

Chapter 8

Introduction to Mass Transfer Operations

INTRODUCTION

This first chapter in Part Two provides introductory information on mass transfer operations.

Three important topics are reviewed:

- 1 Classification of mass transfer operations
- 2 Mass transfer equipment
- 3 Characteristics of mass transfer operations

The chapters that follow treat specific mass transfer operations. As noted in the introduction to Part Two, individual chapters are devoted to several mass transfer topics, including what the authors consider the three main operations: distillation, absorption, and adsorption.

CLASSIFICATION OF MASS TRANSFER OPERATIONS

Mass transfer operations are generally applicable to processes that essentially involve either componential or physical change, or both. A substantial number of these operations are concerned with changing the composition of solutions and mixtures through methods that do not involve chemical reactions; these are defined as componential separation processes. It is also often desirable to separate the original substance into its component parts by phase. Such separations may be entirely mechanical, such as the separation of a solid from a liquid during filtration or the classification of a granular solid into fractions of different particle size by screening. On the other hand, if the operation(s) involve the aforementioned changes in the composition of solutions, they are defined as componential separation operations, and it is with these processes that the bulk of this Part of the book is primarily concerned.

It is also useful to classify mass transfer operations and to cite examples of each. These separations may be brought about by three principle mechanisms. There are nine different phase combinations (see Table 6.1 provided earlier). The individual mass transfer operations falling under these nine classifications are numerous and exceedingly diversified. However, since the underlying principles in all these operations and the general methods of applying them are often the same, these cases will be first grouped together for a study of the factors common to all. Later chapters in this Part will provide specific details on these processes. These nine classifications are now considered in relation to the three mechanisms below.⁽¹⁻³⁾

- 1 Contact of two immiscible phases, with mass transfer or diffusion through the interface between the phases.
- 2 Indirect contact of miscible phases separated by a permeable or semi-permeable membrane, with diffusion through the membrane.
- 3 Direct contact of miscible phases.

These three topics receive treatment below.

Contact of Immiscible Phases

The bulk of the real-world industrial mass transfer operations reside in this category of immiscible phases. It is primarily these mass transfer processes that are addressed in this Part. The various categories are briefly described below.

Gas–Gas

Since all gases are completely soluble in each other, this category of operation cannot generally be practically realized.

Gas–Liquid

If all components of the system are present in appreciable amounts in both gas and liquid phases, an operation known as *distillation* may be employed. In this instance, a gas phase can be formed from the liquid phase by the application of heat. For example, if a liquid solution of acetic acid and water is partially vaporized by heating, it is found (as discussed in Chapter 6) that the newly created vapor phase and the residual liquid both contain acetic acid and water, but in proportions that are different for the two phases and different from those in the original solution. If the vapor and residual liquid are separated physically from one another and the vapor is condensed, two liquid solutions, one “richer” and the other “poorer” in acetic acid, are obtained. In this way, a certain degree of separation of the original components is accomplished. Conversely, should a vapor mixture of the two substances be partially condensed, the newly formed liquid phase and the residual vapor will differ in composition. An interdiffusion of both components between the phases eventually establishes their final composition in both instances. It should be noted; however, that distillation is only feasible when the components to be separated have appreciably differing boiling points.

However, all the components of the solutions discussed above may not be present in appreciable amounts in both the gas and liquid phases. If the liquid phase is a pure liquid containing one component and the gas contains two or more, the operation can be classified as *humidification* or *dehumidification*, depending upon the direction of the transfer. For example, the contact of dry air with liquid water results in evaporation of some of the water into the air (humidification of the air). Conversely, the contact of very moist air with pure liquid water may result in the condensation of part of the moisture in the air (dehumidification). Relatively little air dissolves in the water in both cases, and for most practical purposes it is assumed that only water vapor diffuses from one phase to the other.

Both phases may also be solutions, each containing only one common component that is distributed between phases. For example, if a mixture of ammonia and air is brought into contact with liquid water (see Chapter 6), a large portion of the ammonia, but relatively little air, will dissolve in the liquid, and in this way the air–ammonia mixture may be separated. This operation is known as *gas absorption*. On the other hand, if air is brought into contact with an ammonia–water solution, some of the ammonia leaves the liquid and enters the gas phase. This operation is known as *desorption*, or *stripping*, a common wastewater treatment method.

To complete this classification, consider the case where the gas phase contains but one component and the liquid several, as in evaporation of a saltwater solution by boiling. Here the gas phase contains only water vapor, since the salt is essentially nonvolatile. Such operations do not depend on concentration gradients, but rather on the rate of heat transfer to the boiling solution, and are consequently not considered diffusional separations. Should the salt solution be separated by diffusion of the water into an air stream, however, the operation then becomes one of *desorption*, or *stripping*.

Gas–Solid

It is convenient to classify mass transfer operations in the gas–solid category according to the number of components that appear in the two phases. If a solid solution were to be partially vaporized without the appearance of a liquid phase, the newly formed vapor phase and the residual solid would each contain all the original components but in different proportions. The operation is then *fractional sublimation*. As in distillation, the final compositions are established by interdiffusion of the components between the phases. Although such an operation is theoretically possible, it is usually not practical because of the inconvenience of dealing with solid phases in this manner. However, all components may be present in both phases.

If a solid that is moistened with a volatile liquid is exposed to a relatively dry gas, the liquid leaves the solid and diffuses into the gas, an operation generally known as *drying*, or sometimes as *desorption*. An example of this process is the drying of laundry by exposure to air. There are many industrial counterparts such as the drying of lumber or the removal of moisture from a wet filter cake by exposure to dry gas. In these cases, the transfer is, of course, from the solid to the gas phase. If the diffusion takes place in the opposite direction, the operation is known as *gaseous adsorption*. For example, if a mixture of water vapor and air is brought into contact with silica gel, the water vapor diffuses to the solid, which retains it, and the air is thus dried.

In other instances, a gas mixture may contain several components, each of which is adsorbed on a solid but to different extents (*fractional adsorption*). For example, if a mixture of propane and propylene gases is brought into contact with a molecular sieve, the two hydrocarbons are both adsorbed, but to different extents, thus leading to a separation of the gas mixture.

