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Clarification of Some Concepts in Chemical Diffusion, or Darken, Kirkendall, and Other Sources of Difficulties and Confusion in Diffusion*

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The assumptions of Kirkendall interdiffusion theory are reviewed and it is shown that this theory does not apply to chemical diffusion experiments in which the stoichiometry changes, but one sublattice is inert. We then summarize the theory of ambipolar chemical diffusion and apply it to the examples CoO, UO_2, CdS, YSZ, and the system B–Si. For UO_2 we reevaluate recently published calculations and show that the correct theory gives better agreement with experiments. © 1984 Academic Press, Inc.

Introduction

The purpose of this paper is to discuss chemical diffusion and interdiffusion and the relation between them and to clarify some badly defined and/or wrongly used concepts which occur in the literature. It seems that they occur so frequently because diffusion is based on thermodynamics and the latter lends itself all too easily to drawing wrong conclusions from valid but very general formulae.

Chemical diffusion is defined as diffusion in a chemical concentration gradient. It therefore includes interdiffusion of two materials forming a solid solution as in Kirkendall experiments and in chemical doping of semiconductors as well as experiments in which the stoichiometry of a compound changes, such as oxidation/reduction of CoO_{1+x} to CoO_{1+y}, with $y \neq x$. In this article we shall use the term "chemical diffusion" in the restricted sense as applying only to experiments where the stoichiometry changes and use the name "interdiffusion" for the other cases.

An equation derived by Darken (*1*) to explain the Kirkendall effect in interdiffusion experiments, has sometimes been applied to chemical diffusion processes. We shall show that this is not permitted. In order to do this we shall first review briefly the important equations of interdiffusion.

Interdiffusion and the Kirkendall Effect

In a Kirkendall experiment one constructs a diffusion couple made of two pieces of an alloy AB with different compositions and measures as a function of time the distance between inert markers placed at the original boundary of the two pieces and the ends of the couple. A good discus-

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sion of the principles involved is found in Manning (*2*). Here we shall not repeat the derivation of the equations, but would like to stress that an important and necessary assumption in the derivation is that the total number of atoms per unit volume is constant (*1*). Let us assume that the diffusion is by a vacancy mechanism, then the concentration of vacancies must be independent of x and t.

Darken showed that the following equation gives the rate at which the concentration gradient of the diffusion couple tends to smooth out

$$J'_{\mathrm{A}} = -(N_{\mathrm{A}} D^{\mathrm{I}}_{\mathrm{B}} + N_{\mathrm{B}} D^{\mathrm{I}}_{\mathrm{A}})\ \partial[\mathrm{A}]/\partial x. \quad (1)$$

The effective diffusion constant, which we shall call D^{Dar}, is therefore

$$D^{\mathrm{Dar}} = N_{\mathrm{A}} D^{\mathrm{I}}_{\mathrm{B}} + N_{\mathrm{B}} D^{\mathrm{I}}_{\mathrm{A}} \quad (2)$$

this is known as Darken's equation.

In these equations J'_{A} is the flux of component A measured with respect to the ends of the couple (because of the above assumption about atoms per unit volume the length of the couple does not change with time), [A] is the concentration of component A (measured in units of particles/m^3), $N_{\mathrm{A}} = [\mathrm{A}]/([\mathrm{A}] + [\mathrm{B}])$, $N_{\mathrm{B}} = [\mathrm{B}]/([\mathrm{A}] + [\mathrm{B}])$, and $D^{\mathrm{I}}_{\mathrm{A}}$ is the so-called (*2*) intrinsic diffusion coefficient defined by

$$J_{\mathrm{A}} = -D^{\mathrm{I}}_{\mathrm{A}}\ \partial[\mathrm{A}]/\partial x \quad (3)$$

with a similar definition for $D^{\mathrm{I}}_{\mathrm{B}}$. These D^{I}'s which are called "diffusivities" by Darken, depend on the composition, i.e., on the ratio [A]/[B]. J, in contrast to J', is the flux density measured with respect to the lattice, i.e., operationally with respect to inert markers in the sample (*1*).

Manning showed that Eq. (2) can be transformed as follows (his Eq. (5.87))

$$D^{\mathrm{Dar}} = (N_{\mathrm{A}} D^{\mathrm{Tr}}_{\mathrm{B}} + N_{\mathrm{B}} D^{\mathrm{Tr}}_{\mathrm{A}}) \frac{d \ln a_{\mathrm{A}}}{d \ln N_{\mathrm{A}}} R \quad (4)$$

with

$$R = 1 + \frac{(1 - f) N_{\mathrm{A}} N_{\mathrm{B}} (D^{\mathrm{Tr}}_{\mathrm{A}} - D^{\mathrm{Tr}}_{\mathrm{B}})^2}{f(N_{\mathrm{A}} D^{\mathrm{Tr}}_{\mathrm{B}} + N_{\mathrm{B}} D^{\mathrm{Tr}}_{\mathrm{A}})(N_{\mathrm{A}} D^{\mathrm{Tr}}_{\mathrm{A}} + N_{\mathrm{B}} D^{\mathrm{Tr}}_{\mathrm{B}})}.$$

