SEPARATION PROCESS PRINCIPLES

Part 1

Fundamental Concepts

In the first five chapters, fundamental concepts are presented that apply to processes for the separation of chemical mixtures. Emphasis is on industrial processes, but many of the concepts apply to small-scale separations as well. In Chapter 1, the role of separation operations in chemical processes is illustrated. Five general separation techniques are enumerated, each being driven by energy and/or the addition of mass to alter properties important to separation. For each technique, equipment types are briefly described. Various ways of specifying separation operations are discussed, including component recovery and product purity, and the use of these specifications in making mass balances is illustrated. The selection of feasible equipment for a particular separation problem is briefly covered.

The degree to which a separation can be achieved depends on differing rates of mass transfer of the individual components of the mixture, with limits dictated by thermodynamic phase equilibrium. Chapter 2 is a review of thermodynamics applicable to separation operations, particularly those involving fluid phases. Chapter 3 is an extensive discussion of mass transfer of individual components in binary mixtures under stagnant, laminar-flow, and turbulent-flow conditions, by analogy to conductive and convective heat transfer wherever possible.

Many separation operations are designed on the basis of the limit of attaining thermodynamic phase equilibrium. Chapter 4 covers mass-balance calculations for phase equilibrium in a single contacting stage that may include vapor, liquid, and/or solid phases. Often the degree of separation can be greatly improved by using multiple contacting stages, with each stage approaching equilibrium, in a cascade and/or by using a sequence of two or more different types of separation methods in a hybrid system. These are of great importance to industrial separation processes and are briefly described in Chapter 5, before proceeding to subsequent chapters in this book, each focusing on detailed descriptions and calculations for a particular separation operation. Included in Chapter 5 is a detailed discussion of degrees-of-freedom analysis, which determines the number of allowable specifications for cascades and hybrid systems. This type of analysis is used throughout this book, and is widely used in process simulators such as ASPEN PLUS, CHEMCAD, and HYSYS.

Chapter 1

Separation Methods

The separation of chemical mixtures into their constituents has been practiced, as an art, for millennia. Early civilizations developed techniques to (1) extract metals from ores, perfumes from flowers, dyes from plants, and potash from the ashes of burnt plants, (2) evaporate sea water to obtain salt, (3) refine rock asphalt, and (4) distill liquors. The human body could not function for long if it had no kidney, a membrane that selectively removes water and waste products of metabolism from blood.

Separations, including enrichment, concentration, purification, refining, and isolation, are important to chemists and chemical engineers. The former use *analytical separation methods,* such as chromatography, to determine compositions of complex mixtures quantitatively. Chemists also use small-scale *preparative separation techniques,* often similar to analytical separation methods, to recover and purify chemicals. Chemical engineers are more concerned with the manufacture of chemicals using economical, large-scale separation methods, which may differ considerably from laboratory techniques. For example, in a laboratory, chemists separate and analyze light-hydrocarbon mixtures by gas–liquid chromatography, while in a large manufacturing plant a chemical engineer uses distillation to separate the same hydrocarbon mixtures.

This book presents the principles of large-scale component separation operations, with emphasis on methods applied by chemical engineers to produce useful chemical products economically. Included are treatments of classical separation methods, such as distillation, absorption, liquid–liquid extraction, leaching, drying, and crystallization, as well as newer methods, such as adsorption and membrane separation. Separation operations for gas, liquid, and solid phases are covered. Using the principles of separation operations, chemical engineers can successfully develop, design, and operate industrial processes.

Increasingly, chemical engineers are being called upon to deal with industrial separation problems on a smaller scale, e.g., manufacture of specialty chemicals by batch processing, recovery of biological solutes, crystal growth of semiconductors, recovery of valuable chemicals from wastes, and the development of products (such as the artificial kidney) that involve the separation of chemical mixtures. Many of the separation principles for these smaller-scale problems are covered in this book and illustrated in examples and homework exercises.

1.0 INSTRUCTIONAL OBJECTIVES

After completing this chapter, you should be able to:

- Explain the role of separation operations in an industrial chemical process.
- Explain what constitutes the separation of a chemical mixture and enumerate the five general separation techniques.
- Explain the use of an energy-separating agent (ESA) and/or a mass-separating agent (MSA) in a separation operation.
- Explain how separations are made by phase creation or phase addition and list the many separation operations that use these two techniques.
- Explain how separations are made by introducing selective barriers and list several separation operations that utilize membranes.
- Explain how separations are made by introducing solid agents and list the three major separation operations that utilize this technique.
- Explain the use of external fields to separate chemical mixtures.
- Calculate component material balances around a separation operation based on specifications of component recovery (split ratios or split fractions) and/or product purity.

- Use the concepts of key components and separation power to measure the degree of separation between two key components.
- Make a selection of feasible separation operations based on factors involving the feed, products, property differences among chemical components, and characteristics of different separation operations.

1.1 INDUSTRIAL CHEMICAL PROCESSES

The chemical industry manufactures products that differ in chemical content from process feeds, which can be (1) naturally occurring raw materials, (2) plant or animal matter, (3) chemical intermediates, (4) chemicals of commerce, or (5) waste products. Especially common are oil refineries [1], which, as indicated in Figure 1.1, produce a variety of useful products. The relative amounts of these products produced from, say, 150,000 bbl/day of crude oil depend on the constituents of the crude oil and the types of refinery processes. Processes include distillation to separate crude oil into various boiling-point fractions or cuts, alkylation to combine small hydrocarbon molecules into larger molecules, catalytic reforming to change the structure of medium-size hydrocarbon molecules, fluid catalytic cracking to break apart large hydrocarbon molecules, hydrocracking to break apart even larger molecules, and other processes to convert the crude-oil residue to coke and lighter fractions.

A chemical process is conducted in either a *batchwise, continuous,* or *semicontinuous* manner. The operations may be classified as *key operations,* which are unique to chemical engineering because they involve changes in chemical composition, or *auxiliary operations,* which are necessary to the success of the key operations but may be designed by mechanical engineers as well because the auxiliary operations do not involve changes in chemical composition. The key operations are (1) chemical reactions and (2) separation of chemical mixtures. The auxiliary operations include phase separation, heat addition or removal (to change temperature or phase condition), shaft-work addition or removal (to change pressure), mixing or dividing of streams or batches of material, solids agglomeration, size reduction of solids, and separation of solids by size.

The key operations for the separation of chemical mixtures into new mixtures and/or essentially pure components are of central importance. Most of the equipment in the average chemical plant is there to purify raw materials, intermediates, and products by the separation techniques described briefly in this chapter and discussed in detail in subsequent chapters.

Block-flow diagrams are used to represent chemical processes. They indicate, by square or rectangular blocks, chemical reaction and separation steps and, by connecting lines, the major process streams that flow from one processing step to another. Considerably more detail is shown in *process-flow diagrams,* which also include auxiliary operations and utilize symbols that depict more realistically the type of equipment employed. The block-flow diagram of a continuous process for manufacturing hydrogen chloride gas from evaporated chlorine and electrolytic hydrogen [2] is shown in Figure 1.2. The heart of the process is a chemical reactor, where the high-temperature gas-phase combustion reaction, $H_2 + Cl_2 \rightarrow 2HCl$, occurs. The only auxiliary equipment required consists of pumps and compressors to deliver feeds to the reactor and product to storage, and a heat exchanger to cool the product. For this process, no separation operations are necessary because complete conversion of chlorine occurs in the reactor. A slight excess of hydrogen is used, and the product, consisting of 99% HCl and small amounts of H_2, N_2, H_2O, CO, and CO_2, requires no purification. Such simple commercial processes that require no separation of chemical species are very rare.

Some industrial chemical processes involve no chemical reactions, but only operations for separating chemicals and phases, together with auxiliary equipment. A block-flow diagram for such a process is shown in Figure 1.3, where wet natural gas is continuously separated into six light-paraffin

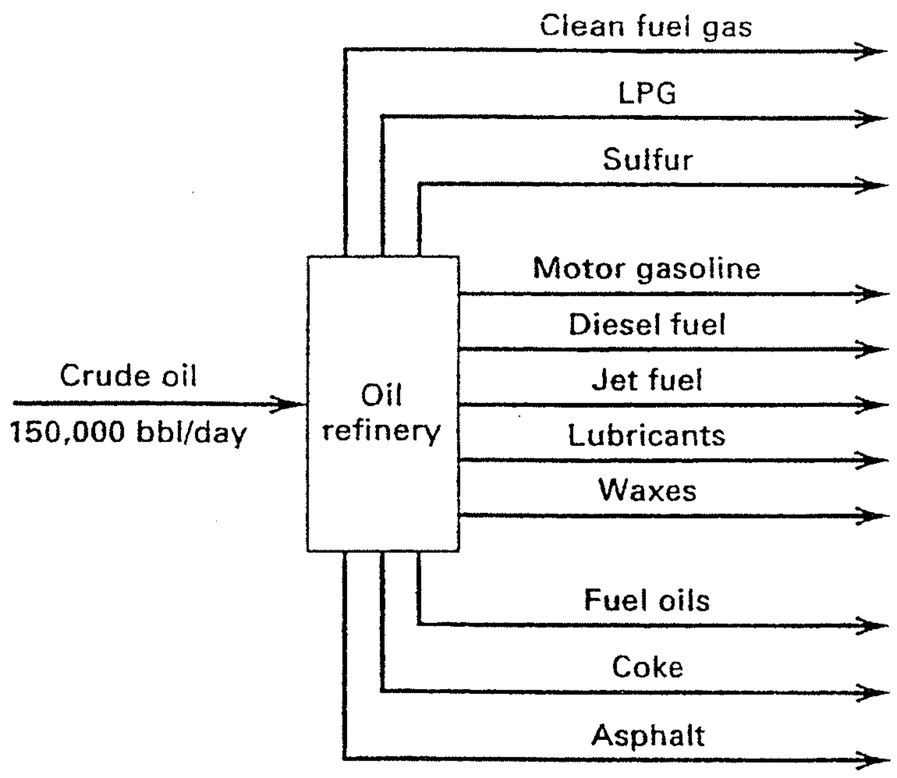


Figure 1.1 Refinery for converting crude oil into a variety of marketable products.

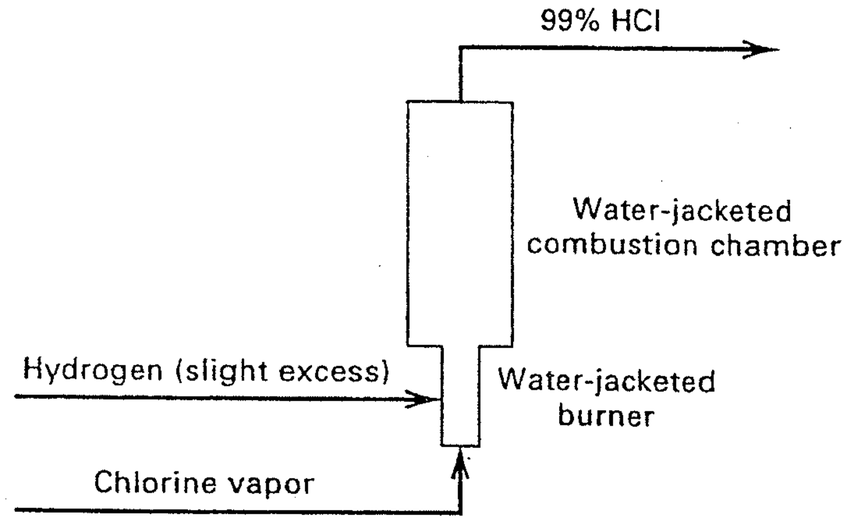


Figure 1.2 Synthetic process for anhydrous HCl production.

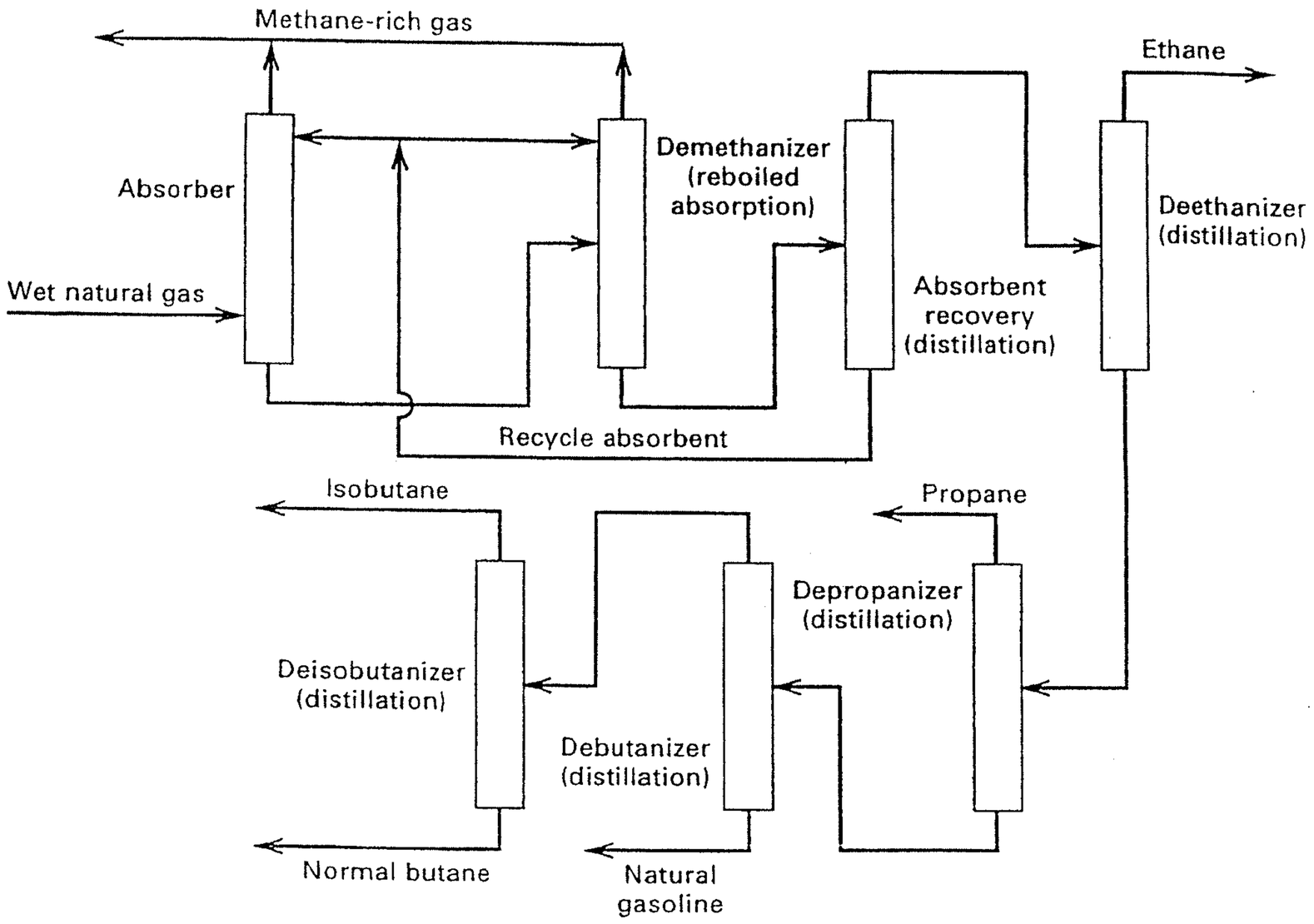


Figure 1.3 Process for recovery of light hydrocarbons from casinghead gas.

hydrocarbon components and mixtures by a train of separators [3]. A train or sequence of separators is used because it is often impossible to produce more than two products with a single piece of separation equipment.

