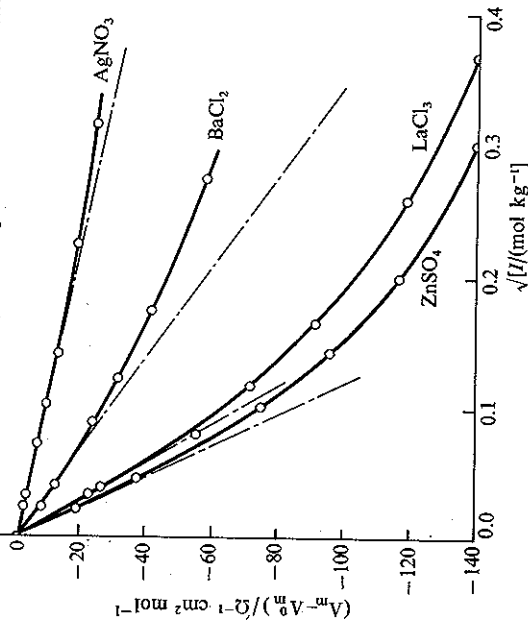


Fig. 26.8. Experimental and theoretical molar conductivity



• *Comment.* The result is not at all bad considering the theoretical difficulties of dealing with a dynamical system of this complexity. Note that the plot of Λ_m against \sqrt{c} is a useful way of making the extrapolation to find Λ_m^∞ .

Equation (26.1.18) has the same $c^{1/2}$ concentration-dependence as the empirical Kohlrausch expression, eqn (26.1.3). Furthermore, the slopes of the curves are predicted to depend on the valence type (z) appears in the constants A and B . Some comparisons between theory and experiment are shown in Fig. 26.8, and this shows how well the theory accounts for the observations at low concentrations.

The success of the Debye-Hückel-Onsager equation suggests that the model of ion-ion interactions is substantially correct. A further test is obtained by investigating what happens when the effect of the ionic atmosphere is eliminated. This can be done in a variety of ways. In one the conductivities are measured at very high frequencies; then the central ion is moved backwards and forwards very rapidly, and the retarding effects of the ionic atmosphere ought to average to zero. This is the *Debye-Falkenhagen effect*, and the predicted increase in mobility at high frequencies has been observed. The other way of eliminating the effect of the atmosphere is to move the ions so rapidly that no atmosphere has time to build up. The *Wien effect* is the observation of higher mobilities at very high electric fields. (There are two Wien effects. The *first Wien effect* is the one just described; the *second Wien effect* is the enhancement of the degree of ionization of an ionogen, or weak electrolyte, by the applied field.)

This model of the interactions fails when the concentration becomes large, because ions tend to stick together in pairs, and even triples. This can be seen quite clearly from X-ray analysis of ionic solution, where peaks of scattering can be interpreted in terms of definite ion-ion distances

26.2 Fundamental aspects of molecular transport

In this section we begin to draw together the threads of the discussion in this chapter and the last. We do so on the basis of thermodynamic and statistical principles and find that we can make a variety of important and useful connections between properties relating to the motion of molecules and ions in fluids.

Diffusion: the thermodynamic view. In Part 1 it was shown that the thermodynamic property that governs the direction of spontaneous change is the thermodynamic chemical potential (p. 182). When unit amount of solute is shifted from a region where its chemical potential is $\mu(1)$ to one where it is $\mu(2)$ the work required is $w = \mu(2) - \mu(1)$. Suppose the chemical potential depends on the position x in the system, then the work involved in transferring unit amount of material from x to $x + dx$ is

$$dw = \mu(x + dx) - \mu(x) = [\mu(x) + (d\mu/dx)dx] - \mu(x) = (d\mu/dx)dx.$$

(The derivatives ought strictly to be partial derivatives, and the transfer ought to be carried out under conditions of constant pressure and temperature—see p. 258 for details.) In classical mechanics the work required to shift an object through a distance dx against a force \mathcal{F} is

$$dw = -\mathcal{F} dx.$$

By comparing the last two equations we see that *the gradient of the chemical potential acts like a force*. We shall therefore write

$$\mathcal{F} = -(d\mu/dx). \quad (26.2.1)$$

There is no real force pushing molecules down the slope of chemical potential, for that is their natural drift as a consequence of the Second Law and the hunt for maximum entropy: nevertheless, thinking in terms of these phantom, effective, thermodynamic forces can be very useful, as we shall see.

