Appendix B

Cation Diffusion Kinetics in Ionic Solids

B.1 Thermodynamic Treatment

The description of Sections 2.5 and 2.6 is applied to the ternary solid solution (A,B)O in which cations A and B have the same valence. The anion sublattice is treated as immobile, and provides a solvent-fixed reference frame. For a p-type oxide, the species fluxes to be considered are those of the two cations, vacancies and positive holes. Because sites and charge are conserved,

$$J_A + J_B + J_V = 0 = J_O \qquad \text{[B1]}$$

$$2J_V = J_h \qquad \text{[B2]}$$

the fluxes are clearly not independent.

The entropy source expression

$$T\dot{s} = -\sum_{i=1}^{n} J_i \nabla \eta_i \qquad \text{[2.98]}$$

leads to

$$-T\dot{s} = J_{A_M}\nabla\eta(A_M) + J_{B_M}\nabla\eta(B_M) + J_V\nabla\eta(V) + J_h\nabla\eta(h) + J_{O_O}\nabla\eta(O_O) \qquad \text{[B3]}$$

For clarity, the charges have been omitted from the point defect symbols. Application to Eq. [B3] of the constraints Eq. [B1], Eq. [B2] leads immediately to

$$-T\dot{s} = J_{A_M}\nabla\{\eta(A_M) - \eta(V) - 2\eta(h)\} + J_{B_M}\nabla\{\eta(B_M) - \eta(V) - 2\eta(h)\} \qquad \text{[B4]}$$

thereby identifying a set of relative building units (Section 3.4) whose potential gradients define the driving forces in a reduced set of flux equations

$$J_A = -L_{11}\nabla\{\eta(A_M) - \eta(V) - 2\eta(h)\} - L_{12}\nabla\{\eta(B_M) - \eta(V) - 2\eta(h)\}$$

$$J_B = -L_{21}\nabla\{\eta(A_M) - \eta(V) - 2\eta(h)\} - L_{22}\nabla\{\eta(B_M) - \eta(V) - 2\eta(h)\}$$

$$\text{[B5]}$$

The defect reaction equilibria

$$A_{(g)} + V''_M + 2h^. = A^X_M \tag{3.28}$$

$$B_{(g)} + V''_M + 2h^. = B^X_M \tag{3.29}$$

then allow simplification of Eq. [B5] to

$$J_A = -L_{11}\nabla\mu_A - L_{12}\nabla\mu_B \tag{B6}$$

$$J_B = -L_{21}\nabla\mu_A - L_{22}\nabla\mu_B \tag{B7}$$

Evaluation of the kinetic coefficients from absolute rate theory (Section 2.6) is now considered.

B.2 Evaluation of Onsager Coefficients

B.2.1 No Oxygen Potential Gradient

Consider first the simple system in which no free carriers exist and consequently no net flux of vacancies is possible. Interchanges between nearest neighbours only are considered, and it is sufficient to examine two adjacent lattice planes normal to the diffusion direction, as shown in Fig. B1. The site interchange mechanism automatically obeys the site conservation restraint. However, each interchange involves the movement of a vacancy and must be balanced by a countercurrent vacancy movement. Because vacancy concentrations are low, the immediate return of the first vacancy to its former plane is the most likely mechanism. To contribute to diffusion, such a mechanism must involve the two different cation species. The simplest microscopic mechanism which can fulfil these requirements is seen in Fig. B1 to involve two successive steps.
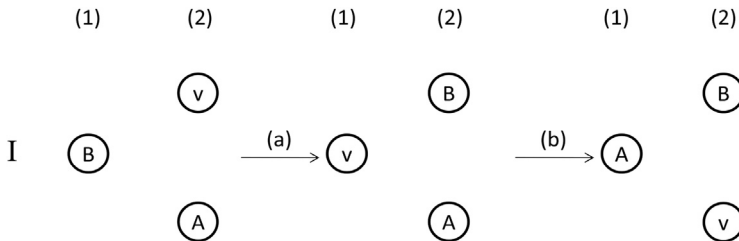

FIGURE B1 Site exchange model for diffusion in ternary oxide (A,B)O with fixed anion lattice. Vacancy indicated as V.

