



## Review

## Some basic matters on the heat effects at electrode–electrolyte interfaces

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## ARTICLE INFO

## Article history:

Received 6 September 2010

Received in revised form

31 December 2010

Accepted 12 January 2011

Available online 26 January 2011

## Keywords:

Electrode–electrolyte interface

Electrochemical Peltier heat

Electrochemical Peltier coefficients

Absolute scale

Entropy change

Standard hydrogen electrode

Single electrode process

## ABSTRACT

Some basic matters concerning with the heat effect at electrode–electrolyte interface are briefly introduced in this paper. They include the concepts and definition about the electrochemical Peltier heat (EPH) and the Peltier coefficient for the electrode process, the absolute scale, the fundamental equations on this scale for thermoelectrochemistry, and the issues of the entropy changes on this scale and EPHs for the standard hydrogen electrode reaction as well as other standard electrode reactions. The EPH of electrode–electrolyte interface is specially emphasized to be a quantity related to reversible process; thereupon it can be measured and also be calculated by the change in the function of state, or entropy, on the absolute scale. The changes in entropy on the absolute scale, EPHs and the electrochemical Peltier coefficients for some of the most common standard electrode reactions in aqueous solution at 298.15 K are given.

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## 1. Introduction

Recently, the exploration for thermoelectrochemistry is fast developing in the aspect of new instruments and new techniques [1,2]. However, in the studies on the heat effects of reaction, there are still two basic problems that have not been resolved so far. One is that the heat effects for a reversible reaction,  $Q$  can be calculated by the formula  $Q = T\Delta S$  where  $\Delta S$  is the entropy change of this reaction and  $T$  temperature in Kelvin. Undoubtedly this is true for many reactions. Nonetheless, for a reversible electrode reaction (i.e. half-cell reaction), its heat effect measured experimentally is far from the value calculated by the formula [3–7]. That is, the experimental values are not in agreement with those calculated on the current thermodynamic databank of ions. Another is that there is

no effective method to be able to calculate the “real” heat effect of a standard reversible electrode reaction. These two problems should be resolved in thermoelectrochemical discipline.

The thermoelectric phenomena, such as the Seebeck effect, the Peltier effect and the Thomson effect, can be dated back to more than 100 years ago [8]. A few of the experimental studies on the heat effects for the electrochemical cells had also been presented soon after that [9–14]. In the second half of the 20th century a number of the studies on the Peltier heats was widely extended to the electrochemical reactions, especially to the electrode reactions. Even so, these investigations were still mainly focused on the designs of research apparatus and the exploration of research methods at that time [15–35]. These methods include thermoelectric power measurements [15,16], electrolytic calorimeter [17–20], controlled-potential and controlled-current polarizations [21], potentiodynamic and galvanostatic transient techniques [22], the non-stationary temperature wave method

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[23], cyclic-voltammetry [18], lumped-heat-capacity analysis [25,26], steady state electrolysis [27], non-isothermal cell [28], and differential voltammetric scanning thermometry [29] to obtain the electrochemical Peltier heat (EPH) of the electrode reactions.

In order to identify EPH of the cell or electrode reaction from the experimental information, there were two mainly approaches of treatments. One is based on the heat balance under the steady state or quasi-stationary conditions. This treatment considers all heat effects including the characteristic EPH and the heat dissipation related to the various processes such as the ionic and electronic heats of transport, Joule heat, and heat conductivity and convection due to the polarization [19,30]. And these quantities related to the processes are also generally ignored in the data-processing, because they are thought to be too small to affect EPH under some given conditions. The treatment like this always brings certain errors more or less. Another treatment concerns with the irreversible thermodynamics and the Onsager reciprocal relations [15,17], on which the heat flux due to temperature gradient, the component fluxes due to concentration gradient and the electric current density due to potential gradient and some active components' transfer are simply assumed to be directly proportional to these driving forces. Numerical simulation with a finite element program for the complex heat and mass flow at the heated electrode is also used [36]. Although these methods can determine EPH of electrode reaction under some assumptions, they are helpless to answer those problems presented above. A number of "contradictions" in the experimental data, for example the first problem stated above, also lacks explanations. Besides, in these approaches, the quantities such as the change in enthalpy and the change in Gibbs free energy (or the maximum electric work done) of the considered reactions, which are related to the changes in the state of system, were considered less. The regularity of the phenomena observed was little summarized. With the understanding thermoelectrochemistry, its application has now been extended in many areas, especially in the surface-electrochemical treatment of the functional materials and electrode modifying, the charge and discharge-control of the redox batteries, and more thought on the heat effects at the electrode–electrolyte interfaces during reactions is indispensable.

Thermoelectrochemistry is a subject that combines the theories and methods of both thermo- and electro-chemistry to investigate the cell and electrode reactions. That is, the parameters of thermodynamics [3–6,37] and kinetics [38–40] of the electrochemical reactions can be obtained by the simultaneous measurements and analysis of heat flow, electrode potential, electric current and time signals under the various conditions. For example, the curves of temperature and the potentials of the electrode against time under the constant current for the system  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  were simultaneously measured by an electrochemical calorimeter and are given in Fig. 1 from where more significant results have been acquired [3]. Therefore, the thermoelectrochemistry can provide the available and comprehensively additional information more for the analysis of electrode reactions. It compensates the insufficiency for a single electrochemical study or a single thermochemical research to some extent.

The purpose of this article is to clarify some vague understanding that still exists in this subject.