In a case in which the gas phase is a pure vapor, such as in the sublimation of a volatile solid from a mixture with one that is non-volatile, the operation is dependent more on the rate of application of heat than on the concentration gradient. This process is essentially a nondiffusional separation. The same is true of the condensation of a vapor to a pure solid, where the rate of condensation depends on the rate of heat removal.

Liquid–Liquid

Separations involving the contact of two insoluble liquid phases are known as *liquid-extraction* operations. A simple example is a familiar laboratory procedure: if an acetone–water solution is shaken in a separatory funnel with carbon tetrachloride and the liquids are allowed to settle, a large portion of the acetone will be found in the carbon-tetrachloride-rich phase and will thus have been separated from the water. A small amount of the water will also have been dissolved by the carbon tetrachloride, and a small amount of the latter will have entered the water layer, but these effects are relatively minor and can usually be neglected. In another example, a solution of acetic acid and acetone may be separated by adding the solution to an insoluble mixture of water and carbon tetrachloride. After shaking and settling, both acetone and acetic acid will be found in both liquid phases, but in different proportions. Such an operation is known as *fractional extraction*.

Liquid–Solid

Fractional solidification of a liquid, where the solid and liquid phases are both of variable composition containing all components but in different proportions, is theoretically possible but is not ordinarily carried out because of practical difficulties in handling the solid phase and the very slow transfer rates in the solid.

Cases involving the distribution of a substance between the solid and liquid phases are common, however. Dissolution of a component from a solid mixture by a liquid solvent is known as *leaching* (sometimes called *solvent extraction*). The leaching of gold from ore by cyanide solutions and the leaching of cottonseed oil from cottonseeds by hexane are two examples of this class of leaching process. Diffusion is, of course, from the solid to the liquid phase. If the concentration gradient driving diffusion is in the opposite direction, the operation is known as *liquid adsorption*. Thus, colored material that contaminates impure cane sugar solutions may be removed by contacting the liquid solutions with activated carbon, whereupon the colored substances are retained on the surface of the solid carbon and removed from solution.

When the solid phase is a pure substance and the liquid solution is being separated, the operation is called *crystallization*; but as ordinarily carried out, crystallization rates are more dependent on heat-transfer rates than on solution concentrations. The

reverse operation is *dissolution*. No known operation is included in the category involving a pure liquid phase.

Solid–Solid

Because of the extraordinarily slow rates of diffusion within solid phases, there is at present no major practical industrial separation operation in this (solid–solid) category.

Miscible Phases Separated by a Membrane

In operations involving miscible phases separated by a membrane, the membrane is necessary to prevent intermingling of the phases. It must be permeable differently to the components of the solutions if diffusional separations are to be possible. Three different phases combinations are briefly discussed below. Additional information can be found in Chapter 15.

Gas–Gas

The operation in the gas–gas category is known as *gaseous diffusion*, *gas permeation*, or *effusion*. If a gas mixture whose components are of different molecular weights is brought into contact with a porous diaphragm, the various components of the gas will diffuse through the pores at different rates. This leads to different compositions on opposite sides of the diaphragm and, consequently, to separation of the gas mixture. In this manner, large-scale separation of the isotopes of uranium, in the form of uranium hexafluoride, can be carried out.

Liquid–Liquid

The separation of a crystalline substance from a colloid, by contact of the solution with a liquid solvent with an intervening membrane permeable only to the solvent and the dissolved crystalline substance, is known as *dialysis*. For example, aqueous beet sugar solutions containing undesired colloidal material are freed of the latter by contact with water with an intervening semipermeable membrane. Sugar and water diffuse through the membrane, but the larger colloidal particles cannot. *Fractional dialysis* for separating two crystalline substances in solution makes use of the difference in membrane permeability of the substances. If an electromotive force is applied across the membrane to assist in the diffusion of charged particles, the operation is *electrodialysis*. If a solution is separated from the pure solvent by a membrane that is permeable only to the solvent, the solvent diffuses into the solution—an operation that has come to be defined as *osmosis*. This is not a separation operation, of course, but if the flow of solvent is reversed by superimposing a pressure to oppose the osmotic pressure, the process is labeled *reverse osmosis*.

Solid–Solid

The operation in the solid–solid category has found little, if any, practical application in the chemical process industry.

Direct Contact of Miscible Phases

Operations involving direct contact of miscible phases are not generally considered practical industrially except in unusual circumstances because of the difficulty in maintaining concentration gradients without mixing of the fluid.

Thermal diffusion involves the the formation of a concentration difference within a single liquid or gaseous phase by the imposition of a temperature gradient upon the fluid, thus making possible a separation of the components of the solution. This process has been used, for example, in the separation of uranium isotopes in the aforementioned form of uranium hexafluoride.

If a condensable vapor, such as steam, is allowed to diffuse through a gas mixture, it will preferentially carry one of the components along with it, thus making a separation by the operation known as *sweep diffusion*. If the two zones within the gas phase, where the concentrations are different, are separated by a screen containing relatively large-size openings, the operation is called *atmolysis*.

If a gas mixture is subjected to a very rapid centrifugation, the components will be separated because of the slightly different forces acting on the various molecules, owing to their different masses. The heavier molecules thus tend to accumulate at the periphery of the centrifuge.

ILLUSTRATIVE EXAMPLE 8.1

Discuss why the “doughboys” in World War I employed gas masks to prevent problems with poisonous gas releases.

SOLUTION: The gas masks caused the ambient air being drawn in for breathing purposes to pass through a canister filled with activated carbon, which is a highly porous, granular or pelleted form of carbon. The activated carbon readily adsorbed the organic molecules that constituted the poisonous gases released but essentially did not adsorb oxygen and nitrogen, which passed through the canister freely. Thus, the gas mask can be thought of as a small scale version of an industrial gas adsorption unit.

