

16-9 A triple-effect evaporator is to be used to produce a 50 percent NaOH solution from a feed containing 25 percent NaOH. Steam is available at 320°F, and the vapor from the last stage is condensed at 120°F. Backward feed is used. (a) If equal amounts of water are removed in effect, what would be the concentrations in the intermediate effects, the boiling-point elevation in each effect, and the net temperature differences available for heat transfer? (b) With the same terminal temperatures and more than three effects, what would be the maximum number of effects that could be used?

16-10 A vapor-recompression evaporator is to concentrate a very dilute aqueous solution. The feed rate is to be 30,000 lb/h; the evaporation rate will be 20,000 lb/h. The evaporator will operate at atmospheric pressure, with the vapor mechanically compressed as shown in Fig. 16-13 except that a natural-circulation calandria will be used. If steam costs \$7 per 1,000 lb, electricity costs 2.3 cents per kilowatt-hour, and heat-transfer surface in the heater costs \$50 per square foot, calculate the optimum pressure to which the vapor should be compressed. The overall compressor efficiency is 70 percent. Assume all other costs are independent of the pressure of the compressed vapor. To how many effects will this evaporator be equivalent?

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SECTION FOUR

MASS TRANSFER AND ITS APPLICATIONS

A group of operations for separating the components of mixtures is based on the transfer of material from one homogeneous phase to another. Unlike purely mechanical separations, these methods utilize differences in vapor pressure or solubility, not density or particle size. The driving force for transfer is a concentration difference or a concentration gradient, much as a temperature difference or a temperature gradient provides the driving force for heat transfer. These methods, covered by the term *mass-transfer operations*, include such techniques as distillation, gas absorption, dehumidification, liquid extraction, leaching, crystallization, and a number of others not discussed in this book.

The function of *distillation* is to separate, by vaporization, a liquid mixture of miscible and volatile substances into individual components or, in some cases, into groups of components. The separation of a mixture of alcohol and water into its components; of liquid air into nitrogen, oxygen, and argon; and of crude petroleum into gasoline, kerosene, fuel oil, and lubricating stock are examples of distillation.

In *gas absorption* a soluble vapor is absorbed by means of a liquid in which the solute gas is more or less soluble, from its mixture with an inert gas. The washing of ammonia from a mixture of ammonia and air by means of liquid water is a typical example. The solute is subsequently recovered from the liquid by distillation, and the absorbing liquid can be either discarded or reused. When a solute is transferred from the solvent liquid to the gas phase, the operation is known as *desorption* or *stripping*. In *adsorption* a solute is removed from either a liquid or gas through contact with a solid adsorbent, the surface of which has a special affinity for the solute. In *dehumidification* a pure liquid is partially removed from an inert or carrier gas by condensation.

Usually the carrier gas is virtually insoluble in the liquid. Removal of water vapor from air by condensation on a cold surface and the condensation of an organic vapor such as carbon tetrachloride out of a stream of nitrogen are examples of dehumidification. In humidification operations the direction of transfer is from the liquid to the gas phase. In the *drying* of solids, a liquid, usually water, is separated by the use of hot, dry gas (usually air) and so is coupled with the humidification of the gas phase. In *liquid extraction*, sometimes called *solvent extraction*, a mixture of two components is treated by a solvent that preferentially dissolves one or more of the components in the mixture. The mixture so treated is called the *raffinate* and the solvent-rich phase is called the *extract*. The component transferred from raffinate to extract is the *solute*, and the component left behind in the raffinate is the *diluent*. The solvent in the extract leaving the extractor is usually recovered and reused.

In extraction of solids, or *leaching*, soluble material is dissolved from its mixture with an inert solid by means of a liquid solvent. The dissolved material, or *solute*, can then be recovered by crystallization or evaporation.

Crystallization is used to obtain materials in attractive and uniform crystals of good purity. Since the formation of crystals separates a solute from a melt or a solution and leaves impurities behind, it is a separation operation. Modern theories and models of industrial crystallization from solution, however, are focused on the processes occurring at the crystal-solution interface and the characteristics of particulate solids; this operation is therefore discussed, with other operations on solid particles, in Section 5.

The quantitative treatment of mass transfer is based on material and energy balances, equilibria, and rates of heat and mass transfer. Certain concepts applicable generally are discussed here. More specialized topics are discussed in the following chapters.

TERMINOLOGY AND SYMBOLS

It is conventional to refer generally to the two streams in any one operation as the *L* phase and the *V* phase. It is also customary to choose the stream having the higher density as the *L* phase and the one having the lower density as the *V* phase. An exception may appear in liquid extraction, where the raffinate always is taken as the *L* phase and the extract as the *V* phase, even when the raffinate happens to be lighter than the extract. In drying, the *L* phase is the stream consisting of the solid and the liquid retained in or on the solid. Table A shows how the streams are designated in the various operations.

Note on concentrations Strictly speaking, concentration means mass per unit volume. Mass may be in pounds or kilograms and volume in cubic feet or cubic meters. Pound moles or kilogram moles are often used for mass. In this book the context will make clear what quantity—mole or ordinary mass—is used. It is convenient to extend the use of the word "concentration" to include mole or mass fractions. The relation between concentration and mole or mass fraction of a component *i* is

$$c_i = \rho x_i$$

Table A Terminology for streams in mass-transfer operations

Operation	V phase	L phase
Distillation	Vapor	Liquid
Gas absorption, dehumidification	Gas	Liquid
Adsorption	Gas or liquid	Solid
Liquid extraction	Extract	Raffinate
Leaching	Liquid	Solid
Crystallization	Mother liquor	Crystals
Drying	Gas (usually air)	Wet solid

where x_i = mole or mass fraction of component *i*

ρ = molar or mass density of mixture

c_i = corresponding concentration of component *i*

The mole fraction is the ratio of the moles of the component to the total number of moles in the mixture, with a corresponding definition for mass fraction. By definition, all mole or mass fractions in a mixture sum to unity. If there are *r* components, $r - 1$ of the mole fractions may be chosen independently; the mole fraction of the remaining component is thereby fixed and equals 1 less the sum of the others.

General symbols are needed for flow rates and concentrations. For all operations, use *V* and *L* for the flow rates of *V* and *L* phases, respectively. Use *A*, *B*, *C*, etc., to refer to the individual components. If only one component is transferred between phases, choose component *A* as that component. Use *x* for the concentration of a component in the *L* phase, and *y* for the concentration in the *V* phase. Thus, y_A is the concentration of component *A* in a *V* phase and x_B is that of component *B* in an *L* phase. When only two components are present in a phase, the concentration of component *A* is *x* or *y*, and that of component *B* is $1 - x$ or $1 - y$, and the subscripts *A* and *B* are unnecessary.

Terminal quantities Since in steady-flow mass-transfer operations there are two streams and each must enter and leave, there are four terminal quantities. To identify them, use subscript *a* to refer to that end of the process where the *L* phase enters and *b* to refer to that end where the *L* phase leaves. Then, for *countercurrent* flow, the terminal quantities are as shown in Table B. If there are only two components in a stream, the subscript *A* can be dropped from the concentration terms.

