

PART I

THE FORMALISM OF MODERN THERMODYNAMICS

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1 BASIC CONCEPTS AND THE LAWS OF GASES

Introduction

Adam Smith's *Wealth of Nations* was published in the year 1776. Seven years earlier James Watt (1736–1819) had obtained a patent for his version of the steam engine. Both men worked at the University of Glasgow. Yet, in Adam Smith's great work the only use for coal was in providing heat for workers [1]. The machines of the eighteenth century were driven by wind, water and animals. Nearly 2000 years had passed since Hero of Alexandria made a sphere spin with the force of steam; but still fire's power to generate motion and drive machines remained hidden. Adam Smith (1723–1790) did not see in coal this hidden wealth of nations.

The steam engine revealed a new possibility. Wind, water and animals converted one form of motion to another. The steam engine was fundamentally different: it converted heat to mechanical motion. Its enormous impact on civilization not only heralded the industrial revolution, it also gave birth to a new science: *thermodynamics*. Unlike the science of Newtonian mechanics, which had its origins in theories of motion of heavenly bodies, thermodynamics was born out of a more practical interest: generating motion from heat.

Initially, thermodynamics was the study of heat and its ability to generate motion; then it merged with the larger subject of energy and its interconversion from one form to another. With time, thermodynamics evolved into a theory that describes transformations of states of matter in general, motion generated by heat being a consequence of particular transformations. It is founded on essentially two fundamental laws, one concerning *energy* and the other *entropy*. A precise definition of energy and entropy, as measurable physical quantities, will be presented in the Chapters 2 and 3 respectively. In the following two sections we will give an overview of thermodynamics and familiarize the reader with the terminology and concepts that will be developed in the rest of the book.

Every system is associated with an energy and an entropy. When matter undergoes transformation from one state to another, the total amount of energy in the system and its exterior is conserved; total entropy, however, can only increase or, in idealized cases, remain unchanged. These two simple-sounding statements have far-reaching consequences. Max Planck (1858–1947) was deeply influenced by the breadth of the conclusions that can be drawn from them and devoted much of himself to the study of thermodynamics. In reading this book, I hope the reader will come to appreciate the significance of the following often-quoted opinion of Albert Einstein (1879–1955):

A theory is more impressive the greater the simplicity of its premises is, the more different kinds of things it relates, and the more extended its area of applicability. Therefore the deep impression which classical thermodynamics made upon me. It is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown.

The thermodynamics of the nineteenth century, which so impressed Planck and Einstein, described static systems that were in thermodynamic equilibrium. It was formulated to calculate the initial and final entropies when a system evolved from one equilibrium state to another. In this ‘Classical Thermodynamics’ there was no direct relationship between natural processes, such as chemical reactions and conduction of heat, and the rate at which entropy changed. During the twentieth century, Lars Onsager (1903–1976), Ilya Prigogine (1917–2003) and others extended the formalism of classical thermodynamics to relate the *rate* of entropy change to *rates* of processes, such as chemical reactions and heat conduction. From the outset, we will take the approach of this ‘Modern Thermodynamics’ in which thermodynamics is a theory of irreversible processes, not merely a theory of equilibrium states.

1.1 Thermodynamic Systems

A thermodynamic description of natural processes usually begins by dividing the world into a ‘system’ and its ‘exterior’, which is the rest of the world. This cannot be done, of course, when one is considering the thermodynamic nature of the entire universe – however, although there is no ‘exterior’, thermodynamics can be applied to the entire universe. The definition of a thermodynamic system depends on the existence of ‘boundaries’, boundaries that separate the system from its exterior and restrict the way the system interacts with its exterior. In understanding the thermodynamic behavior of a system, the manner in which it exchanges energy and matter with its exterior, is important. Therefore, thermodynamic systems are classified into three types: isolated, closed and open systems (Figure 1.1) according to the way they interact with the exterior.

Isolated systems do not exchange energy or matter with the exterior. Such systems are generally considered for pedagogical reasons, while systems with extremely slow exchange of energy and matter can be realized in a laboratory. Except for the universe as a whole, truly isolated systems do not exist in nature.

Closed systems exchange energy but not matter with their exterior. It is obvious that such systems can easily be realized in a laboratory: A closed flask of reacting chemicals which is maintained at a fixed temperature is a closed system. The Earth, on a time-scale of years, during which it exchanges negligible amounts matter with its exterior, may be considered a closed system; it only absorbs radiation from the sun and emits it back into space.

Open systems exchange both energy and matter with their exterior. All living and ecological systems are open systems. The complex organization in open systems is

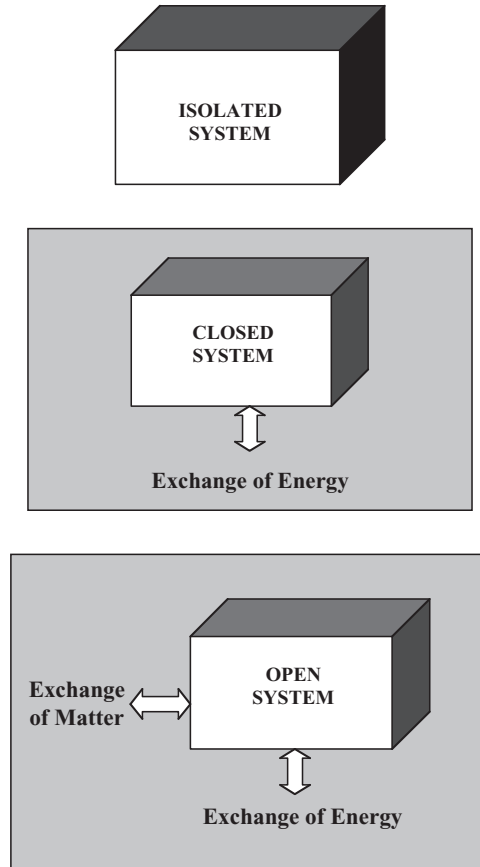


Figure 1.1 Isolated, closed and open systems. Isolated systems exchange neither energy nor matter with the exterior. Closed systems exchange heat and mechanical energy but not matter with the exterior. Open systems exchange both energy and matter with the exterior

a result of exchange of matter and energy and the entropy generating irreversible processes that occur within.

In thermodynamics, the **state** of a system is specified in terms of macroscopic **state variables**, such as volume V , pressure p , temperature T , and moles N_k of chemical constituent k , which are self-evident. These variables are adequate for the description of equilibrium systems. When a system is not in thermodynamic equilibrium, more variables, such as rate of convective flow or of metabolism, may be needed to describe it. The two laws of thermodynamics are founded on the concepts of energy U , and entropy S , which, as we shall see, are **functions of state variables**.

Since the fundamental quantities in thermodynamics are functions of many variables, thermodynamics makes extensive use of calculus of many variables. A brief summary of some basic properties of functions of many variables is given in Appendix A1.1 (at the end of this chapter). Functions of state variables, such as U and S , are often called **state functions**.

It is convenient to classify thermodynamic variables into two categories. Variables such as volume and amount of a substance (moles), which indicate the size of the system, are called **extensive variables**. Variables such as temperature T and pressure p , which specify a local property, which do not indicate the system's size, are called **intensive variables**.

If the temperature is not uniform, then heat will flow until the entire system reaches a state of uniform temperature. Such a state is the state of **thermal equilibrium**. The state of thermal equilibrium is a special state towards which all isolated systems will inexorably evolve. A precise description of this state will be given later in this book. In the state of thermal equilibrium, the values of total internal energy U and entropy S are completely specified by the temperature T , the volume V and the amounts of the system's chemical constituents N_k (moles):

$$U = U(T, V, N_k) \quad \text{or} \quad S = S(T, V, N_k) \quad (1.1.1)$$

The values of an extensive variable, such as total internal energy U or entropy S , can also be specified by other extensive variables:

$$U = U(S, V, N_k) \quad \text{or} \quad S = S(U, V, N_k) \quad (1.1.2)$$

As we shall see in the following chapters, intensive variables can be expressed as derivatives of one extensive variable with respect to another. For example, we shall see that the temperature $T = (\partial U / \partial S)_{V, N_k}$. The laws of thermodynamics and the calculus of many-variable functions give us a rich understanding of many phenomena we observe in nature.

1.2 Equilibrium and Nonequilibrium Systems

It is our experience that if a physical system is isolated, its state – specified by macroscopic variables such as pressure, temperature and chemical composition – evolves *irreversibly* towards a time-invariant state in which we see no further physical or chemical change. This is the state of **thermodynamic equilibrium**. It is a state characterized by a uniform temperature throughout the system. The state of equilibrium is also characterized by several other physical features that we will describe in the following chapters.

The evolution of a system towards the state of equilibrium is due to **irreversible processes**, such as heat conduction and chemical reactions, which act in a specific direction but not its reverse. For example, heat always flows from a higher to a lower temperature, never in the reverse direction; similarly, chemical reactions cause

compositional changes in a specific direction not its reverse (which, as we shall see in Chapter 4, is described in terms of ‘chemical potential’, a quantity similar to temperature, and ‘affinity’, a thermodynamic force that drives chemical reactions). At equilibrium, these processes vanish. Thus, a nonequilibrium state can be characterized as a state in which irreversible processes are taking place driving the system towards the equilibrium state. In some situations, especially during chemical transformations, the rates at which the state is transforming irreversibly may be extremely small, and an isolated system might appear as if it is time invariant and has reached its state of equilibrium. Nevertheless, with appropriate specification of the chemical reactions, the nonequilibrium nature of the state can be identified.

Two or more systems that interact and exchange energy and/or matter will eventually reach the state of thermal equilibrium in which the temperature within each system is spatially uniform and the temperature of all the systems are the same. If a system A is in thermal equilibrium with system B and if B is in thermal equilibrium with system C, then it follows that A is in thermal equilibrium with C. This ‘transitivity’ of the state of equilibrium is sometimes called the **zeroth law**. Thus, equilibrium systems have a well-defined, spatially uniform temperature; for such systems, the energy and entropy are functions of state as expressed in (1.1.1).

Uniformity of temperature, however, is not a requirement for the entropy or energy of a system to be well defined. For **nonequilibrium systems**, in which the temperature is not uniform but is well defined locally at every point x , we can define densities of thermodynamic quantities such as energy and entropy. Thus, the energy density at x

$$u[T(x), n_k(x)] = \text{internal energy per unit volume} \quad (1.2.1)$$

can be defined in terms of the local temperature $T(x)$ and the concentration

$$n_k(x) = \text{moles of constituent } k \text{ per unit volume} \quad (1.2.2)$$

Similarly, an entropy density $s(T, n_k)$ can be defined. The atmosphere of the Earth, shown in Box 1.1, is an example of a nonequilibrium system in which both n_k and T are functions of position. The total energy U , the total entropy S and the total amount of the substance N_k are

$$S = \int_V s[T(x), n_k(x)] dV \quad (1.2.3)$$

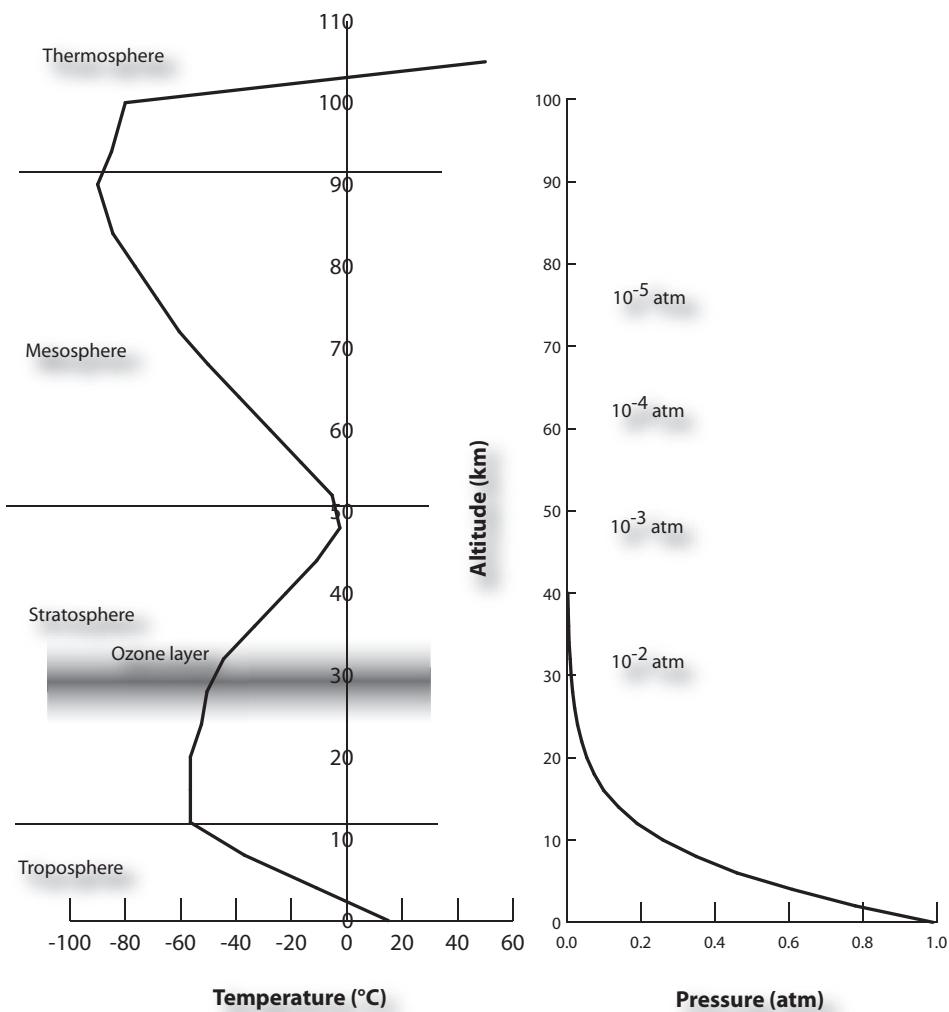
$$U = \int_V u[T(x), n_k(x)] dV \quad (1.2.4)$$

$$N_k = \int_V n_k(x) dV \quad (1.2.5)$$

In nonequilibrium (non-uniform) systems, the total energy U is no longer a function of other extensive variables such as S , V and N_k , as in (1.1.2), and obviously one cannot define a single temperature for the entire system because it may not uniform.

