Sum-Rule Relationships among Phenomenological Coefficients: Simplifications for the Analysis of Segregation and Chemical Diffusion

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In this review article, the authors first introduce the phenomenological transport coefficients, and the relationships between them and the tracer diffusion coefficients. Next, the authors discuss a sum rule relating phenomenological coefficients themselves in the random-alloy model. The authors then consider several applications of the sum rule to diffusion problems. These applications include intrinsic diffusion in multicomponent alloys, chemical diffusion in strongly ionic mixed cation crystals, and the segregation (demixing) of cations in mixed oxides in an oxygen potential gradient and/or an electric field. In each case, a substantial simplification is possible as a result of the sum rule.

1. Introduction

It is well known that an implication of Fick's first law is that once the concentration gradient for the diffusing species i reaches zero, the flux of species i must also cease. While frequently true, it is in fact a too restrictive condition for equilibrium. In general, the net flux of a diffusing species ceases only when all direct and indirect forces on that species are zero. The Onsager flux equations of irreversible processes achieve this through the postulate of linear relations between the fluxes and the driving forces (e.g., Ref 1 and 2):

$$J_i = \sum_j L_{ij} X_j \qquad \text{(Eq 1)}$$

where the L_{ij} are the phenomenological transport coefficients and the X_j are the driving forces. The matrix of phenomenological transport coefficients is frequently simply called the L matrix. The Onsager flux equations have been used very extensively in theoretical treatments of collective diffusion problems such as chemical diffusion and ionic conductivity, especially in multicomponent systems. The great importance of the phenomenological transport coefficients stems from their independence of driving force. Although highly desirable on this account, unfortunately, the experimental determination of the L matrix is most difficult for the solid state due to the difficulty in measuring chemical potential gradients, which are the usual solid-state driving forces. Gaining access to diffusion coefficients is much

more straightforward because concentrations (and their gradients) are of course readily measurable. Accordingly, this has first of all prompted interest in finding relations between the phenomenological coefficients and the (measurable) diffusion coefficients.

2. Relations between Phenomenological Coefficients and Tracer Diffusion Coefficients

The first relations between the phenomenological transport coefficient and tracer diffusion coefficients were the relations of Darken.[3] In essence, the Darken assumption is the neglect of any off-diagonal phenomenological transport coefficients. The remaining diagonal phenomenological transport coefficients are then related to the corresponding tracer diffusion coefficients; for example, in a binary AB alloy, L_{AA} is then simply related to the tracer diffusion coefficient of A, D_A^*:

$$L_{AA} = C_A D_A^* / kT \qquad \text{(Eq 2a)}$$

$$L_{AB} = 0 \qquad \text{(Eq 2b)}$$

In principle, the off-diagonal phenomenological transport coefficients can make a large difference in the value of a given flux and can even change the sign. Accordingly, whether the neglect of the off-diagonal phenomenological transport coefficient is a reasonable thing to do, or not, depends very much on the context. In highly ordered stoichiometric AB intermetallic compounds, where it is believed that there are concatenated sequences of jumps (e.g., the six-jump cycle[4]), it is known that the off-diagonal phenomenological transport coefficients take values that are very close to zero anyway,[5] and so ignoring them is not likely to make much difference. In other situations, such as the "five-frequency" model for a solute in an electric field, ignoring the off-diagonal phenomenological transport coefficient can in principle give the wrong direction for the solute flux. It is generally accepted, however, that as a first

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rough approximation it is not unreasonable to ignore the off-diagonal phenomenological transport coefficients.

The second set of relations between the phenomenological transport coefficients and tracer diffusion coefficient are the relations of Manning,[6] which were developed originally for the random alloy in which the various atomic species and the isolated vacancy are randomly mixed, and where the atom-vacancy frequencies depend only on the identity of the atom jumping. In the relations of Manning, the phenomenological transport coefficients are directly related to the tracer diffusion coefficients by the expressions:

$$L_{ii} = \frac{C_i D_i^*}{kT} \left(1 + \frac{2C_i D_i^*}{M_0 \sum_k C_k D_k^*} \right) \qquad \text{(Eq 3a)}$$

