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Comment on "How to interpret Onsager cross terms in mixed ionic electronic conductors" by I. Riess, *Phys. Chem. Chem. Phys.*, 2014, **16**, 22513

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Abstract

Here, we show that the Onsager cross terms for ion-electron interaction are not an artifact, but the necessity to phenomenologically completely describe the mass/charge transport of a mixed ionic-electronic conductor in terms of mobile charged components which are the only experimentally operable species. The use of an appropriate comprehensive defect model may help to reduce the cross terms (which depend on the choice of the formal charge of the mobile defects), but it cannot obviate them if long-range Coulombic interaction is in action among defects.

According to irreversible thermodynamics, [1-3] all the isothermal transport phenomena of a mixed ionic electronic conductor (MIEC), e.g., $A_{1-\delta}O_v$, having one of the ionic components, e.g., O^{2-} (=i) and holes h^+ (=h) as mobile charged components must be phenomenologically completely described as

$$\begin{pmatrix} J_i \\ J_h \end{pmatrix} = \begin{pmatrix} L_{ii} & L_{ih} \\ L_{hi} & L_{hh} \end{pmatrix} \begin{pmatrix} -\nabla \eta_i \\ -\nabla \eta_h \end{pmatrix} \quad (1)$$

where J_k and η_k denote the flux and electrochemical potential of the mobile charged component k (= i, h), respectively. Here, the coupling coefficient matrix L is symmetric, due to Onsager [4], or

$$L_{ih} = L_{hi} \quad (2)$$

Authors [5,6] often define the ionic charge-of-transport, α_i^* as

$$\alpha_i^* \equiv \left(\frac{J_h}{J_i} \right)_{\nabla \eta_h = 0} \equiv \frac{L_{hi}}{L_{ii}} \quad (3)$$

which phenomenologically corresponds to the number of holes (or electrons) dragged by an anion (or cation) upon its transfer in the absence of their own driving force ($\nabla \eta_h = 0$). The transport coefficients, and thus also the charge-of-transport, depend on the choice of the formal charge number z_i of the mobile ions, but their measurable effective charge number $z_i + \alpha_i^*$ is invariant [6]. In any description of transport in mixed conductors $A_{1-\delta}O_v$, the formal charge of the ionic species is usually chosen on the basis of chemical intuition and experience. In the case of oxygen ions typically the formal charge number $z_i = -2$ is chosen. Due to interaction with other mobile species the effective charge may differ, which is then properly taken into account by the Onsager cross terms.

Recently, Chatzichrostodoulou et al. [7] have measured all the L-coefficients on the system of $Ce_{0.8}Pr_{0.2}O_{2-\delta}$ at 800°C by the semi-blocking method which was first proposed by Wagner [3] and first implemented experimentally by Miyatani [8]. Using the formal charge numbers $z_i = -2$ for oxygen ions and $z_h = +1$ for holes, they have found that α_i^* decreases from a value close to +1 to near 0 as the oxygen activity decreases from $\log a_{O_2} = 0.0$ to -2.5.

In a recent paper, Riess [9] discusses the Onsager cross terms and concludes implicitly that the dependence of the cross terms on the choice of the formal charge number makes the cross terms an "artifact". Obviously, this conclusion is incorrect, and in the following we clarify the meaning of the cross terms.

On the work by Chatzichrostodoulou [7] "*and references cited therein*":

1) Riess [9] first claims that "... in most cases $L_{ih} = 0$."

This statement could be misleading. Up until now, the attempt to measure L_{ih} has been made only on nine or so limited number of systems and the general conclusion is that $L_{ih} \neq 0$ the magnitude of which depends on the thermodynamic state of the system, see Refs. [3,8,10-18]. Even though the mobile ionic defects are fully ionized, $L_{ih} \neq 0$ if there are long-range inter-defect interactions, see below and Appendix. A correct statement would rather be that L_{ih} can become small by

mathematical transformation if short range interactions (association) lead to an ionic defect with smaller charge number, e.g., the formation of V_O^{\square} by association of V_O^{\square} and e' , and if this is the majority defect. If the concentrations of V_O^{\square} and V_O^{\square} are comparable, the cross term becomes appreciable in order to account for the deviation of the effective charge from the integer formal charge, see Eq. (4) below.