Box 1.1 The Atmosphere of the Earth.

Blaise Pascal (1623–1662) explained the nature of atmospheric pressure. The pressure at any point in the atmosphere is due to the column of air above it. The atmosphere of the Earth is not in thermodynamic equilibrium: its temperature is not uniform and the amounts of its chemical constituents (N_2 , O_2 , Ar, CO_2 , etc.) are maintained at a nonequilibrium value through cycles of production and consumption.



In general, each of the variables, the total energy U , entropy S , the amount of substance N_k and the volume V , is no longer a function of the other three variables, as in (1.1.2). But this does not restrict in any way our ability to assign an entropy to a system that is not in thermodynamic equilibrium, as long as the temperature is locally well defined.

In texts on classical thermodynamics, when it is sometimes stated that entropy of a nonequilibrium system is not defined, it is meant that S is not a function of the variables U , V and N_k . If the temperature of the system is locally well defined, then indeed the entropy of a nonequilibrium system can be defined in terms of an entropy density, as in (1.2.3).

1.3 Biological and Other Open Systems

Open systems are particularly interesting because in them we see spontaneous self-organization. The most spectacular example of self-organization in open systems is life. Every living cell is an open system that exchanges matter and energy with its exterior. The cells of a leaf absorb energy from the sun and exchange matter by absorbing CO_2 , H_2O and other nutrients and releasing O_2 into the atmosphere. A biological open system can be defined more generally: it could be a single cell, an organ, an organism or an ecosystem. Other examples of open systems can be found in industry; in chemical reactors, for example, raw material and energy are the inputs and the desired and waste products are the outputs.

As noted in the previous section, when a system is not in equilibrium, processes such as chemical reactions, conduction of heat and transport of matter take place so as to drive the system towards equilibrium. And all of these processes generate entropy in accordance with the Second Law (see Figure 1.2). However, this does not mean that the entropy of the system must always increase: the exchange of energy and matter may also result in the net output of entropy in such a way that the entropy of a system is maintained at a low value. One of the most remarkable aspects of nonequilibrium systems that came to light in the twentieth century is the phenomenon of self-organization. Under certain nonequilibrium conditions, systems can spontaneously undergo transitions to organized states, which, in general, are states with lower entropy. For example, nonequilibrium chemical systems can make a transition to a state in which the concentrations of reacting compounds vary periodically, thus becoming a ‘chemical clock’. The reacting chemicals can also spatially organize into patterns with great symmetry. In fact, it can be argued that most of the ‘organized’ behavior we see in nature is created by irreversible processes that dissipate energy and generate entropy. For these reasons, these structures are called **dissipative structures** [1], and we shall study more about them in Chapter 11. In an open system, these organized states could be maintained indefinitely, but only at the expense of exchange of energy and matter and increase of entropy outside the system.

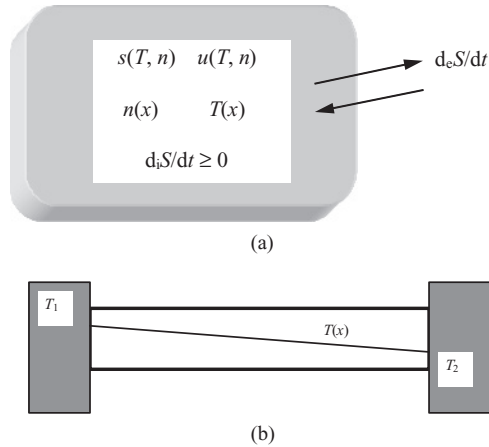


Figure 1.2 (a) In a nonequilibrium system, the temperature and number density $n_k(x)$ may vary with position. The entropy and energy of such a system may be described by an entropy density $s(T, n_k)$ and an energy density $u(T, n_k)$. The total entropy $S = \int_V s[T(x), n_k(x)] dV$, the total energy $U = \int_V u[T(x), n_k(x)] dV$, and the total molenumber $N_k = \int_V n_k(x) dV$. For such a nonequilibrium system, the total entropy S is not a function of U , N and the total volume V . The term $d_i S/dt$ is the rate of change of entropy due to chemical reactions, diffusion, heat conduction and other such irreversible processes; according to the second law, $d_i S/dt$ can only be positive. In an open system, entropy can also change due to exchange of energy and matter; this is indicated by the term $d_e S/dt$, which can be either positive or negative. (b) A system in contact with thermal reservoirs of unequal temperatures is a simple example of a nonequilibrium system. The temperature is not uniform and there is a flow of heat due to the temperature gradient. The term $d_e S/dt$ is related to the exchange of heat at the boundaries in contact with the heat reservoirs, whereas $d_i S/dt$ is due to the irreversible flow of heat within the system

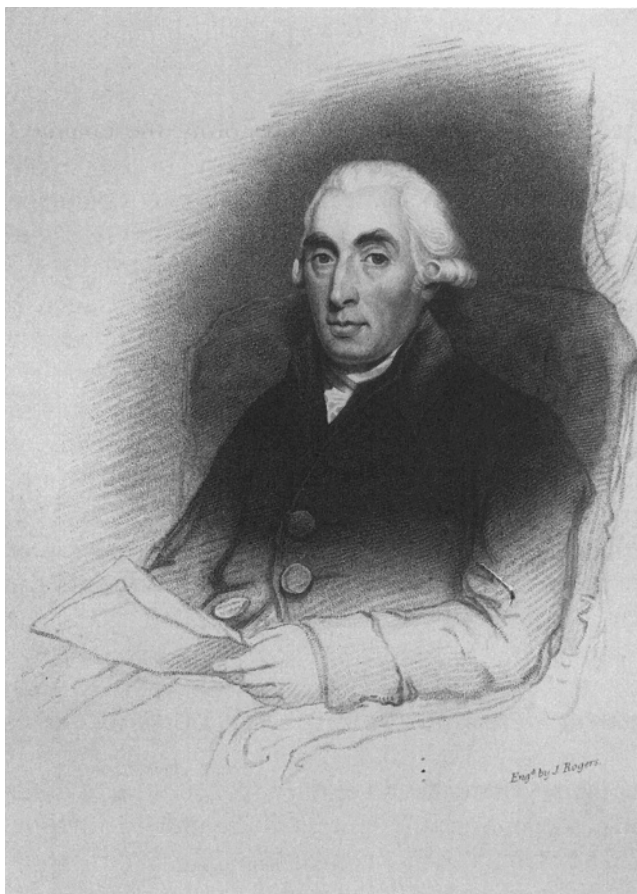
1.4 Temperature, Heat and Quantitative Laws of Gases

During the seventeenth and eighteenth centuries, a fundamental change occurred in our conception of Nature. Nature slowly but surely ceased to be solely a vehicle of God's will, comprehensible only through theology. The new 'scientific' conception of Nature based on rationalism and experimentation gave us a different world view, a view that liberated the human mind from the confines of religious doctrine. In the new view, Nature obeyed simple and universal laws, laws that humans can know and express in the precise language of mathematics. Right and wrong were decided through experiments and observation. It was a new dialogue with Nature. Our questions became experiments, and Nature's answers were consistent and unambiguous.

It was during this time of great conceptual change that a scientific study of the nature of heat began. This was primarily due to the development of the thermometer, which was constructed and used in scientific investigations since the time of Galileo Galilei (1564–1642) [2, 3]. The impact of this simple instrument was considerable. In the words of Sir Humphry Davy (1778–1829), 'Nothing tends to the advancement of knowledge as the application of a new instrument'.

The most insightful use of the thermometer was made by Joseph Black (1728–1799), a professor of medicine and chemistry at Glasgow. Black drew a clear distinction between temperature, or degree of hotness, and the quantity of heat (in terms of current terminology, temperature is an intensive quantity whereas heat is an extensive quantity). His experiments using the newly developed thermometers established the fundamental fact that *the temperatures of all the substances in contact with each other will eventually reach the same value, i.e. systems that can exchange heat will reach a state of thermal equilibrium*. This idea was not easily accepted by his contemporaries because it seems to contradict the ordinary experience of touch, in which a piece of metal felt colder than a piece of wood even after they had been in contact for a very long time. But the thermometer proved this point beyond doubt. With the thermometer, Black discovered **specific heat**, laying to rest the general belief at his time that the amount of heat required to increase the temperature of substance by a given amount depended solely on its mass, not specific to its makeup. He also discovered latent heats of fusion and evaporation of water – the latter with the enthusiastic help from his pupil James Watt (1736–1819) [4].

Though the work of Joseph Black and others established clearly the distinction between heat and temperature, the nature of heat remained an enigma for a long time. Whether heat was an indestructible substance without mass, called the 'caloric', that moved from substance to substance or whether it was a form of microscopic motion was still under debate as late as the nineteenth century. After considerable debate and experimentation it became clear that heat was a form of energy that could be transformed to other forms, and so the caloric theory was abandoned – though we still measure the amount of heat in 'calories', in addition to using the SI units of joules.



Joseph Black (1728–1799) (Reproduced with permission from the Edgar Fahs Smith Collection, University of Pennsylvania Library)

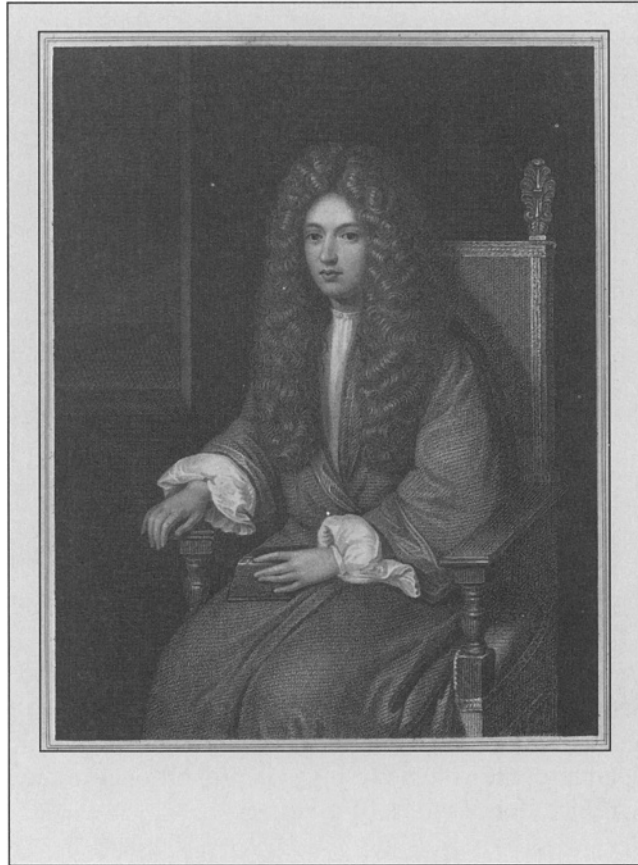
Temperature can be measured by noting the change of a physical property, such as the volume of a fluid (such as mercury), the pressure of a gas or the electrical resistance of a wire, with degree of hotness. This is an *empirical* definition of temperature. In this case, the uniformity of the unit of temperature depends on the uniformity with which the measured property changes as the substance gets hotter. The familiar Celsius scale, which was introduced in the eighteenth century by Anders Celsius (1701–1744), has largely replaced the Fahrenheit scale, which was also introduced in the eighteenth century by Gabriel Fahrenheit (1686–1736). As we shall see in the following chapters, the development of the Second Law of thermodynamics during the middle of the nineteenth century gave rise to the concept of an *absolute scale of temperature* that is independent of material properties. Thermodynamics is formulated in terms of the absolute temperature. We shall denote this absolute temperature by T .

THE LAWS OF GASES

In the rest of this section we will present an overview of the laws of gases without going into much detail. We assume the reader is familiar with the laws of ideal gases and some basic definitions are given in Box 1.2.

One of the earliest quantitative laws describing the behavior of gases was due to Robert Boyle (1627–1691), an Englishman and a contemporary of Isaac Newton (1642–1727). The same law was also discovered by Edmé Mariotte (1620(?)–1684) in France. In 1660, Boyle published his conclusion in his ‘New experiments physico-mechanical, touching the spring of the air and its effects’: at a fixed temperature T , the volume V of a gas was inversely proportional to the pressure p , i.e.:

$$V = \frac{f_i(T)}{p} \quad f_i(T) \text{ is some function of the temperature } T \quad (1.4.1)$$



Robert Boyle (1627–1691) (Reproduced with permission from the Edgar Fahs Smith Collection, University of Pennsylvania Library)

Box 1.2 Basic Definitions.

