Zeroth Law of Thermodynamics and Equations of State

CHAPTER 1

Physical chemistry is concerned with understanding the quantitative aspects of chemical phenomena. To introduce physical chemistry, we will start with the most accessible properties of matter—those that can readily be measured in the laboratory. The simplest of these are the properties of matter at equilibrium. Thermodynamics deals with the properties of systems at equilibrium, such as temperature, pressure, volume, and amounts of species; but it also deals with work done on a system and heat absorbed by a system, which are not properties of the system but measures of changes. The amazing thing is that the thermodynamic properties of systems at equilibrium obey all the rules of calculus and are therefore interrelated. The principle involved in defining temperature was not recognized until the establishment of the first and second laws of thermodynamics, and so it is referred to as the zeroth law. This leads to a discussion of the thermodynamic properties of gases and liquids. After discussing the ideal gas, we consider the behavior of real gases. The thermodynamic properties of a gas or liquid are represented by an equation of state, such as the virial equation or the van der Waals equation. The latter has the advantage that it provides a description of the critical region, but much more complicated equations are required to provide an accurate quantitative description.

1.1 STATE OF A SYSTEM

A thermodynamic system is that part of the physical universe that is under consideration. A system is separated from the rest of the universe by a real or idealized **boundary.** The part of the universe outside the boundary of the system is referred to as the **surroundings,** as illustrated in Fig. 1.1. The boundary between the system and its surroundings may have certain real or idealized characteristics. For example, the boundary may conduct heat or be a perfect insulator. The boundary may be rigid or it may be movable so that it can be used to apply a specified pressure. The boundary may be impermeable to the transfer of matter between the system and its surroundings, or it may be permeable to a specified species. In other words, matter and heat may be transferred between system and surroundings, and the surroundings may do work on the system, or vice versa. If the boundary around a system prevents interaction of the system with its surroundings, the system is called an **isolated** system.

If matter can be transferred from the surroundings to the system, or vice versa, the system is referred to as an **open** system; otherwise, it is a **closed** system.

When a system is under discussion it must be described precisely. A system is **homogeneous** if its properties are uniform throughout; such a system consists of a single phase. If a system contains more than

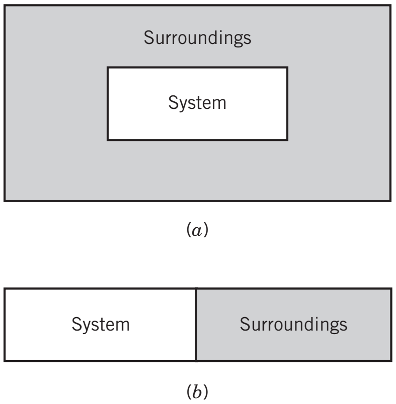

FIGURE 1.1 (*a*) A system is separated from its surroundings by a boundary, real or idealized. (*b*) As a simplification we can imagine the system to be separated from the surroundings by a single wall that may be an insulator or a heat conductor. Later, in Sections 6.7 and 8.3 (see Fig. 8.6), we will consider semipermeable boundaries so that the system is open to the transfer of matter.

one phase, it is **heterogeneous.** A simple example of a two-phase system is liquid water in equilibrium with ice. Water can also exist as a three-phase system: liquid, ice, and vapor, all in equilibrium.

Experience has shown that the macroscopic state of a system at equilibrium can be specified by the values of a small number of macroscopic variables. These variables, which include, for example, temperature T, pressure P, and volume V, are referred to as **state variables** or **thermodynamic variables.** They are called state variables because they specify the state of a system. Two samples of a substance that have the same state variables are said to be in the same state. It is remarkable that the state of a homogeneous system at equilibrium can be specified by so few variables. When a sufficient number of state variables are specified, all of the other properties of the system are fixed. It is even more remarkable that these state variables follow all of the rules of calculus; that is, they can be treated as mathematical functions that can be differentiated and integrated. Thermodynamics leads to the definition of additional properties, such as internal energy and entropy, that can also be used to describe the state of a system, and are themselves state variables.

The thermodynamic state of a specified amount of a pure substance in the fluid state can be described by specifying properties such as temperature T, pressure P, and volume V. But experience has shown that only two of these three properties have to be specified when the amount of pure substance is fixed. If T and P, or P and V, or T and V are specified, all the other thermodynamic properties (including those that will be introduced later) are fixed and the system is at equilibrium. More properties have to be specified to describe the thermodynamic state of a homogeneous mixture of different species.

Note that the description of the microscopic state of a system containing many molecules requires the specification of a very large number of variables. For example, to describe the microscopic state of a system using classical mechanics, we would have to give the three coordinates and three components of the momentum of each molecule, plus information about its vibrational and rotational motion. For one mole of gas molecules, this would mean more than 6×10^{23} numbers. An important thing to notice is that we can use a small number of state variables to describe the equilibrium thermodynamic state of a system that is too complicated to describe in a microscopic way.

Thermodynamic variables are either intensive or extensive. **Intensive variables** are independent of the size of the system; examples are pressure, density, and temperature. **Extensive variables** do depend on the size of the system and double if the system is duplicated and added to itself; examples are volume, mass, internal energy, and entropy. Note that the ratio of two extensive variables is an intensive variable; density is an example. Thus we can talk about the **intensive state of the system,** which is described by intensive variables, or the **extensive state of a system,** which is described by intensive variables plus at least one extensive variable. The intensive state of the gas helium is described by specifying its pressure and density. The extensive state of a certain amount of helium is described by specifying the amount, the pressure, and the density; the extensive state of one mole of helium might be represented by 1 mol He(P, ρ), where P and ρ represent the pressure and density, respectively. We can generalize this by saying that the intensive state of a pure substance in the fluid state is specified by $N_s + 1$ variables, where N_s is the number of different kinds of species in the system. The extensive state is specified by $N_s + 2$ variables, one of which has to be extensive.

In chemistry it is generally more useful to express the size of a system in terms of the amount of substance it contains, rather than its mass. **The amount of substance *n* is the number of entities (atoms, molecules, ions, electrons, or specified groups of such particles) expressed in terms of moles.** If a system contains N molecules, the amount of substance $n = N/N_A$, where N_A is the Avogadro constant (6.022×10^{23} mol^{-1}). The ratio of the volume V to the amount of substance is referred to as the molar volume: $\overline{V} = V/n$. The volume V is expressed in SI units of m^3, and the molar volume $\overline{V}$ is expressed in SI units of m^3 mol^{-1}. We will use the overbar regularly to indicate molar thermodynamic quantities.

Comment:

Since this is our first use of physical quantities, we should note that the value of a physical quantity is equal to the product of a numerical factor and a unit:

$$\textit{physical quantity} = \textit{numerical value} \times \textit{unit}$$

The values of all physical quantities can be expressed in terms of SI base units (see Appendix A). However, some physical quantities are dimensionless, and so the symbol for the SI unit is taken as 1 because this is what you get when units cancel. Note that, in print, physical quantities are represented by italic type and units are represented by roman type.

When a system is in a certain state with its properties independent of time and having no fluxes (e.g., no heat flowing through the system), then the system is said to be at **equilibrium.** When a thermodynamic system is at equilibrium its state is defined entirely by the state variables, and **not by the history of the system.** By history of the system, we mean the previous conditions under which it has existed.

Since the state of a system at equilibrium can be specified by a small number of state variables, it should be possible to express the value of a variable that has not been specified as a function of the values of other variables that have been specified. The simplest example of this is the ideal gas law.

For some systems, more than two intensive variables must be stated to specify the state of the system. If there is more than one species, the composition has to be given. If a liquid system is in the form of small droplets, the surface area has to be given. If the system is in an electric or magnetic field, this may have an effect on its properties, and then the electric field strength and magnetic field strength become state variables. We will generally ignore the effect of the earth's gravitational field on a system, although this can be important, as we will see in the special topic at the end of this chapter. Note that the properties used to describe the state of a system must be independent; otherwise they are redundant. Independent properties are separately controllable by the investigator.

The pressure of the atmosphere is measured with a barometer, as shown in Fig. 1.2*a*, and the pressure of a gaseous system is measured with a closed-end manometer, as shown in Fig. 1.2*b*.

1.2 THE ZEROTH LAW OF THERMODYNAMICS

Although we all have a commonsense notion of what temperature is, we must define it very carefully so that it is a useful concept in thermodynamics. If two closed systems with fixed volumes are brought together so that they are in thermal contact, changes may take place in the properties of both. Eventually a state is reached in which there is no further change, and this is the state of **thermal equilibrium.** In this state, the two systems have the same temperature. Thus, we can readily determine whether two systems are at the same temperature by bringing them into thermal contact and seeing whether observable changes take place in the properties of either system. If no change occurs, the systems are at the same temperature.

Now let us consider three systems, A, B, and C, as shown in Fig. 1.3. It is an experimental fact that if system A is in thermal equilibrium with system C, and system B is also in thermal equilibrium with system C, then A and B are in thermal equilibrium with each other. It is not obvious that this should be true, and so this empirical fact is referred to as the **zeroth law of thermodynamics.**

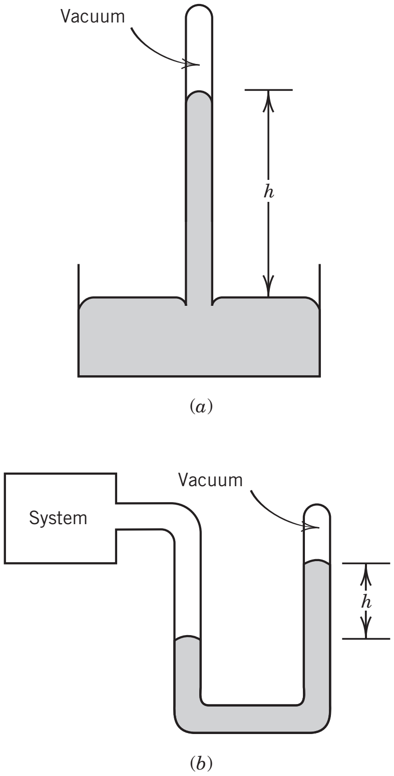

FIGURE 1.2 (*a*) *The pressure* exerted by the atmosphere on the surface of mercury in a cup is given by $P = h\rho g$ (see Example 1.1). (*b*) The pressure of a system is given by the same equation when a closed-end manometer is used.

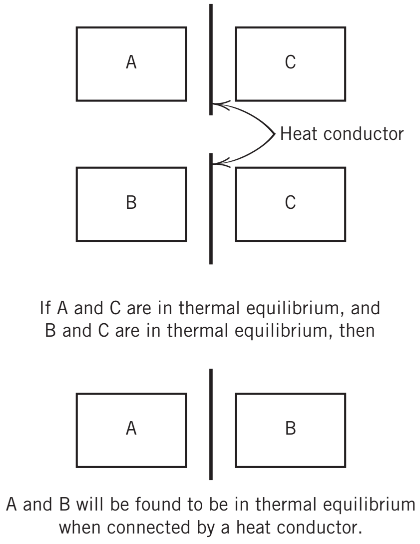

FIGURE 1.3 The zeroth law of thermodynamics is concerned with thermal equilibrium between three bodies.

