Molecules in motion

21

One of the simplest types of molecular motion to describe is the random motion of molecules of a perfect gas. We see that a simple theory accounts for the pressure of a gas and the rates at which molecules and energy migrate through gases. Molecular mobility is particularly important in liquids. Another simple kind of motion is the largely uniform motion of ions in solution in the presence of an electric field. Molecular and ionic motion have common features and, by considering them from a more general viewpoint, we derive expressions that govern the migration of properties through matter. One of the most useful consequences of this general approach is the formulation of the diffusion equation, which is an equation that shows how matter and energy spread through media of various kinds. Finally, we build a simple model for all types of molecular motion, in which the molecules migrate in a series of small steps, and see that it accounts for many of the properties of migrating molecules in both gases and condensed phases.

The general approach we describe in this chapter provides techniques for discussing the motion of all kinds of particles in all kinds of fluids. We set the scene by considering a simple type of motion, that of molecules in a perfect gas, and go on to see that molecular motion in liquids shows a number of similarities. We shall concentrate on the **transport properties** of a substance, its ability to transfer matter, energy, or some other property from one place to another. Four examples of transport properties are

Diffusion, the migration of matter down a concentration gradient.

Thermal conduction, the migration of energy down a temperature gradient.

Electric conduction, the migration of electric charge along an electrical potential gradient.

Viscosity, the migration of linear momentum down a velocity gradient.

It is convenient to include in the discussion **effusion**, the emergence of a gas from a container through a small hole.

Molecular motion in gases

Here we present the kinetic model of a perfect gas as a starting point for the discussion of its transport properties. In the **kinetic model** of gases we assume 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 deduced.

21.1 **The kinetic model of gases**

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.

(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

$$pV = \tfrac{1}{3}nMc^2 \tag{21.1}°$$

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:
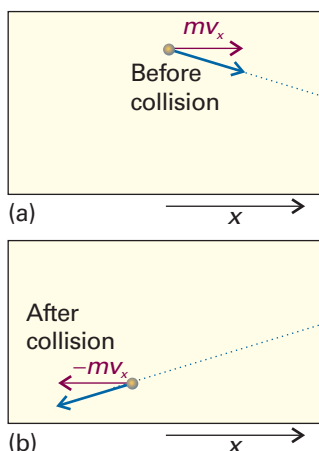
$$c = \langle v^2 \rangle^{1/2} \tag{21.2}$$

(a)

(b)

Fig. 21.1 The pressure of a gas arises from the impact of its molecules on the walls. In an elastic collision of a molecule with a wall perpendicular to the x-axis, the x-component of velocity is reversed but the y- and z-components are unchanged.
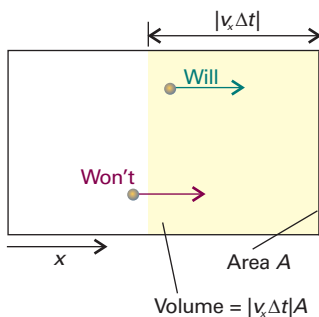
Fig. 21.2 A molecule will reach the wall on the right within an interval Δt if it is within a distance $v_x \Delta t$ of the wall and travelling to the right.

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Justification 21.1 *The pressure of a gas according to the kinetic model*

Consider the arrangement in Fig. 21.1. 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 (the product of its mass and its velocity) 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 by the number of molecules that reach the wall during the interval.

Because a molecule with velocity component v_x can travel a distance $v_x \Delta t$ along the x-axis in an interval Δt, all the molecules within a distance $v_x \Delta t$ of the wall will strike it if they are travelling towards it (Fig. 21.2). It follows that, if the wall has area A, then all the particles in a volume $A \times v_x \Delta t$ will reach the wall (if they are travelling towards it). The number density of particles is nN_A/V, where n is the total amount of molecules in the container of volume V and N_A is Avogadro's constant, so the number of molecules in the volume $Av_x \Delta t$ is $(nN_A/V) \times Av_x \Delta t$.

At any instant, half the particles are moving to the right and half are moving to the left. Therefore, the average number of collisions with the wall during the interval Δt is $\tfrac{1}{2}nN_A Av_x \Delta t/V$. The total momentum change in that interval is the product of this number and the change $2mv_x$:

$$\text{Momentum change} = \frac{nN_A Av_x \Delta t}{2V} \times 2mv_x = \frac{nmAN_A v_x^2 \Delta t}{V} = \frac{nMA v_x^2 \Delta t}{V}$$

where $M = mN_A$.

Next, to find the force, we calculate the rate of change of momentum, which is this change of momentum divided by the interval Δt during which it occurs:

$$\text{Rate of change of momentum} = \frac{nMA v_x^2}{V}$$

This rate of change of momentum is equal to the force (by Newton's second law of motion). It follows that the pressure, the force divided by the area, is

$$\text{Pressure} = \frac{nMv_x^2}{V}$$

Not all the molecules travel with the same velocity, so the detected pressure, p, is the average (denoted $\langle \ldots \rangle$) of the quantity just calculated:

$$p = \frac{nM\langle v_x^2 \rangle}{V}$$

This expression already resembles the perfect gas equation of state.

To write an expression of the pressure in terms of the root mean square speed, c, we begin by writing the speed of a single molecule, v, as $v^2 = v_x^2 + v_y^2 + v_z^2$. Because the root-mean-square speed, c, is defined as $c = \langle v^2 \rangle^{1/2}$ (eqn 21.2), it follows that

$$c^2 = \langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle$$

However, because the molecules are moving randomly, all three averages are the same. It follows that $c^2 = 3\langle v_x^2 \rangle$. Equation 21.1 follows immediately by substituting $\langle v_x^2 \rangle = \frac{1}{3}c^2$ into $p = nM\langle v_x^2 \rangle/V$.

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Equation 21.1 is one of the key results of the kinetic model. 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 (Section 1.2). Moreover, for eqn 21.1 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

$$c = \left(\frac{3RT}{M} \right)^{1/2} \tag{21.3}°$$

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. Sound waves are pressure waves, and for them to propagate the molecules of the gas must move to form regions of high and low pressure. Therefore, we should expect the root mean square speeds of molecules to be comparable to the speed of sound in air (340 m s⁻¹). The root mean square speed of N_2 molecules, for instance, is found from eqn 21.3 to be 515 m s⁻¹.

Equation 21.3 is an expression for the mean square speed of molecules. However, in an actual gas the speeds of individual molecules span a wide range, and the collisions in the gas continually redistribute the speeds among the molecules. Before a collision, a molecule may be travelling rapidly, but after a collision it may be accelerated to a very high speed, only to be slowed again by the next collision. The fraction of molecules that have speeds in the range v to $v + dv$ is proportional to the width of the range, and is written $f(v)dv$, where $f(v)$ is called the **distribution of speeds**.

The precise form of f for molecules of a gas at a temperature T was derived by J.C. Maxwell, and is

$$f(v) = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-Mv^2/2RT} \tag{21.4}$$
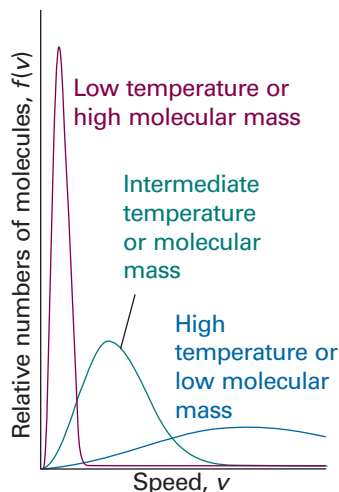
Fig. 21.3 The distribution of molecular speeds with temperature and molar mass. Note that the most probable speed (corresponding to the peak of the distribution) increases with temperature and with decreasing molar mass, and simultaneously the distribution becomes broader.

Exploration (a) Plot different distributions by keeping the molar mass constant at 100 g mol^{-1} and varying the temperature of the sample between 200 K and 2000 K. (b) Use mathematical software or the *Living graph* applet from the text's web site to evaluate numerically the fraction of molecules with speeds in the range 100 m s^{-1} to 200 m s^{-1} at 300 K and 1000 K. (c) Based on your observations, provide a molecular interpretation of temperature.

This expression is called the **Maxwell distribution of speeds** and is derived in the following *Justification*. Let's consider its features, which are also shown pictorially in Fig. 21.3:

1 Equation 21.4 includes a decaying exponential function, the term e$^{-Mv^2/2RT}$. Its presence implies that the fraction of molecules with very high speeds will be very small because e$^{-x^2}$ becomes very small when x^2 is large.

2 The factor $M/2RT$ multiplying v^2 in the exponent is large when the molar mass, M, is large, so the exponential factor goes most rapidly towards zero when M is large. That is, heavy molecules are unlikely to be found with very high speeds.

3 The opposite is true when the temperature, T, is high: then the factor $M/2RT$ in the exponent is small, so the exponential factor falls towards zero relatively slowly as v increases. In other words, a greater fraction of the molecules can be expected to have high speeds at high temperatures than at low temperatures.

4 A factor v^2 (the term before the e) multiplies the exponential. This factor goes to zero as v goes to zero, so the fraction of molecules with very low speeds will also be very small.

5 The remaining factors (the term in parentheses in eqn 21.4 and the 4π) simply ensure that, when we add together the fractions over the entire range of speeds from zero to infinity, then we get 1.

To use eqn 21.4 to calculate the fraction of molecules in a given narrow range of speeds, Δv, we evaluate $f(v)$ at the speed of interest, then multiply it by the width of the range of speeds of interest; that is, we form $f(v)\Delta v$. To use the distribution to calculate the fraction in a range of speeds that is too wide to be treated as infinitesimal, we evaluate the integral:

$$\text{Fraction in the range } v_1 \text{ to } v_2 = \int_{v_1}^{v_2} f(v)\mathrm{d}v \tag{21.5}$$

This integral is the area under the graph of f as a function of v and, except in special cases, has to be evaluated numerically by using mathematical software (Fig. 21.4).

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Justification 21.2 *The Maxwell distribution of speeds*

The Boltzmann distribution is a key result of physical chemistry and is treated fully in Section 16.1. It implies that the fraction of molecules with velocity components v_x, v_y, v_z is proportional to an exponential function of their kinetic energy, which is

$$E = \tfrac{1}{2}mv_x^2 + \tfrac{1}{2}mv_y^2 + \tfrac{1}{2}mv_z^2$$

Therefore, we can use the relation $a^{x+y+z+\cdots} = a^x a^y a^z \cdots$ to write

$$f = K\mathrm{e}^{-E/kT} = K\mathrm{e}^{-(\frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2)/kT} = K\mathrm{e}^{-mv_x^2/2kT}\mathrm{e}^{-mv_y^2/2kT}\mathrm{e}^{-mv_z^2/2kT}$$

where K is a constant of proportionality (at constant temperature) and $f\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z$ is the fraction of molecules in the velocity range v_x to $v_x + \mathrm{d}v_x$, v_y to $v_y + \mathrm{d}v_y$, and v_z to $v_z + \mathrm{d}v_z$. We see that the fraction factorizes into three factors, one for each axis, and we can write $f = f(v_x)f(v_y)f(v_z)$ with

$$f(v_x) = K^{1/3}\mathrm{e}^{-mv_x^2/2kT}$$

and likewise for the two other directions.

To determine the constant K, we note that a molecule must have a velocity somewhere in the range $-\infty < v_x < \infty$, so

$$\int_{-\infty}^{\infty} f(v_x)\mathrm{d}v_x = 1$$

Substitution of the expression for $f(v_x)$ then gives

$$1 = K^{1/3} \int_{-\infty}^{\infty} e^{-mv_x^2/2kT} dv_x = K^{1/3} \left(\frac{2\pi kT}{m} \right)^{1/2}$$

where we have used the standard integral

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \frac{\pi}{a}$$

Therefore, $K = (m/2\pi kT)^{3/2} = (M/2\pi RT)^{3/2}$, where M is the molar mass of the molecules. At this stage we know that

$$f(v_x) = \left(\frac{M}{2\pi RT} \right)^{1/2} e^{-Mv_x^2/2RT} \qquad (21.6)$$

The probability that a molecule has a velocity in the range v_x to $v_x + dv_x$, v_y to $v_y + dv_y$, v_z to $v_z + dv_z$ is

$$f(v_x)f(v_y)f(v_z)dv_x dv_y dv_z = \left(\frac{M}{2\pi RT} \right)^{3/2} e^{-Mv^2/2RT} dv_x dv_y dv_z$$

where $v^2 = v_x^2 + v_y^2 + v_z^2$. The probability $f(v)dv$ that the molecules have a speed in the range v to $v + dv$ regardless of direction is the sum of the probabilities that the velocity lies in any of the volume elements $dv_x dv_y dv_z$ forming a spherical shell of radius v and thickness dv (Fig. 21.5). The sum of the volume elements on the right-hand side of the last equation is the volume of this shell, $4\pi v^2 dv$. Therefore,

$$f(v) = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-Mv^2/2RT}$$
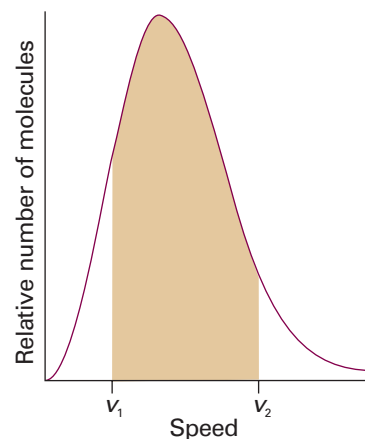
as given in eqn 21.4.

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Fig. 21.4 To calculate the probability that a molecule will have a speed in the range v_1 to v_2, we integrate the distribution between those two limits; the integral is equal to the area of the curve between the limits, as shown shaded here.
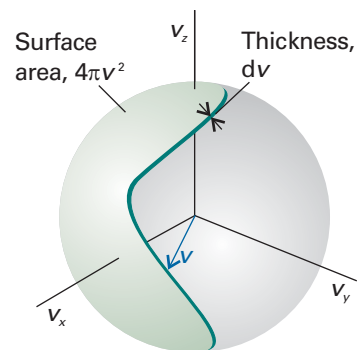

Fig. 21.5 To evaluate the probability that a molecule has a speed in the range v to $v + dv$, we evaluate the total probability that the molecule will have a speed that is anywhere on the surface of a sphere of radius $v = (v_x^2 + v_y^2 + v_z^2)^{1/2}$ by summing the probabilities that it is in a volume element $dv_x dv_y dv_z$ at a distance v from the origin.

Example 21.1 *Calculating the mean speed of molecules in a gas*

What is the mean speed, $\bar{c}$, of N_2 molecules in air at 25°C?

Method We need to use the results of probability theory summarized in *Appendix 2*. In this case, we are asked to calculate the mean speed, not the root mean square speed. A mean speed is calculated by multiplying each speed by the fraction of molecules that have that speed, and then adding all the products together. When the speed varies over a continuous range, the sum is replaced by an integral. To employ this approach here, we note that the fraction of molecules with a speed in the range v to $v + dv$ is $f(v)dv$, so the product of this fraction and the speed is $vf(v)dv$. The mean speed, $\bar{c}$, is obtained by evaluating the integral

$$\bar{c} = \int_0^{\infty} vf(v)dv$$

with f given in eqn 21.4.

Answer The integral required is

$$\bar{c} = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} \int_0^{\infty} v^3 e^{-Mv^2/2RT} dv$$

$$= 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} \times \frac{1}{2} \left(\frac{2RT}{M} \right)^2 = \left(\frac{8RT}{\pi M} \right)^{1/2}$$
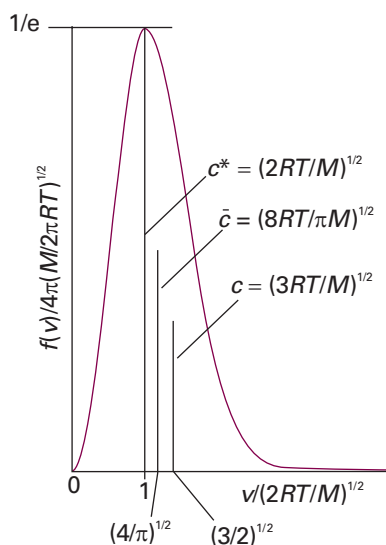
Fig. 21.6 A summary of the conclusions that can be deduced from the Maxwell distribution for molecules of molar mass M at a temperature T: c^* is the most probable speed, $\bar{c}$ is the mean speed, and c is the root mean square speed.

Comment 21.1

To find the location of the peak of the distribution, differentiate f with respect to v and look for the value of v at which the derivative is zero (other than at $v = 0$ and $v = \infty$).

where we have used the standard result from tables of integrals (or software) that

$$\int_0^\infty x^3 e^{-ax^2}\,dx = \frac{1}{2a^2}$$

Substitution of the data then gives

$$\bar{c} = \left(\frac{8 \times (8.3141 \text{ J K}^{-1}\text{ mol}^{-1}) \times (298 \text{ K})}{\pi \times (28.02 \times 10^{-3}\text{ kg mol}^{-1})}\right)^{1/2} = 475 \text{ m s}^{-1}$$

where we have used $1 \text{ J} = 1 \text{ kg m}^2\text{ s}^{-2}$.

Self-test 21.1 Evaluate the root mean square speed of the molecules by integration. You will need the integral

$$\int_0^\infty x^4 e^{-ax^2}\,dx = \frac{3}{8}\left(\frac{\pi}{a^5}\right)^{1/2} \qquad\qquad [c = (3RT/M)^{1/2}, 515 \text{ m s}^{-1}]$$

As shown in Example 21.1, we can use the Maxwell distribution to evaluate the **mean speed**, $\bar{c}$, of the molecules in a gas:

$$\bar{c} = \left(\frac{8RT}{\pi M}\right)^{1/2} \tag{21.7}$$

We can identify the **most probable speed**, c^*, from the location of the peak of the distribution:

$$c^* = \left(\frac{2RT}{M}\right)^{1/2} \tag{21.8}$$

Figure 21.6 summarizes these results.

The **relative mean speed**, $\bar{c}_{\text{rel}}$, the mean speed with which one molecule approaches another, can also be calculated from the distribution:

$$\bar{c}_{\text{rel}} = 2^{1/2}\bar{c} \tag{21.9}$$

This result is much harder to derive, but the diagram in Fig. 21.7 should help to show that it is plausible. The last result can also be generalized to the relative mean speed of two dissimilar molecules of masses m_A and m_B:

$$\bar{c}_{\text{rel}} = \left(\frac{8kT}{\pi\mu}\right)^{1/2} \qquad \mu = \frac{m_A m_B}{m_A + m_B} \tag{21.10}$$

Note that the molecular masses (not the molar masses) and Boltzmann's constant, $k = R/N_A$, appear in this expression; the quantity μ is called the **reduced mass** of the molecules. Equation 21.10 turns into eqn 21.7 when the molecules are identical (that is, $m_A = m_B = m$, so $\mu = \frac{1}{2}m$).

The Maxwell distribution has been verified experimentally. For example, molecular speeds can be measured directly with a velocity selector (Fig. 21.8). The spinning cylinder has channels that permit the passage of only those molecules moving through them at the appropriate speed, and the number of molecules can be determined by collecting them at a detector.

(b) The collision frequency

A qualitative picture of the events taking place in a gas was first described in Section 1.2. The kinetic model enables us to make that picture more quantitative. In particular,
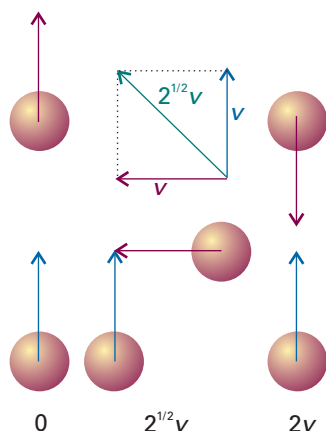
Fig. 21.7 A simplified version of the argument to show that the mean relative speed of molecules in a gas is related to the mean speed. When the molecules are moving in the same direction, the mean relative speed is zero; it is $2v$ when the molecules are approaching each other. A typical mean direction of approach is from the side, and the mean speed of approach is then $2^{1/2}v$. The last direction of approach is the most characteristic, so the mean speed of approach can be expected to be about $2^{1/2}v$. This value is confirmed by more detailed calculation.
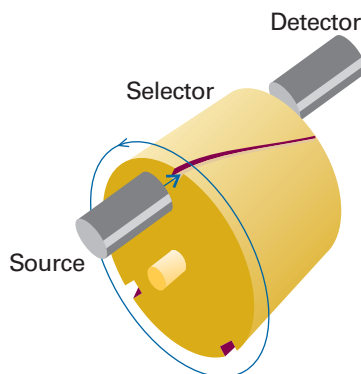

Fig. 21.8 A velocity selector. The molecules are produced in the source (which may be an oven with a small hole in one wall), and travel in a beam towards the rotating channels. Only if the speed of a molecule is such as to carry it along the channel that rotates into its path will it reach the detector. Thus, the number of slow molecules can be counted by rotating the cylinder slowly, and the number of fast molecules counted by rotating the cylinder rapidly.

