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DIFFUSION IN SOLIDS

PART ONE: INTRODUCTION TO THE THEORY OF DIFFUSION

by
R. Metselaar
Eindhoven University of Technology

Intermod Descriptors

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2. <u>Author</u> – R. Metselaar, Eindhoven University of Technology

3. <u>Correspondent</u> – EMMSE Coordinator, Materials Research Laboratory, The Pennsylvania State University, University Park, PA 16802

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10. <u>Skills and Knowledge Taught</u> – Upon completion of this module, the student should be able to: (1) explain the difference between self-diffusion, tracer diffusion and chemical diffusion; (2) Derive a relation for the temperature dependence of the diffusion coefficients in terms of the atomic jump mechanism, both for diffusion via an interstitial mechanism and for a vacancy mechanism; (3) Denote the influence of impurity concentration and of partial gas pressure on the diffusion coefficients in ceramic materials; (4) Use the solutions of Fick's equations to calculate the tracer diffusion

coefficient from experimentally determined concentration profiles.

11. <u>Prerequisites</u> – Completion of: general physics and chemistry (sophomore level); elementary materials science

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Objectives

Upon successful completion of this module, the student should be able to:

(1) explain the difference between self-diffusion, tracer diffusion and chemical diffusion;

(2) Derive a relation for the temperature dependence of the diffusion coefficients in terms of the atomic jump mechanism, both for diffusion via an interstitial mechanism and for a vacancy mechanism;

(3) Denote the influence of impurity concentration and of partial gas pressure on the diffusion coefficients in ceramic materials;

(4) Use the solutions of Fick's equations to calculate the tracer diffusion coefficient from experimentally determined concentration profiles.

Prerequisites

The reader should have completed a general chemistry course, introductory courses in differential calculus and an elementary course in thermodynamics. The reader should be acquainted with the elementary concepts of defect chemistry, e.g. vacancies, interstitials; a study of the modules on point defects by R.F. Davis is recommended.

Glossary of Terms

lattice

volume or bulk diffusion coefficient refers to any diffusion process within the bulk of the crystal

short-circuit diffusion

refers to any diffusion process not occurring within the bulk of the crystal e.g. along a surface, a grain boundary, a dislocation

self-diffusion

(or auto-diffusion) refers to the random walk diffusion process; D_{self}

tracer diffusion

refers to diffusion of a tracer isotope in very dilute concentration in an otherwise homogeneous crystal without chemical potential gradients; D^*. If the tracer atoms are of the same species as the nontracer atoms $D^* = D_{self}$

chemical coefficient

(or interdiffusion coefficient) refers to diffusion in a chemical-potential gradient; $\tilde{D}$

interstitial mechanism

denotes a movement of an atom from one interstitial position to another

interstitialcy mechanism

denotes a movement of an atom from an interstitial position to a normal lattice position

DIFFUSION IN SOLIDS
PART ONE: INTRODUCTION TO THE THEORY OF DIFFUSION

R. Metselaar
Department of Chemical Technology
Eindhoven University of Technology
Eindhoven, The Netherlands

Introduction

When a person wearing perfume sits some distance apart from you, you will smell the perfume after some time -- even if there are no apparent air currents or movements. This is a well-known example of diffusion in a gas. The kinetic theory of gas describes this phenomenon as a random movement of colliding molecules. In liquids this random movement can be easily demonstrated using the Brownian movements of suspended particles. Likewise in solids the atoms move through the material. However, there is a large difference in the distance per unit of time travelled by an atom in these three different states. If the displacement of a gas molecule is 1 m in a given time, it will be about 1 cm in a liquid and of the order of 10-100 μm in a solid. Yet, despite these small relative distances, diffusion in solids plays an important role. For instance, the rate of solid state reactions, the growth rate of oxide scales on metals, the sintering rate, and the high-temperature creep rate of materials are all determined by diffusion.

In this module we shall first look at the possible mechanisms for the atomic movements. After a discussion

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of the jump frequencies of the atoms, we will define
diffusion coefficients and derive quantitative expressions
for these quantities.

Mechanisms for Atomic Displacements in Solids

In a crystalline solid there is a regular array of
lattice sites. These sites are low-energy positions for
the atoms. Atoms move by jumping from one lattice site to
another. Different jump mechanisms are possible,
depending on the nature of the moving atom and on the
crystal lattice. A number of possible mechanisms are
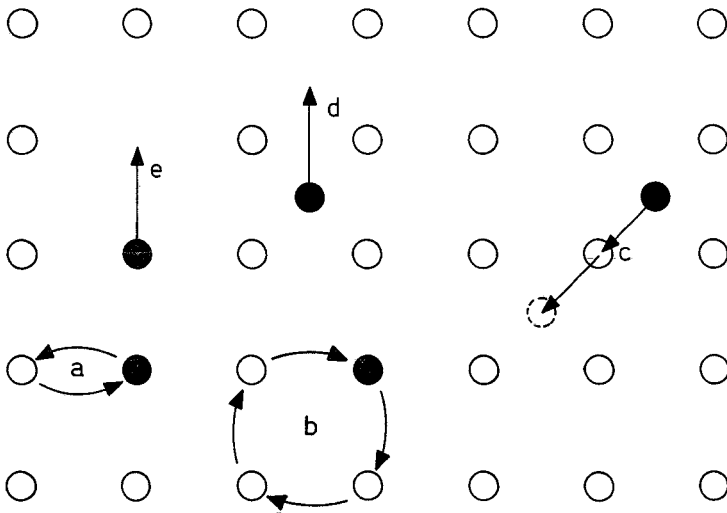shown in Fig. 1.

