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The electrochemical Peltier heat of the standard hydrogen electrode reaction

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ABSTRACT

A method for measuring the electrochemical Peltier heat (EPH) of a single electrode reaction has been developed and an absolute scale is suggested to obtain EPH of the standard hydrogen electrode. The scale is based on $\phi_0^* = 0$ and $\Delta S_0^* = 0$ for any electrode reaction at zero Kelvin, in accord with the third law of thermodynamics. The relationships between entropy, enthalpy and free energy changes on this scale and on the conventional scale are derived. Calorimetric experiments were made on the $Fe(CN)_6{}^{3-}/Fe(CN)_6{}^{4-}$ system at five different concentrations at 298.15 K, and EPH for the standard hydrogen electrode reaction is obtained. EPHs and the entropy change on the absolute scale for the studied redox are linearly related to concentration of electrolyte. The reversible electric work is almost concentration independent in the range of concentration studied.

1. Introduction

The heat effects of half-cell reactions including conducting polymer electrode [1], molten salt system [2], electricity generating leaching of minerals [3], determination of transfer functions [4], and studies of kinetics and mechanism of electrode reactions [5,6], have been explored. Several methods have been applied to the electrochemical Peltier heat (EPH) measurement for electrode reactions [7–13], but EPH was defined as the heat effect observed when electric current passes through the interface between electrode and electrolyte [14–17], including the entropy change due to electrochemical polarization. The reported methods for determining EPH were mostly based on heat or entropy balance in an electrode process [7,18]. Based on these definitions and methods it is very difficult to obtain reliable EPH of an electrode reaction because of some irreversible effects such as Joule heating related to current intensity, type and concentration of supporting salt. These EPH values are not always easy to compare [19]. The results would be hard to obtain even for the same system, and therefore, the validity of the EPH values cannot be ensured because there is no appropriate criterion. Especially for the standard hydrogen electrode reaction, it is difficult to keep the experimental conditions at the standard state. This paper aims to give a definition of EPH that can be experimentally reproduced and to determine EPH of the standard hydrogen electrode reaction by measuring the heat evolved by the $Fe(CN)_6{}^{3-}/Fe(CN)_6{}^{4-}$ redox during the charge flow.

2. Theoretical consideration

Consider the isothermal process of the standard hydrogen electrode (SHE) reaction at constant pressure:

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

All species participating in the process are at each standard state, i.e. the activity of hydrogen ion at unit (molality) concentration is 1, hydrogen is a hypothetical ideal gas at unit fugacity, and a hypothetically ideal electron gas with unit fugacity in metal is for electron. Traditionally, the electrode potential of reaction (1) is assigned as zero at all temperatures, although a value other than zero exists at every temperature. Let the potential of reaction (1) be denoted as $\phi^*(H^+/H_2)$ as a reference on the absolute scale at a given temperature. The relationship between the potential ϕ (vs. SHE) on the conventional and ϕ^* on the absolute scale for any electrode at the same temperature and pressure is

$$\phi^* = \phi \quad (\text{vs.}\quad \text{SHE}) + \phi^*(H^+/H_2) \qquad (2)$$

and

$$\Delta L^* = \Delta L + z\Delta L^*(H^+/H_2) \qquad (3)$$

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where ΔL^* represents the Gibbs free energy change ΔG^*, the entropy change ΔS^* or the enthalpy change ΔH^* on the absolute scale; ΔL are ΔG, ΔS or ΔH on the conventional scale, and z is electron transfer number. The EPH of an electrode reaction, $\prod$ is

$$\Pi = T(\Delta S^*)_{i\to 0} \tag{4}$$

where ΔS^* is the absolute entropy change (AEC) and T is the temperature in Kelvin. The current $i \to 0$ indicates that the electrode reaction carries out reversibly. EPH is the reversible heat effect of the redox reaction. At any temperature except absolute zero, $\prod(H^+/H_2)$ is not equal to zero and can be measured directly, i.e. AEC is not zero.