In a solution where the concentration is c the chemical potential of an ideal solute is (p. 226).

$$\mu = \mu^\ominus + RT \ln(c/\text{mol dm}^{-3}). \quad (26.2.2)^\circ$$

If the concentration depends on position, the thermodynamic force acting is

$$\begin{aligned} \mathcal{F} &= -(d/dx)[\mu^\ominus + RT \ln(c/\text{mol dm}^{-3})] \\ &= -(RT/c)(dc/dx) \end{aligned} \quad (26.2.3)^\circ$$

because μ^\ominus is independent of position, and $d \ln f/dx = (1/f) df/dx$.

The form of the last equation lets us derive Fick's Law of Diffusion (that flux is proportional to the concentration gradient, eqn (25.3.1)) from a thermodynamic viewpoint. We suppose that the flux is the response of the molecules to some force. If the force per unit amount is \mathcal{F} , the force

flux of material, $J(\text{matter})$, is proportional to the impressed force, the $J(\text{matter}) \propto c\mathcal{F}$. But the effective force is given by eqn (26.2.3), and

$$J(\text{matter}) \propto -RT(dc/dx) = -kT(d\mathcal{N}/dx)$$

and we have the flux as proportional to the concentration gradient, in accord with Fick's Law (\mathcal{N} is the number density of molecules, $\mathcal{N} = \rho/\mu$).

It is more convenient to develop a different line of argument, and to interpret the flux of particles as the product $v\mathcal{N} = v c L$, where v is their average velocity and c their concentration. Then Fick's Law,

$$v\mathcal{N} = J = -D(d\mathcal{N}/dx) = -DL(dc/dx)$$

reads

$$cv = -D(dc/dx)$$

or, using eqn (26.2.3),

$$v = -(D/c)(dc/dx) = (D/kT)\mathcal{F}.$$

Therefore, in response to a unit force, the molecules diffuse with a drift velocity of magnitude D/kT . We know, however, that the mobility of an ion is related to the electrical force on it. Since the mobility is defined through $s = uE$, and since the electrical force is $e z E$, it follows that

$$s = uE = (u/ze)(ezE) = (u/ze)\mathcal{F},$$

and therefore the drift speed under the influence of unit force is (u/ze) . The nature of the force is irrelevant; therefore the two drift speeds $(D/kT)\mathcal{F}$ and $(u/ze)\mathcal{F}$ may be identified: then

$$u/ze = D/kT,$$

and so we arrive at the very important result, known as the

$$\text{Einstein relation: } D = ukT/ez$$

connecting the diffusion constant and the mobility.

The last relation can be developed further in two directions. In the first place it can be used to relate the molar conductivity to the diffusion constants of the ions, D_+ and D_- . We write (for 1:1 salts)

$$\Lambda_m = zF(u_+ + u_-) = (z^2 e^2 F/kT)(D_+ + D_-)$$

and so arrive at the

$$\text{Nernst-Einstein relation: } \Lambda_m = (z^2 F^2/RT)(D_+ + D_-) \quad (26.2.5)^\circ$$

One application of these expressions is to the determination of the ionic diffusion constants from conductivity measurements; the other is to the calculation of conductivities on the basis of models of ionic diffusion (see below).

the mobility to the viscosity. By combining the expressions

$$s = ezE/6\pi\eta a \quad \text{and} \quad s = uE,$$

the first being the expression for the drift speed defined in eqn (26.1.9), we are able to write

$$u = ez/6\pi\eta a.$$

Since the Einstein relation is $u = ezD/kT$, the two may be equated and combined into the

$$\text{Stokes-Einstein relation: } D = kT/6\pi\eta a$$

which connects the diffusion constant and the viscosity of liquids. An important feature of this result is that it is independent of the charge of the diffusing species, and therefore it also applies in the limit of vanishingly small charge, or neutral molecules. This means that we may use the Stokes-Einstein relation to estimate the diffusion constant from measurements of the viscosity. It must not be forgotten, however, that it is an approximation, being based on the assumption of the validity of the Stokes formula for the viscous drag. Some diffusion coefficients are listed in Table 26.4.

Table 26.4. Diffusion coefficients at 25°C, $D/10^{-9} \text{ m}^2 \text{ s}^{-1}$

I ₂ in hexane	4.05	H ₂ in CCl ₄	9.75
I ₂ in benzene	2.13	N ₂ in CCl ₄	3.42
CCl ₄ in n-heptane	3.17	O ₂ in CCl ₄	3.82
Glycine in water	1.055	Ar in CCl ₄	3.63
Dextrose in water	0.673	CH ₄ in CCl ₄	2.89
Sucrose in water	0.521	Water in water	2.26
		Methanol in water	1.58
		Ethanol in water	1.24
Ions in water:			
H ⁺	9.31	OH ⁻	5.30
Li ⁺	1.03	F ⁻	1.46
Na ⁺	1.33	Cl ⁻	2.03
K ⁺	1.96	Br ⁻	2.08
		I ⁻	2.05

Source: *American Institute of Physics Handbook*, McGraw-Hill, and (for the ions) eqn (26.2.4) and Table 26.2.

