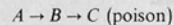


From this information determine the constants k_0 and E in the following expression for the second-order rate constant

$$k_2 = k_0 \exp(-E/RT)$$

9-12 Derive an expression for the rate as a function of time for first-order main and poisoning reactions in a slurry reactor. The reactor operates batchwise for both solid catalyst particles and the liquid reaction mixture. Deactivation occurs by blocking of active sites with poison C , which is produced from reactant A in parallel with the production of desired product B . (The solution is simplified by dividing the rate equations for production of B and for C to eliminate time as a variable. Note that for a batch reactor the deactivation time is equal to the reaction time.)

9-13 Reconsider Prob. 9-12 for series poisoning where the reactions are:



For this case assume that the rate of production of C is much less than the rate of formation of B from A (slow poisoning). This means that the concentration of B is equal to the initial concentration of A , at any time.

EXTERNAL TRANSPORT PROCESSES
IN HETEROGENEOUS REACTIONS

No matter how active a catalyst particle is, it can be effective only if the reactants can reach the catalytic surface. The transfer of reactant from the bulk fluid to the outer surface of the catalyst particle requires a driving force, the concentration difference. Whether this difference in concentration between bulk fluid and particle surface is significant or negligible depends on the velocity pattern in the fluid near the surface, on the physical properties of the fluid, and on the intrinsic rate of the chemical reactions at the catalyst; that is, it depends on the mass-transfer coefficient between fluid and surface and the rate constant for the catalytic reaction. The concentration of reactant is less at the surface than in the bulk fluid. Hence the observed rate, the *global* rate, is less than the intrinsic rate evaluated at the concentration of reactant in the *bulk* fluid.

The same reasoning suggests that there will be a temperature difference between bulk fluid and catalyst surface. Its magnitude will depend on the heat-transfer coefficient between fluid and catalyst surface, the reaction-rate constant, and the heat of reaction. If the reaction is endothermic, the temperature of the catalyst surface will be less than that in the bulk fluid (Fig. 10-1), and the observed rate will be less than that corresponding to the bulk-fluid temperature; the resistance to mass and energy transfer supplement each other. If the reaction is exothermic, the temperature of the catalyst surface will be greater than that of the bulk fluid. Now the global rate may be higher or lower than that corresponding to bulk-fluid conditions; it is increased because of the temperature rise and reduced because of the drop in reactants concentration.

In this chapter our objective is to study quantitatively how these external physical processes affect the global rate, which is the rate that we need in order to design heterogeneous reactors. Such processes are designated as *external* to signify that they are completely separated from, and in series with, the chemical reaction

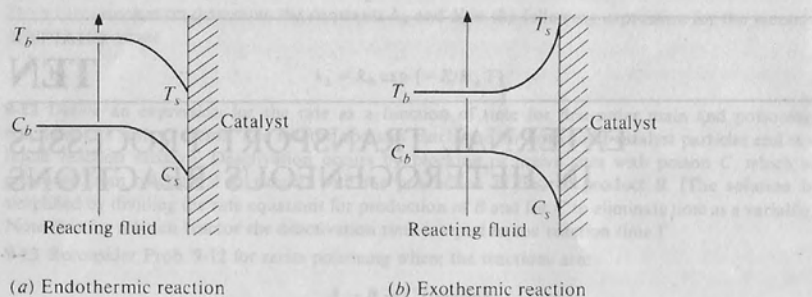


Figure 10-1 External concentration and temperature profiles for fluid-solid catalytic reactions.

on the catalyst surface. For porous catalysts both reaction and heat and mass transfer occur at the same internal location *within* the catalyst pellet. The quantitative analysis in this case requires *simultaneous* treatment of the physical and chemical steps. The effect of these internal physical processes will be considered in Chap. 11.

Mass- and heat-transfer coefficients between fluid and catalyst depend upon the flow and geometric arrangement of fluid and catalyst particle. In other words, they depend upon the type of reactor. For example, such coefficients are different in a fixed-bed arrangement, where the fluid flows around stationary particles, from those in a fluidized bed where both particles and fluid are in motion. In this chapter the fixed-bed case is considered first and this is followed by fluidized beds and 3-phase (slurry and trickle-bed) reactors.

In designing a reactor we suppose that an equation is known for the *intrinsic* rate, that is, the rate in terms of concentrations and temperature at the surface of the catalyst. With respect to external transport effects, the problem is to evaluate a *global* rate for any set of bulk fluid concentrations and temperatures. This is accomplished by using equations for heat and mass transfer to evaluate concentrations and temperature at the catalyst surface. Then the surface C and T are used in the intrinsic rate equation to determine the global rate. The other form of the problem is the interpretation of laboratory measurements to obtain an intrinsic rate equation. Here the global rate is known for a set of bulk concentrations and temperature. The heat- and mass-transfer equations are now used to evaluate surface concentrations and temperature. These values can then be associated with the measured rate to seek an intrinsic rate equation, according to the methods of Chap. 9. Both types of problems are considered in the examples in this chapter.

FIXED-BED REACTORS

Fixed- (or packed-) bed reactors refer to two-phase systems in which the reacting fluid flows through a tube filled with stationary catalyst particles or pellets. In such reactors there will be regions near the outer surface of the particles where the fluid velocity is very low. In these regions, which are particularly evident near points of contact between particles, mass and energy transfer between bulk fluid

and pellet surface will be primarily by conduction. Away from the surface a convective mechanism will be dominant. The complexity of flow patterns around an individual pellet suspended in a fluid stream is considerable. When this is combined with interactions between pellets, as in a fixed-bed reactor, the problem of predicting or correlating *local* velocities is, at present, beyond solution. Therefore transport rates are normally defined in terms of an *average* heat- or mass-transfer coefficient. Even though experimental data show that variations exist, it will be assumed that the average coefficient can be applied to *all* the outer surface of a pellet. With these assumptions a single value of the heat- or mass-transfer coefficient can be used to describe the rates of transfer between bulk fluid and pellet surface.

The error introduced in using an average coefficient is not as serious as might be expected, since the correlations for the mass-transfer coefficient k_m and heat-transfer coefficient h are based on experimental data for beds of particles (see Sec. 10-2). That is, the experimental results are, in general, for average values of the coefficients. Gillespie et al.,[†] however, have carried out an interesting study of the variation of heat-transfer coefficients with respect to the position of the pellet in the bed and the location on the surface of a single pellet. The results showed that h values were lower for the first two layers of pellets (measured from the entrance) than for the remainder of the bed. In addition, the coefficient was higher near the wall of the bed than in the central section of the cylindrical tube, presumably because of the higher velocity about one pellet diameter from the wall.[‡] The local coefficients also varied with position; the highest values were obtained for the surface perpendicular to the direction of bulk flow in the bed. The status of analytical attempts to predict local variations in h are described by Petersen.[§]

In reactor design the rate at the interior catalyst site is presumed to be known from the rate equation (see Chap. 9). Also the temperature and concentrations in the bulk fluid are known. The global rate is then calculated by simultaneous solution of the equations for the rate of reaction and mass and energy transfer, and in the process the unknown concentrations at the surface of the catalyst pellet are eliminated. If all the equations are linear in the surface concentrations and temperatures, an analytical solution is possible, as illustrated by Eqs. (10-5) and (10-6). If some equations are nonlinear, numerical solution is necessary. When the objective is an intrinsic rate equation, the global rate is directly obtained from the experimental measurements; for example, from differential or integral reactor data, as explained in Sec. 4-3, or from other types of laboratory reactors, as described in Chap. 12. Such rates are then used with the equations for mass and energy transfer to determine the concentrations and temperature at the surface of the catalyst pellet. These surface values are correlated with the observed rate in order to establish the form of the rate equation by the procedure described in Chap. 9.

[†] B. M. Gillespie, E. D. Crandall, and J. J. Carberry, *AIChE J.*, **14**, 483 (1968).

[‡] C. E. Schwartz and J. M. Smith, *Ind. Eng. Chem.*, **45**, 1209 (1953).

[§] E. E. Petersen, "Chemical Reaction Analysis," pp. 129-164, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965.

Before we proceed with quantitative illustrations, let us consider the qualitative effect of external resistances on reaction rates (Sec. 10-1) and then summarize the available information for mass- and heat-transfer coefficients (Sec. 10-2).

10-1 The Effect of Physical Processes on Observed Rates of Reaction

Suppose an irreversible gaseous reaction on a *solid* catalyst pellet is of order n . At steady state the rate, expressed per unit mass of pellet, may be written either in terms of the diffusion rate from the bulk gas to the surface or in terms of the rate on the surface. These expressions (C = reactant concentration) are:

$$r_p = k_m a_m (C_b - C_s) \quad (10-1)$$

$$r_p = k C_s^n \quad (10-2)$$

where C_b and C_s are the concentrations in the bulk gas and at the surface, respectively. In the first expression k_m (for example, in centimeters per second) is the mass-transfer coefficient between bulk gas and solid surface, and a_m is the external surface area per unit mass of the pellet. Suppose that the reaction-rate constant k (per unit mass of catalyst) is very much greater than $k_m a_m$. Under these conditions C_s approaches zero and Eq. (10-1) shows that the rate per pellet is

$$r_p = k_m a_m C_b \quad (10-3)$$

At the other extreme, k is very much less than $k_m a_m$. Then C_s approaches C_b , and the rate, according to Eq. (10-2), is

$$r_p = k C_b^n \quad (10-4)$$

Equation (10-3) represents the case when diffusion controls the overall process. The rate is determined by $k_m a_m$; the kinetics of the chemical step at the catalyst surface are unimportant. Equation (10-4) gives the rate when the mass-transfer resistance is negligible with respect to that of the surface step; i.e., the kinetics of the surface reaction control the rate.

Consider a situation where the true order of the surface reaction is 2 [according to Eq. (10-2)] but the rate is diffusion controlled, so that Eq. (10-3) is applicable. Experimental data plotted as rate vs. C_b would yield a straight line. If diffusion were not considered, and Eq. (10-2) were used to interpret the data, the order would be identified as unity—a false conclusion. This simple example illustrates how erroneous conclusions can be reached about kinetics of a catalytic reaction if external mass transfer is neglected.

When both diffusion and reaction resistance are significant, and for a first-order reaction, Eqs. (10-1) and (10-2) can be easily solved for the unknown surface concentration. This result for C_s can be substituted in Eq. (10-1) to obtain an expression for the rate in terms of the bulk concentration C_b . This was done in Chap. 7 (see Sec. 7-1 and Fig. 7-1) with the results

$$C_s = \frac{k_m a_m}{k + k_m a_m} C_b \quad (7-3)$$

$$r_p = k_0 C_b = \frac{1}{1/k + 1/k_m a_m} C_b \quad (7-4) \text{ or } (10-5)$$

where

$$\frac{1}{k_0} = \frac{1}{k} + \frac{1}{k_m a_m} \quad (10-6)$$

Equations (10-5) and (10-6) show that for this intermediate case the observed rate is a function of both the rate-of-reaction constant k and the mass-transfer coefficient k_m . In a design problem k and k_m would be known, so that Eqs. (10-5) and (10-6) give the global rate in terms of C_b . Alternately, in interpreting laboratory kinetic data k_0 would be measured. If k_m is known, k can be calculated from Eq. (10-6). In the event that the reaction is not first order Eqs. (10-1) and (10-2) cannot be combined easily to eliminate C_s . The preferred approach is to utilize the mass-transfer coefficient to evaluate C_s and then apply Eq. (10-2) to determine the order of the reaction n and the numerical value of k .[†] One example of this approach is described by Olson et al.[‡]

Diffusion effects can also lead to a false activation energy. Suppose global reaction rates are measured for a nonporous catalyst pellet at different temperatures and that the surface rate is first order. The observed rates can be used to calculate the overall rate constant k_0 from Eq. (10-5). If external diffusion is arbitrarily neglected, an apparent activation energy E' could then be calculated from the Arrhenius equation.

$$k_0 = A' e^{-E'/R_g T} \quad (10-7)$$

where A' is the apparent frequency factor. This result would give an erroneous value for E if external diffusion were a significant resistance. In fact, the data points for different temperatures would not form a straight line, but would give a curve, as indicated by the solid line in Fig. 10-2. This can be seen by writing Eq. (10-6) as

$$\frac{1}{k_0} = \frac{1}{k} + \frac{1}{k_m a_m} = \frac{e^{E/R_g T}}{A} + \frac{1}{k_m a_m}$$

or

$$k_0 = \frac{A k_m a_m e^{-E/R_g T}}{k_m a_m + A e^{-E/R_g T}} \quad (10-8)$$

where $A e^{-E/R_g T}$ has been substituted for the rate constant k of the surface step. Here E is the true activation energy of the surface reaction. Since the mass-transfer coefficient is relatively insensitive to temperature, Eq. (10-8) shows that k_0 approaches a nearly constant value equal to $k_m a_m$ at high temperatures. At low temperatures $k_0 \approx A e^{-E/R_g T}$, since $k_m a_m$ is the dominant term in the denominator, and a straight line is obtained on the Arrhenius plot. Figure 10-2 illustrates these results. At low temperatures the slope of the straight line gives the correct activation energy E of the surface reaction. As the temperature increases, a curve which

[†] Note that the kinetics of the surface reaction need not be expressed as a simple case of order n , as in Eq. (10-2). The procedure is equally applicable to the form of rate equation developed in Chap. 9 [e.g., Eq. (9-21)].

[‡] R. W. Olson, R. W. Schuler, and J. M. Smith, *Chem. Eng. Progr.*, **46**, 614 (1950).

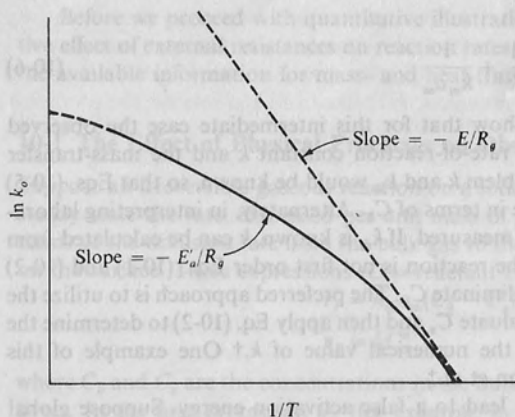


Figure 10-2 True (E) and apparent (E') activation energies.

ultimately flattens to a nearly horizontal line is obtained. In this region E' would vary with the temperature. When experimental rate data for fluid-solid catalytic reactions show a curved line, as in Fig. 10-2, it is possible that external diffusion resistances are important.

These illustrations of the significance of external mass-transfer resistances have been based on isothermal conditions. Temperature differences due to external heat-transfer resistance can also be important. Nonisothermal situations will be considered in Sec. 10-3.

10-2 Mass- and Heat-Transfer Coefficients (Fluid-Particle) in Packed Beds

Average transport coefficients between the bulk stream and particle surface can be correlated in terms of dimensionless groups which characterize the flow conditions. For mass transfer the Sherwood number, $k_m \rho / G$, is an empirical function of the Reynolds number $d_p G / \mu$, and the Schmidt number $\mu / \rho D$. It is common practice to correlate experimental data in terms of j -factors which are defined as the following functions of the Sherwood and Schmidt numbers:

$$j_D = \frac{k_m \rho}{G} \left(\frac{a_m}{a_t} \right) \left(\frac{\mu}{\rho D} \right)^{2/3} \quad (10-9)$$

The ratio (a_m/a_t) allows for the possibility that the effective mass-transfer area, a_m , may be less than the total external area, a_t , of the particles.[†]

[†] In experimental studies of mass transfer only the product $k_m a_m$ can be directly measured. However, it is this product that is needed to evaluate mass transfer effects in reactors, as indicated by Eqs. (10-5) or (10-8).

There have been many experimental studies*[†] of mass transfer in fixed beds along with critical summaries and analyses of the results.**^{††} For Reynolds numbers greater than 10, the following relationship^{††} between j_D and the Reynolds number well represents available data:

$$j_D = \frac{0.458}{\epsilon_B} \left(\frac{d_p G}{\mu} \right)^{-0.407} \rightarrow Re \quad (10-10)$$

G = mass velocity (superficial) based upon cross-sectional area of empty reactor ($G = u\rho$)

d_p = diameter of catalyst particle for spheres^{††}

μ = viscosity of fluid

ρ = density of fluid

D = molecular diffusivity of component being transferred

ϵ_B = void fraction of the interparticle space (void fraction of the bed)

Heat transfer between a fluid and particle surface in a packed bed occurs by the same molecular and convective processes as describe mass transfer. For heat transfer the equation analogous to Eq. (10-9) is

$$j_H = \frac{h}{c_p G} \left(\frac{a_m}{a_t} \right) \left(\frac{c_p \mu}{k_f} \right)^{2/3} \quad (10-11)$$

The heat-transfer coefficient h is defined in terms of the temperature difference and particle surface

$$Q'_L = h a_m (T_s - T_b) \quad (10-12)$$

where Q' is the heat-transfer rate per unit mass of catalyst. While literature correlations sometimes make a distinction between j_H and j_D , the validity of the difference (in the absence of radiation) is uncertain. Hence, Eq. (10-10) may also be used for j_H , in accordance with the original analogy proposed by Chilton and Colburn.§§ At temperatures above about 400°C and for large ($\geq \frac{1}{4}$ ") particles heat transfer by radiation may be significant.¶¶

The relationship between the temperature and concentration differences between fluid and pellet surface can be established by combining the correlations for k_m and h . An energy balance on the pellet requires, for steady state,

$$k_m a_m (C_b - C_s)(-\Delta H) = h a_m (T_s - T_b) \quad (10-13)$$

* D. Thoenes and H. Kramers, *Chem. Eng. Sci.*, **8**, 271 (1958).

† R. D. Bradshaw and C. O. Bennett, *AIChE J.*, **7**, 48 (1961).

†† J. J. Carberry, *AIChE J.*, **6**, 460 (1960).

‡ L. J. Petrovic and G. Thodos, *Ind. Eng. Chem. Fundam.*, **7**, 274 (1968).

§ E. J. Wilson and C. J. Geankoplis, *Ind. Eng. Chem.*, **5**, 9 (1966).

¶ S. Whitaker, *AIChE J.*, **18**, 361 (1972).

†† P. N. Dwivedi and S. N. Upadhyay, *Ind. Eng. Chem. Proc. Des. Dev.*, **16**, 157 (1977).

§§ For other shapes, an approximate value of d_p is that of a sphere with the same external area as the nonspherical particle.

¶¶ T. C. Chilton and A. P. Colburn, *Ind. Eng. Chem.*, **26**, 1183 (1934).

¶¶ W. B. Argo and J. M. Smith, *Chem. Engr. Prog.*, **49**, 443 (1953).

Using Eqs. (10-9) and (10-11) for k_m and h yields

$$T_s - T_b = (C_b - C_s) \frac{-\Delta H}{c_p \rho} \left(\frac{c_p \mu / k_f}{\mu / \rho \mathcal{D}} \right)^{2/3} \left(\frac{j_D}{j_H} \right) \quad (10-14)$$

This expression can be used to evaluate the temperature difference from $C_b - C_s$. For many gases the Lewis number, the ratio of the Prandtl and Schmidt numbers, is about 1.0 and also $j_H \sim j_D$. Hence for most gases Eq. (10-14) reduces approximately to

$$T_s - T_b = \frac{-\Delta H}{c_p \rho} (C_b - C_s) \quad (10-15)$$

If the global rate is influenced by diffusion, so that $C_b - C_s$ is appreciable, Eq. (10-15) shows that significant temperature differences between fluid and pellet are possible. In fact the arrangement of properties in Eq. (10-14) is such that $T_s - T_b$ may be appreciable when $C_b - C_s$ is very small.† Hence, external heat transfer can have an effect on the global rate when the external mass-transfer resistance is negligible. For example, experiments‡ on the oxidation of hydrogen ($\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$) with a platinum-on-alumina catalyst gave $T_s - T_b$ values of as high as 115°C while the fractional concentration difference $(C_b - C_s)/C_b$ was less than 5%. When mass-transfer resistance is not negligible, even larger $T_s - T_b$ are observed.§ In the extreme case where external mass-transfer controls the global rate [$C_s \rightarrow 0$], Eq. (10-15) shows that the maximum $T_s - T_b$ would be that corresponding to the adiabatic temperature rise, $(-\Delta H)C_b/c_p\rho$, for the reaction.

A variation of the fixed-bed reactor is an assembly of screens or gauze of catalytic solid over which the reacting fluid flows. Such an arrangement is sometimes employed for oxidation reactions; for example, the oxidations of acetaldehyde to acetic acid using silver screens as a catalyst. These reactions are frequently characterized by a high rate constant, so that mass transfer of reactants from fluid to solid surface can be a significant part of the total resistance. Data on mass transfer from single screens has been reported by Gay and Maughan.¶ Their correlation is of the form

$$j_D = \frac{\varepsilon k_m \rho}{G} \left(\frac{\mu}{\rho \mathcal{D}} \right)^{2/3} = C \left(\frac{4G}{\beta \mu} \right)^{-m} \quad (10-16)$$

where ε is the porosity of the single screen and β is the external-heat-transfer area of the screen per unit volume, i.e., the reciprocal of the hydraulic radius of the screen, and the other symbols are defined as in Eq. (10-9). The coefficients C and m are given in Table 10-1 for the four screen sizes investigated. Heat-transfer results were obtained for similar screens by Coppage and London.††

† John Hutchings and J. J. Carberry, *AIChE J.*, **12**, 20 (1966).

‡ J. Maymo and J. M. Smith, *AIChE J.*, **12**, 845 (1966).

§ C. N. Satterfield and H. Resnick, *Chem. Eng. Progr.*, **50**, 504 (1954); F. Yoshida, D. Ramaswami and O. A. Hougen, *AIChE J.*, **8**, 5 (1962).

¶ B. Gay and R. Maughan, *Intern. J. Heat Mass Transfer*, **6**, 277 (1963).

