

Physical Chemistry 1

Thermodynamics by Atkins

Second Stage

The Properties of Gases

Dr. Ahmed Mishaal Mohammed

Department of Chemistry - College of Science

University of Anbar

The properties of gases

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This chapter establishes the properties of gases that will be used throughout the text. It begins with an account of an idealized version of a gas, a perfect gas, and shows how its equation of state may be assembled experimentally. We then see how the properties of real gases differ from those of a perfect gas, and construct an equation of state that describes their properties.

The simplest state of matter is a **gas**, a form of matter that fills any container it occupies. Initially we consider only pure gases, but later in the chapter we see that the same ideas and equations apply to mixtures of gases too.

The perfect gas

We shall find it helpful to picture a gas as a collection of molecules (or atoms) in continuous random motion, with average speeds that increase as the temperature is raised. A gas differs from a liquid in that, except during collisions, the molecules of a gas are widely separated from one another and move in paths that are largely unaffected by intermolecular forces.

1.1 The states of gases

The **physical state** of a sample of a substance, its physical condition, is defined by its physical properties. Two samples of a substance that have the same physical properties are in the same state. The state of a pure gas, for example, is specified by giving its volume, V , amount of substance (number of moles), n , pressure, p , and temperature, T . However, it has been established experimentally that it is sufficient to specify only three of these variables, for then the fourth variable is fixed. That is, it is an experimental fact that each substance is described by an **equation of state**, an equation that interrelates these four variables.

The general form of an equation of state is

$$p = f(T, V, n) \quad (1.1)$$

This equation tells us that, if we know the values of T , V , and n for a particular substance, then the pressure has a fixed value. Each substance is described by its own equation of state, but we know the explicit form of the equation in only a few special cases. One very important example is the equation of state of a 'perfect gas', which has the form $p = nRT/V$, where R is a constant. Much of the rest of this chapter will examine the origin of this equation of state and its applications.

The perfect gas

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Comment 1.1

The International System of units (SI, from the French *Système International d'Unités*) is discussed in Appendix 1.

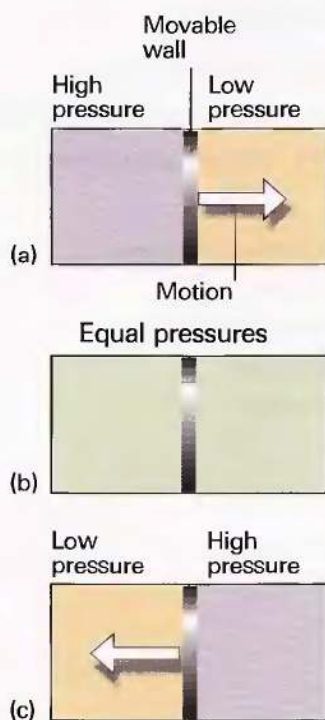


Fig. 1.1 When a region of high pressure is separated from a region of low pressure by a movable wall, the wall will be pushed into one region or the other, as in (a) and (c). However, if the two pressures are identical, the wall will not move (b). The latter condition is one of mechanical equilibrium between the two regions.

Table 1.1 Pressure units

Name	Symbol	Value
pascal	1 Pa	$1 \text{ N m}^{-2}, 1 \text{ kg m}^{-1} \text{ s}^{-2}$
bar	1 bar	10^5 Pa
atmosphere	1 atm	101.325 kPa
torr	1 Torr	$(101\,325/760) \text{ Pa} = 133.32 \dots \text{ Pa}$
millimetres of mercury	1 mmHg	$133.322 \dots \text{ Pa}$
pound per square inch	1 psi	$6.894\,757 \dots \text{ kPa}$

(a) Pressure

Pressure is defined as force divided by the area to which the force is applied. The greater the force acting on a given area, the greater the pressure. The origin of the force exerted by a gas is the incessant battering of the molecules on the walls of its container. The collisions are so numerous that they exert an effectively steady force, which is experienced as a steady pressure.

The SI unit of pressure, the *pascal* (Pa), is defined as 1 newton per metre-squared:

$$1 \text{ Pa} = 1 \text{ N m}^{-2} \quad [1.2a]$$

In terms of base units,

$$1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2} \quad [1.2b]$$

Several other units are still widely used (Table 1.1); of these units, the most commonly used are atmosphere ($1 \text{ atm} = 1.013\,25 \times 10^5 \text{ Pa}$ exactly) and bar ($1 \text{ bar} = 10^5 \text{ Pa}$). A pressure of 1 bar is the **standard pressure** for reporting data; we denote it p^\ominus .

Self-test 1.1 Calculate the pressure (in pascals and atmospheres) exerted by a mass of 1.0 kg pressing through the point of a pin of area $1.0 \times 10^{-2} \text{ mm}^2$ at the surface of the Earth. *Hint.* The force exerted by a mass m due to gravity at the surface of the Earth is mg , where g is the acceleration of free fall (see endpaper 2 for its standard value). [0.98 GPa, $9.7 \times 10^3 \text{ atm}$]

If two gases are in separate containers that share a common movable wall (Fig. 1.1), the gas that has the higher pressure will tend to compress (reduce the volume of) the gas that has lower pressure. The pressure of the high-pressure gas will fall as it expands and that of the low-pressure gas will rise as it is compressed. There will come a stage when the two pressures are equal and the wall has no further tendency to move. This condition of equality of pressure on either side of a movable wall (a ‘piston’) is a state of **mechanical equilibrium** between the two gases. The pressure of a gas is therefore an indication of whether a container that contains the gas will be in mechanical equilibrium with another gas with which it shares a movable wall.

