

5. Diffusion

Introduction

Numerous chemical reactions and microstructural changes in solids take place through solid state diffusion. In crystalline solids, the diffusion takes place because of the presence of defects; vacancies and interstitials. Diffusion also takes place along 1- and 2-dimensional defects which include dislocations, grain boundaries and surfaces. As diffusion along linear, planar and surface defects is generally faster than in the lattice, they are also termed high diffusivity or easy diffusion paths. Another frequently used term is short-circuit diffusion.

The relative contributions of the different types of diffusion in oxides and other inorganic compounds are functions of the temperature, partial pressures or activities of the constituents of the compounds, the microstructure, grain size, porosity etc. Grain boundary and dislocation diffusion generally have smaller activation energies than lattice diffusion and as a result they become increasingly important the lower the temperature in solids with a given microstructure.

In the literature on diffusion and diffusion-controlled reactions or processes one encounters many different terms that describe the diffusional behaviour under different experimental conditions: tracer and self-diffusion of atoms and ions, diffusion of defects, chemical diffusion, ambipolar diffusion, a.o. In the following chapters these phenomena and terms will be described in more detail. Here we will start out with a few simple phenomenological descriptions that will help us comprehend diffusion.

Models of diffusion

Fourier's law of heat flux

It is a well known phenomenon that heat flows from hot to cold regions. Such a flow of heat in a one-dimensional temperature gradient is described by Fourier's law

$$j_q = -\kappa \frac{dT}{dx} \quad (5.1)$$

where j_q is the heat flux density, i.e., the flow of heat per unit area of the plane through which the heat traverses per second, $\frac{dT}{dx}$ is the temperature gradient, and

κ (kappa) is the thermal conductivity. It may be noted that the minus sign reflects that the heat flows from high to low temperatures (downhill).

Fick's first law

The expression for the flow of particles from high to low concentrations is analogous to that for the flow of heat and is given by Fick's first law:

$$j = -D \frac{dc}{dx} \quad (5.2)$$

Here, j is the particle flux density, $\frac{dc}{dx}$ the concentration gradient of the particles, and D the diffusion coefficient. As in the equation for the heat flux, the minus sign reflects that the particles flow from high to low concentration of particles (downhill). This relation is named after A. Fick who first formulated this relation. The particle flux and gradient is illustrated schematically in Figure 5-1.

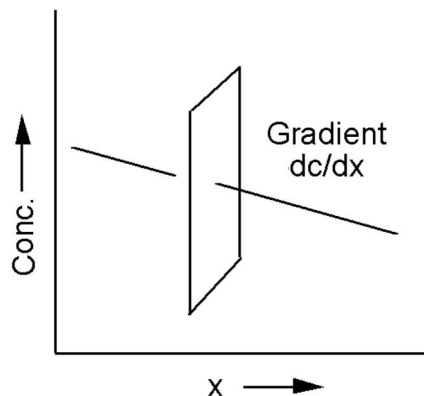


Figure 5-1. Schematic illustration of Fick's first law. The negative of the particle concentration gradient is the "driving force" of the diffusion.

j represents the number (or moles) of particles crossing a unit area (cm^2 or m^2) per unit time (seconds). If the concentration of particles is expressed in number of particles (or moles) per cm^3 and the distance x in cm , the diffusion coefficient D has the dimension cm^2s^{-1} . In SI units the concentration is expressed in number per m^3 and the diffusion coefficient has the dimension m^2s^{-1} .

In Fick's first law in Eq. (5.2) the negative particle gradient, $-\frac{dc}{dx}$, may be considered to be an expression of the "driving force" for the particle flux. The larger the concentration gradient, the larger the particle flux. When Fick's first law is applied to uncharged (neutral) and independently diffusing particles, it is valid in the sense that the coefficient is a constant (independent of concentration and gradient). This may apply e.g. to dilute solutions of neutral defects in solids. Such

defects may be vacancies, interstitials, and impurities in metals. In ionic solids they may comprise neutral interstitial impurities, homovalent substituents, or isotopic species. The applicability or inapplicability of Fick's first law will become clearer later in this chapter and in the forthcoming chapters.

Potential gradients as the driving force

More generally, the driving force for the diffusion constitutes the chemical potential gradient of the particles that diffuse (provided that no other forces act on the particles). Correspondingly, the driving force for the transport of electrical charges is the electrical potential gradient. In the following is given a brief derivation of Fick's first law using a potential gradient as the driving force, in detail in the case of a chemical potential gradient.

Let us consider the transport of particles of type "i" across a plane under a driving force F . The particle flux density through a plane is given by the product of the volume concentration c_i of the particles at the plane and the average migration or drift velocity v_i of the particles, e.g.

$$j_i \text{ (number of particles cm}^{-2} \text{ s}^{-1}\text{)} = c_i \text{ (number of particles cm}^{-3}\text{)} \cdot v_i \text{ (cm s}^{-1}\text{)} \quad (5.3)$$

For uncorrelated movements the drift velocity v_i of a particle is proportional to the driving force F_i exerted on the particle:

$$v_i = B_i F_i \quad (5.4)$$

The proportionality factor B_i is termed the mobility ("Beweglichkeit") of the particles and is defined as the average drift velocity per unit driving force. It is often referred to as mechanical mobility to differentiate it from other types of mobility. It basically says something about how easy it is to move the particle.

The driving force is, in turn, given by the negative of the potential gradient normal to the cross-sectional area in the plane

$$F_i = -\frac{dP_i}{dx} \quad (5.5)$$

where P is a potential. The negative sign is, as above, due to the fact that the transport takes place from higher to lower values of P , see Figure 5-2.

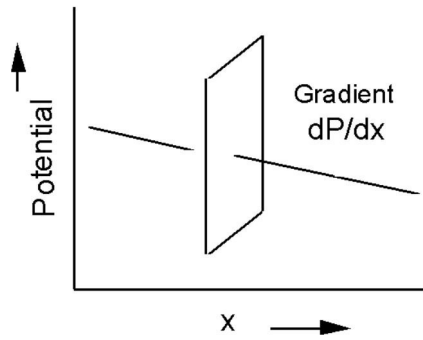


Figure 5-2. Schematic illustration of flux through a plane in a potential gradient.

When one combines Eqs. 5.3 - 5.5, the particle flux density becomes

$$j_i = c_i v_i = -c_i B_i \frac{dP_i}{dx} \quad (5.6)$$

Chemical potential gradient acting on neutral particles

If the particle moves in a chemical potential gradient, the potential P equals the chemical potential of particles of type i : $P_i = \mu_i$. Equation 5.6 then takes the form

$$j_i = c_i v_i = -c_i B_i \frac{d\mu_i}{dx} \quad (5.7)$$

The chemical potential μ_i is related to the chemical activity a_i of species i through

$$\mu_i = \mu_i^o + kT \ln a_i \quad (5.8)$$

If ideal conditions can be assumed, the activity can be expressed by the concentration divided by the concentration in the reference (standard) state:

$$a_i = \frac{c_i}{c_i^o} \quad (5.9)$$

and the chemical potential gradient is then given by

$$\frac{d\mu_i}{dx} = kT \frac{d \ln c_i}{dx} = \frac{kT}{c_i} \frac{dc_i}{dx} \quad (5.10)$$

When one substitutes the expression for the chemical potential gradient in Eq. 5.7, the particle flux density becomes

$$j_i = -c_i B_i \frac{d\mu_i}{dx} = -B_i kT \frac{dc_i}{dx} \quad (5.11)$$

$B_i kT$ is termed the diffusion coefficient D_i of particles i :

$$D_i = B_i kT \quad (5.12)$$

By combination with Eq. 5.12, Eq. 5.11 takes the form of Fick's first law as given in Eq. 5.2:

$$j_i = -D_i \frac{dc_i}{dx} \quad (5.2)$$

It is important to realise that Fick's 1st law, Eq. 5.2, is fully valid only for ideal cases of diffusion of neutral particles in chemical potential gradients. If the particles are charged, we need to take into account both the electrical potential gradient and requirements to the combination of fluxes to maintain a given total current and electroneutrality. These cases will be treated later on.