FIG. 1

Possible atomic movements contributing to diffusion.
(a) exchange, (b) ring, (c) interstitialcy,
(d) interstitial, (e) vacancy mechanism.

Figure 1a illustrates the so-called exchange
mechanism, where the elementary jump consists of an
exchange of two neighboring atoms. The ring mechanism,
shown in Fig. 1b is a variant of the exchange mechanism.

It will be clear that in most cases the direct exchange is energetically improbable due to steric hindrance. For the ring mechanism the lattice disturbance is less, but this mechanism is also rather unlikely. The two mechanisms discussed allow atomic movements in perfect crystals. However, in actual crystals, at $T > OK$, there always exists a finite number of point defects e.g. interstitial atoms or vacancies. In this case other jump mechanisms which are energetically more favorable may occur. Figure 1c illustrates the interstitialcy mechanism. Here, an interstitial atom moves onto a lattice site, thereby forcing the atom off the lattice site into a new interstitial position. Also direct jumps from one interstitial site to another interstitial site are possible (Fig. 1d). One of the most important mechanisms is the vacancy mechanism, illustrated in Fig. 1e. An atom jumps from a lattice site into an adjacent vacant lattice site. Remember that vacancies are always present in the crystal.

In a solid where Schottky defects (vacancies in the cation and anion sublattices) are the main point defects, one can expect vacancy diffusion. Similarly, interstitial diffusion can be important in solids with Frenkel defects (vacancies and interstitial ions in one sublattice).

QUESTION 1:

In pure metals diffusion occurs generally via the vacancy mechanism. In alloys this is not always the case. Could you suggest examples of alloys where diffusion occurs via an interstitial mechanism?

So far we have discussed diffusion within the regular lattice structure, so-called volume diffusion (also called lattice- or bulk-diffusion). However, reality is always more complicated. In practice diffusion can also occur in disturbed regions of the crystal. As such we consider jumps along the surface, at grain boundaries, along dislocations or cracks. These processes are summarized under the name short-circuit diffusion. Since the lattice in these regions is less densely packed, short-circuit diffusion often makes a major contribution to the atom

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displacements. As a result, diffusion in polycrystalline materials often proceeds much faster than in single crystals. We shall show later that diffusion can be characterized by a diffusion coefficient D, a quantity with dimension m^2s^{-1}. For single crystal Al_2O_3 at 1500°C the diffusion of oxygen is characterized by a value $D = 4.10^{-20} m^2s^{-1}$ while in polycrystalline samples $D = 6.10^{-18} m^2s^{-1}$.

QUESTION 2:

The relative contributions of lattice diffusion and short—circuit diffusion change with temperature. We shall prove in Section 6 that $D = D_{o_2} exp(-Q/RT)$, where D is a constant (dimension m^2s^{-1}), Q an activation enthalpy (in $J\ mol^{-1}$), the gas constant $R = 8.3\ J\ K^{-1}\ mol^{-1}$, T the temperature (in K). Make a plot of $^{10}log\ D$ versus 1000/T for volume diffusion and grain boundary diffusion in silver, using D_{Ag} (grain boundary) = $2.3 \times 10^{-9}\ exp(-110/RT)\ m^2s^{-1}$ and D_{Ag} (volume) = $8.95 \times 10^{-5}\ exp(-192/RT)\ m^2s^{-1}$, with in Q in $kJ\ mol^{-1}$. Vary 1000/T between 0.8 (melting point of Ag) and 3.0. Compare the relative magnitude of lattice diffusion and short—circuit diffusion.

Jump Frequencies

The atoms in the crystal lattice occupy positions with a relative minimum in the potential energy. In Fig. 2a such positions are p and r. However, the atoms are not fixed in the minimum energy positions. Due to the thermal energy they perform a vibrational motion with a frequency f. If an atom is transferred from position p to position r, it has to pass over an energy barrier G_m. According to Boltzmann statistics the chance to make such a jump is $exp(-G_m/kT)$. Therefore the jump frequency is given by:

$$p_o = f\ exp(-G_m/kT) \tag{1}$$

In case there are no driving forces acting on the atoms, a jump to the right is equally probable as a jump to the

left. In this case the jumps are completely at random with no preferred direction, i.e. each atom follows a random walk. We call this self-diffusion or auto-diffusion. We have to distinguish this completely random movement from a movement under the influence of an external force e.g. a gradient in the concentration c or a gradient in the electrical potential ϕ. In the first case the force F is given by F = -grad c, in the second case F = -grad ϕ.
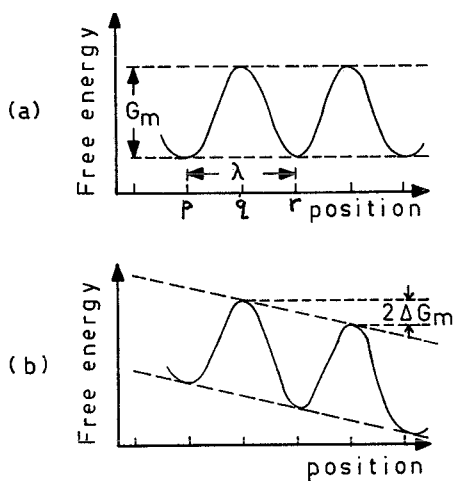
FIG. 2

Gibbs energy as a function of position in a lattice; λ is the jump distance. (a) Without external forces; (b) With an external potential gradient.

QUESTION 3:

Which other forces can you think of in this context?

