1.1 IMPORTANCE OF SEPARATIONS

Why does chemical engineering require the study of separation techniques? Because separations are crucial in chemical engineering. A typical chemical plant is a chemical reactor surrounded by separators, as diagramed in the schematic flow sheet of Figure 1-1. Raw materials are prepurified in separation devices and fed to the chemical reactor; unreacted feed is separated from the reaction products and recycled back to the reactor. Products must be further separated and purified before they can be sold. This type of arrangement is very common. Examples for a variety of traditional processes are illustrated by Couper et al. (2005), Shreve and Austin (1984), Matar and Hatch (2001), Turton et al. (2003), Chenier (2002), and Speight (2002), whereas recent processes often are shown in Chemical Engineering magazine. Chemical plants commonly have from 40% to 70% of both capital and operating costs in separations (Humphrey and Keller, 1997).

Since separations are ubiquitous in chemical plants and petroleum refineries, chemical engineers must be familiar with a variety of separation methods. We will first focus on some of the most common chemical engineering separation methods: flash distillation, continuous column distillation, batch distillation, absorption, stripping, and extraction. These separations all contact two phases and can be designed and analyzed as equilibrium stage processes. Several other separation methods that can also be considered equilibrium stage processes will be briefly discussed. Chapters 16 and 17 explore two important separations—membrane separators and adsorption processes—that do not operate as equilibrium stage systems.

The equilibrium stage concept is applicable when the process can be constructed as a series of discrete stages in which the two phases are contacted and then separated. The two separated phases are assumed to be in equilibrium with each other. For example, in distillation, a vapor and a liquid are commonly contacted on a metal plate with holes in it. Because of the intimate contact between the two phases, solute can transfer from one phase to another. Above the plate the vapor disengages from the liquid. Both liquid and vapor can be sent to additional stages for further separation. Assuming that the stages are equilibrium stages, the engineer can calculate concentrations and temperatures without detailed knowledge of flow
patterns and heat and mass transfer rates. Although this example shows the applicability of the equilibrium stage method for equipment built with a series of discrete stages, we will see that the staged design method can also be used for packed columns where there are no discrete stages. This method is a major simplification in the design and analysis of chemical engineering separations that is used in Chapters 2 to 14.

A second useful concept is that of a unit operation. The idea here is that although the specific design may vary depending on what chemicals are being separated, the basic design principles for a given separation method are always the same. For example, the basic principles of distillation are always the same whether we are separating ethanol from water, separating several hydrocarbons, or separating liquid metals. Consequently, distillation is often called a unit operation, as are absorption, extraction, etc.

A more general idea is that design methods for related unit operations are similar. Since distillation and absorption are both liquid-vapor contacting systems, the design is much the same for both. This similarity is useful because it allows us to apply a very few design tools to a variety of separation methods. We will use stage-by-stage methods where calculation is completed for one stage and then the results are used for calculation of the next stage to develop basic understanding. Matrix solution of the mass and energy balances will be used for detailed computer simulations.

1.2 CONCEPT OF EQUILIBRIUM

The separation processes we are studying in Chapters 1 to 14 are based on the equilibrium stage concept, which states that streams leaving a stage are in equilibrium. What do we mean by equilibrium?

Consider a vapor and a liquid that are in contact with each other as shown in Figure 1-2. Liquid molecules are continually vaporizing, while vapor molecules are continually condensing. If two chemical species are present, they will, in general, condense and vaporize at different rates. When not at equilibrium, the liquid and the vapor can be at different pressures and temperatures and be present in different mole fractions. At equilibrium the temperatures, pressures, and fractions of the two phases cease to change. Although molecules continue to evaporate and condense, the rate at which each species condenses is equal to the rate at which
it evaporates. Although on a molecular scale nothing has stopped, on the macroscopic scale, where we usually observe processes, there are no further changes in temperature, pressure, or composition.

Equilibrium conditions can be conveniently subdivided into thermal, mechanical, and chemical potential equilibrium. In thermal equilibrium, heat transfer stops and the temperatures of the two phases are equal.

\[ T_{\text{liquid}} = T_{\text{vapor}} \quad \text{(at equilibrium)} \]

In mechanical equilibrium, the forces between vapor and liquid balance. In the staged separation processes we will study, this usually implies that the pressures are equal. Thus for the cases in this book,

\[ p_{\text{liquid}} = p_{\text{vapor}} \quad \text{(at equilibrium)} \] (1-2)

If the interface between liquid and vapor is curved, equal forces do not imply equal pressures. In this case the Laplace equation can be derived (e.g., see Levich, 1962).