$$L_{ij} = \frac{2C_i D_i^* C_j D_j^*}{kT(M_0 \sum_k C_k D_k^*)} \text{ for } i \neq j \qquad \text{(Eq 3b)}$$

where $M_0 = 2f_0/(1-f_0)$, and f_0 is the geometric tracer correlation factor for the lattice [e.g., $f_0 = 0.78146...$ for the face-centered cubic (fcc) lattice].[7] The extra factor in Eq 3a compared with Eq 2a should be noted. It is worth noting too that the Manning relations can also be obtained on the basis of two somewhat intuitive assumptions without recourse to the random-alloy model,[8] thereby suggesting that they have rather more general validity than the random-alloy model might suppose. That this is indeed the case has been shown in various computer simulations even for ordered alloys, at least at low levels of order before concatenated mechanisms such as the six-jump cycle[4] start to become important.[9-11] The Manning relations have also been rederived specifically for ordered B1-B2 alloys.[12]

The self-consistent theory of Moleko et al.[13] also provides relations between the phenomenological coefficients and the tracer diffusion coefficients for the random-alloy model, but these relations are not expressible in a convenient closed form. Nonetheless, it is still possible to use straightforward numerical methods to find all of the L_{ij} from a given set of tracer diffusion coefficients for all of the atomic species.[14] Computer simulations[15] have shown these relations to be considerably more accurate than those provided by Manning[6] that were described above. The differences between the results of the self-consistent theory and the Manning theory are mainly apparent at more extreme ratios of the atom-vacancy exchange frequencies.

The third relationship between the phenomenological transport coefficients and the tracer diffusion coefficients is the Heumann relation.[16] This relation was determined after consideration of the five-frequency model (see also Ref 1). This model (e.g., Le Claire and Lidiard[17]) is very useful for describing solute and host diffusion kinetics in fcc metals and fcc sublattices in ionic crystals when the vacancy-solute interaction is localized. The five frequencies in the model refer to the following conditions: a vacancy-host atom (A) exchange frequency, w_0; a vacancy-host (A) exchange frequency, w_1, referring to a "rotational jump" around a solute atom (i.e., from one nearest-neighbor site to

another of the solute); a vacancy-solute (B) exchange frequency, w_2; a vacancy-host (A) atom exchange frequency, w_3, that brings the vacancy to a site neighboring the solute atom (this is usually called the *associative jump*); and finally a vacancy-host atom (A) exchange frequency, w_4, that is the reverse of the w_3 jump (this is usually called the *dissociative jump*). It can be shown that for a dilute alloy in the limit where the solute concentration $C_B \to 0$, the ratio of $L_{AB}(0)/L_{BB}(0)$ is given by[16]:

$$\frac{L_{AB}(0)}{L_{BB}(0)} = \frac{D_A^*(0)}{D_B^*(0)} \left(f_0^{-1} - \frac{D_A^I(0)}{D_A^*(0)} \right) \qquad \text{(Eq 4)}$$

where $D_A^*(0)$, $D_B^*(0)$ are the tracer diffusion coefficients of A and B, respectively, and $D_A^I(0)$ is the intrinsic diffusion coefficient of A in the dilute alloy at the limit $C_B \to 0$.

3. Relations among Phenomenological Coefficients: The Sum Rule

Various relations have been identified between the phenomenological coefficients themselves in randomly mixed systems, in effect reducing the number of independent coefficients. These are of great interest, first of all because the assumption of random mixing in diffusion problems is a very common one indeed in solving diffusion problems analytically. Second, experience gained from many Monte Carlo computer simulations indicates that a nonrandom distribution of components does not actually change the basic diffusion kinetics behavior very much unless long-range order or clustering is present. In other words, the effect on the jump frequency and the correlation factors, tracer or collective, of a nonrandom distribution itself is relatively small. Indeed, the main effect of a change in the distribution of the components is in fact in the thermodynamic factor that typically appears in expressions for the chemical diffusion coefficient. This factor can in general be factored out and treated quite separately from the jump frequency and the correlation parts. It has been found that a considerable simplification is often possible in collective diffusion problems through the use of such relations. The first of these relations was the exact sum rule identified in 1988 by Moleko and Allnatt[18] for the multicomponent random alloy with the monovacancy mechanism operating at an arbitrary vacancy concentration. This sum rule was implied in earlier work on diffusion kinetics in the random-alloy model at a very low vacancy concentration (e.g., the formalism of Manning[6] of the early 1970s) but was simply not identified as such at the time.

