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Short communication

Response to “Comment on ‘The electrochemical Peltier heat of the standard hydrogen electrode reaction’ by Zheng Fang et al.” [Thermochimica Acta V 490 (1–2) (2009) 82–84]

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ABSTRACT

In response to Rockwood’s query about the standard state of electron and the handling of the entropy of electron on the absolute scale, an answer is made. Usually, the standard state for a chemical substance is specified based on a classical physical law. The standard state of electron on the absolute scale is determined according to the free electron model on the Fermi–Dirac statistics. However, the thermodynamic handling of the same particle on the different scales must be completely identical, and the difference is only designated values of the thermodynamic parameters. For the standard hydrogen electrode reaction, the electron entropy and the partial molar entropy of hydrogen ion, respectively, are 65.29 J mol^{-1} K^{-1} and zero on the conventional scale, and zero and about −22.3 J mol^{-1} K^{-1} on the absolute scale at 298.15 K. The other query, related to units used for fugacity, the conversion entropy of electron from gas-phase to metal-phase, the partial molar entropy of electron in the platinum, and the Peltier heat at the platinum/copper joint, is also expatiated.

In the article discussed [1], Fang and his co-workers reported a thermo-electrochemical experiment on the half-cell reaction of the ferrocyanide–ferricyanide couple, and from this they obtained the result that the entropy of the standard hydrogen electrode reaction on the absolute scale is evaluated.

In a comment [2] to this article, Rockwood presented following six issues, such as incomplete specification of the thermodynamic state of the electron, omission of units used for fugacity, absence of a description of calculation of solution-phase ionic entropies, omission of a necessary term in the calculation of solution-phase ionic entropies, namely the partial molar entropy of electron in the electrode metal, overlooking relevant literature on the determination of partial molar entropies of solution-phase ions, and failure to cite relevant literature that had previously treated absolute half cell entropies. Summarily, these issues are mainly involved in two aspects, (1) the standard state of electron; (2) the entropy of electron taking part in the standard hydrogen electrode reaction. Unfortunately, the arguments used are not entirely correct, which may mislead the reader regarding the nature and significance of our work. We think that Rockwood apparently does fail to notice what we do in our experiment.

1. On the standard state of electron

1.1. The standard state of electron

As well known, in the field of chemical thermodynamics, the most standard states for solid, liquid, gas, solvent and solute, may be not physically realizable. However, every type of these substances at least obeys a definite physical law, for example, $(PV)_{P\to 0} = RT$ for one-molar gas with pressure P, volume V, gas constant R and temperature T in Kelvin, and Henry’s law for dilute solution. Although, a standard state can be discretional, usually, the value of a thermodynamic parameter at the state, physically unrealizable in most cases, can be quantified by the ideal extrapolation according to a definite physical law, and the thermodynamic parameter at other states can conveniently be related to that under the standard state. So, the standard states given on a certain physical law can be commonly accepted or accredited.

As for electron, except a few literatures, in most of the physicochemical references, handbooks and textbooks, its standard state is not referred to, when one concerns the standard hydrogen electrode (SHE). In my opinion, there are maybe twofold reasons. Firstly, electron, as a kind of elementary particles, obeys the quantum statistics principle. It is hard to obtain an accredited standard state of electron based on a classical physical law (not the quantum mechanics). Secondly, specifying a standard state is to look for a reference point to which the thermodynamic parameter at other states can be related.

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Take the chemical potential of substance i in a mixture, μ_i, for example:

$$\mu_i = \mu_i^{\varnothing} + RT\ \ln\left(\frac{f_i}{f_i^{\varnothing}}\right), \tag{1}$$

where, $\mu_i^{\varnothing}$ is the chemical potential of the substance at its standard state, f_i fugacity at a given state, and $f_i^{\varnothing}$, fugacity at the standard state. The standard state is only to choose a convenient reference, to which the relative value of the chemical potential of substance i at other state can be determined easily. For electron, there is no need to know such reference in normal thermodynamic analysis. On the conventional scale, it is just under an underlying assumption to handle electron, i.e. these values of thermodynamic parameters for electron are always considered to be equal, no matter what metal or what state electrons lie in, even under various conditions (like pressure of gaseous substance). For example, for the half-cells of Cu^{2+}/Cu and Zn^{2+}/Zn, we have the electrode reactions, respectively, as follows:

$$\text{Zn(pure metal)} - 2e^- = \text{Zn}^{2+}\text{(any activity)}, \tag{2a}$$

$$\text{Cu}^{2+}\text{(any activity)} + 2e^- = \text{Cu(pure metal)}. \tag{2b}$$

When the Daniell cell is set up, the whole reaction of the cell usually is written as

$$\text{Zn(pure metal)} + \text{Cu}^{2+}\text{(any activity)} = \text{Zn}^{2+}\text{(any activity)} + \text{Cu(pure metal)}, \tag{2}$$

where electron in both sides of the equation is canceled, indicating that the thermodynamic parameters including entropy of electron in the two metals or under different states are all considered to be equal or at least the difference between them is negligibly small. Otherwise, electron cannot be all canceled.