## 2. Electrochemical Peltier heat of a cell reaction

The Peltier heat was first found by the French physicist Peltier. The Peltier effect shows that the heat flow would be generated on the junction between two different metals in an electric current circumstance. The junction acts as a heat sink or as a heat source,

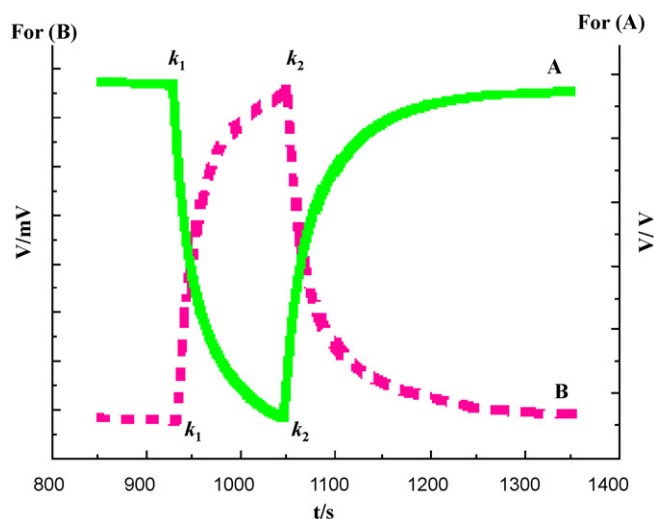


Fig. 1. The typical curves for electrode potentials against time (A) and for potential signals of temperature difference against time (B) at given constant electric current for the system  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ ; a constant current passing through interface between electrode and electrolyte started from point  $k_1$  and ended at point  $k_2$ .

which depends on the direction of the electric current. And the strength of the heat is proportional to the current intensity. This effect is a reverse effect of the Seebeck effect that was discovered by the German physicist Seebeck at earlier period. Seebeck discovered that a potential difference will be resulted between two connection points in a loop composed of two dissimilar metals, if the two junctions are maintained at different temperatures. Obviously, both of them are a kind of physical effects that does not concern with chemical change of components of the studied system.

As is well known, a chemical reaction is accompanied by the "old" chemical bond breaking and the "new" chemical bond establishment, and apparently, this must generate the heat effects. Electrochemical reaction is no exception. Its occurrence must be accompanied by heat release and heat absorption at the electrode–electrolyte interface.

Clearly, this phenomenon is not only a purely physical effect, because the electric charge moves and the electrons transfer at the electrode–electrolyte interface accompanied by the change of chemical substances and the change in entropy of the electrode reaction. This type of heat is an extension of the Peltier heat happen on the junction of two dissimilar conductors when the electric current passes. Therefore, it was called as EPH. All including the migration of charged particle, overpotential, and solution resistance and thermal physical effects can cause the heat effects at the interface. This heat absorption and release arising from various factors that include the change in the valence of substance and some irreversible effects was widely known as EPH in the earlier period. In history, EPH was even defined as one observed when electric current passes through [40–43]. Obviously, the heat effect that could be observed must involve the irreversible ingredients. Undoubtedly, if some irreversible factors are considered, this will make the meaning of the EPH effects between the electrode–electrolyte interface undefined. It should be said that this heat is not the factual EPH.

Vetter has elegantly defined [44] EPH to be the heat arising out or the heat consumption in a reversible cell reaction, i.e.

$$-T \left( \frac{\partial(\Delta G)}{\partial T} \right)_p = zFT \left( \frac{\partial \varepsilon_0}{\partial T} \right)_p \quad (1)$$

where  $\Delta G$  is the free energy change,  $z$  the electron transfer number,  $F$  the Faraday constant,  $\varepsilon_0$  the cell voltage,  $T$  the absolute temperature and  $P$  the pressure.

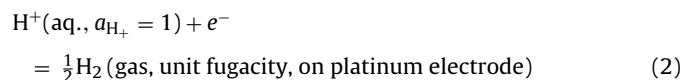
In this definition, there are two points worth noting. One is that EPH is defined as a reversible reaction heat, which essentially eliminates the various uncertainties arising from the irreversible factors such as the overvoltage, Joule heat, thermal conductivity and concentration gradient, and makes the physical quantity more definite and comparable. This indicates that EPH is a characteristic measure of a cell reaction, because the term  $(\partial(\Delta G)/\partial T)_p$  is an amount independent on reaction process, and only related to changes in the function of state. That is to say, EPH completely is determined by the initial and final states of the substances taking part in reaction on the electrode–electrolyte interface, no matter what irreversible factors, such as ions and electrons transfer, are accompanied.

Another one is that the thermodynamic functions of the standard hydrogen electrode (SHE) are taken as the reference of  $\Delta G$  and  $\varepsilon_0$  in the definition. This reference is called the “conventional scale” where all thermodynamic functions of SHE reaction including its change in free energy, change in enthalpy and change in entropy as well as its electrode potential are designated to zero at any temperature [45].

This definition where  $\varepsilon_0$  emerges also reflects that EPH differs from the physically Peltier heat, although the terminology of EPH originated in the physical phenomena. The physically Peltier heat mostly concerns with the electron transfer from an energy level (material I) to another level (material II), and it is as the difference of the “heats of evaporation” of electrons in the dissimilar conductors, I and II, there being no electric potential difference and no component change on the contact interface between the two conductors. But EPH mostly concerns with the atom reorganization and the change in valence of the active element by redox of substances under the action of the cell voltage,  $\varepsilon_0$ . Compared with EPH, the physical one is so small that it generally can be ignored.

