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## Introduction to the book

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The basic objective of this chapter is to describe the organization of this book vis-à-vis separations from a chemical engineering perspective. Separation, sometimes identified as concentration, enrichment or purification, is employed widely in large industrial-scale as well as small laboratory-scale processes. Here we refer primarily to physical separation methods. However, chemical reactions, especially reversible ones, can enhance separation and have therefore received significant attention in this book. Further, we have considered not only separation of mixtures of molecules, but also mixtures of particles and macromolecules.

The number of different separation processes, methods and techniques is very large. Further new techniques or variations of older techniques keep appearing in industries, old and new. The potential for the emergence of new techniques is very high. Therefore, the approach taken in this book is focused on understanding the basic concepts of separation. Such an approach is expected not only to help develop a better understanding of common separation processes, but also to lay the foundation for deciphering emerging separation processes/techniques. The level of treatment of an individual separation process is generally elementary. Traditional equilibrium based separation processes have received considerable but not overwhelming attention. Many other emerging processes, as well as established processes dealing with particles and external forces, are not usually taught to chemical engineering students; these are integral parts of this book. To facilitate the analysis of processes over such a broad canvas, a somewhat generalized structure has been provided. This includes a core set of equations of change for species concentration, particle population and particle trajectory. These equations are expected to be quite useful in general; however, separation systems are quite often very complicated, thereby limiting the direct utilization of such equations.

Separation and purification are two core activities of chemical engineers. The first wave of textbooks on separation/mass transfer (until the early 1980s) concentrated on

distillation, absorption and extraction, with some attention to adsorption/ion exchange/chromatography. The second wave expanded the treatment of adsorption/ion exchange/chromatography and incorporated an introduction to membrane processes. The overwhelming emphasis in these books was on chemical separations. Simultaneously, a series of textbooks emerged focusing on bioseparations. In these textbooks, the treatment of particle based separations appears briefly under mechanical separations, or under the equilibrium based process of crystallization, or as special operations under bioseparations.

Fundamental principles that facilitate understanding of a variety of different separations have, however, been emerging in the literature for quite some time. It is useful to structure the learning of separation around these basic principles. Forces present in the separation system act on molecules, macromolecules or particles and make them migrate at different velocities and sometimes in different directions. When such velocities/forces interact with the bulk velocity of the individual phase(s)/region(s) present in the separation system, molecular species or particles follow different trajectories or concentrate in different phase(s)/region(s), leading to separation. This book will systematically develop this overall framework of a few important configurations of bulk flow direction vis-à-vis the direction of the force(s) for open separators. Chemical thermodynamics provides the local boundaries/limits in such configurations for chemical separations. The individual separation processes/techniques will then be illustrated in each such configuration of bulk flow direction vs. force direction in three categories of processes: phase equilibrium driven; external force driven; membrane processes.

These three basic categories of separation processes rely on three different types of separation phenomena. These different types of separation phenomena achieve different extents of separation when coupled with particular configurations of bulk flow vs. force pattern. The description of each process/technique generally includes

its conventional treatment and often elementary process/equipment design considerations.

This illustrative framework is preceded by a few chapters that provide the basic tools for achieving this goal. In earlier literature, a broad category of separation techniques is identified as a mechanical separation process. These techniques are invariably restricted to the separation of particles in a fluid or drops in another fluid subjected generally to an external force. In this book, particle separations have been studied along with chemical separations when a particular external force is considered. Therefore the structure of this book is somewhat different. The following section provides a brief introduction to each chapter in the book.

### Introduction to chapters

What happens to a perfectly mixed binary mixture of two species in a closed vessel as separation takes place is introduced in Chapter 1. How one describes the extent of separation achieved in the closed vessel is illustrated via a few common separation indices. The separation indices are based on the notion of different species-specific regions in the separation system, and their differing compositions and capacities. Double subscript based notation, with the first subscript  $i$  referring to a component and the second subscript  $j$  referring to a region/phase/fraction, is introduced here. This notation has been used throughout the book as often as possible. Use of these separation indices is illustrated for three basic classes of separation systems without any particles: immiscible phases; membrane-containing systems; and systems having the same phase throughout the separation system. A description of separation in multicomponent systems has been included along with the notion of a separating agent required for separation.

Chapter 2 presents the description of quantities needed to quantify separation in open systems with flow(s) in and out of single-entry and double-entry separators for binary, multicomponent and continuous chemical mixtures, as well as a size-distributed particle population. Separation indices useful for describing separation in open systems with or without recycle or reflux are illustrated for steady state operation (Sections 2.2 and 2.3); those for a particle population are provided in Section 2.4. At the end (Section 2.5), indices for description of separation in time-dependent systems, e.g. chromatography, have been introduced.

