CHAPTER 1

Introduction

The objective of this book is to develop the concepts and solution methods that are required to determine the distribution of material and energy flows in a chemical process. These so-called material and energy balance calculations are both the most elementary and the most frequently performed computations carried out by chemical engineers. They are as basic a tool of the chemical engineer as are ledger-book balancing methods to an accountant. This book will help the reader to develop a mastery of this basic tool both for use in manual calculations as well as for implementation on computers. The consideration of solution strategies appropriate for computer implementation is given special attention because the use of computers to perform "bread-and-butter" balance calculations is growing in the field and is clearly the way of the future. However, our study of computer-oriented strategies is at the conceptual level, stopping short of delving into coding details. Hence, prior mastery of any specific programming language is not a prerequisite.

In this first chapter, we begin with a discussion of the role of chemical engineers in general and of the place of balance calculations both in the work of the professional engineer as well as in the curriculum required of B.S. Chemical Engineering graduates. In the following section, we review some of the basic concepts derived from chemistry, physics, and mathematics that are employed in balance calculations. The chapter concludes with a preview of the organization of the contents of the remainder of the text.

1.1 THE ROLE OF THE CHEMICAL ENGINEER

The two primary functions of the chemical engineer are to develop and design processes that convert raw materials and basic energy sources into desired chemical products or higher energy forms and to improve and operate existing processes so that they become as safe, reliable, efficient, and economical as possible. The design function involves the synthesis of appropriate sequences of chemical and physical transformation steps and the selection of the conditions under which these transformations are to take place given basic information about the chemical reactions and physical properties of the materials to be processed. The responsibility of the chemical engineer–designer thus begins with the basic chemical and physical information developed by chemists on a laboratory scale and concludes with the specifications of equipment for a full-scale plant. These specifications are then implemented by mechanical and structural engineers in fabricating the actual mechanical devices and constructing the finished plant. The chemical engineer thus has the challenging job of translating a laboratory concept into a full-scale commercial plant.

The duties of the chemical engineer in an existing plant include identifying and correcting malfunctions in the process, devising improved operating schedules and procedures, finding ways of increasing plant safety or reliability, and selecting new operating conditions to accommodate changes in feed conditions, product requirements, or unit performance characteristics. Execution of these duties requires a knowledge of the chemical and physical operations that are embodied in the process, the ability to interpret plant operating data as well as to select the measurements that should be taken, and the skill to perform the necessary engineering calculations that will allow values of unaccessible process variables to be deduced or plant performance to be predicted. The responsibility of the process engineer is thus to translate basic operating information and objectives into concrete action that can be taken by the plant operators, maintenance staff, or structural and mechanical engineering crews.

The following two examples are intended to illustrate both the types of technical problems addressed by chemical engineers and the general structure of chemical processes themselves.

Example 1.1 Ethylene Glycol Process Design It is known that the important chemical ethylene glycol, $C_2H_4(OH)_2$, widely used as automobile antifreeze, can be produced by reacting ethylene oxide, C_2H_4O, with water in the liquid phase. The ethylene oxide intermediate can in turn be obtained by partial oxidation of ethylene, C_2H_4. This gas-phase reaction can be made to proceed at moderate temperatures by using a silver catalyst. The formation of the oxide is however accompanied by the undesirable complete oxidation reaction in which only CO_2 and H_2O are products. Based on further laboratory information about the relative yields of C_2H_4O and CO_2 as well as data on the properties of the various chemical species, the job of chemical engineers would be to design a two-step process which uses ethylene, air, and water as primary feeds, as shown in Figure 1.1.

Solution Based on an analysis of laboratory reactor data, the design group might conclude that in order to minimize the formation of CO_2, the concentrations of C_2H_4 and O_2 in the feed to the oxidation reactor should be kept low. The N_2 present in the air would conveniently act as dilutent for this purpose. In addition, the fraction of the C_2H_4 that is allowed to react would be kept small. As a result, however, the reactor product would be dilute in C_2H_4O and would contain unconverted C_2H_4 and O_2 as well as the species CO_2, H_2O, and N_2. Clearly it will

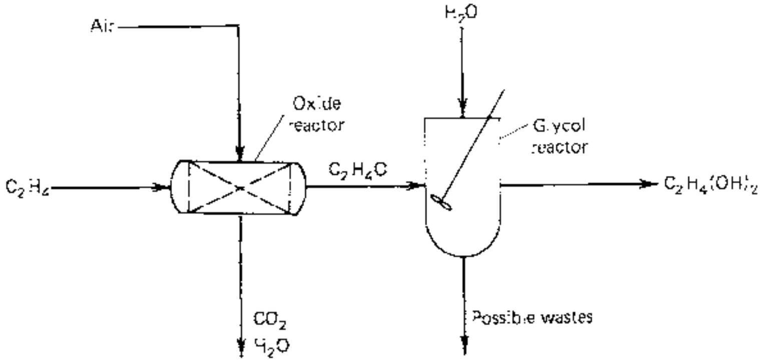


Figure 1.1 Two-stage conceptual glycol processes.

be necessary to devise means of separating these chemical species. The C_2H_4O must be recovered in relatively pure form to be used in the glycol formation reactor. The unconverted C_2H_4 and O_2 should be reclaimed for recycle to the oxide reactor, while the undesirable CO_2 and N_2 should be isolated and removed as waste products.

One possible separation scheme is shown in the process schematic given in Figure 1.2. The schematic consists of symbols representing process equipment units and of lines connecting these units representing physical pipes or ducts through which materials are transferred from unit to unit. These lines are commonly referred to as *streams* and are characterized by the flow rate of material, the composition of the species in the flowing mixture, temperature, and pressure. Schematics of the type of Figure 1.1 are commonly referred to as *flow diagrams* or *flowsheets* and will be used extensively throughout this book.

In the flowsheet of Figure 1.2, the stream leaving the oxide reactor is cooled by exchanging heat with the incoming feed to the reactor and is sent to an absorber unit. This unit separates C_2H_4O and a portion of the CO_2 from the remaining species in the product stream by absorption into cold water. This separation thus exploits the much higher solubility in water of C_2H_4O and CO_2 compared to the solubilities of the other species.

The solution from the absorber is fed to another separation device in which C_2H_4O and CO_2 are boiled off and the remaining water is recycled back to the absorber after being cooled using the cold absorber solution. The C_2H_4O and CO_2 are next separated by distillation at lower temperatures. The CO_2 and other light impurities are discarded as a waste stream while stream 12, the mixture of oxide and water, is transferred directly to the glycol reactor.

Returning to the gas stream leaving the oxide-absorber unit, a portion of that stream is split off and will be eliminated by incineration since there is no simple way of separating N_2 from the other gaseous species. (Such a separated waste stream is often called a *purge* stream.) The CO_2 in the remaining portion of the gas stream is removed by absorption into a solution of ethanolamine and water, which has a special affinity for CO_2. The resulting C_2H_4–O_2–N_2 mixture is com-

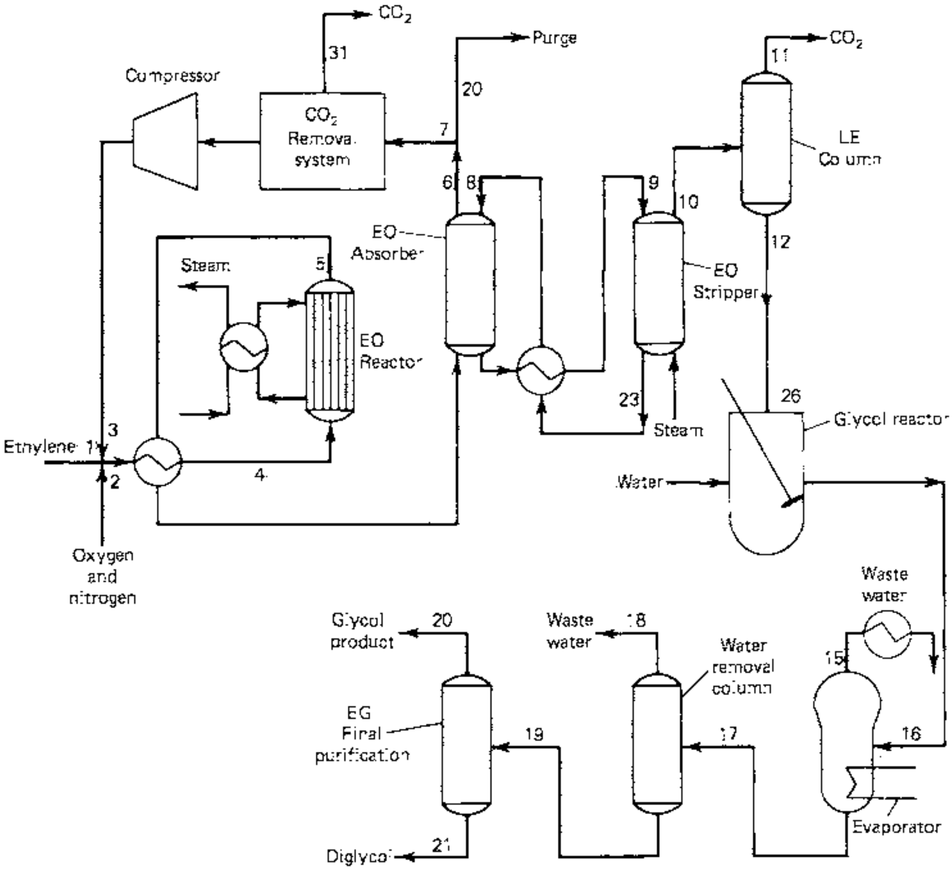


Figure 1.2 Process for manufacture of ethylene glycol.

pressed to make up for the pressure losses sustained in the previous processing of the gas stream, is mixed with fresh air and C_2H_4, and becomes the feed to the oxide reactor. The reader will note that in order to have devised the above separation scheme, knowledge of the relative solubilities of the species in water or ethanolamine solutions as well as information on the boiling points of C_2H_4O and CO_2 were indispensible.

