Chapter 1

Introduction

1.1 MASS TRANSFER

Chemical process industries are concerned with the transformation of raw materials into useful products. The products include a wide variety of materials such as petroleum products and petrochemicals, inorganic and organic chemicals, paints and pigments, fertilizers and pesticides, pulp and paper, rubber and plastics, soaps and detergents, synthetic fibres, drugs and pharmaceuticals, minerals, metals and semiconductors. These products are either directly used in our day-to-day life, or they serve as raw materials or intermediates for further processing. The materials undergo several processing steps which include physical operations and chemical conversions, before the final products of the desired quality and specifications are obtained. The raw materials reaching a processing unit may require some pre-processing treatments. The products leaving the reactors may sometimes be contaminated by the undesired by-products that have to be removed, or they should be treated to recover valuable side products. The unconverted reactants and the impurities brought into the system by the feed materials have to be separated from the products. These operations, whether they are the pre-processing of raw materials, recovery of the by-products or the final purification of the desired products, involve certain separation operations.

The objectives of the separation operations are purification, isolation, recovery, refining, concentration, or enrichment of the materials at various stages of their processing. The separation is usually achieved by exploiting the differences in one or other of the properties of the substances such as the size, density, volatility, solubility, diffusivity, electrical charge, etc. The separation processes in the chemical process industries fall into one of the following broad categories.

- Mechanical separations
- Diffusional separations

Mechanical separations are generally used for separating one phase from another. For example, filtration is used to separate a solid phase from a liquid phase. They employ the differences in the size, density, velocity, etc. to effect separation. Filtration, screening, sedimentation, magnetic separation, centrifuging, etc. are examples of mechanical separations. Diffusional separations also known as *mass transfer operations*, on the other hand, are used for separating the components of a homogeneous solution. The differences in the properties such as the volatility, solubility, diffusivity, etc. of the constituent species, are utilised in achieving the separation. The concentration difference existing in a homogeneous phase can cause movement of material from one region to another. This transfer of material from the region of higher concentration to the region of lower concentration is termed diffusion which is the basic mechanism of mass transfer. However, this transfer is incapable to achieve separation of the given substance into the products with distinct properties. Since mixing of substances to form a solution is a highly irreversible process, the separation of a homogeneous solution into its components will not occur spontaneously. For separation to be effective, the material is to be transferred to a second phase. The second phase necessary to effect the separation is either generated from the original solution by supplying energy or it is introduced into the system as an external agent. Certain components of the original solution get transferred to the new phase, thus effecting separation. Thus the mass transfer operations generally involve the diffusion process within a homogeneous phase followed by the interphase transport. Majority of the separations in chemical process industries are carried out by mass transfer; a variety of mass transfer operations such as distillation, absorption, extraction, adsorption, crystallisation, etc. are employed for this purpose. Mass transfer operations play such an important role in chemical processing that in a large scale chemical process industry, the capital investment on the mass transfer equipment generally far exceeds the investment on the reaction vessels and the related equipment.

Mass transfer operations are employed for separation of the components of a solution. The solution so separated may be a solid, gas or a liquid. In the majority of separations, the transfer of mass occurs between the two insoluble phases which are in *direct contact*. The common mass transfer operations falling under this category are distillation, liquid–liquid extraction, gas absorption, leaching, drying, adsorption, humidification and dehumidification, crystallisation, ion-exchange, etc. If the phases are allowed to be in contact for a sufficiently long time, they eventually reach the equilibrium state, a state in which there is no further net transfer of material. In the *membrane separation operations*, the phases are prevented from coming into contact and kept separated from each other by a semipermeable membrane; the membrane acts as a barrier to the hydrodynamic flow of the phases, but permits through it, the migration of certain components of the solution in preference to the others. Microfiltration, ultrafiltration, reverse osmosis, electrodialysis, pervaporation and gas permeation are examples of membrane separations. Since the membranes achieve the separation by size exclusion as well as by diffusion, their role as separation techniques lie somewhere between the mechanical separations and the conventional mass transfer operations.