To see how the zeroth law leads to the definition of a temperature scale, we need to consider thermal equilibrium between systems A, B, and C in more detail. Assume that A, B, and C each consist of a certain mass of a different fluid. We use the word **fluid** to mean either a gas or a compressible liquid. Our experience is that if the volume of one of these systems is held constant, its pressure may vary over a range of values, and if the pressure is held constant, its volume may vary over a range of values. Thus, the pressure and the volume are independent thermodynamic variables. Furthermore, suppose that the experience with these systems is that their intensive states are specified completely when the pressure and volume are specified. That is, when one of the systems reaches equilibrium at a certain pressure and volume, all of its macroscopic properties have certain characteristic values. It is quite remarkable and fortunate that the macroscopic state of a given mass of fluid of a given composition can be fixed by specifying only the pressure and the volume.*

If there are further constraints on the system, there will be a smaller number of independent variables. An example of an additional constraint is thermal equilibrium with another system. Experience shows that if a fluid is in thermal equilibrium with another system, it has only one independent variable. In other words, if we set the pressure of system A at a particular value P_A, we find that there is thermal equilibrium with system C, in a specified state, only at a particular value of V_A. Thus, system A in thermal equilibrium with system C is characterized by a **single** independent variable, pressure or volume; one or the other can be set arbitrarily, but not both. The plot of all the values of P_A and V_A for which there is equilibrium with system C is called an **isotherm.** Figure 1.4 gives this isotherm, which we label Θ_1. Since system A is in thermal equilibrium with system C at any P_A, V_A on the isotherm, we can say that each of the pairs P_A, V_A on this isotherm corresponds with the same temperature Θ_1.

When heat is added to system C and the experiment is repeated, a different isotherm is obtained for system A. In Fig. 1.4, the isotherm for the second experiment is labeled Θ_2. If still more heat is added to system C and the experiment is repeated again, the isotherm labeled Θ_3 is obtained.

Figure 1.4 illustrates Boyle's law, which states that PV = constant for a specified amount of gas at a specified temperature. Experimentally, this is strictly true only in the limit of zero pressure. Charles and Gay-Lussac found that the volume of a gas varies linearly with the temperature at specified pressure when the temperature is measured with a mercury in glass thermometer, for example. Since it would be preferable to have a temperature scale that is independent of the properties of particular materials like mercury and glass, it is better to say that the ratio of the P_2V_2 product at temperature Θ_2 to P_1V_1 at temperature Θ_1 depends only on the two temperatures:

$$\frac{P_2V_2}{P_1V_1} = \phi(\Theta_1, \Theta_2) \tag{1.1}$$

where ϕ is an unspecified function. The simplest thing to do is to take the ratio of the PV products to be equal to the ratio of the temperatures, thus defining a temperature scale:

$$\frac{P_2V_2}{P_1V_1} = \frac{T_2}{T_1} \quad \text{or} \quad \frac{P_2V_2}{T_2} = \frac{P_1V_1}{T_1} \tag{1.2}$$

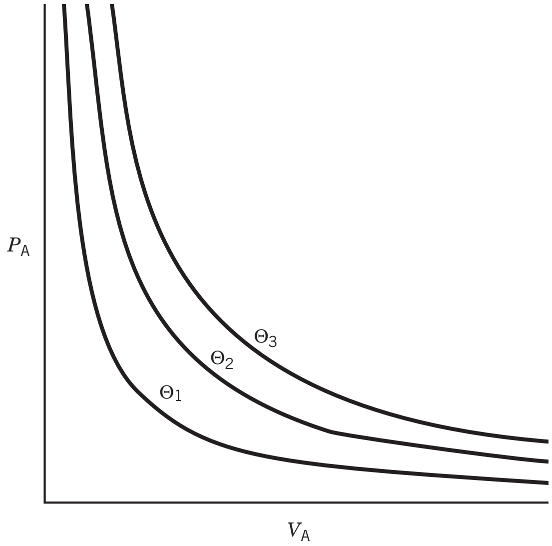

FIGURE 1.4 Isotherms for fluid A. This plot, which is for a hypothetical fluid, might look quite different for some other fluid.

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*This is not true for water in the neighborhood of 4°C, but the state is specified by giving the temperature and the volume or the temperature and the pressure. See Section 6.1.

Here we have introduced a new symbol T for the temperature because we have made a specific assumption about the function ϕ. Equations 1.1 and 1.2 are exact only in the limit of zero pressure, and so T is referred to as the ideal gas temperature.

Since, according to equation 1.2, PV/T is a constant for a fixed mass of gas and since V is an extensive property,

$$PV/T = nR \tag{1.3}$$

where n is the amount of gas and R is referred to as the **gas constant.** Equation 1.3 is called the ideal gas **equation of state.** An equation of state is a relation between the thermodynamic properties of a substance at equilibrium.

1.3 THE IDEAL GAS TEMPERATURE SCALE

The ideal gas temperature scale can be defined more carefully by taking the temperature T to be proportional to $P\overline{V} = PV/n$ in the limit of zero pressure. Since different gases give slightly different scales when the pressure is about one bar (1 bar = 10^5 Pascal = 10^5 Pa = 10^5 N m^{-2}), it is necessary to use the limit of the $P\overline{V}$ product as the pressure approaches zero. When this is done, all gases yield the same temperature scale. We speak of gases under this limiting condition as **ideal.** Thus, the **ideal gas temperature** T is defined by

$$T = \lim_{P\to 0}(P\overline{V}/R) \tag{1.4}$$

The proportionality constant is called the gas constant R. The unit of thermodynamic temperature, 1 Kelvin or 1 K, is defined as the fraction 1/273.16 of the temperature of the triple point of water.* Thus, the temperature of an equilibrium system consisting of liquid water, ice, and water vapor is 273.16 K. The temperature 0 K is called absolute zero. According to the current best measurements, the freezing point of water at 1 atmosphere (101 325 Pa; see below) is 273.15 K, and the boiling point at 1 atmosphere is 373.12 K; however, these are experimental values and may be determined more accurately in the future. The Celsius scale t is formally defined by

$$t/^\circ\mathrm{C} = T/\mathrm{K} - 273.15 \tag{1.5}$$

The reason for writing the equation in this way is that temperature T on the Kelvin scale has the unit K, and temperature t on the Celsius scale has the unit °C, which need to be divided out before temperatures on the two scales are compared. In Fig. 1.5, the molar volume of an ideal gas is plotted versus the Celsius temperature t at two pressures.

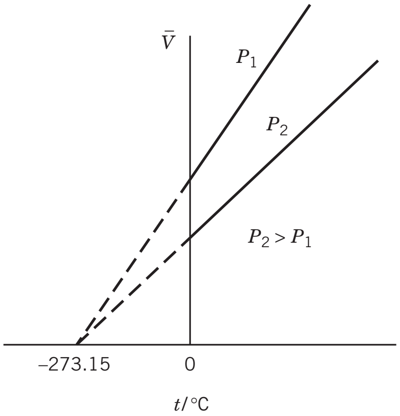

FIGURE 1.5 Plots of $\overline{V}$ versus temperature for a given amount of a real gas at two low pressures P_1 and P_2, as given by Gay-Lussac's law.

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[*] The triple point of water is the temperature and pressure at which ice, liquid, and vapor are in equilibrium with each other in the absence of air. The pressure at the triple point is 611 Pa. The freezing point in the presence of air at 1 atm is 0.0100 °C lower because (1) the solubility of air in liquid water at 1 atm (101 325 Pa) is sufficient to lower the freezing point 0.0024 °C (Section 6.7), and (2) the increase of pressure from 611to101 325 Pa lowers the freezing point 0.0075 °C, as shown in Example 6.2. Thus, the ice point is at 273.15 K.

We will find later that the ideal gas temperature scale is identical with one based on the second law of thermodynamics, which is independent of the properties of any particular substance (see Section 3.9). In Chapter 16 the ideal gas temperature scale will be identified with that which arises in statistical mechanics.

The gas constant R can be expressed in various units, but we will emphasize the use of SI units. The SI unit of **pressure** (P) is the Pascal, Pa, which is the pressure produced by a force of 1 N on an area of 1 m^2. In addition to using the prefixes listed in the back cover of the book to express larger and smaller pressures, it is convenient to have a unit that is approximately equal to the atmospheric pressure. This unit is the bar, which is 10^5 Pa. Earlier the atmosphere, which is defined as 101 325 Pa, had been used as a unit of pressure.

Example 1.1

Express one atmosphere pressure in SI units

Calculate the pressure of the earth's atmosphere at a point where the barometer reads 76 cm of mercury at 0°C and the acceleration of gravity g is 9.806 65 m s^{-2}. The density of mercury at 0°C is 13.5951 g cm^{-3}, or 13.5951×10^3 kg m^{-3}.

Pressure in chemistry is a force exerted by the substance per area on another substance. The pressure of a gas is the force that the gas exerts on the walls of its container.

Therefore, pressure P is force f divided by area, as defined previously, A:

$$P = f/A$$

The force exerted by a column of air over an area A is equal to the mass m of mercury in a vertical column with a cross section A times the acceleration of gravity g:

$$f = mg$$

The mass of mercury raised above the flat surface in Fig. 1.2*a* is ρAh so that

$$f = \rho Ahg$$

Thus, the pressure of the atmosphere is

$$P = hpg$$

If h, ρ, and g are expressed in SI units, the pressure P is expressed in Pascals. Thus, the pressure of a standard atmosphere may be expressed in SI units as follows:

$$\begin{aligned} 1 \text{ atm} &= (0.76 \text{ m})\,(13.5951 \times 10^3 \text{kg m}^{-3})\,(9.806\,65 \text{ m s}^{-2}) \\ &= 101\,325 \text{ N m}^{-2} = 101\,325 \text{ Pa} = 1.013\,25 \text{ bar} \end{aligned}$$

This equality is expressed by the conversion factor 1.013 25 bar atm^{-1}.

To determine the value of the gas constant we also need the definition of a mole. A **mole** is the amount of substance that has as many atoms or molecules as 0.012 kg (exactly) of ^{12}C. The **molar mass** M of a substance is the mass divided by the amount of substance n, and so its SI unit is kg mol^{-1}. Molar masses can also be expressed in g mol^{-1}, but it is important to remember that in making calculations in which all other quantities are expressed in SI units, the molar mass must be expressed in kg mol^{-1}. The molar mass M is related to the molecular mass m by $M = N_A m$, where N_A is the **Avogadro constant** and m is the mass of a single molecule.

Until 1986 the recommended value of the gas constant was based on measurements of the molar volumes of oxygen and nitrogen at low pressures. The accuracy of such measurements is limited by problems of sorption of gas on the walls of the glass vessels used. In 1986 the recommended value* of the gas constant

$$R = 8.314\,51\,\mathrm{J\,K^{-1}\,mol^{-1}} \tag{1.6}$$

was based on measurements of the speed of sound in argon. The equation used is discussed in Section 17.4. Since pressure is force per unit area, the product of pressure and volume has the dimensions of force times distance, which is work or energy. Thus, the gas constant is obtained in joules if pressure and volume are expressed in Pascals and cubic meters; note that 1 J = 1 Pa $\mathrm{m^3}$.

Example 1.2

Express the gas constant in various units

Calculate the value of R in cal $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$, L bar $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$, and L atm $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$.