As an aside, the authors note that the random-alloy model is a very important model because it is a convenient vehicle for describing the diffusion kinetics in concentrated multicomponent alloys and also for sublattices in compounds that exhibit random mixing of two or more components. In its original form, the vacancy concentration was infinitely small. In its more general form, where the vacancy concentration can be arbitrary (and where it is often called the *lattice gas*) the model is useful for describing the mobile

sublattice of a fast ion conductor or a mixed adsorption system. In the random-alloy model, the atom vacancy exchange frequencies w_i can be considered in two rather different ways. In the first way, the frequencies can be classified simply as explicit frequencies that depend only on the species of the atom and not the surroundings. For example, in the binary random alloy, w_A then simply represents the A atom vacancy exchange frequency of a given A atom in all compositions and environments. In the second, and more general, way, one considers that the w_i represents an average frequency of species i at a given composition. For example, in the binary random alloy, w_A would then represent the average frequency of a given A atom as it migrates through the lattice sampling the various environments. Because the average environment of an atom will obviously change with composition, then the w_i can also be expected to change with composition (e.g., Murch and Belova[19]).

Moleko and Allnatt[18] identified the following sum rule for the M-component random alloy with the vacancy mechanism operating at an arbitrary vacancy concentration:

$$\sum_{i=1}^{M} L_{ij} w_j / w_i = A c_V w_j C_j, \quad ij = 1, \ldots, M \tag{Eq 5}$$

where A is given by $A = z\, a^2/6kT$ (z is the coordination number, a is the jump distance for a vacancy jump, and k and T have their usual meanings), and c_V is the vacancy fraction. In effect, the sum rule relates the phenomenological coefficients to the vacancy-atom exchange frequencies and, in so doing, reduces the number of independent phenomenological coefficients. For example, in the binary random alloy, there is only one independent phenomenological coefficient, not three.

Thus in the binary alloy AB the sum-rule relation is:

$$L_{AA} + \frac{w_A}{w_B} L_{AB} = L_{AA}^{(0)} = c_V C_A w_A A \tag{Eq 6a}$$

$$L_{BB} + \frac{w_B}{w_A} L_{AB} = L_{BB}^{(0)} = c_V C_B w_B A \tag{Eq 6b}$$

For the case of the very frequently used hopping model, where the atoms thermalize with the surroundings between hops or jumps, the phenomenological transport coefficients can be conveniently partitioned into a correlated part (a correlation function, frequently called the *collective correlation factor* due to its similarity to a tracer correlation factor) and an uncorrelated part (principally containing the jump frequency):

$$L_{ij} = f_{ij}^{(j)} L_{jj}^{(0)} \tag{Eq 7}$$

where $f_{ij}^{(j)}$ is the collective correlation factor, and $L_{jj}^{(0)}$ is the uncorrelated phenomenological transport coefficient.

The sum rule can then also be restated in terms of these collective correlation factors as:

$$\sum_{i=1}^{M} f_{ij}^{(j)} w_j / w_i = 1, \quad j = 1, \ldots, M \tag{Eq 8}$$

The derivation of this sum rule is beyond the scope of this overview, but the authors can describe it qualitatively. Consider a random alloy with the vacancy mechanism operating and assume that an atom of species i has just made a jump. The authors accept this jump as the initial point in time and take a snapshot of the system. Then, for each quantity like L_{ij}, consider how the system changes from the initial configuration (after the jump of the i atom) during the jumping of the vacancies: that is, after the first jump, the second jump and so on. At each moment in time, choose a vacancy randomly from the current configuration (there is a specific probability for the system to get to this configuration starting with the initial one), then choose a *random direction* and find an atom of some type (or another vacancy). Accordingly, for each direction there is a defined probability that the vacancy makes an exchange with the atom there. If this is an atom of species j, then a contribution to the cosine of the angle between the first jump of the i atom and the final jump of the j atom (the basic quantity in the correlated part of L_{ij} [see Eq 7]) is equal to the probability for a system to get to the current configuration multiplied by the vacancy concentration and multiplied by the vacancy-atom j exchange frequency (and divided by the coordination number). Therefore, each contribution of this type for a different atomic species j differs from one another only by the corresponding exchange frequency. After all of the summations are done, the authors end up with the sum-rule relation, as shown in Eq 5.