Example (Objective 12, 13, 14). Find the diffusion coefficient, the molar conductivity, and the effective hydrodynamic radius of the SO₄²⁻ ion in water at 25°C.

• *Method.* In Table 26.2 the mobility of the ion is given as $8.29 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$. Relate this to D through eqn (26.2.4). Then use eqn (26.2.5) to relate D (now written D_-) to λ_- (the anion contribution to Λ_m). Calculate the effective radius a_- from

$$\begin{aligned}
 &= \frac{(8.29 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}) \times (1.3807 \times 10^{-23} \text{ J K}^{-1}) \times (298.15 \text{ K})}{2 \times (1.6022 \times 10^{-19} \text{ C})} \\
 &= 1.065 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}
 \end{aligned}$$

From eqn (26.2.5),

$$\lambda_- = \frac{(9.6485 \times 10^4 \text{ C mol}^{-1})^2 \times (1.065 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1})}{(8.3144 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})}$$

$$= 160.0 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

From eqn (26.2.6),

$$a_- = \frac{kT}{6\pi\eta D_-} = \frac{(1.3807 \times 10^{-23} \text{ J K}^{-1}) \times (298.15 \text{ K})}{6\pi \times (1.00 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}) \times (1.065 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1})}$$

$$= 2.051 \times 10^{-10} \text{ m} \text{ or } 205 \text{ pm} \text{ or } 2.05 \text{ \AA}$$

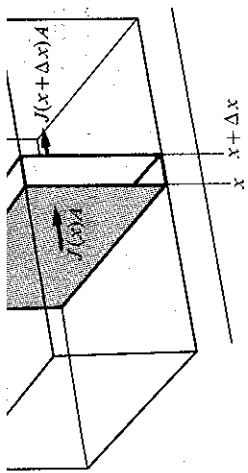
• *Comment.* The bond length in SO_4^{2-} is 144 pm, and so the radius calculated here (the radius of a sphere representing the molecule) is plausible and compatible with only a small degree of solvation.

Some experimental support for these ideas comes from conductivity measurements, because the empirical *Walden's rule* is that the product $\Lambda_m^0 \eta$ should be approximately constant for the same ions in different solvents. Since $\Lambda_m^0 \propto u$, and $u \propto 1/\eta$, we can see the theoretical basis of this rule. Its applicability is muddled by the role of solvation: different solvents solvate ions to different extents, and so the ions' effective hydrodynamic radii depend on their nature: both a and η vary with the solvent.

Diffusion as a time-dependent process. We turn now to the discussion of time-dependent diffusion processes, in which some distribution of concentration, or of temperature, etc., is established at some moment, and then allowed to disperse without replenishment. One example is a metal bar heated rapidly at one end and then allowed to reach equilibrium, and another is when a layer of solute is spread on the surface of a solvent and the concentration distribution in the solution changes as it dissolves.

In order to treat a time-dependent diffusion process we shall concentrate on the diffusion of matter, but the arguments are easily modified to apply to other properties. We fix our attention on a small slab of the system extending from x to $x + \Delta x$, and of cross-sectional area A , Fig. 26.9. Let the concentration at x be $\mathcal{N}(x, t)$ at the time t , then the increase in concentration inside the slab (of volume $A\Delta x$) by virtue of the flux from the left is

$$\partial \mathcal{N}(x, t) / \partial t = J(x, t) A / A\Delta x = J(x, t) / \Delta x$$



because JA is the number of particles that enter through a window of area A in each unit time interval. There is also a flow out of the right-hand window; if the flux is $J(x + \Delta x)$ the concentration inside the slab changes due to this efflux with a rate

$$\partial \mathcal{N}(x, t) / \partial t = -J(x + \Delta x, t) A / A\Delta x = -J(x + \Delta x, t) / \Delta x,$$

the negative sign appearing because the concentration in the slab decreases when the flow is to the right (J positive). Therefore the total rate of change of concentration is

$$\partial \mathcal{N}(x, t) / \partial t = J(x, t) / \Delta x - J(x + \Delta x, t) / \Delta x.$$