Table B Terminal quantities for counter-current flow

Stream	Flow rate	Concentration component <i>A</i>
<i>L</i> phase, entering	L_a	x_{Aa}
<i>L</i> phase, leaving	L_b	x_{Ab}
<i>V</i> phase, entering	V_b	y_{Ab}
<i>V</i> phase, leaving	V_a	y_{Aa}

DIFFUSIONAL PROCESSES AND EQUILIBRIUM STAGES

Mass-transfer problems can be solved by two distinctly different methods, one utilizing the concept of equilibrium stages, the other based on diffusional rate processes. The choice of the method depends on the kind of equipment in which the operation is carried out. Distillation, leaching, and sometimes liquid extraction are performed in equipment such as mixer-settler trains, diffusion batteries, or plate towers, which contain a series of discrete processing units, and problems in these areas are commonly solved by equilibrium-stage calculations. Gas absorption and other operations which are carried out in packed towers and similar equipment are usually handled using the concept of a diffusional process. All mass-transfer calculations, however, involve a knowledge of the equilibrium relationships between phases.

Phase Equilibria

A limit to mass transfer is reached if the two phases come to equilibrium and the net transfer of material ceases. For a practicable process, which must have a reasonable production rate, equilibrium must be avoided, as the rate of mass transfer at any point is proportional to the driving force, which is the departure from equilibrium at that point. To evaluate driving forces, a knowledge of equilibria between phases is therefore of basic importance. Several kinds of equilibria are important in mass transfer. In all situations, two phases are involved, and all combinations are found except two gas phases or two solid phases. In phases in bulk the effects of surface area or surface curvature are negligible, and the controlling variables are the intensive properties temperature, pressure, and concentrations. Equilibrium data can be shown in tables, equations, or graphs. For most operations considered in this text, the pertinent equilibrium relationships can be shown graphically.

Classification of equilibria To classify equilibria and to establish the number of independent variables or degrees of freedom available in a specific situation, the phase rule is useful. It is

$$\mathcal{F} = \mathcal{C} - \mathcal{P} + 2$$

where \mathcal{F} = number of degrees of freedom

\mathcal{C} = number of components

\mathcal{P} = number of phases

In the following paragraphs the equilibria used in mass transfer are analyzed in terms of the phase rule. Usually there are two phases, and so $\mathcal{F} = \mathcal{C}$.

The number of degrees of freedom, or variance \mathcal{F} , is the number of independent intensive variables—temperature, pressure, and concentrations—that must be fixed to define the equilibrium state of the system. If fewer than \mathcal{F} variables are fixed, an infinite number of states fit the assumptions; if too many are arbitrarily chosen, the system will be overspecified. When there are only two phases, as is usually the case, $\mathcal{F} = \mathcal{C}$; in systems of two components, therefore, $\mathcal{F} = 2$. If the pressure is fixed, only one variable—the liquid-phase concentration, for example—can be changed independently; the temperature and gas-phase composition (if the two phases are liquid

and gas) must follow. For such systems equilibrium data are presented in temperature-composition diagrams which apply at constant pressure, or by plotting y_e , the V -phase concentration, against x_e , the L -phase composition. Such plots are called *equilibrium curves*. If there are more than two components, the equilibrium relationship cannot be represented by a single curve.

Distillation Assume that there are two components, so $\mathcal{C} = 2$, $\mathcal{P} = 2$, and $\mathcal{F} = 2$. Both components are found in both phases. There are four variables: pressure, temperature, and the concentrations of component A in the liquid and vapor phases (the concentrations of component B are unity less those of component A). If the pressure is fixed, only one variable, e.g., liquid-phase concentration, can be changed independently and temperature and vapor-phase concentration follow.

Gas absorption Assume that only one component is transferred between phases. There are three components, and $\mathcal{F} = 3$. Neglect both the solubility of the inert gas in the liquid and the presence of vapor from the liquid in the gas. Then there are four variables: pressure, temperature, and the concentrations of component A in liquid and gas. The temperature and pressure may be fixed; one concentration may be chosen as the remaining independent variable. The other concentration is then determined, and an equilibrium curve y_e vs. x_e plotted. All points on the curve pertain to the same temperature and pressure. Equilibrium data for various temperatures may also be presented in the form of solubility charts, in which the partial pressure of the solute in the gas phase is plotted as the ordinate.

Adsorption As in gas absorption, there are three components when only one component is transferred, and two phases; hence $\mathcal{F} = 3$. Typically the temperature and pressure are fixed, as well as the concentration of component A in the liquid or gas. The concentration of A on the adsorbent, in equilibrium with the fluid phase, is then determined by the equilibrium relation. Equilibrium plots of y_e vs. x_e , often in dimensionless form, are made for specified constant temperatures and are called *isotherms* (See Fig. 24-3.)

Dehumidification The solubility of the carrier gas may be neglected. There are two components, the carrier gas and the volatile liquid, so $\mathcal{C} = \mathcal{P} = 2$ and $\mathcal{F} = 2$. One phase, the liquid, is pure, and the variables are temperature, pressure, and the concentration of the vapor in the V phase. If the pressure is held constant, either the temperature or the vapor-phase concentration may be varied and the value of the other variable follows, so that a unique plot of temperature vs. concentration gives an equilibrium relationship. The equilibrium between water and moist air at 1 atm is shown in Fig. 23-1.

Liquid extraction The minimum number of components is 3, so $\mathcal{F} = 3$. All three components may appear in both phases. The variables are temperature, pressure, and four concentrations. Either temperature or pressure may be taken as a constant, and two or more concentrations chosen as independent variables. The pressure usually is assumed constant, and the temperature then varies somewhat. The relations between

these variables are given by various graphical methods, examples of which are shown in Figs. 19-10 to 19-13.

Leaching Two situations are found in leaching. In the first, the solvent available is more than sufficient to dissolve all the solute, and at equilibrium all the solute is in solution. There are, then, two phases, the solid and the solution. The number of components is 3, and $\mathcal{F} = 3$. The variables are temperature, pressure, and concentration of solute in the liquid. All are independently variable.

In the second situation, the solvent available is insufficient to dissolve all the solute, and the excess solute remains as a solid phase in equilibrium with the liquid. Then, $\mathcal{P} = 3$, so $\mathcal{F} = 2$. The variables are temperature, pressure, and concentration of the saturated solution. If the pressure is fixed, the concentration depends on the temperature. This relation is the ordinary solubility curve.

Drying In drying a water-wet solid, free liquid water may or may not be present. If it is, there are three phases—vapor, solid, and liquid—and three components, so $\mathcal{F} = 2$. At constant pressure a unique relationship exists between temperature and concentration of water in the vapor, just as in air-water contacts.

The water in hygroscopic solids or in natural materials like wood or leather may be in loose combination with the solid, and no liquid water may be present. Then there are two phases and three components, and $\mathcal{F} = 3$. The variables are temperature, pressure, and the concentrations of water in solid and vapor. If the temperature and pressure are fixed, these two concentrations can be plotted as an equilibrium curve. Typical curves for 1 atm and 25°C are shown in Fig. 25-3.

CHAPTER SEVENTEEN EQUILIBRIUM-STAGE OPERATIONS

One class of mass-transfer devices consists of assemblies of individual units, or stages, interconnected so that the materials being processed pass through each stage in turn. The two streams move countercurrently through the assembly; in each stage they are brought into contact, mixed, and then separated. Such multistage systems are called *casca*des. For mass transfer to take place the streams entering each stage must not be in equilibrium with each other, for it is the departure from equilibrium conditions that provides the driving force for transfer. The leaving streams are usually not in equilibrium either but are much closer to being so than the entering streams are. The closeness of the approach to equilibrium depends on the effectiveness of mixing and mass transfer between the phases. To simplify the design of a cascade, the streams leaving each stage are often assumed to be in equilibrium, which, by definition, makes each stage *ideal*. A correction factor or efficiency is applied later to account for any actual departures from equilibrium.