Since the discovery of the first sum rule, various other closely related sum rules have been identified for a number of other mechanisms and situations including the dumb-bell interstitial mechanism in the binary random alloy,[20] the divacancy mechanism in the fcc random alloy,[21] the vacancy-pair mechanism in strongly ionic materials with randomly mixed cations,[22] the vacancy mechanism for a model of an intermetallic compound (with randomly mixed sublattices), and certain parts of a reduced five-frequency model for solute and solvent diffusion in the fcc lattice with the vacancy mechanism operating.[23,24] In the remainder of this review, some of the applications of the first sum rule to several collective diffusion problems are reviewed.

4. The Sum Rule and the Intrinsic Diffusion Coefficients in Multicomponent Alloys

In this example, the authors consider intrinsic diffusion in a random N-component alloy with the vacancy mechanism operating. We write the driving forces X_i as $-\nabla\mu_I$, where μ_i is the chemical potential of species i (assume there are no external driving forces), and make the usual assumption that the sources and sinks of vacancies are sufficiently numerous that the gradient of the chemical potential of the vacancies $\nabla\mu_V \approx 0.0$.

Using the Gibbs-Duhem relation, Eq 1 can then readily be transformed into:
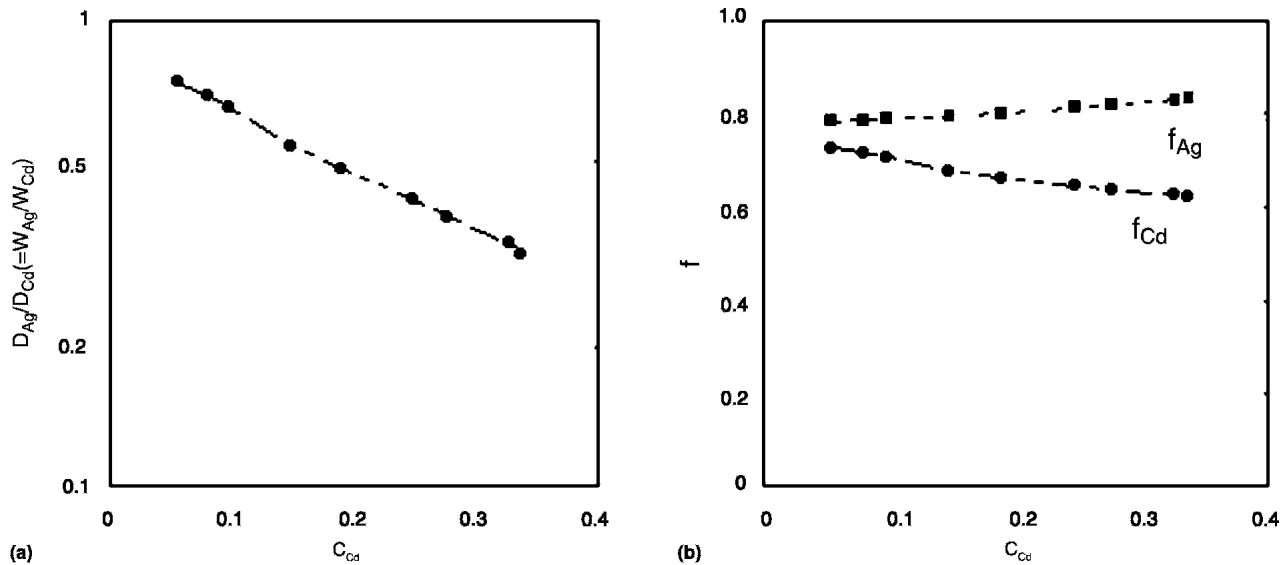
Fig. 1 (a) The ratio D_{Ag}/D_{Cd} ($= w_{Ag}/w_{Cd}$) as a function of c_{Cd} at 873 K[26]; (b) corresponding tracer correlation factors using the Moleko et al.[13] self-consistent formalism for the random alloy