†† J. E. Coppage and A. L. London, *Chem. Eng. Progr.*, **52**, 57 (1956).

Table 10-1 Coefficients C and m in Eq. (10-16)

Screen mesh size	C	m	ε	β , ft ⁻¹
10	2.62	0.73	0.817	390
16	4.26	0.85	0.795	535
24	2.80	0.81	0.763	858
60	1.46	0.77	0.690	2,030

For a matrix of 20 or more screens heat-transfer data were found† to follow the j_H lines of Fig. 10-3. The curves given are for extremes of porosity. For intermediate porosities the curves were located between the two shown in the figure. The Reynolds number for Fig. 10-3 is defined as

$$\text{Re}' = \frac{4r_H G}{\mu} \quad (10-17)$$

where r_H , the hydraulic radius, is

$$r_H = L \frac{A_f}{A_h} \quad (10-18)$$

L = length of matrix of screens in the direction of flow

A_f = total cross-sectional area of screen multiplied by porosity ε_m of matrix of screens

A_h = heat-transfer area of matrix of screens

G = mass velocity based on A_f

† A. L. London, J. W. Mitchell, and W. A. Sutherland, *ASME J. Heat Transfer*, **82**, 199 (1960).

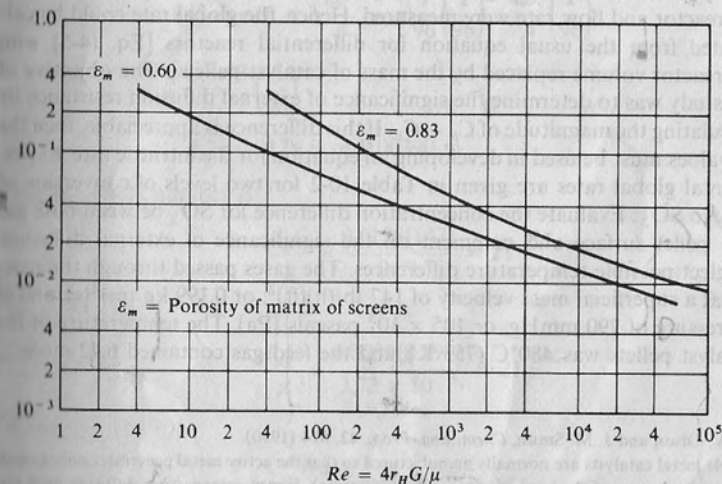


Figure 10-3 Heat-transfer correlation for matrix of screens.

10-3 Quantitative Treatment of External Transport Effects

Four equations are needed to treat external transport effects: one each for the rate of mass and energy transfer to the catalyst surface, and two rate of reaction equations, one for the mass converted and one for the energy involved due to reaction. We will assume first-order kinetics for the reaction equations, for simplicity, but note that the method of using the equations is the same for nonlinear kinetics (see Example 10-2). We also limit the discussion in this section to single reactions; selectivity in multiple reaction systems is considered in Sec. 10-5.

The rates of mass and energy transfer are Eqs. (10-1) and (10-12) and the mass converted by reaction is given by Eq. (10-2) with $n = 1$. The corresponding energy evolved by reaction is

$$Q'_R = (-\Delta H)r_p = (-\Delta H)A(e^{-E/R_g T_s})C_s \quad (10-19)$$

where the second equality is obtained by expressing k in terms of the Arrhenius function of temperature.

A. Isothermal behavior Applications of these equations to the design problem of calculating the global rate and to the problem of interpreting laboratory kinetics data are illustrated in Examples (10-2) and (10-1) for isothermal behavior. For this treatment only equations such as (10-1) and (10-2) for transfer and conversion of mass of reactant are needed. Then in Examples (10-3) and (10-4) nonisothermal behavior is analyzed.

Example 10-1 Rates of oxidation of SO_2 with air have been measured[†] in a differential, fixed-bed reactor. The platinum catalyst was deposited only in the outer surface[‡] of the $\frac{1}{8}$ -in. \times $\frac{1}{8}$ -in. cylindrical Al_2O_3 pellets so that intraparticle transport effects were negligible. Bulk gas compositions entering and leaving the reactor and flow rate were measured. Hence, the global rate could be calculated from the usual equation for differential reactors [Eq. (4-5) with the reactor volume replaced by the mass of catalyst pellets]. The objective of the study was to determine the significance of external diffusion resistance by calculating the magnitude of $C_b - C_s$. If this difference is appreciable, then the C_s values must be used in developing an equation for the intrinsic rate. Experimental global rates are given in Table 10-2 for two levels of conversion of SO_2 to SO_3 . Evaluate the concentration difference for SO_2 between bulk gas and pellet surface and comment on the significance of external diffusion. Neglect possible temperature differences. The gases passed through the reactor at a superficial mass velocity of 147 lb/(h)(ft)², or 0.199 kg/(m)²(s), and at a pressure of 790 mmHg, or 105×10^3 pascals (Pa). The temperature of the catalyst pellets was 480°C (753 K), and the feed gas contained 6.42 mole %

[†] R. W. Olson and J. M. Smith, *Chem. Eng. Prog.*, **42**, 614 (1950).

[‡] Noble metal catalysts are normally manufactured so that the active metal penetrates only a small distance into the pores of the inert carrier (such as alumina). Hence, intraparticle diffusion does not reduce the effectiveness of the catalyst (see Chap. 11).

Table 10-2

Mean conversion of SO_2	r_p , g moles SO_2 /(h) (g catalyst)	P_b , atm		
		SO_2	SO_3	O_2
0.1	0.0956	0.0603	0.0067	0.201
0.6	0.0189	0.0273	0.0409	0.187

NO_2 and 93.58 mole % air. Assume that the gas properties are those of air. The external area of the catalyst pellets was 5.12 ft²/(lb of pellets), and the void fraction of the bed was 0.43.

SOLUTION For interpretation of laboratory data where the rate r_p has been measured, only Eq. (10-1) is needed to evaluate $C_b - C_s$. If $k_m a_m$ is eliminated from this equation by using the correlation for mass-transfer data, Eq. (10-9), the result is

$$C_b - C_s = \frac{r_p (d/\rho D)^{2/3}}{a_i (G/\rho) j_D} \quad (10-20)$$

To calculate $C_b - C_s$ for SO_2 from this equation we need to evaluate the Reynolds and Schmidt numbers. At 480°C the viscosity of air is about 0.09 lb/(h)(ft) or 3.72×10^{-5} (Pa)(s). The particle diameter to employ is the diameter of the sphere with the same area as that of the cylindrical pellets. Hence πd_p^2 will equal the sum of the areas of the lateral and end surfaces of the cylinder:

$$\pi d_p^2 = \pi dL + 2 \frac{\pi d^2}{4} = \pi \frac{1}{96} \left(\frac{1}{96} \right) + \frac{2\pi}{4} \left(\frac{1}{96} \right)^2$$

$$d_p^2 = \frac{3}{2} \left(\frac{1}{96} \right)^2$$

$$d_p = 0.0128 \text{ ft or } 0.00390 \text{ m.}$$

The Reynolds number is

$$\frac{d_p G}{\mu} = \frac{0.0128(147)}{0.09} = 21$$

or, in SI units,

$$\frac{d_p G}{\mu} = \frac{0.0039(0.199)}{3.72 \times 10^{-5}} = 21$$

From Eq. (10-10)

$$j_D = \frac{0.458}{0.43} (21)^{-0.407} = 0.31$$

In the Schmidt group the correct value for \mathcal{D} would be the molecular diffusivity of sulfur dioxide in a mixture of nitrogen, oxygen, and sulfur trioxide, in which O_2 and SO_3 would also be diffusing. Procedures are available† for evaluating diffusivities in such complex systems. However, in this instance little error will be introduced by considering \mathcal{D} the binary diffusivity of SO_2 in air. This may be estimated from the Chapman-Enskog kinetic theory. The equation for \mathcal{D} and illustrations of its use are given in Sec. 11-1. From Example 11-1, the molecular diffusivity of SO_2 -air is $0.629 \text{ cm}^2/\text{s}$, or $2.44 \text{ ft}^2/\text{h}$ ($6.30 \times 10^{-5} \text{ m}^2/\text{s}$).

The density of air will be

$$\rho = \frac{28.9}{359} \left(\frac{790}{480 + 273} \right) \left(\frac{790}{760} \right) = 0.0304 \text{ lb/ft}^3 (0.487 \text{ kg/m}^3)$$

Then the Schmidt group is

$$\frac{\mu}{\rho \mathcal{D}} = \frac{0.09}{0.0304(2.44)} = 1.21 \quad \text{or} \quad \frac{3.72 \times 10^{-5}}{0.487(6.30 \times 10^{-5})} = 1.21$$

For 10% conversion $r_p = 0.0956 \text{ g mol}/(\text{h})(\text{g})$, or $\text{lb mol}/(\text{h})(\text{lb})$, and $a_m = 5.12 \text{ ft}^2/\text{lb}$. Substituting all these results in Eq. (10-20) yields

$$C_b - C_s = \frac{0.0956}{5.12} \frac{(1.21)^{2/3}}{0.31(147/0.0304)} = 1.40 \times 10^{-5} \text{ lb mol}/\text{ft}^3 (16.0 \text{ g mol}/\text{m}^3)$$

The numerical results are more meaningful if they are converted to partial pressures. In atmospheres, the difference between bulk and surface pressures of sulfur dioxide is

$$\begin{aligned} (p_b - p_s)_{SO_2} &= R_g T (C_b - C_s) = 0.73 [1.8(480 + 273)] (1.40 \times 10^{-5}) \\ &= 0.0139 \text{ atm} \\ p_s &= 0.0603 - 0.0139 = 0.0464 \text{ atm (or } 4.7 \times 10^3 \text{ Pa)} \end{aligned}$$

Thus p_s is about 23% less than p_b .

If the Δp for 60% conversion is calculated in the same manner, the results at the two conversions can be summarized as in Table 10-3. The relatively large values of $p_b - p_s$ indicate that external-diffusion resistance is significant, although the effect is less at the higher conversion because the rate is less.

If external diffusion were neglected in Example 10-1 and C_b values were used to relate the surface rate and composition (i.e., to obtain an equation for the chemical step at the surface), serious errors would result, particularly at low conversions. The high temperature, low mass velocity, and relatively fast reaction, lead to large external-diffusion resistances in this case. At lower temperatures the surface rate would be lower, and at higher velocities k_m would increase; both

Table 10-3

Conversion level	Partial pressures of SO_2 , atm			
	p_b	$p_b - p_s$	p_s	$(p_b - p_s)/p_b$
0.1	0.0603	1.39×10^{-2}	0.0464	0.23
0.6	0.0273	0.27×10^{-2}	0.0246	0.10

effects would reduce $C_b - C_s$. In laboratory investigations it is customary to make preliminary measurements at a series of increasing mass velocities. If all other conditions are constant during this series of runs, the importance of external diffusion will decrease with increasing mass velocity. When the experimental rate no longer increases as G is increased, external diffusion is negligible and $C_s \approx C_b$. If rate measurements are made at this mass velocity, bulk concentrations can be used to obtain an expression for the chemical step at the surface. The critical velocity must be determined at the maximum temperature if diffusion resistance is to be negligible at all other temperatures. Other methods of eliminating external resistances in laboratory reactors are described in Chap. 12. Instead of eliminating these resistances by choice of experimental conditions, we may account for them by calculating the surface values of concentration (and temperature), as illustrated in Example 10-1. However, this introduces uncertainty in the results to the extent that the correlations for k_m (and h) are in error.

Example 10-2 Suppose that a fixed-bed reactor is to be designed for the oxidation of SO_2 using a platinum/ Al_2O_3 catalyst. The intrinsic rate equation is that developed in Example 9-2 from experimental rate data. Intraparticle transport effects are negligible, but external concentration and temperature differences may be important. We will assume isothermal conditions at 480°C in order to simplify the calculations, even though this assumption is unrealistic (see Example 10-3). The superficial mass velocity of gas through the bed will be $147 \text{ lb}/(\text{h})(\text{ft}^2)$. To demonstrate the procedure for accounting for external mass-transport limitation, calculate the global rate at a location in the reactor where the bulk partial pressures are those given in Table 10-2 (corresponding to 10% conversion).

SOLUTION Equation (F) of Example 9-2 gives the Langmuir-Hinshelwood, intrinsic rate equation. Since the feed composition is fixed, the several partial pressures are uniquely related to each other by the stoichiometry of the reaction. Hence, Eq. (F) can be expressed as Eq. (K) of Example 9-2, which is written

$$r = \frac{p_{SO_2} p_{O_2}^{1/2} - (1/K) p_{SO_3}}{(0.176 + 12.9 p_{SO_3})^2} \Big|_s, \text{ g mol}/(\text{h})(\text{g catalyst}) \quad (\text{A})$$

The partial pressures (in atm) in this expression are at the catalyst surface. We must use Eqs. (10-1) and (A) to evaluate these surface pressures from the

† R. C. Reid, J. M. Prausnitz, and T. K. Sherwood, "The Properties of Gases and Liquids," 3d ed., Chap. 11, McGraw-Hill Book Company, New York, 1977.

known bulk values (in Table 10-2). Nonlinear Eq. (A) replaces Eq. (10-2) for this problem. Hence a numerical solution is necessary. One procedure is to assume a value of the global rate, and then calculate p_s for each component from Eq. (10-1). In this particular problem there is no uncertainty about the initial assumption for the rate since the experimental value [$r = 0.0956 \text{ g mol SO}_2/(\text{h})(\text{g catalyst})$ or $2.66 \times 10^{-5} \text{ kg mol}/(\text{s})(\text{kg catalyst})$] is available from Table 10-2. Equation (10-1) with Eq. (10-9) for $k_m a_m$ becomes Eq. (10-20). We have already used this equation [in Example (10-1)] to calculate $(p_b - p_s)$ for SO_2 . The result is

$$(p_b - p_s) = 0.0139 \text{ atm (1.408 Pa)}$$

or

$$(p_s)_{\text{SO}_2} = 0.0603 - 0.0139 = 0.0464 \text{ atm (4.70 Pa)}$$

For oxygen the rate will be $0.0956/2 \text{ g mol}/(\text{h})(\text{g catalyst})$ so that Eq. (10-20) becomes

$$(C_b - C_s)_{\text{O}_2} = \frac{(0.0956)/2}{5.12} \frac{(0.81)^{2/3}}{0.31(147/0.0304)} = 5.4 \times 10^{-6} \text{ lb mol}/\text{ft}^3$$

or

$$(p_b - p_s)_{\text{O}_2} = R_g T (C_b - C_s)_{\text{O}_2} = 0.73[1.8(753)]5.4 \times 10^{-6} \\ = 0.0054 \text{ atm (or 550 Pa)}$$

$$(p_s)_{\text{O}_2} = 0.201 - 0.005 = 0.196 \text{ atm}$$

In SI units

$$(C_b - C_s)_{\text{O}_2} = \frac{2.66 \times 10^{-5}}{1.05} \frac{(0.81)^{2/3}}{0.31(0.199/0.427)} = 8.7 \times 10^{-5} \text{ kg mol}/\text{m}^3$$

and

$$(p_b - p_s)_{\text{O}_2} = R_g T (C_b - C_s)_{\text{O}_2} = 8.314(1000)(753)(8.7 \times 10^{-5}) \\ = 550 \text{ Pa}$$

A similar calculation for SO_3 , gives

$$(p_b - p_s)_{\text{SO}_3} = 0.0130 \text{ atm}$$

and

$$(p_s)_{\text{SO}_3} = 0.0067 + 0.0150 = 0.0217 \text{ atm}$$

With these values for the partial pressures at the catalyst surface we can employ Eq. (A) to check the assumed rate.

$$r = \frac{0.0464(0.196)^{1/2} - (1/73)(0.0217)}{[0.176 + 12.9(0.0217)]^2} \\ = 0.097 \text{ lb mol}/(\text{h})(\text{g catalyst})$$

Since this result is close to the assumed value, it is the desired global rate for a location in the reactor where the conversion is 10%.

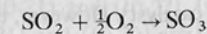
B. Nonisothermal behavior At steady state the heat loss Q'_L from a catalyst, given by Eq. (10-12), is equal to the heat Q'_R evolved due to reaction as given by Eq. (10-19). This equality establishes the temperature difference $T_s - T_b$ in terms of the heat- and mass-transfer coefficients and the properties (ΔH , k , E) of the reaction system. Thus, if we equate Q'_L and Q'_R , and also equate r_p from Eqs. (10-1) and (10-2), two expressions are obtained. For a first-order reaction they are:

$$\underbrace{h a_m (T_s - T_b)}_{\text{Eq. (10-12) for } Q'_L} = \underbrace{r_p (-\Delta H)}_{\text{Eq. (10-19) for } Q'_R} = (-\Delta H) A (e^{-E/R_g T_s}) C_s \quad (10-21)$$

$$\underbrace{k_m a_m (C_b - C_s)}_{\text{Eq. (10-1)}} = \underbrace{r_p}_{\text{Eq. (10-2)}} = A (e^{-E/R_g T_s}) C_s \quad (10-22)$$

In a design problem, A , E , ΔH , h , k_m and a_m would be known. The global rate is to be calculated for a given bulk concentration and temperature. Equations (10-21) and (10-22) can be solved numerically for the unknown C_s and T_s . Then the rate is given by either Eq. (10-1) or (10-2). The problem of interpreting laboratory data to determine an intrinsic rate equation is more direct. Here, A and E are unknown, the global rate and C_b and T_b are measured, and T_s and C_s are to be found. We calculate C_s and T_s directly from the left-hand side equalities in Eqs. (10-22) and (10-21). Examples (10-3) and (10-4) illustrate the calculations.

Example 10-3 The temperature reported in Example 10-1 was measured by inserting thermocouples in the catalyst pellets, thus giving T_s . Calculate the temperature difference $T_s - T_b$ for the conditions of Example 10-1. The heat of reaction for



is approximately $-23,000 \text{ cal/g mol}$ at 480°C , and the activation energy may be taken as $20,000 \text{ cal/g mol}$.

SOLUTION $T_s - T_b$ can be obtained from Eq. (10-21). Thus

$$T_s - T_b = \frac{r_p (-\Delta H)}{h a_m} \quad (A)$$

Expressing h in terms of j_H and using Eq. (10-11) gives

$$T_s - T_b = \frac{r_p (-\Delta H) (c_p \mu / k_f)^{2/3}}{a_i j_H c_p G} \quad (B)$$

For air at 480°C the Prandtl number is $c_p \mu / k = 0.70$ and $c_p = 0.26 \text{ Btu}/\text{lb}^\circ\text{F}$. From Example 10-1, the Reynolds number is 21. Then from Eq. (10-10) $j_H = j_D = 0.31$. Using the data given in Example 10-1, we find for the 0.1 conversion level

$$T_s - T_b = \frac{0.0956 \cdot 23,000 (1.8) (0.70)^{2/3}}{5.12 \cdot 0.31 (0.26) (147)} = 51^\circ\text{F or } 28^\circ\text{C}$$

$$T_b = T_s - 28 = (480 + 273) - 28 = 725 \text{ K or } 452^\circ\text{C}$$

The temperature difference could also have been obtained from the concentration difference (calculated in Example 10-1) by using the energy balance of Eq. (10-14).

$$T_s - T_b = 1.40 \times 10^{-5} \frac{23,000(1.8)}{0.26(0.0304)} \left(\frac{0.70}{1.21} \right)^{2/3} = 51^\circ\text{F or } 28^\circ\text{C}.$$

With an activation energy of 20,000 cal/g mol, a 28°C temperature drop would cause a 40% decrease in rate at a temperature level of 480°C . Hence, a significant error in rate would be made by neglecting the temperature difference between bulk fluid and catalyst surface.

According to Eq. (B) the temperature difference is proportional to the rate. Hence, at the 60% conversion level

$$T_s - T_b = \frac{0.0189}{0.0956} 28 = 5^\circ\text{C}.$$

Because of the low rate, the external temperature difference is now of little significance. Note that in Example 10-1 we found that the external concentration difference was also small at 60% conversion.

Example 10-4 The general treatment of the problem of predicting the global rate at given bulk conditions accounts for both mass- and heat-transfer effects. Let us treat this generalization of Example 10-2 by supposing that we know $T_b = 452^\circ\text{C}$ ($T_b = 725\text{ K}$) and the bulk concentrations given for the 10% conversion level in Table 10-2. We also presume that the intrinsic rate equation [Eq. (K) of Example 9-2] is available. The objective is to calculate a global rate. It is known from the data in Table 10-2 that the answer is $r_p = 0.0956\text{ g mol/(h) g catalyst}$. However, to illustrate this type of problem, we will pretend that we don't know the rate, just as we did in Example 10-2.

SOLUTION As in Example (10-2), one method of solution is to assume a rate. Then calculate T_s and C_s (for each component) from the left-hand-side equalities in Eqs. (10-21) and (10-22). Finally, check the assumed rate by using these values of T_s and C_s in the expression for the intrinsic rate.

