

Absorption

The most common use of the mass transfer coefficients developed in Chapter 8 is the analytical description of large-scale separation processes like gas absorption and liquid–liquid extraction. These mass transfer coefficients describe the absorption of a solute vapor like SO_2 or NH_3 from air into water. They describe the extraction of waxes from lubricating oils, the leaching of copper from low-grade ores, and the efficiency of the distillation of xylene isomers.

Mass transfer coefficients are useful because they describe how fast these separations occur. They thus represent a step beyond thermodynamics, which establishes the maximum separations that are possible. They are a step short of analyses using diffusion coefficients, which have a more exact fundamental basis. Mass transfer coefficients are accurate enough to correlate experimental results from industrial separation equipment, and they provide the basis for designing new equipment.

All industrial processes are affected by mass transfer coefficients but to different degrees. Gas absorption, the focus of this chapter, is an example of what is called “differential contacting” and depends directly on mass transfer coefficients. Distillation, the focus of the next chapter, is an example of what is called “stage-wise contacting” and is less influenced by mass transfer. Extraction and adsorption, the subjects of Chapters 11–12, may be effected in either differential or staged contactors.

Understanding absorption is the key to all four operations. This understanding is usually clouded by presenting the ideas completely in algebraic terms. All chemistry and all simple limits are implied rather than explained. As a result, novices often understand every step of the analysis but have a poor perspective of the overall problem. To avoid this dislocation, we begin, in Section 9.1, with a description of the gases to be absorbed and the liquid solvents that absorb them. A few of these liquids depend only on the solubility of the gas; many more liquids react chemically with the components of the gas.

Once this chemical problem is stated, we turn, in Section 9.2, to the physical equipment used. This physical equipment is simple, but it is constrained by the fluid mechanics of the gas and liquid flowing past each other. These flows are complicated, described largely by empirical correlations. The best strategy may be to follow the turnkey procedure to solve the fluid mechanics.

In Section 9.3 we turn to the simple case of dilute absorption and in Section 9.4 to the parallel case of concentrated absorption. For the dilute solution case, we assume a linear isotherm, that is, that a solute’s solubility in liquid is directly proportional to its partial pressure in gas. This leads to a simple analytical solution. For the concentrated case, we do not assume the isotherm is linear and we recognize that the liquid and gas flows change within the equipment. Now the solution requires numerical integration. These two sections mirror our earlier discussion of diffusion, where the simple case of dilute diffusion in Chapter 2 gave way to the concentrated and more general results in Chapter 3. Understanding the dilute case is the key to the concentrated case.

9.1 The Basic Problem

When you drive by a chemical plant at night, the most impressive part is the lights. They outline every piece of equipment. When you look more closely, you can often see three types of silhouettes. The tallest are the thin distillation columns, which are described in the next chapter. The next tallest are the fat gas absorption columns, which are the subject of this chapter. Ironically, the shortest silhouettes are the chemical reactors, charged with reagents to make the desired products.

This relative size has a moral: while the chemical plant would not exist without the chemical reactors, the biggest expense — the biggest equipment — will often be in the separation equipment. This separation equipment centers on distillation and gas absorption, the two most important unit operations. The analysis and the design of these operations is central to the entire chemical industry.

I have found that distillation is better understood than gas absorption. I believe that this is because everyone knows that distillation is how you concentrate ethanol from water: Distillation is how you turn wine into brandy. In contrast, few know what gas absorption is for. What specific gases are absorbed, anyway? What liquids absorb the gases? What happens to the liquids afterwards? I find this ignorance ironic because of increased environmental concerns. Gas absorption is the chief method for controlling industrial air pollution, yet many with environmental interests remain ignorant of its nature.

In this section, I want to begin to remove this ignorance. I want to list the gases that we most often seek to remove and to give rough limits for the inlet and exit concentrations. I want to explain where these gas mixtures occur. I will do so qualitatively, without equations; there are more than enough equations in later sections. I do want to make one point now about cost. In these systems, the cost of absorption is usually log linear. It costs twice as much to remove 99% as it does to 90%, and it costs twice as much to remove 99.9% as it does to remove 99%. This increasing cost should be a key in environmental legislation.

9.1.1 Which Gases Are Absorbed

Most gas absorption aims at separation of acidic impurities from mixed gas streams. These acidic impurities include carbon dioxide (CO_2), hydrogen sulfide (H_2S), sulfur dioxide (SO_2), and organic sulfur compounds. The most important of these are CO_2 and H_2S , which occur at concentrations of five to fifty percent. The organic sulfur compounds include carbonyl sulfide (COS) and mercaptans, which are like alcohols with a sulfur atom in place of the oxygen. Mercaptans stink: For example, butyl mercaptan is responsible for the stench of skunks.

Other impurities vary widely. One common impurity is water, which can be removed by either absorption or adsorption. Another is ammonia (NH_3), which is basic, rather than acidic. Sulfur trioxide (SO_3), prussic acid (HCN), and nitrogen oxides (NO_x) are of concern because of their high chemical reactivity. Oxygen must be removed from some reagent streams, and nitrogen can be absorbed to upgrade natural gas.

The occurrence of these streams and the targets for their removal are summarized in Table 9.1-1. The ubiquitous presence of H_2S reflects the fact that fossil fuels, especially coal and petroleum, contain large amounts of sulfur. Moreover, as the world becomes more industrialized, the targets will decrease. This is particularly true for SO_2 in flue gas, which is the source of acid rain.

Process

Ammonia man
Coal gas
High Btu g
Low Btu g
Ethylene man
Flue gas desul
Hydrogen man
Natural gas de
Oil desulfuriz
Refinery desu
Syn gas for ch

9.1.1

The
mixture and
high, perhaps
nonreactive
concentration
fast, reversib
referred to as
we may be fo
produce solid

These gen
concentrated fee
carbonate, wh
commonly us
amine

H_2N

As you can s
species react
solvents. Fin
aqueous solu

Gas absorp
This common
at. Often,
through the
cost of heatin
begin using
pressure can
sensitive abs

Both temp
The disposal

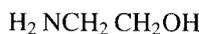
Table 9.1-1. Gas treating in major industrial processes

