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# Theory and Application of Thermoelectrochemistry

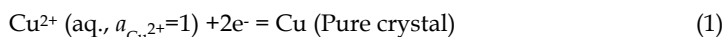
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## 1. Introduction

Thermoelectrochemistry (TEC) is a subject that combines the theories and techniques of both thermo- and electro-chemistry to investigate the cell and electrode reactions [1]. That is, the parameters of thermodynamics [2-4] and kinetics [5] 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. Therefore, TEC can provide the available and expansively additional information more for electrochemical reactions. It compensates the insufficiency for a single electrochemical study or a single thermochemical research to some extent. In earlier period, a lot of techniques and instruments used to research the heat effects of cell and half-cell was set up [6-30], such as thermoelectric power measurements [6,7], electrolytic calorimeter [8], controlled-potential and controlled-current polarizations [9], Kinetic method on the stationary heat effect [10], non-stationary temperature wave method [11], cyclic-voltammetry-thermometry[12], Lumped-heat-capacity analysis [13], steady state electrolysis [14], differential voltammetric scanning thermometry [15], acoustic calorimetry[16], thermistor probe determination[17], potentiodynamic and galvanostatic transient techniques [18], non-isothermal cell [19], etc to obtain the electrochemical Peltier heat (EPH) of the electrode reactions.

In these researches, a mainly purpose is to acquire EPHs of cell or half-cell reactions. The EPH could be considered as a basic issue of TEC. Before the identification of this problem there had been two puzzled questions, 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. However, this formula that is valid for most reactions is not viable at least for a reversible single electrode reaction in aqueous solution. For a reversible single electrode reaction, the experimental value of the heat effect is not in agreement with that calculated on the current thermodynamic databank of ions, that is, with which, the product of the calculated entropy change and the temperature of the electrode reaction always differs from the experimental measurements [2]. For example, for the electrode reaction at the standard state:



where  $a_{\text{Cu}^{2+}}$  is activity of copper ions, and metal copper and its ions lie to the each standard state. Its change in entropy is calculated to be about  $\Delta S^\ominus = S^\ominus_{\text{Cu}} - 2S^\ominus_{\text{e}^-} - S^\ominus_{\text{Cu}^{2+}} = 2.2 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . The heat effects,  $Q$  should be  $T\Delta S^\ominus = 0.65 \text{ kJ}\cdot\text{mol}^{-1}$  at 298.15K, but it was evaluated by an experimental as  $52.8 \text{ kJ}\cdot\text{mol}^{-1}$ . The difference of both is bigger. Another problem is that there had been no workable method that could be used to calculate or predict the “real” heat effect of a standard reversible electrode reaction by means of the current thermodynamic knowledge. For example, we did not know how to get the value of heat effects,  $52.8 \text{ kJ}\cdot\text{mol}^{-1}$  for reaction (1) except the experiment at least up to now. These two problems should be resolved in TEC discipline.

In order to identify EPHs of the cell or electrode reactions from the experimental information, there had been two principal approaches of treatments. One was based on the heat balance under the steady state or quasi-stationary conditions [6, 11, 31]. This treatment considered all heat effects including the characteristic Peltier heat and the heat dissipation due to polarization or irreversibility of electrode processes such as the so-call heats of transfer of ions and electron, the Joule heat, the heat conductivity and the convection. Another was to apply the irreversible thermodynamics and the Onsager's reciprocal relations [8, 32, 33], 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. Of course, there also were other methods, for instance, the numerical simulation with a finite element program for the complex heat and mass flow at the heated electrode was also used [34].

## 2. Electrochemical Peltier heat and the absolute scale

### 2.1 The electrochemical Peltier heat of cell reaction

The terminology of EPH originated from the thermoelectric phenomena in Physics. Dated back to more than 100 years ago, such as the Seebeck effect, the Peltier effect and the Thomson effect were successively discovered. The Peltier heat was first found by the French physicist Peltier in 1834. 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, which depends on the direction of the electric current. And the strength of the heat was found to be proportional to the current intensity. The Peltier effect can express as [35]

$$dQ(T)/dt = \pi_{\text{I-II}} i \quad (2)$$

where  $i$  is electric current,  $Q(T)$ , Peltier heat dependent on temperature,  $T$  in Kelvin,  $t$ , time and  $\pi_{\text{I-II}}$ , the Peltier coefficient which, sometimes, is considered as the difference of the “heats of evaporation” of electrons in the dissimilar metals, I and II.

The Peltier effect is a reverse one of the Seebeck effect that was discovered by the German physicist Seebeck at earlier period (1822). 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. Thereafter, in 1854, the English physicist Lord Kelvin (W. Thomson) was to discover that a uniform conductor with electric current passing through will suck heat up from the surrounding when there has a temperature gradient in the conductor, which is called as the Thomson effect.

In 1877, Mill called the heat effects in the electrochemical reactions as the electrochemical Peltier heats. Later, Bouty and Jahn demonstrated experimentally the EPH effects. Subsequently, a few of experimental studies on the heat effects for the electrochemical cells had also been presented. However, the heat effects in physics are different from those in electrochemical reactions. No distinct definition for EPH was given in history, except it was defined as the heat effects observed when electric current passes through. Obviously, this definition is not precise.

Vetter has elegantly defined the EPH effect to be the heat arising out or the heat consumption in a reversible cell reaction[36], i.e.

$$-T \left( \frac{\partial (\Delta G)}{\partial T} \right)_P = z \mathcal{F} T \left( \frac{\partial \varepsilon_0}{\partial T} \right)_P \quad (3)$$

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

Two features of this definition are worth noting. One is that EPH is defined as the heat of a reversible reaction, which essentially eliminates the various uncertainties arising from the irreversible factors such as overvoltage, Joule heat, thermal conductivity, concentration gradient and forced transfer of various particles like ions and electrons in electrical field, and makes the physical quantity more definite and comparable. This indicates that EPH is a characteristic measure of a cell reaction, because the term  $\left( \frac{\partial (\Delta G)}{\partial T} \right)_P$  is an amount independent on reaction process, and only related to changes in the function of state. That is to say, EPH is determined only by the initial and the final states of the substances taking part in the reaction that occurs on the electrode-electrolyte interfaces, although other heats due to irreversible factors are accompanied. EPH is, unlike the heat of dissipation (Joule heat and the heats due to irreversibility of electrode processes and transfer processes), one of the fundamental characteristics of the electrode process.

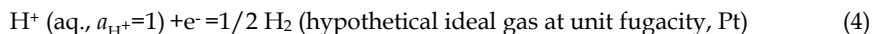
Another one is that the thermodynamic functions of the standard hydrogen electrode (SHE) are taken as the reference of  $\Delta G$  and  $\varepsilon_0$  in this definition. This reference is called the "conventional scale" where all thermodynamic functions of SHE reaction including its free energy change,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

This definition, where  $\varepsilon_0$  emerges, also reflects that EPH differs from the physically Peltier heat, although the terminology of "Peltier heat" originated from the physical phenomena. The physically Peltier heat mostly concerns with the electron transfer from an energy level (material I) to another level (material II), there being no electric potential difference and no change in composition of substances on the contact interfaces between two conductors, so that it is called as the difference of the "heats of evaporation" of electrons in the materials, I and II. But, EPH mostly concerns with the atom reorganization and the change of valence of the active element by redox of substances under the action of the cell voltage,  $\varepsilon_0$ . Compared with EPH, the physically Peltier heat is so small that it generally can be ignored. Like the contact point between copper and silver, the Peltier coefficient is about  $100 \times 10^{-6}$  volt [35] according to Fermi-Dirac statistics used to free electron gas in metal, while the electrochemical Peltier coefficient of the redox between copper and its ions is 0.274 volt [1].

## 2.2 The electrochemical Peltier heat of electrode reaction and the absolute scale

When applying the 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 free energy change and the

electrode potential. Otherwise, for the SHE reaction itself, we will draw a conclusion that the heat effects of the reaction are 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 [1]. Then where does the problem come from? Look at the SHE reaction:



In the conventional scale, the entropy of the hydrogen ion and the change in entropy of this reaction are all arbitrarily set at zero [37], 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 taken as 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 based on 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 to the experimental data, we should adopt a new reference scale, i.e. the “absolute scale” as the reference, in which the enthalpy change, the entropy change, the free energy and its standard electrode potential for the SHE reaction are not able to be arbitrarily specified as zero. Define the reversible electrode potential of any electrode,  $\phi^*$ , in the absolute scale as follows [38]:

$$\phi^* = \phi (\text{vs. SHE}) + \phi^*(\text{H}^+/\text{H}_2), \quad (5)$$

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  $\phi$  (vs. SHE) on the conventional scale. And both  $\phi^*$  and  $\phi^*(\text{H}^+/\text{H}_2)$  are designated to zero when  $T \rightarrow 0$  [2].

