

# Chapter 24

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## Fluid–Fluid Reactors: Design

We must first choose the right kind of contactor, then find the size needed. There are two kinds of contactor—towers and tanks, and Fig. 24.1 shows some examples. As may be expected, these contactors have widely different  $G/L$  volume ratios, interfacial areas,  $k_g$  and  $k_l$ , and concentration driving forces. The particular properties of the system you are dealing with, the solubility of gaseous reactant, the concentration of reactants, etc.—in effect the location of the main resistance in the rate equation—will suggest that you use one class of contactor and not the other.

Table 24.1 shows some of the characteristics of these contactors.

### Factors to Consider in Selecting a Contactor

(a) **Contacting pattern.** We idealize these as shown in Fig. 24.2.

- Towers approximate plug  $G$ /plug  $L$ .
- Bubble tanks approximate plug  $G$ /mixed  $L$ .
- Agitated tanks approximate mixed  $G$ /mixed  $L$ .

As we shall see, towers have the largest mass transfer driving force and in this respect have an advantage over tanks. Agitated tanks have the smallest driving force.

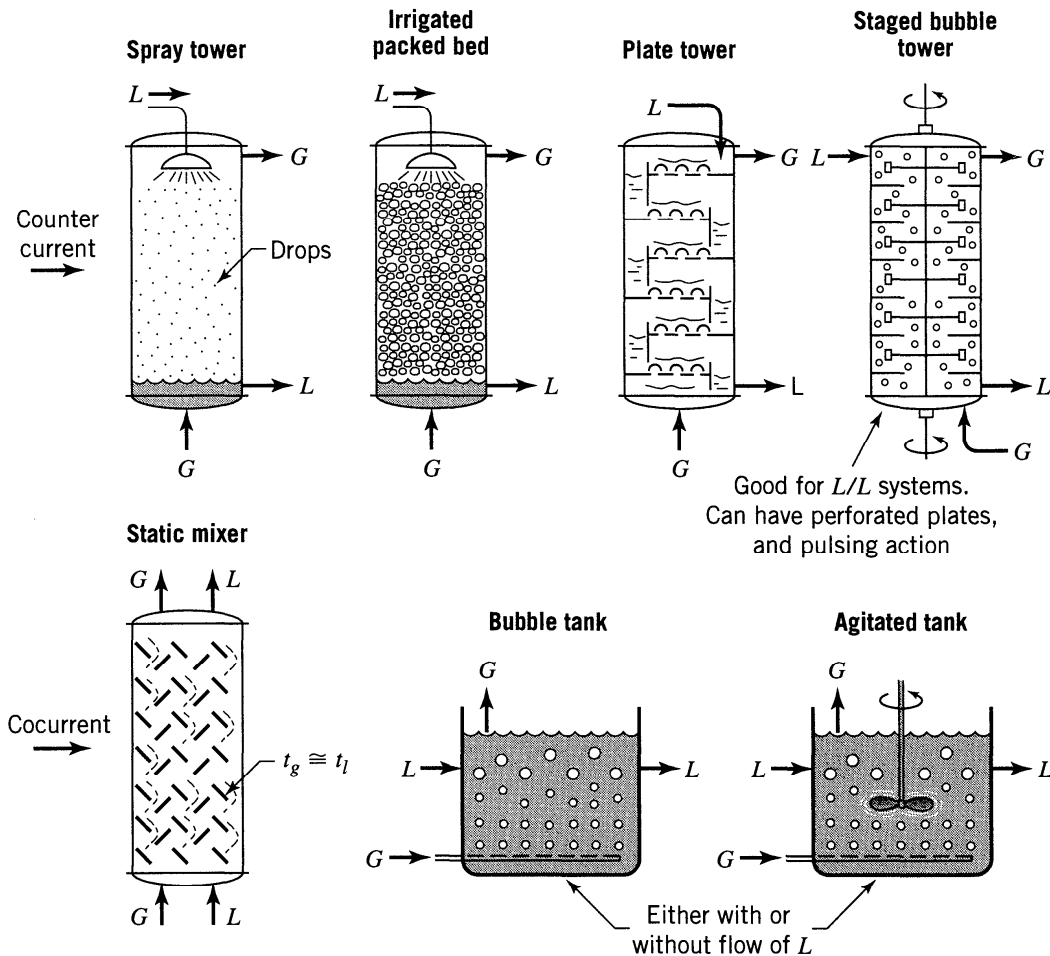
(b)  **$k_g$  and  $k_l$ .** For liquid droplets in gas  $k_g$  is high,  $k_l$  is low. For gas bubbles rising in liquid  $k_g$  is low,  $k_l$  is high.

(c) **Flow rates.** Packed beds work best with relative flow rates of about  $F_l/F_g \cong 10$  at 1 bar. Other contactors are more flexible in that they work well in a wider range of  $F_l/F_g$  values.

(d) **If the resistance is in the gas and/or liquid films** you want a large interfacial area “a,” thus most agitated contactors and most columns. If the  $L$  film dominates, stay away from spray contactors. If the  $G$  film dominates stay away from bubble contactors.

(e) **If the resistance is in the main body of the  $L$**  you want large  $f_l = V_l/V_r$ . Stay away from towers. Use tank contactors.

(f) **Solubility.** For very soluble gases, those with a small value of Henry’s law constant  $H$  (ammonia, for example), gas film controls, thus you should



**Figure 24.1** Tower and tank contactors for  $G/L$  reactions.

avoid bubble contactors. For gases of low solubility in the liquid, thus high  $H$  value ( $O_2$ ,  $N_2$ , as examples) liquid film controls, so avoid spray towers.

**(g) Reaction lowers the resistance of the liquid film, so**

- For absorption of highly soluble gases, chemical reaction is not helpful.
- For absorption of slightly soluble gases, chemical reaction is helpful and does speed up the rate.

**Nomenclature.** We use the following symbols in our development.

$A_{cs}$  = cross-sectional area of column.

$a$  = interfacial contact area per unit volume of reactor ( $m^2/m^3$ ).

$f_l$  = volume fraction of liquid (-).

$i$  = any participant, reactant or product, in the reaction.

A, B, R, S = participants in the reaction.

U = carrier or inert component in a phase, hence neither reactant nor product.

$T$  = total moles in the reacting (or liquid) phase.

$Y_A = p_A/p_U$ , moles A/mole inert in the gas (-).

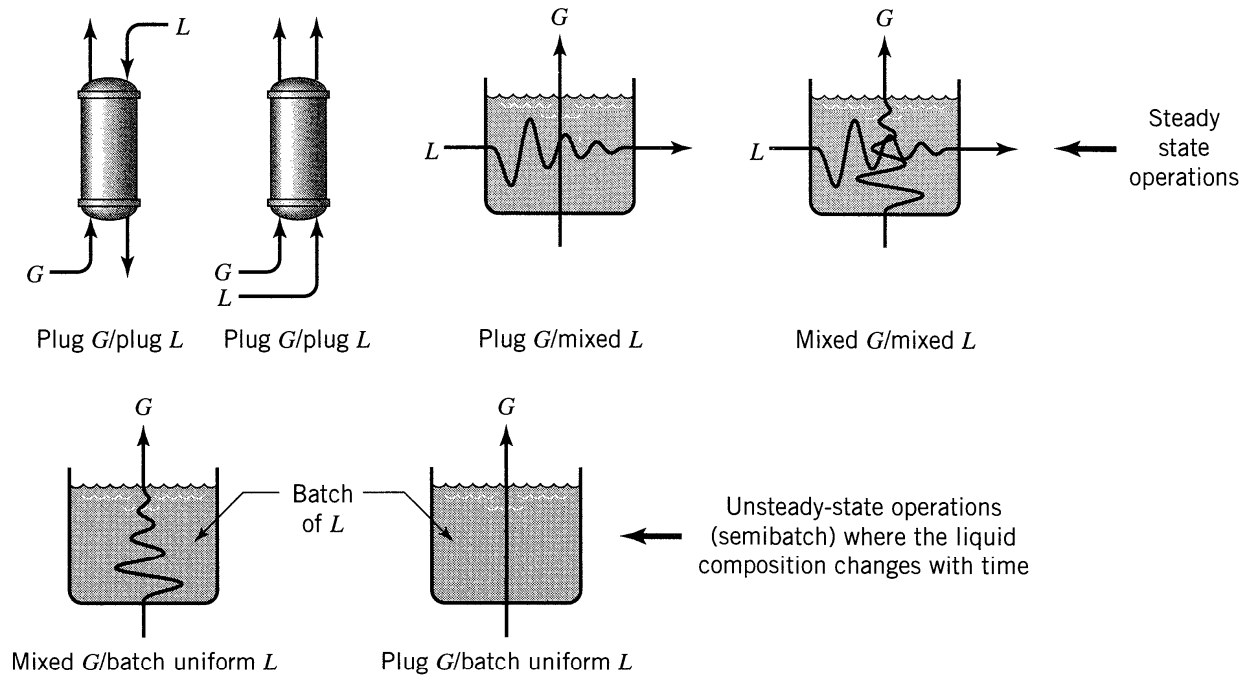
$X_A = C_A/C_U$ , moles A/mole inert in the liquid (-).