As a result of the first part of the process, the intermediate C_2H_4O has been produced in a form suitable for reaction to ethylene glycol. As shown in Figure 1.2, the C_2H_4O solution is combined with a suitable amount of water in the glycol reactor. Since the oxide is quite reactive, there is no difficulty in achieving virtually 100% conversion. However, the concentration of C_2H_4O must be kept low to reduce the formation of diglycol, $(C_2H_4OH)_2O$, via a side reaction of ethylene oxide with the preferred product, the ethylene glycol, $C_2H_4(OH)_2$. Again, laboratory data are necessary to identify the C_2H_4O concentration as well as temperature which would be most advantageous. After reaction, the mixture of glycol, diglycol, and water must be separated to obtain a high-purity (say, 99%) glycol product. This is accomplished in several steps. First, an evaporator is used to boil off the bulk of the water. Next, a distillation unit is used to remove the residual water; and finally, a second distillation unit is used to separate glycol and diglycol. Having deduced the sequence of operations that are appropriate for this process, the design group will next proceed with detailed design calculations to determine the size and capacity of each of the individual equipment items as well as the composition, flow, temperature, and pressure of each of the streams flowing between the units. The design group will also perform some trade-off studies to examine the effects of changes in some of the design parameters. For instance, decreasing the ethylene oxide, C_2H_4O, concentrations in the glycol reactor feed will reduce the formation of diglycol, $(C_2H_4OH)_2O$, but will increase the amount of water that must be removed per unit of product formed in subsequent separation units. Thus, a balance must be found between loss of C_2H_4O to diglycol and water separation costs.

Another very important part of the design process is the determination of treatment methods for process waste streams, such as the water obtained in the glycol separation operations or the vent-gas stream produced in the light-ends columns. Finally, careful attention must be given to safety considerations such as the possibility of attaining explosive mixture proportions in the feed to the oxide reactor as well as the possibility of leaks of ethylene oxide, which is a very reactive substance. These considerations are no less critical in determining a good design than the selection of the main processing steps and their conditions.

The preceding example primarily illustrates the type of considerations involved in the development and design of a process. The following example presents issues which might have to be addressed by chemical engineers once the plant is built and operating.

Example 1.2 Ethylene Glycol Process Studies The plant of Figure 1.2 is constructed, started up, and operates for a period of time. After some period of time, the following problems are posed to the plant process engineers:

(a) The yield of ethylene oxide decreases gradually. What is causing the decrease?
(b) A profitable market is found for diglycol. How can the operating conditions be altered to favor joint diglycol production?
(c) The price of ethylene doubles. What can be done to improve ethylene utilization?
(d) The demand for glycol declines because of reduced automotive sales. However, high-purity ethylene oxide is needed for polymerization applications. What can be done to recover a high-purity ethylene oxide intermediate product?

Solution In case (a), plant tests might show that the silver catalyst is becoming less active because of fouling. The engineer would need to determine why this occurs and how to prevent fouling. Perhaps there are trace impurities introduced through the CO_2 removal system solution. Perhaps the reactor cooling system is malfunctioning and hot spots are occurring in the reactor. Suppose that as a result of measurements and possibly a few confirming laboratory-scale experiments, temperature control is found to be at fault. Then, modifications of the existing conditions or hardware will need to be proposed to correct the problem.

In case (b), the glycol-reactor feed concentration will need to be changed, as will the reactor operating temperature. These changes will affect the conditions in the downstream separation units. For instance, the evaporator will need to process a more concentrated solution thus requiring changes in heating rate and operating temperature. Moreover, depending upon the desired diglycol purity, an additional distillation unit may have to be added to the separation sequence. The new set of operating conditions will need to be carefully established and implemented. Equipment modifications may be necessary and a new column may have to be designed.

The improved ethylene utilization indicated in case (c) could be obtained in two ways: reduction in direct losses of ethylene and improved yields of products in each of the reactors. For instance, it might be desirable to develop a method of recovering C_2H_4 from the purge stream, say, by absorption into a heavier oil. Alternatively, since yield of C_2H_4O increases with a decrease in the fraction of C_2H_4 that is reacted in the oxide reactor, adjustment of the fraction reacted might be appropriate. Of course, this will increase the flow rate of the recycle stream and hence increase the load on the units processing the recycle flow. Perhaps an extra parallel compressor or extra heat exchange equipment may be desirable.

In the last case, case (d), three questions need to be considered.

1. The addition of separation units to purify a portion of the oxide solution which will then bypass the glycol production train, as shown in Figure 1.3.
2. The effects of reduced processing rates in the glycol production train. To what extent can the units be throttled down? Might it be necessary to only operate the glycol section periodically?
3. The possibility of increased production of ethylene oxide by scaling up the flows. What operations will prove to be the bottleneck?

In addressing these types of operational issues, the engineer will need to have insight into the process, to be able to anticipate trouble spots, to orchestrate the gathering of plant and laboratory data that guide the analysis process, and to perform the engineering calculations that will predict plant performance under the modified conditions.

Of course, chemical engineers are also involved in other important activities: research to further the understanding of the physical and chemical phenomena affecting new and existing processes; management of plant operating personnel; industrial sales and technical support for customer applications; and technical training of other chemical engineers. However, while these activities are both interesting and important, the core chemical engineering tasks remain process development and design as well as process engineering.

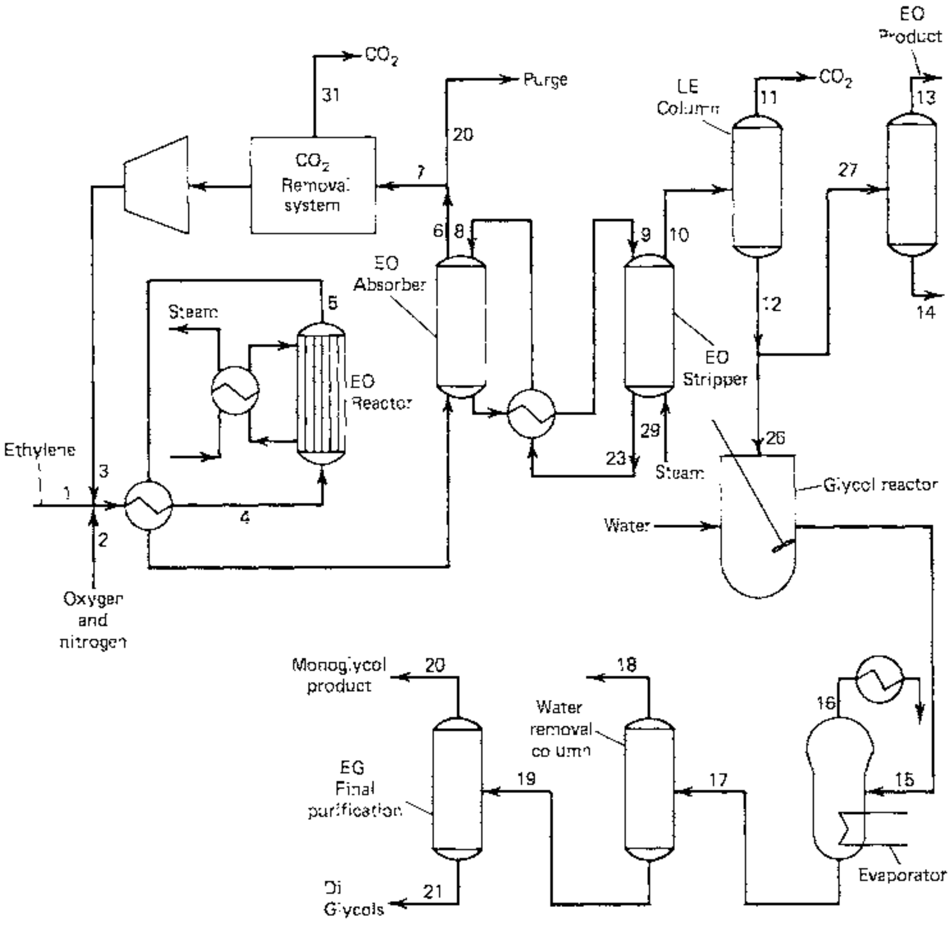


Figure 1.3 Process for manufacture of ethylene oxide and ethylene glycol.

1.2 THE ROLE OF BALANCE CALCULATIONS

Balance calculations are the computations based on the principles of conservation of mass and energy that serve to determine the flows, compositions, and temperatures of all streams in a flowsheet given selected or assumed information about the performance of some process equipment items or the properties of some streams. Since knowledge of the input streams and desired output streams to each process equipment item is essential information in the design of each such piece of equipment, it is clear that balance computations are of central importance in design. Similarly, since it is impractical or impossible to measure all streams in an existing process, balance calculations can be used to determine the flows and compositions of the unmeasured or unmeasurable streams in the process from known information about selected measured streams. Balance calculations thus have an important role in preliminary design, in final design, and in process operations. The following few examples illustrate the types of questions that can be answered using the methods discussed in this book.

Example 1.3 Space Station Life Support System[1] In designing equipment for manned space missions, considerable attention must be devoted to the supply of air, water, and food as well as the disposal of respiratory and bodily wastes. While for short-term missions supply needs can be met from onboard caches and wastes can simply be stored or vented, for long-term missions recycle of waste products becomes important in order to minimize the need for large supply caches. The most important waste recycle systems involve recovery of respiratory CO_2 for reprocessing into O_2 and recovery and reuse of water from respiration and urine. Figure 1.4 shows the key elements of such a reprocessing system.

