

MONOGRAFIAS DE FÍSICA

XII

DIFFUSION IN SOLIDS

by

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FOREWORD

During the month of August, 1962, a series of five lectures was given at the Centro Brasileiro de Pesquisas Físicas, Rio de Janeiro. These lectures were intended to present some rather practical aspects of the measurement and interpretation of diffusion coefficients in inorganic crystals. Special emphasis was placed on the metallic oxides, which have been under investigation by the Solid State Research Group at Indiana University for the past ten years. The important subject of diffusion in metals and alloys was hardly mentioned. Clearly, therefore these lectures were not intended to provide a systematic introduction to the entire field, but were more in the nature of a personal commentary on some interesting current research problems.

I wish to thank the National Science Foundation for a travel grant which permitted me to take part in the Solid State Program at the Centro Brasileiro de Pesquisas Físicas.

Walter J. Moore

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Lecture 1

DIFFUSION IN SOLIDS

Diffusion is the fundamental rate process in the solid state. Whereas in gaseous systems, and usually in liquids, diffusion of reactants is so rapid that it is not a rate determining step, in solids the overall rate of a reaction is usually controlled by the rate of diffusion of reactant species. Examples of diffusion-controlled processes are (a) sintering (b) gaseous corrosion of metals (c) annealing of radiation damage. As a consequence, experimental and theoretical studies of solid-state diffusion are of basic importance in materials research. Another field of important applications is solid-state electronics.

The first investigation of diffusion in solid metals was by W. C. Roberts-Austen¹, the English metallurgist. He found a surprising result: the interdiffusion of gold and lead at about 400 °C was as fast as that of salt in water at room temperature. How could atomic movements be so fast in a rigid solid? This problem was solved by the recognition of the fact that crystals are not perfect but contain point defects. These defects were first described by W. Schottky and I. Frenkel (1930 to 1935). Thus diffusion can occur

* Notes on lectures given at Centro Brasileiro de Pesquisas Físicas, Rio de Janeiro, August, 1962.

by the process of jumping of atoms from normal lattice sites into defects such as vacancies or interstitials. In its simplest formulation, we can consider a diffusion coefficient D to be the product of two terms,

$$D = X_i D_i$$

where X_i is the atom fraction of defects and D_i is the diffusion coefficient of a defect. The term X_i is purely thermodynamic, an equilibrium quantity, given by

$$X_i \propto e^{-\Delta G^\circ/RT} = e^{\Delta S^\circ/R} e^{-\Delta H^\circ/RT}$$

where ΔG° , ΔS° and ΔH° are the free energy, entropy and enthalpy of formation of the defect. The term D_i , from transition state theory, would be

$$D_i = \frac{kT}{h} a^2 e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT}$$

where a is the jump distance in the elementary diffusion step, and ΔH^\ddagger and ΔS^\ddagger are the enthalpy and entropy of activation.

It is evident that a knowledge of the defect mechanism of a given diffusion process, together with a knowledge of ΔH° , ΔS° , ΔH^\ddagger and ΔS^\ddagger can lead to quite a deep understanding of the nature of the solid state of the substance being studied.

Definition of Diffusion Coefficients

The definition of the diffusion coefficient D is given by Fick's First law as the factor of proportionality between J_{AX} the

flux of a constituent A in the χ direction and the negative gradient in the concentration of A in that direction,

$$J_{A\chi} = -D_{A\chi} \left(\frac{\partial C_A}{\partial \chi} \right) \quad (1)$$

We know from first principles of irreversible thermodynamics that the flux should depend on the gradient of chemical potential ($\partial \mu_A / \partial \chi$), so that $D_{A\chi}$ in eq. (1) will not in general be a constant, but a function of the concentration.

In the limit, as the gradient $\rightarrow 0$, we can define the self-diffusion coefficient as

$$D_{A\chi} = \lim_{(\partial C_A / \partial \chi) \rightarrow 0} \left[\frac{-J_A}{(\partial C_A / \partial \chi)} \right]_{C_A} \quad (2)$$

We cannot measure this quantity directly, but in a few cases it can be determined from broadening of NMR peaks or from the electrical mobility, μ , of a particle of charge q through the Nernst-Einstein relation,

$$\frac{D}{\mu} = \frac{kT}{q} \quad (3)$$

The quantity which in fact is most usually measured is the tracer diffusion coefficient. In his excellent review article, D. Lazarus² develops the theory for a tracer atom A^* diffusing in a solid of atoms A. The flux of A^* is given by,

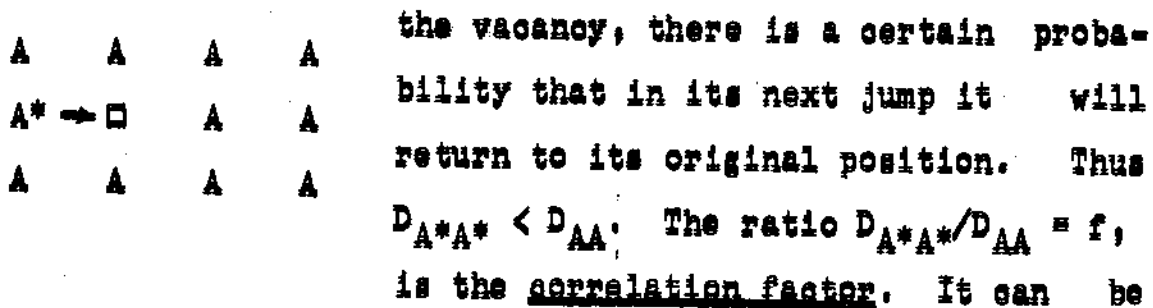
$$J_{A^*} = - b_{A^*A^*} \frac{\partial \mu_{A^*}}{\partial x} - b_{A A^*} \frac{\partial \mu_A}{\partial x}$$

where the b's are the mobilities. Note that in addition to the first term, the diffusion current, there is a second term which gives the flux of A* due to a gradient in chemical potential of A. It turns out that

$$D_{A^*A^*} = D_{AA} - D_{AA^*} \quad (4)$$

tracer diffusion	self diffusion	cross term giving effect of correlation between tracer and solvent atom jumps.
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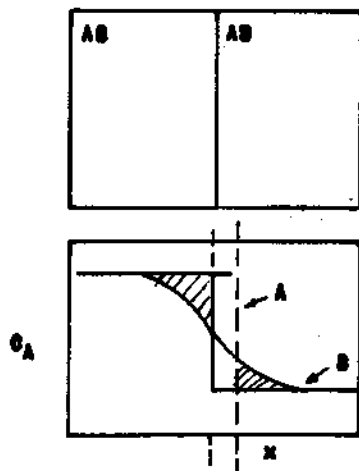
The correlation term can be very useful in deciding between alternative mechanism of diffusion. We can see how it arises in the simple case of vacancy diffusion. If a tracer atom jumps into



as low as 0.3. For a simple exchange mechanism it would be 1.0. The usual way to measure f is by a comparison of the tracer diffusion coefficient with the D calculated from eq. (3) from conductivity data.

If we consider diffusion between two binary solutions of different concentration we can define as interdiffusion coefficient, D^0 .

$$\frac{\partial c_A}{\partial t} = \frac{\partial}{\partial x} \left(D^c \frac{\partial c_A}{\partial x} \right) \quad (5)$$



This D^c measures the interdiffusion of A and B. In general it is a function of the concentration. In the particular case of an ideal solution, and one in which the Fick First Law applies, we have

$$D^c = X_A D_B + X_B D_A$$

where X_A and X_B are the atom fractions and D_A and D_B are called the intrinsic diffusion coefficients. Note that the usual interdiffusion experiment does not allow one to find either D_B or D_A directly. In the special case where $X_A \ll 1$ and $D_B/D_A < 1$, $D^c \approx D_A$. This is the case of impurity diffusion under the influence of a gradient in chemical composition.

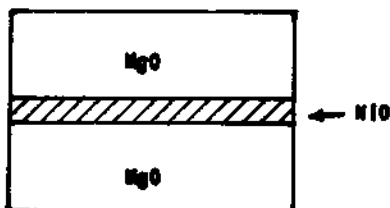
Even in this ideal case, D_B and D_A are functions of concentration so that only the values at very low dilution can be obtained.