Figure 2b shows the Gibbs energy diagram in case there is a driving force F making the atom jump preferentially to the right. Without external force the barrier between p and r has a height G_m and the jump frequency from p to r and vice versa is given by Eq. (1). Under the influence of the force the barrier for a jump in

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the direction of the force is lowered to $(G_m - \Delta G_m)$, where

$$\Delta G_m = 1/2 \ \lambda F \tag{2}$$

As a result the jump frequency from p to r becomes

$$p_{pr} = f \ \exp(\frac{-G_m + \Delta G_m}{kT}) = p_0 \ \exp(\frac{\Delta G_m}{kT})$$

In most cases of practical interest $\Delta G_m \ll kT$, so that we can expand $\exp(\Delta G_m/kT) \approx 1 + (\Delta G_m/kT)$, and

$$p_{pr} \approx p_0 \ (1 + \frac{\Delta G_m}{kT})$$

For an atom jumping in the opposite direction the barrier height is $(G_m + \Delta G_m)$, so

$$p_{rp} \approx p_0 \ (1 - \frac{\Delta G_m}{kT})$$

So, to first order approximation the net jump rate becomes

$$p_{net} = p_{pr} - p_{rp} = p_0 \ \frac{2\Delta G_m}{kT}$$

and from Eq. (2)

$$p_{net} = p_0 \ \frac{F\lambda}{kT}$$

The net velocity of the atoms then is $v = \lambda p_{net}$. By multiplying the velocity by the number of atoms per unit volume c, one obtains the atom flux J, i.e. the number of

atoms passing a unit area per unit time. So,

$$J = p_o \frac{F\lambda^2 c}{kT} = f \frac{F\lambda^2 c}{kT} \exp(-G_m/kT) \qquad (3)$$

As discussed previously, f is the vibration frequency of the atom, λ the jump distance and G_m the barrier height.

QUESTION 4:

Check the dimensions of the flux equation.

Diffusion Coefficients

Let us have a closer look at the self-diffusion process. In all diffusion processes the driving force is the decrease in Gibbs energy. However, in the case of self-diffusion the enthalpy remains constant and only the entropy S_m changes. The atomic motions lead to a random distribution, which is statistically the most probable state.

Experimentally we cannot measure self-diffusion directly. Instead we use a trick, viz. we use tracer atoms to reveal the movements we want to study. As such we can use radioactive isotopes. Assume that we want to study the self-diffusion of Ag atoms in pure silver. We can then take a bar of silver and deposit a few radioactive Ag^{110} atoms on one end of the bar. After an annealing experiment we can measure the radiation emitted by the Ag atoms as a function of the distance along the bar and so follow the progress of the diffusing atoms.

In such a diffusion couple of the type A/A* (where A* denotes the radioactive tracer atoms) we can define the flux of the isotopes. It seems reasonable to assume that the flux is proportional to the gradient in the concentration of A*, analogous to the case of a heat flux under a temperature gradient. We define a diffusion coefficient D by

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$$J = -D \text{ grad } c \qquad (4)$$

This equation is known as Fick's first law.

J is the flux of atoms, grad c the concentration gradient of the diffusing atoms. This equation defines the diffusion coefficient D. J has the dimension $[\text{time·area}]^{-1}$ e.g. $m^{-2}s^{-1}$ and grad c has the dimension $[\text{vol·length}]^{-1}$ e.g. m^{-4}, so D is expressed as [area/time], i.e. in units $m^2 s^{-1}$. The minus sign in Eq. (4) expresses that the atom flux is in the direction of decreasing concentration. In general, in a crystal, J depends on the crystallographic direction, so D is a tensor. However, in this module we will only discuss one dimensional diffusion. In that case, Eq. (4) can be simplified to

$$J = J_z = -D(\delta c/\delta z) \qquad (5)$$

where the diffusion is chosen along the z-direction.

In the case of diffusion of a tracer isotope, discussed above, the diffusion coefficient measured is designated as D* and is called the "tracer diffusion coefficient." If the tracer atoms are isotopically identical with the other atoms of the crystal D is called the self-diffusion or auto-diffusion coefficient. In principle the word self-diffusion is restricted to diffusion in the absence of a gradient in chemical potential. The tracer diffusion coefficient D* gives a good approximation of D when only a very small amount of A* (in practice for instance a layer of less than 50 nm thickness) is deposited on A (or on an alloy AB). In this case there is a concentration gradient, but it rapidly becomes extremely small so that it is a justified approximation to call this autodiffusion.

We can also use Eq. (4) or (5) to define a diffusion coefficient for the case of diffusion under the influence of a gradient in the chemical potential. A well known example is that of diffusion in a couple of the type A/B, where A and B are two metals, alloys or compounds. If the total volume remains constant, the flux of moles of component i across any section, fixed with respect to the origin, can be expressed by

$$J_i = -\tilde{D} \; (\delta c_i / \delta z) \tag{6}$$

This equation defines the chemical or interdiffusion coefficient D. This coefficient is theoretically less simple since it contains contributions from both A and B. In part II of this module we will consider how the interdiffusion coefficient D can be built up from so-called intrinsic diffusion coefficients D_A and D_B. If we have a couple A/AB with a sufficiently low concentration of B, we measure $\tilde{D} \sim D_B$. For an ideal solution $\tilde{D}_B^* \sim D_B^*$, the diffusion coefficient obtained when a very small amount of the tracer B* diffuses through A.