In the following, ideal conditions will be assumed and concentrations will be used for activities of atoms, ions and various types of defects. But it should be recalled that this always represents an approximation.

Simplified model for one-dimensional diffusion

Following Eq.5.2 the diffusion coefficient represents the proportionality constant between the particle flux and the concentration gradient. In order to describe the process of diffusion of particles or atoms in solids we need to realise that the diffusion represents the sum of a large number of particles or atoms that each make a large number of jumps. We will therefore attempt to describe the diffusion coefficient in terms of the number of jumps per unit time (the jump frequency) and the distance that each particle or atom moves in each jump.

For this purpose let us consider a simplified one-dimensional model where particles jump between parallel planes separated by a distance s as illustrated in Figure 5-3. The two neighbouring planes under consideration are termed plane 1

and 2. The number of particles per unit area in plane 1 and 2 is termed n_1 and n_2 , respectively. Let us further assume that $n_1 > n_2$.

Consider now that the particles in plane 1 and 2 may jump from one plane to a neighbouring plane at a jump frequency Γ (gamma). The particles in plane 1 have an equal probability of jumping to plane 2 and to the neighbouring plane in the opposite direction. The total number of particles jumping out of a unit area of plane 1 per unit time is equal to the product of number of particles per unit area times the jump frequency: $n_1\Gamma$. As the particles may jump in opposite directions, the number of particles jumping from plane 1 to 2 is given by $\frac{1}{2} n_1\Gamma$. Correspondingly, the number of particles jumping from unit area of plane 2 to plane 1 is given by $\frac{1}{2} n_2\Gamma$. The difference in the jump rates is equal to the net flux density of particles:

$$j = \frac{1}{2}(n_1 - n_2)\Gamma \quad (5.13)$$

As all particles have the same jump frequency, there is a net flow of particles from plane 1 to 2 because there are more atoms per unit area in plane 1 than in plane 2.

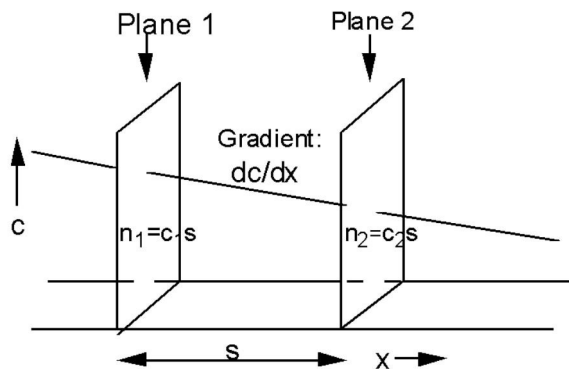


Figure 5-3. Schematic illustration of simplified model for one-dimensional diffusion

The number of particles n_1 belonging to unit area of plane 1 is given by the volume concentration at plane 1, c_1 , times the extension in the x direction, i.e., the plane separation s :

$$n_1 = c_1s \quad \text{and} \quad n_2 = c_2s \quad (5.14)$$

By combining Eqs.5.13 and 5.14 the particle flux density becomes

$$j = \frac{1}{2}(c_1 - c_2)s\Gamma \quad (5.15)$$

The concentration gradient normal to the planes is termed $\frac{dc}{dx}$. The relation between c_1 and c_2 can then be expressed by seeing that a difference is equal to the gradient times the length;

$$c_2 - c_1 = s \frac{dc}{dx} \quad (5.16)$$

By insertion of this into Eq. 5.15 we obtain

$$j = -\frac{1}{2} s^2 \Gamma \frac{dc}{dx} \quad (5.17)$$

This expression applies to one-dimensional diffusion of particles, and the factor $\frac{1}{2}$ reflects that only half of all jumps occur in the direction we consider as the flux direction.

If the diffusion can take place in the three orthogonal directions, only one third of the particles jump in one direction, and in the three-dimensional case the net flux in one direction is $\frac{1}{3}$ of the flux of that when all atoms jump in one direction only:

$$j = -\frac{1}{6} s^2 \Gamma \frac{dc}{dx} \quad (5.18)$$

By comparing with Fick's first law, Eq. 5.2, it is seen that the diffusion coefficient D in the three-dimensional case is given by

$$D = \frac{1}{6} s^2 \Gamma \quad (5.19)$$

If we consider a large number of jumps, n , which occurs during the time t , then

$$\Gamma = \frac{n}{t} \quad (5.20)$$

and inserting this in Eq.5.19, one obtains

$$ns^2 = 6Dt \quad (5.21)$$

The expression for the diffusion coefficient in Eqs. 5.19 and 5.21 provides a qualitative description of how far diffusion proceeds. By way of example, the diffusion coefficient for interstitial diffusion of oxygen atoms in niobium metal at 800 °C is approximately $D = 7 \cdot 10^{-8} \text{ cm}^2 \text{ s}^{-1}$. The jump distance can be assumed to be 1.65 Å ($1.65 \cdot 10^{-8} \text{ cm}$), and then from Eq. 5.19 the jump frequency Γ is about $1.54 \cdot 10^9 \text{ s}^{-1}$. Thus, each oxygen atom makes a tremendously large number of jumps per second. But it should then also be recalled that the atoms vibrate with a (Debye) frequency of $10^{12} - 10^{13} \text{ s}^{-1}$, and thus only a small fraction - about 1 in 1000 or 10,000 - of the vibrations leads to a jump. We shall consider this in more detail when the different atomistic mechanisms are treated below.

Although the number of jumps is very large, the mean displacement of each atom is relatively small – most of the time it moves back and forth. In the diffusion process it is not possible to observe the individual jumps of the atoms, and it is necessary to find a relation between the individual atom jumps for large number of atoms and the diffusion phenomena which may be observed on a macroscopic scale. The problem is to find how far a large number of atoms will move from their original sites after having made a large number of jumps. Such relations may be derived statistically by means of the so-called random walk approach.

Random diffusion

Let us consider that the jumps of the atoms are random, i.e. that the jumps of the atoms are independent of all the previous jumps and can occur in all directions. In that case the displacement of a diffusing atom from the starting point after n number of jumps, R_n , is given by the algebraic sum of the individual jump vectors:

$$\vec{R}_n = \vec{s}_1 + \vec{s}_2 + \dots + \vec{s}_n = \sum_{j=1}^n \vec{s}_j \quad (5.22)$$

If the individual jumps take place with equal probability in all directions and the individual jump distances are equal, this algebraic sum equals zero. This does not mean that the diffusing atom remains at its starting point after n jumps, but only that jumps in "positive" and "negative" directions are equally probable. In fact the total displacement may have any value between zero and $\pm ns$.