The physicochemical basis for separation is the primary focus of Chapter 3. Separation happens via species-specific force driven relative displacement of molecules of one species in relation to other species into species-specific region in the separation system. Particles of different sizes/properties similarly undergo relative displacements. To develop this perspective, Chapter 3 (Section 3.1) identifies various external forces and chemical potential gradient based

force generating different migration/terminal velocities and fluxes for chemical species and particles. Integrated flux expressions for molecular diffusion and convection for single-phase systems, mass-transfer coefficients and empirical correlations for mass-transfer coefficients are introduced. Chapter 3 (Section 3.2) further points out the role of the spatial profile of the potential attributable to the force in developing a multicomponent separation capability. The criteria for achieving equilibrium between different phases and regions in the separation system with or without an external force and various types of phase equilibria are discussed in Section 3.3. The presentation of the partitioning of a species between two phases is at a phenomenological level. The molecular basis of this partitioning via intermolecular interactions has not been considered. This is followed by species flux expressions in interphase transport, including membrane transport (Section 3.4). The notion of an overall mass-transfer coefficient and its relation to single-phase mass-transfer coefficients are introduced here.

Chapter 4 provides a quantitative exposition of how much separation is achieved at equilibrium in a closed vessel for three broad classes of separation systems: phase equilibrium between two phases (Section 4.1); single phase or a particle suspension in an external force field (Section 4.2); two regions separated by a membrane (Section 4.3). The phase equilibrium systems considered are: gas-liquid, vapor-liquid, liquid-liquid, liquid-solid, interfacial adsorption systems, liquid-ion exchanger and the supercritical fluid-solid/liquid phase. The external force fields and configurations studied are: centrifuges, isopycnic sedimentation, isoelectric focusing, gravity (sedimentation, inclined settlers), acoustic forces and thermal diffusion. In the case of a membrane based system of dialysis and gas permeation if separation is to be achieved, we come across the need for an open system. Chapter 5 focuses on the beneficial effects of chemical reactions in phase equilibrium and membrane based separation systems. A few common types of reactions, such as ionizations, acid-base reactions and different types of complexation equilibria, are found to influence strongly the separation achieved across the whole spectrum of separations involving molecules and macromolecules. The phase equilibrium systems studied are: gas-liquid, vapor-liquid, liquid-liquid, liquid-solid, surface adsorption and Donnan equilibrium. Reaction based enhancement in the rates of interphase transport as well as membrane transport has been illustrated for a variety of systems.

Separation is most often implemented in open systems/devices with bulk flow(s) in and out. The treatment of separation achieved in such separators is carried out in Chapters 6, 7 and 8. Chapter 6 begins with the sources and the nature of bulk flow in separation systems in a multiscale context as well as the feed introduction mode vis-à-vis time (Section 6.1). The various equations of change for species concentration in a mixture, the equation of motion of a particle in a fluid and the general

equation of change for a particle population, including that in a continuous stirred tank separator, are provided in Section 6.2. Section 6.3 covers the separation processes/techniques in which the direction of the bulk flow is parallel to the direction of the force(s). Figure 6.3.1 illustrates the widespread use of this flow vs. force configuration for three basic classes of separation systems. External force based processes of elutriation, capillary electrophoresis, centrifugal elutriation, inertial impaction and electrostatic separation of fine particles are introduced first. Chemical potential gradient driven processes of flash/vaporization/devolatilization, batch distillation, liquid-liquid extraction, zone melting, normal freezing and drying are studied next. The membrane based processes covered are: cake filtration/microfiltration, ultrafiltration, reverse osmosis, pervaporation and gas permeation. In the final section (Section 6.4), Chapter 6 considers the continuous stirred tank separator (CSTS) as a special category of bulk flow vs. force configurations; the separation processes studied are: crystallization (precipitation), solvent extraction, ultrafiltration and gas permeation.

The nature and extent of separation achieved when the direction of flow of the feed-containing fluid phase is perpendicular to the direction of the force(s) are studied in Chapter 7. This treatment illustrates the basic separation mechanism clearly, even though the particulars vary widely, as in, for example, free-flow electrophoresis, electrostatic precipitators, electrostatic separation of plastic mixtures, laser excitation of isotopes and flow cytometry (all of them driven by an electrical force field perpendicular to the bulk flow). Figure 7.0.1 provides this broad perspective across all three classes of separation processes: phase equilibrium driven, membrane based, external force driven. This chapter begins (Section 7.1) with the treatment of fixed-bed adsorption processes, pressure-swing adsorption, parametric pumping and chromatography. Crossflow membrane processes considered next (Section 7.2) are: gas permeation, reverse osmosis, ultrafiltration, microfiltration; this has been followed by granular filtration. The external force field based processes studied in Section 7.3 involve electrical force (mentioned earlier), centrifugal force (centrifuges, cyclones), gravity (gravity based settlers), magnetic force field (high-gradient magnetic separation) and optical force. Field-flow fractionation as a special case of a force perpendicular to bulk flow interacting with the velocity profile in a novel way has also been treated; a variety of forces may be used.

