**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 *a priori* the defect structure of a mixed conducting oxide, say, $AO_{1-\delta}$, 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:

$$O_O^x, \; V_O^x, \; V_O^g, \; V_O^{gg}; \; e_C', \; h_C^x \qquad\qquad (A.1)$$
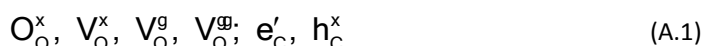
where particularly e_C' stands for electrons in the conduction band (C) and h_C^x for holes in C, the electronic regular SE corresponding to the ionic regular SE, O_O^x. These SEs will be henceforth labelled as k=1,2,…,6 in order.

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

$$T\sigma \neq \sum_{k=1}^{6} j_k X_k \qquad\qquad (A.2)$$

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

$$j_k = \sum_{m=1}^{6} l_{km} X_m . \qquad\qquad (A.3)$$

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 l-coefficients, which are subjected to redundancies due to the constraints upon the SE-fluxes j_k and local quasi-chemical equilibria.

Firstly, they are

$$\sum_{k=1}^{4} j_k \equiv 0 \; ; \; \sum_{k=5}^{6} j_k \equiv 0 \qquad\qquad (A.4)$$

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),

$$\sum_{k=1}^{4} l_{km} \equiv 0 \; ; \; \sum_{k=5}^{6} l_{km} \equiv 0 \quad \text{(m=1-6)} \qquad\qquad (A.5)$$

Secondly, substitution of Eq. (A5) into Eq. (A.3) leads to

$$j_k = \sum_{m=1}^{3} l_{km}\left(X_m - X_4\right) + l_{k5}\left(X_5 - X_6\right). \qquad (A.6)$$

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,

$$\sum_{m=1}^{4} l_{km} \equiv 0 \;;\; \sum_{m=5}^{6} l_{km} \equiv 0 \quad (k=1-6) \qquad (A.7)$$

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

$$l_{km} = l_{mk}. \qquad (A.8)$$

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:

$$O_O^x - V_O^{\bullet\bullet} \, f \quad O^{2-} : \quad X_1 - X_4 = X_i$$

$$e'_C - h_C^x \, f \quad e^- = -h^+ : \quad X_5 - X_6 = X_e = -X_h$$

$$V_O^x - V_O^{\bullet\bullet} \, f \quad 2e^- = -2h^+ : \quad X_2 - X_4 = 2X_e = -2X_h$$

$$V_O^{\bullet} - V_O^{\bullet\bullet} \, f \quad e^- = -h^+ : \quad X_3 - X_4 = X_e = -X_h \qquad (A.9)$$

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

$$j_k = l_{k1} X_i + \sum_{m=1}^{6} l_{km} \beta_m X_e \qquad (A.10)$$

where the number of electrons associated with SE m, β_m takes the numerical values:

$$\beta_1 = \beta_4 = \beta_6 = 0; \; \beta_2 = 2; \; \beta_3 = \beta_5 = 1 \qquad (A.11)$$

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,

$$T\sigma = \sum_{k=1}^{6} j_k X_k = j_i X_i + j_e X_e, \qquad (A.12)$$

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

$$J_i = j_1 \ ; \ J_e = \sum_{k=1}^{6} j_k \beta_k \qquad (A.13)$$

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[1],

$$\begin{pmatrix} J_i \\ J_e \end{pmatrix} = \begin{pmatrix} L_{ii} & L_{ie} \\ L_{ei} & L_{ee} \end{pmatrix} \begin{pmatrix} X_i \\ X_e \end{pmatrix} \qquad (A.14)$$

where the Onsager L-coefficients are each expressed in terms of l_{km} as:

$$\begin{pmatrix} L_{ii} & L_{ie} \\ L_{ei} & L_{ee} \end{pmatrix} = \begin{pmatrix} l_{11} & \sum_{m=1}^{6} l_{1m} \beta_m \\ \sum_{k=1}^{6} \beta_k l_{k1} & \sum_{k=1}^{6} \sum_{m=1}^{6} \beta_k l_{km} \beta_m \end{pmatrix} \qquad (A.15)$$

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, α_i^* ($=L_{ie}/L_{ii}$). By replacing l_{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

$$\alpha_i^* = \frac{L_{ie}}{L_{ii}} = \frac{-\sum_{k=2}^{4} \sum_{m=2}^{5} l_{km} \beta_m}{\sum_{k=2}^{4} \sum_{m=2}^{4} l_{km}} \qquad (A.16)$$

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

$$\alpha_i^* = \frac{\sum_{k=2}^{4} (-\beta_k) \, l_{kk}}{\sum_{k=2}^{4} l_{kk}} \qquad (A.17)$$

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

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[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.