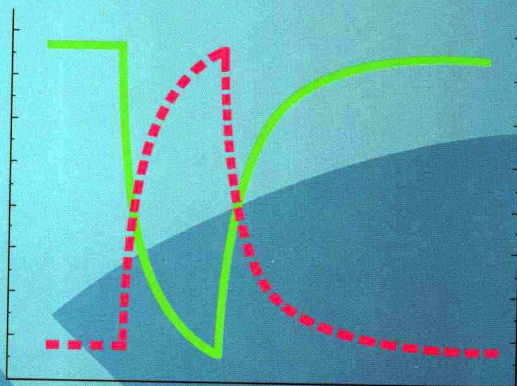


Thermodynamics

— How much are the real heats of electrode reaction?

Zheng FANG

Central South University, China



$$\Delta S^{\circ} = 87.6 \quad \Delta S^{\circ} = 87.6 \quad \Delta S^{\circ} = 87.6 \quad \Delta S^{\circ} = 87.6$$



Central South University Press

www.csupress.com.cn

Thermodynamics

—How much are the real heats of
electrode reaction?

Zheng FANG

Central South University, China



Central South University Press
www.csupress.com.cn

图书在版编目(CIP)数据

热力学——电极反应的真实热效应 Thermodynamics—How much are the real heats of electrode reaction?: 英文/方正著. —长沙:中南大学出版社,2012. 10

ISBN 978-7-5487-0705-9

I. 热... II. 方... III. 电极反应-热效应-文集-英文
IV. 0646. 54-53

中国版本图书馆 CIP 数据核字(2012)第 242466 号

热力学——电极反应的真实热效应

方正 著

☐责任编辑 周兴武

☐责任印制 周颖

☐出版发行 中南大学出版社

社址:长沙市麓山南路

邮编:410083

发行科电话:0731-88876770

传真:0731-88710482

☐印 装 长沙利君漾印刷厂

☐开 本 720 × 1000 B5 ☐印张 19 ☐字数 373 千字

☐版 次 2012 年 10 月第 1 版 ☐2012 年 10 月第 1 次印刷

☐书 号 ISBN 978-7-5487-0705-9

☐定 价 78.00 元

图书出现印装问题,请与经销商调换

Preface

The volume named *Thermodynamics—How much are the real heats of electrode reaction?* is an anthology on a scholarly topic, which embodies the outcome of the author's original research over the years and shows his some fresh ideas in the area of physicochemistry in process metallurgy.

The author's academic work has been mainly focusing on the heats of electrode reaction. In the research into this project, the author has discovered that the heat release and heat absorption of an electrode process could not really be predicted according to the current knowledge of the thermodynamics or electrochemistry, although this type of heats can truthfully be measured by experiments and a fairly accurate forecast of the released or absorbed heats for a cell reaction can also be given. Certainly, the settlement of this problem has to do with the entropy change of an electrode reaction. Therefore, the issue becomes very basic. For example, whether is it always appropriate in all cases to stipulate the entropy change for the standard hydrogen electrode reaction to be zero at any temperature? What is the exact expression of the first and second laws of thermodynamics when they are used to an electrode reaction? In order to predict and experimentally measure the real heats of electrode reaction, the author proposed the concept of the absolute scale first on which the entropy change for standard hydrogen electrode reaction at room temperature has been given. Besides, the content is also complete with the studies of "solution chemistry", "phase boundaries of multicomponent system", "oxygen potential of buffer gases" and "thermodynamic properties of substances". Among them, there are the discussions on the thermodynamic models of aqueous solution of electrolyte and molten salt system, the relationship between the probability-distribution function of water molecules near the solute ion and the osmotic coefficients of electrolyte solution, the complete computation and analytic expression for partial molar properties of components along the phase boundaries, the new representation for the chemical potentials of oxygen, which is different from the classical one, and can be applied to construction of the diagram of oxygen potential against temperature, etc.

