

Diffusion in Ionic Solids

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1 Introduction

All experimental and theoretical work in the field of diffusion is ultimately concerned with the basic question of how the diffusing species gets from place to place through the diffusion medium. In gases, where the molecules are to a first approximation independently-moving particles, the well-established kinetic theory has led to a treatment of gaseous diffusion in which the process is described in terms of average velocities and mean free paths of the gaseous species. For liquid diffusion the treatment is more complex since the restraints imposed by near neighbour interactions invalidate the simple assumptions applicable to gases. In crystalline solids the regularity of the lattice enables the possible motions of the atoms or ions to be restricted to simple geometrical considerations; also the forces between the species are usually well represented in classical terms, so that the diffusion problem again becomes amenable to a precise and detailed treatment.

Experimental studies in solid state diffusion have many varied applications. Thus in metals and alloys the diffusion processes are intimately related to the structural behaviour of the materials; in the technology of solid-state devices, the control of the diffusion of impurities is of crucial importance in the manufacturing process, and in ionic solids the mechanism of the diffusion is of importance in the control of solid state reactions such as the oxidation of metals. Each of these particular applications tends to have its own special problems and, as a result, developments often appear to take place independently in the different fields. Nevertheless, all such studies in solid state diffusion are covered by the same basic models and theories, and in addition to specific applied problems, the pursuance of such studies greatly enhances fundamental knowledge of the physics and chemistry of solids.

It is convenient to divide diffusion studies into two groups:

- (i) Isothermal diffusion. In this the migration of the diffusing species is followed through a solid kept at a constant known temperature. The diffusing species may be an isotopically labelled atom or ion of the host material (self diffusion) *e.g.* K in K, K^+ in KCl, or it may be a species which is chemically distinct from the host material (impurity or chemical diffusion) *e.g.* Ca^{2+} in NaCl, Au in Pb. These studies can provide direct and detailed information about the mechanism of the diffusion process.
- (ii) Thermal diffusion. In this the migration of a solute species is followed in a solid which has a thermal gradient maintained along it. If a solid which has a uniform concentration of impurity atoms or ions throughout is

maintained in a temperature gradient, then one component of the solid will diffuse preferentially towards the higher temperature region, thus establishing a concentration gradient. This effect, called the Soret effect, is analogous to the redistribution of electrons which results in thermoelectric effects when a conductor is held in a temperature gradient. Although thermal diffusion studies also provide detailed information about the migration processes, the information is not so direct or so unambiguous as that obtained from isothermal methods. Much of the work in thermal diffusion is devoted to testing the applicability of the equations of irreversible thermodynamics to the process, and to the formulation of acceptable molecular interpretations of the parameters obtained from these equations. Thermal diffusion has been reviewed elsewhere¹ and in this article attention will be restricted to isothermal diffusion in ionic crystals.

2 Theory

A. Diffusion equations.—The quantitative treatment of diffusion is still based on the successful approach pioneered by Adolf Fick in 1855. Fick supposed that the flow or flux of diffusing species was proportional to the concentration gradient of that species in the diffusion medium. This is expressed as:

$$J_1 = - D_1 \left(\frac{\partial c_1}{\partial x} \right)_t \quad (1)$$

where J_1 is the flux of component 1 across a given plane and $(\partial c_1/\partial x)_t$ is the concentration gradient of that component in the direction x at time t . The constant of proportionality D_1 is the diffusion coefficient of the process. In a steady state when $(\partial c_1/\partial x)_t = 0$, equation (1) may be used directly, but more often the concentration gradient changes with time, in which case equation (1) is in an inconvenient form. In the case of variable concentration gradient, it is readily shown that:

$$\frac{\partial C_1}{\partial t} = D_1 \left(\frac{\partial^2 C_1}{\partial x^2} \right) \quad (2)$$

This is often called Fick's Second Law, and is the equation most frequently used for following isothermal diffusion processes. Equation (2) enables the concentration of the diffusing species at various positions (x) and times (t), to be related to the diffusion coefficient of the process. However, the solution of equation (2) is strongly dependent on the boundary conditions imposed, and therefore on the physical form of the diffusion system. Detailed treatments of these solutions are given elsewhere^{2,3} and only a brief description will be given here of commonly used conditions.

(i) *Diffusion into a semi-infinite solid.* If a bar of solid B has a thin film of solid A

¹ A. R. Allnat and A. V. Chadwick, *Chem. Rev.*, 1967, **67**, 681.

² W. Jost, 'Diffusion in Solids, Liquids, and Gases', Academic Press, 1952.

