

# Gases and Vapors

Gases and vapors are naturally associated with foods and food-processing systems. The equilibrium between food and water vapor determines temperatures achieved during processing. Dissolved gases in foods such as oxygen affect shelf life. Gases are used to flush packages to eliminate oxygen and prolong shelf life. Modified atmospheres in packages have been used to prolong shelf life of packaged foods. Air is used for dehydration. Gases are used as propellants in aerosol cans and as refrigerants. The distinction between gases and vapors is very loose because theoretically all vapors are gases. The term “vapor” is generally used for the gaseous phase of a substance that exists as a liquid or a solid at ambient conditions.

## 4.1 EQUATIONS OF STATE FOR IDEAL AND REAL GASES

Equations of state are expressions for the relationship between pressure, volume, temperature and quantity of gases within a given system. The simplest equation of state, the ideal gas equation, closely approximates the actual behavior of gases at near ambient temperature and pressure where the effect of molecular interactions is minimal. At high pressures and temperatures, however, most gases deviate from ideal behavior, and several equations of state have been proposed to fit experimental data. In this section, two equations of state will be discussed: the ideal gas equation and one of the most used equation of state for real gases, van der Waal’s equation.

### 4.1.1 The Kinetic Theory of Gases

The fundamental theory governing the behavior of gases, the kinetic theory, was first proposed by Bernoulli in 1738 and was tested and extended by Clausius, Maxwell, Boltzman, van der Waal, and Jeans. The postulates of the kinetic theory are as follows:

1. Gases are composed of discrete particles called *molecules*, which are in constant random motion, colliding with each other and with the walls of the surrounding vessel.
2. The force resulting from the collision between the molecules and the walls of the surrounding vessel is responsible for the *pressure* of the gas.

3. The lower the pressure, the farther apart the molecules, thus, attractive forces between molecules have reduced influence on the overall properties of the gas.
4. The average kinetic energy of the molecules is directly proportional to the absolute temperature.

#### 4.1.2 Absolute Temperature and Pressure

The pressure ( $P$ ) of a gas is the force of collisions of gas molecules against a surface in contact with the gas. Because pressure is force per unit area, pressure is proportional to the number of gas molecules and their velocity. This pressure is the absolute pressure.

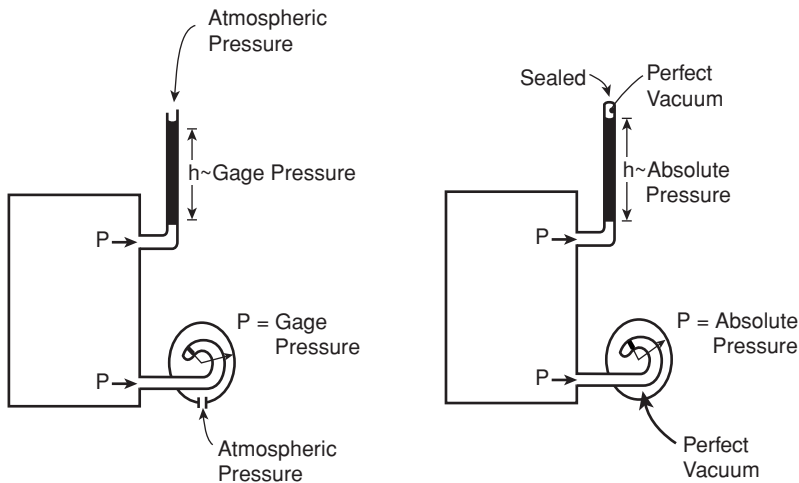
Pressure is often expressed as *gauge pressure* when the measured quantity is greater than atmospheric pressure, and as *vacuum* when below atmospheric. Measurement of gauge and atmospheric pressure is shown in Fig. 4.1.

Two types of pressure-measuring devices are depicted: a manometer and a Bourdon tube pressure gauge. On the left of the diagram, the pressure of the gas is counteracted by atmospheric pressure, such that if pressure is atmospheric, the gauges will read zero. The reading given by these type of gauges is the *gauge pressure*. In the American Engineering System of measurement, gauge pressure is expressed as “psig” or pound force per square inch gauge. In the SI system, gauge pressure is expressed as “kPa above atmospheric.”

The diagram on the right in Fig. 4.1 shows the measuring element completely isolated from the atmosphere. The pressure reading from these gauges represents the actual pressure or force of collision of gas molecules, the *absolute pressure*. In the American Engineering System, absolute pressure is expressed as “psia” or pound force per square inch absolute. In SI, it is expressed as “kPa absolute.”

Conversion from gauge to absolute pressure is done using the following equation:

$$P_{\text{gauge}} = P_{\text{absolute}} - P_{\text{atmospheric}} \quad (4.1)$$



**Figure 4.1** Diagram showing differences in measurement of gauge and absolute pressure.

The term “vacuum” after a unit of pressure indicate how much the pressure is below atmospheric pressure. Thus, vacuum may be interpreted as a negative gauge pressure and is related to the atmospheric pressure and absolute pressure as follows:

$$P_{\text{absolute}} = P_{\text{atmospheric}} - P_{\text{vacuum}} \quad (4.2)$$

Pressure is sometimes expressed in *atmospheres* (atm) instead of the traditional force/area units. This has led to some confusion between a pressure specified in atmospheres and atmospheric pressure. Unless otherwise specified, the pressure term “atm” refer to a *standard atmosphere*, the mean atmospheric pressure at sea level, equivalent to 760 mm Hg, 29.921 in. Hg, 101.325 kPa, or 14.696 lb<sub>f</sub>/in.<sup>2</sup>. A *technical atmosphere* is a pressure of 1 kg<sub>f</sub>/cm<sup>2</sup>. Some technical articles express pressure in *Bar*, which is equivalent to 100 Pa. *Atmospheric pressure* is actual pressure exerted by the atmosphere in a particular location and varies with time and location. Atmospheric pressure must be specified if it is different from a standard atmosphere.

**Example 4.1.** Calculate the absolute pressure inside an evaporator operating under 20 in. Hg vacuum. Atmospheric pressure is 30 in. Hg. Express this pressure in SI and in the American Engineering System of units.

