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Introduction

1.1 Background and Scope

Engineering can be defined as "the science or art of practical applications of the knowledge of pure sciences such as physics, chemistry, and biology."

Compared with civil, mechanical, and other forms of engineering, chemical engineering is a relatively young branch of the subject that has been developed since the early twentieth century. The design and operation of efficient chemical plant equipment are the main duties of chemical engineers. It should be pointed out that industrial-scale chemical plant equipment cannot be built simply by enlarging the laboratory apparatus used in basic chemical research. Consider, for example, the case of a chemical reactor – that is, the apparatus used for chemical reactions. Although neither the type nor the size of the reactor will affect the rate of chemical reaction *per se*, they will affect the overall or apparent reaction rate, which involves effects of physical processes, such as heat and mass transfer and fluid mixing. Thus, in the design and operation of plant-size reactors, knowledge of such physical factors – which is often neglected by chemists – is important.

G. E. Davis, a British pioneer in chemical engineering, described in his book, *A Handbook of Chemical Engineering* (1901, 1904), a variety of physical operations commonly used in chemical plants. In the United States, physical operations such as distillation, evaporation, heat transfer, gas absorption, and filtration were termed "unit operations" in 1915 by A. D. Little of the Massachusetts Institute of Technology (MIT), where the instruction of chemical engineering was organized via unit operations. The first complete textbook of unit operations entitled *Principles of Chemical Engineering* by Walker, Lewis, and McAdams of MIT was published in 1923. Since then, the scope of chemical engineering has been broadened to include not only unit operations but also chemical reaction engineering, chemical engineering thermodynamics, process control, transport phenomena, and other areas.

Bioprocess plants using microorganisms and/or enzymes, such as fermentation plants, have many characteristics similar to those of chemical plants. Thus, a chemical engineering approach should be useful in the design and operation of various plants that involve biological systems, if differences in the physical properties of some materials are taken into account. Furthermore, chemical engineers

are required to have some knowledge of biology when tackling problems that involve biological systems.

Since the publication of a pioneering textbook [1] in 1964, some excellent books [2, 3] have been produced in the area of the so-called biochemical or bioprocess engineering. Today, the applications of chemical engineering are becoming broader to include not only bioprocesses but also various biological systems involving environmental technology and even some medical devices, such as artificial organs.

1.2 Dimensions and Units

A quantitative approach is important in any branch of engineering. However, this does not necessarily mean that engineers can solve everything theoretically, and quite often they use empirical rather than theoretical equations. Any equation – whether theoretical or empirical – that expresses some quantitative relationship must be dimensionally sound, as stated below.

In engineering calculations, a clear understanding of dimensions and units is very important. *Dimensions* are the basic concepts in expressing physical quantities. Dimensions used in chemical engineering are length (L), mass (M), time (T), the amount of substance (n), and temperature (θ). Some physical quantities have combined dimensions; for example, the dimensions of velocity and acceleration are $L\,T^{-1}$ and $L\,T^{-2}$, respectively. Sometimes, force (F) is also regarded as a dimension; however, as the force acting on a body is equal to the product of the mass of that body and the acceleration acting on the body in the direction of the force, F can be expressed as $M\,L\,T^{-2}$.

Units are measures for dimensions. Scientists normally use the centimeter (cm), gram (g), second (s), mole (mol), and degree Celsius (°C) as the units for length, mass, time, amount of substance, and temperature, respectively (the CGS (centimeter–gram–second) system), whereas the units often used by engineers are m, kg, h, kmol, and °C. Traditionally, engineers have used the kilogram as the unit for both mass and force. However, this practice sometimes causes confusion, and to avoid this, a designation of kilogram-force (kg_f) is recommended. The unit for pressure, $kg\,cm^{-2}$, often used by plant engineers should read $kg_f\ cm^{-2}$. Mass and weight are different entities; the *weight* of a body is the gravitational force acting on the body, that is, (mass) (gravitational acceleration g). Strictly speaking, g – and hence weight – will vary slightly with locations and altitudes on the Earth. It would be much smaller in a space ship.