Food, which is represented as C_2H_2 because the carbon/hydrogen ratio in the average diet is about unity, is oxidized by the mission crew to produce CO_2 and H_2O using the O_2 in the cabin atmosphere.

The reclaimed water is electrolyzed to produce O_2 and H_2 gases in an electrolysis cell. The O_2 is returned for use in the metabolism of food, while the H_2 is used to reduce CO_2 to form methane, CH_4, and H_2O.

The CO_2 reduction reaction is known as the Sabatier reaction and can be carried out over a ruthenium catalyst in a tubular reactor. The products of reaction can easily be separated, with the water being recycled to the electrolysis cell while the CH_4 can be vented to space.

The foremost question to be answered in considering the system of Figure 1.4 is, assuming all reactions go to completion and all separations are perfect, which chemical species, O_2, H_2, or H_2O, must be stored to sustain the system. The next question is how much of that species must be provided per unit of food (C_2H_2) metabolized.

Solution The material balance calculations discussed in Chapters 2 and 3 of this book can readily provide answers to both of these questions. Through such calculations, it can be shown that the system is H_2 deficient. Hence, a cache of H_2 must in principle be provided. An alternate and more convenient solution is to store the H_2 as water, H_2O, by using ordinary frozen foods. The use of water provides extra oxygen atoms, allowing some of the food carbon to be vented to space in the form of CO_2 and thus lowering the duty on the Sabatier reactor. The precise ratio of CO_2 to CH_4 which will be vented can, again, be computed using material balance calculations.

After these preliminary calculations, it is next necessary to select the equipment which will be used to reclaim H_2O and CO_2 from the space cabin atmosphere and

[1] P. J. Lunde, "Modeling, Simulation, and Operation of a Sabatier Reactor," Paper 56E, AIChE 74th National Meeting, New Orleans, March 1973.

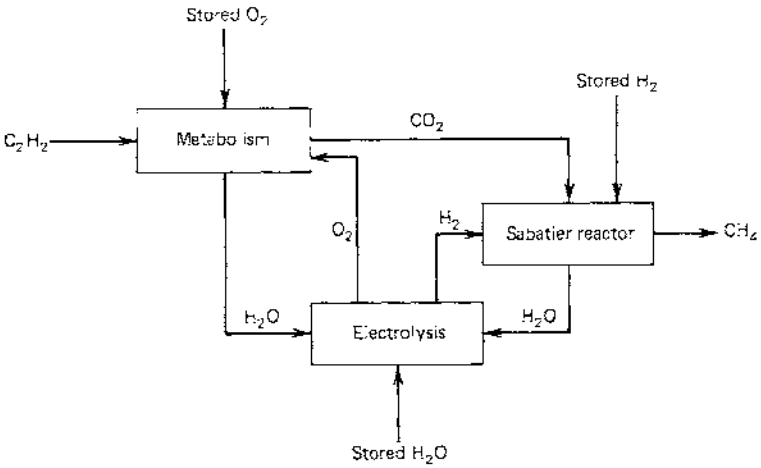


Figure 1.4 Conceptual life support system.

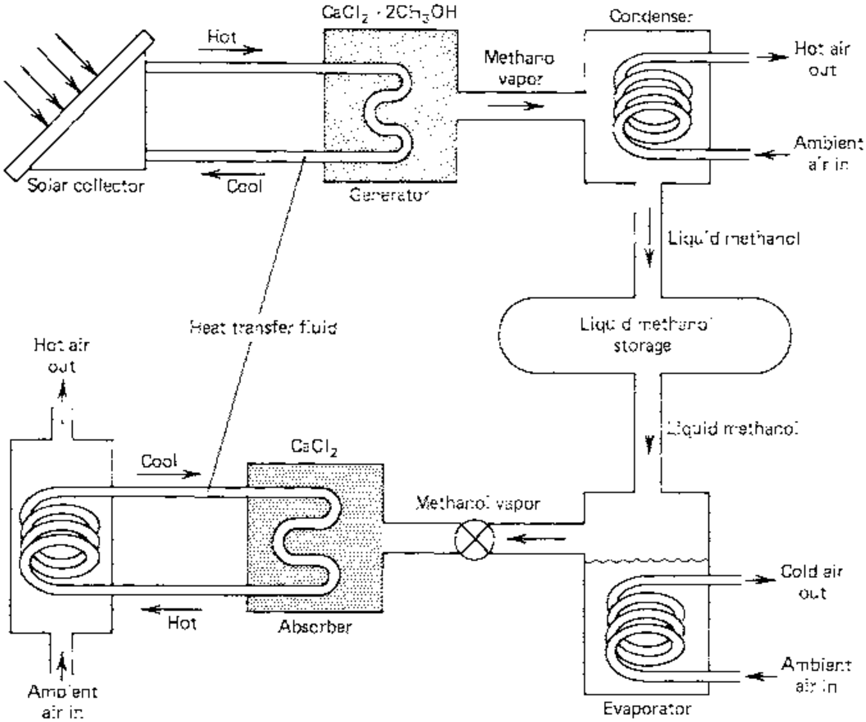
urine, to separate the Sabatier reactor products, and to carry out the electrolysis. Each of these real devices performs less than ideally, and the actual performance data must then be incorporated into final balance calculations which will yield the actual species flows for the life support system. Thus, material balance calculations prove useful both in the preliminary and in the final design stages of the system.

Example 1.4 Solar-Powered Chemical Heat Pump[2] The system shown in Figure 1.5 and developed for the U.S. Department of Energy[2] uses solar energy, outside air, and a reversible chemical reaction to provide heating or cooling as well as hot water for homes. The reaction of methanol with anhydrous calcium chloride to produce the solid calcium chloride methanolate, $CaCl_2 \cdot 2CH_3OH$, is employed as follows.

Solar energy is used to heat a heat-transfer fluid to 130°C. The hot fluid is circulated through a bed of methanolate pellets to which it transfers heat, resulting in the decomposition of the methanolate. The released hot methanol vapor is cooled to form a liquid in the condenser unit. In the winter, this cooling is accomplished by heating inside air from, say, 20° to 40°C. In the summer, outside air can be used for this purpose provided it is at no more than 35°C. In either case, the liquid methanol is stored in a tank for use when needed in the second half of the process.

When either heating or cooling is desired, the valve to a bed of anhydrous calcium chloride, $CaCl_2$, will be opened allowing methanol vapor from the evaporator unit to be absorbed and reacted with the $CaCl_2$. As vapor is consumed, more liquid will be evaporated to replace it. The evaporation process requires heat, which is supplied in the summer by cooling inside air or in the winter by cooling outside air (provided it is above −15°C). The reaction of CH_3OH vapor with $CaCl_2$

[2] "Chemical Heat Pump Cools as well as Heats," *Chem. Eng. News*, 36-37 Anon., (Oct. 20, 1980).



Note: Generator and absorber beds are exchanged on alternate cycles.

Figure 1.5 Solar powered chemical heat pump (reproduced from *Chemical & Engineering News*, Oct. 20, 1980).

releases heat, which is recovered from the bed using a heat-transfer fluid and is transferred either to a hot-water heater, to inside air, or to outside air depending upon requirements. The $CaCl_2$ bed and the reservoir of liquid methanol represent stored energy because, when they are allowed to combine, heating and/or cooling can be made to take place. A system of this type would use several beds of anhydrous $CaCl_2$ which would be used as generators or absorbers in alternating cycles.

Given a system of this type with fixed solar collector area, known average solar flux, and known outside air temperature, the answers to the following questions would be of interest.

1. If the inside air is available at 20°C and is heated to 40°C, how many cubic meters of air can be processed per hour?
2. How much liquid methanol could be accumulated over an average winter day? How much heat could be provided overnight?
3. If the inside air is available at 30°C and is cooled to 20°C, how many cubic meters of air can be processed per hour?
4. What is the pressure inside the evaporator when the inside air is cooled to 20°C?

Solution These questions having to do with predicting the flows and conditions in an operating or proposed system can be readily answered using the energy balance calculations discussed in Chapters 6 through 8 of this book. Note that in this case, given the rate at which solar energy is delivered and certain measured stream properties (the temperatures), balance calculations would be used to determine the remaining unknown flows or properties.

The preceding two examples considered chemical engineering systems which involve relatively few streams and a relatively small number of distinct chemical species. In other process applications, such as the flowsheet of Figure 1.3, there may be many streams and the process may involve a substantial number of chemical species. The calculations required to determine all of the stream flows, compositions, and temperatures can become quite laborious and complex. Consequently, it is expedient to computerize the balance calculations using methods discussed in Chapters 5 and 9 of this text.

We conclude this section with a brief discussion of the place of material and energy balance calculations in the curriculum required of B.S. Chemical Engineers. Normally, the topics discussed in this book form the core of the first course in Chemical Engineering. The balance equations themselves are subsequently employed in the thermodynamics course, the reactor design course, the staged separations course, as well as the transfer operations courses. However, in these courses material and energy balances will normally only be developed for the individual units or operations studied in that particular course. The more extensive application of the subject matter of this text typically occurs in the process design course. In the design course, attention is again focused on entire process flowsheets of the type of Figure 1.3; and hence flowsheet balance calculations, particularly the methods discussed in Chapters 5 and 9, become quite important. Thus, material and energy balance concepts permeate the chemical engineering curriculum and find their heaviest utilization in the capstone design course. To compensate for the information loss which can occur because of the wide temporal separation between the first Chemical Engineering course and the capstone design course, the student may find it quite beneficial to review key chapters of this book, especially Chapters 5 and 9, prior to beginning the design course.