³ J. Crank, 'Mathematics of diffusion', Oxford University Press, 1956.

deposited on one end face and the couple annealed at a known temperature T for a given time t , then the concentration profile of A along the direction x into the solid B is:

$$C = \frac{C_0}{(\pi Dt)^{\frac{1}{2}}} \exp - \left(\frac{x^2}{4Dt} \right) \quad (3)$$

where C_0 = the initial concentration of A on the surface ($x = 0$). This solution to equation (2) satisfies the boundary conditions for this particular example *viz* that:

- (i) when $x = 0$ and $t = 0$, $C = \infty$ *i.e.* the entire amount of A is concentrated on the plane $x = 0$.
- (ii) for $t \rightarrow 0$ and $C \rightarrow 0$ then $x > 0$, *i.e.* diffusion takes place in the positive direction of x .
- (iii) the total amount of A present is constant, however it is distributed, since

$$\int_{-\infty}^{\infty} C dx = C_0$$

From equation (3) the diffusion coefficient D may be obtained from the slope of the line obtained by plotting $\ln(C)$ against x^2 . Essentially the same solution applies to diffusion from a thin film into a pair of semi-infinite solids as would be the case if the sample A were sandwiched between two bars of B .

(ii) *Diffusion of one semi-infinite solid into another.* Another common situation occurs when a bar of solid A is in contact with a bar of solid B , the dimensions of both being $\gg (Dt)^{\frac{1}{2}}$. The boundary conditions for this situation are:

- (i) $C = C_0$ when $t = 0$ and $x < 0$
- (ii) $C = 0$ when $x > 0$ and $t = 0$

The solution to equation (2) for these conditions is

$$C_{(x,t)} = \frac{C_0}{2} \left\{ 1 - \operatorname{erf} \left(\frac{x}{2(Dt)^{\frac{1}{2}}} \right) \right\}$$

Values of the Gaussian Error Function

$$\operatorname{erf} \left[\frac{x}{2(Dt)^{\frac{1}{2}}} \right]$$

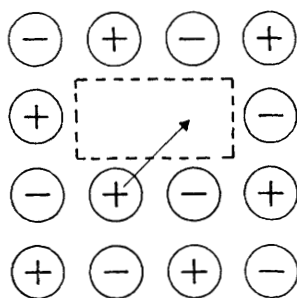
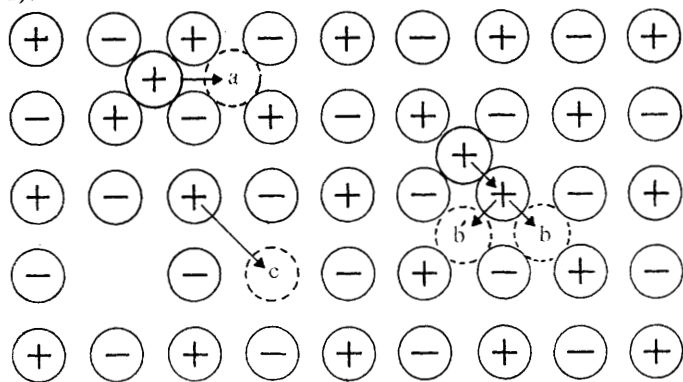
are available in standard tables, so that D can be computed from measurements of $C_{(x,t)}$ for various values of x .

B. Description of basic diffusion mechanisms.—The diffusion coefficients introduced in the previous section give no clue as to the mechanisms whereby an ion migrates from place to place in the crystal lattice. These mechanisms are best understood in terms of the lattice defects which are present in every ionic crystal above absolute zero. The basic types of lattice defect found in ionic systems are:

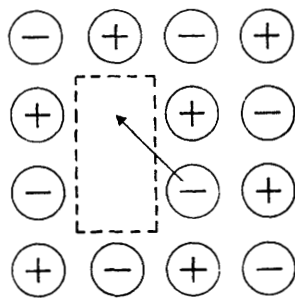
- (i) Schottky Defects—equivalent numbers of anion and cation vacancies.

(ii) Frenkel Defects—equal numbers of interstitials and corresponding vacancies in either the anion or cation lattice,

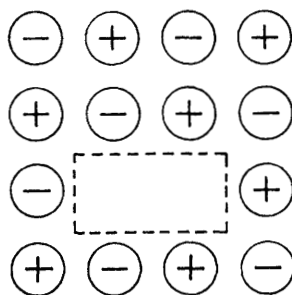
Based on these, the following mechanisms for diffusion can be distinguished (Figure 1):



d₁



d₂



d₃

Figure 1 Basic diffusion mechanisms. (a) interstitial, (b) collinear interstitialcy, (b') non-collinear interstitialcy, (c) vacancy, (d) vacancy pair mechanisms. (The three situations shown at d₁ d₂ d₃ illustrate the different orientations of the vacancy pair after successive cation and anion jumps.)

(i) The Interstitial mechanism, in which an ion in an interstitial position hops to any one of the neighbouring interstitial sites without permanently displacing any other ion.

(ii) The Interstitialcy mechanism, in which an interstitial ion displaces a neighbouring lattice ion (of its own kind) into the next interstitial position, and itself takes up the vacated lattice site. The two variations of this process, the collinear and non-collinear mechanisms, are illustrated in Figure 1b.