The author has attempted to systematize the papers in different points. This will be indispensable to researchers in the field to grasp these contents more deeply and to

understand the contribution in treatment and development of some basic issues. Of course, those conclusions in the collected papers might not be utterly strict and cautious. Some of them still need more deeply academic researches and further experiments to be improved. For example, whether it is appropriate and reasonable to specify both all the entropy change and electrode potential of a reversible electrode reaction to be zero when the temperature in Kelvin approaches zero.

The volume as a valuable reference reading could be useful for student study and postgraduate study of the related specialist area, especially for those interested in mastering the experimental and theoretical aspects of physicochemistry in process metallurgy. The publishing of the book is also expected to be able to enlighten them to know that there might be still something that hampers further development of the discipline, even for the relatively mature discipline and some knowledge that has been more widely accepted.

At the time when the book is published, the author would like to thank the National Natural Science Foundation of China for financial support. It is the support that has created a great surrounding, where the author is able to meditate on the some academic issues in the related projects. The author also wishes to express his appreciation to the State Education Committee of P. R. China and the University of Manitoba of Canada for the researches during the study abroad, and to the research collaborators who give the valuable help.

Professor Xinmin CHEN was my doctoral advisor. He was a well-known scientist of physicochemistry in process metallurgy and the member of the Chinese Academy of Sciences. This year is just the centennial of his birth. To him I dedicate this volume in token of affection and gratitude.

Zheng FANG

Contents

Chapter 1 On Thermoelectrochemistry	(1)
1.1 Theory and Application of Thermoelectrochemistry	(2)
1.2 Some Basic Matters on the Heat Effects at Electrode-Electrolyte Interfaces	(26)
1.3 Thermoelectrochemistry and Its Application to Metallurgical Research	(41)
1.4 The Electrochemical Peltier Heat of the Standard Hydrogen Electrode Reaction	(50)
1.5 Response to “Comment on ‘The Electrochemical Peltier Heat of the Standard Hydrogen Electrode Reaction’ by Zheng Fang et al”	(62)
1.6 Basic Equations for Thermo-electrochemistry and the Entropy Change of the Standard Hydrogen Electrode Reaction	(71)
1.7 The Peltier Heat and the Standard Electrode Potential of Ferro- ferricyanide Couple at 298.15K Determined by Electrochemical- calorimetry	(75)
1.8 Determination of the Entropy Changes for Electrode Reaction and Dilute Enthalpy of Some Ions by Thermoelectrochemical Technology ...	(88)
References	(93)
 Chapter 2 On Solution Chemistry	 (99)
2.1 A New Model for Predicting Thermodynamic Properties of Ternary Metallic Solution from Binary Components	(100)
2.2 A Metallic Solution Model with Adjustable Parameter for Describing Ternary Thermodynamic Properties from Its Binary Constituents ...	(110)
2.3 A Model Describing the Osmotic Coefficients and the Activities of Water for Electrolyte Solutions	(121)

2 / Thermodynamics—How much are the real heats of electrode reaction?

