Chapter 22

G/L Reactions on Solid Catalysts: Trickle Beds, Slurry Reactors, and Three-Phase Fluidized Beds

These multiphase reactions are of the type

$$\mathrm{A}(g \xrightarrow{\text{dissolve}} l) + \mathrm{B}(l) \xrightarrow[\text{catalyst}]{\text{on solid}} \text{products}$$

and they can be run in a number of ways, as shown in Fig. 22.1. The packed bed contactors use large solid particles, the slurry reactors very fine suspended solids, while the fluidized bed can use either depending on the flow rates.

Flow pattern: Overall, all other things equal (which they are not) countercurrent plug flow is the most desirable flow pattern while the worst of all in terms of driving forces is mixed/mixed flow.

22.1 THE GENERAL RATE EQUATION

Consider the following reaction and stoichiometry

$$\mathrm{A}(g \rightarrow l) + b\mathrm{B}(l) \xrightarrow[\text{surface}]{\text{on catalyst}} \text{products} \cdot \cdot \cdot b = \left(\frac{\text{mol B}}{\text{mol A}}\right) \tag{1}$$

$$\left.\begin{aligned} -r'''_{\mathrm{A}} &= k'''_{\mathrm{A}} C_{\mathrm{A}} C_{\mathrm{B}} \\ -r'''_{\mathrm{B}} &= k'''_{\mathrm{B}} C_{\mathrm{A}} C_{\mathrm{B}} \end{aligned}\right\} \text{where} \left.\begin{aligned} -r'''_{\mathrm{A}} &= -r'''_{\mathrm{B}}/b \cdot \cdot \cdot \text{mol A/m}^3\,\text{cat} \cdot \text{s} \\ k'''_{\mathrm{A}} &= k'''_{\mathrm{B}}/b \cdot \cdot \cdot \text{m}_l^6/\text{mol B} \cdot \text{m}^3\,\text{cat} \cdot \text{s} \end{aligned}\right\}$$

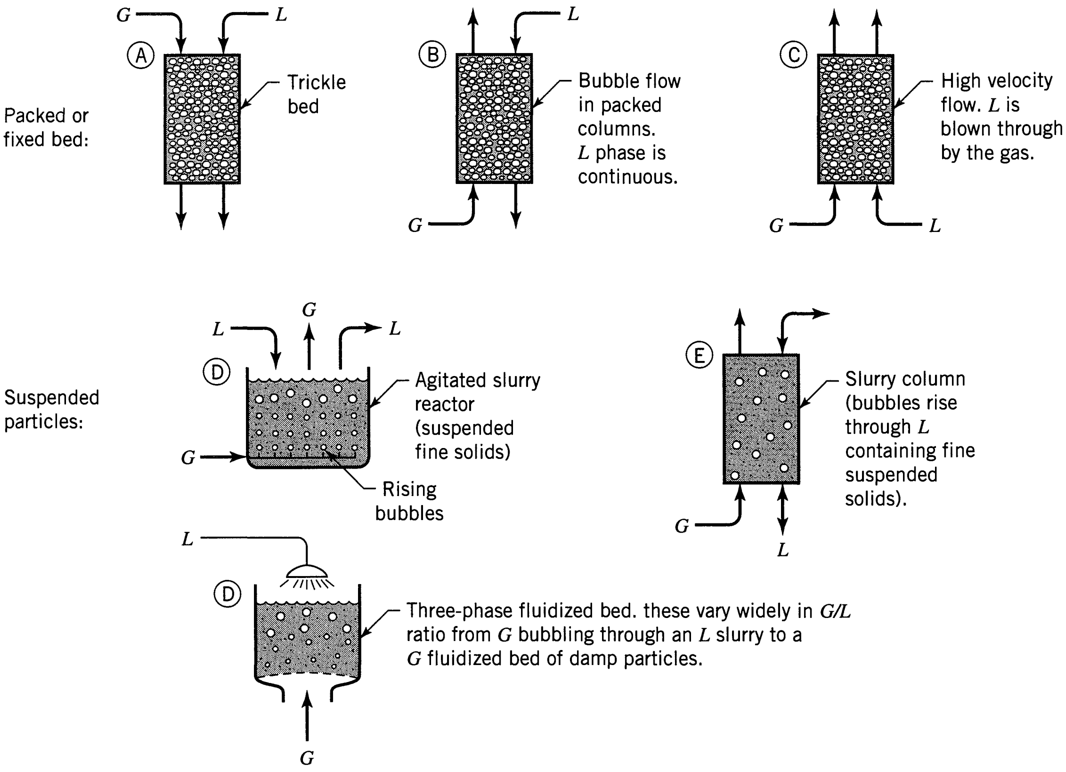
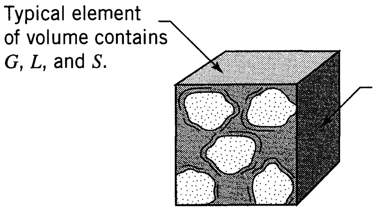


Figure 22.1 Various ways of running G/L reactions catalyzed by solids.

Gas reactant must first dissolve in the L, then both reactants must diffuse or move to the catalyst surface for reaction to occur. Thus the resistance to transfer across the G/L interface and then to the surface of solid both enter the general rate expression.

To develop the rate equation, let us draw on the two-film theory, and let us use the following nomenclature:



$$H_A = \frac{p_A}{C_A}, \text{ Henry's law constant [Pa} \cdot \text{m}^3\text{l/mol]}$$

$$a_i = \frac{\text{gas–liquid interfacial area}}{\text{volume of reactor}}$$

$$a_c = \frac{\text{external surface of particles}}{\text{volume of reactor}} \quad \frac{\text{for}}{\text{spheres}} \quad \frac{6f_s}{d_p}$$

$$f_s = \frac{\text{volume of particles}}{\text{volume of reactor}}, \text{ called solid loading}$$

$$f_l = \frac{\text{volume of liquid}}{\text{volume of reactor}}, \text{ called liquid holdup}$$