The net species flux from plane (1) to plane (2) in step (a) is found from Eq. [2.110] to be

$$J^{(a)} = -\frac{m\lambda^2}{RT} \nu_{Bv} K_{Bv} a_B a_v \{\nabla\eta_B - \nabla\eta_v\} \qquad [B8]$$

Similarly, it is found that

$$J^{(b)} = -\frac{m\lambda^2}{RT} \nu_{Av} K_{Av} a_A a_v \{\nabla\eta_A - \nabla\eta_v\} \qquad [B9]$$

In addition, one can formulate an expression for the species flux as a single-step correlated transition from the initial to the final state of the mechanism, using an activated complex at equilibrium with each of these two states. Then for species B

$$J_2 = -m\lambda\nu_1 K_1 \left\{ a_B^{(1)} a_v^{(2)} a_A^{(2)} - a_A^{(1)} a_B^{(2)} a_v^{(2)} \right\} \qquad [B10]$$

which after Taylor series expansion and retention of linear terms becomes

$$J_2 = -\frac{m\lambda^2}{RT} \nu_I K_I a_A a_B a_v \{\nabla\eta_A - \nabla\eta_B\} \qquad [B11]$$

The quantity ν_I is found from the steady-state condition

$$J_2 = J^{(a)} = J^{(b)} \qquad [B12]$$

to be

$$\nu_I = \left\{ \frac{K_I a_A}{\nu_{Bv} K_{Bv}} + \frac{K_1 a_B}{\nu_{Av} K_{Av}} \right\}^{-1} \qquad [B13]$$

This expression is simplified by introducing the new variables, m_i', which for Henrian solutions are strictly proportional to the species concentration,

$$m_i' = a_i \nu_{iv} K_{iv} \qquad [B14]$$

Then Eq. [B13] becomes

$$\nu_I = \frac{\nu_{Av} \nu_{Bv}}{m_A' + m_B'} \qquad [B15]$$

Substitution of Eq. [B15] together with the relationship

$$K_I = K_{Av} K_{Bv} \qquad [B16]$$

into Eq. [B11] yields

$$J_2 = \frac{m\lambda^2}{RT} \frac{m_A' m_B'}{m_A' + m_B'} a_v \{\nabla\mu_A - \nabla\mu_B\} \qquad [B17]$$

In the absence of free carriers, Eq. [B1] and Eq. [B2] imply that $J_A = -J_B$, and the system is essentially a binary. Thus Eq. [B6] and Eq. [B7] reduce to

$$J_B = -L_{11}\{\nabla\mu_B - \nabla\mu_A\} \tag{B18}$$

Comparison of Eq. [B17] with Eq. [B18] yields

$$L_{11} = \frac{m\lambda^2}{RT} \frac{m'_A m'_B}{m'_A + m'_B} a_v \tag{B19}$$

Extension of this description to multicomponent systems is straightforward [1] and leads for a quaternary oxide (A,B,C)O to the result

$$J_2 = -(\phi_{AB} + \phi_{BC})\{\nabla\mu_B - \nabla\mu_A\} + \phi_{BC}\{\nabla\mu_C - \nabla\mu_A\} \tag{B20}$$

$$J_3 = \phi_{BC}\{\nabla\mu_B - \nabla\mu_A\} - (\phi_{AC} + \phi_{BC})\{\nabla\mu_C - \nabla\mu_A\} \tag{B21}$$

where

$$\phi_{ij} = \frac{m\lambda^2}{RT} \frac{m'_i m'_j}{m'_i + m'_j} a_v \tag{B22}$$

Thus

$$L_{22} = \phi_{AB} + \phi_{BC}$$

$$L_{23} = L_{32} = -\varphi_{BC} \tag{B23}$$

$$L_{33} = \phi_{AC} + \phi_{BC}$$

and the Onsager reciprocal relationships are explicit.

The above treatment is applicable to a diffusion experiment conducted at uniform oxygen activity. Even when positive holes are present, their concentration and that of the cation vacancies are uniform as a result of the equilibrium:

$$O_O^X + V''_M + 2h^{\cdot} = \frac{1}{2}O_{2(g)} \tag{3.30}$$
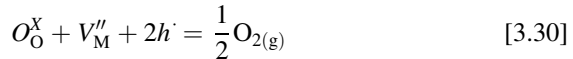
We now consider the oxide scaling process, where an oxygen potential gradient exists, and both vacancies and positive holes will move.