Synoptic table 21.1* Collision cross-sections

	σ/nm^2
C_6H_6	0.88
CO_2	0.52
He	0.21
N_2	0.43

* More values are given in the *Data section*.

it enables us to calculate the frequency with which molecular collisions occur and the distance a molecule travels on average between collisions.

We count a 'hit' whenever the centres of two molecules come within a distance d of each other, where d, the **collision diameter**, is of the order of the actual diameters of the molecules (for impenetrable hard spheres d is the diameter). As we show in the following *Justification*, we can use kinetic model to deduce that the **collision frequency**, z, the number of collisions made by one molecule divided by the time interval during which the collisions are counted, when there are N molecules in a volume V is

$$z = \sigma \bar{c}_{rel} \mathcal{N} \qquad (21.11a)°$$

with $\mathcal{N} = N/V$ and $\bar{c}_{rel}$ given in eqn 21.10. The area $\sigma = \pi d^2$ is called the **collision cross-section** of the molecules. Some typical collision cross-sections are given in Table 21.1 (they are obtained by the techniques described in Section 18.6). In terms of the pressure,

$$z = \frac{\sigma \bar{c}_{rel} p}{kT} \qquad (21.11b)°$$

Fig. 21.9 In an interval Δt, a molecule of diameter d sweeps out a tube of radius d and length $\bar{c}_{rel}\Delta t$. As it does so it encounters other molecules with centres that lie within the tube, and each such encounter counts as one collision. In reality, the tube is not straight, but changes direction at each collision. Nevertheless, the volume swept out is the same, and this straightened version of the tube can be used as a basis of the calculation.

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Justification 21.3 *Using the kinetic model to calculate the collision frequency*

We consider the positions of all the molecules except one to be frozen. Then we note what happens as one mobile molecule travels through the gas with a mean relative speed $\bar{c}_{rel}$ for a time Δt. In doing so it sweeps out a 'collision tube' of cross-sectional area $\sigma = \pi d^2$ and length $\bar{c}_{rel}\Delta t$, and therefore of volume $\sigma \bar{c}_{rel}\Delta t$ (Fig. 21.9). The number of stationary molecules with centres inside the collision tube is given by the

volume of the tube multiplied by the number density $\mathcal{N} = N/V$, and is $\mathcal{N}\sigma\bar{c}_{rel}\Delta t$. The number of hits scored in the interval Δt is equal to this number, so the number of collisions divided by the time interval, is $\mathcal{N}\sigma\bar{c}_{rel}$. The expression in terms of the pressure of the gas is obtained by using the perfect gas equation to write

$$\mathcal{N} = \frac{N}{V} = \frac{nN_A}{V} = \frac{pN_A}{RT} = \frac{p}{kT}$$

Equation 21.11a shows that, at constant volume, the collision frequency increases with increasing temperature. The reason for this increase is that the relative mean speed increases with temperature (eqns 21.9 and 21.10). Equation 21.11b shows that, at constant temperature, the collision frequency is proportional to the pressure. Such a proportionality is plausible, for the greater the pressure, the greater the number density of molecules in the sample, and the rate at which they encounter one another is greater even though their average speed remains the same. For an N_2 molecule in a sample at 1 atm and 25°C, $z \approx 5 \times 10^9$ s^{-1}, so a given molecule collides about 5×10^9 times each second. We are beginning to appreciate the timescale of events in gases.

(c) The mean free path

Once we have the collision frequency, we can calculate the **mean free path**, λ (lambda), the average distance a molecule travels between collisions. If a molecule collides with a frequency z, it spends a time $1/z$ in free flight between collisions, and therefore travels a distance $(1/z)\bar{c}$. It follows that the mean free path is

$$\lambda = \frac{\bar{c}}{z} \tag{21.12}$$

Substitution of the expression for z in eqn 21.11b gives

$$\lambda = \frac{kT}{2^{1/2}\sigma p} \tag{21.13}$$

Doubling the pressure reduces the mean free path by half. A typical mean free path in nitrogen gas at 1 atm is 70 nm, or about 10^3 molecular diameters. Although the temperature appears in eqn 21.13, in a sample of constant volume, the pressure is proportional to T, so T/p remains constant when the temperature is increased. Therefore, the mean free path is independent of the temperature in a sample of gas in a container of fixed volume. The distance between collisions is determined by the number of molecules present in the given volume, not by the speed at which they travel.

In summary, a typical gas (N_2 or O_2) at 1 atm and 25°C can be thought of as a collection of molecules travelling with a mean speed of about 500 m s^{-1}. Each molecule makes a collision within about 1 ns, and between collisions it travels about 10^3 molecular diameters. The kinetic model of gases is valid (and the gas behaves nearly perfectly) if the diameter of the molecules is much smaller than the mean free path ($d \ll \lambda$), for then the molecules spend most of their time far from one another.

IMPACT ON ASTROPHYSICS
I21.1 The Sun as a ball of perfect gas

The kinetic model of gases is valid when the size of the particles is negligible compared with their mean free path. It may seem absurd, therefore, to expect the kinetic model and, as a consequence, the perfect gas law, to be applicable to the dense matter of stellar interiors. In the Sun, for instance, the density at its centre is 1.50 times that of liquid water and comparable to that of water about half way to its surface. However,

we have to realize that the state of matter is that of a *plasma*, in which the electrons have been stripped from the atoms of hydrogen and helium that make up the bulk of the matter of stars. As a result, the particles making up the plasma have diameters comparable to those of nuclei, or about 10 fm. Therefore, a mean free path of only 0.1 pm satisfies the criterion for the validity of the kinetic theory and the perfect gas law. We can therefore use $pV = nRT$ as the equation of state for the stellar interior.

As for any perfect gas, the pressure in the interior of the Sun is related to the mass density, $\rho = m/V$, by $p = \rho RT/M$. Atoms are stripped of their electrons in the interior of stars so, if we suppose that the interior consists of ionized hydrogen atoms, the mean molar mass is one-half the molar mass of hydrogen, or 0.5 g mol^{-1} (the mean of the molar mass of H^+ and e^-, the latter being virtually 0). Half way to the centre of the Sun, the temperature is 3.6 MK and the mass density is 1.20 g cm^{-3} (slightly denser than water); so the pressure there works out as 7.2×10^{13} Pa, or about 720 million atmospheres.

We can combine this result with the expression for the pressure from the kinetic model (eqn 21.1). Because the total kinetic energy of the particles is $E_K = \frac{1}{2}Nmc^2$, we can write $p = \frac{2}{3}E_K/V$. That is, the pressure of the plasma is related to the *kinetic energy density*, $\rho_K = E_K/V$, the kinetic energy of the molecules in a region divided by the volume of the region, by $p = \frac{2}{3}\rho_K$. It follows that the kinetic energy density half way to the centre of the Sun is about 0.11 GJ cm^{-3}. In contrast, on a warm day (25°C) on Earth, the (translational) kinetic energy density of our atmosphere is only 0.15 J cm^{-3}.

21.2 Collisions with walls and surfaces

The key result for accounting for transport in the gas phase is the rate at which molecules strike an area (which may be an imaginary area embedded in the gas, or part of a real wall). The **collision flux**, Z_W, is the number of collisions with the area in a given time interval divided by the area and the duration of the interval. The **collision frequency**, the number of hits per second, is obtained by multiplication of the collision flux by the area of interest. We show in the *Justification* below that the collision flux is

$$Z_W = \frac{p}{(2\pi mkT)^{1/2}} \tag{21.14}°$$

When $p = 100$ kPa (1.00 bar) and $T = 300$ K, $Z_W \approx 3 \times 10^{23}$ cm^{-2} s^{-1}.

....

Justification 21.4 *The collision flux*

Consider a wall of area A perpendicular to the x-axis (as in Fig. 21.2). If a molecule has $v_x > 0$ (that is, it is travelling in the direction of positive x), then it will strike the wall within an interval Δt if it lies within a distance $v_x\Delta t$ of the wall. Therefore, all molecules in the volume $Av_x\Delta t$, and with positive x-component of velocities, will strike the wall in the interval Δt. The total number of collisions in this interval is therefore the volume $Av_x\Delta t$ multiplied by the number density, $\mathcal{N}$, of molecules. However, to take account of the presence of a range of velocities in the sample, we must sum the result over all the positive values of v_x weighted by the probability distribution of velocities (eqn 21.6):

$$\text{Number of collisions} = \mathcal{N}A\Delta t \int_0^\infty v_x f(v_x)\,dx$$

The collision flux is the number of collisions divided by A and Δt, so

$$Z_W = \mathcal{N} \int_0^\infty v_x f(v_x)\,dx$$

Then, using the velocity distribution in eqn 21.6,

$$\int_0^\infty v_x f(v_x) \mathrm{d}v_x = \left(\frac{m}{2\pi kT}\right)^{1/2} \int_0^\infty v_x \mathrm{e}^{-mv_x^2/2kT} \mathrm{d}v_x = \left(\frac{kT}{2\pi m}\right)^{1/2}$$

where we have used the standard integral

$$\int_0^\infty x \mathrm{e}^{-ax^2} \mathrm{d}x = \frac{1}{2a}$$

Therefore,

$$Z_W = \mathcal{N}\left(\frac{kT}{2\pi m}\right)^{1/2} = \tfrac{1}{4}\bar{c}\mathcal{N} \tag{21.15}°$$

where we have used eqn 21.7 in the form $\bar{c} = (8kT/\pi m)^{1/2}$, which implies that $\tfrac{1}{4}\bar{c} = (kT/2\pi m)^{1/2}$. Substitution of $\mathcal{N} = nN_A/V = p/kT$ gives eqn 21.14.

21.3 The rate of effusion

The essential empirical observations on effusion are summarized by **Graham's law of effusion**, which states that the rate of effusion is inversely proportional to the square root of the molar mass. The basis of this result is that, as remarked above, the mean speed of molecules is inversely proportional to $M^{1/2}$, so the rate at which they strike the area of the hole is also inversely proportional to $M^{1/2}$. However, by using the expression for the rate of collisions, we can obtain a more detailed expression for the rate of effusion and hence use effusion data more effectively.

When a gas at a pressure p and temperature T is separated from a vacuum by a small hole, the rate of escape of its molecules is equal to the rate at which they strike the area of the hole (which is given by eqn 21.14). Therefore, for a hole of area A_0,

$$\text{Rate of effusion} = Z_W A = \frac{pA_0}{(2\pi mkT)^{1/2}} = \frac{pA_0 N_A}{(2\pi MRT)^{1/2}} \tag{21.16}°$$

where, in the last step, we have used $R = N_A k$ and $M = mN_A$. This rate is inversely proportional to $M^{1/2}$, in accord with Graham's law.

Equation 21.16 is the basis of the **Knudsen method** for the determination of the vapour pressures of liquids and solids, particularly of substances with very low vapour pressures. Thus, if the vapour pressure of a sample is p, and it is enclosed in a cavity with a small hole, then the rate of loss of mass from the container is proportional to p.

Example 21.2 *Calculating the vapour pressure from a mass loss*

Caesium (m.p. 29°C, b.p. 686°C) was introduced into a container and heated to 500°C. When a hole of diameter 0.50 mm was opened in the container for 100 s, a mass loss of 385 mg was measured. Calculate the vapour pressure of liquid caesium at 500 K.

Method The pressure of vapour is constant inside the container despite the effusion of atoms because the hot liquid metal replenishes the vapour. The rate of effusion is therefore constant, and given by eqn 21.16. To express the rate in terms of mass, multiply the number of atoms that escape by the mass of each atom.

Answer The mass loss Δm in an interval Δt is related to the collision flux by

$$\Delta m = Z_W A_0 m \Delta t$$

where A_0 is the area of the hole and m is the mass of one atom. It follows that

$$Z_W = \frac{\Delta m}{A_0 m \Delta t}$$

Because Z_W is related to the pressure by eqn 21.14, we can write

$$p = \left(\frac{2\pi RT}{M}\right)^{1/2} \frac{\Delta m}{A_0 \Delta t}$$

Because $M = 132.9$ g mol^{-1}, substitution of the data gives $p = 11$ kPa (using 1 Pa = 1 N m^{-2} = 1 J m^{-1}), or 83 Torr.

Self-test 21.2 How long would it take 1.0 g of Cs atoms to effuse out of the oven under the same conditions? [260 s]

21.4 Transport properties of a perfect gas

Transport properties are commonly expressed in terms of a number of 'phenomenological' equations, or equations that are empirical summaries of experimental observations. These phenomenological equations apply to all kinds of properties and media. In the following sections, we introduce the equations for the general case and then show how to calculate the parameters that appear in them.

(a) The phenomenological equations

The rate of migration of a property is measured by its **flux**, J, the quantity of that property passing through a given area in a given time interval divided by the area and the duration of the interval. If matter is flowing (as in diffusion), we speak of a **matter flux** of so many molecules per square metre per second; if the property is energy (as in thermal conduction), then we speak of the **energy flux** and express it in joules per square metre per second, and so on.

Experimental observations on transport properties show that the flux of a property is usually proportional to the first derivative of some other related property. For example, the flux of matter diffusing parallel to the z-axis of a container is found to be proportional to the first derivative of the concentration:

$$J(\text{matter}) \propto \frac{d\mathcal{N}}{dz} \tag{21.17}$$

where $\mathcal{N}$ is the number density of particles with units number per metre cubed (m^{-3}). The SI units of J are number per metre squared per second (m^{-2} s^{-1}). The proportionality of the flux of matter to the concentration gradient is sometimes called **Fick's first law of diffusion**: the law implies that, if the concentration varies steeply with position, then diffusion will be fast. There is no net flux if the concentration is uniform ($d\mathcal{N}/dz = 0$). Similarly, the rate of thermal conduction (the flux of the energy associated with thermal motion) is found to be proportional to the temperature gradient:

$$J(\text{energy}) \propto \frac{dT}{dz} \tag{21.18}$$

The SI units of this flux are joules per metre squared per second (J m^{-2} s^{-1}).

A positive value of J signifies a flux towards positive z; a negative value of J signifies a flux towards negative z. Because matter flows down a concentration gradient, from high concentration to low concentration, J is positive if $d\mathcal{N}/dz$ is negative (Fig. 21.10).
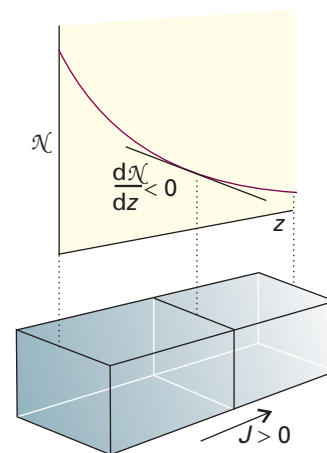

Fig. 21.10 The flux of particles down a concentration gradient. Fick's first law states that the flux of matter (the number of particles passing through an imaginary window in a given interval divided by the area of the window and the duration of the interval) is proportional to the density gradient at that point.

Synoptic table 21.2* Transport properties of gases at 1 atm

	κ/(J K^{-1} m^{-1} s^{-1})	η/(μP)†	
	273 K	273 K	293 K
Ar	0.0163	210	223
CO$_2$	0.0145	136	147
He	0.1442	187	196
N$_2$	0.0240	166	176

* More values are given in the *Data section*.
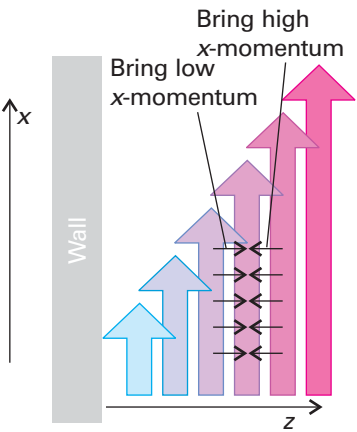$\dagger$ 1 μP = 10^{-7} kg m^{-1} s^{-1}.

Fig. 21.11 The viscosity of a fluid arises from the transport of linear momentum. In this illustration the fluid is undergoing laminar flow, and particles bring their initial momentum when they enter a new layer. If they arrive with high *x*-component of momentum they accelerate the layer; if with low *x*-component of momentum they retard the layer.

Therefore, the coefficient of proportionality in eqn 21.18 must be negative, and we write it $-D$:

$$J(\text{matter}) = -D\frac{d\mathcal{N}}{dz} \tag{21.19}$$

The constant D is the called the **diffusion coefficient**; its SI units are metre squared per second (m^2 s^{-1}). Energy migrates down a temperature gradient, and the same reasoning leads to

$$J(\text{energy}) = -\kappa\frac{dT}{dz} \tag{21.20}$$

where κ is the **coefficient of thermal conductivity**. The SI units of κ are joules per kelvin per metre per second (J K^{-1} m^{-1} s^{-1}). Some experimental values are given in Table 21.2.

To see the connection between the flux of momentum and the viscosity, consider a fluid in a state of **Newtonian flow**, which can be imagined as occurring by a series of layers moving past one another (Fig. 21.11). The layer next to the wall of the vessel is stationary, and the velocity of successive layers varies linearly with distance, z, from the wall. Molecules ceaselessly move between the layers and bring with them the x-component of linear momentum they possessed in their original layer. A layer is retarded by molecules arriving from a more slowly moving layer because they have a low momentum in the x-direction. A layer is accelerated by molecules arriving from a more rapidly moving layer. We interpret the net retarding effect as the fluid's viscosity.

Because the retarding effect depends on the transfer of the x-component of linear momentum into the layer of interest, the viscosity depends on the flux of this x-component in the z-direction. The flux of the x-component of momentum is proportional to dv_x/dz because there is no net flux when all the layers move at the same velocity. We can therefore write

$$J(x\text{-component of momentum}) = -\eta\frac{dv_x}{dz} \tag{21.21}$$

The constant of proportionality, η, is the **coefficient of viscosity** (or simply 'the viscosity'). Its units are kilograms per metre per second (kg m^{-1} s^{-1}). Viscosities are often reported in poise (P), where 1 P = 10^{-1} kg m^{-1} s^{-1}. Some experimental values are given in Table 21.2.

(b) The transport parameters

As shown in *Further information* 21.1 and summarized in Table 21.3, the kinetic model leads to expressions for the diffusional parameters of a perfect gas.

Table 21.3 Transport properties of perfect gases

Property	Transported quantity	Simple kinetic theory	Units
Diffusion	Matter	$D = \frac{1}{3}\lambda\bar{c}$	m^2 s^{-1}
Thermal conductivity	Energy	$\kappa = \frac{1}{3}\lambda\bar{c}C_{V,m}[A]$	J K^{-1} m^{-1} s^{-1}
		$= \dfrac{\bar{c}C_{V,m}}{3\sqrt{2}\sigma N_A}$	
Viscosity	Linear momentum	$\eta = \frac{1}{3}\lambda\bar{c}m\mathcal{N}$	kg m^{-1} s^{-1}
		$= \dfrac{m\bar{c}}{3\sqrt{2}\sigma}$	

The diffusion coefficient is

$$D = \tfrac{1}{3}\lambda\bar{c} \tag{21.22}°$$

As usual, we need to consider the significance of this expression:

1 The mean free path, λ, decreases as the pressure is increased (eqn 21.13), so D decreases with increasing pressure and, as a result, the gas molecules diffuse more slowly.

2 The mean speed, $\bar{c}$, increases with the temperature (eqn 21.7), so D also increases with temperature. As a result, molecules in a hot sample diffuse more quickly than those in a cool sample (for a given concentration gradient).

3 Because the mean free path increases when the collision cross-section of the molecules decreases (eqn 21.13), the diffusion coefficient is greater for small molecules than for large molecules.

Similarly, according to the kinetic model of gases, the thermal conductivity of a perfect gas A having molar concentration [A] is given by the expression

$$\kappa = \tfrac{1}{3}\lambda\bar{c}C_{V,\mathrm{m}}[\mathrm{A}] \tag{21.23}°$$

where $C_{V,\mathrm{m}}$ is the molar heat capacity at constant volume. To interpret this expression, we note that:

1 Because λ is inversely proportional to the pressure, and hence inversely proportional to the molar concentration of the gas, the thermal conductivity is independent of the pressure.

2 The thermal conductivity is greater for gases with a high heat capacity because a given temperature gradient then corresponds to a greater energy gradient.

The physical reason for the pressure independence of κ is that the thermal conductivity can be expected to be large when many molecules are available to transport the energy, but the presence of so many molecules limits their mean free path and they cannot carry the energy over a great distance. These two effects balance. The thermal conductivity is indeed found experimentally to be independent of the pressure, except when the pressure is very low, when $\kappa \propto p$. At low pressures λ exceeds the dimensions of the apparatus, and the distance over which the energy is transported is determined by the size of the container and not by the other molecules present. The flux is still proportional to the number of carriers, but the length of the journey no longer depends on λ, so $\kappa \propto [\mathrm{A}]$, which implies that $\kappa \propto p$.