Process	Gases to be removed	Common targets (% Acid gas)
Ammonia manufacture	CO ₂ , NH ₃ , H ₂ S	<16 ppm CO ₂
Coal gas		
High Btu gas	CO ₂ , H ₂ S, COS	500 ppm CO ₂ ; 0.01 ppm H ₂ S
Low Btu gas	H ₂ S	100 ppm H ₂ S
Ethylene manufacture	H ₂ S, CO ₂	<1 ppm H ₂ S, 1 ppm CO ₂
Flue gas desulfurization	SO ₂	90% removal
Hydrogen manufacture	CO ₂	<0.1% CO ₂
Natural gas upgrading	H ₂ S, CO ₂ , N ₂ , RSH	<4 ppm H ₂ S; <1% CO ₂
Oil desulfurization	H ₂ S	100 ppm H ₂ S
Refinery desulfurization	CO ₂ , H ₂ S, COS	10 ppm H ₂ S
Syn gas for chemicals feedstock	CO ₂ , H ₂ S	<500 ppm CO ₂ ; <0.01 ppm H ₂ S

9.1.2 What Are the Absorbing Liquids?

The choice of a liquid absorbent depends on the concentrations in the feed gas mixture and on the percent removal desired. If the impurity concentration in the feed gas is high, perhaps ten to fifty percent, we can often dissolve most of the impurity in a nonvolatile, nonreactive liquid. Such a nonreactive liquid is called a physical solvent. If the impurity concentration is lower, around one to ten percent, we will tend to use a liquid capable of fast, reversible chemical reaction with the impurity. Such a reversibly reactive liquid is referred to as a "chemical solvent." If the impurity concentration in the feed is lower still, we may be forced to use a liquid that reacts irreversibly, an expensive alternative that may produce solid waste.

These generalizations may be clearer if we consider the case of H₂S. If we have a concentrated feed stream, we can dissolve the H₂S in liquids like ethylene glycol or propylene carbonate, which are physical solvents. At lower feed concentrations of H₂S, we would commonly use aqueous solutions of alkylamines. One common example is monoethanol amine



As you can see, this is like ammonia but with one proton replaced with ethanol. Such species react reversibly with acid gases like H₂S, so their aqueous solutions are chemical solvents. Finally, if the H₂S is present only in traces, we can remove these traces with an aqueous solution of NaOH. This will produce a waste stream of NaHS, which is discarded.

Gas absorption processes produce a liquid containing high concentrations of the impurity. This commonly is removed — stripped — by heating the liquid so that the impurity bubbles out. Often, this removal is accelerated by pumping an inert gas — a sweep stream — through the hot liquid. Recently, chemical companies have been bothered by the high cost of heating the large volumes of absorbing liquids. To avoid these costs, they have begun using absorbants whose chemical reactivity is pressure sensitive. Because swings in pressure can be less expensive than swings in temperature, I expect the switch to pressure sensitive absorbants will continue.

Both temperature and pressure swings yield a concentrated impurity requiring disposal. The disposal is again illustrated by the example of H₂S. The H₂S is normally stripped from

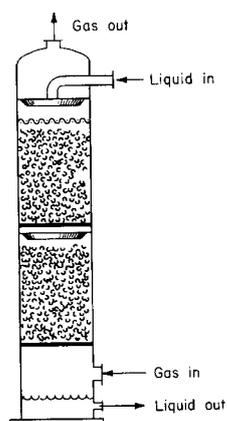
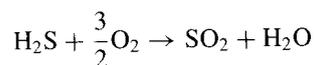


Fig. 9.2-1. A packed tower used for gas absorption. A gas mixture enters the bottom of the tower and flows out the top. Part of this mixture is absorbed by liquid flowing countercurrently, from top to bottom.

amines by heating; the concentrated H_2S stream is split into two. The first stream is burned:



This product gas is reacted catalytically with the remaining H_2S :



The H_2S is converted into solid sulfur, which can be sold. This "Claus process" has been the key to sulfur recovery for almost a century.

Thus gas absorption centers on removing an impurity from a gas stream into a liquid. In the rest of this chapter, we will discuss the analysis and design of equipment for this task. Our discussion will be entirely on physical solvents, that is, on nonreactive liquids. Gas absorption in physical solvents is almost twenty times less common than absorption in chemical solvents, that is, in reacting liquids. We focus our discussion on physical solvents because they are much simpler; we will explore chemical solvents in Chapter 16.

9.2 Absorption Equipment

Gas absorption at an industrial scale is most commonly practiced in packed towers like that shown in Fig. 9.2-1. A packed tower is essentially a piece of pipe set on its end and filled with inert material or "tower packing." Liquid poured into the top of the tower trickles down through the packing; gas pumped into the bottom of the tower flows countercurrently upward. The intimate contact between gas and liquid achieved in this way effects the gas absorption.

Analyzing a packed tower involves both mass transfer and fluid mechanics. The mass transfer, detailed in the following section, determines the height of the packed tower. This mass transfer is described as molar flows, partly because of the chemical reactions that often occur. The fluid mechanics, described in this section, determines the cross-sectional area of the packed tower. The fluid mechanics is described as mass flows, a consequence of the

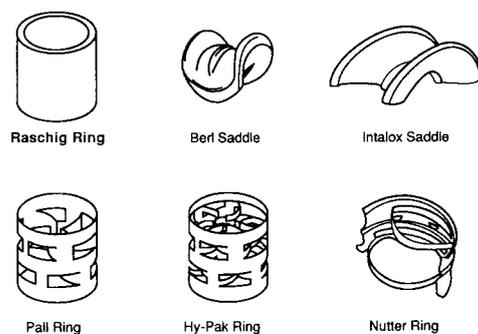


Fig. 9.2-2. Six types of random packing. These packings aim to resolve the conflicting goals of fast flow and large interfacial areas.

physics that control the process. To describe the physics, we discuss the tower packing, the flows themselves, and the estimation of the tower's cross section.

9.2.1 Tower Packing

The fluid mechanics in the packed tower is dominated by the inert material in the packed tower. This material can be small pieces dumped randomly or larger structures carefully stacked inside the tower. Random packing is cheaper and more common; structured packing is more expensive but more efficient. The efficiency is typically improved by around thirty percent, a significant gain when producing commodity chemicals at very low margins. Still, because structured packings vary widely, we will stress the more common random packings here.

Typical random packings, shown in Fig. 9.2-2, replace the crushed material used in early chemical processing. These packings try to permit both high fluid flow and high interfacial area between the gas and the liquid. These goals are in conflict: High fluid flow implies a few large channels through the tower, and high interfacial area requires many small channels. Thus tower packings are compromises, developed with eighty years of empiricism. Sometimes, the Raschig rings and the Berl saddles are described as first-generation packings, the Intalox saddles and Pall rings are second generation, and the Nutter rings are third generation. All aim at the same goal: fast flow with big area.

