1A The perfect gas

Contents

➤ Why do you need to know this material?

Equations related to perfect gases provide the basis for the development of many equations in thermodynamics. The perfect gas law is also a good first approximation for accounting for the properties of real gases.

➤ What is the key idea?

The perfect gas law, which is based on a series of empirical observations, is a limiting law that is obeyed increasingly well as the pressure of a gas tends to zero.

➤ What do you need to know already?

You need to be aware of the concepts of pressure and temperature introduced in *Foundations* A.

In molecular terms, a gas consists of a collection of molecules that are in ceaseless motion and which interact significantly with one another only when they collide. The properties of gases were among the first to be established quantitatively (largely during the seventeenth and eighteenth centuries) when the technological requirements of travel in balloons stimulated their investigation.

1A.1 Variables of state

The **physical state** of a sample of a substance, its physical con tion, is defined by its physical properties. Two samples of same substance that have the same physical properties are the same state. The variables needed to specify the state of a s tem are the amount of substance it contains, n, the volume occupies, V, the pressure, p, and the temperature, T.

(a) Pressure

The origin of the force exerted by a gas is the incessant batteri of the molecules on the walls of its container. The collisions a so numerous that they exert an effectively steady force, whic is experienced as a steady pressure. The SI unit of pressure, th *pascal* (Pa, 1 Pa = 1 N m^{-2}) is introduced in *Foundations* A. A discussed there, several other units are still widely used (Tab 1A.1). A pressure of 1 bar is the **standard pressure** for repor ing data; we denote it $p^{\ominus}$.

If two gases are in separate containers that share a commo movable wall (a 'piston', Fig. 1A.1), the gas that has the highe pressure will tend to compress (reduce the volume of) the ga that has lower pressure. The pressure of the high-pressure ga will fall as it expands and that of the low-pressure gas wi rise as it is compressed. There will come a stage when the tw pressures are equal and the wall has no further tendency t move. This condition of equality of pressure on either side c a movable wall is a state of **mechanical equilibrium** betwee the two gases. The pressure of a gas is therefore an indica tion of whether a container that contains the gas will be i mechanical equilibrium with another gas with which it share a movable wall.

Table 1A.1 Pressure units*

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

* Values in bold are exact.

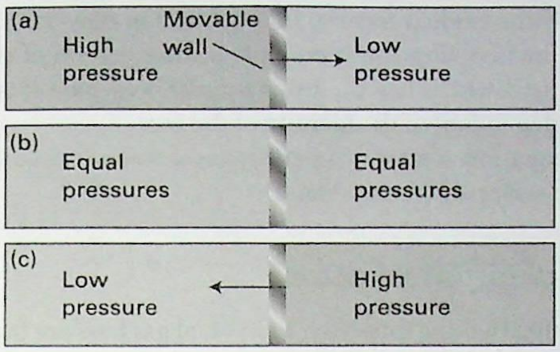


Figure 1A.1 When a region of high pressure is separated from a region of low pressure by a movable wall, the wall will be pushed into one region or the other, as in (a) and (c). However, if the two pressures are identical, the wall will not move (b). The latter condition is one of mechanical equilibrium between the two regions.

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 1A.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. The pressure exerted by a column of liquid is commonly called the 'hydrostatic pressure'.

Method According to *Foundations* A, the pressure is the force, F, divided by the area, A, to which the force is applied: $p=F/A$. For a mass m subject to a gravitational field at the surface of the earth, $F=mg$, where g is the acceleration of free fall. 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

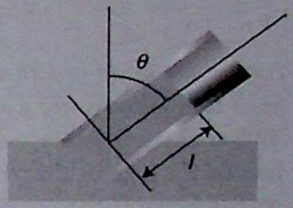
$$F=mg=\rho Ahg$$

The pressure at the base of the column is therefore

$$p=\frac{F}{A}=\frac{\rho Agh}{A}=\rho gh \qquad \text{Hydrostatic pressure} \qquad (1A.1)$$

Note that the hydrostatic 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 1A.1 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**).