Finally, the kinetic model leads to the following expression for the viscosity (see *Further information* 21.1):

$$\eta = \tfrac{1}{3}M\lambda\bar{c}[\mathrm{A}] \tag{21.24}°$$

where [A] is the molar concentration of the gas molecules and M is their molar mass. We can interpret this expression as follows:

1 Because $\lambda \propto 1/p$ (eqn 21.13) and $[\mathrm{A}] \propto p$, it follows that $\eta \propto \bar{c}$, independent of p. That is, the viscosity is independent of the pressure

2 Because $\bar{c} \propto T^{1/2}$ (eqn 21.7), $\eta \propto T^{1/2}$. That is, the viscosity of a gas *increases* with temperature.

The physical reason for the pressure-independence of the viscosity is the same as for the thermal conductivity: more molecules are available to transport the momentum, but they carry it less far on account of the decrease in mean free path. The increase of viscosity with temperature is explained when we remember that at high temperatures the molecules travel more quickly, so the flux of momentum is greater. By contrast, as
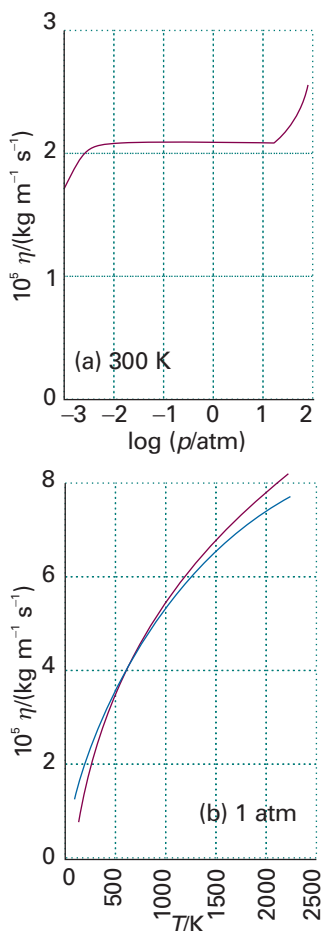
Fig. 21.12 The experimental results for (a) the pressure dependence of the viscosity of argon, and (b) its temperature dependence. The blue line in the latter is the calculated value. Fitting the observed and calculating curves is one way of determining the collision cross-section.

we shall see in Section 21.6, the viscosity of a liquid *decreases* with increase in temperature because intermolecular interactions must be overcome.

There are two main techniques for measuring viscosities of gases. One technique depends on the rate of damping of the torsional oscillations of a disc hanging in the gas. The half-life of the decay of the oscillation depends on the viscosity and the design of the apparatus, and the apparatus needs to be calibrated. The other method is based on **Poiseuille's formula** for the rate of flow of a fluid through a tube of radius r:

$$\frac{dV}{dt} = \frac{(p_1^2 - p_2^2)\pi r^4}{16l\eta p_0} \tag{21.25}$$

where V is the volume flowing, p_1 and p_2 are the pressures at each end of the tube of length l, and p_0 is the pressure at which the volume is measured.

Such measurements confirm that the viscosities of gases are independent of pressure over a wide range. For instance, the results for argon from 10^{-3} atm to 10^2 atm are shown in Fig. 21.12, and we see that η is constant from about 0.01 atm to 20 atm. The measurements also confirm (to a lesser extent) the $T^{1/2}$ dependence. The blue line in the illustration shows the calculated values using $\sigma = 22 \times 10^{-20}$ m^2, implying a collision diameter of 260 pm, in contrast to the van der Waals diameter of 335 pm obtained from the density of the solid. The agreement is not too bad, considering the simplicity of the model, especially the neglect of intermolecular forces.

Illustration 21.1 *Using the Poiseuille formula*

In a Poiseuille flow experiment to measure the viscosity of air at 298 K, the sample was allowed to flow through a tube of length 100 cm and internal diameter 1.00 mm. The high-pressure end was at 765 Torr and the low-pressure end was at 760 Torr. The volume was measured at the latter pressure. In 100 s, 90.2 cm^3 of air passed through the tube. The viscosity of air at 298 K is found by reorganizing the Poiseuille formula, eqn 21.25, into

$$\eta = \frac{(p_1^2 - p_2^2)\pi r^4}{16lp_0(dV/dt)}$$

and substituting the data (after converting the pressures to pascals by using 1 Torr = 133.3 Pa):

$$\eta = \frac{\{(765 \times 133.3\ \text{Pa})^2 - (760 \times 133.3\ \text{Pa})^2\} \times \pi \times (5.00 \times 10^{-4}\ \text{m})^4}{16 \times (1.00 \times 10^{-1}\ \text{m}) \times (760 \times 133.3\ \text{Pa}) \times \left(\dfrac{9.02 \times 10^{-5}\ \text{m}^3}{100\ \text{s}}\right)}$$

$$= 1.82 \times 10^{-4}\ \text{kg m}^{-1}\ \text{s}^{-1}$$

where we have used 1 Pa = 1 kg m^{-1} s^{-2}. The kinetic model expression gives $\eta = 1.4 \times 10^{-5}$ kg m^{-1} s^{-1}, so the agreement is reasonably good. Viscosities are commonly expressed in centipoise (cP) or (for gases) micropoise (μP), the conversion being 1 cP = 10^{-3} kg m^{-1} s^{-1}; the viscosity of air at 20°C is about 180 μP.

Self-test 21.3 What volume would be collected if the pressure gradient were doubled, other conditions remaining constant?   [181 cm^3]

Molecular motion in liquids

We outlined what is currently known about the structure of simple liquids in Section 17.6. Here we consider a particularly simple type of motion through a liquid, that of an ion, and see that the information that motion provides can be used to infer the behaviour of uncharged species too.

21.5 Experimental results

The motion of molecules in liquids can be studied experimentally by a variety of methods. Relaxation time measurements in NMR and EPR (Chapter 15) can be interpreted in terms of the mobilities of the molecules, and have been used to show that big molecules in viscous fluids typically rotate in a series of small (about 5°) steps, whereas small molecules in nonviscous fluids typically jump through about 1 radian (57°) in each step. Another important technique is **inelastic neutron scattering**, in which the energy neutrons collect or discard as they pass through a sample is interpreted in terms of the motion of its particles. The same technique is used to examine the internal dynamics of macromolecules.

More mundane than these experiments are viscosity measurements (Table 21.4). For a molecule to move in a liquid, it must acquire at least a minimum energy to escape from its neighbours. The probability that a molecule has at least an energy E_a is proportional to $e^{-E_a/RT}$, so the mobility of the molecules in the liquid should follow this type of temperature dependence. Because the coefficient of viscosity, η, is inversely proportional to the mobility of the particles, we should expect that

$$\eta \propto e^{E_a/RT} \tag{21.26}$$

(Note the positive sign of the exponent.) This expression implies that the viscosity should decrease sharply with increasing temperature. Such a variation is found experimentally, at least over reasonably small temperature ranges (Fig. 21.13). The activation energy typical of viscosity is comparable to the mean potential energy of intermolecular interactions.

One problem with the interpretation of viscosity measurements is that the change in density of the liquid as it is heated makes a pronounced contribution to the temperature variation of the viscosity. Thus, the temperature dependence of viscosity at constant volume, when the density is constant, is much less than that at constant pressure. The intermolecular interactions between the molecules of the liquid govern the magnitude of E_a, but the problem of calculating it is immensely difficult and still largely unsolved. At low temperatures, the viscosity of water decreases as the pressure is increased. This behaviour is consistent with the rupture of hydrogen bonds.

21.6 The conductivities of electrolyte solutions

Further insight into the nature of molecular motion can be obtained by studying the motion of ions in solution, for ions can be dragged through the solvent by the application of a potential difference between two electrodes immersed in the sample. By studying the transport of charge through electrolyte solutions it is possible to build up a picture of the events that occur in them and, in some cases, to extrapolate the conclusions to species that have zero charge, that is, to neutral molecules.

(a) Conductance and conductivity

The fundamental measurement used to study the motion of ions is that of the electrical resistance, R, of the solution. The **conductance**, G, of a solution is the inverse of its

Synoptic table 21.4* Viscosities of liquids at 298 K

	$\eta/(10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}})$
Benzene	0.601
Mercury	1.55
Propane	0.224
Water†	0.891

* More values are given in the *Data section*.
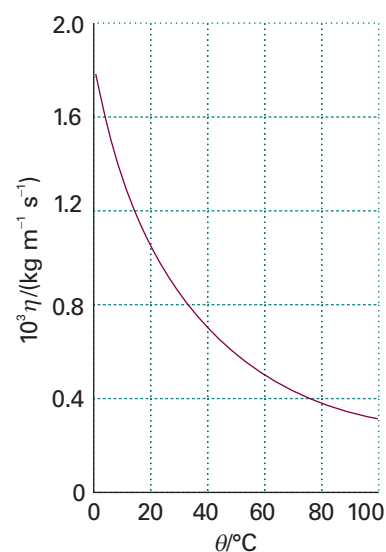† The viscosity of water corresponds to 0.891 cP.

Fig. 21.13 The experimental temperature dependence of the viscosity of water. As the temperature is increased, more molecules are able to escape from the potential wells provided by their neighbours, and so the liquid becomes more fluid. A plot of $\ln \eta$ against $1/T$ is a straight line (over a small range) with positive slope.

resistance R: $G = 1/R$. As resistance is expressed in ohms, Ω, the conductance of a sample is expressed in Ω^{-1}. The reciprocal ohm used to be called the mho, but its official designation is now the siemens, S, and $1\,S = 1\,\Omega^{-1} = 1\,C\,V^{-1}\,s^{-1}$. The conductance of a sample decreases with its length l and increases with its cross-sectional area A. We therefore write

$$G = \frac{\kappa A}{l} \tag{21.27}$$

where κ is the **conductivity**. With the conductance in siemens and the dimensions in metres, it follows that the SI units of κ are siemens per metre ($S\,m^{-1}$).

The conductivity of a solution depends on the number of ions present, and it is normal to introduce the **molar conductivity**, Λ_m, which is defined as

$$\Lambda_m = \frac{\kappa}{c} \tag{[21.28]}$$

where c is the molar concentration of the added electrolyte. The SI unit of molar conductivity is siemens metre-squared per mole ($S\,m^2\,mol^{-1}$), and typical values are about $10\,mS\,m^2\,mol^{-1}$ (where $1\,mS = 10^{-3}\,S$).

The molar conductivity is found to vary with the concentration. One reason for this variation is that the number of ions in the solution might not be proportional to the concentration of the electrolyte. For instance, the concentration of ions in a solution of a weak acid depends on the concentration of the acid in a complicated way, and doubling the concentration of the acid added does not double the number of ions. Secondly, because ions interact strongly with one another, the conductivity of a solution is not exactly proportional to the number of ions present.

The concentration dependence of molar conductivities indicates that there are two classes of electrolyte. The characteristic of a **strong electrolyte** is that its molar conductivity depends only slightly on the molar concentration (and in general decreases slightly as the concentration is increased, Fig. 21.14). The characteristic of a **weak electrolyte** is that its molar conductivity is normal at concentrations close to zero, but falls sharply to low values as the concentration increases. The classification depends on the solvent employed as well as the solute: lithium chloride, for example, is a strong electrolyte in water but a weak electrolyte in propanone.
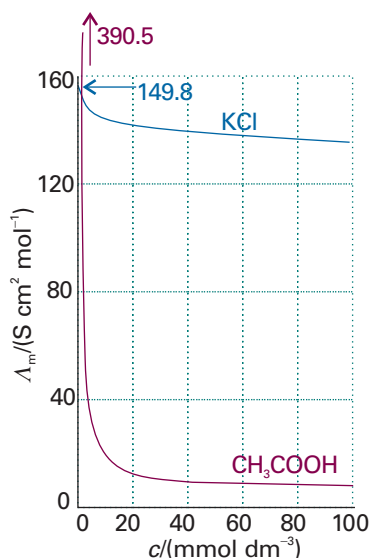

Fig. 21.14 The concentration dependence of the molar conductivities of (a) a typical strong electrolyte (aqueous potassium chloride) and (b) a typical weak electrolyte (aqueous acetic acid).

(b) Strong electrolytes

Strong electrolytes are substances that are virtually fully ionized in solution, and include ionic solids and strong acids. As a result of their complete ionization, the concentration of ions in solution is proportional to the concentration of strong electrolyte added.

In an extensive series of measurements during the nineteenth century, Friedrich Kohlrausch showed that at low concentrations the molar conductivities of strong electrolytes vary linearly with the square root of the concentration:

$$\Lambda_m = \Lambda_m^\circ - \mathcal{K}c^{1/2} \tag{21.29}$$

This variation is called **Kohlrausch's law**. The constant Λ_m° is the **limiting molar conductivity**, the molar conductivity in the limit of zero concentration (when the ions are effectively infinitely far apart and do not interact with one another). The constant $\mathcal{K}$ is found to depend more on the stoichiometry of the electrolyte (that is, whether it is of the form MA, or M_2A, etc.) than on its specific identity. In due course we shall see that the $c^{1/2}$ dependence arises from interactions between ions: when charge is conducted ionically, ions of one charge are moving past the ions of interest and retard its progress.

Synoptic table 21.5* Limiting ionic conductivities in water at 298 K

	$\lambda/(\text{mS m}^2\text{ mol}^{-1})$		$\lambda/(\text{mS m}^2\text{ mol}^{-1})$
H^+	34.96	OH^-	19.91
Na^+	5.01	Cl^-	7.63
K^+	7.35	Br^-	7.81
Zn^{2+}	10.56	SO_4^{2-}	16.00

* More values are given in the *Data section*.

Kohlrausch was also able to establish experimentally that Λ_m° can be expressed as the sum of contributions from its individual ions. If the limiting molar conductivity of the cations is denoted λ_+ and that of the anions λ_-, then his **law of the independent migration of ions** states that

$$\Lambda_m^\circ = v_+\lambda_+ + v_-\lambda_- \tag{21.30}°$$

where v_+ and v_- are the numbers of cations and anions per formula unit of electrolyte (for example, $v_+ = v_- = 1$ for HCl, NaCl, and CuSO$_4$, but $v_+ = 1$, $v_- = 2$ for MgCl$_2$). This simple result, which can be understood on the grounds that the ions migrate independently in the limit of zero concentration, lets us predict the limiting molar conductivity of any strong electrolyte from the data in Table 21.5.
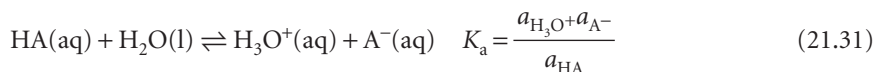

Illustration 21.2 *Calculating a limiting molar conductivity*

The limiting molar conductivity of BaCl$_2$ in water at 298 K is

$$\Lambda_m^\circ = (12.72 + 2\times 7.63)\text{ mS m}^2\text{ mol}^{-1} = 27.98\text{ mS m}^2\text{ mol}^{-1}$$

(c) Weak electrolytes

Weak electrolytes are not fully ionized in solution. They include weak Brønsted acids and bases, such as CH$_3$COOH and NH$_3$. The marked concentration dependence of their molar conductivities arises from the displacement of the equilibrium

$$\text{HA(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+\text{(aq)} + \text{A}^-\text{(aq)} \quad K_a = \frac{a_{\text{H}_3\text{O}^+}a_{\text{A}^-}}{a_{\text{HA}}} \tag{21.31}$$

towards products at low molar concentrations.

The conductivity depends on the number of ions in the solution, and therefore on the **degree of ionization**, α, of the electrolyte; when referring to weak acids, we speak instead of the **degree of deprotonation**. It is defined so that, for the acid HA at a molar concentration c, at equilibrium

$$[\text{H}_3\text{O}^+] = \alpha c \qquad [\text{A}^-] = \alpha c \qquad [\text{HA}] = (1-\alpha)c \tag{21.32}$$

If we ignore activity coefficients, the acidity constant, K_a, is approximately

$$K_a = \frac{\alpha^2 c}{1-\alpha} \tag{21.33}°$$

from which it follows that

$$\alpha = \frac{K_a}{2c}\left\{\left(1 + \frac{4c}{K_a}\right)^{1/2} - 1\right\} \tag{21.34}°$$

Comment 21.2

It will be familiar from introductory chemistry that a *Brønsted acid* is a proton donor and a *Brønsted base* is a proton acceptor. In eqn 21.31, HA(aq) is a Brønsted acid and H$_2$O(l) is a Brønsted base. The equilibrium constant for the reaction between HA(aq) and H$_2$O(l) is the *acidity constant K_a* of HA. Acids with $K_a < 1$, indicating only a small extent of deprotonation in water, are classified as *weak acids*.

The acid is fully deprotonated at infinite dilution, and its molar conductivity is then Λ_m°. Because only a fraction α is actually present as ions in the actual solution, the measured molar conductivity Λ_m is given by

$$\Lambda_m = \alpha\Lambda_m^\circ \qquad (21.35)^\circ$$

with α given by eqn 21.34.

Illustration 21.3 *Using molar conductivity data to calculate an acidity constant*

The molar conductivity of 0.0100 M $CH_3COOH(aq)$ at 298 K is $\Lambda_m = 1.65$ mS m^2 mol^{-1}. The degree of deprotonation, α, is calculated from eqn 21.35 with $\Lambda_m^\circ = 39.05$ mS cm^2 mol^{-1} (Table 21.5). It follows that $\alpha = 0.0423$. The acidity constant, K_a, is calculated by substitution of α into eqn 21.33, which gives $K_a = 1.9 \times 10^{-5}$.

Self-test 21.4 The molar conductivity of 0.0250 M $HCOOH(aq)$ is 4.61 mS m^2 mol^{-1}. Determine the $pK_a = -\log K_a$ of the acid.   [3.44]

Once we know K_a, we can use eqns 21.34 and 21.35 to predict the concentration dependence of the molar conductivity. The result agrees quite well with the experimental curve in Fig. 21.14. More usefully, we can use the concentration dependence of Λ_m in measurements of the limiting molar conductance. First, we rearrange eqn 21.33 into

$$\frac{1}{\alpha} = 1 + \frac{\alpha c}{K_a} \qquad (21.36)^\circ$$

Then, by using eqn 21.35, we obtain **Ostwald's dilution law**:

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^\circ} + \frac{\Lambda_m c}{K_a(\Lambda_m^\circ)^2} \qquad (21.37)^\circ$$

This equation implies that, if $1/\Lambda_m$ is plotted against $c\Lambda_m$, then the intercept at $c = 0$ will be $1/\Lambda_m^\circ$ (Fig. 21.15).

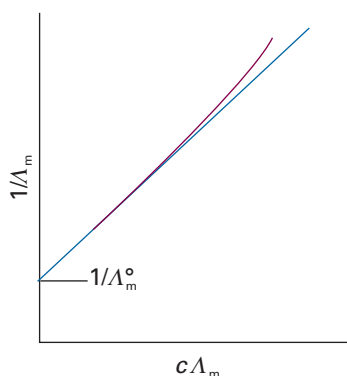**Fig. 21.15** The graph used to determine the limiting value of the molar conductivity of a solution by extrapolation to zero concentration.

21.7 **The mobilities of ions**

To interpret conductivity measurements we need to know why ions move at different rates, why they have different molar conductivities, and why the molar conductivities of strong electrolytes decrease with the square root of the molar concentration. The central idea in this section is that, although the motion of an ion remains largely random, the presence of an electric field biases its motion, and the ion undergoes net migration through the solution.

(a) **The drift speed**

When the potential difference between two electrodes a distance l apart is $\Delta\phi$, the ions in the solution between them experience a uniform electric field of magnitude

$$\mathcal{E} = \frac{\Delta\phi}{l} \qquad (21.38)$$

In such a field, an ion of charge ze experiences a force of magnitude

$$\mathcal{F} = ze\mathcal{E} = \frac{ze\Delta\phi}{l} \qquad (21.39)$$

Synoptic table 21.6* Ionic mobilities in water at 298 K

	$u/(10^{-8}\,m^2\,s^{-1}\,V^{-1})$		$u/(10^{-8}\,m^2\,s^{-1}\,V^{-1})$
H^+	36.23	OH^-	20.64
Na^+	5.19	Cl^-	7.91
K^+	7.62	Br^-	8.09
Zn^{2+}	5.47	SO_4^{2-}	8.29

* More values are given in the *Data section*.

