

Chapter 4

Process Variables

INTRODUCTION

The authors originally considered the title “State, Physical, and Chemical Properties” for this chapter. However, since these three properties have been used interchangeably and have come to mean different things to different people, it was decided to employ the title “Process Variables.” The three aforementioned properties were therefore integrated into this all-purpose title and eliminated the need for differentiating between the three.

This chapter provides a review of some basic concepts from physics, chemistry, and engineering in preparation for material that is covered in later chapters. All of these topics are vital in some manner to mass transfer operations. Because many of these topics are unrelated to each other, this chapter admittedly lacks the cohesiveness of chapters covering a single topic. This is usually the case when basic material from widely differing areas of knowledge such as physics, chemistry, and engineering are surveyed. Though these topics are widely divergent and covered with varying degrees of thoroughness, all of them will find use later in this text. If additional information on these review topics is needed, the reader is directed to the literature in the reference section of this chapter.

ILLUSTRATIVE EXAMPLE 4.1

Discuss the traditional difference between chemical and physical properties.

SOLUTION: Every compound has a unique set of *properties* that allows one to recognize and distinguish it from other compounds. These properties can be grouped into two main categories: *physical* and *chemical*. *Physical properties* are defined as those that can be measured without changing the identity and composition of the substance. Key properties include viscosity, density, surface tension, melting point, boiling point, and so on. *Chemical properties* are defined as those that may be altered via reaction to form other compounds or substances. Key chemical properties include upper and lower flammability limits, enthalpy of reaction, autoignition temperature, and so on.

These properties may be further divided into two categories—*intensive* and *extensive*. *Intensive properties* are not a function of the quantity of the substance, while *extensive properties* depend on the quantity of the substance. ■

The remainder of the chapter addresses a variety of process variables.

TEMPERATURE

Whether in the gaseous, liquid, or solid state, all molecules possess some degree of kinetic energy, i.e., they are in constant motion—vibrating, rotating, or translating. The kinetic energies of individual molecules cannot be measured, but the combined effect of these energies in a very large number of molecules can. This measurable quantity is known as *temperature*, which is a macroscopic concept only and as such does not exist on the molecular level.

Temperature can be measured in many ways; the most common method makes use of the expansion of mercury (usually encased inside a glass capillary tube) with increasing temperature. (However, in most industrial systems, thermocouples or thermistors are more commonly employed.) The two most commonly used temperature scales are the Celsius (or Centigrade) and Fahrenheit scales. The Celsius scale is based on the boiling and freezing points of water at 1 atm pressure; to the former, a value of 100°C is assigned, and to the latter, a value of 0°C. On the older Fahrenheit scale, these temperatures correspond to 212°F and 32°F, respectively. Equations (4.1) and (4.2) show the conversion from one temperature scale to the other:

$$^{\circ}\text{F} = 1.8(^{\circ}\text{C}) + 32 \quad (4.1)$$

$$^{\circ}\text{C} = (^{\circ}\text{F} - 32)/1.8 \quad (4.2)$$

where $^{\circ}\text{F}$ = a temperature on the Fahrenheit scale

$^{\circ}\text{C}$ = a temperature on the Celsius scale

Experiments with gases at low-to-moderate pressures (up to a few atmospheres) have shown that, if the pressure is kept constant, the volume of a gas and its temperature are linearly related (Charles' law, see later section) and that a decrease of 0.3663% or (1/273) of the initial volume is experienced for every temperature drop of 1°C. These experiments were not extended to very low temperatures, but if the linear relationship were extrapolated, the volume of the gas would *theoretically* be zero at a temperature of approximately -273°C or -460°F . This temperature has become known as *absolute zero* and is the basis for the definition of two *absolute* temperature scales. (An *absolute* scale is one that does not allow negative quantities.) These absolute temperature scales are known as the Kelvin (K) and Rankine ($^{\circ}\text{R}$) scales; the Kelvin scale is defined by shifting the Celsius scale by 273°C so that 0 K is equal to -273°C . Equation (4.3) shows the relationship described above:

$$\text{K} = ^{\circ}\text{C} + 273 \quad (4.3)$$

The Rankine scale is defined by shifting the Fahrenheit scale 460° , so that

$$^\circ\text{R} = ^\circ\text{F} + 460 \quad (4.4)$$

The relationships among the various temperature scales are shown in Figure 4.1.

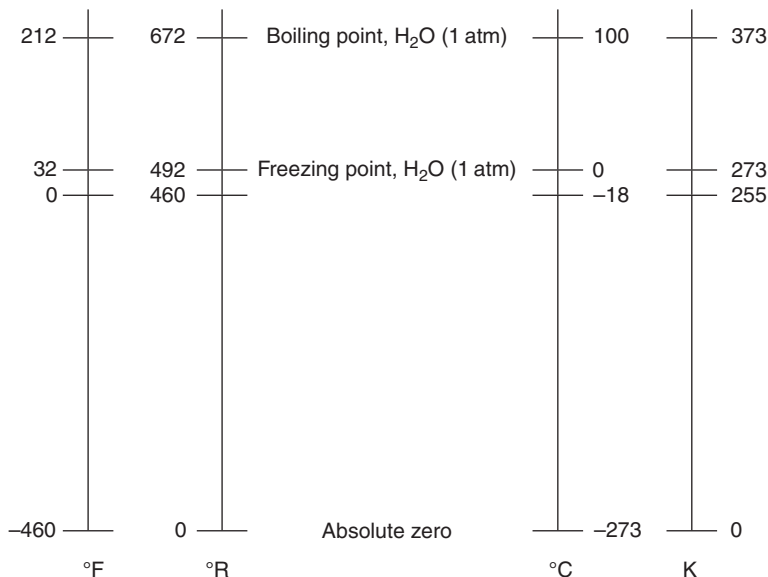


Figure 4.1 Temperature scales.