In order to obtain a value for the magnitude (length) of the sum vector, one squares Eq. 5.22:

$$R_n^2 = \vec{R}_n \cdot \vec{R}_n = \sum_{j=1}^n \vec{s}_j \cdot \vec{s}_j + 2 \sum_{j=1}^{n-1} \sum_{k=j+1}^n \vec{s}_j \cdot \vec{s}_k \quad (5.23)$$

If, as above, the individual jump vectors are equal, i.e., $|s_1| = |s_2| \dots |s_j| = s$, as, for instance, in crystals with cubic symmetry, and if they are random and uncorrelated, then the second term on the right hand side of the equality sign in Eq. 5.23 will approach zero for large numbers of jumps, as on an average s_j and s_k have an equal chance of being positive and negative. The first term on the right hand side, on the other hand, is always non-zero and positive, and thus represents the average displacement length for a large number of jumps:

$$R_n^2 = \sum_{j=1}^n \overrightarrow{s_j}^2 = ns^2 \quad (5.24)$$

The mean displacement is given by the square root of R_n^2 and is termed the root mean square displacement:

$$\overline{R_n} = \sqrt{R_n^2} = \sqrt{n} s \quad (5.25)$$

From this it is seen that the mean displacement is proportional to the square root of the number of jumps times the individual jump distance. Figure 5-4 illustrates the relationship between individual jumps and total displacement.

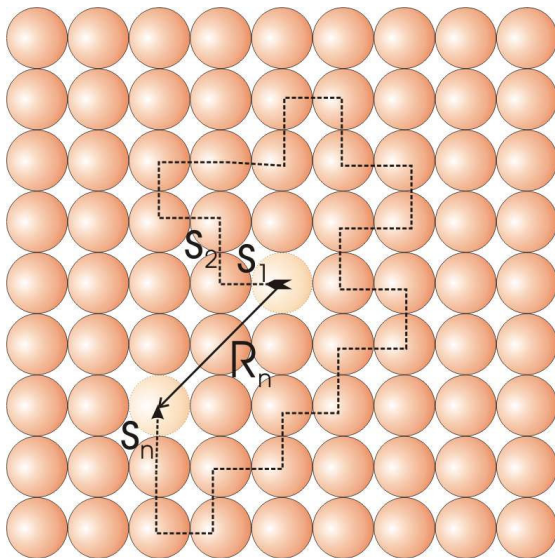


Figure 5-4. Random diffusion by n jumps each of distance s gives a long travelled distance s_n but a relatively short displacement R_n from the starting point.

By combining Eqs. 5.21 and 5.24 we may express the random diffusion in terms of the diffusion coefficient we dealt with in diffusion down a concentration gradient in the 3-dimensional cubic case:

$$R_n^2 = ns^2 = 6D_r t \quad (5.26a)$$

$$R_n = \sqrt{6D_r t} \quad (5.26b)$$

where t is the time during which the mean-square-displacement takes place. One may note that we have now started terming the diffusion coefficient D_r (r for random walk). R_n is the radius of the sphere that a diffusing atom on average will distance itself by from the starting point after time t .

Let us now consider the displacement in a single dimension (e.g. the x-direction) as a result of this three-dimensional displacement in the cubic case. From simple geometry we have $R_n^2 = 3x^2$ where x^2 is the mean square displacement in each orthogonal direction. Thus, the mean diffusion length in one direction in a three-dimensional cubic crystal is:

$$x = \sqrt{2D_r t} \quad (5.27)$$

This length is thus shorter than the displacement radius, since displacements in the y and z directions are “wasted” for displacement in the x direction.

As described above and using oxygen diffusion in niobium as an example, the oxygen atoms on an average exchange positions approximately $1.54 \cdot 10^9$ times per second at 800 °C. From the same considerations one may also estimate that an oxygen atom has randomly covered total jump distances of 25.4 cm and 914.7 m after 1 second and 1 hour, respectively. But what is the mean displacement? From Eq 5.27 one may estimate that the one-dimensional root-mean-square displacement after 1 hour only amounts to 0.022 cm. Thus, the mean displacement is very small and on an average the oxygen atoms spend most of their time jumping “back and forth”.

What we did above was to consider random jumps, and then we related jumps, times and distances to a term we recognised from earlier, namely the diffusion coefficient, and we named it the random diffusion coefficient D_r . The diffusion coefficient was in turn something we recognised – while considering diffusion down a one-dimensional concentration gradient – from Fick’s first law. One should note, however, that random diffusion and the random diffusion coefficient can be considered and expressed and quantified also in the absence of a concentration gradient and also for charged particles.

As will be described below, diffusion is often measured by using tracer atoms and one then obtains values of the diffusion coefficient of the tracer atoms. Depending on the diffusion mechanism the tracer diffusion is in most cases not completely random, but is to some extent correlated with previous jumps. This will be further discussed later on.

Fick's second law

As described above, Fick's 1st law assumes a fixed concentration gradient across the plane through which the flux of particles take place. But in numerous practical cases the concentration and concentration gradient changes with time. Such cases are covered by Fick's 2nd law. This is shown schematically in Figure 5-5 which illustrates the change in the concentration gradient through the solid. As shown in the figure let us consider a region within a solid, enclosed between planes separated by the distance dx . The net particle flux density from the region of higher concentration into dx is j_1 and the net particle flux density out of dx towards lower concentration is j_2 . When j_1 is greater than j_2 the particle concentration in dx increases with time. This requires that the concentration gradient in plane 1 is larger than in plane 2, since Fick's 1st law applies in both planes (and at any position) at any time. The process is illustrated in Figure 5-5.

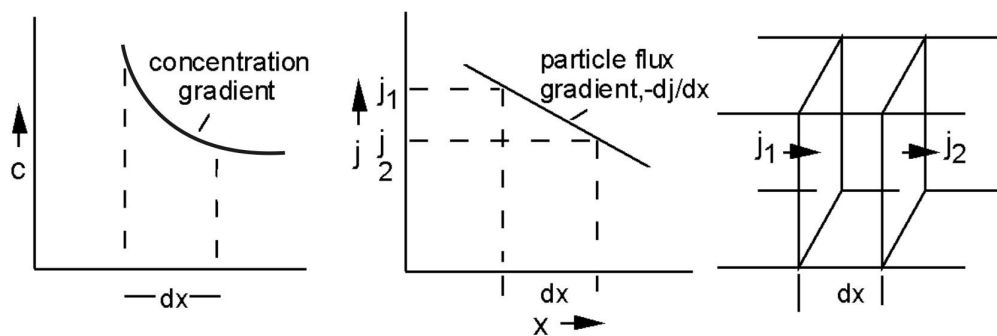


Figure 5-5. Schematic illustration of Fick's 2nd law; the concentration gradient changes with time.

The change in concentration per unit time at any position is proportional to the gradient in flux at that position

$$\frac{\partial c}{\partial t} = -\frac{\partial j}{\partial x} \quad (5.28)$$

Although the concentration and concentration gradient change with time, Fick's 1st law is valid at any one time and position and thus

$$\frac{\partial c}{\partial t} = -\frac{\partial j}{\partial x} = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right) \quad (5.29)$$

If D can be considered to be independent of concentration then

$$\frac{\partial c}{\partial t} = -\frac{\partial j}{\partial x} = D \frac{\partial^2 c}{\partial x^2} \quad (5.30)$$

The intuition of the qualitative arguments as well as the double derivative of the concentration in Eq. 5.30 tell us that particles will flow from convex to concave regions in terms of distribution of particles.

Equations 5.29 and 5.30 are representations of Fick's 2nd law. It may be solved explicitly under certain boundary conditions that may be closely approximated experimentally (Crank 1956). A couple of examples of this are given in the following.