$F'_g, F'_l$  = molar flow rate of all the gas and the liquid (mol/s).

$F_g = F'_g p_U/\pi$ , upward molar flow rate of inerts in the gas (mol/s).

**Table 24.1** Characteristics of  $G/L$  Contactors (from Kramers and Westerterp, 1961).

Flow Pattern	Contactors	$a$ ( $\text{m}^2/\text{m}^3$ )	$f_t = \frac{V_l}{V}$ (-)	Capacity	Comments
Counter Current Flow	Spray tower	60	0.05	Low	Good for very soluble gases high $k_g/k_l$
	Packed bed	100	0.08	High	Good all rounder, but must have $F_l/F_g \cong 10$
	Plate tower	150	0.15	Medium-high	
Cocurrent flow	Staged bubble column	200	0.9	Low	Needs mechanical mixer or pulsing device. Good for slightly soluble gases and $L_1/L_2$ . Has low $k_g/k_l$ .
	Static mixer	200	0.2-0.8	Very high	Very flexible, little reported data $\bar{t}_g \cong \bar{t}_l$ .
	Bubble tank	20	0.98	Medium	Cheap to build
Mixed flow of $L$	Agitated tank	200	0.9	Medium	Cheap to build but needs a mechanical agitator



**Figure 24.2** Contacting patterns for  $G/L$  contactors.

$F_l = F'_l C_U / C_T$ , downward molar flow rate of inerts in the liquid phase (mol/s).

With this nomenclature, we have the following relationships among the various concentration measures.

$$\pi = p_A + p_B + \cdots + p_U$$

$$C_T = C_A + C_B + \cdots + C_U$$

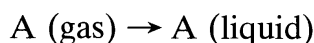
$$dY_A = d\left(\frac{p_A}{p_U}\right) = \frac{p_U dp_A - p_A dp_U}{p_U^2} \stackrel{\text{dilute}}{\approx} \frac{dp_A}{p_U}$$

$$dX_A = d\left(\frac{C_A}{C_U}\right) = \frac{C_U dC_A - C_A dC_U}{C_U^2} \stackrel{\text{dilute}}{\approx} \frac{dC_A}{C_U}$$

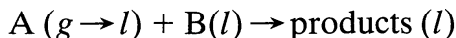
The performance equations which are written in terms of  $F_g$  and  $F_l$  are useful when the flowing streams have inert carrier material. The equation written in terms of  $F'_g$  and  $F'_l$  are useful when the flowing streams only contain reactive materials and no inerts.

## 24.1 STRAIGHT MASS TRANSFER

Since the approach for reacting systems is a straightforward extension of straight mass transfer, let us first develop equations for absorption alone of A by liquid



then go to reacting systems.



Note the similarity in the performance equations.

### Plug Flow *G*/Plug Flow *L*—Countercurrent Flow in a Tower

To develop the performance equation, we combine the rate equation with the material balance. Thus for steady-state countercurrent operations we have for a differential element of volume

$$(\text{A lost by gas}) = (\text{A gained by liquid}) = (-r_A''')dV_r$$

or

$$\frac{F_g dY_A}{(\pi - p_A)^2} = d\left(\frac{F'_g p_A}{\pi}\right) = \frac{F_g dp_A}{\pi - p_A} = \frac{F_l dX_A}{(C_T - C_A)^2} = (-r_A''')dV_r \quad (1)$$

$\frac{F_g \pi dp_A}{(\pi - p_A)^2} = d\left(\frac{F'_g p_A}{\pi}\right) = \frac{F_g dp_A}{\pi - p_A}$ 
 $\frac{F_l dX_A}{(C_T - C_A)^2}$ 
 $(-r_A''')a = k_{A_g} a(p_A - p_{A_i}) = k_{A_l} a(C_{A_i} - p_A)$

Integrating for the whole tower gives

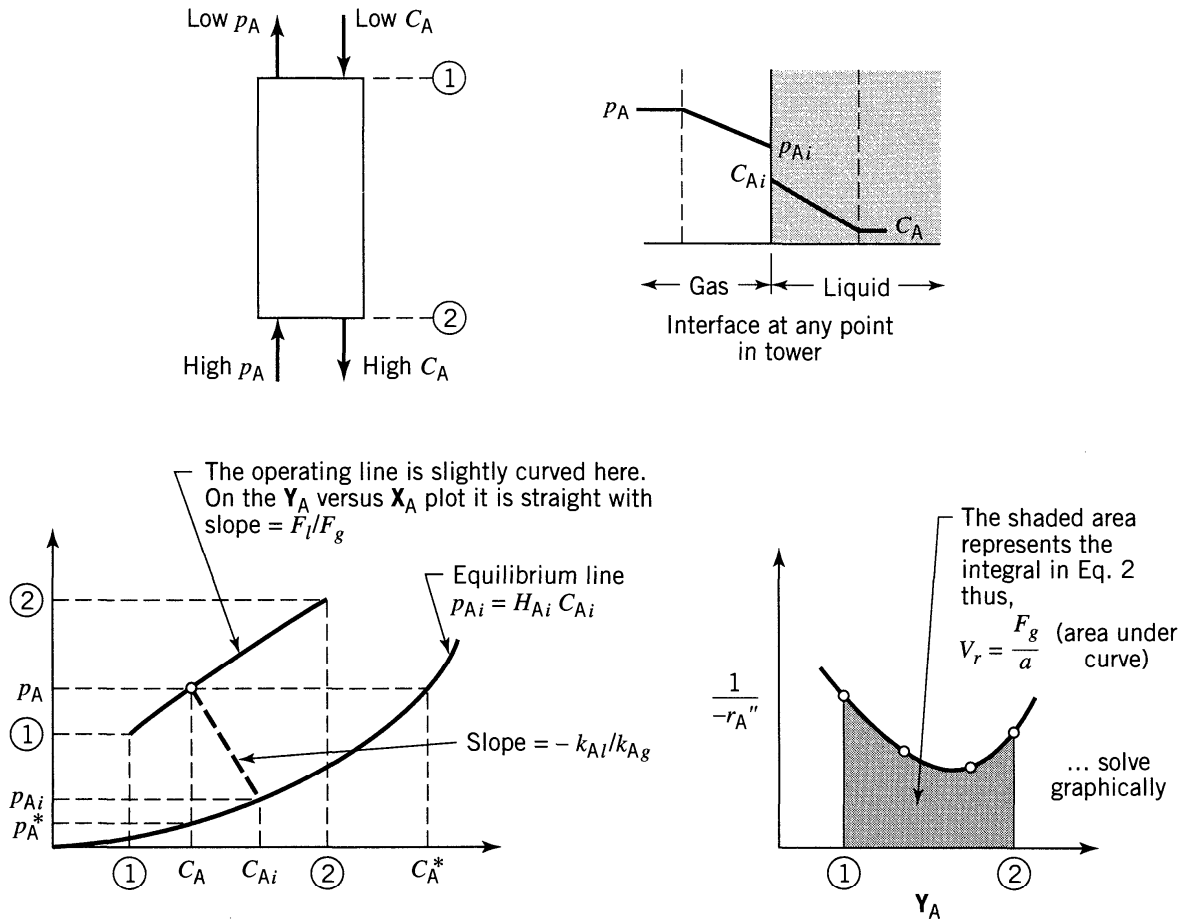
$$\begin{aligned} V_r &= \frac{F_g}{a} \int_{Y_{A1}}^{Y_{A2}} \frac{dY_A}{\pi - p_A} = \frac{F_l}{a} \int_{X_{A1}}^{X_{A2}} \frac{dX_A}{C_T - C_A} \\ &= F_g \pi \int_{p_{A1}}^{p_{A2}} \frac{dp_A}{k_{A_g} a (\pi - p_A)^2 (p_A - p_{A_i})} = \int_{p_{A1}}^{p_{A2}} \frac{F'_g dp_A}{k_{A_g} a (\pi - p_A) (p_A - p_{A_i})} \\ &= F_l C_T \int_{C_{A1}}^{C_{A2}} \frac{dC_A}{k_{A_l} a (C_T - C_A)^2 (C_{A_i} - C_A)} = \int_{C_{A1}}^{C_{A2}} \frac{F'_g dC_A}{k_{A_l} a (C_T - C_A) (C_{A_i} - C_A)} \end{aligned} \quad (2)$$