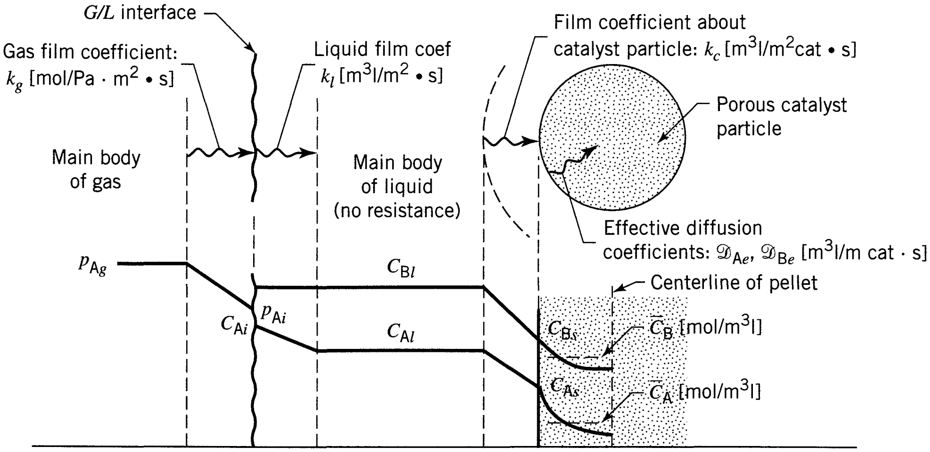


Figure 22.2 Sketch showing the resistances involved in the G/L reaction on a catalyst surface.

Graphically we show the resistances as in Fig. 22.2. We can then write the following general rate equations:

For A:

$$-r_A''' = \frac{1}{\dfrac{1}{k_{Ag}a_i} + \dfrac{H_A}{k_{Al}a_i} + \dfrac{H_A}{k_{Ac}a_c} + \dfrac{H_A}{(k_A'''\overline{C}_B)\mathscr{E}_A f_s}} p_{Ag} \tag{2}$$

effectiveness factor for the first-order reaction of A with rate constant $(k_A'''\overline{C}_B)$

Henry's law constant $H_A = p_A/C_A$

these rates are related by $-r_A''' = \dfrac{-r_B'''}{b}$

For B:

$$-r_B''' = \frac{1}{\dfrac{1}{k_{Bc}a_c} + \dfrac{1}{(k_B'''\overline{C}_A)\mathscr{E}_B f_s}} C_{Bl} \tag{3}$$

mol B/m³ reactor·s

effectiveness factor for the first order reaction of B with rate constant $(k_B'''\overline{C}_A)$

Now either Eq. 2 or Eq. 3 should give the rate of reaction. Unhappily, even with all the system parameters known (k, a, f, etc.) we still cannot solve these expressions without trial and error because $\overline{C}_B$ is not known in Eq. 2 and $\overline{C}_A$ is not known in Eq. 3. However, we usually encounter either of two simplifying extremes, which are very useful.

Extreme 1: $C_{Bl} \gg C_{Al}$. In systems with pure liquid B and slightly soluble gas A we can take

$$C_{Bs} = \overline{C}_{B,\text{within pellet}} = C_{Bl} \cdots \text{same value everywhere}$$

With C_B constant the reaction becomes first order with respect to A overall and the above rate expressions with their required trial and error all reduce to one directly solvable expression

$$-r'''_A = \frac{1}{\dfrac{1}{k_{Ag}a_i} + \dfrac{H_A}{k_{Al}a_i} + \dfrac{H_A}{k_{Ac}a_c} + \dfrac{H_A}{\underbrace{(k'''_A C_{Bl})}_{\substack{\text{first-order rate}\\ \text{constant for A}}}\mathscr{E}_A f_s}} p_{Ag} \tag{4}$$

Extreme 2: $C_{Bl} \ll C_{Al}$. In systems with dilute liquid reactant B, highly soluble A, and high pressure, we can take

$$C_{Al} = \frac{p_{Ag}}{H_A} \cdot \cdot \cdot \text{throughout the reactor}$$

The rate then becomes first order with respect to B and reduces to

$$\underset{\text{mol B/m}^3\,\text{reactor}\cdot\text{s}}{-r'''_B} = \frac{1}{\dfrac{1}{k_{Bc}a_c} + \dfrac{1}{\underbrace{\left(\dfrac{k'''_B p_{Ag}}{H_A}\right)}_{\substack{\text{first-order rate constant which}\\ \text{is used to calculate } \mathscr{E}_B}}\mathscr{E}_B f_s}} C_{Bl} \tag{5}$$

How to Test Whether these Extremes Apply, and Other Comments

(a) By the unequal signs $\gg$ or $\ll$ we mean two or three times as large.

(b) More generally compare the rates calculated from Eqs. 4 and 5 and use the smaller one. Thus,

- if $r''''_{\text{Eq. 4}} \ll r''''_{\text{Eq. 5}}$, then C_{Bl} is in excess and extreme 1 applies.
- if $r''''_{\text{Eq. 4}} \gg r''''_{\text{Eq. 5}}$, then Eq. 5 gives the rate of reaction.

(c) Nearly always does one or other of the extremes apply.

22.2 PERFORMANCE EQUATIONS FOR AN EXCESS OF B

All types of contactors—trickle beds, slurry reactors, and fluidized beds—can be treated at the same time. What is important is to recognize the flow patterns of the contacting phases and which component, A or B, is in excess. First consider an excess of B. Here the flow pattern of liquid is not important. We only have to consider the flow pattern of the gas phase. So we have the following cases.

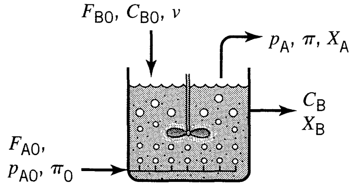


Figure 22.3 Gas bubbles swim around the bed; hence, gas is in mixed flow.

Mixed Flow *G*/Any Flow *L* (excess of B)

Here we have the situation shown in Fig. 22.3. A material balance about the whole reactor gives

$$\boxed{\underbrace{F_{A0}X_A}_{\substack{\text{I}\\ \text{rate of}\\ \text{loss of A}}} = \underbrace{\frac{1}{b}F_{B0}X_B}_{\substack{\text{II}\\ \text{rate of}\\ \text{loss of B}}} = \underbrace{(-r''''_A)V_r}_{\substack{\text{III}\\ \text{rate of}\\ \text{reaction}}}} \qquad (6)$$

Solution is straightforward. Just combine I and III or II and III.