The fluxes can now be related to the concentration gradients at each window. Using Fick's Law we can write

$$\begin{aligned}
 J(x, t) - J(x + \Delta x, t) &= \{-D[\partial \mathcal{N}(x, t) / \partial x]\} - \{-D[\partial \mathcal{N}(x + \Delta x, t) / \partial x]\} \\
 &= -D \left(\frac{\partial \mathcal{N}(x, t)}{\partial x} \right) + D \frac{\partial}{\partial x} \left[\mathcal{N}(x, t) + \left(\frac{\partial \mathcal{N}(x, t)}{\partial x} \right) \Delta x \right] \\
 &= D(\partial^2 \mathcal{N}(x, t) / \partial x^2) \Delta x.
 \end{aligned}$$

Substituting this back into the expression for the rate of change of the concentration in the slab leads to the

$$\text{diffusion equation: } (\partial \mathcal{N}(x, t) / \partial t) = D(\partial^2 \mathcal{N}(x, t) / \partial x^2) \quad (26.2.7)$$

This is also sometimes called *Fick's Second Law*.

First, a word about the general form of this equation. We see that the rate of change of the concentration is proportional to the curvature (the second-derivative) of the concentration dependence on the distance. If the concentration changes rapidly from point to point the rate at which the concentration changes with time is correspondingly rapid. If the curvature is zero, the concentration does not change with time. For example, if the concentration falls linearly with distance, the concentration at any point remains constant because the inflow of concentration is balanced by the outflow. The diffusion equation can be regarded as a mathematical

eqn (26.2.6). The viscosity of water at 25°C is 1.00 cp ($1.00 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$). Remember that $J = C V$ and $V A^{-1} = \Omega$.

• Answer. From eqn (26.2.4),

$$D_- = u_- kT / ez = \frac{(8.29 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}) \times (1.3807 \times 10^{-23} \text{ J K}^{-1}) \times (298.15 \text{ K})}{2 \times (1.6022 \times 10^{-19} \text{ C})} = 1.065 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}.$$

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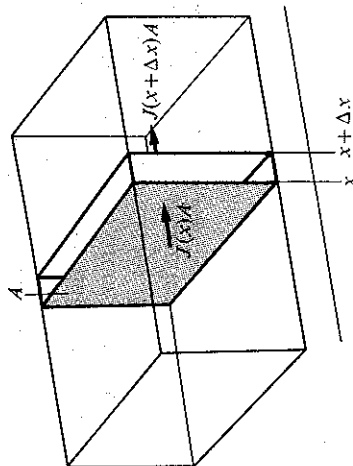
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$$\partial \mathcal{N}(x, t) / \partial t = J(x, t) A / A\Delta x = J(x, t) / \Delta x$$

Fig. 26.9. The diffusion of material into a region.



because JA is the number of particles that enter through a window of area A in each unit time interval. There is also a flow out of the right-hand window; if the flux is $J(x + \Delta x)$ the concentration inside the slab changes due to this efflux with a rate

$$\partial \mathcal{N}(x, t) / \partial t = -J(x + \Delta x, t) A / A\Delta x = -J(x + \Delta x, t) / \Delta x,$$

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Substituting this back into the expression for the rate of change of the concentration in the slab leads to the

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eliminate the wrinkles in a distribution.

The diffusion equation is a second-order differential equation in space and first-order in time, and therefore in order to arrive at a solution we have to specify two boundary conditions for the spatial dependence and a single initial condition for the time dependence. This can be illustrated by the specific example of a solvent in which the solute is coated on one surface. At time zero the initial condition is that all the N_0 solute particles are concentrated on the yz -plane at $x = 0$. The boundary conditions are that the concentration must be everywhere finite, and the total number present must be N_0 at all times. The solution of the diffusion equation having these as conditions is

$$\mathcal{N}(x, t) = \{N_0/A(\pi Dt)^{1/2}\} \exp(-x^2/4Dt) \quad (26.2.8)$$

as may be verified by direct substitution. The form of the result at different times is shown in Fig. 26.10, and it is clear that the concentration of particles spreads through the material as time advances. The use of the diffusion equation is that, with its aid, the concentration can be predicted at any point in the system at any time.