(iii) The Vacancy mechanism. Here, a cation in any site round a cation vacancy (or an anion in any site round an anion vacancy) may exchange places with the vacant site.

(iv) The Divacancy mechanism. The anion and cation vacancies have a net positive and negative charge respectively, and in some circumstances they may associate into vacancy pairs *i.e.* where two neighbouring sites in the crystal are empty. Diffusion *via* this defect can occur by anion and cation hopping into the appropriate 'half' of the vacancy pair, which then has a different orientation in the lattice. As diffusion proceeds, the vacancy pair moves through the crystal in an irregular series of end over end 'flip flop' motions. (Figure 1d).

Various other diffusion mechanisms are possible, *e.g.* a direct interchange between two ions of like sign, or a ring mechanism involving the co-operative exchange of site between a number of like ions. These and other mechanisms are very unlikely in ionic crystals, and attention may be restricted to those described.

The motion of a given ion (and its corresponding lattice defect) by any of the above mechanisms leads to a net displacement which is the vector sum of all the individual jump processes. Provided that these jumps are in random directions then the diffusion process can be treated as a random walk problem, and the macroscopic diffusion coefficient will then be a function of the jump frequency, the distance travelled per jump, and the total number of migrating species. A detailed treatment of random walk diffusion is given in several standard texts,^{4,5} but the relationship between the macroscopic diffusion coefficient and the ionic parameters may be shown by the following simplified approach.

Consider two adjacent planes of spacing λ in a simple cubic lattice. Let n_1 and n_2 be the numbers of diffusing ions per unit area in the planes 1 and 2 respectively. If Γ_{12} is the jump frequency for an ion from a given site in plane 1 to the corresponding site in plane 2, then the flux of ions from plane 1 to 2 per unit area per unit time is $j_{12} = n_1\Gamma_{12}$. Similarly the flux from plane 2 to 1 is $j_{21} = n_2\Gamma_{21}$ where Γ_{21} is the corresponding jump frequency.

The net flux of ions between the two planes is

$$J = j_{12} - j_{21} = (n_1\Gamma_{12} - n_2\Gamma_{21})$$

If the process is truly random so that the jump frequency is independent of direction then

$$J = (n_1 - n_2)\Gamma \text{ where } \Gamma = \Gamma_{21} = \Gamma_{12}$$

⁴ P. G. Shewmon, 'Diffusion in Solids', McGraw Hill, 1963.

⁵ J. R. Manning, 'Diffusion kinetics for atoms in crystals', Van Nostrand, 1968.

The ion concentration per unit area n_1 and n_2 may be written as concentrations per unit volume.

$$n_1 = \lambda c_1 \text{ and } n_2 = \lambda c_2 \text{ and } (n_1 - n_2) = \lambda(c_1 - c_2)$$

The concentration difference ($c_1 - c_2$) may be expressed in terms of the concentration gradient in the x direction by

$$(c_1 - c_2) = -\lambda \frac{\partial c}{\partial x}$$

so that $J = -\lambda^2 \Gamma \frac{\partial c}{\partial x}$

The jump frequency in the x direction is related to the total jump frequency ν by

$$\Gamma = \frac{1}{Z} \nu$$

where Z , the total number of possible choices of jump open to the diffusing ion is equal to the number of like neighbouring sites. In the simple cubic system being considered here $Z = 6$ so that

$$J = -\frac{1}{6} \lambda^2 \nu \frac{\partial c}{\partial x} \quad (5)$$

When this is compared with Fick's first law, equation (1), it is seen that in general

$$D = \frac{1}{Z} \lambda^2 \nu \quad (6)$$

where Z is dependent on crystal structure.

The frequency ν with which an ion jumps to an adjacent lattice site involves two probabilities:

(i) that the site to which it moves is vacant (in the case of a vacancy mechanism)

(ii) that the ion has sufficient thermal energy to surmount the surrounding potential barrier.

The first of these probabilities dictates the number of ions which are free to move according to the appropriate mechanism, and this number can clearly be equated to the concentration of defects per unit volume (n_d). The second probability determines the fraction of the jump attempts which are successful; this is governed by the usual Boltzmann factor and may be written as:

$$p = w \exp - \frac{\Delta g_m}{kT} \quad (7)$$

where w is the jump attempt frequency *i.e.* the normal lattice ion vibration in the direction of the contemplated jump, and Δg_m is a Gibbs free energy of activation for the motion of the ion from one potential minimum in the lattice, through a saddle point to the next potential minimum. The diffusion coefficient for the process can now be written

$$D = \frac{1}{Z} \lambda^2 n_a w \exp - \frac{\Delta g_m}{kT} \quad (8)$$

It is possible to extend the relation further by considering the concentration of defects n_a . The formation of a lattice defect is also a thermally activated process, and it is readily shown⁶ that in a lattice with Schottky defects the equilibrium number of cation vacancies or anion vacancies is given by

$$n_{v+} = n_{v-} = N \exp - \left(\frac{\Delta g_f}{2kT} \right) \quad (9)$$

where n_{v+} and n_{v-} are the numbers of cation and anion vacancies, N is the total number of sites per unit volume, and Δg_f is the Gibbs free energy of formation of the isolated Schottky pair. A similar relationship holds for Frenkel defects.

