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Introduction and Background

Thermodynamics is the only science about which I am firmly convinced that, within the framework of the applicability of its basic principles, it will never be overthrown.

Albert Einstein

Thermodynamics derives from consideration of energy. Because the study of thermodynamics is much more meaningful when it is applied to familiar substances, we briefly discuss the properties of various materials in this chapter. At low and moderate pressures, the ideal gas is an excellent approximation to real gases and a good introduction to the properties of materials at equilibrium. Although thermodynamics deals with bulk matter, a microscopic or molecular description of matter is often used to understand and predict bulk properties of materials. Using the kinetic theory of gases, a description of temperature and pressure on the molecular level is obtained. Because deviations from ideal gas behavior become more pronounced at high pressure and temperatures, the equations of van der Waals, Berthelot, and Redlich and Kwong are introduced to describe real gas behavior. These equations are used to discuss properties of real substances, such as condensation and critical phenomena, that are due to the interactions between molecules. Gas mixtures are discussed and the generation of

pressure variation in an extended gas (the atmosphere) due to a gravitational field is calculated. The influence of pressure, temperature, and forces on the properties of solids and liquids are illustrated.

1.1 Introduction

1.1.1 Scope

With knowledge comes power, but knowledge soon becomes overwhelming; there is just too much to be known. We need principles to organize and extend our knowledge. In the study of matter and its transformations, a body of knowledge that is often called chemistry, there are a number of basic principles by which knowledge is organized. It is interesting that these principles are, in reality, only approximations.

One of these principles is the immutability of atomic species, which enables us to consider chemical transformations as rearrangements of atoms, the basic building blocks of matter. Most readers know that atomic species are really not immutable. In fact, nuclear physics deals largely with changes of one atomic species into another. Nevertheless, immutability is a very good and convenient approximation in the low-energy environment of our everyday experience, and we do not hesitate to make use of it in the science that applies to that realm.

Another principle that we use with impunity in chemistry is conservation of mass. Since Lavoisier, mass balance has been assumed in considerations of chemical transformations, even though Einstein's theory of relativity assures us that it is only an approximation. The point is that in chemistry and other fields that consider only relatively low-energy phenomena, conservation of mass is a very good approximation indeed!

The present volume deals with a number of exceedingly useful principles for organizing and extending our knowledge of matter and its transformations. These principles are based on considerations of energy, and are called the *laws of thermodynamics*. These laws are generalization of our experience and are taken as the basic postulates of thermodynamics. There are four of these laws, and at least three of these are approximations. One law, conservation of energy, is an approximation in the same sense as is conservation of mass, because, by relativity, we know that mass and energy are interconvertible. A second law is only true in a statistical sense (but in a very, very good statistical sense), and a third law allows exception. For the most part, we will be able to use these laws and the mathematical relationships that follow from them with no consideration of their approximate nature.

Thermodynamics was developed early in the industrial revolution to aid in improving engines. Originally, it dealt with transformations of heat and work. However, over time, the laws of thermodynamics have been used to deduce

powerful mathematical relationships applicable to a broad range of phenomena. Thermodynamics has been found to be an infallible guide for indicating which processes can occur in nature. Processes not ruled out by thermodynamics can occur, but may occur so slowly that they can be completely neglected. The science dealing with the rates of processes is called *kinetics* and will not be discussed in this book.

Our approach to matter and its transformations will be macroscopic and phenomenological. Thus, we will consider nitrogen as a substance with a certain group of properties that can be measured and other properties that can be calculated from the measured ones using thermodynamics. It is also possible to calculate the properties of materials from their microscopic description. For example, we know that nitrogen is made up of diatomic molecules that are rotating, vibrating, translating, and occasionally colliding with other nitrogen molecules. However, except for translation, accurate description of these motions requires *quantum mechanics*, which will not be treated in this volume. We do, in [Chapter 5](#), establish basic relations between the microscopic and macroscopic worlds, and these can be used once the requisite quantum background is obtained.

1.1.2 Plan of the Book

We begin by presenting some experimental results dealing with the properties of different types of matter. This is necessary—so that we have something to which we can apply our thermodynamic relations. A digression into the simplest molecular description of ideal gases allows us to develop some intuitive feeling for the very important bulk properties—temperature and pressure. The four laws of thermodynamics are then presented. The zeroth law allows us to define a unique temperature scale, and the first law is conservation of energy. The idea that energy has quality, as well as quantity, is then introduced. The second law is presented as the quality of energy being reduced as we use it. This reduction in quality of energy is called entropy increase. The third law deals with very low temperatures and permits us to discuss absolute values for entropy. The use of free energies greatly simplifies the application of the laws of thermodynamics. Each of the laws of thermodynamics is expressed in mathematical form, and useful relations between thermodynamic variables are derived. Extensive application of multivariable calculus is made in the text. A short presentation of this subject is given in [Appendix A](#).

Entropy is interpreted as the number of microscopic arrangements included in the macroscopic definition of a system. The second law is then used to derive the distribution of molecules and systems over their states. This allows macroscopic state functions to be calculated from microscopic states by statistical methods.

The laws of thermodynamics are applied to a number of topics. These include elastic properties of polymeric materials and surface effects in liquids. Phase transformations (melting, boiling, and sublimation) of single-component systems are treated, followed by chemical reactions in gases. Chemical potentials are defined and used to treat these problems, and general conditions for equilibrium are developed. For treating solutions, two ideal limits are introduced and used to calculate solution properties. The concept of activity is used to treat deviations from ideal behavior, and many of the thermodynamic relations are rephrased in terms of this variable. In ionic solutions, deviation from ideal behavior is large, even at very low concentrations, and methods are introduced for treating this behavior. Electrochemical cells are treated both for their practical importance and for their ability to provide measurements of many thermodynamic parameters. Surface effects are discussed and their thermodynamics analyzed by use of the concept of a two-dimensional surface phase. Finally, we explore the thermodynamics of steady-state systems, in which matter and/or energy continually pass through the system boundaries. Such systems are important models for chemical processes and living systems.

1.2 The Ideal Gas

One of the first quantitative relations established from experimental measurements was Boyle's observation in 1662 that for most gases, under the conditions that they could conveniently be studied in his laboratory (pressures of a few atmospheres or less), volume is inversely proportional to pressure:

$$V \propto \frac{1}{P} \quad (1)$$

Boyle's measurements were made on a fixed sample of gas over a short time, so that his laboratory temperature could be considered constant. Soon after, Charles explicitly investigated the effect of temperature variation.¹ He found that if pressure was held constant, the volume varied linearly with temperature:

$$V \propto 1 + kt \quad (2)$$

where k was found to have the value $1/273.15^\circ\text{C}$. This equation implies that if it holds to a temperature of -273.15°C (it does not), the volume of gases would be zero at that temperature. Because negative volumes are not meaningful, $t = -273.15^\circ\text{C}$ could be considered the lowest temperature attainable and was called *absolute zero*. A new temperature, T , was defined as

$$T \equiv t + 273.15 \quad (3)$$

and termed the *absolute temperature*, or the *ideal gas temperature*.² When Eqs. (1)–(3) are combined, we have

$$V \propto \frac{T}{P} \quad (4)$$

Additional information was supplied by Avogadro's hypothesis that the volume of a gas (at constant T and P) was proportional to the number of molecules, N , in the gas sample. Because in the 17th century, the number of molecules in a given gas sample was not known, it was customary to deal with an arbitrary number of molecules called the mole. Although the definition of the number of molecules in a mole has changed slightly over time, at present the number of atoms in exactly 12 g of the isotope ^{12}C is chosen as the standard, resulting in 6.02214×10^{23} molecules/mol. This quantity is called *Avogadro's number* and given the symbol N_A . In order to deal with an equation, rather than a proportionality, we include a constant R , the *gas constant* in our final gas equation:

$$V = \frac{nRT}{P} \quad (5)$$

The value of R depends on the units chosen for V and P . Scientists have agreed to move toward adopting the SI (Système International d'Unités) units, with V in cubic meters (m^3) and P in *Pascal* ($\text{Pascal} = \text{Pa} = \text{Newton}/\text{m}^2$) and R is $8.314 \text{ m}^3 \text{ Pa}/\text{mol K} = 8.314 \text{ J}/\text{mol K}$, where the joule (J) is the SI unit of energy. Because Eq. (5) only holds exactly in the limit of zero pressure, where molecules are infinitely far apart and their interactions can be neglected, it is called the *ideal gas law*. For most gases, it is an excellent approximation for the conditions generally used in laboratory experiments. Under high-pressure conditions that occasionally hold in the laboratory and are usually employed in industrial processes, Eq. (5) is often a very poor approximation. The Pascal is a very small pressure; 100,000 Pa is called a *bar*, which is very similar to an *atmosphere* ($1.0 \text{ atm} = 1.013 \times 10^5 \text{ Pa} = 1.013 \text{ bar}$). It is important to distinguish between the atmosphere, a fixed unit of pressure, roughly equal to the average atmospheric pressure at sea level, and "atmospheric pressure," which depends on the place and time being discussed.

