Commentary

Comments on "The Seebeck coefficient and the Peltier effect in a polymer electrolyte membrane cell with two hydrogen electrodes" by S. Kjelstrup, P.J.S. Vie, L. Akyalcin, P. Zefeniya, J.G. Pharoah, O.S. Burnheim [Electrochim. Acta 99 (2013) 166]

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Kjelstrup et al. recently applied non-equilibrium thermodynamics to analyze the thermodynamic relationships for thermo-electrochemical effects in certain electrochemical cells [Electrochim. Acta 99 (2013) 166–175]. The present paper considers whether one can extend such relationships to establish equivalence between certain non-equilibrium thermodynamic properties, such as transported entropies, and equilibrium thermodynamic properties, such as partial molar entropies. If so it would enable the use of thermo-electrochemical measurements to determine certain quantities that have heretofore been considered "un-measurable", such as partial molar entropies of ions in solution. It would also provide a unifying principle between non-equilibrium thermodynamics and reversible thermodynamics, and it could lead one to consider the possibility of an additional law or principle of thermodynamics.

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1. Introduction

Kjelstrup et al. recently published a paper in this journal on thermo-electrochemical effects, focusing on the Peltier effect and the Seebeck coefficient in a polymer electrolyte fuel cell [1]. The authors applied the methods of non-equilibrium thermodynamics to determine thermodynamic relationships for the process

$$\frac{1}{2}\text{H}_2 \rightarrow \text{H}^+ + \text{e}^- \tag{1}$$

where for the time being, I have omitted phase-specifying subscripts from the symbols for the reactant and two products. From non-equilibrium thermodynamic theory they derived expressions that included quantities such as S_{H_2}, $S_{\text{H}^+}^*$, and $S_{\text{e}^-}^*$, where the * superscript on certain quantities specifies that they are "transported entropies" which are not necessarily considered to be equilibrium thermodynamic quantities.

In this comment I propose to extend the thermodynamic analysis of thermo-electrochemical processes one step further, i.e. to consider a possible relationship between transported entropies, which are quantities from non-equilibrium thermodynamics, and partial molar entropies, which are quantities from equilibrium thermodynamics.

2. Theoretical development

Consider the process of transferring electrons between two homogeneous isotropic conductors A and B.

$$\text{e}_A^- \rightarrow \text{e}_B^- \tag{2}$$

If carried out slowly under isothermal conditions the reaction is reversible, and the entropy of the process is therefore related to the heat of reaction according to the following expression

$$\Delta S = \frac{Q_{\text{rev}}}{T} \tag{3}$$

From fundamental chemical thermodynamics the entropy of transfer of a component from one phase to another equals to the difference in partial molar entropies, which for the transfer of electrons between two conductors is

$$\Delta S = S_{\text{e}^-,B} - S_{\text{e}^-,A} \tag{4}$$

where $S_{\text{e}^-,B}$ and $S_{\text{e}^-,A}$ are the partial molar entropies of the electron in phases B and A, respectively.

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The heat of the same process is also given by the following thermoelectric relationships

$$Q_{rev} = F\Pi_A - F\Pi_B = FT\sigma_A - FT\sigma_B = TS^*_{e-,B} - TS^*_{e-,A} \tag{5}$$

where F is Faraday's constant, Π_A and Π_B are the Peltier coefficients for phases A and B, respectively, σ_A and σ_B are the absolute Seebeck coefficients for phases A and B, respectively, and $S^*_{e-,A}$ and $S^*_{e-,B}$ are the transported entropies for electrons in phases A and B, respectively. The quantities σ and S^*_{e-} are essentially equivalent, other than a difference of sign and a multiplication of σ by Faraday's constant. The asterisk in the notation is used to distinguish transported entropies from partial molar entropies. The symbol σ is used in this paper to denote the absolute Seebeck coefficient rather than the more customary symbol S to avoid confusing it with the symbol for partial molar entropies. The absolute Seebeck coefficient is also known as the absolute thermoelectric power.

Calculating the entropy of the process from the reversible heat given in Eq. (5) we have

$$\Delta S = \frac{Q_{rev}}{T} = \frac{F\Pi_A}{T} - \frac{F\Pi_B}{T} = F\sigma_A - F\sigma_B = S^*_{e-,B} - S^*_{e-,A} \tag{6}$$

Equating the entropy in Eqs. (4) and (6), one obtains the following relationship between partial molar entropies and absolute Seebeck coefficients for electrons in any two arbitrarily chosen conductors.

$$S_{e-,B} - S_{e-,A} = F\sigma_A - F\sigma_B \tag{7}$$

For this equation to hold for all possible pairs of conductors one must necessarily conclude that

$$S = -F\sigma + G(T) \tag{8}$$

where the subscripts have been removed from symbols S and σ to indicate that the relationship holds for electrons in all conductors. The function $G(T)$ may depend on the temperature but not on the material. It is therefore a universal function, so evaluating $G(T)$ for even a single case would establish it for all cases. Eq. (8) was obtained previously, and its validity depends only on the macroscopic laws of reversible and irreversible thermodynamics [2,3].