1.3 REVIEW OF BASIC CONCEPTS

In this section, we briefly summarize the elementary concepts drawn from chemistry, physics, and mathematics that underly balance computations. Specifically, we consider the conservation principles, elementary chemical stoichiometry, equation solving, and manipulation of dimensional quantities. The primary purpose of this review is to outline the prerequisites for the developments given in subsequent chapters. The reader who finds the discussion of this section too terse is strongly encouraged to refer to basic chemistry, physics, algebra, and calculus texts for expanded treatments of selected topics.

1.3.1 The Conservation Principles

One of the major accomplishments of the theory of relativity is the formulation of the principle that the total of the mass and energy of a system is conserved. This principle, which forms the basis of material and energy balance calculations, is of course a hypothesis since it has never been conclusively demonstrated. However, it is a very solid hypothesis since it has never been disproved experimentally.

A precise statement of the principle of conservation of mass and energy requires a careful definition of terms. First, the term *system* is understood to mean that bounded portion of the universe which is under study. The mass m of the system refers to the amount of matter at zero velocity relative to some selected reference point (sometimes called *rest mass*). The energy E of the system refers to energy in *all* possible forms. Finally, it is understood that a quantity is *conserved* if it can neither be created nor destroyed. Thus, all changes in the amount of the conserved quantity present in a system can be accounted for by simply measuring the tranfer of that quantity back and forth across the system boundaries.

Let $(d/dt)(m + E)_S$ denote the rate of change of the mass and energy of the system with time at a given point in time. Furthermore, let $(\dot{m} + \dot{E})_I$ and $(\dot{m} + \dot{E})_O$ denote the input and output rates of mass and energy into and out of the system. Then, the principle of mass and energy conservation reduces to the single statement

$$\frac{d}{dt}(m + E)_S = (\dot{m} + \dot{E})_I - (\dot{m} - \dot{E})_O \tag{1.1}$$

In the absence of nuclear reactions or speeds approaching that of light, the extent of interconversion between mass and energy is negligible. Consequently, the single conservation equation can be separated into two statements:

$$\frac{d}{dt}m_s = \dot{m}_I - \dot{m}_O \tag{1.2}$$

and

$$\frac{d}{dt}E_s = \dot{E}_I - \dot{E}_O \tag{1.3}$$

The first is refered to as the *principle of conservation of mass*, and the second, as the *principle of conservation of energy*. These two principles were in fact postulated by early researchers in chemistry and mechanics and were considered to be independent laws. The theory of relativity showed that this is not the case in general. However, for most chemical engineering applications, excluding those involving nuclear reactors, the separation of the general conservation principle into two independent principles is an excellent and very convenient approximation. Equation (1.2) is the starting point for the material balance portion of this text; eq. (1.3) is the basis for the energy balance portion.

Special Cases The conservation principle equations given above are written for the general case in which both sides of each equality are time-varying functions.

Such systems are said to be *dynamic*. In most of the applications to be considered in subsequent chapters, it is assumed that the system is at *steady state*, that is, that all properties of the system are invariant with time. For steady-state systems, it follows that the time derivatives dm_s/dt and dE_s/dt, often called the *accumulation terms*, are identically equal to zero. Thus, the conservation equations reduce to

$$\dot{m}_I = \dot{m}_O$$

$$\dot{E}_I = \dot{E}_O$$

or, the rate of mass transfer (energy transfer) into the system must be equal to the rate of mass transfer (energy transfer) out of the system. The difference between steady-state and dynamic systems is illustrated in the following example.

Example 1.5 Consider the system consisting of a barrel which has a capacity of 100 kg water, is empty at time $t = 0$, and is filled at the rate of 10 kg water per minute. At time $t = 10$ min, the barrel is full and commences to overflow. For t less than 10 min, water enters at $\dot{m}_I = 10$ kg/min, but $\dot{m}_O = 0$. Thus, from the mass conservation equation, eq. (1.2),

$$\frac{dm_s}{dt} = 10 - 0 = 10 \text{ kg/min}$$

Although the input and output mass transfer rates are time invariant, the accumulation term is nonzero, and therefore the system is *not* at steady state. The barrel is a *dynamic* system.

For times greater than 10 min, the barrel is filled to the rim, and hence the mass of water in the system is constant with time, that is, $dm_s/dt = 0$. Since the input rate remains constant at 10 kg/min, the mass conservation equation reduces to

$$\frac{dm_s}{dt} = 0 = 10 \text{ kg/min} - \dot{m}_O$$

or

$$\dot{m}_O = 10 \text{ kg/min}$$

The system has reached a *steady state*: all flows and properties are time invariant.

Systems can further be classified based on the occurrence of mass transfer across the system boundaries. An *open* system is one in which there is transfer of mass into or out of the system. A *closed* system is one in which there is no transfer of mass across the system boundaries. For a closed system, both m_I and m_O are equal to zero. Thus, eq. (1.2) reduces to the form

$$\frac{dm_s}{dt} = \dot{m}_I - \dot{m}_O = 0$$

or m_s is constant with time. Although a closed system must have constant mass, it can be either steady state or dynamic in terms of the properties having to do with energy. Thus, the full dynamic form of the energy conservation equation may be applicable. A system is said to be *isolated* if it is closed and, in addition, there is no energy transfer across the system boundaries. For an isolated system, $\dot{E}_I = \dot{E}_O = 0$ and eq. (1.3) reduces to the form,

$$\frac{d\dot{E}_s}{dt} = \dot{E}_I - \dot{E}_O = 0$$

Thus, an isolated system has both constant mass and constant energy level.

Example 1.6 Suppose at $t = 20$ min, the input flow of water to the barrel of Example 1.5 is shut off. Providing there are no leaks in the barrel, the output flow also becomes zero. Thus,

$$\frac{dm_s}{dt} = 0$$

and the system clearly is closed with constant mass of 100 kg. The system need not be isolated. If the sun shone upon it, the water in the barrel would warm up. If the outside air temperature would drop below freezing, the water in the barrel would eventually turn to ice. In both cases, the energy content of the system would change with time. For the system to become isolated, it would be necessary to cover the barrel and to insulate it so that no transfer of energy as heat or any other form could occur.

In subsequent chapters, we largely deal with open steady-state systems. Such systems typically represent the desired operating mode of large-scale chemical plants of the type of Figure 1.3.

1.3.2 Chemical Stoichiometry

In most applications of balance calculations, it is not sufficient to deal with mixtures on the basis of total mass alone. Particularly in systems involving chemical transformations it is necessary to focus on the individual chemical compounds or species of which the mixtures are composed. In this section, we summarize the basic facts from the atomic theory of matter and the notions of molecular formula, stoichiometric equations, and atomic and molecular weight which are prerequisites for applying the principle of conservation of mass to individual chemical species.

Molecules and Reactions Under the atomic theory of matter, chemical compounds are composed of bonded aggregates, called *molecules*, consisting of atoms of one or more of the 103 known types of basic chemical building blocks called elements. Each molecule contains an integral number of atoms of its constituent elements and can thus in large part be characterized by the number and type of its atoms. This information is conveniently expressed in terms of a construction called a *molecular formula* which has the general form $A_aB_bC_c$, where each capital letter denotes the symbol for a specific element and the lower-case subscript indicates the number of atoms of that element per molecule of that chemical compound. A standard set of element symbols has been agreed upon and is summarized in Appendix 1. Using that symbol library and the molecular formula convention, the compound benzene, consisting of six carbon and six hydrogen atoms per molecule, is denoted C_6H_6.

The *chemical reaction* of two species to form one or more new product species is a process in which the reacting molecules are rearranged and their constituent elements are redistributed to result in the desired product species molecules. This process occurs in such a way as to preserve the identity of the atoms of the different elements. Thus, under the atomic theory of matter, the atoms of each type of elements are *conserved* during a chemical reaction.

Stoichiometric Equations Since atoms are conserved and since the product molecules also contain integral numbers of atoms of the elements present in the reactant molecules, it follows that the reactant molecules must combine to form the product molecules in ratios that are integers or simple fractions. A compact way of expressing both the ratios in which specific compounds combine to form specific product compounds and the molecular formulas of the compounds themselves is the *stoichiometric reaction equation*.

If a molecules of compound with molecular formula A combine with b molecules of compound with molecular formula B to form c and d molecules of products C and D, respectively, then the stoichiometric equation for this reaction is

$$aA + bB \rightarrow cC + dD$$

The coefficients a, b, c, and d are called *stoichiometric coefficients* of their respective species.

By convention, the direction of the arrow indicates the products of the irreversible reaction. A reversible reaction is denoted by a double arrow. For example, the stoichiometric equation for the reversible reaction of carbon monoxide and hydrogen to form methane plus water is

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$$

Since atoms must be conserved during reaction, the stoichiometric coefficients appearing in the stoichiometric equation must result in the occurrence of the same number of atoms of any given element on each side of the reaction equation. A stoichiometric equation for which this is true is said to be *balanced*.

Example 1.7 The reaction

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$$

is balanced. There is a single C atom, two O atoms, and eight H atoms on each side of the equation.

The reaction

$$C_3H_6 + 4O_2 \rightarrow 3CO_2 + 3H_2O$$

is not balanced. There are eight O atoms in the reactant side and nine O atoms on the product side. The stoichiometric coefficient of O_2 should be changed to $\frac{9}{2}$ for the equation to represent a valid reaction.

The stoichiometric equation very clearly and compactly summarizes several important features of a system undergoing reaction.

1. Since the numbers of atoms of each type of element are unchanged, the mass of each type of element in the system is unchanged, that is, it is conserved.
2. Since the number of molecules of each type of chemical compound involved in the reaction will change, the mass of each reacting compound is *not* conserved.
3. Since species that do not appear in the stoichiometric equation are by definition unaffected by the reaction, the mass of each such inert species will be conserved.