In recent engineering research papers, units with the International System of Units (SI) are generally used. The SI system is different from the CGS system often used by scientists or from the conventional metric system used by engineers [4]. In the SI system, kilogram is used for mass only, and newton (N), which is the unit for force or weight, is defined as $kg\,m\,s^{-2}$. The unit for pressure, Pa (pascal), is defined as $N\,m^{-2}$. It is roughly the weight of an apple distributed over the area of $1\,m^2$. As it is generally too small as a unit for pressure, kPa (kilopascal) (i.e., 1000 Pa) and MPa (megapascal) (i.e., 10^6 Pa) are more often used. One bar, which is equal to 0.987 atm, is 100 kPa = 0.1 MPa = 1000 hPa (hectopascal).

The SI unit for energy or heat is the joule (J), which is defined as $J = N\,m = kg\,m^2\,s^{-2} = Pa\,m^3$. In the SI system, the calorie is not used as a unit of heat, and hence no conversion between heat and work, such as $1\,cal = 4.184\,J$, is needed. Power is defined as energy per unit time, and the SI unit for power is W (watt) $= J\,s^{-1}$. Since W is usually too small for engineering calculations, the kilowatt (=1000 W) is more often used. Although use of the SI units is preferred, we shall also use in this book the conventional metric units that are still widely used in engineering practice. The English engineering unit system is also used in engineering practice, but we do not use it in this book. Values of the conversion factors between various units that are used in practice are listed in Appendix A, at the back of this book.

Empirical equations are often used in engineering calculations. For example, the following type of equation can relate the specific heat capacity c_p ($J\,kg^{-1}\,K^{-1}$) of a substance with its absolute temperature T (K).

$$c_p = a + bT \tag{1.1}$$

where a ($kJ\,kg^{-1}\,K^{-1}$) and b ($kJ\,kg^{-1}\,K^{-2}$) are empirical constants. Their values in the kcal, kg, and °C units are different from those in the kJ, kg, and K units. Equations such as Equation 1.1 are called *dimensional equations*. The use of dimensional equations should preferably be avoided; hence, Equation 1.1 can be transformed to a nondimensional equation such as

$$\left(\frac{c_p}{R}\right) = a' + b'\left(\frac{T}{T_c}\right) \tag{1.2}$$

where R is the gas law constant with the same dimension as c_p, and T_c is the critical temperature of the substance in question. Thus, as long as the same units are used for c_p and R and for T and T_c, respectively, the values of the ratios in the parentheses as well as the values of coefficients a' and b' do not vary with the units used. Ratios such as those in the above parentheses are called *dimensionless numbers* (groups), and equations involving only dimensionless numbers are called *dimensionless equations*.

Dimensionless equations – some empirical and some with theoretical bases – are often used in chemical engineering calculations. Most dimensionless numbers are usually called by the names of person(s) who first proposed or used such numbers. They are also often expressed by the first two letters of a name, beginning with a capital letter; for example, the well-known Reynolds number, the values of which determine conditions of flow (laminar or turbulent), is usually designated as Re, or sometimes as N_{Re}. The Reynolds number for flow inside a round straight tube is defined as $dv\rho/\mu$, in which d is the inside tube diameter (L), v is the fluid velocity averaged over the tube cross section ($L\,T^{-1}$), ρ is the fluid density ($M\,L^{-3}$), and μ is the fluid viscosity ($M\,L^{-1}\,T^{-1}$) (this is defined in Chapter 2). Most dimensionless numbers have some significance, usually ratios of two physical quantities. How known variables could be arranged in a dimensionless number in an empirical dimensionless equation can be determined by a mathematical procedure known as *dimensional analysis* [5], which is not described in this text. Examples of some useful dimensionless equations or correlations appear in the following chapters of the book.

Example 1.1 A pressure gauge reads 5.80 kg_f cm^{-2}. What is the pressure in SI units?