ILLUSTRATIVE EXAMPLE 4.2

Perform the following temperature conversions:

- Convert 55°F to (a) Rankine, (b) Celsius, and (c) Kelvin
- Convert 55°C to (a) Fahrenheit, (b) Rankine, and (c) Kelvin

SOLUTION:

- $^\circ\text{R} = ^\circ\text{F} + 460 = 55 + 460 = 515$
 - $^\circ\text{C} = \frac{5}{9}(^\circ\text{F} - 32) = \frac{5}{9}(55 - 32) = 12.8$
 - $\text{K} = \frac{5}{9}(^\circ\text{F} + 460) = \frac{5}{9}(55 + 460) = 286$
- $^\circ\text{F} = 1.8(^\circ\text{C}) + 32 = 1.8(55) + 32 = 131$
 - $^\circ\text{R} = 1.8(^\circ\text{C}) + 492 = 1.8(55) + 492 = 591$
 - $\text{K} = ^\circ\text{C} + 273 = 55 + 273 = 328$



PRESSURE

Molecules possess a high degree of translational kinetic energy in the gaseous state, which means they are able to move quite freely throughout the body of the gas. If the gas is in a container of some type, the molecules are constantly bombarding the walls of the container. The macroscopic effect of this bombardment by a tremendous number of molecules—enough to make the effect measurable—is called *pressure*. The natural units of pressure are force per unit area. In the example of the gas in a container, the *unit area* is a portion of the inside solid surface of the container wall and the *force*, measured perpendicularly to the unit area, is the result of the molecules hitting the unit area and losing momentum during the sudden change of direction.

There are a number of different methods used to express a pressure measurement. Some of them are natural units (i.e., based on a force per unit area) and include pound (force) per square inch (abbreviated lb_f/in^2 or psi) and dyne per square centimeter (dyn/cm^2). Others are based on a fluid height such as inches of water (in H_2O) or millimeters of mercury (mm Hg). These latter units are convenient when the pressure is indicated by a difference between two levels of a liquid as in a *manometer* or *barometer*. *Barometric pressure* and *atmospheric pressure* are synonymous and measure the ambient air pressure. *Standard barometric pressure* is the average atmospheric pressure at sea level, 45° north latitude at 32°F . It is used to define another unit of pressure called the atmosphere (atm). Standard barometric pressure is 1 atm and is equivalent to 14.696 psi and 29.921 in Hg. As one might expect, barometric pressure varies with weather and altitude.

Measurements of pressure by most gauges indicate the difference in pressure either above or below that of the atmosphere surrounding the gauge. *Gauge pressure* is the pressure indicated by such a device. If the pressure in the system measured by the gauge is greater than the pressure prevailing in the atmosphere, the gauge pressure is expressed positively; if lower than atmospheric pressure, the gauge pressure is a negative quantity; the term *vacuum* designates a negative gauge pressure. Gauge pressures are often identified by the letter “g” after the pressure unit, e.g., psig (pounds per square inch gauge) is a gauge pressure in psi units.

Since gauge pressure is the pressure relative to the prevailing atmospheric pressure, the sum of the two yields the *absolute pressure*, indicated by the letter “a” after the unit, e.g., psia (pounds per square inch absolute):

$$P = P_a + P_g \quad (4.5)$$

where P = absolute pressure (psia)

P_a = atmospheric pressure (psia)

P_g = gauge pressure (psig)

The absolute pressure scale is absolute in the same sense that the absolute temperature scale is absolute, i.e., a pressure of zero psia is the lowest possible pressure theoretically achievable—a perfect vacuum.

ILLUSTRATIVE EXAMPLE 4.3

Consider the following pressure calculations.

- 1 A liquid weighing 100 lb held in a cylindrical column with a base area of 3 in² exerts what pressure at the base in lb_f/ft²?
- 2 If the pressure is 35 psig (pounds per square inch gauge), what is the absolute pressure?

SOLUTION:

- 1 Refer to Chapter 3.

$$\begin{aligned} F &= mg/g_c = 100 \text{ lb} (1 \text{ lb}_f/\text{lb}) \\ &= 100 \text{ lb}_f \end{aligned}$$

As discussed in Chapter 3, g_c is a conversion factor equal to 32.2 lb · ft/lb_f · s²; g is the gravitational acceleration, which is equal, or close to, 32.2 ft/s² on Earth's surface. Therefore,

$$\begin{aligned} P &= F/S = 100 \text{ lb}_f/3 \text{ in}^2 \\ &= 33.33 \text{ lb}_f/\text{in}^2 \\ &= 4800 \text{ lb}_f/\text{ft}^2 \end{aligned}$$

where S = surface area onto which force is applied.