We assume $r = 0.0956$ and evaluate $k_m a_m$ and $h a_m$ from Eqs. (10-9) and (10-11), using Eq. (10-10) with $j_D = j_H$. Substituting these results in Eqs. (10-21) and (10-22) we obtain

$$T_s - T_b = \frac{r_p(-\Delta H)}{h a_m} = 28^\circ\text{C}$$

$$T_s = T_b + 28 = (452 + 273) + 28 = 753\text{ K}$$

$$(C_b - C_s)_{\text{SO}_2} = 1.40 \times 10^{-5}\text{ lb mol/ft}^3$$

or

$$(p_b - p_s)_{\text{SO}_2} = 0.0139\text{ atm}$$

The numerical values shown are those already determined in Examples (10-3) for ΔT and (10-1) for ΔC . Similar ΔC values for oxygen and sulfur trioxide

are also available from Example 10-2. In summary, the corresponding p_s values are

$$(p_s)_{\text{SO}_2} = 0.0603 - 0.0139 = 0.0464\text{ atm}$$

$$(p_s)_{\text{O}_2} = 0.201 - 0.0045 = 0.196\text{ atm}$$

$$(p_s)_{\text{SO}_3} = 0.0067 + 0.0150 = 0.0217\text{ atm}$$

We check the assumed rate by using these surface partial pressures and T_s in the intrinsic rate equation

$$r_p = \frac{p_{\text{SO}_2} p_{\text{O}_2}^{1/2} - (1/K) p_{\text{SO}_3}}{[A + B p_{\text{SO}_2}]^2} = \frac{0.0464(0.196)^{1/2} - (1/73)0.0217}{[0.176 + 12.9(0.0217)]^2} \quad (\text{A})$$

$$= 0.097\text{ lb mol/(h)(g catalyst)}$$

This result agrees well with the assumed value. In the normal case where a good initial estimate for r_p is not available, iterative calculations would probably be required. In such cases the *initial* estimate for r_p could be that value calculated from the intrinsic rate equation assuming $p_s = p_b$ and $T_s = T_b$. Note also that the two "constants" in the intrinsic rate equation are temperature dependent. Thus, in the normal case it is necessary to know how A and B in Eq. (A) vary with temperature and to use the values corresponding to the calculated surface temperature. In our calculations this was unnecessary because $A = 0.176$ and $B = 12.9$ were the correct values for $T_s = 753\text{ K}$ (480°C).

For first-order reactions another method of calculation of T_s and C_s values may be used. This is to employ the equality of the left-hand and right-hand terms in Eqs. (10-21) and (10-22). In this method a rate is not assumed; instead Eqs. (10-21) and (10-22) are solved simultaneously for T_s and C_s .

Hougen† has summarized many aspects of the problem of external-mass- and energy-transfer resistances and has included figures for predicting when such resistances need to be considered. This was done for mass transfer by eliminating k_m from Eqs. (10-9) and (10-1), thus establishing $(C_b - C_s)C_b$ in terms of the rate of reaction, the Reynolds number, and the Schmidt number, $\mu\rho/\mathcal{D}$. If this concentration ratio is less than, say, 0.1, diffusion resistance is unimportant. In a similar way, Eqs. (10-11), (10-12), and (10-19) were used to prepare a plot of $T_s - T_b$ as a function of the rate, the Reynolds number, and the Prandtl number. The exponential effect of temperature on the rate means that small values of $T_s - T_b$ can have a large effect on the rate. Thus care must be taken when external heat-transfer resistances are neglected. The safest procedure is to evaluate the rate at T_s and at T_b and note whether the difference is significant, as was done in Example 10-2. These methods for evaluating external resistances are applicable for any form of rate equation, since they utilize an experimental rate of reaction.

† O. A. Hougen, *Ind. Eng. Chem.*, 53, 509 (1961).

10-4 Stable Operating Conditions

The requirement that $Q'_R = Q'_L$ at steady state introduces interesting questions about stable operating conditions. The problem is similar to the situation in stirred-tank reactors, discussed in Sec. 5-5. We consider this problem for two cases: negligible and finite external-diffusion resistance.

✦ **Negligible mass transfer resistance** The equality of Q'_L and Q'_R given by Eq. (10-21), and equality of rates of mass transfer and reaction given by Eq. (10-22) establish steady-state values of C_s and T_s . While an analytical solution cannot be achieved, the intersection of curves of Q'_L and Q'_R vs. $T_s - T_b$, or vs. the dimensionless temperature rise $\theta = (T_s - T_b)/T_b$, determines T_s . When the external mass transfer resistance is negligible, $C_s = C_b$, and Eq. (10-21) alone gives T_s for a given T_b and C_b . According to Eq. (10-19), Q'_R will be an exponential curve in θ , as shown in Fig. 10-4 for an exothermic reaction. Equation (10-12) for Q'_L is linear in θ . It could intersect Q'_R as indicated by curves Q'_{L1} or Q'_{L2} , or it could be below Q'_R , as shown by curve Q'_{L3} , depending on the magnitude of h and the location of Q'_R .

The curves in Fig. 10-4 were originally proposed by Frank-Kamenetski† and are useful for describing regions where multiple values of T_s are possible. If the relative position is as described by curves Q'_R and Q'_{L1} , stable operation occurs at point A_1 . If the rate of heat transfer from solid to fluid is less, so that the system is given by Q'_R and Q'_{L2} , there can be two temperatures for stable operation, given by A_2 and B_2 . The region between A_2 and B_2 is unstable in that the heat loss is greater than the heat of reaction. An initial condition in this region would stabilize

† D. A. Frank-Kamenetski, "Diffusion and Heat Exchange in Chemical Kinetics," chap. IX, Princeton University Press, Princeton, N.J., 1955.

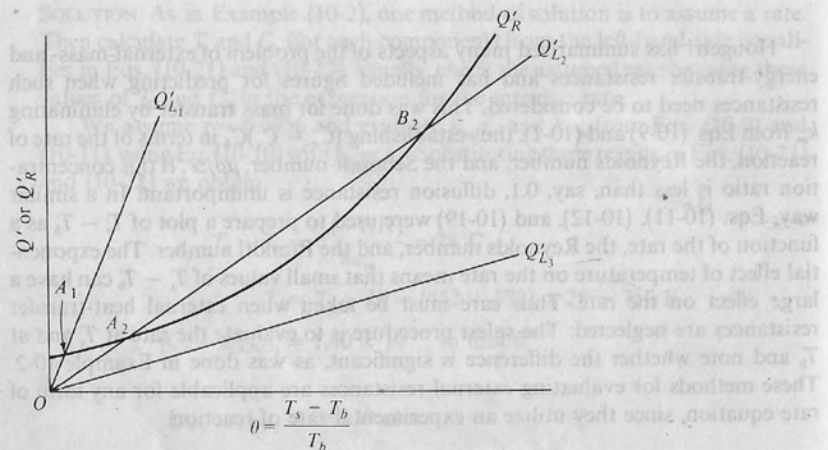


Figure 10-4 Temperature difference between bulk fluid and surface of catalyst pellet (negligible diffusion resistance).

at A_2 . An initial condition above B_2 would be unstable, with no temperature of stabilization, because $Q'_R > Q'_{L2}$. Similarly, the Q'_R and Q'_{L2} system is not usually stable, since Q'_R is greater than Q'_{L3} at any reasonable value of $T_s - T_b$.

✦ **Finite mass transfer resistance** In this case $C_s < C_b$ so that Eqs. (10-21) and (10-22) must be solved simultaneously. Solving Eq. (10-22) for C_s and substituting the result for C_s in Eq. (10-19) for Q'_R gives

$$Q'_R = \frac{(-\Delta H)C_b}{(1/A)e^{E/R_0T_s} + (1/k_m a_m)} \quad (10-23)$$

The steady-state value of T_s is determined by the intersection of the curve of Q'_R vs. $(T_s - T_b)/T_b$, from Eq. (10-23), and the curve for Q'_L given by Eq. (10-12).

The curve for Q'_R tends to flatten as $T_s - T_b$ increases to a high value, because the $(1/k_m a_m)$ term in the denominator of Eq. (10-23) becomes dominant. Physically this means that the rate is so high that $C_s \rightarrow 0$ and mass transfer determines the global rate. In comparison with the Q'_R curves in Fig. 10-4, we see that mass transfer tends to quench the reaction; i.e., the rate reaches a plateau corresponding to the flat portion of the Q'_R curve in Fig. 10-5. Both Q'_R and Q'_L curves are shown in Fig. 10-5. The relative position of the Q'_R and Q'_L curves is illustrated by drawing several lines for Q'_L . For the set $Q'_{L1} - Q'_R$ the stable operating point is at A_1 . If the initial temperature is on either side of this point, the pellet will cool or heat until A_1 is reached. For the set $Q'_R - Q'_{L2}$ initial T_s values below point A_2 will increase to A_2 , and initial T_s values above B_2 will fall to B_2 . Intersection C_2 is, in theory, another stable condition. However, it is pseudostable, because small perturbations below C_2 force the temperature to A_2 , while slight deviations above force the temperature to B_2 . In practice, the entire region between A_2 and B_2 is

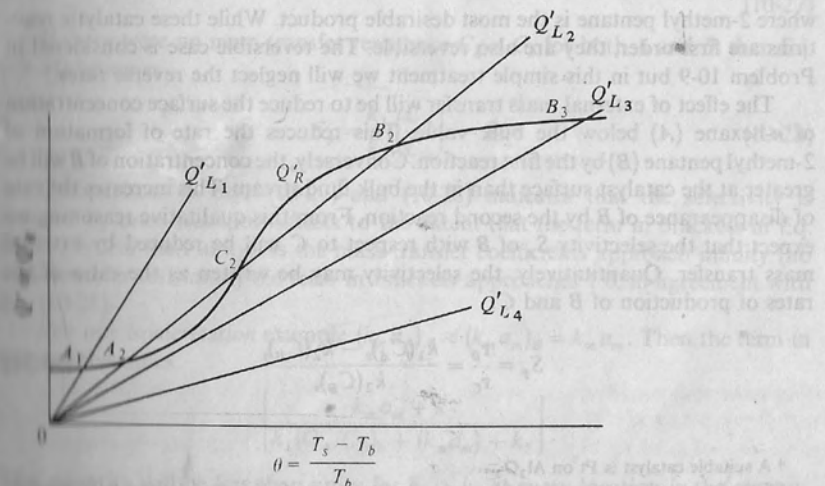


Figure 10-5 Temperature differences between bulk fluid and surface of catalyst pellet (general case).

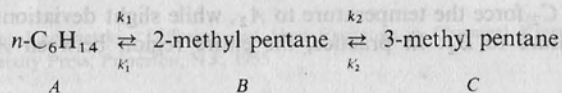
unstable. For $Q'_R - Q'_{L_3}$ stable operation occurs only at a high value of $T_s - T_b$ corresponding to B_3 . Here the Q'_R curve is nearly flat and is determined by the diffusion term $1/k_m$ in Eq. (10-23). Frank-Kamenetski termed this region the *diffusion-controlled regime* and the region at A_1 and A_2 the *reaction-controlled regime*. For the set $Q'_R - Q'_{L_4}$ there is usually no stable region, because the heat transfer away from the pellet is normally less than the heat of reaction. Regions of large $(T_s - T_b)/T_b$ are frequently encountered for combustion, since $(-\Delta H)$ for these systems is high. However, hydrogenations and other reactions can exhibit both reaction and diffusion regimes at feasible operating conditions.

The same type of stability behavior is observed for gas-solid *noncatalytic* reactions, such as the combustion of carbon pellets in air. This problem is a dynamic one, however, because the carbon reactant and size of pellet changes with time. This class of heterogeneous reactions is discussed in Chap. 14.

10-5 Effect of External Transport Processes on Selectivity

When more than one reaction occurs, the effect of external transport on selectivity is important. The local, or point, selectivity, S_p , at any location in a reactor has been defined (Sec. 2-11) as the ratio of the rates of the desirable to the undesirable product. To illustrate the effect of transport processes we consider parallel and consecutive reactions for isothermal and nonisothermal conditions.

Consecutive reactions—isothermal Consider the production of high-octane, branched chain hydrocarbons by the isomerization reactions:[†]



where 2-methyl pentane is the most desirable product. While these catalytic reactions are first order, they are also reversible. The reversible case is considered in Problem 10-9 but in this simple treatment we will neglect the reverse rates.[‡]

The effect of external mass transfer will be to reduce the surface concentration of n -hexane (A) below the bulk value. This reduces the rate of formation of 2-methyl pentane (B) by the first reaction. Conversely, the concentration of B will be greater at the catalyst surface than in the bulk fluid stream. This increases the rate of disappearance of B by the second reaction. From this qualitative reasoning we expect that the selectivity S_p of B with respect to C will be reduced by external mass transfer. Quantitatively, the selectivity may be written as the ratio of the rates of production of B and C :

$$S_p = \frac{r_B}{r_C} = \frac{k_1(C_A)_s - k_2(C_B)_s}{k_2(C_B)_s} \quad (10-24)$$

[†] A suitable catalyst is Pt on Al_2O_3 .

[‡] For a more realistic treatment of hexane isomerization see A. Voorhies, Jr., and R. G. Beecher, paper 20B, 61st Annual Meeting of A.I.Ch.E., Los Angeles, Calif., Dec. 1-5, 1968.

The surface concentrations can be expressed in terms of bulk values by writing mass balances for A and B . For A ,

$$(k_m a_m)_A (C_b - C_s)_A = k_1 C_{A_s}$$

or

$$C_{A_s} = \frac{(k_m a_m)_A}{(k_m a_m)_A + k_1} (C_A)_b \quad (10-25)$$

Component B is produced by reaction 1 and disappears by reaction 2. Hence, the mass balance for B is

$$(k_m a_m)_B (C_s - C_b)_B = k_1 (C_A)_s - k_2 (C_B)_s$$

Solving this expression for $(C_B)_s$ gives

$$(C_B)_s = \frac{k_1 (C_A)_s + (k_m a_m)_B (C_B)_b}{(k_m a_m)_B + k_2}$$

With Eq. (10-25) for $(C_A)_s$ this expression for $(C_B)_s$ becomes:

$$(C_B)_s = \frac{k_1 (k_m a_m)_A (C_A)_b + (k_m a_m)_B (C_B)_b}{(k_m a_m)_A + k_1 + (k_m a_m)_B + k_2} \quad (10-26)$$

Equations (10-25) and (10-26) can be substituted in Eq. (10-24) to yield an expression for S_p in terms of bulk concentrations. The result is

$$S_p = \frac{k_1}{k_2} \left(\frac{C_A}{C_B} \right)_b \left[\frac{1 + k_2 / (k_m a_m)_B}{\left[\frac{k_1 / (k_m a_m)_B}{(C_A/C_B)_b} + \left[\frac{1 / (k_m a_m)_A}{(k_m a_m)_A + k_1} \right] \right]} \right] - 1 \quad (10-27)$$

If there were no mass-transfer resistance $C_s = C_b$ for both A and B , then Eq. (10-24) becomes

$$S'_p = \frac{k_1}{k_2} \left(\frac{C_A}{C_B} \right)_b - 1 \quad (10-28)$$

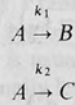
Comparison of eqs. (10-27) and (10-28) indicates that the selectivity is reduced by mass-transport effects to the extent that the term in brackets in Eq. (10-27) is less than unity. As the mass-transfer coefficients approach infinity (no mass-transfer resistance) the term in brackets approaches 1.0, in agreement with Eq. (10-28).

For our isomerization example $(k_m a_m)_A \approx (k_m a_m)_B = k_m a_m$. Then the term in brackets becomes

$$\left[\frac{k_m a_m + k_2}{k_1 (C_A/C_B)_b + (k_m a_m) + k_1} \right]$$

This quantity will be less than unity for $k_1 > k_2$ at every location in the reactor, that is, regardless of the value of $(C_A/C_B)_b$.

Parallel reactions—isothermal Consider parallel reactions with a common reactant (A):

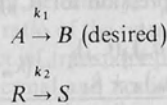


where B is the desired product. The selectivity of B with respect to C is given by the ratio of the rates

$$S_p = \frac{r_B}{r_C} = \frac{k_1(C_A)_s}{k_2(C_A)_s} = \frac{k_1}{k_2} \quad (10-29)$$

Regardless of how much the surface concentration is reduced by mass transfer Eq. (10-29) shows that the selectivity is unaffected. Thus, Eq. (10-29) is identical with Eq. (2-74), which ignored mass-transfer effects. For this type of parallel reactions the rate is reduced by mass transfer but the *selectivity* is unchanged.

If the parallel reactions are completely independent:



Equation (10-25) can be used to express the surface concentration of both A and R in terms of bulk values. Then the selectivity is

$$S_p = \frac{r_B}{r_S} = \frac{k_1(C_A)_s}{k_2(C_R)_s} = \frac{(1/k_m a_m)_R + 1/k_2}{(1/k_m a_m)_A + 1/k_1} \frac{(C_A)_b}{(C_R)_b} \quad (10-29a)$$

For no external resistances, the selectivity S'_p is

$$S'_p = \frac{k_1(C_A)_b}{k_2(C_R)_b} \quad (10-29b)$$

Hence the effect of external mass transport on selectivity is given by the ratio

$$\frac{(S_p)}{(S'_p)} = \frac{[(k_m a_m)_R + k_2]}{[(k_m a_m)_A + k_1]} \frac{(k_m a_m)_A}{(k_m a_m)_R} \quad (10-29c)$$

The two mass-transfer coefficients will be nearly the same for most reaction systems. Hence, the selectivity will be reduced by external mass transfer if $k_1 > k_2$. There will be little effect for low mass-transfer resistances since $k_m a_m$ becomes large with respect to k_1 or k_2 and the ratio in Eq. (10-29c) approaches unity.

Nonisothermal conditions Equations (10-27) and (10-29) are applicable when external temperature differences are significant, but the rate constants k_1 and k_2 must be evaluated at the surface temperature. The effect of heat transfer on selectivity will then depend upon the activation energies of the reactions. In general, the selectivity is increased by mass-transfer resistances for an exothermic reaction

when the activation energy, E_1 , for the desired reaction is larger than E_2 for the by-product reaction. For example, for parallel reactions, Eq. (10-29) gives

$$S_p = \frac{A_1 e^{-E_1/R_g T_s}}{A_2 e^{-E_2/R_g T_s}} \quad (10-30)$$

If there were no heat-transfer resistance $T_s = T_b$. Hence the ratio of selectivities with and without considering external temperature differences would be

$$\frac{(S_p)_{T_s}}{(S_p)_{T_b}} = \frac{\exp \left[\frac{E_1}{R_g} \left(\frac{T_s - T_b}{T_s T_b} \right) \right]}{\exp \left[\frac{E_2}{R_g} \left(\frac{T_s - T_b}{T_s T_b} \right) \right]} \quad (10-31)$$

When the net heat of the reactions is exothermic, $T_s - T_b$ is positive. Hence, if $E_1 > E_2$, the selectivity at T_s will be greater than that at T_b . For a net endothermic heat effect the effect of heat transfer would be to reduce the selectivity when $E_1 > E_2$.

For consecutive reactions the same conclusions apply. Suppose that mass transfer is important as well as heat transfer. Then the selectivity is reduced by the mass-transfer resistance and increased by the heat-transfer resistance, provided $E_1 > E_2$ and the reaction is exothermic. The temperature effect will be the dominant factor for moderate or high heats of reaction. As an illustration, imagine that the conditions (heats of reaction, heat-transfer coefficient) are such that $(T_s - T_b) = 25^\circ\text{C}$ for a set of *consecutive* reactions. Suppose that the mass-transfer resistance is relatively low. Typical values for the outer conditions might be:

$$(k_m a_m)_A = (k_m a_m)_B = 50 \text{ cm}^3/(\text{s})(\text{g catalyst})$$

$$E_1 = 20 \text{ kcal/g mol}$$

$$E_2 = 15 \text{ kcal/g mol}$$

$$A_1 = 6.2 \times 10^8 \text{ cm}^3/(\text{s})(\text{g catalyst})$$

$$A_2 = 1.9 \times 10^6 \text{ cm}^3/(\text{s})(\text{g catalyst})$$

$$T_b = 500 \text{ K}$$

$$(C_A/C_B)_b = 2.$$

If external mass and heat transfer are both neglected, the selectivity is, from Eq. (10-28),

$$\begin{aligned} S_p &= \frac{k_1}{k_2} \frac{(C_A)_b}{(C_B)_b} - 1 \\ &= \frac{6.2 \times 10^8 \exp[-20,000/R_g(500)]}{1.4 \times 10^6 \exp[-15,000/R_g(500)]} (2) - 1 \\ &= 4.2 - 1 = 3.2 \end{aligned}$$

The combined effects of both mass and heat transfer are given by Eq. (10-27) with k_1 and k_2 evaluated at $T_s = 525$ K. These values are $k_1 = 2.87$ and $k_2 = 1.07 \text{ cm}^3/(\text{s})(\text{g catalyst})$. Hence

$$S_p = \frac{2.87}{1.07} (2) \left[\frac{1 + (1.07)/50}{(2.87/50)(2) + (50 + 2.87)/50} \right] - 1$$

$$= 5.36[0.87] - 1 = 3.7$$

The term in brackets indicates that the effect of mass transfer reduces the selectivity about 13% [1 vs. 0.87]. However, the effect of temperature is to increase S_p by $(5.36 - 4.2)/4.2$ or 30%. The net result is an increase from 3.2 to 3.7.

FLUIDIZED-BED REACTORS

In the fixed-bed reactor the catalyst particles are relatively large and stationary. In contrast, in a fluidized-bed reactor, Fig. 1-8, the small particles (50 to 250 microns) move about in a manner dependent on the velocity of the reacting fluid. Figure 10-6† shows the range of behavior of particles in a vertical tube through which fluid flows. At very low velocities the particles are not disturbed so that, in essence, fixed-bed behavior is observed. At the other extreme the velocity is so high that the particles are carried out the top of the reactor with the fluid.‡ In this

† Adapted from Fig. 1, Chap. 1, "Fluidization Engineering," Daizo Kunii and Octave Levenspiel, John Wiley & Sons, New York, 1969.

‡ F. A. Zenz and D. F. Othmer, "Fluidization and Fluid-Particle Systems," Reinhold Publishing Corporation, New York, 1960.