Even for the processes that involve ions and electron shown in Eqs. (2a) or (2b), no quantity about electron as an independent variable is included in the well-known Nernst equation that is suitable for these half-cell reactions. This means that the change in thermodynamic quantities of electrode reaction is affected only by metal sort and state of reactants (activities), while the effect of electron state would not be considered.

Just like other disciplines, there also always exist some underlying assumptions in the chemical thermodynamics. For example, the thermodynamic parameters of a system with static mass, such as enthalpy, entropy, and Gibbs free energy, are never considered to be a function of place with different gravitation potential and velocity of the system (except some extremely cases), in spite of the particle's state in the system it is really different under various velocity and at various place of the system from the view point of physics. Well then, whether should we give a "standard state" related to place and velocity? Academically, this is what we should be doing, but practically, it is unnecessary to do so in the normal analysis to these parameters. The changes of them in a chemical process would be much bigger than those due to change of place and velocity of the system.

Proceeding from a deliberation that the thermodynamic state of SHE should be fully characterized, as well as the repeated requirement that standard state of electron must be well defined to the manuscript of the paper [1] by one of the reviewers, we defined the standard state of electron in the revision of the manuscript as an ideal electron gas with unit fugacity in metal based on the free electron model, which is successful in explaining many experimental phenomena. In this model, valence electrons are assumed to be completely detached from their ions, but not got away from crystal lattice, forming an ideal electron gas. The expression "in metal" in the presented definition means that the gaseous electrons lie in a potential well of metal ions and also presents a difference between electron gas with quantum effect and the ordinary gases (in paper [3], the standard state of electron gas was similar to that of an ordinary gas). State like this with quantum effect is chosen as the standard state of electron, so that one can obtain the thermodynamic parameter of it at non-standard state much conveniently by an ideal extrapolation on quantum rule. In my opinion, this definition for the standard state (i.e. electron with quantum characteristic) would be better than that on the classical meanings, on which the transform of thermodynamic parameter of electron from a non-standard to standard might be more difficult or more complicated. However, this never indicates that electron, as mentioned by Rockwood, is placed in the gas-phase or in the metal-phase.

It is worth noting that treating electronic thermodynamics on the absolute scale must be similar to that on the conventional scale except the differently designated values of thermodynamic parameters on these two scales. Just like hydrogen ion, the definition of its standard state on the conventional scale must be similar to that on the absolute scale, but both numerical values of thermodynamic functions are different, as mentioned below. Therefore, although defining a standard state of electron on the absolute scale, there still is a way similar to the conventional handling to electronic thermodynamics. From experimental point of view, the entropy change of electron from a state or a kind of metal to another state or another kind of metal would be practically not considered in absolute scale due to the negligibly small value.

In fact, there is a worthy argument, i.e. whether the standard state of electron chosen to both of the conventional scale and the absolute scale is reasonable or not, because no final conclusion has yet been reached on this matter in chemical thermodynamics. If this standard state of electron can be accepted, it is still necessary to consider that the energy of potential well or which type of potential well should be specified, whether the tunnel effect of electron should be omitted, etc. Rockwood referred the previous literature [3] where the standard state of electron is defined as hypothetical 1-atm ideal gas and criticized the author and his co-workers overlooking citing this relevant publication. This standard sate of electron advocated by Ref. [3] is similar to that of the ordinary gases such as gaseous hydrogen, and gaseous oxygen. Well then, whether the electron gas with Fermi–Dirac distribution can be thought completely to be the same as these ordinary gases with Maxwell–Boltzmann distribution. How will the entropy of electron gas with quantum effects under non-standard state be related to the entropy under the standard state with classical meanings?

1.2. Units used for fugacity

The comment oppugns that the fugacity of unit for standard state of gaseous species is not the only choice, it may be bar or others. It is well known and codified by IUPAC that there are at least two terms on the standard states of gas [4], i.e. *standard conditions for gases* and *standard pressure*. They have unambiguously ordained the meaning of the standard state of gaseous species, and recommended the denoted symbol $p^{\varnothing}$ or p^{o} and numerical value, i.e. $p^{\varnothing} = 10^5$ Pa or 1 bar. When discussing the standard state of gas, naturally, the prescription by IUPAC from the symbol to the numerical value should be a tacit recognition under no specific statement. Although prior to 1982 the value 101,325 Pa (=1 atm) was usually used, IUPAC recommends that "the pressure of 1 atm as standard pressure (equivalent to 1.01325×10^5 Pa) should be discontinued" [4].

