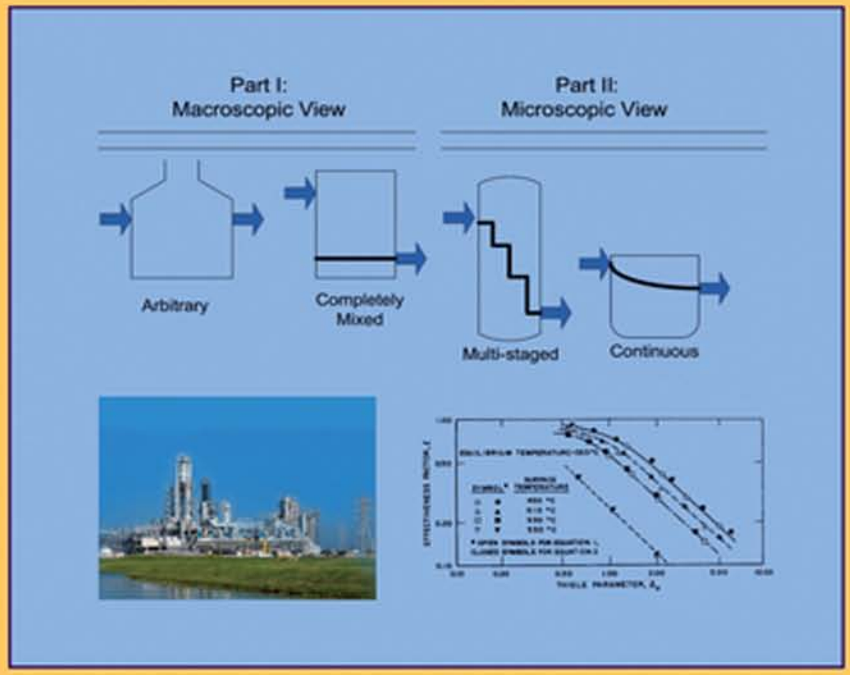
Principles of Chemical Engineering Practice

George DeLancey



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This book is dedicated to my darling wife, Lynn, who nurtured every page and every moment with her generosity, encouragement, and unfaltering support.

CONTENTS

PREFACE

This book is about the application of scientific principles and engineering experience to chemical processing. Major chemical engineering operations are organized under the principles of analysis in order to facilitate the consideration of new technologies from a chemical engineering point of view.

New applications have emerged in chemical engineering practice. Microchemical systems, for example, require attention to design parameters not important at larger scales. The shift from commodity chemicals to chemical products by many smaller companies is creating a demand for chemical engineers with a broader view of design than the traditional capstone design experience (Cussler and Moggridge, 2001). Biocatalysis and the chiral technology industry call for the support of undergraduate curricula. Opportunities for the chemical engineering graduate in the development of medical devices and drug manufacture call for more emphasis on the life sciences and physiology.

There is therefore a call to introduce a degree of flexibility into traditional undergraduate chemical engineering curricula for those who wish to serve a broader industrial base. An alternative is to concentrate the basic chemical engineering training in a minimal core designed to secure the distinguishing technical character of the chemical engineer and to provide the ground both for further specialization in traditional chemical engineering and for coherent studies in other areas. The minimization decisions regarding the required topics and the depth of coverage are local decisions that reflect the mission of the program.

This text can support such a local decision process as a consolidation of normally separate courses in material and energy balances, transport phenomena, reactor design, and separations. While not a replacement for these courses, it is a functional treatment of the underlying skills that characterize them. The selection of major operations reflects the intention of establishing a minimum competency level required to be differentiated as a chemical engineer in an undergraduate engineering curriculum.

Although the book is primarily meant for chemical engineering undergraduates, it may be appropriate for conversion programs designed to prepare graduates of other engineering and science programs for matriculation in chemical engineering master's programs.

