7

Diffusion

- What is steady-state diffusion?
- How does one obtain a quick estimate of the distance moved by diffusing atoms?
- How does the energy barrier for ionic diffusion change when an electric field is present?

Diffusion originally described the way in which heat (believed to be a fluid) flowed through a solid. Later the same ideas were applied to describe the way in which a gas would spread out to fill the available volume. In solids, diffusion is the transport of atoms, ions or molecules under the influence of a driving force that is usually a concentration gradient. Diffusion takes place in solids at a much slower rate than in gases or liquids and, in the main, it is a high-temperature process. However, this is not always so, and in some solids the rate of diffusion at room temperature is considerable.

Movement through the body of a solid is called volume, lattice or bulk diffusion. In a gas or liquid, the diffusion is usually the same in all directions and the material is described as isotropic. This is also true in amorphous or glassy solids and in cubic crystals. In all other crystals, the rate of diffusion depends on the direction taken, and is anisotropic. Moreover, atoms can also diffuse along surfaces, between crystallites or along dislocations. As the regular crystal geometry is disrupted in these regions, atom movement is often much faster than for volume diffusion. Diffusion by way of these pathways is often collectively referred to as short-circuit diffusion. In the following sections, volume diffusion along a single direction in an isotropic medium will be described.

Diffusion is studied by measuring the concentration of the atoms at different distances from the release point after a given time has elapsed. Raw experimental data thus consist of concentration and distance values. The speed at which atoms or ions move through a solid is usually expressed in terms of a diffusion coefficient, D, with units of $m^2\ s^{-1}$. In general, it has been found that D depends on position and concentration, and hence D varies throughout the solid. In this chapter, attention is confined to diffusion when the concentration of the diffusing species is very small, so that concentration effects are not important, or where the diffusion coefficient does not depend on concentration or position. This is equivalent to stipulating that the diffusion coefficient is a constant.

7.1 Self-diffusion, tracer diffusion and tracer impurity diffusion

When atoms in a pure crystal diffuse under no concentration gradient or other driving force, the process is called self-diffusion. In such a case, the

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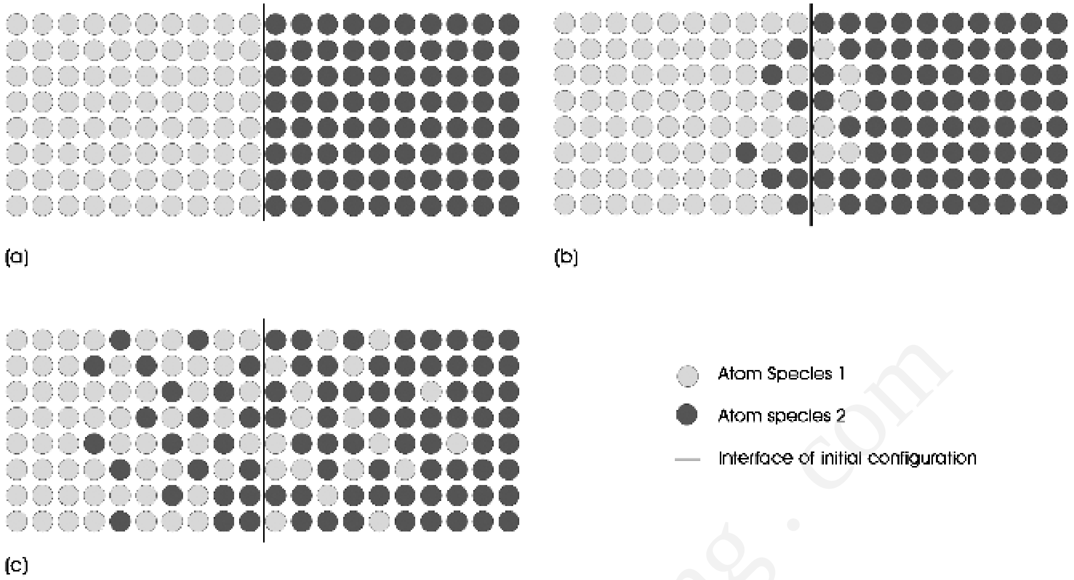

Figure 7.1 The diffusion of atoms: (a) initial configuration; (b) configuration after heating for shorter times; (c) configuration after heating for longer times; the interface becomes blurred as a result of interdiffusion of the two atom species

atomic movements are random, with motion in one direction just as likely as in another (Figure 7.1). The relevant diffusion coefficient is called the self-diffusion coefficient and is given the symbol D_{self}.

It is by no means easy to measure the self-diffusion coefficient of an atom because it is not possible to keep track of the movements of one atom in a crystal composed of many identical atoms. However, it is possible to measure something that is a very good approximation to the self-diffusion coefficient if some of the atoms can be uniquely labelled and their movement tracked. In this case, the diffusion coefficient that is measured is called the tracer diffusion coefficient, written D^*.

The experiment can be repeated with impurity tracer atoms, A, to yield the tracer impurity diffusion coefficient, D^*_{A}.

To illustrate this, consider the determination of the tracer diffusion coefficient of magnesium atoms in magnesium oxide, MgO, which crystallises with the *halite* (NaCl) structure. Initially, a thin layer of radioactive magnesium, which consists of the tracer atoms, is evaporated onto the surface of a carefully polished single crystal of MgO. This layer is oxidised to MgO by exposing the layers to oxygen gas, after which another carefully polished single-crystal slice of MgO is placed on top to form a diffusion couple (Figure 7.2).

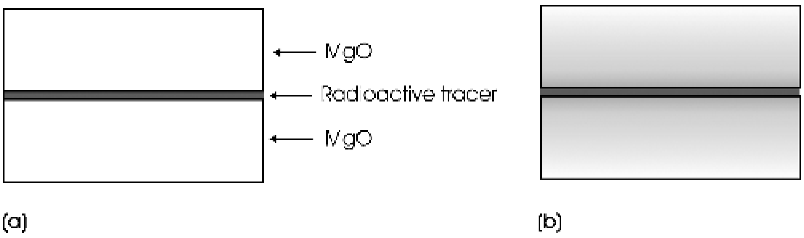

Figure 7.2 A diffusion couple formed by two crystals of MgO separated by radioactive material: (a) initially and (b) after heating

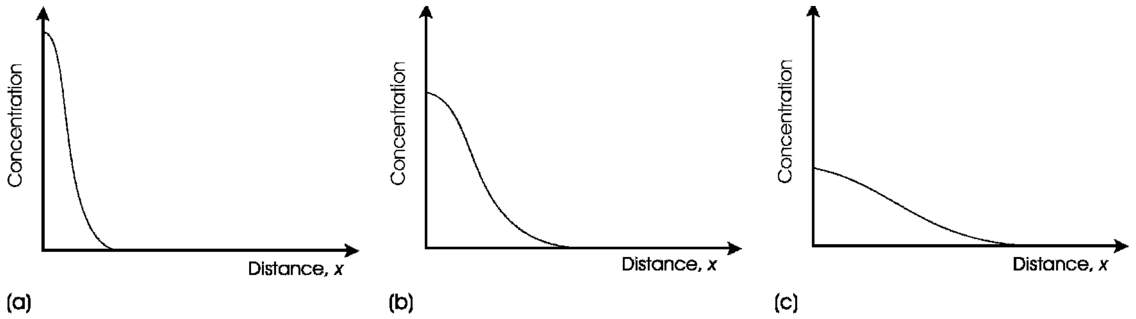

Figure 7.3 Diffusion profiles at gradually increased heating times, t_i: (a) t_1, (b) t_2 and (c) t_3, where $t_1 < t_2 < t_3$

The crystal sandwich is heated for a known time at the temperature for which the diffusion coefficient is required. The whole slab is then carefully sliced parallel to the original interface containing the radioactive MgO layer and the radioactivity of each slice, which is a measure of the concentration of radioactive magnesium in each section, is determined. A graph of the concentration of the radioactive component is then plotted against the distance from the interface to give a diffusion profile, or concentration profile (Figure 7.3). Note that the concentration of the tracer at any point, x, changes over time.