An Example of Measurement of Impurity Diffusion

An example of such a study is the recent work of Wuensch and Vasilos³ on diffusion of Fe, Co, Ni into single crystals of MgO. They used a "sandwich couple" but did not specify the thickness of the NiO layer, except to say it was "very thin". They used the

solution for plane source of initial activity M ,

$$C = \frac{M}{2(\pi Dt)^{\frac{1}{2}}} \exp(-x^2/4Dt) \quad (7)$$



They could have used the correct solution for a source of thickness h , initial concentration C_0 ,

$$C = \frac{1}{2} C_0 \left\{ \operatorname{erf} \frac{h-x}{2\sqrt{Dt}} + \operatorname{erf} \frac{h+x}{2\sqrt{Dt}} \right\} \quad (8)$$

They analyzed the specimen with x-ray emission using a microprobe of diameter $< 1\mu$. Typical data gave a linear plot of $\log c$ vs. x^2 except for an initial region. At $X = .01$, equation (6) would give

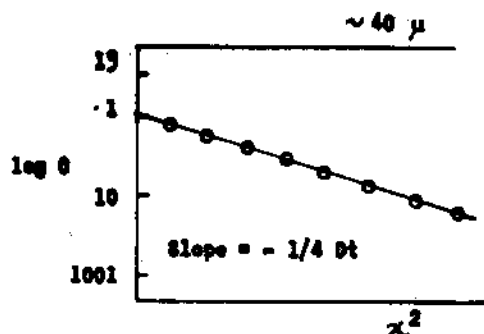
$$D^c = 0.01 D_{Mg} + 0.99 D_{Ni}$$

in this case. $D_{Mg} < D_{Ni}$ so that

$$D^c \approx D_{Ni}$$

Although the treatment given by these authors is not exact, they apparently did measure the intrinsic diffusion coefficients

as stated. Clearly, however, one must be very careful in such an

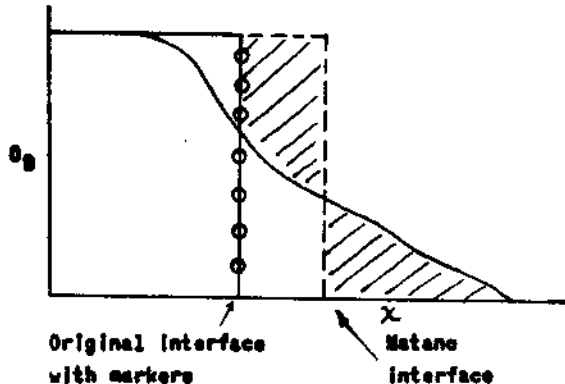


experiment and it is better to use the more exact mathematical treatment of the data, and not to rely on "intuition".

Marker Movements

In principle it should be possible to determine intrinsic diffusion coefficients from the interdiffusion coefficient and the rate of movement of markers placed at the interface of the diffusion couple.

(Kirkendall effect). If $D_A \neq D_B$ the boundary must move with respect to the Matano interface. The velocity of boundary movement (if local defect equilibrium is maintained) would be



$$v = (D_A - D_B) \frac{\partial c_A}{\partial x} \quad (9)$$

Hence, from equation (6) and (9) we should be able to get

both D_A and D_B . In practice, this method has had limited usefulness. The assumption of local defect equilibrium does not always hold. For example, Hermann and Walther⁴ put markers throughout the system and found motion not only at interface but also at ends of the diffusion zone.

Relation Between D and Mobility b

$$J_{Ax} = C_A b_{Ax} (\partial \mu_A / \partial x)$$

$$\mu_A = \mu_A^\circ + kT \ln \gamma_A C_A$$

$$J_{Ax} = -kT C_A b_{Ax} \left(\frac{\partial \ln C_A}{\partial x} + \frac{\partial \ln \gamma_A}{\partial x} \right)$$

$$= -kT C_A b_{Ax} \left(\frac{1}{C_A} \frac{\partial C_A}{\partial x} + \frac{\partial \ln \gamma_A}{\partial C_A} \frac{\partial C_A}{\partial x} \right)$$

$$= -kT b_{Ax} \left(1 + \frac{\partial \ln \gamma_A}{\partial \ln C_A} \right) \frac{\partial C_A}{\partial x}$$

By comparison with Fick's First Law,

$$D_{Ax} = kT b_{Ax} \left(1 + \frac{\partial \ln \gamma_A}{\partial \ln C_A} \right) \quad (10)$$

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Lecture 2

EXPERIMENTAL METHODS

We shall give a concise survey of some of the methods most often used to study tracer diffusion.

A. Tracer Diffusion - Surface Activity Methods

(1) A thin source covers the surface of the specimen which is sectioned after the diffusion anneal. The method is good for $D \gg 10^{-12} \text{ cm}^2 \text{ s}^{-1}$. Notes on experimental technique:

- a. A precision grinder is accurate to 0.1μ . For high D , a lathe can be used.
- b. A microbalance or semimicrobalance is useful for determining thickness of sections.
- c. One should use a single crystal. If noncubic its orientation must be known.
- d. Precautions must be taken to eliminate effects of surface diffusion. Best method is to remove and count surface layers separately.
- e. Probably best tracer is a fairly hard γ emitter. Then no absorption correction is needed and counting can be done in well type scintil-

lation counter.

The equations to evaluate D have already been given in eqs. (7) and (8). The same basic method can also be used with some other method of analysis perpendicular to the section, for example, autoradiography in suitable cases.

(2) Method of decline in surface activity. We need to know the absorption coefficient, μ . Then the surface activity becomes

$$A = \int_0^{\infty} c(x) e^{-\mu x} dx \quad (11)$$

The method requires a homogeneous radiation, although we could use a mixed radiation and fit the data numerically. If β radiation is used, we must be sure we are in the exponential region of absorption curve. Eq. (11) with eq. (7) yields

$$A/A_0 = \exp(\mu^2 Dt) \left\{ 1 - \operatorname{erf}(\mu \sqrt{Dt}) \right\} \quad (12)$$

This method is probably at its best with quite soft γ -rays. The counting must be done carefully and geometric corrections made. C. E. Birchenall and R. H. Condit⁵ gave a detailed discussion of the errors and corrections for this method.

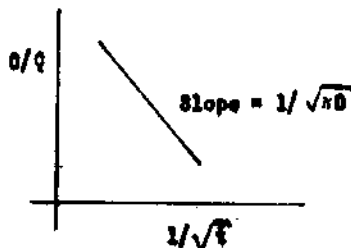
(3) Method of activity after sectioning. It was originally used by Gruzin. Recently it was used by Choi and Moore⁶ for nickel oxide. The surface activity after removal of a section of thickness X_1 is

$$A = \int_{X_1}^{\infty} \frac{1}{\sqrt{\pi Dt}} \exp(-x^2/4Dt) e^{-\mu x} dx \quad (13)$$

A convenient treatment of the data for the case $x^2/4Dt \ll 1$ is given in the paper cited. This method is convenient and more accurate than method (2). Geometric factors need to be carefully considered in the counting procedure.

(4) Method of extremely thin surface sample. This method was given by Joukhovitsky and Geodakyan. If surface sample is thin enough, eq. (7) reduces to

$$C = Q/\sqrt{\pi Dt} \quad (14)$$



Then a plot of C/Q vs. $t^{-1/2}$ gives D . The surface sample must be taken by an electrographic method or some similar technique.

(5) Method of activities on both sides of a thin slice. Kriakov and Joukhovitsky give this method, which eliminates the absorption coefficient. The ratio of the activities on the active side and on the reverse side of a slice of thickness l is:

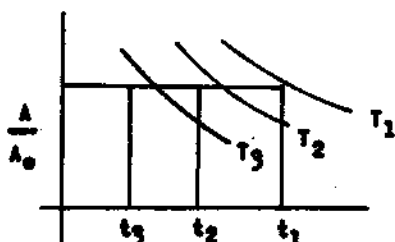
$$\frac{A_1}{A_2} = \frac{1 + B \exp(-\pi^2 Dt/l^2)}{1 - B \exp(-\pi^2 Dt/l^2)} \quad (15)$$

It follows that:

$$\log \frac{A_1 - A_2}{A_1 + A_2} = f(t)$$

The function is linear with slope $-\pi^2 D/l^2$. With a slice $\sim 100\mu$, the method is suitable for $D > 10^{-11} \text{ cm}^2 \text{ s}^{-1}$.

(6) Method for activation energies. Joukhovitsky also gave a rapid method for getting the activation energy of diffusion. He uses the surface activity method to get a set of curves of A vs. t for different temperatures. He reads the



times for a fixed fraction of original activity and plots these as $t = t_0 e^{-E/RT}$ ($\ln t$ vs T^{-1}) to get E .

B. Tracer Diffusion - Exchange Methods.

We were led to use this method to study oxygen diffusion in oxides with the tracer ^{18}O , since sectioning methods would be extremely difficult and tedious. We also used it to study diffusion in ZnO in an atmosphere of zinc vapor. In oxygen diffusion we exposed single crystals of oxide to enriched oxygen (about 5% ^{18}O usually) and analyzed the gas with a mass spectrometer. In case of ^{65}Zn we made radioactive ZnO crystals, exposed them to inactive Zn vapor, and measured the loss in activity of the crystal. Morrison⁷ used radioactive NaCl crystals and directly measured the appearance of activity in a current of Cl_2 gas passed over the crystals.

(1) Exchange of plane sheet with limited amount of fluid.

If $\lambda = n_g/n_s$, the ratio of number of moles of exchanging component in gas and in solid, the total uptake of activity M_t at time t is given by (with l = thickness of sheet):

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2\lambda(1+\lambda)}{1+\lambda+\lambda^2 q_n^2} \exp(-Dq_n^2 t/l^2) \quad (16)$$

with

$$\tan q_n + \lambda q_n = 0.$$

Solutions are also available for spheres and parallelepipeds. Note that it is not necessary to use a single large sheet. Pieces of crystal will suffice, provided the area of the flat surfaces greatly exceeds that of the sides. However, it is important to secure free mixing of the gas and circulation of the gas over both sides of the sheets. A source of possible error is evaporation of the crystals. The evaluation of the data must be made numerically, although curves exist for rapid checking of approximate D values from exchange data [Crank gives examples and references].