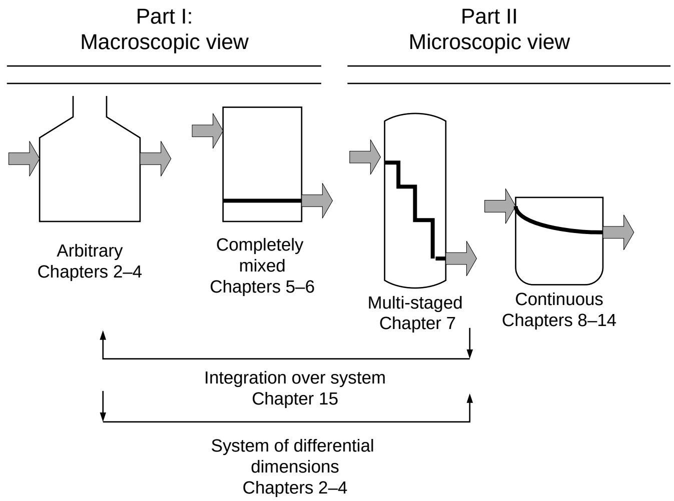
Graduate engineers in both academic and industrial positions may find it convenient to have a single resource with wide coverage.

CONTENT

The principles referred to above consist of the conservation of mass, energy, and momentum at the macroscopic and microscopic levels as well as the principle of the increase of entropy and characterization of equilibrium states by equilibrium thermodynamics. The production of entropy provides an important measure of process efficiency and underpins the conservation laws by providing a theoretical foundation for the nonconvective flows. In addition, the balance equations and equilibrium relations are used to develop models of the chemical process operations from the rate or equilibrium stage point of view, respectively. Efficiency is a link between the two.

The chemical engineering operations that are discussed in the text are as follows:

- Separators
- Heat exchangers.



Organization.

A process flow diagram for the manufacture of acrylic acid is presented at the outset and used for an introduction to chemical processing and equipment. Reference to the acrylic acid process is continued thereafter for presentation of new material in a process context. Example calculations in the text are compared with simulator results pertaining to equipment sizes and operating conditions in the acrylic acid plant.

Heuristics are regarded as fundamental tools and are stated extensively. They are used in calculations and are compared with some independent calculations. Degrees of freedom are employed throughout the earlier sections of the book.

Process control, economics, and safety are not included.

ORGANIZATION

Two major divisions of the subject matter in the text are made on the basis of a macroscopic and a microscopic view: The balance equations for mass, energy, momentum, and entropy are applied at the macroscopic level confined to the equipment ports, through completely mixed and staged systems to the continuous variations within equipment (see Organization).

The “macroscopic view” ensures the conservation of mass, energy, and momentum at the equipment and process levels with consideration only of the conditions at the entrances and exits of the process equipment. The exception is completely mixed systems where the uniform interior conditions appear at the outlet. The macroscopic view is taken at the level of process synthesis where the conditions are consistently set for each processing step to establish the overall process design and economics. The microscopic view is subsequently adopted to arrive at the detailed design of the processing equipment and the final economics. This viewpoint can provide conditions at every location within the equipment boundaries. For multistaged systems consisting of completely mixed subsystems, the conditions vary stepwise throughout the equipment. The microscopic view ensures the local conservation of mass, energy, and momentum. The macroscopic view is therefore the net effect of this local role, which can be seen by integration over the system volume, thereby “closing the circle.”

CALCULATIONS

Many examples are provided within the chapters throughout the text to elucidate the discussion. Two process-related threads are carried through the examples (see Tables 1.7 and 1.8) in order to provide a broad process perspective for the calculations. Questions for discussion and encouragement to complete the argument or calculation appear periodically. A variety of problems are suggested at the end of chapters in order to initiate the problem-solving activity as a learning tool and to provide experience with scientific and engineering databases. The collection can be augmented to meet specific course objectives or a desired orientation without modifications to the chapters.

Scientific Notebook (MacKichan Software) and Microsoft Excel are primarily used in the example calculations. Scientific Notebook was chosen because the students who used the notes had prior experience with this software in their mathematics courses and they preferred this software over others that were available to them. Moreover, this software is particularly compatible with the notation used throughout this book.

Excel was used because the ease with which objects could be moved on graphs, the magnification options, and the ability to construct multifunctional plots greatly facilitated stepping off stages and other graphical constructions. The tabular formulation of recursive calculations is readily accomplished in Excel.

Some experience with the use of this software in an introductory course is available in DeLancey (1999).