The last column of Table I gives some examples of values of D at a fixed temperature. For Zn two figures are given. Zn is an element which crystallizes with a hexagonal crystal structure. From the table we see that tracer diffusion of Zn atoms parallel to the c-axis is faster than diffusion in the plane perpendicular to the c-axis. It can also be seen that the D-values cover a wide range. Since the diffusion coefficient is strongly temperature dependent we cannot compare data for different materials. A comparison can be made, however, for different species diffusing in the same matrix. For instance, the high D value for H in Ag, compared with Ag or Cu in Ag, points at a difference in diffusion mechanism. The small H atom diffuses via interstitial sites, while Ag and Cu move via a vacancy mechanism.

In Table I we have also included data for some binary compounds. Here it is interesting to note the high D-value for Ag^+ in α-AgI. This results in α-AgI being a very good Ag ion conductor. The data in the third and fourth column of this table, D_o and Q, will be discussed later.

An Expression for D in Terms of Atomic Jumps

We have seen that the atom flux can be expressed in terms of atomic jumps. Therefore it should be possible to derive an equation for the diffusion coefficient expressed in jump frequencies and distances. We will show this for

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TABLE I
Values of Diffusion Coefficients for Different Materials.

Matrix	Diffusing Species	D_0 $(m^2 s^{-1})$	Q $(kJ\ mol^{-1})$	D at 800K $(m^2 s^{-1})$
Ag	Ag	4.0×10^{-5}	185	3.6×10^{-17}
	Cu	1.2×10^{-4}	193	3.0×10^{-17}
	H	2.8×10^{-7}	31	2.5×10^{-9}
α-Fe	Fe	1.9×10^{-4}	239	4.7×10^{-20}
	H	8.8×10^{-8}	13	1.2×10^{-8}
	C	2.0×10^{-6}	84	6.6×10^{-12}
Zn	Zn//c-axis	1.3×10^{-5}	91	* 6.2×10^{-13}
	Zn$\perp$c-axis	5.8×10^{-5}	102	* 4.0×10^{-13}
Ge	Ge	7.8×10^{-4}	287	1.4×10^{-22}
	Li	1.3×10^{-7}	45	1.5×10^{-10}
	P	2.5×10^{-4}	239	6.2×10^{-20}
NaCl	Na^+	5.0×10^{-5}	155	3.9×10^{-15}
	Ni^{++}	2.0×10^{-6}	126	1.3×10^{-14}
	Cl^-	1.1×10^{-2}	215	1.0×10^{-16}
α-AgI	Ag^+	1.6×10^{-8}	9	4.1×10^{-9}
	I^-	4.8×10^{-9}	61	5.0×10^{-13}
Cu_2O	Cu^+	4.3×10^{-6}	151	5.9×10^{-16}
	O^{--}	6.5×10^{-7}	164	1.3×10^{-17}

* D-value at 650K, 40K below the melting point of Zn.

the case of one-dimensional diffusion with a concentration gradient $(\delta c/\delta z)$.

We consider two adjacent lattice planes 1 and 2, at a distance λ (Fig. 3). Plane 1 contains n_1 diffusing atoms per unit area, plane 2 contains n_2. The jump probability from plane 1 to plane 2 is p_{12}, and is p_{21} from plane 2 to plane 1.

The net flux of atoms is

$$J = n_1 p_{12} - n_2 p_{21} \quad .$$

In the case of a random-walk process, i.e. in the absence of driving forces $p_{12} = p_{21}$. In this simple lattice, jumps to left and right are equally probable. Therefore the total jump probability p_0 is
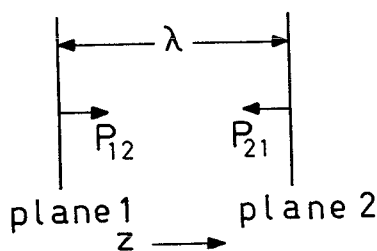

FIG. 3

Two lattice planes at distance λ with different densities of diffusing atoms. The jump probability from plane i to j is p_{ij}.

$$p_{12} = p_{21} = 1/2 p_0$$

Noting that the atom concentration per unit area (n) can be expressed in concentration per unit volume (c) by $n = \lambda c$, $J = 1/2 \lambda p_0 (c_1 - c_2)$.

Since $(c_1 - c_2)/\lambda = -(\delta c/\delta z)$

$$J = -1/2 \lambda^2 p_0 (\frac{\delta c}{\delta z}) \tag{7}$$

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Comparison with Eq. (5) gives

$$D = 1/2 \; \lambda^2 p_0 \tag{8}$$

If the jumps occur in three equivalent directions, as in a simple cubic lattice, Eq. (8) becomes

$$D = 1/6 \; \lambda^2 p_0 \tag{9}$$

For a general crystal structure, instead of 1/6, a geometric factor g must be included.

$$D = g\lambda^2 p_0 \tag{10}$$

According to Eq. (1) the jump probability p_0 can be written as

$$p_0 = f \; \exp(-G_m/kT)$$

so

$$D = g\lambda^2 \; f \; \exp \; (-G_m/kT) \tag{11}$$

With typical values $g = 1/6$, $\lambda = 2\text{Å} = 2 \times 10^{-10}$ m, $f = 10^{13} s^{-1}$, $G_m = 100$ kJ mol^{-1}, $T = 1200$K, we obtain $p_0 = 4.4 \times 10^8 s^{-1}$ and $D = 2.9 \times 10^{-12} m^2 s^{-1}$.