During the war, these charcoal and other solid adsorbents were employed in chemical warfare. The use of these materials for adsorption of gases became widely introduced in industrial plants as a result of improvements made during the war in the manufacture of activated charcoal, silica gel and other highly active adsorbents. ■

MASS TRANSFER EQUIPMENT

There are numerous types of mass transfer equipment employed in industry. Some of the more common devices found in mass transfer processes are briefly introduced below. A comprehensive review, including design and predictive equations, follows in Chapters 9–16. The reader is referred to the cited literature for additional details on not only those listed below but also those not covered in this section.

Distillation

Distillation is probably the most widely used separation process in the chemical industry. Its application ranges from the rectification of alcohol, which has been practiced since antiquity, to the fractionation of crude oil. The separation of liquid mixtures by distillation is based on differences in volatilities among components; the greater the relative volatilities, the easier the separations.

In continuous distillation, vapor flows up the column and liquid flows countercurrently down the column (see Fig. 8.1). The vapor and liquid are brought into contact on plates or inert packing material. A portion of the condensate from the condenser is returned to the top of the column to provide liquid that flows down the column. Similarly, at the base of the column some liquid is vaporized in the reboiler and returned to provide the vapor flow.

In the *stripping section*, which lies below the feed, the more volatile components are stripped from the liquid. Above the feed, in the *enrichment* or *rectifying section*, the concentration of the more volatile components is increased in the vapor phase. Figure 8.1 shows a distillation column producing two product streams, referred to as tops and bottoms, from a single feed, as well as with multiple feeds and with sidestreams withdrawn at points throughout the column (see Fig. 8.1b). This does not alter the basic operation, but it does complicate the analysis of the process to some extent. If the process requirement is to strip a volatile component from a relatively non-volatile solvent, the rectifying section may be omitted, and the column is then called a *stripping column*.

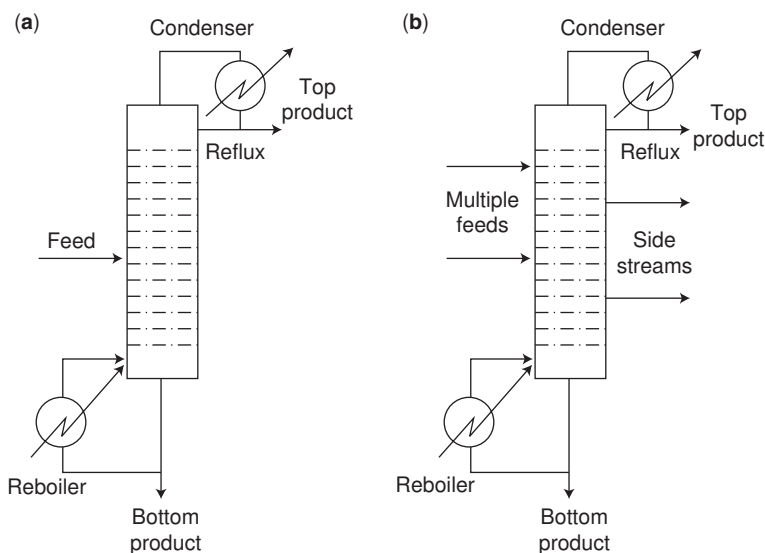


Figure 8.1 Common distillation column configurations. (a) Basic column. (b) Multiple feeds and side streams.

In some operations where the top product is required as a vapor, the liquid condensed is sufficient only to provide the reflux (return) flow to the column, and the condenser is referred to as a *partial condenser*. When the liquid is totally condensed, the liquid returned to the column will have the same composition as the top product. In a partial condenser, the reflux is in equilibrium with the vapor leaving the condenser. Virtually pure top and bottom products can be achieved by using multiple distillation stages or, sometimes, additional columns.

A detailed treatment of distillation can be found in the next chapter.

Absorption

The process of absorption conventionally refers to the intimate contacting of a gaseous mixture with a liquid so that part of one or more of the constituents of the gas will dissolve in the liquid. The contact usually takes place in some type of packed column.

Packed columns are used for the continuous contact between liquid and gas. The countercurrent packed column is the most common type of unit encountered in gaseous pollutant control for the removal of undesirable gas, vapor, or odor. This type of column has also found widespread application in the chemical industry. The gas stream moves upward through the packed bed against an absorbing or reacting liquid that is introduced at the top of the packing. This results in the highest possible recovery efficiency. Since the concentration in the gas stream decreases as it rises through the column, there is constantly fresher liquid available for contact. This provides a maximum average driving force for the transfer process throughout the bed. The opposite of gas absorption is stripping (or desorption) where a component in the liquid phase is transferred to the gas phase. The reader is directed to Chapter 10 of this text where additional information is provided.

Adsorption

In the adsorption process, one or more components in a mixture are preferentially removed from the mixture by a solid (referred to as the adsorbent). Adsorption is influenced by the surface area of the adsorbent, the nature of the compound being adsorbed, the pressure of the operating system (gaseous application), and the temperature of operation. These are important parameters to be aware of when designing or evaluating an adsorption process.

The adsorption process is normally performed in a column. The column can be run as either a packed or fluidized bed. The adsorbent, after it has reached the end of its useful life, can either be discarded or regenerated. This operation can be applied to either a gas mixture or a liquid mixture. The reader is directed to Chapter 11 where additional information is provided.

Extraction

Extraction (referred to by some as leaching) encompasses liquid–liquid as well as solid–liquid systems. Liquid–liquid extraction involves the transfer of solutes from

one liquid phase into another liquid solvent. It is normally conducted in mixer–settler stages and agitated-tower contacting equipment, or packed or spray towers. In the pharmaceutical industries, antibiotics in an aqueous fermentation solution are often removed with an organic solvent. Liquid–solid extraction, in which a liquid solvent is passed over a solid phase to remove some solute, is carried out in fixed-bed, moving-bed, or agitated-solid columns. A bench-scale example of leaching is the coffee pot, where boiling and/or hot water dissolves the soluble coffee from the insoluble coffee grounds. See Chapter 12 for a detailed treatment of both liquid–liquid and solid–liquid extraction processes.

Humidification and Drying

Some mass transfer operations involve simultaneous heat and mass transfer. In the humidification process, water or another liquid is vaporized, and the required heat of vaporization must be transferred to the liquid. Dehumidification is the condensation of water vapor from air, or, in general, the condensation of any vapor from a gas.