In mass transfer, material is transferred on a molecular scale, and this transfer is quite different from the bulk transport of material from one location to another. Moving the material by means of say, a pump or a blower, involves the bulk transfer of material facilitated by the pressure difference created externally. This bulk transport of mass is distinct from the mass transfer, which involves the relative movement of the components due to a concentration difference. For example, inhalation of air by the lungs is bulk transport where as transfer of oxygen from the air to the blood by diffusion is mass transfer. When ammonia is absorbed from a mixture of ammonia and air using water as the solvent, ammonia moves relative to the air from the gas phase to the liquid phase. When oil is extracted from the oil cake using a solvent such as hexane, there is relative movement of components between the solid and the liquid phases. The transfer of ammonia is due to the concentration difference for the ammonia existing between the gas and the liquid phases and the transfer of oil from the oil cake is due to the concentration difference between the solid and the liquid phases. In these examples, the transfer of ammonia is by the mass transfer operation called *gas absorption* and the transfer of oil is by the operation called *leaching*.

We know that the heat transfer between two planes comes to a stop when the temperatures at the planes become identical. Therefore, we can treat the temperature difference to be the true driving force in heat transfer. We can see that the driving forces in the gas absorption and leaching are the concentration differences between the two insoluble phases. The concentration difference between the two immiscible phases which are in direct contact is responsible for the transfer of materials in the operations such as absorption, distillation, humidification, extraction, leaching, drying, adsorption and crystallisation which are discussed in Chapters 4 through 11 of this book. However, the concentration difference cannot be treated as the true driving force for mass transfer between phases; if it were so, the concentration in both phases would have been the same when the equilibrium is established and the transfer of material no longer occurs. This does not happen in mass transfer. For example, in the absorption of ammonia from an ammonia-air mixture using water as the solvent, the concentration of ammonia in the gas and liquid phases will be different even after the phases were allowed to be in contact for an infinitely long time for the equilibrium to be attained.

1.2 THEORETICAL FOUNDATION

Equilibrium

Thermodynamics requires that when different phases of a solution coexist in equilibrium, the *chemical potentials* of the components in the different phases should be equal. Since the chemical potentials in different phases are related to the concentrations differently, the concentrations of the components in the phases need not be equal when this criterion of equilibrium is satisfied. Concentration difference is thus a measure of the driving force for mass transfer between the phases, but not the true driving force. The true driving force is determined by the difference in the chemical potential of the species in the different phases. Thus thermodynamics, particularly the phase equilibrium thermodynamics plays a very important role in determining the driving force for mass transfer. The discussion of the mass transfer operations in the following chapters will begin with a detailed analysis of the equilibrium characteristics of the system under consideration.

While thermodynamic equilibrium determines the theoretical extent of a given mass transfer operation, the actual rate of mass transfer depends upon other additional factors. The rate is influenced by the flow pattern within the system and the diffusivities of the constituent species.

Molecular Diffusion and Interphase Transport

Chapter 2 discusses the theory of molecular diffusion which is the basic mechanism of mass transfer in a homogeneous phase. Molecular diffusion is the movement of molecules from the region of higher concentration to the region of lower concentration when a concentration gradient exists in a homogeneous solution; the ultimate condition attained by the system is a uniformity of concentration throughout. Molecular diffusion in mass transfer is in several ways analogous to conduction in heat transfer and the molecular transport of momentum in momentum transfer. The Fick's law of diffusion predicts a direct relationship between the rate of mass transport and the concentration gradient, just as the Fourier's law of conduction gives the direct proportionality between the rate of heat conduction and the temperature gradient and Newton's law of viscosity predicts the relationship between the rate of momentum transfer and the velocity gradient. Chapter 2 also discusses the influence of temperature and pressure on mass diffusivity which can be treated as the transport coefficient of mass. The various techniques available for the estimation of mass diffusivity in the gaseous and the liquid phases are also reviewed in this chapter. Chapter 3 is concerned with the convective transport and the interphase mass transfer. Molecular diffusion is a very slow process; even in a homogeneous phase originally consisting of regions of non-uniform compositions, it will take a very long time for attaining the uniformity of concentration, if the transfer were due to the molecular diffusion alone. We cannot wait for such an infinitely long time for the completion of the process; neither can we have infinitely large vessels for carrying out the transfer process. In order to carry out the process in a reasonable time and in equipment of manageable sizes, the practicable solution is to increase the rate of transfer by introducing the convective transport in the system by external means. In all the separation equipment used in industries, the mass transfer takes place predominantly by the convective transport. The mass transfer coefficient serves as an index for measuring the rate of convective transport. The concept of mass transfer coefficient, the different types of mass transfer coefficients in use and their interrelationship are explained in Chapter 3. The chapter also discusses how the concept of mass transfer coefficient is different from that of the heat transfer coefficient, the theories of mass transfer and the methods of estimating the coefficient for different geometrical systems.