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PART I

MACROSCOPIC VIEW

1

CHEMICAL PROCESS PERSPECTIVE

The objective of this chapter is to provide an introduction to chemical processing and chemical processing equipment and to establish a realistic context for much of the more quantitative developments of the same topics appearing in the remaining chapters. A preliminary design of an acrylic acid process (Turton et al., 2003) with a complete flow sheet and stream table provides this context. A connected set of examples and exercises concerned with equipment sizing, material and energy balances, or stream and operating conditions threaded throughout the text are related to the acrylic acid process. The location and nature of these examples are summarized in Table 1.7.

Catalytic aspects of chemical processing are raised in the acrylic acid process and in biocatalytic systems with an introduction to enzyme catalysis. Industrial biotransformations are discussed and the production of hexyl glucoside is selected to provide the context for a second connected thread of examples and exercises throughout the text. In contrast to the acrylic acid thread, this selection is based on a proposed new process with much less information. The examples are therefore in the categories of scale up and process development. The location and nature of the examples in the subsequent chapters are summarized in Table 1.8.

1.1 SOME BASIC CONCEPTS IN CHEMICAL PROCESSING

It will be useful in the following discussion to have in mind what is meant by equilibrium, the steady state, and driving force. These ideas primarily underpin the steps in chemical processing and fall into the three thermodynamic categories: thermal, chemical, and mechanical. The first two categories are discussed below. The third is left to the reader (see Problem 1.1).

Thermal Refer to Figure 1.1a. Here we imagine that two fluids not necessarily of the same phase are introduced into the two chambers of a rigid insulated container with impermeable walls. The two chambers are separated by a rigid dimensionless barrier (to allow the transfer of heat without mass transfer) and the fluids fill the two mixed chambers. The temperature of the hot fluid (A) will decrease and the temperature of the cold fluid (B) will increase, each approaching the same temperature at the equilibrium state.

If, on the other hand, the fluids are drawn at the same rate they are fed, they will reach a **steady-state** temperature that is constant throughout each phase except for a narrow region near the dimensionless diathermal wall where the temperature decreases continuously from the high to the low value. The same equilibrium temperature is approached from either side of the interface. The two phases are prevented from reaching the intermediate state by the continual replacement and removal of the transferred energy.

If the flows are stopped, the system will equilibrate as in Figure 1.1a. We therefore think of the steady state being subjected to a **driving force** proportional to the distance from equilibrium as in Figure 1.1c where the flux of thermal energy is the response to the force. Since each approaches zero together, we take the linear approximation that the flux is proportional to the force.

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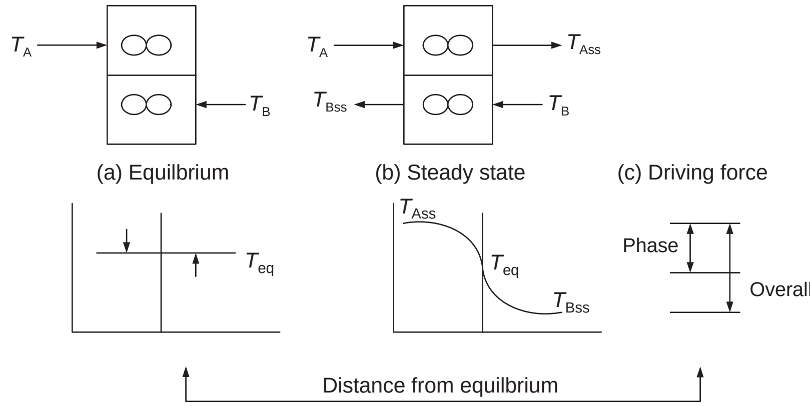

FIGURE 1.1 Rate and equilibrium in thermal processes.

We can focus on one phase and think of the driving force as the distance from the equilibrium value or we can think of the overall driving force as the difference between the phase temperatures. Both driving forces refer to the same flow of energy at steady state and each approaches zero at equilibrium.

Chemical—Unreactive Reaction Refer to Figure 1.2a. We again consider an insulated container with rigid impermeable walls. Here we charge the container with two immiscible liquid phases containing components that are partially soluble in both phases. We will assume for simplicity that the dissolution process of any one of the components in either phase involves no heat effect. Otherwise we would need to repeat the "thermal" discussion. We also assume that no reactions take place. Chemical reactions will be discussed separately.