(b) The measurement of pressure

The pressure exerted by the atmosphere is measured with a **barometer**. The original version of a barometer (which was invented by Torricelli, a student of Galileo) was an inverted tube of mercury sealed at the upper end. When the column of mercury is in mechanical equilibrium with the atmosphere, the pressure at its base is equal to that

exerted by the atmosphere. It follows that the height of the mercury column is proportional to the external pressure.

Example 1.1 Calculating the pressure exerted by a column of liquid

Derive an equation for the pressure at the base of a column of liquid of mass density ρ (rho) and height h at the surface of the Earth.

Method Pressure is defined as $p = F/A$ where F is the force applied to the area A , and $F = mg$. To calculate F we need to know the mass m of the column of liquid, which is its mass density, ρ , multiplied by its volume, V : $m = \rho V$. The first step, therefore, is to calculate the volume of a cylindrical column of liquid.

Answer Let the column have cross-sectional area A ; then its volume is Ah and its mass is $m = \rho Ah$. The force the column of this mass exerts at its base is

$$F = mg = \rho Ahg$$

The pressure at the base of the column is therefore

$$p = \frac{F}{A} = \frac{\rho Ahg}{A} = \rho gh \quad (1.3)$$

Note that the pressure is independent of the shape and cross-sectional area of the column. The mass of the column of a given height increases as the area, but so does the area on which the force acts, so the two cancel.

Self-test 1.2 Derive an expression for the pressure at the base of a column of liquid of length l held at an angle θ (theta) to the vertical (1). $[p = \rho gl \cos \theta]$

The pressure of a sample of gas inside a container is measured by using a pressure gauge, which is a device with electrical properties that depend on the pressure. For instance, a *Bayard–Alpert pressure gauge* is based on the ionization of the molecules present in the gas and the resulting current of ions is interpreted in terms of the pressure. In a *capacitance manometer*, the deflection of a diaphragm relative to a fixed electrode is monitored through its effect on the capacitance of the arrangement. Certain semiconductors also respond to pressure and are used as transducers in solid-state pressure gauges.

(c) Temperature

The concept of temperature springs from the observation that a change in physical state (for example, a change of volume) can occur when two objects are in contact with one another, as when a red-hot metal is plunged into water. Later (Section 2.1) we shall see that the change in state can be interpreted as arising from a flow of energy as heat from one object to another. The **temperature**, T , is the property that indicates the direction of the flow of energy through a thermally conducting, rigid wall. If energy flows from A to B when they are in contact, then we say that A has a higher temperature than B (Fig. 1.2).

It will prove useful to distinguish between two types of boundary that can separate the objects. A boundary is **diathermic** (thermally conducting) if a change of state is observed when two objects at different temperatures are brought into contact.¹ A

¹ The word *dia* is from the Greek for ‘through’.

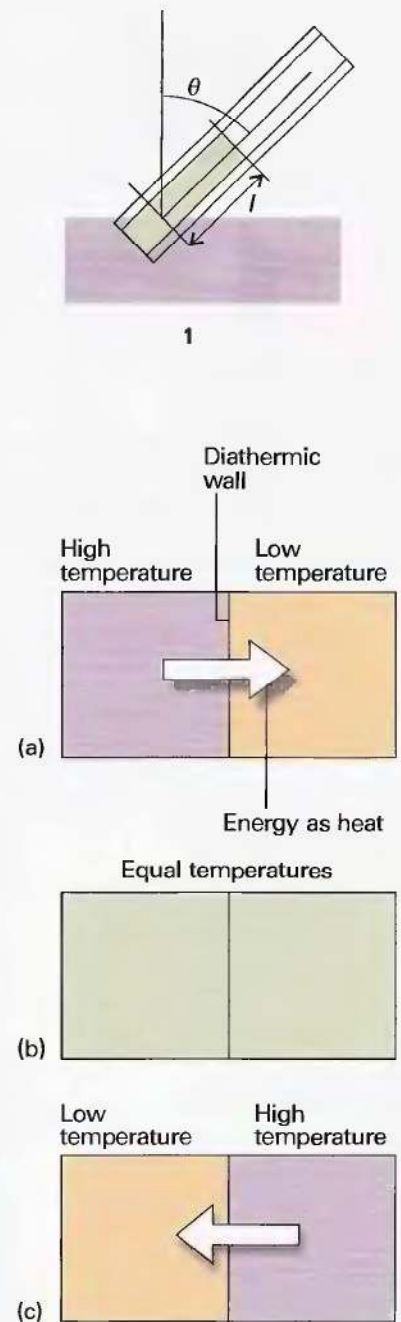


Fig. 1.2 Energy flows as heat from a region at a higher temperature to one at a lower temperature if the two are in contact through a diathermic wall, as in (a) and (c). However, if the two regions have identical temperatures, there is no net transfer of energy as heat even though the two regions are separated by a diathermic wall (b). The latter condition corresponds to the two regions being at thermal equilibrium.