These observations will prove quite central in our formulation of material balance equations.

Atomic and Molecular Weights While the stoichiometric equation indicates the proportions in which molecules must be combined to form products, it is necessary to deal with the mass or mass flow rate of each reactant when actually preparing the reactant mixtures. To relate ratios of molecules to actual masses of each compound, it has proved convenient to use the concepts of atomic weight, molecular weight, and mole.

The *atomic weight* of an element is the relative mass of one atom of that element based on a standard but arbitrary scale which sets the mass of one atom of the carbon-12 isotope at exactly 12.

The *molecular weight* of a compound is the sum of the products of the atomic weight of each constituent element times the number of atoms of that element present in one molecule of the compound.

Both the atomic weight and the molecular weight are relative numbers, as they are based on the value of 12 assigned to carbon-12. The atomic weights of the elements are tabulated in Appendix 1.

Example 1.8 Calculate the molecular weight of C_3H_6 using Appendix 1.

Solution The atomic weights of carbon and hydrogen are 12.0115 and 1.00797, respectively. The atomic weight of C is not 12 exactly because the standard atomic weights are determined using the mixture of isotopes of that element that occurs naturally. By definition, the molecular weight of C_3H_6 is equal to

$$3(12.01115) + 6(1.00797) = 42.08127$$

In practice, one would typically round this number to the nearest tenth.

A *gram mole*, or simply *mole*, of a substance is the amount of that substance that contains as many elementary entities as there are atoms in 12 g carbon-12. If the substance is an element, the elementary species will be atoms. If the substance is a compound, the entities will be molecules.

Since the gram mole and the molecular weight of a compound are both defined relative to carbon-12, the mass of one mole of a compound can be calculated as the product of the mass of one mole of carbon-12 times the molecular weight of the compound. That is,

$$\text{One gram mole} = 12\text{ g carbon-12} \times \frac{\text{molecular weight of } x}{12}$$
$$= (\text{molecular weight of } x) \text{ grams}$$

where the number 12 in the denominator is the basis of the scale of atomic and molecular weights, the number assigned to carbon-12.

Because the gram mole is defined in terms of a specific amount of carbon-12 expressed in grams, one could equally define moles in terms of other measures of mass, for example, a kilogram mole or a milligram mole. For instance, 1 kgmol would be defined in terms of the number of atoms in 12 kg carbon-12. Thus, 1 kgmol would be equal to 10^3 gmol.

Example 1.9 Suppose the new unit of mass called the gold brick is defined as one gold brick = 1000/3 g.

(a) Calculate the mass in gold bricks of one gold-brick mole of H_2O.
(b) Calculate the number of gram moles per gold-brick mole.

Solution By definition, one gold-brick mole of water is the mass of water which contains as many molecules as there are atoms in 12 gold bricks of carbon-12. Since the molecular weight of H_2O is about 18, we have

$$\text{One gold-brick mole} = 12 \text{ gold bricks of carbon-12} \times \frac{18}{12}$$
$$= 18 \text{ gold bricks of } H_2O$$

Since 1 gold brick = 1000/3 g, it follows that one gold-brick mole = 18 gold bricks of $H_2O \times \frac{1000}{3}$ g/gold brick = 6000 g H_2O. But from the definition of the gram mole,

$$\text{One gram mole} = 18 \text{ g } H_2O$$

Therefore,

$$\text{One gold-brick mole} = \frac{6000 \text{ g } H_2O}{18 \text{ g } H_2O/\text{gmol}}$$
$$= \frac{1000}{3} \text{ gmol}$$

The above example shows that the definitions of the mole in terms of different mass units will lead to a mole unit of different total mass. Since the mass of a carbon-12 atom is a fixed quantity, changing the unit of mass on the reference mass of carbon-12 will change the number of atoms that are contained in one mole of carbon-12. The number of atoms in one gram mole of carbon-12 is known as Avogadro's number, A, and its most accurately known value[3] is $6.0220943 \times 10^{23} \pm 6.3 \times 10^{17}$. Since

$$\frac{12 \text{ g carbon} \quad 12/\text{gmol}}{\text{Mass of one carbon} - 12 \text{ atom}} = \text{A atoms/gmol}$$

the number of elementary entities in 1 kgmol will be equal to 10^3A, in one gold-brick mole will be equal to 1000/3A, and so on. Fortunately, the calculations of the mole–mass equivalences use the relative atomic/molecular weights and do not explicitly require Avogadro's number or its multiples. Thus, knowledge of its precise numerical value is not essential for most calculations.

The key points to retain from the preceding discussion are the following. First, although the standard mole is the gram mole, mole units can be defined in terms of any desired unit of mass. Second, the mole-to-mass conversion factor for any compound in any mass unit will always be numerically equal to the molecular weight of the compound. For instance, for water there are 18 g per gmol, 18 kg/kgmol, 18 gold bricks/gold-brick mole, and so forth. For this reason, the molecular weight is often directly written as the mass–mole conversion factor with an assigned set of units, although strictly speaking it is dimensionless. We employ this loose practice in subsequent chapters because of its widespread usage in the field.

1.3.3 Equation-Solving Concepts

The application of the conservation laws to steady-state systems ultimately requires the solution of sets of balance equations for the values of unknown process flow rates. In general, the equations will be algebraic, may be linear or nonlinear, and their number may be quite large. Since the solution of such equation sets can be a formidable task, it is appropriate to devote attention to the study of efficient solution strategies and methods, as is done in subsequent chapters. For the present, we briefly recall some elementary equation-solving concepts which ought to be familiar to the reader.

Linear Equations A linear equation of the variables x_1 through x_N is a function of the form

$$a_1x_1 + a_2x_2 + \cdots + a_Nx_N = b$$

where the coefficients a_i and the right-hand side b are known constants. Each term in the function contains a single variable, and each variable occurs to the first power. If the linear equation contains but a single unknown, say, x_1, then the unique solution to the equation can be obtained by mere division, that is, $x_1 = b/$

[3] Anon., "Metrology: A More Accurate Value of Avogadro's Number," *Science*, *183*, 1037–1038 (Sept. 20, 1974).

a_{ii}. If the linear equation contains more than one variable, then it will have an infinite number of solutions since we can always set all variables but one to arbitrary values and solve the resulting single-variable equation for the remaining unknown.

The process of setting $N - 1$ variables to fixed values is equivalent to augmenting the multivariable linear equation with $N - 1$ trivial equations of the form $x_i = c_i$. This is but a special instance of the well-known fact that a *system* of linear equations has a unique solution if and only if the system contains as many independent equations as there are unknowns. A set of linear equations is *independent* if and only if no one equation in the system can be obtained by adding together multiples of any of the remaining equations.

Example 1.10 The system of equations

$$x_1 + 0x_2 = 1$$
$$0x_1 + 1x_2 = 2$$

is *independent* because neither equation can be expressed as a multiple of the other.

The system of equations

$$x_1 + 0x_2 = 1$$
$$0x_1 + 1x_2 = 2$$
$$1x_1 + 1x_2 = 3$$

is dependent because the third is equal to the sum of the first two.

The solution of systems of linear equations can be accomplished in two ways: by Cramer's rule or by variable elimination.

Cramer's Rule Cramer's rule is a classical construction which expresses the solution of a system of linear equations in terms of ratios of determinants of the array of coefficients of the equations. In the case of a system of two equations in two unknowns,

$$a_{11}x_1 + a_{12}x_2 = b_1$$
$$a_{21}x_1 + a_{22}x_2 = b_2$$

The solution will be given by

$$x_1 = \frac{\det\begin{vmatrix} b_1 & a_{12} \\ b_2 & a_{22} \end{vmatrix}}{\det\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix}} = \frac{b_1a_{22} - b_2a_{12}}{a_{11}a_{22} - a_{12}a_{21}}$$

$$x_2 = \frac{\det\begin{vmatrix} a_{11} & b_1 \\ a_{21} & b_2 \end{vmatrix}}{\det\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix}} = \frac{b_2a_{11} - b_1a_{21}}{a_{11}a_{22} - a_{12}a_{21}}$$

The form of the solution extends in an obvious way to larger systems. In each case, the denominator of the ratios will consist of the determinant of the array of variable coefficients, while the numerator for the ith variable will consist of the determinant of the array formed when the ith column of the array of variable coefficients is replaced by a column of right-hand side constants. Unfortunately, the evaluation of determinants becomes quite cumbersome and error prone for systems larger than 2. Hence, the use of Cramer's rule is not recommended beyond the case $N = 2$.

Variable Elimination The solution strategy for linear equation sets which is always applicable is successively to solve one of the equations of the set for one of the unknowns and to eliminate that variable from the remaining equations by substitution. The elimination process is continued until the system is reduced to a single equation in one unknown. This approach is considerably simplified if each of the original equations contains only a few of the unknowns.

Example 1.11 Solve the system of equations given below using elimination.

$$\begin{aligned} 2x_1 + 2x_2 + 4x_3 &= 5 \\ x_1 \qquad\quad + x_3 &= 2 \\ x_1 + 3x_2 \qquad\quad &= 7 \end{aligned}$$

Solution Suppose we solve the second equation for x_3:

$$x_3 = 2 - x_1$$

and the third equation for x_2:

$$x_2 = \tfrac{1}{3}(7 - x_1)$$

The results can be substituted into the first equation to obtain a single equation in x_1. That is,

$$2x_1 + 2(\tfrac{1}{3}(7 - x_1)) + 4(2 - x_1) = 5$$

Collecting terms, we obtain

$$-\tfrac{8}{3}x_1 = -\tfrac{23}{3}$$

or

$$x_1 = \tfrac{23}{8}$$

The values of the remaining variables can then be obtained by back-substituting the value of x_1 in the expressions for x_2 and x_3. Thus, $x_2 = \frac{11}{8}$ and $x_3 = -\frac{7}{8}$. The solution can and always should be checked by substituting it into the three equations.