In brief, the design procedure is summarized in Fig. 24.3. For dilute systems  $C_A \ll C_T$  and  $p_A \ll \pi$ , so  $F'_g \cong F_g$  and  $F'_l \cong F_l$ . In this situation the differential material balance becomes

$$\frac{F_g}{\pi} dp_A = \frac{F_l}{C_T} dC_A = -r_A'''' dV_r \quad (3)$$

and for any two points in the absorber

$$p_{A2} - p_{A1} = \frac{F_l \pi}{F_g C_T} (C_{A2} - C_{A1}) \quad (4)$$



**Figure 24.3** Illustration of the design procedure for straight mass transfer in countercurrent towers.

The rate expression reduces to

$$\begin{aligned}
 -r_A''' &= (-r_A'')a = \left( \frac{1}{\frac{1}{k_{Ag}a} + \frac{H_A}{k_{Al}a}} \right) (p_A - p_A^*) \\
 &= K_{Ag}a(p_A - p_A^*) = K_{Al}a(C_A^* - C_A)
 \end{aligned} \tag{5}$$

Thus the general integrated rate expression of Eq. 2 becomes, with Eq. 3,

$$\begin{aligned}
 V_r = hA_{cs} &= \frac{F_g}{\pi} \int_{p_{A1}}^{p_{A2}} \frac{dp_A}{-r_A'''} = \frac{F_l}{C_T} \int_{C_{A1}}^{C_{A2}} \frac{dC_A}{-r_A'''} \\
 &= \frac{F_g}{\pi K_{Ag}a} \int_{p_{A1}}^{p_{A2}} \frac{dp_A}{p_A - p_A^*} = \frac{F_l}{C_T K_{Al}a} \int_{C_{A1}}^{C_{A2}} \frac{dC_A}{C_A^* - C_A}
 \end{aligned} \tag{6}$$

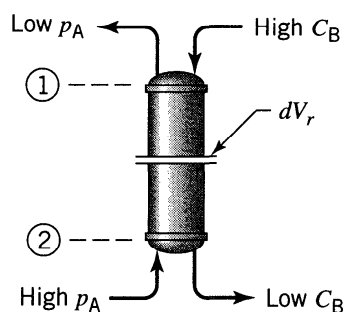
coefficient on gas basis  $\frac{1}{K_{Ag}} = \frac{1}{k_{Ag}} + \frac{H_A}{k_{Al}}$       gas in equilibrium with liquid  $C_A$ , or  $p_A^* = H_A C_A$       coefficient on liquid basis  $\frac{1}{K_{Al}} = \frac{1}{H_A k_{Ag}} + \frac{1}{k_{Al}}$       liquid in equilibrium with gas  $p_A$ , or  $C_A^* = p_A / H_A$

For the other contacting patterns of Fig. 24.2 plug  $G$ /plug  $L$  cocurrent, mixed  $G$ /mixed  $L$ , plug  $G$ /mixed  $L$ , mixed  $G$ /plug  $L$ , mixed  $G$ /batch  $L$  see Levenspiel (1996) Chapter 42, or recall the equations and methods from your lessons in mass transfer and unit operations.

## 24.2 MASS TRANSFER PLUS NOT VERY SLOW REACTION

Here we only treat the reaction  $A(g \rightarrow l) + bB(l) \rightarrow \text{products}(l)$ . We assume that the rate is fast enough so that no unreacted  $A$  enters the main body of the liquid. This assumes that the Hatta modulus is not very much smaller than unity.

### Plug Flow $G$ /Plug Flow $L$ —Mass Transfer + Reaction in a Countercurrent Tower



For a differential slice of absorber-reactor we write

$$\frac{\text{(A lost by gas)}}{\text{I}} = \frac{1}{b} \frac{\text{(B lost by liquid)}}{\text{II}} = \frac{\text{(disappearance of A by reaction)}}{\text{III}}$$

or

$$F_g dY_A = -\frac{F_l dX_B}{b} = (-r_A''') dV_r \quad (7)$$

**For Dilute Systems.**  $p_U \cong \pi$  and  $C_U \cong C_T$  in which case the above expressions simplify to

$$\frac{F_g}{\pi} dp_A = -\frac{F_l}{bC_T} dC_B = (-r_A'') a dV_r \quad (8)$$

Rearranging and integrating I and II, II and III, I and III gives the following:

In general

$$V_r = F_g \int_{Y_{A1}}^{Y_{A2}} \frac{dY_A}{(-r_A'')a}$$

$$= \frac{F_l}{b} \int_{X_{B2}}^{X_{B1}} \frac{dX_B}{(-r_B'')a} \quad \dots \text{with} \quad F_g(Y_{A2} - Y_{A1}) = \frac{F_l}{b}(X_{B1} - X_{B2}) \quad (9)$$

For dilute systems

$$V_r = \frac{F_g}{\pi} \int_{p_{A1}}^{p_{A2}} \frac{dp_A}{(-r_A'')a}$$

$$= \frac{F_l}{bC_T} \int_{C_{B2}}^{C_{B1}} \frac{dC_B}{(-r_A'')a} \quad \dots \text{with} \quad \frac{F_g}{\pi}(p_{A2} - p_{A1}) = \frac{F_l}{bC_T}(C_{B1} - C_{B2}) \quad (10)$$

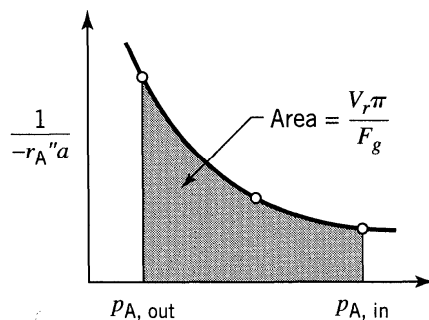
also good from point 1 to and point  $i$  in the tower

**To Solve for  $V_r$**

- pick a few  $p_A$  values, usually  $p_{A1}$ ,  $p_{A2}$  and one intermediate value are enough, and for each  $p_A$  find the corresponding  $C_B$ .
- evaluate the rate for each point from

$$(-r_A'')a = \left[ \frac{1}{\frac{1}{k_{Ag}a} + \frac{H_A}{k_{Al}aE} + \frac{H_A}{kC_Bf_l}} \right] p_A$$

- integrate the performance equation graphically



### Plug Flow $G$ /Plug Flow $L$ —Mass Transfer + Reaction in a Cocurrent Tower

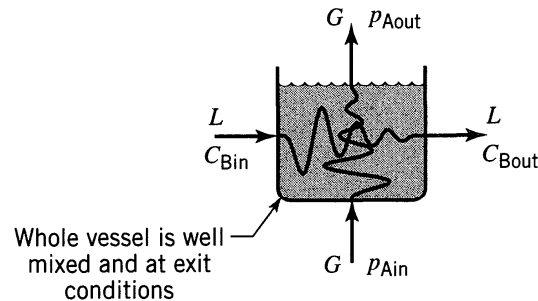
Here simply change  $F_l$  to  $-F_l$  (for upflow of both streams) or  $F_g$  to  $-F_g$  (for downflow of both streams) in the equations for countercurrent flow. Be sure to find the proper  $C_B$  value for each  $p_A$ . The rest of the procedure remains the same.