(2) Exchange with surface reaction rate controlling. In the exchange method, it is necessary to test to determine whether the exchange is in fact controlled by diffusion. It is possible in some cases, particularly at lower temperatures, to have the overall exchange controlled by the rate of the surface exchange reaction. The test is to vary the dimensions of the specimen. For example, if we double the thickness we do not affect the rate of surface reaction, but we decrease by a factor of 1/4 the half

time for an exchange controlled reaction.

An interesting case in theory, which probably has not yet been found experimentally, is an exchange reaction controlled by the rate of the solid-state reaction itself. Consider, for example, the interstitial diffusion of tracer M^* in an oxide MO . The M^* might diffuse rapidly from one interstitial site to the next, but only slowly exchange with lattice M . The theory of such a process of interstitial diffusion coupled with exchange was given by R. W. Reddington⁸ for case of diffusion of Ba in BaO . We can think of it as a diffusion coupled with a trapping process. We shall discuss it further when we consider interstitial mechanisms.

The most extensive treatment of surface reaction coupled with diffusion has been that of Haul and coworkers⁹.

For the case of spherical particles, they give

$$\frac{M - M_0}{M_\infty - M_0} = \frac{1 + \beta}{2\beta} \operatorname{eerfc} \left\{ (1 - \beta) \alpha t^{\frac{1}{2}} \right\} - \frac{1 - \beta}{2\beta} \operatorname{eerfc} \left\{ (1 + \beta) \alpha t^{\frac{1}{2}} \right\} \quad (17)$$

Here,

$$\alpha = K/2D^{\frac{1}{2}}, \quad \beta = \left(1 - \frac{4DS}{K} \right)^{\frac{1}{2}} \quad \lambda = n_g/n_s$$

K is the surface reaction rate constant in cm s^{-1} ; S is the surface area of crystals. The function $\operatorname{eerfc}(x) = \exp x^2 (1 - \operatorname{erf} x)$. They used this theory to study interaction of $^{18}\text{O}_2$ with CdO at 630 to 855 °C, and gave values for both K and D . In our work with

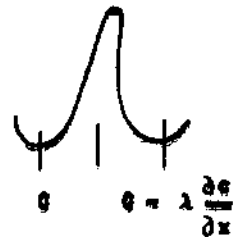
NiO we preferred to use larger crystals (small S) and high temperature. Thus there was no influence of surface reactions. What one would really like to see is an extension of the results of Haul to higher temperatures (and larger crystals) at which D alone determines the rate, and to lower temperatures (and smaller crystals) at which K alone is important. Until this is done we cannot be sure that he is not simply curve fitting to a two parameter function without the physical significance he assigns to it.

* * *

Lecture 3

TEMPERATURE DEPENDENCE

Probably the most important insight into the mechanisms of diffusion is given by measurements of the temperature dependence of D . We can discuss this temperature dependence in terms of the transition-state theory. The number of particles moving per cm^2 per sec in the forward direction is $Nc\lambda k_1$. In reverse direction, $N\left(c - \lambda \frac{\partial c}{\partial x}\right) \lambda k_1$. Therefore, the net flow is $N\lambda^2 k_1 \frac{\partial c}{\partial x}$. Thus, $D = \lambda^2 k_1$ where k_1 is the rate constant, the number of times per second a molecule jumps. From the theory of Eyring,



$$k_1 = \frac{kT}{h} e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT}$$

Hence,

$$D^E = \lambda^2 \frac{kT}{h} e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT} \quad (18)$$

An alternative formulation was given by Zener¹⁰, leading to

$$D^Z = \lambda^2 \bar{\nu} e^{-\Delta S^*/R} e^{-\Delta H^*/RT} \quad (19)$$

The Zener interpretation is that ΔG^* is the isothermal work required to move the diffusing atom from the initial state to the activated state, with the constraint that the moving atom can vibrate only in a plane normal to its direction of motion. It turns out that

$$\Delta H^* (\text{Zener}) = \Delta H^\ddagger (\text{Eyring}) + RT \quad (20)$$

The Zener ΔH^* is the average energy above the ground state; the Eyring ΔH^\ddagger is the height of the barrier.

The simple expression $D = D_0 e^{-E/RT}$ is often used. We see that this apparent activation energy, $E = \Delta H^\ddagger + RT = \Delta H^*$.

The treatment of Zener was extended by Vineyard¹¹. He considered the jump process as a generalized many-body transition in phase space and obtained for the jump frequency,

$$\bar{\nu} = \prod_{i=1}^N \nu_i / \prod_{i=1}^{N-1} \nu_i^* \quad (21)$$

The ν_i are the N normal frequencies of the system in the ground state and the ν_i^* are the $N-1$ normal frequencies in the excited state (i.e. at the saddle point). This treatment seems physically reasonable in that it considers the motion of the atoms that constitute the barrier as well as the motion of the diffusing atom. The difficulty, however, is that we have no way of readily computing the ν_i^* or even the ν_i . Vineyard applied his formulation to the problem of the mass dependence of

the diffusion coefficient (in particular the isotope effect) He gives for the jump probability an expression,

$$\Gamma = \frac{c'}{\sqrt{m^*}} \exp - [\phi(P) - \phi(A)]/kT \quad (22)$$

where P refers to the saddle point and A to the initial point, and m^* is an effective mass,

$$m^* = c_1^2 + (1 - c_1^2) m_2$$

Here m_1 is the mass of the diffusing atom and m_2 is the mass of the atoms on the host lattice. The factor c_1 is the cosine of the angle between the normal to the reaction coordinate at P and a suitably chosen axis 1. No method is provided, however, for calculating c_1 . It is evident that m^* must be between m_1 and m_2 .

The theories of Eyring, Zener, and Vineyard are all based on the assumption that the transition state in the diffusive process can be treated as an equilibrium state. A nonequilibrium or dynamical method of treating diffusion has been developed by Alan R. Allnatt and Stuart A. Rice. In this theory, attention is focused on a particular atom in a subvolume consisting of its neighbors, and the condition for a jump is the occurrence of a sufficiently large amplitude of vibration in the direction of motion, with a corresponding out of phase motion of the barrier atom in the subvolume. For a vacancy mechanism, Rice obtained the following expression for the jump frequency,

$$\Gamma = \bar{\nu} \phi \exp - \left[\left(V_0 + \sum_j V_j + \sum_{k>l} W_{kl} \right) / RT \right] \quad (24)$$

Here ϕ is the site fraction of vacancies, $\bar{\nu}$ is a weighted mean frequency of contributing normal modes of vibration, V_j is the energy required by j 'th barrier atom to move from its equilibrium position, V_0 is the critical energy required for the diffusion atom to attain the necessary amplitude, W_{kl} is the interaction energy, the potential of the mean force acting between all pairs of atoms. The term W_{kl} can be considered as a Gibbs free energy of activation,

$$W_{kl} = \Delta H_{kl} - T\Delta S_{kl}$$

Finally, this treatment gives for the pre-exponential factor D_0 an apparent activation energy Q of the diffusion coefficient:

$$D_0 = \gamma d^2 \bar{\nu} \exp \left[\left(\Delta S_1 + \sum \Delta S_{kl} \right) / R \right] \quad (25)$$

$$Q = \frac{\Delta H_1 + V_0 + \sum V_j + \sum \Delta H_{kl}}{RT}$$

The ΔH_1 and ΔS_1 are the enthalpy and entropy of formation of the vacancies.

Another dynamical model of diffusion has been proposed recently by Prigogine and Bak¹³. A curious result of this theory is its prediction that D should depend inversely on the

square of the mass of the diffusing atom. This result contrasts with the inverse dependence on the square root of the mass in the Zener theory. Although data on isotopic effects in diffusion are scanty, there is no experimental evidence for such a marked effect as that predicted by Prigogine and Bak.

