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Coupling microcalorimeter with electrochemical instruments for thermoelectrochemical research

Hengzhong Zhang*, Pinming Zhang, Zheng Fang

Department of Chemistry, Central South University of Technology, Changsha, Hunan 410083, People's Republic of China

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Abstract

A measurement system that couples a commercial microcalorimeter with usual electrochemical instruments was established for electrochemical calorimetry of electrode reactions. Apparent enthalpy change of anodic oxidation of ferrocyanide ion to ferricyanide ion and apparent enthalpy change of cathodic reduction of hydrogen ion to hydrogen gas were determined with this system. The difference between the apparent enthalpy change and the value calculated with conventional thermodynamic data of aqueous ions was found to be a constant at a given temperature. This system can further be used to determine unknown standard enthalpy changes of electrode reactions. © 1997 Elsevier Science B.V.

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1. Introduction

Special electrochemical calorimeters were employed to investigate the enthalpy changes and the entropy changes of electrode reactions [1–3]. Unfortunately these apparatus have not been widely used for the reason that too many calibrations were needed in addition to the complicated design and manufacture. Furthermore, inconsistent experimental principles were adopted, which resulted in the experimentally deduced enthalpy and entropy data being not comparable with each other and especially with conventional thermodynamic data. These differences have been bridged by the newly derived thermoelectrochemical equations [4]. In the present work we will establish a measurement system that couples a Calvet microcalorimeter with usual electrochemical instruments out of the consideration that a commercial calorimeter is of sensitive detection limit, high measurement precision, good reproducibility and easy to operate. Several electrode systems will be tested with this coupling under constant current polarization. Such a measurement system is expected for more common and wider uses.

2. Experimental

The following equation applies to the calorimetry of an electrode reaction [4]:

$$Q_{p,i} \pm \int \phi_i(\mathrm{vs\,SHE}) I\mathrm{d}t = \frac{\Delta_\mathrm{r} H_{m,i}}{z_i F} \cdot \int I\mathrm{d}t - R_i \int I^2\mathrm{d}t \quad (+ : i = a, - : i = c) \qquad (1)$$

where the foot note i denotes the anodic reaction (i=a) or cathodic reaction (i=c), $Q_{p,i}$ the endothermic process heat, ϕ_i the electrode potential vs. the standard

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*Corresponding author.

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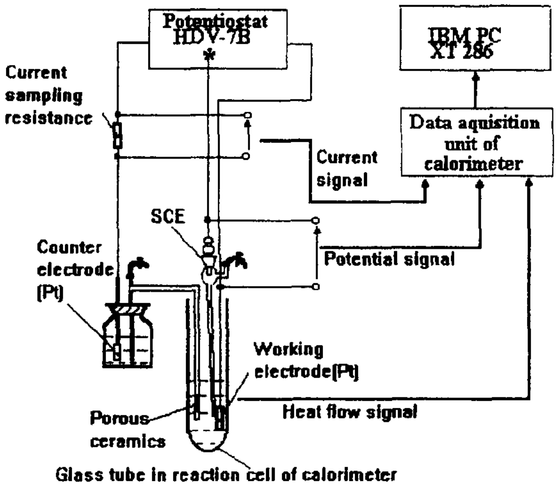

Fig. 1. A set-up that couples a microcalorimeter with electrochemical instruments

hydrogen electrode (SHE), I the polarization current (I>0), t the time, z_i the stoichiometric coefficient of electron in the electrode reaction, F the Faraday constant, $\Delta_r H_{m,i}$ the molar apparent enthalpy change of the reaction, and R_i the effective electrical resistance of anode or cathode compartment. With the thermoelectrochemical signals, the heat flow h, the potential ϕ_i and the current I obtained from electrochemical calorimetry, the apparent enthalpy change of the electrode reaction can then be figured out. These signals can be measured by coupling a microcalorimeter with the usual electrochemical instruments. Fig. 1 shows the combination.