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

$$\Delta S^*_T = z \mathcal{F} (\partial \phi^*_T / \partial T)_P, \quad (6)$$

When integrating Eq.(6), the integral constant,  $\Delta S^*_0$  is appointed to zero at  $T \rightarrow 0$  based on the third law of thermodynamics.

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

$$\Pi = z \mathcal{F} T (\partial \phi^* / \partial T)_{P, i \rightarrow 0}, \quad (7)$$

or

$$\Pi = -T (\partial (\Delta G^*) / \partial T)_P = T (\Delta S^*)_{P, i \rightarrow 0}, \quad (8)$$

where  $i \rightarrow 0$  indicates that the considered electrode reaction progresses in the reversible manner. It should be noted that in this scale, the electronic entropy is specified to be zero. It will be seen below that this is a designation close to truth.

The definition of EPH for the electrode reaction given by Eq.(7) or Eq.(8) is all similar to that of a cell reaction except on the absolute scale. These equations indicate that EPH of a half-cell, just like that of the cell reaction, is also a characteristic quantity that only relates to changes in the function of state, i.e. the entropies on the absolute scale, of substances taking part in the reaction. The heat effect occurs on the electrode-electrolyte interfaces. Evidently, when Eq.(7) or Eq.(8) is applied to a cell reaction, the terms,  $\phi^*(\text{H}^+/\text{H}_2)$  in Eq.(5), common to both electrodes of the cell, does not appear explicitly because they are deleted ultimately.

The  $\phi^*$  in Eq.(5) will be replaced by the corresponding function on the conventional scale; the expression is reduced to Vetter's definition. It is obvious that the definition based on Eq. (3) is a special case of Eq. (7) or Eq. (8) which could be more widely used.

The establishment of the absolute scale is dependent on determination of  $\Delta S^*_T$  according to Eq.(6) which can be rewritten as

$$\phi^*_T = \int \Delta S^*_T dT / (z F) \quad (9)$$

with the integral range from zero to a designated temperature  $T$ .

It should be pointed out that a specified reference is  $\phi^*_T \rightarrow 0$  and  $\Delta S^*_T \rightarrow 0$  when  $T \rightarrow 0$  on the absolute scale. This merely is for expedience to identify other values at other than zero in Kelvin experimentally. According to Nernst, for an isothermal process of the condensed system, the third law of thermodynamics can be expressed as

$$\lim_{T \rightarrow 0} (\Delta S)_T = 0 \quad (10)$$

Although the formula is confirmed to be correct in many cases, for the electrode reaction where the hydrated ions and the electrons would take part in it, the validity is to be confirmed. Even,  $\phi^*_T$  might have an own individual value for each electrode when  $T \rightarrow 0$ .

### 3. The basic equations for thermochemistry and experiments for determination of the entropy change of SHE on absolute scale

#### 3.1 The basic equations for thermochemistry

It has been mentioned above that two methods, the heat balance under the steady state or quasi-stationary conditions, and the irreversible thermodynamics and Onsager's reciprocal relations, had been used to treat the heat effects in the electrochemical reactions. Although these methods can determine EPH of electrode reaction under some assumption, they are helpless to answer those problems presented in introduction.

Here a method based on the equilibrium thermodynamics will be introduced. In Eq.(5), a relationship between the electrode potentials on the absolute scale and the conventional scale is given. According to the relationship, the thermodynamic functions such as the entropy  $S$ , the free energy  $G$  and the enthalpy  $H$ , can be written as:

$$\Delta S^* = \Delta S + z \Delta S^*(H^+/H_2), \quad (11)$$

$$\Delta G^* = \Delta G + z \Delta G^*(H^+/H_2), \quad (12)$$

$$\Delta H^* = \Delta H + z \Delta H^*(H^+/H_2), \quad (13)$$

where  $\Delta S^*(H^+/H_2)$ ,  $\Delta G^*(H^+/H_2)$  and  $\Delta H^*(H^+/H_2)$  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.

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

$$\Delta G^* = \Delta H^* - T \Delta S^*, \quad (14)$$

Combined with the equations (8), (12), (13) and (14), and noting that  $\Delta G = -W_e$  (vs. SHE) =  $-z F \phi$ , we have

$$\Pi - W_e (\text{vs. SHE}) = \Delta H^\square, \quad (15)$$

or

$$\Pi - z \mathcal{F}\phi (\text{vs. SHE}) = \Delta H^\square, \quad (16)$$

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

According to Faraday law, for more than or less than one mole change, Eq. (8) and (15) can be, respectively, rewritten as

$$\Pi = T \Delta S^* \left( \int i dt / (z \mathcal{F}) \right)_{i \rightarrow 0} \quad (17)$$

$$\Pi - W_e (\text{vs. SHE}) = \Delta H^\square \int i dt / (z \mathcal{F}), \quad (18)$$

where  $i$  is electric current,  $t$  time and the integral range from zero to  $t$ . Eq. (17) and (18) are the fundamental equations for the electrode reaction.

When a small electric current passes through, Eq. (17) can be approximately written, as

$$Q = T \Delta S^* \int i dt / (z \mathcal{F}) \quad (19)$$

Being differential on both sides of Eq. (19) and letting  $i \rightarrow 0$ , we get

$$\Delta S^* = \kappa (q/i)_{i \rightarrow 0} \quad (20)$$

where  $\kappa = z \mathcal{F} T$  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 called as the Peltier coefficient and represented by the symbol,  $\pi$ . The definition of the Peltier coefficient is completely similar to one in physics in format. The Peltier heat effect can be obtained by the product of the electric quantity and the Peltier coefficient, *i.e.*  $z \mathcal{F} (q/i)_{i \rightarrow 0} = z \mathcal{F} \pi$ . The formula (20) is also a fundamental equation to obtain the entropy change on the absolute scale and the Peltier heat for an electrode reaction.

### 3.2 An experiment for evaluation of the entropy change of SHE on the absolute scale

As shown by Eq. (9), if  $\Delta S^*_T$  at various temperatures are experimentally obtained,  $\phi^*_T$  at a designated temperature  $T$  can be determined. The problem is how to obtain  $\Delta S^*_T$  experimentally at any temperature except zero in Kelvin. According to Eq. (11), if  $\Delta S^*(\text{H}^+/\text{H}_2)$  can be determined experimentally,  $\Delta S^*_T$ , subsequently, can be obtained. Take the evaluation of  $\Delta S^*(\text{H}^+/\text{H}_2)$  at 298.15K as an example. A work has done on the thermoelectrochemical experiment on the ferro-ferricyanide couple and from this the result of the entropy change of SHE on the absolute scale has been evaluated.

The heat effects were determined by temperature-rise calorimetry. The experimental setup is shown by Fig. 1.

A three-electrode system with a platinum working (H), a platinum auxiliary (K) and a reference saturated calomel electrode (F) was placed in a U-type compartment (M) in an isothermal water bath (E). Two platinum wires jointing with the working and auxiliary electrodes, respectively, straight reached to electrolyte outside and connected to two copper wires which linked with the electrochemical workstation (B). The reference electrode was used to track the change in potential of electrode (H). A thermo-sensitive resistor (L)

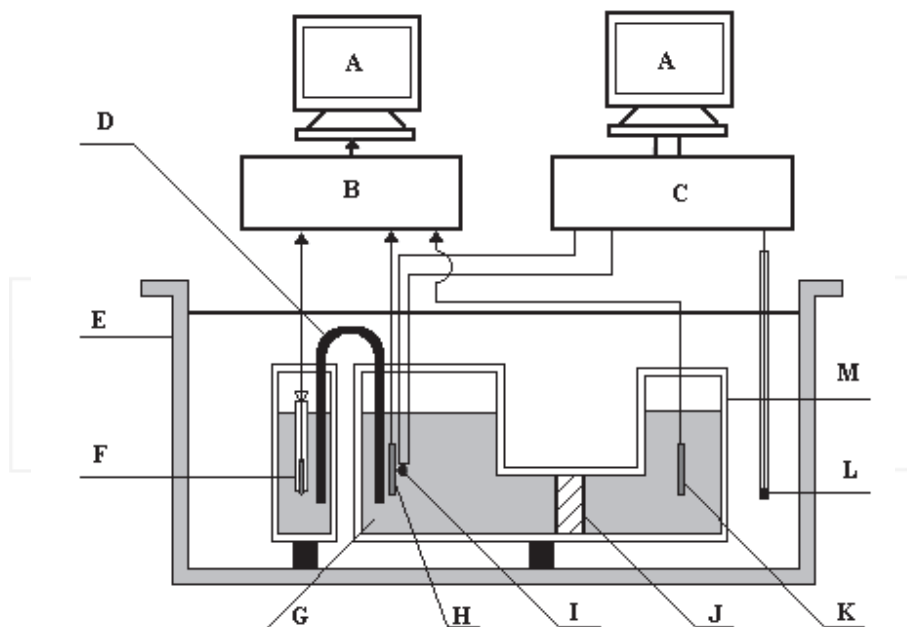


Fig. 1. Schematic diagram of experimental apparatus for measuring  $\Delta S^*(H^+/H_2)$  (A) computer, (B) electrochemical workstation, (C) solution-reaction isoperibol calorimeter, (D) salt bridge, (E) isothermal water bath, (F) saturated calomel electrode, (G) electrolyte, (H) working electrode, (I) thermo-sensitive resistor, (J) porous ceramics, (K) auxiliary electrode, (L) thermo-sensitive resistor, and (M) U-type compartment.