Pressure Dependence

Not many experimental measurements of pressure dependence have yet been made, but it should be important in the future. Noteworthy is the work of Nachtrieb¹⁴. The pressure coefficient of D is determined by the activation volume, ΔV^\ddagger .

$$\left(\frac{\partial G}{\partial P} \right)_T \approx \left(\frac{\partial A}{\partial P} \right)_T = V$$

$$D = \frac{kT}{h} \lambda^2 e^{-\Delta G^\ddagger / RT}$$

$$\left(\frac{\partial \ln D}{\partial P} \right)_T = \frac{\Delta V^\ddagger}{RT} \quad (26)$$

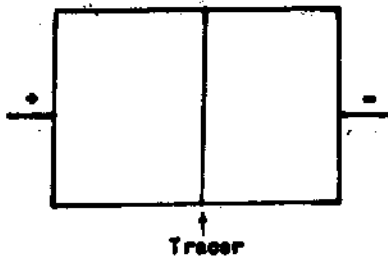
Effect of Electric Fields

For particles of mobility μ in an electric field E ,

$$\frac{\partial c}{\partial t} = -\mu E \frac{\partial c}{\partial x} + D \frac{\partial^2 c}{\partial x^2}$$

The solution for a thin layer of tracer at $x = 0, t = 0$, is

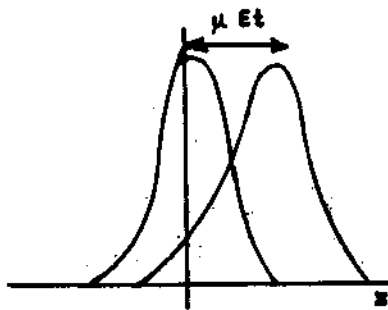
$$C(x,t) = \frac{C_0}{(\pi Dt)^{\frac{1}{2}}} \exp \left\{ \frac{-(x - \mu Et)^2}{4 Dt} \right\} \quad (27)$$



This gives a distribution of the same form as in the absence of the field, except that the origin is displaced by μEt . Thus it is possible to get μ and D from a single experiment and to determine whether the diffusing species

is charged. Such experiments were made by M. Chemla¹⁵ on monovalent and bivalent impurities in NaCl. For Cs in NaCl he found

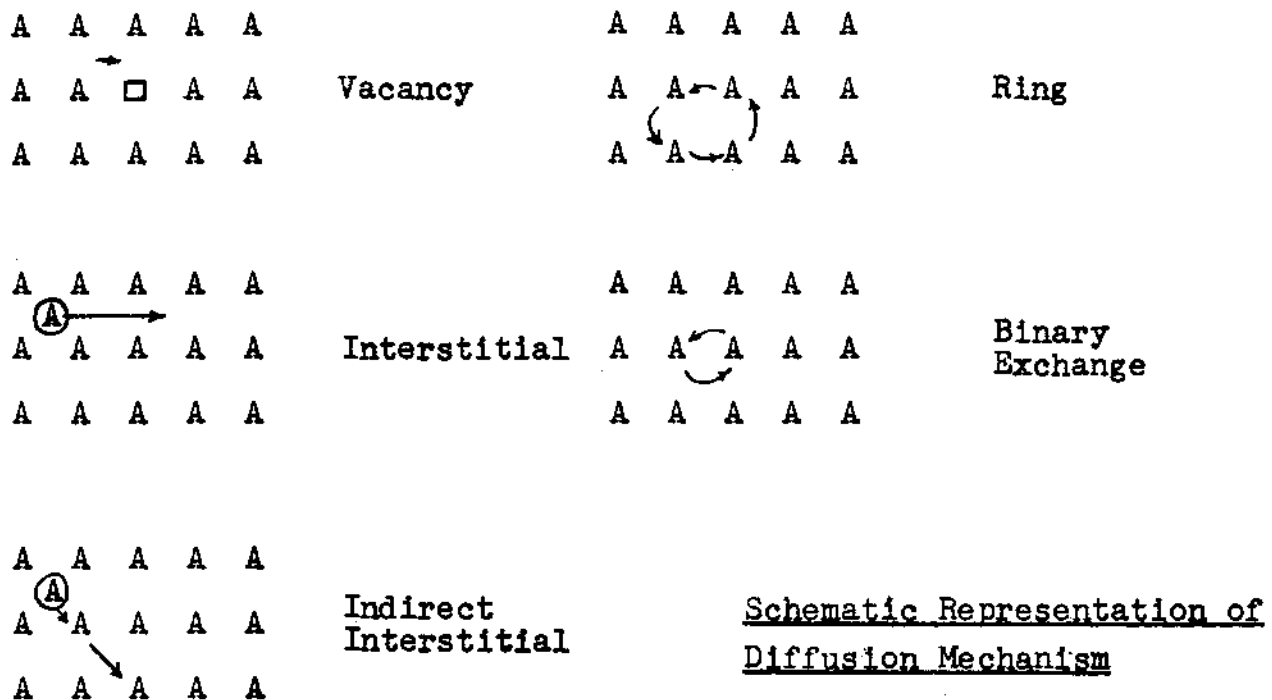
$\mu/D \approx e/kT$ as predicted by the Nernst-Einstein equation. For Zn^{+2} however, "e" was only 0.28 instead of "2" for a doubly charged ion. The interpretation is that diffusion occurs via a vacancy - Zn^{+2} pair which is neutral. This "ex-



planation" leaves some questions unanswered, however, especially the computation of the value of the apparent charge.

Defect Mechanisms

There have been several calculations of the energy required to move atoms in the solid state. They indicate that a direct binary exchange of two atoms would require much too high an energy to be a possible process. The first calculations made by M. B. Huntington and F. Seitz in the case of copper have since been refined, but their conclusion remains unchanged. The most likely mechanism is through vacancies, which in a typical metal (Cu) require an energy of about 2 eV to form and 2 eV to move.



In the metals, and probably in alkali halides and silver halides, the point defects are those of the Frenkel and Schottky types, which are generated thermally without changing the stoichiometry of the crystals. In oxides, sulfides, etc., however, the

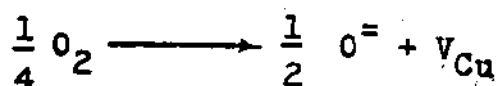
defect concentrations are mainly determined by departures from exact stoichiometry. We distinguish metal-excess compounds and metal deficient compounds. Typical examples are ZnO and Cu_2O .

Zn	O^-	Zn	O	Zn^+	O	Crystal contains excess Zn. Whether this is interstitial or oxygen vacancies or both is not known with certainty.
O	Zn_i	O	Zn	\square	Zn	
Zn	O	Zn	O	Zn	O	

Cu	Cu	Cu	Cu	Cu	Cu	In Cu_2O the principal defect is certainly the cation vacancy, but there is probably also interstitial O_i in smaller amount.
	O		O		O	
Cu	\square	Cu^{+2}	Cu	Cu	Cu	
	O		O		O	

Defect Equilibria

As an example of the formation of defects by departure from stoichiometry let us consider the solution of excess oxygen in cuprous oxide:



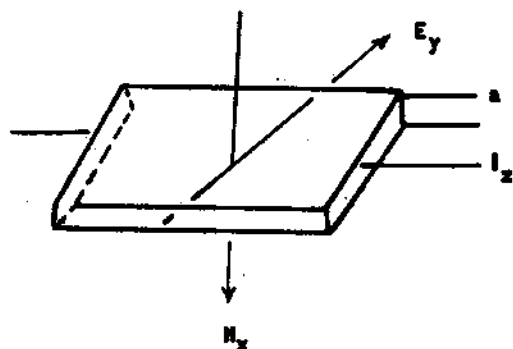
$$\frac{[V_{Cu}^+][O^-]^{\frac{1}{2}}}{p^{1/4} O_2} = K_1$$

Thus, $[V_{Cu^+}] = K_1 P_{O_2}^{1/4}$. We found experimentally a dependence on $P_{O_2}^{1/3.7}$. For the reaction above,

$$\Delta H = 21.7 \pm 1.5 \text{ kcal}$$

$$\Delta S = 12.1 \text{ cal deg}^{-1}$$

What is the nature of the defects in Cu_2O ? (a) they are not paramagnetic (b) the Hall effect was measured.



The Hall voltage is E_y

$$E_y = R I_x H_x / a$$

$$R = \frac{-3\pi}{8e} \frac{n\mu_n^2 - p\mu_p^2}{(\mu_n + \mu_p)^2}$$

with $p \gg n$,

$$R_p = \frac{3\pi}{8e} \frac{1}{p}$$

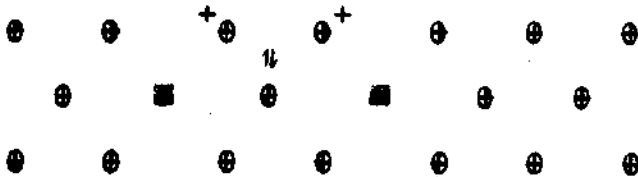
Actually R becomes so small as to be unmeasurable at $T > 400^\circ K$. Hence p must be large and μ small. At room temperature $\mu \sim 30 \text{ cm}^2 \text{ v s}^{-1}$. Extrapolated to $1000^\circ C$, $\mu \sim 7$. If $p = N_v$, $\mu \approx 0.7$. Consequently we can say that the number of vacancies = number of holes. The lack of paramagnetism leads to the idea that the holes are associated with spins coupled. This explanation, however, ran up against a great difficulty which it took us a long time to see through. The $\sigma \sim P_{O_2}^{1/7}$. This result was always interpreted in terms of holes dissociated from vacancies. Our suggestion, however, is that μ itself is pressure dependent, so that $\sigma = \text{con-}$

stant $P^x \mu(P)$, where P^x represents true pressure dependence of number of holes. Hence the activation energy E depends on pressure:

$$E = 0.66 + 0.105 \ln P \text{ (eV)}$$

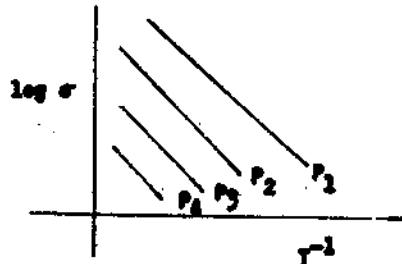
$$\sigma = \text{const. } P^x \exp[(-0.66 - 0.105 \ln P)/kT]$$

$$m = \partial \ln \sigma / \partial \ln P = x - \frac{0.0105}{kT} \text{ with } x = 0.25$$



By this analysis we find that the pressure dependence of the number of holes is indeed the same as that of the

excess oxygen.