Since the calorie is defined as 4.184 J,

$$\begin{aligned} R &= 8.314\,51\,\mathrm{J\,K^{-1}\,mol^{-1}}/4.184\,\mathrm{J\,cal^{-1}} \\ &= 1.987\,22\,\mathrm{cal\,K^{-1}\,mol^{-1}} \end{aligned}$$

Since the liter is 10^{-3} $\mathrm{m^3}$ and the bar is 10^5 Pa,

$$\begin{aligned} R &= (8.314\,51\ \mathrm{Pa\ m^3K^{-1}mol^{-1}})\,(10^3\mathrm{L\ m^{-3}})\,(10^{-5}\mathrm{bar\ Pa^{-1}}) \\ &= 0.083\,145\,1\ \mathrm{L\ bar\ K^{-1}mol^{-1}} \end{aligned}$$

Since 1 atm is 1.013 25 bar,

$$\begin{aligned} R &= (0.083\,145\,1\,\mathrm{L\ bar\ K^{-1}mol^{-1}})/(1.013\,25\,\mathrm{bar\ atm^{-1}}) \\ &= 0.082\,057\,8\ \mathrm{L\ atm\ K^{-1}mol^{-1}} \end{aligned}$$

1.4 IDEAL GAS MIXTURES AND DALTON'S LAW

Equation 1.3 applies to a mixture of ideal gases as well as a pure gas, when n is the total amount of gas. Since $n = n_1 + n_2 + \cdots$, then

$$\begin{aligned} P &= (n_1 + n_2 + \cdots)RT/V \\ &= n_1RT/V + n_2RT/V + \cdots \\ &= P_1 + P_2 + \cdots = \sum_i P_i \end{aligned} \tag{1.7}$$

where P_1 is the partial pressure of species 1. Thus, the total pressure of an ideal gas mixture is equal to the sum of the partial pressures of the individual gases; this is **Dalton's law.** The partial pressure of a gas in an ideal gas mixture is the pressure that it would exert alone in the total volume at the temperature of the mixture:

$$P_i = n_iRT/V \tag{1.8}$$

A useful form of this equation is obtained by replacing RT/V by P/n:

$$P_i = n_iP/n = y_iP \tag{1.9}$$

The dimensionless quantity y_i is the mole fraction of species i in the mixture, and it is defined by n_i/n. Substituting equation 1.9 in 1.7 yields

$$1 = y_1 + y_2 + \cdots = \sum_i y_i \tag{1.10}$$

so that the sum of the mole fractions in a mixture is unity.

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*E. R. Cohen and B. N. Taylor, The 1986 Adjustment of the Fundamental Physical Constants, *CO DATA Bull.* 63:1(1986);1 *Phys. Chem. Ref Data* 17:1795 (1988).

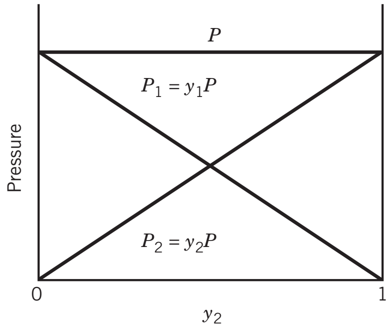

FIGURE 1.6 Total pressure P and partial pressures P_1 and P_2 of components of binary mixtures of gases as a function of the mole fraction y_2 of the second component at constant total pressure. Note that $y_1 = 1 - y_2$.

Figure 1.6 shows the partial pressures P_1 and P_2 of two components of a binary mixture of ideal gases at various mole fractions and at constant total pressure. The various mixtures are considered at the same total pressure P.

The behavior of real gases is more complicated than the behavior of an ideal gas, as we will see in the next section.

Example 1.3

Calculation of partial pressures

A mixture of 1 mol of methane and 3 mol of ethane is held at a pressure of 10 bar. What are the mole fractions and partial pressures of the two gases?

$$y_\mathrm{m} = 1\ \mathrm{mol}/4\ \mathrm{mol} = 0.25$$
$$P_\mathrm{m} = y_\mathrm{m}P = (0.25)(10\ \mathrm{bar}) = 2.5\ \mathrm{bar}$$
$$y_\mathrm{e} = 3\ \mathrm{mol}/4\ \mathrm{mol} = 0.75$$
$$P_\mathrm{e} = y_\mathrm{e}P = (0.75)(10\ \mathrm{bar}) = 7.5\ \mathrm{bar}$$

Example 1.4

Express relative humidity as mole fraction of water

The maximum partial pressure of water vapor in air at equilibrium at a given temperature is the vapor pressure of water at that temperature. The **actual** partial pressure of water vapor in air is a percentage of the maximum, and that percentage is called the relative humidity. Suppose the relative humidity of air is 50% at a temperature of 20°C. If the atmospheric pressure is 1 bar, what is the mole fraction of water in the air? The vapor pressure of water at 20°C is 2330 Pa. Assuming the gas mixture behaves as an ideal gas, the mole fraction of H_2O in the air is given by

$$yH_2O = P_i/P = (0.5)(2330\ \mathrm{Pa})/10^5\mathrm{Pa} = 0.0117$$

1.5 REAL GASES AND THE VIRIAL EQUATION

Real gases behave like ideal gases in the limits of low pressures and high temperatures, but they deviate significantly at high pressures and low temperatures. The **compressibility factor** $Z = P\overline{V}/RT$ is a convenient measure of the deviation from ideal gas behavior. Figure 1.7 shows the compressibility factors for N_2 and O_2 as a function of pressure at 298 K. Ideal gas behavior, indicated by the dashed line, is included for comparison. As the pressure is reduced to zero, the compressibility factor approaches unity, as expected for an ideal gas. At very high pressures the compressibility factor is always greater than unity. This can be understood in terms of the finite size of molecules. At very high pressures the molecules of the gas are pushed closer together, and the volume of the gas is larger than expected for an ideal gas because a significant fraction of the volume is occupied by the molecules themselves. At low pressure a gas may have a smaller compressibility factor than an ideal gas. This is due to intermolecular attractions. The effect of intermolecular attractions disappears in the limit of zero pressure because the distance between molecules approaches infinity.

Figure 1.8 shows how the compressibility factor of nitrogen depends on temperature, as well as pressure. As the temperature is reduced, the effect of intermolecular attraction at pressures of the magnitude of

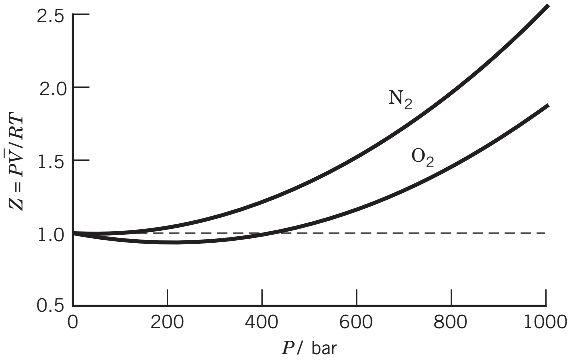

FIGURE 1.7 Influence of high pressure on the compressibility factor, $P\overline{V}/RT$, for N_2 and O_2 at 298 K. (See Computer Problem 1.D.)

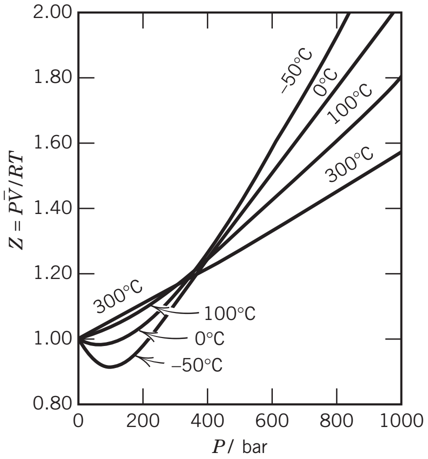

FIGURE 1.8 Influence of pressure on the compressibility factor, $P\overline{V}/RT$, for nitrogen at different temperatures (given in °C).

100 bar increases because the molar volume is smaller at lower temperatures and the molecules are closer together. All gases show a minimum in the plot of compressibility factor versus pressure if temperature is low enough. Hydrogen and helium, which have very low boiling points, exhibit this minimum only at temperatures much below 0°C.

A number of equations have been developed to represent P–V–T data for real gases. Such an equation is called an **equation of state** because it relates state properties for a substance at equilibrium. Equation 1.3 is the equation of state for an ideal gas. The first equation of state for real gases that we will discuss is closely related to the plots in Figs. 1.7 and 1.8, and is called the virial equation.

In 1901 H. Kamerlingh-Onnes proposed an equation of state for real gases, which expresses the compressibility factor Z as a power series in $1/\overline{V}$ for a pure gas:

$$Z = \frac{P\overline{V}}{RT} = 1 + \frac{B}{\overline{V}} + \frac{C}{\overline{V}^2} + \cdots \tag{1.11}$$

The coefficients B and C are referred to as the second and third virial coefficients, respectively.* For a particular gas these coefficients depend only on the temperature and not on the pressure. The word *virial* is derived from the Latin word for force.

The second and third virial coefficients at 298.15 K are given in Table 1.1 for several gases. The variation of the second virial coefficient with temperature is illustrated in Fig. 1.9.

For many purposes, it is more convenient to use P as an independent variable and write the virial equation as

$$Z = \frac{P\overline{V}}{RT} = 1 + B'P + C'P^2 + \cdots \tag{1.12}$$

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*Statistical mechanics shows that the term $B/\overline{V}$ arises from interactions involving two molecules, the $C/\overline{V}^2$ term arises from interactions involving three molecules, etc. (Section 16.11).

Table 1.1 Second and Third Virial Coefficients at 298.15 K

Gas	$B/10^{-6}$ m^3 mol^{-1}	$C/10^{-12}$ m^6 mol^{-2}
H_2	14.1	350
He	11.8	121
N_2	−4.5	1100
O_2	−16.1	1200
Ar	−15.8	1160
CO	−8.6	1550

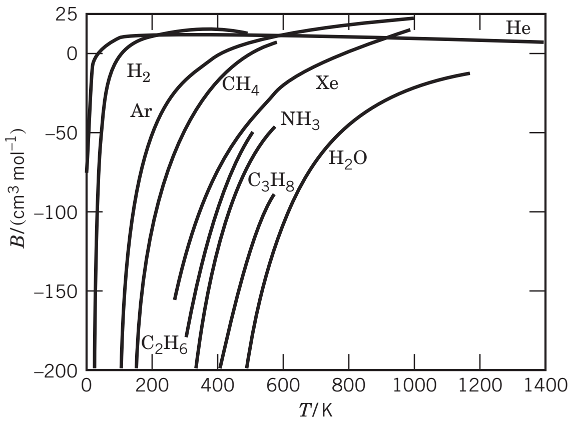

FIGURE 1.9 Second virial coefficient B. (From K. E. Bett, J. S. Rowlinson, and G. Saville, *Thermodynamics for Chemical Engineers*. Cambridge, MA: MIT Press, 1975. Reproduced by permission of The Athlone Press.) (See Computer Problem 1.E.)

Example 1.5

Derive the relationships between two types of virial coefficients

Derive the relationships between the virial coefficients in equation 1.11 and the virial coefficients in equation 1.12.