A number of important features of the diffusion process can be explained on the basis of the diffusion equation, and in particular with the help of the simple solution just quoted. For example, we can ask what is the *mean distance* through which the solute has spread after a time t . The number of molecules in the slab of thickness dx at x is $\mathcal{N}(x, t)A dx$, and so the probability that any of the N_0 molecules is there is $\mathcal{N}(x, t)A dx/N_0$. If the molecule is there it has travelled a distance x from the origin; therefore the mean distance travelled is

$$\begin{aligned} \langle x \rangle &= \int_0^\infty x \mathcal{N}(x, t) A dx / N_0 = (1/\pi Dt)^{1/2} \int_0^\infty x e^{-x^2/4Dt} dx \\ &= 2(Dt/\pi)^{1/2}. \end{aligned} \quad (26.2.9)$$

The average distance varies as the *square root* of the time lapse. This is an important general result which we shall return to later. If we use the Stokes-Einstein relation for the diffusion constant the mean distance covered in a solvent of viscosity η by particles of radius a is

$$\langle x \rangle = (2kT/3\pi^2\eta a)^{1/2} \sqrt{t}. \quad (26.2.10)$$

The *root mean square distance* covered is $\bar{x} = \sqrt{\langle x^2 \rangle}$, and its value is

$$\bar{x} = \sqrt{\langle x^2 \rangle} = \sqrt{\int_0^\infty x^2 \mathcal{N}(x, t) A dx} / N_0 = (2Dt)^{1/2}. \quad (26.2.11)$$

This is a valuable measure of the spread of the particles when they are allowed to migrate in both directions (for then $\langle x \rangle = 0$). The value of \bar{x} for molecules having $D = 5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ is shown in Fig. 26.11: you can see how long it takes for diffusion to increase \bar{x} to about 1 cm in an unstirred solution. The *proportion* of particles which remain within a distance \bar{x} of

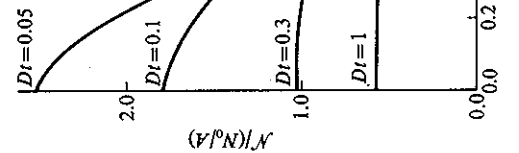


Fig. 26.10. Diffusion of a solute from a plane surface.

the origin is a useful number to have, because the mean might not convey enough information. Since the number in the slab at x is $\mathcal{N}(x, t)A dx$, the number in all the slabs up to the one at \bar{x} is the sum (integral)

$$N(x \leq \bar{x}, t) = \int_0^{\bar{x}} \mathcal{N}(x, t) A dx = (0.68 \dots) (N_0/A),$$

where \bar{x} has been replaced by $(2Dt)^{1/2}$, and the integral evaluated numerically.* It follows that the proportion of molecules inside the range $0 \leq x \leq \bar{x}$ is 0.68. Therefore, over two-thirds of the molecules are still clustered around the origin, and only 32 per cent have escaped beyond \bar{x} (but do not forget that the value of \bar{x} grows with time).

The diffusion equation can be solved for more complicated arrangements, for example, when ions are continuously generated at a plane electrode dipped in the solution, or when ions are deposited on an electrode and withdrawn from the solution. Calculations like these play an important part in the discussion of rates of reactions at electrodes (Chapter 30).

Diffusion: the statistical view. An intuitive picture of the mechanism of diffusion is one in which particles move in a series of small steps, and gradually migrate away from their original position. We shall build a model of diffusion on the basis that the particles can jump through a distance d , and do so in a time τ . This means that the distance covered by a molecule in a time t is $(t/\tau)d$. This does *not* mean that the particle will be found at

* The integral can be simplified by substituting $y = x/(2Dt)^{1/2}$, for then it becomes

$$N(x \leq \bar{x}, t) = \{N_0/A(\pi Dt)^{1/2}\} \int_0^{\bar{x}} dx e^{-x^2/4Dt} = (N_0/A)(2/\pi^{1/2}) \int_0^{1/2} e^{-y^2} dy.$$

It happens that the integral $(2/\pi^{1/2}) \int_0^y e^{-y^2} dy$ is a standard mathematical form known as the *error function*, and written $\text{erf } z$. Standard tables of these are available, Table 25.1, and the value of $\text{erf}(1/2)^{1/2}$, which is what we require, is 0.68.

LLLL LLRL LLRR LRLR LRRR RRRR
 LLRL LRLR RLRL
 LRLL LRRR RRLR
 RLLL RLLR RRLL
 RLRL
 RRLR

and clearly there are 6 ways of taking 2 steps to the right and 2 to the left, which tallies with the expression $4!/2!2! = 6$. The probability that the particle is at the origin after 4 steps is therefore $6/16$. The probability that it is at $x = 4d$ is $1/16$ because, in order to be there, all four steps must be towards the right, and there is only one way of organizing that.