1.3 EQUIPMENT AND METHODS OF OPERATION

Direct contact separation methods always involve bringing into contact two immiscible phases that are initially not in equilibrium. Mass gets transferred from one phase to the other until equilibrium is established between these two phases. The phases in contact can be a gas, a liquid or a solid. Thus we have gas–liquid contact operations, liquid–liquid contact operations, solid–liquid contact operations and gas–solid contact operations. The basic principles of interphase transport, the two-resistance theory, the different modes of contacting the phases, salient features of *stage contact* and *continuous contact* are also discussed in Chapter 3 under interphase transport.

Based on the mode of operation, the mass transfer processes can be classified as *batch process*, *semi-batch process* or *continuous process*. In batch operation, definite quantities of the materials are introduced into the equipment for intimate mixing, the phases are allowed to be in contact for a sufficiently long time and the product streams are withdrawn when the desired extent of separation is achieved. Batch operations are *unsteady-state operations* in the sense that the concentration of the phases at a given point inside the equipment change with the time. In contrast, in continuous operation, the feed streams are introduced continuously and products are also withdrawn continuously from the equipment. Since the concentrations at a given point in the vessel remain constant and do not change with the time, the continuous operations are also *steady-state operations*. In the semi-batch operation, one of the phases is allowed to flow continuously through the equipment which holds a definite quantity or batch of the other phase. *Drying* a wet solid by passing hot air continuously across a batch of the wet feed taken on a tray is a semi-batch operation.

In the continuous operation, the changes in the concentration of the phases can be achieved either continuously or intermittently in stages. The *plate column* is an example of a stage contact equipment for gas–liquid and liquid–liquid contact and the *packed column* is a continuous contact equipment. In the plate columns, the tall vertical vessel is separated into different stages by means of the horizontal plates which allow the intimate contact of the gas and liquid streams or two immiscible liquid streams. The streams are in contact only on the plates and after mass transfer, they are separated and led to the next stage as distinct phases. The streams thus undergo concentration changes intermittently in discrete quantities only over the plates. In packed columns, on the other hand, streams are in contact at all points inside the vessel and they undergo concentration change continuously. A wide variety of stage contact and continuous contact equipment are in operation and they are discussed in detail when specific operations are considered in Chapters 4 through 11. Table 1.1 gives a list of different separation operations, their major industrial applications and important equipment for carrying out these operations.

Gas–liquid Contact Operations

In *gas absorption*, components of a gas mixture are separated by absorbing in liquid solvents. The absorption operation makes use of the difference in the solubility of the components in the liquid. The components with greater solubilities get dissolved in the solvent in preference to the others, thereby achieving the separation. Gas absorption is a typical gas–liquid contact operation which can be carried out as a multistage continuous operation in plate columns or continuous contact operation in packed columns. Chapter 4 discusses the gas absorption in detail with an elaborate account of the gas–liquid contact equipment which are also applicable for the other gas–liquid contact operations. *Stripping or*