Many industrial chemical processes involve at least one chemical reactor accompanied by one or more separation trains. An example is the continuous, direct hydration of ethylene to ethyl alcohol [4]. The heart of the process is a reactor packed with solid-catalyst particles, operating at 572 K and 6.72 MPa (570°F and 975 psia), in which the hydration reaction, $C_2H_4 + H_2O \rightarrow C_2H_5OH$, takes place. Because of thermodynamic equilibrium limitations, the conversion of ethylene is only 5% per pass through the reactor. The unreacted ethylene is recovered in a separation step and recycled back to the reactor. By this recycle technique, which is common to many industrial processes, essentially complete conversion of the ethylene fed to the process is achieved. If pure ethylene were available as a feedstock and no side reactions occurred, the relatively simple process in Figure 1.4 could be constructed, in which two by-products (light ends and waste water) are also produced. This process uses a reactor, a partial condenser for ethylene recovery, and distillation to produce aqueous ethyl alcohol of near-azeotropic composition (93 wt%). Unfortunately, a number of factors frequently combine to increase the complexity of the process, particularly with respect to separation-equipment requirements. These factors include impurities in the ethylene feed, and side reactions involving both ethylene and feed impurities such as propylene. Consequently, the separation system must also deal with diethyl ether, isopropyl alcohol, acetaldehyde, and other chemicals. The resulting industrial process, shown in Figure 1.5, is much more complicated. After the hydration reaction, a partial condenser and high-pressure water absorber recover unreacted ethylene for recycling. The pressure of the liquid from the bottom of the absorber is reduced, causing partial vaporization. Vapor is separated from the

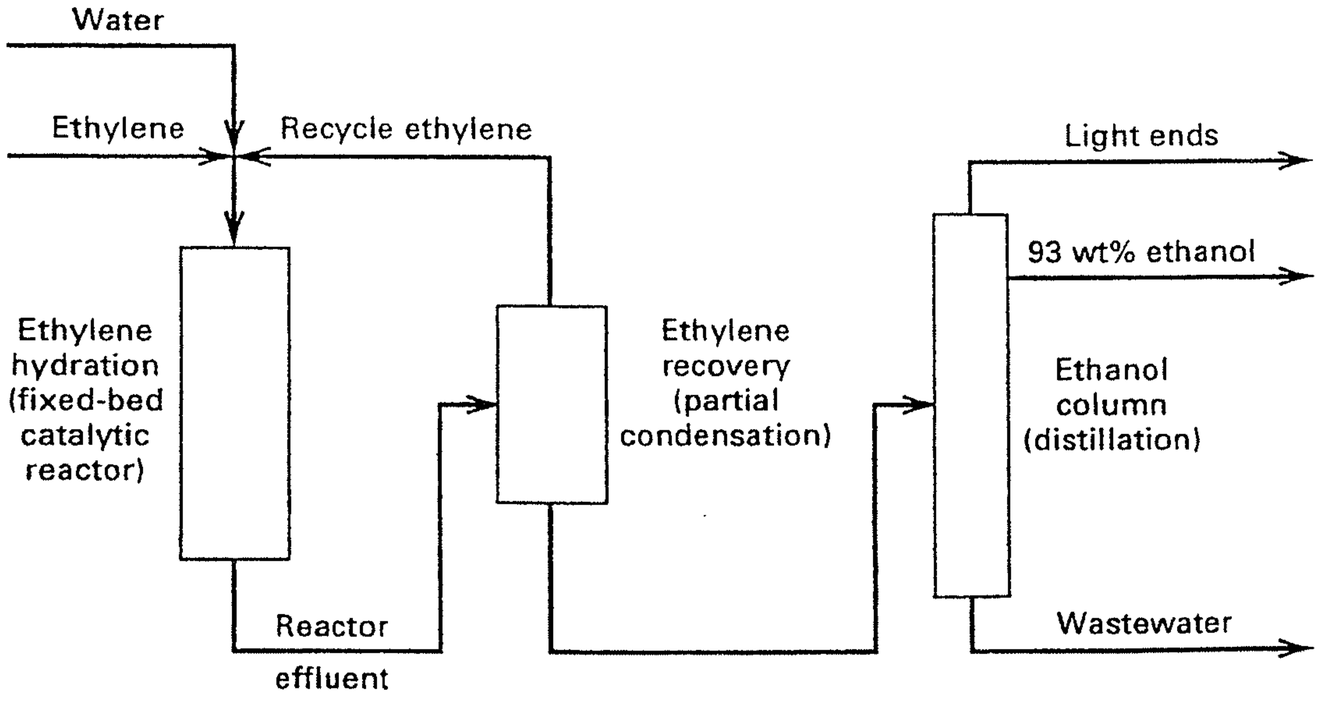


Figure 1.4 Hypothetical process for hydration of ethylene to ethanol.

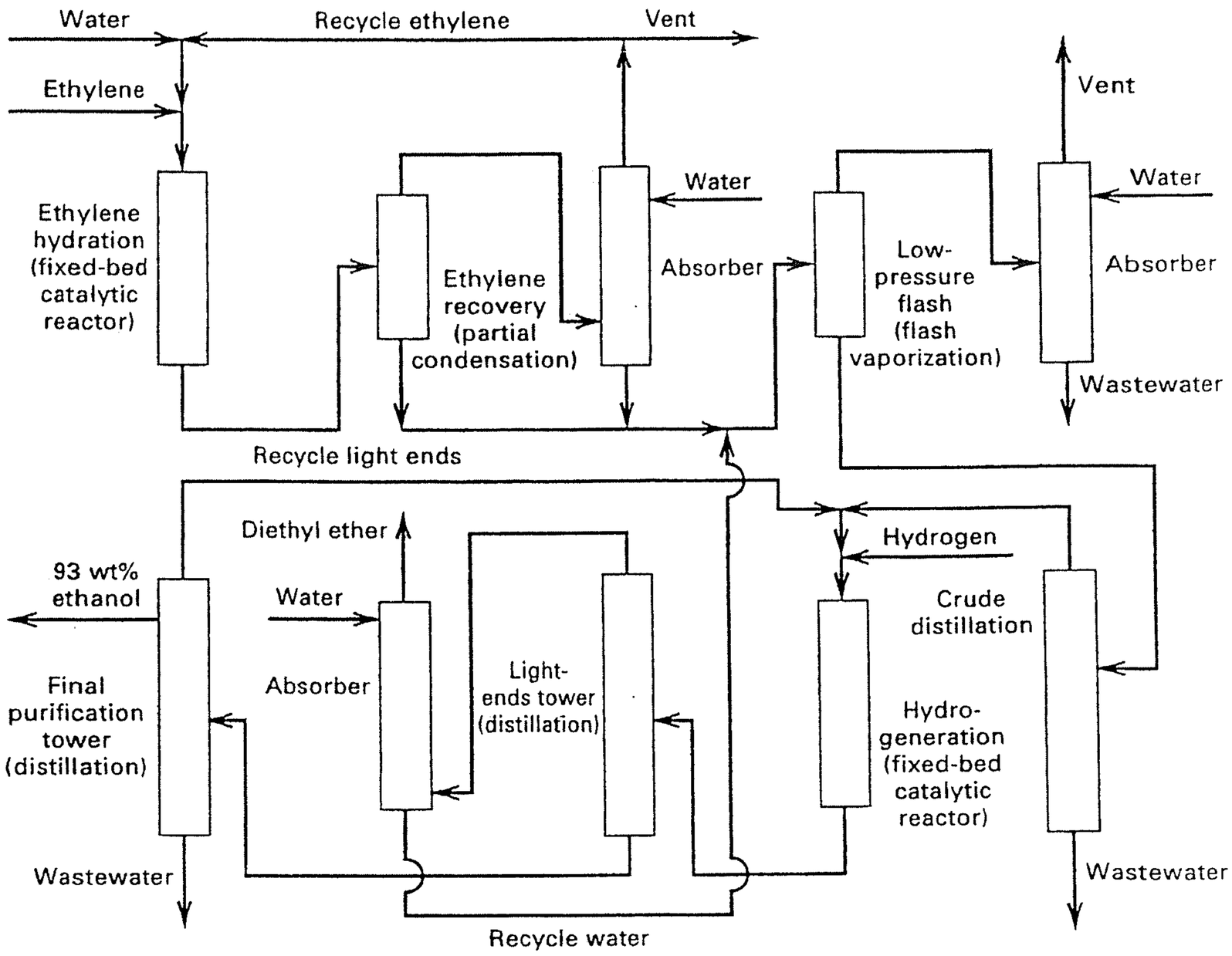


Figure 1.5 Industrial process for hydration of ethylene to ethanol.

remaining liquid in the low-pressure flash drum. Vapor from the low-pressure flash is scrubbed with water in an absorber to remove alcohol and prevent its loss to the vent gas. Crude, concentrated ethanol containing diethyl ether and acetaldehyde is distilled overhead in the crude-distillation (stripper) column and then catalytically hydrogenated in the vapor phase to convert acetaldehyde to ethanol. Diethyl ether is removed by distillation in the light-ends tower and scrubbed with water in an absorption tower. The final product is prepared by distillation in the final-purification tower, where 93 wt% aqueous ethanol product is withdrawn several trays below the top tray, light ends are concentrated in the so-called pasteurization-tray section above the product-withdrawal tray and recycled to the catalytic-hydrogenation reactor, and wastewater is removed from the bottom of the tower. Besides the separation equipment shown, additional separation steps may be necessary to concentrate the ethylene feed to the process and remove impurities that poison the catalysts. In the development of a new process from the laboratory stage through the pilot-plant stage, experience shows that more separation steps than originally anticipated are usually needed.

The above examples serve to illustrate the importance of separation operations in industrial chemical processes. Such operations are employed not only to separate a feed mixture into other mixtures and relatively pure components, to recover solvents for recycle, and to remove wastes, but also, when used in conjunction with chemical reactors, to purify reactor feeds, recover reactants from reactor effluents for recycle, recover by-products, and recover and purify products to meet required specifications. Sometimes a separation operation, such as absorption of SO_2 by limestone slurry, may be accompanied by a chemical reaction that serves to facilitate the separation. In this book, emphasis is on separation operations that do not rely on concurrent chemical reactions; however, reactive distillation is discussed in Chapter 11.

Chemical engineers also design products. A significant product that involves the separation of chemicals is the espresso machine for making a cup of coffee that is superior to that made in a filter-drip machine. The goal in coffee making is to leach from the coffee beans the best oils, leaving behind ingredients responsible for acidity and bitterness in the cup of coffee. The espresso machine accomplishes this by conducting the leaching operation rapidly in 20–30 seconds with water at high temperature and pressure. If the operation is carefully controlled, the resulting cup of espresso, if immediately consumed, has: (1) a topping of creamy foam that traps the extracted chemicals, (2) a fullness of body due to emulsification, and (3) a richness of aroma. Typically, 25% of the coffee bean is extracted and the espresso contains less caffeine than filtered coffee. Cussler and Moggridge [13] and Seider, Seader, and Lewin [14] discuss many other examples of products designed by chemical engineers, some of which involve the separation of chemicals.

1.2 MECHANISM OF SEPARATION

Mixing of chemicals is a spontaneous, natural process that is accompanied by an increase in entropy or randomness. The inverse process, the separation of that mixture into its

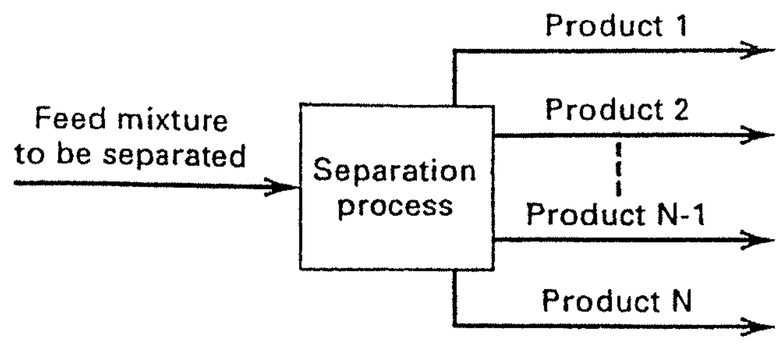


Figure 1.6 General separation process.

constituent chemical species, is not a spontaneous process; it requires an expenditure of energy. A mixture to be separated usually originates as a single, homogeneous phase (solid, liquid, or gas). If it exists as two or more immiscible phases, it is often best to first use a mechanical means based on gravity, centrifugal force, pressure reduction, or an electric and/or magnetic field to separate the phases. Then, appropriate separation techniques are applied to each phase.

A schematic diagram of a general separation process is shown in Figure 1.6. The feed mixture can be vapor, liquid, or solid, while the two or more products may differ in composition from each other and the feed, and may differ in phase state from each other and/or from the feed. The separation is accomplished by forcing the different chemical species in the feed into different spatial locations by any of five general separation techniques, or combinations thereof, as shown in Figure 1.7. The most common industrial technique, Figure 1.7a, involves the creation of a second phase (vapor, liquid, or solid) that is immiscible with the feed phase. The creation is accomplished by energy (heat and/or shaft-work) transfer to or from the process or by pressure reduction. A second technique, Figure 1.7b, is to introduce the second phase into the system in the form of a solvent that selectively dissolves some of the species in the feed. Less common, but of growing importance, is the use of a barrier, Figure 1.7c, which restricts and/or enhances the movement of certain chemical species with respect to other species. Also of growing importance are techniques that involve the addition of solid particles, Figure 1.7d, which act directly or as inert carriers for other substances so as to cause separation. Finally, external fields, Figure 1.7e, of various types are sometimes applied for specialized separations.

For all the techniques of Figure 1.7, separations are achieved by enhancing the rate of mass transfer by diffusion of certain species relative to mass transfer of all species by bulk movement within a particular phase. The driving force and direction of mass transfer by diffusion is governed by thermodynamics, with the usual limitations of equilibrium. Thus, both transport and thermodynamic considerations are crucial in separation operations. The rate of separation is governed by *mass transfer,* while the extent of separation is limited by *thermodynamic equilibrium.* These two topics are treated in Chapters 2, 3, and 4. Fluid mechanics and heat transfer also play important roles, and applicable principles are included in appropriate chapters, particularly with respect to phase separation, phase change, pressure drop, temperature change, and entrainment.