* * *

Lecture 4

DEFECT MECHANISMS IN NONSTOICHIOMETRIC CRYSTALS

Diffusion in oxides, sulfides and halides is interesting from the standpoint of solid-state theory, because it provides a method for investigating the defect structure and defect kinetics in these crystals. Also, however, there are important practical applications, such as the relation of the measured diffusion coefficients to the sintering of ceramics and the gaseous corrosion of metals at high temperatures.

Carl Wagner¹⁶ gave the first detailed theory of the formation of tarnish layers on metals. He first related the mobilities of ions and electrons in the product layer to the electrical conductivity σ and the transference numbers t_1 , t_2 of cations and anions, and t_3 of electrons. He obtained thereby for the number of equivalents of metal reacting per unit time and unit cross section,

$$n_{\text{eq}} = \frac{K_R}{\Delta y} = \frac{300}{\Delta y F L e} \int_{\mu'_x}^{\mu''_x} \frac{1}{|z_2|} (t_1 + t_2) t_3 \sigma d\mu_x \quad (28)$$

where K_R is the so-called rational rate constant and Δy is the

thickness of product layer; F is the Faraday, L is the Avogadro number, $|Z_2|$ is the valence of the anions, and μ_X^I and μ_X^{II} are the equilibrium values of the chemical potentials of the nonmetal at the inner and outer interfaces of the layer.

For many cases of interest (especially among oxides and sulfides) the compound is almost a purely electronic conductor, so that $t_3 \cong 1$. Since t_1 and t_2 would be extremely difficult to measure in such instances, it is preferable to relate the ionic mobilities to the ionic diffusion coefficients, by $t_1 \sigma / FkT = D/Z_1 e$. With the relation $d\mu_X = RT d \ln a_X$ and

$$|Z_2| d \ln a_{Me} + Z_1 d \ln a_X = 0$$

This gives

$$K_R = C_{eq} \int_{a_{Me}''}^{a_{Me}'} \left(D_1^* + \frac{|Z_2|}{Z_1} D_2^* \right) d \ln a_{Me} \quad (29)$$

where C_{eq} is the concentration of metal ions in equivalents per cm^3 . In terms of the interdiffusion coefficient D_Δ ,

$$K_R = S \int_{\Delta''}^{\Delta'} D_\Delta d\Delta \quad (30)$$

where Δ is the deviation from stoichiometry. It follows also that

$$D_\Delta = S(b_1 + b_2) (d\mu_m / d\Delta) \quad (31)$$

The difficulty in applying any of these equations to inter

diffusion problems has been our lack of information that would allow us to integrate the equation across the product layer. The relation between the tracer diffusion coefficient D^* and the mobility b holds only if D^* has been measured in the absence of any chemical potential gradient. This measurement can be made readily enough, but it would need to be made at different defect concentrations to measure the variation of D_1^* and D_2^* with concentration. Next we should have to know how the activity a_{Me} varies across the product layer. This would require, probably, that we know first of all how the concentration (or Δ) varies across such a layer, and then how a_{Me} varies with Δ . A valuable advance toward the quantitative treatment of these problems has been made in a series of papers by R. F. Brebrick, which will be discussed in some detail.

First, however, we should mention that a most sensitive test of some of these equations can be obtained by means of an experiment first described by Bardeen, Brattain and Shockley¹⁷ in which one measures the distribution of radioactive tracer in a growing product layer on a crystal. Conceptually, this is an important experiment, but as a matter of fact it has never been done with the experimental care necessary to secure reliable data. In principle, the experiment should allow us to measure the variation of the mobility b_A or b_C (in suitable cases) as functions of the gradient of chemical potential in the growing film.

In one case only do we have some experimental data on the variation of defect concentration across a growing oxide layer.

Measurements by Engell¹⁸ showed a linear variation of excess oxygen across a layer of FeO. The neutron diffraction experiments of Roth¹⁹ indicated a structure in which about 88% of the cation sites were occupied, with one interstitial iron atom for every two vacancies. If we accept this surprising and rather unlikely conclusion, the interpretation of the formation of FeO by the simple vacancy model of Wagner, as used by Engell, seems open to doubt.

The theory of Brebrick

Brebrick considers the special case of a 1-1 ionic crystal (such as NiO) with the possibility of vacancies on both the anion and the cation sublattices. Then two equilibrium conditions apply,

$$V_C V_A = k_s \quad (k \text{ is the Schottky constant}) \quad (32)$$

$$n_p = n_i^2 \quad (n_i \text{ is the intrinsic carrier concentration}) \quad (33)$$

He has derived the following expressions for the chemical potentials of the metallic and nonmetallic components:

$$\mu_m = kT \ln (S/V_C) + \mu_e + f_1 (T) \quad (34)$$

$$\mu_x = kT \ln (S/V_A) - \mu_e + f_2 (T) \quad (35)$$

Here S is the concentration of sites on either cation or anion sublattice, and μ_e is the electron chemical potential (Fermi level). We note that μ_m and μ_x can vary over an energy range at least as large as the separation of the valence and conduction bands. However, the free energy of the crystal, $\mu_m + \mu_x$, is to a

good approximation a function only of the temperature and does not depend significantly on the departure from stoichiometry.

$$\mu_m + \mu_x = kT \ln (S^2/k_s) + f(T) \approx F(t). \quad (36)$$

This is an important fact, since it shows that large departures from the behaviour expected for ideal solutions can occur for metallic and nonmetallic components (in an oxide, for example) which can lead to large effects on the observed interdiffusion coefficients (in accord with the Darken equation).

Brebrick considers explicitly a nondegenerate semiconductor in the "exhaustion range", i.e. with the donors all ionized. If N_C and N_A are the concentrations of cations and anions,

$$N_C - N_A = n - p \quad (37)$$

The deviation from stoichiometry is

$$\Delta = N_C - N_A \quad (38)$$

The electron chemical potential was given by Longini and Greene²⁰ as

$$\mu_e = kT \ln \left[\frac{\Delta}{2n_1} + \left(\left(\frac{\Delta}{2n_1} \right)^2 + 1 \right)^{\frac{1}{2}} \right] + \mu_e^1(T) \quad (39)$$

The concentration of lattice sites,

$$N_C + V_C = N_A + V_A = S \quad (40)$$

The flow of the deviation from stoichiometry is the difference between the cation and the anion flows,

$$J_{\Delta} = J_C - J_A = -D_{\Delta} \text{ grad } \Delta \quad (41)$$

where D_{Δ} is the interdiffusion coefficient. For example, a crystal of nickel oxide is annealed in a vacuum and then oxygen gas is admitted. The rate at which the oxygen is taken into the crystal is governed by the flow of the deviation from stoichiometry, J_{Δ} .

For a semiconductor, with electronic transference number $t_e \approx 1$, the interdiffusion coefficient is given by eq. (31). The individual tracer diffusion coefficients are related to the mobilities b by

$$\begin{aligned} D_C^* &= kT b_C \\ D_A^* &= kT b_A \end{aligned} \quad (42)$$

Application of eqs. (31), (39) and (42) yields

$$D_{\Delta} = \left(\frac{S}{V_A + V_C} \right) (D_C^* + D_A^*) \left(1 + \left[\frac{\Delta^2 + 4 K_s}{\Delta^2 + 4 n_1^2} \right]^{\frac{1}{2}} \right) \quad (43)$$

This result differs from equations previously employed by the inclusion of the term in square brackets. This term will alter the ratio of the interdiffusion coefficient to the tracer diffusion coefficient, by a factor which depends on the extent of deviation from stoichiometry. This factor will range from 1 to about 10.

At the stoichiometric composition, $\Delta = 0$, eq. (43) becomes:

$$D_{\Delta}/D_C^* = \frac{1}{2} (1 + b_A/b_C) (S/k_s^{\frac{1}{2}} + S/n_1) \quad (44)$$

For the case of PbS, a minimum value of D_{Δ} can be found from eq. (44) by setting $b_A/b_C = 0$. At 823 °K, $D_C^* = 2 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$, $k_s = 5.8 \times 10^{32}$, and $n_1 = 4 \times 10^{17}$, $S = 2 \times 10^{22}$. Hence,

$$D_{\Delta} > 9 \times 10^{-6}$$

The measured value was 2×10^{-6} . Note that D_{Δ} is about 10^5 times greater than D_C^* .

This result has been obtained by a general phenomenological (thermodynamic) argument, without reference to the mechanism of diffusion. We can, however, give a reasonable mechanistic interpretation simply by pointing out that for a vacancy mechanism of diffusion, $b_C = \lambda^2 k_c V_c/S$, where λ is the jump distance and k_c is a characteristic rate constant for the cation jump.