2.4	The Mean Activity Coefficients of LaCl_3 in Dilute Aqueous Solution at 298.15 K	(139)
2.5	A Simplified Regular Solution Model for Solubility of Nonmetal (2) in Metal(1) – Metal(3) Alloy Systems	(151)
2.6	Modeling of Thermodynamic Properties of Multicomponent Electrolyte Solutions	(159)
2.7	A Simplified Subregular Solution Model Describing the Activities of MgCl_2 in Both $\text{KCl} - \text{MgCl}_2 - \text{LiCl}$ and $\text{CaCl}_2 - \text{MgCl}_2 - \text{NaCl}$ Molten Salt Systems	(167)
2.8	A Model for the Activity Coefficients of Water in Aqueous Solution of $\text{HCl} - \text{MCl}_n$ ($M = \text{Ni}, \text{Cu}, \text{Na}, \text{and Fe}$) with Constant Concentration Ratio $X_{\text{HCl}}/X_{\text{MCl}_n}$	(173)
2.9	A Prediction of the Excess Partial Molar Free Energies of MgCl_2 in the $\text{KCl} - \text{MgCl}_2 - \text{LiCl}$ Molten Salt System Containing MgCl_2 below 0.5 from Thermodynamic Properties of Binary Systems	(178)
	References	(184)
Chapter 3 On Phase Boundaries of Multicomponent System		(187)
3.1	Complete Integration of Gibbs-Duhem Equation along Phase Boundaries in Multicomponent System	(188)
3.2	Activities on Phase Boundaries in Multicomponent Systems—A Recursion Formula for Calculation of Activities	(192)
3.3	An Analogue Margules Equation on Phase Boundaries in Multicomponent Systems	(201)
	References	(208)
Chapter 4 On Oxygen Potentials of Buffer Gases		(209)
4.1	Oxygen Potentials and Oxygen-potential Diagrams for Buffer Gas System at Normal Pressure	(210)
4.2	Effect of Oxygen Contents on Oxygen Potentials of $\text{H}_2\text{O} - \text{H}_2$ and $\text{H}_2\text{O} - \text{H}_2 - \text{Inerts}$ Gas Mixtures	(222)

4.3	Oxygen Potentials of CO_2 , $\text{H}_2\text{O}(\text{g})$ and $\text{CO}_2 - \text{CO}$ Gas Mixtures —with Extension of Application of Ellingham Diagram	(234)
	References	(248)
Chapter 5	On Thermodynamic Properties of Substances	(250)
5.1	A Study on Thermodynamic Properties in the System $\text{MoO}_2 - \text{Mo}$ by Gas Equilibration Method	(251)
5.2	Equilibria of the System $\text{MoO}_3 - \text{MoO}_2 - \text{H}_2\text{O} - \text{H}_2$ and Phase Diagram for the System $\text{Mo} - \text{O}$ between 400 and 700°C	(262)
5.3	Equilibrium between Non-stoichiometric MoO_2 and Mo with Application of Sieverts' Law Constant to Smiltens' Integration	(270)
5.4	A New Molybdenum Oxide Phase	(274)
5.5	Recovery of Gallium from Coal Fly Ash	(279)
	References	(294)

Chapter 1

On Thermoelectrochemistry

1.1 Theory and Application of Thermoelectrochemistry^{*}

Abstract: Thermoelectrochemistry (TEC) is a subject that combines the theories and methods of both thermo- and electro-chemistry to investigate the cell and electrode reactions. The parameters of thermodynamics and kinetics 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. TEC can provide the available and comprehensive additional information more for electrode reactions, and compensates the insufficiency for a single electrochemical study or a single thermochemical research to some extent. The exploration for TEC is fast developing, especially in the aspect of new instruments and new techniques. One of the purposes of this paper to discuss some theoretical concepts of TEC, such as the Peltier heat of electrochemical reaction and electrode reaction, the reference point or the absolute scale for research into electrode process, the fundamental equations for reversible electrode reaction in TEC, data-processing for the experiments as well as clarify some vague understanding that still exists in this subject, for example, how much are the real heats of an electrode reaction? whether the definition that the entropy of the standard hydrogen electrode is designated to be zero is reasonable or not in theoretical determination of the real heats of electrode reactions. Furthermore, some applications of TEC to hydrometallurgy and thermodynamics of electrode reaction are mentioned, which are focused on the electrogenerative and simultaneous leaching of mineral.

Keywords: Electrode-electrolyte interface; Electrochemical Peltier heat; Electrochemical Peltier coefficients; Absolute scale; Entropy change; Standard hydrogen electrode; Single electrode process; Power generation leaching

^{*} The original text published in *Thermodynamics-Physical Chemistry of Aqueous System* edited by Juan Carlos Moreno-Pirajan IN TECH Press in 2011. The author is Z. Fang (Chemistry and Chemical Engineering College, Central South University).