According to Faraday's law, moles of reaction are $\int i\,dt/(zF)$ integrated from zero to t with Faraday's constant F and time t. Eq. (4) can be rewritten as

$$\Pi = T\Delta S^* \left(\int \frac{i\,dt}{zF} \right)_{i\to 0} \tag{5}$$

In the absolute scale, we have

$$\Delta G^* = \Delta H^* - T\Delta S^* \tag{6}$$

and

$$\Delta G^* = -z\phi^* \mathcal{F} \tag{7}$$

3. $\Delta S^*(H^+/H_2)$ for standard hydrogen electrode reaction

Combination of Eqs. (7), (6), (2) and (3) yields

$$-zF\phi \text{ (vs. SHE)} = (\Delta H + z\Delta H^*(H^+/H_2) + zF\phi^*(H^+/H_2)) - T\Delta S^* \tag{8}$$

Rearranging Eq. (8) and considering $\prod = T\Delta S^*$ and $\Delta H^* + zF\phi^* = T\Delta S^*$, we have

$$\Pi - W_e = \Delta H^{\square} \tag{9}$$

where $\Delta H^{\square} = \Delta H + zT\Delta S^*(H^+/H_2)$, which is the thermo-electrochemical apparent molar enthalpy change of reaction and electric work is $W_e = zF\phi$ (vs. SHE).

For more than or less than a molar change, Eq. (9) changes to

$$\Pi - W_e = \Delta H^{\square} \int i\,dt/(z\mathcal{F}) \tag{10}$$

Note that Eq. (10) is strictly correct only under the condition of $i \to 0$. When a small electric current passes through, Eq. (10) can be approximately written as

$$Q - W_e' = \Delta H^{\square\prime} \int i\,dt/(z\mathcal{F}) \tag{11}$$

where electric work $W_e' = \int i((\phi + \eta)$ (vs. SHE) dt with equilibrium potential ϕ and overpotential η, Q is the total heat effect including irreversible effects such as Joule heat, and $\Delta H^{\square\prime}$ corresponds to $\Delta H^{\square}$ but includes irreversibility. Clearly, $Q \to \prod$, $W_e' \to W_e$ (or $\eta \to 0$), $\Delta H^{\square\prime} \to \Delta H^{\square}$ and Eq. (11) reduces to (10) when $i \to 0$. With the extrapolated $\Delta H^{\square}$ value and ΔH of the studied reaction on the conventional scale, $\Delta S^*(H^+/H_2)$ and then $\prod(H^+/H_2)$ can be calculated based on the definition of $\Delta H^{\square}$ and Eq. (4), respectively. This shows that EPH of reaction (1) can be obtained by measurement of the thermo-electrochemical apparent molar enthalpy change $\Delta H^{\square}$ of any reversible electrode reaction.

Eq. (5) can also be applied to obtain $\Delta S^*(H^+/H_2)$ and $\prod(H^+/H_2)$. Note that the equation is strictly correct under the condition of $i \to 0$. When a small electric current passes through, the equation can be approximately written as

$$Q = T\Delta S^* \int \frac{i\,dt}{zF} \tag{12}$$

where the meaning of Q is the same as that in Eq. (11). Also, $Q \to \prod$ and Eq. (12) reduces to (5) as $i \to 0$. Using the $\prod$ value from extrapolation and ΔS on the conventional scale, $\Delta S^*(H^+/H_2)$ and $\prod(H^+/H_2)$ can be calculated according to Eqs. (3) and (4).

Differentiating both sides of Eq. (5) with respect to t at constant temperature and letting $i \to 0$, we acquire Eq. (13):

$$\Delta S^* = K \left(\frac{q}{i} \right)_{i\to 0} \tag{13}$$

where $K = zF/T$ and $q = d\prod/dt$ or heat flow. When an electrode reaction reversibly carries out, the ratio of heat flow to electric current, $(q/i)_{i\to 0}$ is just electrochemical Peltier coefficient π (EPC). Eq. (13) is fundamental for obtaining EPH, too.