Plug Flow *G*/Any Flow *L* (excess of B)

With a large excess of B, C_B stays roughly constant throughout the reactors shown in Fig. 22.4 even though the concentration of A in the gas phase changes as the gas flows through the reactors. For a thin slice of reactor as shown in Fig.

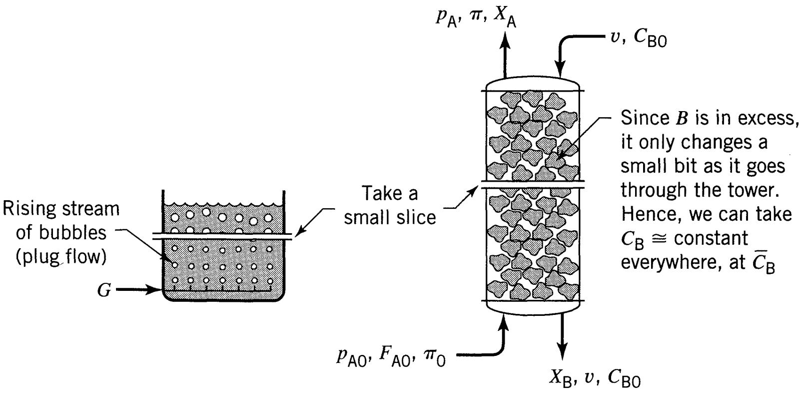


Figure 22.4 Gas rises in plug flow in these two contactors.

22.4, we can write

$$F_{A0}\,dX_A = (-r''''_A)dV_r \tag{7}$$

where

$$1 - X_A = \frac{p_A(\pi_0 - p_{A0})}{p_{A0}(\pi - p_A)} \underset{\text{only}}{\overset{\text{dilute}}{=\!=\!=}} \frac{p_A\pi_0}{p_{A0}\pi} \underset{\pi\,=\,\text{const.}}{\overset{\text{dilute}}{=\!=\!=\!=\!=}} \frac{p_A}{p_{A0}} \tag{8}$$

and

$$-dX_A = \frac{\pi(\pi_0 - p_{A0})\,dp_A}{p_{A0}(\pi - p_A)^2} \overset{\text{dilute}}{=\!=\!=} \frac{\pi_0\,dp_A}{p_{A0}\pi} \underset{\pi\,=\,\text{const.}}{\overset{\text{dilute}}{=\!=\!=\!=\!=}} \frac{dp_A}{p_{A0}} \tag{9}$$

Overall, around the whole reactor

$$\boxed{\frac{V_r}{F_{A0}} = \int_0^{X_A} \frac{dX_A}{\underset{\text{use } \overline{C}_B \text{ here}}{(-r'''_A)}} \quad \text{... with ...} \quad F_{A0}X_A = \frac{F_{B0}}{b}\,\underset{\frac{v}{b}C_{B0}-C_B}{X_B}} \tag{10}$$

Mixed Flow *G*/Batch *L* (excess of B)

With throughflow of *L* its composition stays roughly constant when B is in excess. However, with a batch of *L* its composition slowly changes with time as B is being used up, but B is roughly constant in the reactor at any time, as shown in Fig. 22.5. Here the material balance at any time *t* becomes

$$\boxed{\underset{\text{I}}{F_{A0}X_{A,\text{exit}}} = \underset{\text{II}}{\frac{V_l}{b}\left(-\frac{dC_B}{dt}\right)} = \underset{\text{III}}{(\overset{\text{mol A/m}^3\text{ reactor}\cdot\text{s}}{-r''''_A})V_r}} \tag{11}$$

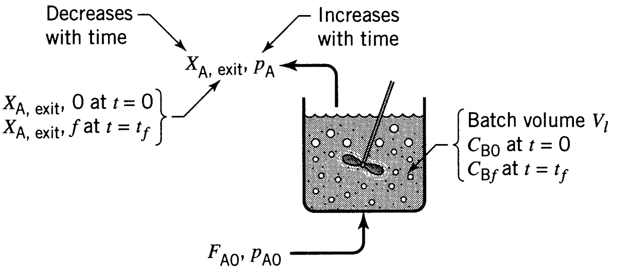


Figure 22.5 Gas bubbles through a batch of liquid, B in excess.

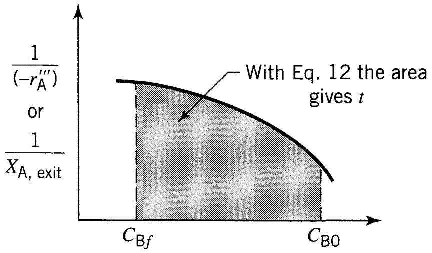


Figure 22.6 Evaluation of the reaction time for a batch of liquid.

The general procedure for finding the processing time is as follows:

Pick a number of C_B values	From III calculate	From I and II calculate
C_{B0}	$(-r_A)_0$	$X_{A,\,exit,\,0}$
—	—	—
—	—	—
C_{Bf}	$(-r_A)_f$	$X_{A,\,exit,\,f}$

Then from II and III, or I and II solve for t

$$\boxed{t = \frac{V_l}{bV_r}\int_{C_{Bf}}^{C_{B0}}\frac{dC_B}{(-r_A'''')} = \frac{V_l}{bF_{A0}}\int_{C_{Bf}}^{C_{B0}}\frac{dC_B}{X_{A,\,exit}}} \tag{12}$$

as shown in Fig. 22.6.

Plug Flow *G*/Batch *L* (excess of B)

As with the previous case, C_B changes slowly with time; however, any element of gas sees the same C_B as it flows through the reactor, as shown in Fig. 22.7.

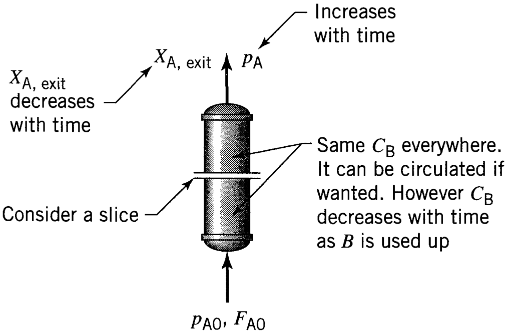


Figure 22.7 Plug flow of gas through a batch of liquid.