- 2 $P = P_a + P_g = 14.7 + 35$
= 49.7 psia

MOLES AND MOLECULAR WEIGHT

An atom consists of protons and neutrons in a nucleus surrounded by electrons. An electron has such a small mass relative to that of the proton and neutron that the weight of the atom (called the *atomic weight*) is approximately equal to the sum of the weights of the particles in its nucleus (the protons and neutrons). Atomic weight may be expressed in *atomic mass units (amu) per atom* or *in grams per gram atom*. One gram atom contains 6.02×10^{23} atoms (Avogadro's number). The atomic weights of the elements are available in the literature.^(1,2)

The *molecular weight (MW)* of a compound is the sum of the atomic weights of the atoms that make up the molecule. Units of atomic mass units per molecule (amu/molecule) or grams per gram mole (g/gmol) are used for molecular weight. One gram mole (gmol) contains an Avogadro's number of molecules. For the English system, a pound mole (lbmol) contains $454 \times 6.023 \times 10^{23}$ molecules.

Molal units are used extensively in mass transfer calculations as they greatly simplify material balances where chemical reactions are occurring. For mixtures of substances (gases, liquids, or solids), it is also convenient to express compositions in mole fractions or mole percentages instead of mass fractions. The mole fraction is

the ratio of the number of moles of one component to the total number of moles in the mixture. Equations (4.6)–(4.9) express these relationships:

$$\begin{aligned} \text{moles of A} &= \frac{\text{mass A}}{\text{molecular weight of A}} \\ n_A &= \frac{m_A}{(\text{MW})_A} \end{aligned} \quad (4.6)$$

$$\begin{aligned} \text{mole fraction A} &= \frac{\text{moles A}}{\text{total moles}} \\ y_A &= \frac{n_A}{n} \end{aligned} \quad (4.7)$$

$$\begin{aligned} \text{mass fraction A} &= \frac{\text{mass A}}{\text{total mass}} \\ w_A &= \frac{m_A}{m} \end{aligned} \quad (4.8)$$

$$\begin{aligned} \text{volume fraction A} &= \frac{\text{volume A}}{\text{total volume}} \\ v_A &= \frac{V_A}{V} \end{aligned} \quad (4.9)$$

The reader should note that, in general, mass fraction (or percent) is *NOT* equal to mole fraction (or percent).

ILLUSTRATIVE EXAMPLE 4.4

A 55-gal tank contains 20.0 lb of water.

- 1 How many pound moles of water does it contain?
- 2 How many gram moles does it contain?
- 3 How many molecules does it contain?

SOLUTION: The molecular weight of the water is

$$\begin{aligned} \text{MW} &= (2)(1.008) + (15.999) = 18.015 \text{ g/gmol} \\ &= 18.015 \text{ lb/lbmol} \end{aligned}$$

$$1 \quad (20.0 \text{ lb}) \left(\frac{1 \text{ lbmol}}{18.015 \text{ lb}} \right) = 1.11 \text{ lbmol water}$$

$$2 \quad (20.0 \text{ lb}) \left(\frac{453.593 \text{ g}}{1 \text{ lb}} \right) \left(\frac{1 \text{ gmol}}{18.015 \text{ g}} \right) = 503.6 \text{ gmol water}$$

$$3 \quad (503.6 \text{ gmol}) \left(\frac{6.023 \times 10^{23} \text{ molecules}}{1 \text{ gmol}} \right) = 3.033 \times 10^{26} \text{ molecules} \quad \blacksquare$$

MASS, VOLUME, AND DENSITY

The *density* (ρ) of a substance is the ratio of its mass to its volume and may be expressed in units of pounds per cubic foot (lb/ft^3), kilograms per cubic meter (kg/m^3), etc. For solids, density can be easily determined by placing a known mass of the substance in a liquid and determining the displaced volume. The density of a liquid can be measured by weighing a known volume of the liquid in a volumetric flask. For gases, the ideal gas law, to be discussed later in this chapter, can be used to calculate the density from the pressure, temperature, and molecular weight of the gas.

Unlike gases, the densities of pure solids and liquids are relatively independent of temperature and pressure and can be found in standard reference books.^(1,2) The *specific volume* (v) of a substance is its volume per unit mass (ft^3/lb , m^3/kg , etc.) and is therefore the inverse of its density.

Two key densities that the practicing engineer should be familiar with are that for air and water. Although the effect of temperature and pressure can be obtained directly from the ideal gas law, the following equation can be used to estimate the density of air at atmospheric conditions⁽¹⁾:

$$\rho_{\text{air}} \text{ (kg/m}^3\text{)} = 1.30 - 4.68 \times 10^{-3}(T) - 1.40 \times 10^{-5}(T)^2; \quad T \equiv ^\circ\text{C} \quad (4.10)$$

As one might expect, the effect of temperature on liquid water is negligible. However, the following equation may be employed to account for any temperature variation⁽¹⁾:

$$\begin{aligned} \rho_{\text{H}_2\text{O}} \text{ (kg/m}^3\text{)} &= 999.85 + 6.1474 \times 10^{-2}(T) - 8.3633 \times 10^{-3}(T)^2 \\ &+ 6.6805 \times 10^{-5}(T)^3 - 4.3869 \times 10^{-7}(T)^4 \\ &+ 1.3095 \times 10^{-9}(T)^5; \quad T \equiv ^\circ\text{C} \end{aligned} \quad (4.11)$$

The reader should note that the density of a gas is denoted by ρ , ρ_V , or ρ_G in this text. The term ρ will generally be employed, but the other notations appear in certain situations for clarity. In addition, the density of a liquid is represented as ρ_L .