Returning now to the general case we see that the probability of being at x after n steps, each of length d , is

$$P(x) = n! / n_R!(n - n_R)! 2^n,$$

with $n = n_R + n_L$ and $x/d = n_R - n_L$. Since

$$n_R = \frac{1}{2}(n + x/d), \quad n - n_R = \frac{1}{2}(n - x/d),$$

it follows that

$$P(x) = n! / \left\{ \left[\frac{1}{2}(n + s) \right]! \left[\frac{1}{2}(n - s) \right]! 2^n \right\}, \quad (26.2.12)$$

where $s = x/d$.

This expression does not seem to resemble the Gaussian distribution of probability, such as eqn (26.2.8), and so it looks as though the model of a random walk underlying a diffusion process is quite wrong. This, however, is not the case: the last equation becomes *identical* to the Gaussian distribution when we examine the limit in which the number of steps becomes very large.

The algebraic manipulation of this equation is based on the approximate formula for factorials of large numbers first used in Chapter 20 (p. 668). When N is a large number it is possible to use *Stirling's approximation*:

$$\ln N! \approx (N + \frac{1}{2}) \ln N - N + \ln(2\pi)^{1/2}. \quad (26.2.13)$$

This is a more accurate form of the approximation than the one used earlier. Even when N is quite small this expression is quite good. For example, instead of $10! = 3.629 \times 10^6$ it gives $10! \approx 3.60 \times 10^6$, when larger numbers are involved we can be very confident indeed about the results it gives. Taking logarithms of eqn (26.2.12), and then allowing n to be large, leads (after quite a lot of algebra) first from

$$\ln P = \ln n! - \ln \left[\left(\frac{1}{2}(n + s) \right)! \right] - \ln \left[\left(\frac{1}{2}(n - s) \right)! \right] - n \ln 2$$

to

$$\ln P \approx \ln(2/\pi n)^{1/2} - \frac{1}{2}(n + s + 1) \ln(1 + s/n) - \frac{1}{2}(n - s + 1) \ln(1 - s/n).$$

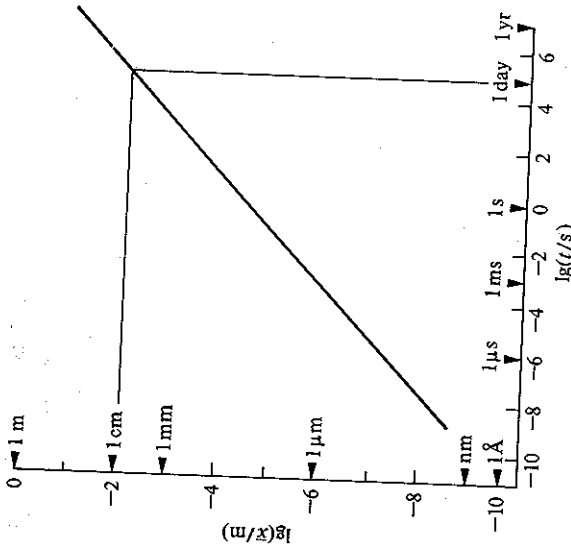


Fig. 26.11. Root mean square distance covered by particles with $D = 5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

that distance from the origin. The direction of the steps is different on each occasion and so the net distance of diffusion must take this into account. We shall simplify the discussion by allowing the particle to move only along a straight line, the x -coordinate, but we must not forget that in a real system a particle is free to move in three dimensions. We shall also confine our attention to a model in which the particle can jump with equal probability through a distance d to the right or d to the left. This is called the *one-dimensional random walk*; we first met it in Chapter 24.

Our task is to find the probability that a molecule will be found at a distance x from the origin at a time t . During that time interval it will have taken t/τ steps: we shall write $n = t/\tau$. Many of these steps were steps to the right; many were steps to the left. If n_R is the number of steps to the right and n_L the number to the left, not only can we write the total number of steps as $n = n_R + n_L$, but we can also write the net distance travelled as $x = n_R d - n_L d$.

The probability of being at x after n steps of length d is the probability that of the n steps, n_R occurred to the right, n_L occurred to the left, and $n_R - n_L = x/d$.

What is the *total number of possibilities* for left or right steps? Since each step may occur in either of two directions (left or right) the total number of possibilities is 2^n .

How many ways are there of taking n_R of the n steps to the right? This is the same as the number of ways of choosing n_R objects from n possibilities, irrespective of the order: this is $n! / n_R!(n - n_R)!$. We can check this in the case of 4 steps, and ask what is the number of ways of taking 2 right steps. There are 2^4 possible step sequences:

If we allow s/n to be a small number (so that x must not be a great distance from the origin) we can use the approximation $\ln(1+y) \approx y$, and obtain

$$\ln P \approx \ln(2/\pi n)^{1/2} - s^2/2n,$$

or

$$P \approx (2/\pi n)^{1/2} \exp(-s^2/2n),$$

which is already of a Gaussian form.