controlled the isothermal surrounding with 0.001 K fluctuations. Another thermo-sensitive resistor (I) was cemented to the back of working electrode (H) immersed in electrolyte (G). A precision resistor inside the solution-reaction calorimeter (C) with  $\pm 0.001K$  was the reference. The electric bridge of the calorimeter measured change in temperature of the working electrode. At the beginning of every run, the electric bridge was balanced by adjusting the inner reference resistor. The potential signals for temperature of the working electrode (H) were output when a small electric current passed through the loop consisting of electrodes (H) and (K). The relation between output potentials and temperature change was predetermined by a calibration experiment. The potential signals of temperature change, electric currents and electrode potentials as a function of time were simultaneously collected by calorimeter (C) and the electrochemical workstation (B), and were recorded by means of computers (A). The temperature change was used for determining  $Q$  and the electric currents and the potential for  $We'$ .

The  $[Fe(CN)_6]^{3-/4-} + 1 mol \cdot dm^{-3}$  KCl solutions were prepared with equal molar concentrations of the two negative ions being  $0.075 mol \cdot dm^{-3}$ ,  $0.15 mol \cdot dm^{-3}$ ,  $0.2 mol \cdot dm^{-3}$ ,  $0.25 mol \cdot dm^{-3}$  and  $0.3 mol \cdot dm^{-3}$ , respectively. The experiments were done at 298.15K. The experimental data are in table 1, and the typical experimental curves for electrode potentials against time and the potential signals for temperature difference against time for the  $0.2 mol \cdot dm^{-3}$   $[Fe(CN)_6]^{3-/4-}$  system are shown in Fig. 2.



$c$ /mol.dm <sup>-3</sup>	$i$ /mA	$\int_0^t i dt$ /A.S	$\frac{\int_0^t (\Delta V + 6.9 \times 10^{-6}) dt}{\int_0^t i dt}$ /V.A <sup>-1</sup>	$\frac{\int_0^t i(\phi + \eta)(SHE) dt}{\int_0^t i dt}$ /V	$-k$ /A
0.075	$i \rightarrow 0$		0.732	0.484	0.566
	0.5	0.060	0.761	0.470	
	0.8	0.096	0.763	0.463	
	1.0	0.120	0.770	0.459	
	1.3	0.156	0.775	0.451	
	1.5	0.180	0.788	0.448	
	1.7	0.204	0.812	0.443	
	2.3	0.276	0.829	0.423	
0.15	$i \rightarrow 0$		0.675	0.489	0.715
	1.0	0.12	0.689	0.471	
	1.5	0.18	0.716	0.466	
	2.5	0.30	0.726	0.451	
	3.5	0.42	0.747	0.442	
	4.0	0.48	0.748	0.436	
	4.5	0.54	0.764	0.421	
	5.0	0.60	0.785	0.406	
0.20	$i \rightarrow 0$		0.698	0.494	0.750
	1.0	0.12	0.707	0.481	
	2.0	0.24	0.733	0.471	
	2.5	0.30	0.735	0.467	
	3.5	0.42	0.750	0.457	
	4.0	0.48	0.752	0.453	
	5.0	0.60	0.760	0.443	
	6.0	0.72	0.778	0.430	
0.25	$i \rightarrow 0$		0.724	0.491	0.783
	1.0	0.12	0.734	0.484	
	1.5	0.18	0.741	0.480	
	2.5	0.30	0.743	0.473	
	3.0	0.36	0.746	0.470	
	3.5	0.42	0.753	0.466	
	4.0	0.48	0.763	0.462	
	4.5	0.54	0.760	0.458	
0.30	$i \rightarrow 0$		0.814	0.497	0.751
	1.0	0.12	0.826	0.486	
	2.0	0.24	0.829	0.483	
	3.0	0.36	0.845	0.474	
	4.0	0.48	0.858	0.467	
	4.5	0.54	0.864	0.464	
	6.0	0.72	0.871	0.451	
	8.0	0.96	0.895	0.433	

\* :  $6.9 \times 10^{-6}$  (V) originated from experimental calibration  $\Delta V(\text{mV}) = 170.199 \Delta T(\text{K}) - 0.0069$ . From Ref. [2]

Table 1. The experimental data and results for  $[\text{Fe}(\text{CN})_6]^{3-/4}$  system.

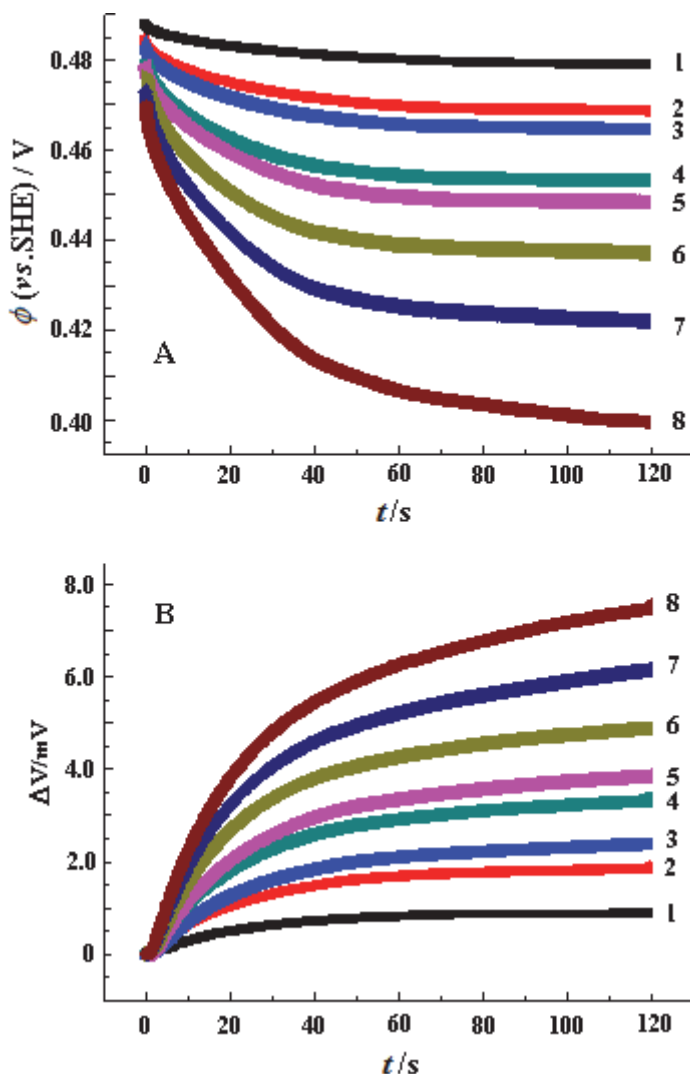


Fig. 2. Plots of the electrode potentials and the potential signals for temperature difference against time for the  $0.2 \text{ mol.dm}^{-3} [\text{Fe}(\text{CN})_6]^{3-/-4}$  system at various electric currents, (A) the electrode potentials *vs.* time, (B) the potential signals for temperature difference *vs.* time; the curves from No.1 to No.8 correspond to currents 1.0, 2.0, 2.5, 3.5, 4.0, 5.0, 6.0 and 7.0 mA, respectively

### 3.3 Experimental data-processing and evaluation of entropy change of SHE on the absolute scale

The redox equation considered in this experiment is as follows:



When a small electric current passes through, Eq. (18) can be approximately written as

$$Q - W_e' \text{ (vs. SHE)} = \Delta H^{\square'} \int i dt / (z \mathcal{F}), \quad (22)$$

where  $Q$  denotes the observed heats including all heat dissipation due to the various polarizations,  $W_e' \text{ (vs. SHE)} = \int i (\phi + \eta) \text{ (vs. SHE)} dt$  with equilibrium potential  $\phi$  and overpotential  $\eta$ , and  $\Delta H^{\square'}$ , a quantity corresponding to  $\Delta H^{\square}$  but includes the change due to irreversible effects. Apparently,  $Q \rightarrow \Pi$ ,  $W_e' \rightarrow W_e$  (or  $\eta \rightarrow 0$ ) and  $\Delta H^{\square'} \rightarrow \Delta H^{\square}$  and Eq. (22) reduces to Eq. (18) when  $i \rightarrow 0$ . The both sides of Eq. (22) being simultaneously divided by the term,  $\int i dt / (z \mathcal{F})$  gives

$$Q / (\int i dt / (z \mathcal{F})) - W_e' \text{ (vs. SHE)} / (\int i dt / (z \mathcal{F})) = \Delta H^{\square'}, \quad (23)$$

Noting that  $Q / (\int i dt / (z \mathcal{F})) \rightarrow \Pi$  and  $W_e' \text{ (vs. SHE)} / (\int i dt / (z \mathcal{F})) \rightarrow W_e \text{ (vs. SHE)}$  at  $i \rightarrow 0$ , and extrapolating the electric current to zero,  $\Pi$  can be determined from a series values of  $Q / (\int i dt / (z \mathcal{F}))$  at different currents. Similarly,  $W_e \text{ (vs. SHE)}$  can be also obtained. Therefore, according to Eq. (15)  $\Delta H^{\square}$  is identified. The  $\Delta H^{\square}$  obtained by the extrapolation treatment is merely at a given concentration of active electrolyte, and denoted by  $\Delta H^{\square}(c)$ . When further extrapolating the concentration to zero, we will acquire  $\Delta H^{\square}$  at the infinite dilution, i.e.  $\Delta H^{\square}(c \rightarrow 0)$ . Based on the definition of the apparent enthalpy change, we have

$$\Delta H^{\square}(c \rightarrow 0) = \Delta H(c \rightarrow 0) + z T \Delta S^*(\text{H}^+/\text{H}_2), \quad (24)$$

Considering a thermodynamic principle which holds that the enthalpy of the solute at unlimited dilution is always equal to that at the standard state, when the standard state is designated to a hypothetical solution which obeys Henry's law at unit molal concentration of solute [39], we can write

$$\Delta H(c \rightarrow 0) = \Delta H^{\ominus} \quad (25)$$

where  $\Delta H^{\ominus}$  is the standard enthalpy change of the considered electrode reaction. Consequently, Eq. (24) can be rewritten as

$$\Delta H^{\square}(c \rightarrow 0) = \Delta H^{\ominus} + z T \Delta S^*(\text{H}^+/\text{H}_2), \quad (26)$$

The values of  $\Delta H^{\square}(c)$  for  $[\text{Fe}(\text{CN})_6]^{3-/4}$  redox system at various concentrations have been calculated from the experimental data, as shown in table 2.

$c / \text{mol} \cdot \text{dm}^{-3}$	0.075	0.15	0.20	0.25	0.30
$-\Delta H^{\square}(c) / \text{kJ} \cdot \text{mol}^{-1}$	86.67	93.75	98.17	102.07	106.96
$-\Pi(c) / \text{kJ} \cdot \text{mol}^{-1}$	39.97	46.57	50.51	54.70	58.98

Table 2. Some thermodynamic functions for  $[\text{Fe}(\text{CN})_6]^{3-/4}$  system. From Ref. [2].

From table 2, plot  $\Delta H^{\square}(c)$  against concentration, as shown in Fig.3 where it can be seen that  $\Delta H^{\square}(c)$  is good linearly related to concentration.  $\Delta H^{\square}(c \rightarrow 0)$  can be obtained to be  $-80.16 \text{ kJ} \cdot \text{mol}^{-1}$  by the linear extrapolation of concentration to zero. From the literature,  $\Delta H^{\ominus} = \Delta H^{\ominus}(\text{Fe}(\text{CN})_6^{4-}) - \Delta H^{\ominus}(\text{Fe}(\text{CN})_6^{3-}) = -106.3 \text{ kJ} \cdot \text{mol}^{-1}$  can be obtained, then the entropy change of SHE reaction on the absolute scale,  $\Delta S^*(\text{H}^+/\text{H}_2)$  is calculated as  $87.6 \pm 1.0 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  at  $298.15 \text{ K}$  according to Eq. (26).

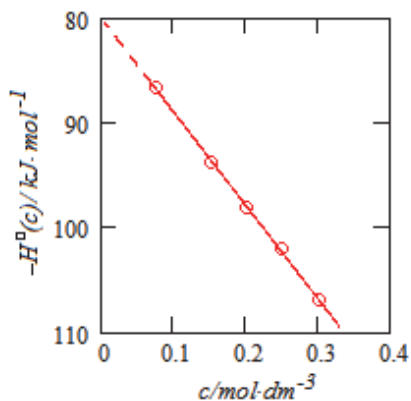


Fig. 3. Plot of  $\Delta H^0(c)$  vs. concentration for the  $[\text{Fe}(\text{CN})_6]^{3-/4}$  system.

### 3.4 Relationship between the quantities determined by TEC technology and those calculated with the current thermodynamic databank of ions

A mathematical expression of the first law of thermodynamics for an infinitesimal process is as follows

$$dU = \delta Q - \delta W \quad (27)$$

where  $dU$  is the change in thermodynamic energy,  $\delta Q$  and  $\delta W$  are, respectively, the heat transferred and work done to the system which includes the expansion work done due to volume change of the system and the other work done except expansion due to the change in surface area, charge in electrochemical cell, magnetic moment in the magnetic field, etc. Considering a system where there are only the electric work done and the expansion work at constant pressure, Eq. (27) can be written as

$$\delta Q = dU + \delta W_e + p dV \quad (28)$$

or

$$\delta Q = dH + \delta W_e \quad (29)$$

where  $H$  is the enthalpy function,  $p$ , pressure and  $V$ , volume. For a system where a certain amount of change occurs, Eq. (29) can be written as

$$Q - W_e (\text{vs. SHE}) = \Delta H \quad (30)$$

where the electric work done is appointed to the reference of SHE. This is an expression of the first law of thermodynamics.

When the law is used to an electrode reaction with the given electron transfer number at the given temperature, the enthalpy change calculated based on the electric work done and the heat effect obtained experimentally differs from that calculated by Eq.(30) on the current thermodynamic databank including the ion data. The difference between them is almost a constant. For this phenomenon it has been not yet explained reasonably so far, and this greatly influenced the development of thermochemistry.

It should be seen from Eq.(15) that the value on TEC experiments is the apparent enthalpy change, while the value calculated by Eq.(30) on the current thermodynamic databank is the

enthalpy change of the electrode reaction on the conventional scale. They just differ by a constant that is  $z T\Delta S^*(\text{H}^+/\text{H}_2)$ . If adding  $z T\Delta S^*(\text{H}^+/\text{H}_2)$  to both sides of Eq. (30) at same time and noting that  $Q = T\Delta S$  and  $I = T\Delta S^*$ , we will get Eq. (15). The difference between the two terms about the enthalpy changes,  $\Delta H^\square$  and  $\Delta H$ , in Eq. (15) and Eq.(30) is just a constant that is EPH of the SHE reaction at temperature  $T$ ,  $zT\Delta S^*(\text{H}^+/\text{H}_2)$ .

In Eq. (30),  $Q$  is a product of temperature  $T$  and the entropy change derived from the current thermodynamic databank including the ion data which is constructed on the conventional scale, and can be named as "the traditional heat effect"; while in Eq. (15),  $I$  is the heat effect identified by the experiments, called as "the measured heat effect". The difference between them is  $z T\Delta S^*(\text{H}^+/\text{H}_2)$ . Consequently, the first problem mentioned above, why is this formula,  $Q = T\Delta S$ , unsuitable for a reversible single electrode reaction, is answered.

### 3.5 About the absolute value of thermodynamic function on the absolute scale

When these thermodynamic functions on the absolute scale are applied to a cell reaction, all terms concerning with SHE on the absolute scale, such as  $\Delta S^*(\text{H}^+/\text{H}_2)$ ,  $\Delta G^*(\text{H}^+/\text{H}_2)$  and  $\Delta H^*(\text{H}^+/\text{H}_2)$  in Eq.(11), (12) and (13), common to both electrodes of the cell, are cancelled ultimately. It will be not any impact to the normal thermodynamic analysis of the cell reaction.