The diffusion process usually occurs by the migration of one type of defect, and if the expression for the concentration of defects of the appropriate type is substituted in equation (8) we have:

$$D = \frac{1}{Z} \lambda^2 w \exp \left(\frac{-\Delta g_f}{2kT} \right) \exp \left(\frac{-\Delta g_m}{kT} \right) \quad (10)$$

If the free energy terms are resolved into the corresponding enthalpies and entropies this becomes

$$\begin{aligned} D &= \frac{1}{Z} \lambda^2 w \exp \left(\frac{\Delta S_m + \frac{1}{2} \Delta S_f}{k} \right) \exp - \left(\frac{\Delta h_m + \frac{1}{2} \Delta h_f}{kT} \right) \\ &= D_0 \exp - \left(\frac{\Delta h_m + \frac{1}{2} \Delta h_f}{kT} \right) \end{aligned} \quad (11)$$

where all the entropy and other temperature independent constants have been included in the pre-exponential factor. This equation shows the validity of the linear relationship between $\ln D$ and $1/T$ which has long been recognised empirically.

Equation (11) has been derived on the assumption that the number of defects is the equilibrium concentration. At temperatures less than about 0.6 T_m (T_m = melting temperature) this is often untrue, due to the inevitable presence of impurities with higher valence than that of the host crystal ions. In a crystal of NaCl, any cation impurity such as Ca^{2+} will cause an extra cation vacancy because of the electroneutrality requirements. Such impurity-controlled defects are present in a constant, temperature independent concentration $n' \gg n$ (equilibrium) and in this region the diffusion will be determined by the migration of defects already present, with the diffusion coefficient given by

$$D = D'_0 \exp - \left(\frac{\Delta h_m}{kT} \right)$$

⁶ A. B. Lidiard, 'Ionic Conductivity', Handbuch der Physik, Springer-Verlag, 1957, 20, 246.

As the temperature is increased, the number of defects produced thermally eventually outweighs those present due to impurities, and the diffusion obeys equation (11). A plot of $\ln D$ against $1/T$ will show a break into two regions described as Intrinsic (high temperature) and Extrinsic (low temperature) and in principle, the activation enthalpies Δh_m and Δh_f can thus be determined from the two slopes. Although ionic diffusion in some solids shows this behaviour clearly, the parameters relating to defect mobility and formation are more easily obtained from ionic conductivity measurements.⁸

3 Correlation Effects

Probably the most important single concept to evolve in the study of solid state diffusion since the idea of the lattice defect by Frenkel in 1926⁷ is that of the Correlation Effect. This concept was introduced by Bardeen and Herring in 1951⁸ and results from the realisation that ion (or atom) migration in a solid is not necessarily a random process, but that a given jump direction may depend on the direction of the previous jump. When this is so, the random walk equations are modified by the introduction of a Correlation Factor f , which may be defined in general terms as the ratio of the diffusion coefficient actually observed to that which would be expected on the basis of a truly random walk migration. The subject of correlation effects is reviewed comprehensively by Manning⁵ and by LeClaire,⁹ but in this section a general summary of the topic is given. Consider a plane in a simple ionic lattice (Figure 2a) and assume that the lattice contains a cation vacancy, with a tracer cation on a neighbouring cation site. The process of diffusion can occur by any of the numbered cations 1—4 exchanging positions with the vacancy. This vacancy has no preference for exchange with any one of its neighbours so that its first jump is entirely random. Since we follow the diffusion process by the movement of the tracer, assume that the first jump of the vacancy is by exchange with position 2 leading to the situation (Figure 2b). The next jump of the tracer is not a random process since it is still a next neighbour of the vacancy (which continues its random motion), but the cation sites 1, 3, 4 are no longer next neighbours of the vacancy and there is a probability greater than random that the tracer will move back to 2 rather than jump to 1, 3, or 4. These latter jumps would require that the vacancy had moved round to 1, 3, or 4 before the tracer makes its next jump to one of these sites, and this requires either 2 separate jumps (to 1 or 3) or 3 separate jumps (to site 4) of the vacancy. It is therefore seen that of the choices available to the tracer (as at Figure 2b), a jump back to 2 is that of highest probability, jumps to 1 and 3 have equal and lower probability, and the jump to 4 has the lowest probability. When this non-random motion is considered over many consecutive jumps (n) the mean square displacement of the tracer, $\overline{R}_n^2(t)$, will be less than that of the vacancy, $\overline{R}_n^2(v)$, which took the same number of jumps. This means that the observed diffusion coefficient of

⁷ I. Frenkel, *Z. Physik*, 1926, **35**, 652.