The pressures can be eliminated from equation 1.12 by use of equation 1.11 in the following forms:

$$P = \frac{RT}{\overline{V}} + \frac{BRT}{\overline{V}^2} + \frac{CRT}{\overline{V}^3} + \cdots \tag{1.13}$$

$$P^2 = \left(\frac{RT}{\overline{V}}\right)^2 + \frac{2B(RT)^2}{\overline{V}^3} + \cdots \tag{1.14}$$

Substituting these expressions into equation 1.12 yields

$$Z = 1 + B'\left(\frac{RT}{\overline{V}}\right) + \frac{B'BRT + C'(RT)^2}{\overline{V}^2} + \cdots \tag{1.15}$$

When we compare this equation with equation 1.11 we see that

$$B = B'RT \tag{1.16}$$

$$C = BB'RT + C'(RT)^2 \tag{1.17}$$

Thus

$$B' = B/RT \tag{1.18}$$

$$C' = \frac{C - R^2}{(RT)^2} \tag{1.19}$$

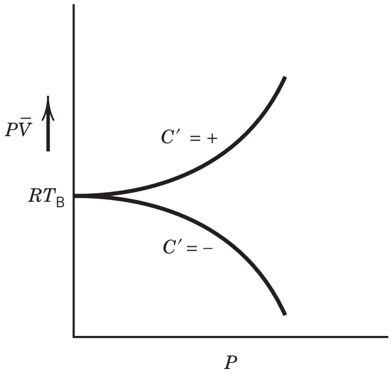

FIGURE 1.10 At the Boyle temperature ($B = 0$), a gas behaves nearly ideally over a range of pressures. The curvature at higher pressures depends on the sign of the third virial coefficient.

Table 1.2 Critical Constants and Boyle Temperatures

Gas	T_c/K	P_c/bar	$\overline{V}_c$ / L mol^{-1}	Z_c	*T/B/K*
Helium-4	5.2	2.27	0.0573	0.301	22.64
Hydrogen	33.2	13.0	0.0650	0.306	110.04
Nitrogen	126.2	34.0	0.0895	0.290	327.22
Oxygen	154.6	50.5	0.0734	0.288	405.88
Chlorine	417	77.0	0.124	0.275	
Bromine	584	103.0	0.127	0.269	
Carbon dioxide	304.2	73.8	0.094	0.274	714.81
Water	647.1	220.5	0.056	0.230	
Ammonia	405.6	113.0	0.0725	0.252	995
Methane	190.6	46.0	0.099	0.287	509.66
Ethane	305.4	48.9	0.148	0.285	
Propane	369.8	42.5	0.203	0.281	
n-Butane	425.2	38.0	0.255	0.274	
Isobutane	408.1	36.5	0.263	0.283	
Ethylene	282.4	50.4	0.129	0.277	624
Propylene	365.0	46.3	0.181	0.276	
Benzene	562.1	49.0	0.259	0.272	
Cyclohexane	553.4	40.7	0.308	0.272	

The second virial coefficient B for nitrogen is zero at 54°C, which is consistent with Fig. 1.8. A real gas may behave like an ideal gas over an extended range in pressure when the second virial coefficient is zero, as shown in Fig. 1.10. The temperature at which this occurs is called the **Boyle temperature** T_B. The Boyle temperatures of a number of gases are given in Table 1.2.

1.6 P–$\overline{V}$–T SURFACE FOR A ONE-COMPONENT SYSTEM

To discuss more general equations of state, we will now look at the possible values of P, $\overline{V}$, and T for a pure substance. The state of a pure substance is represented by a point in a Cartesian coordinate system with P, $\overline{V}$, and T plotted along the three axes. Each point on the surface of the three-dimensional model in Fig. 1.11 describes the state of a one-component system that contracts on freezing. We will not be concerned here with the solid state, but will consider that part of the surface later (Section 6.2). Projections of this surface on the $P-\overline{V}$ and P–T planes are shown. There are three two-phase regions on the surface: S + G, L + G, and S + L (S is solid, G gas, and L liquid). These three surfaces intersect at the **triple point** t where vapor, liquid, and solid are in equilibrium.

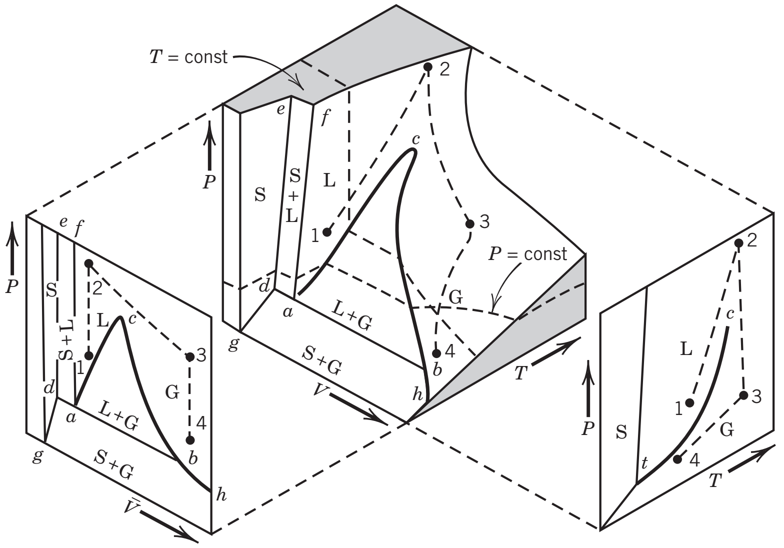

FIGURE 1.11 $P - \overline{V} - T$ surface for a one-component system that contracts on freezing. (From K. E. Bett, J. S. Rowlinson, and G. Saville, *Thermodynamics for Chemical Engineers.* Cambridge, MA: MIT Press, 1975. Reproduced by permission of The Athlone Press.)

The projection of the three-dimensional surface on the P–T plane is shown to the right of the main diagram in Fig. 1.11. The vapor pressure curve goes from the triple point t to the **critical point** c (see Section 1.7). The sublimation pressure curve goes from the triple point t to absolute zero. The melting curve rises from the triple point. Most substances contract on freezing, and for them the slope $\mathrm{d}P/\mathrm{d}T$ for the melting line is positive.

At high temperatures the substance is in the gas state, and as the temperature is raised and the pressure is lowered the surface is more and more closely represented by the ideal gas equation of state $P\overline{V} = RT$. However, much more complicated equations are required to describe the rest of the surface that represents gas and liquid. Before discussing equations that can represent this part of the surface, we will consider the unusual phenomena that occur near the critical point. Any realistic equation of state must be able to reproduce this behavior at least qualitatively.

1.7 CRITICAL PHENOMENA

For a pure substance there is a critical point (P_c, T_c) at the end of the liquid-gas coexistence curve where the properties of the gas and liquid phases become so nearly alike that they can no longer be distinguished as separate phases. Thus, T_c is the highest temperature at which condensation of a gas is possible, and P_c is the highest pressure at which a liquid will boil when heated.

The critical pressures P_c, volumes $\overline{V}_c$, and temperatures T_c of a number of substances are given in Table 1.2, along with the compressibility factor at the critical point $Z_c = P_c\overline{V}_c/RT_c$, and the Boyle temperature T_B.

Critical phenomena are most easily discussed using the projection of the three-dimensional surface in Fig. 1.11 on the $P - \overline{V}$ plane. Figure 1.12 shows only the parts of the $P - \overline{V}$ plot labeled L, G, and L + G. When the state of the system is represented by a point in the L + G region of this plot, the system contains two phases, one liquid and one gas, in equilibrium with each other. The molar volumes of the liquid and gas can be obtained by drawing a horizontal line parallel to the $\overline{V}$ axis through the point representing the state of the system and noting the intersections with the boundary line for the L + G region. Such a line, which connects the state of one phase with the state of another phase with which it is in equilibrium, is called a **tie line.** Two tie lines are shown in Fig. 1.12. The pressure in this case is the equilibrium vapor pressure of the liquid. As the temperature is raised, the tie line becomes shorter, and the molar volumes of the liquid and gas approach each other. At the critical point c the tie line vanishes and the distinction between liquid and gas is lost. At temperatures above the critical temperature, there is a single fluid phase. Above the critical point a gas may have a very high density, and it may be characterized as a supercritical fluid.

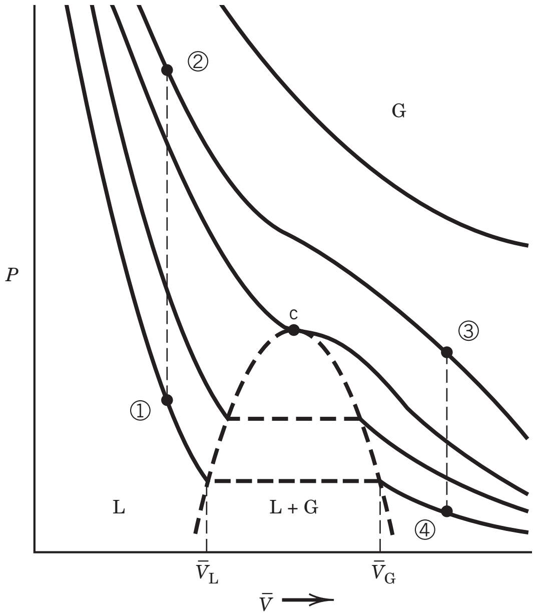

FIGURE 1.12 Pressure-molar volume relations (e.g., isotherms) in the region of the critical point. The dashed horizontal lines in the two-phase region are called tie lines. The path 1–2–3–4 shows how a liquid can be converted to a gas without the appearance of a meniscus. If liquid at point 4 is compressed isothermally, the volume decreases until the two-phase region is reached. At this point there is a large decrease in volume at constant pressure (the **vapor pressure** of the liquid) until all of the gas has condensed to liquid. As the liquid is compressed, the pressure rises rapidly.

The isotherm that goes through the critical point has the following two properties: It is horizontal at the critical point,

$$\left(\frac{\partial P}{\partial V}\right)_{T=T_c} = 0 \tag{1.20}$$

and it has a point of inflection at the critical point,

$$\left(\frac{\partial^2 P}{\partial^2 V}\right)_{T=T_c} = 0 \tag{1.21}$$

Figures 1.11 and 1.12 also show how a liquid at point 1 can be converted to a gas at point 4 without the appearance of an interface between two phases. To do this, liquid at point 1 is heated at constant volume to point 2, then expanded at constant temperature to point 3, and finally cooled at constant volume to point 4, where it is a gas. Thus, liquid and vapor phases are really the same in terms of molecular organization, and so when the densities of these two phases for a substance become equal, they cannot be distinguished and there is a critical point. On the other hand, a solid and a liquid have different molecular organizations, and the two phases do not become identical even if their densities are equal. Therefore, solid-liquid, solid-gas, and solid-solid equilibrium lines do not have critical points as do gas-liquid lines.

At the critical point the **isothermal compressibility** [$\kappa = -\bar{V}^{-1}(\partial \bar{V}/\partial P)_T$; see Problem 1.17] becomes infinite because $(\partial P/\partial \bar{V})_{T_c} = 0$. If the isothermal compressibility is very large, as it is in the neighborhood of the critical point, very little work is required to compress the fluid. Therefore, gravity sets up large differences in density between the top and bottom of the container, as large as 10% in a column of fluid only a few centimeters high. This makes it difficult to determine $P\bar{V}$ isotherms near the critical point. These large differences, or **spontaneous fluctuations**, in the density can extend over macroscopic distances. The distance may be as large as the wavelength of visible light or larger. Since fluctuations in density are accompanied by fluctuations in refractive index, light is strongly scattered, and this is called **critical opalescence**.