Now replace s by x/d and n by t/τ . We obtain

$$P(x, t) = (2\tau/\pi t)^{1/2} \exp(-x^2\tau/2td^2), \quad (26.2.14)$$

and this has precisely the form of $\mathcal{N}(x, t)/N_0$ given in eqn (26.2.8) as a solution of the diffusion equation. (The differences of detail arise from allowing the particle to migrate in both directions away from $x = 0$, and letting it be found only at discrete points separated by d instead of being anywhere on a continuous line.) Therefore we can be confident that the diffusion can be interpreted as the result of a very large number of small steps in random directions. This also indicates the region of invalidity of the diffusion equation: we should not expect it to apply at times so short that the particles have had time to take only a few steps.

Finally we can make use of the identity of form of the two distributions to obtain yet another expression for D . Comparison of the two exponents leads to the identification

$$2d^2/\tau = 4D,$$

and therefore we come to the

$$\text{Einstein-Smoluchowski relation: } D = \frac{1}{2}d^2/\tau. \quad (26.2.15)$$

Example (Objective 17). Suppose that the SO_4^{2-} ion jumps through about its own diameter every time it makes a move in aqueous solution. How often does it change position?

• *Method.* The diffusion coefficient was found in the last Example to be $1.065 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, and the effective radius was found there to be 205 pm. Find τ from eqn (26.2.15).

• *Answer.* From eqn (26.2.15),

$$\tau = d^2/2D \\ = (2 \times 205 \times 10^{-12} \text{ m})^2 / 2 \times (1.065 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}) = 7.89 \times 10^{-11} \text{ s}.$$

• *Comment.* The big, heavy SO_4^{2-} ion jumps through its diameter in about 8×10^{-11} s. If the ion were imagined as jumping through a distance equal to the diameter of a water molecule (≈ 150 pm) the jump time would be about 1.1×10^{-11} s.

The Einstein-Smoluchowski relation is a central connection between the microscopic properties of the size (d) and rate ($1/\tau$) of a molecular

jump and the macroscopic properties of diffusion constant and viscosity (via the Stokes-Einstein relation eqn (26.2.6)). This also brings the discussion full circle and back to the properties of gases. For if d/τ is interpreted as a mean velocity of the molecules undergoing diffusion, and the jump length d is called a mean free path and written λ , the Einstein-Smoluchowski equation reduces to $D = \frac{1}{2}\lambda\bar{c}$, which is the same as that obtained for the diffusion constant from the kinetic theory of gases. This shows that the diffusion of a perfect gas can also be interpreted as a random walk through an average path length λ .

Summary of the general conclusions. The chapter began by examining various aspects of the motion of ions in solution. We saw that the conductivity could be expressed in terms of the mobility of the ions. We also saw that any species could be regarded as moving under the influence of an effective force \mathcal{F} if its chemical potential varied from place to place, and we identified \mathcal{F} with $-d\mu/dx$, eqn (26.2.1). The thermodynamic force led to the construction of *Fick's First Law of Diffusion*. We saw on quite general arguments, that if the particle was subjected to a unit force, it acquired a drift speed D/kT . This led to the *Einstein relation* between D and the mobility, eqn (26.2.4), and the *Nernst-Einstein relation*, eqn (26.2.5), between conductivity and D , see Box 26.1. Incorporation of the Stokes frictional force into the argument led to the *Stokes-Einstein relation*, eqn (26.2.6), between D and the viscosity, valid for molecules of any charge (including zero). We next set up equations for dealing with time-dependent diffusional processes, and derived the basic *diffusion equation*, eqn (26.2.7). The solutions of this equation could be reproduced, we found, if we modelled the diffusion process as a series of small steps of length d occurring with a frequency

Box 26.1

Transport properties in solution

Einstein-Smoluchowski relation between jump size d and jump time τ .

$$D = d^2/2\tau.$$

Stokes-Einstein relation between diffusion coefficient D and solution viscosity η .

$$D = kT/6\pi\eta a.$$

Einstein relation between diffusion coefficient and ion mobility u_{\pm} .

$$D_{\pm} = u_{\pm} kT/ez = u_{\pm} RT/zeF.$$

Nernst-Einstein relation between diffusion coefficient and ion conductivity λ_{\pm} .

$$\lambda_{\pm} = (z^2 F^2 / RT) D_{\pm}.$$

$1/\tau$; the solutions became the same when $\frac{1}{2}d^2/\tau$ was identified with the diffusion constant D ; this is the *Einstein-Smoluchowski relation* (26.2.15). With this connection established we can interpret viscosity, ion mobility, conductivity, and diffusion processes in general in terms of microscopic, dynamical parameters d and τ .