Pressure is defined as the force per unit area. The pascal is the SI unit of pressure:

$$\text{pascal (Pa)} = 1 \text{ Nm}^{-2}$$

The pressure due to a column of fluid of uniform density ρ and height h equals $h\rho g$, where g is the acceleration due to gravity (9.806 ms^{-2}). The pressure due to the Earth's atmosphere changes with location and time, but it is often close to 10^5 Pa at the sea level. For this reason, a unit called the **bar** is defined:

$$1 \text{ bar} = 10^5 \text{ Pa} = 100 \text{ kPa}$$

The atmospheric pressure at the Earth's surface is also nearly equal to the pressure due to a 760 mm column of mercury. For this reason, the following units are defined:

torr = pressure due to 1.00 mm column of mercury

$$1 \text{ atmosphere (atm)} = 760 \text{ torr} = 101.325 \text{ kPa}$$

1 atm equals approximately 10 N cm^{-2} (1 kg weight/cm^2 or 15 lb/inch^2). The atmospheric pressure decreases exponentially with altitude (see Box 1.1).

Temperature is usually measured in kelvin (K), Celsius ($^{\circ}\text{C}$) or Fahrenheit ($^{\circ}\text{F}$). The Celsius and Fahrenheit scales are empirical, whereas (as we shall see in Chapter 3) the kelvin scale is an absolute scale based on the Second Law of thermodynamics: 0 K is the absolute zero, the lowest possible temperature. Temperatures measured in these scales are related as follows:

$$T/^{\circ}\text{C} = (5/9)[(T/^{\circ}\text{F}) - 32] \quad T/\text{K} = (T/^{\circ}\text{C}) + 273.15$$

On the Earth, the highest recorded temperature is 57.8°C , or 136°F ; it was recorded in El Azizia, Libiya, in 1922. The lowest recorded temperature is -88.3°C , or -129°F ; it was recorded in Vostok, Antarctica. In the laboratory, sodium gas has been cooled to temperatures as low as 10^{-9} K , and temperatures as high as 10^8 K have been reached in nuclear fusion reactors.

Heat was initially thought to be an indestructible substance called the **caloric**. According to this view, caloric, a fluid without mass, passed from one body to another, causing changes in temperature. However, in the 19th century it was established that heat was not an indestructible caloric but a form of energy that can convert to other forms of energy (see Chapter 2). Hence, heat is measured in the units of energy. In this text we shall mostly use the SI units in which heat is measured in **joules**, though the calorie is an often-used unit of heat. A calorie was originally defined as the amount of heat required to increase the temperature of 1 g of water from 14.5°C to 15.5°C . The current practice is to *define* a thermo-chemical calorie as 4.184 J.

The **gas constant** R appears in the ideal gas law, $pV = NRT$. Its numerical values are:

$$R = 8.314 \text{ J K mol}^{-1} \text{ (or Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1}) = 0.08314 \text{ bar L K}^{-1} \text{ mol}^{-1} \\ = 0.0821 \text{ atm L K}^{-1} \text{ mol}^{-1}$$

The **Avogadro number** $N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$. The **Boltzmann constant** $k_B = R/N_A = 1.3807 \times 10^{-23} \text{ J K}^{-1}$.

(Though the temperature that Boyle knew and used was the empirical temperature, as we shall see in Chapter 3, it is appropriate to use the absolute temperature T in the formulation of the law of ideal gases. To avoid excessive notation we shall use T whenever it is appropriate.) Boyle also advocated the view that heat was not an indestructible substance (caloric) that passed from one object to another but was ‘. . . intense commotion of the parts . . .’ [5].

At constant pressure, the variation of volume with temperature was studied by Jacques Charles (1746–1823) who established that

$$\frac{V}{T} = f_2(p) \quad f_2(p) \text{ is some function of the pressure } p \quad (1.4.2)$$

In 1811, Amedeo Avogadro (1776–1856) announced his hypothesis that, under conditions of the same temperature and pressure, equal volumes of all gases contained equal numbers of molecules. This hypothesis greatly helped in explaining the changes in pressure due to chemical reactions in which the reactants and products were gases. It implied that, at constant pressure and temperature, the volume of a gas is proportional to the amount of the gas. Hence, in accordance with Boyle’s law (1.4.1), for N moles of a gas:

$$V = N \frac{f_1(T)}{p} \quad (1.4.3)$$



Jacques Charles (1746–1823) (Reproduced with permission from the Edgar Fahs Smith Collection, University of Pennsylvania Library)

A comparison of (1.4.1), (1.4.2) and (1.4.3) leads to the conclusion that $f_i(T)$ is proportional to T and to the well-known **law of ideal gases**:

$$pV = NRT \quad (1.4.4)$$

in which R is the gas constant. Note: $R = 8.31441 \text{ J K}^{-1} \text{ mol}^{-1}$ (or $\text{Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1}$) = $0.08314 \text{ bar L K}^{-1} \text{ mol}^{-1} = 0.0821 \text{ atm L K}^{-1} \text{ mol}^{-1}$.

As more gases were identified and isolated by the chemists during the eighteenth and nineteenth centuries, their properties were studied. It was found that many obeyed Boyle's law approximately. For most gases, this law describes the experimentally observed behavior fairly well for pressures to about 10 atm. As we shall see in the next section, the behavior of gases under a wider range of pressures can be described by modifications of the ideal gas law that take into consideration the molecular size and intermolecular forces.

For a *mixture* of ideal gases, we have the **Dalton's law of partial pressures**, according to which the pressure exerted by each component of the mixture is independent of the other components of the mixture, and each component obeys the ideal gas equation. Thus, if p_k is the partial pressure due to component k , we have

$$p_k V = N_k RT \quad (1.4.5)$$

Joseph-Louis Gay-Lussac (1778–1850), who made important contributions to the laws of gases, discovered that a dilute gas expanding into vacuum did so without change in temperature. James Prescott Joule (1818–1889) also verified this fact in his series of experiments that established the equivalence between mechanical energy and heat. In Chapter 2 we will discuss Joule's work and the law of conservation of energy in detail. When the concept of energy and its conservation was established, the implication of this observation became clear. Since a gas expanding into vacuum does not do any work during the processes of expansion, its energy does not change. The fact that the temperature does not change during expansion into vacuum while the volume and pressure do change implies that the energy of a given amount of ideal gas depends only on its temperature T , not on its volume or pressure. Also, a change in the ideal gas temperature occurs only when its energy is changed through exchange of heat or mechanical work. These observations lead to the conclusion that the energy of a given amount of ideal gas is a function only of its temperature T . Since the amount of energy (heat) needed to increase the temperature of an ideal gas is proportional to the amount of the gas, the energy is proportional to N , the amount of gas in moles. Thus, the energy of the ideal gas, $U(T, N)$, is a function only of the temperature T and the amount of gas N . It can be written as

$$U(T, N) = NU_m(T) \quad (1.4.6)$$

in which U_m is the total internal energy per mole, or **molar energy**. For a mixture of gases the total energy is the sum of the energies of the components:



Joseph-Louis Gay-Lussac (1778–1850) (Reproduced with permission from the Edgar Fahs Smith Collection, University of Pennsylvania Library)

$$U(T, N) = \sum_k U_k(T, N_k) = \sum_k N_k U_{mk}(T) \quad (1.4.7)$$

in which the components are indexed by k . Later developments established that

$$U_m = cRT + U_0 \quad (1.4.8)$$

to a good approximation, in which U_0 is a constant. For monatomic gases, such as He and Ar, $c = 3/2$; for diatomic gases, such as N_2 and O_2 , $c = 5/2$. The factor c can be deduced from the kinetic theory of gases, which relates the energy U to the motion of a gas molecules.

The experiments of Gay-Lussac also showed that, at constant pressure, the relative change in volume $\delta V/V$ due to increase in temperature had nearly the same value

for all dilute gases; it was equal to $1/273^\circ\text{C}^{-1}$. Thus, a gas thermometer in which the volume of a gas at constant pressure was the indicator of temperature t had the quantitative relation

$$V = V_0(1 + \alpha t) \quad (1.4.9)$$

in which $\alpha = 1/273$ is the coefficient of expansion at constant pressure. In Chapter 3 we will establish the relation between the temperature t , measured by the gas thermometer, and the absolute temperature T .

The above empirical laws of gases played an important part in the development of thermodynamics. They are the testing ground for any general principle and are often used to illustrate these principles. They were also important for developments in the atomic theory of matter and chemistry.

For most gases, such as CO_2 , N_2 , and O_2 , the ideal gas law was found to be an excellent description of the experimentally observed relation between p , V and T only for pressures up to about 20 atm. Significant improvements in the laws of gases did not come until the molecular nature of gases was understood. In 1873, more than 200 years after Boyle published his famous results, Johannes Diderik van der Waals (1837–1923) proposed an equation in which he incorporated the effects of attractive forces between molecules and molecular size on the pressure and volume of a gas. We shall study van der Waals' equation in detail in the next section, but here we would like to familiarize the reader with its basic form so that it can be compared with the ideal gas equation. According to van der Waals, p , V , N and T are related by

$$\left(p + a \frac{N^2}{V^2}\right)(V - Nb) = NRT \quad (1.4.10)$$

In this equation, the constant a is a measure of the attractive forces between molecules and b is proportional to the size of the molecules. For example, the values of a and b for helium are smaller than the corresponding values for a gas such as CO_2 . The values of the constants a and b for some of the common gases are given in Table 1.1. Unlike the ideal gas equation, this equation explicitly contains molecular parameters and it tells us how the ideal gas pressure and volume are to be 'corrected' because of the molecular size and intermolecular forces. We shall see how van der Waals arrived at this equation in the next section. At this point, students are encouraged to pause and try deriving this equation on their own before proceeding to the next section.

As one might expect, the energy of the gas is also altered due to forces between molecules. In Chapter 6 we will see that the energy U_{vw} of a van der Waals gas can be written as

$$U_{\text{vw}} = U_{\text{ideal}} - a \left(\frac{N}{V}\right)^2 V \quad (1.4.11)$$

Table 1.1 Van der Waals constants a and b and critical constants T_c , p_c and V_{mc} for selected gases

Gas	$a/\text{bar L}^2 \text{mol}^{-2}$	$b/\text{L mol}^{-1}$	T_c/K	p_c/bar	$V_{mc}/\text{L mol}^{-1}$
Acetylene (C_2H_2)	4.516	0.0522	308.3	61.39	0.113
Ammonia (NH_3)	4.225	0.0371	405.5	113.5	0.072
Argon (Ar)	1.355	0.0320	150.9	49.55	0.075
Carbon dioxide (CO_2)	3.658	0.0429	304.1	73.75	0.094
Carbon monoxide (CO)	1.472	0.0395	132.9	34.99	0.093
Chlorine (Cl_2)	6.343	0.0542	416.9	79.91	0.123
Ethanol ($\text{C}_2\text{H}_5\text{OH}$)	12.56	0.0871	513.9	61.32	0.167
Helium (He)	0.0346	0.0238	5.19	2.22	0.057
Hydrogen (H_2)	0.245	0.0265	32.97	12.93	0.065
Hydrogen chloride (HCl)	3.700	0.0406	324.7	83.1	0.081
Methane (CH_4)	2.300	0.0430	190.5	46.04	0.099
Nitric oxide (NO)	1.46	0.0289	180	64.8	0.058
Nitrogen (N_2)	1.370	0.0387	126.2	33.9	0.090
Oxygen (O_2)	1.382	0.0319	154.59	50.43	0.073
Propane (C_3H_8)	9.385	0.0904	369.82	42.50	0.203
Sulfur dioxide (SO_2)	6.865	0.0568	430.8	78.84	0.122
Sulfur hexafluoride (SF_6)	7.857	0.0879	318.69	37.7	0.199
Water (H_2O)	5.537	0.0305	647.14	220.6	0.056

Source: An extensive listing of van der Waals constants can be found in D.R. Lide (ed.), *CRC Handbook of Chemistry and Physics*, 75th edition. 1994, CRC Press: Ann Arbor, MI.

The van der Waals equation was a great improvement over the ideal gas law, in that it described the observed liquefaction of gases and the fact that, above a certain temperature, called the critical temperature, gases could not be liquefied regardless of the pressure, as we will see in the following section. But still, it was found that the van der Waals equation failed at very high pressures (Exercise 1.13). The various improvements suggested by Clausius, Berthelot and others are discussed in Chapter 6.

1.5 States of Matter and the van der Waals Equation

The simplest transformations of matter caused by heat is the melting of solids and the vaporization of liquids. In thermodynamics, the various states of matter (solid, liquid, gas) are often referred to as **phases**. Every compound has a definite temperature T_m at which it melts and a definite temperature T_b at which it boils. In fact, this property can be used to identify a compound or separate the constituents of a mixture. With the development of the thermometer, these properties could be studied with precision. As noted earlier, Joseph Black and James Watt discovered another interesting phenomenon associated with the changes of phase: at the melting or the boiling temperature, the heat supplied to a system does not result in an increase in temperature; it only has the effect of converting the substance from one phase to another. This heat that lays ‘latent’ or hidden without increasing the temperature was called the **latent heat**. When a liquid solidifies, for

example, this heat is given out to the surroundings. This phenomenon is summarized in Figure 1.3.