The extent of separation achieved between or among the product phases for each of the chemical species present in the feed depends on the exploitation of differences in molecular, thermodynamic, and transport properties of the

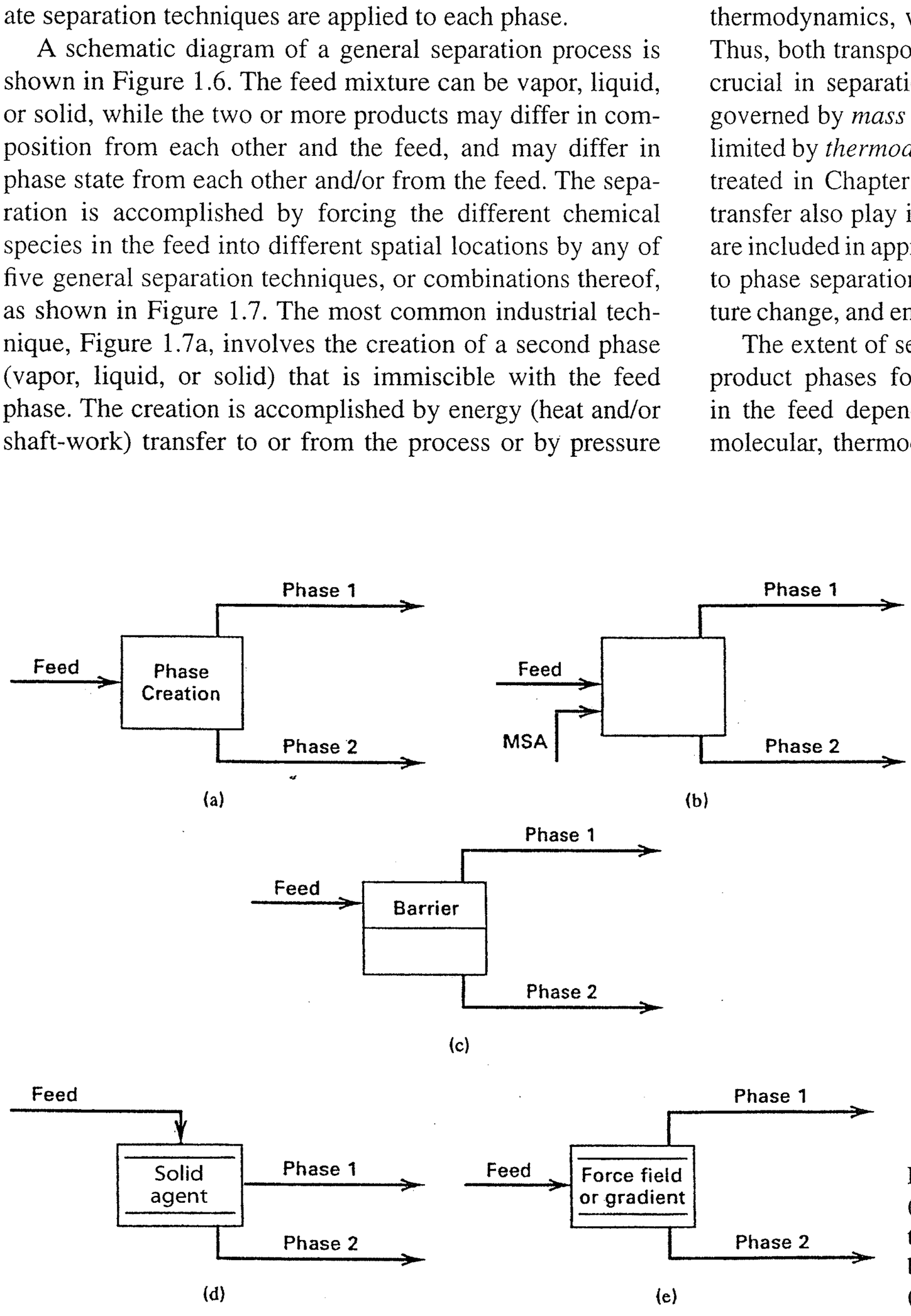


Figure 1.7 General separation techniques: (a) separation by phase creation; (b) separation by phase addition; (c) separation by barrier; (d) separation by solid agent; (e) separation by force field or gradient.

species in the different phases present. Some properties of importance are:

1. Molecular properties

Molecular weight	Polarizability
van der Waals volume	Dielectric constant
van der Waals area	Electric charge
Molecular shape (acentric factor)	Radius of gyration
Dipole moment	

2. Thermodynamic and transport properties

Vapor pressure	Adsorptivity
Solubility	Diffusivity

Values of these properties for many substances are available in handbooks, specialized reference books, and journals. Many of these properties can also be estimated using computer-aided, process-simulation programs. When they are not available, these properties must be estimated or determined experimentally if a successful application of the appropriate separation operation(s) is to be achieved.

1.3 SEPARATION BY PHASE ADDITION OR CREATION

If the feed mixture is a homogeneous, single-phase solution (gas, liquid, or solid), a second immiscible phase must often be developed or added before separation of chemical species can be achieved. This second phase is created by an *energy-separating agent* (ESA) and/or added as a *mass-separating agent* (MSA). Application of an ESA involves heat transfer and/or transfer of shaft work to or from the mixture to be separated. Alternatively, vapor may be created from a liquid phase by reducing the pressure. An MSA may be partially immiscible with one or more of the species in the mixture. In this case, the MSA frequently remains the constituent of highest concentration in the added phase. Alternatively, the MSA may be completely miscible with a liquid mixture to be separated, but may selectively alter the partitioning of species between liquid and vapor phases. This facilitates a more complete separation when used in conjunction with an ESA, as in extractive distillation.

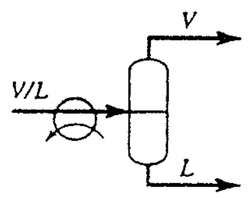
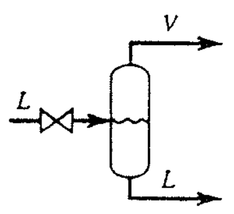
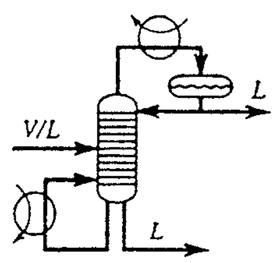
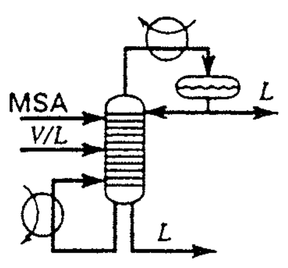
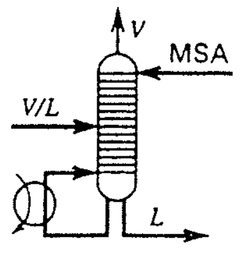
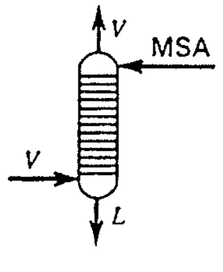
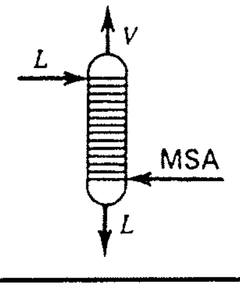
Although separations that use an ESA are generally preferred, an MSA can make possible a separation that is not feasible with an ESA. Disadvantages of the use of an MSA are: (1) need for an additional separator to recover the MSA for recycle, (2) need for MSA makeup, (3) possible contamination of the product with the MSA, and (4) more difficult design procedures.

When two immiscible fluid phases are contacted, intimate mixing of the two phases is important in enhancing mass-transfer rates so that the thermodynamic-maximum degree-of-partitioning of species can be approached more rapidly. After phase contact, the separation operation is completed by employing gravity and/or an enhanced technique, such as centrifugal force, to disengage the two phases. Table 1.1 is a compilation of the more common industrial-separation operations based on interphase mass transfer between two phases, one of which is created by an ESA or added as an MSA. Graphic symbols that are suitable for process-flow diagrams are included in the table. Vapor and liquid and/or solid phases are designated by *V*, *L*, and *S*, respectively. Design procedures have become fairly routine for the operations prefixed by an asterisk (*) in the first column of Table 1.1. Such procedures have been incorporated as mathematical models into widely used commercial computer-aided, chemical-process simulation and design (CAPD) programs for continuous, steady-state operations and are treated in considerable detail in subsequent chapters of this book. Batchwise modes of these operations are also treated in this book when appropriate.

When the feed mixture includes species that differ widely in their tendency to vaporize and condense, *partial condensation* or *partial vaporization,* Separation Operation (1) in Table 1.1 may be adequate to achieve the desired separation or recovery of a particular component. A vapor feed is partially condensed by removing heat, and a liquid feed is partially vaporized by adding heat. Alternatively, partial vaporization can be caused by *flash vaporization,* Operation (2), by reducing the pressure of the feed with a valve. In both of these operations, after partitioning of species by interphase mass transfer has occurred, the resulting vapor phase is enriched with respect to the species that are most volatile (most easily vaporized), while the liquid phase is enriched with respect to the least volatile species. After this single contact, the two phases, which, except near the critical region, are of considerably different density, are separated by gravity.

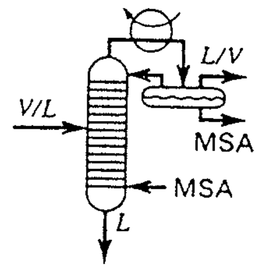
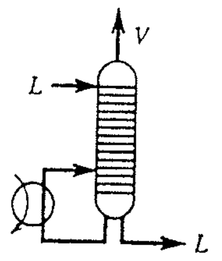
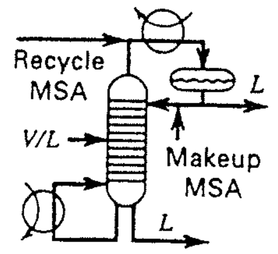
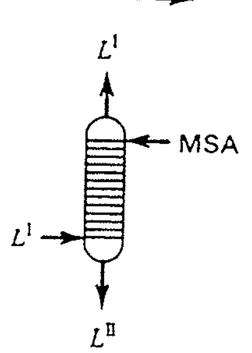
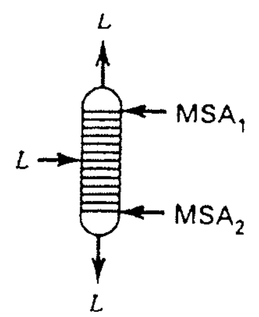
Often, the degree of species separation achieved by a single, partial vaporization or partial condensation step is inadequate because the volatility differences among species in the feed are not sufficiently large. In that case, it may still be possible to achieve a desired separation of the species in the feed mixture, without introducing an MSA, by employing *distillation,* Operation (3) in Table 1.1, the most widely utilized industrial separation method. Distillation involves multiple contacts between countercurrently flowing liquid and vapor phases. Each contact consists of mixing the two phases to promote rapid partitioning of species by mass transfer, followed by phase separation. The contacts are often made on horizontal trays (referred to as *stages*) arranged in a vertical column as shown in the symbol for distillation in Table 1.1. Vapor, while flowing up the column, is increasingly enriched with respect to the more volatile species. Correspondingly, liquid flowing down the column is increasingly enriched with respect to the less-volatile species. Feed to the distillation column enters on a tray somewhere between the top and bottom trays, and often near the middle of the column. The portion of the column above the feed entry is called the *enriching* or *rectification section,* and that below is the *stripping section*. Feed vapor starts up the column; feed liquid starts down. Liquid is required for making contacts with vapor above the feed tray, and vapor is required for making contacts with liquid below the feed tray.

Table 1.1 Separation Operations Based on Phase Creation or Addition

Separation Operation	Symbol[a]	Initial or Feed Phase	Created or Added Phase	Separating Agent(s)	Industrial Example[b]
Partial condensation or vaporization* (1)		Vapor and/or liquid	Liquid or vapor	Heat transfer (ESA)	Recovery of H_2 and N_2 from ammonia by partial condensation and high-pressure phase separation (Vol. 2, pp. 494–496)
Flash vaporization* (2)		Liquid	Vapor	Pressure reduction	Recovery of water from sea water (Vol. 24, pp. 343–348)
Distillation* (3)		Vapor and/or liquid	Vapor and liquid	Heat transfer (ESA) and sometimes work transfer	Purification of styrene (Vol. 21, pp. 785–786)
Extractive distillation* (4)		Vapor and/or liquid	Vapor and liquid	Liquid solvent (MSA) and heat transfer (ESA)	Separation of acetone and methanol (Suppl. Vol., pp. 153–155)
Reboiled absorption* (5)		Vapor and/or liquid	Vapor and liquid	Liquid absorbent (MSA) and heat transfer (ESA)	Removal of ethane and lower molecular weight hydrocarbons for LPG production (Vol. 14, pp. 384–385)
Absorption* (6)		Vapor	Liquid	Liquid absorbent (MSA)	Separation of carbon dioxide from combustion products by absorption with aqueous solutions of an ethanolamine (Vol. 4, pp. 730–735)
Stripping* (7)		Liquid	Vapor	Stripping vapor (MSA)	Stream stripping of naphtha, kerosene, and gas oil side cuts from crude distillation unit to remove light ends (Vol. 17, pp. 199–201)

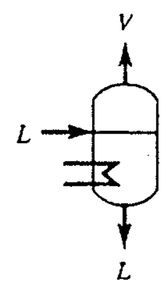
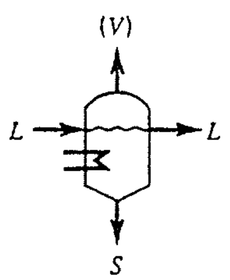
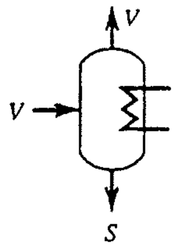
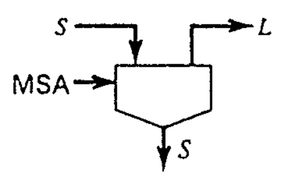
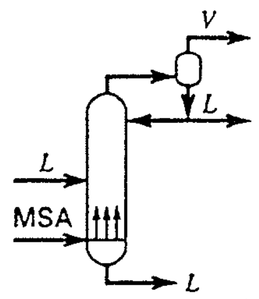
(*Continued*)

Table 1.1 (*Continued*)

Separation Operation	Symbol[a]	Initial or Feed Phase	Created or Added Phase	Separating Agent(s)	Industrial Example[b]
Refluxed stripping (steam distillation)* (8)		Vapor and/or liquid	Vapor and liquid	Stripping vapor (MSA) and heat transfer (ESA)	Separation of products from delayed coking (Vol. 17, pp. 210–215)
Reboiled stripping* (9)		Liquid	Vapor	Heat transfer (ESA)	Recovery of amine absorbent (Vol. 17, pp. 229–232)
Azeotropic distillation* (10)		Vapor and/or liquid	Vapor and liquid	Liquid entrainer (MSA) and heat transfer (ESA)	Separation of acetic acid from water using *n*-butyl acetate as an entrainer to form an azeotrope with water (Vol. 3, pp. 365–368)
Liquid–liquid extraction* (11)		Liquid	Liquid	Liquid solvent (MSA)	Recovery of aromatics (Vol. 9, pp. 707–709)
Liquid–liquid extraction (two-solvent)* (12)		Liquid	Liquid	Two liquid solvents (MSA_1 and MSA_2)	Use of propane and cresylic acid as solvents to separate paraffins from aromatics and naphthenes (Vol. 17, pp. 223–224)
Drying (13)		Liquid and often solid	Vapor	Gas (MSA) and/or heat transfer (ESA)	Removal of water from polyvinylchloride with hot air in a fluid-bed dryer (Vol. 23, pp. 901–904)

(*Continued*)

Table 1.1 (*Continued*)

Separation Operation	Symbol[a]	Initial or Feed Phase	Created or Added Phase	Separating Agent(s)	Industrial Example[b]
Evaporation (14)		Liquid	Vapor	Heat transfer (ESA)	Evaporation of water from a solution of urea and water (Vol. 23, pp. 555–558)
Crystallization (15)		Liquid	Solid (and vapor)	Heat transfer (ESA)	Crystallization of *p*-xylene from a mixture with *m*-xylene (Vol. 24, pp. 718–723)
Desublimation (16)		Vapor	Solid	Heat transfer (ESA)	Recovery of phthalic anhydride from noncondensible gas (Vol. 17, pp. 741–742)
Leaching (liquid–solid extraction) (17)		Solid	Liquid	Liquid solvent	Extraction of sucrose from sugar beets with hot water (Vol. 21, pp. 907–908)
Foam fractionation (18)		Liquid	Gas	Gas bubbles (MSA)	Recovery of detergents from waste solutions (Vol. 10, pp. 544–545)

*Design procedures are fairly well accepted.

[a]Trays are shown for columns, but alternatively packing can be used. Multiple feeds and side streams are often used and may be added to the symbol.

[b]Citations refer to volume and page(s) of *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed., John Wiley and Sons, New York (1978–1984).

Often, vapor from the top of the column is condensed in a condenser by cooling water or a refrigerant to provide contacting liquid, called *reflux*. Similarly, liquid at the bottom of the column passes through a reboiler, where it is heated by condensing steam or some other heating medium to provide contacting vapor, called *boilup*.

When volatility differences between species to be separated are so small as to necessitate more than about 100 trays in a distillation operation, *extractive distillation,* Operation (4), is often considered. Here, an MSA, acting as a solvent, is used to increase volatility differences between selected species of the feed, thereby reducing the number of required trays. Generally, the MSA, which must be completely miscible with the liquid phase throughout the column, is less volatile than any of the species in the feed mixture and is introduced to a stage near the top of the column. Reflux to the top tray is utilized to minimize MSA content in the top product. A subsequent separation operation, usually distillation, is used to recover the MSA for recycling back to the extractive distillation column.