1.8 THE VAN DER WAALS EQUATION

Although the virial equation is very useful, it is important to have approximate equations of state with only a few parameters. We turn now to the equation that was introduced by van der Waals in 1877, which is based on plausible reasons that real gases do not follow the ideal gas law. The ideal gas law can be derived for point particles that do not interact except in elastic collisions (see Chapter 17, Kinetic Theory of Gases). The first reason that van der Waals modified the ideal gas law is that molecules are not point particles.

Therefore $\overline{V}$ is replaced by $\overline{V} - b$, where b is the volume per mole that is occupied by the molecules. This leads to

$$P(\overline{V} - b) = RT \tag{1.22}$$

which corresponds to equation 1.12 with $B' = b/RT$ and C' and higher constants equal to zero. This equation can represent compressibility factors greater than unity, but it cannot yield compressibility factors less than unity.

The second reason for modifying the ideal gas law is that gas molecules attract each other and that real gases are therefore more compressible than ideal gases. The forces that lead to condensation are still referred to as van der Waals forces, and their origin is discussed in Section 11.10. Van der Waals provided for intermolecular attraction by adding to the observed pressure P in the equation of state a term $a/\overline{V}^2$, where a is a constant whose value depends on the gas.

The **van der Waals equation** is*

$$(P + a/\overline{V}^2)(\overline{V} - b) = RT \tag{1.23}$$

When the molar volume $\overline{V}$ is large, b becomes negligible in comparison with $\overline{V}$, $a/\overline{V}^2$ becomes negligible with respect to P, and the van der Waals equation reduces to the ideal gas law, $P\overline{V} = RT$.

The van der Waals constants for a few gases are listed in Table 1.3. They can be calculated from experimental measurements of P, $\overline{V}$, and T or from the critical constants, as shown later in equations 1.32 and 1.33. The van der Waals equation is very useful because it exhibits phase separation between gas and liquid phases.

Figure 1.13 shows three isotherms calculated using the van der Waals equation. At the critical temperature the isotherm has an inflection point at the critical point. At temperatures below the critical temperature each isotherm passes through a minimum and a maximum. The locus of these points shown by the dotted line has been obtained from $(\partial P/\partial \overline{V})_T = 0$. The states within the dotted line have $(\partial P/\partial \overline{V})_T > 0$, that is, the volume increases when the pressure increases. These states are therefore mechanically unstable and do not exist. Maxwell showed that states corresponding to the points between A and B and those

Table 1.3 Van der Waals Constants

Gas	a/L^2 bar mol^{-2}	B/L mol^{-1}	Gas	a/L^2 bar mol^{-2}	b/L mol^{-1}
H_2	0.247 6	0.026 61	ch_4	2.283	0.042 78
He	0.034 57	0.023 70	c_2h_6	5.562	0.063 80
N_2	1.408	0.039 13	c_3h_8	8.779	0.084 45
O_2	1.378	0.031 83	QHio(rc)	14.66	0.122 6
Cl_2	6.579	0.056 22	C_4Hio(iso)	13.04	0.114 2
NO	1.358	0.027 89	$C_5H_{12}(n)$	19.26	0.146 0
NO_2	5.354	0.044 24	CO	1.505	0.039 85
H_2O	5.536	0.030 49	CO_2	3.640	0.042 67

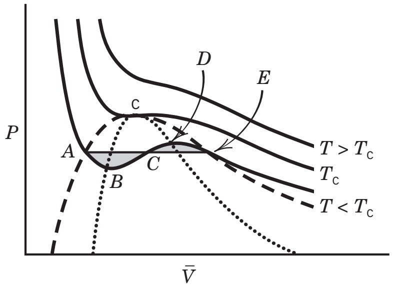

FIGURE 1.13 Isotherms calculated from the van der Waals equation. The dashed line is the boundary of the L + G region.

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*The van der Waals equation can also be written in the form $(P + an^2/V^2)(V - nb) = nRT$.

between D and E are metastable, that is, not true equilibrium states. The dashed line is the boundary of the two-phase region; the part of the isotherm to the left of A represents the liquid and that to the right of E, gas. The horizontal line ACE that produces two equal areas (ABC and CDE) is referred to as the Maxwell construction. It connects the thermodynamic properties of the liquid phase (A) with the properties of the gas phase (E) that is in equilibrium with it.

The compressibility factor for a van der Waals gas is given by

$$\begin{aligned} Z = \frac{P\overline{V}}{RT} &= \frac{\overline{V}}{\overline{V} - b} - \frac{a}{RT\overline{V}} \\ &= \frac{1}{1 - b/\overline{V}} - \frac{a}{RT\overline{V}} \end{aligned} \tag{1.24}$$

At low pressures, $b/\overline{V} << 1$ so that we can expand the first term using $(1 - x)^{-1} = 1 + x + x^2 + \cdots$.

Example 1.6

Expansion of $(1 - x)^{-1}$ using the Maclaurin series

Since we will use series like

$$1/(1 - x) = 1 + x + x^2 + \cdots$$

a number of times, it is important to realize that functions can often be expressed as series by use of the Maclaurin series

$$f(x) = f(0) + \left(\frac{\mathrm{d}f}{\mathrm{d}x}\right)_{x=0} x + \frac{1}{2!}\left(\frac{\mathrm{d}^2 f}{\mathrm{d}x^2}\right)_{x=0} x^2 + \cdots$$

In this case,

$$\begin{aligned} &f(0) = 1 \\ &\left(\frac{\mathrm{d}f}{\mathrm{d}x}\right) = \frac{1}{(1 - x)^{-2}} \quad \text{and} \quad \left(\frac{\mathrm{d}f}{\mathrm{d}x}\right)_{x=0} = 1 \\ &\left(\frac{\mathrm{d}^2 f}{\mathrm{d}x^2}\right) = 2(1 - x)^{-3} \quad \text{and} \quad \left(\frac{\mathrm{d}^2 f}{\mathrm{d}x^2}\right)_{x=0} = 2 \end{aligned}$$

Equation 1.24 then yields the virial equation in terms of volume:

$$Z = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{\overline{V}} + \left(\frac{b}{\overline{V}}\right)^2 + \cdots \tag{1.25}$$

From this equation we can see that the value of a is relatively more important at low temperatures, and the value of b is relatively more important at high temperatures. To obtain the virial equation in terms of pressure, we can replace $\overline{V}$ in the second term by the ideal gas value to obtain, to first order in P,

$$Z = 1 + \frac{1}{RT}\left(b - \frac{a}{RT}\right)P + \cdots \tag{1.26}$$

but this approximation is not good enough to give the correct coefficient for the P^2 term. At the Boyle temperature the second virial coefficient is zero, and so for a van der Waals gas

$$T_B = \frac{a}{bR} \tag{1.27}$$

The values of the van der Waals constants may be calculated from the critical constants for a gas, as shown in the following example.

Example 1.7

Van der Waals constants expressed in terms of critical constants

Derive the expressions for the van der Waals constants in terms of the critical constants for a gas.

The van der Waals equation may be written

$$P = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2} \tag{1.28}$$

Differentiating with respect to molar volume and evaluating these equations at the critical point yields

$$\left(\frac{\partial P}{\partial \overline{V}}\right)_{T_c} = \frac{-RT_c}{(\overline{V}_c - b)^2} + \frac{2a}{\overline{V}_c^3} = 0 \tag{1.29}$$

$$\left(\frac{\partial^2 P}{\partial \overline{V}^2}\right)_{T_c} = \frac{2RT_c}{(\overline{V}_c - b)^3} + \frac{6a}{\overline{V}_c^4} = 0 \tag{1.30}$$

A third simultaneous equation is obtained by writing equation 1.28 for the critical point:

$$P_c = \frac{RT_c}{\overline{V}_c - b} - \frac{a}{\overline{V}_c^2} \tag{1.31}$$

These three simultaneous equations may be combined to obtain expressions for *a* and *b* in terms of T_c and P_c or T_c and $\overline{V}_c$:

$$a = \frac{27R^2T_c^2}{64P_c} = \frac{9}{8}RT_c\overline{V}_c \tag{1.32}$$

$$b = \frac{RT_c}{8P_c} = \frac{\overline{V}_c}{3} \tag{1.33}$$

Example 1.8

Critical constants expressed in terms of van der Waals constants

Derive the expressions for the molar volume, temperature, and pressure at the critical point in terms of the van der Waals constants.

Equation 1.33 shows that

$$\overline{V}_c = 3b$$

Equation 1.32 shows that

$$T_c = \frac{8a}{9R\overline{V}_c} = \frac{8a}{27Rb}$$

Equation 1.33 shows that

$$P_c = \frac{RT_c}{8b} = \frac{a}{27b^2}$$

Example 1.9

Calculation of the molar volume using the van der Waals equation

What is the molar volume of ethane at 350 K and 70 bar according to (*a*) the ideal gas law and (*b*) the van der Waals equation?

(a) $\overline{V} = RT/P = (0.083145 \text{ L bar K}^{-1}\text{ mol}^{-1})(350 \text{ K})/(70 \text{ bar})$
$= 0.416 \text{ L mol}^{-1}$

(b) The van der Waals constants are given in Table 1.3.

$$P = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2}$$

$$70 = \frac{(0.08315)(350)}{\overline{V} - 0.06380} - \frac{5.562}{\overline{V}^2}$$

This is a cubic equation, but we know it has a single real, positive solution because the temperature is above the critical temperature. This cubic equation can be solved using a personal computer with a mathematical application. This yields two complex roots and one real root, namely 0.2297 L mol^{-1} (see Computer Problem 1.G).

We will see later that equations of state are very important in the calculation of various thermodynamic properties of gases. Therefore, a variety of them have been developed. To represent the P–V–T properties of a one-component system over a wide range of conditions it is necessary to use an equation with many more parameters. As more parameters are used they lose any simple physical interpretation. The van der Waals equation does not fit the properties of any gas exactly, but it is very useful because it does have a simple interpretation and the qualitatively correct behavior.

The van der Waals equation fails in the immediate neighborhood of the critical point. The coexistence curve (see Fig. 1.12) is not parabolic in the neighborhood of the critical point. The van der Waals equation indicates that near T_c, $\overline{V}_c - \overline{V} = k(T_c - T)^{1/2}$, but experiments show that the exponent is actually 0.32. Other properties in the neighborhood of the critical point vary with $(T_c - T)$ with exponents that differ from what would be expected from the van der Waals equation. These exponents are the same for all substances, which shows that the properties in the neighborhood of the critical point are universal.

1.9 DESCRIPTION OF THE STATE OF A SYSTEM WITHOUT CHEMICAL REACTIONS

In Section 1.1 we observed that the intensive state of a one-phase system can be described by specifying $N_s + 1$ intensive variables, where N_s is the number of species (an ion or a molecule). Another term that is widely used for the species is the **constituent** of a system. A mixture of ethanol and water has two constituents. The constituent is not the same as the component. A **component** is chemically independent constituent of a system. The **phase** of a system defines a state of matter that is uniform throughout, namely in chemical composition and in physical state.