Pressure, volume, temperature, and number of moles are *thermodynamic properties* or *thermodynamic variables* of a system—in this case, a gas sample. Their values are measured by experimenters using thermometers, pressure gauges, and other instruments *located outside the system*. The properties are of two types: those that increase proportionally with the size of the system, such as n and V , called *extensive properties*, and those defined for each small region in the system, such as P and T , called *intensive properties*. Terms that are added together or are on opposite sides of an equal sign must contain the same number of

extensive variables. The quotient of two extensive variables is an intensive variable.

When a property, such as T or P , is assigned to a system, it is implied that it is uniform (has the same value) throughout the system. These conditions are called *thermal equilibrium* and *mechanical equilibrium* for temperature and pressure, respectively. In [Chapter 10](#), we will deal with systems in which intensive properties are not uniform.

By dividing both sides of Eq. (5) by n , it can be expressed completely in terms of intensive variables:

$$\frac{V}{n} \equiv V_m = \frac{RT}{P} \quad (6)$$

where V_m is called the *molar volume*. Any extensive property divided by the number of moles is called the “molar property.” We can write $V_m(P, T)$, indicating that the molar volume is a function of P and T . Additional variables (concentrations) are needed for multicomponent systems. The *density* of a gas, ρ , is its mass per volume:

$$\rho = \frac{nM}{V} = \frac{PM}{RT} \quad (7)$$

The ideal gas law is an example of an *equation of state* (i.e., an equation relating different properties of a form of matter). Such equations are not obtained from thermodynamics. They result either from empirical measurements of the related quantities or from calculations based on molecular models.

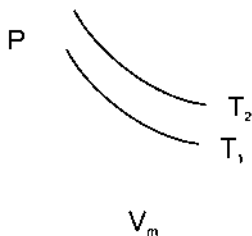
For some purposes, a graphical presentation of information is preferable to an equation. As shown in Eq. (6), the ideal gas law is a relation among three variables. In order to represent this equation in a two-dimensional plot, one variable must be held constant. The plots are called *isotherms*, *isobars*, or *isochores*, depending on whether temperature, pressure, or volume, respectively, is held constant. The plots for an ideal gas are shown in [Fig. 1](#).

1.3 Thermal Expansion Coefficient and Isothermal Compressibility

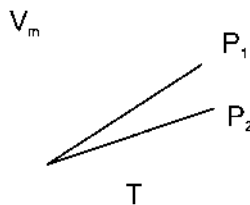
Several partial derivatives of state functions are used so often that they have been given names. The *thermal expansion coefficient*, α , is defined as

$$\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (8)$$

a) Isotherms, $T_2 > T_1$



b) Isobars, $P_2 > P_1$



c) Isochores, $V_{m,2} > V_{m,1}$

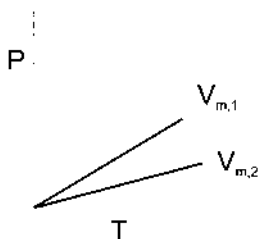


Figure 1 Isotherms, isobars, and isochores of an ideal gas.

and the *isothermal compressibility*, κ , as

$$\kappa \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (9)$$

Both of these partial derivatives are divided by V to make them intensive quantities. The SI units of α are K^{-1} and those of κ are Pa^{-1} . A negative sign is used in the definition of κ , because volumes always decrease as pressure increases, and we would prefer to tabulate positive quantities.

Example 1. Find expressions for the thermal expansion coefficient and the isothermal compressibility of an ideal gas.

Solution:

$$\begin{aligned} V &= \frac{nRT}{P}, & \left(\frac{\partial V}{\partial T} \right)_P &= \frac{nR}{P}, & \left(\frac{\partial V}{\partial P} \right)_T &= -\frac{nRT}{P^2} \\ \alpha &\equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{V} \frac{nR}{P} = \frac{1}{T}, & \kappa &\equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = \frac{1}{V} \frac{nRT}{P^2} = \frac{1}{P} \end{aligned}$$

1.4 A Simple Model of the Ideal Gas

Thermodynamics deals with relations among bulk (macroscopic) properties of matter. Bulk matter, however, is comprised of atoms and molecules and, therefore, its properties must result from the nature and behavior of these microscopic particles. An explanation of a bulk property based on molecular behavior is a *theory* for the behavior. Today, we know that the behavior of atoms and molecules is described by quantum mechanics. However, theories for gas properties predate the development of quantum mechanics. An early model of gases found to be very successful in explaining their equation of state at low pressures was the kinetic model of noninteracting particles, attributed to Bernoulli. In this model, the pressure exerted by n moles of gas confined to a container of volume V at temperature T is explained as due to the incessant collisions of the gas molecules with the walls of the container. Only the translational motion of gas particles contributes to the pressure, and for translational motion Newtonian mechanics is an excellent approximation to quantum mechanics. We will see that ideal gas behavior results when interactions between gas molecules are completely neglected.

The development first considers what happens when a single molecule hits a wall of a container. This result is then summed over all of the molecules in the container. A number of simplifications will be made in the presentation; most of these can be relaxed to give a much more complicated, but perhaps more satisfying, derivation.³

Consider a cubical box of side L , as shown in Fig. 2. We will first consider only the z component of motion of a single molecule of mass m . Because all interactions between particles are neglected, a molecule moving in the positive z direction will travel unimpeded until it hits the right wall of the container. It will

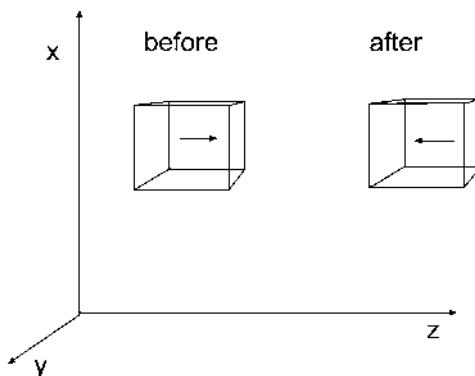


Figure 2 Elastic collision of a molecule with a wall.

be assumed that the collision with this wall is perfectly elastic, resulting in the molecule losing no translational kinetic energy. In addition, we will consider walls that are perfectly smooth and, thus, exert no forces in the x or y directions. With these assumptions, the only possible result of the collision is for the molecular velocity to reverse direction but keep the same magnitude, as shown in Fig. 2. The change of momentum of the molecule in a single collision is $-mv_z - (mv_z) = -2mv_z$. The force required to change the momentum of the molecule is provided by the right-hand wall of the box during the collision. Newton's third law equates the force to the rate of change of momentum. The force only occurs during the very short time of the collision and is highly variable. The impulsive nature of the force that occurs each time the molecule hits the right-hand wall is shown in Fig. 3.

We can also equate the time-averaged force exerted by the wall on the molecule to the time-averaged rate of change of momentum of the molecule, which is the momentum change in a single collision, times the rate of colliding with this wall. The latter quantity is molecular velocity divided by the distance the molecule travels between successive collisions with a given wall, $2L$:

$$f_{z,w \rightarrow m} = -(2mv_z)\left(\frac{v_z}{2L}\right) = -\frac{mv_z^2}{L} = -f_{z,m \rightarrow w} \quad (10)$$

The final equality results from Newton's law.⁴ $f_{z,m \rightarrow w}$ is the time-averaged force exerted on the wall by a single molecule, say molecule i . To find the total force, we have to add up the contribution from each of the N molecules in the box. Dropping the $m \rightarrow w$ subscript, this sum is

$$F_z = \sum_i f_{z,i} = \frac{m}{L} \sum_i v_{z,i}^2 = \frac{mN}{L} \langle v_z^2 \rangle \quad (11)$$

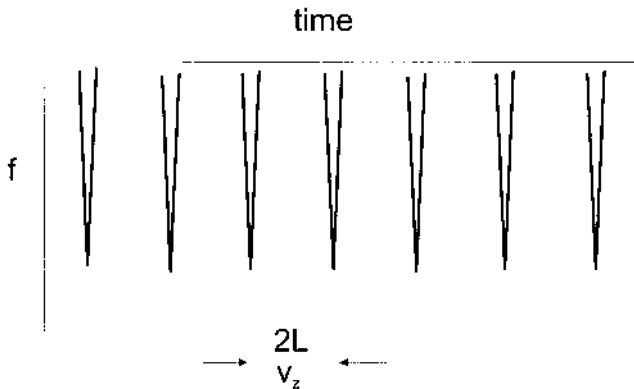


Figure 3 Instantaneous force exerted by right-hand wall on a molecule.

using the definition of the average value of a molecular property⁵

$$\langle g \rangle \equiv \frac{1}{N} \sum_{i=1}^N g_i \quad (12)$$

The pressure on the right-hand wall is just the force on this wall divided by its area, L^2 :

$$P = \frac{mN}{L^3} \langle v_z^2 \rangle = \frac{mN}{V} \langle v_z^2 \rangle. \quad (13)$$

The pressure due to a macroscopic number of molecules (of the order of 10^{22}) appears perfectly steady, as no pressure gauge can respond fast enough to record the individual collisions.