B.2.2 Oxygen Potential Gradient

Consider first a binary metal deficit oxide $M_{1-\delta}O$ containing divalent cation vacancies and positive holes as the only defects. An immobile anion sublattice is again taken to provide a solvent-fixed reference frame, and we examine only the cation sublattice in the microscopic kinetic model shown in Fig. B2.
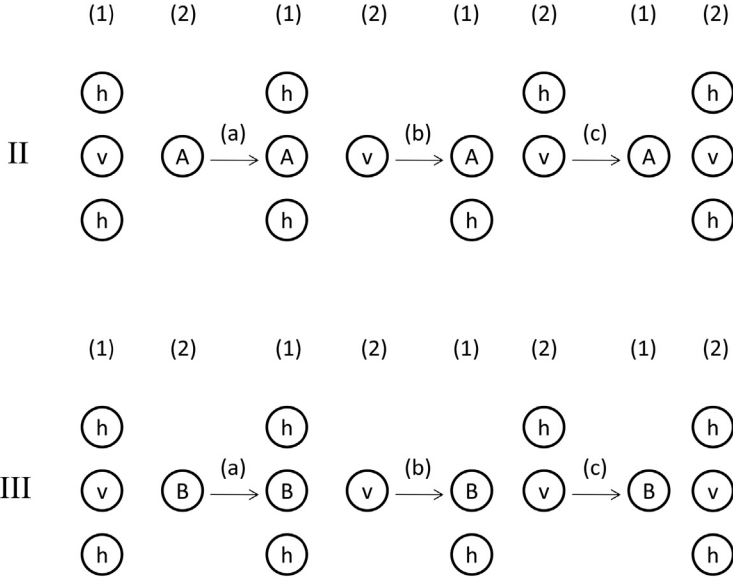
FIGURE B2   Site exchange models for diffusion of doubly charged vacancies and positive holes.

Mechanism II is seen to obey both the zero net current constraint and the local charge neutrality condition through the correlated motion of matching numbers of vacancies and positive holes.

Using the same procedures as above, we find the component fluxes due to this mechanism to be

$$J_V^{II} = \omega_A\{\nabla\mu_A - 2\nabla\mu_h - \nabla\mu_V\} \qquad [B24]$$

$$J_A^{II} = \frac{1}{2}J_h^{II} = -J_V^{II} \qquad [B25]$$

where

$$\omega_1 = \frac{m\lambda^2}{RT}\frac{m_A' m_h'}{m_h' + 2m_A' a_V} \qquad [B26]$$

and

$$m_h' = a_h v_h K_h \qquad [B27]$$

and the relations

$$\mu_A = \eta_A, \quad \mu_V + 2\mu_h = \eta_V + 2\eta_h$$

have been employed. Comparison reveals that

$$L_{11} = \omega_A \qquad [B28]$$

in this binary system.

This description is extended to a ternary metal deficit oxide $(A,B)_{1-\delta}O$ in which cation vacancies and positive holes are the only defects. A microscopic kinetic model for the motion of the second cation is shown as mechanism III in Fig. B2. By analogy with Eq. [B24],

$$J_V^{III} = \omega_B\{\nabla\mu_B - 2\nabla\mu_h - \nabla\mu_V\} \qquad [B29]$$

$$J_B^{III} = -\frac{1}{2}J_h^{III} = -J_V^{III} \quad J_A^{III} = 0 \qquad [B30]$$