Here D^{Tr}_i is the radioactive tracer diffusion coefficient of component i, measured at the composition of the alloy, which is of course a function of x. The a_{A} is the activity of component A, defined through the chemical potential μ_{A} by $\mu_{\mathrm{A}} = kT \ln a_{\mathrm{A}}$. The f is the correlation factor for tracer diffusion in the lattice considered, it relates the mechanical mobility b_i (with dimensions m sec^{-1} Nt^{-1}) to D^{Tr}_i by $D^{\mathrm{Tr}}_i = f_i kT b_i$ $(1 \geq f \geq \frac{1}{2})$. R, which is a measure of the "vacancy flow" (*2*), usually differs from 1 by less than 10%. Equation (4), without the factor R, had already been derived by Darken (see Appendix A). The expression $d \ln a_{\mathrm{A}}/d \ln N_{\mathrm{A}}$ is known as the thermodynamic factor. If the solution of A in B is ideal (this implies that the entropy is configurational only), then

$$\mu_{\mathrm{A}} = kT \ln N_{\mathrm{A}} + \text{const.} \quad (5)$$

and the thermodynamic factor is 1. Since the vacancy concentration is constant it does not appear in Eq. (5). Compare also with Eq. (15), below.

From Eq. (4) we can calculate D^{Dar} for any composition provided $D^{\mathrm{Tr}}_{\mathrm{A}}$, $D^{\mathrm{Tr}}_{\mathrm{B}}$, f, and the factor $d \ln a_{\mathrm{A}}/d \ln N_{\mathrm{A}}$ are all known for the composition of interest.

Two special cases will help to understand the concepts involved:

A. Measurement with radioactive tracers of the self-diffusion in an element. We can regard this as interdiffusion of the radioactive and the nonradioactive isotope. In Eq. (4) the two diffusion coefficients are the same and the value of the thermodynamic factor is 1, since the solution is ideal. Also $R = 1$, as can be verified from Eq. (4). We get therefore $D^{\mathrm{Dar}} = D^{\mathrm{Tr}}$, as can be expected.

B. Diffusion doping of a semiconductor, e.g., boron diffusing into silicon. Here we have interdiffusion of a minor constituent (the dopant, A) and a major constituent (the semiconductor, B). Therefore $N_A \ll N_B$ and R can be shown to be 1 in this case. Equation (4) gives now

$$D^{\mathrm{Dar}} = D_A^{\mathrm{Tr}} \frac{d \ln a_A}{d \ln N_A} \tag{6}$$

and because of the low concentration we would expect $d \ln a_A = d \ln N_A$, i.e., $D^{\mathrm{Dar}} = D_A^{\mathrm{Tr}}$. Since, however, dopants in semiconductors diffuse usually not as atoms, but as ions and electrons, the relation is more complicated. The value of the factor multiplying D_A^{Tr} for this situation will be discussed later.

Non-Applicability of Darken's Equation to Chemical Diffusion

Let us now discuss a simple system, namely a hypothetical binary compound MX in which we have a low concentration of vacancies V_M on the M sublattice. V_M is a neutral vacancy and causes diffusion of the M atoms. We assume that the X atoms stay in place so that the X sublattice is completely inert and can serve as reference lattice.

We now make an experiment which looks like a Kirkendall experiment (but is not, see below). We construct a diffusion couple with a step in the concentration of M-atoms (see Fig. 1). It consists of a left part containing initially $[V_M]^1$ vacancies and $[M_M]^1$ atoms and a right part containing $[V_M]^2$ vacancies and $[M_M]^2$ atoms, and we have $[M_M] + [V_M] = \text{const}$.

The couple will equilibrate with an effective diffusion coefficient $\tilde{D}$, the vacancies and the atoms will eventually be distributed uniformly. We see that this fits our definition of a chemical diffusion process so that $\tilde{D}$ is the chemical diffusion coefficient. $\tilde{D}$ can be measured as usual by comparing a measured concentration profile with a solution of the diffusion equation

$$\frac{\partial[M_M]}{\partial t} = \frac{\partial}{\partial x}\left(\tilde{D}\,\frac{\partial[M_M]}{\partial x}\right). \tag{7}$$

We note here that $\tilde{D}$ does not have an index. One usually measures relative rather than absolute concentrations so that there is no way of telling from the equilibration experiment whether the M atoms or the X atoms are mobile.

We now ask whether we can use Eq. (2), or the equivalent Eq. (4), to calculate $\tilde{D}$, as was done for closely related equilibration experiments among others by Wagner (*3*) who discussed FeO, by Steele (*4*) (for CdS), and more recently by Breitung (*5*) (for UO_2).