* * *

Lecture 5

EXAMPLES OF DIFFUSION MEASUREMENTS AND MECHANISMS

Alkali Halides

Although it is possible to obtain large single crystals of the alkali halides of high purity, we do not yet have nearly enough accurate data on diffusion in such crystals. The only comprehensive study was made by Bénard and Laurent²¹. Although their results with NaCl have been confirmed by other measurements, there are discrepancies in the case of KCl, so that further measurements with alkali halide crystals would be desirable. The results of Bénard and Laurent are summarized in the following table:

Table 5.1

Tracer Diffusion in Single Crystals of Alkali Halides

	D_0 , cm ² sec ⁻¹		E(kcal)	
	Anion	Cation	Anion	Cation
KI	1.2×10^{-9}	1.0×10^{-5}	25.7	14.8
KBr	2×10^{-2}	1.0×10^{-2}	33.0	29.0
KCl	10	4×10^{-2}	46.0	34.0
KF		9		41.0
NaCl	110	0.5	51.4	37.0
CaCl (NaCl type)	0.7	1.0×10^{-1}	36.0	32.0
CaF		4		38.5

Maurer and Mapother²² studied the diffusion of ^{24}Na in NaCl. Above 550 °C they found $D = 3.13 \exp(-41.4 \text{ kcal}/RT)$. Below 550 °C, they found $D = 1.6 \times 10^{-5} \exp(-17.7/RT)$. From an analysis of conductivity data, Dreyfus and Nowick²³ concluded that the best value for the activation energy of the migration of Na^+ in NaCl at high temperatures was 43.4 kcal. Morrison, Harrison and Rudham from the exchange of $^{37}\text{Cl}_2$ with NaCl crystals found the E_a for diffusion of Cl in NaCl to be 53.0. We may conclude that the E for Cl diffusion is 52 ± 2 and that for Na diffusion is 42 ± 2 . The high temperature ionic conductivity and diffusion is almost always interpreted as the consequence of Schottky defects in the crystals, with the activation energy $E_1 = E_m + (E_s/2)$. The energy of formation of a Schottky defect in NaCl is estimated to be 50 kcal. Hence $E_m = 17$ for Na^+ and 27 for Cl^- in NaCl.

The situation for KCl is not so satisfactory. The conductivity data yield $E_1 = 45.5$ for K^+ , which is much higher than the $E_1 = 34.0$ given by Bénard from diffusion data. The E_s for KCl is estimated as 52 kcal. Thus E_m would be 20 for K^+ in KCl from the conductivity data, but only 8 from the diffusion data. It would appear that the E for diffusion of K^+ in KCl is in error. This apparent error casts some doubt on the other values reported by Bénard and Laurent. Actually their diffusion value for Cl^- is 46. This is reasonable, being almost the same as the conductivity value for K^+ . These two ions are almost the same size and it seems likely that the activation energy for either one to jump into a vacancy would be almost the same.

At low temperatures the ionic conductivity and diffusion in alkali halides is believed to be due to the presence of bivalent metal impurities, which are associated with cation vacancies. Indeed, a NaCl crystal doped with CdCl_2 will show the behavior expected on this model, but detailed doping studies combined with diffusion measurements are not yet available.

Correlation Factors

As we pointed out in the first lecture, the tracer diffusion coefficient may differ from the self-diffusion coefficient as a consequence of correlation effects in the successive jumps that comprise the diffusion process. The theory and application of the correlation factor has recently been reviewed by R. J. Friauf²⁵.

If vacancy motion is the only factor that contributes to both diffusion of radioactive tracer and to conductivity, the Nernst-Einstein relation becomes

$$D_c^* = f(kT/Nq^2) \sigma = f D_v$$

The correlation factor f for vacancy migration in a face-centered cubic crystal is 0.781. This factor is so close to unity that it does not provide a satisfactory experimental test for the vacancy mechanism in alkali halide crystals.

In the case of interstitial mechanisms, however, the factor f can be smaller, and it has been used as a criterion of mechanism in the silver halides. The direct interstitial mechanism has $f=1$. The mechanism of a colinear interstitialcy has $f = 1/3$. The dif-

ference in these factors should be sufficient to diagnose the mechanism. (In part the low value of $1/3$ is due to the larger effective jump distance for conductivity and not, properly speaking, to correlation).

Silver Halides

Compton and Maurer²⁶ made extensive measurements of diffusion of ^{110}Ag in AgCl crystals of fair purity (reagent grade; no analyses cited). They also made a few measurements of diffusion of ^{36}Cl . The silver diffusion was measured from about 120 to 430 °C; the chloride diffusion from 320 to 430 °C. The results were:

$$D^{\text{Ag}} = 1.4 \exp(-20.8/RT)$$

$$D^{\text{Cl}} = 2.1 \times 10^2 \exp(-37.7/RT)$$

The principal significance of these results is to show that the mobility of the Cl is so much less than that of Ag that we can set $t_{\text{Cl}^-} = 0$. Measurements by Tubandt²⁷ indicated that electronic transport in AgCl was also essentially zero. Thus one can set $t_{\text{Ag}^+} = 1$. If AgCl is doped with CdCl_2 , cation vacancies can be introduced and interstitial Ag^+ suppressed. Experiments of this kind indicated that the interstitial mobility was much greater than the vacancy mobility. The next question was whether the interstitial mechanism was direct or indirect.

In AgBr the diffusion of ^{82}Br was measured by Tannhauser²⁸ from 332 to 415 °C, with crystals grown from reagent

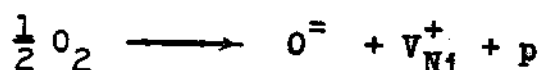
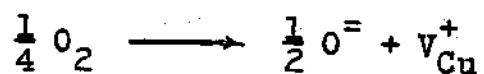
grade materials. Even over this short temperature range, the apparent activation energy was not constant, ranging from 45 to 60 kcal. The D for Ag is much larger than that for Br (R. J. Friauf)²⁹ The plot of $\log D$ vs T^{-1} in this case also gave a variable activation energy with an average value of about $E = 18$ kcal. The values of E for diffusion of Ag^+ in AgCl and AgBr are so low that most of the observed activation energy must be ascribed to the formation of the Frenkel defects. The activation energy for the interstitial jump itself is believed to be closed to zero. It would be desirable to check this interesting conclusion by an independent method, e.g. study of internal friction or dielectric loss.

Friauf found that he could explain the results with AgBr by introducing two types of interstitialcy motion, colinear and noncolinear, with different correlation factors. In addition some of the motion of Ag^+ was ascribed to a vacancy mechanism. By doping with $CdBr_2$ (0.028 mole %) he could in a narrow temperature range obtain evidence for a vacancy mechanism alone. The picture obtained for diffusion of Ag in AgBr is thus very detailed, but it has required the introduction of several types of defect and a variety of parameters without independent confirmation. It is worth mentioning again, however, that the analysis in terms of correlation factors depends on the assumed validity of the Nernst-Einstein relation with a unit positive charge for the Ag^+ ion. It would therefore be worthwhile to study the diffusion of radioactive Ag in AgCl or AgBr in the presence of an electric field

(Chemla experiment) to determine directly the effective charge by another method.

Diffusion of Cations in Cuprous, Nickel and Cobalt Oxides

In these three cases we have some quite reliable data on cationic diffusion in single crystals and on the departure from stoichiometry. These crystals all contain excess oxygen except perhaps in the highest vacuum at elevated temperatures. The excess oxygen is universally believed to be in the form of vacancies at cation sites, but there is no unequivocal proof of such an assignment, e.g. detailed x-ray analysis. Consequently we cannot say much about the structure of the vacancies and the extent of relaxation of the structure surrounding them. The reactions which form the vacancies can be written:



We have expressed the tracer diffusion coefficient of the cation as

$$D_c = kT b_c$$

with

$$b_c = \lambda^2 k_c V_c / S$$

The apparent free energy of activation for diffusion, ΔG^* , will be the sum of the free energy of formation per mole of vacancies (ΔG_V^0) and the free energy of activation for the rate constant

$k_c (\Delta G_V^*)$. These quantities in turn can be broken into energetic and entropic contributions, as $\Delta G = \Delta H - T\Delta S$. The results for the three oxide crystals are summarized in Table 5.2.

Table 5.2

Diffusion Parameters in Oxides with Cationic Vacancies

	ΔH_V°	ΔS_V°	ΔH_V^*	ΔS_V^*
Cu_2O	21.7	4.9	12.1	-1.5
CoO	10	-12	27	-0.8
NiO	36	-14	25	-1.0

References: Cu_2O - O'Keefe and Moore, J. Chem. Phys. 36, 3009 (1962)
 NiO - Choi and Moore, J. Phys. Chem. 66, 1308 (1962)
 CoO - Carter and Richardson, Trans. A.I.M.E. 194, 1244 (1954)

The diffusion measurements in cuprous oxide were made some years ago with polycrystalline specimens. They should now be repeated over a range of oxygen pressures with single crystals of highest purity.