Here an issue is whether or not the potential of single electrode on the absolute scale is a "real" value? It should be said that the potential of electrode is not its "real" value in absolute sense, and the thermodynamic functions on the absolute scale like  $\Delta S^*$ ,  $\Delta G^*$  and  $\Delta H^*$  of an electrode reaction are not the "real" values either, although the words, "real" and "absolute", are used to this text. The scale is called as "absolute scale" that is only compared with "conventional scale". They are also some relative quantities obtained based on this reference, i.e.  $\phi_T^* \rightarrow 0$ ,  $\Delta S_T^* \rightarrow 0$  when  $T \rightarrow 0$ , and the assumption of zero electronic entropy [40, 41]. It, called as "absolute scale", is merely that these values on the scale much more close to "reality" than on the conventional scale. In the conventional scale, the entropy of the hydrogen ion and the entropy change of the SHE reaction are all arbitrarily set at zero, which would result in a bigger difference between these quantities and the "verity". However, based on the "absolute scale", the partial molal entropy of the hydrogen ion is calculated as  $-22.3 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  (see below), the entropy change of SHE reaction (Eq. (4)),  $87.6 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  at  $298.15\text{K}$ , and the electronic entropy is specified as zero. All of these quantities are much more close to "verity" than those on the "conventional scale". In the conventional scale the electronic entropy is calculated as  $65.29\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  [41] according to a principle which states that the algebraic sum of the entropies of all substances taking part in the reaction (4) equals to zero. This result, obviously, is far from the "really" electronic entropy that can approximately be considered to be zero according to Fermi-Dirac statistics theory applied to the electron gas in metal. Therefore, we call the scale that is more close to the "verity" as the "absolute scale".

## 4. Some application of the basic equations for thermoelectrochemistry

### 4.1 The partial molal entropies of hydrogen ion and some other hydrated ions on the absolute scale

According to Eq.(4),

$$\Delta S^*(\text{H}^+/\text{H}_2) = S^\ominus(1/2\text{H}_2) - \tilde{S}^*(\text{e}^-) - \tilde{S}^*(\text{H}^+) \quad (31)$$

where  $\tilde{S}^*(e^-)$  and  $\tilde{S}^*(H^+)$  are the partial molal entropy of electron and hydrogen ion on the absolute scale, respectively. Substituting the corresponding data, 87.6, 65.29 and 0 for  $\Delta S^*(H^+/H_2)$ ,  $S^\ominus(1/2H_2)$  and  $\tilde{S}^*(e^-)$ , respectively,  $\tilde{S}^*(H^+)$  is calculated to be  $-22.3 \text{ J.K}^{-1}.\text{mol}^{-1}$  which is very good in agreement with the value reported previously on some other experimental methods. Therefore, the entropies of other hydrated ions on the conventional scale can be recalculated to be those on the absolute scale with  $\tilde{S}^*(H^+)$ . The formula used for conversion is as follows:

$$\tilde{S}^*(N^z) = \tilde{S}^\ominus(N^z) - 22.3.z \quad (32)$$

where  $N^z$  represents ion with the  $z$  valence of positive ( $z > 0$ ) or negative ( $z < 0$ ) ion. Table 3 gives the entropies for some hydrated ions on absolute scale based on the data for ion entropies from Ref. [42].

Ion	$\tilde{S}_i$	$\tilde{S}_i^*$	Ion	$\tilde{S}_i$	$\tilde{S}_i^*$	Ion	$\tilde{S}_i$	$\tilde{S}_i^*$
H <sup>+</sup>	0	-22.3	Be <sup>2+</sup>	-129.7	-174.3	Al <sup>3+</sup>	-325.0	-391.9
Li <sup>+</sup>	12.24	-10.0	Mg <sup>2+</sup>	-137.4	-182.0	Fe <sup>3+</sup>	-315.9	-382.8
Na <sup>+</sup>	58.45	36.2	Ca <sup>2+</sup>	-56.2	-100.8	S <sub>2</sub> <sup>2-</sup>	-14.6	30.0
K <sup>+</sup>	101.2	78.9	Sr <sup>2+</sup>	-32.6	-77.2	HS <sup>-</sup>	67.0	89.3
Rb <sup>+</sup>	121.75	99.5	Ba <sup>2+</sup>	9.6	-35.0	F <sup>-</sup>	-13.8	8.5
Cs <sup>+</sup>	132.1	109.8	Fe <sup>2+</sup>	-137.7	-182.3	Cl <sup>-</sup>	56.6	78.9
Ag <sup>+</sup>	72.45	50.2	Co <sup>2+</sup>	-113.0	-157.6	Br <sup>-</sup>	82.55	104.8
Cu <sup>+</sup>	40.6	18.3	Ni <sup>2+</sup>	-128.9	-173.5	I <sup>-</sup>	106.45	128.7

Table 3. The partial molal entropies for some hydrated ions on the conventional scale and on absolute scale ( $\text{J.K}^{-1}.\text{mol}^{-1}$ ).

#### 4.2 The electrochemical Peltier heats and the Peltier coefficients of the standard electrode reactions

Similar to the  $[\text{Fe}(\text{CN})_6]^{3-/4}$  redox couple, EPH of an electrode reaction can directly be measured by the thermochemical experiments. However, it is hard to measure EPH of an electrode reaction at the standard state directly, because the standard state chosen usually in thermodynamics is even physically unrealizable in most cases. According to Eq.(8), EPH of a standard electrode reaction can be determined provided that  $\Delta S^*$  of the reaction is known. For example, for the  $[\text{Fe}(\text{CN})_6]^{3-/4}$  couple at each standard state of the components, its entropy change is calculated as  $\Delta S^\ominus([\text{Fe}(\text{CN})_6]^{3-/4}) = -240.6 \text{ J.K}^{-1}.\text{mol}^{-1}$ , therefore,  $\Delta S^*( [\text{Fe}(\text{CN})_6]^{3-/4} ) = -153.0 \text{ J.K}^{-1}.\text{mol}^{-1}$ , and  $\Pi^\ominus([\text{Fe}(\text{CN})_6]^{3-/4}) = -45.6 \text{ kJ.mol}^{-1}$ . The EPHs of some standard electrode reactions at 298.15K are given in table 4. Similarly, the electrochemical Peltier coefficient, a characteristic quantity of electrode reaction, can be also determined by Eq.(20).

Like this, the second problem mentioned in introduction, that is, how to seek a feasible method to calculate or predict the "real" heat effect of a standard reversible electrode reaction, is also resolved.