2) Riess [9] claims that "... **no explanation for a mutual effect** [$L_{ih} \neq 0$]... **Indeed there is none.**"

This claim ignores all of the earlier works on this subject. It is Wagner [3] who first set up the thermodynamic equations of motion for an MIEC in terms of the mobile charged components, Eq. (1), first proposed the experiments to determine the L-coefficients, and first considered the physicochemical origin of the mutual effect. He says that "*appropriate models of lattice defects are considered in order to see under which condition the cross coefficients may be ignored or yield significant contributions.*" And he clearly points out that the "*finite cross coefficients are due to coupling of transport processes*" not only in short range (i.e., defect association), but also in long range. For example, as a transfer of V_O^{\bullet} corresponds to a coupled transfer of $V_O^{\bullet\bullet}$ and e' , one would have $\alpha_1^* = 1$ if V_O^{\bullet} and e' were in the majority. Otherwise, one would have to consider the "*long-range energetic interaction among charged defects according to Coulomb's law*" which "*results in a coupling of the motions of the individual defects due to Debye, Hückel, Onsager and Fuoss for aqueous solutions.*"

Later on, Yoo et al. [6] showed that the cross coefficients include the contributions of any possible defect "d" (structure elements) with different effective charges: In the absence of long-range interaction, one has a non-vanishing charge-of-transport,

$$\alpha_1^* = \frac{\sum_d \beta_d D_d c_d}{\sum_d D_d c_d} \quad (4)$$

if defects with variable charges (due to association) are formed. Here, β_d , D_d and c_d stand for the number of electrons (holes) associated with, self diffusivity of, and concentration of the defect "d", respectively. The validity of Eq. (4) was then checked to reveal that the cross coefficient is not totally due to short-range interaction or inter-defect association, but that long range interaction adds up to the short term interaction. [6,19]

In order to rationalize the influence of long range interaction, Janek et al. [20,21] subsequently applied the Debye-Hückel-Onsager-Fuoss theory [22,23] to solid-state MIECs. The major conclusion is that α_1^* corresponds to the number of holes or electrons in the electronic charge cloud surrounding the central ionic defect. This may be written for the system of e.g., $\{V_0^{\bullet\bullet}, e'\}$ (as in $\text{CeO}_{2-\delta}$) or $\{V_{\text{Co}}^{\bullet\bullet}, h^\bullet\}$ (as in $\text{Co}_{1-\delta}\text{O}$) as

$$\alpha_1^* = \frac{e_o^2(1 - 1/\sqrt{3})}{6\pi\epsilon_0\epsilon_r kT} \cdot \frac{1}{\kappa^{-1} + a} \quad (5)$$

where $\epsilon_0\epsilon_r$ is the dielectric constant of the system, κ^{-1} the Debye length, "a" the distance of the closest approach between an ionic defect and an electron or hole, and the others have their usual meaning. The theory has also been extended to systems with more than two defects, e.g. $\{V_0^{\bullet\bullet}, V_0^\bullet, e'\}$ [20]. It has later been found that Eq. (5) explains the results more convincingly than Eq. (4) for $\text{Co}_{1-\delta}\text{O}$ [24] and $\text{TiO}_{2-\delta}$ [25].

The present status of understanding is, thus, evenhandedly that the non-vanishing cross effect is partly due to short-range interaction, Eq. (4) and partly due to the long-range interaction, Eq. (5), but the latter takes precedence with increasing defect concentrations.[3] (Of course, $\lim_{c_d \rightarrow 0} \alpha_1^* = 0$ because then electronic-ionic defect association renders negligible and $\kappa^{-1} \rightarrow \infty$ as well.) In this light, Riess's claim [9] is incorrect and also misleading. We like to add that, for materials with high defect concentrations, even the distinction of short- and long-range interaction becomes arbitrary and the more important becomes the consideration of the phenomenological cross terms. It is required to get a complete description of charge transport.