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Answer: $p=\rho gl\cos\theta$

The pressure of a sample of gas inside a container is measured by using a pressure gauge, which is a device with properties that respond to 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.

(b) Temperature

The concept of temperature is introduced in *Foundations* A. 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 (theta) and expressed in *degrees Celsius* (°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** introduced in Topic 3A, 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 °K). Thermodynamic and Celsius temperatures are related by the exact expression

$$T/\mathrm{K}=\theta/{}^{\circ}\mathrm{C}+273.15$$ Definition of Celsius scale (1A.2)

This relation 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 $T=0\,\mathrm{K}$ 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.

Brief illustration 1A.1 Temperature conversion

To express 25.00 °C as a temperature in kelvins, we use eqn 1A.4 to write

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

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); see *The chemist's toolkit* A.1 of *Foundations*. Multiplication of both sides by the unit K then gives $T=298.15$ 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 $(25.00\,{}^{\circ}\mathrm{C})/{}^{\circ}\mathrm{C}=25.00$ in this illustration. Units may be multiplied and cancelled just like numbers.

1A.2 Equations of state

Although in principle the state of a pure substance is specified by giving the values of n, V, p, and T, 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

$$p=f(T,V,n)$$ General form of an equation of state (1A.3)

This equation tells us that if we know the values of n, T, and V 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 specia cases. One very important example is the equation of state of 'perfect gas', which has the form $p=nRT/V$, where R is a constant independent of the identity of the gas.

The equation of state of a perfect gas was established by combining a series of empirical laws.

(a) The empirical basis

We assume that the following individual gas laws are familiar:

Boyle's law: $pV=\text{constant, at constant } n,\ T$ (1A.4a

Charles's law: $V=\text{constant}\times T,\ \text{at constant } n, p$ (1A.4b

$p=\text{constant}\times T,\ \text{at constant } n,\ V$ (1A.4c

Avogadro's principle:

$V=\text{constant}\times n \text{ at constant } p, T$ (1A.4d

Boyle's and Charles's laws are examples of a **limiting law**, a la that is strictly true only in a certain limit, in this case $p\rightarrow$ For example, if it is found empirically that the volume of substance fits an expression $V=aT+bp+cp^2$, then in the lim of $p\rightarrow 0$, $V=aT$. Throughout this text, equations valid in th limiting sense are labelled with a blue equation number, as i these expressions. Although these relations are strictly tru only at $p=0$, they are reasonably reliable at normal pressur ($p\approx 1$ bar) and are used widely throughout chemistry.

Avogadro's principle is commonly expressed in the for 'equal volumes of gases at the same temperature and pressu contain the same numbers of molecules'. It is a principle rathe than a law (a summary of experience) because it depends o the validity of a model, in this case the existence of molecule Despite there now being no doubt about the existence of mo ecules, it is still a model-based principle rather than a law.

Figure 1A.2 depicts the variation of the pressure of a sample of gas as the volume is changed. Each of the curves in th

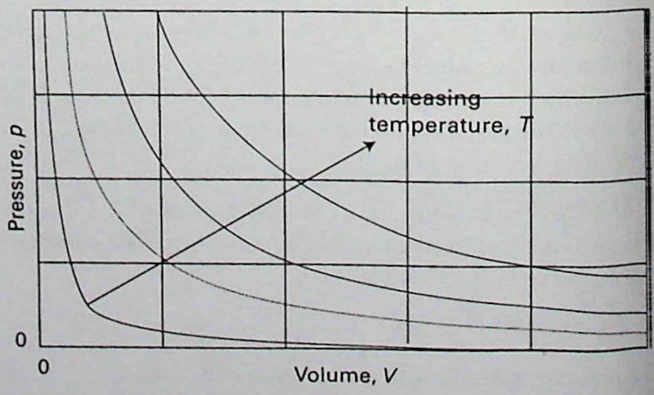

Figure 1A.2 The pressure–volume dependence of a fixed amount of perfect gas at different temperatures. Each curve is a hyperbola (pV=constant) and is called an isotherm.