$$J_i = -\sum_{j=1}^{N-1} n D_{ij}^N \nabla c_j, \; i = 1, \dots, N \qquad \text{(Eq 9)}$$

where D_{ij}^N is the intrinsic diffusion coefficients. For binary *AB* alloys, the ratio of the intrinsic diffusivities D_A and D_B can be expressed in terms of the phenomenological coefficients in the usual way (e.g., Philibert[1]):

$$\frac{D_A}{D_B} = \frac{c_B L_{AA} - c_A L_{AB}}{c_A L_{BB} - c_B L_{AB}} \qquad \text{(Eq 10)}$$

Application of the sum rule (Eq 5) to Eq 10 immediately gives the surprisingly simple and exact result for the binary random-alloy model[25]:

$$\frac{D_A}{D_B} = \frac{w_A}{w_B} \qquad \text{(Eq 11)}$$

It is seen that, despite the appearance of the off-diagonal phenomenological coefficients in Eq 10, no correlation factors or vacancy wind factors appear in Eq 11. Similarly, for ternary *ABC* alloys, the sum rule gives that[25]:

$$\frac{D_{BA}^C D_{CB}^C - D_{BB}^C D_{CA}^C}{D_{AA}^C D_{BB}^C - D_{AB}^C D_{BA}^C} = \frac{w_C}{w_A} \qquad \text{(Eq 12a)}$$

$$\frac{D_{AB}^C D_{CA}^C - D_{AA}^C D_{CB}^C}{D_{AA}^C D_{BB}^C - D_{AB}^C D_{BA}^C} = \frac{w_C}{w_B} \qquad \text{(Eq 12b)}$$

where D_{AA}^C and others are the ternary intrinsic diffusivities in the *ABC* ternary alloy, and *C* is, by convention, the dependent concentration variable.

The general expression (for an *N* atomic component alloy) can be written as:

$$\mathbf{D}^{-1} \times \begin{bmatrix} D_{N1}^N \\ D_{N2}^N \\ \dots \\ D_{NN-1}^N \end{bmatrix} = \begin{bmatrix} w_N/w_1 \\ w_N/w_2 \\ \dots \\ w_N/w_{N-1} \end{bmatrix} \qquad \text{(Eq 13)}$$

where **D** is a matrix with elements D_{kl}^N and $k, l \neq N$.

There has been a very long tradition in solid-state diffusion research of gaining access to the tracer correlation factors, if possible, because these factors give rather direct information on the relative degrees of correlation in the random walks of the various atomic species. It is well-known that tracer correlation factors in materials can frequently be inferred directly from isotope effect experiments[26] and, for ionic conductors, from measurements of the Haven ratio.[27] It is rather less well known that tracer correlation factors can also be obtained in concentrated disordered alloys, specifically from ratios of the tracer diffusivities and the value of the geometric tracer correlation factor f_0 using a diffusion kinetics theory in the random-alloy model, such as that of Manning[6] or the more recent self-consistent theory of Moleko et al.[13] However, it can now be seen that tracer correlation factors can also be obtained by way of the ratio of the intrinsic diffusivities in the random alloy and one of the diffusion kinetics theories just cited. As an example of this, in Fig. 1(a) the authors show the ratio of the atom-vacancy exchange frequencies as deduced directly from the measured intrinsic diffusivities (Eq 11) in the Cd-Ag system at 873 K,[28] and in Fig. 1(b) the corresponding tracer correlation factors obtained from the ratio of the exchange frequencies by way of the diffusion kinetics theory of Moleko et al.[13] It can be seen that at low

Cd compositions the tracer correlation factors are similar, indicating that the Ag and Cd atoms are similarly correlated in their motion. As the Cd composition increases, Ag atoms have the higher tracer correlation factors (they have the lower atom-vacancy exchange frequencies), indicating that they are less correlated in their motion than the Cd atoms.