### 3. Electrochemical Peltier heat of electrode reaction and the absolute scale

When applying Vetter's definition to a reversible electrode (or half-cell) reaction, it is no longer able to use the conventional scale as the reference of the change in free energy and the electrode potential. Otherwise, for the SHE reaction itself, we will draw a conclusion that the heat effect of the reaction is always zero in all temperatures. Obviously this is not true, because even the SHE reaction, certainly there are the “old” chemical bond fracturing and a “new” chemical bond constructing process accompanied by the emergence of the heat effect. Then, where does the problem come from? Look at the SHE reaction [45]:



In the conventional scale, the entropy of the hydrogen ion and the change in entropy of the reaction are all arbitrarily set at zero, which would result in a bigger difference between these quantities and the “real” values. Just this entropy that is arbitrarily specified to the hydrogen ion is prescribed as the reference point of the other ion entropies once again. This will also make the calculated entropy change differ from the “real” value for other electrode reaction. Therefore, the heat effect calculated by the change in entropy of the reaction must differ from that obtained experimentally. In this case, in order to make the calculated result much approximate the experimental data, we should adopt a new scale, i.e. the “absolute scale” for reference, in which the enthalpy change, the entropy change, the free energy change and its standard electrode potential for the SHE reaction are no longer specified as zero [3]. Define the reversible electrode potential of any electrode,  $\phi^*$  in the absolute

scale is as follows:

$$\phi^* = \phi(\text{vs. SHE}) + \phi^* \left( \frac{\text{H}^+}{\text{H}_2} \right) \quad (3)$$

where the amount marked with an asterisk is on the “absolute scale” (the same below),  $\phi^*(\text{H}^+/\text{H}_2)$  the electrode potential of SHE on this scale and  $\phi(\text{vs. SHE})$  on the conventional scale. And designate both  $\phi^*$  and  $\phi^*(\text{H}^+/\text{H}_2)$  at  $T \rightarrow 0$  as zero.

On this scale, the entropy change for a single-electrode reaction,  $\Delta S^*_T$  will be characterized as:

$$\Delta S^*_T = zF \left( \frac{\partial \phi^*_T}{\partial T} \right)_p \quad (4)$$

When integrating of Eq. (4), the integral constant,  $\Delta S^*_T$  approaches to zero at  $T \rightarrow 0$  based on the third law of thermodynamics.

The corresponding EPH of the electrochemical reaction,  $\Pi$  is defined as

$$\Pi = -T \left( \frac{\partial(\Delta G^*)}{\partial T} \right)_p = T(\Delta S^*)_{i \rightarrow 0}, \quad (5)$$

or

$$\Pi = zFT \left( \frac{\partial \phi^*_T}{\partial T} \right)_{p, i \rightarrow 0}, \quad (6)$$

where  $i \rightarrow 0$  indicates that the considered electrode reaction progresses in reversible manner. It should be noted that in this scale, the electronic entropy is specified as zero [46,47].

The EPH of the electrode reaction defined by Eq. (5) or Eq. (6) is all similar to that of a cell except on the absolute scale. These equations indicate that EPH of a half-cell, just like that of the cell reaction, is also a quantity only related to the changes in the function of state, i.e. in entropy on the absolute scale, of substances taking part in reaction. Even for the adsorption of hydrogen between the electrode and solution, the stepwise change of the Peltier heats is related to the change in entropy of hydrogen species with gradually change in bonded strengths in the reversible process [21]. For a reversible equilibrium, all charge transfer across the phase boundaries between solid or gaseous electrode and solution, any quantity related to process, such as the transferring heats of ions or electrons, and the entropy production due to these factors can entirely be ignored. In the data-processing [3,17], all of those quantities due to the various polarization (irreversibility) are eliminated by extrapolating the electric current to zero, removing thoroughly the impact of the irreversible factors.

According to the relationship between the electrode potentials on the absolute scale and the conventional scale (Eq. (3)), for the thermodynamic functions such as the free energy  $G$ , the entropy  $S$  and the enthalpy  $H$ , we have:

$$\Delta S^* = \Delta S + z\Delta S^* \left( \frac{\text{H}^+}{\text{H}_2} \right), \quad (7)$$

$$\Delta G^* = \Delta G + z\Delta G^* \left( \frac{\text{H}^+}{\text{H}_2} \right), \quad (8)$$

$$\Delta H^* = \Delta H + z\Delta H^* \left( \frac{\text{H}^+}{\text{H}_2} \right), \quad (9)$$

where  $\Delta S^*(\text{H}^+/\text{H}_2)$ ,  $\Delta G^*(\text{H}^+/\text{H}_2)$  and  $\Delta H^*(\text{H}^+/\text{H}_2)$  are the corresponding thermodynamic functions of the SHE reaction with a single electron transfer on the absolute scale,  $z$  is the electron transfer number of the considered electrode reaction.

According to Eq. (5), the change in entropy,  $\Delta S^*_T$ , of an electrode reaction on the absolute scale at any temperature except the absolute zero can be identified by electrochemical-calorimetry

measurement of  $\prod$  at constant temperature. Then  $\phi_T^*$  can be obtained by means of the integral of Eq. (4) with integral interval from the absolute zero to a specified temperature  $T$  at constant pressure:

$$\phi_T^* = \int \left[ \frac{\Delta S_T^* dT}{zF} \right]_p \quad (10)$$

When integrating of Eq. (10),  $\Delta S_0^*$  and the integral constant  $\phi_0^*$  all approach zero at  $T \rightarrow 0$ .