If condensation of vapor leaving the top of a distillation column is not easily accomplished by heat transfer to cooling water or a refrigerant, a liquid MSA called an *absorbent* may be introduced to the top tray in place of reflux. The resulting separation operation is called *reboiled absorption,* (5). If the feed is all vapor and the stripping section of the column is not needed to achieve the desired separation, the operation is referred to as *absorption,* (6). This operation may not require an ESA and is frequently conducted at ambient temperature and high pressure. Constituents of the vapor feed dissolve in the absorbent to varying extents depending on their solubilities. Vaporization of a small fraction of the absorbent also generally occurs.

The inverse of absorption is *stripping,* Operation (7) in Table 1.1. Here, a liquid mixture is separated, generally at elevated temperature and ambient pressure, by contacting liquid feed with a stripping agent. This MSA eliminates the need to reboil the liquid at the bottom of the column, which may be important if the liquid is not thermally stable. If contacting trays are also needed above the feed tray in order to achieve the desired separation, a *refluxed stripper,* (8), may be employed. If the bottoms product from a stripper is thermally stable, it may be reboiled without using an MSA. In that case, the column is called a *reboiled stripper,* (9). Additional separation operations are required to recover, for recycling, MSAs used in absorption and stripping operations.

The formation of minimum-boiling azeotropic mixtures makes *azeotropic distillation,* (10), another useful tool where separation by distillation is not feasible. In the example cited in Table 1.1, the MSA, *n*-butyl acetate, which forms a heterogeneous (i.e., two liquid phases present), minimum-boiling azeotrope with water, is used as an entrainer to facilitate the separation of acetic acid from water. The azeotrope is taken overhead and then condensed and separated into acetate and water layers. The MSA is recirculated, and the distillate water layer and bottoms acetic acid are removed as products.

Liquid–liquid extraction, (11) and (12), using one or two solvents, respectively, is widely used when distillation is impractical, especially when the mixture to be separated is temperature-sensitive and/or more than about 100 distillation stages would be required. When one solvent is used, it selectively dissolves only one or a fraction of the components in the feed mixture. In a two-solvent extraction system, each solvent has its own specific selectivity for dissolving the components of the feed mixture. Thus, if a feed mixture consists of species A and B, solvent C might preferentially dissolve A, while solvent D dissolves B. As with extractive distillation, additional separation operations are generally required to recover, for recycling, solvent from streams leaving the extraction operation.

A variation of liquid–liquid extraction is *supercritical-fluid extraction,* where the extraction temperature and pressure are slightly above the critical point of the solvent. In this region, solute solubility in the supercritical fluid changes drastically with small changes in temperature and pressure. Following extraction, the pressure of the extract can be reduced to release the solvent, which is then recycled. For the processing of foodstuffs, the supercritical fluid is an inert substance such as CO_2, which will not contaminate the product.

Since many chemicals are processed wet but sold as dry solids, one of the more common manufacturing steps is *drying,* (13), which involves removal of a liquid from a solid by vaporization of the liquid. Although the only basic requirement in drying is that the vapor pressure of the liquid to be evaporated be higher than its partial pressure in the gas stream, the design and operation of dryers represents a complex problem in heat transfer, fluid mechanics, and mass transfer. In addition to the effect of such external conditions as temperature, humidity, air flow rate, and degree of solid subdivision on drying rate; the effect of internal conditions of liquid and vapor diffusion, capillary flow, equilibrium moisture content, and heat sensitivity in the solid must be considered. Although drying is a multiphase mass-transfer process, equipment-design procedures differ from those of any of the other processes discussed in this chapter because the thermodynamic concepts of equilibrium are difficult to apply to typical drying situations, where the concentration of vapor in the gas is so far from saturation, and concentration gradients in the solid are such that mass-transfer driving forces are undefined. Also, heat transfer rather than mass transfer may well be the limiting rate process. Therefore, the typical dryer design procedure is for the process engineer to send a few tons of representative, wet sample material for pilot-plant tests by one or two reliable dryer manufacturers and to purchase the equipment that produces a satisfactorily dried product at the lowest cost. The types of commercial dryers are discussed in detail in *Perry's Chemical Engineers' Handbook* [5] and Chapter 18.

Evaporation, Operation (14) in Table 1.1, is generally defined as the transfer of volatile components of a liquid into a gas by volatilization caused by heat transfer. Humidification and evaporation are synonymous in the scientific sense; however, *humidification* or *dehumidification* implies that

one is intentionally adding vapor to or removing vapor from a gas. Major applications of evaporation are humidification, conditioning of air, cooling of water, and the concentration of aqueous solutions.

Crystallization, (15), is carried out in many organic, and almost all inorganic, chemical manufacturing plants where the desired product is a finely divided solid. Since crystallization is essentially a purification step, the conditions in the crystallizer must be such that impurities do not precipitate with the desired product. In *solution crystallization,* the mixture, which includes a solvent, is cooled and/or the solvent is evaporated to cause crystallization. In *melt crystallization,* two or more soluble species, in the absence of a solvent, are separated by partial freezing. A particularly versatile melt crystallization technique is *zone melting* or *refining,* which relies on selective distribution of impurity solutes between a liquid and a solid phase to achieve a separation. Many metals are refined by this technique, which, in its simplest form, involves moving a molten zone slowly through an ingot by moving the heater or drawing the ingot past the heater. The manufacture of single crystals has been a vital development in the semiconductor industry in recent years. Typically single crystals of very high purity silicon are produced worldwide by the Czochralski technique, wherein a single crystal is pulled from a melt. Typical crystal dimensions, after shaping into a uniform rod with diamond grinding machines, are 150-mm diameter × 1-m long, from which wafers of 675-micron thickness are sawed.

Sublimation is the transfer of a substance from the solid to the gaseous state without formation of an intermediate liquid phase, usually at a relatively high vacuum. Major applications have been in the removal of a volatile component from an essentially nonvolatile one. Examples are separation of sulfur from impurities, purification of benzoic acid, and freeze-drying of foods. The reverse process, *desublimation,* (16), is also practiced, for example, in the recovery of phthalic anhydride from gaseous reactor effluent. The most common application of sublimation in everyday life occurs in the use of Dry Ice as a refrigerant for storing ice cream, vegetables, and other perishables. The sublimed gas, unlike water, does not puddle and spoil the frozen materials.

Liquid–solid extraction, often referred to as *leaching,* (17), is widely used in the metallurgical, natural product, and food industries under batch, semicontinuous, or continuous operating conditions. The major problem in leaching is to promote diffusion of the solute out of the solid and into the liquid solvent. The most effective way of doing this is to reduce the dimensions of the solid to the smallest feasible particle size. For large-scale applications, in the metallurgical industries in particular, large, open tanks are used in countercurrent operation. The major difference between solid–liquid and liquid–liquid systems centers about the difficulty of transporting the solid, or the solid slurry, from stage to stage. For this reason, the solid may be left in the same tank, with only the liquid transferred from tank to tank. In the pharmaceutical, food, and natural-product industries, countercurrent solid transport is provided by complicated mechanical devices. A supercritical fluid is sometimes used as the solvent in leaching.

In adsorptive-bubble separation methods, surface-active material collects at solution interfaces, establishing a concentration gradient between a solute in the bulk and in the surface layer. If the (very thin) surface layer can be collected, partial solute removal from the solution will have been achieved. The major application of this phenomenon is in ore flotation processes, where solid particles migrate to and attach themselves to rising gas bubbles and literally float out of the solution. This is essentially a three-phase system. *Foam fractionation,* (18), a two-phase adsorptive-bubble separation method, is a process where natural or chelate-induced surface activity causes a solute to migrate to rising bubbles and is, thus, removed as a foam. This method is not covered in this book.

Each equipment symbol shown in Table 1.1 corresponds to the simplest configuration for the operation represented. More complex versions are possible and frequently desirable. For example, a more complex version of the reboiled absorber, Separation Operation (5) in Table 1.1, is shown in Figure 1.8. This reboiled absorber has two feeds, an intercooler, a side stream, and both an interreboiler and a bottoms reboiler. Acceptable design procedures must handle such complex situations. It is also possible to conduct chemical reactions simultaneously with separation operations in a single column. Siirola [6] describes the evolution of an advanced commercial process for producing methyl acetate by the esterification of methanol and acetic acid. The process is conducted in a single column in an integrated process that involves three reaction zones and three separation zones.

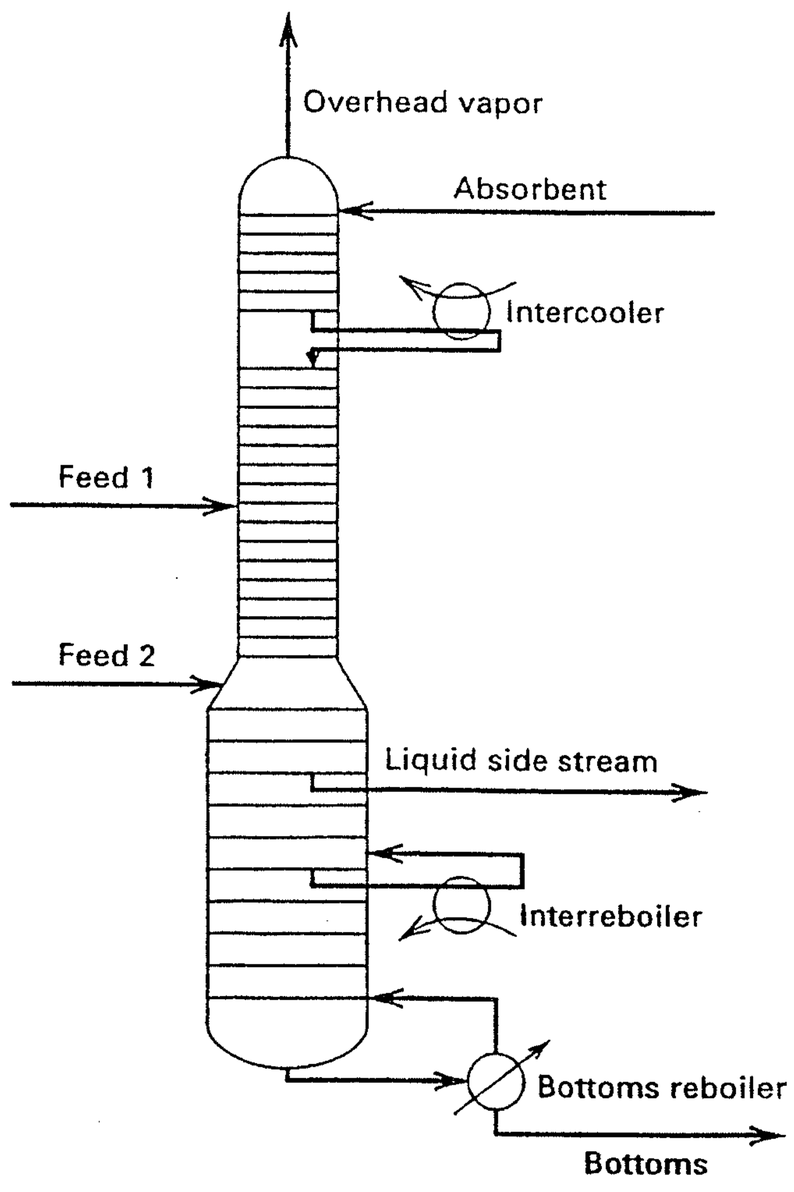


Figure 1.8 Complex reboiled absorber.

1.4 SEPARATION BY BARRIER

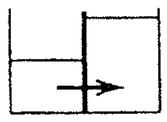
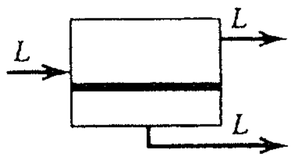
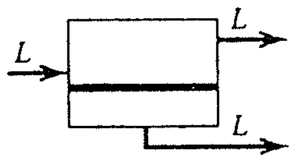
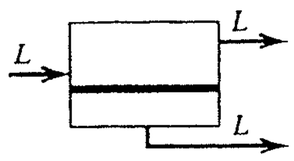
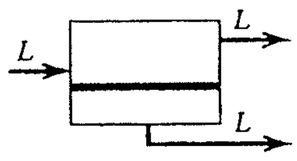
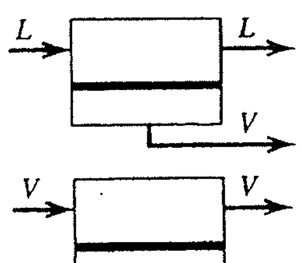
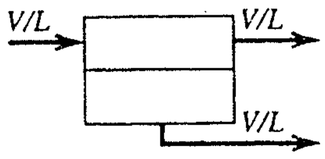
The use of microporous and nonporous membranes as semipermeable barriers for difficult and highly selective separations is rapidly gaining adherents. Membranes are fabricated from natural fibers, synthetic polymers, ceramics, or metals, but may also consist of liquid films. Solid membranes are fabricated into flat sheets, tubes, hollow fibers, or spiral-wound sheets, which are incorporated into commercial modules or cartridges, generally available only in certain sizes. For microporous membranes, separation is effected by differing rates of diffusion through the pores; while for nonporous membranes, separation occurs because of differences in both solubility in the membrane and rate of diffusion through the membrane. The most complex and selective membranes are found in the trillions of cells in the human body.

Table 1.2 lists the more widely used membrane separation operations. *Osmosis,* Operation (1) in Table 1.2, involves transfer, by a concentration gradient, of a solvent through a membrane into a mixture of solute and solvent. The membrane is almost nonpermeable to the solute. In *reverse osmosis,* (2), transport of solvent in the opposite direction is effected by imposing a pressure, higher than the osmotic pressure, on the feed side. Using a nonporous membrane, reverse osmosis successfully desalts water. *Dialysis,* (3), is the transport, by a concentration gradient, of small solute molecules, sometimes called crystalloids, through a porous membrane. The molecules unable to pass through the membrane are small, insoluble, nondiffusible particles, sometimes referred to as colloids.

Microporous membranes can be used in a manner similar to reverse osmosis to selectively allow small solute molecules and/or solvents to pass through the membrane and to prevent large dissolved molecules and suspended solids from passing through. *Microfiltration,* (4), refers to the retention of molecules typically in the size range from 0.02 to 10 μm. *Ultrafiltration,* (5), refers to the range from 1 to 20 nm. To retain molecules down to 0.1 nm, reverse osmosis, sometimes called *hyperfiltration,* can be used.

Although reverse osmosis can be used to separate organic and aqueous-organic liquid mixtures, high pressures are required. Alternatively, *pervaporation,* (6), in which the species being absorbed by and transported through the nonporous membrane are evaporated, can be used. This method, which uses much lower pressures than reverse osmosis, but

Table 1.2 Separation Operations Based on a Barrier

Separation Operation	Symbol[a]	Initial or Feed Phase	Separating Agent	Industrial Example[b]
Osmosis (1)		Liquid	Nonporous membrane	—
Reverse osmosis* (2)		Liquid	Nonporous membrane with pressure gradient	Desalinization of sea water (Vol. 24, pp. 349–353)
Dialysis (3)		Liquid	Porous membrane with pressure gradient	Recovery of caustic from hemicellulose (Vol. 7, p. 572)
Microfiltration (4)		Liquid	Microporous membrane with pressure gradient	Removal of bacteria from drinking water (Vol. 15, p. 115)
Ultrafiltration (5)		Liquid	Microporous membrane with pressure gradient	Separation of whey from cheese (Vol. 15, pp. 562–564)
Pervaporation* (6)		Liquid	Nonporous membrane with pressure gradient	Separation of azeotropic mixtures (Vol. 15, pp. 116–117)
Gas permeation* (7)		Vapor	Nonporous membrane with pressure gradient	Hydrogen enrichment (Vol. 20, pp. 709–710)
Liquid membrane (8)		Vapor and/or liquid	Liquid membrane with pressure gradient	Removal of hydrogen sulfide (Vol. 15, p. 119)

*Design procedures are fairly well accepted.

[a]Single units are shown. Multiple units can be cascaded.

[b]Citations refer to volume and page(s) of *Kirk–Othmer Encyclopedia of Chemical Technology,* 3rd ed., John Wiley and Sons, New York (1978–1984).

where the heat of vaporization must be supplied, is used to separate azeotropic mixtures.