To illustrate the principle of an equilibrium-stage cascade, two typical countercurrent multistage devices, one for distillation and one for leaching, are described here. Other types of mass-transfer equipment are discussed in later chapters.

Typical distillation equipment A plant for continuous distillation is shown in Fig. 17-1. Reboiler *A* is fed continuously with the liquid mixture to be distilled. The liquid is converted partially into vapor by heat transferred from the heating surface *B*. The vapor formed in the reboiler is richer in low boiler than the unevaporized liquid, but unless the two components differ greatly in volatility, the vapor contains substantial quantities of both components, and if it were condensed, the condensate would be far from pure. To increase the concentration of low boiler in the vapor, the vapor stream from the still is brought into intimate countercurrent contact with a descending stream of boiling liquid in the column, or tower, *C*. This liquid must be rich enough in low boiler so that there is mass transfer of the low boiler from the liquid to the vapor at each stage of the column. Such a liquid can be obtained simply by condensing the overhead vapors and returning some of the liquid to the top of the column. This return liquid is called *reflux*. The use of reflux increases the purity of the overhead product, but not without some cost, since the vapor generated in the reboiler must

Reflux is sometimes provided by partial condensation of the overhead vapor; the reflux then differs in composition from the vapor leaving as overhead product. If an azeotrope is not formed, the vapor reaching the condenser can be brought to complete purity as desired by using a tall tower and a large reflux.

From the reboiler, liquid is withdrawn which contains most of the high boiling component, because little of this component escapes with the overhead product unless the product is an azeotrope. The liquid from the reboiler, which is called the *bottom product* or *bottoms*, is not nearly pure, however, because there is no provision in the equipment of Fig. 17-1 for rectifying this stream. A method for obtaining nearly pure bottom product by rectification is described in Chap. 18.

The column shown in Fig. 17-1 often contains a number of perforated plates, stacked one above the other. A cascade of such trays is called a *sieve-plate column*. A single sieve plate is shown in Fig. 17-2. It consists of a horizontal tray *A* carrying a downpipe, or downcomer, *C*, the top of which acts as a weir, and a number of holes *B*. The holes are all of the same size, usually $\frac{1}{4}$ to $\frac{1}{2}$ in. in diameter. The downcomer *D* from the tray above reaches nearly to tray *A*. This construction leads to the following flow of liquid and vapor. Liquid flows from plate to plate down the column, passing through downcomers *D* and *C* and across the plates. The weir maintains a minimum depth of liquid on the tray, nearly independent of the rate of flow of liquid. Vapor flows upward from tray to tray through the perforations. Except at very low vapor rates, well below the normal operating range, the vapor velocity through the perforations is sufficient to prevent leakage or "weeping" of the liquid through the holes. The vapor is subdivided by the holes into many small bubbles and passes in intimate contact through the pool of liquid on the tray. Because of the action of the vapor bubbles, the liquid is actually a boiling, frothy mass. Above the froth and below the next tray is fog from collapsing bubbles. This fog for the most part settles back into the liquid, but some is entrained by the vapor and carried to the plate above. Sieve-plate columns are representative of an entire class of equipment called *plate columns*.

Typical leaching equipment In leaching, soluble material is dissolved from its mixture with an inert solid by means of a liquid solvent. A diagrammatic flowsheet of a typical

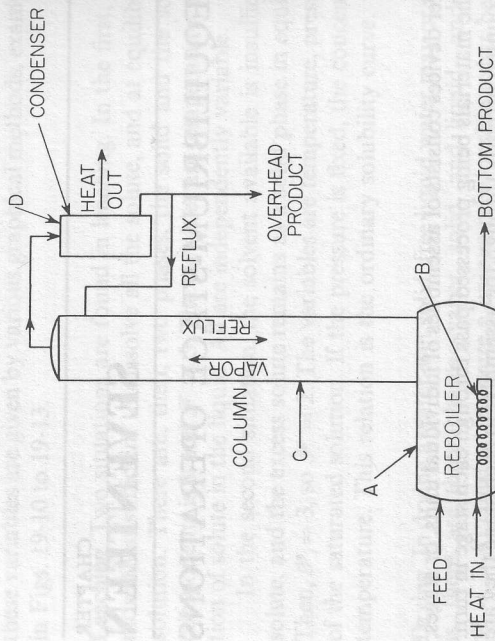


Figure 17-1 Reboiler with fractionating column: A, reboiler; B, heating surface; C, column; D, condenser. provide both reflux and overhead product, and this energy cost is a large part of the total cost of separation by distillation.

The reflux entering the top of the column is often at the boiling point; but if it is cold, it is almost immediately heated to its boiling point by the vapor. Throughout the rest of the column, the liquid and vapor are at their boiling and condensing temperatures, respectively, and the temperatures increase on going down the column because of the increase in high boiler concentration, and in some cases, because of increase in pressure.

Enrichment of the vapor occurs at each stage because the vapor coming to a stage has a lower concentration of the low boiler than the vapor that would be in equilibrium with the liquid fed to that stage. For example, considering the top stage, the vapor coming to this stage is less rich than the overhead product, and the reflux, which has the same composition as the product, has an *equilibrium vapor composition* which is even richer than the product. Therefore, vapor passing through the top stage will be enriched in low boiler at the expense of the reflux liquid. This makes the reflux poorer in low boiler, but if the flow rates have been adjusted correctly, the liquid passing down to the second stage will still be able to enrich the lower quality vapor coming up to the second stage. Then at all stages in the column, some low boiler diffuses from the liquid into the vapor phase, and there is a corresponding diffusion of high boiler from the vapor to the liquid. The heat of vaporization of the low boiler is supplied by the heat of condensation of the high boiler, and the total flow rate of vapor up the column is nearly constant.

The enrichment of the vapor stream as it passes through the column in contact with reflux is called *rectification*. It is immaterial where the reflux originates, provided its concentration in low boiler is sufficiently great to give the desired product. The usual source of reflux is the condensate leaving condenser *D*. Part of the condensate is withdrawn as the product, and the remainder returned to the top of the column

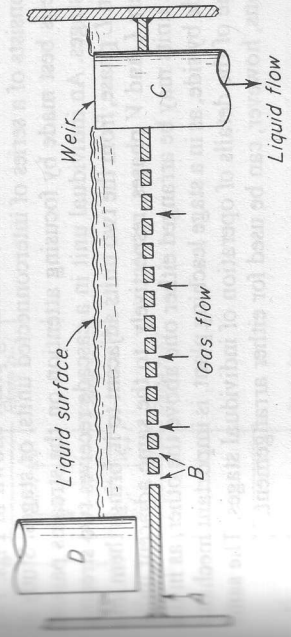


Figure 17-2 Sieve plate: A, tray or plate; B, perforations; C, downcomer to plate below; D, downcomer from plate above.