### Mixed Flow *G*/Mixed Flow *L*—Mass Transfer + Reaction in an Agitated Tank Contactor

Since the composition is the same everywhere in the vessel make an accounting about the vessel as a whole. Thus,

$$\left( \begin{array}{c} \text{A lost} \\ \text{by gas} \end{array} \right) = \frac{1}{b} \left( \begin{array}{c} \text{B lost} \\ \text{by liquid} \end{array} \right) = \left( \begin{array}{c} \text{disappearance of} \\ \text{A by reaction} \end{array} \right)$$



In symbols these equalities become

$$F_g(\mathbf{Y}_{Ain} - \mathbf{Y}_{Aout}) = \frac{F_l}{b}(\mathbf{X}_{Bin} - \mathbf{X}_{Bout}) = (-r_A''''')|_{\text{at exit conditions for both } G \text{ and } L} V_r \quad (11)$$

and for dilute systems

$$\frac{F_g}{\pi}(p_{Ain} - p_{Aout}) = \frac{F_l}{bC_T}(C_{Bin} - C_{Bout}) = (-r_A''''')|_{\text{at exit}} V_r \quad (12)$$

**To find  $V_r$** , the solution is direct; evaluate  $-r_A'''''$  from known stream compositions and solve Eq. 11 or 12.

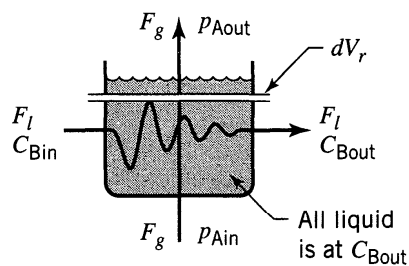
**To find  $C_{Bout}$  and  $p_{Aout}$  given  $V_r$** , guess  $p_{Aout}$ , evaluate  $C_{Bout}$ , then  $-r_A'''''$ , then  $V_r$ . Compare the calculated  $V_r$  value with the true value. If different, guess another  $p_{Aout}$ .

### Plug Flow *G*/Mixed Flow *L*—Mass Transfer + Reaction in Bubble Tank Contactors

Here we must make two accountings, a differential balance for the loss of A from the gas because *G* is in plug flow, and an overall balance for B because *L* is in mixed flow.

Focusing on a bit of rising gas, we have

$$\left( \begin{array}{c} \text{A lost} \\ \text{by gas} \end{array} \right) = \left( \begin{array}{c} \text{disappearance of} \\ \text{A by reaction} \end{array} \right) \quad \dots \text{ or } \dots \quad F_g d\mathbf{Y}_A = (-r_A''''')|_{L \text{ at exit conditions}} dV_r \quad (13)$$



For the liquid as a whole and for the gas as a whole, a balance about the whole reactor gives

$$\left( \begin{array}{l} \text{all A lost} \\ \text{by gas} \end{array} \right) = \frac{1}{b} \left( \begin{array}{l} \text{all B lost} \\ \text{by liquid} \end{array} \right) \quad \dots \text{ or } \dots \quad F_g \Delta Y_A = \frac{F_l}{b} \Delta X_B \quad (14)$$

Integrating Eq. 13 along the path of the bubble and also using Eq. 14 gives

In general

$$V_r = F_g \int_{Y_{Aout}}^{Y_{Ain}} \frac{dY_A}{(-r_A'')a} \quad \dots \text{with} \dots \quad F_g(Y_{Ain} - Y_{Aout}) = \frac{F_l}{b}(X_{Bin} - X_{Bout}) \quad (15)$$

for liquid at  $C_{Bout}$

For dilute systems

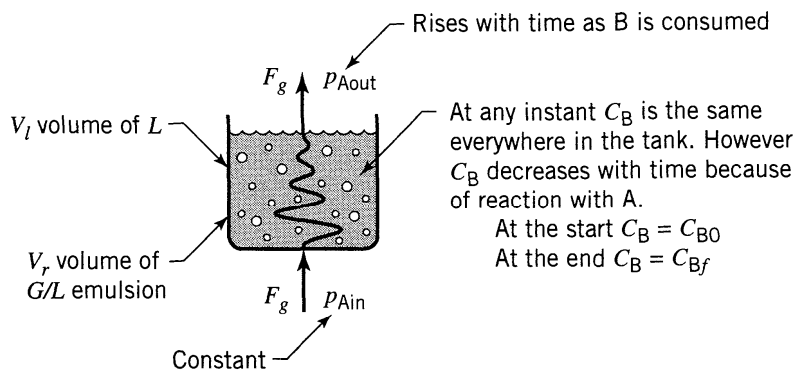
$$V_r = \frac{F_g}{\pi} \int_{p_{Aout}}^{p_{Ain}} \frac{dp_A}{(-r_A'')a} \quad \dots \text{with} \dots \quad \frac{F_g}{\pi}(p_{Ain} - p_{Aout}) = \frac{F_l}{bC_T}(C_{Bin} - C_{Bout}) \quad (16)$$

If  $V_r$  is to be found and the exit conditions are known, then the procedure is direct. Pick a number of  $p_A$  values and integrate graphically.

If  $p_{Aout}$  and  $C_{Bout}$  are to be found in a reactor of known volume  $V_r$  then we require a trial and error solution. Simply guess  $C_{Bout}$  and then see if  $V_{calculated} = V_{given}$ .

### Mixed Flow $G$ /Batch Uniform $L$ —Absorption + Reaction in a Batch Agitated Tank Contactor

Since this is not a steady-state operation, composition and rates all change with time, as shown in Fig. 24.4. At any instant the material balance equates the three



**Figure 24.4** History of a batch of reacting liquid.

quantities shown below and thus in general

$$\frac{F_g(Y_{Ain} - Y_{Aout})}{\text{I}} = \frac{V_l dC_B}{b dt} = (-r_A''''')V_r \quad (17)$$

II
III

loss of A from gas
decrease of B with time in L
disappearance of A or B by reaction. In the rate expression use  $p_{Aout}$  since G is in mixed flow.

For dilute systems

$$\frac{F_g}{\pi}(p_{Ain} - p_{Aout}) = -\frac{V_l dC_B}{b dt} = (-r_A''''')V_r \quad (18)$$

### To Find the Time Needed for a Given Operation

- Choose a number of  $C_B$  values, say  $C_{B0}$ ,  $C_{Bf}$  and an intermediate  $C_B$  value. For each  $C_B$  value guess  $p_{Aout}$ .
- Next calculate  $M_H$ ,  $E_i$ , and then  $E$  and  $-r_A'''''$ . This may require trial and error, but not often.
- See if terms I and III are equal to each other

$$(-r_A''''')V_r \stackrel{?}{=} F_g \left( \frac{p_{Ain}}{\pi - p_{Ain}} - \frac{p_{Aout}}{\pi - p_{Aout}} \right)$$

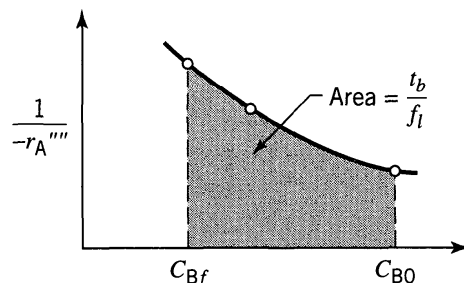
and keep adjusting  $p_{Aout}$  until they do.

As a shortcut: if  $p_A \ll \pi$  and if  $E = M_H$  then  $E$  is independent of  $p_A$  in which case I and III combine to give

$$-r_A''''' = p_{Ain} / \left( \frac{\pi V_r}{F_g} + \frac{1}{k_{Ag}a} + \frac{H_A}{k_{Al}aE} + \frac{H_A}{kC_{Bf}l} \right)$$

- Next combine terms II and III to find the processing time

$$t = \frac{f_l}{b} \int_{C_{Bf}}^{C_{B0}} \frac{dC_B}{-r_A'''} \quad \dots \text{solve graphically} \quad (19)$$



- This time can be compared with the minimum needed if all A reacts and none escapes the vessel. This situation is represented by  $p_{Aout} = 0$  at all times. Thus

$$t_{\min} = \frac{\frac{1}{b} V_l (C_{B0} - C_{Bf})}{F_g \left( \frac{p_{Ain}}{\pi - p_{Ain}} \right)} = \frac{\frac{1}{b} \left( \text{amount of B reacted} \right)}{\left( \text{amount of A entering} \right)} \quad (20)$$

(the vessel in unit time)

- Combining  $t$  and  $t_{\min}$  gives the efficiency of utilization of A. Thus

$$\left( \begin{array}{l} \text{percent of entering A} \\ \text{which reacts with B} \end{array} \right) = \frac{t_{\min}}{t} \quad (21)$$

Example 24.6 illustrates this procedure for batch absorber-reactors.