In considering motion in three dimensions, we can assume that the system is isotropic and the components of velocity are independent, so that

$$\langle c^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = 3 \langle v_z^2 \rangle \quad (14)$$

where c is the molecular *speed*, the magnitude of the velocity. Using the average translational kinetic energy of the molecules in the box,

$$\langle \varepsilon \rangle = \frac{m}{2} \langle c^2 \rangle \quad (15)$$

$$P = \frac{mN \langle c^2 \rangle}{3V} = \frac{2N \langle \varepsilon \rangle}{3V} = \frac{2nN_A \langle \varepsilon \rangle}{3V} \quad (16)$$

Comparing Eq. (16) with Eq. (5), the ideal gas law, we see that for them to be the same,

$$\langle \varepsilon \rangle = \frac{m}{2} \langle c^2 \rangle = \frac{3}{2} \frac{RT}{N_A} = \frac{3}{2} kT \quad (17)$$

k , the ratio of the gas constant to Avogadro's number, is called the Boltzmann constant and has the value 1.38066×10^{-23} J/K. The Boltzmann constant, however, is more than just a ratio of two constants. In the microscopic world, it plays a fundamental role in the definition of entropy, a subject of major interest in this book.

Equation (17) gives us physical intuition into the microscopic meaning of temperature. Temperature is a measure of the average translational kinetic energy of molecules! However, note that it is only the absolute (or ideal gas) temperature that is directly related to the motion of molecules in this way. In [Chapter 5](#), we will generalize this principle, showing that, under certain conditions, the absolute temperature is also a measure of the average of other types of energy (rotation and vibration) of molecules. This microscopic picture of energy will be an important adjunct to its thermodynamic definition.

From Eq. (17), we can also obtain

$$c_{\text{rms}} \equiv \sqrt{\langle c^2 \rangle} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}} \quad (18)$$

where c_{rms} , the *root-mean-square velocity*,⁶ is one measure of the velocity of the molecules.

Example 2. Calculate c_{rms} of N_2 at 298 K. Compare your result with the velocity of sound at ambient conditions, 340 m/s.

Solution:

$$\begin{aligned} c_{\text{rms}} &= \left(\frac{3(8.314 \text{ J/mol K})(298 \text{ K}) [\text{kg m}^2/\text{s}^2]}{0.028 \text{ kg/mol [J]}} \right)^{1/2} \\ &= 515 \frac{\text{m}}{\text{s}} \end{aligned}$$

The speed of sound is about two-thirds of the root-mean-square molecular speed. This is reasonable because sound travels by moving molecules by reorienting, but not changing, the magnitude of their velocity. Sound can therefore travel no faster than the molecules through which it is traveling.

Note that the molecular weight of N_2 must be expressed in SI units in this calculation. Neglect of this is a very common cause of errors in such calculations. Having an intuitive feeling for the size of molecular velocities is also a good way to avoid errors.

One ramification of Eq. (18) is *Graham's law of effusion*, which deals with the rate at which gaseous molecules pass through a small hole in the wall of their enclosure (effusion). According to Graham, the rate per unit concentration is proportional to velocity and, thus, directly proportional to the square root of the absolute temperature and inversely proportional to the square root of the molecular mass.

Example 3. A small hole is punched in the wall of a container containing an equimolar mixture of H_2 and N_2 . What is the initial ratio of the rate of effusion of H_2 to that of N_2 ?

Solution: The rate at which molecules pass through the hole is proportional to the product of their concentration in the container times their root-mean-square velocity. The concentrations are equal and molecules in the same container have the same temperature, so that only the mass dependence must be considered:

$$\frac{\text{Rate}_{H_2}}{\text{Rate}_{N_2}} = \sqrt{\frac{M_{N_2}}{M_{H_2}}} = \sqrt{\frac{28}{2}} = 3.74$$

Actually, effusion (molecules passing through a hole without colliding with each other or the walls) only holds at very low pressures. At higher pressures, many collisions of the molecules with the walls and with each other occur as the molecules pass through the hole. This process is called *diffusion*, but it has the same dependence on temperature and mass as does effusion. Gaseous diffusion has been of great importance in separating the isotopes of uranium⁷ for military and electric power generating purposes. The separation is performed using gaseous UF₆ and requires many stages, as the mass differences for the different uranium-isotope variations of this compound are very small.

Before leaving this topic, we should note that Bernoulli's model was not the only theory put forth to explain gas behavior. Sir Isaac Newton, the scientific giant of the 17th and 18th centuries, proposed that the ideal gas law could be explained by postulating a repulsive force between stationary molecules. Newton's reputation was so great that there was at first little support for Bernoulli's kinetic model and, in fact, it was ridiculed when first presented before the Royal Society by Waterson. The kinetic theory, however, has proven to be so powerful in explaining many properties of gases that gradually its acceptance won out, notwithstanding Newton's reputation.

1.5 Real Gases: The van der Waals Equation

Although the ideal gas equation is both extremely simple and useful, we know that forces between molecules play an important role in the behavior of matter. What else holds molecules together in liquids and solids? As a first step in treating such forces, we will consider real gases (i.e., gases under conditions in which they do not obey the ideal gas law). It was not too long after the discovery of the ideal gas law that experimental measurements began to indicate that, for some gases (e.g., CO₂) at high pressures or low temperatures, noticeable deviations from ideal gas behavior were exhibited. A satisfying explanation of these deviations in terms of intermolecular forces was first given by van der Waals in 1873.

There are two types of intermolecular forces: *repulsive forces* and *attractive forces*. These are represented by plots of potential energy versus intermolecular separation in Fig. 4, where the forces are given by the negative of the slopes of the curves: $-dV/dr$.

The slope of the potential energy curve for repulsive forces is negative, indicating that the force is in the positive direction (i.e., tending to increase the distance between molecules). Repulsive forces are very short range. They only become important when molecules are very close to each other, but they rise quickly to very large values over a very short distance. Because of this, van der Waals treated the repulsive forces using the concept of an *excluded volume*, [i.e.,

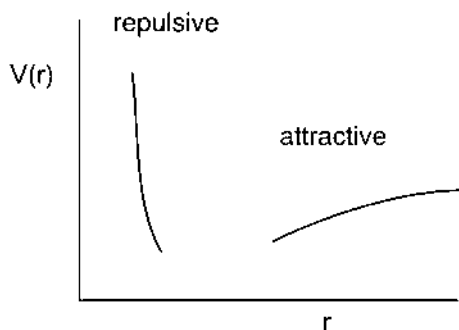


Figure 4 Attractive and repulsive forces.

a region around each molecule into which another molecule cannot penetrate (equivalent to an infinite repulsive force at the boundary of the region)]. Because the translational motion of a particle is the motion of its center of mass, it is the center of mass of one molecule that cannot enter into the excluded volume around another molecule. The van der Waals model treats gaseous molecules as attracting billiard balls.

Van der Waals reasoned that when using an ideal-gas-like treatment, the excluded volume should be subtracted from the actual volume of the container to give the free volume in which the molecules could undergo translational motion. As the excluded volume is proportional to the number of molecules (or moles) in the container, it is written as nb , where b is the excluded volume per mole, and the free volume is $V - nb$. Thus, according to van der Waals, the repulsive force modifies the ideal gas equation to

$$P = \frac{nRT}{V - nb} \quad (19)$$

and results in an increase in pressure over what would be obtained for an ideal gas.

As seen in Fig. 4, the attractive forces between molecules are weaker, but much longer range than the repulsive forces.⁸ To find the form of the contribution from the attractive forces to the pressure, van der Waals noted that pressure results from collisions between molecules and the walls of the container. For a molecule colliding with a wall, attractive forces between molecules would result in a force directed toward other molecules in the container and away from the wall. The attractive forces thus result in a reduction in pressure. For any one molecule colliding with the wall, the pressure reduction should be proportional to the density of molecules pulling it back into the gas during collision (N/V). However, the rate at which molecules collide with the walls is also proportional

to N/V , giving a reduction in pressure proportional to $(N/V)^2$. Writing this in terms of the number of moles gives the van der Waals equation as

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2} \quad (20)$$

This equation can be written more concisely in terms of molar volume, V_m :

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad (21)$$

Van der Waals' treatment makes no mention of three or more molecules interacting at the same time, and a billiard-ball-type of excluded volume is quite unreasonable for the "fuzzy" electron clouds required by quantum mechanics. Nevertheless, it still finds extensive use as a first correction to the ideal gas law. The equation is called *semiempirical*, in that, although it is based on physical arguments, it contains two constants, specific for each molecule, which must be evaluated by comparison with experimental data. Values for some of these constants are listed in Table 1. The numbers in such tables may vary somewhat, depending on the pressure and temperature regime in which the fitting to experimental data has been performed. Predictions of the van der Waals equation will be more accurate close to the conditions under which the constants have been determined.