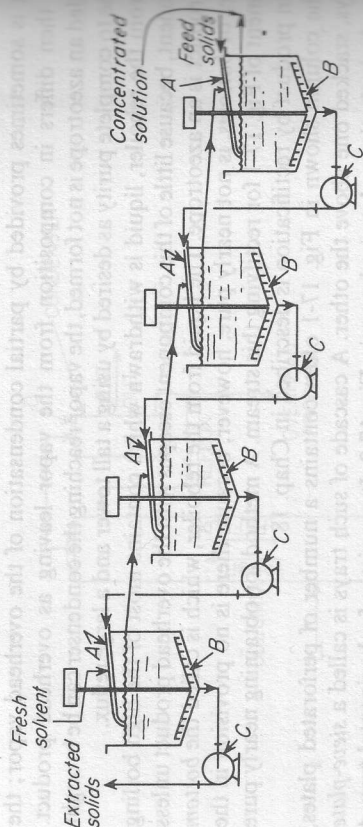


Figure 17-3 Countercurrent leaching plant: A, launder; B, rake; C, slurry pump.

countercurrent leaching plant is shown in Fig. 17-3. It consists of a series of units, in each of which the solid from the previous unit is mixed with the liquid from the succeeding unit and the mixture allowed to settle. The solid is then transferred to the next succeeding unit, and the liquid to the previous unit. As the liquid flows from unit to unit, it becomes enriched in solute, and as the solid flows from unit to unit in the reverse direction, it becomes impoverished in solute. The solid discharged from one end of the system is well extracted, and the solution leaving at the other end is strong in solute. The thoroughness of the extraction depends on the amount of solvent and the number of units. In principle, the unextracted solute can be reduced to any desired amount if enough solvent and a sufficient number of units are used.

Any suitable mixer and settler can be chosen for the individual units in a countercurrent leaching system. In those shown in Fig. 17-3 mixing occurs in launders A and in the tops of the tanks, rakes B move solids to the discharge, and slurry pumps C move slurry from tank to tank.

PRINCIPLES OF STAGE PROCESSES

In the sieve-plate tower and the countercurrent leaching plant shown in Figs. 17-1 and 17-3, the cascade consists of a series of interconnected units, or stages. Study of the assembly as a whole is best made by focusing attention on the streams passing between the individual stages. An individual unit in a cascade receives two streams, one a V phase and one an L phase, from the two units adjacent to it, brings them into close contact, and delivers L and V phases, respectively, to the same adjacent unit. The fact that the contact units may be arranged either one above the other, as in the sieve-plate column, or side by side, as in a stage leaching plant, is important mechanically and may affect some of the details of operation of individual stages. The same material-balance equations, however, can be used for either arrangement.

Terminology for stage-contact plants The individual contact units in a cascade are numbered serially, starting from one end. In this book, the stages are numbered in the

direction of flow of the L phase, and the last stage is that discharging the L phase. A general stage in the system is the n th stage, which is number n counting from the entrance of the L phase. The stage immediately ahead of stage n in the sequence is stage $n - 1$ and that immediately following it is stage $n + 1$. Using a plate column as an example, Fig. 17-4 shows how the units in a cascade are numbered. The total number of stages is N , and the last stage in the plant is therefore the N th stage.

To designate the streams and concentrations pertaining to any one stage, all streams originating in that stage carry the number of the unit as a subscript. Thus, for a two-component system, y_{n+1} is the mole fraction of component A in the V phase leaving stage $n + 1$, and L_n is the molal flow rate of the L phase leaving the n th stage. The streams entering and leaving the cascade and those entering and leaving stage n in a plate tower are shown in Fig. 17-4. Quantities $V_a, L_b, y_a,$ and x_b in Table B, page 449, are equal to $V_1, L_N, y_1,$ and x_N , respectively. This can be seen by reference to Fig. 17-4.

Material balances Consider the portion of the cascade that includes stages 1 through n , as shown by the section enclosed by the dashed line in Fig. 17-4. The total input of material to this section is $L_a + V_{n+1}$ mol/h, and the total output is $L_n + V_a$ mol/h. Since, under steady flow, there is neither accumulation nor depletion, the input and the output are equal and

$$L_a + V_{n+1} = L_n + V_a \quad (17-1)$$

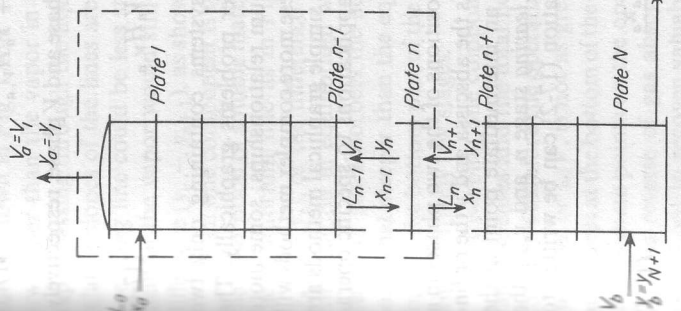


Figure 17-4 Material-balance diagram for plate column.

Equation (17-1) is a total material balance. Another balance can be written by equating input to output for component A . Since the number of moles of this component in a stream is the product of the flow rate and the mole fraction of A in the stream, the input of component A to the section under study, for a two-component system, is $L_n x_a + V_{n+1} y_{n+1}$ mol/h, the output is $L_n x_n + V_a y_a$ mol/h, and

$$L_n x_a + V_{n+1} y_{n+1} = L_n x_n + V_a y_a \quad (17-2)$$

A material balance can also be written for component B , but such an equation is not independent of Eqs. (17-1) and (17-2), since if Eq. (17-2) is subtracted from Eq. (17-1), the result is the material-balance equation for component B . Equations (17-1) and (17-2) yield all the information that can be obtained from material balances alone written over the chosen section.

Overall balances covering the entire cascade are found in the same manner:

$$\text{Total material balance:} \quad L_a + V_b = L_b + V_a \quad (17-3)$$

$$\text{Component } A \text{ balance:} \quad L_a x_a + V_b y_b = L_b x_b + V_a y_a \quad (17-4)$$

Enthalpy balances In many equilibrium-stage processes the general energy balance can be simplified by neglecting mechanical potential energy and kinetic energy. If, in addition, the process is workless and adiabatic, a simple enthalpy balance applies. Then, for a two-component system, for the first n stages,

$$L_n H_{L,a} + V_{n+1} H_{V,n+1} = L_n H_{L,n} + V_a H_{V,a} \quad (17-5)$$

where H_L and H_V are the enthalpies per mole of the L phase and V phase, respectively. For the entire cascade,

$$L_a H_{L,a} + V_b H_{V,b} = L_b H_{L,b} + V_a H_{V,a} \quad (17-6)$$

Graphical methods for two-component systems For systems containing only two components it is possible to solve many mass-transfer problems graphically. The methods are based on material balances and equilibrium relationships; some more complex methods require enthalpy balances as well. These more complex methods will be discussed in Chap. 18. The principles underlying the simple graphical methods are discussed in the following paragraphs. Their detailed applications to specific operations are covered in later chapters.