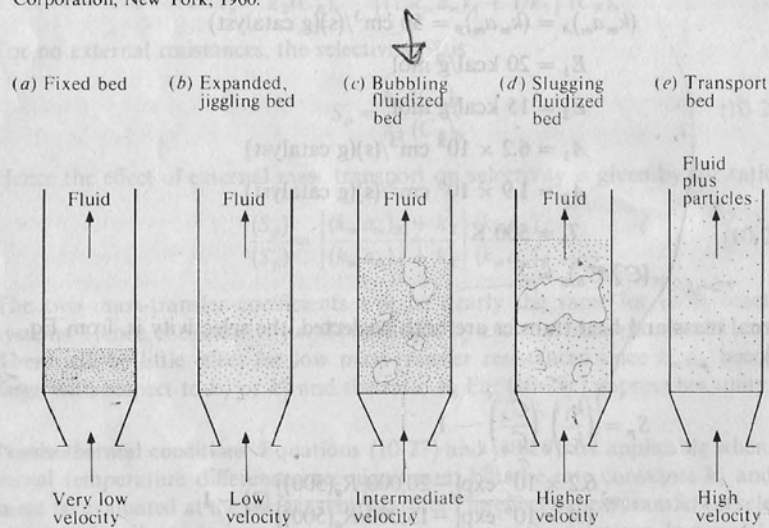


Figure 10-6 Particle motion in tubular-flow reactor.

condition the system operates as a transport, or transfer-line reactor. In most fluidized-bed catalytic reactors, the fluid is a gas and the normal operating condition is in the bubbling regime. In this condition the gas moves through the reactor in two ways: as "bubbles" containing relatively few solid particles and moving at above the average velocity, and as a continuous "dense" or "emulsion" phase where the particle concentration is high.† Kunii and Levenspiel‡ have described this behavior in terms of a "bubbling-bed model" and used the model for design of reactors.§ We will consider the design problem later in Chap. 13. Here we are interested in mass- and heat-transfer rates between the fluid and the solid particles.

10-6 Particle-Fluid Mass and Heat Transfer

An important characteristic of fluidized beds is the near uniformity of temperature throughout the reactor. This is due to the mixing in the emulsion phase, caused by the gas bubbles, and to the very high heat-transfer area, per unit mass of catalyst, that is associated with the small particles. The same large area is available for mass transfer. Therefore, the temperature and concentration differences between fluid and particle surface are usually negligible. This is in direct contrast to the result for fixed-bed reactors even though the mass- and heat-transfer coefficients in fluidized beds are less than those in fixed beds. As a result, external concentration and temperature effects are not very significant in design of fluidized-bed reactors. The more important problem is accounting for the bypassing of the catalyst by the gas "bubbles" and the mass transfer between bubble and dense phases as discussed in Chap. 13.

Kunii and Levenspiel¶ have summarized available mass- and heat-transfer data in the form of graphs of Sherwood and Nusselt numbers vs. Reynolds number. Typical of the results are those of Chu et al.,†† which may be expressed in terms of j factors as

$$j_D \text{ or } j_H = 1.77 \left[\frac{d_p G}{\mu(1 - \epsilon_B)} \right]^{-0.44} \quad (10-32)$$

for the range $30 < d_p G / \mu(1 - \epsilon_B) < 5,000$. Here j_D and j_H are as defined in Eqs. (10-9) and (10-11) and

ϵ_B = void fraction in the bed

G = superficial mass velocity

d_p = average particle diameter

This correlation is based on data for both liquid-solid and gas-solid beds.

† J. van Deemter, *Chem. Eng. Sci.*, **13**, 343 (1961).

‡ Op. cit.

§ F. Davidson and D. Harrison, in "Fluidized Solids," Cambridge University Press, London, 1961, also proposed a bubble and emulsion phase model to describe fluidized-bed reactor behavior.

¶ Op. cit.

†† J. C. Chu, J. Kail, and W. A. Wetterath, *Chem. Eng. Prog.*, **49**, 141 (1953).

Example 10-5 Estimate the ratio of mass-transfer rates, per unit volume, for fixed-bed and fluidized-bed reactors at reasonable operating conditions. Suppose these conditions are:

	Fluidized bed	Fixed bed
Particle size, d_p , cm	0.0063 (250 mesh)	0.635 ($\frac{1}{4}$ in.)
Void fraction of the bed, ϵ_B	0.90	0.40
Fluid mass velocity, G g/cm ² (s)	0.02	0.10

SOLUTION The mass transfer rate per unit *volume* of reactor is, from Eq. 10-1):

$$r_v = \rho_p(1 - \epsilon_B)r_p = \rho_p(1 - \epsilon_B)k_m a_m (C_b - C_s) \quad (\text{A})$$

where ρ_p is the density of the particles themselves. For spherical particles of diameter d_p , the external area per unit mass, a_m , is $6/d_p\rho_p$. Hence Eq. (A) becomes

$$r_v = \frac{6(1 - \epsilon_B)}{d_p} k_m (C_b - C_s) \quad (\text{B})$$

The ratio of the mass-transfer rates can be obtained by using Eq. (10-9) for k_m in Eq. (B). For the same fluid and the same concentration difference, the result is

$$\frac{r_{\text{fluid}}}{r_{\text{fixed}}} = \frac{[(1 - \epsilon_B)/d_p]_{\text{fluid}}(Gj_D)_{\text{fluid}}}{[(1 - \epsilon_B)/d_p]_{\text{fixed}}(Gj_D)_{\text{fixed}}} \quad (\text{C})$$

Substituting Eqs. (10-32) and (10-10) for j_D ,

$$\frac{r_{\text{fluid}}}{r_{\text{fixed}}} = \frac{[1.77(1 - \epsilon_B)^{1.44} G^{0.56} d_p^{-1.44}]_{\text{fluid}}}{[(0.458/\epsilon_B)(1 - \epsilon_B) G^{0.593} d_p^{-1.407}]_{\text{fixed}}} \quad (\text{D})$$

Substituting numerical values

$$\frac{r_{\text{fluid}}}{r_{\text{fixed}}} = 32$$

Thus the mass-transfer rate between particle and fluid for a fluidized bed can be an order of magnitude greater than that for a fixed bed. With this large transport rate it is evident that $C_b - C_s$, calculated by the methods described in Sec. 10-3, will be negligible. A similar result applies for external temperature differences.

SLURRY REACTORS

Heretofore in this chapter external transport has been analyzed for two-phase systems, fluid and solid catalyst. When there are both volatile and nonvolatile reactants, or when a liquid solvent is necessary with all gaseous reactants, three-phase reactors are needed. Examples are hydrogenation of oils with a nickel catalyst, oxidation of liquids (or pollutants dissolved in liquids) with metal oxide catalysts, and polymerization of ethylene or propylene in a slurry of solid catalyst particles in liquid cyclohexane. External transport effects can be especially important in three-phase reactors because more interphase steps exist; a gaseous reactant must be transferred from gas to liquid and then from liquid to solid catalyst before reaction occurs.

The two common forms of three-phase reactors are the slurry† and trickle-bed‡ types described briefly in Chap. 1 (Fig. 1-6). The design of three-phase reactors consists of the usual two steps associated with heterogeneous systems: formulation of an expression for the global rate of reaction, applicable at any location, followed by using this expression to predict overall reactor performance. By using the global rate, the second step can be carried out with the procedures for homogeneous reactors presented in Chaps. 3 to 5. In this chapter we discuss only the first step of accounting for external transport in formulating a global rate equation, first for slurry reactors and then for trickle beds. Then in Chap. 13 the prediction of reactor performance is considered.

The distinguishing feature of a slurry reactor is that *small* particles (~100 microns) of catalyst are suspended in a liquid. In a three-phase system bubbles of gas rise through the agitated slurry, as indicated in Fig. 10-7. Unlike the fluidized bed, there is little relative movement between particles and fluid, even though the liquid is agitated mechanically. The particles tend to move with the liquid. The small particle size, low diffusivities in liquids, and low relative velocity all reduce the mass transfer coefficient. Hence external mass transfer can significantly retard the global rate. However, the relatively high thermal conductivity of liquids increases the heat transfer coefficient. This coupled with the small heat of reaction per unit *volume* of the slurry means that there is little temperature difference between particle and liquid. Thus, external temperature differences can normally be neglected in slurry reactors. Note that the relative importance of heat- and mass-transfer effects in slurries is the opposite of that in fixed-bed reactors.§

A similar situation exists for heat and mass transfer between gas bubble and liquid. The bubble velocity with respect to the liquid may be large, but the area for

† Another form of the slurry reactor is the two-phase type where all the reactants are liquid.

‡ The term trickle bed means cocurrent downflow of gas and liquid over a fixed bed of catalyst particles (see Fig. 1-6b). Downward flow of liquid and countercurrent, upflow of gas, and cocurrent upflow of both gas and liquid are possible alternatives of three-phase reactors.

§ For other treatments of slurry reactors see C. N. Satterfield and T. K. Sherwood, "The Role of Diffusion in Catalysis," pp. 43-55, Addison-Wesley Publishing Co., Inc., Reading, Mass., 1963; C. N. Satterfield, "Mass Transfer in Heterogeneous Catalysis," pp. 107-122, Massachusetts Institute of Technology Press, Cambridge, Mass., 1970; Y. T. Shah, "Gas-Liquid-Solid Reactor Design," pp. 111-115, McGraw-Hill Book Company, New York, 1979.

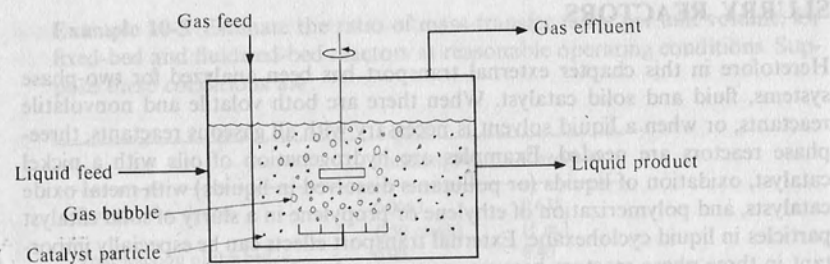


Figure 10-7 Three-phase slurry reactor.

mass transfer with respect to that of the particles is often small.† Hence, bubble-liquid mass transfer can also significantly retard the global rate.

It is reasonable to assume that the liquid and catalyst particles in a slurry reactor are well mixed (as in a stirred-tank). However, the gas bubbles rise through the liquid without complete mixing. Therefore, the concentration of gaseous reactant in the bubble will change with position (unless the gas is a pure component, as in hydrogenations). As a result, the global rate can change with vertical position in the reactor.‡ At one position, the overall reaction consists of the following processes in series:§

1. Mass transfer from the bulk concentration in the gas bubble to the bubble-liquid interface
2. Mass transfer from the bubble interface to the bulk-liquid phase
3. Mixing and diffusion in the bulk liquid
4. Mass transfer to the external surface of the catalyst particles
5. Reaction at the catalyst surface¶

As mentioned, the rise of the bubbles through the liquid, along with mechanical agitation is normally sufficient to achieve uniform conditions in the bulk liquid. Hence the resistance of step 3 can be neglected.†† The global rate can be expressed in terms of the known bulk concentrations by writing rate equations for

† For a wide range of operating conditions the vertical velocity of bubbles rising through a liquid is about 20 cm/s. Also, the bubble diameter is 1–3 mm (much larger than the particle size) and varies but little [D. Mistic and J. M. Smith, *Ind. Eng. Chem. Fundam.*, **10**, 380 (1971)]. Hence the bubble surface per unit volume of slurry can be much smaller than the particle surface.

‡ When there is no gas phase, that is, there are only liquid reactants, and the slurry is well mixed, the global rate is the same throughout the reactor.

§ For an irreversible reaction. For a reversible case, the reverse transport processes for the limiting product would be added.

¶ Since our concern in this chapter is only with external (to the catalyst particle) resistances, the possibility of resistances within a porous catalyst particle is not included. The particles are inherently small, so that intraparticle mass-transfer resistance may be unimportant. The conditions for establishing the significance of such internal resistances are given in Chap. 11.

†† This conclusion has been verified experimentally by H. Kolbel and W. Siemes [*Umschau*, **24**, 746 (1957)] and by W. Siemes and W. Weiss [*Dechema Monographien*, **32**, 451 (1959)].

each of the four remaining steps. The rates of all the steps will be identical at steady state, and this equality permits elimination of the unknown interfacial concentrations. The procedure is the same as that employed in developing Eq. (10-5) for a single mass-transfer step. As in that situation, a simple explicit equation for the global rate can be written only for a first-order reaction at the catalyst surface.§ If we make the assumption of a first-order irreversible catalytic reaction, the rate per unit volume of bubble-free slurry may be written

$$r_v = k a_c C_s \quad \text{reaction at surface} \quad (10-33)$$

where a_c = external area of catalyst particles per unit volume of liquid (bubble free)

k = first-order rate constant

C_s = concentration of reactant (hydrogen) at the outer surface of the catalyst particle

The rates of the three mass-transfer processes may be expressed as

$$r_v = k_g a_g (C_g - C_{ig}) \quad \text{bulk gas to bubble interface} \quad (10-34)$$

$$r_v = k_L a_g (C_{il} - C_L) \quad \text{bubble interface to bulk liquid} \quad (10-35)$$

$$r_v = k_c a_c (C_L - C_s) \quad \text{bulk liquid to catalyst surface} \quad (10-36)$$

where a_g is the gas bubble-liquid interfacial area per unit volume of bubble-free liquid and k_g , k_L , and k_c are the appropriate mass-transfer coefficients. The various concentrations are shown schematically in Fig. 10-8 for a single bubble-

§ For hydrogenation reactions the low solubility of hydrogen usually means that it is the limiting component. Then first-order behavior is expected.

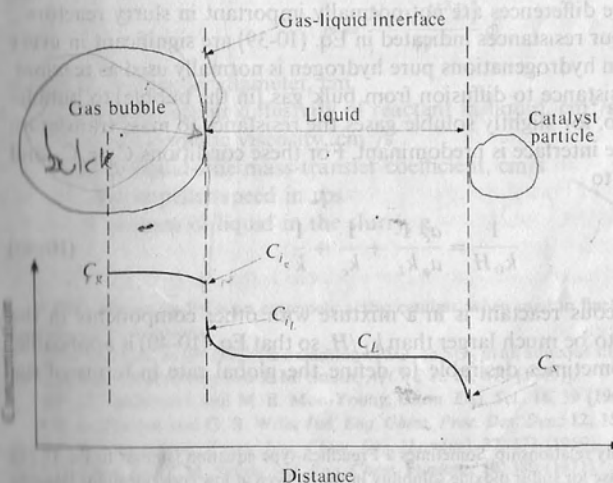


Figure 10-8 Concentration profiles in a slurry reactor.

particle combination. If equilibrium exists at the bubble-liquid interface, C_{ig} and C_{il} are related by Henry's law,[†]

$$C_{ig} = HC_{il} \quad (10-37)$$

These five equations can be combined to eliminate C_{ig} , C_{il} , C_L , and C_s . Then the rate can be expressed solely in terms of the concentration of reactant in the gas:

$$r_v = k_0 a_c C_g \quad (10-38)$$

and

$$\frac{1}{k_0} = \frac{a_c}{a_g} \frac{1}{k_g} + \frac{a_c}{a_g} \frac{H}{k_L} + H \left(\frac{1}{k_c} + \frac{1}{k} \right) \quad (10-39)$$

Equation (10-39) shows that the global k_0 is a function of the three mass-transfer coefficients, the specific reaction rate k , and the area ratio a_c/a_g . The rate will increase as this ratio falls, which corresponds to increasing the concentration of gas bubbles in the slurry. The rate is enhanced by increasing the concentration of catalyst particles in the slurry, because this increases a_c in Eq. (10-38). For low concentration of catalyst there is a sufficient supply of dissolved reactant for mass transfer to each particle to be independent of the number of particles. Under these circumstances the global rate is linear in catalyst concentration (particles per unit volume of reactor), since a_c in Eq. (10-38) is directly proportional to this concentration. As the catalyst concentration increases to higher values, there is competition between particles for reactant, and the rate ultimately approaches a constant upper limit.

The rate constant k is sensitive to temperature and, in principle, should be associated with the temperature of the catalyst particle. However, as mentioned, the catalyst temperature is essentially the same as that of the liquid. Hence, external temperature differences are not normally important in slurry reactors.

Not all of the four resistances indicated in Eq. (10-39) are significant in every case. For example, in hydrogenations pure hydrogen is normally used as reactant. Then there is no resistance to diffusion from bulk gas (in the bubble) to bubble-liquid interface. Also, for slightly soluble gases the resistance to mass transfer on the liquid side of the interface is predominant. For these conditions $C_g = C_{ig}$ and Eq. (10-39) reduces to

$$\frac{1}{k_0 H} = \frac{a_c}{a_g} \frac{1}{k_L} + \frac{1}{k_c} + \frac{1}{k} \quad (10-40)$$

Even when the gaseous reactant is in a mixture with other components in the bubbles, k_g appears to be much larger than k_L/H , so that Eq. (10-40) is applicable. In this case it is sometimes desirable to define the global rate in terms of the

[†] For a linear solubility relationship. Sometimes a Freundlich-type equation [similar to Eq. (7-21)] is indicated. This is the case for sulfur dioxide solubility in water, even at low concentrations [Hiroshi Komiyama and J. M. Smith, *AIChE J.*, **21**, 664 (1975)].

liquid-phase concentration in equilibrium with C_g , that is, $(C_L)_{eq}$. Since $C_{ig} = C_g = H(C_L)_{eq}$, Eq. (10-38) may be written

$$r_v = k_0 H a_c (C_L)_{eq} \quad (10-41)$$

where $k_0 H$ is given by Eq. (10-40).

If the catalyst is very active,[‡] k will be much greater than k_c or k_L/H . Then the global rate is determined by the mass-transfer coefficients k_L and k_c . In contrast, for some chemical systems and for common bubble and particle concentrations, all three rate coefficients, k_L , k_c , and k may be significant.[§] In any event, the important mass-transport parameters are k_L and k_c . Available data for these coefficients are summarized in Secs. 10-7 and 10-8.

10-7 Mass-Transfer Coefficients: Gas Bubble to Liquid (k_L)

Data for the coefficient k_g in Eq. (10-39) are meager. Fortunately, accurate values are seldom required. Even when the bubble is a gas mixture, the major resistance to transport for slightly soluble gases is in the liquid. Hence k_L is usually the important coefficient in gas bubble-to-liquid mass transfer. Several experimental studies and correlations^{§-§§} for k_L are available. Its value depends somewhat on the geometry of the reactor system (especially the dimensions of the stirrer and baffles) and the stirrer speed. In one correlation[†] these effects were accounted for in terms of a mild dependence on the energy dissipation rate using the following dimensional equation.

$$k_L = 0.592 \mathcal{D}_A^{1/2} (\sigma/W)^{1/4} \quad (10-42)$$

The energy dissipation rate σ per unit of mass of liquid [in erg/(s)(g)] is given by

$$\sigma = \frac{N_p \rho_L N^3 D_I^5}{W} \phi \quad (10-43)$$

where D_I = impeller diameter, cm

\mathcal{D}_A = molecular diffusivity of reactant in liquid, cm^2/s

ν = kinematic viscosity, cm^2/s

k_L = liquid-side mass-transfer coefficient, cm/s

N = impeller speed in rps

W = mass of liquid in the slurry, g

[†] For example, nickel is an extremely active catalyst, when used in finely divided form, for many hydrogenation reactions.

[‡] For example, in the catalytic oxidation of SO_2 to SO_3 in an aqueous slurry of activated carbon at 25°C [Hiroshi Komiyama and J. M. Smith, *AIChE J.*, **21**, 670 (1975)].

[§] P. H. Calderbank and M. B. Moo-Young, *Chem. Eng. Sci.*, **16**, 39 (1961).

^{§§} B. D. Prasher and G. B. Wills, *Ind. Eng. Chem. Proc. Des. Dev.*, **12**, 351 (1973).

^{††} P. H. Calderbank, *Trans. Inst. Chem. Eng. (London)*, **37**, 173 (1959).

^{†††} D. Misis and J. M. Smith, *Ind. Eng. Chem. Fundam.*, **10**, 380 (1971).

^{††††} V. A. Juvekar and M. M. Sharma, *Chem. Eng. Sci.*, **28**, 825 (1973).

N_p = power number, defined by the expression

$$N_p = \frac{P}{\rho_L N^3 D_i^5} \quad (10-44)$$

This number depends upon the design (number and size) of baffles, geometry of baffles and vessel, but frequently is about 10. P is the power input, erg/s.

ϕ = a correction factor ($0 < \phi < 1$) to account for the decrease in energy dissipation rate due to gas bubbles. For $Q/ND_i^3 < 0.035$, Calderbank gives†

$$\phi = 1 - 12.6Q/ND_i^3 \quad (10-45)$$

where Q is the gas flow rate (cm^3/s).

This method of correlation seems to account for variations in impeller speed, baffles, and impeller geometry but requires a measurement of the energy dissipation rate by determining the torque of the agitator.

In the absence of mechanical agitation and for bubbles whose diameter is less than 2.5 mm (the usual size range for slurry reactors), the following correlation is available

$$k_L \left(\frac{\mu_L}{\rho_L g} \right)^{2/3} = 0.31 \left(\frac{\Delta\rho \mu_L g}{\rho_L^2} \right)^{1/3} \quad (10-46)^\ddagger$$

where $\Delta\rho$ = difference in density between liquid phase and gas bubbles, $\text{g}/(\text{cm})^3$

μ_L = viscosity of liquid phase, $\text{g}/(\text{cm})(\text{s})$

g = acceleration of gravity, $\text{g}/(\text{s})^2$

ρ_L = density of liquid phase, $\text{g}/(\text{cm})^3$

k_L = mass-transfer coefficient, cm/s

This correlation is for bubbles rising through the liquid phase because of gravitational force. Equation (10-46) has been applied with apparent success to transport from bubbles to liquid in systems containing catalyst particles in slurry form.§

In the absence of gravitational force, mass transfer from a stagnant bubble would be by molecular diffusion through the surrounding stagnant liquid. Then the Sherwood number is $Sh = d_b k_1 / \mathcal{D} = 2$, where d_b is the diameter of the bubble. Other correlations have been developed by modifying this relation to include the effect of turbulence, in the liquid phase, induced by mechanical stirring or gravitational force. Hughmark¶ proposed this type of correlation for the Sherwood number when the turbulence was due to gravitational force. Both Eq. (10-46) and Hughmark's correlation are for column-type reactors, where gas bubbles rise through an appreciable height.