Consider a slice of contactor in a short time interval in which C_B is practically unchanged. Then a material balance gives

$$F_{A0}\,dX_A = (-r''''_A)dV_r \tag{13}$$

Integrating gives the exit conversion of A

$$\boxed{\frac{V_r}{F_{A0}} = \int_0^{X_{A,\text{exit}}} \frac{dX_A}{(-r''''_A)}} \tag{14}$$

Considering B we may now write

$$F_{A0}X_{A,\text{exit}} = \frac{V_l}{b}\left(-\frac{dC_B}{dt}\right), \qquad \left[\frac{\text{mol}}{\text{s}}\right]$$

and on integrating we find the processing time to be

$$\boxed{t = \frac{V_l}{bF_{A0}} \int_{C_{Bf}}^{C_{B0}} \frac{dC_B}{X_{A,\text{exit}}}} \tag{15}$$

The procedure is as follows:

Choose C_B	Solve Eq. 14 to Give $X_{A,\text{exit}}$
C_{B0}	$X_{A,\text{exit}}\ (t = 0)$
—	—
—	—
C_{Bf}	$X_{A,\text{exit}}$ (at t)

Then solve Eq. 15 graphically to find the time as shown in Fig. 22.8.

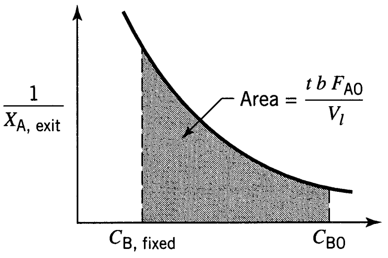


Figure 22.8 Evaluation of the reaction time in a batch L reactor.

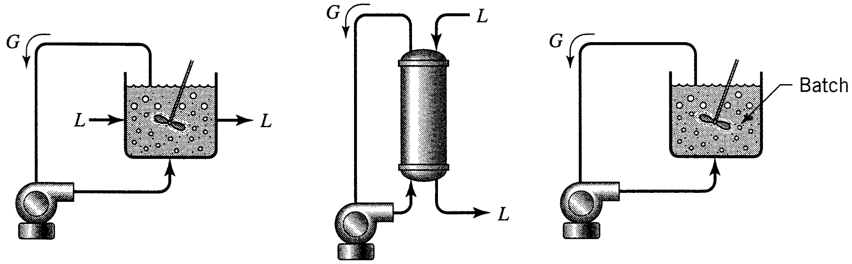


Figure 22.9 Pure gaseous A can be recompressed and recycled.

Special Case of Pure Gaseous A (excess of B)

One often encounters this situation, especially in hydrogenations. Here one usually recycles the gas, in which case p_A and C_A stay unchanged; hence, the preceding equations for both batch and flow systems simplify enormously, see Fig. 22.9. When solving problems, it is suggested that one write down the basic material balances and then carefully see what simplifications apply . . . is p_A constant? . . . and so on.

Comments The rate expressions used so far have been first order with respect to A and first order with respect to B. But how do we deal with more general rate forms, for example:

$$A(g) + bB(l) \xrightarrow[\text{catalyst}]{\text{on solid}} \ldots, \quad -r_A''' = -\frac{r_B'''}{b} = k_A''' C_A^n C_B^m \tag{16}$$

To be able to combine the chemical step with the mass transfer steps in simple fashion, we must replace the above awkward rate equation with a first-order approximation, as follows:

$$-r_A''' = k_A''' C_A^n C_B^m \Rightarrow -r_A''' = [(k_A''' \bar{C}_B^m) \bar{C}_A^{n-1}] C_A \tag{17}$$

mean values at
locations where
reaction occurs

This approach is not completely satisfactory, but it is the best we can do. Thus, instead of Eq. 4, the rate form to be used in all the performance expressions will be

$$-r_A'''' = \frac{1}{\dfrac{1}{H_A k_{Ag} a_i} + \dfrac{1}{k_{Al} a_i} + \dfrac{1}{k_{Ac} a_c} + \dfrac{1}{(k_A''' \bar{C}_B^m \bar{C}_A^{n-1}) \mathscr{E}_A f_s}} \frac{p_A}{H_A} \tag{18}$$

22.3 PERFORMANCE EQUATIONS FOR AN EXCESS OF A

Here the flow pattern of gas is of no concern. All we need to worry about is the flow pattern of liquid.

Plug Flow *L*/Any Flow *G* (tower and packed bed operations)

Making the material balances gives on integration

$$\frac{V_r}{F_{B0}} = \int_0^{X_B} \frac{dX_B}{\underset{\uparrow\ \text{given by Eq. 5}}{-r''''_B}} \qquad \text{where} \qquad 1 - X_B \cong \frac{C_B}{C_{B0}} \tag{19}$$

Mixed Flow *L*/Any Flow *G* (tank operations of all types)

Here the performance equation is simply

$$\frac{V_r}{F_{B0}} = \frac{\overset{1-\frac{C_B}{C_{B0}}}{\overset{\downarrow}{X_B}}}{\underset{\uparrow\ \text{given by Eq. 5}}{-r'''_B}} \tag{20}$$

Batch *L*/Any Flow *G*

Noting that $C_A \cong$ constant throughout time (because it is in excess), the performance equation for B becomes

$$-\frac{dC_B}{dt} = -r_B = \frac{V_r}{V_l}(-r''''_B) \cdots \quad \text{or} \quad \cdots t = \int_0^t \frac{dC_B}{-r_B} \tag{21}$$

22.4 WHICH KIND OF CONTACTOR TO USE

The selection of a good contactor depends on

- where the controlling resistance lies in the rate expression,
- the advantages of one contacting pattern over another, and
- the difference in auxiliary equipment needed.

The overall economics which accounts for these three factors will determine which set up and reactor type is best. Let us briefly look at these factors in turn.

The Rate: We should favor the contactor which favors the weakest step in the rate. For example,

- if the main resistance lies in the *G/L* film, use a contactor with large interfacial surface area.
- if the resistance lies at the *L/S* boundary, use a large exterior surface of solid, thus large f_s or small particles.
- if the resistance to pore diffusion intrudes, use tiny particles.

From prediction we can find the weakest step by inserting all transfer coefficients (k_g, k_l, . . .) and system parameters (a_i, a_s, . . .) into the rate equation and then see which resistance term dominates. Unfortunately, the values for these quantities usually are not well known.