Chapter 8 deals with the configuration of bulk flows of two phases/regions (one of which may be solid) perpendicular to the direction of force(s). The directions of motion of the two phases may be parallel to each other in either countercurrent or cocurrent fashion, or they may be in crossflow. Figures 8.1.1–8.1.4 illustrate the countercurrent flow vs. force configuration for all three classes of separation systems. Conventional countercurrent devices/processes of gas absorption/stripping, column distillation

with a condenser and reboiler, solvent extraction in columns, melt crystallization, adsorption and simulated moving beds, dialysis and electrodialysis, liquid membrane separation, gas permeation, gas centrifuge, thermal diffusion and mass (sweep) diffusion are studied in Section 8.1. How cocurrent flow of the two phases/flows changes the separation achieved is considered vis-à-vis a few systems in Section 8.2. Local multicomponent feed injection in a crossflow format in fluid-solid systems leads to the achievement of continuous chromatography. Overall crossflow of two phases is exemplified by a crossflow distillation plate (Section 8.3).

Although countercurrent multistaged processes of distillation, gas absorption, solvent extraction, etc. have been studied in some detail in Chapter 8, the subject of multistaging/cascades is considered briefly in Chapter 9. Ideal cascades and constant or variable cross-sectional area are introduced, as are cascades of multistage columns for non-binary systems. Chapter 10 describes at an elementary level the minimum energy required for separation by different separation processes. Additional topics discussed in Chapter 10 include the consideration of various concepts that reduce the energy required for separation, recovering the free energy of mixing via a dialytic battery and additional deliberations for treating dilute solutions in the context of bioseparations. In many real-life applications, sequences of different separation processes are employed with and without reaction processes. Chapter 11 illustrates such sequences of separation processes for bioseparations, water treatment, chemical and petrochemical industries and hydrometallurgical separations.

Each of these chapters provides a particular aspect/perspective of the broad subject of separations. One is often interested, however, in a particular separation process/technique in all of its aspects, beginning with the basic concept and ending with devices designed to implement the separation. Tables are therefore provided at the end of this chapter that identify the essential and important components located in different chapters for a given separation process. Obviously it is not possible to provide a comprehensive treatment of every process, and a few commonly used separation processes have received much more attention than others. However, the treatment of each such commonly used separation process is at a level illustrative of the basic principles relevant to the particular chapter. Furthermore, the treatments are not exhaustive. Readers interested in greater detail are encouraged to go to major texts on such separation processes identified along with their treatments.

### Linked footprints of a separation process/technique

We provide in this section seven tables; they appear at the end of this chapter. Each table has nine columns. The first column identifies the name of a particular separation

process in a particular row (e.g. 'Absorption' in row 1 of Table 1). The second column focuses on Chapters 1 and 2. Six more columns are identified progressively with each of the Chapters 3–8. The final ninth column covers the much smaller Chapters 9–11. Each row in the tables is dedicated to a particular separation process. The entry in a box for a given row and a given column identifies sections in the chapter where that particular separation process or fundamental material needed to understand the transport and thermodynamics for that process has been presented. In Chapters 1 and 2 and in Sections 3.1, 3.2, 3.3.1–3.3.6, 6.1 and 6.2, general features or fundamental relations valid for a variety of separation processes are presented. Therefore, entries for a given separation process under columns 2, 3 and 6, specifically Sections 3.1, 3.2, 3.3.1–3.3.6, 6.1 and 6.2, providing fundamental information on the description of separation species/particle transport, thermodynamics relations, balance/conservation equations and equations of change, respectively, for species/particles are not tied in general specifically to that separation process; however, any entry will be useful for understanding that separation process.