From the table of conversion factors, Appendix Table A.1, the following conversion factors are obtained:

$$\begin{aligned} \frac{0.4912 \text{ lb}_f/\text{in.}^2}{\text{in.Hg}}; \frac{3.38638 \times 10^3 \text{ Pa}}{\text{in. Hg}} P_{\text{absolute}} &= P_{\text{atmospheric}} - P_{\text{vacuum}} = (30 - 20) \text{ in. Hg} = 10 \text{ in. Hg} \\ &= 10 \text{ in.Hg} \frac{0.4912 \text{ lb}_f/\text{in.}^2}{\text{in.Hg}} = 4.912 \text{ psia} = 10 \text{ in.Hg} \frac{3386.38 \text{ Pa}}{\text{in.Hg}} = 33.863 \text{ kPa absolute} \end{aligned}$$

Temperature (T) is a thermodynamic quantity related to the velocity of motion of molecules. The temperature scales are based on the boiling (liquid-gas equilibrium) and freezing points (solid, liquid, gas equilibrium) of pure substances such as water at 1 standard atmosphere (101.325 kPa) pressure. The Kelvin (K) is defined as the fraction, 1/273.16, of the thermodynamic temperature of the triple point of water. The absolute temperature scales are based on a value on the scale that is zero at the temperature when the internal energy of molecules is zero. These are the Kelvin, in SI, and the Rankine (R) in the American Engineering System. Conversion from the commonly used Celsius and Fahrenheit temperature scales to the absolute or thermodynamic scales are as follows:

$$K = ^\circ\text{C} + 273.16$$

$$^\circ\text{R} = ^\circ\text{F} + 460$$

In common usage, the conversion to Kelvin is rounded off to:

$$K = ^\circ\text{C} + 273$$

The absolute temperature is used in equations of state for gases.

### 4.1.3 Quantity of Gases

The quantity of gases is often expressed as volume at a specific temperature and pressure. Because molecules of a gas have very weak attraction toward each other, they will disperse and occupy all

space within a confining vessel. Thus, the volume (V) of a gas is the volume of the confining vessel and is not definitive of the quantity of the gas unless the pressure and temperature are also specified.

The most definitive quantification of gases is by mass, or as the number of moles,  $n$ , which is the quotient of mass and the molecular weight. The unit of mass is prefixed to mole (e.g., kgmole), to indicate the ratio of mass in kg and the molecular weight. The number of molecules in 1 gmole is the *Avogadro number*,  $6.023 \times 10^{23}$  molecules/gmole.

At 273 K and 760 mm Hg pressure (101.325 kPa), 1 gmole, kgmole, and lbmole occupies 22.4 L, 22.4 m<sup>3</sup>, and 359 ft<sup>3</sup>, respectively.

#### 4.1.4 The Ideal Gas Equation

The ideal gas equation is the simplest equation of state and was originally derived from the experimental work of Boyle, Charles, and Guy-Lussac. The equation will be derived based on the kinetic theory of gases.

Pressure, the force of collision between gas molecules and a surface, is directly proportional to temperature and the number of molecules per unit volume. Expressing the proportionality as an equation, and using a proportionality constant,  $R$ :

$$P \propto \frac{n}{V}T; \quad P = R \frac{n}{V}T$$

Rearranging:

$$PV = nRT \tag{4.3}$$

Equation (4.3) is the *ideal gas equation*.  $R$  is the gas constant and has values of 0.08206 L(atm)/(gmole  $\cong$  K); or 8315 N(m)/(kgmole  $\cong$  K) or 1545 ft(lbf)/(lbmole  $\cong$  °R).

##### 4.1.4.1 P-V-T Relationships for Ideal Gases

When a fixed quantity of a gas that follows the ideal gas equation (Eq. 4.3) undergoes a process where the volume, temperature, or pressure is allowed to change, the product of the number of moles  $n$  and the gas constant  $R$  is a constant and:

$$\frac{PV}{T} = \text{constant}$$

If initial temperature, pressure, and volume are known and designated by subscript 1, these properties at another point in the process will be expressed by:

$$\frac{PV}{T} = \frac{P_1 V_1}{T_1} \tag{4.4}$$

Ideality of gases predicted by Equations (4.3) and (4.4) occur only under conditions close to ambient or under processes that span a relatively narrow range of temperature and pressure. Thus, these equations are useful in problems usually encountered when using gases in food processing or packaging.

**Example 4.2.** Calculate the quantity of oxygen entering a package in 24 hours if the packaging material has a surface area of  $3000 \text{ cm}^2$  and an oxygen permeability  $100 \text{ cm}^3/(\text{m}^2)(24 \text{ h})$  STP (standard temperature and pressure =  $0^\circ\text{C}$  and 1 standard atmosphere of  $101.325 \text{ kPa}$ ).

**Solution:**

Solving for the volume of oxygen permeating through the package in 24 hours:

$$V = \frac{100 \text{ cm}^3}{\text{m}^2(24 \text{ h})}(24 \text{ h}) \frac{1 \text{ m}^2}{(100)^2 \text{ cm}^2} (3000 \text{ cm}^2) \\ = 30 \text{ cm}^3$$

Using Equation (4.3):  $n = PV/RT$

Use  $R = 0.08206 \text{ L(atm)/(gmole} \cdot \text{K)}$

$$n = \frac{1 \text{ atm}(30 \text{ cm}^3)}{[0.08206 \text{ L(atm)/(gmole} \cdot \text{K)}](273 \text{ K})} \frac{1 \text{ L}}{1000 \text{ cm}^3} = 0.001339 \text{ gmoles}$$

**Example 4.3.** Calculate the volume of  $\text{CO}_2$  in  $\text{ft}^3$  at  $70^\circ\text{F}$  and 1 atm, which would be produced by vaporization of 1 lb of dry ice.

**Solution:**

Dry ice is solid  $\text{CO}_2$  (mol. wt. =  $M = 44 \text{ lb/lbmole}$ ).  $T = 70^\circ\text{F} + 460 = 530^\circ\text{R}$ .

$$n = \frac{W}{M} = \frac{1 \text{ lb}}{44 \text{ lb/lbmole}} = 0.02273 \text{ lbmole}$$

$$P = 1 \text{ atm} = \frac{14.7 \text{ lb}_f}{\text{in}^2} \frac{144 \text{ in}^2}{\text{ft}^2} = 2116.8 \text{ lb}_f/\text{ft}^2$$

Substituting in the ideal gas equation:  $V = nRT/P$

$$V = 0.02273 \text{ lbmole} \frac{1545 \text{ ft lb}_f}{\text{lbmole}(\text{R})} \frac{530^\circ\text{R}}{2116 \text{ lb}_f/\text{ft}^2} = 8.791 \text{ ft}^3$$

**Example 4.4.** Calculate the density of air ( $M = 29$ ) at  $70^\circ\text{F}$  and 1 atm in (a) American Engineering and (b) SI units.