VISCOSITY

Viscosity is a property associated with a fluid's resistance to flow. More precisely, this property accounts for energy losses that result from shear stresses occurring between different portions of the fluid which are moving at different velocities.⁽³⁻⁵⁾ The *absolute viscosity* (μ) has units of mass per length \cdot time; the fundamental unit is the *poise* (P), which is defined as $1 \text{ g}/\text{cm} \cdot \text{s}$. This unit is inconveniently large for many practical purposes and viscosities are frequently given in *centipoises* (0.01 poise), which is abbreviated to cP. The viscosity of pure water at 68.6°F is 1.00 cP. In English units, absolute viscosity is expressed either as pounds (mass) per foot \cdot second ($\text{lb}/\text{ft} \cdot \text{s}$) or pounds per foot \cdot hour ($\text{lb}/\text{ft} \cdot \text{h}$). The absolute viscosity depends primarily on temperature and to a lesser degree on pressure. The *kinematic viscosity* (ν) is the absolute viscosity divided by the density of the fluid and is useful in certain fluid

flow problems. The units for this quantity are length squared per time, e.g., square foot per second (ft^2/s) or square meters per hour (m^2/h). A kinematic viscosity of $1 \text{ cm}^2/\text{s}$ is called a *stoke* (S). For pure water at 70°F , $\nu = 0.983 \text{ cS}$ (centistokes). Because fluid viscosity changes rapidly with temperature, a numerical value of viscosity has no significance unless the temperature is specified.

Liquid viscosity is usually measured by the amount of time it takes for a given volume of liquid to flow through an orifice. The *Saybolt universal viscometer* is the most widely used device in the United States for the determination of the viscosity of fuel oils and liquid wastes. It should be stressed that Saybolt viscosities, which are expressed in *Saybolt seconds (SSU)*, are not even approximately proportional to absolute viscosities except in the range above 200 SSU; hence, converting units from Saybolt seconds to other units requires the use of special conversion tables. As the time of flow through a viscometer decreases, the deviation becomes more marked. In any event, viscosity is an important property because of possible flow problems with viscous liquids.

The viscosities of air at atmospheric pressure and water are presented as functions of temperature in Tables 4.1 and 4.2, respectively. Viscosities of other substances are available in the literature⁽⁶⁾ and the Appendix. Several simple equations for directly calculating viscosities are presented below.

Equation (4.12) is used to calculate the viscosity of air:

$$\mu_{\text{air}} (\text{N} \cdot \text{s}/\text{m}^2) = 1.71 \times 10^{-5} + 5.0 \times 10^{-8}T; \quad T \equiv ^\circ\text{C} \quad (4.12)$$

Regarding the viscosity of water, Equation (4.13) applies when the temperature is greater than 0°C and less than or equal to 20°C :

$$\log \mu_{\text{H}_2\text{O}} (\text{kg}/\text{m} \cdot \text{s}) = \frac{1301}{998.333 + 8.1855(T - 20) + 5.85 \times 10^{-3}(T - 20)^2} - 1.30233; \quad T \equiv ^\circ\text{C} \quad (4.13)$$

This equation may be rearranged to give

$$\mu_{\text{H}_2\text{O}} = 10^{\left[\frac{1301}{998.333 + 8.1855(T - 20) + 5.85 \times 10^{-3}(T - 20)^2} \right] - 1.30233} \quad (4.14)$$

Table 4.1 Viscosity of Air at 1 Atmosphere^a

T ($^\circ\text{C}$)	Viscosity, micropoise (μP)
0	170.8
18	182.7
40	190.4
54	195.8
74	210.2
229	263.8

^a 1 P = 100 cP = $10^6 \mu\text{P}$; 1 cP = $6.72 \times 10^{-4} \text{ lb}/\text{ft} \cdot \text{s}$.

Table 4.2 Viscosity of Water

T ($^{\circ}\text{C}$)	Viscosity, centipoise (cP)
0	1.792
5	1.519
10	1.308
15	1.140
20	1.000
25	0.894
30	0.801
35	0.723
40	0.656
50	0.594
60	0.469
70	0.406
80	0.357
90	0.317
100	0.284

The viscosity of the water in the 20°C – 100°C range may be calculated from Equation (4.15)

$$\log \left(\frac{\mu_{\text{H}_2\text{O}@T}}{\mu_{\text{H}_2\text{O}@20^{\circ}\text{C}}} \right) = \frac{1.3272(20 - T) - 1.053 \times 10^{-3}(T - 20)^2}{T + 105}; T \equiv ^{\circ}\text{C} \quad (4.15)$$

The reader should note that, as with density, the viscosity of a gas is denoted by μ , μ_V , and μ_G in this text. In addition, the viscosity of a liquid is represented as μ_L .