The separation of gas mixtures by selective *gas permeation,* (7), through membranes, using pressure as the driving force, is a relatively simple process, first used in the 1940s with porous fluorocarbon barriers to separate $^{235}UF_6$ and $^{238}UF_6$ at great expense because it required enormous amounts of electric power. More recently, nonporous polymer membranes are used commercially to enrich gas mixtures containing hydrogen, recover hydrocarbons from gas streams, and produce nitrogen-enriched and oxygen-enriched air.

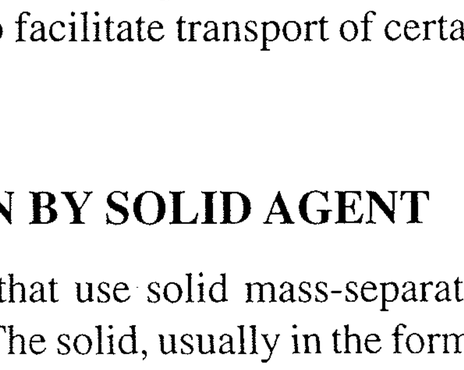
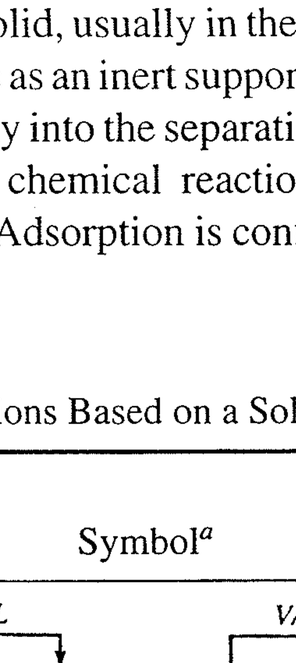
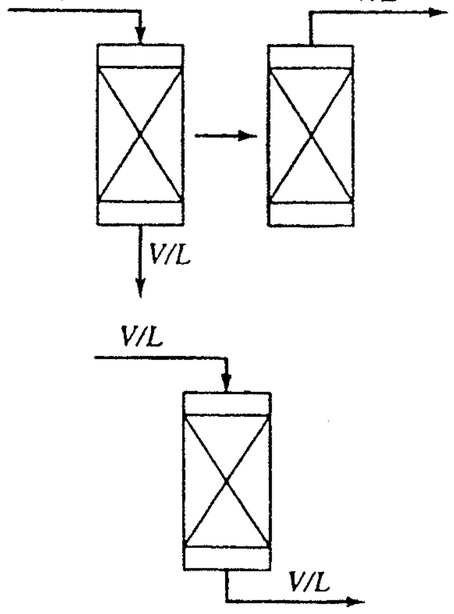
Liquid membranes, (8), of only a few molecules in thickness can be formed from surfactant-containing mixtures that locate at the interface between two fluid phases. With such a membrane, aromatic hydrocarbons can be separated from paraffinic hydrocarbons. Alternatively, the membrane can be formed by imbibing the micropores with liquids that are doped with additives to facilitate transport of certain solutes, such as CO_2 and H_2S.

1.5 SEPARATION BY SOLID AGENT

Separation operations that use solid mass-separating agents are listed in Table 1.3. The solid, usually in the form of a granular material or packing, acts as an inert support for a thin layer of absorbent or enters directly into the separation operation by selective adsorption of, or chemical reaction with, certain species in the feed mixture. Adsorption is confined to the surface of the solid adsorbent, unlike absorption, which occurs throughout the bulk of the absorbent. In all cases, the active separating agent eventually becomes saturated with solute and must be regenerated or replaced periodically. Such separations are often conducted batchwise or semicontinuously. However, equipment is available to simulate continuous operation.

Adsorption, Separation Operation (1) in Table 1.3, is used to remove components present in low concentrations in nonadsorbing solvents or gases and to separate the components in gas or liquid mixtures by selective adsorption on solids, followed by desorption to regenerate the adsorbents, which include activated carbon, aluminum oxide, silica gel, and synthetic sodium or calcium aluminosilicate zeolite adsorbents (molecular sieves). The sieves differ from the other adsorbents in that they are crystalline and have pore openings of fixed dimensions, making them very selective. A simple adsorption device consists of a cylindrical vessel packed with a bed of solid adsorbent particles through which the gas or liquid flows. Regeneration of the adsorbent is conducted periodically, so two or more vessels are used, one vessel desorbing while the other(s) adsorb(s). If the vessel is arranged vertically, it is usually advantageous to employ downward flow of a gas. With upward flow, jiggling of the bed can cause particle attrition and a resulting increase in pressure drop and loss of material. However, for liquid flow, better distribution is achieved by upward flow. Regeneration is accomplished by one of four methods: (1) vaporizing the adsorbate with a hot purge gas (*thermal-swing adsorption*), (2) reducing the

Table 1.3 Separation Operations Based on a Solid Agent

Separation Operation	Symbol[a]	Initial or Feed Phase	Separating Agent	Industrial Example[b]
Adsorption* (1)		Vapor or liquid	Solid adsorbent	Purification of *p*-xylene (Vol. 24, pp. 723–725)
Chromatography* (2)		Vapor or liquid	Solid adsorbent or liquid adsorbent on a solid support	Separation of xylene isomers and ethylbenzene (Vol. 24, pp. 726–727)
Ion exchange* (3)		Liquid	Resin with ion-active sites	Demineralization of water (Vol. 13, pp. 700–701)

*Design procedures are fairly well accepted.

[a]Single units are shown. Multiple units can be cascaded.

[b]Citations refer to volume and page(s) of *Kirk–Othmer Encyclopedia of Chemical Technology,* 3rd ed., John Wiley and Sons, New York (1978–1984).

pressure to vaporize the adsorbate (*pressure-swing adsorption*), (3) inert purge stripping without change in temperature or pressure, and (4) displacement desorption by a fluid containing a more strongly adsorbed species.

Chromatography, Separation Operation (2) in Table 1.3, is a method for separating the components of a feed gas or liquid mixture by passing the feed through a bed of packing. The feed may be volatilized into a carrier gas, and the bed may be a solid adsorbent (gas-solid chromatography) or a solid-inert support that is coated with a very viscous liquid that acts as an absorbent (gas-liquid chromatography). Because of selective adsorption on the solid adsorbent surface or absorption into liquid absorbent, followed by desorption, different components of the feed mixture move through the bed at different rates, thus effecting the separation. In *affinity chromatography,* a macromolecule (called a ligate) is selectively adsorbed by a ligand (e.g., an ammonia molecule in a coordination compound) that is covalently bonded to a solid-support particle. Ligand–ligate pairs include inhibitors–enzymes, antigens–antibodies, and antibodies–proteins. Chromatography in its various forms is finding use in bioseparations.

Ion exchange, (3), resembles adsorption in that solid particles are used and regeneration is necessary. However, a chemical reaction is involved. In water softening, a typical ion-exchange application, an organic or inorganic polymer in its sodium form removes calcium ions by exchanging calcium for sodium. After prolonged use, the (spent) polymer, which becomes saturated with calcium, is regenerated by contact with a concentrated salt solution.

1.6 SEPARATION BY EXTERNAL FIELD OR GRADIENT

External fields can be used to take advantage of differing degrees of response of molecules and ions to forces and gradients. Table 1.4 lists common techniques, with combinations of these techniques with each other and with previously described separation methods also being possible.

Centrifugation, Operation (1) in Table 1.4, establishes a pressure field that separates fluid mixtures according to molecular weight. This technique is used to separate $^{235}UF_6$ from $^{238}UF_6$, and large polymer molecules according to molecular weight.

If a rather large temperature gradient is applied to a homogeneous solution, concentration gradients can be established and *thermal diffusion,* (2), is induced. It has been used to enhance the separation of uranium isotopes in gas permeation processes.

Natural water contains 0.000149 atom fraction of deuterium. When water is decomposed by *electrolysis,* (3), into hydrogen at the cathode and oxygen at the anode, the deuterium concentration in the hydrogen produced is lower than that in the water. Until 1953, this process was the only commercial source of heavy water (D_2O). In *electrodialysis,* (4), cation- and anion-permeable membranes carry a fixed charge, preventing the migration of species of like charge. This operation can be used to desalinize (remove salts from) sea water. A somewhat related process is *electrophoresis,* (5), which exploits the different migration velocities of charged colloidal or suspended species in an electric field. Positively charged species, such as dyes, hydroxide sols, and colloids, migrate to the cathode; while most small, suspended, negatively charged particles are attracted to the anode. By changing the solvent from an acidic to a basic condition, migration direction can sometimes be changed, particularly for proteins. Electrophoresis is a highly versatile method for separating biochemicals.

Another separation technique for biochemicals and difficult-to-separate heterogeneous mixtures of micromolecular and colloidal materials is *field-flow fractionation,* (6). For the mixture to be separated, an electrical field, magnetic field, or thermal gradient is established in a direction perpendicular to a laminar-flow field. Components of the mixture are driven to different locations in the stream; thus, they travel in the flow direction at different velocities, so a separation is achieved.

Table 1.4 Separation Operations by Applied Field or Gradient

Separation Operation	Initial or Feed Phase	Force Field or Gradient	Industrial Example[a]
Centrifugation (1)	Vapor	Centrifugal force field	Separation of uranium isotopes (Vol. 23, pp. 531–532)
Thermal diffusion (2)	Vapor or liquid	Thermal gradient	Separation of chlorine isotopes (Vol. 7, p. 684)
Electrolysis (3)	Liquid	Electrical force field	Concentration of heavy water (Vol. 7, p. 550)
Electrodialysis (4)	Liquid	Electrical force field and membrane	Desalinization of sea water (Vol. 24, pp. 353–359)
Electrophoresis (5)	Liquid	Electrical force field	Recovery of hemicelluloses (Vol. 4, p. 551)
Field-flow fractionation (6)	Liquid	Laminar flow in force field	

[a]Citations refer to volume and page(s) of *Kirk–Othmer Encyclopedia of Chemical Technology,* 3rd ed., John Wiley and Sons, New York (1978–1984).

1.7 COMPONENT RECOVERIES AND PRODUCT PURITIES

Separation operations are subject to the conservation of mass. Accordingly, if no chemical reactions occur and the process operates in a continuous, steady-state fashion, then for each component, i, in a mixture of C components, the molar (or mass) flow rate in the feed, $n_i^{(F)}$, is equal to the sum of the product molar (or mass) flow rates, $n_i^{(p)}$, for that component in the N product phases, p. Thus, referring to Figure 1.6,

$$n_i^{(F)} = \sum_{p=1}^{N} n_i^{(p)} = n_i^{(1)} + n_i^{(2)} + \cdots + n_i^{(N-1)} + n_i^{(N)} \qquad (1\text{-}1)$$

To solve (1-1) for values of $n_i^{(p)}$, from specified values of $n_i^{(F)}$, we need an additional $N - 1$ independent expressions involving $n_i^{(p)}$. This gives a total of NC equations in NC unknowns. For example, if a feed mixture containing C components is separated into N product phases, $C(N - 1)$ additional expressions are needed. General forms of these expressions, which deal with the extent of separation, are considered in this and the next section. If more than one stream is fed to the separation process, $n_i^{(F)}$ is the summation for all feeds.

Equipment for separating components of a mixture is designed and operated to meet desired or required specifications, which are typically given as *component recoveries* and/or *product purities*. In Figure 1.9, the block-flow diagram for a hydrocarbon separation system, the feed is the bottoms product from a reboiled absorber used to deethanize (i.e., remove ethane and components of smaller molecular weight) a mixture of refinery gases and liquids. The separation process of choice in this example is a sequence of three multistage distillation columns. The composition of the feed to the process is included in Figure 1.9, where components are rank-listed by decreasing volatility, and hydrocarbons heavier (i.e., of greater molecular weight) than normal pentane and in the hexane (C_6)-to-undecane (C_{11}) range are lumped together in a so-called C_6^+ fraction. The three distillation columns of Figure 1.9 separate the deethanized feed into four products: a C_5^+-rich bottoms, a C_3-rich distillate, an iC_4-rich distillate, and an nC_4-rich bottoms. For each column, each component in the feed is partitioned between the overhead and the bottoms, according to a unique *split fraction* or *split ratio* that depends on (1) the component thermodynamic and transport properties in the vapor and liquid phases, (2) the number of contacting stages, and (3) the relative vapor and liquid flows through the column. The *split fraction,* SF, for component i in separator k is the fraction of that component found in the first product:

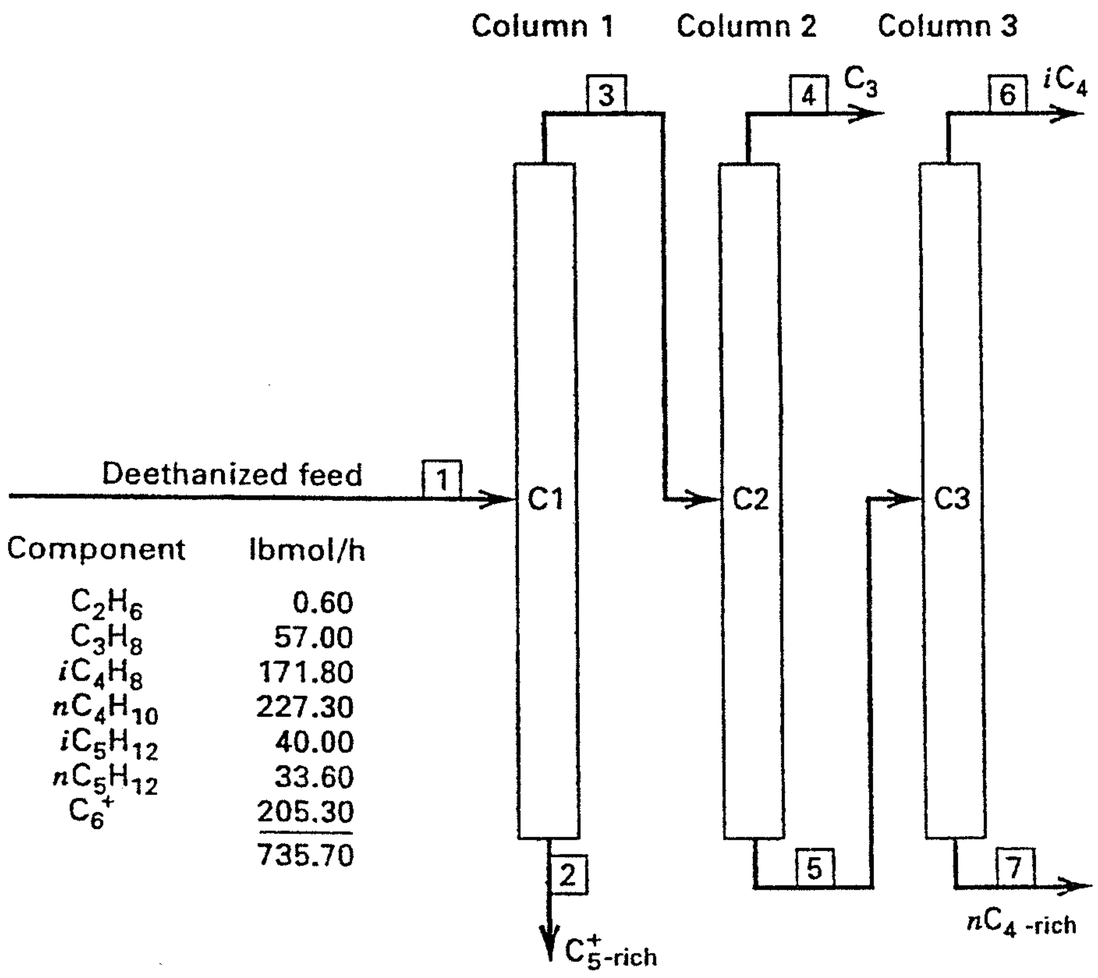
$$\mathrm{SF}_{i,k} = \frac{n_{i,k}^{(1)}}{n_{i,k}^{(F)}} \qquad (1\text{-}2)$$

where $n^{(1)}$ and $n^{(F)}$ refer to component molar flow rates in the first product and the feed, respectively. Alternatively, a *split ratio,* SR, between two products, may be defined as

$$\mathrm{SR}_{i,k} = \frac{n_{i,k}^{(1)}}{n_{i,k}^{(2)}} = \frac{\mathrm{SF}_{i,k}}{(1 - \mathrm{SF}_{i,k})} \qquad (1\text{-}3)$$

where $n^{(2)}$ refers to a component molar flow rate in the second product. Alternatively, SF and SR can be defined in terms of component mass flow rates.