Clearly, the ideal gas equation, good as it is in describing many properties of gases, does not help us to understand why gases convert to liquids when compressed. An ideal gas remains a gas at all temperatures and its volume can be compressed without limit. In 1822, Gay-Lussac's friend Cagniard de la Tour (1777–1859) discovered that a gas does not liquefy when compressed unless its temperature is below a critical value, called the **critical temperature**. This behavior of gases was studied in detail by Thomas Andrews (1813–1885), who published his work in 1869. During this time, atomic theory was gaining more and more ground, while Maxwell, Clausius and others advanced the idea that heat was related to molecular motion and began to find an explanation of the properties of gases, such as pressure and viscosity, in the random motion of molecules. It was in this context that Johannes Diderik van der Waals (1837–1923) sought a single equation of state for the liquid and gas phases of a substance. In 1873, van der Waals presented his doctoral thesis titled 'On the continuity of the gas and liquid state', in which he brilliantly explained the conver-

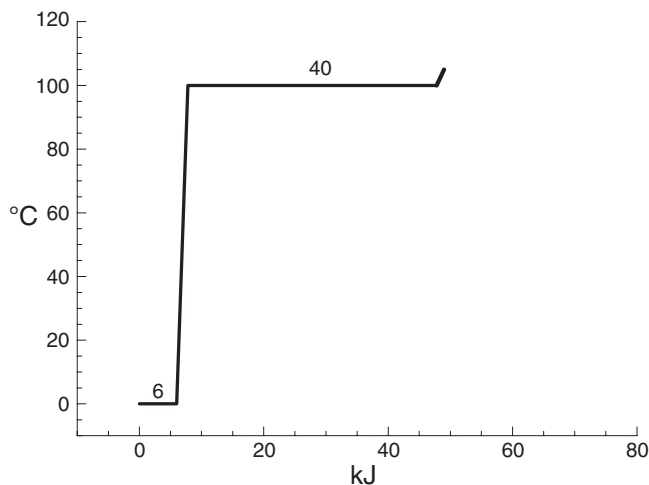


Figure 1.3 The change in temperature of 1 mol of H_2O versus amount of heat, at a pressure of 1 atm. At the melting point, absorption of heat does not increase the temperature until all the ice melts. It takes about 6 kJ to melt 1 mol of ice, the 'latent heat' discovered by Joseph Black. Then the temperature increases until the boiling point is reached, at which point it remains constant until all the water turns to steam. It takes about 40 kJ to convert 1 mol of water to steam

sion of a gas to a liquid and the existence of critical temperature as the consequence of forces between molecules and molecular volume.

Van der Waals realized that two main factors modify the ideal gas equation: the effect of molecular volume and the effect of intermolecular forces. Since molecules have a nonzero volume, the volume of a gas cannot be reduced to an arbitrarily small value by increasing p . The corresponding modification of the ideal gas equation would be $(V - bN) = NRT/p$, in which the constant b is the limiting volume of 1 mol of the gas, as $p \rightarrow \infty$. The constant b is sometimes called the ‘excluded volume’. The effect of intermolecular forces, van der Waals noted, is to decrease the pressure, as illustrated in Figure 1.4. Hence, the above ‘volume-corrected’ equation is further modified to

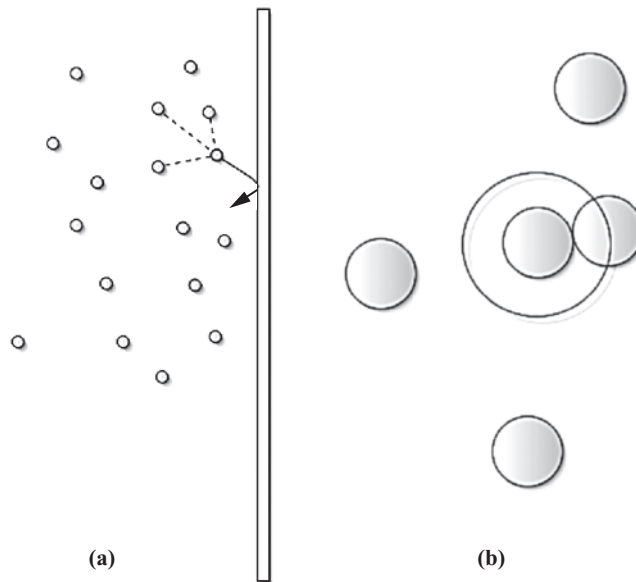
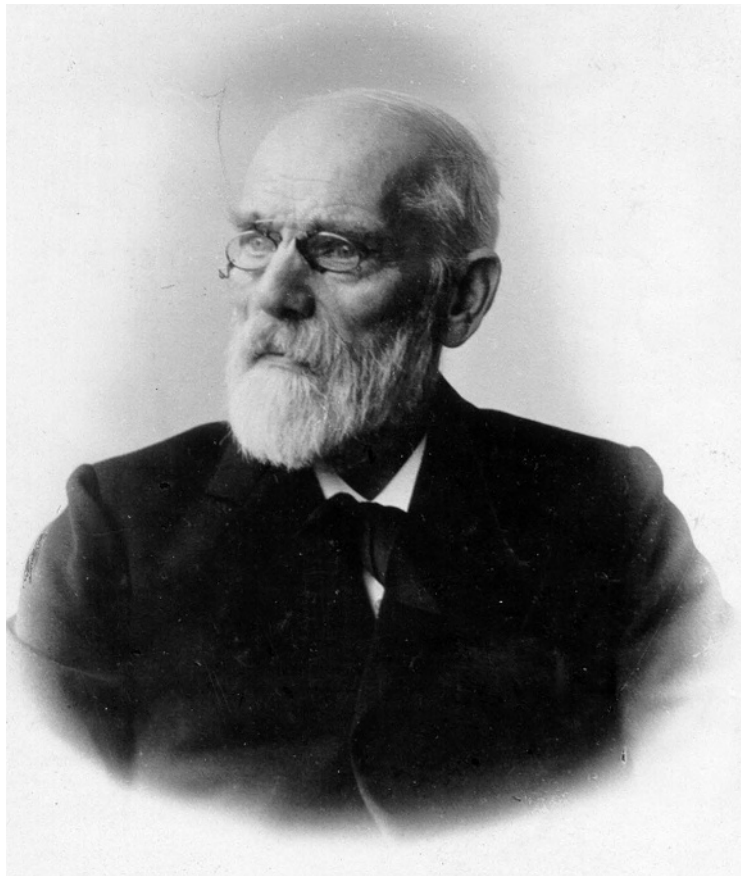


Figure 1.4 Van der Waals considered molecular interaction and molecular size to improve the ideal gas equation. (a) The pressure of a real gas is less than the ideal gas pressure because intermolecular attraction decreases the speed of the molecules approaching the wall. Therefore, $p = p_{\text{ideal}} - \delta p$. (b) Since the molecules of a gas have a nonzero size, the volume available to molecules is less than the volume of the container. Each molecule has a volume around it that is not accessible to other molecules because the distance between the centers of the molecules cannot be less than the sum of the molecular radii. As a result, the volume of the gas cannot decrease below this ‘excluded volume’. Thus, V in the ideal gas equation is replaced with $(V - bN)$ so that as $p \rightarrow \infty$, $V \rightarrow bN$



Johannes van der Waals (1837–1923) (Reproduced with permission from the Edgar Fahs Smith Collection, University of Pennsylvania Library)

$$p = \frac{NRT}{V - bN} - \delta p$$

Next, van der Waals related the factor δp to the number density N/V using the kinetic theory of gases, which showed how molecular collisions with container walls cause pressure. Pressure depends on the number of molecules that collide with the walls per unit area, per unit time; therefore, it is proportional to the number density N/V (as can be seen from the ideal gas equation). In addition, each molecule that is close to a container wall and moving towards it experiences the retarding attractive forces of molecules behind it (see Figure 1.4); this force would also be

proportional to number density N/V ; hence, δp should be proportional to two factors of N/V , so that one may write $\delta p = a(N/V)^2$, in which the constant a is a measure of the intermolecular forces. The expression for pressure that van der Waals proposed is

$$p = \frac{NRT}{V - bN} - a \frac{N^2}{V^2}$$

or, as it is usually written:

$$\left(p + a \frac{N^2}{V^2} \right) (V - Nb) = NRT \quad (1.5.1)$$

This turns out to be an equation of state for both the liquid and the gas phase. Van der Waals' insight revealed that the two phases, which were considered distinct, can, in fact, be described by a single equation. Let us see how.

For a given T , a p - V curve, called the **p - V isotherm**, can be plotted. Such isotherms for the van der Waals equation (1.5.1) are shown in Figure 1.5. They show an important feature: the **critical temperature** T_c studied by Thomas Andrews. If the temperature T is greater than T_c then the p - V curve is always single valued, much like the ideal gas isotherm, indicating that there is no transition to the liquid state. But for lower temperatures, $T < T_c$, the isotherm has a maximum and a minimum. There are two extrema because the van der Waals equation is cubic in V . This region represents a state in which the liquid and the gas phases coexist in thermal equilibrium. On the p - V curve shown in Figure 1.5, the gas begins to condense into a liquid at point A; the conversion of gas to liquid continues until point C, at which all the gas has been converted to liquid. Between A and C, the actual state of the gas does not follow the path AA'BB'C along the p - V curve because this curve represents an unstable supersaturated state in which the gas condenses to a liquid. The actual state of the gas follows the straight line ABC. As T increases, the two extrema move closer and finally coalesce at $T = T_c$. For a mole of a gas, the point (p, V) at which the two extrema coincide is defined as the **critical pressure** p_c and **critical molar volume** V_{mc} . For T higher than T_c , there is no **phase transition** from a gas to a liquid; the distinction between gas and liquid disappears. (This does not happen for a transition between a solid and a liquid because a solid is more ordered than a liquid; the two states are always distinct.) Experimentally, the **critical constants** p_c , V_{mc} and T_c can be measured and they are tabulated (Table 1.1 lists some examples). We can relate the critical parameters to the van der Waals parameters a and b by the following means. We note that if we regard $p(V, T)$ as a function of V , then, for $T < T_c$, the derivative $(\partial p / \partial V)_T = 0$ at the two extrema. As T increases, at the point where the two extrema coincide, i.e. at the critical point $T = T_c$, $p = p_c$ and $V = V_{mc}$, we have an **inflection point**. At an inflection point, the first and second derivatives of a function vanish. Thus, at the critical point:

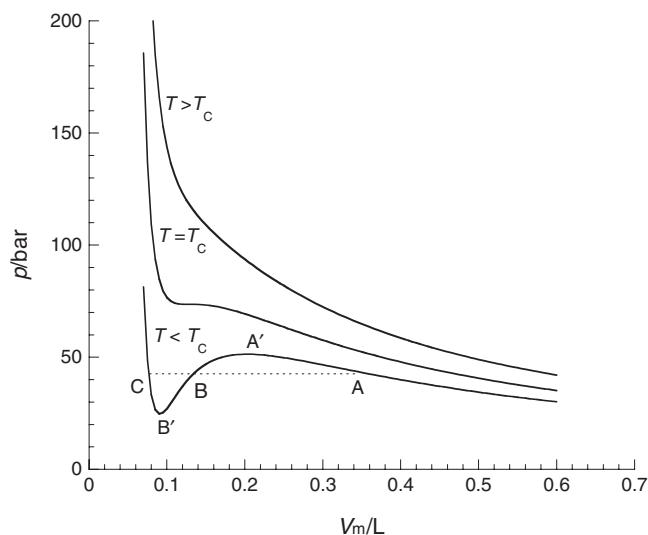


Figure 1.5 The van der Waals isotherms for CO_2 ($T_c = 304.14 \text{ K}$). When $T < T_c$, there is a region $AA'BB'C$ in which, for a given value of p , the van der Waals equation does not specify a unique volume V ; in this region, the gas transforms to a liquid. The segment $A'BB'$ is an unstable region; states corresponding to points on this segment are not experimentally realizable. Experimentally realizable states are on the dotted line ABC . The observed state follows the path ABC . A detailed description of this region is discussed in Chapter 7

$$\left(\frac{\partial p}{\partial V}\right)_T = 0 \quad \left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0 \quad (1.5.2)$$

Using these equations one can obtain the following relations between the critical constants and the constants a and b (Exercise 1.17):

$$a = \frac{9}{8} RT_c V_{mc} \quad b = \frac{V_{mc}}{3} \quad (1.5.3)$$

in which V_{mc} is the molar critical volume. Conversely, we can write the critical constants in terms of the van der Waals constants a and b (Exercise 1.17):

$$T_c = \frac{8a}{27Rb} \quad p_c = \frac{a}{27b^2} \quad V_{mc} = 3b \quad (1.5.4)$$

Table 1.1 contains the values of a and b and critical constants for some gases.

THE LAW OF CORRESPONDING STATES

Every gas has a characteristic temperature T_c , pressure p_c , and volume V_{mc} which depend on the molecular size and intermolecular forces. In view of this, one can introduce dimensionless **reduced variables** defined by

$$T_r = \frac{T}{T_c} \quad V_{mr} = \frac{V}{V_{mc}} \quad p_r = \frac{p}{p_c} \quad (1.5.5)$$

Van der Waals showed that, if his equation is rewritten in terms of these reduced variables, one obtains the following ‘universal equation’ (Exercise 1.18), which is independent of the constants a and b :

$$p_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2} \quad (1.5.6)$$

This is a remarkable equation because it implies that gases have corresponding states: *at a given value of reduced volume and reduced temperature, all gases have the same reduced pressure.* This statement is called the **law of corresponding states** or **principle of corresponding states**, which van der Waals enunciated in an 1880 publication. Noting that the reduced variables are defined wholly in terms of the experimentally measured critical constants, p_c , V_{mc} and T_c , he conjectured that the principle has a general validity, independent of his equation of state. According to the principle of corresponding states, then, at a given T_r and V_{mr} the reduced pressures p_r of all gases should be the same (which is not necessarily the value given by (1.5.6)).