9.2.2 Tower Fluid Mechanics

The liquid and gas flows through these random packings cannot be arbitrarily set but must rest within a narrow, empirically defined range. To see why this range is important, imagine you have a tall glass filled with ice. You blow air into the bottom of the glass through a straw, and you pour cola into the glass at the same time. You watch what happens.

If you pour the cola at a very slow rate, it won't flow evenly downward through the ice but will run down in only a few places. Such a flow, called "channeling," occurs when the gas or liquid flow is much greater at some points than at others. Such channeling is undesirable, for it can substantially reduce interfacial area and hence mass transfer. It is usually minor in crushed solid packing and is minimal in commercially purchased random packing, except at very low liquid flows.

If you now pour the cola faster (remember to keep blowing), you get a case where the cola flows through all the ice more evenly, with your breath bubbling up through it. The conditions where these relatively even flows begin is called loading and is a requirement for good mass transfer. When loading begins, the flows may slightly decrease, but the dramatic increase in the gas–liquid area means that mass transfer is fast. You almost always want to operate a packed tower in this loaded condition.

However, if you now begin blowing much harder, you will push in so much air that the cola can't flow into the column, but splashes backward, out of the top of the glass. This condition is called "flooding." It not only reduces mass transfer but also decreases the cola that is flowing into the glass.

These same three conditions — channeling, loading, and flooding — can exist inside of any packed tower. You will want to use liquid flows that are high enough to avoid channeling and achieve loading. You will want to use gas flows that are low enough to avoid flooding. But you will also want flows that are large enough for a specific task, for example, large enough to treat 6000 ft³/min of flue gas. You must choose the packing and the shape of the packed tower to allow these flows without flooding.

9.2.3 Tower Cross-Sectional Area

At this point, we should restate our objective. We aim to analyze industrial gas absorption in packed towers. This analysis depends most strongly on mass balances and rate equations given in subsequent sections of this chapter. It also depends on the fluid mechanics within the tower, which is the subject of this section.

In most cases, the absorption process that interests us will have specified flows of gases and liquids. These flows must load but not flood the tower. We achieve this by changing the tower's cross-sectional area. This changes the gas and liquid fluxes, that is, the amount of fluid per cross-sectional area per time. By increasing the cross-sectional area at constant flows, we decrease the fluxes and the velocities of the gas and liquid flowing past each other.

The empirical correlations most often used for estimating tower cross sections are shown in Fig. 9.2-3. This figure is tricky, a mixture of dimensionless and dimensional quantities. The abscissa, often called the flow parameter is dimensionless:

$$\frac{L'}{G'} \sqrt{\frac{\rho_G}{\rho_L}} = \left[\frac{\frac{1}{2} \rho_L v_L^2}{\frac{1}{2} \rho_G v_G^2} \right]^{1/2} \quad (9.2-1)$$

where $L' (= \rho_L v_L)$ and $G' (= \rho_G v_G)$ are the mass fluxes of liquid and gas, respectively; ρ_L and ρ_G are the corresponding densities; and v_L and v_G are the superficial velocities. Two points about this abscissa merit mention. First, while L' and G' are mass fluxes and hence depend on the tower's cross-sectional area, their ratio L'/G' does not depend on this area. Second, the flow parameter is a measure of relative kinetic energy: It is the square root of the ratio of the liquid's kinetic energy to that in the gas.

The ordinate in Fig. 9.2-3 is more difficult. First of all, it is dimensional, not dimensionless. In particular, the gas flux G' is given in pounds per square foot per second; the densities ρ_G and ρ_L are given in pounds per cubic foot; the viscosity μ is that of the liquid, expressed in centipoise; ψ is the ratio of the density of water to the density of the liquid; the gravitational constant g_c is 32.2; and the packing factor F is roughly inversely proportional to the packing's size. Values for F are listed for common packings in Table 9.2-1.

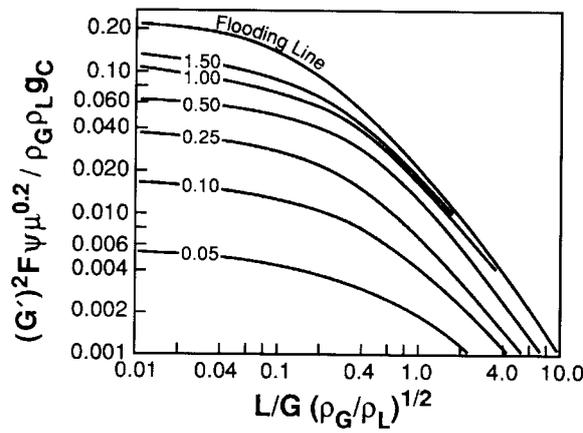


Fig. 9.2-3. Correlation for estimating tower cross sectional area. The correlation implies a mixture of specific units, as explained in the text.

Table 9.2-1. Packing factors *F* and areas per volume (per foot) for random packings

	Nominal packing size (in.)							
	1/2	5/8	3/4	1	1 1/4	1 1/2	2	3
Raschig Rings (Ceramic)	580 (111)	380 (100)	255 (80)	179 (58)		93 (38)	65 (28)	37 (19)
Raschig Rings (1/32 in. Metal)	300 (128)	170	155 (84)	115 (63)				
Raschig Rings (1/16 in. Metal)	410 (118)	300	220 (72)	144 (57)		83 (41)	57 (31)	32 (21)
Berl Saddles (Ceramic)	240 (142)		170 (82)	110 (76)		65 (44)	45 (32)	
Pall Rings (Metal)		81 (104)		56 (63)		40 (39)	27 (31)	18
Pall Rings (Plastic)		95 (104)		55 (63)		40 (39)	26 (31)	17 (26)
Intalox Saddles (Ceramic)	200 (190)		145 (102)	92 (78)		52 (60)	40 (36)	22
Hy-Pak Rings (Metal)				45 (69)		29 (42)	26 (33)	16 (31)

Note: The areas per volume are given in parentheses (abstracted from Strigle, 1987).

This melange of mixed metric and English units is a historical artifact born in the largely American development of the petrochemical industry.

The physical significance of the ordinate is also obscure. We recognize that it is dominated by the ratio

$$\frac{(G')^2 F}{\rho_G \rho_L g_c} \propto \frac{\frac{1}{2} \rho_G v_G^2}{\rho_L g_c (\text{packing size})} \tag{9.2-2}$$

This suggests that the ordinate can be regarded as the ratio of the kinetic energy in the gas to the potential energy in the liquid. The other factors, like $\mu^{0.2}$, are just later empiricisms.