In phase equilibrium, the rate at which each species is vaporizing is just equal to the rate at which it is condensing. Thus there is no change in composition (mole fraction in Figure 1-2). However, in general, the compositions of liquid and vapor are not equal. If the compositions were equal, no separation could be achieved in any equilibrium process. If temperature and pressure are constant, equal rates of vaporization and condensation require a minimum in the free energy of the system. The resulting condition for phase equilibrium is

\[ (\text{chemical potential } i)_{\text{liquid}} = (\text{chemical potential } i)_{\text{vapor}} \]

(1-3)

The development of Eq. (1-3), including the necessary definitions and concepts, is the subject of a large portion of many books on thermodynamics (e.g., Smith et al., 2005; Balzhiser et al., 1972; Denbigh, 1981; Elliott and Lira, 1999; Walas, 1985) but is beyond the scope of this book. However, Eq. (1-3) does require that there be some relationship between liquid and vapor compositions. In real systems this relationship may be very complex and experimental data may be required. We will assume that the equilibrium data or appropriate

1.2 Concept of Equilibrium
equations are known (see Chapter 2), and we will confine our discussion to the use of the equilibrium data in the design of separation equipment.

1.3 MASS TRANSFER

In the vapor-liquid contacting system shown in Figure 1-2 the vapor and liquid will not be initially at equilibrium. By transferring mass from one phase to the other we can approach equilibrium. The basic mass transfer equation in words is

\[ \text{Mass transfer rate} = (\text{area}) \times (\text{mass transfer coefficient}) \times (\text{driving force}) \] \hspace{1cm} (1-4)

In this equation the mass transfer rate will typically have units such as kmoles/hr or lb moles/hr. The area is the area across which mass transfer occurs in m² or ft². The driving force is the concentration difference that drives the mass transfer. This driving force can be represented as a difference in mole fractions, a difference in partial pressures, a difference in concentrations in kmoles/liter, and so forth. The value and units of the mass transfer coefficient depend upon which driving forces are selected. The details are discussed in Chapter 15.

For equilibrium staged separations we would ideally calculate the mass transfer rate based on the transfer within each phase (vapor and liquid in Figure 1-2) using a driving force that is the concentration difference between the bulk fluid and the concentration at the interface. Since this is difficult, we often make a number of simplifying assumptions (see section 15.1. for details), and use a driving force that is the difference between the actual concentration and the concentration we would have if equilibrium were achieved. For example, for the system shown in Figure 1-2 with concentrations measured in mole fractions, we could use the following rate expressions.

\[ \text{Rate / volume} = K_y a(y_A^* - y_A) \] \hspace{1cm} (1-5a)

\[ \text{Rate / volume} = K_x a(x_A^* - x_A) \] \hspace{1cm} (1-5b)

In these equations \( K_y \) and \( K_x \) are overall gas and liquid mass transfer coefficients, \( y_A^* \) is the mole fraction in the gas in equilibrium with the actual bulk liquid of mole fraction \( x_A \), \( x_A^* \) is the mole fraction in the liquid in equilibrium with the actual bulk gas of mole fraction \( y_A \), and the term “a” is the interfacial area per unit volume (m²/m³ or ft²/ft³).

By definition, at equilibrium we have \( y_A^* = y_A \) and \( x_A^* = x_A \). Note that as \( y_A \rightarrow y_A^* \) and \( x_A \rightarrow x_A^* \) the driving forces in Eqs. (1-5) approach zero and mass transfer rates decrease. In order to be reasonably close to equilibrium, the simplified model represented by Eqs. (1-5) shows that we need high values of \( K_y \) and \( K_x \) and/or “a.” Generally speaking, the mass transfer coefficients will be higher if diffusivities are higher, which occurs with fluids of low viscosity. Since increases in temperature decrease viscosity, increasing temperature is favorable as long as it does not significantly decrease the differences in equilibrium concentrations and the materials are thermally stable. Mass transfer rates will also be increased if there is more interfacial area/volume between the gas and liquid (higher “a”). This can be achieved by having significant interfacial turbulence or by using a packing material with a large surface area (see Chapter 10).
Although some knowledge of what affects mass transfer is useful, we don't need to know the details as long as we are willing to assume we have equilibrium stages. Thus, we will delay discussing the details until we need them (Chapters 15, 16 and 17).

1.4 PROBLEM-SOLVING METHODS

To help develop your problem-solving abilities, an explicit strategy, which is a modification of the strategy developed at McMaster University (Woods et al., 1975), will be used throughout this book. The seven stages of this strategy are:

0. I want to, and I can
1. Define the problem
2. Explore or think about it
3. Plan
4. Do it
5. Check
6. Generalize

Step 0 is a motivation and confidence step. It is a reminder that you got this far in chemical engineering because you can solve problems. The more different problems you solve, the better a problem solver you will become. Remind yourself that you want to learn how to solve chemical engineering problems, and you can do it.