Solution
Let $g = 9.807$ m s^{-2}.

$$p = \frac{(5.80)(9.807)}{(0.01^{-2})} = 569\ 000\ \text{Pa} = 569\ \text{kPa} = 0.569\ \text{MPa}$$

1.3 Intensive and Extensive Properties

It is important to distinguish between the intensive (state) properties (functions) and the extensive properties (functions).

Properties that do not vary with the amount of mass of a substance – for example, temperature, pressure, surface tension, and mole fraction – are termed *intensive properties*. On the other hand, those properties that vary in proportion to the total mass of substances – for example, total volume, total mass, and heat capacity – are termed *extensive properties*.

It should be noted, however, that some extensive properties become intensive properties, in case their specific values – that is, their values for unit mass or unit volume – are considered. For example, specific heat (i.e., heat capacity per unit mass) and density (i.e., mass per unit volume) are intensive properties.

Sometimes, capital letters and small letters are used for extensive and intensive properties, respectively. For example, C_p indicates heat capacity (kJ °C^{-1}) and c_p indicates specific heat capacity (kJ kg^{-1} °C^{-1}). Measured values of intensive properties for common substances are available in various reference books [6].

1.4 Equilibria and Rates

Equilibria and rates should be clearly distinguished. *Equilibrium* is the end point of any spontaneous process, whether chemical or physical, in which the driving forces (potentials) for changes are balanced and there is no further tendency to change. *Chemical equilibrium* is the final state of a reaction at which no further changes in composition occur at a given temperature and pressure. As an example of a physical process, let us consider the absorption of a gas into a liquid. When the equilibrium at a given temperature and pressure is reached after a sufficiently long time, the compositions of the gas and liquid phases cease to change. How much of a gas can be absorbed in the unit volume of a liquid at equilibrium – that is, the solubility of a gas in a liquid – is usually given by Henry's law:

$$p = HC \tag{1.3}$$

where p is the partial pressure (Pa) of a gas, C is its equilibrium concentration (kg m^{-3}) in a liquid, and H (Pa m^3 kg^{-1}) is the Henry's law constant, which varies with temperature. Equilibrium values do not vary with the experimental apparatus and procedure.

The *rate* of a chemical or physical process is its rapidity – that is, the speed of spontaneous changes toward the equilibrium. The rate of absorption of a gas into a liquid is the amount of the gas absorbed into the liquid per unit time. Such rates vary with the type and size of the apparatus, as well as its operating conditions. The rates of chemical or biochemical reactions in a homogeneous liquid phase depend on the concentrations of reactants, the temperature, the pressure, and the type and concentration of dissolved catalysts or enzymes. However, in the cases of heterogeneous chemical or biochemical reactions using particles of catalyst, immobilized enzymes or microorganisms, or microorganisms suspended in a liquid medium, and with an oxygen supply from the gas phase in the case of an aerobic fermentation, the overall or apparent reaction rate(s) or growth rate(s) of the microorganisms depend not only on chemical or biochemical factors but also on physical factors such as rates of transport of reactants outside or within the particles of catalyst or of immobilized enzymes or microorganisms. Such physical factors vary with the size and shape of the suspended particles and with the size and geometry of the reaction vessel, as well as with operating conditions such as the degree of mixing or the rate(s) of gas supply. The physical conditions in industrial plant equipment are often quite different from those in the laboratory apparatus used in basic research.

Let us consider, as an example, a case of aerobic fermentation. The maximum amount of oxygen that can be absorbed into the unit volume of a fermentation medium at given temperature and pressure (i.e., the equilibrium relationship) is independent of the type and size of vessels used. On the other hand, the rates of oxygen absorption into the medium vary with the type and size of the fermentor and also with its operating conditions, such as the agitator speeds and rates of oxygen supply.

To summarize, chemical and physical equilibria are independent of the configuration of the apparatus, whereas overall or apparent rates of chemical, biochemical, or microbial processes in industrial plants are substantially dependent on the configurations and operating conditions of the apparatus used. Thus, it is not appropriate to perform the so-called scaling-up using only those data obtained with a small laboratory apparatus.