(In this chapter we disregard the sign of the charge number and so avoid notational complications.) A cation responds to the application of the field by accelerating towards the negative electrode and an anion responds by accelerating towards the positive electrode. However, this acceleration is short-lived. As the ion moves through the solvent it experiences a frictional retarding force, $\mathcal{F}_{fric}$, proportional to its speed. If we assume that the Stokes formula (eqn 19.12) for a sphere of radius a and speed s applies even on a microscopic scale (and independent evidence from magnetic resonance suggests that it often gives at least the right order of magnitude), then we can write this retarding force as

$$\mathcal{F}_{fric} = fs \qquad f = 6\pi\eta a \tag{21.40}$$

The two forces act in opposite directions, and the ions quickly reach a terminal speed, the **drift speed**, when the accelerating force is balanced by the viscous drag. The net force is zero when

$$s = \frac{ze\mathcal{E}}{f} \tag{21.41}$$

It follows that the drift speed of an ion is proportional to the strength of the applied field. We write

$$s = u\mathcal{E} \tag{21.42}$$

where u is called the **mobility** of the ion (Table 21.6). Comparison of eqns 21.41 and 21.42 and use of eqn 21.40 shows that

$$u = \frac{ze}{f} = \frac{ze}{6\pi\eta a} \tag{21.43}$$

Illustration 21.4 *Calculating an ionic mobility*

For an order of magnitude estimate we can take $z = 1$ and a the radius of an ion such as Cs^+ (which might be typical of a smaller ion plus its hydration sphere), which is 170 pm. For the viscosity, we use $\eta = 1.0$ cP (1.0×10^{-3} kg m^{-1} s^{-1}, Table 21.4). Then $u \approx 5 \times 10^{-8}$ m^2 V^{-1} s^{-1}. This value means that, when there is a potential difference of 1 V across a solution of length 1 cm (so $\mathcal{E} = 100$ V m^{-1}), the drift speed is typically about 5 µm s^{-1}. That speed might seem slow, but not when expressed on a molecular scale, for it corresponds to an ion passing about 10^4 solvent molecules per second.

(a)   (b)   (c)
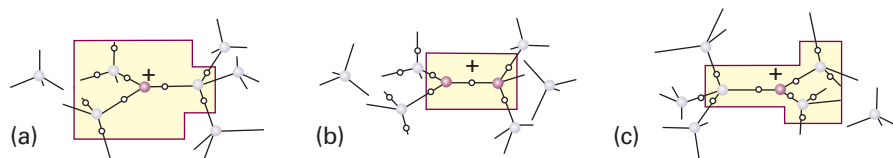
Because the drift speed governs the rate at which charge is transported, we might expect the conductivity to decrease with increasing solution viscosity and ion size. Experiments confirm these predictions for bulky ions (such as R_4N^+ and RCO_2^-) but not for small ions. For example, the molar conductivities of the alkali metal ions increase from Li^+ to Cs^+ (Table 21.6) even though the ionic radii increase. The paradox is resolved when we realize that the radius *a* in the Stokes formula is the **hydrodynamic radius** (or 'Stokes radius') of the ion, its effective radius in the solution taking into account all the H_2O molecules it carries in its hydration sphere. Small ions give rise to stronger electric fields than large ones (the electric field at the surface of a sphere of radius *r* is proportional to ze/r^2 and it follows that the smaller the radius the stronger the field), so small ions are more extensively solvated than big ions. Thus, an ion of small ionic radius may have a large hydrodynamic radius because it drags many solvent molecules through the solution as it migrates. The hydrating H_2O molecules are often very labile, however, and NMR and isotope studies have shown that the exchange between the coordination sphere of the ion and the bulk solvent is very rapid.

The proton, although it is very small, has a very high molar conductivity (Table 21.6)! Proton and ^{17}O-NMR show that the times characteristic of protons hopping from one molecule to the next are about 1.5 ps, which is comparable to the time that inelastic neutron scattering shows it takes a water molecule to reorientate through about 1 rad (1 to 2 ps). According to the **Grotthuss mechanism**, there is an effective motion of a proton that involves the rearrangement of bonds in a group of water molecules. However, the actual mechanism is still highly contentious. Attention now focuses on the $H_9O_4^+$ unit, in which the nearly trigonal planar H_3O^+ ion is linked to three strongly solvating H_2O molecules. This cluster of atoms is itself hydrated, but the hydrogen bonds in the secondary sphere are weaker than in the primary sphere. It is envisaged that the rate-determining step is the cleavage of one of the weaker hydrogen bonds of this secondary sphere (Fig. 21.16a). After this bond cleavage has taken place, and the released molecule has rotated through a few degrees (a process that takes about 1 ps), there is a rapid adjustment of bond lengths and angles in the remaining cluster, to form an $H_5O_2^+$ cation of structure H_2O ···H^+ ···OH_2 (Fig. 21.16b). Shortly after this reorganization has occurred, a new $H_9O_4^+$ cluster forms as other molecules rotate into a position where they can become members of a secondary hydration sphere, but now the positive charge is located one molecule to the right of its initial location (Fig. 21.16c). According to this model, there is no coordinated motion of a proton along a chain of molecules, simply a very rapid hopping between neighbouring sites, with a low activation energy. The model is consistent with the observation that the molar conductivity of protons increases as the pressure is raised, for increasing pressure ruptures the hydrogen bonds in water. The mobility of NH_4^+ is also anomalous and presumably occurs by an analogous mechanism.

Comment 21.3

The H_3O^+ ion is trigonal pyramidal in the gas phase but nearly planar in water.

(b) Mobility and conductivity

Ionic mobilities provide a link between measurable and theoretical quantities. As a first step we establish in the *Justification* below the following relation between an ion's mobility and its molar conductivity:

$$\lambda = zuF \tag{21.44}°$$

where *F* is Faraday's constant ($F = N_Ae$).

Justification 21.5 *The relation between ionic mobility and molar conductivity*

To keep the calculation simple, we ignore signs in the following, and concentrate on the magnitudes of quantities: the direction of ion flux can always be decided by common sense.

Consider a solution of a fully dissociated strong electrolyte at a molar concentration c. Let each formula unit give rise to ν_+ cations of charge z_+e and ν_- anions of charge z_-e. The molar concentration of each type of ion is therefore νc (with $\nu = \nu_+$ or ν_-), and the number density of each type is $\nu c N_A$. The number of ions of one kind that pass through an imaginary window of area A during an interval Δt is equal to the number within the distance $s\Delta t$ (Fig. 21.17), and therefore to the number in the volume $s\Delta t A$. (The same sort of argument was used in Section 21.1 in the discussion of the pressure of a gas.) The number of ions of that kind in this volume is equal to $s\Delta t A \nu c N_A$. The flux through the window (the number of this type of ion passing through the window divided by the area of the window and the duration of the interval) is therefore

$$J(\text{ions}) = \frac{s\Delta t A \nu c N_A}{A\Delta t} = s\nu c N_A$$

Each ion carries a charge ze, so the flux of charge is

$$J(\text{charge}) = zs\nu c e N_A = zs\nu c F$$

Because $s = u\mathcal{E}$, the flux is

$$J(\text{charge}) = zu\nu c F\mathcal{E}$$

The current, I, through the window due to the ions we are considering is the charge flux times the area:

$$I = JA = zu\nu c F\mathcal{E}A$$

Because the electric field is the potential gradient, $\Delta\phi/l$, we can write

$$I = \frac{zu\nu c F A \Delta\phi}{l} \tag{21.45}$$

Current and potential difference are related by Ohm's law, $\Delta\phi = IR$, so it follows that

$$I = \frac{\Delta\phi}{R} = G\Delta\phi = \frac{\kappa A \Delta\phi}{l}$$

where we have used eqn 21.27 in the form $\kappa = Gl/A$. Note that the proportionality of current to potential difference ($I \propto \Delta\phi$) is another example of a phenomenological flux equation like those introduced in Section 21.4. Comparison of the last two expressions gives $\kappa = zu\nu c F$. Division by the molar concentration of ions, νc, then results in eqn 21.44.
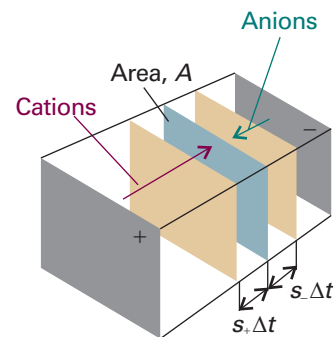

Fig. 21.17 In the calculation of the current, all the cations within a distance $s_+\Delta t$ (that is, those in the volume $s_+A\Delta t$) will pass through the area A. The anions in the corresponding volume the other side of the window will also contribute to the current similarly.

Equation 21.44 applies to the cations and to the anions. Therefore, for the solution itself in the limit of zero concentration (when there are no interionic interactions),

$$\Lambda_m^\circ = (z_+u_+\nu_+ + z_-u_-\nu_-)F \tag{21.46a}°$$

For a symmetrical $z{:}z$ electrolyte (for example, $CuSO_4$ with $z = 2$), this equation simplifies to

$$\Lambda_m^\circ = z(u_+ + u_-)F \tag{21.46b}°$$

Illustration 21.5 *Estimating a limiting molar conductivity*

Earlier, we estimated the typical ionic mobility as $5 \times 10^{-8} \, \mathrm{m^2 \, V^{-1} \, s^{-1}}$; so, with $z = 1$ for both the cation and anion, we can estimate that a typical limiting molar conductivity should be about 10 mS m² mol⁻¹, in accord with experiment. The experimental value for KCl, for instance, is 15 mS m² mol⁻¹.

(c) Transport numbers

The **transport number**, $t_\pm$, is defined as the fraction of total current carried by the ions of a specified type. For a solution of two kinds of ion, the transport numbers of the cations (t_+) and anions (t_-) are

$$t_\pm = \frac{I_\pm}{I} \tag{21.47}$$

where $I_\pm$ is the current carried by the cation (I_+) or anion (I_-) and I is the total current through the solution. Because the total current is the sum of the cation and anion currents, it follows that

$$t_+ + t_- = 1 \tag{21.48}$$

The **limiting transport number**, $t_\pm^\circ$, is defined in the same way but for the limit of zero concentration of the electrolyte solution. We shall consider only these limiting values from now on, for that avoids the problem of ionic interactions.

The current that can be ascribed to each type of ion is related to the mobility of the ion by eqn 21.45. Hence the relation between $t_\pm^\circ$ and $u_\pm$ is

$$t_\pm^\circ = \frac{z_+ v_\pm u_\pm}{z_+ v_+ u_+ + z_- v_- u_-} \tag{21.49a}°$$

However, because $z_+ v_+ = z_- v_-$ for any electrolyte, eqn 21.49a simplifies to

$$t_\pm^\circ = \frac{u_\pm}{u_+ + u_-} \tag{21.49b}°$$

Moreover, because the ionic conductivities are related to the mobilities by eqn 21.44, it also follows from eqn 21.49b that

$$t_\pm^\circ = \frac{v_\pm \lambda_\pm}{v_+ \lambda_+ + v_- \lambda_-} = \frac{v_\pm \lambda_\pm}{\Lambda_m^\circ} \tag{21.50}°$$

and hence, for each type of ion,

$$v_\pm \lambda_\pm = t_\pm^\circ \Lambda_m^\circ \tag{21.51}°$$

Consequently, because there are independent ways of measuring transport numbers of ions, we can determine the individual ionic conductivities and (through eqn 21.44) the ionic mobilities.

There are several ways to measure transport numbers (see *Further reading*). One of the most accurate (and the only one we describe in detail) is the **moving boundary method**, in which the motion of a boundary between two ionic solutions having a common ion is observed as a current flows.

Let MX be the salt of interest and NX a salt giving a denser solution. The solution of NX is called the **indicator solution**; it occupies the lower part of a vertical tube of cross-sectional area A (Fig. 21.18). The MX solution, which is called the **leading**
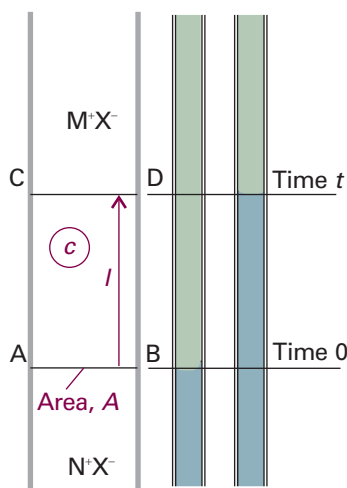
Fig. 21.18 In the moving boundary method for the measurement of transport numbers the distance moved by the boundary is observed as a current is passed. All the M ions in the volume between AB and CD must have passed through CD if the boundary moves from AB to CD. One procedure is to add bromothymol blue indicator to a slightly alkaline solution of the ion of interest and to use a cadmium electrode at the lower end of the vertical tube. The electrode produces Cd²⁺ ions, which are slow moving and slightly acidic (the hydrated ion is a Brønsted acid), and the boundary is revealed by the colour change of the indicator.

solution, occupies the upper part of the tube. There is a sharp boundary between the two solutions. The indicator solution must be denser than the leading solution, and the mobility of the M ions must be greater than that of the N ions. Thus, if any M ions diffuse into the lower solution, they will be pulled upwards more rapidly than the N ions around them, and the boundary will reform. When a current I is passed for a time Δt, the boundary moves from AB to CD, so all the M ions in the volume between AB and CD must have passed through CD. That number is $clAN_A$, so the charge that the M ions transfer through the plane is z_+clAeN_A. However, the *total* charge transferred when a current I flows for an interval Δt is $I\Delta t$. Therefore, the fraction due to the motion of the M ions, which is their transport number, is

$$t_+ = \frac{z_+clAF}{I\Delta t} \tag{21.52}$$

Hence, by measuring the distance moved, the transport number and hence the conductivity and mobility of the ions can be determined.

21.8 Conductivities and ion–ion interactions

The remaining problem is to account for the $c^{1/2}$ dependence of the Kohlrausch law (eqn 21.29). In Section 5.9 we saw something similar: the activity coefficients of ions at low concentrations also depend on $c^{1/2}$ and depend on their charge type rather than their specific identities. That $c^{1/2}$ dependence was explained in terms of the properties of the ionic atmosphere around each ion, and we can suspect that the same explanation applies here too.

To accommodate the effect of motion, we need to modify the picture of an ionic atmosphere as a spherical haze of charge. Because the ions forming the atmosphere do not adjust to the moving ion immediately, the atmosphere is incompletely formed in front of the moving ion and incompletely decayed behind the ion (Fig. 21.19). The overall effect is the displacement of the centre of charge of the atmosphere a short distance behind the moving ion. Because the two charges are opposite, the result is a retardation of the moving ion. This reduction of the ions' mobility is called the **relaxation effect**. A confirmation of the picture is obtained by observing the conductivities of ions at high frequencies, which are greater than at low frequencies: the atmosphere does not have time to follow the rapidly changing direction of motion of the ion, and the effect of the field averages to zero.

The ionic atmosphere has another effect on the motion of the ions. We have seen that the moving ion experiences a viscous drag. When the ionic atmosphere is present this drag is enhanced because the ionic atmosphere moves in an opposite direction to the central ion. The enhanced viscous drag, which is called the **electrophoretic effect**, reduces the mobility of the ions, and hence also reduces their conductivities.

The quantitative formulation of these effects is far from simple, but the **Debye–Hückel–Onsager theory** is an attempt to obtain quantitative expressions at about the same level of sophistication as the Debye–Hückel theory itself. The theory leads to a Kohlrausch-like expression in which

$$\mathcal{K} = A + B\Lambda_m^\circ \tag{21.53a}$$

with

$$A = \frac{z^2eF^2}{3\pi\eta}\left(\frac{2}{\varepsilon RT}\right)^{1/2} \qquad B = \frac{qz^3eF}{24\pi\varepsilon RT}\left(\frac{2}{\varepsilon RT}\right)^{1/2} \tag{21.53b}$$

where ε is the electric permittivity of the solvent (Section 18.3) and $q = 0.586$ for a 1,1-electrolyte (Table 21.7). The slopes of the conductivity curves are predicted to depend
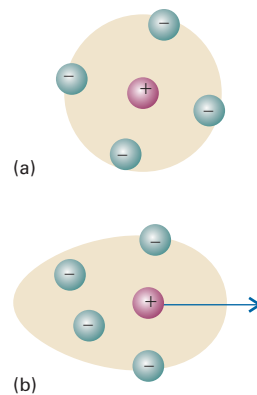
(a)

(b)

Fig. 21.19 (a) In the absence of an applied field, the ionic atmosphere is spherically symmetric, but (b) when a field is present it is distorted and the centres of negative and positive charge no longer coincide. The attraction between the opposite charges retards the motion of the central ion.
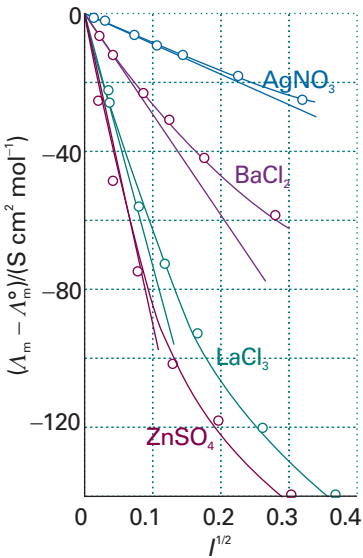
Fig. 21.20 The dependence of molar conductivities on the square root of the ionic strength, and comparison (straight lines) with the dependence predicted by the Debye–Hückel–Onsager theory.

Synoptic table 21.7* Debye–Hückel–Onsager coefficients for (1,1)-electrolytes at 298 K

Solvent	$A/(mS\ m^2\ mol^{-1}/(mol\ dm^{-3})^{1/2})$	$B/(mol\ dm^{-3})^{-1/2}$
Methanol	15.61	0.923
Propanone	32.8	1.63
Water	6.02	0.229

* More values are given in the *Data section*.

on the charge type of the electrolyte, in accord with the Kohlrausch law, and some comparisons between theory and experiment are shown in Fig. 21.20. The agreement is quite good at very low ionic strengths, corresponding to very low molar concentrations (less than about 10^{-3} M, depending on the charge type).

IMPACT ON BIOCHEMISTRY
I21.2 Ion channels and ion pumps

Controlled transport of molecules and ions across biological membranes is at the heart of a number of key cellular processes, such as the transmission of nerve impulses, the transfer of glucose into red blood cells, and the synthesis of ATP by oxidative phosphorylation (*Impact* I7.2). Here we examine in some detail the various ways in which ions cross the alien environment of the lipid bilayer.

Suppose that a membrane provides a barrier that slows down the transfer of molecules or ions into or out of the cell. We saw in *Impact* I7.2 that the thermodynamic tendency to transport an ion through the membrane is partially determined by a concentration gradient (more precisely, an activity gradient) across the membrane, which results in a difference in molar Gibbs energy between the inside and the outside of the cell, and a transmembrane potential gradient, which is due to the different potential energy of the ions on each side of the bilayer. There is a tendency, called **passive transport**, for a species to move down concentration and membrane potential gradients. It is also possible to move a species against these gradients, but now the flow must be driven by an exergonic process, such as the hydrolysis of ATP. This process is called **active transport**.

The transport of ions into or out of a cell needs to be mediated (that is, facilitated by other species) because the hydrophobic environment of the membrane is inhospitable to ions. There are two mechanisms for ion transport: mediation by a carrier molecule and transport through a **channel former**, a protein that creates a hydrophilic pore through which the ion can pass. An example of a channel former is the polypeptide gramicidin A, which increases the membrane permeability to cations such as H^+, K^+, and Na^+.

Ion channels are proteins that effect the movement of specific ions down a membrane potential gradient. They are highly selective, so there is a channel protein for Ca^{2+}, another for Cl^-, and so on. The opening of the gate may be triggered by potential differences between the two sides of the membrane or by the binding of an *effector* molecule to a specific receptor site on the channel.

Ions such as H^+, Na^+, K^+, and Ca^{2+} are often transported actively across membranes by integral proteins called **ion pumps**. Ion pumps are molecular machines that work by adopting conformations that are permeable to one ion but not others depending on the state of phosphorylation of the protein. Because protein phosphorylation requires dephosphorylation of ATP, the conformational change that opens or closes the pump is endergonic and requires the use of energy stored during metabolism.

Let's consider some of the experimental approaches used in the study of ion channels. The structures of a number of channel proteins have been obtained by the now traditional X-ray diffraction techniques described in Chapter 20. Information about the flow of ions across channels and pumps is supplied by the **patch clamp technique**. One of many possible experimental arrangements is shown in Fig. 21.21. With mild suction, a 'patch' of membrane from a whole cell or a small section of a broken cell can be attached tightly to the tip of a micropipet filled with an electrolyte solution and containing an electronic conductor, the so-called *patch electrode*. A potential difference (the 'clamp') is applied between the patch electrode and an intracellular electronic conductor in contact with the cytosol of the cell. If the membrane is permeable to ions at the applied potential difference, a current flows through the completed circuit. Using narrow micropipette tips with diameters of less than 1 μm, ion currents of a few picoamperes ($1 pA = 10^{-12} A$) have been measured across sections of membranes containing only one ion channel protein.

A detailed picture of the mechanism of action of ion channels has emerged from analysis of patch clamp data and structural data. Here we focus on the K^+ ion channel protein, which, like all other mediators of ion transport, spans the membrane bilayer (Fig. 21.22). The pore through which ions move has a length of 3.4 nm and is divided into two regions: a wide region with a length of 2.2 nm and diameter of 1.0 nm and a narrow region with a length of 1.2 nm and diameter of 0.3 nm. The narrow region is called the *selectivity filter* of the K^+ ion channel because it allows only K^+ ions to pass.