A Calvet heat flux microcalorimeter (Setaram HT1000) was used. The major electrochemical instrument used is a potentiostat (Fujian HDV-7B). In order to carry out electrochemical calorimetry the functions of the calorimeter were expanded, and a corresponding computer software THEL was developed [5]. Beforehand, the temperature measurement and the sensitivity of the calorimeter were carefully calibrated with metallic standards and by Joule effects, and were further confirmed by the enthalpy change of the electrochemical decomposition of water [5]. Digital voltmeters measuring the potential and the current were also carefully calibrated with a standard Weston cell and a potentiometer. High precision (0.01%) electrical resistance was used for current sampling.

An electrode system including a working platinum electrode, a saturated calomel electrode (SCE) for reference, a tube connector to the counter electrode, and about 10 cm^3 electrolyte solution, was placed into

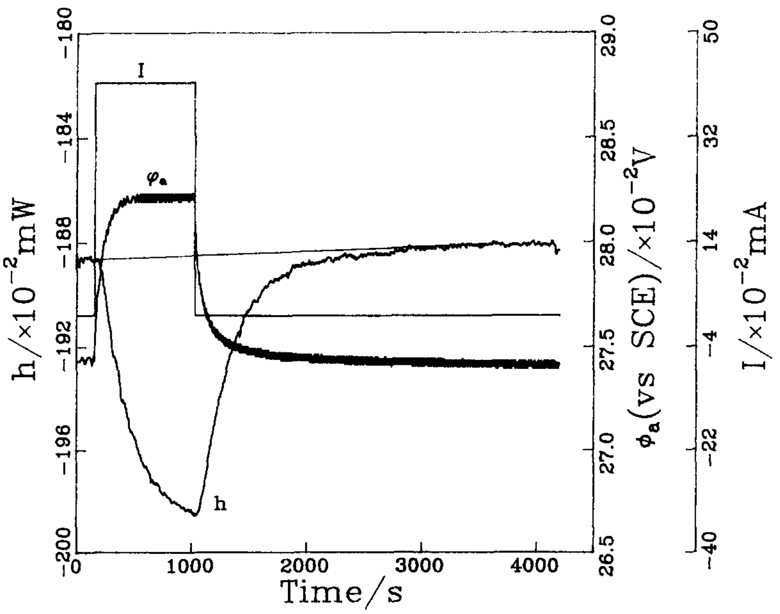

Fig. 2. An experimental record of reaction (4) at active ion concentration 0.10 mol l^{-1}

the glass tube in the reaction cell of the calorimeter. After thermal stabilization, a constant current polarization was enforced to the electrode system by the potentiostat for a period. Then the signals, the heat flow, the electrode potential and the current were all collected simultaneously by a 286 computer. Heat of the process can be obtained by integrating the heat flow. For the same electrode system a series of calorimetry under various constant current polarization were carried out. Data processing is as follows:Eq. (1) can be turned into Eq. (2) at constant current polarization:

$$\frac{Q_{p,i} \pm \int \phi_i(\mathrm{vs\,SHE}) I \mathrm{d}t}{\int I \mathrm{d}t} = \frac{\Delta_r H_{m,i}}{z_i F} - R_i \cdot I \qquad (2)$$

or

$$y = \frac{\Delta_r H_{m,i}}{z_i F} - R_i \cdot I \qquad (3)$$

where y in Eq. (3) represents the left hand side of Eq. (2). Therefore, the apparent enthalpy change can be deduced according to Eq. (3) by linear regression with data of y vs. I.

Anodic process in the aqueous electrolyte solutions potassium ferrocyanide + potassium ferricyanide saturated with potassium chloride, and cathodic process in sulfuric acid solutions were tested. Solutions used were prepared from reagent chemicals. Fig. 2 shows an experimental record.