Table 1 covers many of the common phase equilibrium based separation processes. The entries contain a few separation techniques/processes which are not employed on a large scale or illustrate important conceptual developments, e.g. cycling zone adsorption, foam fractionation, parametric pumping. Table 2 includes membrane separation processes, where different membrane transport rates of different species provide the selectivity in open systems. This table also includes membrane contactor based separation processes, where the basis for separation is the partitioning equilibrium between two fluid phases contacting each other at membrane pore mouths. Tables 3 and 4 identify separation processes driven by centrifugal force and electrical force, respectively. Table 5 is devoted to a few processes driven by magnetic force or gravity. A few separation processes/techniques driven by other forces, such as acoustic force, radiation pressure, inertial force and thermal gradient driven force, are listed in Table 6. Table 7 is devoted to additional separation processes such as field-flow fractionation and mass (sweep) diffusion.

It is useful now to illustrate how the descriptive treatment of a particular separation process, e.g. distillation, has been implemented in an evolutionary fashion via the different chapters as identified in row 7 of Table 1. In Section 1.1, Example I of Figure 1.1.2 illustrates the result of heat addition to an equimolar liquid mixture of benzene–toluene: a benzene-rich vapor phase and a toluene-rich liquid phase. Using definitions of compositions etc. introduced in Section 1.3, separation indices such as the separation factor  $\alpha_{ij}$  (also the equilibrium ratio  $K_i$ ) describe the separation achieved in a closed vessel for the benzene–toluene system and a methanol–water system for various liquid-phase compositions. Section 1.5 illustrates via Example 1.5.1 and the values of various separation indices,  $\alpha_{12}$  and  $\xi$ , the

separation achieved in the benzene–toluene system in a closed vessel. Section 1.6 describes multicomponent mixtures and develops the relations between the compositions of two phases in equilibrium, a result useful for distillation in later chapters.

Section 2.1 introduces various quantities describing flow rates and compositions in an open system; a sieve plate in a distillation column is used as one example, among others, of a double-entry separator. A flash distillation stage with liquid fraction recycle illustrates recycle in a single-entry separator (Section 2.2). Section 2.3 for double-entry separators provides a numerical example of benzene–toluene distillation in a countercurrent column without a condenser or reboiler. This and other examples provide a quantitative background on the separation achieved in a given device without discussing the separation mechanism. The same strategy of description of separation achieved via reflux to a column is pursued in this section to demonstrate that a higher reflux ratio leads to higher separation. Sections 2.4.2 and 2.4.3 introduce indices to describe continuous chemical mixtures and multicomponent mixtures vis-à-vis flash vaporization.

The introductory Section 3.1.2.5 in Chapter 3 identifies the negative chemical potential gradient as the driver of targeted separation, and the relevant species flux expression is developed in Section 3.1.3.2 (see Example 3.1.9 also). Section 3.1.4 introduces molecular diffusion and convection and basic mass-transfer coefficient based flux expressions essential to studies of distillation and other phase equilibrium based separation processes. Section 3.1-5.1 introduces the Maxwell–Stefan equations forming the basis of the rate based approach of analyzing distillation column operation. After these fundamental transport considerations (which are also valid for other phase equilibrium based separation processes), we encounter Section 3.3.1, where the equality of chemical potential of a species in all phases at equilibrium is illustrated as the thermodynamic basis for phase equilibrium (i.e.  $\mu_w = \mu_{il}$ ). Direct treatment of distillation then begins in Section 3.3.7.1, where Raoult's law is introduced. It is followed by Section 3.4.1.1, where individual phase based mass-transfer coefficients are related to an overall mass-transfer coefficient based on either the vapor or liquid phase.

Section 4.1 via Section 4.1.2 formally illustrates vapor–liquid equilibria vis-à-vis distillation in a closed vessel along with bubble-point and dew-point calculations for multicomponent systems. How vapor–liquid equilibrium is influenced by chemical reactions in the liquid phase is treated in Section 5.2.1.2, where two subsections, 5.2.1.2.1 and 5.2.1.2.2, deal with reactions influencing vapor–liquid equilibria in isotopic systems. We next encounter open systems in Chapter 6. The equations of change for any two-phase system (e.g. a vapor–liquid system) are provided in Section 6.2.1.1 based on the pseudo-continuum approach for the dependences of species concentrations

on time and the main axial coordinate (i.e.  $z$ ) direction. Section 6.3.2.1 starts with the simplest of open systems, a flash vaporizer, and illustrates isothermal flash calculations under the constraint of phase equilibrium and bulk flow parallel to (||) the force direction for multicomponent systems and continuous chemical mixtures. Batch distillation without any reflux is then studied as a particular illustration of this flow vs. force configuration for a fixed amount of feed liquid as well as for constant-level batch distillation employed for solvent exchange. Residue curves are introduced here.