If we take the billiard-ball, or hard-sphere, model literally, we can calculate the excluded volume constant, b , from the diameter of the molecular billiard balls, σ . The centers of two billiard balls, each of radius $\frac{1}{2}\sigma$, can come no closer than $r = \sigma$. Therefore, we can consider that around each molecule there is a

TABLE 1 Van der Waals' Constants of Gases

Gas	a (N m ⁴ /mol ²)	b (10 ⁻⁵ m ³ /mol)
Helium	0.0035	2.370
Neon	0.0214	1.709
Argon	0.136	3.219
Krypton	0.235	3.978
Xenon	0.425	5.105
Nitrogen	0.141	3.913
Ammonia	0.422	3.707
Ethane	0.556	6.380
Water	0.554	3.049
Carbon dioxide	0.364	4.267

Source: Data from A James, M Lord. VNR Index of Chemical and Physical Data. New York: Van Nostrand Reinhold, 1992.

sphere of radius σ and volume $4\pi\sigma^3/3$, into which no other ball can penetrate. Using this as the excluded volume for each molecule would mean that, in a collision, both partners would carry the excluded volume, which would double count the exclusion. Thus, we divide this volume by 2, getting, for b , the excluded volume per mole:

$$b = \frac{2\pi\sigma^3 N_A}{3} = 4v_{\text{mol}} N_A \quad (22)$$

where v_{mol} , the volume of a hard-sphere molecule, is

$$\frac{4\pi}{3} \left(\frac{\sigma}{2}\right)^3 = \frac{\pi}{6} \sigma^3$$

The van der Waals b constant should, therefore, be about four times the volume of 1 mol of molecules. Molecular diameters calculated from Eq. (22) are usually in rough agreement with what is expected from molecular theory.

1.6 Real Gases: Other Equations

The van der Waals equation is not the only semiempirical equation of state for gases containing two constants. Another equation is the *Berthelot equation*:

$$P = \frac{RT}{V_m - b'} - \frac{a'}{TV_m^2} \quad (23)$$

This differs from the van der Waals equation by the factor of temperature in the denominator of the second term, which makes the attractive forces relatively less important at high temperature.⁹

A third equation is the *Redlich–Kwong equation*:

$$P = \frac{RT}{V_m - b''} - \frac{a''}{T^{1/2} V_m (V_m + b)} \quad (24)$$

This equation usually gives the best fit to experimental data over a wide range of conditions, although it is difficult to give a physical explanation of the second term. We have used primed and double-primed constants for the Berthelot and Redlich–Kwong equation, respectively, in order to indicate that the constants in the different equations for the same gas are different. In the literature, the constants for all these equations are often designated as a and b . The van der Waals, Berthelot, and Redlich–Kwong equations all approach the ideal gas law at low pressure and high temperature. The van der Waals equation can be solved explicitly for P and T , but it is a cubic in V_m . Solutions for V_m can be obtained by iteration, most easily using a computer program, such as Mathcad or Mathematica. The Berthelot equation is a quadratic in T . Numerical solutions are required for both T and V_m when using the Redlich–Kwong equation.

In Fig. 5, predictions of the ideal gas law, the van der Waals equation, and the Redlich–Kwong equation are shown for ammonia at high (800 K) and low (420 K) temperatures. The high-temperature curves agree well, especially at low densities (high molar volumes). For the low-temperature curves, the ideal gas law is obviously inadequate at all but the largest molar volumes. At this temperature the van der Waals and Redlich–Kwong equations agree very well, except at the highest densities (lowest molar volumes).

A more systematic way of approaching deviations from ideal gas behavior is by means of the *compression factor*, Z , defined as the ratio of the volume of the gas to that of an ideal gas at the same temperature and pressure:

$$Z \equiv \frac{V}{V_{\text{ig}}} = \frac{PV_m}{RT} \quad (25)$$

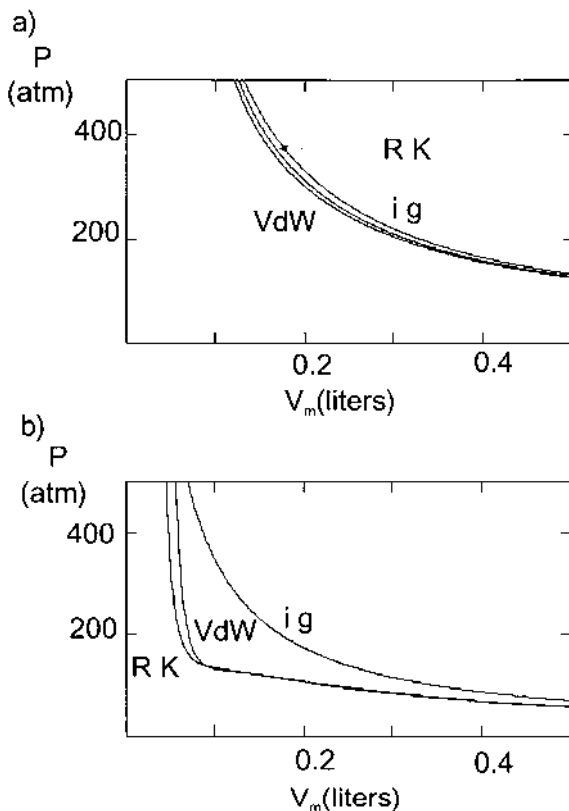


Figure 5 Ideal gas, van der Waals, and Redlich–Kwong equations of state for ammonia: (a) 800 K, (b) 420 K.

[This quantity is often called the *compressibility factor*, a name that is easy to confuse with the isothermal compressibility, defined in Eq. (9).] Z is obviously unity for an ideal gas. At the other extreme, when the pressure or density is very large, excluded volume effects become dominant, $V > V_{\text{ig}}$, and $Z > 1.0$.

Because deviations from ideal gas behavior result from intermolecular forces, which go to zero as the average distance between molecules gets very large, we expect Z to approach unity for real gases, as their molar density, $n/V = 1/V_m$, approaches zero. This suggests that it might be useful to expand Z in a series of powers of the molar density:

$$Z = 1 + B\left(\frac{1}{V_m}\right) + C\left(\frac{1}{V_m}\right)^2 + \dots \quad (26)$$

Another useful expansion for the compression factor is in terms of pressure:

$$Z = 1 + B'P + C'P^2 + \dots \quad (27)$$

These expansions are known as the *virial expansions*,¹⁰ and the coefficients B , B' , C , C' , and so forth, which are functions of temperature, are known as the *virial coefficients*. $B(T)$ and $B'(T)$ are called the *second virial coefficients*. (The first virial coefficient is unity.)

Although the virial expansions might seem very complicated, because they contain an infinite number of terms, their power lies in the fact that usually only a few terms must be considered. As pressure is reduced and molar volume gets very large, the higher terms in the expansion become negligible and only the first two terms need be considered. Equation (26) then becomes

$$Z = \frac{V_m P}{RT} = 1 + \frac{B(T)}{V_m} \quad (28)$$

which can be rearranged to

$$V_m = \frac{RT}{P} + B(T) \frac{RT}{PV_m} \approx \frac{RT}{P} + B(T) \quad (29)$$

The final approximation results from V_m being not too different from the ideal gas molar volume (RT/P) at low and moderate pressures. Equation (29) shows that the second virial coefficient is the first correction to the ideal gas molar volume for real gases. At very low temperature, molecules are strongly influenced by attractive intermolecular forces (in fact, if the temperature is low enough, the gas will liquefy), indicating that the second virial coefficient should be negative at low temperatures. As the temperature is increased, thermal velocities become so large that the weak intermolecular attractive forces can have little effect on molecular motions. The excluded volume, resulting from the repulsive forces, should dominate under these conditions, giving a positive second virial coefficient. The typical variation of B with temperature is shown in Fig. 6. The

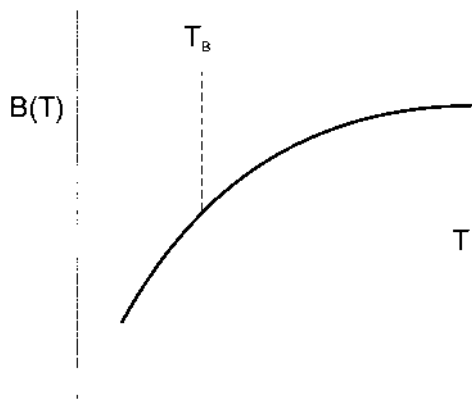


Figure 6 Variation of the second virial coefficient with temperature.

temperature at which the second virial coefficient is zero is called the *Boyle temperature*:

$$B(T_B) = 0 \quad (30)$$

At this temperature, attractive and repulsive influences on the molar volume just cancel and the gas behaves most ideally at low and moderate pressures, for which Eq. (29) is a good approximation.

Example 4. Find an expression for the Boyle temperature of a van der Waals gas.