### EXAMPLE 24.1 TOWERS FOR STRAIGHT ABSORPTION

The concentration of undesirable impurity in air (at 1 bar =  $10^5$  Pa) is to be reduced from 0.1% (or 100 Pa) to 0.02% (or 20 Pa) by absorption in pure water. Find the height of tower required for countercurrent operations.

#### Data

For consistency let us use SI units throughout.

For the packing

$$k_{Ag}a = 0.32 \text{ mol/hr} \cdot \text{m}^3 \cdot \text{Pa}$$

$$k_{Al}a = 0.1/\text{hr}$$

The solubility of A in water is given by Henry's law constant

$$H_A = p_{A_i}/C_{A_i} = 12.5 \text{ Pa} \cdot \text{m}^3/\text{mol}$$

The flow rates per meter squared cross section of tower are

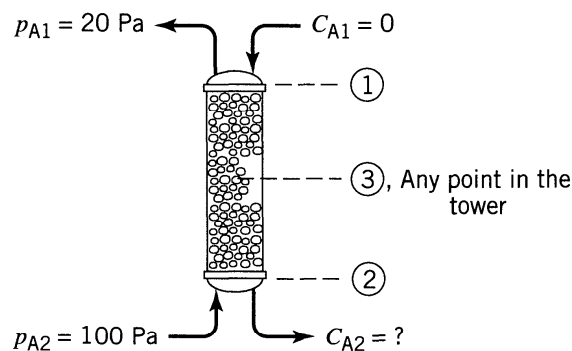
$$F_g/A_{cs} = 1 \times 10^5 \text{ mol/hr} \cdot \text{m}^2$$

$$F_l/A_{cs} = 7 \times 10^5 \text{ mol/hr} \cdot \text{m}^2$$

The molar density of liquid under all conditions is

$$C_T = 56\,000 \text{ mol/m}^3$$

Figure E24.1 shows the quantities known at this point.



**Figure E24.1**

### SOLUTION

Our strategy is to first solve the material balance, then determine the tower height. Since we are dealing with dilute solutions we may use the simplified form of the material balance. So for any point in the tower  $p_A$  and  $C_A$  are related by Eq. 4.

$$p_{A3} - p_{A1} = \frac{(F_l/A_{cs})}{(F_g/A_{cs})} \frac{\pi}{C_T} (C_{A3} - C_{A1})$$

or

$$p_{A3} - 20 = \frac{(7 \times 10^5)(1 \times 10^5)}{(1 \times 10^5)(56\,000)} (C_{A3} - 0)$$

or

$$C_{A3} = 0.08p_{A3} - 1.6 \quad \text{(i)}$$

from which the concentration of A in the liquid leaving the tower is

$$C_{A2} = 0.08(100) - 1.6 = 6.4 \text{ mol/m}^3 \quad \text{(ii)}$$

The expression for tower height is, from Eq. 6,

$$h = \frac{V_r}{A_{cs}} = \frac{(F_g/A_{cs})}{\pi(K_{Ag}a)} \int_{20}^{100} \frac{dp_A}{p_A - p_A^*} \quad \text{(iii)}$$

Now evaluate terms

$$\frac{1}{(K_{Ag}a)} = \frac{1}{(k_{Ag}a)} + \frac{H_A}{(k_{Al}a)} = \frac{1}{0.32} + \frac{12.5}{0.1} = 3.125 + 125 = 128.125$$

This expression shows that

$$G \text{ film resistance} = 3.125/128.125 = 0.024, \text{ or } 2.4\%$$

$$L \text{ film resistance} = 125/128.125 = 0.976, \text{ or } 97.6\%$$

and

$$(K_{Ag}a) = 1/128.125 = 0.0078 \text{ mol/hr} \cdot \text{m}^3 \cdot \text{Pa} \quad \text{(iv)}$$

Next evaluate  $p_A - p_A^*$ . Thus with Eq. (i) we get

$$\begin{aligned} p_A - p_A^* &= p_A - H_A C_A = p_A - 1.25(0.08p_A - 1.6) \\ p_A &= 20 \text{ Pa} \end{aligned} \quad \text{(v)}$$

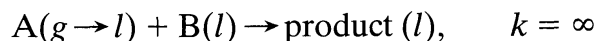
Inserting Eqs. (iv) and (v) in (iii) gives

$$\begin{aligned} h &= \frac{(1 \times 10^5 \text{ mol/hr} \cdot \text{m}^2)}{(10^5 \text{ Pa})(0.0078 \text{ mol/hr} \cdot \text{m}^3 \cdot \text{Pa})} \int_{20}^{100} \frac{dp_A}{20} \\ &= (128.125) \left( \frac{100 - 20}{20} \right) = \underline{\underline{512.5 \text{ m}}} \end{aligned}$$

**Comment.** Here the tower is very high, unacceptably high. Also note that most of the resistance (over 97%) lies in the liquid film, making this a liquid-film-controlling process. However, if we added component B to the liquid which reacts with A, we should be able to speed things up. Let's see if this is so. ■

**EXAMPLE 24.2 TOWERS FOR HIGH CONCENTRATION OF LIQUID REACTANT**

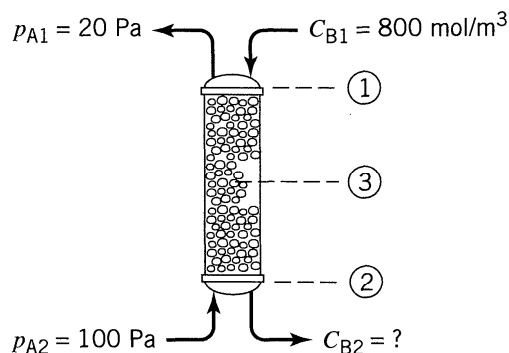
To the water of Example 24.1 add a high concentration of reactant B,  $C_{B1} = 800 \text{ mol/m}^3$  or approximately 0.8 N. Material B reacts with A extremely rapidly



Assume that the diffusivities of A and B in water are the same, thus

$$k_{Al} = k_{Bl} = k_l$$

Figure E24.2 shows what is known at this point.



**Figure E24.2**

**SOLUTION**

The strategy in solving the problem is as follows

**Step 1.** Express the material balance and find  $C_{B2}$  in the exit stream.

**Step 2.** Find which of the many forms of rate equation should be used.

**Step 3.** Determine the tower height.

**Step 1. Material balance.** For dilute solutions with rapid reaction Eq. 6 gives for any point in the tower,  $p_{A3}$ ,  $C_{B3}$

$$(p_{A3} - p_{A1}) = \frac{(F_l/A_{cs})\pi}{(F_g/A_{cs})bC_T} (C_{B1} - C_{B3})$$

or

$$(p_{A3} - 20) = \frac{(7 \times 10^5)(1 \times 10^5)}{(1 \times 10^5)(1)(56\,000)} (800 - C_{A3})$$

or

$$p_{A3} = 10\,020 - 12.5C_{B3}$$

At the bottom of the tower  $p_{A3} = p_{A2}$ , so

$$C_{B2} = \frac{1}{12.5} (10\,020 - 100) = 793.6 \text{ mol/m}^3$$

**Step 2.** *Form of rate equation to use.* Check both ends of the tower:

$$\text{at top} \begin{cases} k_{Ag}ap_A = (0.32)(20) = 6.4 \text{ mol/hr} \cdot \text{m}^3 \\ k_l a C_B = (0.1)(800) = 80 \text{ mol/hr} \cdot \text{m}^3 \end{cases}$$

$$\text{at bottom} \begin{cases} k_{Ag}ap_A = (0.32)(100) = 32 \\ k_l a C_B = (0.1)(793.6) = 79.36 \end{cases}$$

At both ends of the tower  $k_{Ag}p_A < k_l C_B$ ; therefore, gas-phase resistance controls and we have a pseudo first-order reaction as given by Eq. 16 of Chapter 23

$$-r_A''' = k_{Ag}ap_A = 0.32 p_A$$

**Step 3.** *Height of tower.* From Eq. 10

$$\begin{aligned} h &= \frac{(F_g/A_{cs})}{\pi} \int_{p_{A1}}^{p_{A2}} \frac{dp_A}{(-r_A''')} = \frac{10^5}{10^5} \int_{20}^{100} \frac{dp_A}{0.32p_A} \\ &= \frac{1}{0.32} \ln \frac{100}{20} = \underline{\underline{5.03 \text{ m}}} \end{aligned}$$

**Comment.** Even though the liquid phase controls in physical absorption (see Example 24.1), it does not necessarily follow that it should still control when reaction occurs. In fact, we see here in Example 24.2 that it is the gas phase alone which influences the rate of the overall process. Reaction serves merely to eliminate the resistance of the liquid film. Also note the remarkable improvement in performance; 5 versus 500 m.

