CHAPTER 1

The Mass-Transfer Operations

A substantial number of the unit operations of chemical engineering are concerned with the problem of changing the compositions of solutions and mixtures through methods not necessarily involving chemical reactions. Usually these operations are directed toward separating a substance into its component parts. For mixtures, such separations may be entirely mechanical, e.g., the filtration of a solid from a suspension in a liquid, the classification of a solid into fractions of different particle size by screening, or the separation of particles of a ground solid according to their density. On the other hand, if the operations involve changes in composition of solutions, they are known as the mass-transfer operations and it is these which concern us here.

The importance of these operations is profound. There is scarcely any chemical process which does not require a preliminary purification of raw materials or final separation of products from by-products, and for these the mass-transfer operations are usually used. One can perhaps most readily develop an immediate appreciation of the part these separations play in a processing plant by observing the large number of towers which bristle from' a modern petroleum refinery, in each of which a mass-transfer separation operation takes place. Frequently the major part of the cost of a process is that for the separations. These separation or purification costs depend directly upon the ratio of final to initial concentration of the separated substances, and if this ratio is large, the product costs are large. Thus, sulfuric acid is a relatively low-priced product in part because sulfur is found naturally in a relatively pure state, whereas pure uranium is expensive because of the low concentration in which it is found in nature.

The mass-transfer operations are characterized by transfer of a substance through another on a molecular scale. For example, when water evaporates from a pool into an airstream flowing over the water surface, molecules of water vapor diffuse through those of the air at the surface into the main portion of the airstream, whence they are carried away. It is not bulk movement as a result of a pressure difference. as in pumping a liquid through a pipe, with which we are primarily concerned. In the problems at hand, the mass transfer is a result of a concentration difference, or gradient, the diffusing substance moving from a place of high to one of low concentration.

CLASSIFICATION OF THE MASS-TRANSFER OPERATIONS

It is useful to classify the operations and to cite examples of each, in order to indicate the scope of this book and to provide a vehicle for some definitions of terms which are commonly used.

Direct Contact of Two Immscible Phases

This category is by far the most important of all and includes the bulk of the mass-transfer operations. Here we take advantage of the fact that in a two-phase system of several components at equilibrium, with few exceptions the compositions of the phases are different. The various components, in other words, are differently distributed between the phases.

In some instances, the separation thus afforded leads immediately to a pure substance because one of the phases at equilibrium contains only one constituent. For example, the equilibrium vapor in contact with a liquid aqueous salt solution contains no salt regardless of the concentration of the liquid. Similarly the equilibrium solid in contact with such a liquid salt solution is either pure water or pure salt, depending upon which side of the eutectic composition the liquid happens to be. Starting with the liquid solution, one can then obtain a complete separation by boiling off the water. Alternatively, pure salt or pure water can be produced by partly freezing the solution; or, in principle at least, both can be obtained pure by complete solidification followed by mechanical separation of the eutectic mixture of crystals. In cases like these, when the two phases are first formed, they are immediately at their final equilibrium compositions and the establishment of equilibrium is not a time-dependent process. Such separations, with one exception, are not normally considered to be among the mass-transfer operations.

In the mass-transfer operations, neither equilibrium phase consists of only one component. Consequently when the two phases are initially contacted, they will not (except fortuitously) be of equilibrium compositions. The system then attempts to reach equilibrium by a relatively slow diffusive movement of the constituents, which transfer in part between the phases in the process. Separations are therefore never complete, although, as will be shown, they can be brought as near completion as desired (but not totally) by appropriate manipulations.

The three states of aggregation, gas, liquid, and solid, permit six possibilities of phase con tact.

Gas-gas: Since with very few exceptions all gases are completely soluble in each other) this category is not practically realized.

Gas-liquid: If all components of the system distribute between the phases at equilibrium, the operation is known as *fractional distillation* (or frequently just *distillation*). In this instance the gas phase is created from the liquid by application of heat; or conversely, the liquid is created from the gas by removal of heat. For example, if a liquid solution of acetic acid and water is partially vaporized by heating, it is found that the newly created vapor phase and the residual liquid both contain acetic acid and water but in proportions at equilibrium which are different for the two phases and different from those in the original solution. If the vapor and liquid are separated mechanically from each other and the vapor condensed, two solutions, one richer in acetic acid and the other richer in water, are obtained. In this way a certain degree of separation of the original components has been accomplished.