From experiment, we can change one or another factor in the rate expression; for example,

- solid loading (this changes f_s alone, hence, only changes the last resistance term in the rate expression)
- size of catalyst particle (affects both $\mathscr{E}$ and a_s)
- intensity of agitation of the liquid (affects the mass transfer terms in the rate)
- π, C_B, p_A.

This should tell which factor strongly affects the rate and which does not.

Boosting the weakest step in the rate by a proper choice of particle size, solid loading and reactor type can strongly affect the overall economics of the process.

Contacting: Plug flow of the limiting component, the one which is not in excess, is certainly better than mixed flow. However, except for very high conversions this factor is of minor importance.

Supporting equipment: Slurry reactors can use very fine catalyst particles, and this can lead to problems of separating catalyst from liquid. Trickle beds don't have this problem, and this is the big advantage of trickle beds. Unfortunately, these large particles in trickle beds mean much lower reaction rates. With regard to rate, the trickle bed can only hold its own

- for very slow reactions on porous solids where pore diffusion limitations do not appear, even for large particles and
- for very fast reactions on nonporous catalyst-coated particles.

Overall, the trickle bed is simpler, the slurry reactor usually has a higher rate, and the fluidized bed is somewhere in between.

22.5 APPLICATIONS

Here is a short list of applications of these reactors.

- The catalytic hydrogenation of petroleum fractions to remove sulfur impurities. Hydrogen is very soluble in the liquid; high pressure is used while the impurity is present in the liquid in low concentration. All these factors tend to lead to extreme 2 (excess of A).

- The catalytic oxidation of liquid hydrocarbons with air or oxygen. Since oxygen is not very soluble in the liquid, while the hydrocarbon could well be present in high concentration we could end up in extreme 1 (excess of B).
- The removal of dissolved organics from industrial waste water by catalytic oxidation as an alternative to biooxidation. Here oxygen is not very soluble in water, but the organic waste is also present in low concentration. It is therefore not clear in what regime the kinetics lie. The catalytic oxidation of phenol is an example of such an operation.
- The removal of airborne pollutants by adsorption and/or reaction. These operations usually lead to extreme 1 (excess of B).
- The illustrative examples and many of the problems which follow are adapted from or are extensions of problems prepared by Ramachandran and Choudhary (1980).

EXAMPLE 22.1 HYDROGENATION OF ACETONE IN A PACKED BUBBLE COLUMN

Aqueous acetone ($C_{B0} = 1000$ mol/m^3 l, $v_l = 10^{-4}$ m^3 l/s) and hydrogen (1 atm, $v_g = 0.04$ m^3 g/s, $H_A = 36845$ Pa·m^3 l/mol) are fed to the bottom of a long, slender column (5-m high, 0.1-m^2 cross section) packed with porous Raney nickel catalyst ($d_p = 5 \times 10^{-3}$ m cat, $\rho_s = 4500$ kg/m^3 cat, $f_s = 0.6$, $\mathscr{D}_e = 8 \times 10^{-10}$ m^3 l/m cat·s) and kept at 14°C, as shown in Fig. E22.1. At these conditions acetone is hydrogenated to propanol according to the reaction

$$\underset{(A)}{\underline{H_2}}\,(g \rightarrow l) + \underset{(B)}{\underline{CH_3COCH_3(l)}} \xrightarrow[\text{catalyst}]{\text{on}} CH_3CHOHCH_3$$

with rate given by

$$-r'_A = -r'_B = k' C_A^{1/2} C_B^0 \qquad \text{and} \ldots k' = 2.35 \times 10^{-3} \frac{\text{m}^3 l}{\text{kg} \cdot \text{s}} \left(\frac{\text{mol}}{\text{m}^3 l} \right)^{1/2}$$

What will be the conversion of acetone in this unit?

Additional Data

The mass transfer rate constants are estimated to be

$$(k_{Ai} a_i)_{g+l} = 0.02 \frac{\text{m}^3 l}{\text{m}^3 r \cdot \text{s}} \qquad k_{Ac} a_c = 0.05 \frac{\text{m}^3 l}{\text{m}^3 r \cdot \text{s}}$$

the sum of the gas + liquid film conductances

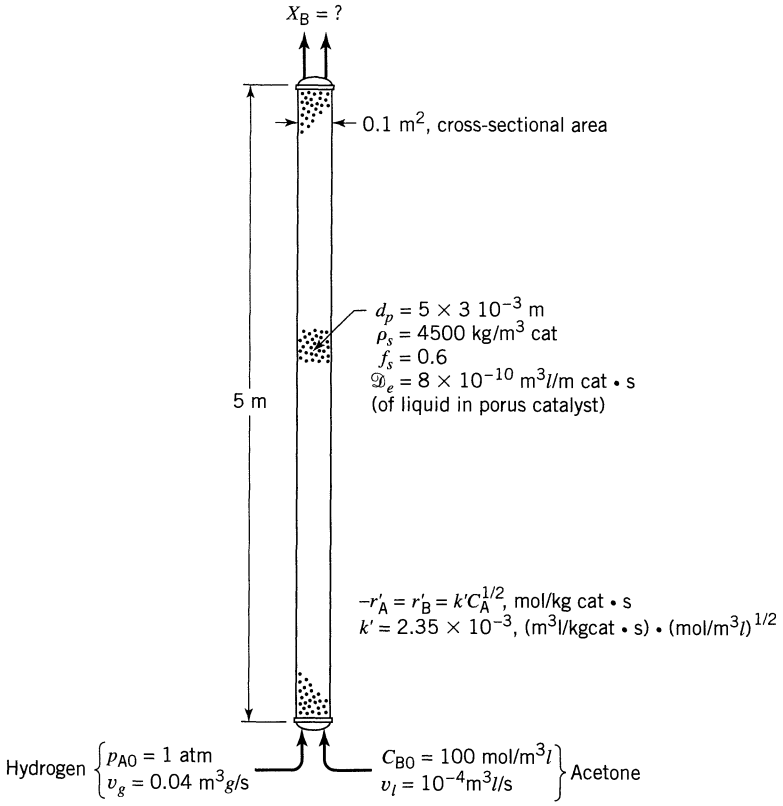


Figure E22.1

SOLUTION

Before rushing to our equations to do the appropriate integrations needed for plug flow, let us consider the situation

- $C_{B0} = 1000$ while C_A is given by Henry's law as

$$C_A = \frac{p_A}{H_A} = \frac{101\,325}{36\,845} = 2.75 \text{ mol/m}^3\, l$$

  Comparing values shows that $C_B \gg C_A$; hence, we are in extreme 1 (excess of B).
- Next, we are dealing with pure hydrogen; thus, p_A is constant throughout the packed column. And since the rate is only dependent on C_A and not on C_B, this means that the rate of reaction is constant throughout the column.