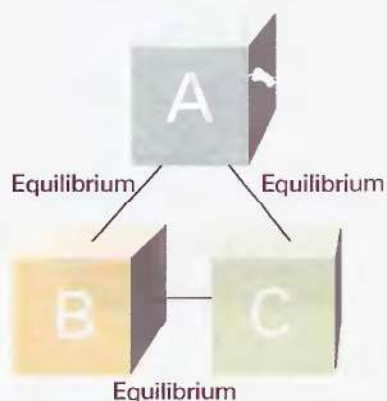


Fig. 1.3 The experience summarized by the Zeroth Law of thermodynamics is that, if an object A is in thermal equilibrium with B and B is in thermal equilibrium with C, then C is in thermal equilibrium with A.

metal container has diathermic walls. A boundary is **adiabatic** (thermally insulating) if no change occurs even though the two objects have different temperatures. A vacuum flask is an approximation to an adiabatic container.

The temperature is a property that indicates whether two objects would be in ‘thermal equilibrium’ if they were in contact through a diathermic boundary. Thermal equilibrium is established if no change of state occurs when two objects A to B are in contact through a diathermic boundary. Suppose an object A (which we can think of as a block of iron) is in thermal equilibrium with an object B (a block of copper), and that B is also in thermal equilibrium with another object C (a flask of water). Then it has been found experimentally that A and C will also be in thermal equilibrium when they are put in contact (Fig. 1.3). This observation is summarized by the **Zeroth Law of thermodynamics**:

If A is in thermal equilibrium with B, and B is in thermal equilibrium with C, then C is also in thermal equilibrium with A.

The Zeroth Law justifies the concept of temperature and the use of a **thermometer**, a device for measuring the temperature. Thus, suppose that B is a glass capillary containing a liquid, such as mercury, that expands significantly as the temperature increases. Then, when A is in contact with B, the mercury column in the latter has a certain length. According to the Zeroth Law, if the mercury column in B has the same length when it is placed in thermal contact with another object C, then we can predict that no change of state of A and C will occur when they are in thermal contact. Moreover, we can use the length of the mercury column as a measure of the temperatures of A and C.

In the early days of thermometry (and still in laboratory practice today), temperatures were related to the length of a column of liquid, and the difference in lengths shown when the thermometer was first in contact with melting ice and then with boiling water was divided into 100 steps called ‘degrees’, the lower point being labelled 0. This procedure led to the **Celsius scale** of temperature. In this text, temperatures on the Celsius scale are denoted θ and expressed in *degrees Celsius* ($^{\circ}\text{C}$). However, because different liquids expand to different extents, and do not always expand uniformly over a given range, thermometers constructed from different materials showed different numerical values of the temperature between their fixed points. The pressure of a gas, however, can be used to construct a **perfect-gas temperature scale** that is independent of the identity of the gas. The perfect-gas scale turns out to be identical to the **thermodynamic temperature scale** to be introduced in Section 3.2c, so we shall use the latter term from now on to avoid a proliferation of names. On the thermodynamic temperature scale, temperatures are denoted T and are normally reported in kelvins, K (not $^{\circ}\text{K}$). Thermodynamic and Celsius temperatures are related by the exact expression

$$T/\text{K} = \theta/^{\circ}\text{C} + 273.15 \quad (1.4)$$

This relation, in the form $\theta/^{\circ}\text{C} = T/\text{K} - 273.15$, is the current definition of the Celsius scale in terms of the more fundamental Kelvin scale. It implies that a difference in temperature of 1°C is equivalent to a difference of 1 K.

A note on good practice We write $T = 0$, not $T = 0 \text{ K}$ for the zero temperature on the thermodynamic temperature scale. This scale is absolute, and the lowest temperature is 0 regardless of the size of the divisions on the scale (just as we write $p = 0$ for zero pressure, regardless of the size of the units we adopt, such as bar or pascal). However, we write 0°C because the Celsius scale is not absolute.

Illustration 1.1 Converting temperatures

To express 25.00°C as a temperature in kelvins, we use eqn 1.4 to write

$$T/\text{K} = (25.00^\circ\text{C})/^\circ\text{C} + 273.15 = 25.00 + 273.15 = 298.15$$

Note how the units (in this case, °C) are cancelled like numbers. This is the procedure called ‘quantity calculus’ in which a physical quantity (such as the temperature) is the product of a numerical value (25.00) and a unit (1°C). Multiplication of both sides by the unit K then gives $T = 298.15 \text{ K}$.

A note on good practice When the units need to be specified in an equation, the approved procedure, which avoids any ambiguity, is to write (physical quantity)/units, which is a dimensionless number, just as $(25.00^\circ\text{C})/^\circ\text{C} = 25.00$ in this *Illustration*. Units may be multiplied and cancelled just like numbers.

1.2 The gas laws

The equation of state of a gas at low pressure was established by combining a series of empirical laws.

(a) The perfect gas law

We assume that the following individual gas laws are familiar:

$$\text{Boyle's law: } pV = \text{constant, at constant } n, T \quad (1.5)^\circ$$

$$\text{Charles's law: } V = \text{constant} \times T, \text{ at constant } n, p \quad (1.6a)^\circ$$

$$p = \text{constant} \times T, \text{ at constant } n, V \quad (1.6b)^\circ$$

$$\text{Avogadro's principle:}^2 V = \text{constant} \times n \text{ at constant } p, T \quad (1.7)^\circ$$

Boyle's and Charles's laws are examples of a **limiting law**, a law that is strictly true only in a certain limit, in this case $p \rightarrow 0$. Equations valid in this limiting sense will be signalled by a ° on the equation number, as in these expressions. Avogadro's principle is commonly expressed in the form ‘equal volumes of gases at the same temperature and pressure contain the same numbers of molecules’. In this form, it is increasingly true as $p \rightarrow 0$. Although these relations are strictly true only at $p = 0$, they are reasonably reliable at normal pressures ($p \approx 1 \text{ bar}$) and are used widely throughout chemistry.

