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Absolute half-cell entropy

Alan L. Rockwood
*Department of Chemistry, University of Houston, Houston, Texas 77004**

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The absolute half-cell entropy is defined here as the entropy of the cell process $M \rightarrow M^+$(solution)$+e^-$(gas). A method of determining absolute half-cell entropies is described. The relationship is discussed for single-ion entropies in solution. ΔS^0 for the hydrogen electrode is provisionally recommended to be -66.6 ± 1.4 J/Kmole at 298 K, based on a previously recommended value for the absolute entropy of H^+ in water. More accurate measurements should be attempted.

INTRODUCTION

An earlier publication defined the absolute half-cell potential in terms of the Gibbs free energy of the generic isothermal one-electron process[1]

$$M(\text{metal}) \rightarrow M^+(\text{solution}) + e^-(\text{gas}) \ . \tag{1}$$

An advantage of this approach is that the thermodynamic states of all species must be well defined, so the approach is well adapted to developing a complete system of absolute half-cell thermodynamics. The present paper develops the theory of absolute half-cell entropy.

THEORETICAL DEVELOPMENT

First, reaction (1) is broken into two parts:

$$M(\text{metal}) \rightarrow M^+(c,\text{solution}) + e^-(\text{metal}) \ , \tag{2}$$

$$e^-(\text{metal}) \rightarrow e^-(\text{gas}) \ , \tag{3}$$

where c specifies the concentration of M^+. The entropy of process (2) can be calculated from the heat of process (2) under reversible conditions:

$$\Delta S_2 = Q_{2,\text{rev}}/T \ . \tag{4}$$

$Q_{2,\text{rev}}$ is the heat absorbed in the vicinity of an electrode during electroplating under reversible low-current conditions, and it depends on the concentration of M^+.

The entropy of process (3) is

$$\Delta S_3 = S_{e^-(\text{gas})} - S_{e^-(\text{metal})} \ , \tag{5}$$

where $S_{e^-(\text{gas})}$ is the entropy of the electron gas and $S_{e^-(\text{metal})}$ is the partial molal entropy of the electron in the metal. The state of the electron gas must be specified in order for Eq. (5) to be meaningful. $S_{e^-(\text{gas})}$ is calculated from

$$S_{e^-(\text{gas})} = R\ln 2 + R\ln\left[\frac{e^{5/2}V}{Lh^3}(2\pi mkT)^{3/2}\right] \ , \tag{6}$$

which is the spin entropy plus the translational entropy of the specified state. (The second term is the Sackur-Tetrode entropy.) In this equation e is the base of the natural log scale, V is the volume, L is Avogadro's number, m is the electron mass, and the other symbols have the usual meanings. Equation (6) assumes that the electron gas is ideal, a point to be discussed later. $S_{e^-(\text{metal})}$ can be obtained from the absolute Seebeck coefficient (the absolute thermoelectric power) using the equation[2]

$$S_{e^-(\text{metal})} = -F\alpha \ , \tag{7}$$

where F is Faraday's constant and α is the absolute Seebeck coefficient of the metal. Old tables of absolute Seebeck coefficients, such as in Ref. 3, should first be corrected to the modern scale.[4] Combining results gives

$$\Delta S_1 = \Delta S_2 + S_{e^-(\text{gas})} - S_{e^-(\text{metal})} \ , \tag{8}$$

where the quantities on the right are given by Eqs. (4), (6), and (7).

Next we find ΔS_1^0, the entropy of reaction when all reactants and products are in their standard states. A convenient set of standard states for absolute half-cell thermodynamics was described elsewhere.[1] Briefly, the standard state of M is the most stable form of the metal at one atmosphere total pressure and the temperature of interest. For M^+ it is the state defined by extrapolating from infinite dilution to unit concentration, assuming the solute obeys Henry's law. The standard state for e^-(gas) is the hypothetical state obtained by extrapolating from zero pressure to unit pressure using the ideal-gas law. We will use units of molality and atmospheres for concentration and pressure. These units are commonly used, but other choices are possible.

Standard states of solutes and gases such as defined here are not physically realizable, but their properties are well defined by the extrapolation.[5] Are the extrapolations which define standard states using ideal laws valid for charged species such as M^+ and e^-? The answer is yes. Although the electrostatic energy does become very large for even a rather small charge imbalance, this has no effect on the definition of the standard state because the electrostatic energy is second order in excess charge and does not show up in the linear extrapolation which defines the standard state.