Operating-line diagram For a binary system, the compositions of the two phases in a cascade can be shown on an arithmetic graph where x is the abscissa and y the ordinate. As shown by Eq. (17-2), the material balance at an intermediate point in the column involves x_n , the concentration of the L phase leaving stage n , and y_{n+1} , the concentration of the V phase entering that stage. Equation (17-2) can be written to show the relationship more clearly:

$$y_{n+1} = \frac{L_n}{V_{n+1}} x_n + \frac{V_a y_a - L_a x_a}{V_{n+1}} \quad (17-7)$$

Equation (17-7) is the operating-line equation for the column; if the points x_n and y_{n+1} for all the stages are plotted, the line through these points is called the *operating line*. Note that if L_n and V_{n+1} are constant throughout the column, the equation is that of a straight line with slope L/V and intercept $y_a - (L/V)x_a$, and the line is easily located. For this case the operating line can also be drawn as a straight line connecting the terminal compositions (x_a, y_a) and (x_b, y_b) . To understand why this is true, extend the dashed line in Fig. 17-4 to include plate N and consider that the stream V_b coming to the bottom stage is equivalent to a stream from a hypothetical stage $N+1$, so that y_b corresponds to y_{N+1} and x_b to x_N . Similarly, the stream L_a at the top of the column can be considered to come from a hypothetical stage numbered zero so that the point (x_0, y_1) or (x_a, y_a) locates the true upper end of the operating line.

When the flow rates are not constant in the column, the operating line on a simple arithmetic plot is not straight. The terminal compositions may still be used to locate the ends of the line, and material-balance calculations over sections of the column are made to establish a few intermediate points. Often only one or two other points are needed because usually the operating line is only slightly curved.

The position of the operating line relative to the equilibrium line determines the direction of mass transfer and how many stages are required for a given separation. The equilibrium data are found by experiment or by thermodynamic calculations, and the equilibrium line is just a plot of the equilibrium values of x_e and y_e . For rectification in a distillation column, the operating line must lie below the equilibrium line, as shown in Fig. 17-5a. Then the vapor coming to any plate contains less of the low boiler than the vapor in equilibrium with the liquid leaving the plate, so that vapor passing through the liquid will be enriched in the low boiling component. The relative slopes of the lines are not important as long as the lines do not touch; the operating line could be less steep than the equilibrium line and progressive enrichment of the vapor would still take place. The driving force for mass transfer is the difference $(y_e - y_{n+1})$, as shown in Fig. 17-5a.

When one component is to be transferred from the V phase to the L phase, as in the absorption of soluble material from an inert gas, the operating line must lie above the equilibrium line as in Fig. 17-5b. The driving force for mass transfer is now $(y_{n+1} - y_e)$, or the difference between the actual vapor composition and the vapor composition in equilibrium with the liquid for that position in the column. In the design of gas absorbers the liquid rate is usually chosen to make the operating line somewhat steeper than the equilibrium line, which gives a moderately large driving force in the bottom part of the column and permits the desired separation to be made with relatively few stages.

In absorbing one component of the gas into a nonvolatile solvent, the total gas rate decreases and the total liquid rate increases as the two phases pass through the column. Therefore the operating line is usually curved, though the percentage change in slope, or L/V , is not as great as the change in either L or V , since both L and V are largest at the bottom of the column and smallest at the top. A method of calculating intermediate points on the operating line is shown later in Example 17-1.

The reverse of gas absorption is called desorption or stripping, an operation carried out to recover valuable solute from the absorbing solution and regenerate

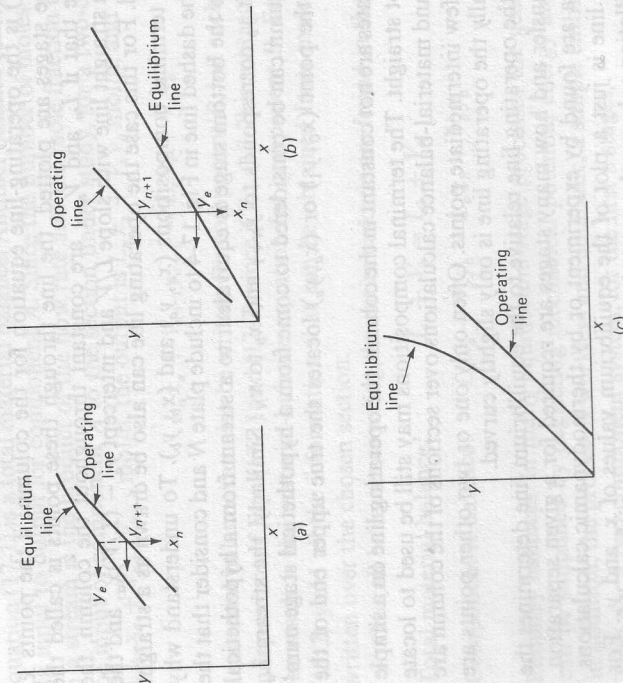


Figure 17-5 Operating and equilibrium lines: (a) for distillation; (b) for gas absorption; (c) for desorption.

the solution. The operating line must then lie below the equilibrium line, as in Fig. 17-5c. Usually the temperature or pressure is changed to make the equilibrium curve much steeper than for the absorption process.

Ideal contact stages The ideal stage is a standard to which an actual stage may be compared. In an ideal stage, the V phase leaving the stage is in equilibrium with the L phase leaving the same stage. For example, if plate n in Fig. 17-4 is an ideal stage, concentrations x_n and y_n are coordinates of a point on the curve of x_e vs. y_e showing the equilibrium between the phases. In a plate column ideal stages are also called *perfect plates*.

To use ideal stages in design it is necessary to apply a correction factor, called the *stage efficiency* or *plate efficiency*, which relates the ideal stage to an actual one. Plate efficiencies are discussed in Chap. 18, and the present discussion is restricted to ideal stages.

Determining the number of ideal stages A problem of general importance is that of finding the number of ideal stages required in an actual cascade to cover a desired range of concentration x_a to x_b or its equivalent, y_a to y_b . If this number can be determined, and if information on stage efficiencies is available, the number of actual stages can be calculated. This is the usual method of designing cascades.

A simple method of determining the number of ideal stages when there are only two components in each phase is a graphical construction using the operating-line

diagram. Figure 17-6 shows the operating line and the equilibrium curve for a typical gas absorber. The ends of the operating line are point a , having coordinates (x_a, y_a) , and point b , having coordinates (x_b, y_b) . The problem of determining the number of ideal stages needed to accomplish the gas-phase concentration change y_b to y_a and the liquid-phase concentration change x_a to x_b is solved as follows.

The concentration of the gas leaving the top stage, which is stage 1, is y_a , or y_1 . If the stage is ideal, the liquid leaving is in equilibrium with the vapor leaving, so the point (x_1, y_1) must lie on the equilibrium curve. This fact fixes point m , found by moving horizontally from point a to the equilibrium curve. The abscissa of point m is x_1 . The operating line is now used. It passes through all points having coordinates of the type (x_n, y_{n+1}) , and since x_1 is known, y_2 is found by moving vertically from point m to the operating line at point n , the coordinates of which are (x_1, y_2) . The step, or triangle, defined by points a , m , and n represents one ideal stage, the first one in this column. The second stage is located graphically on the diagram by repeating the same construction, passing horizontally to the equilibrium curve at point o , having coordinates (x_2, y_2) , and vertically to the operating line again at point p , having coordinates (x_2, y_3) . The third stage is found by again repeating the construction, giving triangle pqb . For the situation shown in Fig. 17-6, the third stage is the last, as the concentration of the gas leaving that stage is y_b , and the liquid leaving it is x_b , which are the desired terminal concentrations. Three ideal stages are required for this separation.