The history of correlation in Fig. 9.2-3 is curious. The original form, due to Sherwood Shipley and Nolloway (1938), was limited to the flooding curve. The curves at constant pressure drop were added by Leva (1954). More recently, many have quarreled over the form, correctly feeling that something with a better-defined physical significance would be preferable. While I agree, I recognize that Fig. 9.2-3 is the starting point for most who are working on absorption design.

To use Fig. 9.2-3 to find the tower's cross-sectional area, we must first know the gas and liquid flows and hence the flow parameter on the figure's ordinate. After we choose a packing from the myriad available, we want to choose a pressure drop in the tower. In conventional practice, absorbers are designed to operate at pressure drops of 0.2 to 0.6 inch H₂O per foot. The lower pressure drop will minimize foaming. Alternatively, we can calculate the column's performance at flooding and arbitrarily choose to operate at a gas flux equal to half the flooding value. In both this method and the previous one, we must make sure to design the tower for the point where the maximum flows of gas and liquid occur. For absorption, this is normally at the tower's bottom; for stripping, it's normally at the top.

Using Fig. 9.2-3 for estimating the tower's cross section is straightforward though complicated. Remember this figure has two major limitations. First, it implies that at large gas flows, the cross sectional area should vary with liquid density and velocity. In fact, it should be independent of these. Second, this figure is largely based on liquid and gas density differences like those of water and air. These tend to give optimistic predictions for nonaqueous systems (i.e., smaller than optimal tower cross sections). Thus in nonaqueous systems, like those involving ethylene and propylene, you may need different methods. Again, make early estimates with the methods in this section, and then discuss your case with equipment suppliers.

Example 9.2-1: Estimating a tower cross-section You are planning to reduce the two percent carbon dioxide in 23 pounds per second of a natural gas stream using absorption in aqueous diethylamine flowing out at 40 pounds per second. You want to use either 1½ inch Raschig rings or 1½ inch Pall rings. In either case, you want to design for a pressure drop of 0.25 inch H₂O per foot, so that foaming is minimized. Under the operating conditions, the densities of the gas and the liquid are 2.8 and 63 lbs/ft³, respectively; the liquid's viscosity is 2 centipoise.

What should the tower's cross-sectional area be?

Solution This problem illustrates the routine use of Fig. 9.2-3. We first calculate the flow parameter:

$$\frac{L'}{G'} \sqrt{\frac{\rho_G}{\rho_L}} = \frac{40 \text{ lbs/sec}}{23 \text{ lbs/sec}} \sqrt{\frac{2.8 \text{ lbs/ft}^3}{63 \text{ lbs/ft}^3}}$$

From Fig. 9.2-3, the capacity factor is thus

$$\frac{(G')^2 F \psi \mu^{0.2}}{\rho_G \rho_L g_c} = 0.015$$

For the 1½ inch R

$$(G')(93$$

$$2.8$$

$$G' = 0.$$

Thus the tower h
of 5.7 feet. For t
However, while t
is a considerable

9.3 AB

We now
we will want to
to use our analy
case, we will bui
allowed estimati

To simplify o
from a gas into
clearest. Becaus
both constants a
key equations:

- (1) a solu
- (2) a solu
- (3) a solu

These three key
equation, respec

We begin w
on a small tow

$$\left(\begin{array}{l} \text{solu} \\ \text{ma} \end{array} \right)$$

$$G.A$$

where y and a
by the volume

$$G \frac{y_1}{x_1}$$

For the $1\frac{1}{2}$ inch Raschig rings, the packing factor F is given in Table 9.2-1 as 93, so

$$\frac{(G')(93) \left(\frac{62.4}{63}\right)^{2.02}}{2.8(63)32.2} = 0.015$$

$$G' = 0.90 \text{ lbs/ft}^2 \text{ sec}$$

Thus the tower has a cross section of $(23/0.90 =) 26 \text{ ft}^2$. This corresponds to a diameter of 5.7 feet. For the Pall rings, the packing factor is 40, so the diameter is smaller, 4.6 feet. However, while there is little difference in the tower diameter for these two packings, there is a considerable change in the tower height, as shown in the next section.

9.3 Absorption of a Dilute Vapor

We now return to the analysis of gas absorption in a packed tower. In many cases, we will want to use the analysis to estimate the tower's height. In other cases, we will want to use our analysis to organize experimental results as mass transfer coefficients. In any case, we will build on the fluid mechanics described in the earlier section, a description that allowed estimating the tower's cross section.

To simplify our analysis, we will begin with the case of a dilute solute vapor absorbed from a gas into a liquid. This focus on the dilute limit makes the physical significance clearest. Because the vapor is dilute, the molar gas flux G and the molar liquid flux L are both constants everywhere within the tower. With this simplification, we then need three key equations:

- (1) a solute mole balance on both gas and liquid,
- (2) a solute equilibrium between gas and liquid, and
- (3) a solute mole balance on either gas or liquid.

These three keys are traditionally called an operating line, an equilibrium line, and a rate equation, respectively.

We begin with a mole balance on the solute in both gas and liquid. We make this balance on a small tower volume $A\Delta z$ located at position z in the tower:

$$\left(\begin{array}{c} \text{solute entering} \\ \text{minus leaving} \\ \text{in gas} \end{array} \right) = \left(\begin{array}{c} \text{solute entering} \\ \text{minus leaving} \\ \text{in liquid} \end{array} \right)$$

$$GA(y|_{z+\Delta z} - y|_z) = LA(x|_{z+\Delta z} - x|_z) \quad (9.3-1)$$

where y and x are the mole fractions in the gas and liquid, respectively. When we divide by the volume $A\Delta z$, we find

$$G \frac{dy}{dz} = L \frac{dx}{dz} \quad (9.3-2)$$

Rearranging,

$$\frac{dx}{dy} = \frac{G}{L} \quad (9.3-3)$$

subject to (at $z = 0$),

$$y = y_0 \quad x = x_0 \quad (9.3-4)$$

where the subscript 0 indicates the streams at the bottom of the tower. Remember that the gas is entering and the liquid is leaving at this position. Integrating,

$$x = x_0 + \frac{G}{L}(y - y_0) \quad (9.3-5)$$

The first key equation, which is nothing more than a mole balance, is called the "operating line."

The second key equation for analyzing absorption is an equilibrium relation for the solute in the gas and in the liquid. Because the solute is dilute, this has the form

$$y^* = mx \quad (9.3-6)$$

where m is closely related to a Henry's law constant. This relation, briefly discussed in Section 8.5, is a frequent source of error because the units of the constant are not carefully considered. Remember also that y^* does not exist at the same tower position as x . In fact, x is the actual liquid mole fraction, y^* is the gas mole fraction which would be in equilibrium with that liquid, and y is the actual gas mole fraction. This second key equation is called the "equilibrium line."