Let us next look at the rate. From Eq. 18.28 we have for a half order reaction

$$M_T = L\sqrt{\frac{n+1}{2}\cdot\frac{k' C_A^{n-1}\rho_s}{\mathscr{D}_e}}$$

$$= \frac{5\times10^{-3}}{6}\sqrt{\frac{1.5}{2}\cdot\frac{(2.35\times10^{-3})(2.75)^{-1/2}(4500)}{8\times10^{-10}}} = 64.4$$

$$\therefore \mathscr{E} = \frac{1}{64.4} = 0.0155$$

Replacing all known values into Eq. 18 gives

$$-r_A'''' = \frac{1}{\dfrac{1}{\underset{\nwarrow 58\%}{0.02}} + \dfrac{1}{\underset{\nwarrow 23\%}{0.05}} + \dfrac{1}{(2.35\times10^{-3})(1)\underset{\nwarrow 19\%}{(2.75)^{-1/2}}(0.0155)(0.6)(4500)}}\;\frac{101\,325}{36\,845}$$

$$= 0.0317 \text{ mol/m}^3\,\text{r}\cdot\text{s}$$

Next, to the material balance of Eq. 11. With constant rate this becomes

$$\underset{\substack{\nwarrow \text{not particularly}\\ \text{useful}}}{\underline{F_{A0}X_A}} = \underset{\substack{\nwarrow \text{use this term in which}\\ F_{B0} = v_l C_{B0} = 10^{-4}(1000) = 0.1 \text{ mol/s}}}{\underline{\frac{F_{B0}X_B}{b}}} = (-r_A''')V_r$$

Thus on rearranging

$$X_B = \frac{b(-r_A'''')V_r}{F_{B0}} = \frac{(1)(0.0317)(5\times0.1)}{0.1}$$

$$= 0.158, \text{ or } \underline{\underline{16\% \text{ conversion}}}$$

■

EXAMPLE 22.2 HYDROGENATION OF A BATCH OF BUTYNEDIOL IN A SLURRY REACTOR

Hydrogen gas is bubbled into an agitated tank (V_r = 2 m$^3 r$) containing liquid butynediol (C_{B0} = 2500 mol/m^3 l) plus a dilute suspension of palladium-impregnated porous catalyst pellets ($d_p = 5\times10^{-5}$ m cat, ρ_s = 1450 kg/m^3 cat, $\mathscr{D}_e = 5\times10^{-10}$ m^3 l/m cat·s, f_s = 0.0055). Hydrogen dissolves in the liquid (H_A =

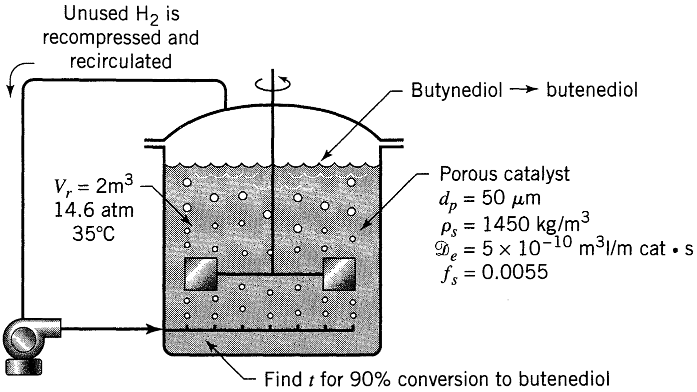


Figure E22.2*a*

148 000 Pa · m³ *l*/mol) and reacts with the butynediol on the catalyst surface as follows (see Fig. E22.2*a*):

$$\underset{\text{(A)}}{\underline{\mathrm{H}_2}}\,(g \rightarrow l) + \underset{\text{(B)}}{\underline{\text{butynediol}}}(l) \xrightarrow[\text{catalyst}]{\text{on}} \text{butynediol}$$

and at 35°C

$$-r'_\mathrm{A} = k' C_\mathrm{A} C_\mathrm{B} \qquad \text{and} \qquad k' = 5 \times 10^{-5}\ \mathrm{m^6}\,l/\mathrm{kg \cdot mol\,cat \cdot s}$$

Unused hydrogen is recompressed and recirculated, and the whole operation takes place at 1.46 atm and 35°C.

Find out how long it will take for 90% conversion of reactant.

Additional Data

The mass transfer rates are given as

$$\underset{\uparrow\ \text{the sum of the gas and liquid films}}{(k_{\mathrm{A}i}a_i)_{g+l}} = 0.277\,\frac{\mathrm{m}^3 l}{\mathrm{m}^3 r \cdot \mathrm{s}} \qquad k_{\mathrm{A}c} = 4.4 \times 10^{-4}\,\frac{\mathrm{m}^3 l}{\mathrm{m}^3 r \cdot \mathrm{s}}$$

SOLUTION

First compare C_A and C_B:

$$\left.\begin{aligned} C_\mathrm{A} &= \frac{p_\mathrm{A}}{H_\mathrm{A}} = \frac{1.46(101\,325)}{148\,000} = 10\ \mathrm{mol/m^3}\,l \\ C_{\mathrm{B}0} &= 2500 \text{ and } C_{\mathrm{B}f} = 250\ \mathrm{mol/m^3}\,l \end{aligned}\right\} \begin{array}{l}\text{Both at the beginning and} \\ \text{at the end of the batch run} \\ C_\mathrm{B} \gg C_\mathrm{A}\text{; therefore, the} \\ \text{system is in extreme 1.}\end{array}$$

Although C_A stays constant throughout the batch run, C_B does not, so we will have a changing rate with time and with C_B. Therefore, let us evaluate the rate at any particular value of C_B.