Appendix: the measurement of transport numbers

The following are brief summaries of the three methods used to measure transport numbers of ions and, through them, individual ion conductivities and mobilities.

(1) *Moving boundary method.* Let MX be the salt of interest. Pour the solution of MX into the lower half of a narrow vertical tube. Select a salt NX where N is less mobile than M; prepare a solution of NX, and pour it on top of the MX solution so that there is a clear boundary. Pass a current I for a time t . The X^- move towards the anode (downwards) and the M^+ and N^+ move towards the cathode (upwards). The amount of cations transported for this amount (It/F) of electricity is $t_+(It/z_+F)$, their charge being z_+ . If they are at a concentration c , the volume swept out is $t_+(It/z_+cF)$. But if the cross-section of the tube is S , and the distance moved by the boundary is x , the volume is also equal to xS . Therefore $t_+(It/z_+cF) = xS$, and monitoring the progress of the boundary for a series of times gives t_+ .

Example (Objective 7). The transport numbers of H^+ and SO_4^{2-} were measured in a moving boundary experiment. The apparatus consisted of a tube of bore 6.40 mm containing aqueous sulphuric acid at a concentration of $0.015 \text{ mol dm}^{-3}$. A steady current of 1.23 mA was passed, and the boundary advanced as follows:

t/s	40	80	120	160	200
x/mm	0.860	1.722	2.586	3.450	4.309

Find t_+ and t_- .

• *Method.* Use the equations set out above.

$$\begin{aligned} \bullet \text{ Answer. } t_+ &= (ScF/I)(x/t) \\ &= \pi \times (3.20 \times 10^{-3} \text{ m})^2 \times (0.015 \text{ mol dm}^{-3}) \times (9.6485 \times 10^4 \text{ C mol}^{-1}) \\ &\quad \times (1/1.23 \times 10^{-3} \text{ A}) \times (x/t) \\ &= 3.785 \times 10^4 \text{ m}^{-1} \text{ s } (x/t) = 37.85 [(x/\text{mm})/(t/s)]. \end{aligned}$$

Draw up the following table:

t/s	40	80	120	160	200
$10^4(x/\text{mm})/(t/s)$	215	215.3	215.5	215.6	215.5

Average: $0.02154 \text{ mm s}^{-1}$. Therefore $t_+(H^+) = 0.815$; and so $t_-(SO_4^{2-}) = 1 - 0.815 = 0.185$.

• *Comment.* These results can be used to recover the mobilities and the individual ionic conductivities, and are the basis of the data in the last *Example*.

(2) *The Hittorf method.* A cell is divided into three compartments and

an amount It of electricity is passed. An amount It/z_+F of cations are discharged at the cathode, but an amount $t_+(It/z_+F)$ of cations move into the cathode region. The net change in the amount of cations near the cathode is $-(It/z_+F) + t_+(It/z_+F) = -(1-t_+)(It/z_+F)$. Therefore, measuring the change in composition in the cathode compartment gives t_+ , the anion transport number. Likewise, the change in composition of anions at the anode is $-t_+(It/z_+F)$.

(3) *E.m.f. measurements.* The e.m.f. of a cell with transference having an electrode reversible with respect to anions is related to the e.m.f. of the cell with the same net reaction but without transference by $E_1 = 2t_+E$ (the argument is similar to that used for the Hittorf method). Therefore set up two cells and compare their e.m.f.s.

Further reading

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Problems

26.1. 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 $7.6 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$ at 25°C and the conductivity of 0.1 mol dm^{-3} aqueous KCl is $1.1639 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1}$. A cell had a resistance of 33.21Ω when filled with 0.1 mol dm^{-3} KCl solution and 300Ω when filled with 0.1 mol dm^{-3} acetic acid. What is the molar conductivity of acetic acid at that concentration and temperature?

26.2. In conductivity measurements it is common to write $\kappa = C/R$, where R is the measured resistance of the sample in the cell and C , the cell constant, is a characteristic of the particular cell in use. Since $\kappa = l/RA$ we see that $C = l/A$. Both l and A may be difficult to determine directly, and so it is normal to calibrate the cell with a sample of known conductivity. In several of the Problems that follow we shall refer to 'the cell'. We shall always mean the cell of this Problem,