In writing the expression for p_0 we have assumed that the attempt frequency f and the barrier height G_m determine the number of jumps. For atoms moving from one interstitial position to another this is generally correct. However, when the atoms move via a vacancy mechanism a jump can only be carried out if a vacancy is present at a neighboring site. Therefore the jump probability is obtained by multiplying p_0 with the probability that the jumping atom has a vacancy as neighbor. This probability is given by the fractional concentration of vacancies $[V] = n_v/N$, where n_v is the number of vacancies and N is the total number of lattice sites (1).

$$D = g\lambda^2 \; f \; [V] \; \exp(-G_m/kT) \tag{12}$$

In the derivation of Eqs. (11) and (12) it is assumed that
the jump probabilities are independent of the directions
of preceding jumps. In reality there is a correlation
between successive atom jumps. We can easily see this if
we look at a vacancy changing place with an adjacent atom.
After the first jump the vacancy can jump to one of Z
surrounding places i.e. there is a chance $1/Z$ that it
jumps back to its previous place. This correlation
reduces the number of effective jumps. Therefore p_o has
to be multiplied by a so-called correlation factor. This
factor is determined by the symmetry of the crystal
structure and by the diffusion mechanism, e.g. for a
vacancy mechanism the correlation factor is 0.65 for
simple cubic, 0.73 for body centered cubic and 0.78 for
face centered cubic lattices. We will absorb this factor
into the constant g in Eqs. (11) and (12).

In the derivation of Eq. (10) and subsequent
equations only self-diffusion was considered. However, in
section 3 we found that the atom flux under an applied
force is expressed by Eq. (3).

For instance, when the driving force is a gradient in
the chemical potential μ_i, we have $F_i = 1/N_A \, d\mu_i/dz$ (N_A =
Avogadro constant). Here, $\mu_i = \mu_o + RT \ln \gamma_i [N_i]$, where
γ_i is the activity coefficient and $[N_i]$ the molar fraction
of i. If the molar volume V_m is constant, and assuming
that $\gamma_i = 1$ (ideal solution), substitution of $N_i = c_i V_m$,
gives $d\mu_i = RT \, d\ln c_i$. From Eq. (3) we then obtain

$$J_i = -f\lambda^2 \exp(-G_m/kT) \cdot (dc_i/dz)$$

or

$$\tilde{D} = f\lambda^2 \exp(-G_m/kT) \qquad (11a)$$

Including a geometrical factor g we arrive at an equation
for chemical diffusion which has the same form as Eq. (11)
[or Eq. (12) in the case of vacancy diffusion].

QUESTION 5:

a. Starting from Eq. (3), derive the contribution to
the electrical conductivity (σ) for an ion i. (Note:

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σ is the electrical current density per unit of electric field.)

b. Derive a relation between σ and D.

Temperature Dependence of Diffusion

The Gibbs energy G_m can be divided into a migration enthalpy term H_m and an entropy term TS_m: $G_m = H_m - TS_m$.

To a first approximation both H_m and S_m are temperature independent. Therefore Eq. (11) for interstitial diffusion becomes

$$D = g\lambda^2 \ f \ \exp(S_m/k) \ \exp(-H_m/kT) \qquad (13)$$

For vacancy diffusion we also have to consider the temperature dependence of the vacancy concentration (1). For pure, elemental solids the number of vacancies in thermal equilibrium is

$$n_v = N \ \exp(-G_f/kT) \qquad (14)$$

where N is the total number of lattice sites and G_f is the Gibbs energy of formation of the defect ($G_f = H_f - TS_f$).

For a stoichiometric crystal MX with Schottky defects the same expression is valid if n_s is the number of anion vacancies, N is the number of ion pairs, G_f is half the Gibbs energy of formation of a Schottky pair.

In either case we get, with $[V] = n_v/N$,

$$D = g\lambda^2 \ f \ \exp[(S_m + S_f)/kT] \ \exp \ [-(H_m + H_f)/kT] \qquad (15)$$

By now it should be obvious that diffusion coefficients can generally be written in the form

$$D = D_o \ \exp \ (-Q/kT) \qquad (16)$$

Note, however that the pre-exponential coefficient D_o and the activation enthalpy Q have different meanings for different diffusion mechanisms: in the case of interstitial diffusion only the free energy of migration is involved, while for diffusion via vacancy mechanism a

sum of migration and formation Gibbs energy contributions is involved.

In Table I we have summarized some experimental data. D_o values for metals are generally in the range 10^{-6}-10^{-3} $m^2 s^{-1}$. Examples are given in this table for self-diffusion in Cu, Ag and Zn. The Q-values for self-diffusion in these metals where a vacancy mechanism applies, can be estimated by way of the empirical rule Q $\approx$ 150 T_m J mol^{-1}, with T_m the melting point in K. Much lower Q values are observed for diffusion of H in Ag or α-Fe, C in α-Fe and Li in Ge because we are dealing with small atoms which occupy interstitial sites and diffuse via the interstitialcy mechanism.

Table II gives some values for migration- and formation enthalpies and entropies. We see that the migration enthalpy and formation enthalpy are of the same order of magnitude (for KCl with Schottky defects the H_f value given is half the enthalpy of formation of a Schottky pair). Data on migration and formation entropy are scarce. The entropy values are positive and are of the order 1-4k where k is the Boltzmann constant (see Table II).

TABLE II
Values of Migration and Formation
Enthalpies and Entropies*.