The same construction can be used for determining the number of ideal stages needed in any cascade, whether it is used for gas absorption, rectification, leaching, or liquid extraction. The graphical step-by-step construction utilizing alternately the operating and equilibrium lines to find the number of ideal stages was first applied to the design of rectifying columns, and is known as the *McCabe-Thiele method*.³ The construction can be started at either end of the column, and in general the last step will not exactly meet the terminal concentrations, as was the case in Fig. 17-6. A fractional step may be assigned, or the number of ideal stages may be rounded up to the nearest whole number.

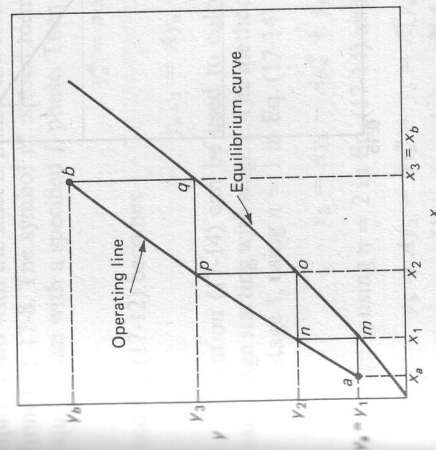


Figure 17-6 Operating-line diagram for gas absorber.

Example 17-1 By means of a plate column, acetone is absorbed from its mixture with air in a nonvolatile absorption oil. The entering gas contains 30 mole percent acetone, and the entering oil is acetone-free. Of the acetone in the air 97 percent is to be absorbed, and the concentrated liquor at the bottom of the tower is to contain 10 mole percent acetone. The equilibrium relationship is $y_e = 1.9x_e$. Plot the operating line and determine the number of ideal stages.

SOLUTION Choose 100 mol of entering gas as a basis, and set this equal to V_0 . The acetone entering is then $0.3 \times 100 = 30$ mol; the air entering is $100 - 30 = 70$ mol. With 97 percent absorbed, the acetone leaving is $0.03 \times 30 = 0.9$ mol and $y_a = 0.9/70.9 = 0.0127$; the acetone absorbed is $30 - 0.9 = 29.1$ mol. With 10 percent acetone in the leaving solution and no acetone in the entering oil, $0.1L_b = 29.1$, and $L_b = 291$ mol. Then $L_a = 291 - 29.1 = 261.9$ mol. To find an intermediate point on the operating line, make an acetone balance around the top part of the tower, assuming a particular value of y , the moles of acetone left in the gas. For 10 mol left in the gas,

$$y = \frac{10}{10 + 70} = 0.125$$

The moles of acetone lost by the gas in this section, $10 - 0.9$, or 9.1 , must equal the moles gained by the liquid. Hence where $y = 0.125$,

$$x = \frac{9.1}{261.9 + 9.1} = 0.0336$$

Similar calculations for $yV = 20$ give $y = 20/90 = 0.222$ and $x = 19.1/(261.9 + 19.1) = 0.068$.

The operating line is plotted in Fig. 17-7. Note that it is only slightly curved, even though the gas flow rate changes almost 30 percent.

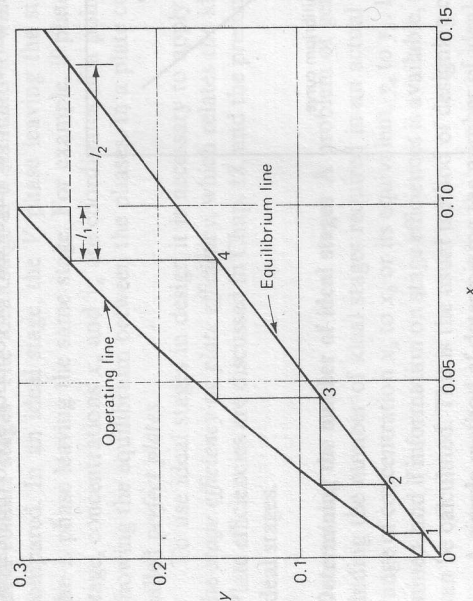


Figure 17-7 Diagram for Example 17-1.

The number of ideal stages is 4 and a fraction. Based on the required change in x relative to the change that would be made in a full step, the fraction is L_1/L_2 , or 0.27. A similar construction based on changes in y gives the fraction 0.33; the values differ because the operating and equilibrium lines are not parallel. The answer would be given as 4.3 stages.

Absorption-factor method for calculating the number of ideal stages When the operating and equilibrium lines are both straight over a given concentration range x_a to x_b , the number of ideal stages can be calculated by formula and graphical construction is unnecessary. Formulas for this purpose are derived as follows.

Let the equation of the equilibrium line be

$$y_e = mx_e + B \tag{17-8}$$

where, by definition, m and B are constant. If stage n is ideal,

$$y_n = mx_n + B \tag{17-9}$$

Substitution for x_n into Eq. (17-7) gives, for ideal stages and constant L/V ,

$$y_{n+1} = \frac{L(y_n - B)}{mV} + y_a - \frac{Lx_a}{V} \tag{17-10}$$

It is convenient to define an absorption factor A by the equation

$$A \equiv \frac{L}{mV} \tag{17-11}$$

The absorption factor is the ratio of the slope of the operating line to that of the equilibrium line. It is a constant when both of these lines are straight. Equation (17-10) can be written

$$\begin{aligned} y_{n+1} &= A(y_n - B) + y_a - Amx_a \\ &= Ay_n - A(mx_a + B) + y_a \end{aligned} \tag{17-12}$$

The quantity $mx_a + B$ is, by Eq. (17-8), the concentration of the vapor that is in equilibrium with the inlet L phase, the concentration of which is x_a . This can be seen from Fig. 17-8. The symbol y_a^* is used to indicate the concentration of a V phase in equilibrium with a specified L phase. Then

$$y_a^* = mx_a + B \tag{17-13}$$

and Eq. (17-12) becomes

$$y_{n+1} = Ay_n - Ay_a^* + y_a \tag{17-14}$$

Equation (17-14) can be used to calculate, step by step, the value of y_{n+1} for each stage starting with stage 1. The method may be followed with the aid of Fig. 17-8.

For stage 1, using $n = 1$ in Eq. (17-14) and noting that $y_1 = y_a$ gives

$$y_2 = Ay_a - Ay_a^* + y_a = y_a(1 + A) - Ay_a^*$$

For stage 2, using $n = 2$ in Eq. (17-14) and eliminating y_2 gives

$$\begin{aligned} y_3 &= Ay_2 - Ay_a^* + y_a = A[y_a(1 + A) - Ay_a^*] - Ay_a^* + y_a \\ &= y_a(1 + A + A^2) - y_a^*(A + A^2) \end{aligned}$$

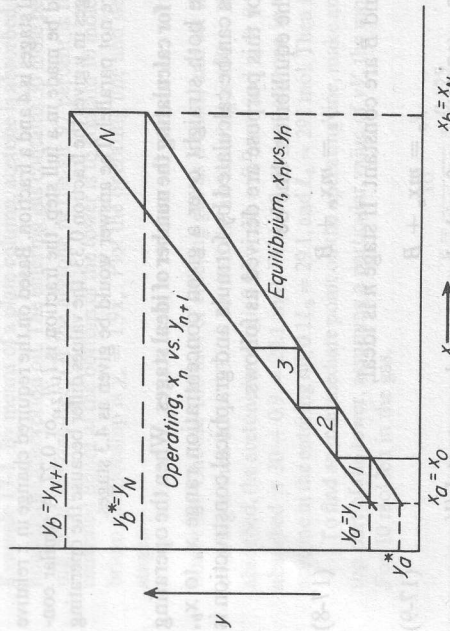


Figure 17-8 Derivation of absorption-factor equation.