Solution: In order to set the second virial coefficient equal to zero, we must put the van der Waals equation into the virial form (i.e., a power series in $1/V_m$). The second term in the van der Waals equation, being proportional to $(1/V_m)^2$, is already in this form. In order to put the term $RT/(V_m - b)$ into the virial form, we write it as

$$\frac{RT}{V_m - b} = \frac{RT}{V_m} \left(\frac{1}{1 - b/V_m} \right)$$

Because b , the excluded volume per mole (the actual size of the molecules) is much less than V_m , $x \equiv b/V_m$ is less than 1 and we can use the Taylor expansion¹¹

$$\frac{1}{1 - x} = 1 + x + x^2 + x^3 + \dots$$

to give

$$P = \frac{RT}{V_m} \left[1 + \left(\frac{b}{V_m} \right) + \left(\frac{b}{V_m} \right)^2 + \dots \right] - \frac{a}{V_m^2}$$

or

$$Z = \frac{PV_m}{RT} = 1 + \left(b - \frac{a}{RT} \right) \left(\frac{1}{V_m} \right) + \dots$$

When this is compared with Eq. (33),

$$B = b - \frac{a}{RT}$$

which is zero at T_B , giving $T_B = a/Rb$.

For most gases (except He, H₂, and Ne), T_B is above 298 K, indicating that at room temperature, $Z < 1.0$ and attractive forces dominate deviations from ideality.

1.7 Condensation and the Critical Point

Condensation refers to the formation of a liquid or solid directly from a gas. (Sometimes, forming a solid directly from a gas is called deposition.) The opposite processes are evaporation or sublimation, respectively. During all of these processes, pressure and temperature cannot be varied separately. If one is fixed, so is the other. It is common experience that water boiling at 1.0 atm pressure remains at 100°C as heat is added and its volume increases, until there is no more liquid remaining in the system. During the process of vaporization, liquid and gaseous water simultaneously exist in the system. The 1.0-atm isobar of water is shown in Fig. 7.

Liquid water has a very small molar volume and a small thermal expansion coefficient, making this part of the isobar almost horizontal. During boiling, liquid and gas coexist, and there is a vertical portion of the isobar as the relative proportions of these two phases change. The isobar acquires its gaseous form only after all of the liquid is converted to gas. As shown in Fig. 8, isotherms show corresponding behavior. If the pressure on water vapor held at 100°C is gradually increased, its molar volume at low pressure will decrease along a hyperbolic curve, similar to those shown in Fig. 1a. At 1.0 atm pressure, when liquid begins to form, the pressure will remain constant until all of the gas condenses.

The pressure at the horizontal part of the curve is known as the *vapor pressure* of the substance at the temperature of the isotherm. The curve representing liquid on the left side of this isotherm is much steeper than that representing gas on the right side of the isotherm. This is due to the much smaller

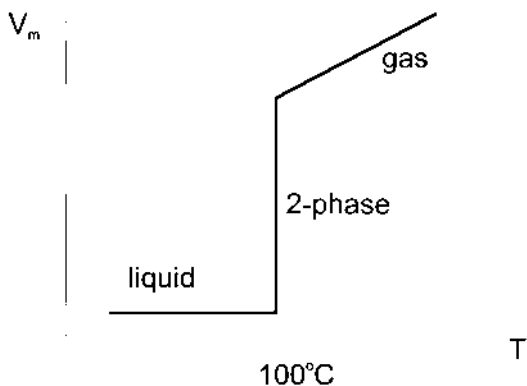


Figure 7 A 1.0-atm isobar of water, showing boiling.

isothermal compressibility, κ , for a liquid than for a gas. In the horizontal segment of this curve, both liquid and gas exist simultaneously in the system. Isobars and isotherms showing vaporization behavior have sudden changes in slope and thus cannot be represented by an analytical equation, such as those we have previously discussed.

If we look at isotherms at successively higher temperatures, we find that the horizontal portion of the isotherm gets shorter and shorter. This results mainly from the fact that at higher temperatures, gaseous molecules must be pushed closer together (to smaller molar volumes) in order for attractive forces to

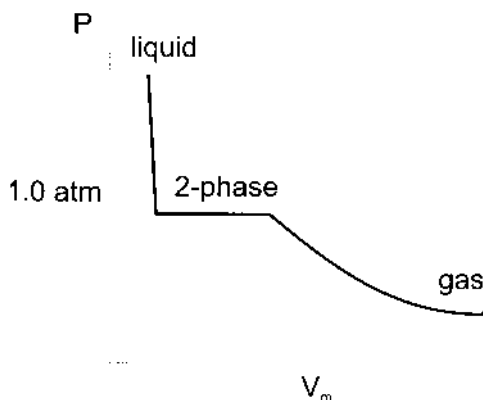


Figure 8 Isotherm, showing condensation of a gas.

overcome their increased kinetic energy. In addition, at higher temperature, thermal expansion gives the liquid a slightly higher molar volume. Eventually, a temperature is reached at which the horizontal segment of the isotherm disappears completely and only an inflection point¹² remains. This is illustrated in Fig. 9, where the width of the 2-phase region decreases at higher temperature. At the inflection point on this isotherm, liquid and gas have the same molar volume and are indistinguishable. The temperature for this limiting isotherm is known as the *critical temperature*, T_c ; the inflection point on this isotherm is known as the *critical point* and it occurs at the *critical pressure*, P_c , and *critical molar volume*, $V_{m,c}$. The critical constants of a number of gases are given in Table 2.

Below the critical temperature, a phase transition occurs when compressing a gas. The formation of a liquid phase is usually first noted by the formation of droplets on the walls of the container. At temperatures above the critical temperature, a substance can be continuously compressed without a separate liquid phase forming. Under such conditions, the substance is a gas, because it continues to fill its container. However, because densities comparable to those of the liquid can be reached by such compression, it is customary to call a substance above its critical temperature a *supercritical fluid*, where the term *fluid* (from flow) refers to either liquid or gas. Supercritical fluids, with densities comparable to liquid and high thermal energy, can be exceedingly good solvents and have found use recently in processes such as decaffeination of coffee.

A substance can be characterized by its *critical constants*, T_c , $V_{m,c}$, and P_c . These constants provide information about the intermolecular potential energy of interaction in the substance, roughly related to the maximum attractive energy, the

TABLE 2 Critical Constants of Gases

Gas	P_c (10^6 Pa)	T_c (K)	$V_{m,c}$ (10^{-4} m ³ /mol)
Helium	0.229	5.2	0.58
Neon	2.72	44.4	0.42
Argon	4.86	150.8	0.75
Krypton	5.50	209.4	0.92
Xenon	5.84	289.7	1.19
Nitrogen	3.40	126.3	0.90
Ammonia	11.28	405.6	0.72
Ethane	4.88	305.4	1.48
Water	22.12	647.4	0.55
Carbon dioxide	7.38	304.2	0.94

Source: Data from A James, M Lord. VNR Index of Chemical and Physical Data. New York: Van Nostrand Reinhold, 1992.

distance at which this maximum occurs, and the variation of the energy with distance, respectively.¹³ The constants in an equation of state, such as that of van der Waals, can be expressed in terms of the critical constants of a gas in the following manner. Because at temperatures just below the critical temperatures, isotherms have a horizontal segment, the critical point must be a horizontal inflection point. In other words, both dP/dV_m and d^2P/dV_m^2 must be zero at the critical point. Applying these conditions to the van der Waals equation [Eq. (21)] gives

$$\frac{dP}{dV} = -\frac{RT_c}{(V_{m,c} - b)^2} + \frac{2a}{V_{m,c}^3} = 0 \quad \text{or} \quad \frac{RT_c}{(V_{m,c} - b)^2} = \frac{2a}{V_{m,c}^3} \quad (31)$$

and

$$\frac{d^2P}{dV^2} = \frac{2RT_c}{(V_{m,c} - b)^3} - \frac{6a}{V_{m,c}^4} = 0 \quad \text{or} \quad \frac{2RT_c}{(V_{m,c} - b)^3} = \frac{6a}{V_{m,c}^4} \quad (32)$$

Dividing Eq. (31) by Eq. (32) gives

$$\frac{V_{m,c} - b}{2} = \frac{V_{m,c}}{3} \quad \text{or} \quad b = \frac{V_{m,c}}{3} \quad (33)$$

Substituting this into Eq. (31) then gives

$$a = \frac{9RT_c V_{m,c}}{8} \quad (34)$$

Equations (33) and (34) are not the optimum method of determining a and b , as $V_{m,c}$ is usually measured with much less accuracy than P_c or T_c . However, substitution of these equations into the van der Waals equation [Eq. (21)], evaluated at the critical point, gives

$$V_{m,c} = \frac{3RT_c}{8P_c} \quad (35)$$

Upon substitution of this into Eq. (33) and (34), we obtain

$$a = \frac{27R^2 T_c^2}{64P_c}, \quad b = \frac{RT_c}{8P_c} \quad \text{for the van der Waals equation} \quad (36)$$

When these values of a and b are used, the van der Waals equation fits the critical point and the slope and curvature of the critical isotherm. By continuity, the equation should also be a good fit to experimental data at temperatures slightly above the critical point. Other values of the constants may provide a better fit to data at conditions far from the critical point. Because it is an analytical function, the van der Waals equation cannot reproduce the discontinuities characteristic of vaporization shown at the two-phase regions in Figs. 7–9. Equation (21) (as well as other two-parameter equations, such as those of Berthelot, and Redlich and