ILLUSTRATIVE EXAMPLE 4.5

What is the kinematic viscosity of a gas whose specific gravity ($\text{SG} = \rho/\rho_{\text{H}_2\text{O}}$) and absolute viscosity are 0.8 and 0.02 cP, respectively?

SOLUTION:

$$\mu = \left(\frac{0.02 \text{ cP}}{1} \right) \left(\frac{6.720 \times 10^{-4} \text{ lb/ft} \cdot \text{s}}{1 \text{ cP}} \right) = 1.344 \times 10^{-5} \text{ lb/ft} \cdot \text{s}$$

$$\rho = (\text{SG})(\rho_{\text{ref}}) = (0.8)(62.43 \text{ lb/ft}^3) = 49.94 \text{ lb/ft}^3$$

$$v = \mu/\rho = (1.344 \times 10^{-5} \text{ lb/ft} \cdot \text{s})/(49.94 \text{ lb/ft}^3)$$

$$= 2.691 \times 10^{-7} \text{ ft}^2/\text{s} \quad \blacksquare$$

ILLUSTRATIVE EXAMPLE 4.6

Calculate the viscosity of water at 10°C .

SOLUTION: Equation (4.13) can be used over the temperature range of 0°C to 20°C. Since the desired temperature is 10°C,

$$\log \mu_{\text{H}_2\text{O}} = \frac{1301}{998.333 + 8.1855(T - 20) + 5.85 \times 10^{-3}(T - 20)^2} - 1.30233 \quad (4.13)$$

Substituting $T = 10^\circ\text{C}$,

$$\begin{aligned} \log \mu_{\text{H}_2\text{O}} &= \frac{1301}{998.333 + 8.1855(10^\circ\text{C} - 20) + 5.85 \times 10^{-3}(10^\circ\text{C} - 20)^2} - 1.30233 \\ &= 0.11633 \\ \mu_{\text{H}_2\text{O}} &= 1.307 \text{ centipoise} \\ &= 1.307 \times 10^{-3} \text{ kg/m} \cdot \text{s} \end{aligned}$$

■

REYNOLDS NUMBER

The Reynolds number, Re , is a dimensionless number that indicates whether a fluid flowing is in the laminar or turbulent flow regime. *Laminar* flow is characteristic of fluids flowing slowly enough so that there are no eddies (whirlpools) or macroscopic mixing of different portions of the fluid. (*Note:* In any fluid, there is always *molecular* mixing due to the thermal activity of the molecules; this is distinct from *macroscopic* mixing due to the swirling motion of different portions of the fluid.) In laminar flow, a fluid can be imagined to flow like a deck of cards, with adjacent layers sliding past one another. *Turbulent* flow is characterized by eddies and macroscopic currents. In practice, moving gases are generally in the turbulent region.⁽⁵⁾ For flow in a pipe, a Reynolds number above 2100 is an indication of turbulent flow.

The Reynolds number is dependent on the fluid velocity, density, viscosity, and some *length* characteristic of the system or conduit; for pipes, this characteristic length is the inside diameter:

$$Re = Dv\rho/\mu = Dv/\nu \quad (4.16)$$

where Re = Reynolds number

D = inside diameter of the pipe (ft)

v = fluid velocity (ft/s)

ρ = fluid density (lb/ft³)

μ = fluid viscosity (lb/ft · s)

ν = fluid kinematic viscosity (ft²/s)

Any consistent set of units may be used with Equation (4.16).

ILLUSTRATIVE EXAMPLE 4.7

Calculate the Reynolds number for a fluid flowing through a 5-inch diameter pipe at 10 fps (feet per second) with a density of 50 lb/ft^3 and a viscosity of 0.65 cP. Is the flow turbulent or laminar?

SOLUTION: By definition

$$\text{Re} = Dv\rho/\mu \quad (4.16)$$

Substitution yields

$$\begin{aligned} \text{Re} &= \left(\frac{50 \text{ lb}}{\text{ft}^3}\right) \left(\frac{10 \text{ ft}}{\text{s}}\right) \left(\frac{5 \text{ in}}{1}\right) \left(\frac{1 \text{ ft}}{12 \text{ in}}\right) \left(\frac{1}{0.65 \text{ cP}}\right) \left(\frac{1 \text{ cP}}{6.720 \times 10^{-4} \text{ lb/ft} \cdot \text{s}}\right) \\ &= (50 \text{ lb/ft}^3)(10 \text{ ft/s})(5/12 \text{ ft})/(0.65 \times 6.72 \times 10^{-4} \text{ lb/ft} \cdot \text{s}) \\ &= 477,000 \end{aligned}$$

The Reynolds number is >2100 ; therefore, the flow is turbulent. ■

pH

An important chemical property of an aqueous solution is pH. The pH measures the acidity or basicity of a solution. In a neutral solution, such as pure water, the hydrogen (H^+) and hydroxyl (OH^-) ion concentrations are equal. At ordinary temperatures, this concentration is

$$C_{\text{H}^+} = C_{\text{OH}^-} = 10^{-7} \text{ gmol/L} \quad (4.17)$$

where C_{H^+} = hydrogen ion concentration
 C_{OH^-} = hydroxyl ion concentration

In all aqueous solutions, whether neutral, basic, or acidic, a chemical equilibrium or balance is established between these two concentrations, so that

$$K_{\text{eq}} = C_{\text{H}^+} C_{\text{OH}^-} = 10^{-14} \quad (4.18)$$

where K_{eq} = equilibrium constant.