Drying involves the *removal* of relatively small amounts of water or organic liquids from a solid phase. The aforementioned humidification process, on the other hand, may be thought of as the *addition* of water to a gaseous phase. Drying can be contrasted to evaporation processes that remove large amounts of water from liquid solutions. In many applications, such as in corn processing, drying equipment follows an evaporation step to provide an ultra high solids content product stream.

Drying, in either a batch or continuous process, removes liquid as a vapor by passing warm gas (usually air) over, or indirectly heating, the solid phase. The drying process is carried out in one of three basic dryer types. The first is a continuous tunnel dryer. In a continuous dryer, supporting trays with wet solids are moved through an enclosed system while warm air blows over the trays. Similar in concept to the continuous tunnel dryer, rotary dryers consist of an inclined rotating hollow cylinder. The wet solids are fed in one side and hot air is usually passed countercurrently over the wet solids. The dried solids then pass out the opposite side of the dryer unit. The final type of dryer is a spray dryer. In spray dryers, a liquid or slurry is sprayed through a nozzle, and fine droplets are dried by a hot gas passed either cocurrently, countercurrently, or co/countercurrently past the falling droplets. This unit has found wide application in air pollution control. Despite the differing methods of heat transfer, the continuous tunnel, as well as indirect, rotary, and spray dryers can all reduce the moisture content of solids to less than 0.01% when designed and operated properly.⁽²⁾

See Chapter 13 for additional details on both humidification and drying.

Other Mass Transfer Unit Operations

In crystallization (Chapter 14), solid crystals are formed from a super-saturated solution, so as to purify and control the physical characteristics of the crystals. Examples include the crystallization of sugar from solution and the crystallization of metal salts in the treatment of metal ore solutions. Fractionation of components of a solution by freeze crystallization (see Chapter 17) is another example; applications

include the separation of xylene isomers and seawater desalination. Membrane separation (Chapter 15) technology provides a physical barrier that selectively allows one component through while stopping the others. Finally, Chapter 16 concludes this Part by examining phase—as opposed to—component separation processes.

ILLUSTRATIVE EXAMPLE 8.2

Discuss the major differences between gaseous adsorption and liquid adsorption.

SOLUTION: Adsorption involves the contact of a fluid (gas or liquid) with a rigid particulate phase which has the property of selectively taking up and storing one or more solute species originally contained in the fluid. Gaseous adsorption is analogous to the condensation of gas molecules at the adsorbent interface, whereas liquid adsorption may be viewed as a crystallization process. ■

ILLUSTRATIVE EXAMPLE 8.3

Provide qualitative differences between gaseous absorption and gaseous stripping.

SOLUTION: Gas absorption is a mass transfer operation in which soluble components of a gas mixture are dissolved in a liquid. Gaseous stripping is the reverse operation. It is employed when it is desired to transfer volatile components from a liquid mixture into a gas. Both processes make use of special equipment and surface area to bring liquid and gas streams into close contact. ■

ILLUSTRATIVE EXAMPLE 8.4

Describe the main differences between gaseous adsorption and gaseous absorption.

SOLUTION: As noted in Illustrative Example 8.2, gaseous adsorption refers to a process where one or more constituents from a mixture are sequestered by a solid substance. The process is influenced by several variables including the surface area of the adsorbent, the nature of the compound being adsorbed, and the system temperature and pressure.

As noted in Illustrative Example 8.3, gaseous absorption refers to the intimate contacting of a mixture of gases with a liquid so that part of one or more of the constituents of the gas will dissolve in the liquid. The process usually occurs in a packed column operated in a counter-current mode. ■

The Selection Decision⁽²⁾

The engineer or scientist faced with the problem of separating the components of a solution must ordinarily choose among several of the aforementioned equipment. Although the choice is usually limited because of the particular physical characteristics of the materials to be handled, the necessity for making this decision nevertheless almost always exists. Until the equipment and the fundamentals of the various

operations are clearly understood, no basis for such a decision is available. Therefore, it would be prudent to establish the nature of the alternatives at this time.

The individual may sometimes choose between using a diffusional operation of the sort discussed in the chapters that follow or a purely mechanical separation method discussed later in this Part. For example, in the separation of a desired mineral from its ore, it may be possible to use either the diffusional operation of leaching with a solvent or the purely mechanical method of flotation. Vegetable oils may be separated from the seeds in which they occur by extraction or by leaching with a solvent. A vapor may be removed from a mixture with a noncondensable gas by the mechanical operation of compression or by the diffusional operations of gas absorption or adsorption. Sometimes, both mechanical and diffusional operations are used, especially where the former are incomplete, as in processes for recovering vegetable oils wherein extraction is followed by leaching. A more commonplace example is the wringing of water from wet laundry followed by air drying. It is characteristic that at the end of a solely mechanical operation, the substance removed is pure, whereas if removed by diffusional separation methods, it is associated with/transferred to another substance.

Frequently, a choice may be made between a diffusional operation and a chemical reaction to bring about a separation. For example, water may be separated from other gases either by absorption in a liquid solvent or by chemical reaction with ferric oxide. Chemical methods ordinarily destroy the substance removed, whereas diffusional methods permit its eventual recovery in an unaltered form without great difficulty.

There are also choices to be made within diffusional operations. For example, a gaseous mixture of oxygen and nitrogen may be separated by preferential adsorption of the oxygen on activated carbon, by absorption, by distillation, or by gaseous effusion. A liquid solution of acetic acid may be separated by distillation, by liquid extraction with a suitable solvent, by absorption with a suitable solvent, or by adsorption with a suitable adsorbent.

The principal basis for choice in most cases is economics: the method that costs least (on an annual basis) is usually the one selected. Other factors, including legal and/or environmental constraints, also influence the decision. The simplest operation, although it may not be the least costly, is sometimes desired because it will be trouble-free. Sometimes, a method will be discarded because imperfect or incomplete knowledge of design methods or the unavailability of data for design will not permit results to be guaranteed. Favorable previous experience with a particular method is often given strong consideration. Cost, however, remains one of the prime factors, and is considered in detail later in Part III—Chapter 18.