Similar to the temperature in thermal phenomena, the concentration of each species will increase or decrease until a steady value is reached in each phase. This is a state of **interphase chemical equilibrium.** A fundamental difference from the thermal case is that the values are not the same in each phase. Whereas the potential for the transfer of thermal energy is the temperature, thermodynamics tells us that the chemical potential is a function of the temperature, pressure, and composition in each phase.

If, as above, the fluids are withdrawn at the same rate they are fed, the concentrations will reach steady-state values that are constant throughout each phase, except for a narrow region near the dimensionless open barrier where the concentrations change stepwise to the vales in the companion phase.

If the flows are stopped, the system will equilibrate as in Figure 1.2a. We therefore think of the steady state being subjected to a **driving force** proportional to the distance from equilibrium as in Figure 1.2c where the flux of mass is the response to the force. Since each approaches zero together, we take the linear approximation that the flux of mass is proportional to the driving force.

We can focus on one phase and think of the driving force as the distance from the equilibrium value for that phase or we can think of the overall driving force as the difference

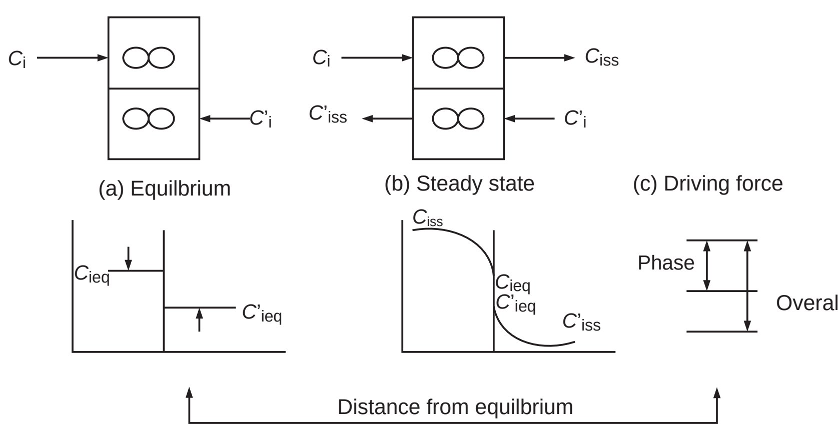

FIGURE 1.2 Rates and equilibrium in chemical processes—interphase phenomena.

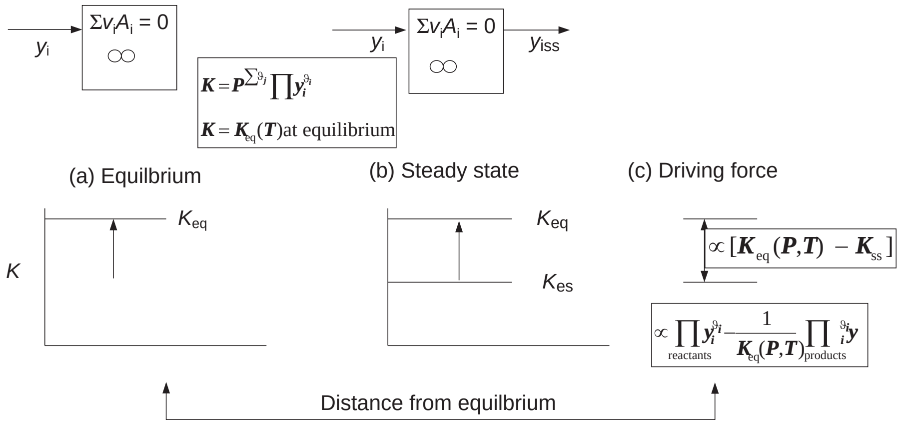

FIGURE 1.3 Reaction rates and equilibrium.

between the phase compositions. Since the interphase equilibrium compositions are not the same, the overall driving force will need to be modified slightly to assure that the rate is the same as that calculated in either phase.