The numerical value for K_{eq} given in Equation (4.18) holds for room temperature and only when the concentrations are expressed in gram mole per liter (gmol/L). In acid solutions, $C_{\text{H}^+} > C_{\text{OH}^-}$; in basic solutions, C_{OH^-} predominates. The pH is a direct measure of the hydrogen ion concentration and is defined by

$$\text{pH} = -\log C_{\text{H}^+} \quad (4.19)$$

Thus, an acidic solution is characterized by a pH below 7 (the lower the pH, the higher the acidity), a basic solution by a pH above 7, and a neutral solution by a pH of 7. It should be pointed out that Equation (4.19) is not the exact definition of pH but is a close approximation. Strictly speaking, the *activity* of the hydrogen ion, a_{H^+} , and not the ion concentration belongs in Equation (4.19). For a discussion of chemical activities, the reader is directed to the literature.^(2,6)

ILLUSTRATIVE EXAMPLE 4.8

Calculate the hydrogen ion and the hydroxyl ion concentrations of an aqueous solution if the pH of the solution is 1.0.

SOLUTION: For a pH of 1.0, apply Equation (4.19):

$$\begin{aligned} \text{pH} &= -\log(C_{\text{H}^+}) \\ C_{\text{H}^+} &= 10^{-\text{pH}} = 10^{-1} = 0.1 \text{ gmol/L} \\ C_{\text{H}^+} \times C_{\text{OH}^-} &= 10^{-14} \\ C_{\text{OH}^-} &= \frac{10^{-14}}{C_{\text{H}^+}} = \frac{10^{-14}}{10^{-1}} \\ &= 10^{-13} \text{ gmol/L} \end{aligned}$$

ILLUSTRATIVE EXAMPLE 4.9

Process considerations require pH control in a 50,000-gal storage tank used for incoming waste mixtures (including liquid plus solids) at a hazardous waste incinerator. Normally, the tank is kept at neutral pH. However, the operation can tolerate pH variations from 6 to 8. Waste arrives in 5000-gal shipments.

Assume that the tank is completely mixed, contains 45,000 gal when the shipment arrives, the incoming acidic waste is fully dissociated, and that there is negligible buffering capacity in the tank. What is the pH of the most acidic waste shipment that can be handled without the need for neutralization?

SOLUTION: The pH of the most acidic waste shipment that can be handled without neutralization is calculated as follows: 5000 gal of waste with a $[\text{H}^+] = X$ is diluted by 45,000 gal at pH = 7 or $[\text{H}^+] = 10^{-7}$. The minimum pH of 6 that can be tolerated is equivalent to a $[\text{H}^+] = 10^{-6}$. From an ion balance:

$$\begin{aligned} [\text{H}^+] &= 10^{-6} = (5000/50,000)X + (45,000/50,000)(10^{-7}) \\ X &= \left(\frac{50,000}{5000}\right) \left[10^{-6} - \frac{45,000(10^{-7})}{50,000}\right] \\ &= 9.1 \times 10^{-6} \\ \text{pH} &= 5.04 \end{aligned}$$

VAPOR PRESSURE

Vapor pressure is an important property of liquids, and, to a much lesser extent, of solids. If a liquid is allowed to evaporate in a confined space, the pressure in the vapor space increases as the amount of vapor increases. If there is sufficient liquid present, a point is eventually reached at which the pressure in the vapor space is exactly equal to the pressure exerted by the liquid at its own surface. At this point, a dynamic equilibrium exists in which vaporization and condensation take place at equal rates and the pressure in the vapor space remains constant. The pressure exerted at equilibrium is equal to the vapor pressure of the liquid. The magnitude of this pressure for a given liquid depends on the temperature, but not on the amount of liquid present. Solids, like liquids, also exert a vapor pressure. Evaporation of solids (*sublimation*) is noticeable only for those with appreciable vapor pressures. This is reviewed in more detail in Chapter 6.

IDEAL GAS LAW⁽⁷⁾

Observations based on physical experimentation often can be synthesized into simple mathematical equations called *laws*. These laws are never perfect and hence are only an approximate representation of reality. The *ideal gas law* (IGL) was derived from experiments in which the effects of pressure and temperature on gaseous volumes were measured over moderate temperature and pressure ranges. This law works well in the pressure and temperature ranges that were used in taking the data; extrapolations outside of the ranges have been found to work well in some cases and poorly in others. As a general rule, this law works best when the molecules of the gas are far apart, i.e., when the pressure is low and the temperature is high. Under these conditions, the gas is said to behave *ideally*, i.e., its behavior is a close approximation to the so-called *perfect* or *ideal gas*: a hypothetical entity that obeys the ideal gas law perfectly. For engineering calculations, the ideal gas law is often assumed to be valid since it generally works well (usually within a few percent of the correct result) up to the highest pressures and down to the lowest temperatures used in many industrial applications.