The third key relation, the rate equation, is found by another solute mole balance on the differential volume $A\Delta z$ but on the gas only:

$$\left(\begin{array}{c} \text{solute} \\ \text{accumulation} \end{array} \right) = \left(\begin{array}{c} \text{solute flow} \\ \text{in minus out} \end{array} \right) - \left(\begin{array}{c} \text{solute lost} \\ \text{by absorption} \end{array} \right) \quad (9.3-7)$$

In symbolic terms, this can be written as

$$0 = GA(y|_z - y|_{z+\Delta z}) - K_G a(A\Delta z)(c_1 - c_1^*) \quad (9.3-8)$$

in which a represents the packing area per volume and K_G is the overall gas phase mass transfer coefficient. Values for a , in ft^2/ft^3 , are given in parentheses for a variety of common packings in Table 9.2-1 (in the previous section). The concentration c_1 is that in the bulk gas, and the concentration c_1^* is the value that the gas would have if it were in equilibrium with the liquid. Again, we divide this equation by the volume $A\Delta z$ and take the limit as this volume goes to zero; we also recognize that the total molar concentration c of the gas is constant. Thus c_1 equals cy , c_1^* equals cy^* , and

$$0 = -G \frac{dy}{dz} - K_G ac(y - y^*) = -G \frac{dy}{dz} - K_y a(y - y^*) \quad (9.3-9)$$

This rate equation, a mole balance on that part of the solute that is in the vapor, is the third key in our analysis.

We now complete our analysis by integrating Eq. 9.3-9. To do so, we first combine it with the equilibrium line in Eq. 9.3-6 and rearrange the result:

$$l = \int_0^l dz = -\frac{G}{K_y a} \int_{y_0}^{y_1} \frac{dy}{y - y^*} = -\frac{G}{K_y a} \int_{y_0}^{y_1} \frac{dy}{y - mx} \quad (9.3-10)$$

where l is the tower height. We further combine this with the operating line, Eq. 9.3-5:

$$l = -\frac{G}{K_y a} \int_{y_0}^{y_1} \frac{dy}{y - m \left[x_0 + \frac{G}{L}(y - y_0) \right]} \quad (9.3-11)$$

The important result can be written in a variety of useful forms:

$$\begin{aligned} l &= \frac{G}{K_y a} \left[\left(\frac{1}{1 - \frac{mG}{L}} \right) \ln \left(\frac{y_0 - y_0^*}{y_1 - y_1^*} \right) \right] \\ &= \frac{G}{K_y a} \left[\left(\frac{1}{1 - \frac{mG}{L}} \right) \ln \left(\frac{y_0 - mx_0}{y_1 - mx_1} \right) \right] \end{aligned} \quad (9.3-12)$$

Solving for the height l is as easy as plugging in the numbers.

This result merits reflection. First, although the analysis repeatedly exploits the assumption of dilute solution, the extension to concentrated solutions should be relatively straightforward. Second, we have implied mass transfer of a solute vapor from a gas into a liquid; such a process is called gas scrubbing. We can repeat the identical analysis for mass transfer of a vapor from a liquid into a gas; such a reversed process is called stripping. Third, we have written the preceding equations in terms of gas-phase mole fractions; we could write completely analogous equations for liquid-phase mole fractions:

$$l = \frac{L}{K_x a} \left[\left(\frac{1}{1 - \frac{L}{mG}} \right) \ln \left(\frac{x_0 - y_0/m}{x_1 - y_1/m} \right) \right] \quad (9.3-13)$$

Note that the overall mass transfer coefficient is different in these two equations. Understanding the difference between the coefficients takes care.

Equations 9.3-12 and 9.3-13 are the basis of most modern analyses of dilute absorption. They are especially appropriate for chemical solvents because reactions of the absorbing solute can be incorporated into the overall mass transfer coefficient. However, especially in the older literature, a relation like Eq. 9.3-12 is sometimes rearranged as

$$l = HTU \cdot NTU \quad (9.3-14)$$

where HTU is a height of a transfer unit defined as

$$HTU = \frac{G}{K_y a} = \frac{v_G}{K_G a} \quad (9.3-15)$$

and NTU is a “number of transfer units” given by

$$\begin{aligned}
 NTU &= \int_{y_l}^{y_0} \frac{dy}{y - y^*} \\
 &= \frac{1}{1 - \frac{mG}{L}} \ln \left(\frac{y_0 - mx_0}{y_l - mx_l} \right) \quad (9.3-16)
 \end{aligned}$$

Other definitions of HTU and NTU can be based on other forms of the overall mass transfer coefficients. The use of “transfer units” is a rough parallel with the use of “stages” in distillation or the term “theoretical plates” in chromatography. As such, it seems a historical genuflection by the more recent absorption analyses in the direction of the older equilibrium theories of distillation.

The use of $HTUs$ and $NTUs$ does have a sound physical interpretation. The $NTUs$ are a measure of the difficulty of the separation, of the distance the final streams will be from equilibrium. If the $NTUs$ are large, the separation is hard. The $HTUs$, on the other hand, give an idea of the efficiency of the equipment. A small HTU is a sign of a good tower, implying, for example, a large surface area per volume. Moreover, because the overall mass transfer coefficient often depends on the velocity, the HTU can be largely independent of flow over the practical range: It tends to be between 0.3 meter and 1.0 meters. Learn to use Eq. 9.3-12 and the idea of an HTU interchangeably.

Example 9.3-1: Carbon dioxide absorption A packed tower uses an organic amine to absorb carbon dioxide. The entering gas, which contains 1.26 mol% CO_2 , is to leave with only 0.04 mol% CO_2 . The amine enters pure, without CO_2 . If the amine left in equilibrium with the entering gas (which it doesn't), it would contain 0.80 mol% CO_2 . The gas flow is 2.3 gmol/sec, the liquid flow is 4.8 gmol/sec, the tower's diameter is 40 centimeters, and the overall mass transfer coefficient times the area per volume $K_y a$ is $5 \cdot 10^{-5}$ gmol/cm³sec. How tall should this tower be?