These equations can be generalized for the *n*th stage, giving

$$y_{n+1} = y_a(1 + A + A^2 + \dots + A^n) - y_a^*(A + A^2 + \dots + A^n) \quad (17-15)$$

For the entire cascade, *n* = *N*, the total number of stages, and

$$y_{N+1} = y_{N+1} = y_b$$

Then

$$y_b = y_a(1 + A + A^2 + \dots + A^N) - y_a^*(A + A^2 + \dots + A^N) \quad (17-16)$$

The sums in the parentheses of Eq. (17-16) are both sums of geometric series. The sum of such a series is

$$S_n = \frac{a_1(1 - r^n)}{1 - r}$$

where *S_n* = sum of first *n* terms of series

*a*₁ = first term

r = constant ratio of each term to preceding term

Equation (17-16) can then be written

$$y_b = y_a \frac{1 - A^{N+1}}{1 - A} - y_a^* A \frac{1 - A^N}{1 - A} \quad (17-17)$$

Equation (17-17) is a form of the Kremser equation.² It can be used as such or in the form of a chart relating *N*, *A*, and the terminal concentrations.^{1,4} It can also be put into a simpler form by the following method.

Equation (17-14) is, for stage *N*,

$$y_b = Ay_N - Ay_a^* + y_a \quad (17-18)$$

It can be seen from Fig. 17-8 that *y_N* = *y_b*^{*} and Eq. (17-18) can be written

$$y_a = y_b - A(y_b^* - y_a^*) \quad (17-19)$$

Collecting terms in Eq. (17-17) containing *A^{N+1}* gives

$$A^{N+1}(y_a - y_a^*) = A(y_b - y_b^*) + (y_a - y_b) \quad (17-20)$$

Substituting *y_a* - *y_b* from Eq. (17-19) into Eq. (17-20) gives

$$A^N(y_a - y_a^*) = y_b - y_b^* - y_a^* + y_a^* = y_b - y_b^* \quad (17-21)$$

Taking logarithms of Eq. (17-21) and solving for *N* gives

$$N = \frac{\log [(y_b - y_b^*) / (y_a - y_a^*)]}{\log A} \quad (17-22)$$

and from Eq. (17-19)

$$\frac{y_b - y_b^*}{y_b - y_a^*} = A \quad (17-23)$$

Equation (17-22) can be written

$$N = \frac{\log [(y_b - y_b^*) / (y_a - y_a^*)]}{\log [(y_b - y_b^*) / (y_b - y_a^*)]} \quad (17-24)$$

The various concentration differences in Eq. (17-24) are shown in Fig. 17-9. When the operating line and the equilibrium line are parallel, *A* is unity and Eqs. (17-22) and (17-24) are indeterminate. In this case the number of steps is just the overall change in concentration divided by the driving force, which is constant.

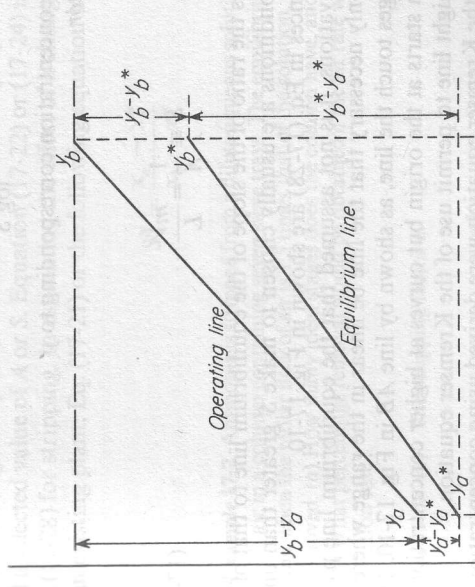


Figure 17-9 Concentration differences in Eq. (17-24).

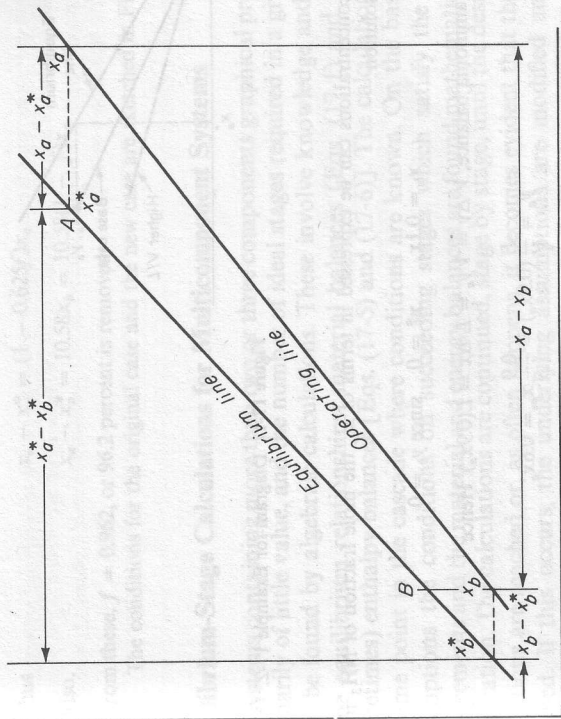


Figure 17-10 Concentration differences in Eq. (17-28).

using mole ratios or mass ratios, defined as the amount of diffusing component divided by the amount of inert nondiffusing components. If this choice of units gives straight equilibrium and operating lines, the same Kremser equations can be used to find the number of ideal stages.

In the design of a plant, N is calculated from the proposed terminal concentrations and a selected value of A or S . Equation (17-22) or (17-24) is used for absorption and Eq. (17-28) for stripping. In estimating the effect of a change in operating conditions of an existing plant, Eq. (17-21) or the following equation in x coordinates is used:

$$S^N = \frac{x_a - x_a^*}{x_b - x_b^*} \tag{17-30}$$

Example 17-2 Ammonia is stripped from a dilute aqueous solution by countercurrent contact with air in a column containing seven sieve trays. The equilibrium relationship is $y_e = 0.8x_e$, and when the molar flow of air is 1.5 times that of the solution, 90 percent of the ammonia is removed. (a) How many ideal stages does the column have, and what is the stage efficiency? (b) What percentage removal would be obtained if the air rate were increased to 2.0 times the solution rate?

SOLUTION (a) The stripping factor is

$$S = \frac{mV}{L} = 0.8 \times 1.5 = 1.2$$

$$N = \frac{y_b - y_a - y_b^* + y_a^*}{y_a - y_a^* - y_b + y_b^*} \tag{17-25}$$

If the operating line has a lower slope than the equilibrium line, A is less than 1.0, but Eqs. (17-22) and (17-24) can still be used by inverting both terms to give

$$N = \frac{\log [(y_a - y_a^*)/(y_b - y_b^*)]}{\log (1/A)} \tag{17-26}$$

$$N = \frac{\log [(y_a - y_a^*)/(y_b - y_b^*)]}{\log [(y_b^* - y_a^*)/(y_b - y_a)]} \tag{17-27}$$

In the design of an absorber, the liquid rate is usually chosen to make the operating line steeper than the equilibrium line or to make A greater than unity. Values of A less than 1.0 can arise when dealing with two or more absorbable components. If the value of A is slightly greater than 1.0 for the major solute, a second component with a much lower solubility (higher value of m) will have a value of A appreciably less than 1.0. If the gas stream and the solution are dilute, the preceding equations can be applied to each component independently.