In the case of nickel oxide, it has not yet been possible to make measurements on single crystals essentially free of trivalent impurities. Thus (as in the case of the alkali halides) we cannot yet be completely certain that the free energy of formation of the vacancies has not been lowered by such impurities of higher valence than that of the cations of the host structure. In the case of CoO , the concentration of vacancies is about 20 times

higher than in NiO, and consequently traces of trivalent impurities would not have an important influence on the defect structure.

There are still certain problems about the defect structure of NiO which need to be resolved. It is commonly assumed that the dark green black color of monocrystalline NiO is due to the excess oxygen it contains, but it has not been demonstrated that this color can be attenuated by removal of this excess oxygen. In fact, the optical properties of this theoretically important crystal have not yet been carefully investigated.

Another topic deserving further work would be tracer diffusion in doped crystal of Cu_2O and NiO. Since such studies have not even been systematically made with the alkali halides, which are presumably much easier to prepare and to handle, we may have to wait some time for results on the oxides.

Zinc Oxide

The problem of the mechanism of diffusion of zinc in zinc oxide has not been satisfactorily resolved. In fact it presents a number of mysterious features which have baffled many investigators³⁰.

From the rate of exchange of crystals containing ^{65}Zn with inactive zinc vapor, Secco and Moore found $D_{\text{Zn}}^* = 4.8 \exp(-73/RT)$ in one atmosphere zinc vapor. From the distribution of ^{65}Zn in crystals heated in radioactive Zn vapor, Lamatsch found $D_{\text{Zn}}^* = 170 \exp(-76/RT)$. The interpretation of these values is a major

problem. There is good evidence that zinc oxide can take up considerable excess interstitial zinc. The x-ray studies of Mohanty and Azaroff³¹ actually purported to show this zinc in octahedral interstitial sites. They estimated a content of 0.35 to 1.4 atom per cent excess zinc. This figure seems to be too high by at least a factor of ten. Nevertheless the studies of Secco and of Lamatsch represent a substitutional diffusion of tracer zinc into a crystal that is saturated with considerable interstitial zinc. The mechanisms possible appear to be: (a) via vacant zinc sites (b) interstitial migration with occasional exchange (c) interstitialcy migration.

In the presence of so much interstitial zinc we would expect vacancies to be repressed. Thomas³² measured the diffusion of indium in zinc oxide. He found $D = 2.5 \times 10^2 \exp(-73/R)$. He believes the indium enters as In^{+3} ions compensated by Zn^{+2} vacancies. Perhaps the occurrence of the magic number 73 here indicates that diffusion of zinc also occurs by a vacancy mechanism. If so, the vacancies must arise from trivalent impurities or some mechanism that does not cost anything energy-wise, since 73 kcal would be the activation energy required to move a Zn^{+2} into a vacancy. However, in the indium doped crystal, the rate determining jump is into a vacancy adjacent to a In^{+3} , and this might have a higher E. Thus the $E = 73$ in the indium doped crystal is at present regarded merely as a coincidence.

If we had an interstitialcy mechanism in ZnO , we might expect the chemical diffusion of Zn into or out of ZnO to have the same activation energy as the tracer diffusion. However, such is

not the case. The chemical diffusion has E from 13 to 39 kcal, depending on the temperature and pretreatment of the crystal, and on whether the zinc is diffusing in or out. In the ordinary interstitial mechanism (cf. analysis of Redington) the tracer $D \approx X_1 D_1$ where X_1 is the fraction of interstitials and D_1 is a "diffusion coefficient" for interstitials. In the case of ZnO, the heat of solution of excess zinc appears to be 5 kcal. Thus the temperature dependence of X_1 would contribute little to the apparent activation energy. Most of the activation energy must be due to the interstitial jump itself. Why, then is the E_a for chemical diffusion so much lower than that for tracer diffusion? In qualitative terms, the answer may be that D_1 is itself strongly dependent on the concentration of interstitials. The E_a for an interstitial or interstitialcy jump is much higher in a crystal saturated with interstitials than in a crystal free of excess zinc. This suggestion does not explain why one gets a good constant D for the studies of chemical diffusion. Perhaps the kind of average obtained weights the faster diffusion processes heavily.

To look at the problem in another way we would ask: how can we lower the E for the chemical diffusion as compared to that of the tracer diffusion? If we disregard mechanism entirely, we can consider the relation between D_Δ and b_c given by Brebrick:

$$D_\Delta = S b_c d \mu_m / d$$

We can write μ_m as

$$\mu_m = kT \ln \left(\frac{N_c}{N_I} \right) - kT \ln \left(1 - \frac{n_{eI}}{N_I} \right) + E_f + \xi_i + U - kT \ln k_c$$

The significance of the terms is as given by Brebrick, except that we have taken the defects to be interstitials (N_I) instead of vacancies. Hence $\Delta = N_I$ and

$$\frac{d\mu_m}{d\Delta} = \frac{-kT}{N_I} + kT \left(1 - \frac{n_{eI}}{N_I} \right)^{-1} \frac{n_{eI}}{N_I^2}$$

$$= \frac{-kT}{N_I} \left(1 - \frac{n_{eI}}{N_I - n_{eI}} \right)$$

If $n_{eI} \ll N_I$,

$$\frac{d\mu_m}{d\Delta} \approx \frac{-kT}{N_I}, \quad \text{and}$$

$$\frac{d \ln D_A}{dT} = \frac{d \ln b_c}{dT} + \frac{d \ln kT}{dT} - \frac{d \ln N_I}{dT}$$

Hence there is no way to avoid the conclusion that $E_a \approx E_b + E_I$. If there is no appreciable ΔH for formation of N_I , the E_I will be simply that for the mobility term.

The problem of chemical diffusion of Zn in ZnO is further complicated by the remarkable observations of Pohl.³³ He followed diffusion of Zn into ZnO by measuring the conductivity. The first diffusion of Zn into a "virgin crystal" was about 100-times slower than the diffusion of zinc outwards on heating the doped crystal in air, or the second diffusion of zinc inwards after this pretreatment. Furthermore, the D for these subsequent diffusions depended on the temperature of the original doping. These results are shown in Fig. 5.1. It would be possible to explain the slow diffusion into the virgin crystal as a surface effect. After the first oxidation step the ZnO crystal should be covered with a thin layer of more finely divided "active zinc oxide". This ad hoc explanation does not serve to explain, however, the dependence of the D on the initial doping temperature. It is evident that further work must be done before we understand diffusion in ZnO crystals.

Oxygen Diffusion in Oxides

In recent years there has been a growing interest in the measurement and interpretation of oxygen diffusion in oxide crystals, measured with the tracer ^{18}O . The measurements reported to date are summarized in Table 5.3.

In all the systems studied by the Indiana group (Cu_2O , ZnO, NiO) the D^{O} increased with the oxygen pressure. The dependence on $P_{\text{O}_2}^{\frac{1}{2}}$ suggested a mechanism due to interstitial oxygen atoms. Interstitial atoms would be presumably much smaller than

Table 5.3

Tracer Diffusion of ^{18}O in Oxides

Oxide	D of ^{18}O		Temperature	Remarks	Reference
	D_0	E_a			
UO_2	1.2×10^3	65 ± 5	550 - 800	$\text{UO}_{2.002}$	1
	2.1×10^{-9}	30 ± 3	320 - 500	$\text{UO}_{2.069}$	
Al_2O_3	1.9×10^3	152	1600 - 1700		2
MgO	2.5×10^{-6}	62	1300 - 1750		3
Cu_2O	6.5×10^{-9}	39 ± 4	1030 - 1120	$\propto P_{\text{O}_2}^{1/2}$	4
NiO	6.2×10^{-4}	57.5	1100 - 1500	$\propto P_{\text{O}_2}^{1/2}$	5
ZnO	6.5×10^{11}	165 ± 6	1100 - 1900	$\propto P_{\text{O}_2}^{1/2}$	6
CdO	8×10^6	93 ± 5	640 - 820	$\propto P_{\text{O}_2}^{1/6}$	7
TiO_2	1.1	79	800 - 1090		8
$\text{Zr}_{.85}\text{Ce}_{.15}\text{O}_{1.85}$	5.1×10^{-9}	90	680 - 900		9
NiCr_2O_4	1.7×10^{-2}	65	1200 - 1550	poly crystalline	10
$\alpha\text{-Fe}_2\text{O}_3$	10^{11}	146	1100 - 1250	poly crystalline	10

References

1. A. B. Auskern and J. Belle, J. Chem. Phys. **28**, 171 (1958)
2. Y. Oishi and W. D. Kingery, J. Chem. Phys. **33**, 480 (1960)
3. Y. Oishi and W. D. Kingery, J. Chem. Phys. **33**, 905 (1960)
4. W. J. Moore, Y. Ebisuzaki, J. A. Sluss, J. Phys. Chem. **62**, 1498 (1958)
5. M. O'Keefe and W. J. Moore, J. Phys. Chem. **65**, 1498 (1961)
6. E. L. Williams and W. J. Moore, Disc. Faraday Soc. **28**, 86 (1959)
7. R. Haul and D. Just, J. Appl. Phys. **33** (Suppl. 1), 487 (1962)
8. R. Haul, D. Just and G. Dumbgen, Proc. 4th Int. Symp. Reactivity of Solids, Amsterdam, 1960, p.6
9. W. D. Kingery, J. Pappis, M. E. Doty, D. G. Hill, J. Am. Ceramic Soc. **42**, 399 (1959)
10. W. D. Kingery, D. G. Hill, R. P. Nelson, J. Am. Ceramic Soc. **43**, 479 (1960)

interstitial oxygen ion, and one would expect an interstitial oxygen to be energetically most unfavorable. In the case of NiO this mechanism is surprising since the structure consists of an essentially close packed array of oxide ions.