### EXAMPLE 24.3 TOWERS FOR LOW CONCENTRATION OF LIQUID REACTANT; CASE A

Repeat Example 24.2 using a feed with  $C_{B1} = 32 \text{ mol/m}^3$ , instead of  $800 \text{ mol/m}^3$ , see Fig. E24.3.



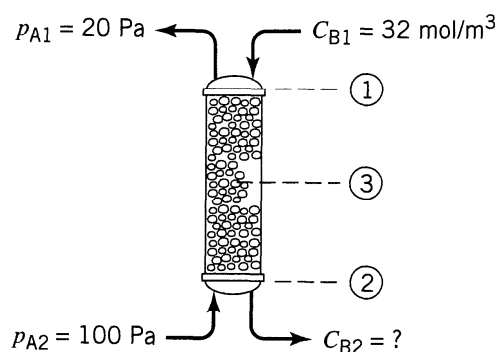


Figure E24.3

**SOLUTION**

As in the previous examples, solve by making a material balance, check the form of rate equation to use, then apply the performance equation to find the tower height.

**Step 1. Material Balance.** As in Example 24.2, for any point in the tower,

$$p_{A3} = 420 - 12.5C_{B3} \quad \text{or} \quad C_{B3} = \frac{420 - p_{A3}}{12.5}$$

and for the bottom of the tower where  $p_A = 100$  Pa,

$$C_{B2} = \frac{320}{12.5} = 25.6 \text{ mol/m}^3$$

**Step 2. Which Rate Form to Use.** Again check both ends of the tower to see which rate form applies

$$\text{at top} \begin{cases} k_{Ag}ap_A = 0.32(20) = 6.4 \\ k_laC_B = 0.1(32) = 3.2 \end{cases}$$

$$\text{at bottom} \begin{cases} k_{Ag}ap_A = 0.32(100) = 32 \\ k_laC_B = 0.1(35.6) = 2.56 \end{cases}$$

At both ends of the tower  $k_{Ag}ap_A > k_laC_B$ , therefore, the reaction takes place within the liquid film and Eq. 13 in Chapter 23 should be used,

$$-r_A''' = \frac{H_A C_B + p_A}{\frac{1}{k_{Ag}a} + \frac{H_A}{k_la}} = \frac{12.5 \left[ \frac{420 - p_{A3}}{12.5} \right] + p_A}{\frac{1}{0.32} + \frac{12.5}{0.1}} = 3.278 \text{ mol/m}^3 \text{ reactor} \cdot \text{hr}$$

**Step 3. Height of Tower.** From Eq. 6,

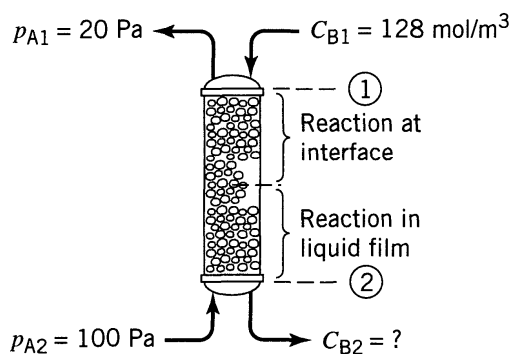
$$h = \frac{V_r}{A_{cs}} = \frac{10^5}{10^5} \int_{20}^{100} \frac{dp_A}{3.278} = \frac{100 - 20}{3.278} = \underline{\underline{24.4 \text{ m}}}$$

### EXAMPLE 24.4 TOWERS FOR INTERMEDIATE CONCENTRATIONS OF LIQUID REACTANT

Repeat Example 24.2 using a feed in which  $C_B = 128 \text{ mol/m}^3$ .

#### SOLUTION

Refer to Fig. E24.4, and solve as with the previous examples.



**Figure E24.4**

**Step 1. Material balance.** As with Examples 24.2 and 24.3 we have at any point in the tower,

$$p_{A3} = 1620 - 12.5C_{B3}$$

and at the bottom of the tower,

$$C_{B2} = \frac{1520}{12.5} = 121.6 \text{ mol/m}^3$$

**Step 2. Form of rate equation to use.** Check both ends of the tower:

$$\text{at top} \begin{cases} k_{Ag}ap_A = 6.4 \text{ mol/hr} \cdot \text{m}^3 \\ k_l a C_B = 12.8 \text{ mol} \cdot \text{hr} \cdot \text{m}^3 \end{cases}$$

$$\text{at bottom} \begin{cases} k_{Ag}ap_A = 32 \\ k_l a C_B = 12.16 \end{cases}$$

At the top  $k_{Ag}p_A < k_l C_B$ ; hence, Eq. 16 in Chapter 23 must be used. At the bottom  $k_{Ag}p_A > k_l C_B$ ; hence, Eq. 13 in Chapter 23 must be used.

Let us now find the condition at which the reaction zone just reaches the interface and where the form of rate equation changes. This occurs where

$$k_{Ag}p_A = k_l C_B \quad \text{or} \quad 0.32p_A = 0.1C_B$$

Solving with the material balance we find that the change occurs at  $p_A = 39.5$  Pa.

**Step 3. Height of Tower.** Writing the performance equation we have, from Eq. 6,

$$h = \frac{(F_g/A_{cs})}{\pi} \int_{p_{A1}}^{p_{A2}} \frac{dp_A}{-r_A'''} \quad \text{(iii)}$$

Noting that two different rate forms must be used, we have

$$\begin{aligned} h &= \frac{(F_g/A_{cs})}{\pi} \int_{20}^{39.5} \frac{dp_A}{(k_{Ag}a)p_A} + \frac{F_g/A_{es}}{\pi} \int_{39.5}^{100} \frac{(1/k_{Ag}a + H_A/k_la)}{C_B H_A + p_A} dp_A \\ &= \frac{10^5}{10^5(0.32)} \ln \frac{39.5}{20} + \frac{10^5}{10^5} \int_{39.5}^{100} \frac{(1/0.32 + 12.5/0.1)}{(1620 - p_A + p_A)} dp_A \\ &= 2.1268 + \frac{128.125}{1620} (100 - 39.5) = \underline{\underline{6.91 \text{ m}}} \end{aligned}$$

**Comment.** In this example we see that two distinct zones are present. Situations may be encountered where even another zone may be present. For example, if the entering liquid contains insufficient reactant, a point is reached in the tower where all this reactant is consumed. Below this point physical absorption alone takes place in reactant-free liquid. The methods of these examples, when used together, deal in a straightforward manner with this three-zone situation and van Krevelens and Hofstijzer (1948) discuss actual situations where these three distinct zones are present.

Comparing solutions for the four examples shows how reaction increases the effectiveness of the absorption process. ■

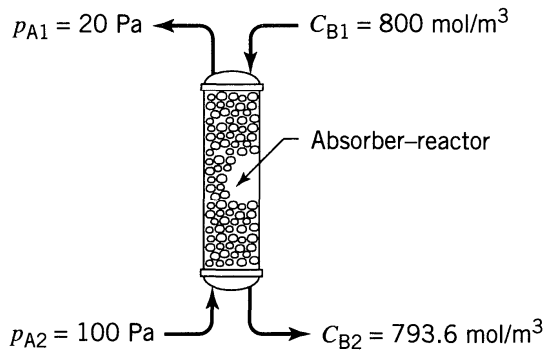
### EXAMPLE 24.5 REDO EXAMPLE 24.2 BY THE GENERAL METHOD

In Example 24.2 we found which of the eight special cases (see Fig. 23.3) applied and then used its corresponding rate equation (it was Eq. 23.16). Alternatively we could have used the general rate expression (Eq. 23.5). This is what we will show here.