L-phase form of Eq. (17-24) The choice of y as the concentration coordinate rather than x is arbitrary. It is the conventional variable in gas-absorption calculations. It may be used for stripping also, but in practice equations in x are more common. They are

$$N = \frac{\log [(x_a - x_a^*)/(x_b - x_b^*)]}{\log [(x_a - x_b)/(x_a^* - x_b^*)]} = \frac{\log [(x_a - x_a^*)/(x_b - x_b^*)]}{\log S} \tag{17-28}$$

where x^* = equilibrium concentration corresponding to y

S = stripping factor

S is defined by

$$S \equiv \frac{mV}{A} = \frac{L}{L} \tag{17-29}$$

The stripping factor is the ratio of the slope of the equilibrium line to that of the operating line, and the conditions are usually chosen to make S greater than unity. The concentration differences in Eq. (17-28) are shown in Fig. 17-10.

As shown in the derivations, it is not assumed that the equilibrium line passes through the origin. It is only necessary that the line be linear in the range where the steps representing the stages touch the line, as shown by line AB in Fig. 17-10. Thus an equilibrium line which starts at the origin but curves at higher concentrations is sometimes fitted by a straight line to permit use of the Kremser equation.

The various forms of the Kremser equation were derived using concentrations in mole fractions, which is the usual choice for distillation or absorption. For some operations, including extraction and leaching, the concentrations may be expressed

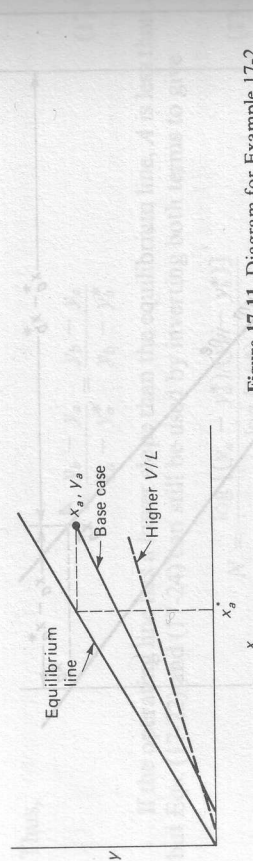


Figure 17-11 Diagram for Example 17-2.

All concentrations can be expressed in terms of x_a , the mole fraction of NH_3 in the entering solution:

$$x_b = 0.1x_a \quad x_b^* = 0, \quad \text{since } y_b = 0$$

From an ammonia balance, $V \Delta y = V y_a = L \Delta x = L(0.9x_a)$. Hence

$$y_a = \frac{L}{V} (0.9x_a) = \frac{0.9}{1.5} x_a = 0.6x_a$$

Also,

$$x_a^* = \frac{y_a}{m} = \frac{0.6x_a}{0.8} = 0.75x_a$$

From Eq. (17-28), using natural logarithms,

$$N = \frac{\log [(x_a - 0.75x_a)/(0.1x_a - 0)]}{\log 1.2} = \frac{\log (0.25x_a/0.1x_a)}{\log 1.2} = 5.02$$

The separation corresponds to 5.02 ideal stages, so the stage efficiency is $5.02/7 = 72$ percent.

(b) If V/L is increased to 2.0 and the number of ideal stages N does not change, $S = 0.8 \times 2.0 = 1.6$. Then

$$\log \frac{x_a - x_a^*}{x_b} = 5.02 \log 1.6 = 2.36$$

$$\frac{x_a - x_a^*}{x_b} = 10.58$$

Let f = fraction of NH_3 removed. Then $x_b = (1 - f)x_a$. By a material balance,

$$y_a = \frac{L}{V} (x_a - x_b) = \frac{1}{2} [x_a - (1 - f)x_a] = \frac{fx_a}{2}$$

$$x_a^* = \frac{y_a}{m} = \frac{0.5fx_a}{0.8} = 0.625fx_a$$

Thus $x_a - x_a^* = (1 - 0.625f)x_a$

Also, $x_a - x_a^* = 10.58x_b = 10.58(1 - f)x_a$

From these, $f = 0.962$, or 96.2 percent is removed.

The conditions for the original case and the new case are sketched in Fig. 17-11.

Equilibrium-Stage Calculations for Multicomponent Systems

For systems containing more than two or three components graphical procedures are ordinarily of little value, and the number of ideal stages required in a given problem must be found by algebraic calculations. These involve knowledge and application of the equilibrium relationships; material balances [Eqs. (17-1) and (17-2)]; and (sometimes) enthalpy balances [Eqs. (17-5) and (17-6)]. The calculations are begun at some point in the cascade where conditions are known. On the basis of certain assumptions the conditions on succeeding stages which satisfy the equilibrium requirements and the material and energy balances are found mathematically, usually by iteration. The calculations are continued, stage by stage, until the desired terminal conditions are reached or, as often happens, it becomes evident that they cannot be reached. If this occurs, the underlying assumptions are modified and the entire calculation repeated until the problem is solved. The large number of repetitive calculations involved are done on a digital computer.

For preliminary calculations on multicomponent systems certain approximate methods are available which greatly reduce the labor involved, but the rigorous computation of multicomponent cascades is an important application of computer technique. (See Chap. 20.)

SYMBOLS

- A Absorption factor, L/mV , dimensionless
- f First term of geometric series
- m Constant in Eq. (17-8)
- f Fraction of ammonia absorbed (Example 17-2)
- H Specific enthalpy, Btu/lb or J/g; H_L of L phase; $H_{L,a}$ at entrance; $H_{L,b}$ at exit; $H_{L,n}$ of L phase leaving stage n ; H_V of V phase; $H_{V,a}$ at exit; $H_{V,b}$ at entrance; $H_{V,n+1}$ of V phase leaving stage $n + 1$
- L Flow rate of L phase, lb mol/h or kg mol/h; L_N from final stage of cascade; L_a at entrance; L_b at exit; L_n from stage n
- m Slope of equilibrium curve, dy/dx
- N Total number of ideal stages
- n Serial number of ideal stage, counting from inlet of L phase
- q Rate of heat flow, Btu/h or W
- r Ratio of succeeding terms of geometric series
- S Stripping factor, mV/L , dimensionless
- Σ Sum of first n terms of geometric series
- V Flow rate of V phase, lb mol/h or kg mol/h; V_a at exit; V_b at entrance; V_{n+1} from stage $n + 1$; V_n leaving first stage of cascade
- x Mole fraction in L phase; used for component A when only two components are present; x_N in L phase from final stage of cascade; x_a at entrance; x_b at exit; x_e at equilibrium; x_n mole fraction in L phase from stage n ; x^* mole fraction in L phase in equilibrium with specified stream of V phase; x_b^* in equilibrium with y_a ; x_b^* in equilibrium with y_b ; x_0 in L phase entering first stage of cascade