Figure 1.4 depicts the variation of the pressure of a sample of gas as the volume is changed. Each of the curves in the graph corresponds to a single temperature and hence is called an **isotherm**. According to Boyle's law, the isotherms of gases are hyperbolas. An alternative depiction, a plot of pressure against $1/\text{volume}$, is shown in Fig. 1.5. The linear variation of volume with temperature summarized by Charles's law is illustrated in Fig. 1.6. The lines in this illustration are examples of **isobars**, or lines showing the variation of properties at constant pressure. Figure 1.7 illustrates the linear variation of pressure with temperature. The lines in this diagram are **isochores**, or lines showing the variation of properties at constant volume.

² Avogadro's principle is a principle rather than a law (a summary of experience) because it depends on the validity of a model, in this case the existence of molecules. Despite there now being no doubt about the existence of molecules, it is still a model-based principle rather than a law.

³ To solve this and other *Explorations*, use either mathematical software or the *Living graphs* from the text's web site.

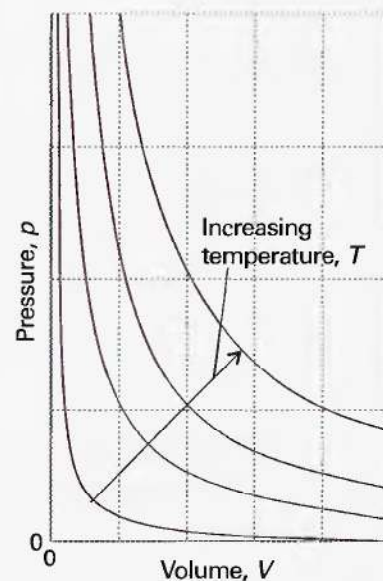


Fig. 1.4 The pressure–volume dependence of a fixed amount of perfect gas at different temperatures. Each curve is a hyperbola ($pV = \text{constant}$) and is called an *isotherm*.

Exploration³ Explore how the pressure of 1.5 mol $\text{CO}_2(\text{g})$ varies with volume as it is compressed at (a) 273 K, (b) 373 K from 30 dm^3 to 15 dm^3 .

Comment 1.2

A hyperbola is a curve obtained by plotting y against x with $xy = \text{constant}$.

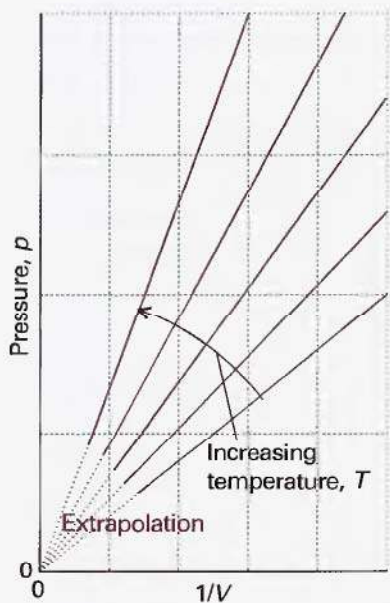



Fig. 1.5 Straight lines are obtained when the pressure is plotted against $1/V$ at constant temperature.

 **Exploration** Repeat *Exploration 1.4*, but plot the data as p against $1/V$.

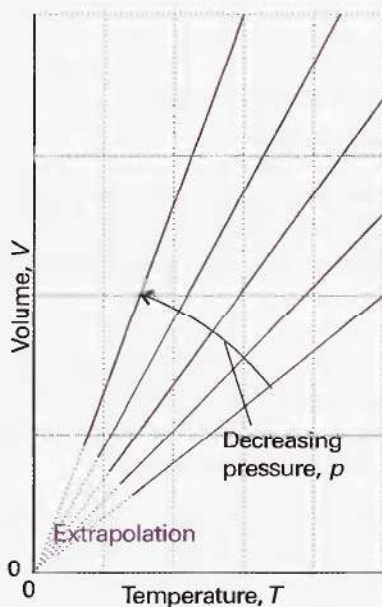



Fig. 1.6 The variation of the volume of a fixed amount of gas with the temperature at constant pressure. Note that in each case the isobars extrapolate to zero volume at $T = 0$, or $\theta = -273^\circ\text{C}$.

 **Exploration** Explore how the volume of 1.5 mol $\text{CO}_2(\text{g})$ in a container maintained at (a) 1.00 bar, (b) 0.50 bar varies with temperature as it is cooled from 373 K to 273 K.

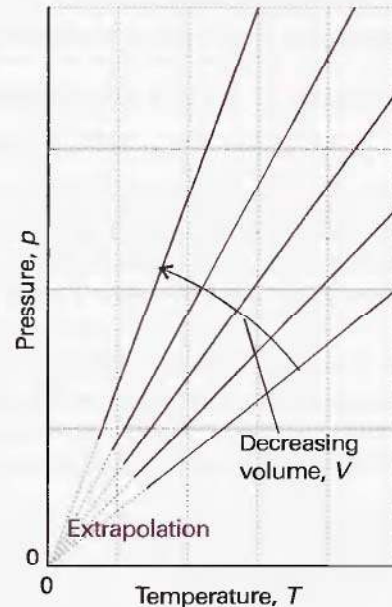



Fig. 1.7 The pressure also varies linearly with the temperature at constant volume, and extrapolates to zero at $T = 0$ (-273°C).