Table 1.1: Mass transfer operations and their applications

Operation	Phases in Contact	Major Equipment	Applications
Gas Absorption	Gas–liquid	Plate columns, packed columns, venturi scrubber, spray towers, bubble columns, centrifugal absorbers	Separation of gases, removal of pollutants and impurities from gases, recovery of valuable chemicals.
Stripping	Gas–liquid	Plate columns, packed columns, spray towers, bubble columns, centrifugal contactors	Regeneration of absorption solvent, recovery of volatile components from oils
Distillation (Fractionation)	Vapour–liquid	Plate columns, packed columns	Petroleum refining, separation of alcohol water solution into components, liquefied air into oxygen and nitrogen, etc.
Humidification/ dehumidification	Gas–liquid	Spray chambers, packed columns, cooling towers	Liquid cooling, gas cooling, air conditioning, solvent recovery, gas drying, water desalination
Extraction	Liquid–liquid	Mixer-settler assemblies, spray, packed and plate columns, rotary-impeller columns, pulse columns, rotating-disk contactors, centrifugal contactors	Separation of close boiling liquids, azeotropes, liquids of poor relative volatility, high boiling mixtures, heat sensitive materials, pharmaceuticals, removal of colour.
Leaching	Solid–liquid	Bollmann extractor, diffuser, extraction battery, Kennedy extractor, rotocell, Pachuca tank, Bonnoto extractor, Hildebrandt extractor	Metallurgical industries, food, pharmaceutical and biological industries, oil extraction from seeds, extraction of sugar from sugar beets, tannin extraction, etc.
Drying	Solid–gas	Tray, truck, agitated pan, rotating batch, vacuum, freeze, turbo, rotary, tunnel, flash, conveyor, fluidized bed and spray dryer	Drying of paper, salt, chemicals, timber, pharmaceutical products, fertilizers, soap, detergents, milk, sugar, etc.
Adsorption	Solid–gas	Fixed bed, moving bed (hypersorber), combined fluidised bed-moving bed adsorber.	Dehumidification of gases, odour removal from industrial gases, pollution control, solvent recovery, separation of nitrogen from air, separation of hydrogen from synthetic gases, control of automobile emissions
Adsorption	Solid–liquid	Agitated vessels, moving bed, (hypersorber), fixed bed, simulated moving bed adsorber	Removal of moisture from gasoline, organic solvents etc., removal of sulphur compounds from organic solutions, removal of organic components from drinking water, decolourisation of petroleum products, sugar solutions, syrups, vegetable oils, etc. removal of objectionable taste and odour, process effluent treatment, recovery of vitamins.
Crystallisation	Solid–liquid	Agitated batch, Swenson-Walker, Oslo evaporative crystalliser, forced circulation evaporator, draft tube-baffle crystallisers	Pharmaceutical and fine chemicals industries, agrochemical industries, cosmetics industries, food industries, etc. desalination of sea water.

desorption is the opposite of absorption; while in absorption, the mass transfer is from the gas to the liquid, in stripping, the transfer is from the liquid to the gas. Ammonia can be absorbed from the ammonia air mixture using water as the solvent; the aqueous ammonia solution can be stripped off the ammonia by a stripping agent such as a hot gas or superheated steam.

Distillation is the most widely used method of separating components of a liquid mixture; its acceptability being attributed to the fact that it is a direct separation technique that does not require an external agent for effecting separation. What is achieved by introducing a solvent or a separating agent in other operations, is achieved in distillation, by the application of heat. When a liquid mixture is boiled, the resulting vapour and liquid will have different compositions, and these compositions are different from the composition of the original feed as well. This difference in the composition of the vapour and liquid phases depends on the volatilities of the constituents of the mixture. In *fractionation*, the vapour produced is continuously enriched in the more volatile component by contacting with a portion of the liquid, called *reflux*, which is obtained by the condensation of the vapour in an external condenser. Similarly, the liquid produced is stripped of the more volatile component by bringing it in contact with the vapours produced by boiling the liquid in an external reboiler. Ultimately, the fractionation columns yield a distillate product containing mostly the more volatile components, and a bottom product containing mostly the less volatile or the high-boiling components. Distillation is a vapour-liquid contact operation where both the vapour and the liquid are produced from the same feed stream. A thorough knowledge of the vapour-liquid equilibrium (VLE) is required for the design and analysis of the distillation processes and equipment. A detailed discussion of VLE is highly warranted and is included in Chapter 5 which contains an exhaustive coverage of distillation theory, design and applications.