If we do so, we get for $\tilde{D}$

$$\tilde{D} = N_M D_X^{\mathrm{I}} + N_X D_M^{\mathrm{I}} \tag{8}$$

and we have in our case $N_M \simeq N_X \simeq \frac{1}{2}$. Since we assumed that $D_X^{\mathrm{I}} = 0$ we get that $\tilde{D} = \frac{1}{2} D_M^{\mathrm{I}}$. However, Eq. (3) is for the M-atoms

$$J_M = -D_M^{\mathrm{I}}\, \partial[M_M]/\partial x. \tag{9}$$

Equation (7) implies that $J'_M = -\tilde{D}\, \partial[M_M]/\partial x$, but in our case J and J' are the same since the X lattice, any plane of which can in principle be marked by radioactive X-atoms, does not move with respect to the ends of the couple. Therefore the effective diffusion coefficient characterizing the equilibration should be $\tilde{D} = D_M^{\mathrm{I}}$, which obviously disagrees with Darken's equation.

We see that Darken's equation is not applicable here, it leads to the wrong result. The basic reason is that Darken's equation applies to a system in which the total number of atoms per unit volume is constant, so

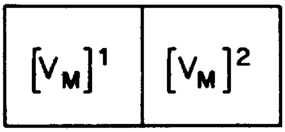

FIGURE 1

that there is a concentration gradient of both M and X, rather than of M alone. Vacancies are then created on one side of the interface and annihilated on the other, whereas in our case vacancies are conserved, only redistributed.

Another way of looking at the same thing is the following: According to Darken (*1*), v_k, the velocity at which the interface of the diffusion couple moves with respect to the ends of the couple, is given by

$$v_k = (D^I_M - D^I_X)\, \partial N_M/\partial x, \qquad (10)$$

where the gradient is evaluated at the interface. In our case v_k is zero, since the X sublattice is immobile. Now N_M is connected with the concentrations by $N_M = [M_M]/([M_M] + [X_X])$ so that $\partial N_M/\partial x$ is obviously not zero. Therefore the factor $(D^I_M - D^I_X)$ should be zero, but we know it is not. Again we conclude that Darken's analysis is not applicable to this case.

We conclude that for our hypothetical experiment the correct expression is

$$\tilde{D} = D^I_M. \qquad (11)$$

Equation (11), with the explicit form of D^I to be derived in the next section, was implicitly used by Steele (*4*) (see below) for CdS, but it should be clear that it is not a limiting case of Eq. (2) as claimed by Steele. Wagner (*3*), who discussed FeO, calculated $\tilde{D}$ according to both Eqs. (2) and (11), neither of which gave a very good fit to the experimental results.

Relation between Chemical and Tracer Diffusion

We shall now relate D^I, and therefore $\tilde{D}$, which is measurable for instance by a thermogravimetric absorption/desorption experiment (Heyne (*6*)) to D^{Tr} of the mobile atoms. We shall do this for a compound MX in which, as in the previous section, the X sublattice stays fixed while the M atoms are mobile. Usually in such a compound, as for instance in CoO or CdS, the atoms move in a dissociated state, i.e., ions and electrons move independently. (Since diffusion always proceeds by a defect mechanism, it is, as we shall see, the ionization state of the defects which matters.) The two charged species try to move at different velocities, but since this would lead to charge separation they cannot get away from each other and the effective motion is still that of neutral atoms. This is known as the ambipolar diffusion mechanism. One cannot in the present case use the derivation leading from Eq. (2) to Eq. (4) because the effective mobility of the atoms is not related anymore to D^{Tr}, which is measured for moving ions. A different approach, taking into account the electric field involved, is needed. The theory of this subject was originally worked out by Wagner in a number of publications (*7, 8*). It has recently been treated by Heyne (*6*) and in a general form by Weppner and Huggins (*9*). We shall summarize the results of the latter authors, but shall assume from the outset that only the M ions and one type of electronic charge carriers (electrons or holes) are mobile in the compound.

Weppner and Huggins showed (see Appendix B) that $\tilde{D}$ in this case is given by

$$\tilde{D} = \frac{D^{Tr}_M}{f_M}\, t_e\, \frac{d \ln a_{M^*}}{d \ln [M^*]}. \qquad (12)$$

In Eq. (12) t_e is the transport fraction of the electronic charge carriers and M* refers to neutral M-atoms. It is important to realize that when M* appears as a concentration it simply means that we can assemble out of the constituents of the sample (e.g., ions and electrons) [M*] atoms/m^{-3}, and not that the lattice is actually made up of neutral atoms. The activity a_{M^*} is defined through the change of Gibbs free energy on introduction of a neutral atom from rest at infinity into the lattice, when one calculates a_{M^*} one has to take into account that the introduction changes the number of defects in the lattice. This will become clearer in the examples. The a_{M^*} is of course also the activity of M-vapor which is in equilibrium with a sample of given defect concentration. Note that no particular defect mechanism is assumed here, however both f_M and the value of the thermodynamic factor $d \ln a_{M^*}/d \ln [M^*]$ depend on the mechanism.

Equation (12) with $t_e = 1$ is the same as Eq. (A4) in Appendix A. The transition to Eq. (A5) cannot be made here since $[M] + [X]$ is not constant.