 **Exploration** Explore how the pressure of 1.5 mol $\text{CO}_2(\text{g})$ in a container of volume (a) 30 dm^3 , (b) 15 dm^3 varies with temperature as it is cooled from 373 K to 273 K.

A note on good practice To test the validity of a relation between two quantities, it is best to plot them in such a way that they should give a straight line, for deviations from a straight line are much easier to detect than deviations from a curve.

The empirical observations summarized by eqns 1.5–7 can be combined into a single expression:

$$pV = \text{constant} \times nT$$

This expression is consistent with Boyle's law ($pV = \text{constant}$) when n and T are constant, with both forms of Charles's law ($p \propto T$, $V \propto T$) when n and either V or p are held constant, and with Avogadro's principle ($V \propto n$) when p and T are constant. The constant of proportionality, which is found experimentally to be the same for all gases, is denoted R and called the **gas constant**. The resulting expression

$$pV = nRT \tag{1.8}^\circ$$

is the **perfect gas equation**. It is the approximate equation of state of any gas, and becomes increasingly exact as the pressure of the gas approaches zero. A gas that obeys eqn 1.8 exactly under all conditions is called a **perfect gas** (or *ideal gas*). A **real gas**, an actual gas, behaves more like a perfect gas the lower the pressure, and is described exactly by eqn 1.8 in the limit of $p \rightarrow 0$. The gas constant R can be determined by evaluating $R = pV/nT$ for a gas in the limit of zero pressure (to guarantee that it is

behaving perfectly). However, a more accurate value can be obtained by measuring the speed of sound in a low-pressure gas (argon is used in practice) and extrapolating its value to zero pressure. Table 1.2 lists the values of R in a variety of units.

Molecular interpretation 1.1 *The kinetic model of gases*

The molecular explanation of Boyle's law is that, if a sample of gas is compressed to half its volume, then twice as many molecules strike the walls in a given period of time than before it was compressed. As a result, the average force exerted on the walls is doubled. Hence, when the volume is halved the pressure of the gas is doubled, and $p \times V$ is a constant. Boyle's law applies to all gases regardless of their chemical identity (provided the pressure is low) because at low pressures the average separation of molecules is so great that they exert no influence on one another and hence travel independently. The molecular explanation of Charles's law lies in the fact that raising the temperature of a gas increases the average speed of its molecules. The molecules collide with the walls more frequently and with greater impact. Therefore they exert a greater pressure on the walls of the container.

These qualitative concepts are expressed quantitatively in terms of the kinetic model of gases, which is described more fully in Chapter 21. Briefly, the kinetic model is based on three assumptions:

1. The gas consists of molecules of mass m in ceaseless random motion.
2. The size of the molecules is negligible, in the sense that their diameters are much smaller than the average distance travelled between collisions.
3. The molecules interact only through brief, infrequent, and elastic collisions.

An *elastic collision* is a collision in which the total translational kinetic energy of the molecules is conserved. From the very economical assumptions of the kinetic model, it can be deduced (as we shall show in detail in Chapter 21) that the pressure and volume of the gas are related by

$$pV = \frac{1}{3}nMc^2 \quad (1.9)^{\circ}$$

where $M = mN_A$, the molar mass of the molecules, and c is the *root mean square speed* of the molecules, the square root of the mean of the squares of the speeds, v , of the molecules:

$$c = \langle v^2 \rangle^{1/2} \quad (1.10)$$

We see that, if the root mean square speed of the molecules depends only on the temperature, then at constant temperature

$$pV = \text{constant}$$

which is the content of Boyle's law. Moreover, for eqn 1.9 to be the equation of state of a perfect gas, its right-hand side must be equal to nRT . It follows that the root mean square speed of the molecules in a gas at a temperature T must be

$$c = \left(\frac{3RT}{M} \right)^{1/2} \quad (1.11)^{\circ}$$

We can conclude that *the root mean square speed of the molecules of a gas is proportional to the square root of the temperature and inversely proportional to the square root of the molar mass*. That is, the higher the temperature, the higher the root mean square speed of the molecules, and, at a given temperature, heavy molecules travel more slowly than light molecules. The root mean square speed of N_2 molecules, for instance, is found from eqn 1.11 to be 515 m s^{-1} at 298 K .

Table 1.2 The gas constant

R	
8.314 47	$\text{J K}^{-1} \text{ mol}^{-1}$
$8.205 74 \times 10^{-2}$	$\text{dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$
$8.314 47 \times 10^{-2}$	$\text{dm}^3 \text{ bar K}^{-1} \text{ mol}^{-1}$
8.314 47	$\text{Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1}$
1 62.364	$\text{dm}^3 \text{ Torr K}^{-1} \text{ mol}^{-1}$
1.987 21	$\text{cal K}^{-1} \text{ mol}^{-1}$

Comment 1.3

For an object of mass m moving at a speed v , the kinetic energy is $E_K = \frac{1}{2}mv^2$. The potential energy, E_p or V , of an object is the energy arising from its position (not speed). No universal expression for the potential energy can be given because it depends on the type of interaction the object experiences.

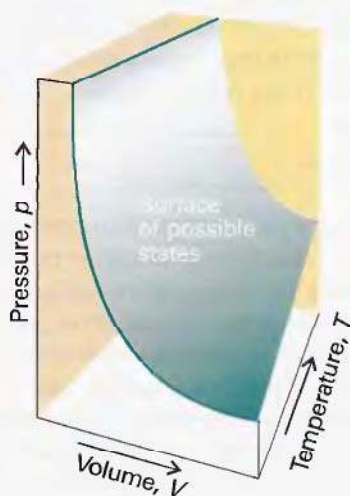


Fig. 1.8 A region of the p, V, T surface of a fixed amount of perfect gas. The points forming the surface represent the only states of the gas that can exist.