Matrix	diffusing species	H_m (kJ mol^{-1})	H_f (kJ mol^{-1})	S_m/k	S_f/k
Ag	vacancy	82	103		
Al	vacancy	43	73		
Cu	vacancy	101	92		
α-Fe	interstitial c	84	--	1.5	
Ge	vacancy	92	200		
K$^+$	KCl	67	125	2.7	4.8
Cl$^-$	KCl	96	125	4.1	4.8
Cu$_2$O	Cu	58	91		

*Entropy is expressed as a dimensionless quantity, by division by the Boltzmann constant k = 1.38x10^{-23} JK^{-1}.

QUESTION 6:

Verify that Eq. (16) also holds for cation diffusion in an ionic crystal with Frenkel defects in the cation sublattice. What is the meaning of Q in this case?

Impurity Dependence of Diffusion

We have shown that the diffusion coefficient is proportional to the fractional vacancy concentration in cases where the particles move via a vacancy mechanism. In metals or in pure, stoichiometric compounds the number of vacancies in thermal equilibrium is determined by the Gibbs energy of formation G_f.

However, in solid solutions or non-stoichiometric compounds the vacancy concentration may be determined extrinsically. We shall consider two examples. First, consider a compound MX, at a fixed temperature, in equilibrium with M atoms in the gas phase with a pressure p_M. It is now possible that the fractional concentration of M vacancies, $[V_M]$ and of X vacancies, $[V_X]$ is controlled via the equilibrium reaction*

$$M(g) \xrightleftharpoons{} M_M + V_X \qquad (17a)$$

For each M atom incorporated on an M site a vacancy is created on an X site The equilibrium position of this equation is governed by the equilibrium constant

$$K = [V_X]/p_M = \exp(-\Delta G_e^o/kT) \qquad (17b)$$

where ΔG_e^o is the standard Gibbs energy change of the reaction. At M pressures where the vacancy concentration is determined by this reaction the diffusion of X atoms is given by

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*If you are not familiar with the use of reaction equations for point defect equilibria, you could study ref. (2).

$$D_X = g\lambda^2 \, f[V_X] \, \exp(-G_m/kT)$$

$$= g\lambda^2 \, f \, p_M \, \exp \, [-(G_m + \Delta G_e^o)/kT] \qquad (18)$$

Next, we consider the case that some NX_2 is dissolved substitutionally in MX. For each molecule of NX_2 incorporated in MX one M vacancy is created. At very low concentrations of NX_2, or at high temperatures, $[V_M]$ is determined by the thermal equilibrium i.e. by the formation enthalpy H_f, and eq. (15) holds. At higher concentrations of NX_2 or at lower temperatures $[V_M]$ is controlled by the substitutional atoms, or $[V_M] = [NX_2] =$ constant. The temperature variation of $[V_M]$ is negligible in this region, so the activation enthalpy Q now only contains H_m. Therefore, a plot of $\ln D_M$ vs. T^{-1} has a slope $-(H_m/k)$ at low temperature and a slope $-(H_m+H_f)/k$ at high temperature.

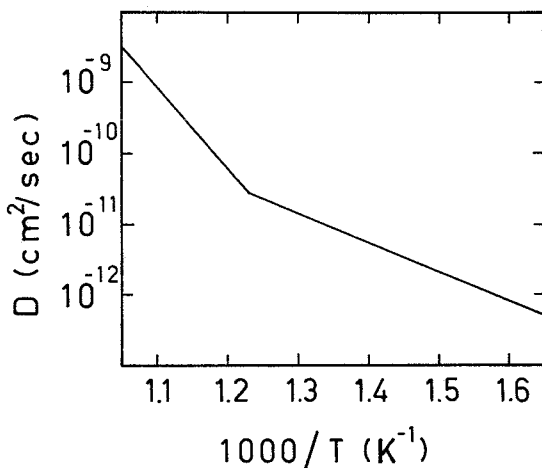Figure 4 gives an example of the temperature dependence for D_{Na+} in NaCl.

FIG. 4

Temperature dependence of the tracer diffusion coefficient of Na^+ in NaCl.

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QUESTION 7:

Calculate the migration enthalpy H_m for Na^+ and the formation enthalpy H_s for a Schottky pair in NaCl, using the data in Fig. 4.

Example Problem: Figure 5 shows the dependence of Mn diffusion in MnO on the partial oxygen pressure. If you are familiar with defect chemistry you can verify from this figure that Mn diffusion in MnO occurs via doubly charged vacancies V''_{Mn}. Try to explain the slope of this plot.
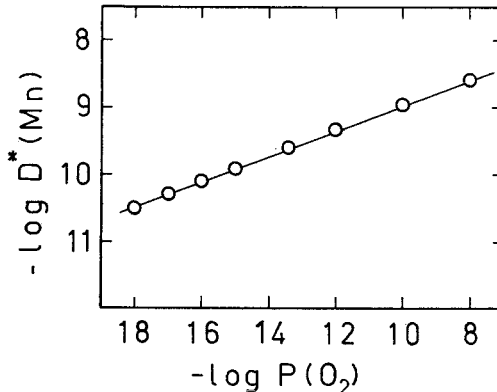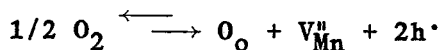

FIG. 5

The tracer diffusion coefficient of Mn^{54} in MnO at 1305K as a function of partial oxygen pressure.

Answer

The slope of log D (Mn) vs. log P_{O_2} yields D(Mn) $\propto$ $p_{O_2}^{1/6}$. This dependence can be explained if transport occurs via vacancies V''_{Mn}. These vacancies are formed via the equilibrium reaction

$$1/2 \; O_2 \; \underset{\longrightarrow}{\longleftarrow} \; O_o + V''_{Mn} + 2h^\cdot$$

Since the electroneutrality equation requires $2[V''_{Mn}]$

$= [h^\cdot]$ we find $[V_{Mn}''] = (1/4K)^{1/3}p_{O_2}^{1/6}$. For this derivation we have used the Kroger-Vink notation (ref. 2).