The two precursors of the ideal gas law were *Boyle's* and *Charles' laws*. Boyle found that the volume of a given mass of gas is inversely proportional to the *absolute* pressure if the temperature is kept constant:

$$P_1 V_1 = P_2 V_2 \quad (4.20)$$

where V_1 = volume of gas at absolute pressure P_1 and temperature T and V_2 = volume of gas at absolute pressure P_2 and temperature T .

Charles found that the volume of a given mass of gas varies directly with the *absolute* temperature at constant pressure:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (4.21)$$

where V_1 = volume of gas at pressure P and absolute temperature T_1 and V_2 = volume of gas at pressure P and absolute temperature T_2 .

Boyle's and Charles' laws may be combined into a single equation in which neither temperature nor pressure need be held constant:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad (4.22)$$

For Equation (4.22) to hold, the mass of gas must be constant as the conditions change from (P_1, T_1) to (P_2, T_2) . This equation indicates that for a given mass of a specific gas, PV/T has a constant value. Since, at the same temperature and pressure, volume and mass must be directly proportional, this statement may be extended to

$$\frac{PV}{mT} = C \quad (4.23)$$

where m = mass of a specific gas and C = constant that depends on the gas.

Moreover, experiments with different gases showed that Equation (4.23) could be expressed in a far more generalized form. If the number of moles (n) is used in place of the mass (m), the constant is the same for all gases:

$$\frac{PV}{nT} = R \quad (4.24)$$

where R = universal gas constant.

Equation (4.24) is called the ideal gas law. Numerically, the value of R depends on the units used for P , V , T , and n (see Table 4.3). Other useful forms of the ideal gas law are shown in Equations (4.25) and (4.26). Equation (4.25) applies to gas flow rather than to gas confined in a container⁽⁷⁾:

$$Pq = \dot{n}RT \quad (4.25)$$

where q = gas volumetric flow rate (ft^3/h), P = absolute pressure (psia), \dot{n} = molar flow rate (lbmol/h), T = absolute temperature ($^\circ\text{R}$), and $R = 10.73 \text{ psia} \cdot \text{ft}^3 / \text{lbmol} \cdot ^\circ\text{R}$.

Equation (4.26) combines n and V from Equation (4.25) to express the law in terms of density:

$$P(MW) = \rho RT \quad (4.26)$$

where MW = molecular weight of the gas (lb/lbmol) and ρ = density of the gas (lb/ft^3).

Volumetric flow rates are often not given at the *actual* conditions of pressure and temperature but at arbitrarily chosen *standard* conditions (*STP, standard temperature and pressure*). To distinguish between flow rates based on the two conditions, the letters "a" and "s" are often used as part of the unit. The units acfm and scfm represent actual cubic feet per minute and standard cubic feet per minute, respectively. The ideal gas law can be used to convert from *standard* to *actual* conditions, but,

Table 4.3 Values of R in Various Units

R	Temperature scale	Units of V	Units of n	Units of P	Units of PV (energy)
10.73	°R	ft ³	lbmol	psia	–
0.7302	°R	ft ³	lbmol	atm	–
21.85	°R	ft ³	lbmol	in Hg	–
555.0	°R	ft ³	lbmol	mm Hg	–
297.0	°R	ft ³	lbmol	in H ₂ O	–
0.7398	°R	ft ³	lbmol	bar	–
1545.0	°R	ft ³	lbmol	psfa	–
24.75	°R	ft ³	lbmol	ft H ₂ O	–
1.9872	°R	–	lbmol	–	Btu
0.0007805	°R	–	lbmol	–	hp · h
0.0005819	°R	–	lbmol	–	kW · h
500.7	°R	–	lbmol	–	cal
1.314	K	ft ³	lbmol	atm	–
998.9	K	ft ³	lbmol	mm Hg	–
19.32	K	ft ³	lbmol	psia	–
62.361	K	L	gmol	mm Hg	–
0.08205	K	L	gmol	atm	–
0.08314	K	L	gmol	bar	–
8314	K	L	gmol	Pa	–
8.314	K	m ³	gmol	Pa	–
82.057	K	cm ³	gmol	atm	–
1.9872	K	–	gmol	–	cal
8.314	K	–	gmol	–	J

since there are many standard conditions in use, the STP being used must be known. Standard conditions most often used are shown in Table 4.4. The reader is cautioned on the incorrect use of acfm and/or scfm. Employing standard conditions is a convenience; when predicting the performance of or designing equipment, the actual conditions *must* be employed. Designs based on standard conditions can lead to disastrous results, with the unit usually underdesigned. For example, for a gas stream at

Table 4.4 Common Standard Conditions

System	Temperature	Pressure	Molar volume
SI	273 K	101.3 kPa	22.4 m ³ /kmol
Universal scientific	0°C	760 mm Hg	22.4 L/gmol
Natural gas industry	60°F	14.7 psia	379 ft ³ /lbmol
American engineering	32°F	1 atm	359 ft ³ /lbmol
Environmental industry	60°F	1 atm	379 ft ³ /lbmol
	70°F	1 atm	387 ft ³ /lbmol

2140°F, the ratio of acfm to scfm (standard temperature = 60°F) is 5.0. Equation (4.27), which is a form of Charles' law, can be used to correct flow rates from standard to actual conditions:

$$q_a = q_s \left(\frac{T_a}{T_s} \right) \quad (4.27)$$

where q_a = volumetric flow rate at actual conditions (ft³/h), q_s = volumetric flow rate at standard conditions (ft³/h), T_a = actual absolute temperature (°R), and T_s = standard absolute temperature (°R).