**Solution:**

Density is mass/volume =  $W/V$ . Using the ideal gas equation:

$$\text{Density} = \frac{W}{V} = \frac{PM}{RT}$$

(a) In the American Engineering System of units:  $P = 2116.8 \text{ lb}_f/\text{ft}^2$ ;  $M = 29 \text{ lb/lbmole}$ ;  $R = 1545 \text{ ft lb}_f/\text{lbmole}(\text{R})$ ; and  $T = 70 + 460 = 530 \text{ ER}$ .

$$\text{Density} = \frac{2116.8 \text{ lb}_f/\text{ft}^2}{1545 \text{ ft lb}_f/(\text{lbmole} \cdot \text{R})} \frac{29 \text{ lb/lbmole}}{530^\circ\text{R}} = 0.07498 \text{ lb/ft}^3$$

(b) in SI,  $P = 101325 \text{ N/m}^2$ ;  $T = (70 - 32)/1.8 = 21.1^\circ\text{C} = 21.1 + 273 = 294.1 \text{ K}$ ;  $V = 1 \text{ m}^3$ ;  $M = 29 \text{ kg/kgmole}$ ; and  $R = 8315 \text{ Nm/(kgmole} \cdot \text{K)}$ .

$$\text{Density} = \frac{101,325 \text{ N/m}^2}{8315 \text{ Nm/(kgmole} \cdot \text{K)}} \frac{29 \text{ kg/kgmole}}{294.1 \text{ K}} = 1.202 \text{ kg/m}^3$$

**Example 4.5.** A process requires  $10 \text{ m}^3/\text{s}$  at 2 atm absolute pressure and  $20^\circ\text{C}$ . Determine the rating of a compressor in  $\text{m}^3/\text{s}$  at STP ( $0^\circ\text{C}$  and  $101325 \text{ Pa}$ ) that must be used to supply air for this process.

**Solution:**

Unless otherwise specified, the pressure term “atm” means a standard atmosphere, or  $101.325 \text{ kPa}$ . Use the P-V-T equation (Eq. 4.4).  $V_1 = 10 \text{ m}^3$ ;  $T_1 = 293 \text{ K}$ ;  $P_1 = 202650 \text{ N/m}^2$ ;  $P = 101325 \text{ N/m}^2$ ;  $T = 273 \text{ K}$ . Solving for V:

$$V = \frac{P_1 T_1}{T_1 P} = \frac{(202,650 \text{ N/m}^2)(2 \text{ m}^3)}{293 \text{ K}} \frac{273 \text{ K}}{101,325 \text{ N/m}^2} = 18.635 \text{ m}^3/\text{s}$$

**Example 4.6.** An empty can was sealed in a room at  $80^\circ\text{C}$  and 1 atm pressure. Assuming that only air is inside the sealed can, what will be the vacuum after the can and contents cool to  $20^\circ\text{C}$ ?

**Solution:**

The quantity of gas remains constant; therefore, the P-V-T equation can be used. The volume does not change, therefore it will cancel out of Equation (4.4).  $P_1 = 101325 \text{ N/m}^2$ ;  $T_1 = 353 \text{ K}$ ;  $T = 293 \text{ K}$ . The pressures to be used in Equation (4.4) will be absolute.

$$P = \frac{101,325 \text{ N/m}^2}{353 \text{ K}} (293 \text{ K}) = 84,103 \text{ Pa absolute.}$$

$$\text{Vacuum} = 17,222 \text{ Pa} \left( \frac{1 \text{ cm Hg}}{1333.33 \text{ Pa}} \right) = 12.91 \text{ cm Hg vacuum}$$

The vacuum in Pa will be  $101,325 - 84,103 = 17,222 \text{ Pa}$ .

#### 4.1.5 van der Waal's Equation of State

The ideal gas equation is based on unhindered movement of gas molecules within the confined space; therefore, at constant temperature when molecular energy is constant, the product of pressure and volume is constant. However, as pressure is increased, molecules are drawn closer, and attractive and repulsive forces between molecules affect molecular motion. When molecules are far apart, attractive forces exist. The magnitude of this attractive force is inversely proportional to the square of the distance between molecules. When molecules collide, they approach a limiting distance of separation when repulsive forces become effective, preventing molecules from directly contacting each other. Molecular contact may cause a chemical reaction, and this occurs only at very high molecular energy levels that exceed the repulsive force. The separation distance between molecules where repulsive forces are effective defines an exclusion zone, which reduces the total volume available for molecules to randomly move. The attractive forces between molecules also restrict molecular motion, and this will have the effect of reducing the quantity and magnitude of impact against the walls of the confining

**Table 4.1** Values of Van der Waal's Constants for Different Gases

Gas	$a$ $\text{Pa (m}^3/\text{kgmole)}^2$	$b$ $\text{m}^3/\text{kgmole}$
Air	$1.348 \times 10^5$	0.0366
Ammonia	$4.246 \times 10^5$	0.0373
Carbon dioxide	$3.648 \times 10^5$	0.0428
Hydrogen	$0.248 \times 10^5$	0.0266
Methane	$2.279 \times 10^5$	0.0428
Nitrogen	$1.365 \times 10^5$	0.0386
Oxygen	$1.378 \times 10^5$	0.0319
Water vapor	$5.553 \times 10^5$	0.0306

Source: Calculated from values in the International Critical Tables.

vessel. These attractive forces are referred to as an internal pressure. At low pressures, molecular distance is large, the internal pressure is small, and the excluded volume is small compared with the total volume, and gas molecules obey the ideal gas equation. However, at high pressures, the pressure-volume-temperature relationship deviates from ideality. Gases that deviate from ideal gas behavior are considered real gases. One of the commonly used equations of state for real gases is the van der Waal's equation.

van der Waal proposed corrections to the ideal gas equation based on the excluded volume,  $nb$ , and a factor,  $n^2a/V^2$ , the internal pressure. The fit between experimental P-V-T relationship and calculated values using van der Waal's equation of state is very good except in the region of temperature and pressure near the critical point of the gas. For  $n$  moles of gas, van der Waal's equation of state is

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT \quad (4.5)$$

Values of the constants  $a$  and  $b$  in SI units are given in Table 4.1.

**Example 4.7.** Calculate the density of air at  $150^\circ\text{C}$  and 5 atm pressure using van der Waal's equation of state and the ideal gas equation.

**Solution:**

Using the ideal gas equation:

$$\begin{aligned} \text{Density} = W &= \frac{PM}{RT}; \quad V = 1 \text{ m}^3 \left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT; \quad n = \frac{W}{M}; \quad V = 1 \\ &= \frac{5(101,325)(29)}{8315(150 + 273)} = 4.1766 \text{ kg/m}^3 \end{aligned}$$

Using van der Waal's equation of state:  $V = 1 \text{ m}^3$

$$\begin{aligned} \left(P + \frac{W^2a}{M^2V^2}\right)\left(V - \frac{W}{M}b\right) &= \frac{W}{M}RT \\ W^3\left(\frac{ab}{M^3V^3}\right) - W^2\left(\frac{a}{M^2V}\right) + W\left(\frac{Pb + RT}{M}\right) - PV &= 0 \end{aligned}$$

Expanding and collecting like terms:

Substituting  $a = 1.348 \times 10^5$ ;  $b = 0.0366$ ;  $R = 8315$ ;  $M = 29$ ;  $P = 5(101325) = 506625 \text{ Pa}$ ;  
 $T = 150 + 273 = 423 \text{ K}$ ;  $V = 1 \text{ m}^3$ .