Fick's Second Law

In the following sections we shall discuss the experimental determination of diffusion coefficients. For this purpose Fick's First Law is generally not convenient since we cannot measure the particle flux directly. Instead we use Fick's Second Law, which relates the concentration of the diffusing species to the time and position coordinates.

Consider a slab of solid with thickness dz, with an incoming particle flux J. If no matter is created or destroyed, the change in concentration in the given volume equals the net flow into this volume i.e.

$$\frac{\delta c}{\delta t} = - \frac{\delta J}{\delta z} \tag{19}$$

Substitution of Fick's First Law [Eq. (5)] into this so-called continuity equation yields

$$\frac{\delta c}{\delta t} = \frac{\delta}{\delta c} (D \frac{\delta c}{\delta z}) \tag{20}$$

This is called Fick's Second Law. If D is independent of c and z

$$\frac{\delta c}{\delta t} = D \frac{\delta^2 c}{\delta z^2} \tag{21}$$

The solution of this second order differential equation leads to an expression for the concentration as a function of position and time. Therefore, from an experimental determination of $c(z,t)$ the diffusion coefficient can be obtained.

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Solutions of the Diffusion Equation

The differential equation (21) can be solved only if the boundary conditions are known. Let us see first how a tracer diffusion experiment can be performed. Suppose that we want to determine the self-diffusion coefficient of Zn in ZnO. To this end we can deposit a very thin layer of Zn^{65} on the end of a ZnO rod (e.g. by evaporation via the gas phase or electrolytically). To avoid interference of grain boundary diffusion a single crystal of ZnO would be preferable. At time t=0 we have a fixed amount M (expressed e.g. in weight or number of atoms per unit area) present at z=0. There are no radioactive Zn atoms present in the rod, therefore the concentration c(z,t) is given by c(o,o) = M and c(z,o) = 0. After heating the rod at a temperature T, during a fixed time t, we rapidly cool the rod to room temperature. Next we measure the concentration c(z,t) of the tracer as a function of the distance from the surface.

The solution of Eq. (19), with the boundary conditions stated above, is

$$c(z,t) = \frac{M}{(\pi Dt)^{1/2}} \exp \left(\frac{-z^2}{4Dt}\right) \qquad (22)$$

QUESTION 8:

Verify by differentiation that Eq. (22) satisfies Eq. (21).

Figure 6 shows the development of the concentration profile with time. It follows from Eq. (22) that a plot of ln c(z,t) vs. z^2 is a straight line with slope 1/4Dt.

QUESTION 9:

The radioactive isotope Ni^{63} is used to determine the self-diffusion coefficient in Ni. A layer of Ni^{63} is deposited on one end of a long Ni bar. After a heat treatment of 1 hr at 1000°C the concentration of Ni^{63} was measured at different positions along the bar.
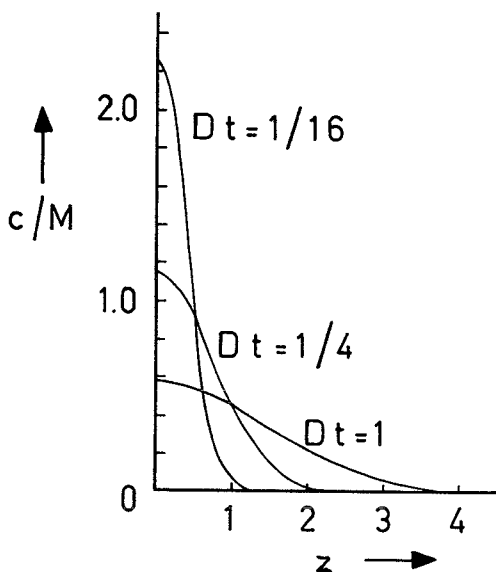
FIG. 6

Development with time of the concentration profile
c(z,t) of a tracer atom deposited in an amount
c(o,o) = M on the end of a long rod [see Eq. (22)].

Determine D_{Ni}^* from the following concentration
profile.

z (cm)	1	2	3	4
c (mg/cm^3)	14.3	10.3	5.8	1.0

This procedure cannot be used to determine the self-
diffusion coefficient of oxygen since there are no stable
radioactive tracers of this element. One possible method
is then to heat the oxide in an atmosphere enriched in O^{18}
and measure the decrease in O^{18} concentration with the aid
of a mass spectrometer.

Measurements of a chemical diffusion coefficient are
often performed with diffusion couples, e.g. a sandwich of
the type AB/A. In these cases the concentration of A at
the interface is kept constant during the experiment i.e.

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the boundary conditions are $c(o,t) = c_o$ and $c(z,o) = 0$. The solution of the differential equation (21) is now given by

$$c(z,t) = c_o \left[1 - \text{erf} \left(\frac{z}{2\sqrt{Dt}}\right)\right] \tag{23}$$

Here erf(y) denotes the integral

$$\text{erf}(y) = \frac{2}{\sqrt{\pi}} \int_o^z e^{-z^2} \, dz \tag{24}$$

the so-called error function. Values for this integral are given in tabular form. One has $\text{erf}(0) = 0$, $\text{erf}(\infty) = 1$. Figure 7 shows the behavior of erf y; the function reaches 1 within 1% for $y = 1.8$.
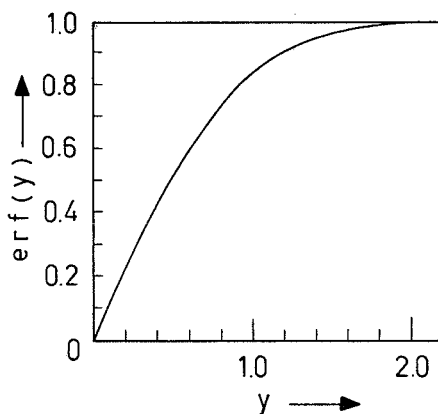

FIG. 7

Erf(y) as a function of y.