CHARACTERISTICS OF MASS TRANSFER OPERATIONS

Treybal⁽³⁾ has discussed the two major characteristic methods of carrying out mass transfer operations. One consideration is the nature of the flow of the phases (whether in steady or unsteady state). However, the flow pattern, i.e., whether the flow direction of the phases is parallel, countercurrent, or cross, must also be considered in the

analysis.⁽³⁾ As important is the method of contacting the phases, i.e., whether it is stagewise or continuous-contact.⁽³⁾ These considerations are briefly described below.

Unsteady-State vs Steady-State Operation

A *steady-state* process is one in which there is no change in conditions (pressure, temperature, composition, etc.) or rates of flow with time at any given point in the system. All other processes are *unsteady-state*. In a *batch* process, a given quantity of matter is placed in a container, and a change occurs by chemical and/or physical means. At the end of the process, the container (or adjustment containers to which material may have been transferred) holds the products. In a *continuous* process, materials are continuously fed to a piece of equipment or to several pieces in series, and products are continuously removed from one or more points. A *continuous* process may or may not be steady-state. A coal-fired power plant, for example, operates continuously. However, because of the wide variation in power demand between peak and slack periods, there is an equally wide variation in the rate at which the coal is fired. For this reason, power plant problems may require the use of average data over long periods of time.

If one examines batch operations, all the phases are stationary from a point of view external to the system or on a “forward flow” basis, although internally there may be relative motion of the phases. A batch reactor, with no flow into or out of the reactor unit during the course of the reaction is one such example. Perhaps a more appropriate mass transfer example is the familiar laboratory extraction procedure involving contact of a solution with an immiscible solvent in a separatory funnel. This a batch operation since, once the liquids are in place, there is no further flow of liquid into or out of the vessel until the operation is completed. The solute diffuses from the solution into the solvent during the course of the extraction and the concentrations in both phases must therefore change with time. Provided the time of contact is sufficient, the maximum change in concentration which is possible occurs when equilibrium exists between the phases, although in practice the operation may be stopped before this occurs. The entire operation is then said to be equivalent to one stage (or step). Many mass transfer operations may be carried out in this general fashion.

In a semibatch operation, one phase is stationary while the other flows continuously into and/or out of the system. A semibatch reactor, with either (but not both) flow into and out of the unit is a simple example. A mass transfer application is the case of a drier where a quantity of wet solid is placed in an air stream which flows continuously into and out of the drier, carrying away the vaporized moisture. The concentration of moisture in the solid and in the exiting air stream must, of course, change with time. Ultimately, if sufficient time is permitted, the stationary phase will come to equilibrium with the influent phase.

It is a characteristic of steady-state operation that system variables at any position in the system remain constant with the passage of time. This requires continuous, invariable flow of all phases into and out of the system and a maintenance of the flow regime within the system. An example here would be a continuous steady-state

tubular flow reactor. It should be noted that most mass transfer operations are (or are assumed to be) steady-state and continuous, and unless otherwise noted, the reader should assume this to be the case.

Flow Pattern

Flow options arise irrespective of whether the unit is operated in the steady- or unsteady-state mode. There are the three basic flow patterns that arise in practice: parallel, countercurrent, and cross. Each of these flow mechanisms are discussed qualitatively below with details provided by Kelly.⁽⁴⁾

In parallel flow, the phases move through the unit in the same direction, entering and leaving together. The net effect insofar as concentrations are concerned is ultimately the same as that for a batch operation: if the phases are in contact long enough, the maximum concentration change will correspond to a state of equilibrium between the effluent phases.

Consider the single-stage cocurrent contacting process represented in Figure 8.2. A steady-state material balance can be used to monitor the separation taking place in the process. Only the transfer of a single component will be considered here. Treating the average compositions of the flows into and out of the system, one can write both an overall (Equation 8.1) and a componential balance (Equation 8.2).

$$V_0 + L_0 = V_1 + L_1 \quad (8.1)$$

$$V_0 y_0 + L_0 x_0 = V_1 y_1 + L_1 x_1 \quad (8.2)$$

The terms V (gas) and L (liquid) refer to the molar flow rates entering and leaving the stage, and x and y are the mole fractions of the transferring component in V and L . Note that these equations may also be written on a mass basis. Also note that the terms V and G (representing the gas flow rate) are used interchangeably in both this text and the literature.

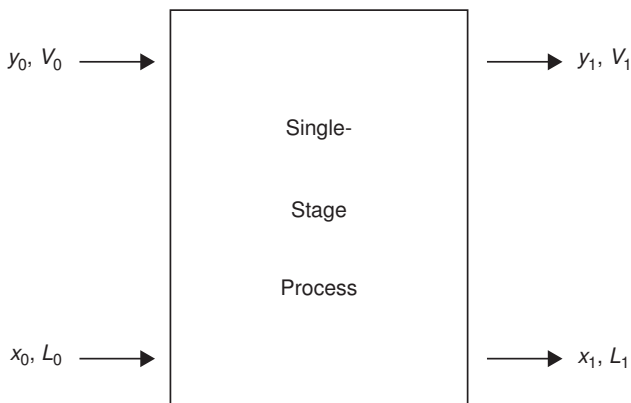


Figure 8.2 Single stage cocurrent contacting process.

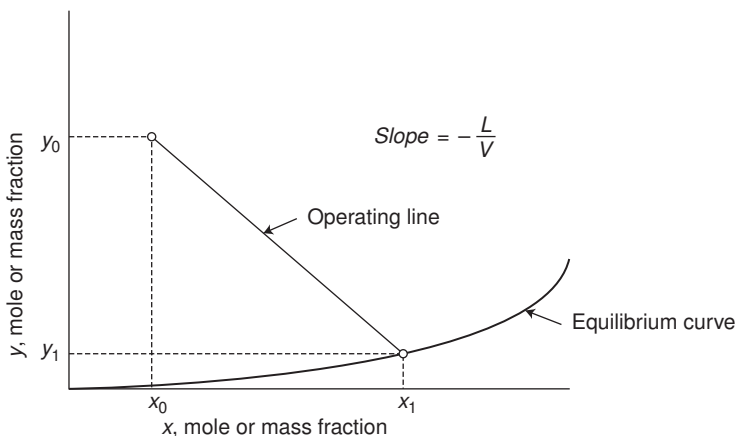


Figure 8.3 Operating diagram: single-stage device.