Column distillation is the most common form of an open separation system in distillation. Here the two phases have, on an overall basis, bulk motions in parallel flow in the countercurrent direction with the forces causing separation being perpendicular ( $\perp$ ) to the directions of bulk flows. The general characteristics of such a separation system are briefly identified in Section 8.1.1, specifically 8.1.1.1–8.1.1.3. We learn the structural consequences of this flow vs. force configuration, namely a distillation column cannot at steady state separate a ternary mixture; we need two columns for a ternary mixture. Further, the particular forms of equations of change for the two phases are obtained from the more general equations in Section 6.2.1.1 (as well as by a control volume analysis). Distillation columns with reflux and recycle are studied in detail in various parts of Section 8.1.3. The conventional approach of assuming ideal equilibrium stages (the stage may have crossflow in an overall countercurrent flow configuration) is adopted in the McCabe–Thiele graphical framework to study the following: operating lines in both sections of a column,  $q$ -line, total reflux, minimum reflux, partial/total reboiler, partial condenser, open steam introduction, Kremser equation and side stream.

The deviation from ideal equilibrium stages is studied next via stage efficiency in Section 8.1.3.4. Vapor–liquid contacting on a plate/tray in a column is considered in Section 8.1.3.5 vis-à-vis estimation of column diameter (with reference to Section 6.3.2.1). Topics such as the rate based approach for modeling distillation and separation of a multicomponent mixture in a column are briefly introduced, the latter via the Fenske equation, the Underwood equation and the Gilliland correlation. Distillation in a packed tower and in a batch vessel with reflux are studied next. Section 8.2.1 briefly touches on distillation in a cocurrent two-phase flow device. Section 8.3.2 studies separation in a crossflow distillation plate employing general equations from Section 6.2.1.1, ultimately yielding the American Institute of Chemical Engineers (AIChE) tray efficiency expression. The total number of worked examples involving distillation in one form or another in Chapters 1–8 is 19. Various other aspects of distillation are considered further in Chapters 9–11. Chapter 9 (Section 9.2) introduces briefly the methodology for multicolumn distillation for separating a mixture containing more than two species. Chapter 10

covers the minimum energy required for distillation, and the concepts of net work consumption, multieffect distillation and heat pump vis-à-vis distillation. Chapter 11.3 introduces very briefly the important role of distillation in the chemical and petrochemical industries.

If the treatment of distillation in a given section of the book needs certain building blocks, it is most likely that those concepts/methods/building blocks have been introduced in an earlier chapter or section of the book. Furthermore, in whichever section distillation appears, it is studied as part of a specific pattern followed by many other separation processes based on phase equilibrium. Such patterns have been emphasized often throughout particular chapters.

A few pointers on phase equilibrium based separation processes are useful. Table 3.3.1 lists possible useful combinations of two bulk immiscible phases for separation such as gas–liquid (vapor–liquid included), gas–solid, liquid–liquid, etc. Quite a few of these combinations form the basis of existing separation processes. In this book, therefore, each chapter, from Section 3.3 onwards, focusing on a particular aspect of the subject of separation, has the subject of phase equilibrium driven separation processes organized along such two immiscible phase combinations. However, all such combinations in practical use do not appear in each chapter.

The treatment of membrane separation processes in this book merits some deliberation. The most commonly used driving force in membrane separation processes is negative chemical potential gradient; a few processes also employ electrical force. Figure 3.4.5 identifies the variety of feed phase–membrane type combinations with variations due to the nature of the permeate phase when negative chemical potential gradient is imposed across the membrane. Section 3.4.2 illustrates the interphase membrane transport aspects of many such configurations. The developments in later chapters follow these feed phase–membrane type permeate phase combinations as often as possible, subject to space limitations. Electrodialysis as an example of an application of electrical force appears in Sections 3.4.2 and 8.1.7. Membrane contactors appear with their phase equilibrium process counterparts in Sections 8.1.2 and 8.1.4, whereas the basic transport considerations in such membrane devices appear much earlier in Sections 3.4.3.1 and 3.4.3.2. A most important item in membrane separation processes is that such devices in the absence of external forces achieve separation when operated as an open system – Sections 4.3.1 and 4.3.3 demonstrate this feature via the processes of dialysis and gas permeation.