It should be emphasized that the establishment of the absolute scale is dependant on the determination of  $\Delta S_T^*$  according to Eq. (10).

For any electrode reaction, the specification of  $\phi_0^* = 0$  and  $\Delta S_0^* = 0$  at  $T \rightarrow 0$  results in  $\Delta G_0^* = -zF\phi_0^* = 0$  and  $\Delta H_0^* = \Delta G_0^* + T\Delta S_0^* = 0$  at this temperature. Therefore, the thermodynamic functions such as  $\Delta G_T^* = -zF\phi_T^*$  and  $\Delta H_T^* = \Delta G_T^* + T\Delta S_T^*$  at the specified temperature  $T$  ( $T \neq 0$ ) can be obtained.

Evidently, when Eq. (5) or (6) is applied to a cell reaction, the terms,  $\phi^*(\text{H}^+/\text{H}_2)$  in Eq. (3) or  $\Delta S^*(\text{H}^+/\text{H}_2)$  in Eq. (7), common to both electrodes of the cell, does not appear explicitly because they are deleted ultimately.  $\Delta S^*$  in Eq. (7) and  $\phi^*$  in Eq. (3) can respectively be replaced by the corresponding functions on the conventional scale; the expression is reduced to Vetter's definition. It is obvious that the definition in Eq. (1) is a special case of Eq. (5) or (6) which could be more widely used.

Here it should be pointed out that the values of thermodynamic functions on the "absolute scale" are or not "real" in the absolute sense. In the previous time, certain definitions on the absolute potentials of a cell or a half-cell proceed from various points of view have been given [48–77], the results of the absolute potential for the SHE reaction were estimated and measured by experiments [65,69,70,72,74], and also recommended by IUPAC. According to these definitions it have been endeavoring to look for the "real" absolute values of the single electrode. But what we do here is only to find a scale for solving how to obtain EPH of a single electrode. The scale is called as "absolute scale" that is merely relative to the "conventional scale". The value of  $\phi_T^*$  in the present scale cannot be said to be a "real" or "absolute" potential, and these thermodynamic functions like  $\Delta S^*$ ,  $\Delta G^*$  and  $\Delta H^*$  are not the "real" values either. They are only the relative quantities that are obtained based on this reference, i.e.  $\phi_T^* \rightarrow 0$  and  $\Delta S_T^* \rightarrow 0$  when  $T \rightarrow 0$ . The "absolute scale" never means it is "absolute" or "real" value, although the words like "absolute" or "real" are used in the text. In fact, any quantity, even so-called the "real" or "absolute", is entirely on a certain reference. In addition, the absolute scale presented here is an exercisable manner on which EPH of an electrode reaction can expediently be obtained by experiments. As considered generally, "the question is not which is the true "absolute" electrode potential, but which provides the most convenient reference for practical impact" [77]. Actually, the Chemists have also tried to uncover the "absolute" value of standard entropy of hydrogen ions [78–81]. They used thermal cell to measure its temperature coefficients, or its electromotive force. However, as stated above, even the absolute entropy, it also takes the assumption of the zero electronic entropy as a Reference [46]. In the conventional scale, according to the ad hoc assumption that the thermodynamic functions such as the Gibbs free energy of formation, the enthalpy of formation, and the entropy of formation of hydrogen ion in water at 25 °C and the standard atmosphere pressure are taken to be zero [82], thus, the electronic entropy is calculated to be 65.29 J mol<sup>-1</sup> K<sup>-1</sup>. This value is far bigger than the electronic entropy obtained by the Fermi-Dirac statistics applied to the electron gas in metal. The electronic entropy obtained on this statistics is so small that it even can approximately be treated as zero. Therefore, the assumption of the zero electronic

entropy in the absolute scale is much close to "verity". In a word, the value in "the absolute scale" is not real one, it still is related to a certain reference, merely it is much close the "real" compared with that based on ad hoc assumption. Just the assumption that the electronic entropy is zero, and  $\phi_T^* \rightarrow 0$  and  $\Delta S_T^* \rightarrow 0$  at  $T \rightarrow 0$ , is much close to "verity", the reference presented in this paper is called as the "absolute scale" in this sense.

#### 4. Fundamental equations for reversible electrode reaction in thermoelectric-chemistry

For a reversible electrode reaction, on the absolute scale, we still have the following relationship:

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (11)$$

Combining Eqs. (5), (7), (8) and (9) with (11), and noting that  $\Delta G = -W_e$  (vs. SHE) =  $-zF\phi$ , we have

$$\prod -W_e \text{ (vs. SHE)} = \Delta H^\circ \quad (12)$$

or

$$\prod -zF\phi \text{ (vs. SHE)} = \Delta H^\circ \quad (13)$$

where  $W_e$  is the reversible electric work done on the conventional scale,  $\Delta H^\circ = \Delta H + zT\Delta S^*(\text{H}^+/\text{H}_2)$ , which is called as the apparent enthalpy change. Note that  $\Delta S^*(\text{H}^+/\text{H}_2)$  at a given temperature is a constant.