Solution We first make an overall carbon dioxide balance to find the exiting liquid concentration:

$$\begin{aligned}
 GA(y_0 - y_l) &= LA(x_0 - x_l) \\
 2.3 \frac{\text{gmol}}{\text{sec}}(0.0126 - 0.0004) &= 4.8 \frac{\text{gmol}}{\text{sec}}(x_0 - 0) \\
 x_0 &= 0.00585
 \end{aligned}$$

Next we find the equilibrium constant

$$\begin{aligned}
 y_0 &= mx_0^* \\
 0.0216 &= m(.0080) \\
 m &= 1.58
 \end{aligned}$$

Now we insert the values given into Eq. 9.3-12:

9.3-16)

$$l = \frac{2.3 \text{ gmol/sec}}{\left[\frac{\pi}{4}(40 \text{ cm})^2\right] 5.10^{-5} \frac{\text{mol}}{\text{cm}^3 \text{sec}}} \left[\left(\frac{1}{1 - \frac{1.58(2.3)}{4.8}} \right) \ln \left(\frac{0.0126 - 1.58(0.00585)}{0.0004 - 1.58(0)} \right) \right]$$

$$= 3.2 \text{ m}$$

The simplicity of this calculation is typical of dilute solutions.

Example 9.3-2: Oxygen stripping You are testing a new packed tower to strip oxygen from water using excess nitrogen. The oxygen-free water is to be used in microelectric manufacture. Your tower is small, about 2 meters high and 0.6 meter in diameter, filled with 1 inch Hy-Pak rings. You expect the value of mG for oxygen is large and the dominant transfer coefficient in the liquid will be $2.2 \cdot 10^{-3}$ centimeters per second. The water flow is to be $300 \text{ cm}^3/\text{sec}$. How much oxygen can we remove with this tower?

Solution To begin, we recognize that because the nitrogen gas flow is in excess, y_1 and y_2 are zero, and (L/mG) is much less than one. As a result, Eq. 9.3-13 becomes

$$l = \frac{L}{K_x a} \left[\ln \left(\frac{x_0}{x_l} \right) \right]$$

From Table 8.2-2 and the fact that mass transfer in the liquid is controlling,

$$K_x = k_x = kc_L$$

From Table 9.2-1, a is $60 \text{ ft}^2/\text{ft}^3$, or $2.26 \text{ cm}^2/\text{cm}^3$. Thus

$$200 \text{ cm} = \frac{300 \frac{\text{cm}^3}{\text{sec}} c_L}{\left[\frac{\pi}{4}(60 \text{ cm})^2\right] 2.2 \cdot 10^{-3} \text{ cm} \cdot \text{sec} c_L} \left[\ln \frac{x_0}{x_l} \right]$$

$$\frac{x_l}{x_0} = 0.016$$

We're removing over ninety-eight percent of the oxygen. An interesting exercise is to check the nitrogen flows implied by this calculation.

Example 9.3-3: Alternative forms of absorption equations Show that Eq. 9.3-12 can be rewritten in the form

$$l = \frac{v_G}{K_G a} \left[\left(\frac{1}{1 - \frac{H v_G}{v_L}} \right) \ln \left(\frac{c_{1G,0} - H c_{1L,0}}{c_{1G,l} - H c_{1L,l}} \right) \right]$$

where v_G and v_L are the superficial velocities of gas and liquid, where K_G is defined by

$$N_1 = K_G (c_{1G} - c_{1G}^*)$$

and the Henry's law constant H is given by

$$c_{1G}^* = H c_{1L}$$

Solution We first recognize that

$$G = c_G v_G$$

$$L = c_L v_L$$

where c_G and c_L are the total molar concentrations in gas and liquid, respectively. We then rewrite Eq. 9.3-6 as

$$\frac{c_{1G}^*}{c_G} = m \frac{c_{1L}}{c_L}$$

so

$$H = \frac{m c_G}{c_L}$$

Finally, from Table 8.2-2,

$$K_G = K_y / c_G$$

Inserting the values of m , K_y , G , and L into Eq. 9.3-12 gives the desired result.

9.4 Absorption of a Concentrated Vapor

In this section, we want to extend the preceding analysis to the case of a concentrated vapor. As before, we plan to accomplish this absorption using a packed tower. As before, we must decide on an appropriate tower packing and on liquid and gas fluxes that will avoid flooding. As before, we depend on a variety of mole balances, though now for concentrated solutions.

Before we develop these new mass balances, we can benefit by looking at our analysis for a dilute vapor in a somewhat different way. This analysis depended on three key equations. A first key equation came from a balance on both liquid and gas (see Eq. 9.3-3):

$$\frac{dy}{dx} = \frac{L}{G} \quad (9.4-1)$$

We integrated this easily:

$$y = y_0 + \frac{L}{G}(x - x_0) \quad (9.4-2)$$

This mole balance, shown in Fig. 9.4-1, is the operating line. A second key equation is the equilibrium condition (see Eq. 9.3-6):

$$y^* = mx \quad (9.4-3)$$

This thermodynamic relation, also shown in Fig. 9.4-1, is the equilibrium line. Finally, from a mass balance on the gas alone, we found (see Eq. 9.3-1)

$$l = \frac{G}{K_y a} \int_{y_1}^{y_0} \frac{dy}{y - y^*} \quad (9.4-4)$$

We combined Eqs. 9.4-2 through 9.4-4 and integrated to find the tower's height l .

In contrast, we could have made use of the graph in Fig. 9.4-1. We begin on the operating line at the point (x_l, y_l) and move vertically until we hit the equilibrium line at the point

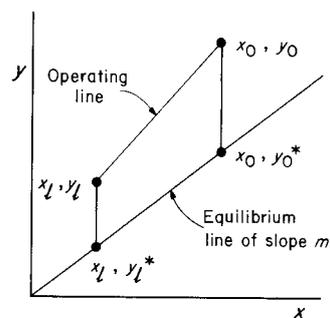


Fig. 9.4-1. Designing an absorption tower for a dilute vapor. The height of the tower is closely related to the area of the trapezoid shown. However, for a dilute vapor, this area is easily calculated analytically using the equations of Section 9.3. The equilibrium line shown here is based on thermodynamics, and the operating line reflects mole or mass balances.

ly. We then

2:

of a concen-
ed tower. As
as fluxes that
gh now for

analysis for
key equations.
-3:

(9.4-1)

(9.4-2)

equation is the

(9.4-3)

ne. Finally,

(9.4-4)

ght l .

the operating
at the point

(x_l, y_l^*) . From these points, we know $y_l - y_l^*$. We repeat this procedure for a lot of values of y . We then use these results to integrate Eq. 9.4-4 by either graphical or numerical means. We thus find the tower height l .

At first glance, this method of calculation using operating and equilibrium lines may seem archaic, an anachronism from the days of slide rules. Certainly, this method was developed to circumvent the elaborate integrals that are often encountered in the analysis of large-scale mass transfer processes. These integrals can now be routinely handled with computers.