If one could evaluate $G(T)$ it would provide a way to evaluate the partial molar entropy of electrons in conductors. Unfortunately, one cannot evaluate $G(T)$ using the known laws of macroscopic thermodynamics. However, it might be possible to evaluate $G(T)$ by stepping outside of the laws of thermodynamics and applying other methods. Here, I will apply microscopic theory to the problem.

In the spirit of this approach, consider the statistical thermodynamics of the degenerate free electron Fermi gas. By a rearrangement of Eqs. (8.2.1) and (8.2.3) from [4] the electrochemical potential is given by

$$\varepsilon_f = C_1 n^{2/3} - \frac{C_2 T^2}{2n^{2/3}} + \cdots \tag{9}$$

where n is the electron number density, and factors C_1 and C_2 depend on some physical and numerical constants. In using this expression one must keep in mind that the electrochemical potential, the Fermi level (εf), and the partial molar Gibbs free energy are synonymous for an ensemble of Fermions. The partial molar entropy is given by the well-known relationship between partial molar entropy and the temperature coefficient of partial molar Gibbs free energy.

$$S = -\frac{\partial \varepsilon_f}{\partial T} = \frac{C_2 T}{n^{2/3}} \tag{10}$$

Only the lowest-order non-zero term is retained in Eq. (10).

Turning to the absolute thermoelectric power of the same model system, using Eqs. (8.2.1), (8.2.3), (8.7.17), (8.7.18), and (8.7.19)

from [4] one obtains, after rearrangement, expansion in a Taylor series, and truncation to the lowest-order term:

$$\sigma = -\frac{C_3 T}{n^{2/3}} \tag{11}$$

where C_3 depends on some physical and numerical constants and assumptions related to collisional relaxation of electrons in the solid.

Combining Eqs. (8), (10) and (11) yields

$$\frac{C_2 T}{n^{2/3}} = F\frac{C_3 T}{n^{2/3}} + G(T) \tag{12}$$

Taking the limit as number density approaches infinity

$$\lim_{n \to \infty} \frac{C_2 T}{n^{2/3}} = 0 = \lim_{n \to \infty} F\frac{C_3 T}{n^{2/3}} + G(T) = 0 + G(T) \tag{13}$$

or

$$G(T) = 0 \tag{14}$$

from which one can further conclude that

$$S = -F\sigma = S^* \tag{15}$$

The negative sign in Eq. (15) arises from the fact that electrons are negatively charged. Tykodi has also reached a similar conclusion to Eqs. (14) and (15) using different methods [3].

The validity of Eq. (15) depends on relatively mild conditions, most importantly that both the thermoelectric power and the partial molar entropy have the limiting behaviors described in Eq. (13). One could also consider whether a model which includes electron–electron interactions, such as a jellium model, would demonstrate similar limiting behavior to Eq. (13) at high number density, namely that both the partial molar electronic entropy and thermoelectric power would approach zero at infinite number density. If so it would further validate the line of thought presented above.

One must keep in mind that $G(T)$ is a universal function. Consequently, it is only necessary to evaluate it for a single material in order to establish it for all materials, even if the other materials would not conform to simple models such as the free electron model or the jellium model. Thus, one need not consider complicating factors such as lattice periodicity or electron-phonon interactions in order to demonstrate the validity of Eq. (15).

3. Applications

If Eq. (15) is valid it would enable one to perform an electrochemical procedure that, at the present time, would seem to be the only practical way to determine partial molar entropies of ions in solution. Consider the following generic electrochemical reaction:

$$M_{metal} \to M^+_{solution} + e^-_{metal} \tag{16}$$

The entropy of reaction is given by combining the partial molar entropies:

$$\Delta S = S_{M^+,solution} + S_{e-,metal} - S_{M,metal} \tag{17}$$

Given that an isothermal electrochemical Peltier experiment can, in principal, be performed under conditions that approach thermodynamic reversibility (e.g. in the limit of zero current) the entropy can also be calculated from the electrochemical Peltier heat:

$$\Delta S = \frac{Q_{reversible}}{T} = \frac{Q_{Peltier}}{T} \tag{18}$$

Substituting this result into Eq. (17) and rearranging the equation one obtains:

$$S_{M^+,solution} = \frac{Q_{Peltier}}{T} + S_{M,metal} - S_{e-,metal} \tag{19}$$