The separation taking place in a single stage process can be represented on an operating diagram which can be drawn in conjunction with phase equilibrium information available for the system. In this example, and for any case where the inlet streams to the process are mixed together, the contacting pattern is said to be cocurrent. An operating diagram for the steady-state mass transfer of a single component between these two phases is provided in Figure 8.3 where it is assumed $V_0 = V_1 = V$ and $L_0 = L_1 = L$. This diagram shows the transfer of a single component from phase V to phase L . For transfer in the other direction, the equilibrium line remains the same, but the *operating line* would be located and appear below the equilibrium relationship from the case shown above. As the end of the operating line representing the exit stream from the process approaches the equilibrium curve, the single-stage process approaches what has come to be defined as an *ideal* or *theoretical stage*. If the operating line reaches the equilibrium curve, the single-stage device is a theoretical stage. It is also important to note that the displacement of an operating point on the operating line from the equilibrium line provides a direct measure of both the driving force and the rate of transfer. Thus, the rate of transfer is highest at x_0, y_0 and zero at x_1, y_1 . The operating line connecting points x_0, y_0 , and x_1, y_1 describes the actual operating state or condition during the transfer process from point 0 to 1.

The shape of the equilibrium curve on the operating diagram arises from the phase equilibria of the system which must reflect changes in temperature, pressure, ionic strength, etc., that occur in the single-stage process. The shape of the operating line reflects changes in the quantity of material in streams V and L as mass (often referred to as the solute) is transferred from one phase to another.

To reduce the degree of curvature of the operating line, the use of mole ratios on a *solute free basis* may be employed instead of mole fractions. This conversion can be obtained by dividing the number of moles of a transferring species (the solute) by the number of moles of those components that are not transferred. Thus,

$$V_0 y_0 = \frac{V_s y_0}{1 - y_0} = V_s Y_0 \quad (8.3)$$

where V_s is the gas nontransferring (solute-free) portion of V_0 and

$$Y_0 = \frac{\text{moles of transferring component}}{\text{moles of nontransferring component}} \quad (8.4)$$

A similar expression can be written for liquid stream L . A component balance can be used to derive an operating line expression in terms of these mole or mass ratios:

$$V_s(Y_0 - Y_1) = L_s(X_1 - X_0) \quad (8.5)$$

or

$$V_s(Y_0 - Y_1) = -L_s(X_0 - X_1) \quad (8.6)$$

An X - Y operating line based on Equation (8.6) would therefore be a straight line passing through points (X_0, Y_0) and (X_1, Y_1) with a slope of $-L_s/V_s$. However, for most applications, the solute-free mole fraction is not employed, particularly when mole fractions are low.

In *countercurrent* flow, the contacted phases flow in opposite directions through the equipment. For example, in gas absorption the gas to be “washed” may flow upward through a tower while the “washing” liquid flows downward through the gas. The reverse transfer occurs in gas *stripping*, where the gas does the “washing.” For the maximum possible transfer, one of the effluent phases will come to equilibrium with the other influent phase, although in practice this condition is never met.

If the exiting streams from a single-stage device are in equilibrium, the single-stage is defined as a *theoretical stage*. It is usually desirable to use several or multiple stages for a given separation. When multiple stages are used, some thought must be given to the pattern of contacting the two phases. Cocurrent contacting (see Fig. 8.2), where the inlet stream from one phase is mixed with the inlet stream of another phase, can provide, at best, the equivalent of only one theoretical stage no matter how many actual stages are used. To maximize driving forces throughout a particular process, countercurrent contacting is often used. In this contacting mode, the inlet stream for one phase is contacted with the outlet stream of the other phase.

A two-stage contacting system for both cocurrent and countercurrent is pictured in Figure 8.4.⁽⁴⁾ The following componential mole balance on a solute free basis is

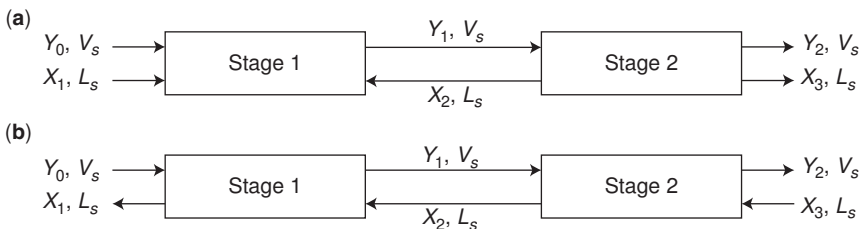


Figure 8.4 Two-stage contacting process. (a) Cocurrent operation. (b) Countercurrent operation.

applied to the overall countercurrent process pictured in Figure 8.4b.

$$V_s Y_0 + V_s X_3 = V_s Y_2 + L_s X_1 \quad (8.7)$$

The operating line for countercurrent contacting is shown in Figure 8.5. Here, the diagram shows the transfer from phase V to phase L . If transfer were in the opposite direction as in a stripping operation, the operating line would, as indicated earlier, be located below the equilibrium line. In general, for a given number of stages, countercurrent contacting yields the highest mass transfer efficiency. The reason for this is that the average mass transfer driving force across the device is greater than would be the case with cocurrent contacting.