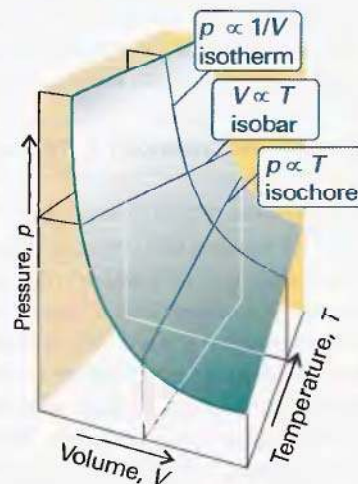


Fig. 1.9 Sections through the surface shown in Fig. 1.8 at constant temperature give the isotherms shown in Fig. 1.4 and the isobars shown in Fig. 1.6.

The surface in Fig. 1.8 is a plot of the pressure of a fixed amount of perfect gas against its volume and thermodynamic temperature as given by eqn 1.8. The surface depicts the only possible states of a perfect gas: the gas cannot exist in states that do not correspond to points on the surface. The graphs in Figs. 1.4 and 1.6 correspond to the sections through the surface (Fig. 1.9).

Example 1.2 Using the perfect gas equation

In an industrial process, nitrogen is heated to 500 K in a vessel of constant volume. If it enters the vessel at 100 atm and 300 K, what pressure would it exert at the working temperature if it behaved as a perfect gas?

Method We expect the pressure to be greater on account of the increase in temperature. The perfect gas law in the form $PV/nT = R$ implies that, if the conditions are changed from one set of values to another, then because PV/nT is equal to a constant, the two sets of values are related by the ‘combined gas law’:

$$\frac{p_1 V_1}{n_1 T_1} = \frac{p_2 V_2}{n_2 T_2} \tag{1.12}^{\circ}$$

The known and unknown data are summarized in (2).

Answer Cancellation of the volumes (because $V_1 = V_2$) and amounts (because $n_1 = n_2$) on each side of the combined gas law results in

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

which can be rearranged into

$$p_2 = \frac{T_2}{T_1} \times p_1$$

	n	p	V	T
Initial	Same	100	Same	300
Final	Same	?	Same	500

2

Substitution of the data then gives

$$p_2 = \frac{500 \text{ K}}{300 \text{ K}} \times (100 \text{ atm}) = 167 \text{ atm}$$

Experiment shows that the pressure is actually 183 atm under these conditions, so the assumption that the gas is perfect leads to a 10 per cent error.

Self-test 1.3 What temperature would result in the same sample exerting a pressure of 300 atm? [900 K]

The perfect gas equation is of the greatest importance in physical chemistry because it is used to derive a wide range of relations that are used throughout thermodynamics. However, it is also of considerable practical utility for calculating the properties of a gas under a variety of conditions. For instance, the molar volume, $V_m = V/n$, of a perfect gas under the conditions called **standard ambient temperature and pressure** (SATP), which means 298.15 K and 1 bar (that is, exactly 10^5 Pa), is easily calculated from $V_m = RT/p$ to be $24.789 \text{ dm}^3 \text{ mol}^{-1}$. An earlier definition, **standard temperature and pressure** (STP), was 0°C and 1 atm; at STP, the molar volume of a perfect gas is $22.414 \text{ dm}^3 \text{ mol}^{-1}$. Among other applications, eqn 1.8 can be used to discuss processes in the atmosphere that give rise to the weather.



IMPACT ON ENVIRONMENTAL SCIENCE

11.1 The gas laws and the weather

The biggest sample of gas readily accessible to us is the atmosphere, a mixture of gases with the composition summarized in Table 1.3. The composition is maintained moderately constant by diffusion and convection (winds, particularly the local turbulence called *eddies*) but the pressure and temperature vary with altitude and with the local conditions, particularly in the troposphere (the 'sphere of change'), the layer extending up to about 11 km.

Table 1.3 The composition of dry air at sea level

Component	Percentage	
	By volume	By mass
Nitrogen, N_2	78.08	75.53
Oxygen, O_2	20.95	23.14
Argon, Ar	0.93	1.28
Carbon dioxide, CO_2	0.031	0.047
Hydrogen, H_2	5.0×10^{-3}	2.0×10^{-4}
Neon, Ne	1.8×10^{-3}	1.3×10^{-3}
Helium, He	5.2×10^{-4}	7.2×10^{-5}
Methane, CH_4	2.0×10^{-4}	1.1×10^{-4}
Krypton, Kr	1.1×10^{-4}	3.2×10^{-4}
Nitric oxide, NO	5.0×10^{-5}	1.7×10^{-6}
Xenon, Xe	8.7×10^{-6}	1.2×10^{-5}
Ozone, O_3 : summer	7.0×10^{-6}	1.2×10^{-5}
winter	2.0×10^{-6}	3.3×10^{-6}

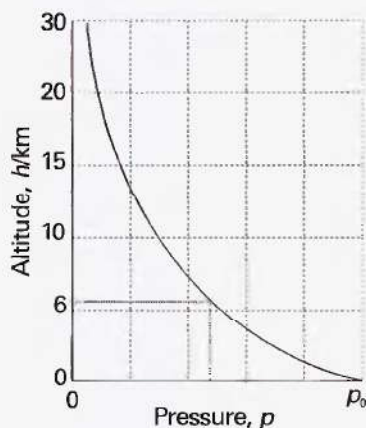


Fig. 1.10 The variation of atmospheric pressure with altitude, as predicted by the barometric formula and as suggested by the ‘US Standard Atmosphere’, which takes into account the variation of temperature with altitude.