⁸ J. Bardeen and C. Herring, 'Atom Movements', A.S.M. Cleveland, 1951.

⁹ A. D. LeClaire, 'Correlation Effects in Diffusion in Solids'. *Physical Chemistry—an advanced treatise*, ed. Eyring *et al.*, 1970 Vol. 10. Chapter 6.

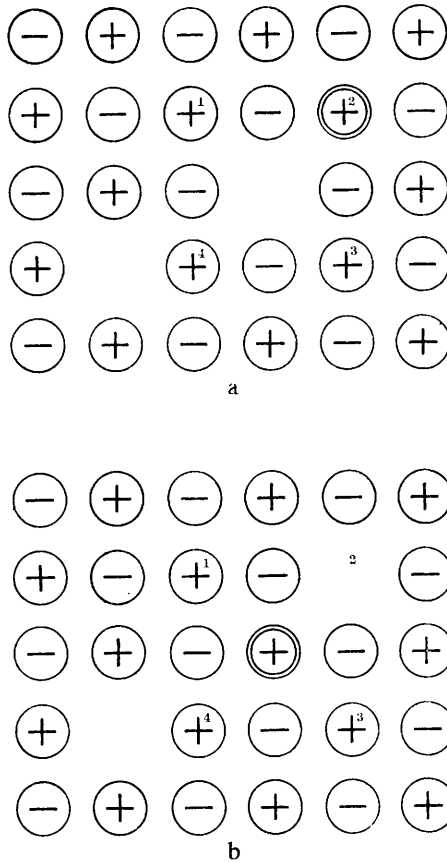


Figure 2 Correlated motion in vacancy diffusion. (\oplus tracer cation)

the tracer is less than if its motion were truly random (like the vacancy) and the correlation factor is given by

$$f = \lim_{n \rightarrow \infty} \frac{\overline{R_n^2(t)}}{\overline{R_n^2(v)}} \tag{12}$$

In the random walk analysis, the mean square displacement expressions are given in terms of the individual jump vectors. If the lattice geometry is such that these jumps are all of the same length then

$$\overline{R_n^2} = n\lambda^2 \{1 + 2(\overline{\text{Cos}\theta_1} + \overline{\text{Cos}\theta_2} + \dots + \overline{\text{Cos}\theta_j})\} \tag{13}$$

where $\overline{\text{Cos}\theta_j}$ is the average value of the cosine of the angle between one jump and the j th jump following. If there is no correlation between the value of θ for any

jump and the previous jump then all possible values of θ are equally allowed, and the summation of $\overline{\text{Cos}\theta_j}$ terms in equation (13) averages out to zero, giving $\overline{R_n^2} = n\lambda^2$.

When the jumps are correlated the $\overline{\text{Cos}\theta_j}$ terms no longer average to zero and f is given simply by the series within the braces in equation (13).

When all the jumps are of the same type, Compaan and Haven¹⁰ have shown for a vacancy mechanism that: $\text{Cos}\theta_j = (\overline{\text{Cos}\theta_1})^j$
so that

$$f = \{1 + 2 \text{Cos}\theta_1 + 2 \text{Cos}\theta_1^2 + 2 \text{Cos}\theta_1^3 + \dots - 2 \text{Cos}\theta_1^j\} \quad (14)$$

which gives by summation of the series,

$$f = \frac{1 + \overline{\text{Cos}\theta_1}}{1 - \overline{\text{Cos}\theta_1}} \quad (15)$$

Since $\text{Cos}\theta_1$ is always negative, f is always less than unity.

In interstitialcy diffusion (Figure 1b) the initial jump of the interstitial ion is a random one, but in the second jump there is a probability greater than random that the displaced ion will jump back to its original site. The third jump again by the original interstitial ion is once more a random one. Jumps for this type of diffusion are thus correlated in pairs and $\overline{\text{Cos}\theta_1}$ becomes zero for half the number of consecutive pairs giving

$$f = 1 + \overline{\text{Cos}\theta_1} \quad (16)$$

Here θ_1 is the average angle between the jump vectors for an interstitial to lattice jump and the succeeding lattice to interstitial jump. In the interstitial process, each jump is a random process with no correlation and so $f = 1$. The exact calculation of f from equation (15) or equation (16) requires evaluation of all the possible jump sequences of the defect from the time it causes a given ion (the tracer) to make a jump until it causes the same ion to make a second jump. The several mathematical procedures which have been adopted for the solution of this problem are summarised by Manning⁵ and by LeClaire⁹ and Table 1 gives the values which have been obtained for different mechanisms in different crystal structures.