In order to obtain the diffusion coefficient from such profiles, we need to use the diffusion equation, also called Fick's second law:

$$\frac{\mathrm{d}c_x}{\mathrm{d}t} = D^* \frac{\mathrm{d}^2 c_x}{\mathrm{d}x^2} \tag{7.1}$$

where c_x is the concentration of the diffusing radioactive ions (atoms m^{-3}) at a distance x from the original interface after time t has elapsed, and D^* is the tracer diffusion coefficient. When D^* is a constant, and does not depend on either concentration or position, the equation can be solved analytically to give an expression for c_x in terms of x. For the experimental arrangement in Figure 7.2, the solution is:

$$c_x = \frac{c_0}{2(\pi D^* t)^{1/2}} \exp\left(\frac{-x^2}{4D^* t}\right) \tag{7.2}$$

where c_0 is the initial concentration on the surface, usually measured in mol m^{-2}. A value for the tracer diffusion coefficient is obtained by taking logarithms of both sides of this equation, to give:

$$\ln c_x = \ln\left[\frac{c_0}{2(\pi D^* t)^{1/2}}\right] - \frac{x^2}{4D^* t} \tag{7.3}$$

This has the form:

$$\ln c_x = \text{constant} - \frac{x^2}{4D^* t}$$

and a plot of $\ln c_x$ versus x^2 will have a gradient of $[-1/(4D^* t)]$ (Figure 7.4). A measurement of the gradient gives a value for the tracer diffusion

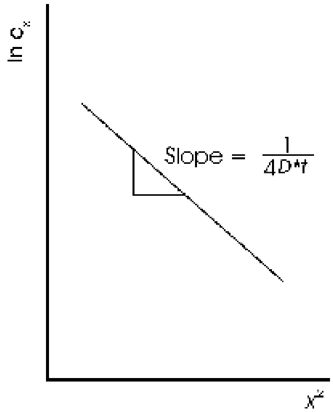

Figure 7.4 A straight-line graph of $\ln c_x$ versus x^2 from a diffusion experiment; the slope of the graph allows a value for the diffusion coefficient, D^*, to be determined

coefficient at the temperature at which the diffusion couple was heated. To obtain the diffusion coefficient over a variety of temperatures the experiments must be repeated.

In this experiment, there is a concentration gradient, because the concentration of the radioactive isotopes in the coating will be different from the concentration of radioactive isotopes, if any, in the original crystal pieces. This is why the term ‘tracer diffusion coefficient’ is used. However, if the layer of tracer atoms is very thin, the concentration gradient will be small and will rapidly become smaller as diffusion takes place and, in these circumstances, D^*, the tracer diffusion coefficient, will be very similar to the self-diffusion coefficient, D_{self}.

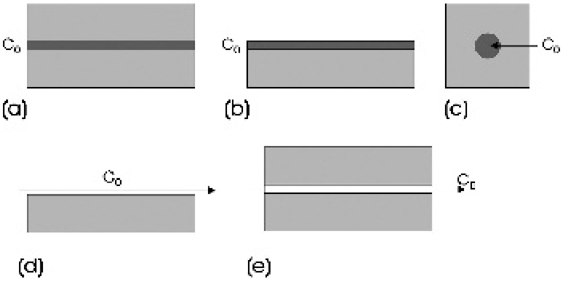

Figure 7.5 Common geometries for nonsteady-state diffusion: (a) thin-film planar sandwich; (b) open planar thin film; (c) small spherical precipitate; (d) open plate; and (e) sandwich plate. In parts (a)–(c) the concentration of the diffusant is unreplenished; in parts (d) and (e) the concentration of diffusant is maintained at a constant value, c_0, by gas or liquid flow

7.2 Nonsteady-state diffusion

The normal state of affairs during a diffusion experiment is one in which the concentration at any point in the solid changes over time, as in the example of tracer diffusion described in Section 7.1. This situation is called nonsteady-state diffusion, and diffusion coefficients are found by solving the diffusion equation. Provided the diffusion coefficient, D, is not dependent on composition and position, analytical solutions can be found. Solutions for some diffusion experiment geometries, sketched in Figure 7.5, are summarised in Table 7.1.

The solution given as Equation (7.2), relevant to the sandwich arrangement described in Section 7.1, is illustrated in Figure 7.5(a). The solution to the

Table 7.1 Solutions of the diffusion equation

Experimental arrangement	Solution
Initial concentration c_0:	
Thin-film planar sandwich	$c_x = \dfrac{c_0}{2(\pi D t)^{1/2}} \exp\left(\dfrac{-x^2}{4Dt}\right)$
Open planar thin film	$c_x = \dfrac{c_0}{(\pi D t)^{1/2}} \exp\left(\dfrac{-x^2}{4Dt}\right)$
Small spherical precipitate	$c_r = \dfrac{c_0}{8(\pi D t)^{3/2}} \exp\left(\dfrac{-r^2}{4Dt}\right)$
Initial concentration, c_0, maintained constant:	
Open plate	$\dfrac{c_x - c_0}{c_s - c_0} = 1 - \operatorname{erf}\left[\dfrac{x}{2(Dt)^{1/2}}\right]$
Sandwich plate	$\dfrac{c_x - c_0}{c_s - c_0} = \frac{1}{2}\left\{1 - \operatorname{erf}\left[\dfrac{x}{2(Dt)^{1/2}}\right]\right\}$

Note: the geometries are shown in Figure 7.5; c_x and c_r, concentration of diffusing species at distance x or r (radial distance); D, diffusion coefficient; t, time; c_s, concentration of diffusing species at the surface diffusion equation for the experimental situation in which the coated surface is uncovered (Figure 7.5b), is:

$$c_x = \frac{c_0}{(\pi D t)^{1/2}} \exp\left(\frac{-x^2}{4 D t}\right)$$

where c_x is the concentration of the diffusing species at a distance of x from the original surface after time t has elapsed, D is the diffusion coefficient, and c_0 is the initial concentration on the surface, usually measured in mol m^{-2}.

A commonly encountered problem concerns the rate at which a precipitate can dissolve in the surrounding medium. In the case of a small spherical precipitate containing c_0 moles of diffusant (Figure 7.5c), in an isotropic matrix, the solution of the diffusion equation is:

$$c_r = \frac{c_0}{8(\pi D t)^{3/2}} \exp[-r^2/4 D t]$$

where c_r is the concentration at a radial distance r from the precipitate as the precipitate dissolves in the surroundings.

In these examples, the initial concentration of the tracer is fixed and the amount remaining as the diffusion progresses will diminish over the course of the experiment. An important case of nonsteady-state diffusion occurs when the initial concentration at the surface is maintained as a constant throughout the experiment. This happens when gas molecules diffuse into a solid and the gas supply is constantly replenished. The solution for diffusion into a plate (Figure 7.5d), provided that no atoms ever reach the opposite side of the solid (i.e. the solid is regarded as infinitely thick) and the diffusion coefficient is a constant, is given by:

$$\frac{c_x - c_0}{c_s - c_0} = 1 - \text{erf}\left[\frac{x}{2(D t)^{1/2}}\right]$$

where c_s is the constant concentration of the diffusing species at the surface, c_0 is the uniform concentration of the diffusing species already present in the solid before the experiment, and c_x is the concentration of the diffusing species at a position x from the surface after time t has elapsed, and D is the (constant) diffusion coefficient of the diffusing species. The function erf $[x/2(D t)^{1/2}]$ is frequently encountered in mathematics and is called the error function. It cannot generally be evaluated analytically, but numerical values are to be found in probability tables. An abbreviated list is given in Table 7.2.

In a pure material in which c_0 is considered to be zero,

$$c_x = c_s\left\{1 - \text{erf}\left[\frac{x}{2(D t)^{1/2}}\right]\right\}$$

If the same constant surface concentration holds, but with a sandwich geometry (Figure 7.4e), the solution is:

$$\frac{c_x - c_0}{c_s - c_0} = \frac{1}{2}\left\{1 - \text{erf}\left[\frac{x}{2(D t)^{1/2}}\right]\right\}$$

Table 7.2 Values of the error function, erf(z)

z	Erf(z)	z	Erf(z)	z	Erf(z)	z	Erf(z)
0	0	0.40	0.4284	0.85	0.7707	1.60	0.9763
0.025	0.0282	0.45	0.4755	0.90	0.7970	1.70	0.9838
0.05	0.0564	0.50	0.5205	0.95	0.8209	1.80	0.9891
0.10	0.1125	0.55	0.5633	1.00	0.8427	1.90	0.9928
0.15	0.1680	0.60	0.6039	1.10	0.8802	2.00	0.9953
0.20	0.2227	0.65	0.6420	1.20	0.9103	2.20	0.9981
0.25	0.2763	0.70	0.6778	1.30	0.9340	2.40	0.9993
0.30	0.3286	0.75	0.7112	1.40	0.9523	2.60	0.9998
0.35	0.3794	0.80	0.7421	1.50	0.9661	2.80	0.9999

Note: erf(z) is equal to 0 when z is equal to 0 and is equal to 1 when z is equal to 2.8; erf($-z$) = $-$erf(z).