According to Faraday's law, for more than or less than one mole change, Eqs. (5) and (12) can be rewritten as

$$\prod = T\Delta S^* \left( \int \frac{idt}{zF} \right)_{i \rightarrow 0} \quad (14)$$

and

$$\prod -W_e \text{ (vs. SHE)} = \Delta H^\circ \int \frac{idt}{zF} \quad (15)$$

where  $i$  is electric current and  $t$  time. Eqs. (14) and (15) are the fundamental equations for the electrode reaction. They are also another expression of the second law and the first law of thermodynamics used to the electrode reaction, respectively.

When a small electric current passes through, Eq. (14) can be approximately written as

$$Q = T\Delta S^* \int \frac{idt}{zF} \quad (16)$$

Being differential on both sides of Eq. (16) and letting  $i \rightarrow 0$ , we get

$$\Delta S^* = k \left( \frac{q}{i} \right)_{i \rightarrow 0} \quad (17)$$

where  $k = zF/T$  and  $q = dQ/dt$  which is called as the heat flow. The ratio of the heat flow to the electric current at  $i \rightarrow 0$ ,  $(q/i)_{i \rightarrow 0}$  is defined as the electrochemical Peltier coefficient and represented by the symbol,  $\pi$ . This definition of the coefficient is completely similar to one in physics in format [83]. Eq. (17) indicates that EPH can be obtained by  $zF(q/i)_{i \rightarrow 0}$ . Formula (17) is also the fundamental equation to obtain the entropy change on the absolute scale and EPH for an electrode reaction.

#### 5. The entropy change and electrochemical Peltier heat for SHE reaction

In a relatively long period of time, the EPHs of a number of electrode reactions were experimentally measured. However, the values of enthalpy changes obtained based on the measured EPHs

are different from those calculated with the currently thermodynamic data of ions. For an electrode reaction with the same temperature and the same electron transfer number, the difference between them is almost a constant [4]. For this phenomenon it has not a reasonable explanation so far, and it greatly influenced the development of thermoelectrochemistry.

According to classical thermodynamics, the first law of thermodynamics at constant pressure can be written as

$$Q - W_e \text{ (vs. SHE)} = \Delta H \quad (18)$$

It can be seen that the calculated value on the current thermodynamic databank of ions is the change in enthalpy of the electrode reaction, while the value on thermoelectrochemical experiments is the apparent enthalpy change (see Eq. (12)). They just differ by a constant that is  $zT\Delta S^*(\text{H}^+/\text{H}_2)$ . If adding  $zT\Delta S^*(\text{H}^+/\text{H}_2)$  to both sides of Eq. (18) at same time and noting that  $Q = T\Delta S$  and  $\Pi = T\Delta S^*$ , we will get Eq. (12). The difference between the two terms about the enthalpy changes,  $\Delta H^\circ$  in Eq. (12) and  $\Delta H$  in Eq. (18), is just a constant that is EPH of the SHE reaction at temperature  $T$ ,  $zT\Delta S^*(\text{H}^+/\text{H}_2)$ . Thus, the difference between  $Q$  and  $\Pi$  for the electrode reaction is  $zT\Delta S^*(\text{H}^+/\text{H}_2)$ .

**Table 1**

The entropy change on absolute scale, EPHs and the electrochemical Peltier coefficients for some standard electrode reactions in aqueous solution at 298.15 K<sup>a</sup>.