Filtering is a subtle process that depends on ionic size and the thermodynamic tendency of an ion to lose its hydrating water molecules. Upon entering the selectivity filter, the K^+ ion is stripped of its hydrating shell and is then gripped by carbonyl groups of the protein. Dehydration of the K^+ ion is endergonic ($\Delta_{dehyd}G^{\ominus} = +203$ kJ mol^{-1}), but is driven by the energy of interaction between the ion and the protein. The Na^+ ion, though smaller than the K^+ ion, does not pass through the selectivity filter of the K^+ ion channel because interactions with the protein are not sufficient to compensate for the high Gibbs energy of dehydration of Na^+ ($\Delta_{dehyd}G^{\ominus} = +301$ kJ mol^{-1}). More specifically, a dehydrated Na^+ ion is too small and cannot be held tightly by the protein carbonyl groups, which are positioned for ideal interactions with the larger K^+ ion. In its hydrated form, the Na^+ ion is too large (larger than a dehydrated K^+ ion), does not fit in the selectivity filter, and does not cross the membrane.

Though very selective, a K^+ ion channel can still let other ions pass through. For example, K^+ and Tl^+ ions have similar radii and Gibbs energies of dehydration, so Tl^+ can cross the membrane. As a result, Tl^+ is a neurotoxin because it replaces K^+ in many neuronal functions.

The efficiency of transfer of K^+ ions through the channel can also be explained by structural features of the protein. For efficient transport to occur, a K^+ ion must enter the protein, but then must not be allowed to remain inside for very long so that, as one K^+ ion enters the channel from one side, another K^+ ion leaves from the opposite side. An ion is lured into the channel by water molecules about halfway through the length of the membrane. Consequently, the thermodynamic cost of moving an ion from an aqueous environment to the less hydrophilic interior of the protein is minimized. The ion is 'encouraged' to leave the protein by electrostatic interactions in the selectivity filter, which can bind two K^+ ions simultaneously, usually with a bridging water molecule. Electrostatic repulsion prevents the ions from binding too tightly, minimizing the residence time of an ion in the selectivity filter, and maximizing the transport rate.

Now we turn our attention to a very important ion pump, the H^+-ATPase responsible for coupling of proton flow to synthesis of ATP from ADP and P_i (*Impact* I7.2). Structural studies show that the channel through which the protons flow is linked in
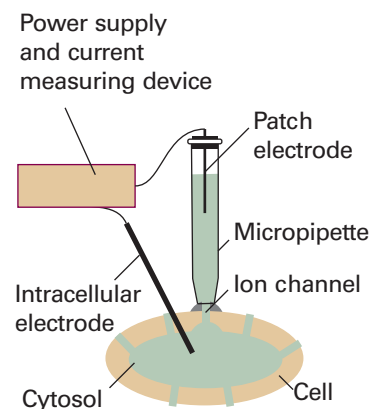
Fig. 21.21 A representation of the patch clamp technique for the measurement of ionic currents through membranes in intact cells. A section of membrane containing an ion channel (shown as a green rectangle) is in tight contact with the tip of a micropipette containing an electrolyte solution and the patch electrode. An intracellular electronic conductor is inserted into the cytosol of the cell and the two conductors are connected to a power supply and current measuring device.

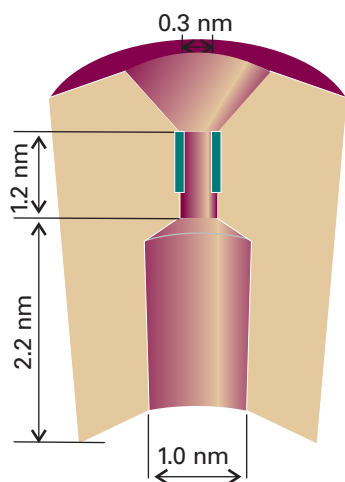**Fig. 21.22** A schematic representation of the cross-section of a membrane-spanning K$^+$ ion channel protein. The bulk of the protein is shown in beige. The pore through which ions move is divided into two regions: a wide region with a length of 2.2 nm and diameter of 1.0 nm, and a narrow region, the *selectivity filter*, with a length of 1.2 nm and diameter of 0.3 nm. The selectivity filter has a number of carbonyl groups (shown in dark green) that grip K$^+$ ions. As explained in the text, electrostatic repulsions between two bound K$^+$ ions 'encourage' ionic movement through the selectivity filter and across the membrane.
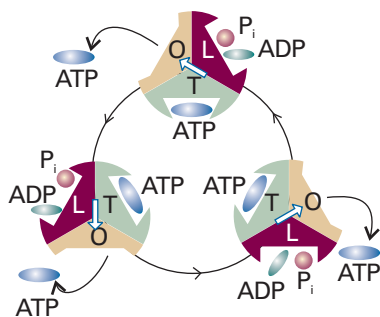

Fig. 21.23 The mechanism of action of H$^+$-ATPase, a molecular motor that transports protons across the mitochondrial membrane and catalyses either the formation or hydrolysis of ATP.

tandem to a unit composed of six protein molecules arranged in pairs of α and β subunits to form three interlocked $\alpha\beta$ segments (Fig. 21.23). The conformations of the three pairs may be loose (L), tight (T), or open (O), and one of each type is present at each stage. A protein at the centre of the interlocked structure, the γ subunit shown as a white arrow, rotates and induces structural changes that cycle each of the three segments between L, T, and O conformations. At the start of a cycle, a T unit holds an ATP molecule. Then ADP and a P$_i$ group migrate into the L site and, as it closes into T, the earlier T site opens into O and releases its ATP. The ADP and P$_i$ in the T site meanwhile condense into ATP, and the new L site is ready for the cycle to begin again. The proton flux drives the rotation of the γ subunit, and hence the conformational changes of the α/β segments, as well as providing the energy for the condensation reaction itself. Several key aspects of this mechanism have been confirmed experimentally. For example, the rotation of the γ subunit has been observed directly by using single-molecule spectroscopy (Section 14.6).

Diffusion

We are now in a position to extend the discussion of ionic motion to cover the migration of neutral molecules and of ions in the absence of an applied electric field. We shall do this by expressing ion motion in a more general way than hitherto, and will then discover that the same equations apply even when the charge on the particles is zero.

21.9 The thermodynamic view

We saw in Part 1 that, at constant temperature and pressure, the maximum non-expansion work that can be done per mole when a substance moves from a location where its chemical potential is μ to a location where its chemical potential is $\mu + d\mu$ is $dw = d\mu$. In a system in which the chemical potential depends on the position x,

$$dw = d\mu = \left(\frac{\partial \mu}{\partial x}\right)_{p,T} dx \tag{21.54}$$

We also saw in Chapter 2 (Table 2.1) that in general work can always be expressed in terms of an opposing force (which here we write $\mathcal{F}$), and that

$$dw = -\mathcal{F}\, dx \tag{21.55}$$

By comparing these two expressions, we see that the slope of the chemical potential can be interpreted as an effective force per mole of molecules. We write this **thermodynamic force** as

$$\mathcal{F} = -\left(\frac{\partial \mu}{\partial x}\right)_{p,T} \tag{21.56}$$

There is not necessarily a real force pushing the particles down the slope of the chemical potential. As we shall see, the force may represent the spontaneous tendency of the molecules to disperse as a consequence of the Second Law and the hunt for maximum entropy.

(a) The thermodynamic force of a concentration gradient

In a solution in which the activity of the solute is a, the chemical potential is

$$\mu = \mu^{\ominus} + RT \ln a$$

If the solution is not uniform the activity depends on the position and we can write

$$\mathcal{F}=-RT\left(\frac{\partial \ln a}{\partial x}\right)_{p,T} \tag{21.57}$$

If the solution is ideal, a may be replaced by the molar concentration c, and then

$$\mathcal{F}=-\frac{RT}{c}\left(\frac{\partial c}{\partial x}\right)_{p,T} \tag{21.58}°$$

where we have also used the relation $d \ln y/dx = (1/y)(dy/dx)$.

Example 21.3 *Calculating the thermodynamic force*

Suppose the concentration of a solute decays exponentially along the length of a container. Calculate the thermodynamic force on the solute at 25°C given that the concentration falls to half its value in 10 cm.

Method According to eqn 21.58, the thermodynamic force is calculated by differentiating the concentration with respect to distance. Therefore, write an expression for the variation of the concentration with distance, and then differentiate it.

Answer The concentration varies with position as

$$c = c_0 e^{-x/\lambda}$$

where λ is the decay constant. Therefore,

$$\frac{dc}{dx} = -\frac{c}{\lambda}$$

Equation 21.58 then implies that

$$\mathcal{F}=\frac{RT}{\lambda}$$

We know that the concentration falls to $\frac{1}{2}c_0$ at $x = 10$ cm, so we can find λ from $\frac{1}{2} = e^{-(10\text{ cm})/\lambda}$. That is, $\lambda = (10 \text{ cm/ln } 2)$. It follows that

$$\mathcal{F}= (8.3145 \text{ J K}^{-1}\text{ mol}^{-1})\times(298\text{ K})\times \ln 2/(1.0\times 10^{-1}\text{ m}) = 17 \text{ kN mol}^{-1}$$

where we have used 1 J = 1 N m.

Self-test 21.5 Calculate the thermodynamic force on the molecules of molar mass M in a vertical tube in a gravitational field on the surface of the Earth, and evaluate $\mathcal{F}$ for molecules of molar mass 100 g mol^{-1}. Comment on its magnitude relative to that just calculated.

$[\mathcal{F}=-Mg, -0.98 \text{ N mol}^{-1}$; the force arising from the concentration gradient greatly dominates that arising from the gravitational gradient.]

(b) Fick's first law of diffusion

In Section 21.4 we saw that Fick's first law of diffusion (that the particle flux is proportional to the concentration gradient) could be deduced from the kinetic model of gases. We shall now show that it can be deduced more generally and that it applies to the diffusion of species in condensed phases too.

We suppose that the flux of diffusing particles is motion in response to a thermodynamic force arising from a concentration gradient. The particles reach a steady drift speed, s, when the thermodynamic force, $\mathcal{F}$, is matched by the viscous drag. This drift speed is proportional to the thermodynamic force, and we write $s \propto \mathcal{F}$. However, the particle flux, J, is proportional to the drift speed, and the thermodynamic force is proportional to the concentration gradient, dc/dx. The chain of proportionalities ($J \propto s$, $s \propto \mathcal{F}$, and $\mathcal{F} \propto dc/dx$) implies that $J \propto dc/dx$, which is the content of Fick's law.

(c) The Einstein relation

If we divide both sides of eqn 21.19 by Avogadro's constant, thereby converting numbers into amounts (numbers of moles), then Fick's law becomes

$$J = -D \frac{dc}{dx} \tag{21.59}$$

In this expression, D is the diffusion coefficient and dc/dx is the slope of the molar concentration. The flux is related to the drift speed by

$$J = sc \tag{21.60}$$

This relation follows from the argument that we have used several times before. Thus, all particles within a distance $s\Delta t$, and therefore in a volume $s\Delta tA$, can pass through a window of area A in an interval Δt. Hence, the amount of substance that can pass through the window in that interval is $s\Delta tAc$. Therefore,

$$sc = -D \frac{dc}{dx}$$

If now we express dc/dx in terms of $\mathcal{F}$ by using eqn 21.58, we find

$$s = -\frac{D}{c} \frac{dc}{dx} = \frac{D\mathcal{F}}{RT} \tag{21.61}$$

Therefore, once we know the effective force and the diffusion coefficient, D, we can calculate the drift speed of the particles (and vice versa) whatever the origin of the force.

There is one case where we already know the drift speed and the effective force acting on a particle: an ion in solution has a drift speed $s = u\mathcal{E}$ when it experiences a force $ez\mathcal{E}$ from an electric field of strength $\mathcal{E}$ (so $\mathcal{F} = N_A ez\mathcal{E} = zF\mathcal{E}$). Therefore, substituting these known values into eqn 21.61 gives

$$u\mathcal{E} = \frac{zF\mathcal{E}D}{RT}$$

and hence

$$u = \frac{zFD}{RT} \tag{21.62}$$

This equation rearranges into the very important result known as the **Einstein relation** between the diffusion coefficient and the ionic mobility:

$$D = \frac{uRT}{zF} \tag{21.63}°$$

On inserting the typical value $u = 5 \times 10^{-8}$ m^2 s^{-1} V^{-1}, we find $D \approx 1 \times 10^{-9}$ m^2 s^{-1} at 25°C as a typical value of the diffusion coefficient of an ion in water.

(d) The Nernst–Einstein equation

The Einstein relation provides a link between the molar conductivity of an electrolyte and the diffusion coefficients of its ions. First, by using eqns 21.44 and 21.63 we write

$$\lambda = zuF = \frac{z^2 D F^2}{RT} \tag{21.64}°$$

for each type of ion. Then, from $\Lambda_{m}^{\circ} = v_{+}\lambda_{+} + v_{-}\lambda_{-}$, the limiting molar conductivity is

$$\Lambda_{m} = (v_{+}z_{+}^2 D_{+} + v_{-}z_{-}^2 D_{-})\frac{F^2}{RT} \tag{21.65}°$$

which is the **Nernst–Einstein equation**. One application of this equation is to the determination of ionic diffusion coefficients from conductivity measurements; another is to the prediction of conductivities using models of ionic diffusion (see below).

(e) The Stokes–Einstein equation

Equations 21.43 ($u = ez/f$) and 21.63 relate the mobility of an ion to the frictional force and to the diffusion coefficient, respectively. We can combine the two expressions into the **Stokes–Einstein equation**:

$$D = \frac{kT}{f} \tag{21.66}$$

If the frictional force is described by Stokes's law, then we also obtain a relation between the diffusion coefficient and the viscosity of the medium:

$$D = \frac{kT}{6\pi\eta a} \tag{21.67}$$

An important feature of eqn 21.66 (and of its special case, eqn 21.67) is that it makes no reference to the charge of the diffusing species. Therefore, the equation also applies in the limit of vanishingly small charge, that is, it also applies to neutral molecules. Consequently, we may use viscosity measurements to estimate the diffusion coefficients for electrically neutral molecules in solution (Table 21.8). It must not be forgotten, however, that both equations depend on the assumption that the viscous drag is proportional to the speed.

Synoptic table 21.8* Diffusion coefficients at 298 K

	$D/(10^{-9}\ m^2\ s^{-1})$
H^+ in water	9.31
I_2 in hexane	4.05
Na^+ in water	1.33
Sucrose in water	0.522

* More values are given in the *Data section*.

Example 21.4 *Interpreting the mobility of an ion*

Use the experimental value of the mobility to evaluate the diffusion coefficient, the limiting molar conductivity, and the hydrodynamic radius of a sulfate ion in aqueous solution.

Method The starting point is the mobility of the ion, which is given in Table 21.6. The diffusion coefficient can then be determined from the Einstein relation, eqn 21.63. The ionic conductivity is related to the mobility by eqn 21.44. To estimate the hydrodynamic radius, a, of the ion, use the Stokes–Einstein relation to find f and the Stokes law to relate f to a.

Answer From Table 21.6, the mobility of SO_4^{2-} is $8.29 \times 10^{-8}\ m^2\ s^{-1}\ V^{-1}$. It follows from eqn 21.63 that

$$D = \frac{uRT}{zF} = 1.1 \times 10^{-9}\ m^2\ s^{-1}$$

From eqn 21.44 it follows that

$$\lambda = zuF = 16 \text{ mS m}^2 \text{ mol}^{-1}$$

Finally, from $f = 6\pi\eta a$ using 0.891 cP (or $8.91 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$) for the viscosity of water (Table 21.4):

$$a = \frac{kT}{6\pi\eta D} = 220 \text{ pm}$$

The bond length in SO_4^{2-} is 144 pm, so the radius calculated here is plausible and consistent with a small degree of solvation.

Self-test 21.6 Repeat the calculation for the NH_4^+ ion.

$$[1.96 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}, 7.4 \text{ mS m}^2 \text{ mol}^{-1}, 125 \text{ pm}]$$

Experimental support for the relations derived above comes from conductivity measurements. In particular, **Walden's rule** is the empirical observation that the product $\eta\Lambda_m$ is very approximately constant for the same ions in different solvents (but there are numerous exceptions). Because $\Lambda_m \propto D$, and we have just seen that $D \propto 1/\eta$, we do indeed predict that $\Lambda_m \propto 1/\eta$, as Walden's rule implies. The usefulness of the rule, however, is muddied by the role of solvation: different solvents solvate the same ions to different extents, so both the hydrodynamic radius and the viscosity change with the solvent.

21.10 **The diffusion equation**

We now turn to the discussion of time-dependent diffusion processes, where we are interested in the spreading of inhomogeneities with time. One example is the temperature of a metal bar that has been heated at one end: if the source of heat is removed, then the bar gradually settles down into a state of uniform temperature. When the source of heat is maintained and the bar can radiate, it settles down into a steady state of nonuniform temperature. Another example (and one more relevant to chemistry) is the concentration distribution in a solvent to which a solute is added. We shall focus on the description of the diffusion of particles, but similar arguments apply to the diffusion of physical properties, such as temperature. Our aim is to obtain an equation for the rate of change of the concentration of particles in an inhomogeneous region.

The central equation of this section is the **diffusion equation**, also called 'Fick's second law of diffusion', which relates the rate of change of concentration at a point to the spatial variation of the concentration at that point:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{21.68}$$

We show in the following *Justification* that the diffusion equation follows from Fick's first law of diffusion.
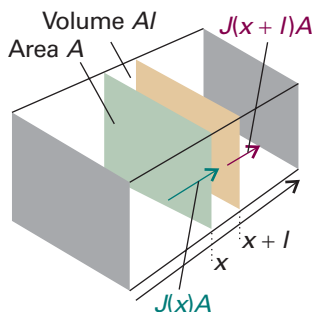

Fig. 21.24 The net flux in a region is the difference between the flux entering from the region of high concentration (on the left) and the flux leaving to the region of low concentration (on the right).

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Justification 21.6 *The diffusion equation*

Consider a thin slab of cross-sectional area A that extends from x to $x+l$ (Fig. 21.24). Let the concentration at x be c at the time t. The amount (number of moles) of particles that enter the slab in the infinitesimal interval $\text{d}t$ is $JA\text{d}t$, so the rate of increase in molar concentration inside the slab (which has volume Al) on account of the flux from the left is

$$\frac{\partial c}{\partial t} = \frac{JA\mathrm{d}t}{Al\mathrm{d}t} = \frac{J}{l}$$

There is also an outflow through the right-hand window. The flux through that window is J', and the rate of change of concentration that results is

$$\frac{\partial c}{\partial t} = -\frac{J'A\mathrm{d}t}{Al\mathrm{d}t} = -\frac{J'}{l}$$

The net rate of change of concentration is therefore

$$\frac{\partial c}{\partial t} = \frac{J - J'}{l}$$

Each flux is proportional to the concentration gradient at the window. So, by using Fick's first law, we can write

$$J - J' = -D\frac{\partial c}{\partial x} + D\frac{\partial c'}{\partial x} = -D\frac{\partial c}{\partial x} + D\frac{\partial}{\partial x}\left\{c + \left(\frac{\partial c}{\partial x}\right)l\right\} = Dl\frac{\partial^2 c}{\partial x^2}$$

When this relation is substituted into the expression for the rate of change of concentration in the slab, we get eqn 21.68.

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The diffusion equation shows that the rate of change of concentration is proportional to the curvature (more precisely, to the second derivative) of the concentration with respect to distance. If the concentration changes sharply from point to point (if the distribution is highly wrinkled) then the concentration changes rapidly with time. Where the curvature is positive (a dip, Fig. 21.25), the change in concentration is positive; the dip tends to fill. Where the curvature is negative (a heap), the change in concentration is negative; the heap tends to spread. If the curvature is zero, then the concentration is constant in time. If the concentration decreases linearly with distance, then the concentration at any point is constant because the inflow of particles is exactly balanced by the outflow.

The diffusion equation can be regarded as a mathematical formulation of the intuitive notion that there is a natural tendency for the wrinkles in a distribution to disappear. More succinctly: Nature abhors a wrinkle.