4. Experimental and data-processing method

The heat effect was determined by temperature-rise calorimetry. The schematic diagram of experimental setup is shown in 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). A platinum wire jointing with working electrode straight reached to electrolyte outside and connected to a copper wire. The reference electrode was used to track the change in potential of electrode (H). A thermo-sensitive resistor (L) 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 SRC-100 Solution-Reaction Calorimeter (C) (Wuhan University, China) with ±0.001 K was the reference. The electric bridge of the calorimeter measured change in temperature of working electrode. At the beginning of every run, the electric bridge was balanced by adjusting the inner reference resistor. The temperature change of working electrode (H) was output when 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. For the present experiment, ΔV (mV) = 170.199ΔT (K) − 0.0069. The potential signals of temperature change, electric currents and electrode potentials as a function of time were simultaneously collected by calorimeter

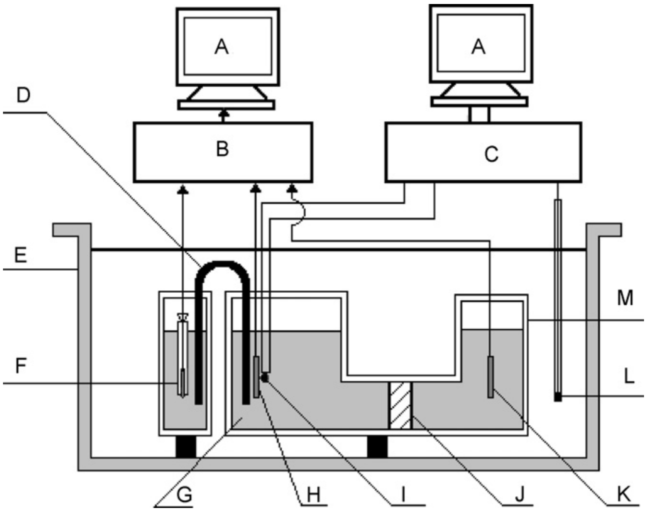

Fig. 1. Schematic diagram of experimental apparatus: (A) computer, (B) CHI660B electrochemical workstation, (C) SRC-100 solution-reaction isoperibol calorimeter, (D) salt bridge, (E) isothermal water bath, (F) saturated calomel electrode, (G) electrolyte, (H) working electrode, (I) thermo-sensitive resistor, (J) porous ceramic, (K) auxiliary electrode, (L) thermo-sensitive resistor, and (M) U-type compartment.

(C) and the CHI660B Electrochemical Workstation (B) (Shanghai Chenhua instrument Co. Ltd.), and were recorded with about 4.6 data points per second by means of the software of computers (A). The temperature change was used for determining Q and electric currents and potential for W_e'. The data-processing method is as follows:

$$Q = \boldsymbol{k}\int \Delta T(t)\,\mathrm{d}t \tag{14}$$

where $\Delta T(t)$ is the change in temperature of the working electrode as a function of time t, and $\boldsymbol{k}$ is a constant related to the apparatus, the heat capacities of solution and electrode, etc. Substituting Eq. (14) into Eq. (11), we have

$$[z\mathcal{F}\boldsymbol{k}\int \Delta T(t)\mathrm{d}t]/\int i\mathrm{d}t = \Delta H^{\square\prime} + z\mathcal{F}W_e'/\int i\mathrm{d}t \tag{15}$$

