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Discussion

Comment on “The electrochemical Peltier heat of the standard hydrogen electrode reaction” by Zheng Fang et al.

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ABSTRACT

Fang et al. recently performed electrochemical Peltier measurements, proposed an absolute entropy scale for the standard hydrogen electrode, and gave a value for the partial molar entropy of hydrogen ions in solution. That paper contains several ambiguities and omissions that should be resolved in order to make the information in the paper more useful. The thermodynamic state of the electron in their treatment is not fully specified, and the method used to calculate the partial molar entropy of solution phase hydrogen ions is not given. Furthermore, the calculation of partial molar entropy of solution phase hydrogen ions apparently omits the partial molar entropy of metal-phase electrons, a term that is necessary for such determinations if the starting point is electrochemical Peltier heat measurements. As a smaller matter, the paper overlooks specifying the units used for fugacity. The paper also overlooks previous work on absolute half-cell entropy.

Using calorimetry, Fang et al. [1] measured the entropy of the following isothermal reaction

$$\mathrm{Fe(CN)_6}^{3-}\,(\text{aqueous}) + e^- \rightarrow \mathrm{Fe(CN)_6}^{4-}\,(\text{aqueous}) \tag{1}$$

and from this determined the entropy of the following isothermal reaction

$$e^- + \mathrm{H}^+\,(\text{aqueous}) \rightarrow \tfrac{1}{2}\mathrm{H_2}\,(\text{gas}) \tag{2}$$

The paper by Fang et al. contains much that is truly interesting and potentially extremely useful. However, there are several ambiguities and omissions that need to be corrected before the paper reaches its full potential.

The first issue concerns the thermodynamic state of electrons. In reference [1] the thermodynamic state of the electron is not fully specified. The authors omitted any state-specifying notations for the electron anywhere in the paper. Although the text mentioned a standard state of the electron to be the “. . . ideal electron gas with unit fugacity in metal.”, it is unclear from this language whether the electron is being placed in the gas-phase or in the metal. Nowhere does paper discuss the thermodynamic properties of gas-phase electrons, so the authors probably intended that electrons be placed in the metal.

If electrons are to be placed in the metal then there are at least two possibilities. One possibility would be to place electrons in the metal under ambient conditions. A second possibility would be to place electrons in a metal equilibrated with an ideal electron gas at unit fugacity. Although the second of these possibilities seems more consistent with the literal language of the paper, this interpretation is untenable because nowhere in the paper do the authors discuss the conversion of their experimental results obtained under ambient conditions, where the fugacity of an equilibrated electron gas would be extremely small, to conditions where the fugacity of the electron gas would equal unit fugacity.

It seems the only interpretation consistent with the actual treatment of data in the paper is that electrons are to be placed in the metal under ambient conditions. This can be a legitimate way to handle the thermodynamics of the electron for some purposes, but whatever the choice for the thermodynamic state for the electron it needs to be clearly stated, and I invite the authors to do so.

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Consistent with the above discussion, and assuming that the authors intended electrons to be placed in the metal under ambient conditions, reactions (1) and (2) become

$$\mathrm{Fe(CN)_6}^{3-}\,(\text{aqueous}) + \mathrm{e}^-\,(\text{metal}) \rightarrow \mathrm{Fe(CN)_6}^{4-}\,(\text{aqueous}) \qquad (3)$$

$$\mathrm{e}^-\,(\text{metal}) + \mathrm{H}^+\,(\text{aqueous}) \rightarrow \tfrac{1}{2}\mathrm{H_2}\,(\text{gas}) \qquad (4)$$

However, even specifying that electrons are to be placed in the metal does not fully characterize the system. The identity of the metal also needs clarification. The paper describes an apparatus in which a copper wire is connected to a platinum wire coming from the cell. The paper does not state whether the copper/platinum junction is in thermal contact with the calorimeter chamber.

If the junction is in thermal contact with the calorimeter chamber, and if one wishes to specify that electrons are to be placed in platinum metal, then one must account for the copper/platinum Peltier heat in the data analysis. The authors have not done this. If the copper/platinum junction is in thermal contact with the calorimeter chamber and one does not account for the copper/platinum Peltier heat then it is equivalent to specifying that electrons are to be placed in copper. If the copper/platinum junction is not in thermal contact with the calorimeter chamber then it is equivalent to specifying that electrons are to be placed in platinum metal. The authors should clarify which of these three possibilities correspond to their system. For the purposes of the rest of this paper it will be assumed that electrons are placed in platinum metal.

Fang et al. specify a fugacity of unity for standard states of gaseous species, but they do not specify the units they are using. Although it is customary these days to specify fugacity in terms of bar, this is not the only choice. The authors should clear up this ambiguity by stating whether they are using bar of some other units for fugacity.