The intensive state of a solution containing species A and species B is completely described by specifying T, P, and n_A/n_B, and so three intensive variables are required. Now that we have discussed several systems, it is time to think about the numbers of intensive variables required to define the thermodynamic states of these more complicated systems. The number of intensive variables that can be changed independently without disturbing the number of phases in equilibrium is represented by F, which is referred to as the **variance** of the system, or the **number of degrees of freedom.** Therefore, for a one-phase system without chemical reactions, $F = N_s + 1$. As we have seen, if $N_s = 1$, the independent intensive properties can be chosen to be T and P. If $N_s = 1$, but the system has two phases at equilibrium, Fig. 1.12 shows that it is sufficient to specify either T or P, but not both, so that $F = 1$. Thus the intensive state of this system is described completely by saying that two phases are at equilibrium and specifying T or P. In defining the ideal gas temperature scale, we saw that water vapor, liquid water, and ice are in equilibrium at a particular T and P. Thus the intensive state of this three-phase system is completely described by saying that three phases are at equilibrium. There are no independent intensive variables, and so $F = 0$.

Table 1.4 shows the relation between the number of degrees of freedom and the number of phases for a one-component system and it suggests a rule relating the degrees of freedom, F, to the number of phases, P, present for a one-component system. This is commonly known as a phase rule

$$F = 3 - p \tag{1.34}$$

Therefore, for a one-component system (i.e., pure water) when only one phase is present, $F = 2$ and both T and P can be changed independently without changing the number of phases. If $F = 1$, then it means that at a given temperature there is a vapor pressure associated with this temperature. When the three phases are in equilibrium, then $F = 0$.

Table 1.4 Rule Relating Degrees of Freedom to Number of Phases

Number of phases present	1	2	3
Degrees of freedom	2	1	0

Earlier we contrasted the thermodynamic description of a system with the classical description of a system in terms of molecules, and now we can see that the description of the thermodynamic state of a system is really quite different. Another interesting aspect of specifying degrees of freedom is that the choice of variables is not unique, although the number is. For example, the intensive state of a binary solution can be described by T, P, and the mole fraction of one of the species.

The preceding paragraph has discussed the intensive state of a system, but it is often necessary to describe the extensive state of a system. The number of variables required to describe the extensive state of a system is given by $D = F + p$, where p is the number of different phases, because the amount of each phase must be specified. For a one-phase system with one species and no reactions, $D = 2 + 1 = 3$, and so a complete description requires T, P, and the amount of the species (n). For a two-phase system with one species, $D = 1 + 2 = 3$, and so it is necessary to specify T or P and the amounts of the two phases. For a three-phase system with one species, $D = 0 + 3 = 3$, and so it is necessary to specify the amounts of the three phases. For a one-phase binary solution, $D = 3 + 1 = 4$, and so it is necessary to specify T, P, n_A/n_B, and the amount of the solution. Phase equilibria and chemical equilibria introduce constraints, and we will see in the next several chapters how these constraints arise and how they are treated quantitatively in thermodynamics.

Comment:

It is a good thing that this issue of the number of variables required to describe the state of a system has come up before we discuss the laws of thermodynamics because the conclusions in this section cannot be derived from the laws of thermodynamics. The fact that $N_s + 2$ *variables are required to describe the extensive state of a homogeneous one-phase system at equilibrium is a generalization of experimental observations, and we will consider it to be a postulate. It is a postulate that has stood the test of time, and we will use it often in discussing thermodynamic systems.*

1.10 PARTIAL MOLAR PROPERTIES

This chapter has mostly been about pure gases, but we need to be prepared to consider mixtures of gases and mixtures of liquids. There is an important mathematical difference between extensive properties and intensive properties of mixtures. These properties can be treated as mathematical functions. A function $f(x_1, x_2, \ldots, x_N)$ is said to be homogeneous of degree k if

$$f(\lambda x_1, \lambda x_2, \ldots, \lambda x_N) = \lambda^k f(x_1, x_2, \ldots, x_N) \tag{1.35}$$

All extensive properties are homogeneous of degree 1. This is illustrated by the volume for which

$$V(\lambda n_1, \lambda n_2, \ldots, \lambda n_N) = \lambda^1 V(n_1, n_2, \ldots, n_N) = \lambda V(n_1, n_2, \ldots, n_N) \tag{1.36}$$

where $n_1, n_2, \ldots$ are amounts of substances. That is, if we increase the amounts of every substance λ-fold, the total volume increases λ-fold. All intensive properties are homogeneous of degree zero. This is illustrated by the temperature for which

$$T(\lambda n_1, \lambda n_2, \ldots, \lambda n_N) = \lambda^0 T(n_1, n_2, \ldots, n_N) = T(n_1, n_2, \ldots, n_N) \tag{1.37}$$

According to **Euler's theorem,** when equation 1.35 applies,

$$kf(x_1, x_2, \ldots, x_N) = \sum_{i=1}^{N} x_i \left(\frac{\partial f}{\partial x_i}\right)_{x_j \neq x_i} \tag{1.38}$$

Thus for the volume of a mixture ($k = 1$),

$$\begin{aligned} V &= \left(\frac{\partial V}{\partial n_2}\right)_{T,P,n_j} n_1 + \left(\frac{\partial V}{\partial n_2}\right)_{T,P,n_j} n_2 + \cdots + \left(\frac{\partial V}{\partial nN}\right)_{T,P,n_j} n_N \\ &= \overline{V}_1 n_1 + \overline{V}_2 n_2 + \cdots + \overline{V}_N n_N \end{aligned} \tag{1.39}$$

where the subscript n_j indicates that the amounts of all other substances are held constant when the amount of one of the substances is changed. These derivatives are referred to as **partial molar volumes.** Since we will use such equations a lot, partial molar properties are indicated by the use of an overbar:

$$\overline{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,\{n_{j \neq i}\}} \tag{1.40}$$

This definition for the partial molar volume can be stated in words by saying that $\overline{V}_i\,\mathrm{d}n_i$ is the change in V when an infinitesimal amount ($\mathrm{d}n_i$) of this substance is added to the solution at constant T, P, and all other n_j. Alternatively, it can be said that $\overline{V}_i$ is the change in V when 1 mol of i is added to an infinitely large amount of the solution at constant T and P.

Note that the partial molar volume depends on the composition of the solution. When the amount of substance 1 is changed by $\mathrm{d}n_1$, the amount of substance 2 is changed by $\mathrm{d}n_2$, etc., and the volume of the solution is changed by

$$\mathrm{d}V = \overline{V}_1\,\mathrm{d}n_1 + \overline{V}_2\,\mathrm{d}n_2 + \cdots + \overline{V}_N\,\mathrm{d}n_N \tag{1.41}$$

Dividing equation 1.39 by the total number of moles in the solution yields

$$\overline{V} = \overline{V}_{{}_1x_1} + \overline{V}_{{}_2x_2} + \cdots + \overline{V}_{{}_Nx_N} \tag{1.42}$$

where $\overline{V}$ is the molar volume of the solution and x_i is the mole fraction of substance i in the solution. In Chapter 6 we will discuss the determination of the partial molar volume of a species in a solution, and we will also see that in ideal solutions the partial molar volume of a substance is equal to its molar volume in the pure liquid.

Example 1.10

The partial molar volume of a gas in an ideal gas mixture

Calculate the partial molar volume of a gas in an ideal gas mixture.

The volume of an ideal gas mixture is

$$V = \frac{RT}{P}(n_1 + n_2 + \cdots)$$

Using equation 1.40 to find the partial molar volume of gas i yields

$$\overline{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,\{n_{j \neq i}\}} = \frac{RT}{P}$$

Thus all of the gases in a mixture of ideal gases have the same partial molar volume. This is not true for nonideal gases or for liquids.

Comment:

Calculus is used so much in physical chemistry that we have included a section on calculus in Appendix D for quick reference. Since the properties of a system depend on a number of variables, it is important to be clear about which properties are held constant for a measurement or a process and to use subscripts on partial derivatives.

1.11 SPECIAL TOPIC: BAROMETRIC FORMULA

In applying thermodynamics, we generally ignore the effect of the gravitational field, but it is important to realize that if there is a difference in height there is a difference in gravitational potential. For example, consider a vertical column of a gas with a unit cross section and a uniform temperature T, as shown in Fig. 1.14. The pressure at any height h is simply equal to the mass of gas above that height per unit area times the gravitational acceleration g. The standard acceleration due to gravity is defined as 9.806 65 m s^{-2}.

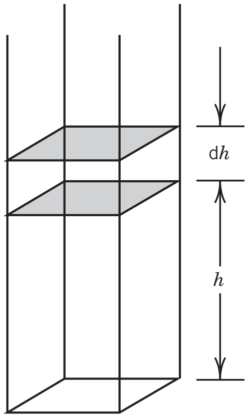

FIGURE 1.14 Column of an ideal gas of uniform temperature and unit cross section.

The difference in pressure dP between h and $h + \mathrm{d}h$ is equal to the mass of the gas between these two levels times g and divided by the area. Thus,

$$\mathrm{d}P = -\rho g\,\mathrm{d}h \tag{1.43}$$

where ρ is the density of the gas. If the gas is an ideal gas, then $\rho = PM/RT$, where M is the molar mass, so that

$$\mathrm{d}P = \frac{PMg}{RT}\mathrm{d}h \tag{1.44}$$

Separating variables and integrating from $h = 0$, where the pressure is P_0, to h, where the pressure is P, yields

$$\int_{P_0}^{P} \frac{\mathrm{d}P}{P} = -\int_0^h \frac{gM}{RT}\,\mathrm{d}h \tag{1.45}$$

$$\ln \frac{P}{P_0} = -\frac{gMh}{RT} \tag{1.46}$$

$$P = P_0\,e^{-gMh/RT} \tag{1.47}$$

This relation is known as the **barometric formula**.

A mathematical note

It is known that $\frac{d}{dx}(e^x) = e^x \Rightarrow \frac{d}{dx}(\ln x) = \frac{1}{x}$; therefore the integral $\int \frac{1}{x}dx = \ln x + C$.

Example 1.11

Pressure and composition of air at 10 km

Assuming that air is 20% O_2 and 80% N_2 at sea level and that the pressure is 1 bar, what are the composition and pressure at a height of 10 km, if the atmosphere has a temperature of 0°C independent of altitude?

$$P = P_0 \exp\left(-\frac{gMh}{RT}\right)$$

For O_2,

$$\begin{aligned} P_{O_2} &= (0.20\,\mathrm{bar}) \exp\left[-\frac{(9.8\,\mathrm{m\,s^{-2}})(32 \times 10^{-3}\,\mathrm{kg\,mol^{-1}})(10^4\,\mathrm{m})}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(273\,\mathrm{K})}\right] \\ &= 0.0503\,\mathrm{bar} \end{aligned}$$

For N_2,

$$P_{N_2} = (0.80)\exp\left(-\frac{9.8 \times 28 \times 10^{-3} \times 10^4}{8.3145 \times 273}\right)$$
$$= 0.239\,\text{bar}$$

The total pressure is 0.289 bar, and $y_{O_2} = 0.173$ and $y_{N_2} = 0.827$.

Figure 1.15 gives the partial pressures of oxygen, nitrogen, and the total pressure as a function of height in feet, assuming the temperature is 273.15 **K** independent of height.