Electrode reaction	$\Delta S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta S^*$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Pi$ (kJ mol <sup>-1</sup> )	$\pi$ (V)
H <sup>+</sup> + e <sup>-</sup> = 0.5H <sub>2</sub>	0	87.6 ± 1.0	26.1 ± 0.3	0.27 <sub>1</sub>
Ag <sup>+</sup> + e <sup>-</sup> = Ag	-95.41	-7.8 ± 1.0	-2.3 ± 0.3	-0.02 <sub>0</sub>
Cu <sup>+</sup> + e <sup>-</sup> = Cu	-72.73	14.9 ± 1.0	4.4 ± 0.3	0.04 <sub>6</sub>
Be <sup>2+</sup> + 2e <sup>-</sup> = Be	8.66	183.9 ± 2.0	54.8 ± 0.6	0.28 <sub>4</sub>
Mg <sup>2+</sup> + 2e <sup>-</sup> = Mg	40.19	215.4 ± 2.0	64.2 ± 0.6	0.33 <sub>3</sub>
Ca <sup>2+</sup> + 2e <sup>-</sup> = Ca	-36.02	139.2 ± 2.0	41.5 ± 0.6	0.21 <sub>5</sub>
Sr <sup>2+</sup> + 2e <sup>-</sup> = Sr	-45.64	129.6 ± 2.0	38.6 ± 0.6	0.20 <sub>0</sub>
Ba <sup>2+</sup> + 2e <sup>-</sup> = Ba	-77.86	97.3 ± 2.0	29.0 ± 0.6	0.15 <sub>0</sub>
Ra <sup>2+</sup> + 2e <sup>-</sup> = Ra	-113.84	61.4 ± 2.0	18.3 ± 0.6	0.09 <sub>5</sub>
Mn <sup>2+</sup> + 2e <sup>-</sup> = Mn (α)	-24.93	150.3 ± 2.0	44.8 ± 0.6	0.23 <sub>2</sub>
Co <sup>2+</sup> + 2e <sup>-</sup> = Co	12.43	187.6 ± 2.0	55.9 ± 0.6	0.29 <sub>0</sub>
Ni <sup>2+</sup> + 2e <sup>-</sup> = Ni	28.16	203.4 ± 2.0	60.6 ± 0.6	0.31 <sub>4</sub>
Cu <sup>2+</sup> + 2e <sup>-</sup> = Cu	2.15	177.4 ± 2.0	52.9 ± 0.6	0.27 <sub>4</sub>
Al <sup>3+</sup> + 3e <sup>-</sup> = Al	154.21	417.0 ± 3.0	124.3 ± 0.9	0.43 <sub>0</sub>
Co <sup>3+</sup> + 3e <sup>-</sup> = Co	139.60	402.4 ± 3.0	120.0 ± 0.9	0.41 <sub>4</sub>
Sc <sup>3+</sup> + 3e <sup>-</sup> = Sc	94.00	356.8 ± 3.0	106.4 ± 0.9	0.36 <sub>8</sub>
Y <sup>3+</sup> + 3e <sup>-</sup> = Y	99.60	362.4 ± 3.0	108.1 ± 0.9	0.37 <sub>3</sub>
La <sup>3+</sup> + 3e <sup>-</sup> = La	78.6	341.4 ± 3.0	101.8 ± 0.9	0.35 <sub>2</sub>
Ce <sup>3+</sup> + 3e <sup>-</sup> = Ce	81.11	343.9 ± 3.0	102.5 ± 0.6	0.35 <sub>4</sub>
Nd <sup>3+</sup> + 3e <sup>-</sup> = Nd	82.37	345.2 ± 3.0	102.9 ± 0.9	0.35 <sub>6</sub>
Sm <sup>3+</sup> + 3e <sup>-</sup> = Sm	85.42	348.2 ± 3.0	103.8 ± 0.9	0.35 <sub>9</sub>
Eu <sup>3+</sup> + 3e <sup>-</sup> = Eu	103.66	366.5 ± 3.0	109.3 ± 0.9	0.37 <sub>7</sub>
Gd <sup>3+</sup> + 3e <sup>-</sup> = Gd	78.06	340.9 ± 3.0	101.6 ± 0.9	0.35 <sub>1</sub>
Tb <sup>3+</sup> + 3e <sup>-</sup> = Tb	103.29	366.1 ± 3.0	109.1 ± 0.9	0.37 <sub>7</sub>
Dy <sup>3+</sup> + 3e <sup>-</sup> = Dy	109.86	372.7 ± 3.0	111.1 ± 0.9	0.38 <sub>4</sub>
Ho <sup>3+</sup> + 3e <sup>-</sup> = Ho	106.22	369.0 ± 3.0	110.0 ± 0.9	0.38 <sub>0</sub>
Er <sup>3+</sup> + 3e <sup>-</sup> = Er	121.65	384.5 ± 3.0	114.6 ± 0.9	0.39 <sub>6</sub>
Tm <sup>3+</sup> + 3e <sup>-</sup> = Tm	120.82	383.6 ± 3.0	114.4 ± 0.9	0.39 <sub>5</sub>
Yb <sup>3+</sup> + 3e <sup>-</sup> = Yb	102.49	365.3 ± 3.0	108.9 ± 0.9	0.37 <sub>6</sub>
Lu <sup>3+</sup> + 3e <sup>-</sup> = Lu	118.68	381.5 ± 3.0	113.7 ± 0.9	0.39 <sub>3</sub>
Am <sup>3+</sup> + 3e <sup>-</sup> = Am	25.88	288.7 ± 3.0	86.1 ± 0.9	0.29 <sub>7</sub>
Ce <sup>4+</sup> + 4e <sup>-</sup> = Ce	112.05	462.5 ± 4.0	137.9 ± 0.9	0.35 <sub>7</sub>
S(orth) + 2e <sup>-</sup> = S <sup>2-</sup>	-176.73	-1.5 ± 2.0	-0.5 ± 0.6	-0.00 <sub>2</sub>
Cl <sub>2</sub> + 2e <sup>-</sup> = 2Cl <sup>-</sup>	-240.58	-65.4 ± 2.0	-19.5 ± 0.6	-0.10 <sub>1</sub>
Br <sub>2</sub> (l) + 2e <sup>-</sup> = 2Br <sup>-</sup>	-117.96	57.2 ± 2.0	17.1 ± 0.6	0.08 <sub>8</sub>
I <sub>2</sub> + 2e <sup>-</sup> = 2I <sup>-</sup>	-24.097	151.1 ± 2.0	45.1 ± 0.6	0.23 <sub>3</sub>
Fe(CN) <sub>6</sub> <sup>3+</sup> + e <sup>-</sup> = Fe(CN) <sub>6</sub> <sup>4-</sup>	-240.6	-153.0 ± 1.0	-45.6 ± 0.3	-0.47 <sub>3</sub>
Co <sup>3+</sup> + e <sup>-</sup> = Co <sup>2+</sup>	127.17	214.8 ± 1.0	64.0 ± 0.3	0.66 <sub>4</sub>
Fe <sup>3+</sup> + e <sup>-</sup> = Fe <sup>2+</sup>	112.95	200.6 ± 1.0	59.8 ± 0.3	0.62 <sub>0</sub>
MnO <sub>4</sub> <sup>-</sup> + e <sup>-</sup> = MnO <sub>4</sub> <sup>2-</sup>	-197.92	-110.3 ± 1.0	-32.9 ± 0.3	-0.34 <sub>1</sub>
CuCl + e <sup>-</sup> = Cu + Cl <sup>-</sup>	-61.85	25.8 ± 1.0	7.7 ± 0.3	0.08 <sub>0</sub>
AgCl + e <sup>-</sup> = Ag + Cl <sup>-</sup>	-62.49	25.1 ± 1.0	7.5 ± 0.3	0.07 <sub>8</sub>
AgBr + e <sup>-</sup> = Ag + Br <sup>-</sup>	-47.42	40.2 ± 1.0	12.0 ± 0.3	0.12 <sub>4</sub>
AgI + e <sup>-</sup> = Ag + I <sup>-</sup>	-26.92	60.7 ± 1.0	18.1 ± 0.3	0.18 <sub>7</sub>
AuCl + e <sup>-</sup> = Au + Cl <sup>-</sup>	-54.29	33.3 ± 1.0	9.9 ± 0.3	0.10 <sub>3</sub>
Au(CN) <sub>2</sub> <sup>-</sup> + e <sup>-</sup> = Au + 2CN <sup>-</sup>	-1.15	86.5 ± 1.0	25.8 ± 0.3	0.26 <sub>7</sub>
AuCl <sub>4</sub> <sup>-</sup> + 3e <sup>-</sup> = Au + 4Cl <sup>-</sup>	-189.47	73.3 ± 3.0	21.9 ± 0.9	0.07 <sub>6</sub>
PtCl <sub>4</sub> <sup>2-</sup> + 2e <sup>-</sup> = Pt + 4Cl <sup>-</sup>	-17.82	157.4 ± 2.0	46.9 ± 0.6	0.24 <sub>3</sub>
Hg <sub>2</sub> Cl <sub>2</sub> + 2e <sup>-</sup> = 2Hg(l) + 2Cl <sup>-</sup>	-58.03	117.2 ± 2.0	34.9 ± 0.6	0.18 <sub>1</sub>
Zn(OH) <sub>2</sub> (β) + 2e <sup>-</sup> = Zn + 2OH <sup>-</sup>	-191.62	-16.4 ± 2.0	-4.9 ± 0.6	-0.02 <sub>5</sub>
Cd(CN) <sub>4</sub> <sup>2-</sup> + 2e <sup>-</sup> = Cd(γ) + 4CN <sup>-</sup>	-24.43	150.8 ± 2.0	45.0 ± 0.6	0.23 <sub>3</sub>
AsO <sub>2</sub> <sup>-</sup> + 2H <sub>2</sub> O + 3e <sup>-</sup> = As(α) + 4OH <sup>-</sup>	-384.99	-122.2 ± 3.0	-36.4 ± 0.9	-0.12 <sub>6</sub>
AsO <sub>4</sub> <sup>3-</sup> + 2H <sub>2</sub> O + 2e <sup>-</sup> = AsO <sub>2</sub> <sup>-</sup> + 4OH <sup>-</sup>	-109.24	66.0 ± 2.0	19.7 ± 0.6	0.10 <sub>2</sub>
Ba(OH) <sub>2</sub> ·8H <sub>2</sub> O + 2e <sup>-</sup> = Ba + 8H <sub>2</sub> O + 2OH <sup>-</sup>	42.80	218.0 ± 2.0	65.0 ± 0.6	0.33 <sub>7</sub>
S(orth) + 2H <sup>+</sup> + 2e <sup>-</sup> = H <sub>2</sub> S(g)	43.68	218.9 ± 2.0	65.3 ± 0.3	0.33 <sub>8</sub>
H <sub>3</sub> BO <sub>3</sub> (aq) + 3H <sup>+</sup> + 3e <sup>-</sup> = B + 3H <sub>2</sub> O	-142.61	120.2 ± 3.0	35.8 ± 0.9	0.12 <sub>4</sub>
WO <sub>3</sub> + 6H <sup>+</sup> + 6e <sup>-</sup> = W + 3H <sub>2</sub> O	-225.22	300.4 ± 6.0	89.6 ± 1.8	0.15 <sub>5</sub>
Al(OH) <sub>3</sub> + 3e <sup>-</sup> = Al + 3OH <sup>-</sup>	-270.93	-8.1 ± 3.0	-2.4 ± 0.9	-0.00 <sub>8</sub>
O <sub>2</sub> + 2H <sub>2</sub> O(l) + 4e <sup>-</sup> = 4OH <sup>-</sup>	-649.03	-298.6 ± 4.0	-89.0 ± 1.2	-0.23 <sub>1</sub>
O <sub>2</sub> + 4H <sup>+</sup> + 4e <sup>-</sup> = 2H <sub>2</sub> O(l)	-326.36	24.0 ± 4.0	7.2 ± 1.2	0.01 <sub>9</sub>