Electrochemical Peltier experiments such as those described by Fang et al., when coupled with additional experimental information, provide the only known experimental method to measure partial molar entropies of ions in solution. Based on their measurements, Fang et al. reported a value for the partial molar absolute entropy of hydrogen ions in solution. However, they did not disclose the equations or methods used to calculate this value, and there is reason to believe that they may have omitted an essential term in the calculation. Specifically, as discussed below one must account for the partial molar entropy of electrons in the electrode metal if one is to use electrochemical Peltier heat measurements to determine partial molar absolute entropies of ions in solution. The relationships between electrochemical Peltier heat measurements, partial molar ionic entropies, partial molar entropies of electrons in metals, and related quantities has been discussed in literature Fang et al. apparently overlooked, such as in Eqs. (4), (8), and (16) of reference [2].

The entropy of reaction (4) (which is also the entropy of reaction (1) in reference [1]) relates to the entropies of the reactants and products as follows:

$$\Delta S_4 = \tfrac{1}{2}S_{\mathrm{H_2}} - S_{\mathrm{H^+}}\,(\text{aqueous}) - S_{\mathrm{e^-}}\,(\text{metal}) \qquad (5)$$

where the terms on the right hand side of Eq. (5) are respectively; one half the molar entropy of H_2 gas, the partial molar entropy of solution-phase hydrogen ions, and the partial molar entropy of metal-phase electrons. ΔS_4 can be measured using methods described by Fang et al., who obtained a value of 87.6 J K^{-1} mol^{-1} when H^+ and H_2 are in standard states of 1 molal ideal solution and 1 bar ideal gas respectively. The entropy of H_2 at 298.15 K is known [3]. After correction from an older standard state of 1 atmosphere to the modern standard state of 1 bar this has a value of 130.79 J K^{-1} mol^{-1}. Substituting these values into Eq. (5) and re-arranging we have:

$$S^\circ_{\mathrm{H^+}}\,(\text{aqueous}) = -22.2\,\mathrm{J\,K^{-1}\,mol^{-1}} - S_{\mathrm{e^-}}\,(\text{metal}) \qquad (6)$$

Clearly, in order to obtain a value for $S^\circ_{\mathrm{H^+}}$ (aqueous) it is necessary to know and use a value for the partial molar entropy of metal-phase electrons, which is $S_{\mathrm{e^-}}$ (metal) in Eq. (6). However, nowhere do Fang et al. discuss this term, so it seems unlikely that they included it in their calculations. Consequently, one must use caution when interpreting the value reported by Fang et al. for the partial molar entropy of the solution-phase hydrogen ion.

Based on their electrochemical Peltier heat measurements Fang et al. reported a value of −22.3 J K^{-1} mol^{-1} for the partial molar absolute entropy of hydrogen ions in solution. This is very close to the value of −22.2 J K^{-1} mol^{-1} one would obtain if by ignoring the electronic entropy term in Eq. (6), and the small difference between −22.2 and −22.3 might be attributable to round off in the calculations. It therefore seems likely that Fang et al. omitted $S_{\mathrm{e^-}}$ (metal) in their calculations.

To date there are no non-controversial methods for obtaining experimental values for $S_{\mathrm{e^-}}$ (metal). However, at least two investigators have argued for the following relationship

$$S_{\mathrm{e^-}}\,(\text{metal}) = -F\alpha_e \qquad (7)$$

where F represents Faraday's constant, and α_e represents the absolute thermoelectric power of the metal [4,5]. The arguments for and against Eq. (7) will not be reviewed here. Let us instead consider the completion of Fang et al.'s calculation of the partial molar entropy of solution-phase ions under the assumption that Eq. (7) is correct.

Using the known value of absolute thermoelectric power of platinum at 298.15 K [6], corrected to the updated scale of thermoelectric power [7], the partial molar entropy of the electron in the platinum electrode material obtained using Eq. (7) is 0.48 J K^{-1} mol^{-1}. Substituting this value into Eq. (6) yields the following value for the partial molar entropy of solution-phase hydrogen ions in a standard state of 1 molal ideal solution.

$$\begin{aligned} S^\circ_{\mathrm{H^+}}\,(\text{aqueous}) &= -22.2\,\mathrm{J\,K^{-1}\,mol^{-1}} - S_{\mathrm{e^-}}\,(\text{metal}) \\ &= -22.7\,\mathrm{J\,K^{-1}\,mol^{-1}} \end{aligned} \qquad (8)$$

Although the partial molar electronic entropy of the metal is relatively small (∼2%) fraction of the calculation for partial molar entropy of aqueous-phase H^+ in its standard state, it is not to be fundamentally ignored, and one can expect it to become relatively more important as the precision and accuracy of measurements improve.

Fang et al. state that they have introduced an absolute scale for half-cell entropy. This claim needs to be considered within a larger historical and scientific context. Fang et al. overlooked citing at least one earlier relevant publication that introduced an absolute scale for half-cell entropy [2].