The variable elimination strategy is quite adequate for manual calculations involving perhaps up to five equations, particularly if each variable is not present in every equation. We use this approach extensively in Chapters 2 and 3 and select, whenever possible, the equations to be solved so that the above condition is met. For computer solution or manual solution of larger problems, formulations of the elimination strategy are available which operate on the array of detached equation coefficients. Such an approach is discussed in Chapter 4.

Nonlinear Equations A nonlinear equation is quite simply any equation that is not linear. As such, a nonlinear equation can take on any of an unlimited number of different forms. For some of these forms, analytical solution formulas are available; hence, determination of the solution of a specific equation is a straightforward matter. For instance, the well-known analytical solution of the quadratic equation

$$f(x) = ax^2 + bx + c = 0$$

given by the formula

$$x = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a}$$

can easily be evaluated for any specific values of the constants a, b, and c. By contrast, the equally elementary equation

$$f(x) = x \exp(ax) - b = 0$$

has no analytical solution formula; hence, for any specific values of a and b, its solution requires the use of either graphical or numerical methods.

Graphical Solution The graphical method for solving a nonlinear equation in a single variable involves the construction of a graph of the function $f(x)$. The construction of the graph of course requires that the function be evaluated at a suitable number of trial points and that a smooth curve be drawn through these trial points. The solution is then obtained as the intersection of the curve with the x axis. In principle, the accuracy of the solution can be improved as desired by repeating the graphical construction using more closely spaced trial points and a graph with a finer scale.

Example 1.12 Obtain an estimate of the solution of the function $f(x) = x \exp(x) - 5 = 0$ graphically.

Solution Since at $x = 0$, $f(x)$ is negative, while at $x = 2$ it is positive, the solution must lie in the interval $0 \leq x \leq 2$. The function can be evaluated at a suitable number of trial points, say, 10 equidistant points in the interval. The resulting (x, y) pairs can then be used to construct the graph shown in Figure 1.6. From the graph, the solution can be estimated to be about 1.33, whereas the solution exact to seven decimals is 1.3267247. At $x = 1.33$, the function value is 0.0288, while at the more exact solution the function value is 3.05×10^{-7}.

Numerical Solution Graphical solution is adequate in applications in which the function is easy to evaluate and a solution with two- or three-figure accuracy is acceptable. Repeated application of graphical constructions is generally inefficient

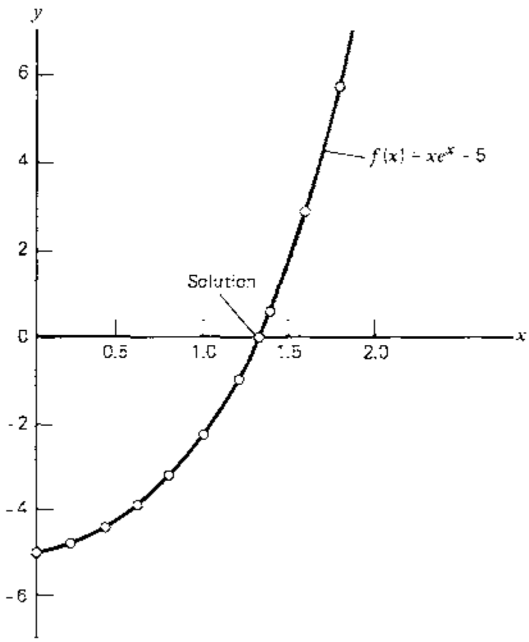


Figure 1.6 Graph of $f(x) = xe^x - 5$.

as a means of improving accuracy. If increased accuracy is desired or if the function is complex to evaluate, then *numerical* methods are much to be preferred. A *numerical method* or *algorithm* is a clearly defined series of logical and algebraic steps which, given an estimate x^{k-1} of the solution, will generate an improved estimate x^k by using information about the function at x^{k-1} as well as possibly at prior solution estimates. The most common type of function information used by numerical algorithms is the value of the function at the previous solution estimates.

The key requirement of a successful numerical method is that it successively improve the solution estimate. In this context, an improved solution estimate is simply one whose function value is closer to zero then that of the previous solution estimate. If the algorithm has this property, then there is some assurance that after repeated application of its steps, a sufficiently accurate solution estimate will be obtained. The algorithm is then said to have *converged*. Normally, an equation-solving algorithm will be terminated when the absolute value of the function at the current solution estimate is less than some specified accuracy parameter ε_1 (say, 10^{-4}). Sometimes, an algorithm might also be terminated if the relative difference between successive solution estimates becomes smaller than some specified tolerance ε_2 (say, 10^{-5}). That is, if x^k is the current estimate and x^{k-1} is the previous estimate of the solution, then one would terminate the application of the numerical method if

$$|f(x^k)| < \varepsilon_1$$

and/or

$$|x^k - x^{k-1}| < \varepsilon_2 |x^k|$$

The simplest of the numerical methods for the solution of the equation $f(x) = 0$ is the *interval halving* or bisection method. In this method, given two solution estimates x^L and x^R, one with a positive function value and the other with a negative function value, the next estimate z of the solution is obtained by setting

$$z = \frac{x^L + x^R}{2}$$

Then, if $f(z) < 0$, the new estimate z is used to replace the point x^L or x^R that has a negative function value. Alternatively, if $f(z) > 0$, the new estimate z is used to replace the point with positive function value. The calculations continue in this fashion until either $f(z)$ becomes sufficiently close to zero or the difference between the points x^L and x^R becomes sufficiently small. Observe that since the interval $x^L \leq x \leq x^R$ within which the solution of $f(x)$ must lie is reduced by one half with each trial point, the size of the interval after N trial points will be $(\overline{x}^R - \overline{x}^L)/2^N$, where $\overline{x}^R$ and $\overline{x}^L$ are the initial estimates with which the bisection method is started. As a result, the desired accuracy of the estimate of the solution x^* can also be controlled by choosing N appropriately. The complete interval halving algorithm is summarized below:

Given N, ε_1, and the bounds x^R and x^L such that $f(x^L)\,f(x^R) < 0$, set $n = 1$.

Step 1 Calculate $z = \dfrac{x^R + x^L}{2}$ and evaluate $f(z)$.

Step 2 If $|f(z)| \leq \varepsilon_1$, stop. The point z is the solution.

Step 3 If $f(z)\,f(x^R) \leq 0$, set $x^L = z$ and go to Step 5. Otherwise, continue.

Step 4 If $f(z)\,f(x^L) < 0$, set $x^R = z$ and continue.

Step 5 If $n = N$, stop. Otherwise, set $n = n + 1$ and continue with Step 1.

Example 1.13 Obtain a solution of $f(x) \equiv x \exp(x) - 5 = 0$ such that $|f(x)| \leq 10^{-2}$ starting with $x^L = 1.2$ and $x^R = 1.4$ using interval halving. As a conservative estimate, set $N = 10$.

Solution At x^L, $f(x^L) = -1.0159$; and at x^R, $f(x^R) = 0.67728$. Following Step 1, we obtain $z = (1.2 - 1.4)/2 = 1.3$ and $f(z) = -0.2299$. Since Step 2 is not satisfied, we check

$$f(z)\,f(x) = (-0.2299)(0.67728) < 0$$

Following Step 3, we set $x^L = z = 1.3$ and continue with Step 1. The results of the next six iterations are summarized below. At the seventh trial point, the requirement $|f(z)| \leq 10^{-2}$ is satisfied and, hence, the calculations are terminated.

x^L	1.3	1.3	1.325	1.325	1.325	1.325
x^R	1.4	1.35	1.35	1.3375	1.33125	1.328125
$f(z)$	0.2075	−0.0151	0.0952	0.03981	0.01229	0.00142

After seven iterations, the solution x^* has been bracketed within the interval $1.326563 \leq x^* \leq 1.328125$. The length of this interval is equal to the initial interval 1.4–1.2 divided by 2^7.

As evident from the example, the performance of the interval halving method is sure but rather slow. Hence, in Chapter 5 we study a broader selection of algorithms for the numerical solution of a single nonlinear equation.

Systems of Equations Solution of systems of nonlinear equations is considerably more difficult than the single equation case. As with linear equations, it is sometimes possible to use the variable elimination strategy to reduce the system to a single nonlinear equation. However, unlike in the linear case, the success of this strategy is not guaranteed since it may simply not be possible to explicitly solve any given nonlinear equation for a single unknown. For instance, the function in the previous example cannot be directly solved for x. In most cases, it is at best only possible to use the elimination strategy to reduce the system of equations to a smaller set; and when this is possible, it is useful to do so. Graphical solution of systems of nonlinear equations is normally not feasible; hence, in most cases numerical solution is the only alternative. In Section 5.2 we discuss such methods and their use with computers. The development of these methods assumes familiarity with the concepts of *derivative* and *partial derivative*. The reader unfamiliar with these concepts is strongly encouraged to consult the introductory chapters of any calculus text.

1.3.4 Dimensional Quantities and Their Manipulation

Scientific measurements and engineering calculations are normally performed using quantities whose magnitudes are expressed in terms of standard units of measure or dimensions. Thus, the mass of water in a barrel might be reported in kilograms or the length of a pipe in meters. While the association of dimensions with physical quantities is essential in removing ambiguities which can arise in communicating and using these quantities, it does require knowledge of the definitions of the standard units, the ability to convert between equivalent units, and the skill to manipulate dimensional quantities in a consistent fashion. In this section, we briefly review these topics.