$$0.2023 W^3 - 160.3 W^2 + 121,923.7 W - 506,625 = 0$$

Dividing through by 0.2023:

$$W^3 - 792.3875 W^2 + 602,687.6 W - 2,504,325.3 = 0$$

Solve using the Newton-Raphson iteration technique:

$$f = W^3 - 792.3875 W^2 + 602,687.6 W - 2,504,325.3$$

$$f' = 3 W^2 - 1584.775 W + 602,687.6$$

Thus, the mass of  $1 \text{ m}^3$  of air at  $150^\circ\text{C}$  and  $5 \text{ atm}$  is  $4.178 \text{ kg} = \text{the density in kg/m}^3$ . Values calculated using the van der Waal's equation of state is more accurate than that obtained using the ideal gas equation. A worksheet in Microsoft Excel to solve this problem is shown in Fig. 4.2

#### 4.1.6 Critical Conditions for Gases

When the pressure of a gas is increased by compression, the molecules are drawn closer together and attractive forces between the molecules become strong enough to restrict movement of the molecules. At a certain temperature and pressure, a saturation point of the gas is reached and an equilibrium condition between gas and liquid can exist. If the energy level in the gas is reduced by removal of the latent heat of vaporization, it will condense into a liquid. The higher the pressure, the higher the saturation temperature of the gas.

If the pressure of the gas is increased as the temperature is maintained following the saturation temperature curve, a point will be reached where gas and liquid become indistinguishable. This particular temperature and pressure is called the critical point. The property of the gas at the critical point is very similar to that of a liquid in terms of dissolving certain solutes, and this property is put into practical use in a process called supercritical fluid extraction, which will be discussed in more detail in Chapter 14.

#### 4.1.7 Gas Mixtures

In this section, the concept of partial pressures and partial volumes will be used to elucidate P-V-T relationships of individual components in a gas mixture.

If components of a gas mixture at constant volume are removed one after the other, the drop in pressure accompanying complete removal of one component is the *partial pressure* of that component.

If  $P_t$  is the total pressure and  $P_a, P_b, P_c \dots P_n$  are partial pressures of the components a, b, c, ... and n, then:

$$P_t = P_a + P_b + P_c + \dots P_n \quad (4.6)$$

Equation (4.6) is *Dalton's law of partial pressures*. Because the same volume is occupied by all components, the ideal gas equation may be used on each component to determine the number of moles of that component, from the partial pressure.

$$P_a V = n_a R T \quad (4.7)$$



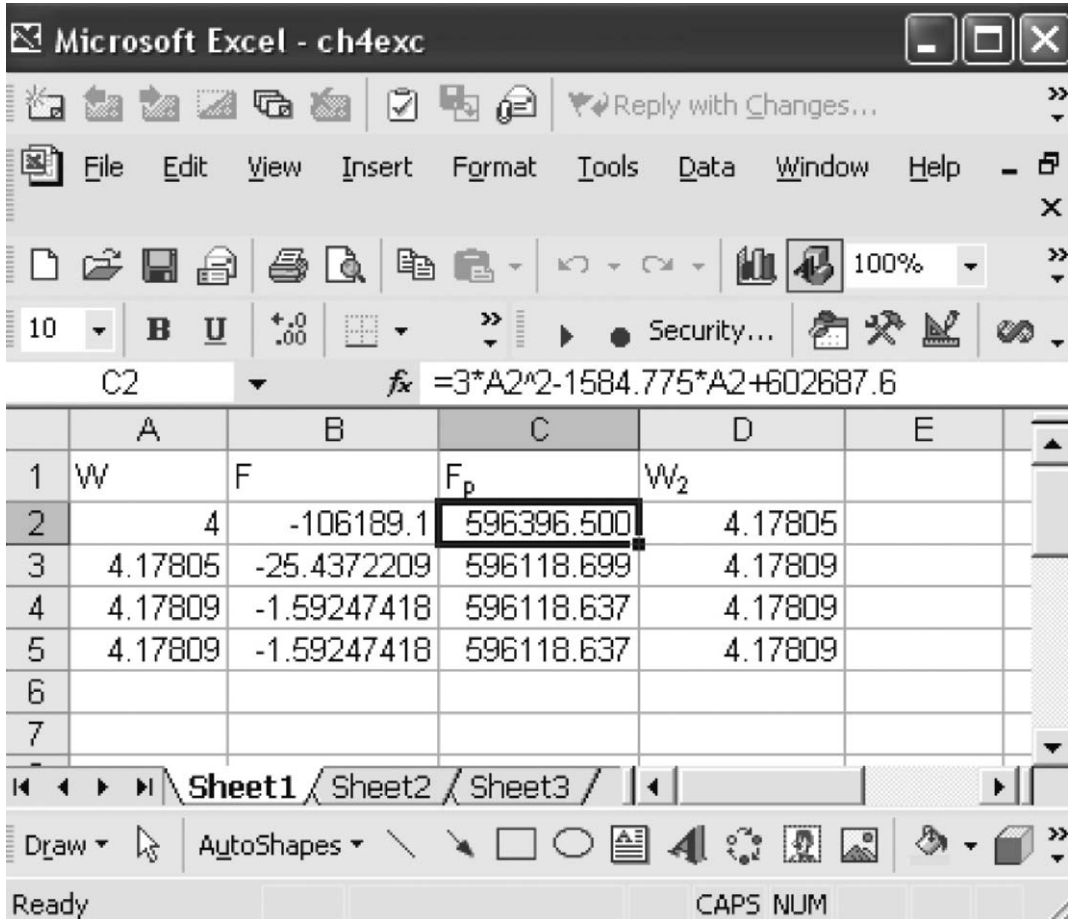


Figure 4.2 Spreadsheet for Newton-Raphson method and van der Waal's equation to calculate air density.

The *partial volume* is the change in volume of a gas mixture when each component is removed separately at constant pressure. If  $V_t$  is the total volume, and  $V_a, V_b, V, \dots V_n$  are the partial volumes of the components, then:

$$V_t = V_a + V_b + V_c + \dots V_n \quad (4.8)$$

Equation (4.8) is *Amagat's law of partial volumes*. The ideal gas equation may also be used on the partial volume of each component to determine the number of moles of that component in the mixture.

$$PV_a = n_a RT \quad (4.9)$$

Compositions of gases are expressed as a percentage of each component by volume. It may be seen from Equation (4.9) that the volume percentage of a gas is numerically the same as the mole percentage.

**Example 4.8.** Calculate the quantity of air in the headspace of a can at 20°C when the vacuum in the can is 10 in. Hg. Atmospheric pressure is 30 in. Hg. The headspace has a volume of 16.4 cm<sup>3</sup>. The headspace is saturated with water vapor.