5. The Sum Rule and Chemical Diffusion in Strongly Ionic Randomly Mixed Crystals

In this example, the authors consider chemical diffusion in strongly ionic mixed cation crystals $(A,B)Y$. We assume Schottky disorder and that the cations A and B diffuse by monovacancies on the cation sublattice (with exchange frequencies w_A and w_B), while the Y anions diffuse independently by single vacancies on the anion sublattice (with exchange frequency w_Y). The flux equations are (we assume for convenience here that the charges on the ions are simply related by $q_A = q_B = -q_Y$):

$$J_A = L_{AA}X_A + L_{AB}X_B$$
$$J_B = L_{AB}X_A + L_{BB}X_B$$
$$J_Y = L_{YY}X_Y \qquad \text{(Eq 14)}$$

where for the internal driving forces we have that:

$$X_A = -\nabla\mu_A + q_A E$$
$$X_B = -\nabla\mu_B + q_B E$$
$$X_Y = -q_Y E \qquad \text{(Eq 15)}$$

where E is the internal (Nernst) electric field. Upon application of the electroneutrality conditions and the Gibbs-Duhem relation, we find that[29]

$$J_A = -D_A N\nabla c_A$$
$$J_B = -D_B N\nabla c_B \qquad \text{(Eq 16)}$$

where the intrinsic diffusion coefficients D_A and D_B are given by:

$$D_A = \frac{\alpha kT c_Y}{N c_A c_B}\left(\frac{L_{AA}L_{BB} - L_{AB}^2 + L_{YY}(L_{AA}c_B - L_{AB}c_A)/c_Y}{L_{AA} + L_{BB} + 2L_{AB} + L_{YY}}\right) \qquad \text{(Eq 17a)}$$

$$D_B = \frac{\alpha kT c_Y}{N c_A c_B}\left(\frac{L_{AA}L_{BB} - L_{AB}^2 + L_{YY}(L_{BB}c_A - L_{AB}c_B)/c_Y}{L_{AA} + L_{BB} + 2L_{AB} + L_{YY}}\right) \qquad \text{(Eq 17b)}$$

and α is a thermodynamic factor. On substitution of the sum rule (Eq 5), the authors soon find that the ratio of these intrinsic diffusion coefficients is given in this case by[29]:

$$\frac{D_A}{D_B} = \frac{w_A(w_B + w_Y)}{w_B(w_A + w_Y)} \qquad \text{(Eq 18)}$$

where w_Y is the anion vacancy exchange frequency. For the limiting case $w_Y \gg w_A$ (w_B), that is, the anion mobility is very high compared with the cation mobility, Eq 18 shows

that the ratio of the intrinsic diffusion coefficients is simply given by w_A/w_B. This is of course exactly the same result obtained for the ratio of the intrinsic diffusivities for the components A and B in the binary metallic alloy described above (Eq 11). This equivalence comes about because the mobility of the vacancies on the anion sublattice is so high that it cannot determine the rate of cation vacancy mobility and therefore cation interdiffusion. This is analogous to noting that the free electrons in the metallic alloy have no influence on the diffusion rate of the atoms themselves. On the other hand, for the other limiting case where $w_Y \ll w_A$ (w_B), that is, the anion mobility is now very low compared with the cation mobility, Eq 18 then shows that the ratio of the intrinsic diffusion coefficients is simply unity (i.e., the two intrinsic diffusion coefficients are now required to be equal). This can be understood as follows. In the interdiffusion experiment with a diffusion couple AY-BY, an essentially immobile Y anion sublattice means there is no anion vacancy mobility. The cation vacancies are restricted in their motion in the sense there can be no cation vacancy flux. The fluxes of the cations A and B must then be exactly equal and opposite. Therefore, there would be no Kirkendall shift. The intrinsic diffusivities of the cations A and B are thus equal and of course equal to the interdiffusion coefficient too.

6. The Sum Rule and Cation Segregation (Demixing) of Mixed Oxides in an Oxygen Potential Gradient and/or an Electric Field

In this example, the authors consider the segregation or demixing of cations in an oxygen potential gradient and/or an electric field of the cations of a mixed oxide $(A,B)O$ taking the rock-salt structure. The authors consider the oxygen potential gradient and the electric field together in the analysis. In these oxides, the oxygen ions are essentially immobile at the temperatures of interest and act as "spectators" for the cation diffusion processes. Consider that one end of the sample is exposed to a higher oxygen partial pressure (which determines the [higher] cation vacancy composition at this end), while the opposite end is exposed to a lower oxygen partial pressure, which again determines the (lower) cation vacancy composition. At high temperatures, where the cations are mobile, there is a resulting vacancy flux across the sample and a cation flux in the opposite direction. Alternatively, a vacancy flux can be obtained by applying an electric field: at high current conditions, there is a cation flux in direct response to the field and a vacancy flux in the opposite direction. In general, the two cations A and B in $(A,B)O$ will have different mobilities (i.e., they have different exchange rates with the vacancies V). As the species of cation diffuse in the flux of vacancies, there will be a demixing of the cations across the sample.