Table 1 Correlation factors for self diffusion

Mechanism	Correlation Factor f
Vacancy (simple cubic lattice)	0.6531
Vacancy (body centred cubic)	0.7272
Vacancy (face centred cubic)	0.7815
Collinear Interstitialcy (face centred cubic)	0.6667
Non-collinear Interstitialcy (face centred cubic)	0.9697

¹⁰ K. Compaan and Y. Haven, *Trans. Faraday Soc.*, 1956, **52**, 786.

Howard¹¹ has computed the correlation factors for diffusion *via* vacancy pairs; there is no single unique value for this quantity since it depends on the ratio of the jump frequencies of the anion and cation into the vacancy pair. Values for some other crystal structures such as tetragonal have been calculated by Mullen¹² but the majority of experimental work has been concerned with systems of higher symmetry which are quoted in Table 1.

So far the discussion of correlation effects has been concerned with self diffusion where all the cation jumps (or anion jumps) have effectively the same frequency, assuming that the small mass difference between the tracer and the host is unimportant (see Section 4B). Many instances occur where it is appropriate to consider the diffusion of an impurity in a host crystal, *e.g.* Sr²⁺ in KBr. In the diffusion of an impurity cation by a vacancy mechanism, the probability of exchange with the vacancy more than once, resulting in a correlation effect, now depends on the relative jump frequencies of the impurity and host cations. Clearly if the neighbouring host cations exchange with the vacancy many times more rapidly than does the impurity cation, then the diffusion of the impurity will be as in the random walk analysis and $f = 1$. If we consider only the first vacancy-impurity exchange then the probability that the impurity will exchange again on the next vacancy jump is $w_2/(w_2 + \sum w_1)$, where w_2 and w_1 are the impurity and host jump frequencies. Substituting this probability for $\overline{\cos\theta_1}$ in equation (15) gives

$$f = \frac{w_1}{w_2 + w_1} \quad (17)$$

A more detailed treatment of the possible solvent jumps gives

$$f = \frac{B}{w_2 + B} \quad (18)$$

where B includes the host jump frequency w_1 and also geometrical and other relevant factors about the surroundings of the vacancy.

The substitution of impurity cations such as Ca²⁺ in a lattice such as NaCl produces equivalent numbers of cation vacancies in addition to those present in thermal equilibrium. The impurity cation here has an effective excess positive charge while the vacancy has an effective negative charge. The two 'defects' have a Coulombic attraction for one another and will tend to occupy adjacent sites, an arrangement known as an impurity-vacancy complex (or pair). If the pair is strongly bound then any solvent-vacancy jumps will tend to be restricted to those which allow the vacancy in its new position to remain as a near neighbour to the impurity. If the binding is not strong then dissociative jumps will be more frequent in which the vacancy wanders away (perhaps only temporarily) from the impurity. When this happens the possibility of the impurity cation moving by exchange with the vacancy has disappeared, and it cannot make another jump

¹¹ R. E. Howard, *Phys. Rev.*, 1966, **144**, 650.

¹² J. G. Mullen, *Phys. Rev.*, 1961, **124**, 1723.

until the vacancy (or another vacancy) arrives back as its near neighbour. To consider such a dissociative process in the correlation factor requires extension of the possible jump sequences to co-ordination shells beyond the nearest and next nearest neighbours. These are factors which contribute to the quantity B in equation (18). Thus for impurity diffusion in a f.c.c. lattice, allowing for dissociative jumps, LeClaire and Lidiard¹³ have shown that

$$f = \frac{w_1 + \frac{7}{2} w_3}{w_2 + w_1 + \frac{7}{2} w_3} \quad (19)$$

where w_3 is the frequency of the dissociative jump. Expressions of this general form are also obtained for impurity-vacancy diffusion in other crystal structures and also for interstitial impurity diffusion.

4 Determination of Diffusion Mechanism

The previous section has indicated the general approach to the calculation of correlation factors. The values so obtained are determined only by the crystal structure and by the mechanism of the diffusion process. Consequently it is seen that when the crystal structure is known, the detailed mechanism of the diffusion can be established by comparing an experimentally determined correlation factor with the theoretically possible values for that particular crystal structure. There are two methods for obtaining an experimental value for the correlation factor. These are:

(i) by comparing the diffusion coefficient obtained directly with that calculated from the ionic conductivity (The Conductivity Method).

(ii) by measuring the diffusion coefficients for two different isotopes of the diffusing species (The Isotope Method).

These two methods are now discussed separately.

A. The Conductivity Method.—The lattice defects discussed in Section 2B can migrate in the presence of an applied electric field giving rise to an ionic conductivity given by

$$\sigma = ne\mu \quad (20)$$

where n is the number of mobile defects per unit volume, e is the effective charge per defect, and μ is the mobility of the defect.

The motion of a defect under an applied e.m.f. involves the same activation processes as were discussed in Section 2B and it is readily shown⁶ that the variation of conductivity with temperature is given by

$$\sigma T = \sigma_0 \exp - \left(\frac{\Delta h_m + \frac{1}{2}\Delta h_f}{kT} \right) \quad (21)$$

¹³ A. D. LeClaire and A. B. Lidiard, *Phil. Mag.*, 1956, 1, 518.

where σ_0 contains entropy factors and other constants similar to those included in D_0 .