If the process shown in Figure 1.9 is part of an operating plant with the measured material balance of Table 1.5, the split fractions and split ratios in Table 1.6 are determined from (1-2) and (1-3). In Table 1.5, it is seen that only two of the four products are relatively pure: C_3 overhead from the second column and iC_4 overhead from the third column. The molar purity of C_3 in the C_3 overhead is (54.80/56.00) or



Component	lbmol/h
C_2H_6	0.60
C_3H_8	57.00
iC_4H_8	171.80
nC_4H_{10}	227.30
iC_5H_{12}	40.00
nC_5H_{12}	33.60
C_6^+	205.30
	735.70

Figure 1.9 Hydrocarbon recovery process.

Table 1.5 Operating Material Balance for Hydrocarbon Recovery Process

	lbmol/h in Stream						
Component	1 Feed to C1	2 C_5^+-rich	3 Feed to C2	4 C_3	5 Feed to C3	6 iC_4	7 nC_4-rich
C_2H_6	0.60	0.00	0.60	0.60	0.00	0.00	0.00
C_3H_8	57.00	0.00	57.00	54.80	2.20	2.20	0.00
iC_4H_{10}	171.80	0.10	171.70	0.60	171.10	162.50	8.60
nC_4H_{10}	227.30	0.70	226.60	0.00	226.60	10.80	215.80
iC_5H_{12}	40.00	11.90	28.10	0.00	28.10	0.00	28.10
nC_5H_{12}	33.60	16.10	17.50	0.00	17.50	0.00	17.50
C_6^+	205.30	205.30	0.00	0.00	0.00	0.00	0.00
Total	735.60	234.10	501.50	56.00	445.50	175.50	270.00

Table 1.6 Split Fractions and Split Ratios for Hydrocarbon Recovery Process

	Column 1		Column 2		Column 3		Overall Percent Recovery
Component	SF	SR	SF	SR	SF	SR	
C_2H_6	1.00	Large	1.00	Large	—	—	100
C_3H_8	1.00	Large	0.9614	24.91	1.00	Large	96.14
iC_4H_{10}	0.9994	1,717	0.0035	0.0035	0.9497	18.90	94.59
nC_4H_{10}	0.9969	323.7	0.00	0.00	0.0477	0.0501	94.94
iC_5H_{12}	0.7025	2.361	0.00	0.00	0.00	0.00	29.75
nC_5H_{12}	0.5208	1.087	0.00	0.00	0.00	0.00	47.92
C_6^+	0.00	Small	—	—	—	—	100

97.86%, while the iC_4 overhead purity is (162.50/175.50) or 92.59% iC_4. The nC_4-rich bottoms from Column 3 has an nC_4 purity of only (215.80/270.00) or 79.93%. Each of the three columns is designed to make a split between two adjacent components (called the *key components*) in the list of components ordered in decreasing volatility. As seen by the horizontal dividing lines in Table 1.6, the three key splits are nC_4H_{10}/iC_5H_{12}, C_3H_8/iC_4H_{10}, and iC_4H_{10}/nC_4H_{10} for Columns 1, 2, and 3, respectively. From the split fractions listed in Table 1.6, it is seen that all splits are relatively sharp (SF $>$ 0.95 for the light key and SF $<$ 0.05 for the heavy key), except for column 1, where the split ratio for the heavy key (iC_5H_{12}) is not sharp at all, and ultimately causes the nC_4-rich bottoms to be relatively impure in nC_4, even though the split between the two key components in the third column is relatively sharp.

In Table 1.6, for each column, values of SF and SR decrease in the order of the ranked component list. It is also noted in Table 1.6 that SF may be a better quantitative measure of degree of separation than SR because SF is bounded between 0 and 1, while SR can range from 0 to a very large value.

Two other common measures of extent of separation can be applied to each column, or to the separation system as a whole. One measure is the *percent recovery* in a designated system product of each component in the feed to the system. These values, as computed from the data of Table 1.5, are listed in the last column of Table 1.6. As shown, the component recoveries are all relatively high (>95%) except for the two pentane isomers. The other measure of extent of separation is *product purity*. These purities for the main component were computed for all except the C_5^+-rich product, which is [(11.90 + 16.10 + 205.30)/234.10] or 99.66% pure with respect to the pentanes and heavier. Such a product is a *multicomponent product*. One of the most common multicomponent products is gasoline.

Product impurity levels and a designation of the impurities are included in product specifications for chemicals of commerce. The product purity with respect to each component in each of the three final products for the hydrocarbon recovery process, as computed from the process operating data of Table 1.5, is given in Table 1.7, where the values are also extremely important because maximum allowable percentages of impurities are compared to the product specifications. The C_5^+ fraction is not included because it is an intermediate that is sent to an isomerization process. From the comparison in Table 1.7, it is seen that two products easily meet their specifications, while the iC_4 product barely meets its specification. If the process is equipped with effective controllers, it might be possible to reduce the energy input to the process and still meet C_3 and nC_4-rich product

Table 1.7 Comparison of Measured Product Purities with Specifications

	mol% in Product					
	Propane		Isobutane		Normal Butane	
Component	Data	Spec	Data	Spec	Data	Spec
C_2H_6	1.07	5 max	0	—	0	—
C_3H_8	97.86	93 min	1.25	3 max	0	1 max
iC_4H_{10}	1.07	2 min	92.60	92 min	83.11	80 min
nC_4H_{10}	0	—	6.15	7 max		
C_5^+	0	—	0	—	16.89	20 max
Total	100.00		100.00		100.00	

specifications. Although the product purities in Table 1.7 are given in mol%, this designation is usually restricted to gas mixtures for which purities in vol% are equivalent to mol%. For liquid mixtures, purities are often specified in wt%. To meet environmental regulations, maximum amounts of impurities in gas, liquid, and solids streams are typically specified in *ppm* (parts per million) or *ppb* (parts per billion), usually by volume (same as moles) for gases and by weight (mass) for liquids and solids. For aqueous solutions, especially those containing acids and bases, common designations for composition are *molarity* or molar concentration (moles of solute per liter of solution, M), *normality* (number of equivalent weights of solute per liter of solution, N), and *molality* (moles of solute per kilogram of solvent). For some chemical products, an attribute, such as color, may be used in place of a purity in terms of composition.

1.8 SEPARATION POWER

Some separations in Table 1.1 are often inadequate for making a sharp split between two key components of a feed mixture, and can only effect the desired recovery of a single key component. Examples are Operations 1, 2, 6, 7, 8, 9, 11, 13, 14, 15, 16, and 17 in Table 1.1. For these, either a single separation stage is utilized as in Operations 1, 2, 13, 14, 15, 16, and 17 or the feed enters at one end (not near the middle) of a multistage separator as in Separation Operations 6, 7, 8, 9, and 11. The split ratio, SR, split fraction, SF, recovery, or purity that can be achieved for the key component depends on a number of factors. For the simplest case of a single separation stage, the factors that influence SR and SF values include: (1) the relative molar amounts of the two phases leaving the separator and (2) thermodynamic, mass transport, and other properties of the key components. For multistage separators, an additional factor must be added, namely, (3) the number of stages and their configuration. The quantitative relationships involving these factors are unique to each type of separator. Therefore, detailed discussion of these relationships is deferred to subsequent chapters, where individual separation operations are discussed in detail. A general but brief discussion of some of the important property factors is given in the next section.

When multistage separators are utilized and the feed mixture enters somewhere near the middle of the separator, such that the separator consists of two sections of stages, one on either side of the feed stage, it is often possible to achieve a relatively sharp separation between two key components. One section acts to remove one key component, while the other section acts to remove the other key component. Examples are Separation Operations 3, 4, 5, 10, and 12 in Table 1.1. For these operations, a convenient measure of the relative degree of separation between two components, i and j, is the *separation power* (also referred to as the relative split ratio and the separation factor), SP, of the separation equipment, defined in terms of the component splits achieved, as measured by the compositions of the two products, (1) and (2):

$$\mathrm{SP}_{i,j} = \frac{C_i^{(1)}/C_i^{(2)}}{C_j^{(1)}/C_j^{(2)}} \tag{1-4}$$

where C is some measure of composition such as mole fraction, mass fraction, or concentration in moles or mass per unit volume. Most commonly, mole fractions or concentrations are used, but in any case, the separation power is readily converted to the following forms in terms of split fractions or split ratios:

$$\mathrm{SP}_{i,j} = \frac{\mathrm{SR}_i}{\mathrm{SR}_j} \tag{1-5}$$

$$\mathrm{SP}_{i,j} = \frac{\mathrm{SF}_i/\mathrm{SF}_j}{(1-\mathrm{SF}_i)/(1-\mathrm{SF}_j)} \tag{1-6}$$

Achievable values of SP depend on the number of stages and the relative thermodynamic and mass transport properties of components i and j. In general, when applied to the two key components, components i and j and products 1 and 2 are selected so that $\mathrm{SP}_{i,j} > 1.0$. Then, a large value corresponds to a relatively high degree of separation or high separation

Table 1.8 Main Separation Factors for Hydrocarbon Recovery Process

Key-Component Split	Column	Separation Factor, SP
nC_4H_{10}/iC_5H_{12}	C1	137.1
C_3H_8/iC_4H_{10}	C2	7103
iC_4H_{10}/nC_4H_{10}	C3	377.6

power; a small value larger than but close to 1.0 corresponds to a low degree of separation power. For example, if SP = 10,000 and $SR_i = 1/SR_j$, then, from (1-5), $SR_i = 100$ and $SR_j = 0.01$, corresponding to a sharp separation. However, if SP = 9 and $SR_i = 1/SR_j$, then $SR_i = 3$ and $SR_j = \frac{1}{3}$, corresponding to a nonsharp separation.

For the hydrocarbon recovery process of Figure 1.9, the values of SP in Table 1.8 are computed from the data in Tables 1.5 or 1.6 for the main split in each of the three separators. The separation factor in Column C1 is relatively small because the split for the heavy key, iC_5H_{12}, is not sharp. The largest separation factor occurs in column C2, where the separation is relatively easy because of the fairly large volatility difference between the two keys. Much more difficult is the butane-isomer split in Column C3, where only a moderately sharp split is achieved.

When applying the conservation of mass principle to separation operations using (1-1), component specifications in terms of component recoveries are easily applied, while those in terms of split ratios and, particularly, purities are more difficult, as shown in the following example.

EXAMPLE 1.1

A feed, F, of 100 kmol/h of air containing 21 mol% O_2 and 79 mol% N_2 is to be partially separated by a membrane unit according to each of the following four sets of specifications. For each case, compute the amounts, in kmol/h, and compositions, in mol%, of the two products (retentate, R, and permeate, P). The membrane is more permeable to the oxygen.

Case 1: 50% recovery of O_2 to the permeate and 87.5% recovery of N_2 to the retentate.

Case 2: 50% recovery of O_2 to the permeate and 50 mol% purity of O_2 in the permeate.

Case 3: 85 mol% purity of N_2 in the retentate and 50 mol% purity of O_2 in the permeate.

Case 4: 85 mol% purity of N_2 in the retentate and a split ratio of O_2 in the permeate to the retentate equal to 1.1.

SOLUTION

The feed is

$$n_{O_2}^{(F)} = 0.21(100) = 21 \text{ kmol/h}$$
$$n_{N_2}^{(F)} = 0.79(100) = 79 \text{ kmol/h}$$

Case 1: This is the simplest case to calculate because two recoveries are given:

$$n_{O_2}^{(P)} = 0.50(21) = 10.5 \text{ kmol/h}$$
$$n_{N_2}^{(R)} = 0.875(79) = 69.1 \text{ kmol/h}$$
$$n_{O_2}^{(R)} = 21 - 10.5 = 10.5 \text{ kmol/h}$$
$$n_{N_2}^{(P)} = 79 - 69.1 = 9.9 \text{ kmol/h}$$

Case 2: With the recovery for O_2 given, calculate its distribution into the two products:

$$n_{O_2}^{(P)} = 0.50(21) = 10.5 \text{ kmol/h}$$
$$n_{O_2}^{(R)} = 21 - 10.5 = 10.5 \text{ kmol/h}$$

Using the purity of O_2 in the permeate, the total permeate is

$$n^{(P)} = 10.5/0.5 = 21 \text{ kmol/h}$$

By a total permeate material balance,

$$n_{N_2}^{(P)} = 21 - 10.5 = 10.5 \text{ kmol/h}$$

By an overall N_2 material balance,

$$n_{N_2}^{(R)} = 79 - 10.5 = 68.5 \text{ kmol/h}$$

Case 3: With two purities given, write two simultaneous material-balance equations, one for each component, in terms of the total retentate and total permeate.

For nitrogen, with a fractional purity of $1.00 - 0.50 = 0.50$ in the permeate,

$$n_{N_2} = 0.85n^{(R)} + 0.50n^{(P)} = 79 \text{ kmol/h} \quad (1)$$

For oxygen, with a fractional purity of $1.00 - 0.85 = 0.15$ in the retentate,

$$n_{O_2} = 0.50n^{(P)} + 0.15n^{(R)} = 21 \text{ kmol/h} \quad (2)$$

Solving (1) and (2) simultaneously for the total products gives

$$n^{(P)} = 17.1 \text{ kmol/h} \qquad n^{(R)} = 82.9 \text{ kmol/h}$$

Therefore, the component flow rates are

$$n_{N_2}^{(R)} = 0.85(82.9) = 70.5 \text{ kmol/h}$$
$$n_{O_2}^{(R)} = 82.9 - 70.5 = 12.4 \text{ kmol/h}$$
$$n_{O_2}^{(P)} = 0.50(17.1) = 8.6 \text{ kmol/h}$$
$$n_{N_2}^{(P)} = 17.1 - 8.6 = 8.5 \text{ kmol/h}$$

Case 4: First compute the O_2 flow rates using the split ratio and an overall O_2 material balance,

$$\frac{n_{O_2}^{(P)}}{n_{O_2}^{(R)}} = 1.1 \qquad 21 = n_{O_2}^{(P)} + n_{O_2}^{(R)}$$

Solving these two equations simultaneously gives

$$n_{O_2}^{(R)} = 10 \text{ kmol/h} \qquad n_{O_2}^{(P)} = 21 - 10 = 11 \text{ kmol/h}$$

Since the retentate contains 85 mol% N_2 and, therefore, 15 mol% O_2, the flow rates for the N_2 are

$$n_{N_2}^{(R)} = \frac{85}{15}(10) = 56.7 \text{ kmol/h} \quad n_{N_2}^{(P)} = 79 - 56.7 = 22.3 \text{ kmol/h}$$

1.9 SELECTION OF FEASIBLE SEPARATION PROCESSES

Selection of a best separation process must be made from among a number of feasible candidates. When the feed mixture is to be separated into more than two products, a combination of two or more operations may be best. Even when only two products are to be produced, a hybrid process of two or more different types of operations may be most economical. Only an introduction to the selection of a separation process is given here. A detailed treatment is given in Chapter 7 of Seider, Seader, and Lewin [14].

Important factors in the selection of feasible separation operations are listed in Table 1.9. These factors have to do with feed and product conditions, property differences that can be exploited, and certain characteristics of the candidate separation operations. The most important feed conditions are composition and flow rate, because the other conditions (temperature, pressure, and phase condition) can be altered by pumps, compressors, and heat exchangers to fit a particular candidate separation operation. In general, however, the vaporization of a liquid feed that has a high heat of vaporization, the condensation of a vapor feed with a refrigerant, and/or the compression of a vapor feed can add significantly to the cost. Some separation operations, such as those based on the use of barriers or solid agents, perform best on feeds that are dilute in the species to be recovered. The most important product conditions are the required purities because, again, the other conditions listed can be altered by energy transfer after the separation is achieved.