Comment:

This is our first contact with exponential functions, but there will be many more. The barometric formula can also be regarded as an example of a Boltzmann distribution, which will be derived in Chapter 16 *(Statistical Mechanics). The temperature determines the way particles distribute themselves over various energy levels in a system.*

1.12 MATHEMATICAL TREATISE: PARTIAL DERIVATIVES

In physical chemistry we deal with functions of two or more variables. The evaluation of a function of several variables is similar to the evaluation of the derivative of a function of a single variable. Let the function, $f(x, y)$ with the y held constant, then the partial derivative of the function, f, with respect to x while y is held constant is,

$$\left(\frac{\partial f}{\partial x}\right)_y = \lim_{\Delta x \to 0} \frac{f(x + \Delta x, y) - f(x, y)}{\Delta x} \tag{1.48}$$

And consequently, the partial derivative of the function, f, with respect to y is

$$\left(\frac{\partial f}{\partial y}\right)_x = \lim_{\Delta y \to 0} \frac{f(x, y + \Delta y) - f(x, y)}{\Delta y} \tag{1.49}$$

In thermodynamics, there are many possible variables, and it is essential to show which variables are being held constant in evaluating partial derivatives. There may be more than two independent variables, $f(x, y, z)$. Then the partial derivative of f with respect to z at constant x and y is:

$$\left(\frac{\partial f}{\partial z}\right)_{x,y} = \lim_{\Delta z \to 0} \frac{f(x, y, z + \Delta z) - f(x, y, z)}{\Delta z} \tag{1.50}$$

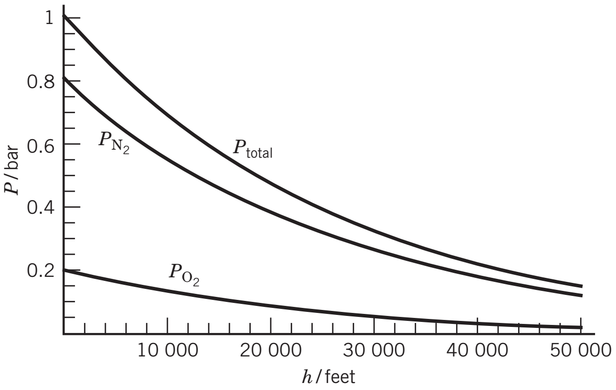

FIGURE 1.15 Partial pressures of oxygen, nitrogen, and the total pressure of the atmosphere as a function of height in feet, assuming the temperature is 273.15 K independent of height (see Computer Problem 1.H).

Example 1.12

(a) Let $z = x^5/y^3$. Evaluate the first and second partial derivatives of z.

$$\frac{\partial z}{\partial x} = \frac{5x^4}{y^3}, \text{then} \frac{\partial^2 z}{\partial x^2} = \frac{20x^3}{y^3} \quad \text{(i)}$$

$$\frac{\partial z}{\partial y} = -\frac{3x^5}{y^4}, \text{then} \frac{\partial^2 z}{\partial y^2} = \frac{12x^5}{y^5} \quad \text{(ii)}$$

$$\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial}{\partial x}\left(-\frac{3x^5}{y^4}\right) = -\frac{15x^4}{y^4} \quad \text{(iii)}$$

$$\frac{\partial^2 z}{\partial y \partial x} = \frac{\partial}{\partial y}\left(\frac{5x^4}{y^3}\right) = -\frac{15x^4}{y^4} \quad \text{(iv)}$$

We observe that $\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x}$. This is a finding that we will encounter later and it is applicable to many problems in physical chemistry.

(b) Let $f(x, y) = e^x \sin xy$ then,

$$\left(\frac{\partial f}{\partial x}\right)_y = e^x \sin xy + ye^x \cos xy \quad \text{and} \quad \left(\frac{\partial f}{\partial y}\right)_x = xe^x \cos xy$$

Let $z = f(x, y)$ and x changes by an infinitesimal amount, $\mathrm{d}x$ while y remains constant. Consequently, the change in z would be given by $\mathrm{d}z = (\partial z/\partial x)_y \mathrm{d}x$. In a similar way if y were to undergo n infinitesimal change while x were held constant, $\mathrm{d}z = (\partial z/\partial y)_x \mathrm{d}y$. If both x and y undergo infinitesimal changes, then the infinitesimal change in z will be,

$$\mathrm{d}z = \left(\frac{\partial z}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial z}{\partial y}\right)_x \mathrm{d}y - \textbf{total differential of } z = f(x, y) \quad (1.51)$$

If there is a function with three variables, $f(x, y, z)$, the total differential is

$$\mathrm{d}f = \left(\frac{\partial f}{\partial x}\right)_{y,z} \mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)_{x,z} \mathrm{d}y + \left(\frac{\partial f}{\partial z}\right)_{x,x} \mathrm{d}z \quad (1.52)$$

Revising Equation 1.51: if y does not change, then $\mathrm{d}y = 0$ and equation 1.51 becomes

$$\mathrm{d}z_y = \left(\frac{\partial z}{\partial x}\right)_y \mathrm{d}x_y \quad (1.53)$$

where the subscript denotes that the infinitesimal change occurs at constant y. Upon dividing by $\mathrm{d}z_y$, we get

$$1 = \left(\frac{\partial z}{\partial x}\right)_y \frac{\mathrm{d}x_y}{\mathrm{d}z_y} = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\mathrm{d}z}\right)_y$$

Therefore,

$$\left(\frac{\partial z}{\partial x}\right)_y = \frac{1}{(\partial x/\partial z)_y} \quad (1.54)$$

For an infinitesimal process where z stays constant, (1.52) becomes

$$0 = \left(\frac{\partial z}{\partial x}\right)_y \mathrm{d}x_z + \left(\frac{\partial z}{\partial y}\right)_z \mathrm{d}y_z \quad (1.55)$$

Upon dividing by $\mathrm{d}y_z$ and keeping in mind that $\mathrm{d}x_z/\mathrm{d}y_z = (\partial x/\partial y)_z$, and using (1.54) with x and y interchanged, we get

$$0 = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial z}{\partial y}\right)_x \quad \text{and} \quad \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial z}{\partial y}\right)_x = -\frac{1}{(\partial y/\partial z)_x}$$

Upon multiplication with $(\partial y/\partial z)_x$, we get

$$\left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial z}\right)_x\left(\frac{\partial z}{\partial x}\right)_y = -1 \qquad \text{(cyclic relation (rule))} \tag{1.56}$$

A function of two independent variables $z(x, y)$ has the following four second partial derivatives

$$\left(\frac{\partial^2 z}{\partial x^2}\right)_y \equiv \left[\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial x}\right)_y\right]_y,\ \left(\frac{\partial^2 z}{\partial y^2}\right)_x \equiv \left[\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial y}\right)_x\right]_x,\ \frac{\partial^2 z}{\partial x \partial y} \equiv \left[\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right)_x\right]_y,\ \frac{\partial^2 z}{\partial y \partial x} \equiv \left[\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right)_y\right]_x$$

In physical chemistry the second derivatives $\frac{\partial^2 z}{\partial x \partial y}$ and $\frac{\partial^2 z}{\partial y \partial x}$ are continuous, then it can be shown that they are equal $\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x}$. Keep in mind that the order of partial differentiation is immaterial. This is shown in Example 1.12.

NINE KEY IDEAS IN CHAPTER 1

1. The state of a macroscopic system at equilibrium can be specified by the values of a small number of macroscopic variables. For a system in which there are no chemical reactions, the intensive state of a one-phase system can be specified by $N_s + 1$ intensive variables, where N_s is the number of different species.
2. According to the zeroth law of thermodynamics, if systems A and B are individually in thermal equilibrium with system C, then A and B are in thermal equilibrium with each other.
3. The ideal gas temperature scale is based on the behavior of gases in the limit of low pressures. The unit of thermodynamic temperature, the Kelvin, represented by K, is defined as the fraction 1/273.16 of the temperature of the triple point of water.
4. The total pressure of a mixture of ideal gases is equal to the sum of the partial pressures of the gases in the mixture.
5. The virial equation of state, which expresses the compressibility factor Z for a gas in terms of powers of the reciprocal molar volume or of the pressure, is useful for expressing experimental data on a gas provided the pressure is not too high or the gas too close to its critical point.
6. The van der Waals equation is useful because it exhibits phase separation between gas and liquid phases, but it does not represent experimental data exactly.
7. For a one-phase system without chemical reactions, we have seen that the number of degrees of freedom F is equal to $N_s + 1$. But if the system contains two phases at equilibrium, $F = N_S$, and if the system contains three phases at equilibrium, $F = N_s - 1$. The number of variables D required to describe the extensive state of a multiphase macroscopic system at equilibrium is $F + p$, where p is the number of phases.
8. The volume of a mixture is equal to the sum of the partial molar volumes of the species it contains each multiplied by the amount of that species.
9. For an isothermal atmosphere, the pressure decreases exponentially with the height above the surface of the earth.

QUESTIONS ON CONCEPTS AND IDEAS

1. Are density, temperature, volume, and refractive index intensive or extensive properties?
2. Is the ratio PV/mT the same in the limit of zero-pressure?
3. Can temperature be measured directly? Explain your reasoning.
4. The parameter, a, in van der Waals equation has the same value for all gases. Is this statement correct?
5. What are the SI units for the parameters a and b for the van der Waals equation?
6. What is the significance of the number of degrees of freedom?
7. Is every isolated system closed and every closed system isolated?

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EXERCISES

Sections 1.1–1.4

1.1 The intensive state of an ideal gas can be completely defined by specifying (1) T, P, (2) T, $\overline{V}$, or (3) P, $\overline{V}$. The extensive state of an ideal gas can be specified in four ways. What are the combinations of properties that can be used to specify the extensive state of an ideal gas? Although these choices are deduced for an ideal gas, they also apply to real gases.

1.2 The ideal gas law also represents the behavior of mixtures of gases at low pressures. The molar volume of the mixture is the volume divided by the amount of the mixture. The partial pressure of gas i in a mixture is defined as $y_i P$ for an ideal gas mixture, where y_i is its mole fraction and P is the total pressure. Ten grams of N_2 is mixed with 5 g of O_2 and held at 25°C at 0.750 bar. (*a*) What are the mole fractions of N_2 and O_2? (*b*) What are the partial pressures of N_2 and O_2? (*c*) What is the volume of the ideal mixture?

1.3 A mixture of methane and ethane is contained in a glass bulb of 500 cm^3 capacity at 25°C. The pressure is 1.25 bar, and the mass of gas in the bulb is 0.530 g. What is the average molar mass, and what is the mole fraction of methane?

1.4 Nitrogen tetroxide is partially dissociated in the gas phase according to the reaction

$$N_2O_4(g) = 2NO_2(g)$$

A mass of 1.588 g of N_2O_4 is placed in a 500-cm^3 glass vessel at 298 K and dissociates to an equilibrium mixture at 1.0133 bar. (*a*) What are the mole fractions of N_2O_4 and NO_2? (*b*) What percentage of the N_2O_4 has dissociated? Assume that the gases are ideal.

Sections 1.5–1.10

1.5 Show that for a gas of rigid spherical molecules, b in the van der Waals equation is four times the molecular volume times Avogadro's constant. If the molecular diameter of Ne is 0.258 nm (Table 17.4), approximately what value of b is expected?