1.5 Batch Versus Continuous Operation

Most chemical, biochemical, and physical operations in chemical and bioprocess plants can be performed batchwise or continuously.

A simple example is the heating of a liquid. If the amount of the fluid is rather small (e.g., 1 kl day^{-1}), then batch heating is more economical and practical, with the use of a tank that can hold the entire liquid volume and is equipped with a built-in heater. However, when the amount of the liquid is fairly large (e.g., 1000 kl day^{-1}), then continuous heating is more practical, using a heater in which the liquid flows at a constant rate and is heated to a required constant temperature. Most unit operations can be carried out either batchwise or continuously, depending on the scale of operation.

Most liquid-phase chemical and biochemical reactions, with or without catalysts or enzymes, can be carried out either batchwise or continuously. For example, if the production scale is not large, then a reaction to produce C from A and B, all of which are soluble in water, can be carried out batchwise in a stirred-tank reactor; that is, a tank equipped with a mechanical stirrer. The reactants A and B are charged into the reactor at the start of the operation. The product C is subsequently produced from A and B as time goes on and can be separated from the aqueous solution when its concentration has reached a predetermined value.

When the production scale is large, the same reaction can be carried out continuously in the same type of reactor or even in another type of reactor (Chapter 7). In this case, the supplies of the reactants A and B and the withdrawal of the solution containing product C are performed continuously, all at constant rates. The washout of the catalyst or enzyme particles can be prevented by installing a filter mesh at the exit of the product solution. Except for the transient start-up and finish-up periods, all the operating conditions such as temperature, stirrer speed, flow rates, and the concentrations of incoming and outgoing solutions remain constant – that is, in the steady state.

1.6 Material Balance

Material (mass) balance, the natural outcome from the law of conservation of mass, is a very important and useful concept in chemical engineering calculations. In usual chemical and/or biological systems, we need not consider nuclear reactions that convert mass into energy.

Let us consider a system that is separated from its surroundings by an imaginary boundary. The simplest expression for the total mass balance for the system is as follows:

$$\text{input} - \text{output} = \text{accumulation} \tag{1.4}$$

The accumulation can be either positive or negative, depending on the relative magnitudes of the input and output. It should be zero for the continuously operated reactor as mentioned in the previous section.

We can also consider the mass balance for a particular component in the total mass. Thus, for a component in a chemical reactor,

$$\text{input} - \text{output} + \text{formation} - \text{disappearance} = \text{accumulation} \tag{1.5}$$

In mass balance calculations involving chemical and biochemical systems, it is sometimes more convenient to use the molar units, such as kilomoles, rather than simple mass units, such as kilograms.

Example 1.2 A flow of 2000 kg h^{-1} of aqueous solution of ethanol (10 wt% ethanol) from a fermentor is to be separated by continuous distillation into the distillate (90 wt% ethanol) and waste solution (0.5 wt% ethanol). Calculate the amounts of the distillate D (kg h^{-1}) and the waste solution W (kg h^{-1}).

Solution
Total mass balance:

$$2000 = D + W$$

Mass balance for ethanol:

$$2000 \times 0.10 = D \times 0.90 + (2000 - D) \times 0.005$$

From these relations, we obtain $D = 212\,\text{kg}\,\text{h}^{-1}$ and $W = 1788\,\text{kg}\,\text{h}^{-1}$.

1.7 Energy Balance

Energy balance is an expression of the first law of thermodynamics – that is, the law of conservation of energy.

For a nonflow system separated from the surroundings by a boundary, the increase in the total energy of the system is given by

$$\Delta(\text{total energy of the system}) = Q - W \tag{1.6}$$

where Q is the net heat supplied to the system and W is the work done by the system. Here, Q and W are both energy in transit and hence have the same dimension as energy. The total energy of the system includes the total internal energy E, potential energy (PE), and kinetic energy (KE). In normal chemical engineering calculations, changes in PE and KE can be neglected. The internal energy E is the intrinsic energy of a substance, including chemical and thermal energy of molecules. Although absolute values of E are unknown, ΔE, the difference from its base values, for example, from those at 0 °C and 1 atm, is often available or can be calculated.