Drawing a straight-line of $\int \Delta T(t)\,\mathrm{d}t/\int i\,\mathrm{d}t$ against $W_e'/\int i\,\mathrm{d}t$ based on the data at various electric currents, $\boldsymbol{k}$ and $\Delta H^{\square\prime}$ can be determined from the slope and intercept of the line, respectively. Considering $Q=(zF\boldsymbol{k}\int \Delta T(t)\,\mathrm{d}t/\int i\,\mathrm{d}t)$, and $Q\rightarrow\prod$ and $\left(zFW_e'/\int i\,\mathrm{d}t\right)\rightarrow W_e$ when $i\rightarrow 0$, $\prod$ and W_e of the reversible electrode reaction studied at a concentration c can be acquired by extrapolating current to zero, and then $\Delta H^{\square}(c)$ is obtained according to Eq. (9). Further extrapolating concentration to zero, $\Delta H^{\square}(c\rightarrow 0)$ in the infinitely dilute electrolyte is acquired from $\Delta H^{\square}(c)$ at different concentrations. Thus $\Delta S^{*}(H^+/H_2)$ at a given temperature was determined based on the difference of $\Delta H^{\square}(c\rightarrow 0)$ and $\Delta H^{\circ}(c\rightarrow 0)$ from the thermodynamic data of ions and substances on the conventional scale.

The chemicals used, $K_3Fe(CN)_6$, $K_4Fe(CN)_6$ and KCl were analytical reagent (Xiangzhong Chemicals Co. Ltd.). Water was redistilled. KCl was used as supporting electrolyte. The $Fe(CN)_6^{3-} + Fe(CN)_6^{4-} + 1$ M KCl solutions were prepared with equal molar concentrations of the two negative ions being 0.075, 0.15, 0.2, 0.25, and 0.3 M. The experiments were done at 298.15 K.

5. Results and discussion

The reaction is

$$Fe(CN)_6^{3-}\ (\text{solution with } 1\,\text{M KCl},\ c) + e^- \rightarrow Fe(CN)_6^{4-}\ (\text{solution with } 1\,\text{M KCl},\ c) \tag{16}$$

with the standard states of solutes all being a hypothetical solution which obeys Henry's law at each unit molality concentration, resulted from ideal extrapolation from infinite dilution, and an idea electron gas with unit fugacity in metal for electron. Typical curves of the electrode potentials and temperature change against time at a given constant current are shown in Fig. 2. The time interval from the starting point 'a' to the ending point 'b' is 120 s. For 0.2 M $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$, the curves for the electrode potentials and the temperature change against time at electric currents from 1.0 to 7.0 mA are shown in Fig. 3A and B, respectively. The curves for other concentrations are similar to the 0.2 M system. The results for different concentrations are listed in Table 1.

The integrals in Table 1, which are automatically computed by software, are from 0 to 120 s. $\boldsymbol{k}$, $\Delta H^{\square\prime}$, $\prod(Fe(CN)_6^{3-}/Fe(CN)_6^{4-}) = (Q)_{i\rightarrow 0}$ and $W_e = (W_e')_{i\rightarrow 0}$ for the corresponding concentration c are listed in Table 1. Plotting $\Delta H^{\square}(c)$ against concentration (Fig. 4A) gives $\Delta H^{\square}(c\rightarrow 0) = -80.2\,\text{kJ mol}^{-1}$, and then $\Delta S^{*}(H^+/H_2)$ according to the thermo-electrochemical apparent molar enthalpy change $\Delta H^{\square}$ of the redox couple and $\Delta H^{\circ} = -106.3\,\text{kJ mol}^{-1}$ calculated from the enthalpy of the substances taking part in the reaction [20]. $\Delta S^{*}(H^+/H_2)$ at 298.15 K is determined as $(87.6 \pm 1.0)\,\text{J K}^{-1}\,\text{mol}^{-1}$, very close to $87.8\,\text{J K}^{-1}\,\text{mol}^{-1}$ determined by thermal cells [21]. The partial molar absolute entropy of hydrogen ions, $(-22.3 \pm 1.0\,\text{J K}^{-1}\,\text{mol}^{-1})$