$$a_c = \frac{6f_s}{d_p} = \frac{6(0.0055)}{5 \times 10^{-5}} = 660\ \text{m}^2\ \text{cat/m}^3\ l$$

therefore,

$$k_{Ac}a_c = 4.4 \times 10^{-4}(660) = 0.29\,\frac{\text{m}^3\ l}{\text{m}^3\ r \cdot \text{s}}$$

and

$$M_T = L\sqrt{\frac{k' C_B \rho_s}{\mathscr{D}_e}} = \frac{5 \times 10^{-5}}{6}\sqrt{\frac{(5 \times 10^{-5})C_B(1450)}{5 \times 10^{-10}}} = 0.1C_B^{1/2} \qquad \textbf{(i)}$$

Replacing in the rate expression of Eq. 18 gives

$$\begin{aligned} -r_A'''' &= \frac{1}{\dfrac{1}{0.277} + \dfrac{1}{0.29} + \dfrac{1}{(5 \times 10^{-5})C_B(1450)(\mathscr{E}_A)(0.0055)}}\;\frac{14.6(101\,325)}{148\,000} \qquad \textbf{(ii)} \\ &= \frac{1}{0.705\,84 + \dfrac{250.8}{C_B(\mathscr{E}_A \text{ at } M_T = 0.1C_B^{1/2})}} \end{aligned}$$

Choose a Number of C_B Values	M_T from Eq. (i)	$\mathscr{E}_A$ from Eq. 18.6	$-r_A''''$ from Eq. (ii)	$1/(-r_A'''')$
2500	5	0.19	0.8105	1.23
1000	3.16	0.29	0.6367	1.57
250	1.58	0.5	0.3687	2.71

Now from Eq. 12 the reaction time is given by

$$t = \frac{V_l}{bV_r}\int_{C_{Bf}}^{C_{B0}} \frac{dC_B}{(-r_A'''')} \qquad \textbf{(12)}$$

With $b = 1$ and $V_l \cong V_r$, making the plot of Fig. E22.2*b*, and taking the area under the curve gives

$$\underline{\underline{t = 3460\ \text{s}}}, \text{ or } \underline{\underline{58\ \text{min}}}$$

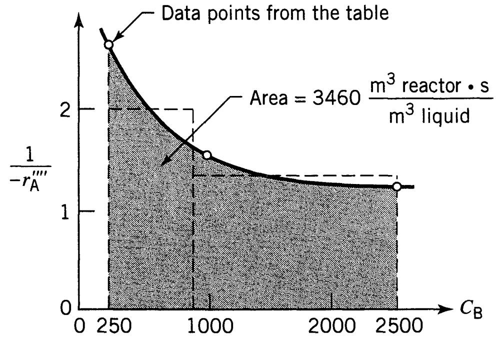


Figure E22.2b

REFERENCE

Ramachandran, P. A., and Choudry, V. R., *Chem. Eng.*, p. 74 (December 1, 1980).

PROBLEMS

22.1. ***Trickle bed oxidation.*** Dilute aqueous ethanol (about 2–3%) is oxidized to acetic acid by the action of pure oxygen at 10 atm in a trickle bed reactor packed with palladium-alumina catalyst pellets and kept at 30°C. According to Sato et al., Proc. First Pacific Chem. Eng. Congress, Kyoto, p. 197, 1972, the reaction proceeds as follows:

$$\underbrace{O_2(g \rightarrow l)}_{(A)} + \underbrace{CH_3CH_2OH(l)}_{(B)} \xrightarrow[\text{catalyst}]{\text{on}} CH_3COOH(l) + H_2O$$

with rate

$$-r'_A = k'C_A, \qquad k' = 1.77 \times 10^{-5}\ \text{m}^3/\text{kg}\cdot\text{s}$$

Find the fractional conversion of ethanol to acetic acid if gas and liquid are fed to the top of a reactor in the following system:

Gas stream: $v_g = 0.01\ \text{m}^3/\text{s}$, $H_A = 86\,000\ \text{Pa}\cdot\text{m}^3/\text{mol}$

Liquid stream: $v_l = 2 \times 10^{-4}\ \text{m}^3/\text{s}$, $C_{B0} = 400\ \text{mol/m}^3$

Reactor: 5 m high, $0.1\ \text{m}^2$ cross section, $f_s = 0.58$

Catalyst: $d_p = 5$ mm, $\rho_s = 1800\ \text{kg/m}^3$
$\mathscr{D}_e = 4.16 \times 10^{-10}\ \text{m}^3/\text{m cat}\cdot\text{s}$

Kinetics: $k_{Ag}a_i = 3 \times 10^{-4}\ \text{mol/m}^3\cdot\text{Pa}\cdot\text{s}$, $k_{Al}a_i = 0.02\ \text{s}^{-1}$
$k_{Ac} = 3.86 \times 10^{-4}\ \text{m/s}$

22.2. ***Slurry column oxidation.*** Instead of using a trickle bed reactor for ethanol oxidation (see previous problem), let us consider using a slurry reactor. For this type of unit

$$(k_{Ag}a_i)_{g+l} = 0.052\ \text{s}^{-1}, \qquad k_{Ac} = 4 \times 10^{-4}\ \text{m/s}$$

$$d_p = 10^{-4}\ \text{m}, \quad f_g = 0.05, \quad f_l = 0.75, \quad f_s = 0.2$$

Take all flows and other values from the previous problem, and then find the expected fractional conversion of ethanol in this reactor.

22.3. ***Slurry tank hydrogenation.*** Predict the conversion of glucose to sorbitol in a stirred slurry reactor using pure hydrogen gas at 200 atm and 150°C. The catalyst used is porous Raney nickel, and under these conditions Brahme and Doraiswamy, *IEC/PDD,* **15,** 130 (1976) report that the reaction proceeds as follows:

$$\underset{\text{(A)}}{H_2(g \rightarrow l)} + \underset{\text{(B)}}{\text{glucose}, C_6H_{12}O_6(l)} \xrightarrow[\text{catalyst}]{\text{solid}} \text{sorbitol}, C_6H_{14}O_6(l)$$

with

$$-r'_A = -r'_B = k' C_A^{0.6} C_B, \quad k' = 5.96 \times 10^{-6} \frac{\text{mol}}{\text{kg} \cdot \text{s}} \left(\frac{\text{m}^3}{\text{mol}}\right)^{1.6}$$

Data:

Gas stream: $v_g = 0.2\ \text{m}^3/\text{s}, \quad H_A = 277\,600\ \text{Pa} \cdot \text{m}^3/\text{mol}$