(a) Diffusion with convection

The transport of particles arising from the motion of a streaming fluid is called **convection**. If for the moment we ignore diffusion, then the flux of particles through an area A in an interval Δt when the fluid is flowing at a velocity v can be calculated in the way we have used several times before (by counting the particles within a distance $v\Delta t$), and is

$$J = \frac{cA\Delta vt}{A\Delta t} = cv \tag{21.69}$$

This J is called the **convective flux**. The rate of change of concentration in a slab of thickness l and area A is, by the same argument as before and assuming that the velocity does not depend on the position,

$$\frac{\partial c}{\partial t} = \frac{J - J'}{l} = \left\{c - \left[c + \left(\frac{\partial c}{\partial x}\right)l\right]\right\}\frac{v}{l} = -v\frac{\partial c}{\partial x} \tag{21.70}$$

When both diffusion and convection occur, the total change of concentration in a region is the sum of the two effects, and the **generalized diffusion equation** is
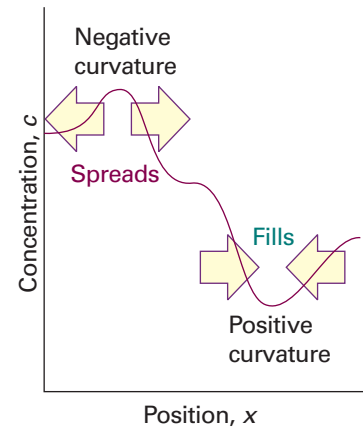
Fig. 21.25 Nature abhors a wrinkle. The diffusion equation tells us that peaks in distribution (regions of negative curvature) spread and troughs (regions of positive curvature) fill in.

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x} \tag{21.71}$$

A further refinement, which is important in chemistry, is the possibility that the concentrations of particles may change as a result of reaction. When reactions are included in eqn 21.71 (Section 24.2), we get a powerful differential equation for discussing the properties of reacting, diffusing, convecting systems and which is the basis of reactor design in chemical industry and of the utilization of resources in living cells.

(b) Solutions of the diffusion equation

The diffusion equation, eqn 21.68, is a second-order differential equation with respect to space and a first-order differential equation with respect to time. Therefore, we must specify two boundary conditions for the spatial dependence and a single initial condition for the time-dependence.

As an illustration, consider a solvent in which the solute is initially coated on one surface of the container (for example, a layer of sugar on the bottom of a deep beaker of water). The single initial condition is that at $t = 0$ all N_0 particles are concentrated on the yz-plane (of area A) at $x = 0$. The two boundary conditions are derived from the requirements (1) that the concentration must everywhere be finite and (2) that the total amount (number of moles) of particles present is n_0 (with $n_0 = N_0/N_A$) at all times. These requirements imply that the flux of particles is zero at the top and bottom surfaces of the system. Under these conditions it is found that

$$c(x,t) = \frac{n_0}{A(\pi D t)^{1/2}} e^{-x^2/4Dt} \tag{21.72}$$

as may be verified by direct substitution. Figure 21.26 shows the shape of the concentration distribution at various times, and it is clear that the concentration spreads and tends to uniformity.

Another useful result is for a localized concentration of solute in a three-dimensional solvent (a sugar lump suspended in a large flask of water). The concentration of diffused solute is spherically symmetrical and at a radius r is

$$c(r,t) = \frac{n_0}{8(\pi D t)^{3/2}} e^{-r^2/4Dt} \tag{21.73}$$

Other chemically (and physically) interesting arrangements, such as transport of substances across biological membranes can be treated (*Impact I21.3*). In many cases the solutions are more cumbersome.

(c) The measurement of diffusion coefficients

The solutions of the diffusion equation are useful for experimental determinations of diffusion coefficients. In the **capillary technique**, a capillary tube, open at one end and containing a solution, is immersed in a well stirred larger quantity of solvent, and the change of concentration in the tube is monitored. The solute diffuses from the open end of the capillary at a rate that can be calculated by solving the diffusion equation with the appropriate boundary conditions, so D may be determined. In the **diaphragm technique**, the diffusion occurs through the capillary pores of a sintered glass diaphragm separating the well-stirred solution and solvent. The concentrations are monitored and then related to the solutions of the diffusion equation corresponding to this arrangement. Diffusion coefficients may also be measured by the dynamic light scattering technique described in Section 19.3 and by NMR.
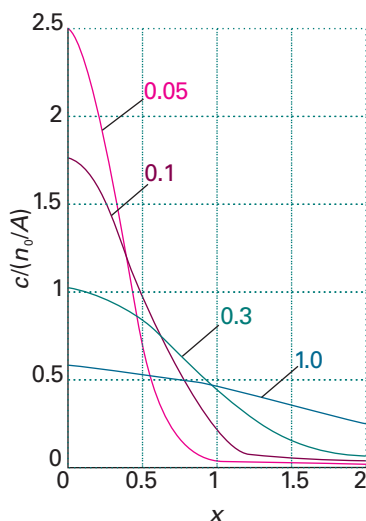
Fig. 21.26 The concentration profiles above a plane from which a solute is diffusing. The curves are plots of eqn 21.72 and are labelled with different values of Dt. The units of Dt and x are arbitrary, but are related so that Dt/x^2 is dimensionless. For example, if x is in metres, Dt would be in metres^2; so, for $D = 10^{-9}$ m^2 s^{-1}, $Dt = 0.1$ m^2 corresponds to $t = 10^8$ s.

Exploration Generate a family of curves similar to that shown in Fig. 21.26 but by using eqn 21.73, which describes diffusion in three dimensions.

IMPACT ON BIOCHEMISTRY

21.3 Transport of non-electrolytes across biological membranes

We saw in *Impact I21.2* how electrolytes are transported across cell membranes. Here we use the diffusion equation to explore the way in which non-electrolytes cross the lipid bilayer.

Consider the passive transport of an uncharged species A across a lipid bilayer of thickness *l*. To simplify the problem, we will assume that the concentration of A is always maintained at $[A] = [A]_0$ on one surface of the membrane and at $[A] = 0$ on the other surface, perhaps by a perfect balance between the rate of the process that produces A on one side and the rate of another process that consumes A completely on the other side. This is one example of a steady-state assumption, which will be discussed in more detail in Section 22.7. Then $\partial[A]/\partial t = 0$ and the diffusion equation simplifies to

$$D\frac{d^2[A]}{dx^2} = 0 \tag{21.74}$$

where *D* is the diffusion coefficient and the steady-state assumption makes partial derivatives unnecessary. We use the boundary conditions $[A](0) = [A]_0$ and $[A](l) = 0$ to solve eqn 21.74 and the result, which may be verified by differentiation, is

$$[A](x) = [A]_0\left(1 - \frac{x}{l}\right) \tag{21.75}$$

which implies that the [A] decreases linearly inside the membrane. We now use Fick's first law to calculate the flux *J* of A through the membrane and the result is

$$J = D\frac{[A]_0}{l} \tag{21.76}$$

However, we need to modify this equation slightly to account for the fact that the concentration of A on the surface of a membrane is not always equal to the concentration of A measured in the bulk solution, which we assume to be aqueous. This difference arises from the significant difference in the solubility of A in an aqueous environment and in the solution–membrane interface. One way to deal with this problem is to define a **partition ratio**, K_D (D for distribution) as

$$K_D = \frac{[A]_0}{[A]_s} \tag{21.77}$$

where $[A]_s$ is the concentration of A in the bulk aqueous solution. It follows that

$$J = DK_D\frac{[A]_s}{l} \tag{21.78}$$

In spite of the assumptions that led to its final form, eqn 21.78 describes adequately the passive transport of many non-electrolytes through membranes of blood cells.

In many cases the flux is underestimated by eqn 21.78 and the implication is that the membrane is more permeable than expected. However, the permeability increases only for certain species and not others and this is evidence that transport can be mediated by carriers. One example is the transporter protein that carries glucose into cells.

A characteristic of a carrier C is that it binds to the transported species A and the dissociation of the AC complex is described by
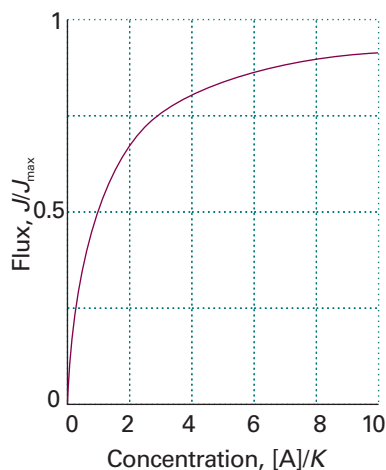
$$AC \rightleftharpoons A + C \qquad K = \frac{[A][C]}{[AC]} \tag{21.79}$$

Fig. 21.27 The flux of the species AC through a membrane varies with the concentration of the species A. The behaviour shown in the figure and explained in the text is characteristic of mediated transport of A, with C as a carrier molecule.

where we have used concentrations instead of activities. After writing $[C]_0 = [C] + [AC]$, where $[C]_0$ is the total concentration of carrier, it follows that

$$[AC] = \frac{[A][C]_0}{[A] + K} \tag{21.80}$$

We can now use eqns 21.80 and 21.78 to write an expression for the flux of the species AC through the membrane:

$$J = \frac{DK_D[C]_0}{l}\frac{[A]}{[A] + K} = J_{max}\frac{[A]}{[A] + K} \tag{21.81}$$

where K_D and D are the partition ratio and diffusion coefficient of the species AC. We see from Fig. 21.27 that when $[A] \ll K$ the flux varies linearly with $[A]$ and that the flux reaches a maximum value of $J_{max} = DK_D[C]_0/l$ when $[A] \gg K$. This behaviour is characteristic of mediated transport.

21.11 **Diffusion probabilities**

The solutions of the diffusion equation can be used to predict the concentration of particles (or the value of some other physical quantity, such as the temperature in a nonuniform system) at any location. We can also use them to calculate the net distance through which the particles diffuse in a given time.

Example 21.5 *Calculating the net distance of diffusion*

Calculate the net distance travelled on average by particles in a time t if they have a diffusion constant D.

Method We need to use the results of probability theory summarized in *Appendix 2*. In this case, we calculate the probability that a particle will be found at a certain distance from the origin, and then calculate the average by weighting each distance by that probability.

Answer The number of particles in a slab of thickness dx and area A at x, where the molar concentration is c, is $cAN_A dx$. The probability that any of the $N_0 = n_0 N_A$ particles is in the slab is therefore $cAN_A dx/N_0$. If the particle is in the slab, it has travelled a distance x from the origin. Therefore, the mean distance travelled by all the particles is the sum of each x weighted by the probability of its occurrence:

$$\langle x \rangle = \int_0^\infty \frac{xcAN_A}{N_0}dx = \frac{1}{(\pi Dt)^{1/2}}\int_0^\infty xe^{-x^2/4Dt}dx = 2\left(\frac{Dt}{\pi}\right)^{1/2}$$

where we have used the same standard integral as that used in Justification 21.4.

The average distance of diffusion varies as the square root of the lapsed time. If we use the Stokes–Einstein relation for the diffusion coefficient, the mean distance travelled by particles of radius a in a solvent of viscosity η is

$$\langle x \rangle = \left(\frac{2kTt}{3\pi^2\eta a}\right)^{1/2}$$

Self-test 21.7 Derive an expression for the root mean square distance travelled by diffusing particles in a time t. $[\langle x^2 \rangle^{1/2} = (2Dt)^{1/2}]$

As shown in Example 21.5, the average distance travelled by diffusing particle in a time t is

$$\langle x \rangle = 2 \left(\frac{Dt}{\pi} \right)^{1/2} \tag{21.82}$$

and the root mean square distance travelled in the same time is

$$\langle x^2 \rangle^{1/2} = (2Dt)^{1/2} \tag{21.83}$$

The latter is a valuable measure of the spread of particles when they can diffuse in both directions from the origin (for then $\langle x \rangle = 0$ at all times). The root mean square distance travelled by particles with a typical diffusion coefficient ($D = 5 \times 10^{-10}$ m^2 s^{-1}) is illustrated in Fig. 21.28, which shows how long it takes for diffusion to increase the net distance travelled on average to about 1 cm in an unstirred solution. The graph shows that diffusion is a very slow process (which is why solutions are stirred, to encourage mixing by convection).
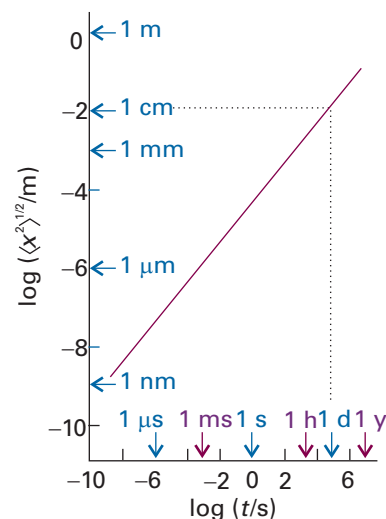
21.12 The statistical view

An intuitive picture of diffusion is of the particles moving in a series of small steps and gradually migrating from their original positions. We shall explore this idea using a model in which the particles can jump through a distance λ in a time τ. The total distance travelled by a particle in a time t is therefore $t\lambda/\tau$. However, the particle will not necessarily be found at that distance from the origin. The direction of each step may be different, and the net distance travelled must take the changing directions into account.

If we simplify the discussion by allowing the particles to travel only along a straight line (the x-axis), and for each step (to the left or the right) to be through the same distance λ, then we obtain the **one-dimensional random walk**. The same model was used in the discussion of a one-dimensional random coil in Section 19.8a.

We show in the *Justification* below that the probability of a particle being at a distance x from the origin after a time t is

$$P = \left(\frac{2\tau}{\pi t} \right)^{1/2} e^{-x^2 \tau/2t\lambda^2} \tag{21.84}$$

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Justification 21.7 *The one-dimensional random walk*

Consider a one-dimensional random walk in which each step is through a distance λ to the left or right. The net distance travelled after N steps is equal to the difference between the number of steps to the right (N_R) and to the left (N_L), and is $(N_R - N_L)\lambda$. We write $n = N_R - N_L$ and the total number of steps as $N = N_R + N_L$.

The number of ways of performing a walk with a given net distance of travel $n\lambda$ is the number of ways of making N_R steps to the right and N_L steps to the left, and is given by the binomial coefficient

$$W = \frac{N!}{N_L! N_R!} = \frac{N!}{\{\frac{1}{2}(N + n)\}! \{\frac{1}{2}(N - n)\}!}$$

The probability of the net distance walked being $n\lambda$ is

$$P = \frac{\text{number of paths with } N_R \text{ steps to the right}}{\text{total number of steps}}$$

$$= \frac{W}{2^N} = \frac{N!}{\{\frac{1}{2}(N + n)\}! \{\frac{1}{2}(N - n)\}! 2^N}$$

Fig. 21.28 The root mean square distance covered by particles with $D = 5 \times 10^{-10}$ m^2 s^{-1}. Note the great slowness of diffusion.

The use of Stirling's approximation (Section 16.1a) in the form

$$\ln x! \approx \ln(2\pi)^{1/2} + (x + \tfrac{1}{2}) \ln x - x$$

gives (after quite a lot of algebra; see Problem 21.33)

$$\ln P = \ln\left(\frac{2}{\pi N}\right)^{1/2} - \tfrac{1}{2}(N + n + 1)\ln\left(1 + \frac{n}{N}\right) - \tfrac{1}{2}(N - n + 1)\ln\left(1 - \frac{n}{N}\right)$$

For small net distances ($n \ll N$) we can use the approximation $\ln(1 \pm x) \approx \pm x - \tfrac{1}{2}x^2$, and so obtain

$$\ln P \approx \ln\left(\frac{2}{\pi N}\right)^{1/2} - \frac{n^2}{2N}$$

At this point, we note that the number of steps taken in a time t is $N = t/\tau$ and the net distance travelled from the origin is $x = n\lambda$. Substitution of these quantities into the expression for $\ln P$ gives

$$\ln P \approx \ln\left(\frac{2\tau}{\pi t}\right)^{1/2} - \frac{x^2 \tau}{2t\lambda^2}$$

which, upon using $e^{\ln x} = x$ and $e^{x+y} = e^x e^y$, rearranges into eqn 21.84.

The differences of detail between eqns 21.72 and 21.84 arise from the fact that in the present calculation the particles can migrate in either direction from the origin. Moreover, they can be found only at discrete points separated by λ instead of being anywhere on a continuous line. The fact that the two expressions are so similar suggests that diffusion can indeed be interpreted as the outcome of a large number of steps in random directions.

We can now relate the coefficient D to the step length λ and the rate at which the jumps occur. Thus, by comparing the two exponents in eqns 21.72 and 21.84 we can immediately write down the **Einstein–Smoluchowski equation**:

$$D = \frac{\lambda^2}{2\tau} \tag{21.85}$$

Illustration 21.6 *Using the Einstein–Smoluchowski equation*

Suppose that a SO_4^{2-} ion jumps through its own diameter each time it makes a move in an aqueous solution; then, because $D = 1.1 \times 10^{-9}$ m^2 s^{-1} and $a = 210$ pm (as deduced from mobility measurements), it follows from $\lambda = 2a$ that $\tau = 80$ ps. Because τ is the time for one jump, the ion makes 1×10^{10} jumps per second.

The Einstein–Smoluchowski equation is the central connection between the microscopic details of particle motion and the macroscopic parameters relating to diffusion (for example, the diffusion coefficient and, through the Stokes–Einstein relation, the viscosity). It also brings us back full circle to the properties of the perfect gas. For if we interpret λ/τ as $\bar{c}$, the mean speed of the molecules, and interpret λ as a mean free path, then we can recognize in the Einstein–Smoluchowski equation exactly the same expression as we obtained from the kinetic model of gases, eqn 21.22. That is, the diffusion of a perfect gas is a random walk with an average step size equal to the mean free path.

Checklist of key ideas

☐ 1. Diffusion is the migration of matter down a concentration gradient; thermal conduction is the migration of energy down a temperature gradient; electric conduction is the migration of electric charge along an electrical potential gradient; viscosity is the migration of linear momentum down a velocity gradient.

☐ 2. The kinetic model of a gas considers only the contribution to the energy from the kinetic energies of the molecules. Important results from the model include expressions for the pressure ($pV = \frac{1}{3}nMc^2$) and the root mean square speed ($c = \langle v^2 \rangle^{1/2} = (3RT/M)^{1/2}$).

☐ 3. The Maxwell distribution of speeds is the function which, through $f(v)dv$, gives the fraction of molecules that have speeds in the range v to $v + dv$.

☐ 4. The collision frequency is the number of collisions made by a molecule in an interval divided by the length of the interval: $z = \sigma \bar{c}_{rel} \mathcal{N}$, where the collision cross-section is $\sigma = \pi d^2$.

☐ 5. The mean free path is the average distance a molecule travels between collisions: $\lambda = \bar{c}/z$.

☐ 6. The collision flux, Z_W, is the number of collisions with an area in a given time interval divided by the area and the duration of the interval: $Z_w = p/(2\pi mkT)^{1/2}$.

☐ 7. Effusion is the emergence of a gas from a container through a small hole. Graham's law of effusion states that the rate of effusion is inversely proportional to the square root of the molar mass.

☐ 8. Flux J is the quantity of a property passing through a given area in a given time interval divided by the area and the duration of the interval.

☐ 9. Fick's first law of diffusion states that the flux of matter is proportional to the concentration gradient, $J(\text{matter}) = -Dd\mathcal{N}/dz$, where D is the diffusion coefficient.

☐ 10. The conductance, G, is the inverse of resistance. The conductivity is the constant κ in $G = \kappa A/l$ and the molar conductivity is written as $\Lambda_m = \kappa/c$.

☐ 11. A strong electrolyte is an electrolyte with a molar conductivity that varies only slightly with concentration. A weak electrolyte is an electrolyte with a molar conductivity that is normal at concentrations close to zero, but falls sharply to low values as the concentration increases.

☐ 12. Kohlrausch's law for the concentration dependence of the molar conductivity of a strong electrolyte is written as $\Lambda_m = \Lambda_m^\circ - \mathcal{K}c^{1/2}$, where the limiting molar conductivity, Λ_m°, is the molar conductivity at zero concentration ($\Lambda_m^\circ = v_+\lambda_+ + v_-\lambda_-$).

☐ 13. The drift speed s is the terminal speed when an accelerating force is balanced by the viscous drag: $s = u\mathcal{E}$, where $u = ze/6\pi\eta a$ is the ionic mobility and a is the hydrodynamic radius (Stokes radius), the effective radius of a particle in solution.

☐ 14. The ionic conductivity is the contribution of ions of one type to the molar conductivity: $\lambda = zuF$.

☐ 15. The transport number is the fraction of total current I carried by the ions of a specified type: $t_\pm = I_\pm/I$.

☐ 16. The Debye–Hückel–Onsager theory explains the concentration dependence of the molar conductivity of a strong electrolyte in terms of ionic interactions.

☐ 17. The Einstein relation between the diffusion coefficient and the ionic mobility is $D = uRT/zF$.

☐ 18. The Nernst–Einstein relation between the molar conductivity of an electrolyte and the diffusion coefficients of its ions is $\Lambda_m = (v_+z_+^2D_+ + v_-z_-^2D_-)(F^2/RT)$.

☐ 19. The Stokes–Einstein equation relates the diffusion coefficient to the frictional force: $D = kT/f$.

☐ 20. Walden's rule states that the product $\eta\Lambda_m$ is very approximately constant for the same ions in different solvents.

☐ 21. The diffusion equation is a relation between the rate of change of concentration at a point and the spatial variation of the concentration at that point: $\partial c/\partial t = D\partial^2 c/\partial x^2$.