In step 1 you want to define the problem. Make sure that you clearly understand all the words. Draw the system and label its parts. List all the known variables and constraints. Describe what you are asked to do. If you cannot define the problem clearly, you will probably be unable to solve it.

In step 2 you explore and think about the problem. What are you really being asked to do? What basic principles should be applied? Can you find a simple limiting solution that gives you bounds to the actual solution? Is the problem over- or underspecified? Let your mind play with the problem and chew on it, and then go back to step 1 to make sure that you are still looking at the problem in the same way. If not, revise the problem statement and continue. Experienced problem solvers always include an explore step even if they don't explicitly state it.

In step 3 the problem solver plans how to subdivide the problem and decides what parts to attack first. The appropriate theory and principles must be selected and mathematical methods chosen. The problem solver assembles required resources such as data, paper, and calculator. While doing this, new subproblems may arise; you may find there are not enough data to solve the problem. Recycle through the problem-solving sequence to solve these subproblems.

Step 4, do it, is often the first step that inexperienced problem solvers try. In this step the mathematical manipulations are done, the numbers are plugged in, and an answer is generated. If your plan was incomplete, you may be unable to carry out this step. In that case, return to step 2 or step 3, the explore or plan steps, and recycle through the process.

In step 5, check your answer. Is it the right order of magnitude? For instance, commercial distillation columns are neither 12 centimeters nor 12 kilometers high. Does the answer seem reasonable? Have you avoided blunders such as plugging in the wrong number or incorrectly punching the calculator? Is there an alternative solution method that can serve as an inde-
pendent check on the answer? If you find errors or inconsistencies, recycle to the appropriate step and solve the problem again.

The last step, generalize, is important but is usually neglected. In this step you try to learn as much as possible from the problem. What have you learned about the physical situation? Did including a particular phenomenon have an important effect, or could you have ignored it? Generalizing allows you to learn and become a better problem solver.

At first these steps will not “feel” right. You will want to get on with it and start calculating instead of carefully defining the problem and working your way through the procedure. Stick with a systematic approach. It works much better on difficult problems than a “start calculating, maybe something will work” method. The more you use this or any other strategy the more familiar and less artificial it will become.

In this book, example problems are solved using this strategy. To avoid repeating myself I will not list step 0, but it is always there. The other six steps will usually be explicitly listed and developed. On the simpler examples some of the steps may be very short, but they are always present.

I strongly encourage you to use this strategy and write down each step as you do homework problems. In the long run this method will improve your problem-solving ability.

A problem solving strategy is useful, but what do you do when you get stuck? In this case heuristics or rules of thumb are useful. A heuristic is a method that is often helpful, but is not guaranteed to help. A large number of problem solving heuristics have been developed. I have listed ten (Wankat and Oreovicz, 1993) that are often helpful to students.

**Problem Solving Heuristics:**

1. Try solving simplified limiting cases.
2. Relate the problem to one you know how to solve. This heuristic encapsulates one of the major reasons for doing homework.
3. Generalize the problem.
4. Try putting in specific numbers. Heuristics 3 and 4 are the opposite of each other. Sometimes it is easier to see a solution path without all the details, and sometimes the details help.
5. Solve for ratios. Often problems can be solved for ratios, but there is not enough information to solve for individual values.
6. Do the solvable parts of the problem. This approach may provide information that allows you to solve previously unsolvable parts.
7. Look for information that you haven’t used.
8. Try guess and check. If you have a strong hunch, this may lead to an answer, but you must check your guess.
9. Take a break. Don’t quit, but do something else for a while. Coming back to the problem may help you see a solution path.
10. Ask someone for a little help. Then complete the problem on your own.

Ten heuristics is probably too many to use on a regular basis. Select four or five that fit you, and make them a regular part of your problem solving method. If you want to read more about problem solving and heuristics I recommend *How to Model It: Problem Solving for the Computer Age* (Starfield *et al.*, 1994).
1.5 PREREQUISITE MATERIAL

No engineering book exists in a vacuum, and some preparatory material is always required. The first prerequisite, which is often overlooked, is that you must be able to read well. If you don't read well, get help immediately.

A second set of prerequisites involves certain mathematical abilities. You need to be comfortable with algebra and the manipulation of equations, as these skills are used throughout the text. Another required mathematical skill is graphical analysis, since many of the design methods are graphical methods. You need to be competent and to feel comfortable plotting curves and straight lines and solving simultaneous algebraic equations graphically. Familiarity with exponential and logarithmic manipulations is required for Chapter 7. The only chapters requiring calculus are Chapters 9, 15, 16, and 17.