**Solution:**

The steam tables (Appendix Table A.4) will give the vapor pressure of water at 20 EC of 2336.6 Pa. Let  $P_t$  be the absolute pressure inside the can.

$$P_t = (30 - 10)\text{in.Hg} \left( \frac{3386.38 \text{ Pa}}{\text{in. Hg}} \right) = 67,728 \text{ Pa}$$

Using the ideal gas equation:  $V = 16.4 \text{ cm}^3 (10^{-6}) \text{ m}^3 / \text{cm}^3 = 1.64 \times 10^{-5} \text{ m}^3$ ;  $T = 20 + 273 = 293 \text{ K}$ .

$$P_{\text{air}} = P_t - P_{\text{water}}$$

$$n_{\text{air}} = \frac{P_{\text{air}} V}{RT} = \frac{(67,728 - 2336.6)(1.64 \times 10^{-5} \text{ m}^3)}{8315/(293)} = 67728 - 2336.6 = 65391.4 \text{ Pa}$$

$$= 4.40 \times 10^{-7} \text{ kgmoles}$$

**Example 4.9.** A gas mixture used for controlled atmosphere storage of vegetables contains 5% CO<sub>2</sub>, 5% O<sub>2</sub>, and 90% N<sub>2</sub>. The mixture is generated by mixing appropriate quantities of air and N<sub>2</sub> and CO<sub>2</sub> gases. 100 m<sup>3</sup> of this mixture at 20°C and 1 atm is needed per hour. Air contains 21% O<sub>2</sub> and 79% N<sub>2</sub>. Calculate the rate at which the component gases must be metered into the system in m<sup>3</sup>/h at 20°C and 1 atm.

**Solution:**

All percentages are by volume. No volume changes occur on mixing of ideal gases. Because volume percent in gases is the same as mole percent, material balance equations may be made on the basis of volume and volume percentages. Let  $X$  = volume O<sub>2</sub>,  $Y$  = volume CO<sub>2</sub>, and  $Z$  = volume N<sub>2</sub>, fed into the system per hour.

$$\text{Oxygen balance: } 0.21(X) = 100(0.05); X = 23.8 \text{ m}^3$$

$$\text{CO}_2 \text{ balance: } Y = 100(0.05); Y = 5 \text{ m}^3$$

$$\text{Total volumetric balance: } X + Y + Z = 100$$

$$Z = 100 - 23.8 - 5 = 71.2 \text{ m}^3$$

## 4.2 THERMODYNAMICS

Thermodynamics is a branch of science that deals with energy exchange between components within a system or between a system and its surroundings. A *system* is any matter enclosed within a boundary. The boundary may be real or imaginary and depends solely upon the part of the process under study. Anything outside the boundary is the *surroundings*. The *properties* of a system determines its state just as a state may imply certain properties. Properties may be *extrinsic* (i.e., it is measurable) or it may be *intrinsic* (i.e., no measurable external manifestations of that property exist). Changes in the intrinsic properties, however, may be measured through changes in energy associated with the change.

*Equilibrium* is a fundamental requirement in thermodynamic transformations. When a system reaches a condition where properties remain constant, a state of equilibrium is attained. The science of thermodynamics deals with a system in equilibrium. Thermodynamics cannot predict how long it will take for equilibrium to occur within a system, it can only predict the final properties at equilibrium.

#### 4.2.1 Thermodynamic Variables

Energy involved in thermodynamic transformations is expressed in terms of *heat* ( $Q$ ), the energy that crosses a system's boundaries due to a difference in temperature, and *work* ( $W$ ), the energy associated with force displacement. The term "internal energy" ( $E$ ) is used to define an intrinsic property, which is energy not associated with either work or heat. Internal energy is not measurable, but changes in internal energy can be measured. An intrinsic property *entropy* ( $S$ ) is also possessed by a system and is a measure of the disorder that exists within a system. The first and second laws of thermodynamics are based on the relationships of the above main thermodynamic variables.

If  $\delta Q$  and  $\delta W$  are small increments of heat and work energy that crosses a system's boundaries, the accompanying differential change in the internal energy of the system is

$$dE = \delta Q - \delta W \quad (4.10)$$

Equation (4.10) is also expressed as:

$$\Delta E = Q - W \quad (4.11)$$

Equations (4.10) or (4.11) are expressions for the *first law of thermodynamics*, a fundamental relationship also known as the law of conservation of energy. The symbol  $\delta$ , called "del," operating on  $W$  and  $Q$  is not a true differential but rather a finite difference. Although it is considered in mathematical operations as a differential operator, integration produces an increment change in a function, rather than an absolute value. This principle is used when integrating functions such as  $E$  and  $S$ , which do not have absolute values but for which increment change associated with a process can be calculated.

Entropy cannot be measured, but the change in entropy is defined as the ratio of the reversible energy ( $Q_{\text{rev}}$ ) which crossed a system's boundaries, and the absolute temperature.

$$dS = \frac{\delta Q_{\text{rev}}}{T}; \quad \Delta S = \frac{Q_{\text{rev}}}{T} \quad (4.12)$$

The *second law of thermodynamics* states that any process that occurs is accompanied by a positive entropy change, and the entropy change approaches zero for reversible processes. If the process is reversible, any change in entropy in a system is compensated by a change in the entropy of the surroundings such that the net entropy change for the system and its surroundings is zero.

The concept of the entropy or state of disorder of a system has several interpretations. One interpretation is that no truly reversible process is possible, because any process produces a more disordered system than what existed before the change. This change in the state of order requires the application of or a loss of energy. Another interpretation of the concept of entropy involves the spontaneity of processes. Spontaneous processes will occur only when there is enough energy available initially to overcome the requirement for increasing the entropy. Thus, process spontaneity always requires a change from a higher to a lower energy state.

Another intrinsic thermodynamic variable is the enthalpy ( $H$ ) defined as:

$$H = E + PV \quad (4.13)$$

In differential form:

$$dH = dE + PdV + VdP \quad (4.14)$$

Because  $PdV = \delta W$ ;  $dE + \delta W = \delta Q$  and:

$$dH = \delta Q + VdP \quad (4.15)$$

For a constant pressure process,  $dP = 0$  and:

$$\delta Q = dH; \delta H = Q \quad (4.16)$$

A specific heat at constant pressure may be defined as follows:

$$C_p = \left. \frac{dQ}{dT} \right|_p \quad (4.17)$$

and as:

$$\Delta H = C_p dT \quad (4.18)$$

Equation (4.18) shows why the enthalpy is referred to as the heat content. In a constant-volume process, work is zero, and Equation (4.10) becomes:

$$dE = \delta Q; \Delta E = Q \quad (4.19)$$

A specific heat at constant volume may be defined as follows:

$$C_v = \left. \frac{dQ}{dT} \right|_v \quad (4.20)$$

and as:

$$\Delta E = C_v dT \quad (4.21)$$

#### 4.2.2 The Relationship Between $C_p$ and $C_v$ for Gases

The relationship between  $C_p$  and  $C_v$  for gases is derived as follows. Substituting  $W = PdV$  for work in Equation (4.10) for a constant pressure process:

$$dE = dQ - PdV \quad (4.22)$$

Taking the derivative with respect to temperature:

$$\frac{dE}{dT} = \left. \frac{dQ}{dT} \right|_p - P \frac{dV}{dT} \quad (4.23)$$

