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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:

$$\mathrm{H}^+\ (\text{solution},\ a_{\mathrm{H}^+} = 1) + \mathrm{e}^- \rightarrow \frac{1}{2}\mathrm{H}_2$$
$$(\text{gas},\ \text{unit fugacity},\ \text{on the platinum electrode}) \qquad (1)$$

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 $\phi^*(\mathrm{H}^+/\mathrm{H}_2)$ 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

$$\phi^* = \phi \quad (\text{vs.}\quad \text{SHE}) + \phi^*(\mathrm{H}^+/\mathrm{H}_2) \qquad (2)$$

and

$$\Delta L^* = \Delta L + z\Delta L^*(\mathrm{H}^+/\mathrm{H}_2) \qquad (3)$$

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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, $\prod(\mathrm{H}^+/\mathrm{H}_2)$ 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 $\int i\,\mathrm{d}t/(zF)$ integrated from zero to t with Faraday's constant F and time t. Eq. (4) can be rewritten as

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

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. $\Delta S^*(\mathrm{H}^+/\mathrm{H}_2)$ for standard hydrogen electrode reaction

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

$$-zF\phi\ (\text{vs. SHE}) = (\Delta H + z\Delta H^*(\mathrm{H}^+/\mathrm{H}_2) + zF\phi^*(\mathrm{H}^+/\mathrm{H}_2)) - T\Delta S^* \tag{8}$$

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 $\Delta H^{\square} = \Delta H + zT\Delta S^*(\mathrm{H}^+/\mathrm{H}_2)$, which is the thermo-electrochemical apparent molar enthalpy change of reaction and electric work is $W_\mathrm{e} = zF\phi$ (vs. SHE).

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

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

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

$$Q - W_e' = \Delta H^{\square\prime} \int i\mathrm{d}t/(z\mathcal{F}) \tag{11}$$

where electric work $W_\mathrm{e}' = \int i((\phi + \eta)\ (\text{vs. SHE})\,\mathrm{d}t$ 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, $Q \to \prod$, $W_\mathrm{e}' \to W_\mathrm{e}$ (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, $\Delta S^*(\mathrm{H}^+/\mathrm{H}_2)$ and then $\prod(\mathrm{H}^+/\mathrm{H}_2)$ 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 $\Delta S^*(\mathrm{H}^+/\mathrm{H}_2)$ and $\prod(\mathrm{H}^+/\mathrm{H}_2)$. 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

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

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, $\Delta S^*(\mathrm{H}^+/\mathrm{H}_2)$ and $\prod(\mathrm{H}^+/\mathrm{H}_2)$ 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 $q = \mathrm{d}\prod/\mathrm{d}t$ 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, $\Delta V\ (\mathrm{mV}) = 170.199\Delta T\ (\mathrm{K}) - 0.0069$. The potential signals of temperature change, electric currents and electrode potentials as a function of time were simultaneously collected by calorimeter

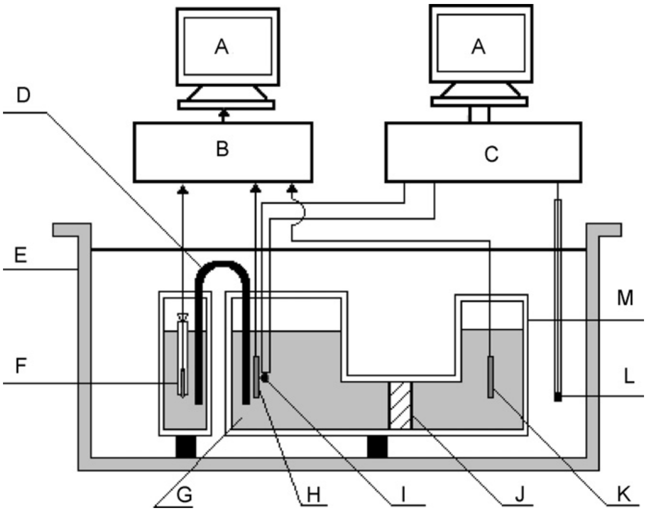

Fig. 1. Schematic diagram of experimental apparatus: (A) computer, (B) CHI660B electrochemical workstation, (C) SRC-100 solution-reaction isoperibol calorimeter, (D) salt bridge, (E) isothermal water bath, (F) saturated calomel electrode, (G) electrolyte, (H) working electrode, (I) thermo-sensitive resistor,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