Measurements of diffusion coefficients by tracer techniques

The use of isotopes or tracers is a common means of studying diffusion. Tracer methods permit measurements of self-diffusion, that is, the diffusion of the crystal components in a crystal. Furthermore, they allow measurements of diffusion in homogenous materials, that is, without imposing chemical gradients (when one disregards the difference in atomic weight between atoms in the crystal and of the tracer).

A common technique is to deposit a very thin film of radioactive isotopes on a plane surface of a sample, and, after subsequent diffusion anneal, determine the activity of diffusion species as a function of distance from the plane surface. If the thickness of the sample is very much larger than the penetration depth of the tracers, the solid can be considered semi-infinite. Furthermore, if the diffusion is homogenous (e.g. taking place by lattice diffusion), the concentration of the diffusing tracers normal to the plane is through solution of Fick's second law with appropriate boundary conditions given by

$$c(x) = \frac{c_0}{2(\pi D_t t)^{1/2}} \exp\left(-\frac{x^2}{4D_t t}\right) \quad (5.31)$$

c is the activity (or concentration) of the tracer at a distance x from the surface, c_0 is the activity originally present on the surface, and t is time of the diffusion anneal. D_t is the tracer diffusion coefficient. Following Eq.5.31 it is determined by plotting $\ln c$ vs x^2 , in which case the resultant straight line has the slope $-\frac{1}{4D_t t}$.

Plots of c vs x and of $\ln c$ vs x^2 according to Eq.5.31 are illustrated in Figure 5-6a and b, respectively. At the point where the activity is half of the activity at the surface, then $x = \sqrt{2.77D_t t}$. This distance corresponds approximately to the root-mean-square penetration distance (Eq. 5.27).

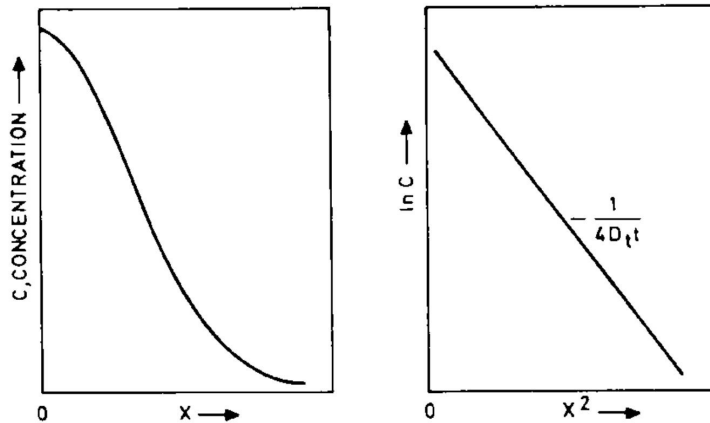


Figure 5-6. Graphical presentation of relationship between activity, c , and penetration distance, x , (Eq.5.31) for homogeneous diffusion of tracer initially deposited as a thin film on the surface the solid. a) c vs. x ; b) $\ln c$ vs. x^2 .

An alternative way of performing the experiment is to have a constant surface composition of the diffusing species. By solving Fick's second law under proper boundary conditions the penetration of the diffusing species is then described by the relationship

$$\frac{c - c_0}{c_s - c_0} = 1 - \operatorname{erf} \frac{x}{2(D_t t)^{1/2}} \quad (5.32)$$

where c is the concentration of the diffusing species at penetration distance x at time t , c_s is the constant surface concentration, and c_0 is the original concentration in the solid. D_s is the diffusion coefficient of the diffusing species. Figure 5-7 shows a graphical penetration of the diffusion profile according to Eq.5.32 in a case where $c_0 = 0$. It may be noted that at the point where $\frac{c - c_0}{c_s - c_0} = 1/2$, that is, at the point where the concentration of the diffusing species is midway between the surface composition and the original composition, then $x/\sqrt{D_t t} = 0.954$. Thus at this point $x \sim \sqrt{D_t t}$.

It may be noted that Eqs. 5.31 and 5.32 involve the dimensionless parameter $x/(2\sqrt{D_t t})$, and accordingly the penetration and the amount of the diffusing species dissolving in the solid are proportional to the square root of time.

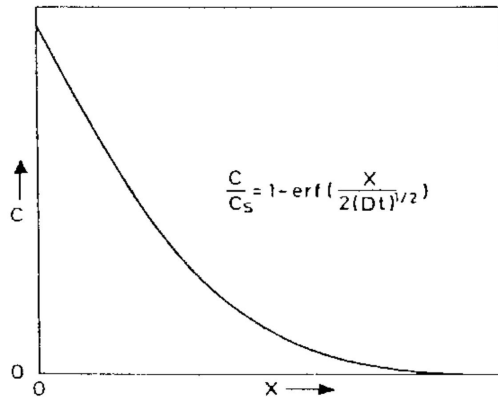


Figure 5-7. Graphical presentation of diffusion profile when the surface concentration of the diffusing species remains constant with time. It is assumed that $c_0=0$ (Eq.5.32).

The penetration by the diffusing species may be measured by means of the so-called sectioning method, that is cutting, grinding or etching off thin sections of layers of the sample parallel to the plane surface and subsequently determining the concentration of the diffusing species in each section. By cutting the specimen normal to or at an angle to the plane surface, the penetration of radioactive tracers may also be measured by means of so-called autoradiography.

Electron microprobe analysis and secondary ion mass spectroscopy (SIMS) combined with sputtering techniques also provide excellent tools for studying penetration and diffusion of foreign ions. As oxygen does not have a radioactive isotope suitable for tracer studies, SIMS is particularly useful for studying oxygen diffusion employing the stable ^{18}O isotope.

In the isotope exchange method the vapour of the diffusing component surrounding the sample is enriched with either a radioactive or an inactive isotope, and the diffusion is measured by following the exchange of the isotope with the sample. The diffusion coefficient may be evaluated if diffusion is the slower process and processes at the surface are rapid. Alternatively, the sample itself may be isotopically enriched, and the increase in concentration of the isotope in the vapour phase may be measured.

Diffusion rates may, in principle, also be determined from any property or reaction which depends on atomic mobility. By way of illustration, ionic conductivity of the anion is directly proportional to the anion diffusion coefficient (see Ch. 6 Electrical conductivity). From high temperature solid state reactions, sintering, oxidation of metals etc. diffusion coefficients may be evaluated provided the detailed mechanism of the processes are known. Examples of this will be given in Ch. 7.

Diffusion mechanisms

Lattice diffusion takes place through the movement of point defects. The presence of different types of defects gives rise to different mechanisms of

diffusion. These are illustrated schematically for elemental solids in the following descriptions. But they also apply to metal oxides and other inorganic compounds when the diffusion is considered to take place in the sublattices of the cations or anions.

Vacancy mechanism

The diffusion is said to take place by the vacancy mechanism if an atom on a normal site jumps into an adjacent unoccupied lattice site (vacancy). This is illustrated schematically in Figure 5-8. It should be noted that the atoms move in the direction opposite the vacancies.

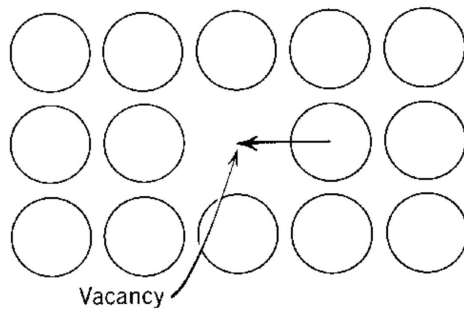


Figure 5-8. Schematic illustration of vacancy diffusion in solids.