When we first noted the similarity in the activation energies of Cu and O and Cu_2O , (36 and 39 kcal) we suggested that perhaps both Cu and O diffused by way of the identical transition state, which occurred when a Cu^+ ion was at the saddle point between a normal site and a cation vacancy. We called this the countervacancy mechanism. As we came to accept the likelihood of interstitial oxygen atoms, we tended to relegate this possible mechanism to the background. Then it appeared again in a quite unexpected system, PbS. G. Simkovich and J. B. Wagner³⁴ found for diffusion in stoichiometric PbS:

$$D_{\text{PbS}}^{\text{Pb}} = 2.3 \times 10^{-4} \exp(-32 \text{ kcal/RT})$$

$$D_{\text{PbS}}^{\text{S}} = 3.8 \times 10^{-5} \exp(-32 \text{ kcal/RT})$$

The D^{S} was higher in crystals containing an excess of S. The possibility of a countervacancy mechanism in this case seems to be excellent.

Enormous Activation Entropies

We shall close these lectures by calling attention again to the interesting problem of the occasional occurrence of enormous activation entropies in diffusion studies in the solid

state. These have been observed too frequently to be considered simply experimental errors. We may cite the cases of barium in barium oxide, oxygen in zinc oxide, sulfur in FeS, phosphorus in indium phosphide, and numerous others. In these cases the apparent activation energy can range up to + 100 calories per degree per mole.

It seems clearly impossible to explain such figures on the basis of any kind of simple point defect or its migration in the crystal structure. In most cases it would appear necessary to call upon a communal entropy of melting, caused either by some kind of an extended defect in which many displaced atoms are contributing to the positive entropy or a similar displacement over a large volume of the crystal structure in the activated state of the diffusion. Another possibility is the occurrence of diffusion short circuits such as dislocation pipes, so that the actual cross sectional area for the diffusion process is much less than that which is used in evaluating the coefficient. It would appear that the further investigation and explanation of these enormous activation entropies may prove to be one of the most rewarding problems in the study of diffusion in the solid state.

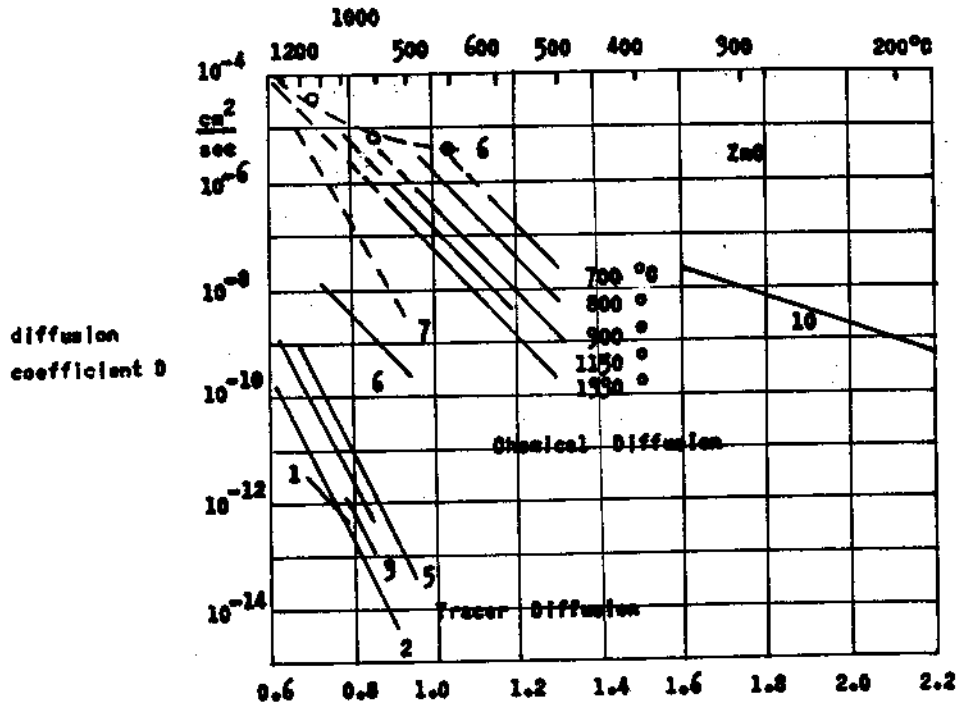


Fig. 5.1 - Diffusion coefficient D of zinc oxide, measured by several authors using different methods:

1. Crystals, tracer, in air, after Moore and Williams.
2. Sintered specimens, tracer, beta-radiation, in air, after Lindner.
3. Crystals, grown with Zn^{65} , tracer, in zinc vapour, of 1 atm, after Seccor and Moore.
4. Sintered specimens, tracer, in air, after Lindner.
5. Crystals, tracer, in saturated zinc vapour, after Lamatch.
6. Crystals, optical absorption after heating in saturated zinc vapour, after Armath.
7. Calculated from curve 5 using the mole fraction of interstitial zinc (conductivity).
8. Extrapolated from curves 9 for $T = 0$.
9. Crystals, decay of conductivity (produced by heating in zinc vapour) during annealing in air at temperature T . Parameter of the different curves is temperature θ of pretreatment in zinc vapour, after Pohl.
10. Crystals, method similar to no 9, after Thomas.

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References

1. W. C. ROBERTS-AUSTEN, Proc. Roy. Soc. London, 59, 277 (1896).
2. D. LAZARUS, Solid State Physics, 10, 71 (1960).
3. WUENSCH and VASILOS, J. Chem. Phys. 36, 2917 (1962).
4. HERMANN and WALTHER, Z. Metallkunde, 48, 151 (1957).
5. C. E. BIRCHENALL and R. H. CONDIT, Princeton University, Metallurgy Reports, 11, (Feb. 1957), 19 (Feb. 1959).
6. CHOI and MOORE, J. Phys. Chem. 66, 1308 (1962).
7. MORRISON, Disc. Faraday Soc. 28, 103 (1959).
8. R. W. REDDINGTON, Phys. Rev. 82, 574 (1951).
9. HAUL and coworkers - a paper with applications to CdO is given in J. Appl. Physics. Suppl. (1) 33, 487 (1962), and a tabulations of the mathematical solutions is in Z. Physik Chemie 31, 310 (1962).
10. ZENER, Phys. Rev. 76, 1169 (1949).
11. VINEYARD, J. Phys. Chem. Solids, 3, 121 (1957).
12. ALAN R. ALLNATT and STUART A. RICE, J. Chem. Phys. 33, 573 (1960).
13. PRIGOGINE and BAK, J. Chem. Phys. 31, 1368 (1959); cf. J. W. PLESNER, *ibid.* 33, 652 (1960).
14. NACHTRIEB, J. Chem. Phys. 23, 1193 (1955).
15. M. CHEMLA, Thèse, University of Paris, 1954; Ann. Phys. (Paris).
16. CARL WAGNER, Z. Phys. Chem. B21, 25 (1933).
17. BARDEEN, BRATTAIN and SHOCKLEY, J. Chem. Phys. 14, 714 (1946).
18. ENGELL, Acta metal. 6, 439 (1958).
19. ROTH, J. Appl. Phys., Suppl. 30, 3035 (1959).
20. LONGINI and GREENE, Phys. Rev. 102, 922 (1956).
21. BÉNARD and LAURENT, J. Phys. Chem. Solids 3, 7 (1957).
22. MAURER and MAPOTHER, Phys. Rev. 73, 1260 (1948).
23. DREYFUS and NOWICK, J. Appl. Phys., Suppl. 33, 473 (1962).

24. MORRISON, HARRISON and RUDHAM, *Trans. Faraday Soc.* 54, 106 (1958).
25. R. J. FRIAUF, *J. Appl. Phys. Suppl.* 33, 494 (1962).
26. COMPTON and MAURER, *J. Phys. Chem. Solids*, 1, 191 (1956).
27. TUBANDT, *Z. Anorg. Allg. Chem.* 115, 113 (1950).
28. TANNHAUSER, *J. Phys. Chem. Solids* 5, 224 (1958).
29. R. J. FRIAUF, *Phys. Rev.* 105, 843 (1957).
30. cf. brief review by HELLAND, *Disc. Faraday Soc.* 28, 123 (1959).
31. MOHANTY and AZAROFF, *J. Chem. Phys.* 35, 1268 (1961).
32. THOMAS, *J. Phys. Chem. Solids* 9, 31 (1958).
33. POHL, *Z. Physik* 155, 120 (1959).
34. G. SIMKOVICH and J. B. WAGNER, Technical Reports, Hammond Metallurgical Laboratory, Yale University.

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