The deviation from ideal gas behavior is usually expressed by defining a **compressibility factor**:

$$Z = \frac{V_m}{V_{m,\text{ideal}}} = \frac{pV_m}{RT}$$

which is the ratio between the actual volume of a gas and that of the ideal gas at a given T and p . Ideal gas behavior corresponds to $Z = 1$. For real gases, at low pressures and temperatures, it is found that $Z < 1$; but for higher pressures and temperatures, $Z > 1$. It is also found that there is a particular temperature, called the Boyle temperature, at which Z is nearly 1 and the relationship between p and V is close to that of an ideal gas (Exercise 1.11). One way to verify the law of corresponding states experimentally is to plot Z as a function of reduced pressure p_r at a given reduced temperature T_r . The compressibility factor Z can be written in terms of the

reduced variables: $Z = (p_c V_{mc}/RT_c)(p_r V_{mr}/T_r)$; if the value of $(p_c V_{mc}/RT_c) = Z_c$ is the same for all gases (for the van der Waals gas $Z_c = (p_c V_{mc}/RT_c) = 3/8$ (Exercise 1.18)) then Z is a function of the reduced variables. Experimental values of Z for different gases could be plotted as a functions of p_r for a fixed T_r . If the law of corresponding states is valid, then at a given value of T_r and p_r the value of Z must be the same for all gases. The plot shown in Figure 1.6 indicates that the validity of the law of corresponding states is fairly general.

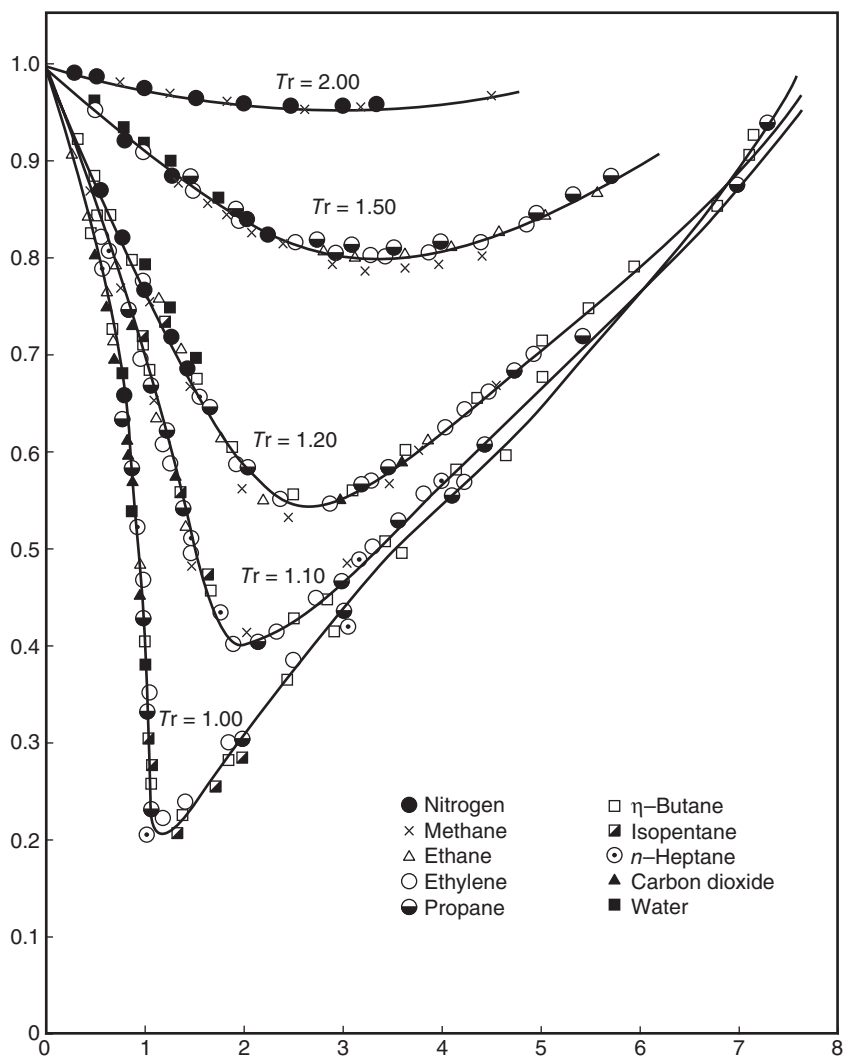


Figure 1.6 Compressibility factor Z as a function of reduced van der Waals' variables. (Reprinted with permission from Goug-Jen Su, *Industrial and Engineering Chemistry*, **38** (1946) 803. Copyright 1946, American Chemical Society)

The van der Waals equation and the law of corresponding states, however, have their limitations, which van der Waals himself noted in his 1910 Nobel Lecture:

But closer examination showed me that matters were not so simple. To my surprise I realized that the amount by which the volume must be reduced is variable, that in extremely dilute state this amount, which I notated b , is fourfold the molecular volume* – but that this amount decreases with decreasing external volume and gradually falls to about half. But the law governing this decrease has still not been found.

Van der Waals also noted that the experimental value of $Z_c = (p_c V_{mc}/RT_c)$ for most gases was not $3/8 = 0.375$, as predicted by his equation, but was around 0.25 (0.23 for water and 0.29 for Ar). Furthermore, it became evident that the van der Waals constant a depended on the temperature – Rudolf Clausius even suggested that a was inversely proportional to T . Thus, the parameters a and b might themselves be functions of gas density and temperature. As a result, a number of alternative equations have been proposed for the description of real gases. For example, engineers and geologists often use the following equation, known as the **Redlich–Kwong equation**:

$$p = \frac{NRT}{V-b} - \frac{a}{\sqrt{T}} \frac{N^2}{V(V-Nb)} = \frac{RT}{V_m-b} - \frac{a}{\sqrt{T}} \frac{1}{V_m(V_m-b)} \quad (1.5.7)$$

The constants a and b in this equation differ from those in the van der Waals equation; they can be related to the critical constants and they are tabulated just as the van der Waals a and b are. We will discuss other similar equations used to describe real gases in Chapter 6.

The limitation of van der Waals-type equations and the principle of corresponding states lies in the fact that molecular forces and volume are quantified with just two parameters, a and b . As explained below, two parameters can characterize the forces between small molecules fairly well, but larger molecules require more parameters.

MOLECULAR FORCES AND THE LAW OF CORRESPONDING STATES

From a molecular point of view, the van der Waals equation has two parameters, a and b , that describe molecular forces, often called **van der Waals' forces**. These forces are attractive when the molecules are far apart but are repulsive when they come into contact, thus making the condensed state (liquid or solid) hard to compress. It is the repulsive core that gives the molecule a nonzero volume. The typical potential energy between two molecules is expressed by the so-called Lennard–Jones energy:

*Molecular volume is the actual volume of the molecules ($N_A 4\pi r^3/3$ for a mole of spherical molecules of radius r).

$$U_{\text{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (1.5.8)$$

Figure 1.7 shows a plot of this potential energy as a function of the distance r between the centers of the molecules. As the distance between the molecules decreases, so U_{LJ} decreases, reaches a minimum, and sharply increases. The decreasing part of U_{LJ} is due to the term $-(\sigma/r)^6$, which represents an attractive force, and the sharply increasing part is due to the term $(\sigma/r)^{12}$, which represents a repulsive core. The Lennard–Jones energy reaches a minimum value of $-\epsilon$ when $r = 2^{1/6}\sigma$ (Exercise 1.20). The two van der Waals parameters, a and b , are related to ϵ and σ respectively, the former being a measure of the molecular attractive force and the latter a measure of the molecular size. In fact, using the principles of statistical thermodynamics, for a given ϵ and σ the values of a and b can be calculated. Such a relationship between the molecular interaction potential and the parameters in the van der Waals equation of state gives us an insight into the limitations of the law of corresponding states, which depends on just two parameters, a and b . If more than two parameters are needed to describe the forces between two molecules adequately, then we can also expect the equation of state to depend on more than two parameters. Lennard–Jones-type potentials that use two parameters are good approximations for small

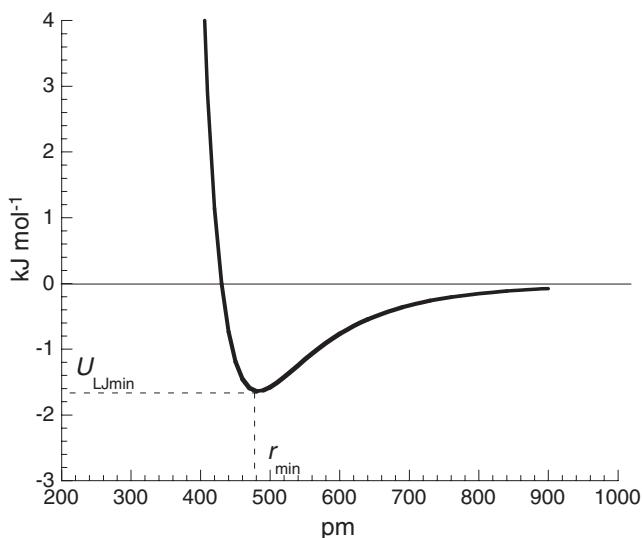


Figure 1.7 Lennard–Jones ‘6–12’ potential energy between two molecules as a function of the distance between their centers. It is common to specify ϵ in units of kelvin using the ratio ϵ/k_{B} , in which k_{B} is the Boltzmann constant. The assumed Lennard–Jones parameter values for the above curve are $\epsilon/k_{\text{B}} = 197 \text{ K}$ (which corresponds to $\epsilon N_{\text{A}} = 1.638 \text{ kJ mol}^{-1}$) and $\sigma = 430 \text{ pm}$. These values represent the approximate interaction energy between CO_2 molecules

molecules; for larger molecules the interaction energy depends not only on the distance between the molecules, but also on their relative orientation and other factors that require more parameters. Thus, significant deviation from the law of corresponding states can be observed for larger molecules.

1.6 An Introduction to Kinetic Theory of Gases

When Robert Boyle published his study on the nature of the ‘spring of the air’ (what we call pressure today) and argued that heat was an ‘intense commotion of the parts’, he did not know how pressure actually arose. During the seventeenth century, a gas was thought to be a continuous substance. A century later, Daniel Bernoulli (1700–1782) published the idea that the mechanism that caused pressure is the rapid collisions of molecules with the walls of the container [5]. In his 1738 publication, *Hydrodynamica*, Bernoulli presented his calculation of the average force on the container walls due to molecular collisions and obtained a simple expression for the pressure: $p = (mnv_{\text{avg}}^2/3)$, in which m is the molecular mass, n is the number of molecules per unit volume and v_{avg} is the average speed of molecules. At that time, no one had any idea how small gas molecules were or how fast they moved, but Bernoulli’s work was an important step in explaining the properties of a gas in terms of molecular motion. It was the beginnings of a subject that came to be known as the kinetic theory of gases.

The kinetic theory of gases was largely developed in the late nineteenth century. Its goal was to explain the observed properties of gases by analyzing the random motion of molecules. Many quantities, such as pressure, diffusion constant and the coefficient of viscosity, could be related to the average speed of molecules, their mass, size, and the average distance they traversed between collisions (called the mean free path). As we shall see in this section, the names of James Clerk Maxwell (1831–1879) and Ludwig Boltzmann (1844–1906) are associated with some of the basic concepts in this field, while, as is often the case in science, several others contributed to its development [4, 5]. In this introductory section we shall deal with some elementary aspects of kinetic theory, such as the mechanism that causes pressure and the relation between average kinetic energy and temperature.

KINETIC THEORY OF PRESSURE

As Daniel Bernoulli showed, using the basic concepts of force and randomness, it is possible to relate the pressure of a gas to molecular motion: pressure is the average force per unit area exerted on the walls by colliding molecules.

We begin by noting some aspects of the random motion of molecules. First, if all directions have the same physical properties, then we must conclude that motion along all directions is equally probable: the properties of molecules moving in one direction will be the same as the properties of molecules moving in any other direction. Let us assume the average speed of the gas molecules is v_{avg} . We denote its x , y and z components of the by $v_{x\text{avg}}$, $v_{y\text{avg}}$, and $v_{z\text{avg}}$. Thus:

$$v_{\text{avg}}^2 = v_{x \text{ avg}}^2 + v_{y \text{ avg}}^2 + v_{z \text{ avg}}^2 \quad (1.6.1)$$

Because all directions are equivalent, we must have

$$v_{x \text{ avg}}^2 = v_{y \text{ avg}}^2 = v_{z \text{ avg}}^2 = \frac{v_{\text{avg}}^2}{3} \quad (1.6.2)$$

The following quantities are necessary for obtaining the expression for pressure:

$$\begin{aligned} N &= \text{amount of gas in moles} \\ V &= \text{gas volume} \\ M &= \text{Molar mass of the gas} \\ m &= \text{mass of a single molecule} = M/N_A \\ n &= \text{number of molecules per unit volume} = NN_A/V \\ N_A &= \text{Avogadro number} \end{aligned} \quad (1.6.3)$$

Now we calculate the pressure by considering the molecular collisions with the wall. In doing so, we will approximate the random motion of molecules with molecules moving with an average speed v_{avg} . (A rigorous derivation gives the same result.) Consider a layer of a gas, of thickness Δx , close to the wall of the container (see Figure 1.8). When a molecule collides with the wall, which we assume is perpendicular to the x -axis, the change in momentum of the molecule in the x direction equals $2mv_{x \text{ avg}}$. In the layer of thickness Δx and area A , because of the randomness of molecular motion, about half the molecules will be moving towards the wall; the rest will be moving away from the wall. Hence, in a time $\Delta t = \Delta x/v_{\text{avg}}$ about half the molecules in the layer will collide with the wall. The number of molecules in the