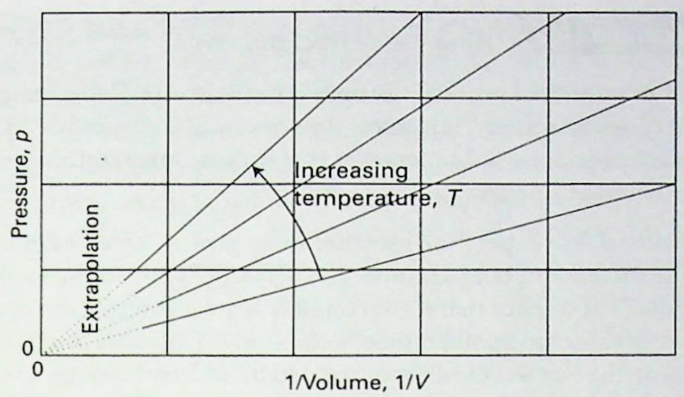

Figure 1A.3 Straight lines are obtained when the pressure is plotted against $1/V$ at constant temperature.

graph corresponds to a single temperature and hence is called an **isotherm**. According to Boyle's law, the isotherms of gases are hyperbolas (a curve obtained by plotting y against x with xy=constant, or y=constant/x). An alternative depiction, a plot of pressure against 1/volume, is shown in Fig. 1A.3. The linear variation of volume with temperature summarized by Charles's law is illustrated in Fig. 1A.4. The lines in this illustration are examples of **isobars**, or lines showing the variation of properties at constant pressure. Figure 1A.5 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.

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 development of expressions that, when plotted, give a straight line is a very important and common procedure in physical chemistry.

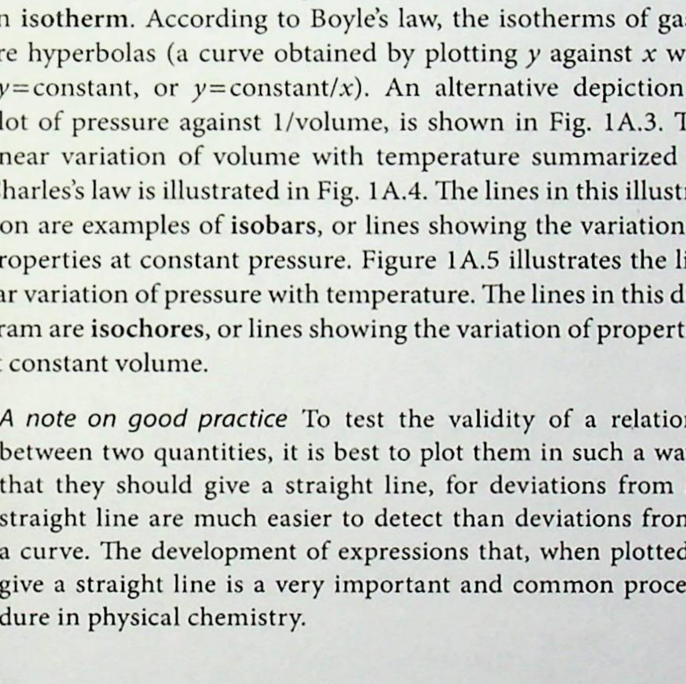

Figure 1A.4 The variation of the volume of a fixed amount of gas with the temperature at constant pressure. Note that in each case the isobars extrapolate to zero volume at $T=0$, or $\theta=-273\,°\mathrm{C}$.

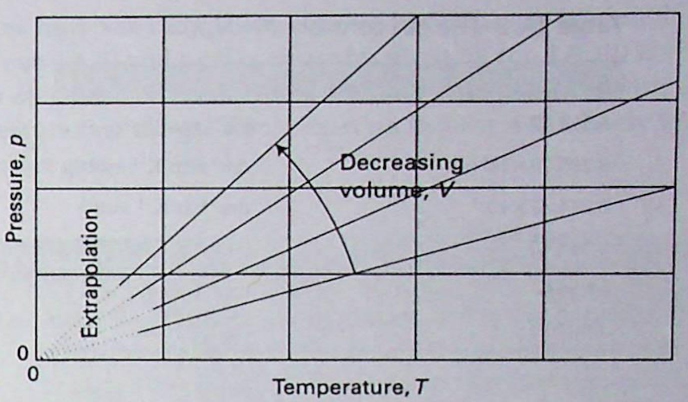

Figure 1A.5 The pressure also varies linearly with the temperature at constant volume, and extrapolates to zero at $T=0$ (−273 °C).