Both phases may be solutions, each containing, however, only one common component (or group of components) which distributes between the phases. For example, if a mixture of ammonia and air is contacted with liquid water, a large portion of the ammonia, but essentially no air, will dissolve in the liquid and in this way the air-ammonia mixture can be separated. The 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, an operation known as *desorption* or *stripping*. The difference is purely in the direction of solute transfer.

If the liquid phase is a pure liquid containing but one component while the gas contains two or more, the operation is *humidification* or *dehumidification*, depending upon the direction of transfer (this is the exception mentioned earlier). For example, contact of dry air with liquid water results in evaporation of some water into the air (humidification of the air). Conversely, contact of very moist air with pure liquid water may result in condensation of part of the moisture in the air (dehumidification). In both cases, diffusion of water vapor through air is involved, and we include these among the mass-transfer operations.

Gas-solid: Classification of the operations in this category according to the number of components which appear in the two phases is again convenient.

If a solid solution is partially vaporized without the appearance of a liquid phase, the newly formed vapor phase and the residual solid each contains all the original components, but in different proportions, and the operation is *fractional sublimation*. As in distillation, the final compositions are established by inter-diffusion of the components between the phases. While such an operation is theoretically possible, practically it is not generally done because of the inconvenience of dealing with solid phases in this manner.

Not all components may be present in both phases, however. If a solid which 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*, sometimes as *desorption*. A homely example is drying laundry by exposure to air, and there are many industrial counterparts such as drying lumber or the removal of moisture from a wet filter cake by exposure to dry gas. In this case, the diffusion is, of course, from the solid to the gas phase. If the diffusion takes place in the opposite direction, the operation is known as *adsorption*. For example, if a mixture of water vapor and air is brought into contact with activated silica gel, the water vapor diffuses to the solid, which retains it strongly, 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 activated carbon. the two hydrocarbons are both adsorbed, but to different extents, thus leading to a separation of the gas mixture.

When the gas phase is a pure vapor, as in the sublimation of a volatile solid from a mixture with one which is nonvolatile, the operation depends more on the rate of application of heat than on concentration difference and is essentially non diffusional. The same is true of the condensation of a vapor to the condition of a pure solid, where the rate 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 the familiar laboratory procedure: if an acetone-water solution is shaken in a separatory funnel with carbon tetrachloride and the liquids 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. As another possibility, a solution of acetic acid and acetone can be separated by adding it to the 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. Another form of fractional extraction can be effected by producing two liquid phases from a single-phase solution by cooling the latter below its critical solution temperature. The two phases which form will be of different composition.

Liquid-solid: When all the constituents are present in both phases at equilibrium, we have the operation of *fractional crystallization*. Perhaps the most interesting examples of this are the special techniques of *zone refining*, used to obtain ultrapure metals and semiconductors, and *adductive crystallization*, where a substance, such as urea, has a crystal lattice which will selectively entrap long straight-chain molecules like the paraffin hydrocarbons but will exclude branched molecules.

Cases where the phases are solutions (or mixtures) containing but one common component occur more frequently. Selective solution of a component from a solid mixture by a liquid solvent is known as *leaching* (sometimes also as solvent extraction), and as examples we cite the leaching of gold from its ores by cyanide solutions and of cottonseed oil from the seeds by hexane. The diffusion is, of course, from the solid to the liquid phase. If the diffusion is in the opposite direction, the operation is known as *adsorption*. Thus, the colored material which contaminates impure cane sugar solutions can be removed by contacting the liquid solutions with activated carbon, whereupon the colored substances are retained on the surface of the solid carbon.

Solid-solid: Because of the extraordinarily slow rates of diffusion within solid phases, there is no industrial separation operation in this category.

Phases Separated by a Membrane

These operations are used relatively infrequently, although they are rapidly increasing in importance. The membranes operate in different ways, depending upon the nature of the separation to be made. In general, however, they serve to prevent intermingling of two miscible phases. They also prevent ordinary hydrodynamic flow, and movement of substances through them is by diffusion. And they permit a component separation by selectively controlling passage of the components from one side to the other.

Gas-gas: In *gaseous diffusion or effusion*, the membrane is microporous. If a gas mixture whose components are of different molecular weights is brought into contact with such a diaphragm, the various components of the gas pass through the pores at rates dependent upon the molecular weights. This leads to different compositions on opposite sides of the membrane and consequent separation of the mixture. In this manner large-scale separation of the isotopes of uranium, in the form of gaseous uranium hexafluoride, is carried out. In *permeation*, the membrane is not porous, and the gas transmitted through the membrane first dissolves in it and then diffuses through. Separation in this case is brought about principally by difference in solubility of the components. Thus, helium can be separated from natural gas by selective permeation through fluorocarbon-polymer membranes.