Reaction	$\Delta S^*$ (J.mol <sup>-1</sup> .K <sup>-1</sup> )	$\pi$ (V)	$\Pi^\ominus$ (kJ.mo l <sup>-1</sup> )	Reaction	$\Delta S^*$ (J.mol <sup>-1</sup> .K <sup>-1</sup> )	$\pi$ (V)	$\Pi^\ominus$ (kJ.mol <sup>-1</sup> )
H <sup>+</sup> + e <sup>-</sup> =0.5H <sub>2</sub>	87.6 ±1.0	0.27 <sub>1</sub>	26.1±0.3	Am <sup>3+</sup> +3e <sup>-</sup> =Am	288.6±3.0	0.29 <sub>7</sub>	86.1±0.9
Ag <sup>+</sup> + e <sup>-</sup> = Ag	-8.6±1.0	-0.02 <sub>7</sub>	-2.6±0.3	Ce <sup>4+</sup> +4e <sup>-</sup> =Ce	462.0±4.0	0.35 <sub>7</sub>	137.8±1.2
Cu <sup>+</sup> + e <sup>-</sup> =Cu	14.9±1.0	0.04 <sub>6</sub>	4.4±0.3	S(orth)+2e <sup>-</sup> =S <sup>2-</sup>	-1.5±2.0	-0.00 <sub>2</sub>	-0.5±0.6
Be <sup>2+</sup> +2e <sup>-</sup> =Be	183.8±2.0	0.28 <sub>4</sub>	54.8±0.6	Cl <sub>2</sub> +2e <sup>-</sup> =2Cl <sup>-</sup>	-75.3±2.0	-0.11 <sub>6</sub>	-22.44±0.6
Mg <sup>2+</sup> +2e <sup>-</sup> =Mg	214.3±2.0	0.33 <sub>1</sub>	63.9±0.6	Br <sub>2</sub> (l)+2e <sup>-</sup> =2Br <sup>-</sup>	57.5±2.0	0.08 <sub>9</sub>	17.2±0.6
Ca <sup>2+</sup> +2e <sup>-</sup> =Ca	142.4±2.0	0.22 <sub>0</sub>	42.5±0.6	I <sub>2</sub> (c)+2e <sup>-</sup> =2I <sup>-</sup>	141.4±2.0	0.21 <sub>8</sub>	42.2±0.6
Sr <sup>2+</sup> +2e <sup>-</sup> = Sr	132.2±2.0	0.20 <sub>4</sub>	39.4±0.6	Fe (CN) <sub>6</sub> <sup>3+</sup> +e <sup>-</sup> = Fe (CN) <sub>6</sub> <sup>4-</sup>	-153.0±1.0	-0.47 <sub>3</sub>	-45.6±0.3
Ba <sup>2+</sup> +2e <sup>-</sup> =Ba	97.5±2.0	0.15 <sub>1</sub>	29.1±0.6	Co <sup>3+</sup> +e <sup>-</sup> =Co <sup>2+</sup>	214.3±1.0	0.66 <sub>2</sub>	63.9±0.3
Ra <sup>2+</sup> +2e <sup>-</sup> =Ra	61.6±2.0	0.09 <sub>5</sub>	18.4±0.6	Fe <sup>3+</sup> +e <sup>-</sup> =Fe <sup>2+</sup>	200.5±1.0	0.62 <sub>0</sub>	59.8±0.3
Mn <sup>2+</sup> +2e <sup>-</sup> = Mn	150.2±2.0	0.23 <sub>2</sub>	44.8±0.6	MnO <sub>4</sub> <sup>-</sup> +e <sup>-</sup> =MnO <sub>4</sub> <sup>2-</sup>	-109.9±1.0	-0.34 <sub>0</sub>	-32.8±0.3
Co <sup>2+</sup> +2e <sup>-</sup> =Co	187.6±2.0	0.29 <sub>0</sub>	55.9±0.6	CuCl+e <sup>-</sup> =Cu+Cl <sup>-</sup>	25.9±1.0	0.08 <sub>0</sub>	7.7±0.3
Ni <sup>2+</sup> +2e <sup>-</sup> =Ni	203.4±2.0	0.31 <sub>4</sub>	60.7±0.6	AgCl+e <sup>-</sup> =Ag+Cl <sup>-</sup>	25.2±1.0	0.07 <sub>8</sub>	7.5±0.3
Cu <sup>2+</sup> +2e <sup>-</sup> =Cu	177.4±2.0	0.27 <sub>4</sub>	52.9±0.6	AgBr+e <sup>-</sup> =Ag+Br <sup>-</sup>	40.3±1.0	0.12 <sub>5</sub>	12.0±0.3
Al <sup>3+</sup> +3e <sup>-</sup> =Al	420.3±3.0	0.43 <sub>3</sub>	125.3±0.9	AgI+ e <sup>-</sup> =Ag+I <sup>-</sup>	55.8±1.0	0.17 <sub>2</sub>	16.6±0.3
Co <sup>3+</sup> +3e <sup>-</sup> =Co	401.9±3.0	0.41 <sub>4</sub>	119.8±0.9	AuCl+e <sup>-</sup> =Au+Cl <sup>-</sup>	33.4±1.0	0.10 <sub>3</sub>	9.9±0.3
Sc <sup>3+</sup> +3e <sup>-</sup> =Sc	356.6±3.0	0.36 <sub>7</sub>	106.3±0.9	Au(CN) <sub>2</sub> <sup>-</sup> +e <sup>-</sup> =Au+2CN <sup>-</sup>	85.9±1.0	0.26 <sub>5</sub>	25.6±0.3
Y <sup>3+</sup> +3e <sup>-</sup> =Y	362.3±3.0	0.37 <sub>3</sub>	108.0±0.9	AuCl <sub>4</sub> <sup>-</sup> +3e <sup>-</sup> =Au+4Cl <sup>-</sup>	73.8±3.0	0.07 <sub>6</sub>	22.0±0.9
La <sup>3+</sup> +3e <sup>-</sup> =La	341.4±3.0	0.35 <sub>2</sub>	101.8±0.9	PtCl <sub>4</sub> <sup>2-</sup> +2e <sup>-</sup> =Pt+4Cl <sup>-</sup>	141.9±2.0	0.21 <sub>9</sub>	42.3±0.6
Ce <sup>3+</sup> +3e <sup>-</sup> =Ce	343.9±3.0	0.35 <sub>4</sub>	102.5±0.6	Hg <sub>2</sub> Cl <sub>2</sub> +2e <sup>-</sup> =2Hg(l)+2Cl <sup>-</sup>	118.0±2.0	0.18 <sub>2</sub>	35.2±0.6
Nd <sup>3+</sup> +3e <sup>-</sup> =Nd	345.2±3.0	0.35 <sub>6</sub>	102.9±0.9	Zn(OH) <sub>2</sub> (β)+2e <sup>-</sup> =Zn+2OH <sup>-</sup>	-16.8±2.0	-0.02 <sub>6</sub>	-5.0±0.6
Sm <sup>3+</sup> +3e <sup>-</sup> =Sm	348.2±3.0	0.35 <sub>9</sub>	103.8±0.9	Cd(CN) <sub>4</sub> <sup>2-</sup> +2e <sup>-</sup> =Cd(γ)+4CN <sup>-</sup>	150.7±2.0	0.23 <sub>3</sub>	44.9±0.6
Eu <sup>3+</sup> +3e <sup>-</sup> =Eu	366.7±3.0	0.37 <sub>8</sub>	109.3±0.9	AsO <sub>2</sub> +2H <sub>2</sub> O+3e <sup>-</sup> =As(α)+4OH <sup>-</sup>	-122.1±3.0	-0.12 <sub>6</sub>	-36.4±0.9
Gd <sup>3+</sup> +3e <sup>-</sup> =Gd	340.9±3.0	0.35 <sub>1</sub>	101.6±0.9	AsO <sub>4</sub> <sup>3-</sup> +2H <sub>2</sub> O+2e <sup>-</sup> =AsO <sub>2</sub> <sup>-</sup> +4OH <sup>-</sup>	64.5±2.0	0.10 <sub>0</sub>	19.2±0.6
Tb <sup>3+</sup> +3e <sup>-</sup> =Tb	366.2±3.0	0.37 <sub>7</sub>	109.2±0.9	Ba(OH) <sub>2</sub> .8H <sub>2</sub> O+2e <sup>-</sup> =Ba+8H <sub>2</sub> O+2OH <sup>-</sup>	217.9±2.0	0.33 <sub>7</sub>	65.0±0.6
Dy <sup>3+</sup> +3e <sup>-</sup> =Dy	373.5±3.0	0.38 <sub>5</sub>	111.4±0.9	S(orth)+2H <sup>+</sup> +2e <sup>-</sup> =H <sub>2</sub> S(g)	218.4±2.0	0.33 <sub>7</sub>	65.1±0.6
Ho <sup>3+</sup> +3e <sup>-</sup> =Ho	369.0±3.0	0.38 <sub>0</sub>	110.0±0.9	H <sub>3</sub> BO <sub>3</sub> (aq)+3H <sup>+</sup> +3e <sup>-</sup> =B+3H <sub>2</sub> O	120.3±3.0	0.12 <sub>4</sub>	35.9±0.9
Er <sup>3+</sup> +3e <sup>-</sup> =Er	384.4±3.0	0.39 <sub>6</sub>	114.6±0.9	WO <sub>3</sub> +6H <sup>+</sup> +6e <sup>-</sup> =W+3H <sub>2</sub> O	300.4±6.0	0.15 <sub>5</sub>	89.6±1.8
Tm <sup>3+</sup> +3e <sup>-</sup> =Tm	383.9±3.0	0.39 <sub>5</sub>	114.5±0.9	Al(OH) <sub>3</sub> +3e <sup>-</sup> =Al+3OH <sup>-</sup>	-8.5±3.0	-0.00 <sub>9</sub>	-2.5±0.9
Yb <sup>3+</sup> +3e <sup>-</sup> =Yb	364.8±3.0	0.37 <sub>6</sub>	108.8±0.9	O <sub>2</sub> +2H <sub>2</sub> O(l)+4e <sup>-</sup> =4OH <sup>-</sup>	-299.4±4.0	-0.23 <sub>1</sub>	-89.3±1.2
Lu <sup>3+</sup> +3e <sup>-</sup> =Lu	381.9±3.0	0.39 <sub>3</sub>	113.9±0.9	O <sub>2</sub> +4H <sup>+</sup> +4e <sup>-</sup> =2H <sub>2</sub> O	24.0±4.0	0.01 <sub>9</sub>	7.2±1.2

Table 4. The entropy change on absolute scale, EPHs and Peltier coefficients for some standard electrode reactions in aqueous solution at 298.15K. From Ref. [1], but recalculating a part of data according to Ref. [42]

### 4.3 Determination of the electric potentials of the standard electrode by $\Delta H^\ominus$ (c→0)

The standard electrode potential of an electrode is a very important electrochemical quantity. Conventionally, it is determined by the extrapolating the electrode potentials of extremely dilute solution along the line predicted by the Debye-Hückel theory. Nevertheless, in the thermoelectrochemistry, it can be obtained by the measurement of the apparent enthalpy change. Based on a thermodynamic principle mentioned above (see Eq. (25)), Eq.(16) can be rewritten as

$$\Pi^\ominus - z F \phi^\ominus (\text{vs. SHE}) = \Delta H^\ominus (c \rightarrow 0) \quad (33)$$

where the superscript “ $\ominus$ ” represents the standard state. Therefore, if  $\Delta H^\ominus$  (c→0) and  $\Pi^\ominus$  are identified, then the standard electrode potential,  $\phi^\ominus$  (vs.SHE) can be determined.