In practice the geometry of the sample can also play a role e.g. for a sphere, a cylinder or a thin plate the dimensions are important parameters too. Solution of Fick's second law for many different cases can be found in the literature (see e.g. ref. 3).

We note that in Eqs. (22) and (23) a dimensionless parameter $(z/\sqrt{Dt})$ occurs. If we want to obtain a quick estimate of the depth z_p where an appreciable change in concentration has occurred after a diffusion time t_p, for a known D, one sets

$$z_p \approx (Dt_p)^{1/2} \tag{25}$$

For example, if the chemical diffusion coefficient of Cr in MgO is 10^{-16} $m^2 s^{-1}$ at 1700K, then the penetration depth of Cr after 1 hr will be of the order of $(3600.10^{-16})^{1/2} = 60.10^{-8}$ m $= 0.6$ μm.

QUESTION 10:

Calculate $c(z_p, t_p)/c(o,o)$ using Eqs. (23) and (24).

In this last section we have learned how to find the diffusion coefficient from experimentally determined concentration profiles. In the preceding sections we discussed the relation between the phenomenological tracer diffusion coefficient and the atomic mechanism. From the atomic jump mechanism we can also understand the temperature and pressure dependence of the diffusion coefficient. Practically no attention was paid to chemical diffusion. We will treat this topic in greater detail in a second module.

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Answer to Questions

Here is a complete list of the answers to the problems found interspersed in the text.

1. Alloys which are interstitial solid solutions. Small atoms like H, B, C, N often occupy interstitial positions. Examples are TiB, ZrB, HfC, NbC, TiNi, ZrN and hydrides of Ti, Zr or Hf.

2. You will find two straight lines crossing at $1000/T = 1.06K^{-1}$.

3. Chemical, magnetic, gravitational and thermal forces.

4. $(time \cdot area)^{-1}$

5a. $\sigma_i = q_i J_i/E$, $F_i = q_i E$
Eq. (3) gives

$$J_i = \frac{f_i \lambda^2 c_i}{kT} q_i E \exp (-G_m/kT)$$

$$so \ \sigma_i = \frac{f_i \lambda^2 q_i^2 c_i}{kT} \exp(-G_m/kT)$$

b. From Eq. (11a) and the equation for σ_i we find $\sigma_i kT = \tilde{D} q_i^2 c_i$. This is called the Nernst-Einstein relation.

6. The number of cations in a crystal with Frenkel defects in the cation sublattice is of the same order of magnitude as the number of available interstitial sites Cf. the module by R.F. Davis, JEMMSE 2 (4):837 (1980)]. Therefore Eq. (11) applies and Q is equal to the migration enthalpy.

7. From the slope of log D vs. T^{-1} in Fig. 4 we find the low temperature region $H_m = 0.76$ eV, and from the high

temperature region $H_m + H_f = 1.94$ eV, so $H_s = 2H_f = 2.36$ eV.

8. By differentiation of Eq. (22) we find

$$\frac{dc}{dt} = D\ \frac{d^2c}{dz^2} = (\frac{Mz^2}{4\pi^{1/2}D^{3/2}t^{5/2}} - \frac{M}{2\pi^{1/2}D^{1/2}t^{3/2}})\ \exp(\frac{-z^2}{4Dt})$$

9. From the slope of ln c vs. z^2, which is a straight line according to Eq. (22), we find $D(Ni) = 6.3 \cdot 10^{-12}$ cm^2 s^{-1}.

10. For $z_p = \sqrt{Dt_p}$ Eq. (23) gives $c(z_p,t_p)/c(0,0) = 1 - erf(1/2)$. From Fig. 7 we find erf $(1/2) = 0.52$.

DIFFUSION IN SOLIDS

References

1. R.F. Davis, Point Defects in Stoichiometric Ceramic Materials, JEMMSE 2(4):837 (1980).
2. A short introduction to the defect notation is given in the module J.H.W. de Wit, High Temperature Oxidation of Metals, JEMMSE 3(2):333 (1981).
   More detailed information can be found e.g. in the book W. van Gool, Principles of Defect Chemistry of Crystalline Solids, Ac. Press, New York (1966).
3. J. Crank, The Mathematics of Diffusion, Oxford University Press, Oxford (1956).

Suggested Reading

Supplementary

1. W.D. Kingery, H.K. Bowen and D.R. Uhlmann, Introduction to Ceramics, 2nd ed., pp. 217-263.

Advanced

2. P.G. Shewmon, Diffusion in Solids, McGraw-Hill, New York (1976).
3. J.R. Manning, Diffusion Kinetics for Atoms in Crystals, Van Nostrand, Princeton (1968).
4. J.P. Stark, Solid State Diffusion, John Wiley and Sons, New York (1976).

Experimental data on diffusion are published regularly in the journal Diffusion and Defect Data, ed. F.H. Wohlbier and D.J. Fisher, Trans. Tech. Publ. Switzerland, USA.