Gas-liquid: These are *permeation* separations where, for example, a liquid solution of alcohol and water is brought into contact with a suitable nonporous membrane, in which the alcohol preferentially dissolves. After passage through the membrane the alcohol is vaporized on the far side.

Liquid-liquid: The separation of a crystalline substance from a colloid, by contact of their 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 for 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 which is permeable only to the solvent, the solvent diffuses into the solution, an operation known as *osmosis*. This is not a separation operation, of course, but by superimposing a pressure to oppose the osmotic pressure the flow of solvent is reversed, and the solvent and solute of a solution can be separated by reverse osmosis. This is one of the processes which may become important in the desalination of seawater.

Direct Contact of Miscible Phases

Because of the difficulty in maintaining concentration gradients without mixing the fluid, the operations in this category are not generally considered practical industrially except in unusual circumstances.

Thermal diffusion involves the formation of a concentration difference within a single liquid or gaseous phase by imposition of a temperature gradient upon the fluid, thus making a separation of the components of the solution possible. In this way, ^{3}He is separated from its mixture with ^{4}He.

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*. 1f the two zones within the gas phase where the concentrations are different are separated by a screen containing relatively large 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. This method is also used for separation of uranium isotopes.

Use of Surface Phenomena

Substances which when dissolved in a liquid produce a solution of lowered surface tension (in contact with a gas) are known to concentrate in solution at the liquid surface. By forming a foam of large surface, as by bubbling air through the solution, and collecting the foam, the solute can be concentrated. In this manner, detergents have been separated from water, for example. The operation is known as *foam separation*. It is not to be confused with the flotation processes of the ore-dressing industries, where insoluble solid particles are removed from slurries by collection into froths.

This classification is not exhaustive but it does categorize all the major mass-transfer operations. Indeed, new operations continue to be developed, some of which can be fit into more than one category. This book includes gas-liquid, liquid-liquid, and solid-fluid operations, all of which involve direct contact of two immiscible phases and make up the great bulk of the applications of the transfer operations.

Direct and indirect operations: The operations depending upon contact of two immiscible phases particularly can be further sub-classified into two types. The *direct* operations produce the two phases from a single-phase solution by addition or removal of heat. Fractional distillation, fractional crystallization, and one form of fractional extraction are of this type. The *indirect* operations involve addition of a foreign substance and include gas absorption and stripping, adsorption, drying, leaching, liquid extraction, and certain types of fractional crystallization.

It is characteristic of the direct operations that the products are obtained directly, free of added substance; these operations are therefore sometimes favored over the indirect if they can be used.

If the separated products are required relatively pure, the disadvantages of the indirect operations incurred by addition of a foreign substance are several. The removed substance is obtained as a solution, which in this case must in turn be separated, either to obtain the pure substance or the added substance for reuse, and this represents an expense. The separation of added substance and product can rarely be complete, which may lead to difficulty in meeting product specifications. In any case, addition of a foreign substance may add to the problems of building corrosion-resistant equipment, and the cost of inevitable losses must be borne. Obviously the indirect methods are used only because they are, in the net, less costly than the direct methods if there is a choice. Frequently there is no choice.

When the separated substance need not be obtained pure, many of these disadvantages may disappear. For example, in ordinary drying, the water vapor-air mixture is discarded since neither constituent need be recovered. In the production of hydrochloric acid by washing a hydrogen chloride-containing gas with water, the acid-water solution is sold directly without separation.

CHOICE OF SEPARATION METHOD

The chemical engineer faced with the problem of separating the components of a solution must ordinarily choose from several possible methods. While the choice is usually limited by the peculiar physical characteristics of the materials to be handled, the necessity for making a decision nevertheless almost always exists. Until the fundamentals of the various operations have been clearly understood, of course, no basis for such a decision is available, but it is well at least to establish the nature of the alternatives at the beginning.

One can sometimes choose between using a mass-transfer operation of the sort discussed in this book and a purely mechanical separation method. For example, in the separation of a desired mineral from its ore, it may be possible to use either the mass-transfer operation of leaching with a solvent or the purely mechanical methods of flotation. Vegetable oils can be separated from the seeds in which they occur by expression or by leaching with a solvent. A vapor can be removed from a mixture with a permanent gas by the mechanical operation of compression or by the mass-transfer operations of gas absorption or adsorption. Sometimes both mechanical and mass-transfer operations are used, especially where the former are incompletet as in processes for recovering vegetable oils wherein expression is followed by leaching. A more commonplace example is wringing water from wet laundry followed by air drying. It is characteristic that at the end of the operation the substance removed by mechanical methods is pure, while if removed by diffusional methods it is associated with another substance.