Kwong) oscillate in the two-phase region. A procedure for interpreting the van der Waals equation in this region will be given in [Chapter 6](#). The Berthelot and Redlich–Kwong equations can be analyzed in a similar manner, giving the following for the characteristic constants of these equations in terms of T_c and P_c :

$$a' = \frac{27R^2T_c^3}{64P_c}, \quad b' = \frac{RT_c}{8P_c} \quad \text{for the Berthelot equation} \quad (37)$$

$$a'' = \frac{R^2T_c^{5/2}}{2.34P_c}, \quad b'' = \frac{0.260RT_c}{3P_c} \quad \text{for the Redlich–Kwong equation} \quad (38)$$

Using Eqs. (35) (solved for R) and (36) to eliminate R , a and b from the van der Waals equation [Eq. (21)] gives

$$\left(\frac{P}{P_c}\right) = \frac{8}{3} \left(\frac{T}{T_c}\right) \left(\frac{V_m}{V_{m,c}} - \frac{1}{3}\right)^{-1} - 3 \left(\frac{V_m}{V_{m,c}}\right)^{-2} \quad (39)$$

This equation is now in a very interesting form. By defining new variables $P_r \equiv P/P_c$ (the *reduced pressure*), $T_r \equiv T/T_c$ (the *reduced temperature*), and $V_{m,r} \equiv V_m/V_{m,r}$ (the *reduced molar volume*), the equation takes the form

$$P_r = \frac{8}{3} T_r \left(V_{m,r} - \frac{1}{3}\right)^{-1} - 3 V_{m,r}^{-2} \quad (40)$$

This equation has a universal form that is seemingly independent of molecular species. We say “seemingly” because, in fact, we need to know the critical constants of the species in order to calculate the reduced variables P_r , T_r , and $V_{m,r}$. Equation (40) is one example of the principle of *corresponding states*, which states that different substances have closely similar properties as functions of reduced variables. The principle is usually applied by using graphs of the compression factor as a function of P_r and T_r , as shown in [Fig. 10](#). These graphs are usually based on a large amount of experimental data, rather than the use of a single equation, such as that of van der Waals.

Example 5. Using the law of corresponding states, as expressed in [Fig. 10](#), calculate the density (g/cm^3) of ethane at 100°C and 100 atm. For ethane, $T_c = 305 \text{ K}$ and $P_c = 49 \text{ atm}$.

Solution:

$$T_r = \frac{(100 + 273) \text{ K}}{305 \text{ K}} = 1.22, \quad P_r = \frac{100 \text{ atm}}{49 \text{ atm}} = 2.04$$

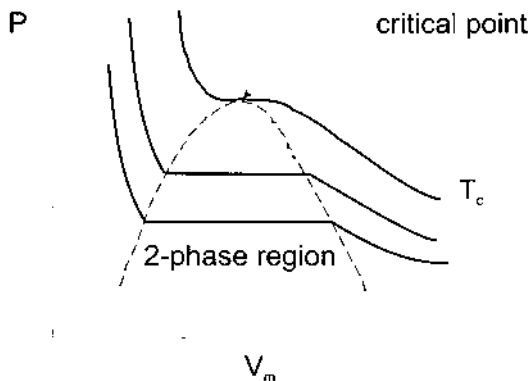


Figure 9 The critical point.

From Fig. 10, on the $T_r = 1.2$ curve at $P_r = 2.0$,

$$\begin{aligned}
 Z &\approx 0.65 = \frac{PV}{nRT} \\
 \rho &= \frac{Mn}{V} = \frac{MP}{ZRT} = \frac{30 \text{ g}}{\text{mol}} \frac{100 \text{ atm}}{0.65} \frac{\text{mol K}}{0.082L \text{ atm}} \frac{1}{373 \text{ K}} \\
 &= 150 \frac{\text{g}}{L} = 0.15 \frac{\text{g}}{\text{cm}^3}
 \end{aligned}$$

1.8 Gas Mixtures

A *solution* is defined as a mixture that is homogeneous on the macroscopic scale. Therefore, gas mixtures are solutions. In the limit of ideal gases, the total force on a wall of the container is the sum of the forces due to the collisions of the molecules of each component of the gas mixture. The total pressure is consequently the sum of the *partial pressures* of the components:

$$P = \sum_i P_i \quad (41)$$

where P_i , the partial pressure of component i in the mixture, is just the pressure that would exist in the container if it only contained the N_i molecules (n_i mol) of species i . This is *Dalton's law of partial pressures*. For an ideal gas, Eq. (41) can be written

$$P = \sum_i \frac{n_i RT}{V} = \frac{n_{\text{tot}} RT}{V} = \sum_i \frac{n_i}{n_{\text{tot}}} \frac{n_{\text{tot}} RT}{V} = \sum_i x_i P \quad (42)$$

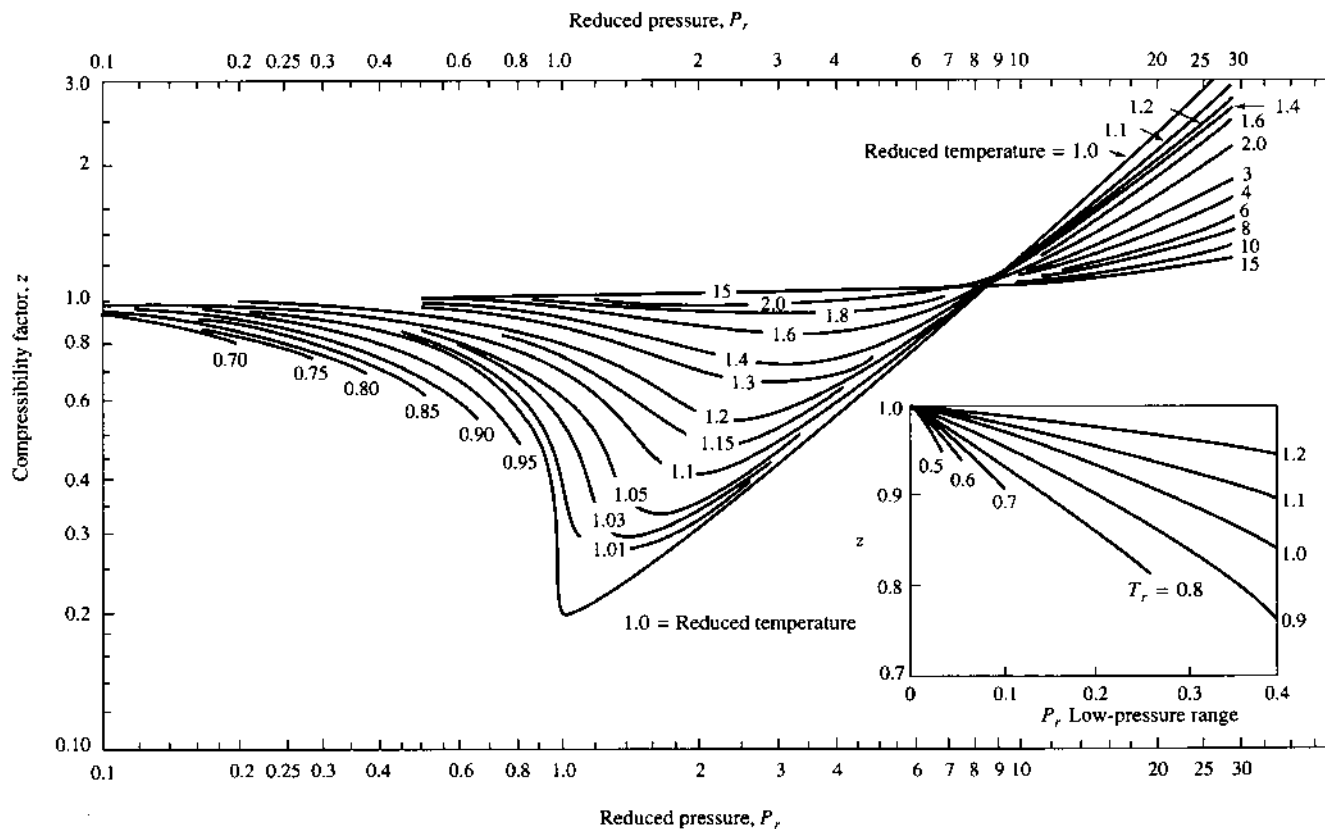


Figure 10 The law of corresponding states, $Z(T_r, P_r)$.

where $x_i = n_i/n_{\text{tot}}$ is the *mole fraction* of species i . A comparison of Eqs. (41) and (42) shows that

$$P_i = x_i P \quad (43)$$

Summing mole fractions gives

$$\sum_i x_i = \sum_i \frac{n_i}{n_{\text{tot}}} = \frac{1}{n_{\text{tot}}} \sum_i n_i = 1 \quad (44)$$

Because mole fractions must sum to unity, in a mixture of k components, only $k - 1$ mole fractions must be specified, in particular, in a *binary* (two-component) mixture, $x_B = 1 - x_A$.

Amagat's law states that the volume of a gas is the sum of the volumes that its components would have, each at the temperature and pressure of the mixture:

$$V = \sum_i V_i, \quad V_i = \frac{n_i RT}{P} \quad (45)$$

the *partial molar volume* of component i .