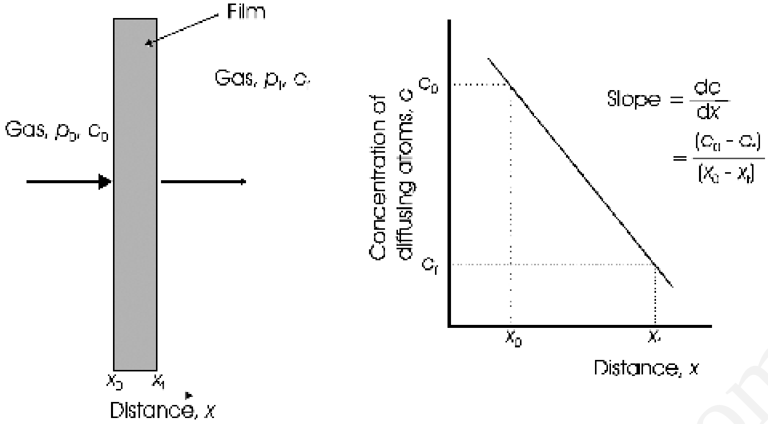

Figure 7.6 Steady-state diffusion. (a) a gas diffusing through a thin film and (b) the resultant diffusion profile. Note: c_0 and c_f, initial and final concentration of gas; p_0 and p_f, initial and final pressure of gas

7.3 Steady-state diffusion

Steady-state diffusion differs from nonsteady-state diffusion in that the concentration of the diffusing atoms at any point, x, and hence the concentration gradient at x, in the solid remains constant (Figure 7.6). Steady-state diffusion can occur when a gas permeates through a metal foil or thin-walled tube. The same situation can occur when oxygen diffuses through a plastic wrapping film. Hydrogen gas, for example, can be purified by allowing it to diffuse through a palladium 'thimble'.

Under steady-state conditions, the diffusion coefficient is obtained by using Fick's first law. This is written:

$$J_i = -D_i \frac{\mathrm{d}c_i}{\mathrm{d}x} \tag{7.4}$$

where D_i is the diffusion coefficient of atom of type i, c_i is the concentration of atoms i, and x is the position in the solid. J_i is called the flux of atoms of type i, that is, the net flow of these atoms through the solid. It is measured in atoms (or a related unit such as grams or moles), per metre squared per second. When the steady state has been reached, the diffusion coefficient across the foil, D, will be given by:

$$D = \frac{J\,l}{c_o - c_f}$$

where the concentrations on each side of the foil are c_o and c_f and the foil thickness is l.

7.4 Temperature variation of the diffusion coefficient

Diffusion coefficients are usually found to vary considerably with temperature. This variation can often be expressed in terms of the Arrhenius equation:

$$D = D_0 \exp\left(\frac{-E}{RT}\right) \tag{7.5}$$

where R is the gas constant, T is the temperature (in kelvin), and D_0 is a constant term referred to as the pre-exponential factor or frequency factor. The term E is called the activation energy of diffusion. Taking logarithms of both sides of this equation gives:

$$\ln D = \ln D_0 - \frac{E}{RT}$$

The activation energy can be determined from the gradient of a plot of ln D *versus* $1/T$ (Figure 7.7).

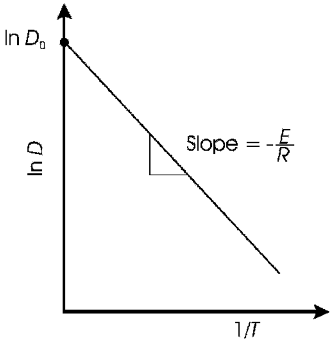

Figure 7.7 An Arrhenius plot of diffusion data: ln D versus $1/T$. Note: D, diffusion coefficient; T, temperature (in kelvin); D_0, pre-exponential, or frequency, factor

Table 7.3 Some representative values for self-diffusion coefficients

Atom	Matrix	Structure type	$D_0/\mathrm{m^2\,s^{-1}}$	$E/\mathrm{kJ\,mol^{-1}}$
Metals and semiconductors				
Cu	Cu	A1	2.0×10^{-5}	200
γ-Fe	Fe	A1	2.0×10^{-5}	269
α-Fe	Fe	A2	1.9×10^{-4}	240
Na	Na	A2	2.4×10^{-5}	44
Si	Si	Diamond	1.5×10^{-1}	455
Ge	Ge	Diamond	2.5×10^{-3}	303
Compounds				
Na^+	NaCl	Halite	8.4×10^{-8}	189
Cl^-	NaCl	Halite	0.17×10^{-4}	245
K^+	KCl	Halite	0.55×10^{-4}	256
Cl^-	KCl	Halite	1.3×10^{-6}	231
Mg^{2+}	MgO	Halite	2.5×10^{-9}	330
O^{2-}	MgO	Halite	4.3×10^{-13}	343
Ni^{2+}	NiO	Halite	4.8×10^{-10}	254
O^{2-}	NiO	Halite	6.2×10^{-12}	241
Pb^{2+}	PbS	Halite	8.6×10^{-13}	147
S^{2-}	PbS	Halite	6.8×10^{-13}	133
Ga	GaAs	Sphalerite	2.0×10^{-10}	400
As	GaAs	Sphalerite	7.0×10^{-5}	309
Zn^{2+}	ZnS	Sphalerite	3.0×10^{-12}	145
S^{2-}	ZnS	Sphalerite	2.1×10^{-4}	304
Cd^{2+}	CdS	Sphalerite	3.4×10^{-8}	193
S^{2-}	CdS	Sphalerite	1.6×10^{-10}	198

Note: literature values for self-diffusion coefficients vary widely, indicating the difficulty of making reliable measurements. The values in this table are intended to be representative only. The values of diffusion coefficients in the literature are mostly given in $\mathrm{cm^2\,s^{-1}}$; to convert the values given here to $\mathrm{cm^2\,s^{-1}}$, multiply by 10^4. D_0, pre-experimental, or frequency, factor; E, activation energy of diffusion.

Such graphs are known as Arrhenius plots. Diffusion coefficients found in the literature are usually expressed in terms of the Arrhenius equation D_0 and E values. Some representative values are given in Table 7.3.

7.5 The effect of impurities

Arrhenius plots for the majority of materials resemble Figure 7.7. However, Arrhenius plots obtained from very pure materials often consist of two straight-line parts with differing slopes (Figure 7.8). The region corresponding to diffusion at lower temperatures has a lower activation energy than the high-temperature region. The point where the two straight lines intersect is called a knee. If a number of different crystals of the same compound are studied, it is found that the position of the knee varies from one crystal to another, and depends on the impurity content. In Figure 7.8, for instance, crystal 1 would have a higher impurity concentration than crystal 2. The part of the plot sensitive to impurity content is called the impurity or extrinsic region. The high-temperature part of the plot is unaffected by the impurities present and is called the intrinsic region. The effect is explained in Section 7.11.

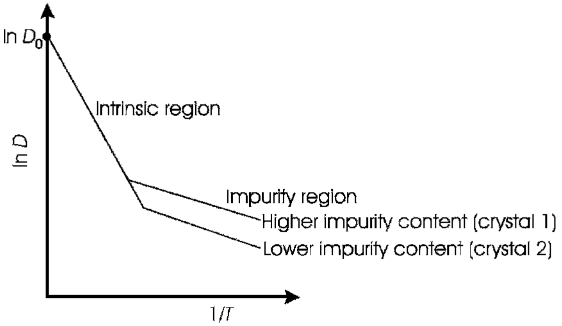

Figure 7.8 A form of Arrhenius plot found for almost-pure crystals with low impurity concentrations. Note: D, diffusion coefficient; T, temeprature (in kelvin); D_0, pre-exponential, or frequency, factor

7.6 The penetration depth

It is of considerable practical importance to have some idea of how far an atom or ion will diffuse into a solid during a diffusion experiment. For example, the electronic properties of integrated circuits are created by the careful diffusion of selected dopants into single crystals of very pure silicon, and metallic machine components are hardened by the diffusion of carbon or nitrogen from the surface into the bulk. An approximate estimate of the depth to which diffusion is significant is given by the penetration depth, x_{P}, which is the depth at which an appreciable change in the concentration of the tracer can be said to have occurred after a diffusion time t. It is obtained by using the equation

$$x_{\mathrm{P}} = (D^{*}t)^{1/2} \qquad (7.6)$$

A value for the distance moved during diffusion by a sequence of random jumps can be calculated. It is found that (Section S3.1.1):

$$\sqrt{(\langle x^2 \rangle)} = \sqrt{(nDt)}$$

where $\sqrt{(\langle x^2 \rangle)}$ is a quantity called the root mean square displacement of x, D is the diffusion coefficient, t is the diffusion time, and the factor n is of the order of 2 to 3. Real systems are more complex, and the approximation given in Equation (7.6) is adequate for practical purposes.