Units of Measure A dimensional quantity is simply one that is defined by a magnitude and the name of a unit of measure. In order for the unit of measure to serve its function, its definition must be held in common by all users. Moreover, the definition should, if possible, be verifiable through standardized physical experiments. These considerations have led to the worldwide adoption of the International System of Units formalized in 1960 and last revised in 1971. The SI system has seven base units: the meter, kilogram, second, ampere, kelvin, mole, and candela. With the exception of the kilogram, these units are defined in terms of appropriate physical experiments.

The definitions of the base units of concern in balance calculations are the following.

The unit of *length*, the *meter* (m), is the length equal to 1,650,763.73 wavelengths in vacuum of the radiation corresponding to the transition between the levels $2p_{10}$ and $5d_5$ of the krypton-86 atom.

The unit of *mass*, the *kilogram* (kg), is the mass of a prototype held by the International Bureau of Weights and Measures in Paris.

The *second* (s) is the duration of 9,192,631,770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the cesium-133 atom.

The *temperature* unit, the *kelvin* (K), is the fraction 1/273.16 of the thermodynamic temperature of the triple point of water.

The definition of the mole was given in Section 1.3.2, while the precise definitions of the remaining units can be found elsewhere.[4]

These SI units can be used with standard prefixes and their symbols to designate decimal submultiples. Preferred submultiples are

$$10^{9} = \text{giga (G)}$$
$$10^{6} = \text{mega (M)}$$
$$10^{3} = \text{kilo (k)}$$
$$10^{3} = \text{milli (m)}$$
$$10^{6} = \text{micro } (\mu)$$
$$10^{9} = \text{nano (n)}$$

Thus, 10^3 m can be called a kilometer and abbreviated km.

The base units can be used in combination to obtain derived units, such as the unit of force, the newton (N), defined as one kilogram meter per second squared.

Other various units of length, mass, time, or temperature which have come into use for historical reasons are by agreement defined in terms of the SI units. For instance, the hour (h) is defined as 3600 s; the ton (t), as 10^3 kg; the liter (l), as 10^{-3} m^3; and the centimeter (cm), as 10^{-2} m. Similarly, the unit of mass, the pound mass (lb_m), until recently widely used in the English-speaking world, is defined as 0.45359237 kg and the unit of length, the foot (ft), as 0.3048 m. Paralleling the definition of the mole given in Section 1.3.2, a molar unit called the pound mole (lbmol) is sometimes used in conjunction with mass quantities expressed in lb_m. Following the discussion given earlier, it is clear that 1 lbmol = 453.59237 gmol.

Manipulation of Dimensional Quantities Since the units of a dimensional quantity are as important as the magnitude of that quantity, both should always be used in reporting. The units should also be explicitly shown for each dimensional quantity involved in a computation as an aid in deducing the units of the result and in verifying the consistency of the units involved in the intermediate steps of the calculation. If the units are shown explicitly along with the magnitudes of the quantities, then the unit symbols can be manipulated just like any other algebraic quantity. Specifically, the manipulation of units takes place via the following rules:

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[4] *ASTM/IEEE Standard Metric Practice*, ASTM E380-75, Institute of Electrical and Electronic Engineers, New York, N.Y., Jan. 30, 1976.

1. The addition or subtraction of quantities all expressed in the same units yields a result expressed in those units. The addition or subtraction of quantities expressed in different units is obviously meaningless.
2. The multiplication or division of quantities expressed in arbitrary units yields a result which will have units given by the product or ratio of the units of those quantities.
3. The division of quantities in the same units gives as result a dimensionless quantity, that is, the units cancel.
4. The product of quantities expressed in the same units yields a result which has these units raised to a suitable exponent.

In short, the units associated with dimensional quantities follow the conventional rules of algebraic manipulation.

Example 1.14 Unit Manipulation Rules

(a) 10 kg/h + 20 kg/h = 30 kg/h.
(b) 10 kg/s − 7200 kg/h is not defined.
(c) 20 m × 10 m × 5 m = 1000 m^3.
(d) 10 kg/s × 3600 s/h = 36,000 kg·s/s·h = 36,000 kg/h.
(e) $\dfrac{15 \text{ m/h} \times 4 \text{ kg/m}^3}{10 \text{ mol/m}^2 \times 25 \text{ kg/mol}} \times 50 \text{ h} = 12 \dfrac{\text{m}^3\cdot\text{mol}\cdot\text{kg}\cdot\text{h}}{\text{m}^3\cdot\text{mol}\cdot\text{kg}\cdot\text{h}} = 12$, where 12 is dimensionless.

Unit Conversion In the above example, the difference 10 kg/s − 7200 kg/h can only be computed if the units of both quantities are the same. Since both quantities have dimensions of mass per unit time, they ought to be expressible in the same units. In particular, since by definition 1 h = 3600 s, the rate of 7200 kg/h can be transformed to a rate expressed in kg/s by multiplying the former by the dimensionless ratio 1 h/3600 s, that is,

$$7200 \text{ kg/h} \times 1 \text{ h/3600 s} = 2 \text{ kg/s}$$

In this manipulation, we have merely rearranged the definition of the hour to a dimensionless ratio and have applied the ratio in such a way as to allow the hour units to cancel out. The process of successive application of the definition of units to transform a quantity in one set of units to the equivalent quantity expressed in another desired set of units is called *unit conversion*. The process of unit conversion is clearly just a special instance of the application of the unit multiplication rule. In material balance computations, the unit conversions required will normally only involve direct interconversion between mass, mole, and time units. In energy balance applications, more involved unit conversions will be required, and these are given special attention in Section 6.4.

Example 1.15 Elementary Unit Conversion

(a) Convert a flow of 10 kg/s to a flow in tons per hour.
(b) Convert a flow of CO_2 of 88 kg/h to pound moles per hour.

Solution

(a) To convert seconds to hours and kilograms to tons, the definitions 1 h = 3600 s and 1 t = 10^3 kg are needed. Applying the definitions successively, we obtain

$$100 \text{ kg/s} \times 1 \text{ t}/10^3 \text{ kg} \times 3600 \text{ s/h} = 360 \text{ t/h}$$

(b) To convert mass to moles, we need the definition of the pound mole. Since the molecular weight of CO_2 is 44, it follows that

$$1 \text{ lbmol } CO_2 = 44 \text{ lb}_m$$

To use this mass-to-mole conversion factor, we first must convert mass in kg to mass in lb_m using the definition 1 lb_m = 0.45359237 kg. The combined result is

$$88 \text{ kg/h} \times 1 \text{ lb}_m/0.45359237 \text{ kg}$$
$$\times 1 \text{ lbmol } CO_2/44 \text{ lb}_m = 4.41 \text{ lbmol } CO_2/\text{h}$$

Composition Conversions One special type of unit conversion which is required quite frequently in material balance computations is that of transforming one measure of the composition of a mixture to another measure. This need arises because composition can be expressed in various ways:

1. Molar concentration $\tilde{c}$, moles of a component per volume of solution.
2. Mass concentration $\hat{c}$, mass of a component per volume of solution.
3. Mole fraction x, moles of one component per mole of mixture.
4. Mass fraction w, mass of one component per unit mass of mixture.
5. Solvent-free mole/mass fractions, moles or mass of a given species per mole of mixture exclusive of the solvent or some other designated component.

While composition can be measured and reported in various units, the principle of conservation of mass only applies to mass of species or to moles in nonreacting cases. Consequently, for material balance purposes it is ultimately necessary and preferable to deal with mole/mass fractions or, better yet, species mole/mass flows rather than with some of the other composition measures.

To carry out the conversions between composition measures, some or all of the following bulk properties of mixtures are required: density, specific or molar volume, and average molecular weight. These properties can simply be viewed as conversion factors which are specific to a given mixture.

The mass or molar *density* of a mixture, designated respectively as $\hat{\rho}$ and $\tilde{\rho}$, is the mass or number of moles of mixture per unit volume of mixture.

The *specific volume* $\hat{V}$ or *molar volume* $\tilde{V}$ of a mixture is, respectively, the reciprocal of the mass or molar density.

The *average molecular weight* of a mixture, $\bar{M}$, is simply the sum of the products of the mole fraction times the molecular weight of each of the mixture components. If x_s indicates the mole fraction of species s and M_s is its molecular weight, then

$$\bar{M} = \sum_s x_s M_s$$

where the sum is over all species s in the mixture. In general, the conversion of concentration measures to mole or mass fractions involves two steps: first, conversion of the unit volume of mixture to mass or mole quantities and second, if appropriate, conversion between the moles/mass of the species in question. Thus, for a given species s,

$$\begin{aligned} x_s &= \tilde{c}_s \text{ (mol/volume) } \tilde{V} \text{ (volume/mol)} \\ &= \hat{c}_s \text{ (mass/volume) } \tilde{V} \text{ (volume/mol) } \frac{1}{M_s} \text{ (mol/mass)} \end{aligned}$$

and

$$\begin{aligned} w_s &= \tilde{c}_s \text{ (mol/volume) } \hat{V} \text{ (volume/mass) } M_s \text{ (mass/mol)} \\ &= \tilde{c}_s \text{ (mol/volume) } \tilde{V} \text{ (volume/mol) } M_s \text{ (mass/mol) } \frac{1}{\bar{M}} \text{ (mol/mass)} \end{aligned}$$

In the last equality, note that the molecular weight of species s, M_s, converts the moles of species s in the concentration to mass of species s. The average molecular weight $\bar{M}$ converts the moles of mixture in the molar volume $\tilde{V}$ to mass of mixture.

Example 1.16 A solution of NaOH in water has a molarity of 2.0 and a density of 53 kgmol/m^3. Calculate the mole fraction of NaOH and the mass density of the solution in tons per cubic meter.