Example 10-6 One method of determining the gas bubble-to-liquid mass-transfer coefficients, k_L , is to introduce a step function of transferable component, A , in the gas stream fed to the slurry reactor (Fig. 10-7). The variation with time of the partial pressure p_L of the component in the effluent gas stream is a function of the rate and equilibrium properties of the system. If no catalyst particles are present, so that the gas bubbles rise through only the liquid, the p_L vs. time relation depends on k_L and the solubility of A .

- Derive an equation for the fraction, $(p_0 - p_L)/p_0$, of A removed from the gas bubbles as a function of t for a well-stirred liquid of height L . Assume that the gas bubbles, which contain a low concentration of A , do not coalesce and are in plug flow. Assume also that A is slightly soluble in the liquid and that its solubility follows Henry's law, $p = H_p C_L$.† In the time required for a bubble to move through the liquid the change in concentration of A in the bubble is large, but the change in concentration in the liquid is negligible. There is no liquid feed or effluent (batch liquid).
- This dynamic method was used‡ to determine k_L for the transfer of benzene from gas bubbles to water at 24°C atm one atmosphere pressure. At $t = 0$ the helium stream bubbling through the water was switched to a He-C₆H₆ stream. Then the concentration of benzene in the effluent gas was measured continuously as a function of time.

Experimental results for one run are given in Table 10-4. The ratio, V_B , (the gas holdup) is a key parameter and is obtained from the gas flow rate Q and the bubble velocity v_B . The total gas holdup in the liquid of volume V_L is

† Note that this definition of Henry's law is in terms of the partial pressure in the gas, not the concentration as in Eq. (10-37).

‡ D. M. Misic and J. M. Smith, op. cit.

Table 10-4 Absorption of benzene from gas bubbles into liquid water (24°C)

Time, min	$(p_0 - p_t)/p_0$
1.5	0.68
3.5	0.47
6.5	0.30
8.0	0.23
12	0.15
16	0.092
18	0.060
23	0.039
25	0.019
33	0.015
38	0.011

† P. H. Calderbank, *Trans. Inst. Chem. Eng.*, **36**, 443 (1958).

‡ P. H. Calderbank, *Trans. Inst. Chem. Engrs. (London)*, **37**, 173 (1959).

§ T. Matsuura, doctoral dissertation, Technische Universitat Berlin, Berlin, 1965.

¶ G. A. Hughmark, *Ind. Eng. Chem., Process Design Develop. Quart.*, **6**, 218 (1967).

$V_B V_L$. This total holdup is also equal to the product of the gas flow rate and the bubble residence time L/v_B :

$$V_B V_L = QL/v_B$$

or

$$V_B = \frac{QL}{v_B V_L}$$

For the given run, $V_L = 50 \text{ cm}^3$ ($50 \times 10^{-6} \text{ m}^3$) and $Q = 50.7 \text{ cm}^3/\text{min}$ ($8.45 \times 10^{-7} \text{ m}^3/\text{s}$). The vertical bubble velocity $V_B = 22.5 \text{ cm/s}$ (0.225 m/s). And $L = 6.0 \text{ cm}$ (0.06 m). The average bubble diameter was 1.8 mm ($1.8 \times 10^{-3} \text{ m}$). Calculate k_L for this run.

SOLUTION

A. For slightly soluble gas A , the concentration C_{iL} (see Fig. 10-7) at the bubble-liquid interface will be that in equilibrium with the pressure p_g in the bulk gas of the bubble. Hence, $C_{iL} = p_g/H_p$. Then Eq. (10-35) for the rate of mass transfer from gas bubble to liquid, per unit volume of bubble-free liquid is

$$r = k_L a_g \left(\frac{p_g}{H_p} - C_L \right) \quad (A)$$

A mass balance of A in the gas phase† according to Eq. (3-1), is

$$-v_B V_B \frac{1}{RT} \left(\frac{\partial p_g}{\partial z} \right) - r = \frac{\partial}{\partial t} \left(\frac{V_B p_g}{RT} \right) \quad (B)$$

The first term represents the net molal flux in and out of the volume element and the last term is the accumulation of A in the gas bubbles within the volume element. The vertical bubble velocity, v_B , and the volume of bubbles per unit volume of liquid, V_B , will be constant for dilute concentrations and small bubble sizes. Also the temperature does not vary. Since the liquid concentration does not change significantly with the residence time of the bubble, but the change in p_g is large, the accumulation term in Eq. (B) may be neglected. Then with Eq. (A) for r , we have

$$-\left(\frac{v_B V_B}{RT} \right) \frac{dp_g}{dz} = k_L a_g \left(\frac{p_g}{H_p} - C_L \right) \quad (C)$$

Since C_L is constant with respect to z (well-stirred liquid) Eq. (C) can be integrated from the bubble entrance, $z = 0$, $p_g = p_0$, to any liquid height z where the partial pressure is $p(z)$. The result is

$$p(z) = H_p C_L + (p_0 - H_p C_L) \exp \left[-\frac{k_L a_g RT z}{H_p V_B v_B} \right] \quad (D)$$

† In a volume element corresponding to a vessel height dz and unit cross-sectional area.

In order to express Eq. (D) in terms of time we need to know how the concentration of A in the liquid varies with time. To do this a mass balance is written for the total volume of bubble-free liquid. According to Eq. (3-1),

$$\frac{V_L}{L} \int_0^L k_L a_g \left(\frac{p(z)}{H_p} - C_L \right) dz = V_L \frac{\partial C_L}{\partial t} \quad (E)$$

The first term represents the total rate of mass transfer from gas bubble to liquid, and the second term is the accumulation of A in the liquid; where V_L is the total liquid volume. Substituting $p(z)$ from Eq. (D) in the left-hand side of Eq. (E), and integrating with respect to z , gives an expression for dC_L/dt as a function of C_L . This differential equation can be integrated from $C_L = 0$ at $t = 0$, to yield the following expression for $C_L(t)$

$$C_L(t) = \frac{p_0}{H} \left[1 - \exp \left\{ -k_L a_g \left(\frac{1 - e^{-\alpha}}{\alpha} \right) t \right\} \right] \quad (F)$$

where α is the dimensionless parameter

$$\alpha = \frac{k_L a_g RT L}{H_p V_B v_B} \quad (G)$$

To obtain p_L Eq. (D) is applied at $z = L$ with C_L expressed in terms of time using Eq. (F). The result may be rearranged to give an equation for the fraction of A removed from the gas bubbles by the liquid:

$$\frac{p_0 - p_L}{p_0} = (1 - e^{-\alpha}) \exp \left[-k_L a_g \frac{1 - e^{-\alpha}}{\alpha} t \right] \quad (H)$$

Equation (H) is the desired result; expressing $p_L(t)$ in terms of the solubility constant H_p and mass-transfer coefficient k_L .

B. Equation (H) suggests that p_L vs. time data plotted as $\ln[(p_0 - p_L)/p_0]$ vs. t should yield a straight line with a slope equal to

$$-k_L a_g (1 - e^{-\alpha})/\alpha.$$

Hence, from experimental data for $(p_0 - p_L)/p_0$ vs. t , a value of α can be determined. Then k_L is calculated from Eq. (G), provided H_p is known. The data plotted in this manner are shown in Fig. 10-9. The slope is $-2.8 \times 10^{-3} \text{ (s)}^{-1}$.

Solubility measurements† for C_6H_6 in water at 24°C gave $H_p = 4.85 \times 10^3 \text{ atm}(\text{cm}^3)/(\text{g mol})$ [$0.491 \text{ (kPa)}(\text{m}^3)/(\text{kg mol})$]. The ratio of interfacial area to bubble volume for the 1.8 mm bubbles is

$$\frac{a_g}{V_B} = \frac{\pi d_b^2}{\pi d_b^3/6} = 33.4 \text{ cm}^{-1} \quad (33.4 \times 10^2 \text{ m}^{-1})$$

† D. M. Misic and J. M. Smith, op. cit.

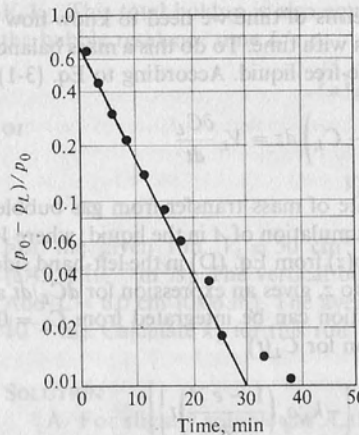


Figure 10-9 Fraction of benzene absorbed in water from helium-benzene gas bubbles.

The bubble volume itself is

$$\underline{V}_B = \frac{QL}{v_B V_L} = \frac{50.7(1/60)6.0}{22.5(50)} = 4.51 \times 10^{-3}$$

Then

$$a_g = 33.4(4.51 \times 10^{-3}) = 0.151 \text{ cm}^{-1} \quad (15.1 \text{ m}^{-1})$$

With these values, Eq. (G) gives for α

$$\alpha = \frac{0.151(82.05)(273 + 24)6.0}{4.85 \times 10^3(4.51 \times 10^{-3})(22.5)} k_L$$

$$= 44.9 k_L$$

From the known slope of the line in Fig. 10-9

$$\text{Slope} = -2.8 \times 10^{-3} = -\frac{k_L a_g (1 - e^{-\alpha})}{\alpha}$$

$$= -\frac{0.151 k_L (1 - e^{-44.9 k_L})}{44.9 k_L}$$

or

$$1 - e^{-44.9 k_L} = \frac{44.9(2.8 \times 10^{-3})}{0.151} = 0.833$$

$$k_L = 4.0 \times 10^{-2} \text{ cm/s} \quad (4.0 \times 10^{-4} \text{ m/s})$$

For comparison, from Eq. (10-46)

$$k_L = 0.31 \frac{[(1.0(0.01)980/1^2)]^{1/3}}{[(0.01/2 \times 10^{-5})]^{2/3}}$$

$$= 1.0 \times 10^{-2} \text{ cm/s} \quad (1.0 \times 10^{-4} \text{ m/s})$$

where the diffusivity of benzene in liquid water is estimated to be $2.0 \times 10^{-5} \text{ cm}^2/\text{s}$ ($2.0 \times 10^{-9} \text{ m}^2/\text{s}$). Equation (10-46) is based upon data in an unstirred liquid which may explain part of the difference between the two values. However, the difference also indicates the difficulty in obtaining accurate values of mass-transfer coefficients in difficult-to-characterize physical situations such as bubbles rising through a liquid phase.

10-8 Mass-Transfer Coefficients: Liquid to Particle (k_c)

The relative velocity between the particles and the liquid determines the extent to which convection increases the Sherwood number above that for stagnant conditions, i.e., above 2. As mentioned, this relative velocity is low in slurries, because the particles are so small that they tend to move with the liquid. In agitated slurries the relative velocity is due primarily to the shearing action induced by the agitator. The basis for correlating k_c as a function of agitation speed and particle size is Kolmogoroff's theory† of isotropic turbulence. According to this theory the Reynolds' number (Re) is defined in terms of the energy dissipation rate [see Eq. (10-43)]. If the eddy size ζ is greater than the particle diameter

$$\text{Re} = \left(\frac{\sigma d_p^4}{\nu^3} \right)^{1/2} \quad \zeta > d_p \quad (10-47)$$

† D. M. Levins and J. R. Glastonbury, *Chem. Eng. Sci.*, **27**, 537 (1972).

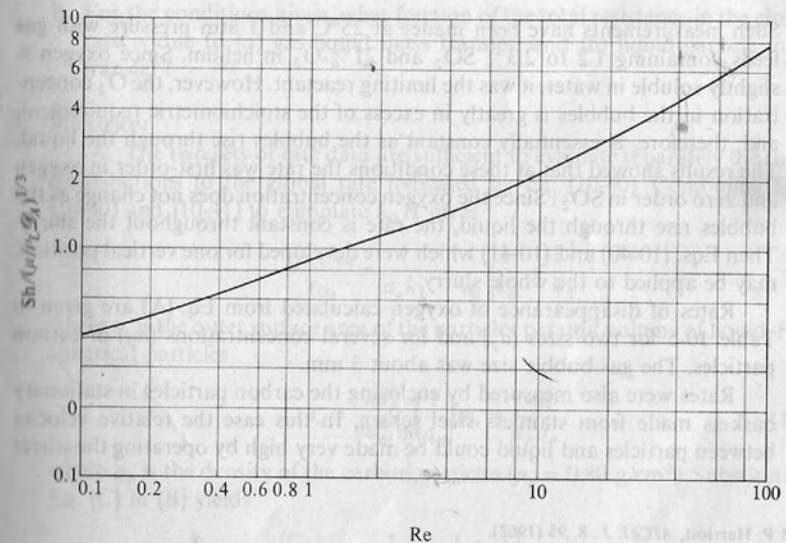


Figure 10-10 Correlation of fluid-particle mass-transfer coefficients in slurries.

or otherwise,

$$\text{Re} = \left(\frac{\sigma d_p^4}{\nu^3} \right)^{1/3} \quad \zeta < d_p \quad (10-48)$$

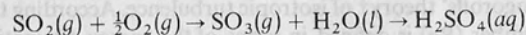
where ζ is a function of σ and the kinematic viscosity ν . Thus

$$\zeta = \left(\frac{\nu^3}{\sigma} \right)^{1/4} \quad (10-49)$$

The experimental data[†] for k_c are well correlated by plotting the Sherwood number ($k_c d_p / \mathcal{D}_A$) vs. the Reynolds number, defined by Eqs. (10-47) or (10-48). Figure 10-10 shows the results.

In three-phase slurries, both bubble-liquid and liquid-particle mass transfer can influence the global rate, as indicated in the following Example.

Example 10-7 The reaction



is catalyzed by activated carbon. Hence, it provides a means of studying mass transfer in a three-phase aqueous slurry of carbon particles. During the steady-state period the rates are calculated [Eq. (4-5)] from the measured concentrations of SO_2 in the gas streams entering (C_{g1}) and leaving (C_{g0}) the reactor. Thus, the rate of disappearance of oxygen is (Q = volumetric gas flow rate; V_L = volume of liquid):

$$\dot{r}_{\text{O}_2} = \frac{1}{2} \dot{r}_{\text{SO}_2} = \frac{1}{2} \frac{Q}{V_L} (C_{g1} - C_{g0})_{\text{SO}_2} \quad (\text{A})$$

Such measurements have been made[‡] at 25°C and 1 atm pressure with gas feeds containing 1.2 to 2.3% SO_2 and 21% O_2 in helium. Since oxygen is slightly soluble in water, it was the limiting reactant. However, the O_2 concentration in the bubbles is greatly in excess of the stoichiometric requirement, and, therefore, is essentially constant as the bubbles rise through the liquid. The results showed that at these conditions the rate was first-order in oxygen and zero order in SO_2 . Since the oxygen concentration does not change as the bubbles rise through the liquid, the rate is constant throughout the slurry. Then Eqs. (10-40) and (10-41) which were developed for one vertical position, may be applied to the whole slurry.

Rates of disappearance of oxygen calculated from Eq. (A) are given in Table 10-5 for two sizes (d_p) and for several concentrations (m_s) of carbon particles. The gas bubble size was about 3 mm.

Rates were also measured by enclosing the carbon particles in stationary baskets made from stainless steel screen. In this case the relative velocity between particles and liquid could be made very high by operating the stirrer

Table 10-5 Rates of SO_2 oxidation in aqueous slurries of activated carbon at 25°C

Carbon particle size, d_p , mm	Particle concentration, m_s , g/(cm ³ of water)	Rate, $r_{\text{O}_2} \times 10^9$, mol/(s)(cm ³ of liquid)
0.099	0.0131	8.4
0.099	0.00560	4.22
0.099	0.00222	1.78
0.030	0.0370	21.0
0.030	0.0111	10.4
0.030	0.00560	7.44
0.030	0.00278	4.11
0.030	0.00139	2.33

at a high speed. Under these conditions the resistance to mass transfer between liquid and particle approaches zero. For $m_s = 0.0333$ g/(cm³ of water) and for $d_p = 0.542$ mm, the rates without and with particles held in the baskets were:

$$\dot{r}_{\text{O}_2} = 5.05 \times 10^{-9} \text{ g mol/(s)(cm}^3 \text{ of water)} \quad (\text{no baskets})$$

$$\dot{r}_{\text{O}_{2,b}} = 6.08 \times 10^{-9} \text{ g mol/(s)(cm}^3 \text{ of water)} \quad (\text{particles in baskets})$$

- Calculate the mass-transfer coefficients k_L and k_c .
- For the conditions given, what fraction of the total resistance in the global rate is due to (a) gas-liquid mass transfer, and (b) liquid-particle mass transfer?

SOLUTION

A. The two sets of rate data are sufficient to evaluate separately the three contributions to the global rate indicated by Eq. (10-40). Combining Eqs. (10-40) and (10-41) to eliminate $k_0 H$ gives

$$\frac{(C_L)_{\text{eq}}}{r_{\text{O}_2}} = \frac{1}{a_g k_L} + \frac{1}{a_c} \left[\frac{1}{k_c} + \frac{1}{k} \right] \quad (\text{B})$$

where a_c is the outer surface area of the particles per unit volume of liquid. For spherical particles

$$a_c = \frac{\pi d_p^2}{\pi d_p^3 / 6} \left(\frac{1}{\rho_p} \right) m_s = \frac{6m_s}{d_p \rho_p} \quad (\text{C})$$

where ρ_p is the density of the carbon particles ($\rho_p = 0.80$ g/cm³). Substituting Eq. (C) in (B) yields

$$\frac{(C_L)_{\text{eq}}}{r_{\text{O}_2}} = \frac{1}{a_g k_L} + \frac{d_p \rho_p}{6m_s} \left[\frac{1}{k_c} + \frac{1}{k} \right] \quad (\text{D})$$

[†] P. Harriott, *AIChE J.*, **8**, 93 (1962).

[‡] P. L. T. Brian, H. B. Hales, and T. K. Sherwood, *AIChE J.*, **15**, 419, 727 (1969).

[§] Hiroshi Komiyama and J. M. Smith, *AIChE J.*, **21**, 670 (1975).

Since $(C_g)_{O_2}$ is constant, r_{O_2} is the same throughout the slurry. Hence, Eqs. (10-40) and (D), which were derived for a fixed position in the slurry, are applicable throughout the liquid. Henry's law constant for oxygen in water at 25°C is $H = 35.4$ [g mol/(cm³ of gas)]/[g mol/cm³ of liquid]. Then

$$(C_L)_{eq} = \left(\frac{C_g}{H}\right)_{O_2} = \frac{0.21}{(82)(298)(35.4)} = 2.43 \times 10^{-7} \text{ g mol/cm}^3$$

Equation (D) indicates that a plot of $1/r_{O_2}$ vs. $1/m_s$ for constant $(C_L)_{eq}$ and d_p should be a straight line with an intercept equal to $1/[(C_L)_{eq} a_g k_L]$. As Fig. 10-11 shows, the data in Table 10-5 when so plotted do establish straight lines with an intercept of about 3.6×10^7 (cm³(s))/(g mol). Then from Eq. (D)

$$\left(\frac{1}{r_{O_2}}\right)_{\text{intercept}} = 3.6 \times 10^7 = [a_g k_L (C_L)_{eq}]^{-1} \quad (E)$$

For spherical bubbles of diameter d_b

$$a_g = \frac{\pi d_b^2}{\pi d_b^3/6} V_B = \frac{6}{d_b} V_B \quad (10-50)$$

where V_B is the gas holdup, as bubble volume per unit volume of liquid. Holdup measurements (measuring the increase in volume when gas is

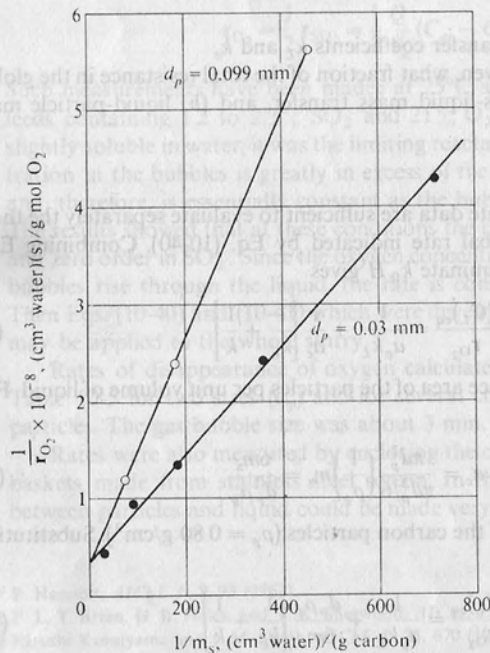


Figure 10-11.

bubbled through the slurry) gave $V_B = 0.070$ cm³ gas/(cm³ of liquid). Hence

$$a_g = \frac{6}{0.3} (0.07) = 1.4 \text{ cm}^{-1}$$

Substituting the values of $(C_L)_{eq}$ and a_g in Eq. (E) gives

$$k_L = \frac{1}{(3.6 \times 10^7)(2.43 \times 10^{-7})1.4} = 0.08 \text{ cm/s}$$

The rate (r_{O_2}) values for runs in which the particles were stationary (held in baskets) can be used to evaluate the liquid-to-particle coefficient k_c . If $k_c a_c$, in Eq. (D), is very high when the particles were held in baskets,

$$\frac{(C_L)_{eq}}{r_{O_2,b}} = \frac{1}{a_g k_L} + \frac{d_p \rho_p}{6m_s} \left(\frac{1}{k_c}\right) \quad (F)$$

With the particles free to move, Eq. (B) is applicable. Subtracting Eq. (F) from (B) yields

$$(C_L)_{eq} \left(\frac{1}{r_{O_2}} - \frac{1}{r_{O_2,b}}\right) = \frac{d_p \rho_p}{6m_s} \left(\frac{1}{k_c}\right) \quad (G)$$

Using the rate data for the $d_p = 0.542$ mm particles, Eq. (G) gives

$$\begin{aligned} \frac{1}{k_c} &= \frac{6m_s(C_L)_{eq}}{d_p \rho_p} \left(\frac{1}{r_{O_2}} - \frac{1}{r_{O_2,b}}\right) \\ &= \frac{6(0.0167)(2.43 \times 10^{-7})}{0.0542(0.80)} \left(\frac{1}{5.05 \times 10^{-9}} - \frac{1}{6.08 \times 10^{-9}}\right) \\ &= 37 \text{ s/cm} \end{aligned}$$

or

$$k_c = 0.027 \text{ cm/s}$$

For comparison, an estimate can be made of k_c from Fig. 10-10. For the particular bubble and stirrer arrangement used by Komiyama† the power number was 9.5 [from Eq. (10-44)]. Then σ calculated from Eq. (10-43) was 2.43×10^4 erg/(s)(g); ϕ was 0.67. From Eq. (10-49) $\zeta = 0.024$ mm. Since $\zeta < d_p$, the Reynolds number is given by Eq. (10-48).

$$Re = \left[\frac{2.43 \times 10^4 (0.0542)^4}{(0.01)^3} \right]^{1/3} = 58$$

From Fig. 10-10

$$Sh = \frac{k_c d_p}{\mathcal{D}_A} = 5.6 \left(\frac{\mu_L}{\rho_L \mathcal{D}_A} \right)^{1/3}$$

† Op. cit.