7.7 Self-diffusion mechanisms

During volume diffusion, an individual atom jumps from one stable position to another . If vacancies are present (Figure 7.9) atoms or ions can jump from a normal site into a neighbouring vacancy and so gradually move through the crystal. Movement of a diffusing atom into a vacant site corresponds to movement of the vacancy in the other direction. This process is therefore frequently referred to as vacancy diffusion. In practice, it is often very convenient, in problems where vacancy diffusion occurs, to ignore atom movement and to focus attention on the diffusion of the vacancies as if they were real particles.

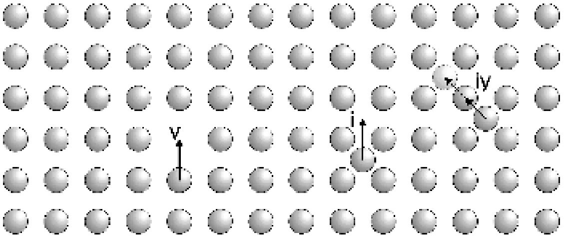

Figure 7.9 Self-diffusion mechanisms. Note: v, vacancy; i, interstitial; iy, interstitialcy

In the case of interstitials, two diffusion mechanisms can be envisaged (Figure 7.9). An interstitial can jump to a neighbouring interstitial position. This is called interstitial diffusion and is the mechanism by which tool steels are hardened by incorporation of nitrogen or carbon. Alternatively, an interstitial can jump to a filled site and knock the occupant into a neighbouring interstitial site. This 'knock-on' process is called interstitialcy diffusion.

Substitutional impurities can also move by way of three mechanisms (Figure 7.10). As well as vacancy diffusion, an impurity can swap places with a neighbouring normal atom, exchange diffusion, and in ring diffusion co-operation between several atoms is needed to make the exchange. These processes have been found to take place during the doping of semiconductor crystals. Interstitial impurities can move by interstitial and interstitialcy jumps similar to those described above (Figure 7.10).

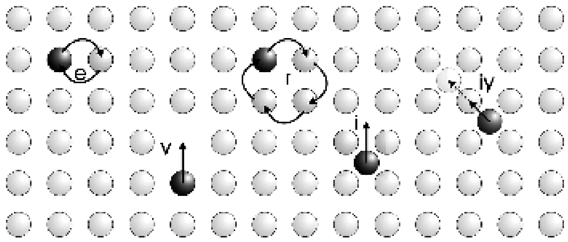

Figure 7.10 Impurity diffusion mechanisms. Note: v, vacancy; e, exchange; r, ring; i, interstitial; iy, interstitialcy

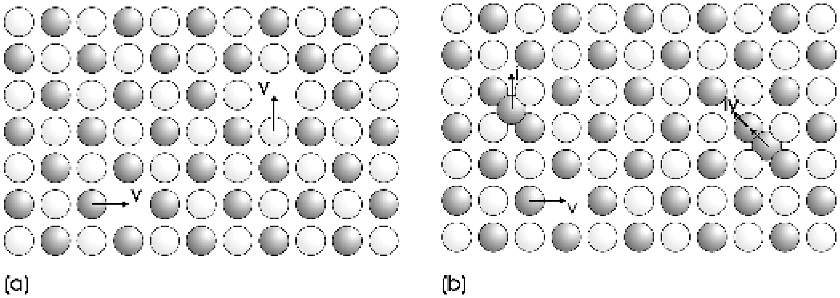

Figure 7.11 (a) Vacancy diffusion, v, in a crystal containing Schottky defects; (b) vacancy diffusion, v, interstitial diffusion, i and interstitialcy diffusion, iy, in crystals containing Frenkel defects

When Schottky defects are present in a crystal, vacancies are found on the cation and the anion sublattices, allowing both cation and anion diffusion to occur (Figure 7.11a). In the case of Frenkel defects, interstitial sites are occuppied and vacancies occur, allowing for interstitial, interstitialcy and vacancy diffusion to take place in the same crystal (Figure 7.11b) so that three migration routes are possible.

7.8 Atomic movement during diffusion

The process of self-diffusion involves the movement of atoms in a random fashion through a crystal. No strong driving force, such as a concentration gradient, is present. Nevertheless, each time an atom moves it will have to overcome an energy barrier. This is because the migrating atoms have to leave normally occupied positions, which are, by definition, the most stable positions for atoms in the crystal, to pass through less stable positions not normally occupied by atoms. Often atoms may be required to squeeze through a bottleneck of surrounding atoms in order to move at all.

For one-dimensional diffusion the energy barrier can be supposed to take the form shown in Figure 7.12, where the height of the barrier is E. Obviously, the larger the magnitude of E the less chance there is that the atom has the necessary energy to make a successful jump.

We can gain an estimate of the probability that an atom will successfully move by using Maxwell–Boltzmann statistics. The probability, p, that a single atom will move from one position of minimum energy to an adjacent position will be given by the equation:

$$p = \exp\left(\frac{-E}{kT}\right) \tag{7.7}$$

where E represents the energy barrier, k is the Boltzmann constant, and T is the absolute temperature. Equation (7.7) indicates that if E is very small

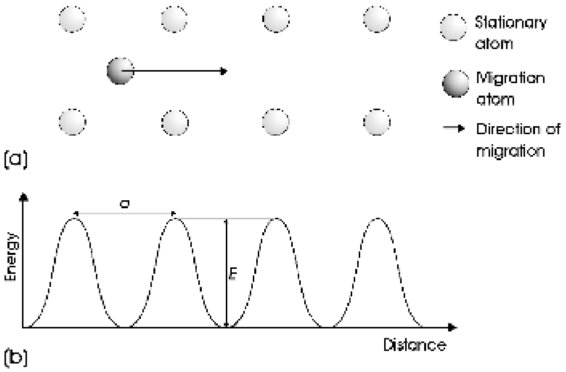

Figure 7.12 (a) An atom migrating from one stable position to another, separated by a distance a. (b) The energy barrier encountered has a periodicity equal to a and is a maximum when the diffusing atom has to pass a 'bottleneck' between two stationary atoms

the probability that the atom will clear the barrier approaches 1.0; if E is equal to kT the probability for a successful jump is about one third; and if E increases above kT the probability that the atom could jump the barrier rapidly becomes negligible.

The atoms in a crystal are vibrating continually with a frequency, ν, which is usually taken to have a value of about 10^{13} Hz at room temperature. It is reasonable to suppose that the number of attempts at a jump, sometimes called the attempt frequency, will be equal to the frequency with which the atom is vibrating. The number of successful jumps that an atom will make per second, Γ, will be equal to the attempt frequency, ν, multiplied by the probability of a successful move, that is,

$$\Gamma = \nu \exp\left(\frac{-E}{kT}\right) \tag{7.8}$$

7.9 Atomic migration and diffusion coefficients

A flow of atoms along the x direction is related to the diffusion coefficient by Fick's first law:

$$J = -D\frac{\mathrm{d}c}{\mathrm{d}x}$$

where J is the number of atoms crossing a unit area in the solid each second (the atom flux), D is the diffusion coefficient, and c is the concentration of the diffusing species at point x after time t has elapsed. An expression for J in terms of atomic jumps is given in Section S3.1.2. The analysis shows that:

$$J = -\frac{1}{2}\Gamma a^2\frac{\mathrm{d}c}{\mathrm{d}x}$$

where Γ is the number of successful jumps that an atom makes per second, and a is the separation of the stable positions. If we now compare this equation with Fick's first law:

$$D = \frac{1}{2}\Gamma a^2$$

Replacing Γ by Equation (7.8) gives:

$$D = \frac{1}{2}a^2\,\nu\exp\left(\frac{-E}{kT}\right)$$

7.10 Self-diffusion in crystals

In real crystals it is necessary to take some account of the three-dimensional nature of the diffusion process. An easy way of doing this is to add a geometrical factor, g, into the equation for D so that it becomes:

$$D = g\,a^2\,\nu\exp\left(\frac{-E}{kT}\right)$$

In the one-dimensional case, the factor 1/2 is a geometrical term to account for the fact that an atom jump can be in one of two directions:

$$D = \frac{1}{2}a^2\,\nu\exp\left(\frac{-E}{kT}\right)$$

In a cubic structure diffusion can occur along six equivalent directions, and a value of g of 1/6 is appropriate:

$$D = \frac{1}{6}a^2\,\nu\exp\left(\frac{-E}{kT}\right)$$

In the foregoing discussion, every possible atom jump is allowed. This may not be true in real crystals. For example, in the case of vacancy diffusion, no movement is possible if the vacancy population is zero. Equation (7.8) for the number of successful jumps ignores this, and should contain a term p_J, that expresses the probability that the jump is possible from a structural point of view:

$$\Gamma = p_J\nu \exp\left(\frac{-E}{kT}\right) \tag{7.9}$$

For example, in the A1 (face-centred cubic) structure of magnesium, each metal atom is surrounded by 12 nearest neighbours. If on average throughout the crystal two of these sites are empty, the probability of a successful jump will be $p_J = 2/12 = 1/6$. The diffusion coefficient is then given by:

$$D = \frac{1}{6} a^2 \nu n \exp\left(\frac{-E}{kT}\right) \tag{7.10}$$

7.11 The Arrhenius equation and the effect of temperature

A comparison of Equations (7.9) and (7.10) with the Arrhenius equation, Equation (7.5), which can be written in terms of the energy per defect rather than molar quantities as:

$$D = D_0 \exp\left(\frac{-E}{kT}\right)$$

shows that the pre-exponential factor D_0 is equivalent to $p_J g a^2 \nu$:

$$D_0 = p_J g a^2 \nu$$

and the activation energy, E, is equivalent to the height of the energy barrier to be surmounted.

The term p_J, which is the probability that a jump can take place for structural reasons, is closely related to the number of defects present. In most ordinary solids, the value of p_J is fixed by the impurity content. Any variation in D_0 from one sample of a material to another is accounted for by the variation of the impurity content. However, the value of p_J does not affect the energy of migration, E, so that Arrhenius plots for crystals will consist of a series of parallel lines (Figure 7.13).

In very pure crystals, another feature becomes important. In this case, the number of intrinsic defects may be greater than the number of defects due to impurities, especially at high temperatures. Under these circumstances, the value of p_J will be influenced by the intrinsic defect population, and can contribute to the observed value of E.

To illustrate this, suppose that cation vacancy diffusion is the predominant migration mechanism and that the crystal, of formula MX, contains Schottky defects as the major type of intrinsic defect. The probability of a jump taking place is equal to the fraction of cation vacancies in the crystal, given by Equation (3.3):

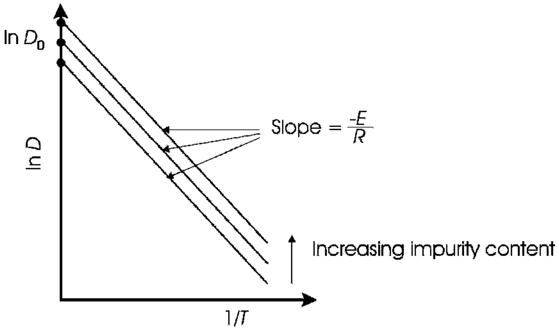

Figure 7.13 The variation of Arrhenius plots with impurity content. Note: D, diffusion coefficient; T, temperature (in kelvin); D_0, pre-exponential, or frequency, factor

$$\frac{n_S}{N} = \exp\left(\frac{-\Delta H_S}{2kT}\right) \tag{7.11}$$

At high temperatures the appropriate form of Equation (7.10) becomes:

$$D = g \nu a^2 \exp\left(\frac{-E_v}{kT}\right) \exp\left(\frac{-\Delta H_S}{2kT}\right)$$

where E_v represents the height of the energy barrier to be overcome in vacancy diffusion, and ΔH_S is the enthalpy of formation of a Schottky defect.

Similarly, at high-temperatures, diffusion in a crystal of formula MX by interstitials will reflect the population of Frenkel defects present, given by Equation (3.6):

$$n_F = (NN^*)^{1/2} \exp\left(\frac{-\Delta H_F}{2kT}\right) \tag{7.12}$$

In these circumstances, the probability factor, p_J, will be proportional to the number of Frenkel defects present, and it is possible to write Equation (7.10) in a form analogous to Equation (7.12):

$$D = g\nu a^2 \exp\left(\frac{-E_i}{kT}\right) \exp\left(\frac{-\Delta H_F}{2kT}\right)$$

where E_i represents the potential barrier to be surmounted by an interstitial atom and ΔH_F is the enthalpy of formation of a Frenkel defect.

Both of these equations retain the form:

$$D = D_0 \exp\left(\frac{-E}{RT}\right)$$

However, the activation energy, E, will consist of the energy required for migration, E_i or E_v, plus the energy of defect formation. For Schottky defects

$$E = E_v + \frac{\Delta H_S}{2}$$

and for Frenkel defects

$$E = E_i + \frac{\Delta H_F}{2}$$

This means that an Arrhenius plot will have a steeper slope at high temperatures where the point defect equilibria are significant, than at low temperatures, where the impurity content dominates. The plot will show a knee between the high-temperature and low-temperature regimes (Figure 7.8). A comparison of the two slopes will allow an estimate both of the energy barrier to migration and of the relevant defect formation energy to be made. Some values found in this way are listed in Table 7.4.

In the foregoing discussion, it has been supposed that the height of the potential barrier will be the same at all temperatures. This is probably not so. As the temperature increases the lattice will expand and, in general, E would be expected to decrease. Moreover, some of the other constant terms in the preceding equations may vary with temperature. For example, an expansion of the crystal is likely to lead to an increase in the vibration frequency, ν. The Arrhenius plots reveal this by being slightly curved.

Table 7.4 Approximate enthalpy values for the formation and movement of vacancies in alkali halide crystals

Material	ΔH/kJ mol^{-1}	E_1/kJ mol^{-1}	E_2/kJ mol^{-1}
(a) Schottky defects			
NaCl	192	84	109
NaBr	163	84	113
KCl	230	75	172
KBr	192	64	46
(b) Frenkel defects			
AgCl	155	13	36
AgBr	117	11	23

Note: for Schottky defects, ΔH is ΔH_S, the enthalpy of formation of a Schottky defect, and E_1 and E_2 are the energy barriers to be surmounted for vacancy diffusion by cations and anions, respectively; for Frenkel defects, ΔH is ΔH_F, the enthalpy of formation of a Frenkel defect, and E_1 and E_2 are the energy barriers to be surmounted for interstitial and vacancy diffusion, respectively.

7.12 Correlation factors for self-diffusion

So far, the diffusion of atoms has been considered to occur in a random fashion throughout the crystal structure. Each step was unrelated to the one before and the atoms were supposed to be jostled solely by thermal energy. However, diffusion of an atom in a solid may *not* be a truly random process and in some circumstances a given jump direction may depend on the direction of the previous jump.

Consider the vacancy diffusion of an atom in a crystal (Figure 7.14). The diffusing atom can be

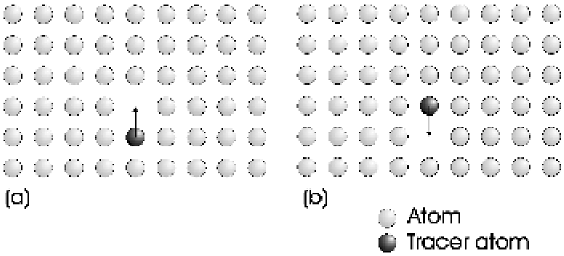

Figure 7.14 Vacancy diffusion of a tracer atom; in both part (a) and part (b) the most probable jump for the tracer is into the adjacent vacancy

regarded as a tracer atom. It is situated next to a vacant site, so that diffusion can take place by jumping into the vacant site (Figure 7.14a). The next jump of the tracer is not, now, an entirely random process. It is still next to the vacancy and it is more likely that the tracer will move back to the vacancy (Figure 7.14b), recreating the original situation. Hence, of the choices available to the tracer in Figure 7.14(b), a jump back to the situation shown in Figure 7.14(a) is of highest probability.

If attention is focused on the vacancy, a different result is found. Considering the situation in Figure 7.14(a), diffusion can occur by way of any of the atoms around the vacancy moving into the empty site. The vacancy, of course, does not prefer any of its neighbours so that its first jump is entirely random. The same is true of the succeding situation (Figure 7.14b). The vacancy will have no need to prefer a jump to the tracer position. Thus, the vacancy can always move to an adjacent cation site and hence can follow a truly random path.

When these processes are considered over many jumps, the mean square displacement of the tracer will be less that that of the vacancy, even though both have taken the same number of jumps. Therefore, it is expected that the observed diffusion coefficient of the tracer will be less than that of the vacancy. In these circumstances, the random-walk diffusion equations need to be modified by the introduction of a correlation factor, *f*. The correlation factor is given by the ratio of the values of the mean square displacement of the tracer, $\langle x^2 \rangle_{\text{tracer}}$, to that of the vacancy, $\langle x^2 \rangle_{\text{vacancy}}$, if the number of jumps considered is large:

$$f = \frac{\langle x^2 \rangle_{\text{tracer}}}{\langle x^2 \rangle_{\text{vacancy}}}$$

Correlation factors for vacancy diffusion generally take values of between 0.5 and 0.8.