The empirical observations summarized by eqn 1A.5 can be combined into a single expression:

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

This expression is consistent with Boyle's law (pV=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 (molar) **gas constant**. The resulting expression

$$pV = nRT \qquad \text{Perfect gas law} \qquad (1A.5)$$

is the **perfect gas law** (or *perfect gas equation of state*). 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 1A.5 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 1A.5 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), for the speed of sound depends on the value of R and extrapolating its value to zero pressure. Another route to its value is to recognize (as explained in *Foundations* B) that it is related to Boltzmann's constant, k, by

$$R = N_A k \qquad \text{The (molar) gas constant} \qquad (1A.6)$$

where N_A is Avogadro's constant. There are currently (in 2014) plans to use this relation as the sole route to R, with defined values of N_A and k. Table 1A.2 lists the values of R in a variety of units.

A note on good practice Despite 'ideal gas' being the more common term, we prefer 'perfect gas'. As explained in Topic 5A, in an 'ideal mixture' of A and B, the AA, BB, and AB

Table 1A.2 The gas constant ($R = N_A k$)

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

interactions are all the same but not necessarily zero. In a perfect gas, not only are the interactions all the same, they are also zero.

The surface in Fig. 1A.6 is a plot of the pressure of a fixed amount of perfect gas against its volume and thermodynamic temperature as given by eqn 1A.5. 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. 1A.2 and 1A.4 correspond to the sections through the surface (Fig. 1A.7).

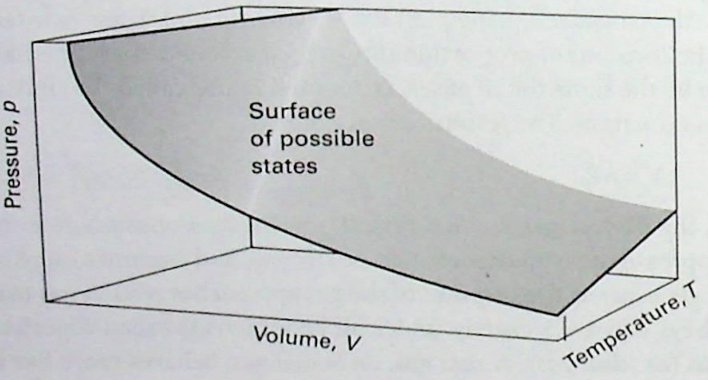

Figure 1A.6 A region of the *p,V,T* surface of a fixed amount of perfect gas. The points forming the surface represent the only states of the gas that can exist.