The reader is again reminded that *absolute* temperatures and *absolute* pressures must be employed in all ideal gas law calculations.

In engineering practice, mixtures of gases are more often encountered than single or pure gases. The ideal gas law is based on the *number* of molecules present in the gas volume; the *kind* of molecules is not a significant factor, only the number. This *ideal* law applies equally well to mixtures and pure gases alike. Dalton and Amagat both applied the ideal gas law to mixtures of gases. Since pressure is caused by gas molecules colliding with the walls of the container, it seems reasonable that the total pressure of a gas mixture is made up of pressure contributions due to each of the component gases. These pressure contributions are called *partial pressures*. Dalton defined the partial pressure of a component as the pressure that would be exerted if the same mass of the component gas occupied the same total volume alone at the same temperature as the mixture. The sum of these partial pressures equals the total pressure:

$$P = p_a + p_b + p_c + \cdots + p_n = \sum_{i=1}^n p_i \quad (4.28)$$

where P = total pressure, n = number of components, and p_i = partial pressure of component i .

Equation (4.28) is known as *Dalton's law*. Applying the ideal gas law to one component (A) only,

$$p_A V = n_A R T \quad (4.29)$$

where n_A = number of moles of component A.

Eliminating R , T , and V between Equations (4.24) and (4.29) yields

$$\frac{p_A}{P} = \frac{n_A}{n} = y_A$$

or

$$p_A = y_A P \quad (4.30)$$

where y_A = mole fraction of component A.

ILLUSTRATIVE EXAMPLE 4.10

What is the density of air at 75°F and 14.7 psia? The molecular weight of air is 29.

SOLUTION: This example is solved using the ideal gas law:

$$PV = nRT = \frac{m}{(MW)}RT$$

$$\frac{P(MW)}{RT} = \frac{m}{V} = \rho$$

or

$$\rho = \frac{P(MW)}{RT} \quad (4.26)$$

Substituting,

$$\rho = \frac{(14.7 \text{ psia})(29 \text{ lb/lbmol})}{(10.73 \text{ ft}^3 \cdot \text{psi/lbmol} \cdot ^\circ\text{R})(75 + 460)}$$

$$= 0.0743 \text{ lb/ft}^3 \quad \blacksquare$$

ILLUSTRATIVE EXAMPLE 4.11

The exhaust gas flow rate from an absorber is 1000 scfm. All of the gas is vented through a small stack that has an inlet area of 1.0 ft². The exhaust gas temperature is 300°F. What is the velocity of the gas through the stack inlet in feet per second? Assume standard conditions to be 70°F and 1.0 atm. Neglect the pressure drop across the stack.

SOLUTION: Note that since the gas is vented through the stack to the atmosphere, the pressure is 1.0 atm. Calculate the actual flow rate, in acfm, using Charles' law:

$$q_a = q_s \left(\frac{T_a}{T_s} \right) \quad (4.27)$$

Substituting

$$= 1000 \left(\frac{460 + 300}{460 + 70} \right)$$

$$= 1434 \text{ acfm}$$

Calculate the velocity of the gas:

$$v = \frac{q_a}{S} = \frac{1434}{1.0}$$

$$= 1434 \text{ ft/min} \quad \blacksquare$$

REFERENCES

1. R. C. WEAST (ed), "CRC Handbook of Chemistry and Physics," 80th edition, CRC Press, Boca Raton, FL, 1999.

36 Chapter 4 Process Variables

2. S. MARON and C. PRUTTON, "*Principles of Physical Chemistry*," 4th edition, MacMillan, New York City, NY, 1970.
3. R. BIRD, W. STEWART, and E. LIGHTFOOT, "*Transport Phenomena*," 2nd edition, John Wiley & Sons, Hoboken, NJ, 2002.
4. L. THEODORE, "*Transport Phenomena for Engineers*," International Textbook Co., Scranton, PA, 1970.
5. P. ABULENCIA and L. THEODORE, "*Fluid Flow for the Practicing Engineer*," John Wiley & Sons, Hoboken, NJ, 2009.
6. D. Green and R. Perry (eds), "*Perry's Chemical Engineers' Handbook*," 8th edition, McGraw-Hill, New York City, NY, 2008.
7. L. THEODORE, F. RICCI, and T. VAN VLIET, "*Thermodynamics for the Practicing Engineer*," John Wiley & Sons, Hoboken, NJ, 2009.

NOTE: Additional problems are available for all readers at www.wiley.com. Follow links for this title. These problems may be used for additional review, homework, and/or exam purposes.