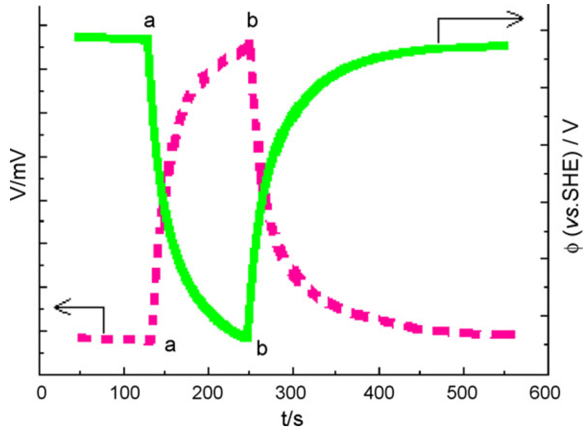

Fig. 2. The typical curves for electrode potentials against time and for potential signals of temperature difference against time at given constant electric current; the current passing through interface between electrode and electrolyte started from point 'a' and ended at point 'b'.

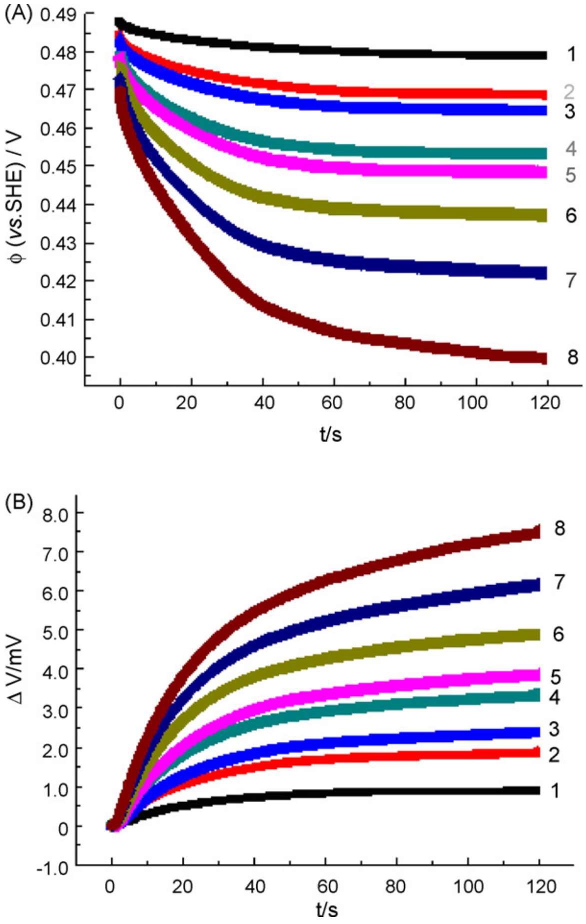

Fig. 3. Plots of the electrode potentials against time (A) and the potential signals for temperature difference against time (B) for the 0.2 M $Fe(CN)_6^{3-}$/0.2 M $Fe(CN)_6^{4-}$ system at various electric currents; the curves from no. 1 to 8 correspond to currents 1.0, 2.0, 2.5, 3.5, 4.0, 5.0, 6.0,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

Table 1
The results for $Fe(CN)_6{}^{3-}/Fe(CN)_6{}^{4-}$ system

C (mol dm^{-3})	i (mA)	$\int_0^t i\,dt$ (A s)	$\dfrac{\int_0^t (\Delta V+6.9\times10^{-6})\,dt}{\int_0^t t\,dt}$ [a] (V A^{-1})	$\dfrac{\int_0^t i(\phi+\eta)(\mathrm{SHE})\,dt}{\int_0^t t\,dt}$ (V)	**k** (A)	$-\Delta H^{\square}(c)$ (kJ mol^{-1})	$-\prod$ (kJ mol^{-1})	W_e (kJ mol^{-1})
0.075	$i\to0$	0	0.732	0.484	−0.566	86.67	39.97	46.70
	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	$i\to0$	0	0.675	0.489	−0.715	93.75	46.57	47.18
	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	$i\to0$	0	0.698	0.494	−0.750	98.17	50.51	47.66
	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				
	7.0	0.84	0.803	0.414				
0.25	$i\to0$	0	0.724	0.491	−0.783	102.07	54.70	47.37
	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				
	5.0	0.60	0.771	0.454				
	5.5	0.66	0.775	0.451				
0.30	$i\to0$	0	0.814	0.497	−0.751	106.96	58.98	47.97
	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				

[a] 6.9×10^{-6} (V) originated from experimental calibration $\Delta V\,(\mathrm{mV}) = 170.199\Delta T\,(\mathrm{K}) - 0.0069$.