The authors define now an "enhancement factor" for diffusion which they call W in honor of Carl Wagner

$$W \equiv t_e \frac{d \ln a_{M^*}}{d \ln [M^*]}. \qquad (13)$$

This factor is the ratio of the chemical diffusion coefficient and the diffusion coefficient D^{Tr}/f calculated via the Einstein relation from the mobility of the ions.[1]

D^{Tr}, t_e, and the thermodynamic factor are often measurable by independent experiments and f can be calculated from the mechanism assumed. We can therefore test the validity of Eq. (12) for chemical diffusion.

Equation (12) with $t_e = 1$ should be applicable to the electronic conductors FeO, CoO, NiO, etc. This was done, as mentioned by Wagner (*3*) as an alternative to using Darken's equation and also by Chu *et al.* (*10*) who got better agreement.

Some Examples of the Enhancement Factor

The enhancement factor is easiest to understand and calculate for a system with low defect concentration. We now evaluate Eq. (12) for a number of examples, including stabilized zirconia in which the defect concentration is high.

1. CoO

CoO contains holes and singly or doubly ionized cobalt vacancies, depending on the range of oxygen pressures (*11*). Introduction of a neutral cobalt atom from rest at infinity corresponds to the reaction

$$\mathrm{Co}\,(\infty) \rightarrow \mathrm{Co}_{\mathrm{Co}}^{x} - V_{\mathrm{Co}}^{z'} - zh^{\cdot} \qquad (z = 1 \text{ or } 2). \qquad (14)$$

We use here the Kroeger–Vink notation in which x, $'$, and $^{\cdot}$ indicative effective charges (relative to the perfect lattice) of zero, $-q$, and $+q$, respectively. The chemical potential μ_{Co^*} is therefore

$$\mu_{\mathrm{Co}^*} = \text{const.} - \mu_{\mathrm{V}} - z\mu_{\mathrm{h}}. \qquad (15)$$

This is of course also the chemical potential of cobalt vapor which is in equilibrium with a CoO sample of given defect concentration. In our defect model $p \equiv [\mathrm{h}] = z[V_{\mathrm{Co}}^{z'}]$ and because of the low concentration

$$\mu_{\mathrm{V}} = kT \ln[V_{\mathrm{Co}}^{z'}] + \text{const.} \qquad (16)$$

and

$$\mu_{\mathrm{h}} = kT \ln p + \text{const.} \qquad (17)$$

Equations (15–17) give

$$\begin{aligned} \mu_{\mathrm{Co}^*} &= kT \ln a_{\mathrm{Co}^*} \\ &= \text{const.} - kT \ln[V_{\mathrm{Co}}^{z'}] - zkT \ln(z[V_{\mathrm{Co}}^{z'}]) \\ &= \text{const.} - (z+1)kT \ln[V_{\mathrm{Co}}^{z'}] - zkT \ln z. \end{aligned} \qquad (18)$$

We have also $d[V_{\mathrm{Co}}^{z'}] = -d[\mathrm{Co}^*]$, therefore

$$\frac{d \ln a_{\mathrm{Co}^*}}{d \ln[\mathrm{Co}^*]} = \frac{d \ln a_{\mathrm{Co}^*}}{d[V_{\mathrm{Co}}^{z'}]} \frac{d[V_{\mathrm{Co}}^{z'}]}{d \ln[\mathrm{Co}^*]} = (z+1) \frac{[\mathrm{Co}^*]}{[V_{\mathrm{Co}}^{z'}]}. \qquad (19)$$

Since in CoO $t_e = 1$, we get from Eq. (12) that

$$\tilde{D} = \frac{1}{f} D_{\mathrm{Co}}^{\mathrm{Tr}} (z+1) \frac{[\mathrm{Co}^*]}{[V_{\mathrm{Co}}^{z'}]}. \qquad (20)$$

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[1] There is an important printing mistake in the more general Eq. (12) of Ref. (*9*). The derivative inside the summation should be with respect to $\ln c_i$ and not $\ln c_j$.

We see that the enhancement factor equals the reciprocal of the relative vacancy concentration times $(z + 1)$. If diffusion was dominated by neutral vacancies we would have $(z + 1) = 1$.

The result of Eq. (20) is more intuitive if one remembers that $D^{\mathrm{Tr}} = fD_V[V_{\mathrm{Co}}^{z'}]/[\mathrm{Co}^*]$. It reads then

$$\tilde{D} = (z + 1)D_V \tag{21}$$

and means that $\tilde{D}$ equals D_V enhanced by a factor $(z + 1)$, depending on the ionization state of the vacancies. For neutral vacancies we would have $\tilde{D} = D_V$.

This result can also be derived from the following modification of Eq. (12), which is valid for low defect and electron concentrations (*6*)

$$\tilde{D} = \frac{([e] + [\mathrm{defect}]z_{\mathrm{def}}^2)D_e D_{\mathrm{def}}}{[e]D_e + [\mathrm{defect}]z_{\mathrm{def}}^2 D_{\mathrm{def}}}. \tag{22}$$

If we define defect ≡ vacancy and use $[e] = z_V[V]$, $D_e \gg D_V$, we get again Eq. (21). However, Eq. (22) is not very useful for slightly more complicated cases, such as CdS, which will be discussed below.