Interstitial mechanism

If an atom on an interstitial site moves to one of the neighbouring interstitial sites, the diffusion occurs by an interstitial mechanism. This is schematically shown in Figure 5-9. Such a movement or jump of the interstitial atom involves a considerable distortion of the lattice, and this mechanism is probable when the interstitial atom is smaller than the atoms on the normal lattice positions. Diffusion of interstitially dissolved light atoms, e.g. H, C, N, and O in metals provides the best known examples of this mechanism.

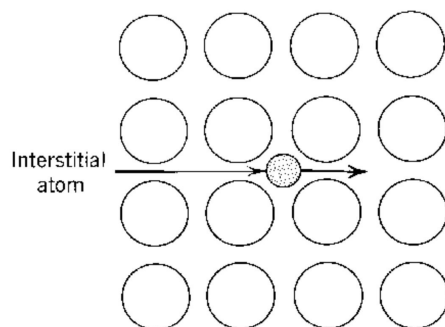


Figure 5-9. Schematic illustration of interstitial diffusion in solids.

Oxides with close-packed oxygen lattices and only partially filled tetrahedral and octahedral sites may also facilitate diffusion of metal ions in the unoccupied, interstitial positions. Finally, even large anions may diffuse interstitially if the anion sublattice contains structurally empty sites in lines or planes which may serve as pathways for interstitial defects. Examples are rare earth sesquioxides (e.g. Y_2O_3) and pyrochlore-type oxides (e.g. $\text{La}_2\text{Zr}_2\text{O}_7$) with fluorite-derived structures and brownmillerite-type oxides (e.g. $\text{Ca}_2\text{Fe}_2\text{O}_5$) with perovskite-derived structure.

Interstitialcy mechanism

If the distortion becomes too large to make the interstitial mechanism probable, interstitial atoms may move by another type of mechanism. In the interstitialcy mechanism an interstitial atom pushes one of its nearest neighbours on a normal lattice site into another interstitial position and itself occupies the lattice site of the displaced atom. This mechanism is illustrated schematically in Figure 5-10.

In the interstitialcy mechanism one may distinguish between two types of movements. If the atom on the normal lattice site is pushed in the same direction as that of the interstitial atom, the jump is termed collinear (Figure 5-10). If the atom is pushed to one of the other neighbouring sites so that the jump direction is different from that of the interstitial atom, the jump is termed non-collinear.

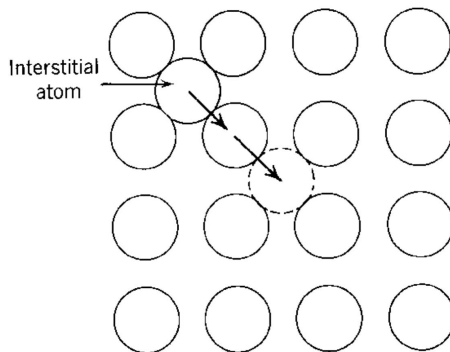


Figure 5-10. Schematic illustration of interstitialcy diffusion in solids. Collinear jump.

Other mechanisms.

In elemental solids also other mechanisms have been proposed. The “crowdion” is a variant of the interstitialcy mechanism. In this case it is assumed that an extra atom is crowded into a line of atoms, and that it thereby displaces several atoms along the line from their equilibrium positions. The energy to move such a defect may be small, but it can only move along the line or along equivalent directions.

For metals it has also been proposed that diffusion may take place through a so-called ring mechanism, but this mechanism is less probable in most oxides or other inorganic compounds. A particular feature of this mechanism is that it can

involve exchange of sites and thus would contribute to tracer diffusion, but that it would not lead to net transport of atoms in any direction. If the atoms were charged (ions) this would then not give rise to net charge transport.

Diffusion of protons in metal oxides.

Protons that dissolve in metal oxides associate with the oxide ions and form hydroxide ions. As the proton has no electron shell, it interacts strongly with the electron cloud of the oxide ion, and in its equilibrium position in the hydroxide ion it is embedded in the valence electron cloud. The O-H bond that is formed has a bond length less than 100 pm; this may be compared with the ionic radius of 140 pm of the oxide ion.

In principle the protons may move by two different mechanisms: i) the free transport mechanism, which is also alternatively termed the Grotthuss mechanism or ii) the vehicle mechanism.

The free transport is the principal mode of transport of protons in oxides, and in this mechanism protons jump from one oxide ion to a neighbouring one. After each jump the proton in the hydroxide rotates such that the proton reorients in the electron cloud and becomes aligned for the next jump. This is illustrated schematically in Figure 5-11. The rotation and reorientation is believed to involve a small activation energy and the jump itself is considered to be the rate-determining step.

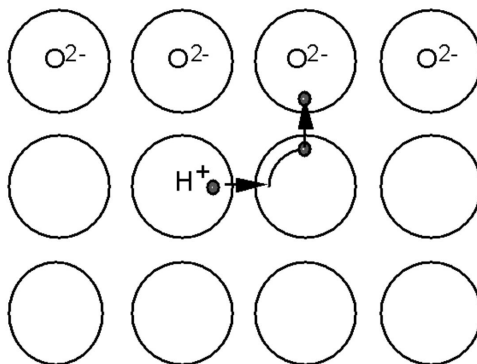


Figure 5-11. Schematic illustration of free transport of protons in metal oxides (Grotthuss mechanism).

In the vehicle mechanism the proton is transported as a passenger on an oxide ion. Thus this mechanism may be considered to constitute transport of hydroxide ions. The hydroxide ion may in principle move by an oxygen vacancy mechanism or as an interstitial hydroxide ion. It may be noted that the hydroxide ion has a smaller radius and charge than the oxide ion and may as such be expected to have a smaller activation energy for diffusion than the oxide ion. Also other species such as water molecules and hydronium ions, H_3O^+ , may serve as vehicles for protonic diffusion, notably in relatively open structures.

Factors that affect the diffusion coefficient in crystalline solids

In Eq. 5.19 we saw that the random diffusion coefficient can be expressed in terms of the jump distance and the number of jumps per unit time:

$$D_r = \frac{1}{6} s^2 \Gamma = \frac{1}{6} s^2 \frac{n}{t} \quad (5.19)$$

We will now further characterise D_r in different crystal structures (lattices or sub-lattices) and subsequently derive expressions for the temperature and oxygen pressure dependence of diffusion in metal oxides.

Vacancy diffusion

Let us consider vacancy diffusion in an elemental solid or in a cation or an anion sub-lattice. The jump frequency (number of jumps per unit time) Γ depends on several factors. First, it depends on the frequency of sufficiently energetic jump attempts ω towards an adjacent site. Furthermore, it is also proportional to the number of adjacent sites Z to which the atom may jump, i.e., the number of nearest neighbour positions of the atom. Finally, the atom may only jump if a vacancy is located on an adjacent site, and this probability is given by the fraction (concentration) of vacancies in the crystal, N_d . Thus, Γ is in this case given by

$$\Gamma = \omega Z N_d \quad (5.33)$$

In crystalline solids the jump distance is a function of the crystal structure and may be expressed as a function of the lattice parameter.