Table 1.9 Factors That Influence the Selection of Feasible Separation Operations

A. Feed conditions
   1. Composition, particularly concentration of species to be recovered or separated
   2. Flow rate
   3. Temperature
   4. Pressure
   5. Phase state (solid, liquid, and/or gas)

B. Product conditions
   1. Required purities
   2. Temperatures
   3. Pressures
   4. Phase states

C. Property differences that may be exploited
   1. Molecular
   2. Thermodynamic
   3. Transport

D. Characteristics of separation operation
   1. Ease of scale-up
   2. Ease of staging
   3. Temperature, pressure, and phase-state requirements
   4. Physical size limitations
   5. Energy requirements

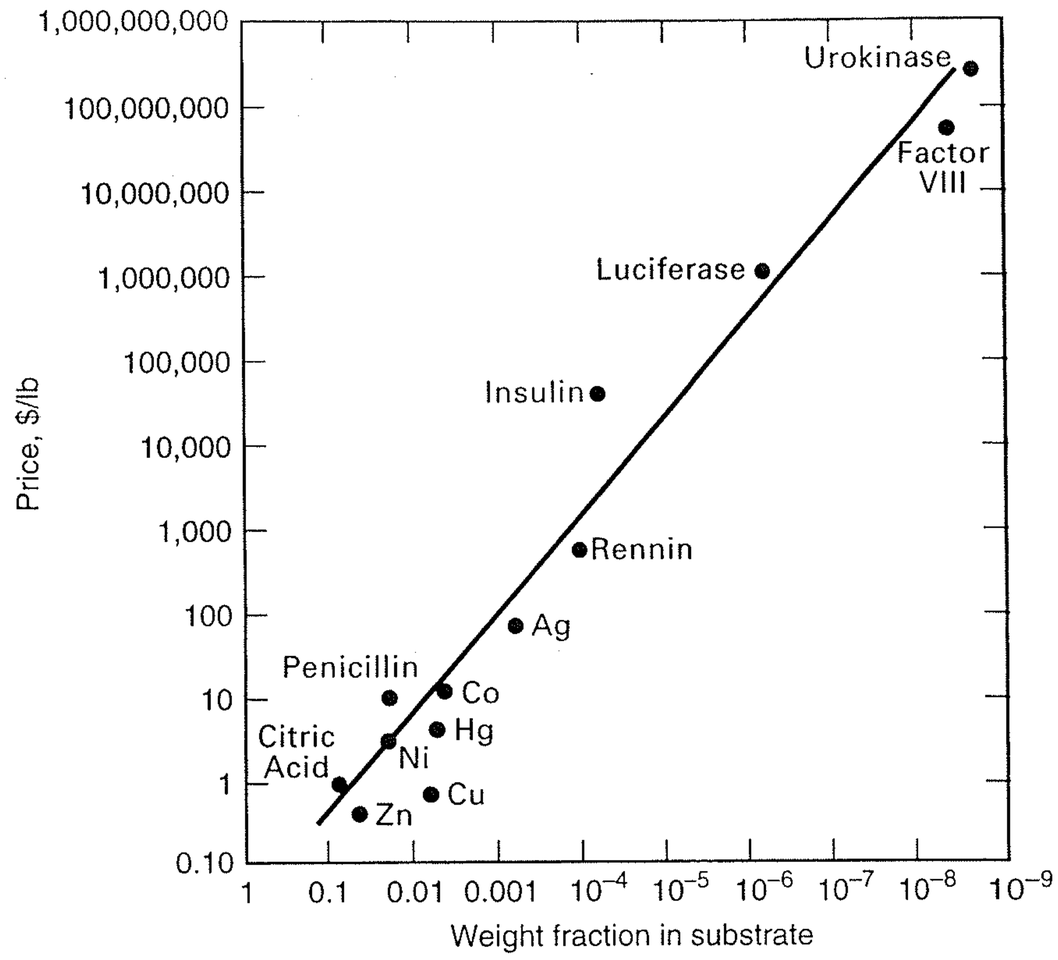


Figure 1.10 Effect of concentration of product in feed material on price [9].

In general, as demonstrated by Sherwood, Pigford, and Wilke [7] and updated recently, using additional data for biological materials from Dwyer [8], by Keller [9], the cost of recovering and purifying a chemical contained in a mixture can depend strongly on the concentration of that chemical in the feed mixture. Keller's correlation is given in Figure 1.10, where it is seen that the more dilute the chemical is in the mixture, the higher is its sales price.

When very pure products are required, either large differences in certain properties must exist or significant numbers of stages must be provided. It is important to consider both molecular and bulk thermodynamic and transport properties, some of which are listed near the end of Section 1.2. Data and estimation methods for many bulk properties are given by Poling, Prausnitz, and O'Connell [10] and for both molecular and bulk properties by Daubert and Danner [11].

Some separation operations are well understood and can be readily designed from a mathematical model and/or scaled up to a commercial size from laboratory data. The results of a survey by Keller [9], shown in Figure 1.11, show that the degree to which a separation operation is technologically mature correlates well with its commercial use. Operations based on a barrier are more expensive to stage than those based on use of a solid agent or the creation or addition of a second phase. Some separation equipment is limited to a maximum size. For capacities requiring a larger size, parallel units must be provided. The choice of single or parallel units must be given careful consideration. Except for size constraints or fabrication problems, the capacity of a single unit can be doubled for an additional investment cost of only about 50%. If two parallel units are installed, the additional investment is 100%. Table 1.10 is a list of the more common separation operations ranked according to ease of scale-up. Those operations ranked near the top are frequently designed without the need for any laboratory data or

Table 1.10 Ease of Scale-up of the Most Common Separation Operations

Operation in Decreasing Ease of Scale-up	Ease of Staging	Need for Parallel Units
Distillation	Easy	No need
Absorption	Easy	No need
Extractive and azeotropic distillation	Easy	No need
Liquid–liquid extraction	Easy	Sometimes
Membranes	Repressurization required between stages	Almost always
Adsorption	Easy	Only for regeneration cycle
Crystallization	Not easy	Sometimes
Drying	Not convenient	Sometimes

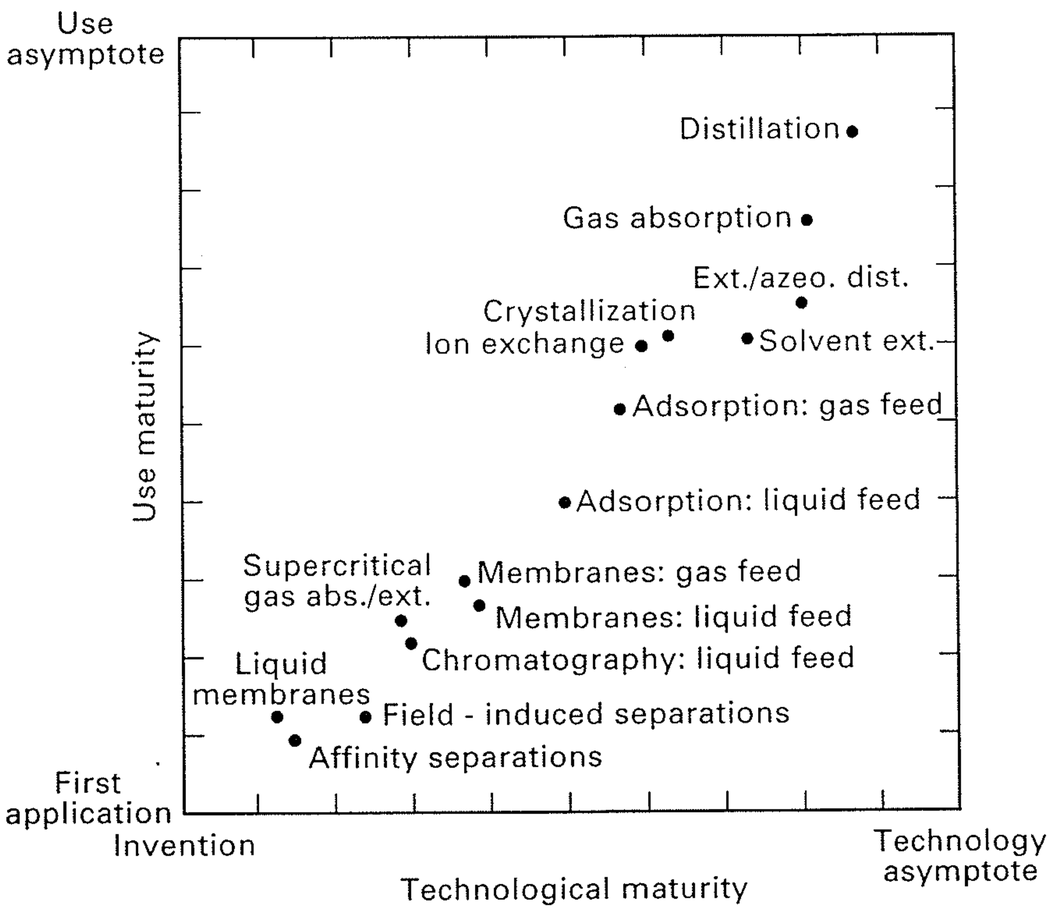


Figure 1.11 Technological and use maturities of separation processes [9].

pilot-plant tests. Operations near the middle usually require laboratory data, while operations near the bottom require pilot-plant tests on actual feed mixtures. Also included in the table is an indication of the ease of providing multiple stages and to what extent parallel units may be required to handle high capacities. A detailed discussion of the selection of alternative techniques for the separation of components from both homogeneous and heterogeneous phases, with many examples, is given by Woods [12]. Ultimately, the process having the lowest operating, maintenance, and capital costs is selected.

EXAMPLE 1.2

Propylene and propane are among the light hydrocarbons produced by thermal and catalytic cracking of heavy petroleum fractions. Propane is valuable as a fuel by itself and in liquefied natural gas (LPG), and as a feedstock for producing propylene and ethylene. Propylene is used to make acrylonitrile monomer for synthetic rubber, isopropyl alcohol, cumene, propylene oxide, and polypropylene. Although propylene and propane have close boiling points, they are traditionally separated by distillation. Representative conditions are shown in Figure 1.12, where it is seen that a large number of stages is needed and the reflux and boilup flow rates compared to the feed flow rate are also large. Accordingly, considerable attention has been given to the possible replacement of distillation with a more economical and less energy-intensive separation operation. Based on the factors in Table 1.9, the characteristics in Table 1.10, and the list of species properties that might be exploited, given at the end of Section 1.2, propose some feasible alternatives to distillation to produce products from the feed in Figure 1.12.

SOLUTION

First, note that the component feed and product flow rates in Figure 1.12 satisfy (1-1), the conservation of mass. Table 1.11 compares properties of the two species, taken mainly from Daubert and Danner [11], where it is seen that the only listed property that might be exploited is the dipole moment. Because of the asymmetric location of the double bond in propylene, its dipole moment is significantly greater than that of propane, making propylene a polar compound, although weakly so (some define a polar compound as one with a dipole moment greater than 1 debye). Separation operations that can exploit this difference are:

1. Extractive distillation with a polar solvent such as furfural or an aliphatic nitrile that will reduce the volatility of propylene (Ref.: U.S. Patent 2,588,056, March 4, 1952).

Table 1.11 Comparison of Properties for Example 1.2

Property	Propylene	Propane
Molecular weight	42.081	44.096
van der Waals volume, m^3/kmol	0.03408	0.03757
van der Waals area, m^2/kmol $\times 10^{-8}$	5.060	5.590
Acentric factor	0.142	0.152
Dipole moment, debyes	0.4	0.0
Radius of gyration, m $\times 10^{10}$	2.254	2.431
Normal melting point, K	87.9	85.5
Normal boiling point, K	225.4	231.1
Critical temperature, K	364.8	369.8
Critical pressure, MPa	4.61	4.25

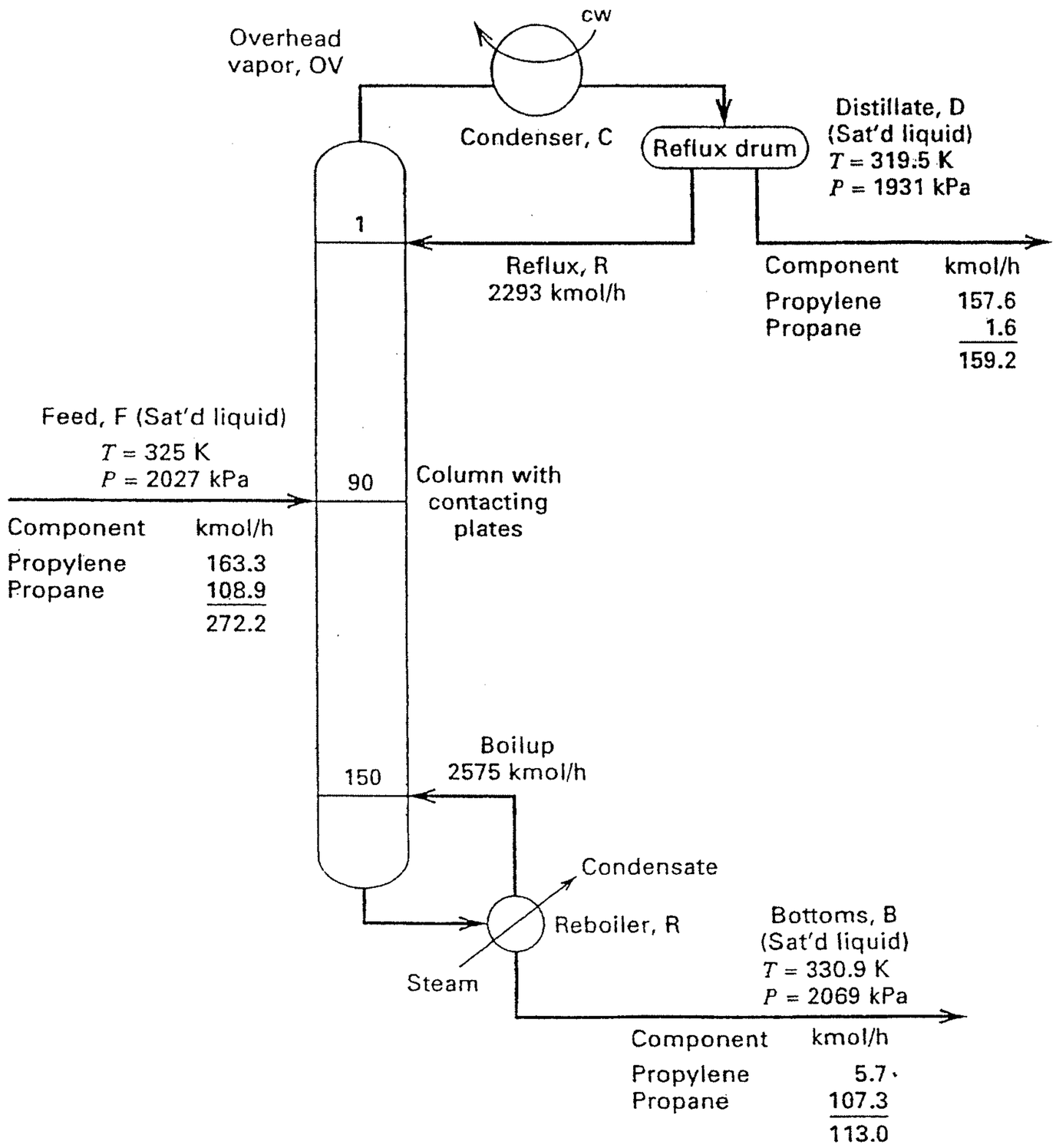


Figure 1.12 Distillation of a propylene–propane mixture.