Exploration How would the graph shown in the illustration change if the temperature variation with altitude were taken into account? Construct a graph allowing for a linear decrease in temperature with altitude.

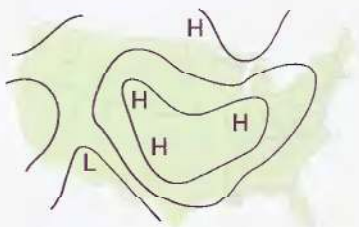


Fig. 1.11 A typical weather map; in this case, for the United States on 1 January 2000.

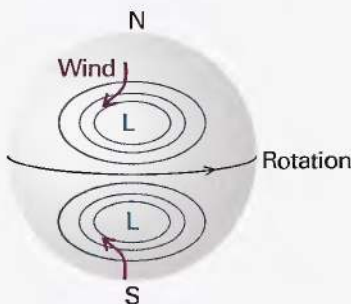


Fig. 1.12 The flow of air (‘wind’) around regions of high and low pressure in the Northern and Southern hemispheres.

In the troposphere the average temperature is 15°C at sea level, falling to -57°C at the bottom of the tropopause at 11 km. This variation is much less pronounced when expressed on the Kelvin scale, ranging from 288 K to 216 K, an average of 268 K. If we suppose that the temperature has its average value all the way up to the tropopause, then the pressure varies with altitude, h , according to the *barometric formula*:

$$p = p_0 e^{-h/H}$$

where p_0 is the pressure at sea level and H is a constant approximately equal to 8 km. More specifically, $H = RT/Mg$, where M is the average molar mass of air and T is the temperature. The barometric formula fits the observed pressure distribution quite well even for regions well above the troposphere (see Fig. 1.10). It implies that the pressure of the air and its density fall to half their sea-level value at $h = H \ln 2$, or 6 km.

Local variations of pressure, temperature, and composition in the troposphere are manifest as ‘weather’. A small region of air is termed a *parcel*. First, we note that a parcel of warm air is less dense than the same parcel of cool air. As a parcel rises, it expands adiabatically (that is, without transfer of heat from its surroundings), so it cools. Cool air can absorb lower concentrations of water vapour than warm air, so the moisture forms clouds. Cloudy skies can therefore be associated with rising air and clear skies are often associated with descending air.

The motion of air in the upper altitudes may lead to an accumulation in some regions and a loss of molecules from other regions. The former result in the formation of regions of high pressure (‘highs’ or anticyclones) and the latter result in regions of low pressure (‘lows’, depressions, or cyclones). These regions are shown as H and L on the accompanying weather map (Fig. 1.11). The lines of constant pressure—differing by 4 mbar (400 Pa, about 3 Torr)—marked on it are called *isobars*. The elongated regions of high and low pressure are known, respectively, as *ridges* and *troughs*.

In meteorology, large-scale vertical movement is called *convection*. Horizontal pressure differentials result in the flow of air that we call *wind* (see Fig. 1.12). Winds coming from the north in the Northern hemisphere and from the south in the Southern hemisphere are deflected towards the west as they migrate from a region where the Earth is rotating slowly (at the poles) to where it is rotating most rapidly (at the equator). Winds travel nearly parallel to the isobars, with low pressure to their left in the Northern hemisphere and to the right in the Southern hemisphere. At the surface, where wind speeds are lower, the winds tend to travel perpendicular to the isobars from high to low pressure. This differential motion results in a spiral outward flow of air clockwise in the Northern hemisphere around a high and an inward counter-clockwise flow around a low.

The air lost from regions of high pressure is restored as an influx of air converges into the region and descends. As we have seen, descending air is associated with clear skies. It also becomes warmer by compression as it descends, so regions of high pressure are associated with high surface temperatures. In winter, the cold surface air may prevent the complete fall of air, and result in a temperature *inversion*, with a layer of warm air over a layer of cold air. Geographical conditions may also trap cool air, as in Los Angeles, and the photochemical pollutants we know as *smog* may be trapped under the warm layer.

(b) Mixtures of gases

When dealing with gaseous mixtures, we often need to know the contribution that each component makes to the total pressure of the sample. The **partial pressure**, p_j , of a gas J in a mixture (any gas, not just a perfect gas), is defined as

$$p_j = x_j p \quad [1.13]$$

where x_J is the **mole fraction** of the component J, the amount of J expressed as a fraction of the total amount of molecules, n , in the sample:

$$x_J = \frac{n_J}{n} \quad n = n_A + n_B + \dots \quad [1.14]$$

When no J molecules are present, $x_J = 0$; when only J molecules are present, $x_J = 1$. It follows from the definition of x_J that, whatever the composition of the mixture, $x_A + x_B + \dots = 1$ and therefore that the sum of the partial pressures is equal to the total pressure:

$$p_A + p_B + \dots = (x_A + x_B + \dots)p = p \quad (1.15)$$

This relation is true for both real and perfect gases.