**SOLUTION**

From Example 24.2 a material balance gives the tower end conditions, as shown in Fig. E24.5. Now the rate of reaction at any point in the tower is, from Eq. 23.5,

$$-r_A''' = \left( \frac{1}{\frac{1}{0.32} + \frac{12.5}{0.1E} + \frac{12.5}{\infty(C_B)}} \right) p_A = \left( \frac{1}{3.125 + \frac{125}{E}} \right) p_A \quad (\text{i})$$



**Figure E24.5**

Evaluate  $E$  at various points in the tower. For this we need to first evaluate  $M_H$  and  $E_i$ .

*At the Top of the Tower.* From Fig. 23.4

$$M_H = \frac{\sqrt{\mathcal{D}_B C_B k}}{k_{A1}} = \infty, \quad \text{because } k = \infty$$

$$E_i = 1 + \frac{\mathcal{D}_B C_B H_A}{\mathcal{D}_A p_{A1}} = 1 + \frac{800(12.5)}{p_{A1}} = \frac{10^4}{p_{A1}} \quad (\text{ii})$$

We have to guess the value of  $p_{A1}$ . It can be anywhere between 0 Pa (gas film controls) up to 20 Pa (liquid film controls). Let us guess no gas-phase resistance. Then  $p_{A1} = p_A$ , in which case

$$E_i = \frac{10^4}{20} = 500$$

and from Fig. 23.4, for  $M_H = \infty$ ,  $E_i = 500$ , we see that

$$E = 500$$

Replacing in Eq. (i) we find

$$-r_A''' = \frac{1}{3.125 + \frac{125}{500}} p_A = \frac{1}{3.125 + 0.25} p_A = 0.296 p_A$$

93%
7%...resistance

Our guess was wrong, so let's try again. Let us guess the other extreme,  $p_{Ai} = 0$ , meaning that the total resistance is in the gas film. Then from Eq. (ii) we see that  $E_i = \infty$ ,  $E = \infty$  and the rate equation becomes

$$-r_A''' = \frac{1}{3.125 + 0} p_A = 0.32 p_A \quad \text{(iii)}$$

↑  
 gas film control

Thus our guess was correct.

**At the Bottom of the Tower.** We follow the same procedure and find the same result. Thus the rate at all points in the tower is given by Eq. (iii). The height of the tower, from Eq. 10, is then (see step 3 of Example 24.2)

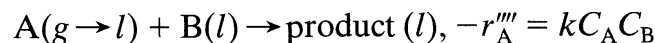
$$\underline{h = 5.03 \text{ m}}$$

**Suggestion.** Whenever  $M_H > E_i$  we end up having to guess  $p_{Ai}$ , and that is tedious. In those cases try to use the special case expressions.

In other cases (and this is what we usually find) the general rate equation is easier to use. ■

### EXAMPLE 24.6 REACTION OF A BATCH OF LIQUID

We wish to lower the concentration of B in the liquid ( $V_l = 1.62 \text{ m}^3$ ,  $C_U = 55555.6 \text{ mol/m}^3$ ) of an agitated tank reactor by bubbling gas ( $F_g = 9000 \text{ mol/hr}$ ,  $\pi = 10^5 \text{ Pa}$ ) containing A ( $p_{Ain} = 1000 \text{ Pa}$ ) through it. A and B react as follows:



- (a) How long must we bubble gas through the vessel to lower the concentration from  $C_{B0} = 555.6$  to  $C_{Bf} = 55.6 \text{ mol/m}^3$ ?
- (b) What percent of entering A passes through the vessel unreacted?

#### Additional Data

$$\begin{array}{ll}
 k_{Ag}a = 0.72 \text{ mol/hr} \cdot \text{m}^3 \cdot \text{Pa} & f_l = 0.9 \text{ m}^3 \text{ liquid/m}^3 \text{ total} \\
 k_{Al}a = 144 \text{ hr}^{-1} & \mathcal{D}_A = \mathcal{D}_B = 3.6 \times 10^{-6} \text{ m}^2/\text{hr}, \quad a = 100 \text{ m}^2/\text{m}^3 \\
 H_A = 10^3 \text{ Pa} \cdot \text{m}^3/\text{mol} & k = 2.6 \times 10^5 \text{ m}^3/\text{mol} \cdot \text{hr}
 \end{array}$$

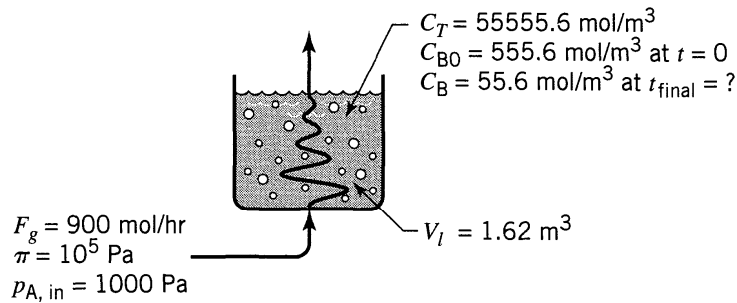


Figure E24.6

**SOLUTION**

Let us sketch what is known in Fig. E24.6.

*At the start*

$$M_H = \frac{\sqrt{\mathcal{D}_B k C_B}}{k_{Al}} = \frac{\sqrt{3.6 \times 10^{-6} (2.6 \times 10^5) (555.6)}}{144/100} = 15.84$$

$$E_i = 1 + \frac{C_B H_A}{p_{Ai}} = \frac{555.6 (10^3)}{1000} = 555.6, \text{ or higher}$$

↑  
or lower

$$\therefore E = M_H = 15.84$$

Since  $p_A \ll \pi$  and  $E = M_H$  the text says we can use the shortcut outlined above Eq. 19. Let us do it.

$$\begin{aligned} -r_A''' &= p_{Ain} / \left( \frac{\pi V_r}{F_g} + \frac{1}{k_{Ag} a} + \frac{H_A}{k_{Al} a E} + \frac{H_A}{k C_B f_l} \right) \\ &= 1000 / \left( \frac{10^5 (1.62)}{9000} + \frac{1}{0.72} + \frac{10^3}{144 (15.84)} + \frac{10^3}{2.6 \times 10^5 (555.6) 0.9} \right) \\ &= 50.44 \text{ mol/m}^3 \cdot \text{hr} \end{aligned}$$

*At the end*, following a similar treatment, we find

$$\left. \begin{aligned} M_H &= 5 \\ E_i &= 55.6, \text{ or higher} \end{aligned} \right\} E = M_H = 5.0$$

$$-r_A''' = 1000 / \left( \frac{10^5 (1.62)}{9000} + \frac{1}{0.72} + \frac{10^3}{144 (5)} + \sim 0 \right) = 48.13 \text{ mol/m}^3 \cdot \text{hr}$$

The rate of reaction at the beginning and at the end of the run is just about the same, so

$$-r_{A, \text{ave}}''' = \frac{50.44 + 48.13}{2} = 49.28$$

Thus the run time needed is

$$t = \frac{f_l}{b} \int_{C_{Bf}}^{C_{B0}} \frac{dC_B}{-r_A'''} = \frac{0.9(555.6 - 55.6)}{49.28} = \underline{\underline{9.13 \text{ hr}}}$$

The minimum time required is

$$t_{\min} = \frac{V_l(C_{B0} - C_{Bf})}{F_g(p_{Ain}/(\pi - p_{Ain}))} = \frac{1.62(555.6 - 55.6)}{9000(1000/(10^5 - 100))} = \underline{\underline{8.91 \text{ hr}}}$$

Thus the fraction of reactant which passes through the tank untreated is

$$\text{Fraction} = \frac{9.13 - 8.91}{8.19} = 0.025 = \underline{\underline{2.5\%}}$$

## REFERENCES

- van Krevelens, D. W., and Hoftijzer, P., *Rec. Trav. Chim.*, **67**, 563 (1948).  
Kramers, H., and Westerterp, K. R., *Elements of Chemical Reactor Design and Operation*,

## PROBLEMS

- 24.1.** The four  $p_A$  versus  $C_A$  sketches of Fig. 24.2 represent various possible ideal contacting schemes of gas with liquid. Sketch the contacting scheme for straight physical absorption corresponding to the  $p_A$  versus  $C_A$  operating lines  $XY$  shown in Fig. P24.1.