The earlier work [2] is based on a defined "absolute half-cell process," which for the hydrogen electrode can be written as:

$$\mathrm{e}^-\,(\text{gas}) + \mathrm{H}^+\,(\text{aqueous}) \rightarrow \tfrac{1}{2}\mathrm{H_2}\,(\text{gas}) \qquad (9)$$

In the present paper the direction of some of the reactions, such as reactions (4) and (9) has been reversed compared to reference [2] in order to be comparable to the direction Fang et al. have written their reactions. Consequently, some of the sign conventions in the present paper are reversed compared to sign conventions in reference [2].

In the approach taken in reference [2] the absolute half-cell entropy of the hydrogen electrode is defined as the entropy of reaction (9). This approach, which places the electron in the gas phase, differs from the approach offered by Fang et al. which apparently leaves the electron in the metal. If the reactants and products of reaction (9) are specified to be in well-defined standard states, such as 1 molal ideal solution for solutes and 1 bar ideal gas for gases, then the entropy of reaction (9) is the absolute half-cell entropy of the standard hydrogen electrode as defined in reference [2].

The definition of absolute half-cell entropy proposed by Fang et al and the one previously introduced in reference [2] are related, and with some additional data, results from the two definitions can be inter-converted. Consider the reaction

$$e^- \,(\text{metal}) \rightarrow e^- \,(\text{gas}) \tag{10}$$

Combining reactions (4) and (10) produces reaction (9). Therefore, the relationship between the two definitions of absolute half-cell entropy is given by the following equation

$$\Delta S_9 = \Delta S_4 - \Delta S_{10} \tag{11}$$

where ΔS_9 is the absolute half-cell entropy as defined in reference [2] and ΔS_4 is the absolute half-cell entropy as defined in reference [1].

The entropy of reaction (10) is

$$\Delta S_{10} = S_{e^-}\,(\text{gas}) - S_{e^-}\,(\text{metal})$$

In an ideal gas standard state S_{e^-} (gas) can be calculated from the Sackur-Tetrode equation for translational entropy plus the spin entropy, and it has a value of 20.98 $\text{J K}^{-1}\,\text{mol}^{-1}$ at 1 bar and 298.15 K. The value of S_{e^-} (metal) can be taken as 0.48 $\text{J K}^{-1}\,\text{mol}^{-1}$ at 298.15 K, as discussed above. Substituting these numbers into Eq. (11) and specifying that the reactants and products are in their standards state gives the numerical relationship between the two definitions of absolute half-cell entropy for the standard hydrogen electrode at 298.15 K:

$$\Delta S_9^\circ = \Delta S_4^\circ - 20.50\,\text{J K}^{-1}\,\text{mol}^{-1}$$

A similar relationship applies to absolute half-cell entropies for all electrode reactions. Using the value of 87.6 $\text{J K}^{-1}\,\text{mol}^{-1}$ for ΔS_4° as measured by Fang et al. one can calculate the value for the absolute half-cell entropy of the standard hydrogen electrode under Rockwood's definition to be:

$$\Delta S_9^\circ = 67.1\,\text{J K}^{-1}\,\text{mol}^{-1}$$

Taking sign conventions and data uncertainties into account this value agrees satisfactorily with a value of 66.7 $\text{J K}^{-1}\,\text{mol}^{-1}$ suggested in reference [2].

To summarize, the measurements of electrochemical Peltier heat, such as those done by Fang et al., can produce extremely useful thermodynamic information. As well as the relationship to absolute half-cell thermodynamics (a relationship discussed by both Fang et al. and earlier authors) such measurements provide valuable information on the entropy of ions in solution, information that is otherwise experimentally inaccessible. Such experiments should be continued and expanded in the future. However, reference [1] contains ambiguities and omissions that limit the usefulness of the paper. Among these are (1) an incomplete specification of the thermodynamic state of the electron, (2) omission of units used for fugacity, (3) absence of a description of how solution-phase ionic entropies were calculated, (4) the likely omission of a necessary term in the calculation of solution-phase ionic entropies, namely the partial molar entropy of electrons in the electrode metal of the half-cell calorimeter, (5) overlooking relevant literature on the determination of partial molar entropies of solution-phase ions, and (6) failure to cite relevant literature that had previously treated absolute half-cell entropies. In clearing up these ambiguities and omissions the authors of reference [1] can make their paper a much more useful addition to the literature.

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References

[1] Z. Fang, S. Wang, Z. Zhang, G. Qiu, Thermochim. Acta 473 (2008) 40–44.
[2] A.L. Rockwood, Phys. Rev. A 36 (1987) 1525–1526.
[3] Handbook of Chemistry and Physics, 61st ed., Chemical Rubber Company, Boca Raton, FL, 1980, p. D-62.
[4] A.L. Rockwood, Phys. Rev. A 30 (1984) 2843–2844.
[5] R.J. Tykodi, Thermodynamics of Systems in Nonequilibrium States, Thinkers' Press, South Dartmouth, MA, 2002, pp. 304–309.
[6] F.J. Blatt, P.A. Schroeder, C.L. Foiles, D. Greig, Thermoelectric Power of Metals, Plenum Press, New York, 1976, pp. 2–3.
[7] R.B. Roberts, Nature 265 (1977) 226–227.