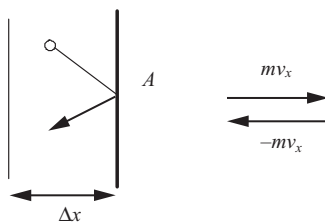


Figure 1.8 Rapid collisions of gas molecules with the walls of the container give rise to pressure. By computing the average momentum transferred to the wall by colliding molecules, pressure can be related to the average of the square of molecular velocity

layer is $(\Delta x A)n$ and the number of molecules colliding with the walls is $(\Delta x A)n/2$. Now, since each collision imparts a momentum $2mv_{x\text{avg}}$, in a time Δt , the total momentum imparted to the wall is $2mv_{x\text{avg}}(\Delta x A)n/2$. Thus, the average force F on the wall of area A is

$$F = \frac{\text{Momentum imparted}}{\Delta t} = \frac{2mv_{x\text{avg}}\Delta x A n}{\Delta t \cdot 2} = \frac{mv_{x\text{avg}}\Delta x A n}{(\Delta x/v_{x\text{avg}})} = mv_{x\text{avg}}^2 n A \quad (1.6.4)$$

Pressure p , which is the force per unit area, is thus

$$p = \frac{F}{A} = mv_{x\text{avg}}^2 n \quad (1.6.5)$$

Since the direction x is arbitrary, it is better to write this expression in terms of the average speed of the molecule rather than its x component. By using (1.6.2) and the definitions (1.6.3), we can write the pressure in terms the macroscopic variables M , V and N :

$$p = \frac{1}{3} mnv_{\text{avg}}^2 = \frac{1}{3} M \frac{N}{V} v_{\text{avg}}^2 \quad (1.6.6)$$

This expression relates the pressure to the square of the average speed. A rigorous description of the random motion of molecules leads to the same expression for the pressure with the understanding that v_{avg}^2 is to be interpreted as the average of the square of the molecular velocity, a distinction that will become clear when we discuss the Maxwell velocity distribution. When Daniel Bernoulli published the above result in 1738, he did not know how to relate the molecular velocity to temperature; that connection had to wait until Avogadro stated his hypothesis in 1811 and the formulation of the ideal gas law based on an empirical temperature that coincides with the absolute temperature that we use today (see Equation (1.4.9)). On comparing expression (1.6.6) with the ideal gas equation, $pV = NRT$, we see that

$$RT = \frac{1}{3} M v_{\text{avg}}^2. \quad (1.6.7)$$

Using the Boltzmann constant $k_B = R/N_A = 1.3807 \times 10^{-23} \text{ J K}^{-1}$ and noting $M = mN_A$, we can express (1.6.7) as a relation between the kinetic energy and temperature:

$$\frac{1}{2} mv_{\text{avg}}^2 = \frac{3}{2} k_B T \quad (1.6.8)$$

This is a wonderful result because it relates temperature to molecular motion, in agreement with Robert Boyle's intuition. It shows us that the average kinetic energy

of a molecule equals $3k_B T/2$. It is an important step in our understanding of the meaning of temperature at the molecular level.

From (1.6.8) we see that the total kinetic energy of 1 mol of a gas equals $3RT/2$. Thus, for monatomic gases, whose atoms could be thought of as point particles that have neither internal structure nor potential energy associated with intermolecular forces (He and Ar are examples), the total molar energy of the gas is entirely kinetic; this implies $U_m = 3RT/2$. The molar energy of a gas of polyatomic molecules is larger. A polyatomic molecule has additional energy in its rotational and vibrational motion. In the nineteenth century, as kinetic theory progressed, it was realized that random molecular collisions result in equal distribution of energy among each of the independent modes of motion. According to this **equipartition theorem**, the energy associated with each independent mode of motion equals $k_B T/2$. For a point particle, for example, there are three independent modes of motion, corresponding to motion along each of the three independent spatial directions x , y and z . According to the equipartition theorem, the average kinetic energy for motion along the x direction is $mv_{x,\text{avg}}^2 = k_B T/2$, and similarly for the y and z directions, making the total kinetic energy $3(k_B T/2)$ in agreement with (1.6.8). For a diatomic molecule, which we may picture as two spheres connected by a rigid rod, there are two independent modes of rotational motion in addition to the three modes of kinetic energy of the entire molecule. Hence, for a diatomic gas the molar energy $U_m = 5RT/2$, as we noted in the context of Equation (1.4.8). The independent modes of motion are often called **degrees of freedom**.

MAXWELL–BOLTZMANN VELOCITY DISTRIBUTION

A century after Bernoulli's *Hydrodynamica* was published, the kinetic theory of gases began to make great inroads into the nature of the randomness of molecular motion. Surely molecules in a gas move with different velocities. According to (1.6.8), the measurement of pressure only tells us the average of the square of the velocities. It does not tell us what fraction of molecules have velocities with a particular magnitude and direction. In the later half of the nineteenth century, James Clerk Maxwell (1831–1879) directed his investigations to the **probability distribution of molecular velocity** that specifies such details. We shall denote the probability distribution of the molecular velocity \mathbf{v} by $P(\mathbf{v})$. The meaning of $P(\mathbf{v})$ is as follows:

$P(\mathbf{v})dv_x dv_y dv_z$ is the fraction of the total number of molecules whose velocity vectors have their components in the range $(v_x, v_x + dv_x)$, $(v_y, v_y + dv_y)$ and $(v_z, v_z + dv_z)$.

As shown in the Figure 1.9, each point in the velocity space corresponds to a velocity vector; $P(\mathbf{v})dv_x dv_y dv_z$ is the probability that the velocity of a molecule lies within an elemental volume dv_x , dv_y and dv_z at the point (v_x, v_y, v_z) . $P(\mathbf{v})$ is called the **probability density** in the velocity space.

The mathematical form of $P(\mathbf{v})$ was obtained by James Clerk Maxwell; the concept was later generalized by Ludwig Boltzmann (1844–1906) to the probability

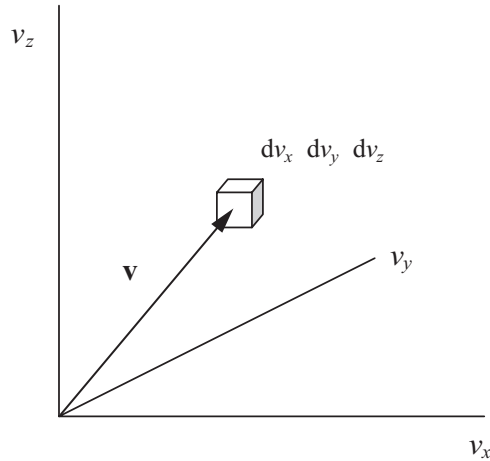


Figure 1.9 The probability distribution for the velocity is defined in the velocity space. $P(\mathbf{v})dv_x dv_y dv_z$ is the probability that the velocity of a molecule is within the shown cube

distribution of the total energy E of the molecule. According to the principle discovered by Boltzmann, when a system reaches thermodynamic equilibrium, the probability that a molecule is in a state with energy E is proportional to $\exp(-E/k_B T)$. If $\rho(E)$ is the number of different states in which the molecule has energy E , then

$$P(E) \propto \rho(E)e^{-E/k_B T} \quad (1.6.9)$$

The quantity $\rho(E)$ is called the **density of states**. Relation (1.6.9), called the **Boltzmann principle**, is one of the fundamental principles of physics. Using this principle, equilibrium thermodynamic properties of a substance can be derived from molecular energies E – a subject called statistical thermodynamics, presented in Chapter 17. In this introductory section, however, we will only study some elementary consequences of this principle.

The energy of a molecule $E = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{int}} + \dots$, in which E_{trans} is the kinetic energy of translational motion of the whole molecule, E_{rot} is the energy of rotational motion, E_{vib} is the energy of vibrational motion, E_{int} is the energy of the molecule's interaction with other molecules and fields such as electric, magnetic or gravitational fields, and so on. According to the Boltzmann principle, the probability that a molecule will have a translational kinetic energy E_{trans} is proportional to $\exp(-E_{\text{trans}}/k_B T)$ (the probabilities associated with other forms of energy are factors that multiply this term). Since the kinetic energy due to translational motion of the molecule is $mv^2/2$, we can write the probability as a function of the velocity \mathbf{v} by which we mean probability that a molecule's velocity is in an elemental cube in velocity space, as shown in the Figure 1.9. For a continuous variable, such as velocity, we

must define a probability density $P(\mathbf{v})$ so that the probability that a molecule's velocity is in an elemental cube of volume $dv_x dv_y dv_z$ located at the tip of the velocity vector \mathbf{v} is $P(\mathbf{v}) dv_x dv_y dv_z$. According to the Boltzmann principle, this probability is

$$P(\mathbf{v}) dv_x dv_y dv_z = \frac{1}{z} e^{-mv^2/2k_B T} dv_x dv_y dv_z \quad (1.6.10)$$

in which $v^2 = v_x^2 + v_y^2 + v_z^2$.

Here, z is the **normalization factor**, defined by

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-mv^2/2k_B T} dv_x dv_y dv_z = z \quad (1.6.11)$$

so that a requirement of the very definition of a probability, $\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} P(\mathbf{v}) dv_x dv_y dv_z = 1$, is met. The normalization factor z , as defined in (1.6.11), can be calculated using the definite integral:

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \left(\frac{\pi}{a}\right)^{1/2}$$

which gives

$$\frac{1}{z} = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \quad (1.6.12)$$

(Some integrals that are often used in kinetic theory are listed at the end of this chapter in Appendix 1.2.) With the normalization factor thus determined, the probability distribution for the velocity can be written explicitly as

$$P(\mathbf{v}) dv_x dv_y dv_z = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv^2/2k_B T} dv_x dv_y dv_z \quad (1.6.13)$$

This is the **Maxwell velocity distribution**. Plots of this function show the well-known Gaussian or 'bell-shaped' curves shown in Figure 1.10a. It must be noted that this velocity distribution is that of a gas at thermodynamic equilibrium. The width of the distribution is proportional to the temperature. A gas not in thermodynamic equilibrium has a different velocity distribution and the very notion of a temperature may not be well defined; but such cases are very rare. In most situations, even if the temperature changes with location, the velocity distribution locally is very well approximated by (1.6.13). Indeed, in computer simulations of gas dynamics it is found that any initial velocity distribution evolves into the Maxwell distribution very quickly, in the time it takes a molecule to undergo few collisions, which in most cases is less than 10^{-8} s.

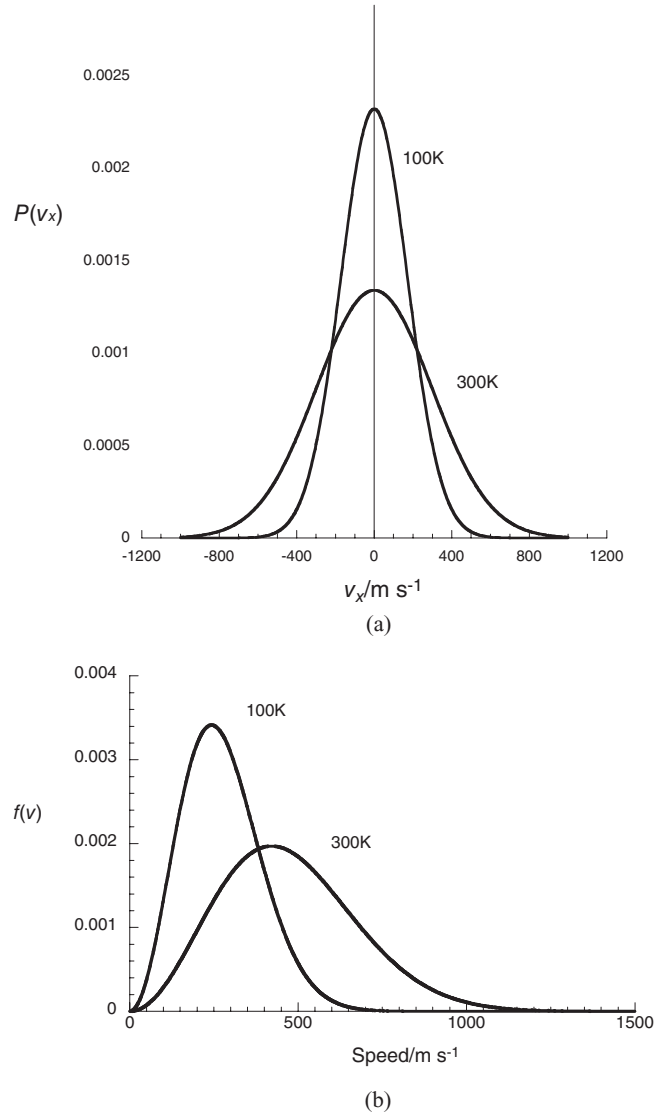


Figure 1.10 Probability distributions of nitrogen. (a) Maxwell velocity distribution of the x -component of the velocity v_x at $T = 100\text{ K}$ and 300 K . The width of the distribution is proportional to T . (b) $f(v)$ versus speed at $T = 100\text{ K}$ and 300 K .