Humidification and *dehumidification* operations are also gas–liquid contact operations, the gas is air and the liquid is pure water, in majority of practical applications. In humidification, the gas gets humidified by receiving the vapours of the liquid with which it is contacted. Since the liquid phase consists of a single component, the mass transfer is restricted to the gas phase; however, the rate of transfer is influenced not only by the mass transfer, but by the heat transfer as well. The concentration difference in the gas phase alone cannot represent the driving force in such a process which is governed by the combined heat and mass transfer mechanisms. Enthalpy difference between the bulk gas and the interface between the gas and the liquid serves as the driving force. In dehumidification, the gas phase from which the vapours are to be removed, is contacted with the liquid phase of the vapour; the vapours get condensed and transferred to the liquid. In humidification, the mass transfer is from the liquid to the gas, whereas in dehumidification, the transfer is in the reverse direction. Chapter 6 covers these operations in detail preceded by a detailed study of the psychrometry, an essential prerequisite for a better understanding of these operations.

Liquid–Liquid Contact Operation

If materials distribute between two immiscible liquid phases in different proportions, liquid solutions consisting of these materials can be separated by *extraction*. Chapter 7 deals with liquid–liquid extraction in detail. Extraction is a liquid–liquid contact operation and its importance as an industrial separation is second only to distillation. As an example of the liquid extraction, we can consider the separation of an aqueous solution of acetic acid by contacting with a solvent such as ethyl acetate with which water is only partially miscible. The preferential distribution of acetic acid between the aqueous and acetate phases results in the separation of the original mixture. In the majority of extraction operations, three components are present in both the phases, and therefore, the ternary liquid–liquid equilibrium forms the thermodynamic basis for the design and analysis of extraction operations. Extraction operations are carried out in equipment similar in construction to the gas–liquid contact equipment. Thus plate columns and packed columns are common in extraction as well, though some specialized equipment are also in use.

Transfer from or to Solids

Operations such as leaching, adsorption, crystallisation, ion exchange, drying, etc. fall under this category. *Leaching* is a solid–liquid contact operation in which the transfer of solutes occurs from the solid phase to the liquid phase, as in the recovery of the oil from the oil-cakes using an organic solvent, or in the extraction of gold from gold ores using the cyanide solution. Since solids are available in different sizes and shapes, the equipment handling solids such as the leaching equipment are in use in a wide variety of designs, which are discussed in detail in Chapter 8. This is true for drying operations discussed in Chapter 9 also. *Drying* is the removal of moisture from the solids by evaporation. In many industries, drying operation is one of the last processes employed just before packaging and dispatch of the products. When moisture is evaporated into a gas stream that is in contact with the solid, the drying becomes a gas–solid contact operation. In general, the drying process is influenced by the simultaneous transfer of heat and mass.

Adsorption involves transfer of solutes onto the surfaces of the solids known as adsorbents from a liquid phase or a gas phase and therefore, can be considered as solid–fluid contact operations. The equilibria in the adsorption operation are popularly known as the *adsorption isotherms*, for representing which theoretical as well as empirical models are available. Adsorption isotherm, adsorption systems, different methods of adsorption operation and equipment are discussed in Chapter 10. *Crystallisation* from solutions is a mass transfer operation in which the solute is transferred from the solution onto solids. *Nucleation and crystal growth* are two distinct processes which govern the rate of crystallisation. The nucleation denotes the birth of crystals and the growth results due to mass transfer. Crystallisation is an important separation technique since it yields relatively very pure products with minimum energy consumption. Chapter 11 deals with crystallisation from solutions.