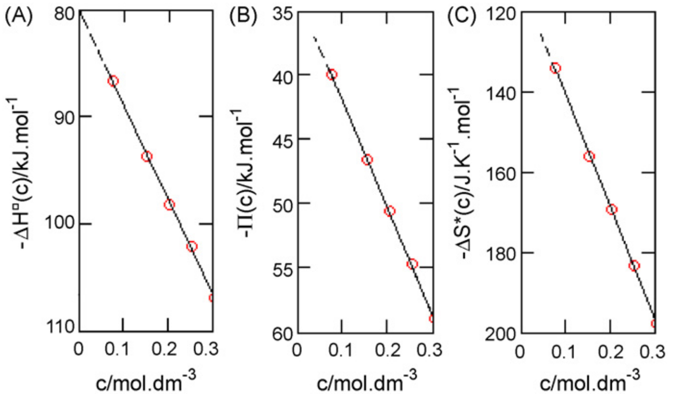

Fig. 4. Plots of $\Delta H^{\square}(c)$ (A), $\prod(c)$ (B), and $\Delta S^{*}(c)$ (C) against concentration for $Fe(CN)_6{}^{3-}/Fe(CN)_6{}^{4-}$ system with the equations of fitted lines: (A) $\Delta H^{\square}(c) = (-89.1c - 80.2) \pm 0.3$ (kJ mol^{-1}); (B) $\prod(c) = (-84.0c - 33.8) \pm 0.3$ (kJ mol^{-1}), and (c) $\Delta S^{*}(c) = (-281.7c - 113.3) \pm 1.0$ (J K^{-1} mol^{-1}).

derived from this value (87.6 ± 1.0 J K^{-1} mol^{-1}) is very close to an average (-22.2 ± 1.4 J K^{-1} mol^{-1}) of the values obtained by Eastman (1926), Lange and Hesse (1933), Li and Dai (1941), Crockford and Hall (1950), Gurney (1951), Criss and Cobble (1964), Brack and Lin (1965) and Ikeda (1965) [21]. EPH for reaction (1) at 298.15 K is (26.1 ± 0.3) kJ mol^{-1}.

$\Delta H^{\square}(c)$ obtained by the linear extrapolation of current approaching zero is based on approximate Ohm's law at small overpotentials and is also linearly related with concentration. W_e is almost concentration independent, therefore, as shown by Fig. 4B and C, $\prod(c)$ and $\Delta S^{*}(c)$ for $Fe(CN)_6{}^{3-}/Fe(CN)_6{}^{4-}$ are also linearity related with concentration in the range of concentration studied.

AEC for reaction (1) and the absolute entropy of hydrogen ions derived from this experiment are in accord with those obtained by other methods, indicating the validity of this method. In our previous studies on the $AgNO_3/Ag$, H_2SO_4/H_2 and $Fe(CN)_6{}^{-3}/Fe(CN)_6{}^{-4}$ systems with different technique [22], the obtained $\Delta S^{*}(H^{+}/H_2)$ at 298.15 K (Table 2) are within the experimental errors in spite of the different systems, demonstrating that EPH is a characteristic value of a given electrode reaction.