In a body centered cubic (bcc) crystal of an elemental solid, for instance, each atom has 8 nearest-neighbour positions or atoms, and thus in this case $Z = 8$. From simple geometrical considerations of the crystal structure it may further be shown that the jump distance is given by $s = a_0 \frac{\sqrt{3}}{2}$, where a_0 is the lattice parameter. When inserting these values of Z and s in Eqs. 5.33 and 5.19 one obtains

$$D_r = a_0^2 \omega N_d \quad (5.34)$$

In general, D_r for a cubic structure is written

$$D_r = \alpha a_0^2 \omega N_d \quad (5.35)$$

where α is a geometrical factor involving the factor 1/6 (from Eq. 5.21), the factor Z from Eq. 5.33 and the relation between the jump distance and the lattice parameter. For vacancy diffusion in a bcc lattice α is thus equal to unity. From the same considerations it may also be shown that $\alpha = 1$ for vacancy diffusion in fcc lattices.

Interstitialcy diffusion

Consider an atom on a normal lattice site of a cation or anion sub-lattice. If this atom is to move by the interstitialcy mechanism, an atom on a nearest neighbour interstitial site has to push the atom on the normal site to a neighbouring interstitial site. Thus for this diffusion mechanism an atom may only diffuse when it has an interstitial atom on a neighbouring site, and as for vacancy diffusion the diffusion coefficient of the atoms is proportional to the fraction (concentration) of defects, in this case interstitial atoms or ions in the sub-lattice.

Interstitial diffusion

When one considers interstitial diffusion of an interstitially dissolved foreign species in dilute solid solution, essentially all the nearest neighbour interstitial sites of the same type are unoccupied and available for occupancy by the diffusing interstitial atoms. Thus the interstitial atom may jump to any of the nearest neighbour interstitial sites and in this case N_d is equal to unity. The diffusion coefficient of the interstitially dissolved foreign species is then given by

$$D_r = \frac{1}{6} s^2 Z \omega \quad (5.36)$$

As mentioned above the best known examples of this mechanism is diffusion of O, N, C, and H atoms interstitially dissolved in metals. By way of example oxygen and nitrogen atoms in bcc metals, e.g. in the group 5 metals V, Nb, and Ta, occupy octahedral sites, and in this case each interstitial atom has 4 nearest neighbour octahedral sites to which they may jump, thus $Z=4$. Furthermore, the jump distance s is equal to $\frac{a_0}{2}$. Inserting these values in Eq. 5.36 the diffusion coefficient for interstitial diffusion between octahedral sites in a bcc lattice becomes

$$D_r = \frac{1}{6} a_0^2 \omega \quad (5.37)$$

Thus in this case $\alpha=1/6$.

Temperature and oxygen pressure dependence of diffusion in metal oxides

We will now address how diffusion coefficients vary with temperature and activity of the components of the compound, mainly the oxygen partial pressure over oxides. In order to evaluate these dependencies one must consider the temperature and activity dependencies of N_d (e.g. cf. Eq.5.35) and the temperature dependence of ω . We start by analysing N_d for some cases.

Dependencies related to the concentration of defects

Vacancies in an elemental solid

For the sake of simplicity let us first consider the case of diffusion by a vacancy mechanism in a pure elemental solid. The diffusing atoms may only make a jump when a neighbouring site is vacant. Thus the jump frequency n/t is proportional to the vacancy concentration and as described in Chapter 3 the fraction of vacancies may be written

$$N_d = \exp\left(\frac{-\Delta G_d}{RT}\right) = \exp\left(\frac{\Delta S_d}{R}\right) \exp\left(\frac{-\Delta H_d}{RT}\right) \quad (5.38)$$

where ΔG_d , ΔS_d , and ΔH_d denote the Gibbs energy, entropy, and enthalpy of formation of the defects – here vacancies. In elemental solids ΔH_d is positive and the vacancy concentration increases with increasing temperature.

Vacancies in an oxygen deficient oxide.

In a nonstoichiometric oxide the concentration of the predominating point defects will be a function of temperature but also of the oxygen pressure. By way of illustration, let us consider an oxygen deficient oxide, $M_aO_{b-\delta}$, in which doubly charged oxygen vacancies are the predominating point defects. If intrinsic ionisation and effects of impurities can be neglected, the concentration of the oxygen vacancies is as described in previous chapters (Eq. 3.57) given by

$$N_d = [v_o^{\bullet\bullet}] = \left(\frac{1}{4}K'_{vo}\right)^{1/3} p_{O_2}^{-1/6} = \left(\frac{1}{4}K'_{vo}\right)^{1/3} \exp\left(\frac{-\Delta H_{vo}^0}{3RT}\right) p_{O_2}^{-1/6} \quad (5.39)$$

where K'_{vo} represents the equilibrium constant for the formation of doubly charged oxygen vacancies, and ΔH_{vo}^0 the enthalpy of formation.

In such an oxide the oxygen vacancy concentration may also be determined by the presence of dopants or a sufficiently large level of impurities with negative effective charge. If the dopant is doubly negatively charged (as, for instance, Ca^{2+} , an acceptor dopant, in ZrO_2), then

$$[v_o^{\bullet\bullet}] = [A_M^{\prime\prime}] \quad (5.40)$$

In this case $[v_o^{\bullet\bullet}]$ will be independent of oxygen pressure and most often temperature (see Chapter 4).

In a similar manner one may obtain the temperature and oxygen pressure dependencies of the concentration of any defect (majority or minority) when the defect structure is known. Of course the concentrations of acceptors or donors will enter when they dominate the defect situation and the water vapour partial pressure may enter when protons are dominating defects.

Temperature dependence of the frequency of sufficiently energetic jump attempts ω

When atoms jump or move between definite sites in the crystal, they have to surmount energy barriers. A large part of this energy barrier involves the strain energy required to displace neighbouring atoms to create a sufficiently large opening between the atoms to permit the atom jump. The potential energy of the atom diffusing from one site to another may be qualitatively illustrated as shown in Figure 5-12. The potential barrier height is ΔH_m and represents the activation energy which the atom has to surmount during the jump. Each atom vibrates in its position, and only during a fraction of time given by the Boltzmann distribution factor $\exp(-\Delta H_m/RT)$, it possesses sufficient energy to overcome the energy barrier. The frequency of sufficiently energetic jump attempts is thus proportional to $\exp(-\Delta H_m/RT)$.

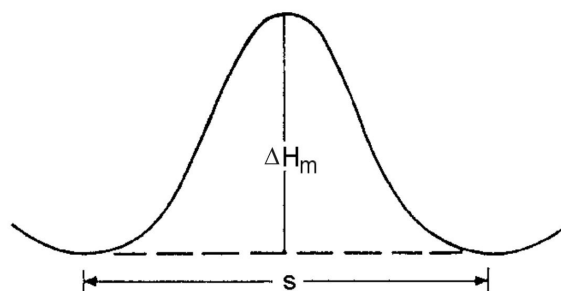


Figure 5-12. Potential energy of atom diffusing in a solid. ΔH_m is the activation enthalpy.

A more complete analysis based on the theory of activated complexes and on statistical mechanics has been given by Zener (1951,1952). He considered the

system or an atom in its initial equilibrium condition and in the activated state at the top of the potential barrier which separates the initial position from its neighbouring equilibrium position. The rate of transition from one equilibrium site to another is given by

$$\omega = \nu \exp \frac{-\Delta G_m}{RT} = \nu \exp \frac{\Delta S_m}{R} \exp \frac{-\Delta H_m}{RT} \quad (5.41)$$

where ΔG_m , ΔS_m , and ΔH_m represent the Gibbs energy, entropy and enthalpy change, respectively, connected with the movement of the atom from the equilibrium position to the top of the potential barrier and ν (“*nu*”) represents the vibration frequency. ν is often assumed to equal the Debye frequency, i.e. about 10^{13} Hz, as an order of magnitude approximation. ΔS_m is often assumed to be a small, positive term (below, say, 10 J/molK).