1.1.1 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 [6–29], 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 ΔS 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

4 / Thermodynamics—How much are the real heats of electrode reaction?

standard state. Its change in entropy is calculated to be about $\Delta S^\ominus = S_{\text{Cu}}^\ominus - 2S_{\text{e}^-}^\ominus - S_{\text{Cu}^{2+}}^\ominus = 2.2 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. The heat effects, Q should be $T\Delta S^\ominus = 0.65 \text{ kJ} \cdot \text{mol}^{-1}$ at 298.15 K, 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, 30]. 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, 31, 32], 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 were 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 [33].

1.1.2 Electrochemical Peltier heat and the absolute scale

1.1.2.1 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 [34]

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

where i is electric current, $Q(T)$, Peltier heat dependent on temperature, T in Kelvin,

t , time and π_{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 [35], i. e.

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

where ΔG is the free energy change of the reaction, z electron transfer number, \mathcal{F} Faraday constant, ε_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 $(\partial(\Delta G)/\partial T)_P$ is an amount independent on reaction process, and only related to changes in the function of state. That is to say, EPH 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

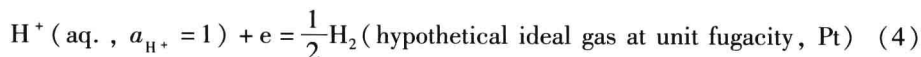
characteristics of the electrode process.

Another one is that the thermodynamic functions of the standard hydrogen electrode (SHE) are taken as the reference of ΔG and ε_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 ε_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, ε_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 100×10^{-6} volt [34] 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].

1.1.2.2 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 [36], 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 the reference point of 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 change 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, φ^* , in the absolute scale as follows [37]:

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

where the amount marked with an asterisk is on the “absolute scale” (the same below), $\varphi^*(\text{H}^+/\text{H}_2)$ the electrode potential of SHE on this scale and $\varphi(\text{vs. SHE})$ on the conventional scale. And both φ^* and $\varphi^*(\text{H}^+/\text{H}_2)$ are designated to zero when $T \rightarrow 0$ [2].

On this scale, the entropy change for a single-electrode reaction, ΔS_T^* will be characterized as:

$$\Delta S_T^* = z\mathcal{F}(\partial\varphi_T^*/\partial T)_P \quad (6)$$

When integrating Eq. (6), the integral constant, ΔS_0^* is appointed to zero at $T \rightarrow 0$ based on the third law of thermodynamics.

The resultant EPH of the electrochemical reaction, Π is defined as

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

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, $\varphi^* (\text{H}^+/\text{H}_2)$ in Eq. (5), common to both electrodes of the cell, does not appear explicitly because they are deleted ultimately. The φ^* 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 ΔS_T^* according to Eq. (6) which can be rewritten as

$$\varphi_T^* = \int \Delta S_T^* dT / (z\mathcal{F}) \quad (9)$$

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

It should be pointed out that a specified reference is $\varphi_T^* \rightarrow 0$ and $\Delta S_T^* \rightarrow 0$ when $T \rightarrow 0$ on the absolute scale. This merely is for expedience to identify other values at temperature 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, φ_T^* might have an own individual value for each electrode when $T \rightarrow 0$.

1.1.3 The basic equations for thermoelectrochemistry and experiments for determination of the entropy change of SHE on absolute scale

1.1.3.1 The basic equations for thermoelectrochemistry

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 on 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 Eqs. (8), (12), (13) and (14), and noting that $\Delta G = -W_e$ (vs. SHE) $= -z\mathcal{F}\varphi$, we have

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

or

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

where W_e is the reversible electric work done on the conventional scale, $\Delta H^\square = \Delta H + zT\Delta S^* (H^+/H_2)$, which is called as the apparent enthalpy change. It should be noted that $\Delta S^* (H^+/H_2)$ 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

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

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

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

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