Liquid stream: $v_l = 0.01\ \text{m}^3/\text{s}, \quad C_{B0} = 2000\ \text{mol/m}^3$

Reactor: $V_r = 2\ \text{m}^3, \quad f_s = 0.056$

Catalyst: $d_p = 10\ \mu\text{m}, \rho_s = 8900\ \text{kg/m}^3, \mathscr{D}_e = 2 \times 10^{-9}\ \text{m}^3/\text{m cat} \cdot \text{s}$

Kinetics: $(k_{Ag}a_i)_{g+l} = 0.05\ \text{s}^{-1}, \quad k_{Ac} = 10^{-4}\ \text{m/s}$

22.4. ***Multistage bubble column hydrogenation.*** In the previous problem, conversion to sorbitol is not as high as desired so let us consider an alternative design, one which uses an upflow of gas and liquid through a long, narrow multistage column 0.25 m^2 in cross section and 8 m high containing suspended solids ($d_p = 10^{-3}$ m and $f_s = 0.4$). What will be the conversion with this arrangement?

Data: $(k_{Ag}a_i)_{g+l} = 0.025\ \text{s}^{-1}, \qquad k_{Ac} = 10^{-5}\ \text{m/s}$

All other values are unchanged from the previous problem.

22.5. ***Three-phase fluidized bed hydrogenation.*** Aniline is to be hydrogenated in a three-phase fluidized bed of porous clay particles impregnated with nickel catalyst. The well-agitated batch of liquid is kept at 130°C by heat exchanger tubes passing through the fluidized bed, and by bubbling hydrogen vigorously and at a high rate through the bed at 1 atm. According to Govindarao and Murthy, *J. Appl. Chem. Biotechnol.* **25,** 196 (1975), at these conditions reaction proceeds as follows:

$$\underbrace{3H_2(g \rightarrow l)}_{(A)} + \underbrace{2\,C_6H_5NH_2(l)}_{(B)} \xrightarrow[\text{catalyst}]{\text{Ni}} \underbrace{C_6H_{11}NHC_6H_5}_{\text{cyclohexyl-aniline}} + NH_3$$

with rate

$$-r'_A = k'C_A, \qquad k' = 0.05\ \text{m}^3/\text{kg cat}\cdot\text{s}$$

Find the time needed for 90% conversion of this batch of aniline.

Data:

Gas stream: pure H_2 at 1 atm, $H_A = 28\,500\ \text{Pa}\cdot\text{m}^3/\text{mol}$

Batch of liquid: $C_{B0} = 1097\ \text{mol/m}^3$

Reactor: $f_g = 0.10,\quad f_l = 0.65,\quad f_s = 0.25$

Catalyst: $d_p = 300\ \mu\text{m},\quad \rho_s = 750\ \text{kg/m}^3$
$\mathscr{D}_e = 8.35 \times 10^{-10}\ \text{m}^3/\text{m cat}\cdot\text{s}$

Kinetics: $(k_{Ag}a_i)_{g+l} = 0.04\ \text{s}^{-1},\quad k_{Ac} = 10^{-5}\ \text{m/s}$

Assume that the fraction of NH_3 in the gas stream is very small at any time.

22.6. ***Bubble column hydrogenation.*** Consider a different design to effect the hydrogenation of the previous problem, one which uses a long, narrow bubble column of semisuspended 3-mm catalyst particles ($f_s = 0.4$, $f_l = 0.5$, $f_g = 0.1$). The batch of liquid aniline is circulated through an external heat exchanger (volume of liquid in the loop outside the reactor equals the total volume of the reactor), and hydrogen is bubbled through the column. Find the time needed for 90% conversion of aniline in this unit.

Data: $(k_{Ag}a_i)_{g+l} = 0.02\ \text{s}^{-1}, \qquad k_{Ac} = 7 \times 10^{-5}\ \text{m/s}$

All other values not mentioned here remain unchanged from the previous problem.

22.7. ***Trickle bed gas absorber-reactor.*** Sulfur dioxide is to be removed from a gas by passing the gas and water through a bed of highly porous activated carbon kept at 25°C. In this system sulfur dioxide and oxygen dissolve in water and react on the solid to give sulfur trioxide, as follows:

$$SO_2(g \rightarrow l) + \frac{1}{2}O_2(g \rightarrow l) \xrightarrow[\text{solid}]{\text{on}} SO_3(l)$$

where

$$-r_{SO_2} = k' C_{\text{oxygen}}, \qquad k' = 0.015\,53\ \mathrm{m^3/kg\cdot s}$$

Find the fraction of sulfur dioxide removed from a gas stream under the following conditions:

Gas stream: $v_g = 0.01\ \mathrm{m^3/s}$, $\pi = 101\,325\ \mathrm{Pa}$
entering $SO_2 = 0.2\%$, $\mathrm{H} = 380\,000\ \mathrm{Pa\cdot m^3/mol}$
entering $O_2 = 21\%$, $\mathrm{H} = 87\,000\ \mathrm{Pa\cdot m^3/mol}$

Liquid stream: $v_l = 2 \times 10^{-4}\ \mathrm{m^3/s}$

Reactor: 2 m high, $0.1\ \mathrm{m^2}$ cross section, $f_s = 0.6$

Catalyst: $d_p = 5\ \mathrm{mm}$, $\rho_s = 850\ \mathrm{kg/m^3}$
$\mathscr{D}_e = 5.35 \times 10^{-10}\ \mathrm{m^3/m}\ s\cdot\mathrm{s}$

Kinetics: $(k_i a_i)_{g+l} = 0.01\ \mathrm{s^{-1}}$, $k_c = 10^{-5}\ \mathrm{m/s}$

22.8. ***Hydrogenation in a slurry reactor.*** The batch hydrogenation of Example 22.2 takes just about an hour to run. Let us suppose that in practical operations we can run eight batches of fluid per day in this unit. Thus, in the long run a batch of fluid is processed every three hours.

Another way of running this reaction is to feed the agitated reactor continuously at such a rate that we get 90% conversion of butynediol. How do these two processing rates compare in the long term? Give your answer as $F_{B0,\,\text{continuous}}/F_{B0,\,\text{batch}}$. Assume that the liquid feed composition, gas composition and pressure, mass transfer and chemical rates are the same in both batch and continuous operations.