The descriptive treatment of the membrane process of reverse osmosis (RO) in the book as identified in Table 2 will be briefly illustrated here. Section 1.1 identifies the basic configuration of RO in Figure 1.1.3. Example 1.5.4 illustrates calculations of separation indices describing separation in RO shown in Figure 1.5.1. Sections 2.1 and 2.2 describe various quantities, as well as the separation indices relevant

for RO; Example 2.2.1(c) is directly applicable to RO. Sections 3.1.2.5, 3.1.3.2 and 3.1.5.1 provide a general transport background. Section 3.1.5.2 is directly relevant to an irreversible thermodynamics based solute and solvent transport through RO membranes. Section 3.3.7.4 provides a membrane-liquid equilibrium relation from an osmotic equilibrium point of view. Section 3.4.2.1 formally introduces transport rates in RO membranes and flux expressions, along with issues of concentration polarization in a feed solution. A closed vessel of Chapter 4 has very limited relevance for RO (Section 4.3.4). Sections 5.4.1 and 5.4.1.1 describe how chemical reactions, such as ionization, in the solutions influence separation in RO processes.

Section 6.3.3.3 studies RO in bulk flow parallel to the force configuration and describes various membrane transport considerations and flux expressions. Practical RO membranes are employed in devices with bulk feed flow perpendicular to the force configuration, as illustrated in Section 7.2.1.2. A simplified solution for a spiral-wound RO membrane is developed: analytical expressions for the water flux as well as for salt rejection are obtained and illustrated through example problem solving. A total of six worked example problems have been provided up to Chapter 7. Chapter 9 (Figure 9.1.5) shows a RO cascade in a tapered configuration. Section 10.1.2 calculates the minimum energy required in reverse osmosis based desalination and compares it with that in evaporation. Section 11.2 covers the sequence of separation steps in a water treatment process for both desalination and ultrapure water production. The very important role played by RO in such plants is clearly illustrated.

The evolution of separation through different chapters due to an external force needs some discussion as well. Whereas negative chemical potential gradient driven distillation is utilized to separate low molecular weight liquids having different volatilities, an external force, such as electrical force arising from a negative gradient of electrical potential, can be used to separate small charged molecules, charged macromolecules, charged cells, charged particles, etc.; the medium may be liquid or gaseous. The canvas is large, and the variety of separation processes/techniques driven by electrical force is significant. Although there is considerable variety also in phase equilibrium processes resulting from a variety of two-phase systems, the separation systems are more often limited to smaller molecules. Separation of proteins/macromolecules via chromatography (Section 7.1.5.1) and biphasic/reverse micellar extraction (Sections 4.1.4 and 4.1.8) provide exceptions; flotation (Section 3.3.8) separates particles with the helping hand of an external force, gravity, as does a Venturi scrubber (Section 8.2.3) via inertial impaction.

Consider the electrophoretic motion of charged molecules/macromolecules/proteins in an aqueous solution/buffer subjected to an electrical force. Three separation techniques, isoelectric focusing, capillary electrophoresis

and continuous free-flow electrophoresis, exploit, among others, electrophoretic transport under the constraints of a closed vessel, bulk flow parallel to force and bulk flow perpendicular to force, respectively. Correspondingly, in Table 4, isoelectric focusing does not appear in Chapters 6–8; capillary electrophoresis is absent from Chapter 8. However, each such technique benefits from relevant discussions in earlier chapters, even though the technique itself is treated in detail in a later chapter; therefore materials in Chapters 2 and (especially) Chapter 3 are identified for each of the three techniques. Capillary electrophoresis appears also in Section 7.1.7.1, where it has been coupled with chromatography where the bulk flow is perpendicular to the force.

### Classification of separation processes

This book has not adopted a comprehensive classification scheme for all separation processes. Readers should go to the references, especially Figure 30 and Table 7 of Lee *et al.* (1977a) and Table 1-1 of King (1980), to that end. What has been adopted here is apparent from the titles of Tables 1–7. Separation processes are classified into three categories based on the three basic types of physicochemical phenomena: (1) phase equilibrium based separation processes; (2) membrane separation processes; (3) external force based separation processes. There are a few processes where there is an overlap. For example, electrodialysis is a membrane-separation process driven primarily by an external force, the electrical potential gradient; most membrane-separation processes are driven by negative chemical potential gradient. There are a few others, e.g. mass diffusion/sweep diffusion, which cannot be neatly put into these three categories; they possess characteristics of different categories.

In this framework of three broad categories of separation processes, further separation development/classification comes about due to the nature of the interaction between the basic separation phenomena in each category and the directions of bulk flow vis-à-vis the direction of force(s) responsible for the basic separation mechanism. Considerable additional separation development is achieved by reflux, recycle, creation of an additional property gradient in an external force field, mode of feed introduction, etc. These aspects have been addressed in the following sections: reflux (Sections 2.3.2, 8.1.1, 8.1.4, 10.1.4.2, 10.2.2.1); recycle (Sections 2.2.2, 2.4.1, 7.2.1.1, 7.2.4, 8.1.1); development of an additional property gradient in an external force field (Sections 4.2.1.3, 4.2.2.1, 4.2.3.3, 7.1.7); mode of feed introduction (Sections 6.1.9, 7.1.5, 7.1.6, 8.1.1, 8.2.2.1, 8.2.2.2, 8.3.1).