1.6 What is the molar volume of n -hexane at 660 K and 91 bar according to (*a*) the ideal gas law and (*b*) the van der Waals equation? For n-hexane, $T_c = 507.7$ K and $P_c = 30.3$ bar.

1.7 Calculate the second virial coefficient of methane at 300 K and 400 K from its van der Waals constants, and compare these results with Fig. 1.9.

1.8 You want to calculate the molar volume of O_2 at 298.15 K and 50 bar using the van der Waals equation, but you don't want to solve a cubic equation. Use the first two terms of equation 1.26. The van der Waals constants of O_2 are $a = 0.138$ Pa m^6 mol^{-1} and $b = 31.8 \times 10^{-6}$ m^3 mol^{-1}. What is the molar volume in L mol^{-1}?

1.9 Calculate the second and third virial coefficients of O_2 from its van der Waals constants in Table 1.3.

1.10 Calculate the critical constants for ethane using the van der Waals constants in Table 1.3.

1.11 Calculate the pressure and composition of air on the top of Mt. Everest, assuming that the atmosphere has a temperature of 0°C independent of altitude ($h = 29141$ ft). Assume that air at sea level is 20% O_2 and 80% N_2.

1.12 A gas follows the van der Waals equation. Derive the relation between the third and fourth virial coefficients and the van der Waals constants.

1.13 Using the van der Waals equation, calculate the pressure exerted by 1 mol of carbon dioxide at 0°C in a volume of (*a*) 1.00 L and (*b*) 0.05 L. (*c*) Repeat the calculations at 100°C and 0.05 L.

1.14 A mole of *n*-hexane is confined in a volume of 0.500 L at 600 K. What will be the pressure according to (*a*) the ideal gas law and (*b*) the van der Waals equation? (See Problem 1.6.)

1.15 A mole of ethane is contained in a 200-mL cylinder at 373 K. What is the pressure according to (*a*) the ideal gas law and (*b*) the van der Waals equation? The van der Waals constants are given in Table 1.3.

1.16 What is the molar volume of $N_2(g)$ at 500 K and 600 bar according to (*a*) the ideal gas law and (*b*) the virial equation? The virial coefficient B of $N_2(g)$ at 500 K is 0.0169 L mol^{-1}.

Section 1.11

1.17 Assuming that the atmosphere is isothermal at 0°C and that the average molar mass of air is 29 g mol^{-1}, calculate the atmospheric pressure at 20 000 ft above sea level.

PROBLEMS

General

1.18 Calculate the pressure due to a mass of 100 kg in the earth's gravitational field resting on an area of (*a*) 100 cm^2 and (*b*) 0.01 cm^2. (c) What area is required to give a pressure of 1 bar?

1.19 Using Fig. 1.9, calculate the compressibility factor Z for $NH_3(g)$ at 400 K and 50 bar.

1.20 **Use** the van der Waals constants for CH_4 in Table 1.3 to calculate the initial slopes of the plots of the compressibility factor Z versus P at 300 and 600 K.

1.21 A mole of air (80% nitrogen and 20% oxygen by volume) at 298.15 K is brought into contact with liquid water, which has a vapor pressure of 3168 Pa at this temperature. (*a*) What is the volume of the dry air if the pressure is 1 bar? (*b*) What is the final volume of the air saturated with water vapor if the total pressure is maintained at 1 bar? (*c*) What are the mole fractions of N_2, O_2, and H_2O in the moist air? Assume the gases are ideal.

1.22 In this chapter we have considered only pure gases, but it is important to make calculations on mixtures as well. This requires information in addition to that for pure gases. Statistical mechanics shows that the second virial coefficient for an N-component gaseous mixture is given by

$$B = \sum_{i=1}^{N} \sum_{j=1}^{N} y_i y_j B_{ij}$$

where y is mole fraction and i and j identify components. Both indices run over all components of the mixture. The bimolecular interactions between i and j are characterized by B_{ij}, and so $B_{ij} = B_{ji}$. Use this expression to derive the expression for B for a binary mixture in terms of y_1, y_2, B_{11}, B_{12}, and B_{22}.

1.23 The densities of liquid and vapor methyl ether in g cm^{-3} at various temperatures are as follows:

$t/°C$	30	50	70	100	120
P_1	0.6455	0.6116	0.5735	0.4950	0.4040
ρ_v	0.0142	0.0241	0.0385	0.0810	0.1465

The critical temperature of methyl ether is 299°C. What is the critical molar volume? (See Problem 1.39.)

1.24 When pressure is applied to a liquid, its volume decreases. Assuming that the isothermal compressibility

$$K = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

is independent of pressure, derive an expression for the volume as a function of pressure.

1.25 Calculate α and κ for a gas for which

$$P(\overline{V} - b) = RT$$

1.26 What is the mean atmospheric pressure in Denver, Colorado, which is a mile high, assuming an isothermal atmosphere at 25°C? Air may be taken to be 20% O_2 and 80% N_2.

1.27 Calculate the pressure and composition of air 100 miles above the surface of the earth assuming that the atmosphere has a temperature of 0°C independent of altitude.

1.28 The density $\rho = m/V$ of a mixture of ideal gases A and B is determined and is used to calculate the average molar mass M of the mixture; $M = \rho RT/P$. How is the average molar mass determined in this way related to the molar masses of A and B?

1.29 Figure 1.13 shows the Maxwell construction for calculating the vapor pressure of a liquid from its equation of state. Since this requires an iterative process, a computer is needed, and J. H. Noggle and R. H. Wood have shown how to write a computer program in Mathematica (Wolfram Research, Inc., Champaign, IL 61820-7237) to do this. Use this method with the van der Waals equation to calculate the vapor pressure of nitrogen at 120 K.

Theoretical

1.30 Although a real gas obeys the ideal gas law in the limit as $P \to 0$, not all of the properties of a real gas approach the values for an ideal gas as $P \to 0$. The second virial coefficient of an ideal gas is zero, and so $\mathrm{d}Z/\mathrm{d}P = 0$ at all pressures. But calculate $\mathrm{d}Z/\mathrm{d}P$ for a real gas as $P \to 0$.

1.31 Derive the expressions for van der Waals constants a and b in terms of the critical temperature and pressure; that is, derive equations 1.32 and 1.33 from 1.29–1.31.

1.32 The isothermal compressibility κ of a gas is defined as $\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ and its value for an ideal gas is shown to be $1/P$. Use implicit differentiation of V with respect to P at constant T to obtain the expression for the isothermal compressibility of a van der Waals gas. Show that in the limit of infinite volume, the value for an ideal gas is obtained.

1.33 The cubic expansion coefficient α is defined by

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

and the isothermal compressibility κ is defined by

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

Calculate these quantities for an ideal gas.

1.34 What is the equation of state for a liquid for which the coefficient of cubic expansion α and the isothermal compressibility κ are constant?

1.35 For a liquid the cubic expansion coefficient α is nearly constant over a narrow range of temperature. Derive the expression for the volume as a function of temperature and the limiting form for temperatures close to T_0.

1.36 (*a*) Calculate $(\partial^2 P/\partial V)_T$ and $(\partial P/\partial T)_V$ for a gas that has the following equation of state:

$$P = \frac{nRT}{V - nb}$$

(*b*) Show that $(\partial^2 P/\partial V \partial T) = (\partial^2 P/\partial T \partial V)$. These are referred to as mixed partial derivatives.

Numerical Methods (Graph)

1.37 Show how the second virial coefficient of a gas and its molar mass can be obtained by plotting P/ρ versus P, where ρ is the density of the gas. Apply this method to the following data on ethane at 300 K.

P/bar	1	10	20
$\rho/10^{-3}$ g cm^{-3}	1.2145	13.006	28.235

1.38 Calculate the second and third virial coefficients for hydrogen at 0°C from the fact that the molar volumes at 50.7, 101.3, 202.6, and 303.9 bar are 0.4634, 0.2386, 0.1271, and 0.090 04 L mol^{-1}, respectively.

1.39 The critical temperature of carbon tetrachloride is 283.1°C. The densities in g/cm^3 of the liquid ρ_l and vapor ρ_v at different temperatures are as follows:

t/°C	100	150	200	250	270	280
P_1	1.4343	1.3215	1.1888	0.9980	0.8666	0.7634
ρ_v	0.0103	0.0304	0.0742	0.1754	0.2710	0.3597

What is the critical molar volume of $CC1_4$? It is found that the mean of the densities of the liquid and vapor does not vary rapidly with temperature and can be represented by

$$\frac{\rho_1 + \rho_v}{2} = A + Bt$$

where A and B are constants. The extrapolated value of the average density at the critical temperature is the critical density. The molar volume $\overline{V}_c$ at the critical point is equal to the molar mass divided by the critical density.

COMPUTER PROBLEMS

1.A Problem 1.7 yields $B = 0.135$ L mol^{-1} and $C = 4.3 \times 10^{-4}$ L^2 mol^{-2} for H_2(g) at 0°C. Calculate the molar volumes of molecular hydrogen at 75 and 150 bar and compare these molar volumes with the molar volume of an ideal gas.

1.B (*a*) Plot the pressure of ethane versus its molar volume in the range $0 < P < 200$ bar and molar volumes up to 0.5 mol L^{-1} using the van der Waals equation at 265, 280, 310.671, 350, and 400 K, where 310.671 K is the critical temperature calculated with the van der Waals constants. (*b*) Discuss the significance of the plots and the extent to which they represent reality. (*c*) Calculate the molar volumes at 400 K and $P = 150$ bar and at 265 K and 20 bar.

1.C This is a follow-up to Computer Problem 1.B on the van der Waals equation. (*a*) Plot the derivative of the pressure with respect to the molar volume for ethane at 265 K. (*b*) Plot the derivative at the critical temperature. (*c*) Plot the second derivative of the pressure with respect to the molar volume at the critical temperature. In each case, what is the significance of the maxima and minima?

1.D (*a*) Express the compressibility factors for N_2 and O_2 at 298.15 K as a function of pressure using the virial coefficients in Table 1.1. (*b*) Plot these compressibility factors versus P from 0 to 1000 bar.

1.E The second virial coefficients of N_2 at a series of temperatures are given by

T/K	75	100	125	150	200	250	300	400	500	600	700
B'/cm^3 mol^{-1}	−274	−160	−104	−71.5	−35.2	−16.2	−4.2	9	16.9	21.3	24

(*a*) Fit these data to the function

$$B' = \alpha + \beta T + \gamma T^2$$

(*b*) Plot this function versus temperature. (*c*) Calculate the Boyle temperature of molecular nitrogen.

1.F Nitrogen tetroxide (N_2O_4) gas is placed in a 500-cm^3 glass vessel, and the reaction $N_2O_4 = 2NO_2$ goes to equilibrium at 25°C. The density of the gas at equilibrium at 1.0133 bar is 3.176 g L^{-1}. Assuming that the gas mixture is ideal, what are the partial pressures of the two gases at equilibrium?

1.G Calculate the molar volume of ethane at 350 K and 70 bar using the van der Waals constants in Table 1.3.

1.H Plot the partial pressures of oxygen, nitrogen, and the total pressure in bars versus height above the surface of the earth from zero to 50 000 feet assuming that the temperature is constant at 273 K.