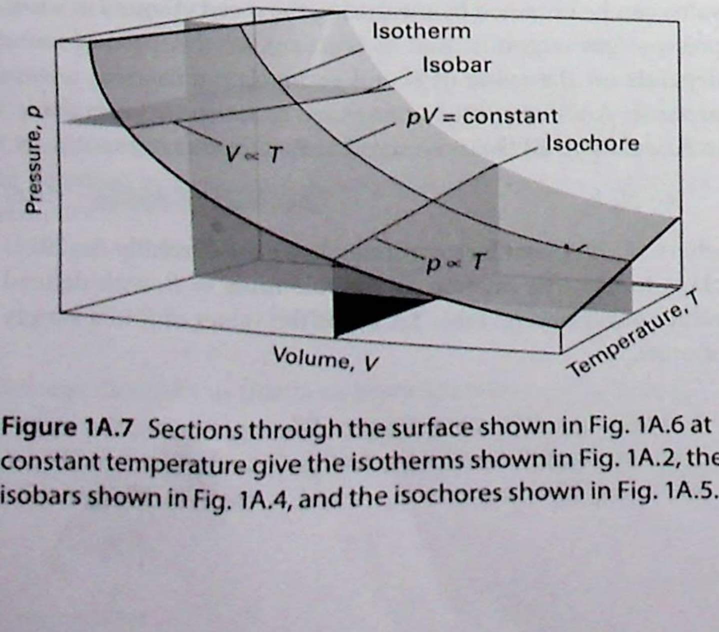

Figure 1A.7 Sections through the surface shown in Fig. 1A.6 at constant temperature give the isotherms shown in Fig. 1A.2, the isobars shown in Fig. 1A.4, and the isochores shown in Fig. 1A.5.

Example 1A.2 Using the perfect gas law

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

Method We expect the pressure to be greater on account the increase in temperature. The perfect gas law in the for $pV/nT = R$ implies that if the conditions are changed from o set of values to another, then because pV/nT is equal to a co stant, the two sets of values are related by the 'combined gas la

$$\frac{p_1 V_1}{n_1 T_1} = \frac{p_2 V_2}{n_2 T_2} \qquad \text{Combined gas law} \quad (1A.7$$

This expression is easily rearranged to give the unknow quantity (in this case p_2) in terms of the known. The know and unknown data are summarized as follows:

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

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

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

which can be rearranged into

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

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 unde these conditions, so the assumption that the gas is perfec leads to a 10 per cent error.

Self-test 1A.2 What temperature would result in the sam sample exerting a pressure of 300 atm?

Answer: 900

The perfect gas law is of the greatest importance in physi chemistry because it is used to derive a wide range of relatio that are used throughout thermodynamics. However, it is al of considerable practical utility for calculating the properties a gas under a variety of conditions. For instance, the molar v ume, $V_m = V/n$, of a perfect gas under the conditions called stan ard ambient temperature and pressure (SATP), which mea

298.15 K and 1 bar (that is, exactly 10^5 Pa), is easily calculated from $V_m = RT/p$ to be 24.789 $dm^3\ mol^{-1}$. 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 $dm^3\ mol^{-1}$.

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 pV 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. For a quantitative account of these relations, see Topic 1B.

(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

$$p_J = x_J p \qquad \textit{Definition} \quad \text{Partial pressure} \qquad (1A.8)$$

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:

$$x_J = \frac{n_J}{n} \qquad n = n_A + n_B + \cdots \qquad \textit{Definition} \quad \text{Mole fraction} \qquad (1A.9)$$

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, $x_A + x_B + \ldots = 1$ and therefore that the sum of the partial pressures is equal to the total pressure:

$$p_A + p_B + \cdots = (x_A + x_B + \cdots)p = p \qquad (1A.10)$$

This relation is true for both real and perfect gases.

When all the gases are perfect, the partial pressure as defined in eqn 1A.9 is also the pressure that each gas would exert 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 exert if it occupied the container alone. Dalton's law

Now, however, the relation between partial pressure (as defined in eqn 1A.8) and total pressure (as given by eqn 1A.10) 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 1A.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 1.20 atm?

Method We expect species with a high mole fraction to have a proportionally high partial pressure. Partial pressures are defined by eqn 1A.8. To use the equation, we need the mole fractions of the components. To calculate mole fractions, which are defined by eqn 1A.9, 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 exactly 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

$$n(N_2) = \frac{75.5\,g}{28.02\,g\,mol^{-1}} = \frac{75.5}{28.02}\,mol = 2.69\,mol$$

$$n(O_2) = \frac{23.2\,g}{32.00\,g\,mol^{-1}} = \frac{23.2}{32.00}\,mol = 0.725\,mol$$

$$n(Ar) = \frac{1.3\,g}{39.95\,g\,mol^{-1}} = \frac{1.3}{39.95}\,mol = 0.033\,mol$$

The total is 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 (1.20 atm):

	N_2	O_2	Ar
Mole fraction:	0.780	0.210	0.0096
Partial pressure/atm:	0.936	0.252	0.012

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

Self-test 1A.3 When carbon dioxide is taken into account, the mass percentages are 75.52 (N_2), 23.15 (O_2), 1.28 (Ar), and 0.046 (CO_2). What are the partial pressures when the total pressure is 0.900 atm?