Equation (4.17) gives  $dQ/dT = C_p$  and Equation (4.21) gives  $dE/dT = C_v$ . From the ideal gas equation, for 1 mole of gas,  $PV = RT$ , and  $dV/dT$  at constant pressure is  $R/P$ . Substituting in Equation (4.23):

$$C_v = C_p - R \quad (4.24)$$

A useful property in calculating P-V-T and other thermodynamic variables involved in expansion and compression of a gas is the specific heat ratio,  $C_p/C_v$ , designated by the symbol  $\gamma$ . The ratio  $C_p/R$  is

expressed in terms of  $Q$  as follows:

$$\frac{C_p}{R} = \frac{\gamma}{\gamma - 1} \quad (4.25)$$

### 4.2.3 P-V-T Relationships for Ideal Gases in Thermodynamic Processes

*Adiabatic processes* are those where no heat is added or removed from the system, therefore,  $\delta Q = 0$ . Equation (4.15) then becomes:  $dH = V dP$ . Because for 1 mole of an ideal gas,  $V = RT/P$ , and because  $dH = C_p dT$ ,

$$C_p dT = RT \left( \frac{dP}{P} \right) \quad (4.26)$$

$$\ln \left[ \frac{P_2}{P_1} \right] = \frac{\gamma}{\gamma - 1} \ln \left[ \frac{T_2}{T_1} \right]$$

$$\frac{C_p}{R} \int_{T_1}^{T_2} \frac{dT}{T} = \int_{P_1}^{P_2} \frac{dP}{P} \quad (4.27)$$

Integrating and substituting  $C_p/R = \gamma / (\gamma - 1)$ .

The ideal gas equation may be used to substitute for  $P$  in Equation (4.27) to obtain an expression for  $V$  as a function of  $T$  in an adiabatic process. Substitute:  $P_1 = nRT_1/V_1$  and  $P_2 = nRT_2/V_2$  in Equation (4.27) and simplifying:

$$\frac{P_2}{P_1} = \left[ \frac{T_2}{T_1} \right]^{\frac{\gamma}{\gamma-1}} \quad (4.28)$$

$$\frac{V_1}{V_2} = \left[ \frac{T_2}{T_1} \right]^{\frac{1}{\gamma-1}} \quad (4.29)$$

Equations (4.28) and (4.29) can be used to derive:

$$\left[ \frac{V_1}{V_2} \right]^\gamma = \left[ \frac{P_2}{P_1} \right] \quad (4.30)$$

*Isothermal processes* are those where the temperature is maintained constant. Thus,  $P_1 V_1 = P_2 V_2$ .

*Isobaric processes* are those where the pressure is maintained constant. Thus,  $V_1/T_1 = V_2/T_2$ .

*Isocratic processes* are those where the volume is maintained constant. Thus,  $P_1/T_1 = P_2/T_2$ .

### 4.2.4 Changes in Thermodynamic Properties, Work, and Heat Associated with Thermodynamic Processes

Adiabatic:

$$\Delta Q = 0; \Delta S = 0; \Delta E = W = \int P dV; \Delta H = \int V dP$$

Isothermal:

$$Q = W = \int P dV; \Delta S = \frac{Q}{T}; \Delta E = 0; \Delta H = 0$$

Isobaric:

$$Q = \int C_p dT = \Delta H; \Delta S = \int C_p \frac{dT}{T}; W = P\Delta V; \Delta E = Q - W$$

Isocratic:

$$Q = \Delta E = \int C_v dT; \Delta S = \int C_v \frac{dT}{T}; W = 0; \Delta E = Q$$

#### 4.2.5 Work and Enthalpy Change on Adiabatic Expansion or Compression of an Ideal Gas

Work and enthalpy changes are important in determining power input into compressors. Adiabatic compression is what occurs during the compression of a refrigerant in a refrigeration cycle.

In adiabatic compression or expansion:

$$W = \int P dV; \Delta H = \int V dP \quad (4.31)$$

Equation (4.30) is rearranged, substituting P and V for  $P_2$  and  $V_2$ .

Solving for V:

$$V = [(P_1)^{\frac{1}{\gamma}} V_1] (P)^{\frac{-1}{\gamma}}$$

Differentiating with respect to P:

$$dV = \frac{-1}{\gamma} [(P_1)^{\frac{1}{\gamma}} V_1] [P]^{\frac{-1}{\gamma}-1}$$

Substituting dV in the expression for work and integrating:

$$W = \int_{P_1}^{P_2} -\frac{1}{\gamma} [(P_1)^{\frac{1}{\gamma}} V_1] [P]^{\frac{-1}{\gamma}-1}$$

The integral is

$$\begin{aligned} & -\frac{1}{\frac{1}{\gamma} + 1} [[P_2]^{\frac{1}{\gamma}+1} - [P_1]^{\frac{1}{\gamma}+1}] \\ & = -\frac{(P_1)^{\frac{1}{\gamma}} V_1}{\gamma} \int_{P_1}^{P_2} (P)^{\frac{-1}{\gamma}} dP \end{aligned}$$

Combining the integral with the multiplier and simplifying:

$$W = \frac{P_1 V_1}{1 - \gamma} \left[ \left[ \frac{P_2}{P_1} \right]^{\frac{(\gamma-1)}{\gamma}} - 1 \right] \quad (4.32)$$

The enthalpy change is determined by evaluating the following integral:

$$\Delta H = V_1 \int_{P_1}^{P_2} \left[ \frac{P_1}{P} \right]^{\frac{1}{\gamma}} dP \quad (4.33)$$

#### 4.2.6 Work and Enthalpy Change on Isothermal Expansion or Compression of an Ideal Gas

$$\Delta H = \left[ \frac{\gamma}{\gamma - 1} \right] (P_1 V_1) \left[ \left[ \frac{P_2}{P_1} \right]^{\frac{(\gamma-1)}{\gamma}} - 1 \right]$$

When an ideal gas is subjected to an isothermal process

$$Q = W = \int P dV \text{ and } \Delta H = \int P dV + \int V dP$$

Because  $T$  is constant,  $P = nRT/V$  and  $dP = -(nRT/V^2) dV$

$$Q = W = \int_{V_1}^{V_2} nRT \frac{dV}{V}$$

$$Q = nRT \ln \left[ \frac{V_2}{V_1} \right]$$

$$\Delta H = W + \int_{V_1}^{V_2} - \left[ nRT \frac{dV}{V} \right] \quad (4.34)$$

The second term in the expression for  $\Delta H$  is exactly the same as the expression for  $W$  but has a negative sign, therefore, in an isothermal process,  $\Delta H = 0$ .

**Example 4.10.**  $N_2$  gas trapped inside a cylinder with a movable piston at 80 atm pressure is then allowed to expand adiabatically (no heat added or removed) until the final pressure is 1 atm. The gas is initially at 303 K and the initial volume is 1 liter. Calculate (a) the work performed by the gas, (b) the entropy change, (c) the enthalpy change, and (d) change in internal energy. The gas has a specific heat ratio,  $\gamma$ , of 1.41.