1.4 MEMBRANE SEPARATIONS

Membrane separations which were considered as unconventional separation techniques, have gained wide acceptability in recent years. Considered to be very unreliable, unselective, slow and expensive operation in the past, membrane separation techniques have now undergone significant transformation. They find wide applications now in industries such as chemical, petrochemical, pharmaceutical, paper, textile, food and beverage, environmental and electronic industries, apart from their application in the medical field as in artificial kidney for haemodialysis and blood-oxygenators. This dramatic development is due to the concerted efforts of physical chemists, material scientists and chemical engineers in developing and adapting membrane materials with high *selectivity and permeability*, in the fabrication methods for high-flux asymmetric or composite membranes, and in the construction of membrane modules capable of accommodating large membrane surface into small volume.

Based on the materials, the membranes can be broadly classified as organic and inorganic membranes. Organic membranes include membranes made from natural or synthetic polymers and the inorganic membranes include ceramic, metal, carbon and zeolite membranes. Membrane separations offer several advantages over the conventional separation techniques. They are ideally suited for the separation of the heat-sensitive materials, as the separation is generally carried out at moderate temperatures. Equipment is modular, compact, require less capital investment, and is less energy intensive than the usual separation operations. The separation is purely physical and requires no foreign substances as separating agents.

The major membrane separation operations are microfiltration, ultrafiltration, nanofiltration, reverse osmosis, dialysis, electrodialysis, pervaporation and gas permeation. These operations involve transfer between two phases, liquid or gas, the direct contact of the phases being prevented by separating them by semipermeable barrier called membrane. Separation of the constituents is achieved by taking advantage of their differences in the rates of movement through the membranes, which in turn depend on the molecular size, shape, electric charge and/or the sorption characteristics of the materials. As such, different driving forces are used to facilitate transport of substances through the membrane. Examples are the applications of high pressure, the maintenance of a concentration gradient on both sides of the membrane and the introduction of an electric potential. The microfiltration, ultrafiltration, nanofiltration, reverse osmosis, pervaporation and the gas permeation are pressure–driven operations, dialysis and osmosis are concentration–driven operations and electrodialysis is an operation involving electric potential gradient across the membrane.

Microfiltration, ultrafiltration, nanofiltration and reverse osmosis are generally referred to as the membrane filtration processes since all rely on the size exclusion principle for separation. The size range of particles retained by the membrane filtration techniques are shown in Fig. 1.1. Table 1.2 gives the classification of membrane separation techniques based on the size range of particles retained. The different driving forces used for effecting separation are also listed in the table.

The membrane separations are discussed in Chapter 12 with emphasis on the basic principles behind the separations, the membranes used, their characteristics and the major industrial applications.

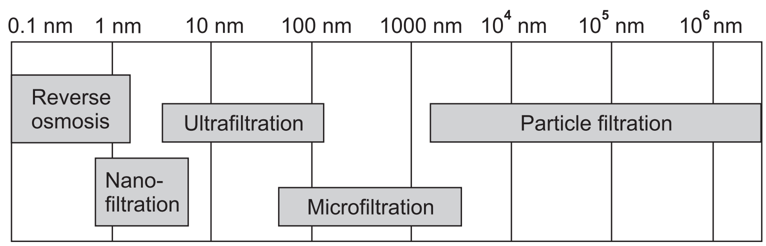

Fig. 1.1: Range of particle sizes separated by membrane filtration techniques

Table 1.2: Classification of membrane processes based on size range of particles separated and driving force of separation

Process	Driving force	Size range of particles retained
Microfiltration	Pressure gradient	> 50 nm
Ultrafiltration	Pressure gradient	> 3 nm
Nanofiltration	Pressure gradient	> 1 nm
Reverse Osmosis	Pressure gradient	> 0.1 nm
Electrodialysis	Electric field gradient	> 5 nm
Dialysis	Concentration gradient	> 5 nm
Pervaporation	Pressure gradient	> 1 nm
Gas permeation	Pressure gradient	> 1 nm