The usual assumption in addressing this problem is to assume that the electronic mobility is far greater than the atomic mobilities and, therefore, is not rate-determining in the diffusion of the cations. We also assume that the cations are randomly mixed (i.e., the cation sublattice is a binary

"random alloy"). The Onsager flux equations (Eq 1) for the cation sublattice system with vacancies can be written as[30]:

$$J_i = -\sum_j L_{ij}(\nabla\mu_j - \nabla\mu_V - F_j), \quad i,j = A,B \qquad \text{(Eq 19)}$$

where the F_j are the electrical driving forces (qE, where q is the charge on the cation and E is the electric field). For convenience here, we will assume that $F_A = F_B = F$.

Once steady-state demixing of the cations has been achieved, the crystal moves with a steady-state velocity, v, with respect to the laboratory frame (which is fixed at an oxygen lattice plane). The condition that leads to the steady state can be expressed as[31]:

$$J_i - vc_i N = 0, \quad i = A,B \qquad \text{(Eq 20)}$$

where c_i is the composition of component i (with respect to the cation sublattice so that $c_A + c_B + c_V = 1.0$), and N is the number of lattice sites per unit volume. Equations 19 and 20 lead to the result:

$$\begin{bmatrix} \nabla(\mu_A - \mu_V - F) \\ \nabla(\mu_B - \mu_V - F) \end{bmatrix} = \begin{bmatrix} L_{AA} & L_{AB} \\ L_{AB} & L_{BB} \end{bmatrix}^{-1} \begin{bmatrix} -c_A vN \\ -c_B vN \end{bmatrix} \qquad \text{(Eq 21)}$$

Equation 21 is the principal demixing equation. We can now make use of the sum rule (Eq 5), and then Eq 21 reduces to:

$$\nabla(\mu_i - \mu_V) = -\frac{vc_i N}{L_{ii}^{(0)}} + F = -\frac{vNkT}{w_i c_V K} + F, \quad i = A,B \qquad \text{(Eq 22)}$$

As in the previous examples, the formal absence of any correlation factors or vacancy-wind factors is especially noted. Next, after converting the chemical potential gradients to composition gradients and assuming thermodynamic ideality (the random-mixing model where $\mu_i - \mu_V = kT ln(c_i/c_V)$). This leads to the following coupled set of ordinary differential equations describing the steady-state composition profiles of the two cations and the vacancies:

$$\frac{dc_i}{d\xi} = \frac{c_i vN}{c_V K}\left(\sum_j \frac{c_j}{w_j} - \frac{1}{w_i}\right) + \frac{c_i c_V F}{kT} \qquad \text{(Eq 23a)}$$

$$\frac{dc_V}{d\xi} = \frac{vN}{K}\sum_j \frac{c_i}{w_i} - \frac{c_V(1 - c_V)F}{kT}, \quad i = A,B \qquad \text{(Eq 23b)}$$

where x represents a coordinate along the length of the moving sample. Equation 23 describes the steady-state composition profiles for cations and vacancies generally (i.e., with, in principle, either an oxygen potential gradient, an electric field operating, or both). Equation 23 is readily solved using standard numerical methods to provide the steady-state atom (and vacancy) composition profiles themselves across the sample.

7. Conclusions

In this overview, the authors have discussed the sum rule for diffusion via vacancies in the random-alloy model and have considered several applications of the sum rule to collective diffusion problems. These applications included intrinsic diffusion in a multicomponent alloy, chemical diffusion in strongly ionic mixed cation crystals, and demixing in an oxygen potential gradient and/or electric field of cations in mixed oxides. In each case, a substantial simplification was possible as a result of the sum rule.

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