THE MAXWELL SPEED DISTRIBUTION

The average velocity of a molecule is clearly zero because every direction of velocity and its opposite are equally probable (but the average of the square of the velocity is not zero). However, the average speed, which depends only on the magnitude of the velocity, is not zero. From the Maxwell velocity distribution (1.6.13) we can obtain the probability distribution for molecular speed, i.e. the probability that a molecule will have a speed in the range $(v, v + dv)$ regardless of direction. This can be done by summing or integrating $P(\mathbf{v})$ over all the directions in which the velocity of a fixed magnitude can point. In spherical coordinates, since the volume element is $v^2 \sin \theta d\theta d\phi dv$, the probability is written as $P(\mathbf{v})v^2 \sin \theta d\theta d\phi dv$. The integral over all possible directions is

$$\int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} P(\mathbf{v})v^2 \sin \theta d\theta d\phi dv = 4\pi P(\mathbf{v})v^2 dv \quad (1.6.14)$$

The quantity $4\pi P(\mathbf{v})v^2$ is the probability density for the molecular speed. We shall denote it by $f(v)$. With this notation, the probability distribution for molecular speeds can be written explicitly as

$$f(v)dv = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\beta v^2} v^2 dv \quad (1.6.15)$$

$$\beta = \frac{m}{2k_B T}$$

Because the molar mass $M = mN_A$ and $R = k_B N_A$, the above expressions can also be written as

$$f(v)dv = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} e^{-\beta v^2} v^2 dv \quad (1.6.16)$$

$$\beta = \frac{M}{2RT}$$

The shape of the function $f(v)$ is shown in the Figure 1.10b. This graphs show that, at a given temperature, there are a few molecules with very low speeds and a few with large speeds; we can also see that $f(v)$ becomes broader as T increases. The speed v at which $f(v)$ reaches its maximum is the most probable speed.

With the above probability distributions we can calculate several average values. We shall use the notation in which the average value of a quantity X is denoted by $\langle X \rangle$. The average speed is given by the integral

$$\langle v \rangle = \int_0^{\infty} v f(v) dv \quad (1.6.17)$$

For the probability distribution (1.6.15), such integrals can be calculated using integral tables or *Mathematica* or *Maple*. While doing such calculations, it is convenient to write the probability $f(v)$ as

$$f(v)dv = \frac{4\pi}{z} e^{-\beta v^2} v^2 dv \quad (1.6.18)$$

$$\beta = \frac{M}{2RT} \quad \frac{1}{z} = \left(\frac{M}{2\pi RT} \right)^{3/2}$$

Using the appropriate integral in Appendix 1.2 at the end of this chapter, the average speed can be obtained in terms of T and the molar mass M (Exercise 1.23):

$$\langle v \rangle = \frac{4\pi}{z} \int_0^{\infty} v^3 e^{-\beta v^2} dv = \frac{4\pi}{z} \frac{1}{2\beta^2} = \sqrt{\frac{8RT}{\pi M}} \quad (1.6.19)$$

Similarly, one can calculate the average energy of a single molecule using m and k_B instead of M and R (Exercise 1.23):

$$\left\langle \frac{1}{2} m v^2 \right\rangle = \frac{m4\pi}{2z} \int_0^{\infty} v^4 e^{-\beta v^2} dv = \frac{m2\pi}{z} \frac{3\sqrt{\pi}}{8\beta^{5/2}} = \frac{3}{2} k_B T \quad (1.6.20)$$

A rigorous calculation of the pressure using the Maxwell–Boltzmann velocity distribution leads to the expression (1.6.6) in which $v_{\text{avg}}^2 = \langle v^2 \rangle$. Also, the value of v at which $f(v)$ has a maximum is the most probable speed. This can easily be determined by setting $df/dv = 0$, a calculation left as an exercise.

What do the above calculations tell us? First, we see that the average speed of a molecule is directly proportional to the square root of the absolute temperature and inversely proportional to its molar mass. This is one of the most important results of the kinetic theory of gases. Another point to note is the simple dependence of the average kinetic energy of a molecule on the absolute temperature (1.6.20). It shows that the average kinetic energy of a gas molecule depends only on the temperature and is independent of its mass.

Appendix 1.1 Partial Derivatives

DERIVATIVES OF MANY VARIABLES

When a variable such as energy $U(T, V, N_k)$ is a function of many variables V , T and N_k , its *partial derivative* with respect to each variables is defined by holding all other variables constant. Thus, for example, if $U(T, V, N) = (5/2)NRT - a(N^2/V)$ then the partial derivatives are

$$\left(\frac{\partial U}{\partial T}\right)_{V,N} = \frac{5}{2}NR \quad (\text{A1.1.1})$$

$$\left(\frac{\partial U}{\partial N}\right)_{V,T} = \frac{5}{2}RT - a\frac{2N}{V} \quad (\text{A1.1.2})$$

$$\left(\frac{\partial U}{\partial V}\right)_{N,T} = a\frac{N^2}{V^2} \quad (\text{A1.1.3})$$

The subscripts indicate the variables that are held constant during the differentiation. In cases where the variables being held constant are understood, the subscripts are often dropped. The change in U , i.e. the differential dU , due to changes in N , V and T is given by

$$dU = \left(\frac{\partial U}{\partial T}\right)_{V,N} dT + \left(\frac{\partial U}{\partial V}\right)_{T,N} dV + \left(\frac{\partial U}{\partial N}\right)_{V,T} dN \quad (\text{A1.1.4})$$

For functions of many variables, there is a second derivative corresponding to every pair of variables: $\partial^2 U/\partial T\partial V$, $\partial^2 U/\partial N\partial V$, $\partial^2 U/\partial T^2$, etc. For the ‘cross-derivatives’ such as $\partial^2 U/\partial T\partial V$, which are derivatives with respect to two different variables, the order of differentiation does not matter. That is:

$$\frac{\partial^2 U}{\partial T\partial V} = \frac{\partial^2 U}{\partial V\partial T} \quad (\text{A1.1.5})$$

The same is valid for all higher derivatives, such as $\partial^3 U/\partial T^2\partial V$; i.e. the order of differentiation does not matter.

BASIC IDENTITIES

Consider three variables x , y and z , each of which can be expressed as a function of the other two variables, $x = x(y, z)$, $y = y(z, x)$ and $z = z(x, y)$. (p , V and T in the ideal gas equation $pV = NRT$ is an example.) Then the following identities are valid:

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{(\partial y/\partial x)_z} \quad (\text{A1.1.6})$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \quad (\text{A1.1.7})$$

Consider a functions of x and y , $f = f(x, y)$, other than z . Then:

$$\left(\frac{\partial f}{\partial x}\right)_z = \left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z \quad (\text{A1.1.8})$$

Appendix 1.2 Elementary Concepts in Probability Theory

In the absence of a deterministic theory that enables us to calculate the quantities of interest to us, one uses probability theory. Let x_k , in which $k = 1, 2, 3, \dots, n$, represent all possible n values of a random variable x . For example, x could be the number of molecules at any instant in a small volume of 1 nm^3 within a gas or the number of visitors at a website at any instant of time. Let the corresponding probabilities for these n values of x be $P(x_k)$. Since x_k , $k = 1, 2, \dots, n$, represents all possible states:

$$\sum_{k=1}^n P(x_k) = 1 \quad (\text{A1.2.1})$$

AVERAGE VALUES

We shall denote the average value of a quantity A by $\langle A \rangle$. Thus, the average value of x would be

$$\langle x \rangle = \sum_{k=1}^n x_k P(x_k) \quad (\text{A1.2.2})$$

Similarly, the average value of x^2 would be

$$\langle x^2 \rangle = \sum_{k=1}^n x_k^2 P(x_k) \quad (\text{A1.2.3})$$

More generally, if $f(x_k)$ is a function of x , its average value would be

$$\langle f \rangle = \sum_{k=1}^n f(x_k) P(x_k)$$

If the variable x takes continuous values in the range (a, b) , then the average values are written as integrals:

$$\langle x \rangle = \int_a^b x P(x) dx \quad \langle f \rangle = \int_a^b f(x) P(x) dx \quad (\text{A1.2.4})$$

For a given probability distribution, the **standard deviation** s is defined as

$$S = \sqrt{\langle (x - \langle x \rangle)^2 \rangle} \quad (\text{A1.2.5})$$

SOME COMMON PROBABILITY DISTRIBUTIONS

Binomial distribution. This is the probability distribution associated with two outcomes H and T (such as a coin toss) with probabilities p and $(1 - p)$. The probability that, in N trials, m are H and $(N - m)$ are T is given by

$$P(N, m) = \frac{N!}{m!(N - m)!} p^m (1 - p)^{N - m} \quad (\text{A1.2.6})$$

Poisson distribution. In many random processes the random variable is a number n . For example, the number of gas molecules in a small volume within a gas will vary randomly around an average value. Similarly, so is the number of molecules undergoing chemical reaction in a given volume per unit time. The probability of n in such processes is given by the Poisson distribution:

$$P(n) = e^{-\alpha} \frac{\alpha^n}{n!} \quad (\text{A1.2.7})$$

The Poisson distribution has one parameter, α ; it is equal to the average value of n , i.e. $\langle n \rangle = \alpha$.

Gaussian distribution. When a random variable x is a sum of many variables, its probability distribution is generally a Gaussian distribution:

$$P(x) dx = \left(\frac{1}{2\pi\sigma^2} \right)^{1/2} \exp\left(-\frac{(x - x_0)^2}{2\sigma^2} \right) dx \quad (\text{A1.2.8})$$

The Gaussian distribution has two parameters, x_0 and σ . The average value of x is equal to x_0 and the standard deviation equals σ .

SOME USEFUL INTEGRALS

$$(a) \quad \int_0^{\infty} e^{-ax^2} dx = \frac{1}{2} \left(\frac{\pi}{a} \right)^{1/2}$$

$$(b) \quad \int_0^{\infty} x e^{-ax^2} dx = \frac{1}{a}$$

$$(c) \quad \int_0^{\infty} x^2 e^{-ax^2} dx = \frac{1}{4a} \left(\frac{\pi}{a} \right)^{1/2}$$

$$(d) \quad \int_0^{\infty} x^3 e^{-ax^2} dx = \frac{1}{2a^2}$$

More generally:

$$(e) \quad \int_0^{\infty} x^{2n} e^{-ax^2} dx = \frac{1 \times 3 \times 5 \times \dots \times (2n-1)}{2^{n+1} a^n} \left(\frac{\pi}{a}\right)^{1/2}$$

$$(f) \quad \int_0^{\infty} x^{2n+1} e^{-ax^2} dx = \frac{n!}{2} \left(\frac{1}{a^{n+1}}\right)$$

Appendix 1.3 Mathematica Codes

The following Mathematica codes show how to define functions, plot them using the 'Plot' command, create numerical text output files using the 'Export' command and do algebraic calculations and evaluate derivatives.

CODE A: EVALUATING AND PLOTTING PRESSURE USING THE EQUATION OF STATE

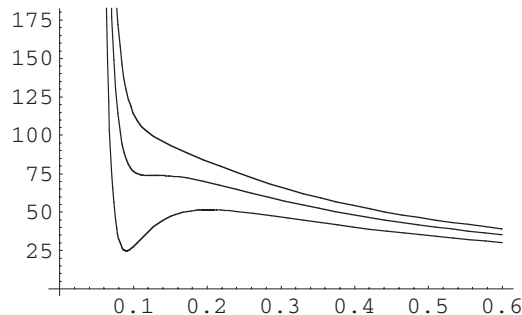
```
(* Values of a and b for CO2; We set N=1 *)
a=3.658;      (* L^2.bar.mol^-2*)
b=0.0429;    (* L.mol^-1*)
R=0.0831;    (* L.bar.K^-1.mol^-1 *)

PVW[V_,T_]:= (R*T/(V-b)) - (a/(V^2));
PID[V_,T_]:= R*T/V;

PID[1.5,300]
PVW[1.5,300]
TC=(8/27)*(a/(R*b))
16.62
15.4835
304.027
```

Using the functions defined above, p - V curves could be plotted using the following command:

```
Plot[{PVW[V,270],PVW[V,304],PVW[V,330]},{V,0.06,0.6}]
```



To write output files for spreadsheets use the 'Export' command and the file format 'CSV'. For more detail, see the Mathematica help file for the 'Export' command. In the command below, the output filename is data.txt. This file can be read by most spreadsheets and graphing software.

```
Export["data.txt", Table[{x, PVW[x, 270], PVW[x, 304], PVW[x, 350]
  {x, 0.07, 0.6, 0.005}}, "CSV"]
```

data.txt

```
Table[{x, PVW[x, 300]}, {x, 0.06, 0.1, 0.01}]/TableForm
```

```
0.06    441.784
0.07    173.396
0.08    100.405
0.09    77.6944
0.1     70.8025
```

CODE B: MATHEMATICA CODE FOR OBTAINING CRITICAL CONSTANTS FOR THE VAN DER WAALS EQUATION

```
Clear[a,b,R,T,V];
```

```
p[V_,T_] := (R*T/(V-b)) - (a/V^2);
```

```
(* At the critical point the first and second derivatives of p
with respect to V are zero*)
```

```
(* First derivative *)
```

```
D[p[V,T],V]
```

$$\frac{2a}{V^3} - \frac{RT}{(-b+V)^2}$$

```
(* Second derivative *)
```

```
D[p[V,T],V,V]
```

$$-\frac{6a}{V^4} + \frac{2RT}{(-b+V)^3}$$

```
Solve[{{(-6*a)/V^4 + (2*R*T)/(-b + V)^3==0,
(2*a)/V^3 - (R*T)/(-b + V)^2==0},{T,V]}
```

$$\left\{ \left\{ T \rightarrow \frac{8a}{27bR}, V \rightarrow 3b \right\} \right\}$$

Now we can substitute these values in the equation for p and obtain p_c .

```
T = (8*a)/(27*b*R); V = 3*b;
```

```
p[V,T]
```

$$\frac{a}{27b^2}$$

Thus, we have all the critical variables: $p_c = a/27b^2$, $T_c = 8a/27bR$, $V_c = 3b$.