2. *UO₂*

In $\mathrm{UO_2}$ oxygen, which diffuses through vacancies, is the mobile ionic species and $t_e = 1$. The relation between oxygen self and chemical diffusion in UO_{2+x} $(x \leq 0.16)$ has recently been discussed by Breitung (*5*). Breitung mistakenly uses Darken's equation and arrives at the result (his Eq. (17))

$$\tilde{D} = D_{\mathrm{O}}^{\mathrm{Tr}} \frac{2 + x}{2RT} \frac{d\,\Delta G(\mathrm{O_2})}{dx}, \tag{23}$$

where $\Delta G(\mathrm{O_2}) \equiv 2RT \ln a_{\mathrm{O}}$. If one uses Eq. (12) of the present paper one gets that

$$\tilde{D} = \frac{D_{\mathrm{O}}^{\mathrm{Tr}}}{f_{\mathrm{O}}} \frac{(2 + x)(3 + x)}{2RT} \frac{d\Delta G(\mathrm{O_2})}{dx} \tag{24}$$

and since $f_{\mathrm{O}} = 0.653$ for the simple cubic oxygen sublattice it follows that $\tilde{D}$ is larger by a factor ~4.5 than the values calculated by Breitung. The mistake originates of course in the use of $\tilde{D} = N_{\mathrm{U}}D_{\mathrm{O}}^{\mathrm{I}} = \frac{1}{3}D_{\mathrm{O}}^{\mathrm{I}}$ by Breitung, instead of $D = D_{\mathrm{O}}^{\mathrm{I}}$, and his neglect of f_{O}. One sees from Fig. 5 of Breitung's paper that the bulk of the experimental results for $\tilde{D}$ lie indeed by a factor of 3 to 4 above the theoretical curve he calculated for $x \leq 0.01$. If one uses the correct theory the agreement is obviously much better.

3. *CdS*

A variation of Eq. (12) can be applied to CdS. This was first mentioned by Steele (*4*), who realized that the kinetic argument used by Kumar and Kroeger (*12*) to explain their measurements is not really necessary. However, Steele's argument is not quite consistent, since he starts mistakenly with Darken's equation. Kumar and Kroeger measured $D_{\mathrm{Cd}}^{\mathrm{Tr}}$ and measured also $\tilde{D}$ through the change of resistance with time when the sample was exposed to various Cd pressures. In the analysis of these measurements there is the complication that it is mainly the sulfur sublattice which changes during the chemical diffusion process. The diffusing defects are highly mobile Cd interstitials, but the dominant defects are sulfur vacancies, i.e., $b_{\mathrm{Cd}}[\mathrm{Cd}_i^{\cdot}] \gg b_{\mathrm{S}}[V_{\mathrm{S}}^{\cdot\cdot}]$, but $[\mathrm{Cd}_i^{\cdot}] \ll [V_{\mathrm{S}}^{\cdot\cdot}]$. The two defect species are related through

$$\mathrm{Cd_{Cd}} + V_{\mathrm{S}}^{\cdot\cdot} + e' \leftrightarrow \mathrm{Cd}_i^{\cdot} \tag{25}$$

which leads to the chemical equilibrium equation

$$[V_{\mathrm{S}}^{\cdot\cdot}]n/[\mathrm{Cd}_i^{\cdot}] = K(T). \tag{26}$$

Because of the neutrality condition

$$[\mathrm{Cd}_i^{\cdot}] + 2[V_{\mathrm{S}}^{\cdot\cdot}] = n, \tag{27}$$

which implies in the present case that

$$n \simeq 2[V_{\mathrm{S}}^{\cdot\cdot}], \tag{28}$$

we get from Eq. (26) that

$$2[V_{\mathrm{S}}^{\cdot\cdot}]^2/[\mathrm{Cd}_i^{\cdot}] = K(T). \tag{29}$$

The concentration of sulfur vacancies therefore changes in parallel with that of Cd interstitials.

If [S*] was constant the measurement of resistance would in effect be a measurement of a chemical diffusion coefficient defined by Eq. (3)

$$\tilde{D} = -\frac{J_{\mathrm{Cd}^*}}{d[\mathrm{Cd}^*]/dx} \tag{30}$$

and Eq. (12) would apply. Since [S*] is not constant the driving force of Cd* diffusion is the gradient of the relative concentration so that we really measure a $\tilde{D}$ defined operationally by

$$\tilde{D} = -J_{\mathrm{Cd}^*}\left[[\mathrm{S}^*]\frac{d}{dx}\left(\frac{[\mathrm{Cd}^*]}{[\mathrm{S}^*]}\right)\right]^{-1} \tag{31}$$