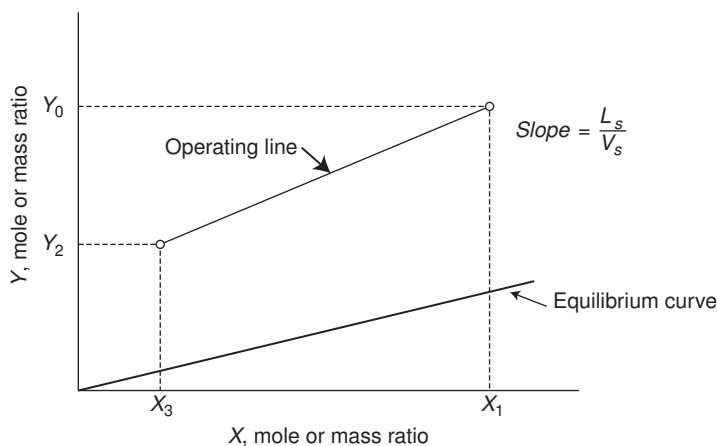


Figure 8.5 Operating diagram: countercurrent contacting operation.

In crossflow, the phases flow at right angles to each other, as in the case of the air and water in some atmospheric water-cooling towers. The maximum possible concentration change occurs if one of the effluent streams comes to equilibrium with the other influent stream. Crosscurrent contacting, which is intermediate in mass transfer efficiency to cocurrent and countercurrent contacting, is shown in Figure 8.6 for a two-stage system.⁽⁵⁾

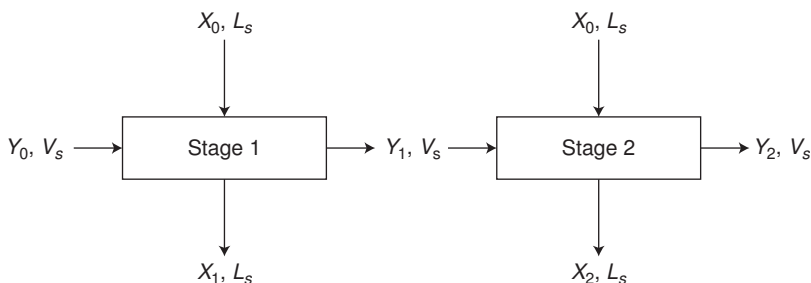


Figure 8.6 Two-stage crossflow contacting process.

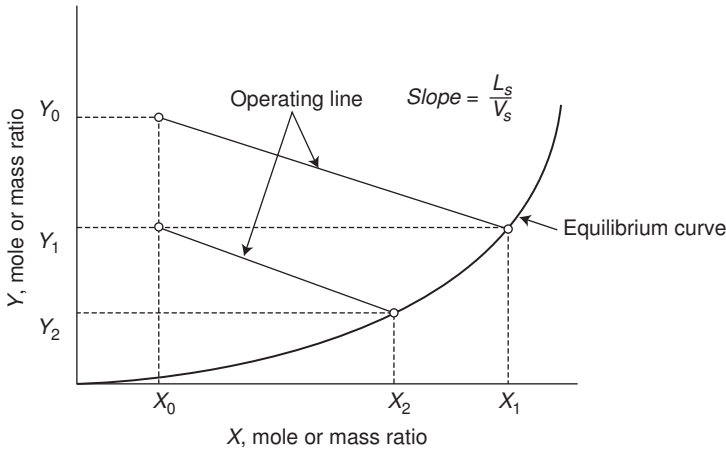


Figure 8.7 Operating diagram: crosscurrent contacting.

Although the liquid L feed to both stages is the same, this need not be the case; the feed rate to each stage can be different as can the composition of that feed stream. To draw the operating line, the following solute free balances can be written:

$$V_s(Y_0 - Y_1) = V_s(X_1 - X_0); \text{ stage 1} \quad (8.8)$$

$$V_s(Y_1 - Y_2) = V_s(X_2 - X_0); \text{ stage 2} \quad (8.9)$$

The component balance for each stage is essentially similar to that for the cocurrent process. However, the stages are coupled. For this case, the operating diagram is presented in Figure 8.7. Crosscurrent contacting is not used as commonly as cocurrent and countercurrent contacting but is employed in extraction, leaching, drying, and air pollution control applications.

ILLUSTRATIVE EXAMPLE 8.5

To illustrate the relative efficiencies of the various contacting modes of operation discussed above, Kelly⁽⁴⁾ considered the following example. Suppose there are two discrete stages that can mix and separate phases, and that the stages can be connected cocurrently, countercurrently, or crosscurrently for gas–liquid contacting. Find the contacting mode that will provide the maximum removal of a single transferring component from a gas phase, V , if a fixed amount of solvent, L , is to be used. Assume the inlet liquid flow, $L = 20$ units/time, inlet liquid composition = 0.0 of the transferring component, inlet gas flow, $V = 20$ units/time, inlet gas composition = Y_0 of the transferring (solute) component on a fractional basis, only one component is transferred between the gas and liquid, each stage can be considered to be an ideal stage, and equilibrium data in terms of mole ratios on a solute free basis is given by $Y = mX$, where X and Y are the mole ratios of the transferring component to the nontransferring component.

SOLUTION: Consider first a single cocurrent stage, as pictured in Figure 8.4a. The ratio of flows of nontransferring components (the liquid to gas ratio on a solute-free basis) is:

$$\frac{L_s}{V_s} = \frac{L_s}{V - VY_0} = \frac{L_s}{V(1 - Y_0)}$$

The outlet mole ratios, X_1 and Y_1 , can be found through graphical construction on an operating diagram by constructing a line of slope $-L_s/V_s$ from (X_0, Y_0) to the equilibrium line since this is a theoretical stage. Since the inlet mole ratio, $X_0 = 0.0$, an analytical expression can also be developed to find X_1 and Y_1 . By material balance,

$$V_s Y_0 + L_s X_0 = V_s Y_1 + L_s X_1 \quad (8.5)$$

But, $X_1 = Y_1/m$ from the given equilibrium relationship. Noting that $X_0 = 0.0$ and rearranging, one obtains

$$Y_1 = \frac{Y_0}{1 + (L_s/V_s)m} = \frac{Y_0}{1 + A}$$

where A is defined as the absorption factor, $A = L_s/V_s m$. Cocurrent contacting, even for a cascade of stages, yields at best one theoretical stage. Since the streams leaving the first stage are in equilibrium, the addition of a second cocurrent stage will not result in any further mass transfer. Thus, the addition of another cocurrent stage does nothing to enhance the transfer of solute as will be the case no matter how many stages are added.