In the case of interstitial diffusion, in which we have only a few diffusing atoms and many available empty interstitial sites, a correlation factor close to 1.0 would be expected. In effect, the interstitial atom moves in a 'sea of vacancies'. In the case of interstitialcy diffusion, this will not be true because the number of vacancies will be equal to the number of interstitials present, which will always be rather small in proportion to the number of filled sites.

Table 7.5 Correlation factors for self-diffusion

Structure	Correlation factor (f)
Vacancy mechanism:	
Diamond	0.50
A2, body-centred cubic	0.7272
A1, face-centred cubic	0.7815
A3, hexagonal close packed	0.7812 (f_x, f_y)
A3, hexagonal close packed	0.7815 (f_z)
Interstitialcy mechanism:	
A1, face-centred cubic	0.80
Fluorite (cations)	1.00
A2, body-centred cubic	0.666
CsCl (cations)	0.832
AgBr (cations)	0.666

Table 7.5 lists some values for a variety of diffusion mechanisms in some common crystal structure types.

The diffusion of an impurity atom in a crystal, say K in NaCl, involves other considerations apart from those of a statistical nature. In such cases, the probability that the impurity will exchange with the vacancy will depend on factors such as the relative sizes of the impurity compared with the host atoms. In the case of ionic movement, the charge on the diffusing species will also play a part. These factors can can also be expressed in terms of the jump frequencies of the host and impurity atoms, in which case one is likely to be greater than the other.

7.13 Ionic conductivity

During ionic conductivity, ions jump from one stable site to another. Hence, the process can be described by equations similar to those for diffusion. The movement of the ions, however, is not random, but is influenced by the presence of an electric field, *V*, so that positive and negative ions move in opposite directions. The electric field

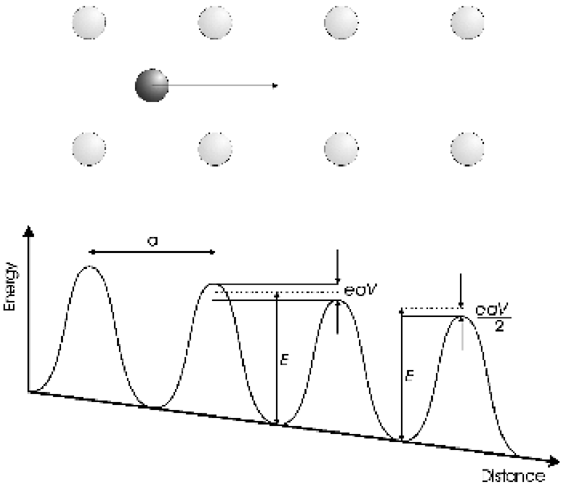

Figure 7.15 The energy barrier to ionic diffusion is higher against the direction of the electric field and lower in the direction of the electric field. The barrier diffference, *eaV*, is for a monovalent ion

changes the potential barrier encountered by a diffusing ion from that in Figure 7.12 to that in Figure 7.15. For monovalent ions, the barrier will be reduced by $\frac{1}{2}\, e\, a\, V$ in one direction and raised by the same amount in the other.

Following the methods set out for random diffusion, it is possible to calulate the relative number of jumps that an ion will make with and against the field and hence obtain the ionic conductivity, σ (see Section S3.1.3). For low field strengths,

$$\sigma = \frac{\sigma_0}{T} \exp\left(\frac{-E}{k\,T}\right) \qquad (7.13)$$

where σ_0 is a constant, E is the mean height of the diffusion barrier, k is the Boltzmann constant, and T is the temperature (in kelvin). The constant, σ_0, is:

$$\sigma_0 = \frac{n\,\nu\,a^2\,e^2}{k} \qquad (7.14)$$

where a is the jump distance, e the charge on the ions, ν is the vibration frequency or jump frequency, k is the Boltmann constant, and n is the number of mobile species present in the crystal.

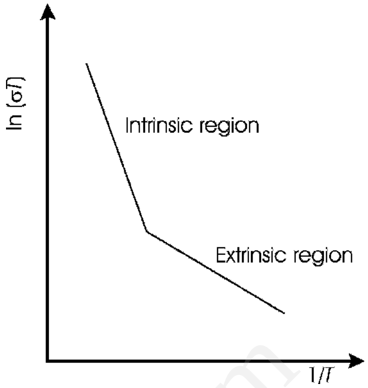

Figure 7.16 Arrhenius-type plot of $\ln(\sigma\,T)$ versus $1/T$ for ionic conductivity in a crystal containing only a small concentration of impurities. Note: σ, ionic conductivity; T, temperature (in kelvin)

Generally, n will be fixed and controlled by the impurity population. When ion migration takes place via a vacancy diffusion mechanism we can write:

$$\sigma_{\mathrm{v}} = \frac{n_{\mathrm{v}}\,\nu\,a^2\,e}{k\,T} \exp\left(\frac{-E_{\mathrm{v}}}{k\,T}\right)$$

and when it takes place by the migration of interstitials we can write:

$$\sigma_{\mathrm{i}} = \frac{n_{\mathrm{i}}\,\nu\,a^2\,e}{k\,T} \exp\left(\frac{-E_{\mathrm{i}}}{k\,T}\right)$$

In this regime, we can obtain measures of $\mathrm{E_v}$ or $\mathrm{E_i}$ directly from the Arrhenius-like plots of $\ln(\sigma T)$ versus $1/T$ (Figure 7.16).

In the case of very pure solids, it is necessary to take into account the number of intrinsic defects, as discussed above. The value of n must then reflect the type of intrinsic defect present. For example, should Schottky defects predominate, substitution of Equation (7.11) [Equation (3.3)] for n in Equations (7.13) and (7.14) gives:

$$\sigma_{\mathrm{S}} = \frac{\nu\,a^2\,e^2\,N}{k\,T} \exp\left(\frac{-E_{\mathrm{v}}}{k\,T}\right) \exp\left(\frac{-\Delta\,H_{\mathrm{S}}}{2\,k\,T}\right)$$

Should Frenkel defects predominate, substituting Equation (7.12) [Equation (3.6)] for n in Equations (7.13) and (7.14) gives:

$$\sigma_F = \frac{\nu a^2 e^2 (N N^*)^{1/2}}{k T} \exp\left(\frac{-E_i}{k T}\right) \exp\left(\frac{-\Delta H_F}{2 k T}\right)$$

In these cases, Arrhenius plots of ln σT versus $1/T$ will show a knee between the low-temperature and high-temperature regions (Figure 7.16). The high-temperature value for E will be composed of two terms; namely,

$$E_S = E_v + \frac{\Delta H_S}{2}$$

for Schottky defects, and

$$E_F = E_i + \frac{\Delta H_F}{2}$$

for Frenkel defects.

7.14 The relationship between ionic conductivity and the diffusion coefficient

If both ionic conductivity and ionic diffusion occur by the same random-walk mechanism, a relationship between the self-diffusion coefficient, D, and the ionic conductivity, σ, can be derived. In the simplest case, assume that processes involve the same energy barrier, E, and jump distance, a (Figures 7.12 and 7.15). Further, if the diffusion is restricted to only one direction, the $+x$ direction, and each jump is allowed, the diffusion coefficient is

$$D = \nu a^2 \exp\left(\frac{-E}{k T}\right)$$

and the ionic conductivity of a monovalent ion is

$$\sigma = \frac{n \nu a^2 e^2}{k T} \exp\left(\frac{-E}{k T}\right)$$

Combining these two equation gives

$$\frac{\sigma}{D} = \frac{n e^2}{k T} \qquad (7.15)$$

where n is the number of mobile ions per unit volume, e is the electronic charge, k is the Boltzmann constant, and T is the temperature (in kelvin). This equation is a simplified form of the Nernst–Einstein equation. For an ion of charge $+z$, the equation becomes

$$\frac{\sigma}{D} = \frac{n z^2 e^2}{k T} \qquad (7.16)$$

The implication is that it is possible to determine the diffusion coefficient from the easier measurement of ionic conductivity. However, the assumption that both processes utilise exactly the same mechanism is important. In general, this is not true. In such a case, the relationship is slightly different from that in Equations (7.15) and (7.16) and depends on the details of the diffusion mechanism. For vacancy diffusion in a cubic structure,

$$\frac{\sigma}{D} = \frac{n z^2 e^2}{f_v k T} \qquad (7.17)$$

where f_v is the correlation factor for vacancy self-diffusion, and n is the number of ions per unit volume on the relevent sublattice. In the case of interstitial diffusion in a cubic crystal, Equation (7.17) applies, with a correlation factor of 1:

$$\frac{\sigma}{D} = \frac{n z^2 e^2}{k T}$$

For interstitialcy diffusion,

$$\frac{\sigma}{D} = \frac{2 n z^2 e^2}{f_{iy} k T}$$

where f_{iy} is the appropriate intersticialcy correlation factor.