Chemical—Single Ideal Gas-Phase Reaction The case of chemical reaction equilibrium is a bit more complicated in that reaction equilibrium is characterized by the chemical affinity, a linear combination of the chemical potentials mentioned in the preceding paragraph. We can, however, arrive at reaction kinetics, which are at least qualitatively correct and sufficient to understand some basic behavior of chemical reactors. We will consider a single ideal gas-phase reaction for which thermodynamics tells us that the ratio K in Figure 1.3a has a specific value at equilibrium $K_{eq}(T)$.

We again consider a container with rigid impermeable walls. Here we take the walls to be diathermal in order to begin and end the reaction process at the same temperature. We charge the container with a reactive ideal gas mixture. The value of K will increase as shown in Figure 1.3a until the equilibrium value is attained after which no further change will take place. This is the **intraphase chemical equilibrium** condition. For irreversible reactions, the value of K is extraordinarily large.

If gases are withdrawn at the same rate they are fed as illustrated in Figure 1.3b, the products will be prevented from accumulating and therefore the value of K_{eq} will be prevented from being reached. The concentrations T and P will reach **steady-state** values that are constant throughout. If the flows are stopped, the system will equilibrate as in Figure 1.3a. We therefore think of the steady state being subjected to a **driving force** proportional to the distance from equilibrium as in Figure 1.3c where the rate of reaction is the response to the force. Since each approaches zero together, we take the linear approximation that the flux of mass is proportional to the driving force. The result shown in Figure 1.3c is the law of mass action.

1.2 ACRYLIC ACID PRODUCTION

Figure 1.4 is a process flow diagram of a continuous process for the manufacture of 50,000 metric ton/year of 99.9 mol% acrylic acid from a one-step oxidation of propylene. One reactor is therefore used, which stands in contrast to the commonly used dual reactor system. The process is based upon the 1986 AIChE Student Contest Problem. The process conditions and equipment sizes are reported by Turton et al. (2003).

There are a number of commercial software packages that are known to produce accurate designs of chemical processes in the hands of experienced engineers (Aspen Plus, Aspen Hysys, Chemcad, etc.). Turton et al. (2003) used Chemcad and expected the results to represent a preliminary process design. We will use the calculated results as if they were actual plant data. Actual plant data at this level of detail are neither available nor needed in light of the sophistication of the software to gain a familiarity with process concepts as well as equipment and basic ideas in chemical engineering analysis and design. However, any comparisons of approximate calculations with these calculations are comparisons with more rigorous calculation procedures, not actual data.

Continuous processes are common in the chemical industry where such products as organic chemicals, plastics, and solvents are produced in large quantities to meet market demands. These products are referred to as bulk or commodity chemicals. Batch processes on the other hand are commonly used by the pharmaceutical industry to produce a wide variety, but small amounts, of pharmaceuticals. These products fall under the category of fine chemicals. Semicontinuous process is the combination of batch and continuous processing, in which the chemical state of one or more chemical compounds is altered stepwise toward a well-defined target. A process flow diagram (PFD) is a schematic representation of the process.