Consider countercurrent contacting with two stages, as pictured in Figure 8.4b. A solute balance around stage 1 yields the following result:

$$Y_1 = \frac{Y_0 + (L_s/V_s)X_2}{1 + A}$$

A balance around stage 2 gives a similar result:

$$Y_2 = \frac{Y_1 + (L_s/V_s)X_3}{1 + A}$$

Recognizing that $X_3 = 0.0$ and that $(L_s/V_s)X_2$ is the same as AY_2 , leads to the following expression:

$$Y_2 = \frac{Y_0}{1 + A + A^2}$$

For crosscurrent contacting with two stages (see Fig. 8.6), a material balance around stage 1, with $X_0 = 0.0$, leads to the following expression for Y_1

$$Y_1 = \frac{Y_0}{1 + A/2}$$

Similarly, for stage 2, with $X_0 = 0.0$,

$$Y_2 = \frac{Y_1}{1 + A/2}$$

By combining the two equations, Y_2 can be expressed as a function of Y_0 :

$$Y_2 = \frac{Y_0}{(1 + A/2)^2}$$

One may now summarize the results for the outlet concentration from each process.

$$\text{Cocurrent, single stage: } Y = \frac{Y_0}{1 + A}$$

$$\text{Crossflow, two stages: } Y = \frac{Y_0}{(1 + A/2)^2} = \frac{Y_0}{\left(1 + A + \frac{A^2}{4}\right)}$$

$$\text{Countercurrent, two stages: } Y = \frac{Y_0}{1 + A + A^2}$$

The results clearly indicate that maximum separation (or the minimum Y) is achieved with countercurrent flow. A similar analysis of these flow modes is available for chemical reactions.^(6,7) ■

ILLUSTRATIVE EXAMPLE 8.6

Formally derive the expression

$$Y_2 = \frac{Y_0}{1 + A + A^2}$$

for the two-stage countercurrent unit described in Illustrative Example 8.5.

SOLUTION: It was previously shown that for stage 1

$$Y_1 = \frac{Y_0 + (L_s/V_s)X_2}{1 + A}$$

and for stage 2

$$Y_2 = \frac{Y_1 + (L_s/V_s)X_3}{1 + A}$$

Noting that $X_3 = 0$ and $(L_s/V_s)X_2 = AY_2$ leads to the equation

$$Y_1 = \frac{Y_0 + AY_2}{1 + A}$$

and

$$Y_2 = \frac{Y_1}{1 + A}$$

Replacing Y_1 in the latter equation with that in the former equation leads to

$$Y_2 = \frac{Y_0 + AY_2}{(1 + A)^2}$$

or

$$Y_2 + 2Y_2A + Y_2A^2 = Y_0 + AY_2$$

Rearranging leads to the final result

$$Y_2(1 + A + A^2) = Y_0$$

or

$$Y_2 = \frac{Y_0}{1 + A + A^2}$$

Stagewise vs Continuous Operation

Stagewise operation is considered first. If two insoluble phases are allowed to come into contact so that the various diffusing components of the mixture distribute themselves between the phases, and if the phases are then mechanically separated, the entire operation—as defined earlier—is said to constitute one stage. Thus, a stage is the unit in which contacting occurs and where the phases are separated; and, a single-stage process is one where this operation is naturally conducted once. As an example, the laboratory batch extraction in a separatory funnel which was described earlier may be cited. However, the operation may be carried on in a continuous as well as in a batchwise fashion. Should a series of stages be arranged so that the phases are frequently contacted and separated once in each stage, the entire multistage assemblage is called a *cascade* and the phases may move through the cascade in parallel, countercurrent, or crossflow mode.

In order to establish a standard for the measurement of performance, the ideal, or theoretical, or equilibrium stage referred to earlier is defined as one where the effluent phases are in equilibrium, so that (any) longer time of contact will bring about no additional change of composition. Thus, at equilibrium, no further net change of composition of the phases is possible for a given set of operating conditions. (In actual industrial equipment, it is usually not practical to allow sufficient time, even with thorough mixing, to attain equilibrium.) Therefore, an *actual* stage does not accomplish as large a change in composition as an equilibrium stage. For this reason, the *fractional stage efficiency* is defined as the ratio of a composition change in an actual stage to that in an equilibrium stage. Stage efficiencies for industrial equipment range between a few percent to that approaching 100 percent.⁽⁵⁾ The approach to equilibrium realized in any stage is then defined as the fractional stage efficiency.

In the case of continuous-contact operation, the phases flow through the equipment in continuous intimate contact throughout the unit, without repeated physical separation and contacting. The nature of the method requires the operation to be either semibatch or steady-state, and the resulting change in compositions may be equivalent to that given by a fraction of an ideal stage or by more than one stage.

Note that equilibrium between two phases at any position in the equipment is generally never completely established.

The essential difference between stagewise and continuous-contact operation may then be summarized. In the case of the stagewise operation, the flow of matter between the phases is allowed to reduce the concentration difference. If allowed to contact for long enough, equilibrium can be established after which no further transfer occurs. The rate of transfer and the time (of contact) then determine the stage efficiency realized in any particular application. On the other hand, in the case of the continuous-contact operation, the departure from equilibrium is deliberately maintained and the transfer between the phases may continue without interruption. Economics plays a significant role in determining the most suitable method.

ILLUSTRATIVE EXAMPLE 8.7

Consider the following two coffee operations. Classify whether they are (a) steady- or unsteady-state; (b) batch, semibatch, or continuous; (c) stagewise or continuous-contact; (d) single- or multistage.

- 1 Coffee is prepared by allowing a portion of hot/boiling water to flow once through a bed of ground coffee beans.
- 2 Coffee is prepared by stirring a sample of ground coffee in a container with hot/boiling water until the desired concentration in the solution is reached and the solid residue filtered from the liquid. The operation is repeated three times with fresh coffee beans.

SOLUTION

Operation 1—Unsteady-state, batch, can be classified either as continuous or stagewise (depending on interpretation and definition), and single-staged (if stagewise).

Operation 2—Unsteady-state, continuous, stagewise, and multistaged. ■

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