It is clear that mechanisms II and III produce no cross-effect between the cations. Nonetheless such an effect arises through the operation of mechanism I, which is also available to this oxide. Summation of component fluxes due to the operation of all three mechanisms leads to

$$J_A = -\omega_A\{\nabla\mu_A - \nabla\mu_V - 2\nabla\mu_h\} - \phi_{AB}\{\nabla\mu_A - \nabla\mu_B\} \qquad [B31]$$

$$J_B = -\omega_B\{\nabla\mu_B - 2\nabla\mu_h - \nabla\mu_V\} - \phi_{AB}\{\nabla\mu_B - \nabla\mu_A\} \qquad [B32]$$

which can be rearranged to yield

$$J_A = -(\omega_A + \phi_{AB})\{\nabla\mu_A - \nabla\mu_V - 2\nabla\mu_h\} + \phi_{AB}\{\nabla\mu_B - \nabla\mu_V - 2\nabla\mu_h\} \qquad [B33]$$

$$J_B = \phi_{AB}\{\nabla\mu_A - \nabla\mu_V - 2\nabla\mu_h\} - (\omega_B + \phi_{AB})\{\nabla\mu_B - \nabla\mu_V - 2\nabla\mu_h\} \qquad [B34]$$

These are of the form of the phenomonological Eq. [B5], and Onsager reciprocity is seen to be explicit. The correlation between cation fluxes is seen to arise through site conservation, whereas the correlation between the net total cation flux and positive hole flux is due to electrostatic coupling.

B.2.3 Chemical and Tracer Diffusion in Ionic Solids

The relationship between diffusion in a multicomponent solid and tracer diffusion in pure binary oxides is sought. The situation of counterdiffusing cations associated with an immobile sublattice is examined.

A tracer diffusion experiment involves interchange of labelled and unlabelled cations in the absence of any oxygen potential gradient. No vacancy flux is generated, and

$$J_{A^*} = -L\nabla(\mu_{A^*} - \mu_A) \qquad [B35]$$

where * denotes the tracer species. The coefficient is evaluated from Eq. [B19], yielding

$$J_{A^*} = -\frac{m\lambda^2}{RT} \frac{m'_A m'_{A^*}}{m'_A + m'_{A^*}} a_v \nabla(\mu_{A^*} - \mu_A) \qquad [B36]$$

A tracer is an ideal solute, and Eq. [B36] is rewritten as

$$J_{A^*} = -\frac{m\lambda^2}{RT} \frac{m'_A m'_{A^*}}{m'_A + m'_{A^*}} a_v \frac{m_A + m_{A^*}}{m_A m_{A^*}} \nabla m_{A^*} \qquad [B37]$$

with m_i the molar concentration of the indicated component. Recalling the definition of m'_i in Eq. [B14], and setting

$$\nu_{AV} K_{AV} = \nu_{A^*V} K_{A^*V}$$

we find from Eq. [B37] that

$$D_{A^*} = \lambda^2 \nu_{AV} K_{AV} a_V \qquad [B38]$$

and a corresponding expression is found for D_{B^*}.

For interdiffusion of two different cations A and B, we use Eq. [B17] to evaluate the flux. Since the cations are of equal valence, $\nabla m_A = -\nabla m_B$ and, for an ideal or Henrian solution (Section 2.3), Eq. [B17] becomes

$$J_A = -\frac{m\lambda^2}{RT} \frac{m'_A m'_B}{m'_A + m'_B} a_v \frac{m_A + m_B}{m_A m_B} \nabla m_A \qquad [B39]$$

Substituting for m'_i from Eq. [B14] and for D_{i^*} from Eq. [B38] we obtain

$$J_A = -\frac{D_{A^*} D_{B^*}}{m_A D_{A^*} + m_B D_{B^*}} (m_A + m_B) \nabla m_A \qquad [B40]$$

whence

$$\widetilde{D} = -\frac{D_{A^*} D_{B^*}}{m_A D_{A^*} + m_B D_{B^*}} (m_A + m_B) \qquad [B41]$$

This description can be extended to quaternary oxides (A,B,C)O [1]. It should be noted that the assumption of Henrian solution behaviour can be in serious error.

An analogous relationship (Eq. [2.135]) was found for binary alloys to result from the differing intrinsic metal mobilities, which led to compensating bulk material flow. No such flow is possible in ionic solids if, as supposed, the anion sublattice is truly immobile. It is instead the electrostatic potential or field (developed by charge separation within the solid) that brings into balance the fluxes of charged species having different mobilities.

REFERENCE

[1]   J.S. Kirkaldy, D.J. Young, Diffusion in the Condensed State, Institute of Metals, London, 1987.