As a more detailed analysis of ν , Zener suggested that ν may be approximated as $\nu = \alpha/a \cdot \sqrt{\Delta H_m / M}$, where α is a structure- and mechanism-dependent factor, a is a lattice parameter, and M is the reduced mass of the oscillator. Intuitively, a particle vibrating in an energy valley will vibrate faster (ν increases) when the walls become steeper (ΔH_m increases). One may also view the particle as vibrating on a spring; the frequency becomes higher when the spring is shorter (α/a decreases), when the spring is stiffer (ΔH_m increases) or the particle becomes lighter (M decreases). Thus, the temperature-independent (pre-exponential) term in the diffusion coefficient increases when ΔH_m increases, so that the two tend to counteract each other. Experimental observations of this is sometimes referred to as the Meyer-Neldel effect (Meyer and Neldel (1937)).

Resulting analysis of the diffusion coefficient D_r

Vacancy diffusion in an elemental solid.

From Eq. 5.35 it is seen that the temperature dependence of D_r for vacancy diffusion in an elemental solid is determined by that of N_d and ω . For an elemental solid with cubic structure, D_r is thus obtained by combining Eqs. 5.35, 5.38 and 5.41:

$$D_r = \alpha a_0^2 \nu \exp \frac{\Delta S_d + \Delta S_m}{R} \exp \frac{-(\Delta H_d + \Delta H_m)}{RT} \quad (5.42)$$

Experimentally determined values of diffusion coefficients are usually obtained as

$$D = D_0 \exp \frac{-Q}{RT} \quad (5.43)$$

where Q is termed the activation energy and D_0 the pre-exponential factor. By comparing Eqs. 5.42 and 5.43 it is seen that the activation energy, Q , in this case comprises

$$Q = \Delta H_d + \Delta H_m \quad (5.44)$$

Correspondingly, D_0 is given by

$$D_0 = \alpha a_0^2 \nu \exp \frac{\Delta S_d + \Delta S_m}{R} \quad (5.45)$$

If experiments are carried out under such conditions that the concentration of defects, N_d , is constant and independent of temperature, e.g. at sufficiently low temperatures that the defect concentration is frozen in, then D_r is given by

$$D_r = \alpha a_0^2 \nu N_{d, \text{frozen}} \exp \frac{\Delta S_m}{R} \exp \frac{-\Delta H_m}{RT} = D_0 \exp \frac{-\Delta H_m}{RT} \quad (5.46)$$

and correspondingly the activation energy is under these conditions given simply by

$$Q = \Delta H_m \quad (5.47)$$

Oxygen vacancy diffusion in oxygen-deficient oxides.

In an oxygen-deficient oxide in which oxygen vacancies predominate and for which effects of impurities can be neglected, the oxygen vacancy concentration is given by Eq. 5.39. Correspondingly, the oxygen diffusion coefficient for random oxygen vacancy diffusion in the oxide in equilibrium with the ambient oxygen gas at a partial pressure becomes

$$D_r = \alpha a_0^2 \nu \left(\frac{1}{4} K'_{0, \text{vO}} \right)^{1/3} p_{\text{O}_2}^{-1/6} \exp \frac{\Delta S_m}{R} \exp \frac{-\left(\frac{\Delta H_{\text{vO}}^0}{3} + \Delta H_m \right)}{RT} \quad (5.48)$$

D_r thus increases with decreasing oxygen pressure. The activation energy for the diffusion is in this case given by

$$Q = \frac{\Delta H_{vO}^0}{3} + \Delta H_m \quad (5.49)$$

If the concentration of oxygen vacancies is determined by lower valent impurities or dopants, e.g. when Eq.5.40 applies, then D_r is given by

$$D_r = \alpha \alpha_0^2 \nu [A_M''] \exp \frac{\Delta S_m}{R} \exp \frac{-\Delta H_m}{RT} \quad (5.50)$$

Thus in this case the activation energy is equal to that of the mobility of the oxygen vacancies: $Q = \Delta H_m$. A similar situation would arise if the vacancy concentration was frozen in rather than determined by acceptor doping.

Such a transition from intrinsic to extrinsic diffusion may take place when the temperature is lowered from high temperatures, where the native point defects predominate, to low temperatures, where the point defect concentrations are determined by the impurity concentration or, in other cases, frozen in. The temperature dependencies and the corresponding change in activation energy of the random diffusion in such a case are illustrated in Figure 5-13.

The above situations represent ideal cases. As the temperature is decreased defect interactions may become increasingly important. This may be treated as formation of associated defects. In the non-stoichiometric (intrinsic) case one may for instance have association between charged vacancies and electrons forming singly charged or neutral vacancies. This will change the oxygen pressure dependency of N_d and probably the temperature dependencies of N_d and ω , but probably not dramatically. Of larger effect, and more frequently observed, are the associations between the mobile vacancies and the relatively stationary acceptors in the extrinsic regime: The associated vacancies can be regarded as immobilised, and the concentration of mobile vacancies (N_d) starts to decrease with decreasing temperature. This is seen as an increasing activation energy of diffusion with decreasing temperature in many heavily doped oxides. One may note that instead of expressing the effect as a changing concentration of free vacancies one may express it as a changing mobility in that the activation energy for diffusion is increased by the trapping energy exerted by the acceptor. However, the simple model of free and stationary (associated) point defects appears capable of explaining most behaviours fairly well.

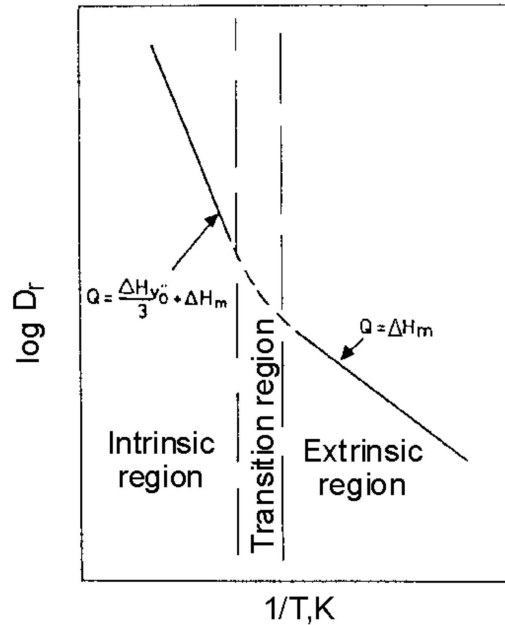


Figure 5-13. The diffusion coefficient for oxygen diffusion by the vacancy mechanism in an oxygen deficient oxide in which oxygen vacancies are the predominant native point defects. At high temperatures the oxide exhibits intrinsic behaviour and at reduced temperatures extrinsic behaviour (i.e. the oxygen vacancy concentration is determined by the concentration of lower valent cations).

Interstitial diffusion of solute.

From Eq.5.36 it is seen that N_d does not enter into the expression for the diffusion coefficient for interstitial diffusion in dilute solutions, thus in this case the activation energy, Q , represents that of the mobility of the diffusing interstitial atoms: $\Delta H_m = Q$.