To determine ΔS_1^0 it is necessary to introduce the process

$$M^+(c,\text{solution}) \rightarrow M^+(c^0,\text{solution}) \ , \tag{9}$$

where c^0 represents the standard state. The result is

$$\Delta S_{\mathrm{I}}^{0}=\Delta S_2+\Delta S_9+S_{e^-(\mathrm{gas})}^{0}-S_{e^-(\mathrm{metal})}^{0} , \tag{10}$$

where $S_{e^-(\mathrm{gas})}^{0}$ is the entropy of the standard state for the electron gas which is calculated using Eq. (6). Equation (10) is not yet usable for determining $\Delta S_{\mathrm{I}}^{0}$ because an equation for the entropy of process (9) has not yet been given. An approximate relation is

$$\Delta S_9 \approx R\ln(C^0/C) . \tag{11}$$

This relation would be exact if the M^+ obeyed Henry's law at nonzero concentration, and it *is* exact in the limit $C \rightarrow 0$. Substituting Eq. (11) into Eq. (10) yields

$$\Delta S_{\mathrm{I}}^{0} \approx \Delta S_2+R\ln(C^0/C)+S_{e^-(\mathrm{gas})}^{0}+S_{e^-(\mathrm{metal})} , \tag{12}$$

which becomes exact in the limit $C \rightarrow 0$:

$$\Delta S_{\mathrm{I}}^{0}=\lim_{C\rightarrow 0}[\Delta S_2+R\ln(C^0/C)+S_{e^-(\mathrm{gas})}^{0}-S_{e^-(\mathrm{metal})}] . \tag{13}$$

In other words, ΔS_2 is measured for a series of dilute solutions, and approximate values for $\Delta S_{\mathrm{I}}^{0}$ are calculated using Eq. (12). These values are then extrapolated to $C=0$ to give the exact value of $\Delta S_{\mathrm{I}}^{0}$. The question of *how* to choose the best practical extrapolation function is outside the scope of the present paper.

DISCUSSION

First, it should be noted that we have not mentioned the counterion for M^+. It is assumed that a counterion is present so that overall charge neutrality exists for the solution-electrode system. However, the extrapolation to $C=0$ insures that the value of $\Delta S_{\mathrm{I}}^{0}$ will be independent of the identity of the counterion. In a microscopic point of view, the reason for this is that in the extrapolation to $C=0$, the short-range forces become unimportant, leaving the Coulomb interaction between the ion and counterion as the last important interaction, and the Coulomb interaction does not depend on ion identity. Finally, in the limit of $C \rightarrow 0$, even the Coulomb interaction ceases to be important. This is a result from Debye-Hueckel theory, which is an exact theory in the limit $C \rightarrow 0$. One could test the assertion that $\Delta S_{\mathrm{I}}^{0}$ is independent of counterion identity by performing appropriate experiments.

A method for determining ΔG^0 was described in an earlier publication,[1] and ΔS^0 can be determined by the method described here. One can find the enthalpy from the relation

$$\Delta H^0=\Delta G^0+T\Delta S^0 , \tag{14}$$

so methods exist for determining three absolute half-cell thermodynamic functions.

Once an absolute half-cell entropy is obtained, single-ion entropies in solution are obtainable from the equation

$$S_{\mathrm{ion}}^{0}=\Delta S_{\mathrm{I}}^{0}+S_{M}^{0}-S_{e^-(\mathrm{gas})}^{0} , \tag{15}$$

where S_M^0 is the absolute entropy of the metal. This is an example of the general relationship between absolute half-cell quantities and single-ion quantities.[1]

Conversely, if single-ion entropies are known, one can backcalculate to obtain absolute half-cell entropies. Values for single-ion entropies have been suggested in the literature.[6] Diverse methods were used to obtain these values. Objections could be raised against most of the methods, and the agreement between the values is only fair. However, the recommendation is probably at least approximately correct, so we will use it for a sample calculation. The value recommended for $S_{\mathrm{H}^+}^{0}$ in water at 298 K is -22.2 ± 1.4 J/K mole. This is for a hypothetical one-molal standard state. From Eq. (6) $S_{e^-}^{0}$ is 20.9 J/K mole for the hypothetical 1-atm ideal gas. The value for half of $S_{\mathrm{H}_2}^{0}$ is 65.3 J/K mole.[7] Using these values, ΔS^0 for the hydrogen electrode reaction

$$\tfrac{1}{2}\mathrm{H}_2(\mathrm{gas}) \rightarrow \mathrm{H}^+(\mathrm{aq})+e^-(\mathrm{gas}) \tag{16}$$

is -66.6 ± 1.4 J/K mole at 298 K.

Conventional half-cell entropies can be converted to the absolute scale by simply adding the absolute half-cell entropy of the hydrogen electrode, taking care to be sure that all values are normalized to the number of electrons transferred in the reaction. Until more accurate measurements are made, the value calculated here for the hydrogen electrode can be considered a provisional recommendation for the absolute half-cell entropy scale. More accurate measurements should be made.

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*Present address: Department of Chemistry, University of Delaware, Newark, DE 19716.

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