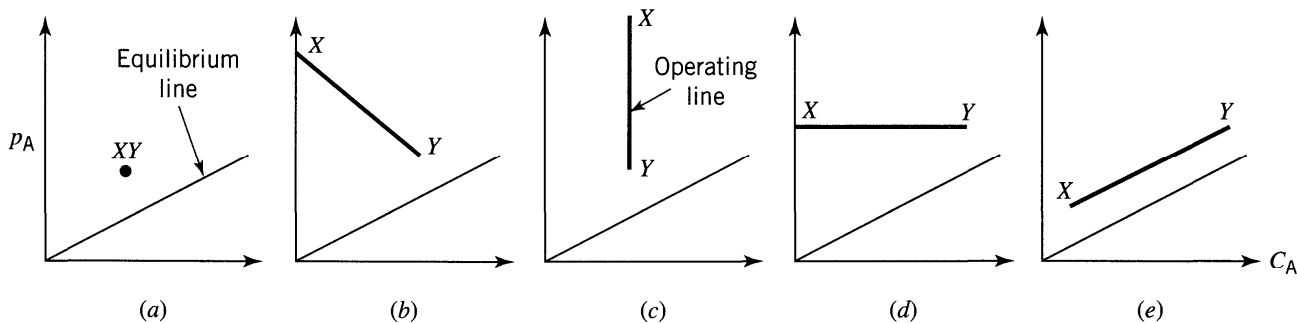
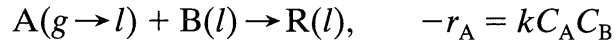


Figure P24.1

We plan to remove about 90% of the A present in a gas stream by absorption in water which contains reactant B. Chemicals A and B react in the liquid as follows:



B has a negligible vapor pressure, hence does not go into the gas phase. We plan to do this absorption in either a packed bed column, or an agitated tank contactor.

- (a) What volume of contactor is needed?  
 (b) Where does the resistance of absorption reaction lie?

### Data

For the gas stream:

$$\begin{aligned} F_g &= 90\,000 \text{ mol/hr at } \pi = 10^5 \text{ Pa} \\ p_{Ain} &= 1000 \text{ Pa} \\ p_{Aout} &= 100 \text{ Pa} \end{aligned}$$

Physical data

$$\begin{aligned} \mathcal{D} &= 3.6 \times 10^{-6} \text{ m}^2/\text{hr} \\ C_U &= 55\,556 \text{ mol H}_2\text{O}/\text{m}^3 \text{ liquid, at all } C_B \end{aligned}$$

For the packed bed

$$\begin{aligned} F_l &= 900\,000 \text{ mol/hr} & k_{Al}a &= 72 \text{ hr}^{-1} \\ C_{Bin} &= 55.56 \text{ mol}/\text{m}^3 & a &= 100 \text{ m}^2/\text{m}^3 \\ k_{Ag}a &= 0.36 \text{ mol/hr} \cdot \text{m}^3 \cdot \text{Pa} & f_l &= V_l/V = 0.08 \end{aligned}$$

For the agitated tank

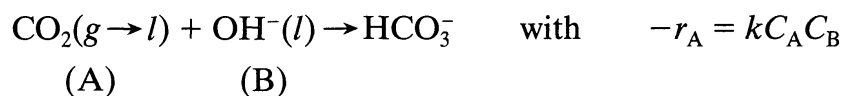
$$\begin{aligned} F_l &= 9000 \text{ mol/hr} & k_{Al}a &= 144 \text{ hr}^{-1} \\ C_{Bin} &= 5556 \text{ mol}/\text{m}^3 \text{ (about 10\% B)} & a &= 200 \text{ m}^2/\text{m}^3 \\ k_{Ag}a &= 0.72 \text{ mol/hr} \cdot \text{m}^3 \cdot \text{Pa} & f_l &= V_l/V = 0.9 \end{aligned}$$

Note that  $F_l$  and  $C_{Bin}$  are very different in packed beds and tank contactors, and here is the reason why. Packed columns need  $F_l/F_g \cong 10$  for satisfactory operations. This means large  $F_l$ , and so as not to waste reactant B, it is introduced in low concentration. On the other hand, tank contactors do not have this flow restriction. Thus we can use low  $F_l$  and high  $C_{Bin}$ , as long as we introduce sufficient B to react with A.



	Henry's Law Constant: $H_A$ , $\text{Pa} \cdot \text{m}^3/\text{mol}$	For Reaction: $k$ , $\text{m}^3/\text{mol} \cdot \text{hr}$	Type of Contactor T = Tower, Countercurrent A = Agitated Tank	
24.2.	0.0	0	In these problems of straight mass transfer assume that no B is present in the system.	A
24.3.	18	0		T
24.4.	1.8	0		T
24.5.	$10^5$	$\infty$		T
24.6.	$10^5$	$2.6 \times 10^7$	A	
24.7.	$10^5$	$2.6 \times 10^5$	A	
24.8.	$10^3$	$2.6 \times 10^3$	T	
24.9.	$10^5$	$2.6 \times 10^7$	T	
24.10.	$10^3$	$2.6 \times 10^5$	T	

24.11. Danckwerts and Gillham, in *Trans. I. Chem. E.*, **44**, 42, March 1966, studied the rate of  $\text{CO}_2$  absorption into an alkaline buffered solution of  $\text{K}_2\text{CO}_3$  and  $\text{KHCO}_3$ . The resulting reaction can be represented as



In the experiment pure  $\text{CO}_2$  at 1 atm was bubbled into a packed column irrigated by rapidly recirculating solution kept at  $20^\circ\text{C}$  and close to constant  $C_B$ . Find the fraction of entering  $\text{CO}_2$  absorbed.

#### Data

Column:  $V_r = 0.6041 \text{ m}^3$                        $f_l = 0.08$        $a = 120 \text{ m}^2/\text{m}^3$   
 Gas:       $\pi = 101\,325 \text{ Pa}$                        $H_A = 3500 \text{ Pa} \cdot \text{m}^3/\text{mol}$        $v_0 = 0.0363 \text{ m}^3/\text{s}$   
 Liquid:       $\bar{C}_B = 300 \text{ mol}/\text{m}^3$                        $\mathcal{D}_{Al} = \mathcal{D}_{Bl} = 1.4 \times 10^{-9} \text{ m}^2/\text{s}$   
 Rates:       $k = 0.433 \text{ m}^3/\text{mol} \cdot \text{s}$        $k_{Al}a = 0.025 \text{ s}^{-1}$

This problem is by Barry Kelly.

24.12. A column packed with 5-cm polypropylene saddles ( $a = 55 \text{ m}^2/\text{m}^3$ ) is being designed for the removal of chlorine from a gas stream ( $G = 100 \text{ mol}/\text{s} \cdot \text{m}^2$ , 2.36%  $\text{Cl}_2$ ) by countercurrent contact with an NaOH solution

( $L = 250 \text{ mol/s} \cdot \text{m}^2$ , 10% NaOH,  $C_B = 2736 \text{ mol/m}^3$ ) at about 40–45°C and 1 atm.

How high should the tower be for 99% removal of chlorine? Double the calculated height to take care of deviations from plug flow.

**Data**

The reaction  $\text{Cl}_2 + 2\text{NaOH} \rightarrow \text{product}$  is very very fast and irreversible. For these very high flow rates (close to the limits allowed) an extrapolation of the correlations in Perry 6th ed., section 14, gives

$$k_g a = 133 \text{ mol/hr} \cdot \text{m}^3 \cdot \text{atm} \quad H_A = 125 \times 10^6 \text{ atm} \cdot \text{m}^3/\text{mol}$$

$$k_l a = 45 \text{ hr}^{-1} \quad \mathcal{D} = 1.5 \times 10^{-9} \text{ m}^2/\text{s}$$

Repeat Example 24.6 with the following two changes

	Henry's Law Constant $H_A, \text{ Pa} \cdot \text{m}^3/\text{mol}$	Second-Order Reaction Rate, Constant $k, \text{ m}^3/\text{mol} \cdot \text{hr}$
<b>24.13.</b>	$10^5$	$2.6 \times 10^5$
<b>24.14.</b>	$10^5$	$2.6 \times 10^9$
<b>24.15.</b>	$10^5$	$2.6 \times 10^3$
<b>24.16.</b>	$10^3$	$2.6 \times 10^{11}$