**Solution:**

(a) Equation (4.31) will be used to calculate the work.  $V_1 = 0.001 \text{ m}^3$ ;  $P_1 = 80(101325) = 8106000 \text{ Pa}$ ;  $P_2 = 101325 \text{ Pa}$ . From Equation (4.31):

$$W = \frac{(8,106,000 \text{ Pa})(0.001 \text{ m}^3)}{-0.41} \left[ \left( \frac{101,325}{8,106,000} \right)^{\frac{0.41}{1.41}} - 1 \right] = -14241.8 \text{ J}$$

(b)  $\Delta S = 0$

$$\Delta H = \left[ \frac{1.41}{0.41} (8,106,000 \text{ Pa})(0.001 \text{ m}^3) \right] \left[ \left[ \frac{101,325}{8,106,000} \right]^{\frac{0.41}{1.41}} - 1 \right]$$

(c) From Equation (4.32):

$$= -20,080.9 \text{ J}$$

(d)  $\Delta E = W = -14241.7 \text{ J}$

### 4.3 VAPOR-LIQUID EQUILIBRIUM

The molecular attraction that holds liquid molecules together is not strong enough to prevent some molecules from escaping, therefore, some molecules will escape in the gaseous form. If the volume of the system containing the liquid and vapor is held constant, eventually equilibrium will be attained

when the rate of escape of molecules from the liquid phase to become vapor equals the rate at which the vapor molecules are recaptured by the liquid phase. This condition of equilibrium exists in all liquids. A liquid will always maintain an envelope of vapor around its surface, and the pressure exerted by that vapor is known as the *vapor pressure*. The pressure exerted by molecules of vapor in equilibrium with a liquid is a function only of temperature. In the absence of any other gas exerting pressure on the liquid surface (e.g., when the liquid is introduced into a container which is under a perfect vacuum), the pressure of the vapor at equilibrium is the vapor pressure. If the total pressure above a liquid is maintained constant at the vapor pressure, heating will not increase the temperature but will cause more liquid molecules to enter the vapor phase. The temperature at a pressure that corresponds to the vapor pressure of a liquid is the *boiling point*, a condition where the whole atmosphere over the liquid surface consists only of gaseous molecules of that liquid. The heat added to the system to generate a unit mass of vapor from liquid at the boiling point is the *heat of vaporization*. When the pressure above the liquid is higher than the vapor pressure, some other gas molecule (e.g., air) would be exerting that pressure in addition to the vapor molecules, therefore the vapor pressure will be the partial pressure of vapor in the gas mixture surrounding the liquid.

### 4.3.1 The Clausius-Clapeyron Equation

The temperature dependence of the vapor pressure is expressed by Equation (4.34), the Clausius-Clapeyron equation:

$$\ln \left[ \frac{P}{P_1} \right] = \left[ \frac{\Delta H_v}{R} \right] \left[ \frac{T - T_1}{TT_1} \right] \quad (4.35)$$

where  $\Delta H_v$  is heat of vaporization;  $P$  is vapor pressure at temperature  $T$ ;  $R$  is gas constant; and  $P_1$  is vapor pressure at temperature  $T_1$ . Equation (4.34) assumes constant heat of vaporization, but in reality, this quantity changes with temperature. Thus, the most useful function of Equation (4.34) is in interpolating between values of vapor pressure listed in abbreviated tables where temperature interval between entries in the table is quite large. The steam tables (Appendix Tables A.3 and A.4) give values of the vapor pressure for water at different temperatures. Because temperature intervals in these tables are rather close, a linear interpolation may be used, instead of a logarithmic function interpolation as suggested by Equation (4.34).

### 4.3.2 Liquid Condensation from Gas Mixtures

When the partial pressure of component in a gas mixture exceeds the vapor pressure of that component, condensation will occur. If the mixture is in a closed container where the volume is constant, condensation will result in a decrease in total pressure. This principle is responsible for the vacuum that results when a hot liquid is filled into a can and sealed. Replacement of air in the headspace by vapors from the product itself or by steam in a system where steam is flushed over the can headspace prior to sealing results in a reduced pressure after the can cools adequately to condense the vapors in the headspace.

**Example 4.11.** A canned food at the time of sealing is at a temperature of 80°C, and the atmospheric pressure is 758 mm Hg. Calculate the vacuum (in mm Hg) formed inside the can when the contents cools down to 20°C.



**Solution:**

Assume there are no dissolved gases in the product at the time of sealing, therefore the only gases in the headspace are air and water vapor. From Appendix Table A.3, the vapor pressure of water at 20°C and 80°C are 2.3366 and 47.3601 kPa, respectively. In the gas mixture in the headspace, air is assumed to remain at the same quantity in the gaseous phase, while water condenses on cooling.

$$P_{\text{air}} = P_t - P_{\text{water}}$$

At 80°C,

$$P_t = 758 \text{ mm Hg} \left( \frac{1 \text{ cm Hg}}{10 \text{ mm Hg}} \right) \left( \frac{1333.33 \text{ Pa}}{\text{cm Hg}} \right) = 101,066 \text{ Pa}$$

Let  $P$  = pressure in the headspace at 20°C.

$$n_{\text{air}} = \frac{PV}{RT} = \frac{(101,064 - 47,360.1)V}{8315(80 + 273)} = 0.018296 \text{ V kgmole}$$

At 20°C,

$$n_{\text{air}} = \frac{PV}{8315(293)} = 4.1046 \times 10^{-7} PV \text{ kgmole}$$

Because the number of moles of air trapped in the headspace is constant:

$$4.1046 \times 10^{-7} P V = 0.018296 V$$

$$P = 44575 \text{ Pa absolute} = 334 \text{ mm Hg absolute}$$

$$\text{Vacuum} = 758 - 334 = 424 \text{ mm Hg vacuum}$$

**Example 4.12.** Air at 5 atm pressure is saturated with water vapor at 50°C. If this air is allowed to expand to 1 atm pressure and the temperature is dropped to 20°C, calculate the amount of water that will be condensed per m<sup>3</sup> of high pressure air at 50°C.

**Solution:**

The vapor pressure of water at 50°C and 20°C are 12.3354 and 2.3366 kPa, respectively. Basis: 1 m<sup>3</sup> air at 5 atm pressure and 50°C. The number of moles of air will remain the same on cooling.

$$n_{\text{air}} = \frac{[5(101,325) - 12,335.4]V}{8315(50 + 273)} = 0.1840 \text{ kgmole}$$

At 20°C:

$$n_{\text{air}} = \frac{(101,325 - 2336.6)V}{8315(20 + 273)} = 0.04063 V$$

Equating:  $0.04063 V = 0.1840$ ;  $V = 4.529 \text{ m}^3$  at 20°C and 1 atm.