<sup>a</sup> The data used in this table are taken from the literature [85].

In Eq. (18),  $Q$  is a product of temperature  $T$  and the change in entropy derived from the current ion thermodynamic data, and is named as “the calculated heat effect”; while in Eq. (12),  $\Pi$  is the heat effect identified by the experiments, called as “the measured heat effect” or EPH of electrode reaction. The difference between them is  $zT\Delta S^*(H^+/H_2)$ .

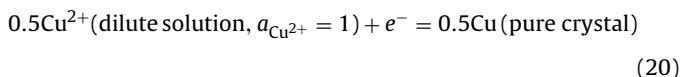
In order to obtain  $\Delta S^*(H^+/H_2)$  of the SHE reaction and its EPH, an experiment of the  $K_3Fe(CN)_6/K_4Fe(CN)_6$  electrode redox with the excellent reversibility was conducted [3]. From this, the change in entropy for SHE reaction with the single-electron transfer on the absolute scale at 298.15 K is achieved to be  $(87.6 \pm 1.0) J K^{-1} mol^{-1}$ , and the corresponding EPH  $(26.1 \pm 0.3) kJ mol^{-1}$ . From this the entropy of hydrogen ions on the absolute scale is derived as  $-22.3 J K^{-1} mol^{-1}$ , which is very close to  $-22.2 J K^{-1} mol^{-1}$ , an average of the results obtained by the researchers from Eastman (1926) to Ikeda (1965) in 40 years [84].