The diffusivity of oxygen in liquid water at 25°C is about 2.6×10^{-5} cm²/s, which corresponds to a Schmidt number, $\mu_L/\rho_L \mathcal{D}_A$, of about 340.

Then

$$k_c = 5.6(340)^{1/3} \frac{2.6 \times 10^{-5}}{0.0542} = 0.019 \text{ cm/s}$$

which is reasonably close to the value of 0.027 cm/s obtained from the rate data.

B. The resistances to the global rate can be estimated from the values of the three terms in Eq. (D). If it is assumed that the particle size does not affect bubble-to-liquid transport (as indicated by the common intercept in Fig. 10-11) the first term is (from Part A)

$$\frac{1}{a_g k_L} = \frac{1}{1.4(0.08)} = 8.9 \text{ s}$$

The liquid-to-particle resistance is

$$\frac{d_p \rho_p}{6m_s} \left(\frac{1}{k_c} \right) = \frac{0.0542(0.80)}{6(0.0333)(0.027)} = 8.0 \text{ s}$$

The reaction resistance is obtained from the rate and Eq. (D):

$$\begin{aligned} \frac{d_p \rho_p}{6m_s} \left(\frac{1}{k} \right) &= \frac{(C_L)_{eq}}{r_{O_2}} - 8.9 - 8.0 \\ &= \frac{2.43 \times 10^{-7}}{5.05 \times 10^{-9}} - 8.9 - 8.0 = 31.2 \text{ s} \end{aligned}$$

Hence, the fractional resistances are: mass transfer, bubble-to-liquid = $(8.9/48.1) \times 100 = 18\%$, mass transfer, liquid-to-particle = $(8.0/48.1) \times 100 = 17\%$, reaction resistance = $(31.2/48.1) \times 100 = 65\%$.

10-9 The Effect of Mass Transfer on Observed Rates

Equation (10-40) shows that the relative importance of diffusion resistances from bubbles to bulk liquid and from liquid to catalyst particle depends on the area ratio. If a large concentration of very small particles is used, a_c/a_g is so large that only the first term is important. Then Eq. (10-40) reduces to

$$\frac{1}{k_o H} = \frac{a_c}{a_g k_L}$$

and the rate is, according to Eq. (10-41)

$$r_v = k_L a_g (C_L)_{eq} \quad (10-51)$$

Calderbank et al.[†] studied the hydrogenation of ethylene using a large concentration of Raney nickel particles in a slurry reactor in order to approach these

conditions. Analysis of the data[†] indicated that the controlling step was the mass transfer of hydrogen from gas bubble to bulk liquid.

Equation (10-51) indicates that the important parameters for this case are k_L and the gas-liquid interfacial area a_g . The latter depends on the size and concentration of bubbles in the slurry. Alternately, it may be expressed in terms of the bubble diameter and gas holdup by Eq. (10-50) (see Example 10-7).

Koide et al.[‡] give the following equation for the diameter of bubbles formed over a porous plate:

$$d_b = 1.35 \frac{u/g \delta}{(\delta u^2 \rho_L / \sigma_L)^{1/2}} \left(\frac{\sigma_L \delta}{g \rho_L} \right)^{1/3} \quad (10-52)$$

where d_b = bubble diameter, cm

u = gas velocity through the porous plate

δ = pore diameter of porous plate

σ_L = surface tension of liquid

ρ_L = density of liquid

Massimilla, Calderbank, and others also have reported experimental data on bubble sizes.[§]

At the other extreme, a large concentration of small gas bubbles (large a_g') might be combined with a low concentration of relatively large active catalyst[¶] particles (low a_c) and poor agitation (low k_c). Then Eq. (10-40) reduces to

$$\frac{1}{k_o H} = \frac{1}{k_c} + \frac{1}{k} \approx \frac{1}{k_c} \quad \text{for very active catalyst} \quad (10-53)$$

The rate is, from Eq. (10-41),

$$r_v = k_c a_c (C_L)_{eq} \quad (10-54)$$

Here the surface area of the catalyst particles is of primary importance, along with k_c . For spherical particles a_c is given by Eq. (C) of Example (10-7); that is,

$$a_c = \frac{6m_s}{d_p \rho_p} \quad (10-55)$$

Under many conditions a_c/a_g would be greater than unity. This follows from the fact that bubble diameters will be of the order of 1 mm, while catalyst particles will be in the order of 0.1 mm (100 microns or 140 mesh). Then for spherical shapes a_c/a_g would be equal to $d_b/d_p = 10$, for equal volumes of bubbles and particles in the slurry. If the gas holdup were 10 times larger than the catalyst volume, a_c/a_g would be reduced to unity, but this ratio of volumes is infrequent. For example, consider the conditions of Example 10-7. For $m_s = 0.0333$ g/cm³ and

[†] D. MacRae, doctoral dissertation, University of Edinburgh, Edinburgh, 1956.

[‡] K. T. Koide, T. Hirahara, and H. Kubata, *Chem. Eng. (Japan)*, **30**, 712 (1966).

[§] L. Massimilla, A. Solimando, and E. Squillace, *Brit. Chem. Eng.*, **6**, 232 (1961); P. H. Calderbank, F. Evans, and J. Rennie, *Proc. Intern. Symp. Distn., Suppl. Trans. Inst. Chem. Engrs. (London)*, p. 51 (1960).

[†] P. H. Calderbank, F. Evans, R. Farley, G. Jepson, and A. Poll, "Proceedings of a Symposium on Catalysis in Practice," p. 66, Institution of Chemical Engineers (London), 1963.

$d_p = 0.0542$ mm, which are very large particles for a slurry, Eqs. (10-50) and (10-55) give

$$\frac{a_c}{a_g} = \frac{m_s/d_p \rho_p}{V_B/d_b} = \frac{0.0333/0.0542(0.8)}{0.07/0.3} = 3.3$$

Except for large particles at low concentrations (low m_s), the effect of k_L on the global rate will be greater than that of k_c . The relative importance of the total mass-transfer process, from gas bubble to particle, on the global rate also will depend on the intrinsic rate, as illustrated in Example 10-8.

Example 10-8 Coenan† has reported rates of hydrogenation of sesame seed oil with a nickel-on-silica catalyst in a slurry reactor. Hydrogen was added at the bottom of a small cylindrical vessel equipped with stator and stirrer blades. Initial rates of reaction were measured as function of catalyst concentration at 180°C, a stirrer speed of 750 rpm, atmospheric pressure, and a hydrogen rate of 60 liters/h. The data, converted to global rates in terms of g mol/(min)(cm³ oil), are given in Table 10-6 (based on an oil density of 0.9 g/cm³). Estimate $k_L a_g/H$ from these data. Comment on the importance of the resistance of hydrogen to solution in the oil and estimate what the reaction rate would be if this resistance could be eliminated for a catalyst concentration of 0.07% Ni in oil.

SOLUTION Equation (10-40) is applicable. Combining it with Eq. (10-38) gives

$$r_v = \frac{a_c C_g}{H[(a_c/a_g)(1/k_L) + 1/k_c + 1/k]} = \frac{C_g}{H[(1/a_g k_L) + (1/a_c)(1/k_c + 1/k)]} \quad (A)$$

Since the gas rate and stirrer speed are constant, k_c , k_L , and a_g will not vary from run to run. Because the temperature is constant, k will also be invariant. The catalyst consists of small particles of silica containing nickel, and its concentration is changed by adding more such particles. The activity per particle is constant. If we assume that the particles do not agglomerate, a_c will

† J. W. E. Coenan, The Mechanism of the Selective Hydrogenation of Fatty Oils, in J. H. deBoer (ed.), "The Mechanism of Heterogeneous Catalysis," p. 126. Elsevier Publishing Company, New York, 1960.

Table 10-6

Catalyst particle concn, % Ni in oil	$r_v \times 10^5$	C_g/r_v , min
0.018	5.2	0.52
0.038	8.5	0.32
0.07	10.0	0.27
0.14	12.0	0.22
0.28	13.6	0.20
1.0	14.6	0.18

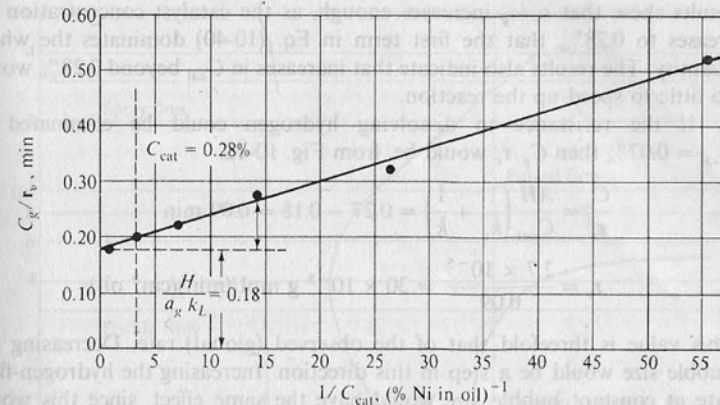


Figure 10-12 Effect of catalyst concentration on rate in a slurry reactor.

be directly proportional to the catalyst concentration, and Eq. (A) may be written

$$\frac{C_g}{r_v} = \frac{H}{a_g k_L} + \frac{AH}{C_{cat}} \left(\frac{1}{k_c} + \frac{1}{k} \right) \quad (B)$$

where A is the proportionality constant. This expression suggests that the data plotted as C_g/r_v vs. $1/C_{cat}$ would yield a straight line. Assuming the ideal-gas law, we have

$$C_g = \frac{p}{R_g T} = \frac{1}{82(273 + 180)} = 2.7 \times 10^{-5} \text{ g mol/cm}^3$$

The data in Table 10-6, when plotted in this way (Fig. 10-12), do yield a linear result. Extrapolation to $1/C_{cat} = 0$ gives an intercept value of 0.18 min. According to Eq. (B),

$$0.18 = \frac{H}{a_g k_L}$$

or

$$\frac{k_L a_g}{H} = 5.7 \text{ min}^{-1}$$

In Fig. 10-12 the resistance to solution of hydrogen in the slurry is represented by the horizontal dashed line. The total resistance is the ordinate of the solid line. At low catalyst concentration the combined resistance of diffusion to the particle and chemical reaction on the catalytic surface is large, although it does not determine the rate by itself. At high concentrations the resistance to transfer of hydrogen from bubble to the bulk liquid dominates the rate. In fact at $C_{cat} = 0.28\%$, $0.18/0.20$, or 90% , of the total resistance is for this step. The

results show that a_c/a_g increases enough, as the catalyst concentration increases to 0.28%, that the first term in Eq. (10-40) dominates the whole quantity. The results also indicate that increases in C_{cat} beyond 0.28% would do little to speed up the reaction.

If the resistance to dissolving hydrogen could be eliminated at $C_{\text{cat}} = 0.07\%$ then C_g/r_v would be, from Fig. 10-12,

$$\frac{C_g}{r_v} = \frac{AH}{C_{\text{cat}}} \left(\frac{1}{k_c} + \frac{1}{k} \right) = 0.27 - 0.18 = 0.09 \text{ min}$$

$$r_v = \frac{2.7 \times 10^{-5}}{0.09} = 30 \times 10^{-5} \text{ g mol/(min)(cm}^3 \text{ oil)}$$

This value is threefold that of the observed (global) rate. Decreasing the bubble size would be a step in this direction. Increasing the hydrogen-flow rate at constant bubble size would have the same effect, since this would increase gas volume and a_g . Better agitation would also reduce the bubble-to-liquid resistance.

TRICKLE-BED REACTORS†

In downflow of liquid and gas over a fixed bed of catalyst particles (see Figs. 1-6b and 10-16), the nature of the flow depends in a complex way upon the liquid and gas flow rates. Figure 10-13 shows approximate boundaries for the different flow regimes. At low liquid and gas mass velocities the gas phase is continuous and the liquid falls in rivulets from one particle to the next (trickle-flow regime). At high liquid rates and low gas rates the liquid phase is continuous and the gas moves in bubbles (dispersed-bubble regime). With very high gas rates and low liquid rates, the liquid falls in droplets through the gas (spray regime). Finally, with high rates of both liquid and gas, the two phases fall in slugs (pulsed-flow regime). The boundary curves in Fig. 10-13 are approximate and more detailed information and discussion about factors that affect flow behavior have been published.‡-††

Mass-transfer rates are available primarily in the trickle-flow regime and our discussion is limited to this region. For trickle flow the concentration profile for a reactant in the gas phase is sketched in Fig. 10-14. This profile is similar to that in Fig. 10-8 for a slurry reactor. However, in Fig. 10-14 a small part of the particle (labeled gas-covered) is shown without a liquid rivulet. Reaction studies in trickle

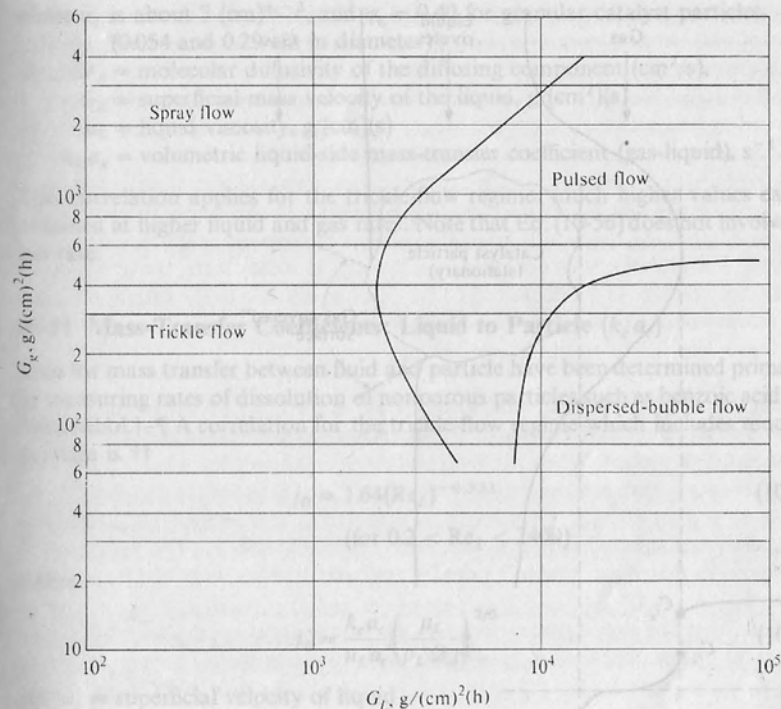


Figure 10-13 Flow regimes in trickle-bed reactors (cocurrent downflow).

beds have demonstrated that such surfaces exist‡ at low liquid rates. On this surface there would be much less mass-transfer resistance for a gaseous reactant. Accounting for the effect of "gas-covered" surface complicates the design of trickle beds. Here and in Chap. 13 it will be supposed that the liquid flow rate is sufficient to cover all of the outer surface. In Secs. 10-10 to 10-12 that follow, we examine mass-transfer effects. Then in Chap. 13 the objective is to combine these transport resistances with the intrinsic rate, and a reactor model, to predict the conversion in the whole reactor.

In trickle beds the external mass-transfer limitations are determined by the two volumetric coefficients: gas-to-liquid, $k_L a_g$, and liquid-to-particle, $k_c a_c$. The areas a_g , a_c refer to the effective mass-transfer surface per unit volume of empty reactor. Since they are difficult to determine experimentally correlations are normally reported in terms of the products $k_L a_g$ or $k_c a_c$.

† For reviews of literature on trickle-bed reactors see: Satterfield, C. N., *AIChE J.*, **21**, 209 (1975); S. Goto, J. Levec, and J. M. Smith, *Cat. Rev.—Sci. Eng.*, **15**, 187 (1977); Y. T. Shah, "Gas-Liquid-Solid Reactor Design," pp. 180-229, McGraw-Hill Book Company, New York, 1979.

‡ E. Talmor, *AIChE J.*, **23**, 868 (1977).

§ Y. T. Sato, H. Hirose, F. Takahashi, M. Toda, and Y. Hashiguchi, *J. Chem. Eng. (Japan)*, **6**, 315 (1973).

¶ J. C. Charpentier and M. Favier, *AIChE J.*, **21**, 1213 (1975).

†† T. S. Chou, F. L. Worley, Jr., and D. Luss, *Ind. Eng. Chem. Proc. Des. Dev.*, **16**, 424 (1977).

‡ M. Herskowitz, R. G. Carbonell, and J. M. Smith, *AIChE J.*, **25**, 272 (1979).

§ W. Sedriks and C. N. Kenny, *Chem. Eng. Sci.*, **28**, 559 (1973).

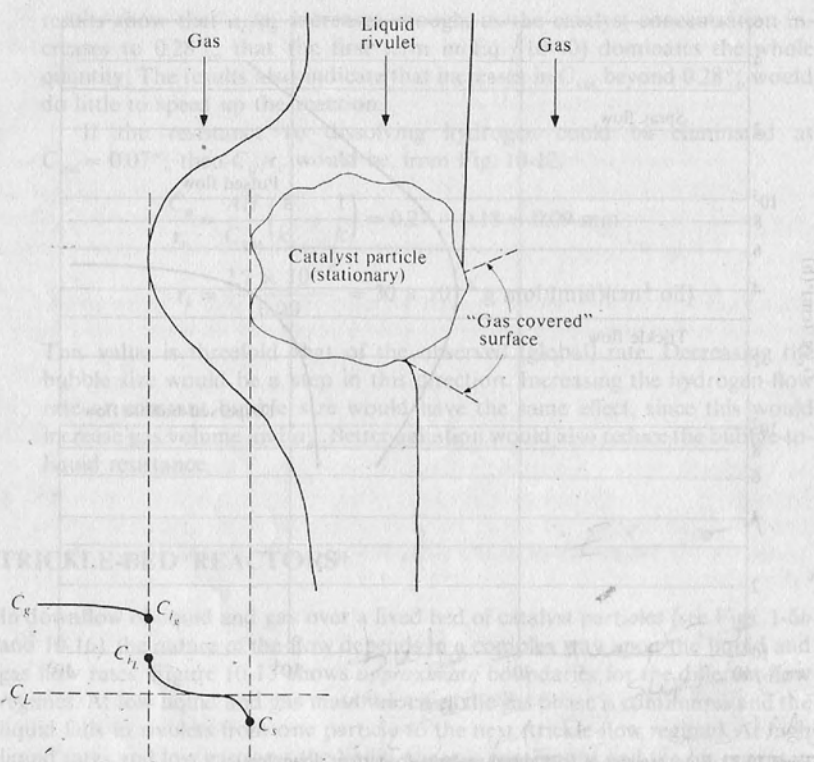


Figure 10-14 Concentration profiles in a trickle-bed reactor (trickle-flow regime).

10-10 Mass-Transfer Coefficients: Gas to Liquid ($k_L a_g$)

In trickle beds the gas phase is often either a nearly pure component (e.g., hydrogenations) or a slightly soluble gas (oxidations). Hence, the most important coefficient for gas-liquid transport is the liquid side value $k_L a_g$. However, correlations are available for the gas-side coefficient $k_g a_g$.^{† ‡ §}

Two types of correlations have been used for $k_L a_g$: one^{† ‡ ¶} relates $k_L a_g$ to the pressure drop for two-phase flow in the reactor, and the other is in terms of the flow velocities. Illustrative of the latter type is the *dimensional* equation^{††}

$$\frac{k_L a_g}{\mathcal{D}_A} = \alpha_L \left(\frac{G_L}{\mu_L} \right)^{\eta_L} \left(\frac{\mu_L}{\rho_L \mathcal{D}_A} \right)^{1/2} \quad (10-56)$$

[†] L. P. Reiss, *Ind. Eng. Chem. Proc. Des. Dev.*, **6**, 486 (1967).

[‡] A. Gianetto, V. Specchia, and G. Baldi, *AIChE J.*, **19**, 916 (1973).

[§] S. Goto, J. Levec, and J. M. Smith, *Ind. Eng. Chem. Proc. Des. Dev.*, **14**, 473 (1975).

[¶] J. C. Charpentier, *Chem. Eng. J.*, **11**, 161 (1976).