☐ 22. In a one-dimensional random walk, the probability P that a molecule moves a distance x from the origin for a period t by taking small steps with size λ and time τ is: $P = (2\tau/\pi t)^{1/2}e^{-x^2\tau/2t\lambda^2}$.

☐ 23. The Einstein–Smoluchowski equation relates the diffusion coefficient to the parameters used in the formulation of the random walk model, $D = \lambda^2/2\tau$.

Further reading

Articles and texts

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Further information

Further information 21.1 *The transport characteristics of a perfect gas*

In this Further information section, we derive expressions for the diffusion characteristics (specifically, the diffusion coefficient, the thermal conductivity, and the viscosity) of a perfect gas on the basis of the kinetic molecular theory.

The diffusion coefficient, *D*

Consider the arrangement depicted in Fig. 21.29. On average, the molecules passing through the area A at $z = 0$ have travelled about one mean free path λ since their last collision. Therefore, the number density where they originated is $\mathcal{N}(z)$ evaluated at $z = -\lambda$. This number density is approximately

$$\mathcal{N}(-\lambda) = \mathcal{N}(0) - \lambda \left(\frac{d\mathcal{N}}{dz} \right)_0 \tag{21.86}$$

where we have used a Taylor expansion of the form $f(x) = f(0) + (df/dx)_0 x + \cdots$ truncated after the second term (see *Appendix* 2). The average number of impacts on the imaginary window of area A_0 during an interval Δt is $Z_W A_0 \Delta t$, with $Z_W = \frac{1}{4}\mathcal{N}\bar{c}$ (eqn 21.15). Therefore, the flux from left to right, $J(L\to R)$, arising from the supply of molecules on the left, is

$$J(L \to R) = \frac{\frac{1}{4}A_0 \mathcal{N}(-\lambda)\bar{c}\Delta t}{A_0 \Delta t} = \frac{1}{4}\mathcal{N}(-\lambda)\bar{c} \tag{21.87}$$

There is also a flux of molecules from right to left. On average, the molecules making the journey have originated from $z = +\lambda$ where the number density is $\mathcal{N}(\lambda)$. Therefore,

$$J(L \leftarrow R) = -\frac{1}{4}\mathcal{N}(\lambda)\bar{c} \tag{21.88}$$

The average number density at $z = +\lambda$ is approximately

$$\mathcal{N}(\lambda) = \mathcal{N}(0) + \lambda \left(\frac{d\mathcal{N}}{dz} \right)_0 \tag{21.89}$$

The net flux is

$$\begin{aligned}
J_z &= J(L \to R) + J(L \leftarrow R) \\
&= \frac{1}{4}\bar{c} \left\{ \left[\mathcal{N}(0) - \lambda \left(\frac{d\mathcal{N}}{dz} \right)_0 \right] - \left[\mathcal{N}(0) + \lambda \left(\frac{d\mathcal{N}}{dz} \right)_0 \right] \right\} \\
&= -\frac{1}{2}\bar{c}\lambda \left(\frac{d\mathcal{N}}{dz} \right)_0
\end{aligned} \tag{21.90}$$

This equation shows that the flux is proportional to the first derivative of the concentration, in agreement with Fick's law.

At this stage it looks as though we can pick out a value of the diffusion coefficient by comparing eqns 21.19 and 21.90, so obtaining $D = \frac{1}{2}\lambda\bar{c}$. It must be remembered, however, that the calculation is quite crude, and is little more than an assessment of the order of magnitude of D. One aspect that has not been taken into account is illustrated in Fig. 21.30, which shows that, although a molecule may
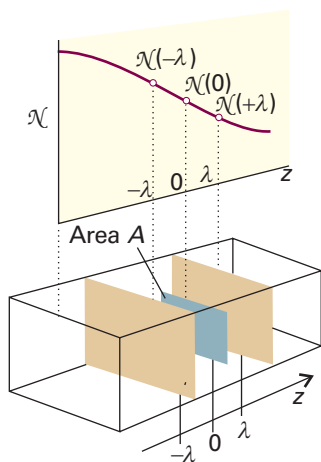

Fig. 21.29 The calculation of the rate of diffusion of a gas considers the net flux of molecules through a plane of area A as a result of arrivals from on average a distance λ away in each direction, where λ is the mean free path.
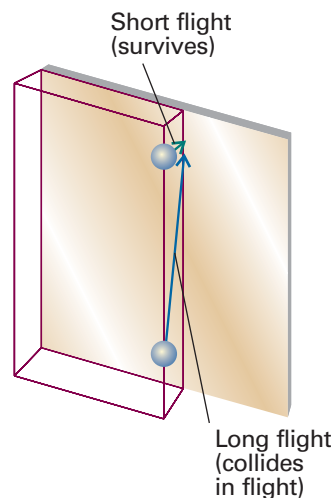

Fig. 21.30 One approximation ignored in the simple treatment is that some particles might make a long flight to the plane even though they are only a short perpendicular distance away, and therefore they have a higher chance of colliding during their journey.

have begun its journey very close to the window, it could have a long flight before it gets there. Because the path is long, the molecule is likely to collide before reaching the window, so it ought to be added to the graveyard of other molecules that have collided. To take this effect into account involves a lot of work, but the end result is the appearance of a factor of $\frac{2}{3}$ representing the lower flux. The modification results in eqn 21.22.

Thermal conductivity

According to the equipartition theorem (Section 17.3), each molecule carries an average energy $\varepsilon = vkT$, where v is a number of the order of 1. For monatomic particles, $v = \frac{3}{2}$. When one molecule passes through the imaginary window, it transports that energy on average. We suppose that the number density is uniform but that the temperature is not. On average, molecules arrive from the left after travelling a mean free path from their last collision in a hotter region, and therefore with a higher energy. Molecules also arrive from the right after travelling a mean free path from a cooler region. The two opposing energy fluxes are therefore

$$J(\text{L} \rightarrow \text{R}) = \tfrac{1}{4}\bar{c}\mathcal{N}\varepsilon(-\lambda) \qquad \varepsilon(-\lambda) = vk\left\{T - \lambda\left(\frac{dT}{dz}\right)_0\right\}$$

$$J(\text{L} \leftarrow \text{R}) = -\tfrac{1}{4}\bar{c}\mathcal{N}\varepsilon(\lambda) \qquad \varepsilon(\lambda) = vk\left\{T + \lambda\left(\frac{dT}{dz}\right)_0\right\} \qquad (21.91)$$

and the net flux is

$$J_z = J(\text{L} \rightarrow \text{R}) + J(\text{L} \leftarrow \text{R}) = -\tfrac{1}{2}vk\lambda\bar{c}\mathcal{N}\left(\frac{dT}{dz}\right)_0 \qquad (21.92)$$

As before, we multiply by $\frac{2}{3}$ to take long flight paths into account, and so arrive at

$$J_z = -\tfrac{1}{3}vk\lambda\bar{c}\mathcal{N}\left(\frac{dT}{dz}\right)_0 \qquad (21.93)$$

The energy flux is proportional to the temperature gradient, as we wanted to show. Comparison of this equation with eqn 21.20 shows that

$$\kappa = \tfrac{1}{3}vk\lambda\bar{c}\mathcal{N} \qquad (21.94)$$

Equation 21.23 then follows from $C_{V,\text{m}} = vkN_A$ for a perfect gas, where [A] is the molar concentration of A. For this step, we use $\mathcal{N} = N/V = nN_A/V = N_A[\text{A}]$.

Viscosity

Molecules travelling from the right in Fig. 21.31 (from a fast layer to a slower one) transport a momentum $mv_x(\lambda)$ to their new layer at $z = 0$;
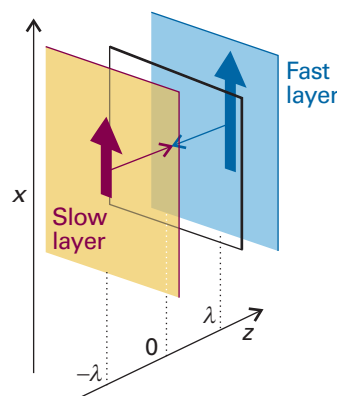

Fig. 21.31 The calculation of the viscosity of a gas examines the net x-component of momentum brought to a plane from faster and slower layers on average a mean free path away in each direction.

those travelling from the left transport $mv_x(-\lambda)$ to it. If it is assumed that the density is uniform, the collision flux is $\frac{1}{4}\mathcal{N}\bar{c}$. Those arriving from the right on average carry a momentum

$$mv_x(\lambda) = mv_x(0) + m\lambda\left(\frac{dv_x}{dz}\right)_0 \qquad (21.95a)$$

Those arriving from the left bring a momentum

$$mv_x(-\lambda) = mv_x(0) - m\lambda\left(\frac{dv_x}{dz}\right)_0 \qquad (21.95b)$$

The net flux of x-momentum in the z-direction is therefore

$$J = \tfrac{1}{4}\mathcal{N}\bar{c}\left\{\left[mv_x(0) - m\lambda\left(\frac{dv_x}{dz}\right)_0\right] - \left[mv_x(0) + m\lambda\left(\frac{dv_x}{dz}\right)_0\right]\right\}$$

$$= -\tfrac{1}{2}\mathcal{N}m\lambda\bar{c}\left(\frac{dv_x}{dz}\right)_0 \qquad (21.96)$$

The flux is proportional to the velocity gradient, as we wished to show. Comparison of this expression with eqn 21.21, and multiplication by $\frac{2}{3}$ in the normal way, leads to

$$\eta = \tfrac{1}{3}\mathcal{N}m\lambda\bar{c} \qquad (21.97)$$

which can easily be converted into eqn 21.24 by using $Nm = nM$ and $[\text{A}] = n/V$.

Discussion questions

21.1 Use the kinetic theory to justify the following observations: (a) the rate of a reaction in the gas phase depends on the energy with which two molecules collide, which in turn depends on their speeds; (b) in the Earth's atmosphere, light gases, such as H_2 and He, are rare but heavier gases, such as O_2, CO_2, and N_2, are abundant.

21.2 Provide a molecular interpretation for each of the following processes: diffusion, thermal conduction, electric conduction, and viscosity.

21.3 Provide a molecular interpretation for the observation that the viscosity of a gas increases with temperature, whereas the viscosity of a liquid decreases with increasing temperature.

21.4 Discuss the mechanism of proton conduction in liquid water.

21.5 Limit the generality of the following expressions: (a) $J = -D(dc/dx)$, (b) $D = kT/f$, and (c) $D = kT/6\pi\eta a$.

21.6 Provide a molecular interpretation for the observation that mediated transport across a biological membrane leads to a maximum flux J_{max} when the concentration of the transported species becomes very large.

21.7 Discuss how nuclear magnetic resonance spectroscopy, inelastic neutron scattering, and dynamic light scattering may be used to measure the mobility of molecules in liquids.

Exercises

21.1a Determine the ratios of (a) the mean speeds, (b) the mean kinetic energies of H_2 molecules and Hg atoms at 20°C.

21.1b Determine the ratios of (a) the mean speeds, (b) the mean kinetic energies of He atoms and Hg atoms at 25°C.

21.2a A 1.0 dm³ glass bulb contains 1.0×10^{23} H_2 molecules. If the pressure exerted by the gas is 100 kPa, what are (a) the temperature of the gas, (b) the root mean square speeds of the molecules? (c) Would the temperature be different if they were O_2 molecules?

21.2b The best laboratory vacuum pump can generate a vacuum of about 1 nTorr. At 25°C and assuming that air consists of N_2 molecules with a collision diameter of 395 pm, calculate (a) the mean speed of the molecules, (b) the mean free path, (c) the collision frequency in the gas.

21.3a At what pressure does the mean free path of argon at 25°C become comparable to the size of a 1 dm³ vessel that contains it? Take $\sigma = 0.36$ nm².

21.3b At what pressure does the mean free path of argon at 25°C become comparable to the diameters of the atoms themselves?

21.4a At an altitude of 20 km the temperature is 217 K and the pressure 0.050 atm. What is the mean free path of N_2 molecules? ($\sigma = 0.43$ nm².)

21.4b At an altitude of 15 km the temperature is 217 K and the pressure 12.1 kPa. What is the mean free path of N_2 molecules? ($\sigma = 0.43$ nm².)

21.5a How many collisions does a single Ar atom make in 1.0 s when the temperature is 25°C and the pressure is (a) 10 atm, (b) 1.0 atm, (c) 1.0 μatm?

21.5b How many collisions per second does an N_2 molecule make at an altitude of 15 km? (See Exercise 21.4b for data.)

21.6a Calculate the mean free path of molecules in air using $\sigma = 0.43$ nm² at 25°C and (a) 10 atm, (b) 1.0 atm, (c) 1.0 μatm.

21.6b Calculate the mean free path of carbon dioxide molecules using $\sigma = 0.52$ nm² at 25°C and (a) 15 atm, (b) 1.0 bar, (c) 1.0 Torr.

21.7a Use the Maxwell distribution of speeds to estimate the fraction of N_2 molecules at 500 K that have speeds in the range 290 to 300 m s⁻¹.

21.7b Use the Maxwell distribution of speeds to estimate the fraction of CO_2 molecules at 300 K that have speeds in the range 200 to 250 m s⁻¹.

21.8a A solid surface with dimensions 2.5 mm × 3.0 mm is exposed to argon gas at 90 Pa and 500 K. How many collisions do the Ar atoms make with this surface in 15 s?

21.8b A solid surface with dimensions 3.5 mm × 4.0 cm is exposed to helium gas at 111 Pa and 1500 K. How many collisions do the He atoms make with this surface in 10 s?

21.9a An effusion cell has a circular hole of diameter 2.50 mm. If the molar mass of the solid in the cell is 260 g mol⁻¹ and its vapour pressure is 0.835 Pa at 400 K, by how much will the mass of the solid decrease in a period of 2.00 h?

21.9b An effusion cell has a circular hole of diameter 3.00 mm. If the molar mass of the solid in the cell is 300 g mol⁻¹ and its vapour pressure is 0.224 Pa at 450 K, by how much will the mass of the solid decrease in a period of 24.00 h?

21.10a A manometer was connected to a bulb containing carbon dioxide under slight pressure. The gas was allowed to escape through a small pinhole, and the time for the manometer reading to drop from 75 cm to 50 cm was 52 s. When the experiment was repeated using nitrogen (for which $M = 28.02$ g mol⁻¹) the same fall took place in 42 s. Calculate the molar mass of carbon dioxide.

21.10b A manometer was connected to a bulb containing nitrogen under slight pressure. The gas was allowed to escape through a small pinhole, and the time for the manometer reading to drop from 65.1 cm to 42.1 cm was 18.5 s. When the experiment was repeated using a fluorocarbon gas, the same fall took place in 82.3 s. Calculate the molar mass of the fluorocarbon.

21.11a A space vehicle of internal volume 3.0 m³ is struck by a meteor and a hole of radius 0.10 mm is formed. If the oxygen pressure within the vehicle is initially 80 kPa and its temperature 298 K, how long will the pressure take to fall to 70 kPa?

21.11b A container of internal volume 22.0 m³ was punctured, and a hole of radius 0.050 mm was formed. If the nitrogen pressure within the vehicle is initially 122 kPa and its temperature 293 K, how long will the pressure take to fall to 105 kPa?

21.12a Calculate the flux of energy arising from a temperature gradient of 2.5 K m⁻¹ in a sample of argon in which the mean temperature is 273 K.

21.12b Calculate the flux of energy arising from a temperature gradient of 3.5 K m⁻¹ in a sample of hydrogen in which the mean temperature is 260 K.

21.13a Use the experimental value of the thermal conductivity of neon (Table 21.2) to estimate the collision cross-section of Ne atoms at 273 K.

21.13b Use the experimental value of the thermal conductivity of nitrogen (Table 21.2) to estimate the collision cross-section of N_2 molecules at 298 K.

21.14a In a double-glazed window, the panes of glass are separated by 5.0 cm. What is the rate of transfer of heat by conduction from the warm room (25°C) to the cold exterior (−10°C) through a window of area 1.0 m²? What power of heater is required to make good the loss of heat?

21.14b Two sheets of copper of area 1.50 m² are separated by 10.0 cm. What is the rate of transfer of heat by conduction from the warm sheet (50°C) to the cold sheet (−10°C). What is the rate of loss of heat?

21.15a Use the experimental value of the coefficient of viscosity for neon (Table 21.2) to estimate the collision cross-section of Ne atoms at 273 K.

21.15b Use the experimental value of the coefficient of viscosity for nitrogen (Table 21.2) to estimate the collision cross-section of the molecules at 273 K.

21.16a Calculate the inlet pressure required to maintain a flow rate of 9.5×10^5 dm³ h⁻¹ of nitrogen at 293 K flowing through a pipe of length 8.50 m

and diameter 1.00 cm. The pressure of gas as it leaves the tube is 1.00 bar. The volume of the gas is measured at that pressure.

21.16b Calculate the inlet pressure required to maintain a flow rate of 8.70 cm³ s⁻¹ of nitrogen at 300 K flowing through a pipe of length 10.5 m and diameter 15 mm. The pressure of gas as it leaves the tube is 1.00 bar. The volume of the gas is measured at that pressure.

21.17a Calculate the viscosity of air at (a) 273 K, (b) 298 K, (c) 1000 K. Take $\sigma \approx 0.40$ nm². (The experimental values are 173 μP at 273 K, 182 μP at 20°C, and 394 μP at 600°C.)

21.17b Calculate the viscosity of benzene vapour at (a) 273 K, (b) 298 K, (c) 1000 K. Take $\sigma \approx 0.88$ nm².

21.18a Calculate the thermal conductivities of (a) argon, (b) helium at 300 K and 1.0 mbar. Each gas is confined in a cubic vessel of side 10 cm, one wall being at 310 K and the one opposite at 295 K. What is the rate of flow of energy as heat from one wall to the other in each case?

21.18b Calculate the thermal conductivities of (a) neon, (b) nitrogen at 300 K and 15 mbar. Each gas is confined in a cubic vessel of side 15 cm, one wall being at 305 K and the one opposite at 295 K. What is the rate of flow of energy as heat from one wall to the other in each case?

21.19a The viscosity of carbon dioxide was measured by comparing its rate of flow through a long narrow tube (using Poiseuille's formula) with that of argon. For the same pressure differential, the same volume of carbon dioxide passed through the tube in 55 s as argon in 83 s. The viscosity of argon at 25°C is 208 μP; what is the viscosity of carbon dioxide? Estimate the molecular diameter of carbon dioxide.

21.19b The viscosity of a chlorofluorocarbon (CFC) was measured by comparing its rate of flow through a long narrow tube (using Poiseuille's formula) with that of argon. For the same pressure differential, the same volume of the CFC passed through the tube in 72.0 s as argon in 18.0 s. The viscosity of argon at 25°C is 208 μP; what is the viscosity of the CFC? Estimate the molecular diameter of the CFC. Take $M = 200$ g mol⁻¹.

21.20a Calculate the thermal conductivity of argon ($C_{V,m} = 12.5$ J K⁻¹ mol⁻¹, $\sigma = 0.36$ nm²) at room temperature (20°C).

21.20b Calculate the thermal conductivity of nitrogen ($C_{V,m} = 20.8$ J K⁻¹ mol⁻¹, $\sigma = 0.43$ nm²) at room temperature (20°C).

21.21a Calculate the diffusion constant of argon at 25°C and (a) 1.00 Pa, (b) 100 kPa, (c) 10.0 MPa. If a pressure gradient of 0.10 atm cm⁻¹ is established in a pipe, what is the flow of gas due to diffusion?

21.21b Calculate the diffusion constant of nitrogen at 25°C and (a) 10.0 Pa, (b) 100 kPa, (c) 15.0 MPa. If a pressure gradient of 0.20 bar m⁻¹ is established in a pipe, what is the flow of gas due to diffusion?

21.22a The mobility of a chloride ion in aqueous solution at 25°C is 7.91×10^{-8} m² s⁻¹ V⁻¹. Calculate the molar ionic conductivity.

21.22b The mobility of an acetate ion in aqueous solution at 25°C is 4.24×10^{-8} m² s⁻¹ V⁻¹. Calculate the molar ionic conductivity.

21.23a The mobility of a Rb⁺ ion in aqueous solution is 7.92×10^{-8} m² s⁻¹ V⁻¹ at 25°C. The potential difference between two electrodes placed in the solution is 35.0 V. If the electrodes are 8.00 mm apart, what is the drift speed of the Rb⁺ ion?

21.23b The mobility of a Li⁺ ion in aqueous solution is 4.01×10^{-8} m² s⁻¹ V⁻¹ at 25°C. The potential difference between two electrodes placed in the solution is 12.0 V. If the electrodes are 1.00 cm apart, what is the drift speed of the ion?

21.24a What fraction of the total current is carried by Li⁺ when current flows through an aqueous solution of LiBr at 25°C?

21.24b What fraction of the total current is carried by Cl⁻ when current flows through an aqueous solution of NaCl at 25°C?