For the  $[\text{Fe}(\text{CN})_6]^{3-/4}$  couple, when  $\Pi^\ominus = -45.6 \text{ kJ}\cdot\text{mol}^{-1}$  (see section 4.2) and  $\Delta H^\ominus(c \rightarrow 0) = -80.2 \text{ kJ}\cdot\text{mol}^{-1}$  (see section 3.3) are substituted to Eq.(33), its standard potential is identified to be +0.3580 volt at 298.15K.

#### 4.4 The enthalpy change and entropy change at designated concentration $c$ , and diluted heats and diluted entropies of ions

The enthalpy change,  $\Delta H(c_2 \rightarrow c_1)$  of an electrode reaction from a designated concentration  $c_2$  to another concentration  $c_1$ , can be evaluated from the measurable quantity  $\Delta H^\ominus(c)$ . Based on the definition of  $\Delta H^\ominus (= \Delta H + z T \Delta S^*(\text{H}^+/\text{H}_2))$ , the dilute enthalpy from concentrations  $c_2$  to  $c_1$  can be computed by the following cycle (Fig. 4) [43] where  $\text{Me}^{n+}$  is a specified metallic ion.

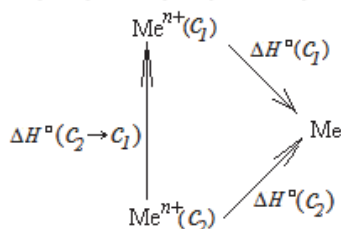


Fig. 4. The thermal cycle for getting dilute enthalpy from concentration  $c_2$  to  $c_1$

According to the thermal cycle, the corresponding computing equations are following

$$\Delta H^\ominus(c_2 \rightarrow c_1) = \Delta H^\ominus(c_2) - \Delta H^\ominus(c_1) \quad (34)$$

Noting that  $\Delta S^*(\text{H}^+/\text{H}_2)$  in the expression of  $\Delta H^\ominus$  at a designated temperature is constant, the dilute enthalpy,  $\Delta H(c_2 \rightarrow c_1)$  is

$$\begin{aligned} \Delta H(c_2 \rightarrow c_1) &= \Delta H^\ominus(c_2) - \Delta H^\ominus(c_1) \\ &= \Delta H(c_2) - \Delta H(c_1) \end{aligned} \quad (35)$$

where  $\Delta H(c)$  is the enthalpy change of the considered electrode reaction at the electrolyte concentration  $c$ . For example, a thermochemical experiment similar to the  $[\text{Fe}(\text{CN})_6]^{3-/4}$  couple was done on the  $\text{Cu}^{2+}/\text{Cu}$  couple in the  $\text{CuCl}_2 + 1 \text{ mol}\cdot\text{dm}^{-3} \text{ KCl}$  solution. The experimental data for the apparent enthalpies of the  $\text{Cu}^{2+}/\text{Cu}$  couple are shown in table 5. The dilute enthalpies of  $\text{Cu}^{2+}$  in the solution are calculated from table 5, and listed in table 6.

$c/\text{mol}\cdot\text{dm}^{-3}$	0.01	0.02	0.03	0.04	0.05
$-\Delta H^\ominus(c)/\text{kJ}\cdot\text{mol}^{-1}$	11.27	9.52	8.25	6.46	5.23

Table 5. Some thermodynamic functions for  $\text{Cu}^{2+}/\text{Cu}$  system. From Z. Yang, *an unpublished work*.

$c/\text{mol}\cdot\text{dm}^{-3}$	0.05	0.04	0.03	0.02	0.01
0.05	0	$1.23 \pm 0.28$	$3.02 \pm 0.28$	$4.29 \pm 0.28$	$6.04 \pm 0.28$

Table 6. Dilute enthalpies  $\Delta H(c)$  ( $\text{kJ}\cdot\text{mol}^{-1}$ ) for  $\text{Cu}^{2+}$  in  $\text{CuCl}_2 + 1 \text{ mol}\cdot\text{dm}^{-3} \text{ KCl}$  electrolyte solution.



Similarly, the dilute entropy,  $\Delta S(c_2 \rightarrow c_1)$  of the electrolyte solution from concentration  $c_2$  to  $c_1$  at the designated temperature can be evaluated from the measurable quantity  $\Delta I I(c)$  according to Eq.(36),

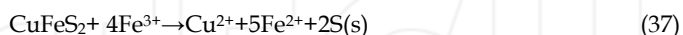
$$\begin{aligned}\Delta S(c_2 \rightarrow c_1) &= \Delta S(c_2) - \Delta S(c_1) \\ &= (I I(c_2) - I I(c_1)) / T\end{aligned}\quad (36)$$

In a word, because the apparent enthalpy,  $\Delta H^\square$  and the Peltier heat,  $I I$  can be measured by the thermoelectrochemical experiments as a function of the function of state, all thermodynamic functions related to these quantities of the considered electrode reaction could be evaluated.

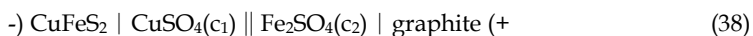
## 5. Application to hydrometallurgy

The Seebeck effect has been used for the power generation practice. This is called as the thermoelectricity. Now, an application of thermoelectrochemistry to hydrometallurgy has been explored. The hydrometallurgy is a kind method that the valuable metals are separated and extracted from the corresponding ores or concentrates mainly by aqueous solution treatment. The leaching is a very important process in this method, by which the valuable metals are transformed into metallic or complex hydrated ions. By the subsequent purified and separated from impurity, the valuable components are extracted. In the direct leaching process, usually, the ores or concentrates are mixed with the acidic or the basic solution or the solution with the redox. A large amount of heats is suck up from surrounding or released out during the leaching. The heats are completely wasted except heating the leaching solution sometimes. The leaching heat effect,  $Q$ , is generally considered to be corresponding to the enthalpy change,  $\Delta H$  of the leaching reaction at the constant pressure. If the leaching is designed as a process that takes place in a galvanic cell, according to Eq.(30), a part of the energy of the leaching reaction would be released as the electric work done. This treatment that takes a galvanic cell to complete the leaching process is named to be the "power generation leaching".

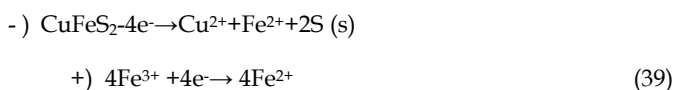
For the wet-extraction of copper, the chalcopyrite ( $\text{CuFeS}_2$ ) is usually used as the raw materials, and the leaching reagent is the ferric sulphate. Its leaching reaction is



In the direct leaching, the released energy due to the disaggregation of the raw materials is educed as the heats. The energy that can do useful work could not be effectively released and functioned. If the power generation leaching is chosen, the galvanic cell could be constructed as shown by the following diagram,



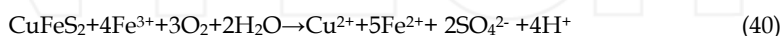
The salt bridge or a kind of ionic membrane suited to the leaching system is located between the anodic and cathodic compartments. The electrode reactions are as follows,



The cell reaction is corresponding to Eq.(37). When the reaction progresses reversibly, the electric work could achieve about 100 kJ.mol<sup>-1</sup> at room temperature.

Apparently, in the power generation leaching, a part of the energy due to the disaggregation of the ores or concentrates will be released as the electric work. Bockris had defined a coefficient as  $\varepsilon_{\max} = \Delta G/\Delta H$  [44] that represents the maximum transfer efficiency of the chemical energy to the electric work done, and it could be a measure as choosing leaching reaction. This also may be a criterion of the efficiency of the power generation leaching.

