Appendix: Reduction of the transport equations from the structure element level to the charged component level

Here we will show, by assuming a simple defect structure, but without sacrificing any generality, how the transport equations on the structure element level are to be reduced to those on the charged component level, Eq. (1), in due thermodynamic course.

Suppose that we know \textit{a priori} the defect structure of a mixed conducting oxide, say, AO\textsubscript{1-\delta}, as comprising oxygen vacancies with every possible effective charges and electrons. The mobile structure elements (SE) may then be listed in the Kroger-Vink notation as:

\[ \text{O}\textsubscript{O}^x, \text{V}\textsubscript{O}^x, \text{V}\textsubscript{O}^\beta, \text{V}\textsubscript{O}^\gamma, \text{e}\textsubscript{C}, \text{h}\textsubscript{C}^x \]  

(A.1)

where particularly \text{e}\textsubscript{C} stands for electrons in the conduction band (C) and \text{h}\textsubscript{C} for holes in C, the electronic regular SE corresponding to the ionic regular SE, \text{O}\textsubscript{O}^x. These SEs will be henceforth labelled as k=1,2,...,6 in order.

Irreversible thermodynamics stipulates that the energy dissipation (T\sigma) due to entropy generation (\sigma) at a temperature (T) be written as

\[ T\sigma = \sum_{k=1}^{6} j_k X_k \]  

(A.2)

where \( j_k \) and \( X_k \) denote the flux and thermodynamic force (=-\nabla \eta_k) of SE k, respectively. Letting \( I_{km} \) denote the coupling transport coefficient on the SE-level,

\[ j_k = \sum_{m=1}^{6} I_{km} X_m \]  

(A.3)

in the linear regime, suggesting that a SE k can be driven to flow by any thermodynamic force \( X_m \). It is noted that there are 36 -coefficients, which are subjected to redundancies due to the constraints upon the SE-fluxes \( j_k \) and local quasi-chemical equilibria.

Firstly, they are

\[ \sum_{k=1}^{4} j_k = 0 \; ; \; \sum_{k=5}^{6} j_k = 0 \]  

(A.4)

as the numbers of lattice sites and electronic energy states should be both conserved (structure condition). For these to be always true for arbitrary \( X_m \) (m=1,2,...,6),

\[ \sum_{k=1}^{4} I_{km} = 0 \; ; \; \sum_{k=5}^{6} I_{km} = 0 \]  

(m=1-6)  

(A.5)

Secondly, substitution of Eq. (A5) into Eq. (A3) leads to
\[ \mathbf{j}_k = \sum_{m=1}^{3} l_{km} (X_m - X_4) + l_{k5} (X_5 - X_6). \]  

(A.6)

This means that for \( X_m = X_4 \) (m=1,2,3) and \( X_5 = X_6 \), \( j_k = 0 \) (k=1-6). For this to be always true,

\[ \sum_{m=1}^{4} l_{km} = 0 \quad ; \quad \sum_{m=5}^{6} l_{km} = 0 \quad (k=1-6) \]  

(A.7)

It now turns out that the 36 \( l \)-coefficients in Eq. (A.3) are subjected to 12 inter-relationships, Eq. (A.4) and another 12, Eq. (A.7). These 24, however, are not independent of each other at all: As the summations over \( m \) of Eq. (A.4) and them over \( k \) of Eq. (A.7) are the same, 4 out of these 24 are rendered redundant, and hence, only 16 out of 36 survive. As these 16 are for the 4 independent fluxes, they are further to satisfy the Onsager reciprocity [1,2,4] or

\[ \sum_{m=1}^{6} \sum_{k=1}^{m} m \mathbf{l}_{km} = 0, \]  

(A.8)

Subsequently, we will choose the fluxes of \( k=1,2,3 \) and 5 as independent ones only for the sake of convenience.