21.25a The limiting molar conductivities of KCl, KNO₃, and AgNO₃ are 14.99 mS m² mol⁻¹, 14.50 mS m² mol⁻¹, and 13.34 mS m² mol⁻¹, respectively (all at 25°C). What is the limiting molar conductivity of AgCl at this temperature?

21.25b The limiting molar conductivities of NaI, NaCH₃CO₂, and Mg(CH₃CO₂)₂ are 12.69 mS m² mol⁻¹, 9.10 mS m² mol⁻¹, and 18.78 mS m² mol⁻¹, respectively (all at 25°C). What is the limiting molar conductivity of MgI₂ at this temperature?

21.26a At 25°C the molar ionic conductivities of Li⁺, Na⁺, and K⁺ are 3.87 mS m² mol⁻¹, 5.01 mS m² mol⁻¹, and 7.35 mS m² mol⁻¹, respectively. What are their mobilities?

21.26b At 25°C the molar ionic conductivities of F⁻, Cl⁻, and Br⁻ are 5.54 mS m² mol⁻¹, 7.635 mS m² mol⁻¹, and 7.81 mS m² mol⁻¹, respectively. What are their mobilities?

21.27a The mobility of a NO₃⁻ ion in aqueous solution at 25°C is 7.40×10^{-8} m² s⁻¹ V⁻¹. Calculate its diffusion coefficient in water at 25°C.

21.27b The mobility of a CH₃CO₂⁻ ion in aqueous solution at 25°C is 4.24×10^{-8} m² s⁻¹ V⁻¹. Calculate its diffusion coefficient in water at 25°C.

21.28a The diffusion coefficient of CCl₄ in heptane at 25°C is 3.17×10^{-9} m² s⁻¹. Estimate the time required for a CCl₄ molecule to have a root mean square displacement of 5.0 mm.

21.28b The diffusion coefficient of I₂ in hexane at 25°C is 4.05×10^{-9} m² s⁻¹. Estimate the time required for an iodine molecule to have a root mean square displacement of 1.0 cm.

21.29a Estimate the effective radius of a sucrose molecule in water 25°C given that its diffusion coefficient is 5.2×10^{-10} m² s⁻¹ and that the viscosity of water is 1.00 cP.

21.29b Estimate the effective radius of a glycine molecule in water at 25°C given that its diffusion coefficient is 1.055×10^{-9} m² s⁻¹ and that the viscosity of water is 1.00 cP.

21.30a The diffusion coefficient for molecular iodine in benzene is 2.13×10^{-9} m² s⁻¹. How long does a molecule take to jump through about one molecular diameter (approximately the fundamental jump length for translational motion)?

21.30b The diffusion coefficient for CCl₄ in heptane is 3.17×10^{-9} m² s⁻¹. How long does a molecule take to jump through about one molecular diameter (approximately the fundamental jump length for translational motion)?

21.31a What are the root mean square distances travelled by an iodine molecule in benzene and by a sucrose molecule in water at 25°C in 1.0 s?

21.31b About how long, on average, does it take for the molecules in Exercise 21.31a to drift to a point (a) 1.0 mm, (b) 1.0 cm from their starting points?

Problems*

Numerical problems

21.1 Instead of the arrangement in Fig. 21.8, the speed of molecules can also be measured with a rotating slotted-disc apparatus, which consists of five coaxial 5.0 cm diameter discs separated by 1.0 cm, the slots in their rims being displaced by 2.0° between neighbours. The relative intensities, I, of the detected beam of Kr atoms for two different temperatures and at a series of rotation rates were as follows:

v/Hz	20	40	80	100	120
I (40 K)	0.846	0.513	0.069	0.015	0.002
I (100 K)	0.592	0.485	0.217	0.119	0.057

Find the distributions of molecular velocities, $f(v_x)$, at these temperatures, and check that they conform to the theoretical prediction for a one-dimensional system.

21.2 Cars were timed by police radar as they passed in both directions below a bridge. Their velocities (kilometres per hour, numbers of cars in parentheses) to the east and west were as follows: 80 E (40), 85 E (62), 90 E (53), 95 E (12), 100 E (2); 80 W (38), 85 W (59), 90 W (50), 95 W (10), 100 W (2). What are (a) the mean velocity, (b) the mean speed, (c) the root mean square speed?

21.3 A population consists of people of the following heights (in metres, numbers of individuals in brackets): 1.80 (1), 1.82 (2), 1.84 (4), 1.86 (7), 1.88 (10), 1.90 (15), 1.92 (9), 1.94 (4), 1.96 (0), 1.98 (1). What are (a) the mean height, (b) the root mean square height of the population?

21.4 Calculate the ratio of the thermal conductivities of gaseous hydrogen at 300 K to gaseous hydrogen at 10 K. Be circumspect, and think about the modes of motion that are thermally active at the two temperatures.

21.5 A Knudsen cell was used to determine the vapour pressure of germanium at 1000°C. During an interval of 7200 s the mass loss through a hole of radius 0.50 mm amounted to 43 μg. What is the vapour pressure of germanium at 1000°C? Assume the gas to be monatomic.

21.6 The nuclide ^{244}Bk (berkelium) decays by producing α particles, which capture electrons and form He atoms. Its half-life is 4.4 h. A sample of mass 1.0 mg was placed in a container of volume 1.0 cm^3 that was impermeable to α radiation, but there was also a hole of radius 2.0 μm in the wall. What is the pressure of helium at 298 K, inside the container after (a) 1.0 h, (b) 10 h?

21.7 An atomic beam is designed to function with (a) cadmium, (b) mercury. The source is an oven maintained at 380 K, there being a small slit of dimensions 1.0 cm × 1.0 × 10^{-3} cm. The vapour pressure of cadmium is 0.13 Pa and that of mercury is 12 Pa at this temperature. What is the atomic current (the number of atoms per unit time) in the beams?

21.8 Conductivities are often measured by comparing the resistance of a cell filled with the sample to its resistance when filled with some standard solution, such as aqueous potassium chloride. The conductivity of water is 76 mS m^{-1} at 25°C and the conductivity of 0.100 mol dm^{-3} KCl(aq) is 1.1639 S m^{-1}. A cell had a resistance of 33.21 Ω when filled with 0.100 mol dm^{-3} KCl(aq) and 300.0 Ω when filled with 0.100 mol dm^{-3} CH$_3$COOH. What is the molar conductivity of acetic acid at that concentration and temperature?

21.9 The resistances of a series of aqueous NaCl solutions, formed by successive dilution of a sample, were measured in a cell with cell constant (the constant C in the relation $\kappa = C/R$) equal to 0.2063 cm^{-1}. The following values were found:

c/(mol dm^{-3})	0.00050	0.0010	0.0050	0.010	0.020	0.050
R/Ω	3314	1669	342.1	174.1	89.08	37.14

Verify that the molar conductivity follows the Kohlrausch law and find the limiting molar conductivity. Determine the coefficient $\mathcal{K}$. Use the value of $\mathcal{K}$ (which should depend only on the nature, not the identity of the ions) and the information that $\lambda(Na^+) = 5.01$ mS m^2 mol^{-1} and $\lambda(I^-) = 7.68$ mS m^2 mol^{-1} to predict (a) the molar conductivity, (b) the conductivity, (c) the resistance it would show in the cell, of 0.010 mol dm^{-3} NaI(aq) at 25°C.

21.10 After correction for the water conductivity, the conductivity of a saturated aqueous solution of AgCl at 25°C was found to be 0.1887 mS m^{-1}. What is the solubility of silver chloride at this temperature?

21.11 What are the drift speeds of Li$^+$, Na$^+$, and K$^+$ in water when a potential difference of 10 V is applied across a 1.00-cm conductivity cell? How long would it take an ion to move from one electrode to the other? In conductivity measurements it is normal to use alternating current: what are the displacements of the ions in (a) centimetres, (b) solvent diameters, about 300 pm, during a half cycle of 1.0 kHz applied potential?

21.12 The mobilities of H$^+$ and Cl$^-$ at 25°C in water are 3.623×10^{-7} m^2 s^{-1} V^{-1} and 7.91×10^{-8} m^2 s^{-1} V^{-1}, respectively. What proportion of the current is carried by the protons in 10^{-3} м HCl(aq)? What fraction do they carry when the NaCl is added to the acid so that the solution is 1.0 mol dm^{-3} in the salt? Note how concentration as well as mobility governs the transport of current.

21.13 In a moving boundary experiment on KCl the apparatus consisted of a tube of internal diameter 4.146 mm, and it contained aqueous KCl at a concentration of 0.021 mol dm^{-3}. A steady current of 18.2 mA was passed, and the boundary advanced as follows:

Δt/s	200	400	600	800	1000
x/mm	64	128	192	254	318

Find the transport number of K$^+$, its mobility, and its ionic conductivity.

21.14 The proton possesses abnormal mobility in water, but does it behave normally in liquid ammonia? To investigate this question, a moving-boundary technique was used to determine the transport number of NH$_4^+$ in liquid ammonia (the analogue of H$_3$O$^+$ in liquid water) at −40°C (J. Baldwin, J. Evans, and J.B. Gill, *J. Chem. Soc.* A, 3389 (1971)). A steady current of 5.000 mA was passed for 2500 s, during which time the boundary formed between mercury(II) iodide and ammonium iodide solutions in ammonia moved 286.9 mm in a 0.013 65 mol kg^{-1} solution and 92.03 mm in a 0.042 55 mol kg^{-1} solution. Calculate the transport number of NH$_4^+$ at these concentrations, and comment on the mobility of the proton in liquid ammonia. The bore of the tube is 4.146 mm and the density of liquid ammonia is 0.682 g cm^{-3}.

21.15 A dilute solution of potassium permanganate in water at 25°C was prepared. The solution was in a horizontal tube of length 10 cm, and at first there was a linear gradation of intensity of the purple solution from the left (where the concentration was 0.100 mol dm^{-3}) to the right (where the concentration was 0.050 mol dm^{-3}). What is the magnitude and sign of the thermodynamic force acting on the solute (a) close to the left face of the container, (b) in the middle, (c) close to the right face? Give the force per mole and force per molecule in each case.

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* Problems denoted with the symbol ‡ were supplied by Charles Trapp, Carmen Giunta, and Marshall Cady.

21.16 Estimate the diffusion coefficients and the effective hydrodynamic radii of the alkali metal cations in water from their mobilities at 25°C. Estimate the approximate number of water molecules that are dragged along by the cations. Ionic radii are given Table 20.3.

21.17 Nuclear magnetic resonance can be used to determine the mobility of molecules in liquids. A set of measurements on methane in carbon tetrachloride showed that its diffusion coefficient is 2.05×10^{-9} m^2 s^{-1} at 0°C and 2.89×10^{-9} m^2 s^{-1} at 25°C. Deduce what information you can about the mobility of methane in carbon tetrachloride.

21.18 A concentrated sucrose solution is poured into a cylinder of diameter 5.0 cm. The solution consisted of 10 g of sugar in 5.0 cm^3 of water. A further 1.0 dm^3 of water is then poured very carefully on top of the layer, without disturbing the layer. Ignore gravitational effects, and pay attention only to diffusional processes. Find the concentration at 5.0 cm above the lower layer after a lapse of (a) 10 s, (b) 1.0 y.

21.19 In a series of observations on the displacement of rubber latex spheres of radius 0.212 μm, the mean square displacements after selected time intervals were on average as follows:

t/s	30	60	90	120
$10^{12}\langle x^2\rangle/m^2$	88.2	113.5	128	144

These results were originally used to find the value of Avogadro's constant, but there are now better ways of determining N_A, so the data can be used to find another quantity. Find the effective viscosity of water at the temperature of this experiment (25°C).

21.20‡ A.K. Srivastava, R.A. Samant, and S.D. Patankar (*J. Chem. Eng. Data* **41**, 431 (1996)) measured the conductance of several salts in a binary solvent mixture of water and a dipolar aprotic solvent 1,3-dioxolan-2-one (ethylene carbonate). They report the following conductances at 25°C in a solvent 80 per cent 1,3-dioxolan-2-one by mass:

NaI

$c/(\text{mmol dm}^{-3})$	32.02	20.28	12.06	8.64	2.85	1.24	0.83
$\Lambda_m/(\text{S cm}^2\text{ mol}^{-1})$	50.26	51.99	54.01	55.75	57.99	58.44	58.67

KI

$c/(\text{mmol dm}^{-3})$	17.68	10.8	87.19	2.67	1.28	0.83	0.19
$\Lambda_m/(\text{S cm}^2\text{ mol}^{-1})$	42.45	45.91	47.53	51.81	54.09	55.78	57.42

Calculate Λ_m° for NaI and KI in this solvent and $\lambda^\circ(\text{Na}) - \lambda^\circ(\text{K})$. Compare your results to the analogous quantities in aqueous solution using Table 21.5 in the *Data section*.

21.21‡ A. Fenghour, W.A. Wakeham, V. Vesovic, J.T.R. Watson, J. Millat, and E. Vogel (*J. Phys. Chem. Ref. Data* **24**, 1649 (1995)) have compiled an extensive table of viscosity coefficients for ammonia in the liquid and vapour phases. Deduce the effective molecular diameter of NH_3 based on each of the following vapour-phase viscosity coefficients: (a) $\eta = 9.08 \times 10^{-6}$ kg m^{-1} s^{-1} at 270 K and 1.00 bar; (b) $\eta = 1.749 \times 10^{-5}$ kg m^{-1} s^{-1} at 490 K and 10.0 bar.

21.22‡ G. Bakale, K. Lacmann, and W.F. Schmidt (*J. Phys. Chem.* **100**, 12477 (1996)) measured the mobility of singly charged C_{60}^- ions in a variety of nonpolar solvents. In cyclohexane at 22°C, the mobility is 1.1 cm^2 V^{-1} s^{-1}. Estimate the effective radius of the C_{60}^- ion. The viscosity of the solvent is 0.93×10^{-3} kg m^{-1} s^{-1}. *Comment.* The researchers interpreted the substantial difference between this number and the van der Waals radius of neutral C_{60} in terms of a solvation layer around the ion.

Theoretical problems

21.23 Start from the Maxwell–Boltzmann distribution and derive an expression for the most probable speed of a gas of molecules at a temperature

T. Go on to demonstrate the validity of the equipartition conclusion that the average translational kinetic energy of molecules free to move in three dimensions is $\frac{3}{2}kT$.

21.24 Consider molecules that are confined to move in a plane (a two-dimensional gas). Calculate the distribution of speeds and determine the mean speed of the molecules at a temperature T.

21.25 A specially constructed velocity-selector accepts a beam of molecules from an oven at a temperature T but blocks the passage of molecules with a speed greater than the mean. What is the mean speed of the emerging beam, relative to the initial value, treated as a one-dimensional problem?

21.26 What is the proportion of gas molecules having (a) more than, (b) less than the root mean square speed? (c) What are the proportions having speeds greater and smaller than the mean speed?

21.27 Calculate the fractions of molecules in a gas that have a speed in a range Δv at the speed $nc^\star$ relative to those in the same range at $c^\star$ itself? This calculation can be used to estimate the fraction of very energetic molecules (which is important for reactions). Evaluate the ratio for $n = 3$ and $n = 4$.

21.28 Derive an expression that shows how the pressure of a gas inside an effusion oven (a heated chamber with a small hole in one wall) varies with time if the oven is not replenished as the gas escapes. Then show that $t_{1/2}$, the time required for the pressure to decrease to half its initial value, is independent of the initial pressure. *Hint.* Begin by setting up a differential equation relating dp/dt to $p = NkT/V$, and then integrating it.

21.29 Show how the ratio of two transport numbers t' and t'' for two cations in a mixture depends on their concentrations c' and c'' and their mobilities u' and u''.

21.30 Confirm that eqn 21.72 is a solution of the diffusion equation with the correct initial value.

21.31 The diffusion equation is valid when many elementary steps are taken in the time interval of interest, but the random walk calculation lets us discuss distributions for short times as well as for long. Use eqn 21.84 to calculate the probability of being six paces from the origin (that is, at $x = 6\lambda$) after (a) four, (b) six, (c) twelve steps.

21.32 Use mathematical software to calculate P in a one-dimensional random walk, and evaluate the probability of being at $x = n\lambda$ for $n = 6, 10, 14, \ldots, 60$. Compare the numerical value with the analytical value in the limit of a large number of steps. At what value of n is the discrepancy no more than 0.1 per cent?

21.33 Supply the intermediate mathematical steps in *Justification* 21.7.

21.34‡ A dilute solution of a weak (1,1)-electrolyte contains both neutral ion pairs and ions in equilibrium (AB ⇌ A$^+$ + B$^-$). Prove that molar conductivities are related to the degree of ionization by the equations:

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m(\alpha)} + \frac{(1-\alpha)\Lambda_m^\circ}{\alpha^2 \Lambda_m(\alpha)^2} \qquad \Lambda_m(\alpha) = \lambda_+ + \lambda_- = \Lambda_m^\circ - \mathcal{K}(\alpha c)^{1/2}$$

where Λ_m° is the molar conductivity at infinite dilution and $\mathcal{K}$ is the constant in Kohlrausch's law (eqn 21.29).

Applications: to astrophysics and biochemistry

21.35 Calculate the escape velocity (the minimum initial velocity that will take an object to infinity) from the surface of a planet of radius R. What is the value for (a) the Earth, $R = 6.37 \times 10^6$ m, $g = 9.81$ m s^{-2}, (b) Mars, $R = 3.38 \times 10^6$ m, $m_{Mars}/m_{Earth} = 0.108$. At what temperatures do H$_2$, He, and O$_2$ molecules have mean speeds equal to their escape speeds? What proportion of the molecules have enough speed to escape when the temperature is (a) 240 K, (b) 1500 K? Calculations of this kind are very important in considering the composition of planetary atmospheres.

21.36‡ Interstellar space is a medium quite different from the gaseous environments we commonly encounter on Earth. For instance, a typical density of the medium is about 1 atom cm^{-3} and that atom is typically H; the effective temperature due to stellar background radiation is about 10 000 K. Estimate the diffusion coefficient and thermal conductivity of H under these conditions. *Comment.* Energy is in fact transferred much more effectively by radiation.

21.37 The principal components of the atmosphere of the Earth are diatomic molecules, which can rotate as well as translate. Given that the translational kinetic energy density of the atmosphere is 0.15 J cm^{-3}, what is the total kinetic energy density, including rotation?

21.38‡ In the *standard model* of stellar structure (I. Nicholson, *The sun*. Rand McNally, New York (1982)), the interior of the Sun is thought to consist of 36 per cent H and 64 per cent He by mass, at a density of 158 g cm^{-3}. Both atoms are completely ionized. The approximate dimensions of the nuclei can be calculated from the formula $r_{\text{nucleus}} = 1.4 \times 10^{-15} A^{1/3}$ m, where A is the mass number. The size of the free electron, $r_e \approx 10^{-18}$ m, is negligible compared to the size of the nuclei. (a) Calculate the excluded volume in 1.0 cm^3 of the stellar interior and on that basis decide upon the applicability of the perfect gas law to this system. (b) The standard model suggests that the pressure in the stellar interior is 2.5×10^{11} atm. Calculate the temperature of the Sun's interior based on the perfect gas model. The generally accepted standard model value is 16 MK. (c) Would a van der Waals type of equation (with $a = 0$) give a better value for T?

21.39 Enrico Fermi, the great Italian scientist, was a master at making good approximate calculations based on little or no actual data. Hence, such calculations are often called 'Fermi calculations'. Do a Fermi calculation on how long it would take for a gaseous air-borne cold virus of molar mass 100 kg mol^{-1} to travel the distance between two conversing people 1.0 m a part by diffusion in still air.

21.40 The diffusion coefficient of a particular kind of t-RNA molecule is $D = 1.0 \times 10^{-11}$ m^2 s^{-1} in the medium of a cell interior. How long does it take molecules produced in the cell nucleus to reach the walls of the cell at a distance 1.0 μm, corresponding to the radius of the cell?

21.41‡ In this problem, we examine a model for the transport of oxygen from air in the lungs to blood. First, show that, for the initial and boundary conditions $c(x,t) = c(x,0) = c_0$, $(0 < x < \infty)$ and $c(0,t) = c_s$, $(0 \leq t \leq \infty)$ where c_0 and c_s are constants, the concentration, $c(x,t)$, of a species is given by

$$c(x,t) = c_0 + (c_s - c_0)\{1 - \text{erf}\,\xi\} \qquad \xi(x,t) = \frac{x}{(4Dt)^{1/2}}$$

where erf ξ is the error function (*Justification 9.4*) and the concentration $c(x,t)$ evolves by diffusion from the yz-plane of constant concentration, such as might occur if a condensed phase is absorbing a species from a gas phase. Now draw graphs of concentration profiles at several different times of your choice for the diffusion of oxygen into water at 298 K (when $D = 2.10 \times 10^{-9}$ m^2 s^{-1}) on a spatial scale comparable to passage of oxygen from lungs through alveoli into the blood. Use $c_0 = 0$ and set c_s equal to the solubility of oxygen in water. *Hint.* Use mathematical software.