At 50°C,

$$n_{\text{water}} = \frac{12,335.4(1)}{8315(323)} = 0.004593$$

At 20°C,

$$n_{\text{water}} = \frac{2336.6(4.529)}{8315(293)} = 0.004344$$

Moles water condensed = 0.004593 - 0.004344 = 0.000249 kg moles.

**Example 4.13.** The partial pressure of water in air at 25°C and 1 atm is 2.520 kPa. If this air is compressed to 5 atm total pressure to a temperature of 35°C, calculate the partial pressure of water in the compressed air.

**Solution:**

Increasing the total pressure of a gas mixture will proportionately increase the partial pressure of each component. Using the ideal gas equation (Equation 4. 3) for the mixture and for the water vapor, let  $V_1$  = the volume of the gas mixture at 25°C and 1 atm;  $P_t$  = total pressure;  $P_w$  = partial pressure of water vapor.

The total number of moles of air and water vapor is

$$n_t = \frac{P_1 V_1}{RT_1} = \frac{P_2 V_2}{RT_2}$$

The number of moles of water vapor is

$$n_{\text{water}} = \frac{P_{w1} V_1}{RT_1} = \frac{P_{w2} V_2}{RT_2}$$

Assuming no condensation, the ratio,  $n_t/n_w$  will be the same in the low-pressure and high-pressure air, therefore:

$$\frac{P_1}{P_{w1}} = \frac{P_2}{P_{w2}}; \quad P_{w2} = P_{w1} \frac{P_2}{P_1}$$

$$P_{w2} = \frac{5 \text{ atm}}{1 \text{ atm}} (2.520 \text{ kPa}) = 12.60 \text{ kPa}$$

The temperature was not used in calculating the final partial pressure of water. The temperature is used in verifying the assumption of no condensation, comparing the calculated final partial pressure with the vapor pressure of water at 35°C. From the steam tables, Appendix Table A.3, the vapor pressure of water at 35°C is the pressure of saturated steam at 35°C, which is 5.6238 kPa. Because the calculated partial pressure of water in the compressed air is greater than the vapor pressure, condensation of water must have occurred and the correct partial pressure of water will be the vapor pressure at 35°C. Thus:  $P_{w2} = 5.6238 \text{ kPa}$ .

## PROBLEMS

- 4.1. Air used for dehydration is heated by burning natural gas and mixing the combustion products directly with air. The gas has a heating value of 1050 BTU/ft<sup>3</sup> at 70°F and 1 atm pressure. Assume the gas is 98% methane and 2% nitrogen.
  - (a) Calculate the quantity of natural gas in ft<sup>3</sup> at 70 EF and 1 atm. needed to supply the heating requirements for a dryer that uses 1500 lb dry air per hour at 170°F and 1 atm. Assume the products of combustion will have the same specific heat as dry air, of 0.24 BTU/(lb  $\cong$  °F).
  - (b) If the air used to mix with the combustion gases is completely dry, what will be the humidity of the air mixture entering the dryer.
- 4.2. A package having a void volume of 1500 cm<sup>3</sup> is to be flushed with nitrogen to displace oxygen prior to sealing. The process used involved drawing a vacuum of 700 mm Hg on the package, breaking the vacuum with nitrogen gas, and drawing another 700 mm Hg vacuum before sealing. The solids in the package prevents total collapse of the package as the vacuum is drawn, therefore the volume of gases in the package may be assumed to remain constant during the process. If the temperature is maintained constant at 25°C during the process, calculate the number of gmoles of oxygen left in the package at the completion of the process. Atmospheric pressure is 760 mm Hg.
- 4.3. Compression of air in a compressor is an adiabatic process. If air at 20°C and 1 atm pressure is compressed to 10 atm pressure, calculate:
  - (a) The temperature of the air leaving the compressor.;
  - (b) The theoretical compressor horsepower required to compress 100 kg of air. The specific heat ratio of air is 1.40; the molecular weight is 29.
- 4.4. Air at 25°C and 1 atm that contains water vapor at a partial pressure that is 50% of the vapor pressure at 25°C (50% relative humidity) is required for a process. This air is generated by saturating room air by passing through water sprays, compressing this saturated air to a certain pressure, P, and cooling the compressed air to 25°C. The partial pressure of water in the cooled saturated air that leaves the compressor is the vapor pressure of water at 25°C. This air is allowed to expand to 1 atm pressure isothermally. Calculate P such that after expansion, the air will have 50% relative humidity.
- 4.5. An experiment requires a gas mixture containing 20% CO<sub>2</sub>, 0.5% O<sub>2</sub>, and 79.5% N<sub>2</sub> at 1 atm and 20°C. This gas mixture is purchased premixed and comes in a 10 L tank at a pressure of 130 atm gauge. The gas will be used to displace air from packages using a packaging machine that operates by drawing a vacuum completely inside a chamber where the packages are placed, displacing the vacuum with the gas mixture, and sealing the packages. The chamber can hold four packages at a time, and the total void volume chamber with the packages in place is 2500 cm<sup>3</sup>. How many packages can be treated in this manner before the pressure in the gas tank drops to 1 atm gauge.
- 4.6. A vacuum pump operates by compressing gases from a closed chamber to atmospheric pressure in order that these gases can be ejected to the atmosphere. A vacuum drier operating at 700 mm Hg vacuum (atmmospheric pressure is 760 mm Hg) and 50°C generates 500 g of water vapor per minute by evaporation from a wet material in the dryer. In addition, the leakage rate for ambient air infiltrating the dryer is estimated to be 1 L/h at 1 atm and 20°C.
  - (a) Calculate the total volume of gases that must be removed by the vacuum pump per minute.
  - (b) If the pump compresses the gas in an adiabatic process, calculate the theoretical horsepower required for the pump. The specific heat ratio for water is 1.30, and that for air is 1.40.

- 4.7. The mass rate of flow of air ( $G$ ) used in correlation equations for heat transfer in a dryer is expressed in  $\text{kg air/m}^2(\text{h})$ . Use the ideal gas equation to solve for  $G$  as a function of the velocity of flow ( $V$ , in  $\text{m/h}$ ) of air at temperature  $T$  and 1 atm pressure.
- 4.8. Use van der Waal's equation of state to calculate the work done on isothermal expansion of a gas from a volume of 10 to  $300 \text{ m}^3$  at  $80^\circ\text{C}$ . The initial pressure was 10 atm. Calculate the entropy change associated with the process.
- 4.9. A supercritical  $\text{CO}_2$  extraction system is being operated at 30.6 Mpa and  $60^\circ\text{C}$  in the extraction chamber. The volume of  $\text{CO}_2$  leaving the system measured at 101.3 kPa and  $20^\circ\text{C}$  is 10 L/min. If the extraction chamber is a tube having a diameter of 50.6 mm and a length of 45 cm., calculate the residence time of the  $\text{CO}_2$  in the extraction chamber. Residence time = volume of chamber/volumetric rate of flow in the chamber.

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#### SUGGESTED READING

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