^{††} S. Goto and J. M. Smith, *AIChE J.*, **21**, 706 (1975).

where α_L is about $7 \text{ (cm)}^{\eta_L-2}$, and $\eta_L = 0.40$ for granular catalyst particles (0.054 and 0.29 cm in diameter)

\mathcal{D}_A = molecular diffusivity of the diffusing component (cm^2/s),

G_L = superficial mass velocity of the liquid, $\text{g}/(\text{cm}^2)(\text{s})$

μ_L = liquid viscosity, $\text{g}/(\text{cm})(\text{s})$

$k_L a_g$ = volumetric liquid-side mass-transfer coefficient (gas-liquid), s^{-1}

This correlation applies for the trickle-flow regime; much higher values can be obtained at higher liquid and gas rates. Note that Eq. (10-56) does not involve the gas rate.

10-11 Mass-Transfer Coefficients: Liquid to Particle ($k_c a_c$)

Data for mass transfer between fluid and particle have been determined primarily by measuring rates of dissolution of nonporous particles such as benzoic acid and β -naphthol.^{†-¶} A correlation for the trickle-flow regime which includes much of the data is ^{††}

$$j_D = 1.64(\text{Re}_L)^{-0.331} \quad (10-57)$$

(for $0.2 < \text{Re}_L < 2400$)

where

$$j_D = \frac{k_c a_c}{u_L a_t} \left(\frac{\mu_L}{\rho_L \mathcal{D}_A} \right)^{2/3} \quad (10-58)$$

and u_L = superficial velocity of liquid

a_t = total external area of particles per unit volume of reactor

$\text{Re}_L = (d_p u_L \rho_L / \mu_L)$

Satterfield et al.^{†††} has obtained data and proposed correlations for $k_c a_c$ for both the trickle- and pulse-flow regimes. In agreement with Eq. (10-57), their results for trickle-flow were nearly independent of gas flow rate.

10-12 Calculation of Global Rate

In Sec. 10-8 (e.g., Example 10-7 involving a slurry reactor) a method was illustrated for extracting mass-transfer coefficients and the intrinsic reaction rate from laboratory data. In the present section we examine the reverse process for a trickle-bed reactor. That is, we want to calculate what is occurring at a particular location in a trickle-bed from intrinsic kinetics and mass-transfer coefficients. The concept of a *global* rate is not particularly helpful in reactor design when there are

[†] D. W. van Krevelan and J. T. C. Krekels, *Rec. Trav. Chim.*, **67**, 512 (1948).

[‡] Y. Sato, T. Hirose, F. Takahashi, and M. Toda, *PACHEC*, Paper 8.3, p. 1187 (1972).

[§] T. Hirose, M. Toda, and Y. Sato, *J. Chem. Eng. (Japan)*, **7**, 187 (1974).

[¶] S. Goto, J. Levec, and J. M. Smith, *Ind. Eng. Chem. Proc. Des. Dev.*, **14**, 473 (1975).

^{††} A. Dharwadkar and N. D. Sylvester, *AIChE J.*, **23**, 376 (1977).

^{†††} C. N. Satterfield, M. W. van Eek, and G. S. Bliss, *AIChE J.*, **24**, 709 (1978).

two or more phases in continuous flow. This is because a global rate expressed in terms of bulk properties of one phase does not describe what is occurring in other moving phases. For design, it is most direct to write conservation equations for each flowing phase and this procedure, which does not involve the global rate, is followed in Chap. 13 for trickle-bed reactors. However, in a trickle-bed where the liquid completely covers the catalyst particles, a global rate can be evaluated in terms of bulk liquid properties. This rate may be compared with the mass-transfer rate between gas and liquid streams. It is helpful to do this since the comparison tells us whether the reactant is being depleted or augmented in the liquid and gas streams. The global rate is obtained by equating, at steady state, the rate of mass transfer of reactant from the liquid to the catalyst particle to the rate of reaction. For a unit volume of reactor the equality may be written

$$r_v = (k_c a_c)(C_L - C_s) = \rho_B r(C_s, T_s) \quad (10-59)$$

where C_L is the bulk concentration in the liquid and $r(C_s, T_s)$ is the intrinsic rate,† per unit mass of catalyst, evaluated at the reactant concentration and temperature at the catalyst surface. When the temperature T_s is known (or when T_b is known and there is no heat-transfer resistance so that $T_s = T_b$) as well as C_L , Eq. (10-59) can be solved for C_s . Then this result, substituted in the function $r(C_s, T_s)$, gives the global rate corresponding to the bulk values C_L and T_b . The procedure is analogous to that illustrated in Examples 10-2 and 10-4 for fixed-bed (two-phase) reactors.

Note that the global rate is obtained without considering the gas phase. This is because the assumption is made that the liquid completely covers the outer surface of the particle. No reaction can occur without transfer of reactant from liquid to particle. In order to evaluate the transfer rate of a gaseous reactant from gas to liquid, mass-transfer coefficient ($k_L a_g$) would be necessary, as indicated in Example 10-9, part B.

In Example 10-9, part A, the global rate is calculated for a system in which one reactant can exist in both gas and liquid phases while the other is only in the liquid. The kinetics are not first order but of the Langmuir-Hinshelwood form.

Example 10-9 The oxidation of dilute aqueous solutions of acetic acid was studied‡ in a trickle-bed reactor using a commercial, iron oxide catalyst. Air and solutions of acetic acid saturated with oxygen (by bubbling air through the solution at atmospheric pressure) flowed at 252°C and 67 atm downward over 0.0541 cm catalyst particles (packed to a depth of 2.2 cm) in a 2.54 cm ID reactor. The flow rates are $Q_L = 0.66 \text{ cm}^3/\text{s}$ and $Q_g = 3.5 \text{ cm}^3/\text{s}$. At the reactor entrance the concentration C_{L, O_2} of oxygen in the liquid is $2.40 \times 10^{-7} \text{ g mol/cm}^3$, that for acetic acid is $C_{L, HA} = 33.7 \times 10^{-7} \text{ g mol/cm}^3$, and the gas is air, saturated with water at 252°C. The bulk density of the catalyst bed is $\rho_B = 1.17 \text{ g/cm}^3$, while the particle density is, $\rho_p = 2.05 \text{ g/cm}^3$.

† For first-order kinetics, $r(C_s, T_s) = k(T_s)C_s$.

‡ Janez Levec and J. M. Smith, *AIChE J.*, **22**, 159 (1976).

For the reaction, $\text{CH}_3\text{COOH}(aq) + 2\text{O}_2(aq) \rightarrow 2\text{CO}_2(aq) + 2\text{H}_2\text{O}$, the intrinsic rate for the disappearance of oxygen is given by

$$r_{O_2}(\text{g mol}/(\text{g catalyst})(\text{s})) = \frac{9.9 \times 10^9 [\exp(-21,000/R_g T)] C_{s, HA} C_{s, O_2}^{1/2}}{1 + 7.2 \times 10^5 C_{s, HA}} \quad (\text{A})$$

where the concentrations are those at the outer surface of the catalyst particle and T is given in degrees Kelvin. Henry's law constant for oxygen in liquid water at 252°C is 0.89 [g mol/(cm³ gas at 25°C, 1 atm)]/[g mol/cm³ liquid]. Other physical properties at 252°C and 67 atm for liquid water are estimated to be:

$$\rho_L = 0.81 \text{ g/cm}^3$$

$$\mu_L = 1.18 \times 10^{-3} \text{ g/(cm)(s)}$$

$$(\mathcal{D}_{O_2}) = 2.1 \times 10^{-4} \text{ cm}^2/\text{s}$$

$$(\mathcal{D}_{HA})_L = 1.2 \times 10^{-4} \text{ cm}^2/\text{s}$$

- From this information calculate the global rate at the reactor entrance.
- Also calculate the rate of mass transfer of oxygen from the gas to the liquid.

SOLUTION The reaction occurs by oxygen and acetic acid in the liquid diffusing to the catalyst particles and reacting. Simultaneously, oxygen (but not nonvolatile acetic acid) is transferred from the air stream to replenish the oxygen in the liquid. Since oxygen is but slightly soluble in water, the overall transfer from gas to liquid may be safely assumed to be governed by the liquid-side coefficient $(k_L a_g)_{O_2}$. Then the rate of oxygen transfer, per unit volume of reactor, from gas to liquid is

$$N_{O_2} \left[\frac{\text{g mol}}{(\text{s})(\text{cm}^3)} \right] = (k_L a_g)_{O_2} (C_{g, O_2}/H - C_{L, O_2}) \quad (\text{B})$$

The concentration difference in this expression is large since C_{L, O_2} in the feed corresponds to saturation with air at atmospheric pressure, while C_{g, O_2} in the feed is for air at 67 atm.

Similarly, the rate of oxygen and acetic acid transfer from liquid to particle are given by the expressions

$$(r_v)_{O_2} = (k_c a_c)_{O_2} (C_{L, O_2} - C_{s, O_2}) \quad (\text{C})$$

$$(r_v)_{HA} = (k_c a_c)_{HA} (C_{L, HA} - C_{s, HA}) \quad (\text{D})$$

A. At steady state the rates of mass transfer from liquid to particle are equal to the rates of reaction. These expressions relate surface and bulk liquid concentrations. Equating Eqs. (A) and (C), and (A), and (D), yields

$$r_{O_2} = (k_c a_c)_{O_2} (C_{L, O_2} - C_{s, O_2}) = \rho_B \frac{9.9 \times 10^9 [\exp(-21,000/R_g T)] C_{s, HA} C_{s, O_2}^{1/2}}{1 + 7.2 \times 10^5 C_{s, HA}} \quad (\text{E})$$

$$r_{HA} = (k_c a_c)_{HA} (C_{L,HA} - C_{s,HA})$$

$$= \frac{9.9 \times 10^9 [\exp(-21,000/R_g T)] C_{s,HA} C_{O_2}^{1/2}}{\rho_B [1 + 7.2 \times 10^5 C_{s,HA}]} \quad (F)$$

Equations (E) and (F) may be solved for the two surface concentrations after $(k_c a_c)_{O_2}$ and $(k_c a_c)_{HA}$ are estimated.

From the data given

$$G_L \approx \frac{0.66(0.81)}{(\pi/4)(2.54)^2} = 0.11 \text{ g/(cm}^2\text{)(s)}$$

$$u_L \approx \frac{0.66}{(\pi/4)(2.54)^2} = 0.13 \text{ cm/s}$$

$$Re_L \approx \frac{d_p u_L \rho}{\mu_L} = \frac{0.0541(0.13)(0.81)}{1.18 \times 10^{-3}} = 4.8$$

$$\mu_L / \rho_L \mathcal{D}_{O_2} \approx \frac{1.18 \times 10^{-3}}{0.81(2.10 \times 10^{-4})} = 6.9$$

$$\mu_L / \rho_L \mathcal{D}_{HA} \approx \frac{1.18 \times 10^{-3}}{0.81(1.2 \times 10^{-4})} = 12.1$$

for spherical particles,

$$a_t = \frac{\pi d_p^2 \rho_B}{(\pi d_p^3 / 6) \rho_p} = \frac{6}{0.0541} \left(\frac{1.17}{2.05} \right) = 63 \text{ cm}^2/\text{cm}^3$$

Substituting these values in Eqs. (10-57) and (10-58) gives

$$(k_c a_c)_{O_2} = j_D (u_L a_t) \left(\frac{\mu_L}{\rho_L \mathcal{D}_{O_2}} \right)^{-2/3}$$

$$= 0.97(0.13)(63)(0.28) = 2.2 \text{ s}^{-1}$$

$$(k_c a_c)_{HA} = 0.97(0.13)(63)(0.19) = 1.5 \text{ s}^{-1}$$

With these mass-transfer coefficients, $T = 252 + 273 = 525 \text{ K}$, and $C_{L,O_2} = 2.40 \times 10^{-7} \text{ g mol/cm}^3$ and $C_{L,HA} = 33.7 \times 10^{-7}$, all quantities in Eqs. (E) and (F) are known except $C_{s,HA}$ and C_{s,O_2} . Numerical solution yields

$$C_{s,HA} = 2.35 \times 10^{-7} \text{ g mol/cm}^3$$

$$C_{s,O_2} = 33.6 \times 10^{-7} \text{ g mol/cm}^3$$

The global rate is then obtained by using these surface concentrations in Eq. (A):

$$r_{O_2} = \frac{9.9 \times 10^9 [\exp(-21,000/525R)] (33.7 \times 10^{-7}) (2.40 \times 10^{-7})^{1/2}}{1 + 7.2 \times 10^5 (33.7 \times 10^{-7})}$$

$$= 8.4 \times 10^{-9} \text{ g mol/(s)(g catalyst)}$$

In this example, the external liquid-particle mass-transfer resistance is relatively small; $(C_{L,O_2} - C_{s,O_2})/C_{L,O_2} = 0.05/2.4 = 0.02$ or 2%. For this particu-

lar case bulk concentrations could have been used in Eq. (A), to calculate the rate. This is because the intrinsic rate is slow.

B. Equation (B) is applicable for evaluating the oxygen-transfer rate from gas to liquid. The coefficient $(k_L a_g)_{O_2}$ is determined from Eq. (10-56).

$$(k_L a_g)_{O_2} = 2.1 \times 10^{-4} (7) \left(\frac{0.11}{1.18 \times 10^{-3}} \right)^{0.40} (6.9)^{1/2}$$

$$= 0.024 \text{ s}^{-1}$$

Note that this coefficient is about two orders of magnitude less than $k_c a_c$. Both $k_L a_g$ and $k_c a_c$ would be much higher at the higher liquid rates normally found in industrial trickle-bed reactors. The concentration of oxygen in the gas at 67 atm and 252°C is†

$$C_g = \frac{p_{O_2}}{R_g T} = \frac{0.21(26.2)}{82(525)} = 1.3 \times 10^{-4} \text{ g mol/cm}^3$$

Henry's law constant is $H_{O_2} = 0.89$ when the gas volume of pure oxygen is measured at 25°C and 1 atm. At $p_{O_2} = 0.21(26.2) = 5.50 \text{ atm}$ and $t = 252^\circ\text{C}$

$$H_{O_2} = 0.89 \frac{5.5}{1} \left(\frac{298}{252 + 273} \right)$$

$$= 2.78 \frac{\text{g mol/(cm}^3 \text{ gas at 5.5 atm, 252}^\circ\text{C)}}{\text{g mol/cm}^3 \text{ of liquid}}$$

Then, from Eq. (B)

$$N_{O_2} = 0.024 \left[\frac{1.3 \times 10^{-4}}{2.78} - 2.4 \times 10^{-7} \right]$$

$$= 0.024(4.59 - 0.02) \times 10^{-5} = 1.1 \times 10^{-6} \text{ g mol/(s)(cm}^3\text{)}$$

Per unit mass of catalyst this is $1.1 \times 10^{-5} / \rho_B = 9.4 \times 10^{-7} \text{ g mol/(s)(g catalyst)}$. Since this rate is much greater than the rate of reaction, r_{O_2} , at the particle surface, the oxygen concentration in the liquid would tend to be augmented at this location in the reactor. This was observed by Leveck‡; the oxygen concentration in the liquid increased in the direction of flow through the reactor. In a similar study§ for the more rapid oxidation of formic acid, the intrinsic rate was much higher. For that situation the rate of depletion of oxygen from the liquid due to reaction was greater than the rate of transfer from gas to liquid in some parts of the reactor. It was observed that C_{L,O_2} decreased in the direction of flow through the reactor. Also in that case the concentration difference $(C_{L,O_2} - C_{s,O_2})$ was significant, in contrast to the results of this example for acetic acid oxidation.

† The vapor pressure of water at 252°C is 40.8 atm. Hence, the pressure of air at 67 atm total pressure (assuming saturation) is 67 - 40.8 = 26.2 atm.

‡ Op. cit.

§ S. Goto and J. M. Smith, *AIChE J.*, 21, 706 (1975).

Since the pertinent parameter that influences external mass transfer in trickle beds is the product of an area as well as a coefficient, for example, $k_c a_c$, the numerous flow and geometric characteristics are important as well as physical properties of the system. Hence, it is difficult to state firm conclusions about the significance of external mass transfer. At low gas and liquid rates with small catalyst particles, $k_L a_g$ seems to be less than $k_c a_c$ so that gas-liquid transport has more of an effect on the global rate than liquid-particle transport (see Example 10-9). For large particles where a_c is reduced, gas-liquid and liquid-particle transport may be of about equal influence.†

Countercurrent and cocurrent upflow of gas and liquid are alternate arrangements to trickle-beds operation. Measurements, at similar rates and for the same reactor and particles, for *cocurrent* flow show about the same ($k_c a_c$) values at low flow rates. For upflow the coefficients increase with gas flow rate; for downflow gas rate seems to have little effect. While data at comparable conditions are meager, it appears that gas-liquid coefficients are higher for upflow than for downflow, particularly at high-flow rates.‡ For countercurrent flow $k_L a_g$ is less than in cocurrent operation, except at high flow rates.

We have not considered the effect of temperature differences between gas and liquid, and liquid and solid, on the global rate in trickle beds. In many cases these differences are negligible because the heat effect is small. In Example 10-9 and in related examples for oxidation of pollutants, the concentrations are so low that the heat evolved due to reaction is negligible, even though ΔH_c (heats of combustion) are high. Similarly, in hydrodesulfurization processes, the concentrations of sulfur components in the liquid are so low that near-isothermal operation results. However, unlike the situation in slurry reactors, a_c is small for large particles. Hence, for high concentrations and heats of reaction (e.g., hydro-cracking of petroleum fractions) significant temperature differences may exist between gas and particle.

PROBLEMS

10-1 To illustrate the effect of mass velocity on external diffusion in the oxidation of sulfur dioxide with a platinum catalyst, consider the following data, all at 480°C.

Mass velocity, lb/(h)(ft ²)	Bulk partial pressures, p_b , atm			Global rate, r_p , g mol SO ₂ /(h)(g catalyst)
	SO ₂	SO ₃	O ₂	
514	0.0601	0.00668	0.201	0.1346
350	0.0599	0.00666	0.201	0.1278
245	0.0603	0.00668	0.201	0.1215
147	0.0603	0.00670	0.201	0.0956

† V. Specchia, G. Baldi, and A. Gianetto, *Proc. 4th Int. Symp. Chem. React. Eng.*, p. 390, Heidelberg, April, 1976.

‡ S. Goto, J. Levec, and J. M. Smith, *Ind. Eng. Chem. Proc. Des. Dev.*, **14**, 473 (1975).

The reactor consisted of a fixed bed of $\frac{1}{8} \times \frac{1}{8}$ -in cylindrical pellets. The pressure was 790 mmHg. The external area of catalyst particles was 5.12 ft²/lb, and the platinum did not penetrate into the interior of the alumina particles. Calculate the partial-pressure difference between the bulk-gas phase and the surface of the catalyst for SO₂ at each mass velocity. What conclusions may be stated with regard to the importance of external diffusion? Neglect temperature differences.

10-2 The global rates of SO₂ oxidation have been measured with a platinum catalyst impregnated on the outer surface of $\frac{1}{8} \times \frac{1}{8}$ -in. cylindrical pellets of Al₂O₃. The data were obtained in a differential reactor consisting of a 2-in.-ID tube packed with the catalyst pellets. The superficial mass velocity of the reaction mixture was 350 lb/(h)(ft²). At constant conversion of 20% of a feed consisting of 6.5 mol % SO₂ and 93.5 mol % air, the rates are as shown below. The total pressure was 790 mmHg. Consider the properties of the mixture to be those of air, except for the Schmidt number for SO₂, which is 1.21.

t , °C	350	360	380	400	420	440	460	480	500
r_p , g mol SO ₂ / (h)(g catalyst)	0.0049	0.00788	0.01433	0.02397	0.0344	0.0514	0.0674	0.0898	0.122

(a) If only the data at 460 to 500°C are used and external diffusion is neglected, what is the apparent activation energy? (b) By calculating $(C_b - C_s)_{SO_2}$ at various temperatures and using all the data above, estimate the true activation energy for the combined adsorption and reaction processes at the catalyst surface. Neglect temperature differences between bulk gas and catalyst surface.

10-3 Predict the global rate of reaction for the oxidation of SO₂ at bulk-gas conditions of 20% conversion at 480°C. Other conditions are as given in Prob. 10-2. The rate at the catalyst surface is to be calculated from Eqs. (G) and (H) of Example 9-2. Assume isothermal conditions. The constants in Eqs. (G) and (H) at 480°C are

$$A = -0.127 \text{ (atm)}^{3/2} \text{ (h)(g catalyst)/g mol}$$

$$B = 15.3 \text{ (atm)}^{1/2} \text{ (h)(g catalyst)/g mol}$$

$$K = K_p = 73 \text{ (atm)}^{-1/2}$$

Also calculate the ratio γ of the global rate and the rate evaluated at bulk conditions.

10-4 For the conditions of Prob. 10-2 predict the temperature difference between bulk gas and pellet surface at 350 and at 500°C. Comment on the validity of the isothermal assumptions made in Probs. 10-1 to 10-3.

10-5 (a) Estimate the maximum temperature difference $T_s - T_b$ for a gas-solid catalytic reaction for which

$$\Delta H = -20,000 \text{ cal/g mol}$$

$$c_p = 8.0 \text{ cal/g mole (K)}$$

$$p_i = 2 \text{ atm}$$

$$T_b = 473 \text{ K (200°C)}$$

The mole fraction of reactant in the bulk gas is 0.25. (b) If external diffusion resistance is not controlling, but $C_b - C_s = C_b/2$, what will be the value of $T_s - T_b$?

10-6 The reaction $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ occurs with a platinum-on-alumina catalyst at low temperatures. Following the work of Maymo and Smith,† suppose that the rate, in g mol O₂/(s)(g catalyst), at the catalyst surface is given by

$$r = 0.327(p_{O_2})_s^{0.804} e^{-5.230/R_s T_s}$$

where p_{O_2} is in atmospheres and T is in degrees Kelvin.