To a very good approximation [Cd*] = [S*] and because of $[\mathrm{Cd}_i] \ll [V_{\mathrm{S}}^{\cdot\cdot}]$ we have $[d\mathrm{S}^*]/dx \gg d[\mathrm{Cd}^*]/dx$. Equation (31) is therefore equivalent to

$$\tilde{D} = J_{\mathrm{Cd}^*}/d[\mathrm{S}^*]/dx. \tag{32}$$

We use again [Cd*] = [S*] and transform Eq. (B7) as follows

$$J_{\mathrm{Cd}^*} = -t_e b_{\mathrm{Cd}} \frac{d\,\mu_{\mathrm{Cd}^*}}{d\ln[\mathrm{S}^*]}\frac{d[\mathrm{S}^*]}{dx} \tag{33}$$

so that $\tilde{D}$ becomes

$$\tilde{D} = -t_e \frac{D_{\mathrm{Cd}}^{\mathrm{Tr}}}{f_{\mathrm{Cd}}}\frac{d\ln a_{\mathrm{Cd}^*}}{d\ln[\mathrm{S}^*]}; \tag{34}$$

this is the form mentioned by Steele.

To evaluate Eq. (34) we use an analog of Eq. (14)

$$\mathrm{Cd}(\infty) \rightarrow \mathrm{Cd}_{\mathrm{Cd}}^{x} + V_{\mathrm{S}}^{\cdot\cdot} + 2e' \tag{35}$$

which gives

$$\mu_{\mathrm{Cd}^*} = \text{const.} + \mu_V + 2\mu_e \tag{36}$$

and get with the help of Eq. (28) that

$$\begin{aligned}\mu_{\mathrm{Cd}^*} &= \text{const.} + kT\ln[V_{\mathrm{S}}^{\cdot\cdot}]\\ &\quad + 2kT\ln n = 3kT\ln[V_{\mathrm{S}}^{\cdot\cdot}] + \text{const.}\end{aligned} \tag{37}$$

We have therefore

$$d\ln a_{\mathrm{Cd}^*} = 3d\ln[V_{\mathrm{S}}^{\cdot\cdot}] = 3\frac{d[V_{\mathrm{S}}^{\cdot\cdot}]}{[V_{\mathrm{S}}^{\cdot\cdot}]} \tag{38}$$

we use also $d\ln[\mathrm{S}^*] = -d[V_{\mathrm{S}}^{\cdot\cdot}]/[\mathrm{S}^*]$ so that

$$\frac{d\ln a_{\mathrm{Cd}^*}}{d\ln[\mathrm{S}^*]} = -3\frac{[\mathrm{S}^*]}{[V_{\mathrm{S}}^{\cdot\cdot}]}. \tag{39}$$

Finally, since $t_e = 1$ and $f_{\mathrm{Cd}} = 1$ for the interstitial mechanism we get

$$\tilde{D} = D_{\mathrm{Cd}}^{\mathrm{Tr}}\,3\frac{[\mathrm{S}^*]}{[V_{\mathrm{S}}^{\cdot\cdot}]} \tag{40}$$

which is the result derived by Kumar and Kroeger. The enhancement factor is therefore $3[\mathrm{S}^*]/[V_{\mathrm{S}}^{\cdot\cdot}]$, it resembles the one for CoO (see Eq. (21)). The ratio $D_{\mathrm{Cd}}^{\mathrm{Tr}}[\mathrm{S}^*]/[V_{\mathrm{S}}^{\cdot\cdot}]$, gives simply an effective diffusion coefficient for sulfur vacancies transporting Cd, which they do in a way, see the paper by Kumar and Kroeger. The factor "3" reflects again the fact that a neutral Cd atom is incorporated as three charged defects according to Eq. (35) rather than as one defect via

$$\mathrm{Cd(gas)} \leftrightarrow V_{\mathrm{S}}^{x} + \mathrm{Cd}_{\mathrm{Cd}}^{x}. \tag{41}$$

One can derive Eq. (34) in a more direct, but less rigorous way. In Eq. (B7) we can interpret [M*] as moles of M per mole of MX, at least for low defect concentrations. If we do so then for CdS $d[\mathrm{Cd}^*] = -d[\mathrm{S}^*]$. We use again $[\mathrm{S}^*] \simeq [\mathrm{Cd}^*]$ and get directly from Eq. (B7) that

$$J_{\mathrm{Cd}^*} = t_e b_{\mathrm{Cd}}\frac{d\mu_{\mathrm{Cd}^*}}{d\ln[\mathrm{S}^*]}\frac{d[\mathrm{Cd}^*]}{dx}. \tag{42}$$

With Eq. (9) and $\tilde{D} = D^{\mathrm{I}}$ we get again Eq. (34).