Still, operating and equilibrium lines remain a focus of everyone's thinking. This is not just the result of mental inertia or academic sloth. Instead, this focus has remained valuable because the operating line summarizes a mass balance and the equilibrium line is a statement based on the second law of thermodynamics. Such a split can make thinking about separation processes easier and more rational.

We want to extend this analysis to absorption in concentrated solutions. We begin with a mole balance on both gas and liquid. The result is a parallel to Eq. 9.3-2:

$$0 = -\frac{d}{dz}(Gy) + \frac{d}{dz}(Lx) \quad (9.4-5)$$

Before, the flux of gas G and that of liquid L were nearly constant because the absorbing species was always dilute. Now, however, we expect that

$$G = G_0 \left(\frac{1}{1-y} \right) \quad (9.4-6)$$

where G_0 is the flux of the nonabsorbing gas. For example, if we are using water to absorb SO_2 out of air, G_0 is the flux of air. Similarly,

$$L = L_0 \left(\frac{1}{1-x} \right) \quad (9.4-7)$$

where L_0 is the flux of the nonvolatile liquid. When we combine these equations and

The tower height l can be found by integrating Eq. 9.4-12, using values of y and y^* read from Fig. 9.4-2. The integration is straightforward but is limited by two key assumptions made during the analysis. These assumptions can have subtle implications and so merit review. First, we are assuming absorption of a single vapor from an inert gas into a nonvolatile liquid. The gas is inert in the sense that only negligible amounts dissolve in the liquid; the liquid is nonvolatile in the sense that only negligible amounts evaporate into the gas. These approximations underlie Eq. 9.4-6 and lead to the factors involving $(1-y)^{-1}$ and $(1-y)^{-2}$ in the analysis. In passing, we should mention that some textbooks use a slightly different set of assumptions and so use slightly different equations (King, 1971; Sherwood et al., 1975; McCabe and Smith, 1975; Treybal, 1980). The differences are caused by these factors and are not often important.

The second key assumption in this analysis is that a mass transfer coefficient can adequately express the mass transfer in a concentrated solution. In other words, it implies that mass transfer coefficients are independent of concentration differences, though they certainly do depend on variables like the Reynolds and Schmidt numbers. This turns out to be only a first approximation. In general,

$$N_1 = K_y \Delta y + K'_y (\Delta y)^2 + \dots \quad (9.4-13)$$

where K'_y is a new correction factor for concentrated solutions.

The reason why mass transfer coefficients may not be accurate in concentrated solution is because mass transfer itself creates convection. Such convection is like that caused by diffusion, as explained in detail in Section 3.1. Extensions of mass transfer coefficients to more concentrated solutions or, more strictly, to situations of fast mass transfer are outlined in Section 13.5. However, these extensions are not often used in practice, even when they are known in principle. Instead, practicing engineers tend to use empirical correlations of actual experimental data. These are usually reliable.

Example 9.4-1: Ammonia scrubbing A gas mixture at 0°C and 1 atmosphere flowing at 1.20 m³/sec, and containing thirty-seven percent NH₃, sixteen percent N₂, and forty-seven percent H₂ is to be scrubbed with water containing a little sulfuric acid at 0°C. The exit gas should contain one percent NH₃ and the exit liquid 23 mol% NH₃.

Design a packed tower to carry out this task. The tower should use 2-inch Berl saddles, which have a surface area per volume 105 m²/m³ (cf. Table 9.2-1). It should operate at fifty percent of flooding. Pilot-plant data suggest that the overall gas-side mass transfer coefficient in this tower will be 0.032 meters per second; this value is larger than normal because of the chemical reaction of ammonia with water.

In this design, answer the following specific questions: (a) What is the flow of pure water into the top of the tower? (b) What tower diameter should be used? (c) How tall should the tower be?

Solution (a) We first find the total flow AG_0 of the nonabsorbed gases (i.e., of N₂ and H₂):

$$\begin{aligned} AG_0 &= 0.63 \left(\frac{1.20 \text{ m}^3/\text{sec}}{22.4 \text{ m}^3/\text{kgmol}} \right) \\ &= 0.0338 \text{ kgmol/sec} \end{aligned}$$

We then find the ammonia transferred:

$$\begin{aligned} \left(\begin{array}{c} \text{NH}_3 \\ \text{absorberd} \end{array} \right) &= 0.37 \left(\frac{1.20 \text{ m}^3/\text{sec}}{22.14 \text{ m}^3/\text{kgmol}} \right) - \left(\frac{0.01(0.0338 \text{ kgmol}/\text{sec})}{0.99} \right) \\ &= 0.0195 \text{ kgmol}/\text{sec} \end{aligned}$$

From this, we find the desired water flow AL_0 :

$$\begin{aligned} AL_0 &= \left(\frac{0.77}{0.23} \right) (0.0195 \text{ kgmol}/\text{sec}) \\ &= 0.0652 \text{ kgmol}/\text{sec} \end{aligned}$$

(b) The risk of flooding is greatest at the bottom of the tower where the flows are greatest. Moreover, because flooding is determined by fluid mechanics, it depends on mass flows, not molar flows. To make this conversion, we first find that the average molecular weight of the gas is 11.7. Then we see that

$$\begin{aligned} \left(\begin{array}{c} \text{total flow} \\ \text{of gas} \end{array} \right) &= \frac{11.7 \text{ kg}}{\text{kgmol}} \left(\frac{0.0338 \text{ kgmol}/\text{sec}}{0.63} \right) \\ &= 0.628 \text{ kg}/\text{sec} \end{aligned}$$

The average molecular weight of the liquid stream (neglecting any H_2SO_4) is 17.8, so

$$\begin{aligned} \left(\begin{array}{c} \text{total flow} \\ \text{of liquid} \end{array} \right) &= \frac{17.8 \text{ kg}}{\text{kgmol}} \left(\frac{0.0652 \text{ kgmol}/\text{sec}}{0.77} \right) \\ &= 1.51 \text{ kg}/\text{sec} \end{aligned}$$

Thus

$$\begin{aligned} \left(\frac{\text{liquid flow}}{\text{gas flow}} \right) \sqrt{\rho_G/\rho_L} &= \frac{1.51 \text{ kg}/\text{sec}}{0.628 \text{ kg}/\text{sec}} \sqrt{0.522 \text{ kg}/\text{m}^3 / 10^3 \text{ kg}/\text{m}^3} \\ &= 0.055 \end{aligned}$$