Answer: 0.703, 0.189, 0.0084, 0.00027 atm

Checklist of concepts

☐ 1. The **physical state** of a sample of a substance, its physical condition, is defined by its physical properties.
☐ 2. **Mechanical equilibrium** is the condition of equality of pressure on either side of a shared movable wall.
☐ 3. An **equation of state** is an equation that interrelates the variables that define the state of a substance.
☐ 4. 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 $p \rightarrow 0$.
☐ 5. An **isotherm** is a line in a graph that corresponds to a single temperature.
☐ 6. An **isobar** is a line in a graph that corresponds to a s gle pressure.
☐ 7. An **isochore** is a line in a graph that corresponds t single volume.
☐ 8. A **perfect gas** is a gas that obeys the perfect gas l under all conditions.
☐ 9. **Dalton's law** states that the pressure exerted by a mi ture of (perfect) gases is the sum of the pressures th each one would exert if it occupied the contain alone.

Checklist of equations

Property	Equation	Comment	Equation number
Relation between temperature scales	$T/\mathrm{K} = \theta/{}^\circ\mathrm{C} + 273.15$	273.15 is exact	1A.2
Equation of state	$p = f(n,V,T)$		1A.3
Perfect gas law	$pV = nRT$	Valid for real gases in the limit $p \rightarrow 0$	1A.5
Partial pressure	$p_J = x_J p$	Valid for all gases	1A.8

1B The kinetic model

Contents

➤ Why do you need to know this material?

This material illustrates an important skill in science: the ability to extract quantitative information from a qualitative model. Moreover, the model is used in the discussion of the transport properties of gases (Topic 19A), reaction rates in gases (Topic 20F), and catalysis (Topic 22C).

➤ What is the key idea?

A gas consists of molecules of negligible size in ceaseless random motion and obeying the laws of classical mechanics in their collisions.

➤ What do you need to know already?

You need to be aware of Newton's second law of motion, that the acceleration of a body is proportional to the force acting on it, and the conservation of linear momentum.

In the **kinetic theory** of gases (which is sometimes called the *kinetic-molecular theory*, KMT) it is assumed that the only contribution to the energy of the gas is from the kinetic energies of the molecules. The kinetic model is one of the most remarkable—and arguably most beautiful—models in physical chemistry, for from a set of very slender assumptions, powerful quantitative conclusions can be reached.

1B.1 The model

The kinetic model is based on three assumptions:

1. The gas consists of molecules of mass m in ceaseless random motion obeying the laws of classical mechanics.
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 elastic collisions.

An **elastic collision** is a collision in which the total translational kinetic energy of the molecules is conserved.

(a) Pressure and molecular speeds

From the very economical assumptions of the kinetic model, we show in the following *Justification* that the pressure and volume of the gas are related by

$$pV = \tfrac{1}{3}nMv_{\mathrm{rms}}^2 \qquad \textit{Perfect gas} \quad \text{Pressure} \qquad (1B.1)$$

where $M = mN_A$, the molar mass of the molecules of mass m, and v_{rms} is the square root of the mean of the squares of the speeds, v, of the molecules:

$$v_{\mathrm{rms}} = \langle v^2 \rangle^{1/2} \qquad \textit{Definition} \quad \text{Root-mean-square speed} \qquad (1B.2)$$

Justification 1.1B The pressure of a gas according to the kinetic model

Consider the arrangement in Fig. 1B.1. When a particle of mass m that is travelling with a component of velocity v_x parallel to the x-axis collides with the wall on the right and is reflected, its linear momentum changes from mv_x before the collision to $-mv_x$ after the collision (when it is travelling in the opposite direction). The x-component of momentum therefore changes by $2mv_x$ on each collision (the y- and z-components are unchanged). Many molecules collide with the wall in an interval Δt, and the total change of momentum is the product of the change in momentum of each molecule multiplied