Thus it can be seen that the entropy value for the SHE reaction is zero and the partial molal entropy of hydrogen ions is zero, too, on the conventional scale, which makes those problems referred to in introduction be hard to resolve; while both of them are not zero on the absolute scale. The “absolute scale” is a successful reference frame to study thermoelectrochemistry. Based on this scale, it is possible to get the entropy change and EPH, which are very close to “real”, for the SHE reaction. Also by means of this scale, it is possible to get these physical quantities for other electrodes, especially, at the standard states (or standard electrode reaction). For the standard electrode reactions, it is hard to measure their EPHs directly before, because the standard states of some substances, such as ions in dilute solution, even are a physically unrealizable in most cases. Even so, according to the absolute scale, we still can estimate their EPHs. Take the following reaction as an example



where all species participating in the process lie to the each standard state. It has been calculated that the standard entropy change of the reaction  $\Delta S^\ominus$  is  $-240.597 J K^{-1} mol^{-1}$  from the literature data [85],  $\Delta S^* = \Delta S^\ominus + \Delta S^*(H^+/H_2) = -153.0 J K^{-1} mol^{-1}$ , and its EPH,  $\Pi$  is equal to  $T\Delta S^* = -45.6 kJ mol^{-1}$  at 298.15 K according to Eq. (5). This value is good in agreement with the experimental result of  $-45.61 kJ mol^{-1}$  [3].

Another example is the standard electrode reaction:



The standard entropy change of the reaction,  $\Delta S^\ominus$  is  $1.075 J K^{-1} mol^{-1}$  [85] and  $\Delta S^* = 88.7 J K^{-1} mol^{-1}$ , thus its EPH,  $\Pi$  at 298.15 K is equal to  $26.45 kJ mol^{-1}$  that is good in agreement with about  $26.5 kJ mol^{-1}$  obtained by our unpublished work of experiment and differs from “calculated heat”  $Q = T\Delta S^\ominus = 0.32 kJ mol^{-1}$ . The entropy changes on the absolute scale, EPHs and the electrochemical Peltier coefficients,  $\pi$  for some of the most common standard electrode reactions in aqueous solution at 298.15 K are listed in Table 1 where all species taking part in the electrode reactions are at each standard state, i.e. the stably pure condensed state at the normal atmosphere pressure for solid or liquid, the hypothetical ideal gas at unit fugacity for gas, and the ideal solution where the activity of ions at unit (molality) concentration is 1 for ions. The data used to calculate the entropy change in Table 1 are taken from the literature [85].

## 6. A final note

In this paper, we discuss EPH of a single electrode process. Firstly, a defined formula different from the electrochemical Peltier heat of the cell reaction is given. The present definition is not only

applicable to a half-cell, but also can cover the original one that only is valid to a cell. From this, an energy conservation equation based on the equilibrium thermodynamics, which is able to be applied to the electrode reaction, is set up. In the new equation, a reference that is called as the absolute scale is established. The change in entropy of SHE on the absolute scale is not arbitrarily set at zero, while determined experimentally to be  $87.6 J K^{-1} mol^{-1}$ . Secondly, the reversible heat effect, or EPH between the electrode–electrolyte interfaces, can be obtained provided that the change in entropy of reaction on the absolute scale is known, although it also can be approximately obtained by means of the heat balance under the steady state or quasi-stationary conditions, as well as by the irreversible thermodynamics. Thirdly, in order to obtain EPH of an electrode reaction, an important treatment is that the electric current needs to be extrapolated to zero in the data-processing. Hence, the irreversible impacts can be totally separated and removed out. The set up of the absolute scale and the evaluation of the change in entropy of SHE on this scale are beneficial to resolve those two questions which are mentioned at the beginning of this paper.

In this paper, we give a concept of the electrode potential on “absolute scale”. Evidently, this is only relative to the conventional scale; therefore, it still is a relative value, although it is labeled to “absolute scale”. The quantity is based on the third law of thermodynamics as well as an assumption that the electronic entropy is designed to zero, which much closer truth than that the potential of SHE is arbitrarily set at zero. Differing from measuring “the absolute potential” of an electrode by the determination of the work functions at present, the method presented here needs to measure the temperature-dependent entropy change of the electrode reaction on the absolute scale to acquire the potential that is called to be one on the “absolute scale”.

In a word, understanding these fundamental issues, one can get the relationship between the thermodynamic functions on the conventional and the absolute scale, and obtain EPHs and the changes in entropy for some electrode reactions on the absolute scale, as a result greatly enriching the thermodynamic database such as the heat effects at the various electrode–electrolyte interfaces under the reversible condition and the changes in entropy on the absolute scale at different temperatures. This also provides a new scale to study the electrode reaction, and can benefit the further development of the thermoelectrochemistry and expand its practical application.

## Acknowledgements

The author would like express his gratitude to the National Natural Science Foundation of China (No. 50874119) which provided the financial support. The author also thanks the Postgraduate, Miss Yan-hua Liu for the data check.

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