Remembering that the values found in Fig. 9.2-3 are not dimensionless, we find that

$$\begin{aligned} \left(\begin{array}{c} \text{gas flux} \\ \text{at flooding} \end{array} \right)^2 &= \frac{0.17 \rho_G \rho_L g_c}{F \mu^{0.2}} \\ &= \frac{0.17 \left(62.4 \frac{\text{lb}}{\text{ft}^3} (0.0326) \frac{\text{lb}}{\text{ft}^3} (32.2) \right)}{45(1.787 \text{ cp})^{0.2}} \end{aligned}$$

or

$$\left(\begin{array}{c} \text{gas flux} \\ \text{at flooding} \end{array} \right) = 2.29 \text{ kg}/\text{m}^2\text{-sec}$$

Because we want to operate at fifty percent flooding, our flux should be half this value, or about $1.15 \text{ kg}/\text{m}^2\text{-sec}$. We now can find the tower's diameter:

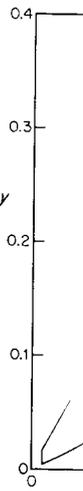


Fig. 9.4-3

$$\frac{\pi}{4} d^2 = \frac{1}{1}$$

$$d = 0$$

The tower's diameter

(c) The

$$HTU =$$

$$=$$

$$=$$

To find the number

shown as the opera

in the figure. V

from $y_0 = 0.37$ to

$$NTU =$$

from Eq. 9.3-14

$$l = (HTU)$$

$$= (0.41)$$

in terms of stripp

equilibrium line.

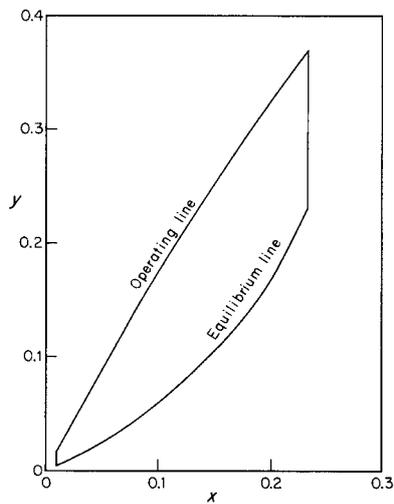


Fig. 9.4-3. Absorption of concentrated ammonia. The values shown are for Example 9.4.1.

$$\frac{\pi}{4}d^2 = \frac{0.628 \text{ kg/sec}}{1.15 \text{ kg/m}^2\text{sec}}$$

$$d = 0.84 \text{ m}$$

The tower's diameter is about 2.7 feet.

(c) The calculation of the tower's height can begin with Eq. 9.4-12. From this,

$$\begin{aligned} HTU &= \frac{G_0}{K_G a c} \\ &= \frac{[0.0338 \text{ kgmol/sec}]/[(\pi/4)(0.84 \text{ m})^2]}{(0.032 \text{ m/sec})(105 \text{ m}^2/\text{m}^3)(1 \text{ kgmol}/22.4\text{m}^3)} \\ &= 0.41 \text{ m} \end{aligned}$$

To find the number of transfer units NTU, we first plot values of y versus x using Eq. 9.4-8, shown as the operating line in Fig. 9.4-3. We also plot y^* versus x , shown as the equilibrium line in the figure. We then read off values of y^* versus y at fixed x , and integrate Eq. 9.4-12 from $y_0 = 0.37$ to $y_1 = 0.01$. The result is

$$NTU = 13$$

From Eq. 9.3-14

$$\begin{aligned} l &= (HTU)(NTU) \\ &= (0.41 \text{ m})(13) = 5.3 \text{ m} \end{aligned}$$

Problems of stripping gases are very similar except that the operating line falls below the equilibrium line.

9.5 Conclusions

This chapter analyzes gas absorption, an important separation process in chemical manufacture and pollution control. Gas absorption commonly is effected in packed towers filled with inert packing that gives a larger interfacial area between gas and liquid. The gas rises through the tower; the liquid trickles countercurrently downward. The liquid is often chemically reactive, binding the solutes being absorbed. For example, acid gases like H_2S are absorbed into aqueous solutions of amines. However, the analysis in this chapter implies nonreactive liquids; reactive liquids are discussed in Chapter 16.

The analysis of gas absorption depends on fluid mechanics and on mass transfer. The fluid mechanics determines the acceptable range of gas and liquid fluxes, which are adjusted by changing the cross-sectional area of the tower. The mass transfer coefficients determine the rate of absorption and hence the height of the packed tower. This height can be estimated by either algebraic or geometric methods. The algebraic formulation is simple for the case of a dilute solute, a case detailed in Section 9.3. This case depends on three key relations: an overall mole balance, a thermodynamic equilibrium, and a rate equation. This dilute case is the easiest way to learn about absorption.

The geometric analysis of absorption is suitable for either dilute or concentrated systems. It also depends on the same three key relations. Almost perversely, the overall mole balance is now called the operating line and the thermodynamic equilibrium is called the equilibrium line. The rate equation sometimes has the mass transfer coefficients rewritten in terms of new quantities called HTUs, height of transfer units, which are measures of the efficiency of the packed tower. These new terms provide occasional physical insight; simultaneously, they are effective at discouraging the inexperienced from trying to learn about gas absorption. If you are inexperienced, don't give up. Work hard on the dilute limit; be encouraged by the fact that the concentrated limit and the geometric analysis are more complicated, but involve no new ideas.

Further Reading

- Kaiser, V. (1994). *Chemical Engineering Progress* **90** (6) 55.
- King, C. J. (1971). *Separation Processes*, New York: McGraw-Hill.
- Kister, H. Z., Larson, K. F., and Yanagi, T. (1994). *Chemical Engineering Progress* **90** (2) 23.
- Kister, H. Z., and Gill, D. R. (1991). *Chemical Engineering Progress* **87** (2) 32.
- Leva, M. (1954). *Chemical Engineering Progress Symposium Series*, **50**, 51.
- McCabe, W., and Smith, J. C. (1975). *Unit Operations of Chemical Engineering*, 3rd ed., New York: McGraw-Hill.
- Perry, R. H., and Chilton, C. H. (1973). *Chemical Engineers Handbook*, 5th ed., New York: McGraw-Hill.
- Robbins, L. A. (1991). *Chemical Engineering Progress* **87** (5) 87.
- Sherwood, T. K., Pigford, R. L., and Wilke, C. R. (1975). *Mass Transfer*. New York: McGraw-Hill.
- Sherwood, T. K., Shipley, G. H., and Holloway, F. A. L. (1938). *Industrial and Engineering Chemistry* **30**, 765.
- Strigle, R. F. (1987). *Random Packings and Packed Towers*, Houston: Gulf Publishing.
- Treybal, R. E. (1980). *Mass Transfer Operations*, 3rd ed. New York: McGraw-Hill.