3) Riess [9] subsequently states, "It turns out that the appearance of finite cross terms and the ability to measure them are due to an incomplete description of the system at hand." For the system of e.g., $\text{Ce}_{0.8}\text{Pr}_{0.2}\text{O}_{2-\delta}$ for which the ionic defects are *known* to be $V_0^{\bullet\bullet}$ and V_0^\bullet in addition to electrons or holes, **"if only two,"** say, $V_0^{\bullet\bullet}$ and electrons (or holes), **"are considered"** as charge carriers, **"the missing information manifests itself as cross terms (L_{ih}) in the theory and leads to misinterpretation of the measurement."**

This is a typical misunderstanding arising when one does not properly take into account the detailed interrelationship between the description on the charged component or building-unit level, Eq. (1), and that on the defect or structure-element level. When the fluxes and forces of all possible structure elements including regular and irregular ones are reduced, in due

thermodynamic course, to the independent ones, one eventually ends up with Eq. (1) on the charged component level, see Appendix. All the defect-level information is, thus, condensed into the three independent, measurable coefficients L_{ii} , $L_{ih}(=L_{hi})$ and L_{hh} , with no information missing, see Refs. [3] and [6]. We like to note that a comprehensive analysis of transport coefficients, emphasizing the description of systems with irregular SE or defects of variable charges, however neglecting long range interaction, has also been provided by Maier [27,28].

It has to be emphasized that the interrelationships between a measurable transport property and the L-coefficients are irrespective of the choice of mobile charged components, e.g., $\{O^{\cdot-}, h^+\}$ instead of $\{O^{2-}, h^+\}$. In particular, the effective charge number of mobile ions, $z_i^* = z_i + \alpha_i^*$, is invariant, in contrast to z_i and α_i^* [6,19]. It is because the entropy creation or energy dissipation rate should remain invariant, and hence, the L-coefficients are only to be transformed in accord with this invariance. [1,2,19]. In more practical terms: Indeed one can choose the formal charge number of ions such that short range order is anticipated and that the cross terms become smaller, but they will still include long range interaction, which, of course, can be small for dilute defect concentrations.

It is further emphasized that what can be experimentally observed or measured is the transport of the charged components, never of the structure elements themselves. It is because our system can interact electrochemically with the surrounding only by exchanging charged components or building units (e.g., $O^{2-} = O_o^{\times} - V_o^{\square}$): Our system can never communicate by exchanging defects or structure elements themselves (e.g., V_o^{\square}) due to the structure condition of the system. [3,26]. Therefore, the cross coefficients are a physical necessity and reality as well on the level of the charged components, not an artifact arising from a deficient choice of defect carriers.

4) Riess [9] finally consummates his argument by saying, "When an appropriate, comprehensive defect model is considered for the MIEC, no cross terms are required."

It is an inherent problem with the defect chemistry and formal description of MIECs that one never knows *a priori* the "appropriate, comprehensive defect model" for a system under study without observing the related phenomena on the charged component level. Thus, this consummation is just in vain or of no practical significance.

Furthermore, even if such a model were at hand, the cross terms are still required as long as there is long-range interaction among defects as described by Eq. (5), see Appendix. They are actually unavoidable particularly as defect concentrations increase typically over 10^{-4} in mole fractions.[3]

Thus, the author's statement [9] is incorrect.

It may help the author [9] understand the situation better to read Wagner [3]: If α_i^* is known with sufficient precision, then *"one obtains additional information for a discussion of the merits of different models of defects to be used in conjunction with other experimental data..."*

In conclusion, Riess's interpretation [9] of the Onsager cross terms is essentially based on the independent migration of differently charged ionic defects and electrons or holes, eventually leading to Eq. (4). This interpretation is nothing new because it has already been fully explored as well as not totally right because of the unavoidable long-range interaction among charged defects leading to Eq. (5). The careless notion of the cross coefficients as "artifacts" is physically incorrect and will mislead the uninformed reader.

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