4. *Stabilized Zirconia*

This material, with a representative composition $\mathrm{Zr}_{0.9}\mathrm{Y}_{0.1}\mathrm{O}_{1.95}$ is an oxygen ion conductor with a high concentration of oxygen vacancies (2½% in the above example) and $t_e \ll 1$ (*6*). Equation (12), which reads for oxygen ions

$$W = t_e \frac{d \ln a_{O^*}}{d \ln [O^*]} \qquad (43)$$

can then be rewritten

$$\begin{aligned} W &= \frac{\sigma_e}{\sigma_i} \frac{d \ln a_{O^*}}{d \ln[O^*]} = \frac{\sigma_e}{4[O^{2-}] b_O q^2} \frac{d \ln a_{O^*}}{d \ln[O^*]} \\ &= \frac{\sigma_e}{4 b_O q^2} \frac{d \ln a_{O^*}}{d[O^*]} \\ &= \frac{\sigma_e f_O kT}{4 D_O^{\mathrm{Tr}} q^2} \frac{d \ln a_{O^*}}{d\,[O^*]}, \end{aligned} \qquad (44)$$

where we have used $[O^{2-}] = [O^*]$. The chemical diffusion coefficient is therefore

$$\tilde{D} = W \frac{D_O^{\mathrm{Tr}}}{f_O} = \frac{\sigma_e kT}{4q^2} \frac{d \ln a_{O^*}}{d[O^*]}. \qquad (45)$$

To evaluate this expression we note that σ_e is determined by holes near $P_{O_2} = 1$ atm, but by electrons at very low oxygen pressures. The incorporation reaction

$$O(\infty) \rightarrow O_O^x - V_O^{\cdot\cdot} + 2h^{\cdot} \qquad (\text{or } -2e') \qquad (46)$$

then leads to

$$\ln a_{O^*} = \text{const.} - \ln a_V + 2 \ln a_h \qquad (\text{or } -2 \ln a_e) \qquad (47)$$

and because of the high $[V_O^{\cdot\cdot}]$, $\ln a_V$ is practically constant. Therefore near $P_{O_2} = 1$ atm

$$\begin{aligned} \frac{d \ln a_{O^*}}{d[O^*]} &= 2 \frac{d \ln a_h}{d[O^*]} \\ &= 2 \frac{d \ln a_h}{dp} \frac{dp}{d[O^*]}. \end{aligned} \qquad (48)$$

Because of $p \ll 1$ we have $\ln a_h = \ln p$. From Eq. (46) we have $dp = -2d[V_O^{\cdot\cdot}] = 2d[O^*]$ so that

$$\frac{d \ln a_{O^*}}{d[O^*]} = \frac{4}{p}. \qquad (49)$$

Equation (45) gives therefore

$$\tilde{D} = \frac{\sigma_e kT}{pq^2} = \frac{p b_h q^2 kT}{pq^2} = b_h kT = D_h \qquad (50)$$

and it can be shown similarly that at low pressures $\tilde{D} = D_e$.

We see that in stabilized zirconia (and similarly in any conductor with $t_e \ll 1$) $\tilde{D}$ is determined only by the diffusion coefficient of the electronic charge carriers and has nothing to do with the tracer diffusion coefficient of the ions. This result, while not new, is very often overlooked, most recently for instance by Manasevit *et al.* (*13*). In zirconia there are complications due to trapping, these are discussed by Heyne (*6*).

5. *Diffusion Doping of Semiconductors*

Boron and similar dopants diffuse into silicon substitutionally. This, as mentioned before, is a case of interdiffusion. Since boron is incorporated not as atoms, but as $B'_{Si} + h^{\cdot}$ we have ambipolar diffusion of the boron. As far as we know, the combination of ambipolar and interdiffusion has not been treated in the literature, though the related problem of KCl–RbCl interdiffusion has been discussed (*14*). In the treatment of diffusion doping the interdiffusion aspect is usually neglected, i.e., the problem is treated as a case of ambipolar diffusion, as follows:

The incorporation reaction

$$B(\infty) \rightarrow B'_{Si} + h^{\cdot} \qquad (51)$$

leads to

$$\mu_{B^*} = \mu_{B'} + \mu_h. \qquad (52)$$

Because of the low concentrations involved we have

$$\mu_{B'} = kT \ln[B'], \quad \mu_h = kT \ln p. \qquad (53)$$

We now have to differentiate between two cases:

(a) If boron diffuses into intrinsic silicon then $p = [B']$. Since $[B'] = [B^*]$ we have in this case $\ln a_{B^*} = 2 \ln[B^*]$ and get from Eq. (12) with $t_e = 1$ that

$$\tilde{D} = 2D_B^{\mathrm{Tr}}/f_B. \qquad (54)$$

(b) If boron diffuses into silicon with a high concentration of holes then p = const. and $\ln a_{B^*} = \ln[B^*]$ + const. In this case we get

$$\tilde{D} = D_{B}^{Tr}/f_{B}. \qquad (55)$$

The simple ambipolar diffusion approach gives therefore an enhancement factor of 2 or 1, depending on the case. We note that in contrast to the case of CoO there is no vacancy concentration in the enhancement factor, the reason being of course that in interdiffusion we do not have a vacancy flow.

The factor f_B in Eqs. (54) and (55) is not really justified since, as mentioned, we have here an interdiffusion mechanism.

Appendix A: Proof of Eq. (4)

The flux density J_A of A-atoms is related to the gradient of their chemical potential, μ_A, by the relation

$$J_A = -[A]b_A\, \partial\mu_A/\partial x. \qquad (A1)$$

It is well known that the mobility b_A is related to D_A^{Tr} by the Einstein relation

$$b_A = D_A^{Tr}/kT. \qquad (A2)$$

We ignore here the correlation factor f_A which depends on the details of the diffusion mechanism. For a treatment which includes f_A see Manning (*2*).