A plot of $\ln(\sigma T)$ against $1/T$ shows the same features as that of $\ln D$ vs. $1/T$, and provides a convenient and frequently used method for evaluation of the enthalpies of defect formation and mobility. The processes of diffusion and conduction are therefore closely related, and from equations (11) and (21) it follows that when the two processes occur by the same mechanism, then for an ionic species i ,

$$\frac{\sigma_i}{D_i} = \frac{Ne^2}{kT} \quad (22)$$

This is a particular form of the general Nernst-Einstein equation relating the diffusion coefficient of a charged species to its mobility.

The diffusion coefficient D_i will include a correlation factor dependent on the diffusion mechanism as discussed previously, but the motion of the defect giving rise to σ_i will not, since the defect moves in a random manner. The value of the diffusion coefficient for a random process can thus be calculated from the conductance and is

$$D_{\text{random}} = (D_i)_\sigma = \frac{\sigma_i kT}{Ne^2} \quad (23)$$

so that

$$f = \frac{D_T}{D_\sigma} \quad (24)$$

where D_T is the directly observed diffusion coefficient of the tracer. Equation (24) holds for mechanisms where the jump process moves an ion and a charge by an equal distance, e.g. vacancy and interstitial mechanisms (Figure 1a, c). In the interstitialcy mechanism (Fig. 1b), however, when the tracer ion moves a distance λ , the charge associated with it moves a distance 2λ , so that

$$f = \frac{2D_T}{D_\sigma} \quad (25)$$

In general then the ratio D_T/D_σ may contain geometrical displacement effects as well as the true correlation effect discussed in Section 3, but for relatively simple diffusion mechanisms where only one type of defect is mobile, the geometrical effects are easily recognised and D_T/D_σ provides a convenient measure of the experimental correlation factor.

One of the most successful applications of the conductivity method has been to AgCl and AgBr.¹⁴ In these salts, conduction is almost entirely cationic, and experiments on doped crystals¹⁵ indicate that they exhibit Frenkel disorder with

¹⁴ R. J. Friauf, *Phys. Rev.*, 1957, **105**, 843.

¹⁵ I. Ebert and J. Teltow, *Ann. Phys.*, 1955, **15**, 268.

both interstitial cations and cation vacancies being mobile. Four distinct mechanisms for the Ag^+ migration are therefore possible.

- (i) Ag^+ interstitial migration ($f = 1.00$)
- (ii) Ag^+ collinear interstitialcy ($f = 0.333$)
- (iii) Ag^+ non-collinear interstitialcy ($f = 0.727$)
- (iv) Ag^+ vacancy migration ($f = 0.781$)

For AgBr Friauf¹⁴ has made precise conduction and cation diffusion measurements as a function of temperature. His results show that f varies from 0.46 at low temperature to 0.65 at higher temperatures. This indicates that the vacancy or interstitial mechanisms cannot be operative, and shows further that both types of interstitialcy mechanisms occur, the collinear mechanism predominating at lower temperatures. By combining these results with Teltow's conduction data on doped crystals, Friauf has determined the activation energies for both types of interstitialcy motion, and also the contributions from each to the total diffusion. The situation in AgCl has been shown to be analogous in a similar analysis by Compton and Maurer.¹⁶ This work on silver halides shows strikingly how much information can be obtained about the detailed mechanism of ion diffusion by the conductivity method. However, few cases are as straightforward as the silver salts, and this is true of the alkali halides which as a group have been extensively studied. It is frequently found that deviations from the Einstein equation occur when D_T/D_σ is substantially greater or less than the values of f for particular mechanisms, and these deviations often provide much information about the diffusion process. Thus any association of defects into neutral entities such as vacancy pairs or impurity ion - host ion vacancy complexes will cause D_T to be greater than fD_σ . This is because the neutral complex cannot contribute to electrical conductivity but will contribute to diffusion. The existence of appreciable contributions from impurity cation - host cation vacancy complexes is shown by measuring impurity cation diffusion coefficients in the crystal. For this type of complex, the value of D for the impurity cation will be the same as for the host cation since the two 'parts' of the complex diffuse together. Similar conclusions apply to anion impurity complexes although these have been less extensively studied than cations. Contributions from anion - cation vacancy pairs are recognised when the anion and cation diffusion coefficients are comparable and have similar activation energies. Further, the anion (and cation) diffusion coefficients will not be changed by doping the crystal with aliovalent impurities; this is because addition of aliovalent cations increases the number of free cation vacancies, decreases the number of free anion vacancies [see equation (9)] but does not alter the number of vacancy pairs.¹⁷

The earlier work on the alkali halides suggested that cation diffusion occurred predominately by a simple vacancy mechanism but more recent work has shown that vacancy pairs contribute appreciably. In particular, Friauf¹⁸ has concluded from diffusion studies in the presence of an electric field that approximately 50%

¹⁶ W. D. Compton and R. J. Maurer, *J. Phys. and Chem. Solids*, 1956, 1, 191.