An additional classification approach considers the nature of the mixture to be separated: mixtures of small molecules and/or ions in solution or gas phase; mixtures of

macromolecules in solution; mixtures of particles, where particles in this book include biological cells (Tables 4.2.1, 7.3.1), cell debris, colloidal material and inorganic and organic particles of varying dimensions (submicron to visible particles, Figure 2.4.1(b)). Of the numerous separation techniques involving different types of macromolecules, the following have received some attention here: separation of proteins from each other/one another or solvent via isoelectric focusing, etc. (Sections 4.2.2.1, 4.2.2.2), ultrafiltration (Sections 6.3.3.2, 6.4.2.1, 7.2.1.3), chromatography (Sections 4.1.6, 4.1.9.4, 7.1.5.1.6, 7.1.5.1.7, 7.1.5.1.8, 7.1.6, 7.1.7), electrophoresis (Section 7.3.1.1), field-flow fractionation (Section 7.3.4), aqueous biphasic extraction (Section 4.1.3) and reverse micelles (Section 4.1.9); separation of nonbiological macromolecules via size exclusion chromatography (Section 7.1.5.1.7), flash devolatilization (Section 6.3.2.1), sol-gel separation (Section 2.4.2); DNA separation via isopycnic sedimentation (Section 4.2.1.3).

It is useful to provide a list of the basic physical or physicochemical properties, each of which could be a basis for separation; it is also useful to list simultaneously the core phenomenon exploiting such a physical or physicochemical property for separation. It is to be noted that this list is not exhaustive; rather, it contains the more familiar properties. Table 8 identifies a variety of these basic properties and lists phenomena employing a particular basic property leading to separation. For each basic property and phenomenon in this table, there are three columns corresponding to three different types of basic separation processes: phase-equilibrium-based separation processes; membrane-separation processes; and external force based separation processes. An entry into these three columns identifies a separation process or processes where the particular basic property is key to separation. References to Tables 1–7, a section in the book or a separate reference have been provided to each entry in these three columns.

There are some items of interest here. A few basic properties are the basis for separation in two different types of basic separation processes. For example, condensability of a vapor/gas species is useful for vapor absorption as well as for membrane gas separation; geometrical partitioning (or partitioning by other means between a pore and an external solution) is useful both in adsorption/chromatography as well as in the membrane processes of dialysis and ultrafiltration, etc. Further, there are many cases where chemical reactions are extraordinarily useful for separation; these are not identified here since chemical reactions can enhance separation only if the basic mechanism for separation exists, especially in phase equilibrium based separations. However, there are a few cases where chemical reactions, especially complexations, provide the fundamental basis for separation, as in affinity chromatography, metal extractions and isotope exchange reactions.

### Additional comments on using the book

This book has 118 separate numerical examples spread over Chapters 1–4 and 6–9. The numerical examples are not in finer print. Chapter 5 has sometimes employed numerical calculations to illustrate the effect of chemical reactions on separations without formal numerical examples. Chapter 10 follows this strategy as well to illustrate the amount of energy required for a particular separation. The total number of problems provided at the ends of all the chapters is 299. The specific separation process relevant for the problem is generally obvious from the introductory sentence in the problem. Further, the sequence of appearance of a problem on a given separation process reflects/follows the sequences of appearance of that separation process in the text.

Footnotes have been employed occasionally. All references used appear at one location in alphabetical order at the end of the book. The symbols and notation employed throughout the book are consistent; any local deviation has been identified. In a few locations, advanced material or additional information has been provided.

### Textbooks, handbooks and major references on separation processes

There is an extraordinarily rich literature on separations. This book has freely drawn material from this literature consisting of textbooks, monographs or extended chapters in multiauthor edited volumes apart from numerous journal articles. Here we list these books and chapters (but no journal articles) under the following categories: separations; chemical separations; bioseparations; membrane separations; particle separations; other books. Such books and relevant journal articles have been cited through each section in each chapter. Occasionally some comments have been attached here to a given reference. Books devoted solely to a given separation process/technique are not, in general, mentioned below. The following list is given in *chronological* order. At the end of each reference, its formal reference has been identified.