The third area of prerequisites concerns mass balances, energy balances, and phase equilibria. Although the basics of mass and energy balances can be learned in a very short time, facility with their use requires practice. Thus, this book will normally be preceded by a course on mass and energy balances. A knowledge of the basic ideas of phase equilibrium, including the concept of equilibrium, Gibb's phase rule, distribution coefficients, familiarity with graphical representations of equilibrium data, and a working knowledge of vapor-liquid equilibrium (VLE) correlations will be helpful.

A fourth area of prerequisites is problem-solving skills. Because the chemical engineer must be a good problem solver, it is important to develop skills in this area. The ability to solve problems is a prerequisite for all chemical engineering courses.

In general, later chapters depend upon the earlier chapters, as shown schematically in Figure 1-3. Chapters 3, 11, 14, 15, 16, and 17 are not required for the understanding of later
chapters and can be skipped if time is short. Figure 1-3 should be useful in planning the order in which to cover topics and for adapting this book for special purposes.

1.6 OTHER RESOURCES ON SEPARATION PROCESS ENGINEERING

Since students have different learning styles, you need to customize the way you use this book to adapt to your learning style. Of course, you will have to take charge of your learning and do this for yourself. If you are interested in exploring your learning style, a good place to start is the Index of Learning Styles, which was developed by Richard M. Felder and Linda K. Silverman. This index is available free on the Internet at www.ncsu.edu/felder-public/ILSpage.html. Alternately, you may search on the term “Felder” using a search engine such as Google.

Since students (and professors) have different learning styles, no single approach to teaching or writing a book can be best for all students. Thus, there will undoubtedly be parts of this book that do not make sense to you. Many students use other students, then the teaching assistant, and finally the professor as resources. Fortunately, a number of good textbooks and Web pages exist that can be helpful since their presentations will differ from those in this textbook. Table 1-1 presents a short annotated bibliography of some of the available handbook and textbook resources. A large number of useful Web sites are available but will not be listed since URLs change rapidly. They can be accessed by searching on the term “separation processes” using any one of the popular search engines.

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<th>Table 1-1. Annotated bibliography of resources on separation process engineering</th>
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1.7 SUMMARY—OBJECTIVES

We have explored some of the reasons for studying separations and some of the methods we will use. At this point you should be able to satisfy the following objectives:

1. Explain how separations are used in a typical chemical plant
2. Define the concepts of equilibrium stages and unit operations
3. Explain what is meant by phase equilibrium
4. List the steps in the structured problem-solving approach and start to use this approach
5. Have some familiarity with the prerequisites

Note: In later chapters you may want to turn to the Summary—Objectives section first to help you see where you are going. Then when you’ve finished the chapter, the Summary—Objectives section can help you decide if you got there.

REFERENCES


References


**HOMEWORK**

**A. Discussion Problems**

**A1.** Return to your successful solution of a fairly difficult problem in one of your previous technical courses (preferably chemical engineering). Look at this solution but from the point of view of the *process* used to solve the problem instead of the technical details. Did you follow a structured method? Most people don’t at first. Did you eventually do most of the steps listed? Usually, the *define, explore, plan, and do it* steps are done sometime during the solution. Rearrange your solution so that these steps are in order. Did you check your solution? If not, do that now. Finally, try *generalizing* your solution.

**A2.** Without returning to the book, answer the following:

a. Define a unit operation. Give a few examples.

b. What is the equilibrium stage concept?

c. What are the steps in the systematic problem solving approach? Explain each step in your own words.

**A3.** Do you satisfy the prerequisites? If not, how can you remedy this situation?

**A4.** Develop a key relations chart (one page or less) for this chapter. A key relations chart is a summary of everything you need to solve problems or answer questions from the chapter. In general, it will include equations, sketches, and key words. Organize it in your own way. The purpose of developing a key relations chart is to force your brain to actively organize the material. This will greatly aid you in remembering the material.
B. **Generation of Alternatives**

B1. List as many products and how they are purified or separated as you can. Go to a large supermarket and look at some of the household products. How many of these could you separate? At the end of this course you will know how to purify most of the liquid products.

C. **Derivatives**

C1. Write the mass and energy balances (in general form) for the separator shown in Figure 1-1. If you have difficulty with this, review a book on mass and energy balances.

D. **Problems**

There are no problems for this chapter.

E. **Complex Problems**

There are no problems for this chapter.

F. **Problems Using Other Resources**

F1. Look through several recent issues of *Chemical Engineering* magazine and find an article that contains a process flow chart. Read the article and write a short (less than one page) critique. Explicitly comment on whether the flow sheet for the process fits (at least approximately) the general flow sheet shown in Figure 1-1.

G. **Simulator Problems**

There are no simulator problems for this chapter.