Solution The molarity is a molar concentration defined in units of gmol/l. Thus, it is first necessary to convert liters to cubic meters and then cubic meters of solution to moles of solution. Thus,

$$\begin{aligned} x_{NaOH} &= \frac{2.0 \text{ gmol NaOH}}{1} \times \frac{1 \text{ l}}{10^{-3} \text{ m}^3} \times \frac{1 \text{ kgmol}}{10^3 \text{ gmol}} \times \frac{1 \text{ m}^3}{53 \text{ kgmol}} \\ &= 0.0377 \text{ kgmol NaOH/kgmol solution} \end{aligned}$$

Since by definition 1 kgmol solution contains 0.0377 kgmol NaOH, the balance, or 0.9623 kgmol, must be water. The average molecular weight is therefore given by

$$\begin{aligned} \bar{M} &= x_{NaOH} M_{NaOH} + x_{H_2O} M_{H_2O} \\ &= 0.0377(40) + 0.9623(18) = 18.83 \end{aligned}$$

The mass density will be equal to

$$\rho\ (\text{kg/m}^3) = \rho\ (\text{kgmol/m}^3)\ M\ (\text{kg/kgmol})$$
$$= 53\ \text{kgmol/m}^3 \times 18.83\ \text{kg/kgmol} = 998.0\ \text{kg/m}^3$$

Since 1 t = 10^3 kg, this is equivalent to 0.998 t/m^3.

Example 1.17 A mixture contains 10 g/l each of toluene and xylene in benzene. If the mixture density is 0.85 g/cm^3, calculate the benzene free mass fraction of toluene.

Solution First the mass concentrations of toluene and xylene must be converted to mass fractions. Then, the benzene free mass fraction can be calculated from its definition. Thus,

$$w_{C_6H_5CH_3} = \frac{10\ \text{g toluene}}{\text{l}} \times \frac{1\ \text{l}}{10^{-3}\ \text{m}^3} \times \frac{\text{cm}^3}{0.85\ \text{g solution}} \times \frac{(10^{-2}\ \text{m})^3}{1\ \text{cm}^3}$$
$$= \frac{10^{-2}}{0.85}\ \frac{\text{g toluene}}{\text{g solution}} = 0.01176$$

It is easy to verify that $w_{C_6H_5(CH_3)_2}$ will also be equal to 0.01176. Then, by definition, the benzene free mass fraction of toluene will be equal to

$$\frac{\text{Mass toluene}}{\text{Mass toluene + mass xylene}}$$
$$= \frac{10^{-2}/0.85\ \text{g toluene/g solution}}{10^{-2}/0.85\ \text{g toluene/g solution} + 10^{-2}/0.85\ \text{g xylene/g solution}} = 0.5$$

Dimensional Equations Since the units of a dimensional quantity are merely labels expressing the scale in terms of which the magnitude of the quantity is to be interpreted, a dimensional quantity need not always be a constant. It can also be a variable. If an equation involves dimensional variables as well as some dimensional constants, then each of the terms of the equation becomes a dimensional quantity. The rules for manipulating dimensional quantities are equally applicable to such terms, and hence to equations, as they are to dimensional constants. In particular, rule 1 (p. 26) indicates that if an equation consists of a sum of terms, then each term must have the same units. Thus, the right-hand side constant of a linear equation must have the same units as each of the terms on the left-hand side of the equation. Moreover, the multiplication or division of factors or variable groupings must also follow rules 2 through 4. An equation which satisfies rules 1 through 4 is said to be *dimensionally homogeneous*. All dimensional equations must be dimensionally homogeneous.

Example 1.18 A mill pond has two inlets, one of which supplies water at 1 ft^3/min, and one outlet which services the mill, as shown in Figure 1.7. If the water flow to the mill is 7440 lb$_m$/h, what must be the additional inlet flow to the pond,

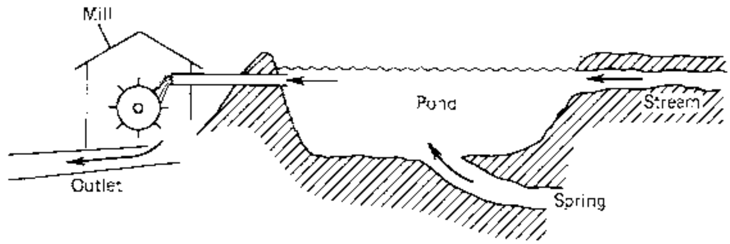

Figure 1.7 Schematic of Example 1.18.

assuming that the pond level is to remain constant? The density of water is 62 lb_m/ft^3.

Solution If the pond level and the flows are constant with time, then the system consisting of the water in the pond must be at steady state. The application of the mass conservation equation, eq. (1.2). Thus yields

$$\text{Flow water in} = \text{flow water out}$$

or

$$1 \text{ ft}^3/\text{min} + x = 7440 \text{ lb}_m/\text{h}$$

where x is the unknown additional water inlet flow. For this equation to be meaningful, the units of both quantities on the left-hand side must be the same. Thus, the unknown flow x must be defined in terms of ft^3/min. Moreover, the units of the right-hand side of the equation must be the same as those of the left-hand side. The flow rate of 7440 lb_m/h must therefore be converted to ft^3/min, that is,

$$7440 \text{ lb}_m/\text{h} \times \text{ft}^3/62 \text{ lb}_m \times 1 \text{ h}/60 \text{ min} = 2 \text{ ft}^3/\text{min}$$

Thus, the dimensionally homogeneous way of writing the above equation is

$$1 \text{ ft}^3/\text{min} + x \, (\text{ft}^3/\text{min}) = 2 \text{ ft}^3/\text{min}$$

The solution is obviously $x = 1$ ft^3/min.

Example 1.19 The density of liquid ethanol in g/cm^3 as a function of temperature T in degrees Kelvin has been correlated via the equation

$$\rho \, (\text{g/cm}^3) = 1.032 - 5.392 \times 10^{-4} T - 8.712 \times 10^{-7} T^2$$

(a) What are the units of the three constants if the equation is dimensionally homogeneous?
(b) How would the correlation be altered to yield liquid density in gmol/l?

Solution (a) For the equation to be dimensionally homogeneous, all three terms on the right-hand side of the equation should have the same units as those of the density (g/cm^3). Therefore, the constant 1.032 should have units of g/cm^3; the constant 5.392 $\times$ 10^{-4} should have the units of g/K $\cdot$ cm^3; and the constant 8.712 $\times$ 10^{-7} should have the units of g/K^2 $\cdot$ cm^3.

(b) Since the molecular weight of C_2H_5OH is 46, it follows that

$$\rho \text{ (gmol/l)} = \rho \text{ (g/cm}^3) \times \frac{10^3 \text{ cm}^3}{1 \text{ l}} \times \frac{\text{gmol}}{46 \text{ g}}$$

$$= \rho \text{ (g/cm}^3) \times \frac{10^3}{46} \text{ (gmol} \cdot \text{cm}^3/\text{g} \cdot \text{l)}$$

Therefore, to convert the correlation to give density in gmol/l, all three constants in the correlation should be multiplied by $10^3/46$.

It should be noted that while each equation in an equation set must be dimensionally homogeneous, it certainly is not necessary that all equations in the set be expressed in the same units. In many cases, this is in fact impossible because the equations will have arisen from different physical laws (e.g., a mass conservation equation and an energy conservation equation) and hence may involve entirely different dimensional quantities. It is however critical that in each instance in which a given variable appears in the equations of the set that variable be expressed in the same units. Thus, if x represents the flow of water into the system in units of m^3/h in one equation, then it must be similarly defined in all other equations.

This completes our review of basic concepts. We conclude the chapter with an overview of the organization of the remainder of the book.

1.4 PREVIEW OF SUBSEQUENT CHAPTERS

The chapters of this book can be divided into three parts. Chapters 2 through 5 deal with the application of the principle of conservation of mass. Chapters 6 through 8 deal with the application of the principle of conservation of energy. Finally, Chapter 9 discusses the solution of problems in which the two types of balances must be solved jointly.

With the exception of Chapter 5, each of the material balance chapters is organized with a dual purpose: to develop the particular structure and properties of a particular type of balance equation and to present analysis and solution strategies for treating increasingly more complex flowsheet problems. Thus, Chapter 2 develops the properties of species material balances for nonreacting systems, Chapter 3 discusses the properties of species material balances for reacting systems, while Chapter 4 presents the characteristics of material balance equations written on the individual chemical elements. Concurrently, as we proceed from Chapters 2 through 4, we advance from the solution of flowsheet problems with just a single processing unit and a few streams to flowsheets with many units and numerous streams. In Chapter 5, we cap the development of material balance concepts with a discussion of iterative and computer-oriented solution strategies.

The energy balance chapters differ from the material balance development principally in that considerable attention must be devoted to a study of the data, correlations, and subsidiary calculations necessary to evaluate the energy content terms in the balance equations. The solution of the energy balances themselves, by contrast, presents relatively few new difficulties. Chapter 6 reviews the separate terms which must be included in the general energy balance equation, introduces the new units and variables involved in energy balances, and develops the general form of the steady-state energy balance equation. Chapter 7 considers the type of thermodynamic information required to solve problems involving nonreacting systems and develops a framework for analyzing single-unit problems. Chapter 8 considers the reacting case, focusing on the additional thermodynamic data required and on the alternate forms of the energy balance equation that can be written for reacting systems. In addition, the multiunit analysis developed in the material balance part is extended to the energy balance case. Finally, Chapter 9, which in large part parallels Chapter 5, discusses iterative and computer-oriented strategies for solving the combined material and energy balances of complete process flowsheets. The reader who masters all of these topics can be confident of having learned the most important family of calculations performed by chemical engineers.