For ideal gases, Amagat's law follows directly from Dalton's law (Problem 12).

Dalton's law is not very accurate under conditions at which deviations from ideal behavior are appreciable. The reason for this is that the densities at which partial pressures are calculated may be considerably different from those existing in the gas mixture. Amagat's law is usually more accurate, because the V_i 's are calculated at the temperature and pressure existing in the mixture.

1.9 Equations of State of Condensed Phases

In liquids and solids, particles are very close together and repulsive forces play a much more important role than they do in gases. It is not surprising, therefore, that equations of state, such as those of van der Waals, and Redlich and Kwong, do not do a good job of predicting liquid and solid phase data. Usually, data for liquids and solid are presented in the form of thermal expansion coefficients and isothermal compressibilities. Some data for α and κ of selected liquids and solids are given in [Table 3](#).

α and κ are usually expressed as power series in temperature and pressure, respectively:

$$\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \alpha_0 + \alpha_1 T + \alpha_2 T^2 + \dots \quad (46)$$

$$\kappa \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = \kappa_0 + \kappa_1 P + \kappa_2 P^2 + \dots \quad (47)$$

TABLE 3 Thermal Expansion Coefficients and Isothermal Compressibility of Liquids and Solids

Substance	α (10^{-6} K $^{-1}$)	κ (10^{-6} atm $^{-1}$)
Water	210	45
Ethanol	1400	110
Copper	50	0.77
Steel (typical)	30	0.6
Rubber (typical)	1500	5000
Glass (typical)	20	2

Source: Data from DR Lide, ed. Handbook of Chemistry and Physics. 1966; EU Condon, H Odishaw, ed. Handbook of Physics. 1958; A James, M Lord. VNR Index of Physical Data. New York: Van Nostrand Reinhold, 1992.

In using tabulated data, it should be noted that the α_n 's are also functions of pressure and the κ_n 's are functions of temperature.

Often for solids, *linear thermal expansion coefficients*, $\alpha_L \equiv (1/L) \times (\partial L/\partial T)_P$, are tabulated. For an *isotropic* substance (the same in all directions), we can relate α_L to the volumetric thermal expansion coefficient, defined in Eq. (8), by considering a cube with $V = L^3$:

$$\alpha_V \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{L^3} 3L^2 \left(\frac{\partial L}{\partial T} \right)_P = 3\alpha_L \quad (48)$$

α_L for copper is 16.6×10^{-6} K $^{-1}$. Special alloys have been designed with α_L as low as 10^{-7} (e.g., Invar alloy = 64% Fe and 36% Ni). For some substances (rubbers under tension), α_L has opposite signs in different directions (see [Chapter 4](#)).

A rather accurate expression for the compressibility of most liquids is the *Tait equation*¹⁴:

$$\kappa = - \frac{C}{V[f(T) + P]} \quad (49)$$

where C is a constant and the function $f(T)$ is usually expressed as a power series in T .

A liquid does not have a fixed shape, so the surface area of a liquid can be easily changed. (The surface area of solids can also be changed by processes such as grinding. However, this requires a considerable amount of energy.) In condensed phases, molecules on the surface have a different environment from molecules in the bulk; therefore, a measure of the surface area is necessary to completely define the state of the system. In [Chapter 11](#), we will discuss surface effect in liquids by use of the *surface tension*, γ , which is the extra energy per unit

increase of surface area of a sample. An empirical equation of state, giving the temperature dependence of γ , is given in [Chapter 11](#).

In liquids and gases, the pressure force at a point is transmitted equally in all directions. This is not the case in solids. The shape of a solid can be changed by applying a force, f , along a particular direction. The volume of a solid can often be considered constant during the application of a force, requiring that as the solid extends in one direction, it contracts in perpendicular directions. The fractional extension of the solid in the direction of the applied force is known as the *strain*, ε :

$$\varepsilon \equiv \frac{l - l_0}{l_0} \quad (50)$$

where l and l_0 are the length and initial length of the solid.

Because a given force is obviously more effective in producing strain when it is applied to an object of small cross-sectional area, we divide the force by the area perpendicular to its application, and obtain the *stress*, f^* :

$$f^* \equiv \frac{f}{a} \quad (51)$$

Note that stress has the same units as pressure; it is a pressure along a single direction.

Young's modulus, E , for a material is defined as

$$E \equiv \frac{df^*}{d\varepsilon} \quad (52)$$

It is the slope of the stress–strain curve. If a material is *elastic*, it recovers to its original length if the applied stress is removed. In general, E depends on the strain of the material. However, for many substances, if the stress is not too large, E is independent of strain. Over this range, the substance is said to obey *Hook's law*:

$$f^* = E\varepsilon \quad (53)$$

A typical stress–strain diagram for a metal is shown in [Fig. 11](#). This metal follows Hook's law up to a *proportional limit* (or *yield strength*) of 2×10^9 Pa. The elastic limit, above which the metal undergoes *plastic deformation*, which is not recoverable when the stress is removed, is close to the proportional limit. The maximum stress that the metal can support is the *ultimate strength* (or *tensile strength*) of the metal, which occurs at the maximum extension of the material.

Nonmetallic substances show a wide variety of stress–strain diagrams, with each type related to the bonding of the particular material. One type, that for an elastomeric rubber, is shown in [Fig. 12](#). Compared to a metal, the rubber can support much larger strains and only much smaller stresses. It follows Hook's law only as a limit at very small displacements. However, displacement is elastic well outside of this range.

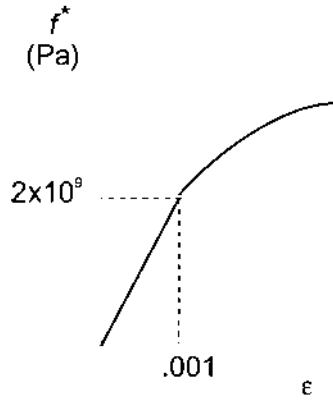


Figure 11 A typical stress-strain diagram for a metal.

Only at very low elongation is there a linear relation between f^* stress and strain. At somewhat higher strain, the curve in Fig. 11 can be represented by

$$f^* = a\varepsilon - b\varepsilon^2 \quad (54)$$

where a and b are constants.

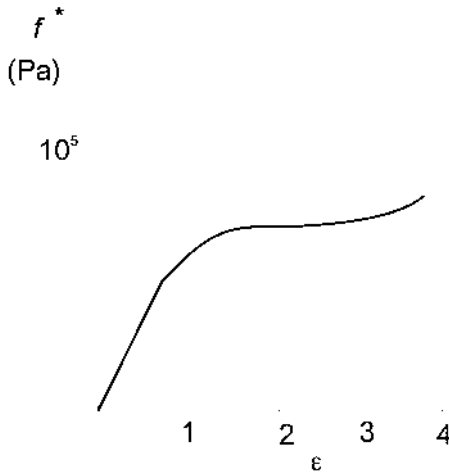


Figure 12 Stress-strain diagram for an elastomer.

1.10 Pressure Variations in Fluids

When external fields are considered, mechanical equilibrium no longer corresponds to a state of uniform pressure. This is most important for systems in a gravitational field. Equating the upward and downward forces on the volume element of fluid shown in Fig. 13 gives

$$PA = (P + dP)A + g\rho A dz \quad (55)$$

or

$$dP = -\rho g dz \quad (56)$$

A liquid can usually be considered *incompressible* (ρ constant). Integrating from $P = P_0$ at $z = 0$ to a distance h below the surface of the liquid ($z = -h$),

$$P \stackrel{\text{liq}}{=} P_0 + \rho gh \quad (57)$$

In a gas, density depends on pressure. Assuming the gas is ideal,

$$\rho = \frac{nM}{V} = \frac{PM}{RT} \quad (58)$$

giving

$$dP \stackrel{\text{ig}}{=} -\frac{PMg}{RT} dz \quad (59)$$

Separating variables and integrating,

$$\int_{P_0}^{P(h)} \frac{dP}{P} = - \int_0^h \frac{Mg}{RT} dz \quad (60)$$

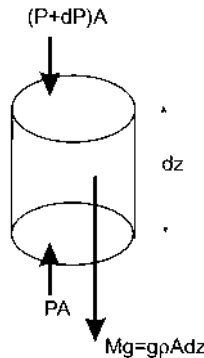


Figure 13 Fluid in a gravitational field.

Integrating with the assumptions of constant temperature and molecular weight,

$$P = P_0 \exp\left(-\frac{Mgh}{RT}\right) \quad (61)$$

This relation is known as the *barometric distribution* and is a first approximation to the pressure distribution in the atmosphere. For a more accurate representation of the pressure variation, Eq. (59) must be integrated, using the known temperature variation in the atmosphere. (The average molecular weight of atmospheric gases is, to a very good approximation, invariant throughout the troposphere and stratosphere, the two lowest regions of the atmosphere.)