¹⁷ A. B. Lidiard, *J. Phys. and Chem. Solids*, 1958, 6, 298.

¹⁸ V. C. Nelson and R. J. Friauf, *J. Phys. and Chem. Solids*, 1970, 31, 825.

of the cation diffusion in NaCl near the melting point is due to vacancy pairs. However, the question of vacancy pair diffusion in alkali halides is still incompletely resolved, and differences of opinion exist as to the concentration and contribution of these complexes.

B. The Isotope Method.—The isotope effect depends on the fact that two different isotopes of the same species will have slightly different diffusion rates and correlation factors, because of the difference in mass (and therefore a difference in jump frequency). In the case of self diffusion, equation (17) may be applied since the tracer ions may be treated as a special type of impurity. The ratio of the diffusion coefficients for two isotopes α and β may be written as

$$\frac{D_{\alpha}}{D_{\beta}} = \frac{w_{\alpha} f_{\alpha}}{w_{\beta} f_{\beta}} \quad (26)$$

where w and f are the jump frequency and correlation factor, and by utilising equation (17) it may be shown that

$$\left(1 - \frac{D_{\alpha}}{D_{\beta}}\right) / \left(1 - \frac{w_{\alpha}}{w_{\beta}}\right) = f_{\alpha} \quad (27)$$

This holds when there is only one type of jump for each tracer, but when more than one type of jump is possible (as for example in interstitialcy motion) then equation (27) is modified with geometrical factors. Since the two diffusing tracers are chemically identical, the ratio of their jump frequencies w_{α}/w_{β} may be written as $(m_{\beta}/m_{\alpha})^{\frac{1}{2}}$ where m is the mass. The general application of the isotope method consists of comparing the experimentally determined left hand side of equation (27) with the possible values of the right hand side.

For true impurity diffusion, f has no single discrete value, but depends on the ratio of solvent : impurity jump frequencies. The right hand side of equation (27) can thus have a series of values even for a given mechanism and consequently the isotope method does not give such direct information about impurity diffusion as it does for self diffusion. However, if the mechanism for impurity diffusion is known from other measurements, then the isotope method gives important information about the relative jump frequencies of host and impurity ions.

Equation (27) holds when the diffusion process involves only one ion, *i.e.* when the diffusing ion moves through the saddle point configuration without sharing its kinetic energy with the surrounding lattice ions. LeClaire¹⁹ has shown when this is not so, then $1 - w_{\alpha}/w_{\beta}$ will be smaller than required by equation (27), with the result that

$$\left(1 - \frac{D_{\alpha}}{D_{\beta}}\right) / \left[1 - \left(\frac{m_{\beta}}{m_{\alpha}}\right)^{\frac{1}{2}}\right] = f \Delta k \quad (28)$$

¹⁹ A. D. LeClaire, *Phil. Mag.*, 1966, **14**, 1271.

In this modification, Δk represents the distribution or sharing of kinetic energy between the diffusing species and the rest of the lattice. The left hand side of equation (28) is again obtained by experiment, but since Δk is not known uniquely, the correlation factor cannot be determined with precision. However, Δk must range from 0 to 1 so for a given mechanism it is possible to put limits on the magnitude of $f\Delta k$ which can then be compared with the left hand side of equation (28). In this way it is often possible to show that only one mechanism gives agreement with the experimental facts.

One application of the Isotope method which may be cited here is that of Barr²⁰ on the isotope effect for cation diffusion in NaCl. A great deal of other evidence has indicated that cation diffusion in NaCl is predominantly by the vacancy mechanism. By diffusing ²²Na and ²⁴Na simultaneously into NaCl, the left hand side of equation (28) has been evaluated and shown to be clearly and unambiguously consistent with the correlation factor required for this mechanism.

5 Summary

This article has outlined some of the important concepts relevant to solid-state diffusion studies, and has indicated briefly some of their applications. Space does not permit any discussion of the general experimental techniques which are used in this field, but useful coverage of this is included in references 14 and 20.

The discussion has indicated the wealth of detail which can be obtained about ionic diffusion processes. In ionic crystals particularly, complimentary studies such as conduction in doped crystals and dielectric relaxation measurements are frequently useful in backing up direct diffusion measurements to provide clear identification of the diffusion mechanism. When the mechanism is known, the isotope method of measuring f has shown up the importance of the quantity Δk . This provides information about the transition state in the solid which cannot at present be obtained in any other way, and it is likely that future studies will be increasingly concerned with this quantity and its interpretation.

²⁰ L. W. Barr and A. D. LeClaire, *Proc. Brit. Ceram. Soc.*, 1964, 109.