One can also frequently choose between a purely mass-transfer operation and a chemical reaction or a combination of both. Water can be removed from an ethanol-water solution either by causing it to react with unslaked lime or by special methods of distillation, for example. Hydrogen sulfide can be separated from other gases either by absorption in a liquid solvent with or without simultaneous chemical reaction or by chemical reaction with ferric oxide. Chemical methods ordinarily destroy the substance removed, while mass-transfer methods usually permit its eventual recovery in unaltered form without great difficulty.

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

The principal basis for choice in any case is cost: that method which costs the least is usually the one to be used. Occasionally other factors also influence the decision, however. The simplest operation, while it may not be the least costly, is sometimes desired because it will be trouble-free. Sometimes a method will be discarded because of imperfect knowledge of design methods or unavailability of data for design, so that results cannot be guaranteed. Favorable previous experience with one method may be given strong consideration.

METHODS OF CONDUCTING THE MASS-TRANSFER OPERATIONS

Several characteristics of these operations influence our method of dealing with them and are described in terms which require definition at the start.

Solute Recovery and Fractionation

If the components of a solution fall into two distinct groups of quite different properties, so that one can imagine that one group of components constitutes the solvent and the other group the solute, separation according to these groups is usually relatively easy and amounts to a *solute-recovery* or *solute-removal* operation. For example, a gas consisting of methane, pentane, and hexane can be imagined to consist of methane as solvent with pentane plus hexane as solute, the solvent and solute in this case differing considerably in at least one property, vapor pressure. A simple gas-absorption operation, washing the mixture with a nonvolatile hydrocarbon oil, will easily provide a new solution of pentane plus hexane in the oil, essentially methane-free; and the residual methane will be essentially free of pentane and hexane. On the other hand, a solution consisting of pentane and hexane alone cannot be classified so readily. While the component properties differ, the differences are small, and to separate them into relatively pure components requires a different technique. Such separations are termed *fractionations*, and in this case we might use fractional distillation as a method.

Whether a solute-recovery or fractionation procedure is used may depend upon the property chosen to be exploited. For example, to separate a mixture of propanol and butanol from water by a gas-liquid contacting method, which depends on vapor pressures, requires fractionation (fractional distillation) be¬cause the vapor pressures of the components are not greatly different. But nearly complete separation of the combined alcohols from water can be obtained by liquid extraction of the solution with a hydrocarbon, using solute-recovery methods because the solubility of the alcohols as a group and water in hydrocarbons is greatly different. The separation of propanol from butanol, however, requires a fractionation technique (fractional extraction or fractional distillation, for example), because all their properties are very similar.

Unsteady-State Operation

It is characteristic of unsteady-state operation that concentrations at any point in the apparatus change with time. This may result from changes in concentrations of feed materials, flow rates, or conditions of temperature or pressure. In any case, *batch* operations are always of the unsteady-state type. In purely batch operations, all the phases are stationary from a point of view outside the apparatus, i.e., no flow in or out, even though there may be relative motion within. The familiar laboratory extraction procedure of shaking a solution with an immiscible solvent is an example. In *semibatch* operations, one phase is stationary while the other flows continuously in and out of the apparatus. As an example, we may cite the case of a drier where a quantity of wet solid is contacted continuously with fresh air, which carries away the vaporized moisture until the solid is dry.

Steady-State Operation

It is characteristic of steady-state operation that concentrations at any position in the apparatus remain constant with passage of time. This requires continuous, invariable flow of all phases into and out of the apparatus, a persistence of the flow regime within the apparatus) constant concentrations of the feed streams, and unchanging conditions of temperature and pressure.

Stage-wise Operation

If two insoluble phases are first allowed to come into contact so that the various diffusing substances can distribute themselves between the phases, and if the phases are then mechanically separated, the entire operation and the equipment required to carry it out are said to constitute one *stage*, e.g., laboratory batch extraction in a separatory funnel. The operation can be carried on in continuous fashion (steady-state) or batch-wise fashion, however. For separations requiring greater concentration changes, a series of stages can be arranged so that the phases flow through the assembled stages from one to the other, e.g.) in counter-current flow. Such an assemblage is called a *cascade*. In order to establish a standard for the measurement of performance, the *equilibrium*, *ideal*, or *theoretical*, stage is defined as one where the effluent phases are in equilibrium, so that a longer time of contact will bring about no additional change of composition. The approach to equilibrium realized m any stage is then defined as the *stage of efficiency*.