Questions

1. Which of the following laws or principles: immutability of atoms, conservation of mass, and Newton's laws, applies to each of the following phenomena:

- (a) Motion of a baseball
- (b) Motion of an electron in an atom
- (c) A thermonuclear explosion

2. Give one reason why Charles' law does not hold to -273.15°C .

3. What is the difference between a pressure of 1.0 atm and atmospheric pressure?

4. Choose a property of materials with which you have some familiarity (e.g., mass, viscosity, thermal conductivity or electrical resistance) and consider how you would measure this property. Are you inside or outside the system when you make the measurement?

5. Classify the following properties of a system as extensive or intensive: volume, pressure, energy, thermal expansion coefficient, and viscosity.

6.* If each of the following was included in the kinetic theory of gases, do you think the result [Eq. (16)] would change? Qualitatively justify your answer.

- (a) Allowing for motion of particles in three dimensions
- (b) Allowing for collisions of point particles
- (c) Allowing for inelastic collisions with the walls

7. Show that the van der Waals equation approaches the ideal gas law as $P \rightarrow 0$ and as $T \rightarrow \infty$. (Hint: As an estimate of the magnitude of V_m , use the value for the ideal gas.)

8. For a strict interpretation of the van der Waals equation, how does the potential energy of interaction of molecules have to vary as a function of intermolecular separation?

9. What are the units of a'' and b'' in the Redlich–Kwong equation?

10. On the corresponding states graph (Fig. 10), where is the critical point? Indicate the region that represents gases. Roughly sketch in the two-phase region and indicate the region that represents liquids.

11. Sketch the compression factor as a function of $1/V_m$ for
 - (a) $T > T_B$
 - (b) $T < T_B$
12. Give two properties of gases that are better explained using the kinetic theory of gases than Newton's idea of gas properties resulting from repulsive forces between stationary gas molecules.
13. Sketch an isochore of a substance showing condensation.
14. What is a typical ratio of the maximum strain of a rubber to that of a metal?
- 15.* The Tait equation predicts that the isothermal compressibility of a liquid approaches zero as the pressure becomes infinitely large. Is this reasonable in terms of the van der Waals model of real fluids?
16. Show that a perfectly elastic substance dissipates zero energy upon repeated stress–strain cycles. Draw a hysteresis diagram (a diagram that shows the states of the material during a full extension–relaxation cycle) on a figure similar to Fig. 11 for a material that relaxes along a different path than that along which it expands. Show that this leads to energy dissipation upon repeated stress–strain cycles.

Problems

1. What is the value of the gas constant in units that use pounds per square inch (psi) for pressure and cubic feet (ft^3) for volume?
2. There are about 20 drops in 1 mL of water. What is the volume of Avogadro's number of drops of water? Compare this with the volume of the Earth's oceans, $1.4 \times 10^{18} \text{ m}^3$.
3. Calculate the mass of the air at standard temperature and pressure (STP) in a room of dimensions $20 \text{ ft} \times 20 \text{ ft} \times 8 \text{ ft}$. You can take 29.0 g/mol as the average molecular weight of air. Compare your result with the mass of water it would require to fill the room.
4. Using the chain rule for partial derivatives [Eq. (7) of Appendix A] express $(\partial P/\partial T)_V$ in terms of the thermal expansion coefficient α and the isothermal compressibility κ .
5. What is the ratio of effusive velocities of $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$? What would be the fraction of the ^{235}U isotopomer effusing from a mixture of hexafluorides that contains 0.50% ^{235}U (the percentage of the isotope in natural abundance)?
6. In a 1.0-L sample of N_2 gas (10.0 cm on a side) at 25°C and 1.0 atm pressure, what is the rms velocity of N_2 molecules? What is the average z component of velocity? Estimate how often a single molecule hits a particular wall. What is the total rate of impacts with this wall? Do you think that there is any pressure gauge that could respond to these individual impacts?
7. Using the van der Waals b constants given in Table 1, calculate the atomic diameter of the noble gases. Do atoms have a definite size?

8.* Use the van der Waals equation for N_2 to determine the following:

- The pressure at 25°C and a molar volume of 2.0 L/mol
- The molar volume at 10 atm and 300 K
- The molar volume at 10 atm and 100 K

Is the ratio of the results in parts (b) and (c) what you would expect? If not, why?

9.* Repeat Problem 9 using the Redlich–Kwong equation. You can calculate the Redlich–Kwong constants for N_2 from its critical constants.

10. Find the Boyle temperature for a gas obeying the Berthelot equation.

11. Show that at the Boyle temperature, $\lim_{P \rightarrow 0}(dZ/dP) = 0$ and $\lim_{P \rightarrow 0}(dZ/dV_m) = 0$.

12. Show that the requirement that Dalton's law holds for an ideal gas leads to Amagat's law also holding.

13. Use Fig. 10 to determine the molar volume of N_2 at the conditions given in Problem 8, parts (b) and (c).

14. Derive Eq. (39) from Eqs. (21), (35), and (36).

15.* For a condensed phase with thermal expansion coefficient given by Eq. (46), show that the volume can be expressed as a function of temperature by $V = V_0(1 + \beta_0 T + \beta_1 T^2 + \dots)$, where V_0 is the volume at 0 K . Find expressions for β_0 and β_1 .

16. If a round metal bar undergoes a strain of 0.001 when a force is applied at constant volume, what is the fractional change of the diameter of the bar?

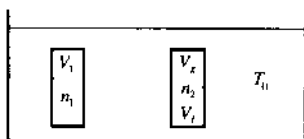
17. Find Young's modulus for a rubber whose stress–strain curve obeys Eq. (54).

18. If the pressure at sea level is 760 mm Hg , what are the pressures 1.0 m and 1.0 km above sea level? Assume an altitude-independent atmospheric temperature of 25°C and an average molecular weight of the atmosphere of 29 g/mol .

19. What is the pressure 1.0 km below the surface of the ocean, assuming a depth-independent density of ocean water of 1.0 g/cm^3 ?

20.* Repeat Problem 18 at 1.0 km for a temperature that drops linearly with elevation at a rate of 6.5°C/km .

21.* Consider the following apparatus used to measure the molar volumes of coexisting liquid and gaseous phases:



Two thick-walled glass tubes of known volumes are each filled with measured amounts of a substance. The temperature of the bath is slowly raised until the liquid phase

in one of the tubes (say tube 1) just disappears. At this temperature, the volumes of the liquid and gaseous phases in the other tube are V_l and V_g . Show that the molar volumes of the coexisting liquid and gaseous phases at T_0 are

$$V_{m,g}(T_0) = \frac{V_1}{n_1}, \quad V_{m,l}(T_0) = \frac{V_1 V_l}{n_2 V_1 - n_1 V_g}$$

22. For a Redlick–Kwong gas, find the following:

(a) $\left(\frac{\partial P}{\partial T}\right)_{V_m}$

(b) $\left(\frac{\partial P}{\partial V_m}\right)_T$

(c) $\alpha = \frac{1}{V_m} \left(\frac{\partial V_m}{\partial T}\right)_P$

23. A mixture of O_2 and F_2 at 520 torr pressure is shaken with mercury. All the F_2 and none of the O_2 reacts and the pressure drops to 430 torr. What was the mole fraction of F_2 in the original mixture?

Notes

1. We will assume that Charles measured temperature with a mercury thermometer calibrated for the centigrade (Celsius) scale.
2. This is sometimes called the Kelvin temperature and measured in degrees Kelvin. More rigorously, the Kelvin temperature scale is defined by the second law of thermodynamics, but, numerically, it is the same as T. We will use the symbol K to designate absolute temperature as defined by Eq. (3).
3. The ideal gas law will also be derived from the point of view of statistical mechanics in [Chapter 5](#).
4. If body A exerts a force on body B, then body B exerts an equal but opposite force on body A.
5. This is called the ensemble average, to distinguish it from the time average.
6. Note that the operations are performed in reverse order from which they occur in the name: square first, then average, and then square root.
7. The ^{235}U isotope undergoes fission, the ^{238}U isotope, which comprises 99.28% of naturally occurring uranium, does not.
8. The forces between neutral molecules have a much shorter range than the forces between charged particles.
9. Because molar volume usually increases with temperature, even the van der Waals equation, where the attractive forces term does not depend on temperature, predicts decreasing influence of these forces at higher temperatures.
10. From Latin, meaning “force.”

11. The general formula for a Taylor expansion is

$$f(x) = f(0) + x \left. \frac{df}{dx} \right|_0 + \frac{1}{2} x^2 \left. \frac{d^2f}{dx^2} \right|_0 + \cdots + \frac{1}{n!} x^n \left. \frac{d^n f}{dx^n} \right|_0 + \cdots$$

The terms represent successive approximations to a function at small values of its argument by the value of the function at the origin, the straight-line approximation of the function at the origin, the parabolic approximation of the function at the origin, and so forth.

12. An inflection point is where a curve changes from concave up to concave down. Mathematically, at an inflection point of a curve $f(x)$, $d^2f/dx^2 = 0$.
13. DA McQuarrie. Statistical Thermodynamics. New York: Harper & Row, 1973, Chap. 12.
14. JO Hirschfelder, CE Curtiss, RB Bird. Molecular Theory of Gases and Liquids. New York: Wiley, 1954, p 261.