In the leaching with the galvanic cell, the element sulfur produced due to its insolubility would cover the surface of ores or the concentrate particles, inhibiting the further progress of the chalcopyrite leaching. When a kind of microorganism, *Acidithiobacillus ferrooxidans* (*A. ferrooxidans*) would be added to the leaching system, the insoluble simple substance could be oxidized to the positive six-valence sulfur, and further forming sulfate group, SO<sub>4</sub><sup>2-</sup> in the oxygen-containing condition [45]. This will reinforce the leaching result, increase the leaching ratio of the mineral and make the amount of the electric work done more. The leaching reaction could be written as,



The maximum electric work done could achieve about 1100 kJ.mol<sup>-1</sup>, when the reaction would be reversible at room temperature. That is to say, the power generation leaching would create a probability that the chemical energy of an electrochemical reaction transfers to the useful electric work.

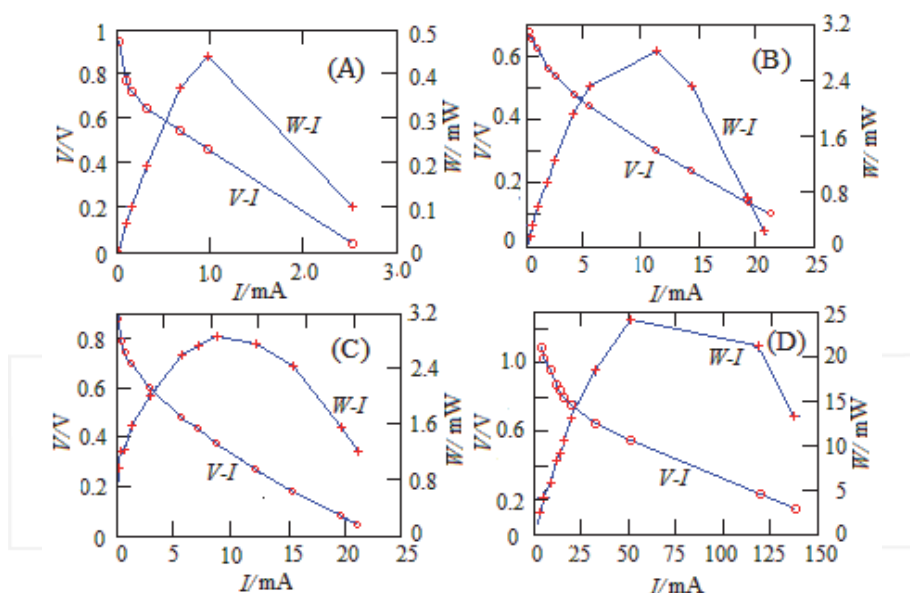


Fig. 5. Potential (V)-power (W)-current (I) curves for (A) Ni<sub>3</sub>S<sub>2</sub>-FeCl<sub>3</sub> system with a salt bridge, (B) PbS (beforehand steeped in Ag<sup>+</sup> solution)-FeCl<sub>3</sub> system, (C) Ni<sub>3</sub>S<sub>2</sub> (beforehand steeped in La<sup>3+</sup> solution)-FeCl<sub>3</sub> system and (D) ZnS (containing acetylene black)-FeCl<sub>3</sub> system with PE anion-selective membrane instead of salt bridge. The figures, (A), (B), (C) and (D) are from H. Zhang, et al, *Nonferrous Met.* 44 (1992) 69; S. Wang, et al, *J. Changsha Univ. Sci. & Technol.* 1 (2004), 87; *ibid* ; and S. Wang, et al, *Electrochem.* 11 (2005) 77, respectively.

In order to make the reaction progress under a high oxidation potential, the bacteria, *A. ferrooxidans* are also added into the cathodic room sometimes because they could be cultivated on the  $\text{Fe}^{2+}$  solution and grow [46]. The bacteria can promote the ferrous ions to oxidize to the ferric ones with the rates  $10^5$  to  $10^6$  times faster than those of inorganic oxidation at the corresponding pH value. This indicates that the high ratio of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  is always kept in catholyte, so that the leaching reaction is also kept under a high strength of the oxidizing potentials to encourage the reaction progress with a fast rate. Leaching experiments have done on such the minerals as  $\text{Cu}_2\text{S}$ ,  $\text{Ni}_3\text{S}_2$ ,  $\text{PbS}$ ,  $\text{FeS}$  and  $\text{ZnS}$  [47]. The researches of the power generation leaching also concern with the simultaneous leaching of two minerals, for example,  $\text{Cu}_2\text{S}$  or other metallic sulfide like  $\text{Ni}_3\text{S}_2$ ,  $\text{PbS}$ ,  $\text{FeS}$  or  $\text{ZnS}$  (as anode) and  $\text{MnO}_2$  (as cathode) [48]. The curves of electric currents-potentials-electric power for the power generation leaching for some metallic sulfides are shown in Fig.5, from where it can be seen that the resulting currents and the electric power obviously increase with improvement of the conditions of leaching.

In a word, this power generation leaching not only can generate electricity, but also reduce the purified steps of the leaching solution and the reagents consumption as well as is able to adjust the reaction evolution by control of the power output. From the point of view of the economy and ecological protection, this is a worthy advocating method.

## 6. Summary

In this chapter, a very important thermodynamic quantity, the electrochemical Peltier heat of a single electrode process, and some concepts related to this quantity have been discussed. They include the definition about EPH and the Peltier coefficient for the electrode process, the absolute scale, and the fundamental equations on this scale for thermoelectrochemistry. The equations on this scale, actually, are a special depiction of the first and second laws of the thermodynamics used to the electrode reactions. Firstly, the energy conservation equation with a new form based on the classical equilibrium thermodynamics is set up. A new reference point for the heat effects and the enthalpy change is designated in the equation, that is both  $\phi^*_T$  and  $\Delta S^*_T$  are zero when  $T \rightarrow 0$  and an assumption of zero electronic entropy. For SHE reaction, the designation of  $\phi^*_{T \rightarrow 0} = 0$  and  $\Delta S^*_{T \rightarrow 0} = 0$  on the absolute scale is as the same as that of  $\phi_{T \rightarrow 0} = 0$  and  $\Delta S_{T \rightarrow 0} = 0$  on the conventional scale. Secondly, EPH on electrode-electrolyte interfaces is specially emphasized to be a quantity related to the function of state. The reversible heat effect, or EPH on the electrode-electrolyte interfaces, can be determined by the change in entropy of reaction on the absolute scale. This is an extension of the second law of thermodynamics. In order to acquire  $\phi^*_T$ , the quantity of  $\Delta S^*_T$ , dependent on temperature, needs to be beforehand identified by the thermoelectrochemistry experiments at different temperatures, and sequentially it is determined as a function of temperature. From this the electrode potential on the absolute scale would be evaluated by means of the relationship of  $\phi^*_T$  and  $\Delta S^*_T$ . Additionally, in the third law of thermodynamics, the change in entropy for a constant temperature process of a condensed system will approach to zero with the temperature moving toward zero according to Eq.(10). If further assumed that the constant temperature process could include the electrode reaction with the hydrated ions and the electrons taking part in, then

$$\lim_{T \rightarrow 0} (\Delta S^*)_T = \lim_{T \rightarrow 0} (\Delta S + z \Delta S^*(\text{H}^+/\text{H}_2))_T = 0 \quad (41)$$

That is, the stipulation of  $\Delta S^*_{T \rightarrow 0} = 0$  would be also fit to the third law of thermodynamics. To sum up, the set up of the absolute scale and the evaluation of the change in entropy of SHE on this scale are useful to resolve those two problems which are mentioned at the beginning of this chapter. From this, one can get the relationship between the thermodynamic functions on the conventional and the absolute scale, and obtain the changes in entropy on the absolute scale and EPHs for electrode reactions, as a result greatly enriching the thermodynamic database. This also provides a new scale to study the electrode reaction, being valuable to the further development of the thermochemistry. Thermochemical applications have now been extended in many areas, especially in the surface-electrochemical treatment of the functional materials, electrode modifying, and the charge and discharge-control of the batteries. The application to hydrometallurgy has also been explored.

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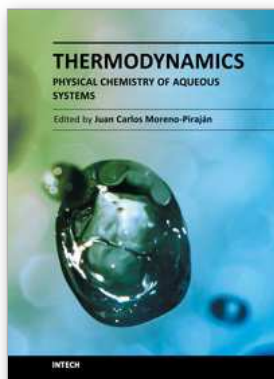
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