The thermodynamic forces are also reduced to those of mobile charged components, \( O^2^- (=i) \) and \( e^- (=e) \) or holes \( h^+ (=h) \) via internal quasi-chemical equilibria:

\[ \begin{align*} 
O^x_o - V^g_o f^O^2^- : X_i - X_4 = X_i \\
e^- _c - h^x _c f^e^- : X_5 - X_8 = X_e = -X_h \\
V^g _o - V^g_o f^2e^- = -2h^+ : X_2 - X_4 = 2X_e = -2X_h \\
V^g _o - V^g_o f^e^- = -h^+ : X_3 - X_4 = X_e = -X_h 
\end{align*} \]  

(A.9)

By substituting Eq. (A.9) into Eq. (A.6), one obtains

\[ \mathbf{j}_k = l_{k1} X_i + \sum_{m=1}^{6} l_{km} \beta_m X_i \]  

(A.10)

where the number of electrons associated with \( SE_m \), \( \beta_m \) takes the numerical values:

\[ \beta_0; \beta_2; \beta_1 \quad 2 = 3 = 5 \]  

(A.11)

Eliminating the dependent fluxes \( j_4 \) and \( j_5 \) due to Eq. (A.4) and substituting Eq. (A.9) for \( X_m, X_4 \) (m=1,2,3) and \( X_5, X_6 \), Eq. (A.2) takes the form,

\[ \mathbf{T} a \mathbf{j} X_i + \sum_{k=1}^{6} j_k X_e + \sum_{k=1}^{6} j_k X_e = 0. \]  

(A.12)

One may, thus, read off from Eq. (A.12) the fluxes of the mobile charged components, ions \( O^2^- \), \( J_i \) and electrons \( e^- \), \( J_e \), corresponding to \( X_i \) and \( X_e \), respectively, as
\[ J = j_i, \quad j_e = \sum_{k=1}^{6} j_k \beta_k \]  

(A.13)

By substituting Eq. (A.10) here, one finally obtains the thermodynamic equations of motion on the level of charged components \((O^{2-}, e^-)\), commensurate with Eq. (1) in the text,

\[
\begin{pmatrix}
J_i \\
J_e
\end{pmatrix} =
\begin{pmatrix}
L_{ii} & L_{ie} \\
L_{ei} & L_{ee}
\end{pmatrix}
\begin{pmatrix}
X_i \\
X_e
\end{pmatrix}
\]  

(A.14)

where the Onsager L-coefficients are each expressed in terms of \(I_{km}\) as:

\[
\begin{pmatrix}
L_{ii} & L_{ie} \\
L_{ei} & L_{ee}
\end{pmatrix} =
\begin{pmatrix}
I_{11} & \sum_{m=1}^{6} I_{1m} \beta_m \\
\sum_{k=1}^{6} \beta_k \beta_k & \sum_{k=1}^{6} \sum_{m=1}^{6} I_{km} \beta_k \beta_m
\end{pmatrix}
\]  

(A.15)

It is noted that Eq. (A.8) leads to the Onsager reciprocity on the charged component level, \(L_{ie} = L_{ei}\) and vice versa.

Let us finally examine the ionic charge-of-transport, \(\alpha_i^* = (\alpha_i / L_k)\). By replacing \(I_{1m}\) for the regular SE \(k=1\) with those for the irregular structure elements or defects by using Eqs. (A.5) and (A.7), one gets

\[
\alpha_i^* = \frac{L_{ie}}{L_{ii}} = \frac{-4}{\sum_{k=2}^{m=2} I_{km} \beta_k} \sum_{k=2}^{m=2} I_{km} \beta_k
\]  

(A.16)

If and only if there were no long-range interactions or \(I_{km} = 0\) for \(k \neq m\), Eq. (A.16) takes the form,

\[
\alpha_i^* = \frac{4}{\sum_{k=2}^{m=2} I_{kk}} \sum_{k=2}^{m=2} (-\beta_k) I_{kk}
\]  

(A.17)

Noting that \(I_{kk} \propto D_k C_k\), one can immediately recognize that Eq. (A.17) is nothing but Eq. (4) in the text. The ionic charge-of-transport \(\alpha_i^*\) would, thus, phenomenologically correspond to the kinetic average of the number of electrons(\(\beta_k\)) or holes(-\(\beta_k\)) associated with all kinds of ionic defects, were it not for long-range interactions among defects (i.e., \(I_{km} \neq 0\) for \(k \neq m\)).

\(^1\) Eq. (1) employs \(h^+\), instead of \(e^-\). One can easily transform \(J_e\) to \(J_h\) simply by taking \(J_e = -J_h\) \(X_e = X_h\) and \(-\beta_m\) as the number of holes associated with SE m.