CODE C: MATHEMATICA CODE FOR THE LAW OF CORRESPONDING STATES

```

Clear[a,b,R,T,V];
T = Tr*(8*a)/(27*b*R); V = Vr*3*b; pc = a/(27*b^2);

(* In terms of these variables the reduced pressure pr = p/pc. This can
now be calculated*)

p[V,T]/pc

```

$$\frac{27b^2 \left(-\frac{a}{9b^2 V_r^2} + \frac{8aTr}{27b(-b+3bV_r)} \right)}{a}$$

$$\text{FullSimplify} \left[\frac{27b^2 \left(-\frac{a}{9b^2 V_r^2} + \frac{8aTr}{27b(-b+3bV_r)} \right)}{a} \right]$$

$$-\frac{3}{V_r^2} + \frac{8Tr}{-1+3V_r}$$

Thus, we have the following relation for the reduced variables, which is the law of corresponding states: $p_r = [8T_r/(3V_r - 1)] - 3/V_r^2$.

CODE D: THE MAXWELL-BOLTZMANN SPEED DISTRIBUTION FOR A GAS OF MASS M AT TEMPERATURE T CAN BE PLOTTED USING THE FOLLOWING CODE

```

Clear[a,b,R,T,V];
M = 28.0*10^-3; (*molar mass in kg*) R = 8.314(*J/K.mol*)
b = M/(2*R);

```

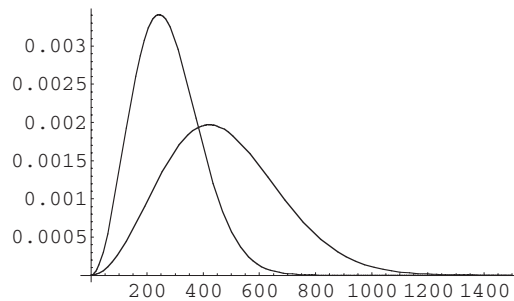
$$p[v_ , T_] := (4.0*Pi) \left(\frac{M}{2*Pi*R*T} \right)^{3/2} v^2 * \text{Exp} \left[\frac{-b*v^2}{T} \right];$$

```

Plot[{p[v,300], p[v,100]}, {v,0,1500}]

```

8.314



- Graphics -

References

1. Prigogine, I., Stengers, I., *Order Out of Chaos*. 1984, Bantam: New York.
2. Mach, E., *Principles of the Theory of Heat*. 1986, D. Reidel: Boston, MA.
3. Conant, J.B. (ed.), *Harvard Case Histories in Experimental Science*, Vol. 1. 1957, Harvard University Press: Cambridge, MA.
4. Mason, S.F., *A History of the Sciences*. 1962, Collier Books: New York.
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Examples

Example 1.1 The atmosphere consists of 78.08% by volume of N_2 and 20.95% of O_2 . Calculate the partial pressures due to the two gases.

Solution The specification ‘percentage by volume’ may be interpreted as follows. If the components of the atmosphere were to be separated, at the pressure of 1 atm, the volume occupied by each component is specified by the volume percent. Thus, if we isolate the N_2 in 1.000 L of dry air, at a pressure of 1 atm its volume will be 0.781 L. According to the ideal gas law, at a fixed pressure and temperature, the amount of gas $N = V(p/RT)$, i.e. the molar amount is proportional to the volume. Hence, percentage by volume is the same as percentage in N , i.e. 1.000 mol of air consists of 0.781 mol of N_2 . According to the Dalton’s law (see (1.4.5)), the partial pressure is proportional to N ; so, the partial pressure of N_2 is 0.781 atm and that of O_2 is 0.209 atm.

Example 1.2 Using the ideal gas approximation, estimate the change in the total internal energy of 1.00 L of N_2 at $p = 2.00$ atm and $T = 298.15$ K if its temperature is increased by 10.0 K. What is the energy required to heat 1.00 mol of N_2 from 0.0 K to 298 K?

Solution The energy of an ideal gas depends only on the amount of gas N and the temperature T . For a diatomic gas such as N_2 the energy per mole equals $(5/2)RT + U_0$. Hence, for N moles of N_2 the change in energy ΔU for a change in temperature from T_1 to T_2 is

$$\Delta U = N(5/2)R(T_2 - T_1)$$

In the above case

$$N = \frac{pV}{RT} = \frac{2.00 \text{ atm} \times 1.00 \text{ L}}{0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}(298.15 \text{ K})} = 8.17 \times 10^{-2} \text{ mol}$$

Hence:

$$\begin{aligned} \Delta U &= (8.17 \times 10^{-2} \text{ mol}) \frac{5}{2} (8.314 \text{ J mol}^{-1} \text{ K}^{-1})(10.0 \text{ K}) \\ &= 17.0 \text{ J} \end{aligned}$$

(Note the different units of R used in this calculation.)

The energy required to heat 1.00 mol of N_2 from 0 K to 298 K is

$$(5/2)RT = (5/2)(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K}) = 6.10 \text{ kJ mol}^{-1}$$

Example 1.3 At $T = 300 \text{ K}$, 1.00 mol of CO_2 occupies a volume of 1.50 L. Calculate the pressures given by the ideal gas equation and the van der Waals equation. (The van der Waals constants a and b can be obtained from Table 1.1.)

Solution The ideal gas pressure is

$$p = \frac{1.00 \text{ mol} \times 0.0821 \text{ atm L mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{1.50 \text{ L}} = 16.4 \text{ atm}$$

The pressure according to the van der Waals equation is

$$p = \frac{NRT}{V - Nb} - a \frac{N^2}{V^2}$$

Since the van der Waals constants a and b given in Table 1.1 are in units of $\text{L}^2 \text{ atm mol}^{-2}$ and L mol^{-2} respectively, we will use the value of $R = 0.0821 \text{ atm L mol}^{-1} \text{ K}^{-1}$. This will give the pressure in atmospheres:

$$p = \frac{1.00(0.0821)300}{1.50 - 1.00(0.0421)} - 3.59 \frac{1.00}{1.50^2} = 15.3 \text{ atm}$$

Exercises

- 1.1 Describe an experimental method, based on the ideal gas law, to obtain the molecular mass of a gas.
- 1.2 The density of dry air at $p = 1.0 \text{ bar}$ and $T = 300 \text{ K}$ is 1.161 kg m^{-3} . Assuming that it consists entirely of N_2 and O_2 and using the ideal gas law, determine the amount of each gas in moles in a volume of 1 m^3 and their mole fractions.
- 1.3 The molecule density of interstellar gas clouds is about 10^4 molecules/mL. The temperature is approximately 10 K. Calculate the pressure. (The lowest vacuum obtainable in the laboratory is about three orders of magnitude larger.)
- 1.4 A sperm whale dives to a depth of more than 1.5 km into the ocean to feed. Estimate the pressure the sperm whale must withstand at this depth. (Express your answer in atmospheres.)

- 1.5** (a) Calculate the amount of gas in moles per cubic meter of atmosphere at $p = 1 \text{ atm}$ and $T = 298 \text{ K}$ using the ideal gas equation.
(b) The atmospheric content of CO_2 is about 360 ppmv (parts per million by volume). Assuming a pressure of 1.00 atm, estimate the amount of CO_2 in a 10.0 km layer of the atmosphere at the surface of the Earth. The radius of the Earth is 6370 km. (The actual amount of CO_2 in the atmosphere is about $6.0 \times 10^{16} \text{ mol}$.)
(c) The atmospheric content of O_2 is 20.946% by volume. Using the result in part (b), estimate the total amount of O_2 in the atmosphere.
(d) Life on Earth consumes about $0.47 \times 10^{16} \text{ mol}$ of O_2 per year. What percentage of the O_2 in the atmosphere does life consume in a year?
- 1.6** The production of fertilizers begins with the Haber processes, which is the reaction $3\text{H}_2 + \text{N}_2 \rightarrow 2\text{NH}_3$ conducted at about 500 K and a pressure of about 300 atm. Assume that this reaction occurs in a container of fixed volume and temperature. If the initial pressure due to 300.0 mol H_2 and 100.0 mol N_2 is 300.0 atm, what will the final pressure be? What will the final pressure be if initially the system contained 240.0 mol H_2 and 160.0 mol N_2 ? (Use the ideal gas equation even though the pressure is high.)
- 1.7** The van der Waals constants for N_2 are $a = 1.370 \text{ L}^2 \text{ atm mol}^{-2}$ and $b = 0.0387 \text{ L mol}^{-1}$. Consider 0.5 mol of $\text{N}_2(\text{g})$ is in a vessel of volume 10.0 L. Assuming that the temperature is 300 K, compare the pressures predicted by the ideal gas equation and the van der Waals equation.
(a) What is the percentage error in using the ideal gas equation instead of the van der Waals equation?
(b) Keeping $V = 10.0 \text{ L}$, use Maple/Mathematica to plot p versus N for $N = 1$ to 100, using the ideal gas and the van der Waals equations. What do you notice regarding the difference between the pressure predicted by the two equations?
- 1.8** For 1.00 mol of Cl_2 in a volume of 2.50 L, calculate the difference in the energy between U_{ideal} and U_{vw} . What is the percentage difference when compared with U_{ideal} ?
- 1.9** (a) Using the ideal gas equation, calculate the volume of 1 mol of a gas at a temperature of 25°C and a pressure of 1 atm. This volume is called the *Avogadro volume*.
(b) The atmosphere of Venus is 96.5% $\text{CO}_2(\text{g})$. The surface temperature is about 730 K and the pressure is about 90 atm. Using the ideal gas equation, calculate the volume of 1 mol of $\text{CO}_2(\text{g})$ under these conditions (Avogadro volume on Venus).
(c) Use Maple/Mathematica and the van der Waals equation to obtain the Avogadro volume on Venus and compare it (find the percentage difference) with the result obtained using the ideal gas equation.

- 1.10** The van der Waals parameter b is a measure of the volume excluded due to the finite size of the molecules. Estimate the size of a single molecule from the data in Table 1.1.
- 1.11** For the van der Waals equation, express the pressure as a power series in $1/V_m$. Using this expression, determine the Boyle temperature T_B at which $p \approx RT_B/V_m$.
- 1.12** For the Redlich–Kwong equation

$$p = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T}} \frac{1}{V_m(V_m - b)}$$

show that there is a critical temperature above which there is no transition to a liquid state.

- 1.13** Though the van der Waals equation was a big improvement over the ideal gas equation, its validity is also limited. Compare the following experimental data with the predictions of the van der Waals equation for 1 mol of CO_2 at $T = 40^\circ\text{C}$. (Source: I. Prigogine and R. Defay, *Chemical Thermodynamics*, 1967, London: Longmans.)

p/atm	$V_m/\text{L mol}^{-1}$
1	25.574
10	2.4490
25	0.9000
50	0.3800
80	0.1187
100	0.0693
200	0.0525
500	0.0440
1000	0.0400

- 1.14** (a) Use Mathematica/Maple to plot the van der Waals p – V curves for Ar, N_2 and C_3H_8 using the data listed in Table 1.1 (see Appendix 1.3 for sample programs). In particular, compare the van der Waals curves for CO_2 and He and the ideal gas equation.
- 1.15** For CO_2 , plot the compressibility factor $Z = pV_m/RT$ as function of the reduced pressure p_r for fixed reduced temperatures $T_r = 1.2$ and $T_r = 1.7$. Verify that the Z – p_r curves are the same for all van der Waals' gases. (This can be plotted using Parametric Plots.)
- 1.16** Using Table 1.1 and the relations (1.5.4) obtain the critical temperature T_c , critical pressure p_c and critical molar volume V_{mc} for CO_2 , H_2 and CH_4 . Write

a *Maple/Mathematica* code to calculate the van der Waals constants a and b given T_c , p_c and V_{mc} for any gas.

- 1.17** (a) From the van der Waals equation, using (1.5.2) obtain (1.5.3) and (1.5.4). (These calculations may also be done using *Mathematica/Maple*). (b) Show that $Z_c = (p_c V_{mc}/RT_c) = 3/8$ a constant for all van der Waals gases.
- 1.18** Using *Mathematica/Maple*, obtain Equation (1.5.6) from (1.5.5).
- 1.19** For CO_2 , plot p - V isotherms for the van der Waals and Redlich–Kwong equations on the same graph for $T = 200\text{ K}$, 300 K and 400 K . The table below lists some constants a and b for the Redlich–Kwong equation (*Source: J.H. Noggle, Physical Chemistry. 1996, Harper Collins*):

	$a/\text{bar L}^2 \text{mol}^{-1} \text{K}^{-1/2}$	$b/\text{L mol}^{-1}$
Ar	16.71	0.0219
CO_2	64.48	0.0296
O_2	17.36	0.0221

- 1.20** Show that the Lennard–Jones energy

$$U_{\text{LJ}}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

has a minimum value equal to $-\varepsilon$ at $r = 2^{1/6}\sigma$.

- 1.21** Estimate the average distance between molecules at $T = 300\text{ K}$ and $p = 1.0\text{ atm}$. (Hint: consider a cube of side 10 cm in which the molecules occupy points on a three-dimensional cubic lattice.)
- 1.22** According to the Graham’s law of diffusion, the rate of diffusion of gas molecules is inversely proportional to the square root of its mass. Explain why this is so using the kinetic theory of gases. How would you expect the diffusion coefficient to depend on the temperature?
- 1.23** (a) Using the integrals in Appendix 1.2, obtain the average speed (1.6.19) and kinetic energy (1.6.20) of a gas molecule.
 (b) Using the Maxwell probability distribution $f(v)$, obtain the most probable speed of a molecule of molar mass M at a temperature T .