Eq. (A1) becomes therefore

$$J_A = -\frac{D_A^{Tr}}{kT}[A]\frac{\partial\mu_A}{\partial x} = -\frac{D_A^{Tr}}{kT}\frac{d\mu_A}{d\ln[A]}\frac{\partial[A]}{\partial x} \qquad (A3)$$

and we get with the help of Eq. (3) and $\mu_A = RT \ln a_A$ that

$$D_A^{I} = D_A^{Tr}\frac{d\ln a_A}{d\ln[A]}. \qquad (A4)$$

Since for [A] + [B] = const. we have $d \ln[A] = d \ln N_A$, this equation can also be written

$$D_A^{I} = D_A^{Tr}\frac{d\ln a_A}{d\ln N_A}. \qquad (A5)$$

Use is now made of the Gibbs–Duhem equation which is valid for a binary system

$$N_A\, d\mu_A + N_B d\mu_B = 0 \qquad (A6)$$

and which together with $dN_A = -dN_B$ leads to

$$\frac{d\ln a_A}{d\ln N_A} = \frac{d\ln a_B}{d\ln N_B}. \qquad (A7)$$

From Eqs. (A5), (A7), and (2) we get Eq. (4), but with $R = 1$.

Because of Eq. (A7) only one factor of the form $d \ln a_A/d \ln N_A$ appears in Eq. (4), even though both components diffuse. We note also the use of full rather than partial derivatives with respect to the composition, in a binary alloy there is only one composition variable.

Appendix B: Proof of Eq. (12)

To derive Eq. (12) for the case of mobile M-ions and electronic charge carriers e (holes or electrons), we start with the particle currents

$$J_M = -[M^{z+}]b_M\frac{\partial\mu_{M^{z+}}}{\partial x} - z_M q[M^{z+}]b_M\frac{\partial\phi}{\partial x} \qquad (B1)$$

$$J_e = -[e]b_e\frac{\partial\mu_e}{\partial x} - z_e q[e]b_e\frac{\partial\phi}{\partial x}, \qquad (B2)$$

where $z_e = 1$ for holes, -1 for electrons. We introduce electrical conductivities defined by

$$\sigma_M \equiv z_M^2 q^2[M^{z+}]b_M \qquad (B3)$$

$$\sigma_e \equiv q^2[e]b_e \qquad (B4)$$

and note that the total electrical current has to be zero, i.e., $z_M J_M + z_e J_e = 0$. This leads to the following expression for the electric field

$$\frac{\partial \phi}{\partial x} = \frac{\frac{1}{z_e}\frac{\sigma_e}{q}\frac{\partial \mu_e}{\partial x} + \frac{\sigma_{\mathrm{M}}}{q z_{\mathrm{M}}}\frac{\partial \mu_{\mathrm{M}^{z+}}}{\partial x}}{\sigma_{\mathrm{M}} + \sigma_e}. \qquad \text{(B5)}$$

Introducing this into Eq. (B1) gives after some algebra

$$J_{\mathrm{M}} = -\frac{\sigma_{\mathrm{M}}\sigma_e}{z_{\mathrm{M}}^2 q^2 (\sigma_{\mathrm{M}} + \sigma_e)} \left(\frac{\partial \mu_{\mathrm{M}^{z+}}}{\partial x} - \frac{z_{\mathrm{M}}}{z_e}\frac{\partial \mu_e}{\partial x}\right). \qquad \text{(B6)}$$

Because of $\mathrm{M}^{\text{atom}} \leftrightarrow \mathrm{M}^{z+} - (z_{\mathrm{M}}/z_e)e$ we have $\mu_{\mathrm{M}^{z+}} - (z_{\mathrm{M}}/z_e)\mu_e = \mu_{\mathrm{M}^*}$. This, together with $\sigma_e/(\sigma_{\mathrm{M}} + \sigma_e) = t_e$ allows us to transform Eq. (B6) to

$$J_{\mathrm{M}} = -t_e[\mathrm{M}^{z+}]b_{\mathrm{M}}\frac{\partial \mu_{\mathrm{M}^*}}{\partial x} \qquad \text{(B7)}$$

using now $[\mathrm{M}^{z+}] = [\mathrm{M}^*]$, $\mu_{\mathrm{M}^*} = kT \ln a_{\mathrm{M}^*}$, $b_{\mathrm{M}} = D_{\mathrm{M}}^{\mathrm{Tr}}/f_{\mathrm{M}}kT$ this becomes

$$J_{\mathrm{M}} = -t_e \frac{D_{\mathrm{M}}^{\mathrm{Tr}}}{f_{\mathrm{M}}} \frac{\partial \ln a_{\mathrm{M}^*}}{\partial \ln[\mathrm{M}^*]} \frac{\partial[\mathrm{M}^*]}{\partial x} \qquad \text{(B8)}$$

so that we get with $J_{\mathrm{M}} = -\tilde{D}\, \partial[\mathrm{M}^*]/\partial x$, Eq. (12).

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