In fact, when referring SHE, the "unit fugacity" for gaseous species often is mentioned in many textbooks and handbooks. Its meanings are never misconstrued in judging the numerical value of unit fugacity, although the numerical value has some revisions with performing new unit system. In fact, when first referring the standard state of electron in the paper [3], Rockwood also used "unit pressure". Then, the author of the paper used "1-atm" to calculate the electron entropy. Rockwood also desired us to give a definite numerical value for pressure of electron gas to calculate the electron entropy under this pressure, and the transform entropy from the “real” pressure derived from free electron model to “unit pressure”, whereas, Rockwood failed to notice that the zero electron entropy assumption (state below) is used in the literature [1].

2. On the entropy of electron and ion

2.1. Calculations of solution-phase ionic entropies

The comment oppugns that the paper [1] omitted an essential term in the calculation of the partial molar entropy of the hydrogen ion, i.e. the entropy of electron. In fact, there are two ionic entropy systems [5], the conventional system and the absolute entropy system. Differing from the convention that all thermodynamic functions for SHE under the standard conditions are zero at all temperatures, these functions on the absolute scale in paper [1] no longer are zero at all temperatures for the same electrode under the same standard conditions. On the former, the entropy change of SHE reaction is specified as zero, the partial molar entropy of hydrogen ion is also assumed as zero and the molar entropy of electron is 65.29 J mol^{-1} K^{-1} at 298.15 K according to a principle that the algebraic sum of the entropies of all substances taking part in a reaction results in the entropy change of the reaction, because the entropy of 0.5 mol H_2 is 65.29 J mol^{-1} K^{-1}. On the latter, according to our experiment, the partial molar entropy of hydrogen ion is about −22.3 J mol^{-1} K^{-1}, and the molar entropy of electron is specified to zero. It should be pointed out that the previously reported partial molar entropy of hydrogen ion on the absolute scale is obtained on the assumption of zero electron entropy [6]. It is on this assumption that the partial molar entropy of hydrogen ion is evaluated in our experiment [1]. According to the reaction in paper [1]

$$\mathrm{H^+}(\text{solution}, a_{\mathrm{H^+}} = 1) + \mathrm{e^-} \rightarrow \tfrac{1}{2}\mathrm{H_2}(\text{gas, unit fugacity, on the platinum electrode}) \quad (3)$$

Under the assumption of zero electron entropy, we have:

$$\Delta S^\circ\left(\frac{\mathrm{H^+}}{\mathrm{H_2}}\right) = \frac{1}{2}S^\circ(\mathrm{H_2}) - S^\circ(\mathrm{H^+}) \quad (4)$$

where $1/2S^\circ(H_2)$ is the entropy of 0.5 molar gaseous hydrogen at its standard state and equals to 65.29 J mol^{-1} K^{-1}, $S^\circ(H^+)$ the partial molar entropy of hydrogen ion at standard state on the absolute scale, and $\Delta S^\circ(H^+/H_2)$ the entropy change of SHE reaction (3) on the absolute scale, i.e. $\Delta S^*(H^+/H_2)$ in paper [1], which has been obtained experimentally as 87.6 J mol^{-1} K^{-1}. From Eq. (4), $S^\circ(H^+) = -22.31$ J mol^{-1} K^{-1}.

Although the second system is called as the absolute scale, yet the entropy of electron is assumed to be zero, not the assignment of a “real value”. Thus, it is very convenient to have a definite reference point for the thermodynamic parameter of variety of single electrode reactions. In fact, this assumption is very close to truth. Compared with other substances taking part in an electrode reaction, the entropy of electron can be omitted after all due to very small value. Based on Fermi–Dirac statistics the electron gas always degenerates higher degree, the heat capacity of electron is very small and basically not affected by temperature. Especially, the capacity and entropy of electron all are zero at absolute zero.

In paper [3] regarded by Rockwood as a relevant literature overlooked by us, an entropy for SHE reaction was calculated as −66.6 J mol^{-1} K^{-1} at 298 K according to the entropies of hydrogen gas, hydrogen ion and electron. Whereas, in the calculation there is an obvious slip, that is, the entropy value of hydrogen ion derived from the zero electron entropy assumption and an electron entropy value other than zero are simultaneously used in Eq. (16) of the paper. This double standard for electron entropy in an equation is unbefitting.