For interstitial diffusion between octahedral sites in bcc metals D_o is by combination of Eqs. 5.37 and 5.41 given by

$$D_o = \frac{1}{6} a_o^2 \nu \exp \frac{\Delta S_m}{R} \quad (5.51)$$

Assuming that $\nu \sim 10^{13} \text{ s}^{-1}$ and $a_o = 1.5 \cdot 10^{-8} \text{ cm}$, and as it is probable that $\Delta S_m > 0$, one may estimate a lower limit of D_o of

$$D_o > \frac{1}{6} a_o^2 \nu = 4 \cdot 10^{-4} \text{ cm}^2 \text{ s}^{-1} \quad (5.52)$$

The diffusion of protons by the free transport mechanism is another case of interstitial diffusion of a solute.

Interstitial diffusion of a constituent

The diffusivity of a constituent such as the host metal or oxide ions by an interstitial mechanism is not only proportional to the probability that the interstitial defect jumps, but also to the probability that a constituent ion is interstitial, i.e., the fractional concentration of interstitials. Thus the diffusion coefficient of the constituent contains the temperature and oxygen pressure dependencies of the concentration of interstitials in addition to the temperature dependency of the diffusivity of the defects. As in the case of vacancy diffusion, the fixation of the defect concentration by doping or freezing as well as association and trapping of defects apply also to interstitial diffusion.

Diffusion coefficients of point defects

In the above treatment of vacancy diffusion, only the diffusion coefficients of the atoms have been considered. For many purposes it may be convenient to consider the diffusion coefficients of the vacancies themselves.

When an atom diffuses by the vacancy mechanism, it can only jump if a vacancy is located on an adjacent site, and the number of jumps per unit time is thus proportional to N_d (Eq. 5.33). However, the vacancy itself can jump to any one of the occupied nearest neighbour positions, provided it is occupied by an atom. Accordingly the vacancy diffusion coefficient D_v for a cubic system is given by (cf. Eq.5.35)

$$D_v = \alpha a_0^2 \omega N \quad (5.53)$$

where N is the fraction of occupied atom positions. In dilute solutions of vacancies, $N \sim 1$, and the diffusion coefficient of the vacancies is then not dependent on N_d .

From Eqs. 5.35 and 5.53 D_v for vacancies is related to D_r for the atoms through the relation

$$D_r N = D_v N_d \quad (5.54)$$

where, as stated above, N denotes the fraction of sites occupied by atoms, often approximated as ~ 1 . This relation can be generalised to be a very important and useful approximation for any point defect:

$$D_r N = D_d N_d \quad (5.55)$$

where D_d is the defect diffusion coefficient. It proves to be a good approximation for component diffusion by the interstitialcy mechanism. It is also a useful approximation for component diffusion by interstitial diffusion in the case of small defect concentrations ($N \sim 1$) but as the concentration of defects increases the term N must reflect the number of unoccupied interstitial sites.

Eq. 5.55 still holds for interstitial diffusion of a dilute solution of an interstitially dissolved solute, such as light elements (H, C etc. in metals or protons in oxides), but in this case the number of solute atoms or ions and the number of defects is of course the same, so that in these cases the diffusion coefficient for the solute and for the (interstitial) defects is the same.

Diffusion of protons in oxides; isotope effects

Transport of protons in an oxide (cf. Fig. 5.11) may be considered according to the principles above. For dilute solutions essentially all nearest neighbour oxide ions are available, and thus in this case N_d is unity. However, the specifications of Z , s and ω are not straightforward in this case. The dynamics of free proton diffusion in oxides are complicated by 1) the multistep process (jump+rotation), 2) the dependency on the dynamics of the oxide ion sublattice, and 3) the quantum mechanical behaviour of a light particle such as the proton.

The uniquely large ratios between the masses of the isotopes of hydrogen give rise to a number of strong isotope effects in the case of diffusion of protons. (These are also in principle operative for diffusion of hydrogen atoms or hydride ions, but they would be essentially negligible for diffusion of protons on a heavier vehicle, such as in OH^- .) The isotope effects for proton diffusion can be classified as follows: The attempt frequency ν (in the pre-exponential of ω) is given as the O-H stretching frequency, and it is given by the inverse of the square root of the reduced mass of the harmonic oscillator. The reduced mass equals $(m_O + m_H)/m_O m_H$ and is roughly inversely proportional to the mass of the hydrogen species. Therefore, the ratios of the pre-exponentials of the diffusion coefficients of protons, deuterons, and tritons are approximately related by $D_{0H} : D_{0D} : D_{0T} = 1 : 1/\sqrt{2} : 1/\sqrt{3}$. This is called the classical effect. Furthermore, the oscillators have different ground-state or zero-point energies, such that diffusion of lighter isotopes may be expected to have a slightly smaller activation energy of jumping. Accordingly, proton diffusion typically has 0.04 - 0.06 eV lower activation energy than deuteron diffusion. This is called the non-classical effect. However, there are more factors involved, connected to the fact that the light proton/deuteron/triton must be treated quantum mechanically and to their dynamics in a dynamic lattice of much heavier oxide ions. For instance, the lighter isotope has a lower sticking probability after an otherwise successful jump. In effect, this reduces the effective diffusivity of all hydrogen isotopes and it can to a varying degree counteract or even seemingly inverse the classical effect. The neglectance of the latter have in general made many investigators ascribe higher diffusivities for protons compared

to deuterons to the classical effect, while in reality the non-classical zero-point energy difference appears to be the main contributor to the observed effect.

The possibility of tunnelling as a major component of diffusion is not expected to apply to protons except at very low temperatures, and the orders-of-magnitude isotope effects that would be expected for proton vs deuteron or triton diffusion have not been reported for oxidic materials at elevated temperatures.

Literature

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Zener (1951,1952).....

Problems

1. Random (self) diffusion

a) The self-diffusion coefficient of a metal with cubic structure can be expressed as

$$D = \frac{1}{6} \frac{n}{t} s^2$$

where n/t represents the jump frequency (i.e. number of jumps n over a time t). Close to the melting point most fcc and bcc metals have $D \approx 10^{-8} \text{ cm}^2/\text{s}$.

i) If the jump distance is 3 \AA , what is the jump frequency near the melting point?

ii) What is the relation between this frequency and the vibrational frequency?

iii) How far has one atom traveled after 1 hour?

iv) What is the root mean square displacement after one hour?

v) What is the root mean square displacement in one dimension after one hour?

b) For a metal with cubic structure the diffusion coefficient can also be expressed as

$$D = \alpha a_0^2 \omega N_d$$

where α is a geometric factor, a_0 the lattice constant, ω is the jump frequency, and N_d is the defect concentration. Derive the value for α for vacancy diffusion in a metal with fcc structure.

2. Defect and self diffusion

TiO₂ is doped with 1 mol% Al³⁺ acceptors substituting the Ti⁴⁺ ions. This is compensated by oxygen vacancies. The diffusivity of oxygen vacancies is at a given temperature equal to $1 \cdot 10^{-8}$ cm²/s.

- a) Find the concentration (ratio) of oxygen vacancies in the doped TiO₂.
- b) Find the self diffusion coefficient of oxygen (oxide ions) in the doped TiO₂.

Answers and hints to selected Problems, Ch. 5

1. a) i) $7 \cdot 10^7 \text{ s}^{-1}$ ii) to be compared to ca 10^{13} s^{-1} iii) 75.6 m iv) 0.015
cm v) 0.0085 cm b) $\alpha = 1$

2. a) 0.005 (site fraction) b) $5 \cdot 10^{-11} \text{ cm}^2/\text{s}$