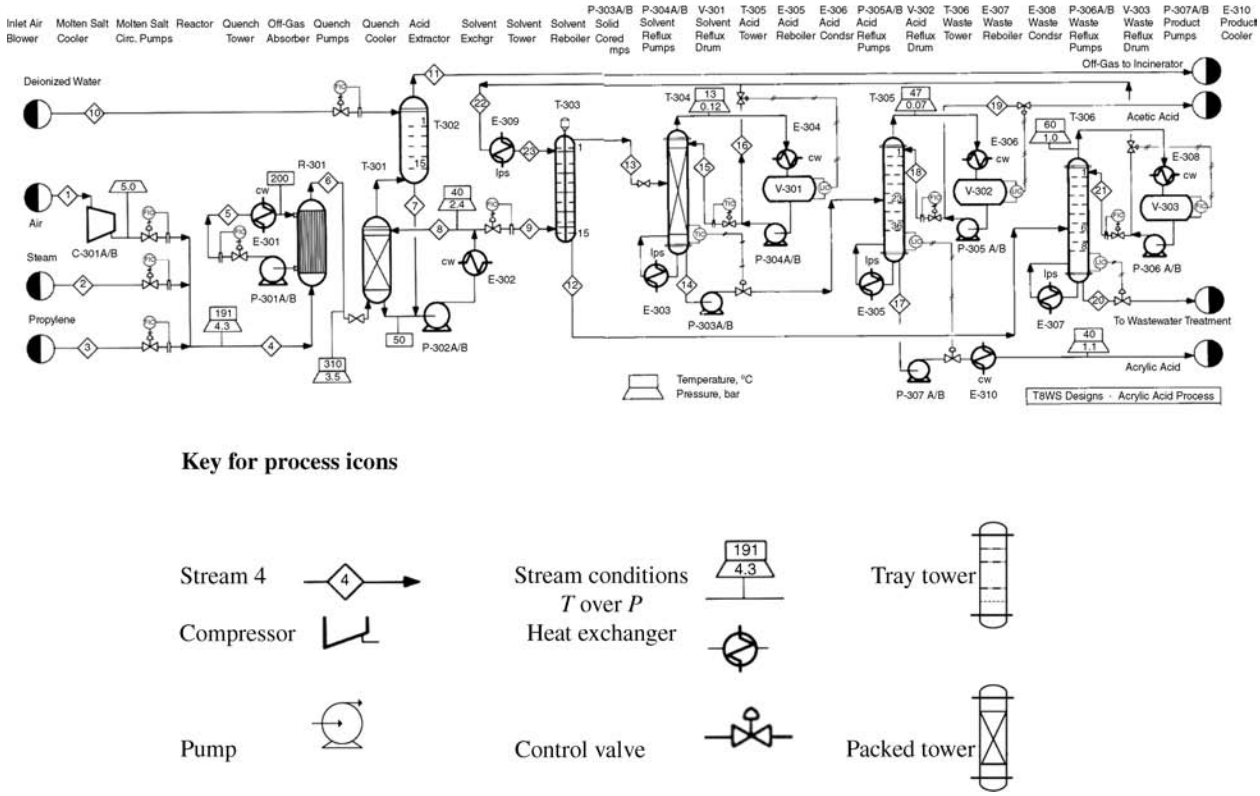

FIGURE 1.4 Process flow diagram for acrylic acid production plant (Turton et al., 2003). Reprinted with permission of Pearson.

In a chemical process, material is moved in streams by mechanical devices such as pumps and compressors from one process unit to another. A summary of the schematic representations of these items is given in Figure 1.4.

The streams are connected to the process units by pipes and ducts for fluids and by screw or belt conveyors in the case of solids, for example. The process units perform operations on the content of the streams to change their temperature, pressure, phase, and/or composition. These units are often referred to as unit operations and are carefully configured by the chemical engineer to transform raw materials into the desired products, economically and safely. Some units are combinations of unit operations.

All of these processes consist of a sequence of operations in which the process streams begin at raw material storage and end with product storage. There are other streams called utilities, which are employed by the process units as sources or sinks of thermal energy. The supply and regeneration of the utility streams may be part of the process or these services may be supplied by a separate facility. In the latter case, the utility streams arrive and are returned after use to the utility site for regeneration.

We will look more carefully into each of these aspects of chemical processing for the production of 50,000 metric ton/year of acrylic acid via the process given in the flow diagram (Figure 1.4). Normally, the adopted chemical route is the result of an intensive search involving technical, economic, and safety considerations. More than one route may be simulated to better evaluate the economics of the final competitors. A two-step process comprised of the oxidation of propylene to acrolein followed by the oxidation of acrolein to acrylic acid (Speight, 2002) is the common industrial choice. In the present case, the partial oxidation of propylene has been selected from other alternative routes to acrylic acid, which may be viewed as an alternative proposition for a single-step process over a new catalyst.

$$C_3H_6 + \frac{3}{2}O_2 \rightarrow C_3H_4O_2 + H_2O \qquad (1.1)$$

An economic view can be initiated at the outset of process development by considering only the raw material costs and product sales price. The net change for the chemical reaction must, of course, be positive or "economically endothermic" before the reaction is even considered to be a possibility for adoption. Some chemical prices are available in the *Chemical Market Reporter*, available online by subscription. Professional publications such as *Chemical and Engineering News* and *Chemical Engineering Progress* publish limited pricing information. In general, there is a cost associated