Answers to introductory questions

What is steady-state diffusion?

Steady-state diffusion differs from nonsteady-state diffusion in that the concentration of the diffusing atoms at any point, x, and hence the concentration gradient at x, in the solid, remains constant. Steady-state diffusion may be achieved when air diffuses through plastic food wrapping film.

Under steady-state conditions, the diffusion coefficient is obtained by using Fick's first law:

$$J_i = -D_i \frac{\mathrm{d}\,c_i}{\mathrm{d}\,x}$$

where D_i is the diffusion coefficient of atom of type i, c_i is the concentration of these atoms, and x is the position in the solid. J_i is the flux of atoms of type i; that is, it is the net flow of these atoms through the solid.

How does one obtain a quick estimate of the distance moved by diffusing atoms?

It is of considerable practical importance to have some idea of how far an atom or ion will diffuse into a solid during a diffusion experiment. An approximate estimate of the depth to which diffusion is significant is given by the penetration depth, x_{P}, which is the depth at which an appreciable change in the concentration of the tracer can be said to have occurred after a diffusion time t. It is obtained by using the equation

$$x_{\mathrm{P}} = (D^* t)^{1/2}$$

This approximation is adequate for practical purposes.

How does the energy barrier for ionic diffusion change when an electric field is present?

During ionic conductivity, ions jump from one stable site to another. Hence, the process can be described by equations similar to those for diffusion. However, the movement of the ions is influenced by the presence of an electric field, V, so that positive and negative ions move in opposite directions. The electric field changes the potential barrier encountered by a diffusing ion from that encountered during diffusion in the following way. For ions with a charge of $z\,e$, the barrier will be reduced by $\frac{1}{2} z\,e\,a\,V$ in one direction and raised by the same amount in the other. When the mechanism of migration is the same, the relationship between the ionic conductivity and the diffusion coefficient for an ion of charge $z\,e$ is given by a simplified form of the Nernst–Einstein equation:

$$\frac{\sigma}{D} = \frac{n\,z^2\,e^2}{k\,T}$$

Further reading

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Problems and exercises

Quick quiz

1 Diffusion through a crystalline structure is called:
   (a) Tracer diffusion
   (b) Volume diffusion
   (c) Self-diffusion

2 Short-circuit diffusion refers to diffusion along:
   (a) Defects
   (b) Lattices
   (c) Planes

3 Self-diffusion is diffusion of:
   (a) Radioactive atoms in a crystal
   (b) Impurity atoms in a crystal
   (c) Native atoms in a pure crystal

4 Tracer diffusion refers to the diffusion of:
   (a) Marked atoms
   (b) Traces of impurities
   (c) Single atoms

5 A radioactive layer between two crystal slabs forms a:
   (a) Difusion pair
   (b) Diffusion couple
   (c) Diffusion probe

6 A diffusion profile is a graph of:
   (a) Concentration versus time
   (b) Concentration versus distance
   (c) Distance versus time

7 In order to obtain the diffusion coefficient from a diffusion profile, use:
   (a) Fick's first law
   (b) The Arrhenius equation
   (c) The diffusion equation

8 What graph would you plot to determine the tracer diffusion coefficient in a diffusion couple:
   (a) c versus x?
   (b) $\ln c$ versus x^2?
   (c) $\ln c$ versus $\ln x$?

9 Nonsteady-state diffusion is characterised by the fact that the concentration at:
   (a) Any point in the solid changes over time
   (b) Any point in the solid is constant
   (c) The surface of the solid changes over time

10 Steady-state diffusion is characterised by the fact that the concentration at:
   (a) Any point in the solid changes over time
   (b) Any point in the solid is constant
   (c) The surface of the solid changes over time

11 In steady-state diffusion the diffusion coefficient is obtained via:
   (a) The diffusion equation
   (b) The Arrhenius equation
   (c) Fick's first law

12 The variation of a diffusion coefficient with temperature is given by:
   (a) The diffusion equation
   (b) Fick's first law
   (c) The Arrhenius equation

13 The activation energy for diffusion can be determined by a plot of:
   (a) $\ln D$ versus $1/T$.
   (b) $\ln c$ versus $1/T$.
   (c) $\ln D$ versus T.

14 The part of an Arrhenius plot above a knee (i.e. the high-temperature part) is called the:
   (a) Extrinsic region
   (b) Intrinsic region
   (c) Impurity region

15 The penetration depth is:
   (a) The distance that an atom can diffuse in a given time
   (b) An estimate of the depth to which diffusion is significant
   (c) The thickness of the surface layer on a crystal before diffusion

16 The mechanism of vacancy diffusion refers to atoms moving into:
   (a) Vacant sites in the crystal structure
   (b) Nonoccupied sites in the crystal structure
   (c) Adjacent atom sites in the crystal structure

17 The mechanism of interstitial diffusion refers to atoms moving into:

  - (a) Vacant sites in the crystal structure
  - (b) Nonoccupied sites in the crystal structure
  - (c) Adjacent atom sites in the crystal structure

18 The diffusion mechanism of exchange involves:
  - (a) Two impurity atoms
  - (b) An impurity atom and a vacancy
  - (c) An impurity atom and a normal atom

19 In crystals containing Frenkel defects:
  - (a) One diffusion mechanism is possible
  - (b) Two diffusion mechanisms are possible
  - (c) Three diffusion mechanisms are possible

20 The geometrical factor in diffusion varies according to:
  - (a) The crystal structure
  - (b) The number of defects present
  - (c) The size of the diffusing atoms

21 Correlation factors take into account:
  - (a) Nonrandom diffusion
  - (b) Impurity content
  - (c) Frenkel and Schottky defects

22 An electric field changes the rate of diffusion of ions in a direction:
  - (a) Perpendicular to the applied electric field
  - (b) Parallel to the unit cell edge
  - (c) Parallel to the electric field

Calculations and questions

7.1 Show that the units of the diffusion coefficient are $m^2\,s^{-1}$. [Note: answer is not provided at the end of this book.]

7.2 Show that the following two equations are equivalent:

$$\frac{c_x - c_0}{c_s - c_0} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{D\,t}}\right)$$

$$\frac{c_s - c_x}{c_s - c_0} = \operatorname{erf}\left(\frac{x}{2\sqrt{D\,t}}\right)$$

[Note: answer is not provided at the end of this book.]

7.3 Radioactive nickel-63 was coated onto a crystal of CoO and made into a diffusion couple. The sample was heated for 30 min at 953 °C. The radioactivity perpendicular to the surface is given in Table 7.6(a). Calculate the impurity tracer diffusion coefficient of nickel-63 in CoO.

7.4 Radioactive cobalt-60 was coated onto a crystal of CoO and made into a diffusion couple. The sample was heated for 30 min at 953 °C. The radioactivity perpendicular to the surface is given in Table 7.6(b). Calculate the tracer diffusion coefficient of cobalt-60 in CoO.

Table 7.6 Diffusion couples: radioactivity perpendicular to the surface for (a) nickel-63 as a crystal of CoO, for Question 7.3; (b) cobalt-60 on a crystal of CoO, for Question 7.4; and (c) iron-59 on (0 0 1) face of a single crystal of TiO_2, for Question 7.5

(a) Question 7.3		(b) Question 7.4		(c) Question 7.5	
activity[a]	distance/µm	activity[a]	distance/µm	activity[a]	distance/µm
80	6	110	10	520	300
50	10	70	20	400	400
20	14	39	30	270	500
6	18	23	40	185	600
5	20	9	50	130	650
				90	700
				53	800

[a] In counts per second.

7.5 Radioactive iron-59 was coated onto the (0 0 1) face of a single crystal of TiO_2 (rutile) (tetragonal) and made into a diffusion couple. The sample was heated for 300 s at 800 °C. The radioactivity perpendicular to the surface is given in Table 7.6(c). Calculate the impurity tracer diffusion coefficient of iron-59 parallel to the *c* axis in rutile.