When all the gases are perfect, the partial pressure as defined in eqn 1.13 is also the pressure that each gas would occupy if it occupied the same container alone at the same temperature. The latter is the original meaning of 'partial pressure'. That identification was the basis of the original formulation of **Dalton's law**:

The pressure exerted by a mixture of gases is the sum of the pressures that each one would exist if it occupied the container alone.

Now, however, the relation between partial pressure (as defined in eqn 1.13) and total pressure (as given by eqn 1.15) is true for all gases and the identification of partial pressure with the pressure that the gas would exert on its own is valid only for a perfect gas.

Example 1.3 Calculating partial pressures

The mass percentage composition of dry air at sea level is approximately N_2 : 75.5; O_2 : 23.2; Ar: 1.3. What is the partial pressure of each component when the total pressure is 1.00 atm?

Method We expect species with a high mole fraction to have a proportionally high partial pressure. Partial pressures are defined by eqn 1.13. To use the equation, we need the mole fractions of the components. To calculate mole fractions, which are defined by eqn 1.14, we use the fact that the amount of molecules J of molar mass M_J in a sample of mass m_J is $n_J = m_J/M_J$. The mole fractions are independent of the total mass of the sample, so we can choose the latter to be 100 g (which makes the conversion from mass percentages very easy). Thus, the mass of N_2 present is 75.5 per cent of 100 g, which is 75.5 g.

Answer The amounts of each type of molecule present in 100 g of air, in which the masses of N_2 , O_2 , and Ar are 75.5 g, 23.2 g, and 1.3 g, respectively, are

$$n(N_2) = \frac{75.5 \text{ g}}{28.02 \text{ g mol}^{-1}} = \frac{75.5}{28.02} \text{ mol}$$

$$n(O_2) = \frac{23.2 \text{ g}}{32.00 \text{ g mol}^{-1}} = \frac{23.2}{32.00} \text{ mol}$$

$$n(\text{Ar}) = \frac{1.3 \text{ g}}{39.95 \text{ g mol}^{-1}} = \frac{1.3}{39.95} \text{ mol}$$

These three amounts work out as 2.69 mol, 0.725 mol, and 0.033 mol, respectively, for a total of 3.45 mol. The mole fractions are obtained by dividing each of the

above amounts by 3.45 mol and the partial pressures are then obtained by multiplying the mole fraction by the total pressure (1.00 atm):

	N ₂	O ₂	Ar
Mole fraction:	0.780	0.210	0.0096
Partial pressure/atm:	0.780	0.210	0.0096

We have not had to assume that the gases are perfect: partial pressures are defined as $p_1 = x_1 p$ for any kind of gas.

Self-test 1.4 When carbon dioxide is taken into account, the mass percentages are 75.52 (N₂), 23.15 (O₂), 1.28 (Ar), and 0.046 (CO₂). What are the partial pressures when the total pressure is 0.900 atm? [0.703, 0.189, 0.0084, 0.00027 atm]

Real gases

Real gases do not obey the perfect gas law exactly. Deviations from the law are particularly important at high pressures and low temperatures, especially when a gas is on the point of condensing to liquid.

1.3 Molecular interactions

Real gases show deviations from the perfect gas law because molecules interact with one another. Repulsive forces between molecules assist expansion and attractive forces assist compression.

Repulsive forces are significant only when molecules are almost in contact: they are short-range interactions, even on a scale measured in molecular diameters (Fig. 1.13). Because they are short-range interactions, repulsions can be expected to be important only when the average separation of the molecules is small. This is the case at high pressure, when many molecules occupy a small volume. On the other hand, attractive intermolecular forces have a relatively long range and are effective over several molecular diameters. They are important when the molecules are fairly close together but not necessarily touching (at the intermediate separations in Fig. 1.13). Attractive forces are ineffective when the molecules are far apart (well to the right in Fig. 1.13). Intermolecular forces are also important when the temperature is so low that the molecules travel with such low mean speeds that they can be captured by one another.

At low pressures, when the sample occupies a large volume, the molecules are so far apart for most of the time that the intermolecular forces play no significant role, and the gas behaves virtually perfectly. At moderate pressures, when the average separation of the molecules is only a few molecular diameters, the attractive forces dominate the repulsive forces. In this case, the gas can be expected to be more compressible than a perfect gas because the forces help to draw the molecules together. At high pressures, when the average separation of the molecules is small, the repulsive forces dominate and the gas can be expected to be less compressible because now the forces help to drive the molecules apart.

(a) The compression factor

The **compression factor**, Z , of a gas is the ratio of its measured molar volume, $V_m = V/n$, to the molar volume of a perfect gas, V_m^o , at the same pressure and temperature:

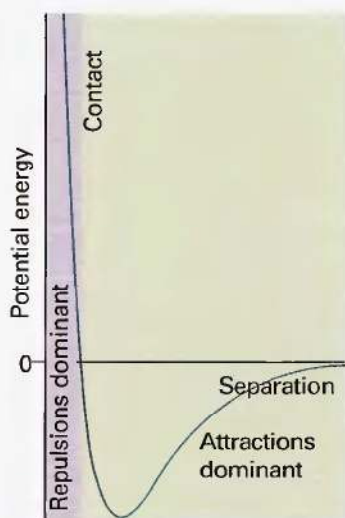


Fig. 1.13 The variation of the potential energy of two molecules on their separation. High positive potential energy (at very small separations) indicates that the interactions between them are strongly repulsive at these distances. At intermediate separations, where the potential energy is negative, the attractive interactions dominate. At large separations (on the right) the potential energy is zero and there is no interaction between the molecules.