2.2. The partial molar entropy of electron in the electrode metal

Rockwood oppugns the evaluation of the entropy of electron mainly on two aspects, (1) the partial molar entropy of metal-phase electron, $S_{\mathrm{e^-},\,\mathrm{metal}}$, is omitted in the calculations and (2) the partial molar entropy of electron in the platinum electrode material obtained using equation $S_{\mathrm{e^-},\mathrm{metal}} = F\alpha_{\mathrm{e}} = 0.48\,\mathrm{J\,mol^{-1}\,K^{-1}}$, should be considered. As stated above, application of the absolute entropy system has interpreted all.

Rockwood thought that the standard state of electron is gaseous, as well as they lie in platinum electrode, so the appended conversion entropy of electron from gases to metal to complete the reference electrode reaction should be considered. In fact, what we do is not directly measuring any thermodynamic function of SHE reaction, but by the experimental data-processing for the ferrocyanide–ferricyanide couple, one obtains the entropy change of SHE reaction called as on the absolute scale. The electron entropy on the absolute scale is zero; naturally, other evaluation for the electron entropy for SHE reaction is excrescent.

Besides, the electron is considered by Rockwood as metal-phase, what means this? We appreciate that electrons, as gaseous species, are completely detached from their ions but still lie in crystal of metal-phase. According to Rockwood, whether can the metal-phase electron be comprehended as a kind of hypothetical solid with a distinct structure or a flowable something? Rockwood calculated the entropy of metal-phase electron in metal platinum to be 0.48 J K^{-1} mol^{-1} using the equation mentioned above, and claimed a need for adding the value to the entropy of electron. With regard to this equation, we do not comment on its validity for the absolute scale here. Even if the equation were applicable here, could this numerical result calculated by Rockwood be directly added to the electron entropy under the standard state? Moreover, we suppose a case. If we used another inert metal electrode for SHE instead of platinum, there would be a different value of $S_{\mathrm{e^-},\,\mathrm{metal}}$ due to the different absolute thermoelectric power $\alpha_{\mathrm{e^-}}$ of the metal. When using the different value, whether one will result in a change in entropy of SHE on the absolute scale at the same temperature and pressure. Thermodynamically, it is unnecessary to consider how do electrons transfer and where do they come from? What we do is only to look for a reference to the studied system of ferrocyanide–ferricyanide, and not to calculate “real value” of the electron entropy in electrode metal.

2.3. The Peltier heat at joint in experimental device

Rockwood also mentioned that one must account for the copper/platinum Peltier heat in the data analysis. In our experimental device, a platinum wire connecting with platinum electrode was connected to a copper wire outside the solution. Certainly, the contact between different metals would produce the Peltier heat as electric current flows. But it should be noted that a completely symmetrical connection also exists on another electrode where the electric current was just reverse, i.e. electric currents flow from copper to platinum on an electrode, and reverse course on the opposite electrode. So net effects would be zero as extrapolating the electric current to zero. In fact, the errors due to these effects were within the experimental uncertainty. Moreover, the transfer entropy of electron in different metals is actually ignored due to the negligibly small value [7,8].

3. Tag

Taking this opportunity, we state the origin of the paper [1]. In the experiments on single electrode reactions such as Zn^{2+}/Zn, Cu^{2+}/Cu, H^+/H_2, $Fe(CN)_6{}^{3-}/Fe(CN)_6{}^{4-}$ [9,10], we have found that the enthalpies derived from the algebraic sum of the heat and the electric work (*vs.* the conventional SHE) are not equal to those calculated by the current thermodynamic data of ions under the *ad hoc* assumption (i.e. the conventional scale) that the Gibbs free energy of formation, the enthalpy of formation, and the entropy of formation of the hydrogen ion in water are all taken to be zero at 298.15 K and unit pressure. There exists an approximate constant between them. When SHE on the absolute scale is taken as the reference to calculate the electric work, the constant can be excellently explained and evaluated to be 87.6 kJ mol^{-1} at 298.15 K. The constant is just the entropy change of SHE reaction on the absolute scale at 298.15 K [1]. In order to prove the validity of the evaluated value, the partial molar entropy of hydrogen ion is derived from it to be -22.3 J mol^{-1} K^{-1}, a value being in good agreement with that before, where the assumption of zero electron entropy has been used. It should be again stated that the aim of the reference [1] is not going to determine or calculate the entropy of electron, but is to obtain the entropy change of SHE reaction in the absolute scale. Although Ref. [1] defined the standard state of electron on the free electron model, no discussion of the model is contained, because in any case, the contents of the standard state of electron are neither the scope of the paper [1] nor to innovate to a standard state. For the Rockwood's query, the author thought that this might be mainly for him to look for the "real" value of electron entropy under different state from the physics point of view (but still need a reference point), while we are looking for the Peltier heats of single electrode, which only concerns the entropy on absolute scale that belongs to the system of zero electron entropy, and checking the validity of the experimental data.

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