7.6 Carbon-14 is diffused into pure α-iron from a gas atmosphere of $CO + CO_2$. The gas pressures are arranged to give a constant surface concentration of 0.75 wt% C. The diffusivity of ^{14}C into α-iron is $9.5 \times 10^{-11}\ m^2\ s^{-1}$ at 827 °C. Calculate the concentration of ^{14}C 1 mm below the surface after a heating time of 2 hours.

7.7 Using the data in Question 7.6, how long would it take to make the carbon content 0.40 wt% 1 mm below the surface?

7.8 An ingot of pure titanium metal is heated at 1000 °C in an atmosphere of ammonia, so that nitrogen atoms diffuse into the bulk. The diffusivity of nitrogen in β-titanium, the stable structure at 1000 °C, is $5.51 \times 10^{-12}\ m^2\ s^{-1}$ at this temperature. What is the thickness of the surface layer of titanium that contains a concentration of nitrogen atoms greater than 0.25 at% after heating for 1 hour?

7.9 Zircalloy is a zirconium alloy used to clad nuclear fuel. How much oxygen will diffuse through each square metre of casing in a day under steady-state diffusion conditions, at 1000 °C, if the following apply: diffusivity of oxygen in zircalloy at 1000 °C, $9.89 \times 10^{-13}\ m^2\ s^{-1}$; concentration of oxygen on the inside of the container, $0.5\ kg\ m^{-3}$; oxygen concentration on the outside of the container, $0.01\ kg\ m^{-3}$; container thickness, 1 cm

7.10 Pure hydrogen is made by diffusion through a Pd-20 %Ag alloy ‘thimble’. What is the mass of hydrogen prepared per hour if: the total area of the thimbles used is 10 m^2; the thickness of each is 5 mm; and the operating temperature is 500 °C? The equilibrium alloy in the surface of the thimble on the hydrogen–rich side has a composition $PdH_{0.05}$, and, on the further side, the hydrogen is swept away rapidly so that the surface is essentially pure metal. The diffusion coefficient of hydrogen in the alloy at 500 °C is $1.3 \times 10^{-8}\ m^2\ s^{-1}$. Pd has the A1 (face-centred cubic) structure, with lattice parameter $a_0 = 0.389$ nm.

7.11 The radioactive tracer diffusion coefficient of silicon atoms in silicon single crystals is given in Table 7.7(a). Estimate the activation energy for diffusion.

7.12 Using the data for Question 7.11, listed in Table 7.7(a), at what temperature in (°C) will the penetration depth be 2 μm after 10 hours of heating?

7.13 The diffusion coefficient of carbon impurities in a silicon single crystal is given in Table 7.7(b). Estimate the activation energy for diffusion.

7.14 Using the data in Question 7.13, listed in Table 7.7(b), at what temperature in (°C) will the penetration depth be 10^{-4} m after 20 hours of heating?

7.15 The diffusion coefficient of radioactive Co^{2+} tracers in a single crystal of cobalt oxide, CoO, is given in the Table 7.7(c). Estimate the activation energy for diffusion.

7.16 The diffusion coefficient of radioactive Cr^{3+} tracers in the refractory oxide Cr_2O_3 is given in the Table 7.7(d). Estimate the activation energy for diffusion.

7.17 The impurity diffusion coefficient of Fe^{2+} impurities in a magnesium oxide, MgO, single crystal is given in Table 7.7(e). Estimate the activation energy for diffusion.

7.18 Calculate the diffusivity of ^{51}Cr in titanium metal at 1000 °C: $D_0 = 1 \times 10^{-7}\ m^2\ s^{-1}$; $E = 158\ kJ\ mol^{-1}$.

7.19 Calculate the diffusivity of ^{51}Cr in a titanium: 18 wt% Cr alloy at 1000 °C; $D_0 = 9 \times 10^{-2}\ m^2\ s^{-1}$; $E = 186\ kJ\ mol^{-1}$.

Table 7.7 Radioactive tracer diffusion coefficients, D^* with temperature, T, for: (a) silicon atoms in silicon single crystals, for Questions 7.11 and 7.12; (b) carbon impurities in a silicon single crystal, for Questions 7.13 and 7.14; (c) radioactive Co^{2+} tracers in a single crystal of CoO, for Question 7.15; (d) radioactive Cr^{3+} tracers in Cr_2O_3, for Question 7.16; and (e) Fe^{2+} impurities in a single crystal of MgO

$T/°C$	$D^*/m^2\,s^{-1}$
(a) Questions 7.11 and 7.12	
1150	8.82×10^{-19}
1200	3.40×10^{-18}
1250	1.20×10^{-17}
1300	3.90×10^{-17}
1350	1.18×10^{-16}
1400	3.35×10^{-16}
(b) Questions 7.13 and 7.14	
900	1.0×10^{-17}
1000	3.0×10^{-16}
1100	4.0×10^{-15}
1200	5.0×10^{-14}
1300	9.0×10^{-13}
1400	5.0×10^{-12}
(c) Question 7.15	
1000	1.0×10^{-13}
1100	3.5×10^{-13}
1200	9.0×10^{-13}
1300	2.0×10^{-12}
1400	4.0×10^{-12}
1500	8.0×10^{-12}
1600	1.5×10^{-11}
(d) Question 7.16	
1050	1.0×10^{-15}
1100	4.6×10^{-15}
1200	1.05×10^{-14}
1300	6.2×10^{-14}
1400	2.7×10^{-13}
1500	6.5×10^{-13}
(e) Question 7.17	
1150	2.0×10^{-14}
1200	3.2×10^{-14}
1250	5.0×10^{-14}
1300	7.5×10^{-14}
1350	1.0×10^{-13}

7.20 Calculate the diffusivity of ^{55}Fe in forsterite, Mg_2SiO_4, at 1150 °C: $D_0 = 4.17 \times 10^{-10}$ m^2 s^{-1}, $E = 162.2$ kJ mol^{-1}.

7.21 Calculate the diffusivity of ^{18}O in Co_2SiO_4 at 1250 °C: $D_0 = 8.5 \times 10^{-3}$ m^2 s^{-1}; $E = 456$ kJ mol^{-1}.

7.22 Calculate the diffusivity of Li in quartz, SiO_2, parallel to the c axis, at 500 °C: $D_0 = 6.9 \times 10^{-7}$ m^2 s^{-1}; $E = 85.7$ kJ mol^{-1}.

7.23 The diffusion coefficient of Ni^{2+} tracers in NiO is 1×10^{-15} m^2 s^{-1} at 1100 °C. Estimate the penetration depth of the radioactive Ni^{2+} ions into a crystal of NiO after heating for 1 hour at 1100 °C

7.24 Ge is diffused into silica glass for fibre optic light guides. How long should a fibre of 0.1 mm diameter be annealed at 1000 °C to be sure that Ge has diffused into the centre of the fibre? The diffusion coefficient of Ge in SiO_2 glass is 1×10^{-11} m^2 s^{-1}.

7.25 What is the probability of a diffusing atom jumping from one site to another at 500 °C and 1000 °C? The activation energy for diffusion is 127 kJ mol^{-1}.

7.26 Estimate the ratio of the ionic conductivity to diffusion coefficient for a monovalent ion diffusing in an ionic solid. Take a typical value for the number of mobile diffusing ions as the number of vacancies present, approximately 10^{22} defects per metre cubed, and T as 1000 K.

7.27 The ionic conductivity of F^- ions in the fast ionic conductor $Pb_{0.9}In_{0.1}F_{2.1}$ at 423 K is $1 \times 10^{-4}\ \Omega^{-1}$ m^{-1}. The cubic unit cell (*fluorite* type) has a cell parameter 0.625 nm, and there are on average, 0.4 mobile F^- anions per unit cell. Estimate the diffusion coefficient of F^- at 423 K.

7.28 The conductivity of SrO, an oxide with the *halite* (B1) structure, $a_0 = 0.5160$ nm, depends upon oxygen partial pressure. The value of the ionic conductivity is $2 \times 10^{-3}\ \Omega^{-1}$ m^{-1} at 900 °C under 0.1 atm O_2. Assuming the ionic conductivity is due to vacancy diffusion of Sr^{2+} ions, estimate the diffusion coefficient of Sr^{2+} at 900 °C.

7.29 The diffusion coefficient is often found to obey an equation of the type:

$$D = D_0 \exp\left(\frac{-E}{RT}\right)$$

Explain each of the terms D, D_0 and E in terms of atomic diffusion. [Note: answer is not provided at the end of this book.]

7.30 A plot of $\ln D$ versus $1/T$ is sometimes found to be composed of two straight-line sections, with differing slopes. Explain how this form of plot arises. [Note: answer is not provided at the end of this book.]