#### Separations

- (1) Karger, B.L., L.R. Snyder and C. Horvath, *An Introduction to Separation Science*, Wiley, New York (1973). Chapter 18 devotes ~19 pages to particle separation; otherwise it covers primarily separations of chemicals and macromolecules. (Karger *et al.*, 1973.)
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Table 1. Relevant sections for each phase equilibrium based separation process

	Chapters 1 & 2 Describe separation	Chapter 3 Basis for separation	Chapter 4 Separation in a closed vessel	Chapter 5 Effect of chemical reaction	Chapter 6 Bulk flow    to force(s) and CSTS	Chapter 7 Bulk flow ⊥ to force(s)	Chapter 8 Bulk flow of two phases ⊥ to force(s)	Chapters 9, 10 & 11 Other aspects
Absorption (and stripping)	1.1-1.4, 2.1, 2.3	3.3.7.1, <sup>a</sup> 3.4.1.1, 3.4.3.1	4.1, 4.1.1.1	5.1, 5.2.1.1, 5.3.1	6.2.1.1	7.1.2.1	8.1.1, 8.1.1.1- 8.1.1.3, 8.1.2, 8.2.1.1, 8.2.2.2	
Adsorption (& simulated moving beds)	1.1-1.4, 2.1, 2.5	3.1.3.2.3, 3.1.3.2.4, <sup>b</sup> 3.3.5, 3.3.7.4, 3.3.7.6, 3.4.1.4	4.1, 4.1.5	5.2.3.2	6.2.1.1	7.1.1-7.1.7.1	8.1.1, 8.1.1.1- 8.1.1.3, 8.1.6	10.1.4.4
Chromatography <sup>c</sup>	1.1-1.4, 2.1, 2.5	3.1.3.2.3, 3.1.3.2.4, 3.2.1, 3.2.2, 3.3.7.4, 3.3.7.6, 3.4.1.4, 3.4.1.5	4.1.3, 4.1.5- 4.1.8, 4.1.9.1	5.2.3.2	6.2.1.1	7.1.1.1, 7.1.5- 7.1.7.1	8.2.2, 8.3.1	11.1
Crystallization <sup>d</sup>	1.1-1.4, 2.1, 2.4.1	3.3.1, 3.3.7.5, 3.4.1.3	4.1.4, 4.1.9.1	5.2.4	6.2.3, 6.4.1.1		8.1.1, 8.1.1.1- 8.1.1.3, 8.1.5	9.1.2.2, 9.1.2.3
Cycling zone <sup>e</sup> adsorption						7.1.4.4		
Devolatization								
Distillation	1.1-1.7, 2.1-2.3, 2.4.2, 2.4.3	3.1.5.1, <sup>a</sup> 3.3.7.1, 3.4.1.1, 3.4.3.1	4.1, 4.1.2 4.1, 4.1.2	5.2.1.2	6.3.2.1 6.2.1.1, 6.3.2.1		8.1.1, 8.1.1.1- 8.1.1.3, 8.1.3, 8.2.1, 8.3.2	10.1.1, 10.1.3, <sup>f</sup> 10.1.4.2, 10.2.1.1, 10.2.1.2, 10.2.1.3, 10.2.2
Drying (and freeze-drying)	1.1-1.4 1.1-1.4, 2.2, Ex. 2.2.2	3.1.4, 3.3.7.5			6.1.4, 6.3.2.4			11.1 10.1.1, 10.2.1
Evaporation								
Extraction	1.1-1.6, 2.1, 2.3	3.2.2, 3.3.7.2, 3.3.7.9, 3.4.1.2, 3.4.3.2	4.1.3, 4.1.7, 4.1.8	5.2.2, 5.3.2	6.2.1.1, 6.3.2.2, 6.4.1.2		8.1.1, 8.1.1.1- 8.1.1.3, 8.1.4	10.1.4.3, 11.4
Flotation		3.3.8						
Foam fractionation	Prob. 2.2.4	3.3.5, 3.3.7.6	4.1.5	5.2.5				
Ion exchange	1.1-1.4, 2.1, 2.5	3.1.3.2, 3.3.7.7, 3.4.1.5, 3.4.2.5	4.1.6	5.2.3.2		7.1.1.4, 7.1.5.1.6	8.1.1, 8.1.6	11.2
Leaching		3.3-7.4	4.1.4					
Melt crystallization	1.1-1.4, 2.1, 2.4.1	3.3.7.5	4.1.4 4.1.4		6.2.1, 6.3.2.3		8.1.1, 8.1.5	
Normal freezing	1.1-1.4, 2.1	3.3.7.5	4.1.4		6.3.2.3			
Parametric pumping (see adsorption)	1.1-1.4, 2.1, 2.5	3.3.7.4, 3.3.7.6, 3.4.1.4	4.1.5		6.2.1.1	7.1.4, 7.1.4.1, 7.1.4.2, 7.1.4.3		