Table 2
$\Delta S^{*}(H^{+}/H_2)$ (J K^{-1} mol^{-1}) from different electrode reactions at 298.15 K [22]

System	$Fe(CN)_6{}^{3-}/Fe(CN)_6{}^{4-}$	$AgNO_3/Ag$	H_2SO_4/H_2
Set 1	88.1		87.2
Set 2	87.9	88.9	
Set 3	87.6 (this work)		

In this approach, an absolute scale is proposed. Strictly speaking, the absolute scale is based on $\phi_0^* = 0$ and $\Delta S_0^* = 0$ for any electrode reaction at zero Kelvin. Accordingly, $\Delta G_0^* = -zF\phi_0^* = 0$, resulting in $\Delta H_0^* = \Delta G_0^* + T\Delta S_0^* = 0$ at this temperature (where subscript 0 represents the quantity at zero Kelvin). Since the entropy change of reaction (1) on the absolute scale at any temperature except absolute zero, ΔS_T^*, can be obtained by experiments, ϕ_T^* can be obtained by means of Eq. (17) with integral range from absolute zero to a designated temperature T at constant pressure:

$$\phi_T^* = \int \left[\frac{\Delta S_T^* \, \mathrm{d}T}{zF} \right]_p \tag{17}$$

Consequently, ΔG_T^* $(= -zF\phi_T^*)$ and ΔH_T^* $(= \Delta G_T^* + T\Delta S_T^*)$ for any electrode reaction at temperature T can be acquired.

Our previous research [23] demonstrated that the difference between the apparent molar enthalpy change $\Delta H^{\square}$ and ΔH was a constant, $zT\Delta S^{*}(H^{+}/H_2)$. According to the first law of thermodynamics at constant pressure:

$$Q - W_e = \Delta H \int \frac{i \, \mathrm{d}t}{zF} \tag{18}$$

Comparing Eq. (18) with Eq. (10), there is a constant difference, $zT\Delta S^{*}(H^{+}/H_2)$ for a redox with the same number of electron transfer at the same temperature. Therefore "the enthalpy change" calculated from the left side of Eq. (18) is $zT\Delta S^{*}(H^{+}/H_2)$ larger than that calculated by Eq. (10) when $i \to 0$.

EPH above was considered as heat effect observed when electric current passes through, making it indefinite due to electrochemical polarization. When defined as $T(\Delta S^{*})_{i\to 0}$ or $\prod/(zF) = (q/i)_{i\to 0}$, EPH is clear and unambiguous, where $i \to 0$ means that the reaction approaches reversibility. The heat effect of a reversible process has a certain value directly related to ΔS^{*} of reaction. As a result, EPH must be definite and can be compared with that by other experimental methods.

Taking electrode polarization into account, Eq. (13) can be transformed as follows:

$$K\left(\frac{q}{i}\right) = \Delta S^* + \Delta_i S^* \tag{19a}$$

or

$$K\left(\frac{q}{i}\right) = K\pi + \Delta_i S^* \tag{19b}$$

where $\Delta_i S^{*}$ is AEC due to irreversible factors such as overpotential, concentration gradient, Joule heat, impedance, etc. and depends on polarization extent. From Eq. (19a) and (19b), the entropy change of irreversible processes due to current flow can be obtained. There are some reports on EPH analyzed by irreversible thermodynamics [10,24,25]. If $\Delta_i S^{*}$ dependent on polarization is not separated from ΔS^{*} and becomes a part of ΔS^{*}, π in this case was indefinite and dependent on polarization extent.

6. Conclusions

A method for determining the EPH of any electrode reaction has been developed. In the approach, an absolute scale for half-cell reaction is introduced. The AEC for any electrode reaction is equal to the sum of the entropy change on the conventional scale and AEC of the standard hydrogen electrode reaction, which equals the difference between the thermo-electrochemical apparent molar enthalpy change of this half-cell reaction and its enthalpy change on the conventional scale. EPH is anew defined as a characteristic quantity related to AEC of an electrode reaction, i.e. the heat equals to the product of AEC and temperature T in Kelvin. A set of experiments measuring the evolved heat and electric work on the $Fe(CN)_6{}^{3-}/Fe(CN)_6{}^{4-}$ redox couple at five different concentrations was made. EPH and AEC for the standard hydrogen electrode reaction with single electron transfer at 298.15 K are obtained by this set of experiments as (26.1 ± 0.3) kJ mol^{-1} and (87.6 ± 1.0) J K^{-1} mol^{-1}, respectively.

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