2. Adsorption with silica gel or a zeolite that will selectively adsorb propylene [Ref.: *J. Am. Chem. Soc.*, **72,** 1153–1157 (1950)].

3. Facilitated transport membranes using impregnated silver nitrate to carry propylene selectively through the membrane [Ref.: *Recent Developments in Separation Science,* Vol. IX, 173–195 (1986)].

SUMMARY

1. Almost all industrial chemical processes include equipment for separating chemicals contained in the process feed(s) and/or produced in reactors within the process.

2. More than 25 different separation operations are commercially important.

3. The extent of separation achievable by a particular separation operation depends on exploitation of the differences in certain properties of the species.

4. The more widely used separation operations involve transfer of species between two phases, one of which is created by energy transfer or the reduction of pressure, or by introduction as a MSA.

5. Less commonly used separation operations are based on the use of a barrier, a solid agent, or a force field to cause species being separated to diffuse at different rates and/or to be selectively absorbed or adsorbed.

6. Separation operations are subject to the conservation of mass. The degree of separation of a component in a separator is indicated by a split fraction, SF, given by (1-2), and/or by a split ratio, SR, given by (1-3).

7. For a sequence, system, or train of separators, overall component recoveries and product purities are of prime importance and are related by material balances to individual SF and/or SR values for the separators in the system.

8. Some separation operations, such as absorption, are capable of only a specified degree of separation for a single species. Other separation operations, such as distillation, can effect a sharp split between two so-called key components.

9. The degree of separation between two key components by a particular separation operation can be indicated by a separation power (separation factor), SP, given by (1-4) and related to SF and SR values by (1-5) and (1-6).

10. For given feed(s) and product specifications, the best separation process must frequently be selected from among a number of feasible candidates. The choice may depend on factors listed in Table 1.9. The cost of recovering and purifying a chemical depends on its concentration in the feed mixture. The extent of industrial use of a separation operation depends on the technological maturity of the operation.

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EXERCISES

Section 1.1

1.1 The book, *Chemical Process Industries,* 4th edition, by R. Norris Shreve and J. A. Brink, Jr. (McGraw-Hill, New York, 1984), contains process descriptions, process flow diagrams, and technical data for processes used commercially in 38 chemical industries. For each of the following processes, draw a block-flow diagram of just the reaction and separation steps and describe the process in terms of just those steps, giving careful attention to the particular chemicals being formed in the reactor and separated in each of the separation operations:

(a) Coal chemicals, pp. 72–74
(b) Natural gas purification, pp. 84–86
(c) Acetylene, pp. 115–117
(d) Magnesium compounds, pp. 174–177
(e) Chlorine and caustic soda, pp. 214–219
(f) Potassium chloride, pp. 269–270
(g) Ammonia, pp. 278–282
(h) Sulfuric acid, pp. 299–310
(i) Fluorocarbons, pp. 321–323
(j) Uranium, pp. 338–340
(k) Titanium dioxide, pp. 388–390
(l) Cottonseed oil, pp. 468–471
(m) Glycerin, pp. 502–503
(n) Industrial alcohol, pp. 530–534
(o) Polyethylene, pp. 587–588
(p) Formaldehyde, pp. 596–598
(q) Styrene, pp. 630–635
(r) Natural-gas liquids, pp. 660–661

Section 1.2

1.2 Explain in detail, using thermodynamic principles, why the mixing of pure chemicals to form a homogeneous mixture is a so-called spontaneous process, while the separation of that mixture into its pure (or nearly pure) species is not.

1.3 Explain in detail, using the first and second laws of thermodynamics, why the separation of a mixture into essentially pure species or other mixtures of differing compositions requires the transfer of energy to the mixture or a degradation of its energy.

Section 1.3

1.4 Compare the advantages and disadvantages of making separations using an ESA versus using an MSA.

1.5 Every other year, the magazine *Hydrocarbon Processing* publishes a petroleum-refining handbook, which gives process-flow diagrams and data for more than 75 commercial processes. For each of the following processes in the November 1990 handbook, list the separation operations of the type given in Table 1.1 and indicate what chemical(s) is(are) being separated:

(a) Hydrotreating (Chevron), p. 114
(b) Ethers (Phillips), p. 128
(c) Alkylation (Exxon), p. 130
(d) Treating of BTX cut (GKT), p. 136

1.6 Every other year, the magazine *Hydrocarbon Processing* publishes a petrochemical handbook, which gives process-flow diagrams and data for more than 50 commercial processes. For each of the following processes in the March 1991 handbook, list the separation operations of the type given in Table 1.1 and indicate what chemical(s) is(are) being separated:

(a) Linear alkylbenzene (UOP), p. 130
(b) Methyl amines (Acid-Amine Technologies), p. 133
(c) Butene-2 (Phillips), p. 144
(d) Caprolactam (SNIA), p. 150
(e) Ethylene glycols (Scientific Design), p. 156
(f) Styrene (Monsanto), p. 188

Section 1.4

1.7 Explain why osmosis is not used as a separation operation.

1.8 The osmotic pressure, π, of sea water is given approximately by the expression $\pi = RTc/M$, where c is the concentration of the dissolved salts (solutes) in g/cm^3 and M is the average molecular weight of the solutes as ions. If pure water is to be recovered from sea water at 298 K and containing 0.035 g of salts/cm^3 of sea water and $M = 31.5$, what is the minimum required pressure difference across the membrane in kPa?

1.9 It has been shown that a liquid membrane of aqueous ferrous ethylenediaminetetraacetic acid, maintained between two sets of microporous, hydrophobic, hollow fibers that are packed in a

permeator cell, can selectively and continuously remove sulfur dioxide and nitrogen oxides from the flue gas of power-generating plants. Prepare a detailed drawing of a possible device to carry out such a separation. Show all locations of inlet and outlet streams, the arrangement of the hollow fibers, and a method for handling the membrane liquid. Should the membrane liquid be left in the cell or circulated? Would a sweep fluid be needed to remove the oxides?

Section 1.5

1.10 Explain the differences, if any, between adsorption and gas–solid chromatography.

1.11 In gas–liquid chromatography, is it essential that the gas flow through the packed tube in plug flow? Discuss in detail.

Section 1.6

1.12 In electrophoresis, explain why most small suspended particles are negatively charged.

1.13 In field-flow fractionation, could a turbulent-flow field be used? Why or why not?

Section 1.7

1.14 The feed to Column C3 of the distillation sequence in Figure 1.9 is given in Table 1.5. However, the separation is to be altered so as to produce a distillate that is 95 mol% pure isobutane with a recovery of isobutane in the distillate (SF) of 96%. Because of the relatively sharp separation in Column C3 between iC_4 and nC_4, assume all propane goes to the distillate and all C_5s goes to the bottoms.

(a) Compute the flow rates in lbmol/h of each component in each of the two products leaving Column C3.

(b) What is the percent purity of the normal butane in the bottoms product?

(c) If the purity of the isobutane in the distillate is fixed at 95%, what percent recovery of isobutane in the distillate will maximize the percent purity of normal butane in the bottoms product?

1.15 Five hundred kmol/h of a liquid mixture of light alcohols containing, by moles, 40% methanol (M), 35% ethanol (E), 15% isopropanol (IP), and 10% normal propanol (NP) is distilled in a sequence of two distillation columns. The distillate from the first column is 98% pure M with a 96% recovery of M. The distillate from the second column is 92% pure E with a 95% recovery of E from the process feed. Assume no propanols in the distillate from Column C1, no M in the bottoms from Column C2, and no normal propanol in the distillate from Column C2.

(a) By material balances, assuming negligible propanols in the distillate from the first column, compute the flow rates in kmol/h of each component in each feed, distillate, and bottoms. Draw a labeled block-flow diagram like Figure 1.9. Include the results of the material balances in a table like Table 1.5 and place the table below your block-flow diagram.

(b) Compute the mole-percent purity of the propanol mixture leaving as bottoms from the second column in the sequence.

(c) If the recovery of ethanol is fixed at 95%, what is the maximum purity that can be achieved for the ethanol in the distillate from the second column?

(d) If instead, the purity of the ethanol is fixed at 92%, what is the maximum recovery of ethanol (based on the process feed) that can be achieved?

1.16 A mixture of ethanol and benzene is separated in a network of distillation and membrane separation steps. In one intermediate step, a near-azeotropic liquid mixture of 8,000 kg/h of 23 wt% ethanol in benzene is fed to a pervaporation membrane consisting of a thin ionomeric film of perfluorosulfonic acid polymer cast on a porous Teflon support. The membrane is selective for ethanol such that the vapor permeate contains 60 wt% ethanol, while the nonpermeate liquid contains 90 wt% benzene.

(a) Draw a flow diagram of the pervaporation step using the appropriate symbol from Table 1.2 and include on the diagram all of the given information.

(b) Compute the component flow rates in kg/h in the feed stream and in the two product streams and enter these results on the diagram.

(c) What separation operation could be used to further purify the vapor permeate?

Section 1.8

1.17 The Prism gas permeation process developed by the Monsanto Company is highly selective for hydrogen when using hollow-fiber membranes of materials such as silicone-coated polysulphone. In a typical application, a gas at 16.7 MPa and 40°C, containing the following components in kmol/h: 42.4 H_2, 7.0 CH_4, and 0.5 N_2, is separated into a nonpermeate gas at 16.2 MPa and a permeate gas at 4.56 MPa.

(a) If the membrane is nonpermeable to nitrogen, the Prism membrane separation index, on a mole basis (SP) for hydrogen relative to methane is 34.13, and the split fraction (SF) for hydrogen to the permeate gas is 0.6038, calculate the kmol/h of each component and the total flow in kmol/h of both the nonpermeate gas and the permeate gas.

(b) Compute the percent purity of the hydrogen in the permeate gas.

(c) Using an average heat capacity ratio, γ, of 1.4, estimate the outlet temperatures of the two exiting gas streams by assuming the ideal gas law and reversible expansions for each gas and no heat transfer between the two exiting gas streams.

(d) Draw a process-flow diagram of the membrane process and indicate on the diagram for each stream the pressure, temperature, and component flow rates.

1.18 Nitrogen gas can be injected into oil wells to increase the recovery of crude oil (enhanced oil recovery). Usually, natural gas is produced with the oil and it is desirable to recover the nitrogen from the gas for reinjection into the well. Furthermore, the natural gas must not contain more than 3 mol% nitrogen if the natural gas is to be put into a pipeline. A total of 170,000 SCFH (based on 60°F and 14.7 psia) of natural gas containing 18% N_2, 75% CH_4, and 7% C_2H_6 at 100°F and 800 psia is to be processed for N_2 removal. A two-step separation process has been proposed consisting of (1) membrane separation with a nonporous glassy polyimide membrane, followed by (2) pressure-swing adsorption using molecular sieves to which the permeate gas is fed. The membrane separator is highly selective for N_2 ($SP_{N_2,CH_4} = 16$) and completely impermeable to ethane. The pressure-swing adsorption step selectively adsorbs methane, giving 97% pure methane product in the adsorbate, with an 85% recovery of CH_4 fed to the adsorber. The nonpermeate (retentate) gas from the membrane step and adsorbate from the pressure-swing adsorption step are combined to give a methane stream that contains 3.0% N_2. The pressure drop across the membrane is 760 psia. The permeate at 20°F is compressed in

two stages to 275 psia and cooled to 100°F before entering the adsorption step. The adsorbate gas, which exits the adsorber during regeneration at 100°F and 15 psia, is compressed in three stages to 800 psia and cooled to 100°F before being combined with nonpermeate gas to give the final pipeline natural gas.

(a) Draw a process-flow diagram of the separation process using appropriate symbols from Tables 1.2 and 1.3. Include the gas compressors and heat exchangers. Label the diagram with all of the data given above, and number all process streams.

(b) Compute by material balances, using the data above, the component flow rates of N_2, CH_4, and C_2H_6 in lbmol/h for all process streams entering and exiting the two separation operations. Place the results in a material-balance table similar to Table 1.5.

Section 1.9

1.19 A mixture of ethylbenzene (EB) and the three isomers (ortho, meta, and para) of xylene is widely available in petroleum refineries.

(a) Based on differences in normal boiling points, verify that the separation between *meta*-xylene (MX) and *para*-xylene (PX) by distillation is far more difficult than the separations between EB and PX, and MX and *ortho*-xylene (OX).

(b) Prepare a list of properties for MX and PX similar to Table 1.11. From that list, which property differences might be the best ones to exploit to separate a mixture of these two xylenes?

(c) Explain why melt crystallization and adsorption are used commercially to separate MX and PX.

1.20 When a mixture of ethanol and water is distilled at ambient pressure, the products are a distillate of ethanol and water of near-azeotrope composition (89.4 mol% ethanol) and a bottoms product of nearly pure water. Based on differences in certain properties of ethanol and water, explain how the following separation operations might be able to recover almost pure ethanol from the distillate:

(a) Extractive distillation

(b) Azeotropic distillation

(c) Liquid–liquid extraction

(d) Crystallization

(e) Pervaporation membrane

(f) Adsorption

1.21 A stream containing 7,000 kmol/h of water and 3,000 parts per million (ppm) by weight of ammonia at 350 K and 1 bar is to be processed to remove 90% of the ammonia. What type of separation operation would you use? If it involves a mass-separating agent, propose one.

1.22 A light-hydrocarbon feed stream contains 45.4 kmol/h of propane, 136.1 kmol/h of isobutane, 226.8 kmol/h of *n*-butane, 181.4 kmol/h of isopentane, and 317.4 kmol/h of *n*-pentane. This stream is to be separated in a sequence of three distillation columns, similar to that in Figure 1.9, into four products: (1) propane-rich, (2) isobutane-rich, (3) *n*-butane-rich, and (4) combined pentanes-rich. However, the distillate from the first column is to be the propane-rich product; the distillate from Column 2 is to be the isobutane-rich product; and the distillate from Column 3 is to be the *n*-butane-rich product, with the combined pentanes being the bottoms from Column 3. The recovery of each main component in each product is to be 98%. For example, 98% of the propane in the feed stream is to appear in the propane-rich product, and 98% of the combined pentanes in the feed stream is to appear in the bottoms product from Column 3.

(a) Draw a process-flow diagram, similar to Figure 1.9.

(b) Complete a material balance for each column and summarize the results in a table similar to Table 1.5. To complete the material balance, you will have to make some assumptions about the flow rates of: (1) isobutane in the distillates for Columns 1 and 3 and (2) *n*-butane in the distillates for Columns 1 and 2, consistent with the specified recoveries. Assume that propane will not be found in the distillate from Column 3 and pentanes will not be found in the distillate from Column 2.

(c) Calculate the mol% purities of each of the products and summarize your results in a table similar to Table 1.7, but without the specifications, which are not given here.

1.23 The need to remove organic pollutants from wastewater is common to many industrial processes. Separation methods that may be considered are: (1) adsorption, (2) distillation, (3) liquid–liquid extraction, (4) membrane separation, (5) stripping with air, and (6) stripping with steam. Discuss the advantages and disadvantages of each method for this application. Be sure to consider the fate of the organic material.

1.24 Many waste gas streams in processing plants contain volatile organic compounds (VOCs), which must be removed. Recovery of the VOCs may be accomplished by several separation methods, including: (1) absorption, (2) adsorption, (3) condensation, (4) freezing, and (5) membrane separation. Discuss the advantages and disadvantages of each method, paying particular attention to the fate of the VOC. For the case of a stream containing 3 mol% acetone in air, draw a flow diagram for a process based on absorption. Choose a reasonable absorbent and include in your process a means to recover the acetone and recycle the absorbent.

1.25 Describe three methods suitable for the separation of air into nitrogen and oxygen.

1.26 What separation methods can be used to separate azeotropic mixtures of water and an organic chemical such as ethanol?

1.27 An aqueous stream contains 5% by weight of magnesium sulfate. Devise a process, complete with a process-flow diagram, for the production of nearly pure magnesium sulfate from this stream.

1.28 Explain why the separation of a stream containing 10 wt% acetic acid in water might be more economical by liquid–liquid extraction with ethyl acetate than by distillation.