Neglecting Δ(PE) and Δ(KE), we obtain from Equation 1.6

$$\Delta E = Q - W \tag{1.7}$$

The internal energy per unit mass e is an intensive (state) function. Enthalpy h, a compound thermodynamic function defined by Equation 1.8, is also an intensive function.

$$h = e + pv \tag{1.8}$$

where p is the pressure and v is the specific volume. For a constant pressure process, it can be shown that

$$\mathrm{d}h = c_\mathrm{p}\mathrm{d}t \tag{1.9}$$

where c_p is the specific heat at constant pressure.

For a steady-state flow system, again neglecting changes in the PEs and KEs, the energy balance per unit time is given by Equation 1.10.

$$\Delta H = Q - W_\mathrm{s} \tag{1.10}$$

where ΔH is the total enthalpy change, Q is the heat supplied to the system, and W_s is the so-called shaft work done by moving fluid to the surroundings, for example, work done by a turbine driven by a moving fluid.

Example 1.3 In the second milk heater of a milk pasteurization plant, 1000 l h^{-1} of raw milk is to be heated continuously from 75 to 135 °C by saturated steam at 500 kPa (152 °C). Calculate the steam consumption (kg h^{-1}), neglecting heat loss. The density and specific heat of milk are 1.02 kg l^{-1} and 0.950 (kcal kg^{-1} $°C^{-1}$), respectively.

Solution
Applying Equation 1.10 to this case, W_s is zero.

$$\Delta H = Q = (0.950)(1.02)(1000)(135 - 75) = 58\,140 \text{ kcal } h^{-1}$$

The heat of condensation (latent heat) of saturated steam at 500 kPa is given in the steam table as 503.6 kcal kg^{-1}. Hence, steam consumption is 58 140/503.6 = 115.4 kg h^{-1}.

Problems

1.1 What are the dimensions and SI units for the following physical quantities?
a) Pressure
b) Power
c) Heat capacity

1.2 Is the following equation dimensionally sound?

$$\frac{dp}{dz} = -\rho g$$

where p is the atmospheric pressure, z is the height above sea level, ρ is the specific density of air, and g is the gravity acceleration.

1.3 Convert the following units.
a) Energy of 1 cm^3 bar into J
b) A pressure of 25.3 lb_f in^{-2} into SI units.

1.4 Explain the difference between mass and weight.

1.5 The Henry constant $H' = p/x$ for NH_3 in water at 20 °C is 2.70 atm. Calculate the value of $H = p/C$, where C is kmol m^{-3}, and $m = y/x$ where x and y are the mole fractions in the liquid and gas phases, respectively.

1.6 It is required to remove 99% of CH_4 from 200 m^3 h^{-1} of air (1 atm, 20 °C) containing 20 mol% of CH_4 by absorption into water. Calculate the minimum amount of water required (m^3 h^{-1}). The Henry's law constant for CH_4 in water $H' = p/x$ at 20 °C is 3.76×10^4 atm.

1.7 A weight with a mass of 1 kg rests at 10 m above ground. It then falls freely to the ground. The acceleration of gravity is 9.8 m s^{-2}. Calculate
a) The PE of the weight relative to the ground
b) The velocity and KE of the weight just before it strikes the ground.

1.8 100 kg h^{-1} of ethanol vapor at 1 atm, 78.3 °C is to be condensed by cooling with water at 20 °C. How much water will be required in the case where the exit water temperature is 30 °C? The heat of vaporization of ethanol at 1 atm, 78.3 °C is 204.3 kcal kg^{-1}.

1.9 In the milk pasteurization plant of Example 1.3, what percentage of the heating steam can be saved, if a heat exchanger is installed to heat fresh milk at 75–95 °C by pasteurized milk at 132 °C?

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Further Reading

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