† J. A. Maymo and J. M. Smith, *AIChE J.*, **12**, 845 (1966).

(a) Calculate the global rate of reaction at a location in a packed-bed reactor where the bulk conditions are

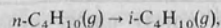
$$\begin{aligned} T_b &= 373 \text{ K (100°C)} \\ p_t &= 1 \text{ atm} \\ (p_{O_2})_b &= 0.060 \text{ atm} \\ (p_{H_2})_b &= 0.94 \text{ atm} \end{aligned}$$

Are external mass- and heat-transfer resistances negligible?

The diameter and mass of the nonporous catalyst pellet are 1.86 cm and 2.0 g, and the superficial mass velocity of the flowing gas is 250 lb/(h)(ft²). At these conditions the molecular diffusivity of oxygen is about 1.15 cm²/s. The properties of the gas mixture are essentially the same as those of hydrogen.

(b) Determine the ratio γ of the global rate to the rate evaluated at bulk-gas conditions.

10-7 The catalytic isomerization of *n*-butane,



is studied in a plug-flow laboratory reactor in which the catalyst is deposited on the walls of the cylindrical tube. Pure *n*-butane (as a gas) is fed to the reactor at a steady rate of F (lb mol/h), and the whole system operates isothermally. Assume that the reaction rate at the catalyst surface is first order and irreversible, according to the expression

$$r = kC_s$$

where r is the rate of formation of iso-butane, lb mol/(h)(ft² tube surface) and C_s is the surface concentration of *n*-butane, lb mol/ft³.

(a) Suppose that the rate of mass transfer radially from the bulk gas, where C_g is the concentration of *n*-C₄H₁₀, to the catalyst wall, where C_s is the concentration, is proportional to the mass-transfer coefficient k_m , in feet per hour. Derive an expression for the conversion of *n*-butane in terms of the reactor length L and other necessary quantities. The constant temperature is $T^\circ\text{R}$ and the pressure is p atmospheres.

(b) Suppose the resistance to mass transfer radially is negligible. What form would the equation for the conversion take?

(c) Suppose the plug-flow model is not valid because axial diffusion is important. Let the effective diffusivity in the axial direction be D_L . Other conditions are as in part (a). Derive an equation whose solution will give the conversion as a function of reactor length and other necessary quantities.

(d) Calculate the conversion of *n*-butane leaving the reactor from the equation derived in part (a) and the conditions

$$\begin{aligned} k &= 446 \text{ ft/h} \\ d &= 6 \text{ in.} \\ t &= 500^\circ\text{F} \\ p_t &= 1 \text{ atm} \\ F &= 20 \text{ lb mol/h} \end{aligned}$$

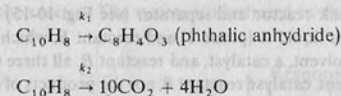
$$\text{Reactor length } L = 10 \text{ ft}$$

Also calculate the conversion from the equation derived in part (c), using the above data, and $D_L/uL = 0.05$. This value of D_L/uL corresponds to an intermediate amount of dispersion.

10-8 Reconsider parts (a) to (c) of Prob. 10-7 for a reversible first-order reaction. It is suggested that the rate equation be written in terms of the equilibrium concentration of *n*-butane. Also show how this concentration is related to the equilibrium constant K .

10-9 The catalytic isomerization of normal hexane to 2-methyl pentane and 3-methylpentane was discussed in Sec. 10-5. The effect of external mass transfer on selectivity was evaluated by assuming that the consecutive reactions were irreversible and first order. In this problem treat the realistic situation of reversible, first-order kinetics. Derive an expression for the selectivity of 2-methylpentane with respect to 3-methylpentane under isothermal conditions and for bulk-fluid concentrations of $(C_A)_b$, $(C_B)_b$, and $(C_C)_b$. Express the result in terms of the two first-order, forward-direction rate constants k_1 and k_2 , the corresponding equilibrium constants K_1 and K_2 , and the necessary mass-transfer coefficients between bulk fluid and catalyst surface.

10-10 Imagine that the catalytic (V_2O_5) oxidation of naphthalene can be approximated by the following irreversible, parallel (not balanced) reactions:



Suppose the activation energies for the two first-order reactions are $E_1 = 117 \text{ kJ/mol}$ and $E_2 = 167 \text{ kJ/mol}$. For reaction 1, $\Delta H_1 = -3770 \text{ kJ/mol}$ and for reaction 2, $\Delta H_2 = -4770 \text{ kJ/mol}$. At one location in a fixed-bed reactor, the temperature difference between catalyst particle and gas phase is 15 K, and the gas temperature is 620 K.

Estimate how much error would be made in the selectivity of phthalic anhydride with respect to carbon dioxide, if the effect of the heat-transfer resistance between gas and particle is neglected.

10-11 Suppose that a temperature difference exists between bulk gas and catalyst surface. How would the equation derived in Prob. 10-9 be modified? What are the additional quantities that would have to be known to evaluate the effect of nonisothermal behavior?

10-12 A. Estimate gas-to-particle mass- and heat-transfer coefficients for a gas (whose properties are those of air) at 373 K and 1 atm flowing through a fixed bed (void fraction = 0.40) of 0.0021 m ($\frac{1}{2}$ -in.) spherical particles. The superficial mass velocity of the gas is 1.47 kg/(s)(m²), or 0.3 lb/(s)(ft²). Compare these coefficients with those for a fluidized bed (void fraction = 0.95) of particles with an average diameter of $8 \times 10^{-5} \text{ m}$ (170–200 mesh size). The superficial mass velocity is 0.29 kg/(s)(m²) [or 0.06 lb/(s)(ft²)].

B. Also compare the mass- and heat-transfer rates, per unit volume of the bed per unit driving force (ΔC or ΔT), for the two beds.

C. Suppose the particles are a catalyst for a reaction that occurs on the outer surface at a rate of $3.0 \times 10^{-7} \text{ (g mol of product produced)/(s)(g catalyst)}$. The heat of reaction is $\Delta H = -20,000 \text{ cal/(g mol of product)}$. Estimate temperature and concentration differences ($C_b - C_s$ and $T_b - T_s$) for the two beds.

D. Comment on the influence of external mass- and heat-transfer effects on the global rate of reaction for the two beds.

10-13 In Example 10-6, part A, an equation was derived for the fraction of component A removed from gas bubbles rising through a height L of liquid. No solid phase was present. Now derive the more general equation applicable when the gas bubbles rise through a slurry of solid particles on which A is absorbed. That is, derive an expression for $(p_0 - p_L)/p_0$ as a function of time. Assume that very rapid physical adsorption occurs on the solid particles. The adsorption follows a linear isotherm, $n = KC_s$, where n is the adsorbed concentration of A , g mol/(g particle). Also assume that rate coefficient $k_2 a_c$ is much greater than $k_L a_g$, so that $C_L - C_s \rightarrow 0$. The mass of particles in the slurry is m_s (g/cm³ of liquid).

All other conditions are the same as in Example 10-6. The slurry liquid is well mixed and the bubbles rise separately in plug flow through the slurry. A is slightly soluble in the liquid and the change in C_L is negligible during the residence time of one bubble.

Show that the derived expression reduces to Eq. (H) of Example 10-6 when there are no solid particles present.

10-14 Estimate the mass-transfer coefficient k_L for bubbles ($d_b = 1.0 \text{ mm}$) of pure hydrogen rising through a liquid ($\mu_L = 2.0$ centipoises, $\rho_L = 0.9 \text{ g/cm}^3$). The system is at 150°C and 5 atm pressure.

Also estimate the value of k_c if the liquid contains catalyst particles of 100 mesh size. The density of the particles is 1.8 g/cm³ and the diffusivity of hydrogen in the liquid is $6 \times 10^{-3} \text{ cm}^2/\text{s}$. The energy dissipation rate evaluated from Eq. (10-43) is $2.0 \times 10^4 \text{ erg/(s)(g of liquid)}$.

10-15 If the intrinsic rate of hydrogenation at the catalyst site is very large for the conditions of Prob. 10-14, calculate the global rate of hydrogenation r_r for the following cases, corresponding to a constant concentration of gas bubbles ($a_g = 3.0 \text{ cm}^{-3}$) and the following catalyst-particle concentrations:

- $a_c/a_g = 100$ (high-particle concentration)
- $a_c/a_g = 10$
- $a_c/a_g = 2.0$ (low-particle concentration)

The solubility of hydrogen in the liquid is such that $C_g/(C_L)_{eq} = 10$ at 150°C.

10-16 If the rate of hydrogenation at the catalyst can be represented by Eq. (10-33) with $k = 0.0020$ cm/s, what are the global rates of reaction for the three cases of Prob. 10-15?

10-17 A continuous, stirred-tank reactor and separator (see Fig. 10-15) are used to study the heterogeneous reaction between pure liquid *A* (phase 1) and reactant *B*, which is dissolved in phase 2 (also liquid). Phase 2 contains the solvent, a catalyst, and reactant *B*, all three substances being completely miscible. However, neither solvent, catalyst, reactant *B*, nor the products of reaction are soluble in phase 1. The reactor operates isothermally at 25°C and at this temperature *A* has a limited solubility in phase 2 of 2.7×10^{-5} g mol/liter. Phase 2 is present in the reactor as bubbles dispersed in phase 1 (continuous phase). The two phases are separated in the separator and phase 1 is recycled. Neglect the reaction that occurs in the separator.

There is good mixing in the reactor but motion within the bubbles of phase 2 is insufficient to eliminate all the mass-transfer resistance within the bubbles. Assume that this mass-transfer resistance is concentrated in a thin film of liquid near the interface between phases 1 and 2, and that this mass-transfer resistance is governed by a mass-transfer coefficient k_g (based on interfacial area of bubbles). From independent mass-transfer measurements it is estimated that the reaction resistance within the bubbles of phase 2 is 75% of the total resistance (mass transfer plus reaction resistances). In a practical example, such a system could represent an alkylation reaction catalyzed by an acid phase.

A. Derive a relationship between the concentration, C_{B_0} , of *B* in the feed stream and in the product (from the separator) stream (concn = C_B) of phase 2.

B. In an alkylation study using this reactor system, the following data were obtained:

Feed rate of phase 2 = $0.2 \text{ cm}^3/\text{s}$

Total liquid volume in reactor = 1500 cm^3

Volume fraction of phase 2 in reactor = 0.24

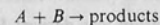
$C_{B_0} = 0.02 \text{ g/liter}$ (feed stream)

$C_B = 0.0125 \text{ g/liter}$ (product stream)

Calculate the value of the reaction-rate constant, k_2 , from these data.

Notes

1. Assume that the reaction is second order and irreversible



2. The liquid density of either phase does not change significantly with reaction.

3. Assume that equilibrium exists at the interface between phases 1 and 2.

10-18 As an example of external mass transfer in catalytic reactors, consider a continuous slurry (two-phase) reactor (well mixed) in which benzaldehyde is adsorbed from an aqueous solution by activated carbon particles at 25°C.

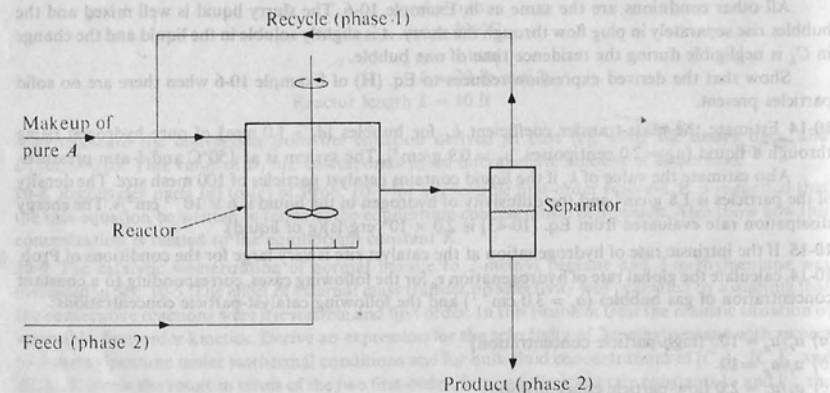
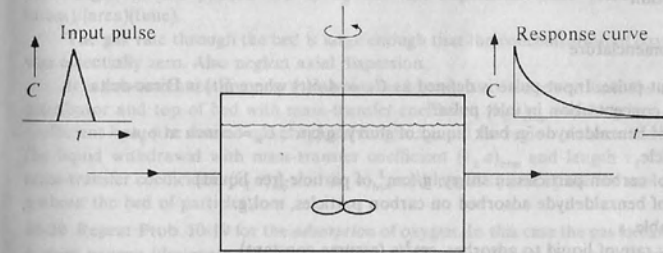


Figure 10-15 Liquid-liquid reaction (alkylation) system (for Prob. 10-17).

One method for evaluating the mass-transfer coefficient, k_c , from liquid to particle surface is by measuring the response curve when a pulse [Dirac-delta function $\delta(t)$] of benzaldehyde solution is introduced into the feed to the reactor. The system is illustrated in the following sketch:



For this chemical system, and the particle sizes studied, it may be assumed that the adsorption process is irreversible and first order and that intraparticle diffusion resistance is negligible. That is, the overall adsorption process depends only on the external mass-transfer process (k_c , cm/s) and the intrinsic rate of adsorption (k , $\text{cm}^3/(\text{g}\cdot\text{s})$). No gas phase is present.

A. Using the nomenclature given later, derive equations for the first (μ_1) and second (μ_2) moments of the response curve. These moments are defined as:

$$\mu_1 = \frac{m_1}{m_0}$$

$$\mu_2 = \frac{m_2}{m_0}$$

where

$$m_n = (-1)^n \lim_{s \rightarrow 0} \frac{d^n \bar{C}(s)}{ds^n}; \quad n = 0, 1, 2, \dots$$

and $\bar{C}(s)$ is the Laplace transform of $C(t)$. For $n = 0$, $d^n \bar{C}(s)/ds^n = \bar{C}(s)$.

B. Experimental values for the first moment were determined from the measured response curve using the equation

$$\mu_1 = \frac{\int_0^{\infty} C t \, dt}{\int_0^{\infty} C \, dt}$$

These experimental results for different particle sizes of an activated carbon are given in the following table.

Experimental data at 25°C

r_p microns	$m_p \times 10^3$ g/cm ³	ρ_p g/cm ³	$(1/\mu_1 - 1/\tau) \times 10^3$ (s) ⁻¹
80	0.471	0.956	2.09
114	0.940	0.956	2.94
192	0.940	0.956	1.49
271	0.940	0.956	1.14
322	0.940	0.956	0.818

From these data and the derivation in part A, calculate a numerical value for k_c .

C. Sketch the shape of the response curves (for comparison) for:

1. Irreversible adsorption
2. Reversible adsorption

Use the following nomenclature

A = strength of input pulse. Input pulse is defined as $C_0 = A \delta(t)$ where $\delta(t)$ is Dirac-delta function; C_0 = concentration in inlet pulse.

C = concentration of benzaldehyde in bulk liquid of slurry, g/cm^3 ; C_s = concn at outer surface of particle.

m_s = concentration of carbon particles in slurry, $\text{g}/(\text{cm}^3 \text{ of particle-free liquid})$.

n = concentration of benzaldehyde adsorbed on carbon particles, mol/g .

s = transform variable, s

Q = volumetric flow rate of liquid to adsorber, cm^3/s (assume constant).

r_s = radius of carbon particle (assume spherical).

t = time, s

V = volume of particle-free liquid in reactor, cm^3

ρ_p = density of carbon particles, g/cm^3

τ = average residence time of liquid in reactor, V/Q , s

S_s = outer surface area of particles per unit volume of particle-free liquid in slurry, cm^{-1}

W = mass of carbon particles in slurry adsorber, g

10-19 Mass transfer between gas and liquid in trickle beds is studied by measuring the *desorption* of oxygen from water into nitrogen as both liquid and gas streams flowed down through a packed bed of particles. The rate of oxygen transfer was determined by measuring the oxygen concentration $C_{L,f}$ in the liquid feed and in the liquid stream leaving the reactor ($C_{L,e}$) when the gas feed was pure nitrogen. However, some mass transfer occurs in the entrance region between the liquid distributor (see Fig. 10-16) and the top of the bed, and also between the bottom of the bed (where the screen holding the particles is located) and the effluent liquid. To account for these end-effects the concentration in the

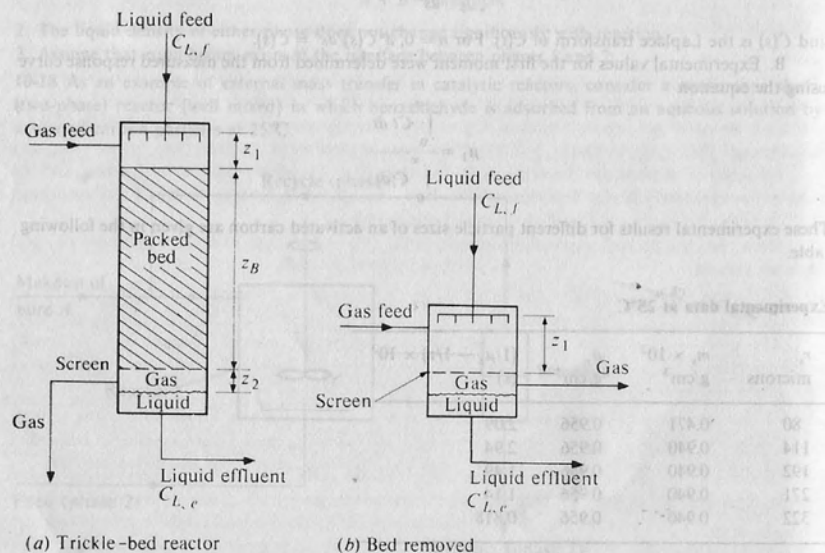


Figure 10-16 Trickle-bed reactor.

effluent is also measured (at the same flow rates and for the same $C_{L,f}$) when the bed of particles was removed and the liquid distributor lowered to the distance z_1 above the screen. If this latter concentration is $C'_{L,e}$, derive an equation for $(k_L a_g)$ for the bed itself in terms of the measured concentrations. The height of the packed bed is z_B and the superficial mass velocity of the liquid is G_L (mass)/(area)(time).

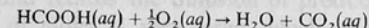
The gas rate through the bed is large enough that the concentration of oxygen in the gas stream was essentially zero. Also neglect axial dispersion.

It is convenient to imagine the apparatus to consist of three sections: the region between liquid distributor and top of bed with mass-transfer coefficient $(k_L a)_{top}$ and length z_1 , the bed proper with coefficient $k_L a_g$ (the desired quantity) and length z_B , and the region between the bottom of the bed and the liquid withdrawal with mass-transfer coefficient $(k_L a)_{bim}$ and length z_2 . Then assume that the mass-transfer coefficients $(k_L a)_{top}$ and $(k_L a)_{bim}$ and length z_1 and z_2 are the same in the runs with and without the bed of particles.

10-20 Repeat Prob. 10-19 for the *adsorption* of oxygen. In this case the gas stream entering the reactor is pure oxygen (designate the concentration of oxygen in water in equilibrium with pure oxygen as $(C_{L,eq})$). The liquid feed is oxygen-free water.

10-21 Consider a trickle-bed reactor for the catalytic oxidation of formic acid (in dilute aqueous solution) with air. The temperature and pressure are 240°C and 40 atm.

A. Calculate the global rate for the reaction



at a location in the reactor where the bulk liquid concentrations are:

$$C_{L,O_2} = 2.70 \times 10^{-7} \text{ g mol}/\text{cm}^3$$

$$C_{L,FA} = 28.7 \times 10^{-7} \text{ g mol}/\text{cm}^3$$

and the gas phase is air saturated with water vapor at 240°C . The gas and liquid flow rates are:

$Q_g = 4.0 \text{ cm}^3/\text{s}$ (at 25°C , and 1 atm) and $Q_L = 2.0 \text{ cm}^3/\text{s}$ in a 1-in. ID reactor. The bed is packed with commercial CuO-ZnO catalyst particles ($d_p = 0.29/\text{cm}$). The particle density is $1.90 \text{ g}/\text{cm}^3$ and the bed density, $\rho_B = 1.05 \text{ g}/\text{cm}^3$.

Assume that the liquid covers all the surface of the particles. Properties of the system at 240°C , and 40 atm are estimated to be:

$$H_{O_2} = 3.82 \text{ [g mol}/(\text{cm}^3 \text{ of oxygen gas at } 25^\circ\text{C, 1 atm})]/(\text{g mol}/\text{cm}^3 \text{ of water)}$$

$$\rho_L = \text{density of water} = 0.79 \text{ g}/\text{cm}^3$$

$$\mu_L = \text{viscosity of water} = 0.92 \text{ g}/(\text{cm})(\text{s})$$

$$(\mathcal{D}_{O_2})_L = \text{diffusivity of } O_2 \text{ in water} = 3.4 \times 10^{-4} \text{ cm}^2/\text{s}$$

$$(\mathcal{D}_{FA})_L = \text{diffusivity of formic acid in water} = 2.7 \times 10^{-4} \text{ cm}^2/\text{s}$$

The intrinsic rate of disappearance of oxygen at the catalyst surface is second order;† at 240°C

$$r_{O_2}(\text{g mol}/(\text{g catalyst})(\text{s})) = 4.37 \times 10^{-6} C_{s,O_2} C_{s,FA}$$

where the concentrations are in the liquid at the outer surface of the catalyst particles.

B. Also calculate the mass transfer rate of oxygen from gas to liquid at the same location in the reactor. Comment on the significance of the values of the global rate (part A) and oxygen transfer rate (part B).

† G. Baldi, S. Goto, C. K. Chow, and J. M. Smith, *Ind. Eng. Chem. Proc. Des. Dev.*, **13**, 447 (1974).