3. Results and discussion

Experimental results are listed in Table 1 for the anodic oxidation of ferrocyanide ion to ferricyanide ion:

$$\mathrm{Fe(CN)_6^{4-}} - \mathrm{e} = \mathrm{Fe(CN)_6^{3-}} \qquad (4)$$

and are listed in Table 2 for the cathodic reduction of hydrogen ion to hydrogen gas:

$$2\mathrm{H^+} + 2\mathrm{e} = \mathrm{H_2(g)} \qquad (5)$$

Dependence of y on I was gained by linear regressions with Eq. (3), regression coefficient r was also given in the Tables. The apparent enthalpy change of the reaction and the effective electrical resistance then can be computed (see Table 1 and Table 2). The apparent enthalpy change of reaction (4) at active ion concentration 0.10 mol l^{-1}, 90.5 kJ mol^{-1}, is close to that obtained by the calorimetry under sweep-current polarization, 94.7 kJ mol^{-1} [6].

It was found that the enthalpy change of a reaction in an aqueous solution changes linearly with the square root of the concentration of an aqueous reagent

Table 1

Calorimetry of the anodic oxidation reaction $\mathrm{Fe(CN)_6^{4-}} - \mathrm{e} = \mathrm{Fe(CN)_6^{3-}}$ at 299.0 ± 0.5 K

Aqueous solution of 0.10 mol l^{-1} $\mathrm{Fe(CN)_6^{4-}}$ + 0.10 mol l^{-1} $\mathrm{Fe(CN)_6^{3-}}$ saturated with KCl

I/mA	0.203	0.303	0.401	0.500	0.605	0.645	0.699
y/V	0.865	0.828	0.786	0.755	0.718	0.710	0.676

$y = 0.938 - 0.365 \cdot I$, $r = -0.998$

$\Delta_r H_{m,a} = 90.5$ kJ mol^{-1}, $R_a = 0.365$ kΩ

Aqueous solution of 0.050 mol l^{-1} $\mathrm{Fe(CN)_6^{4-}}$ + 0.050 mol l^{-1} $\mathrm{Fe(CN)_6^{3-}}$ saturated with KCl

I/mA	0.203	0.203	0.305	0.333	0.450	0.551	0.630
y/V	0.810	0.823	0.741	0.772	0.699	0.641	0.589

$y = 0.921 - 0.514 \cdot I$, $r = -0.986$

$\Delta_r H_{m,a} = 88.9$ kJ mol^{-1}, $R_a = 0.514$ kΩ

Aqueous solution of 0.010 mol l^{-1} $\mathrm{Fe(CN)_6^{4-}}$ + 0.010 mol l^{-1} $\mathrm{Fe(CN)_6^{3-}}$ saturated with KCl

I/mA	0.0590	0.0953
y/V	0.8580	0.8390

$y = 0.886 - 0.491 \cdot I$

$\Delta_r H_{m,a} = 85.5$ kJ mol^{-1}, $R_a = 0.491$ kΩ

Table 2
Calorimetry of the cathodic reduction reaction $2H^+ + 2e = H_2(g)$ at 300.5 ± 0.5 K

Aqueous solution of 0.190 mol l^{-1} H_2SO_4

I/mA	0.104	0.202	0.207	0.302	0.390	0.451
y/V	−0.0714	−0.199	−0.190	−0.253	−0.367	−0.448

$y = 0.0318 - 1.045{\cdot}I$, $r = -0.992$
$\Delta_r H_{m,c} = 6.1$ kJ mol^{-1}, $R_c = 1.045$ kΩ

Aqueous solution of 0.051 mol l^{-1} H_2SO_4

I/mA	0.205	0.302	0.402	0.550	0.698
y/V	−0.812	−1.211	−1.668	−2.220	−3.050

$y = 0.130 - 4.457{\cdot}I$, $r = -0.997$
$\Delta_r H_{m,c} = 25.1$ kJ mol^{-1}, $R_c = 4.457$ kΩ

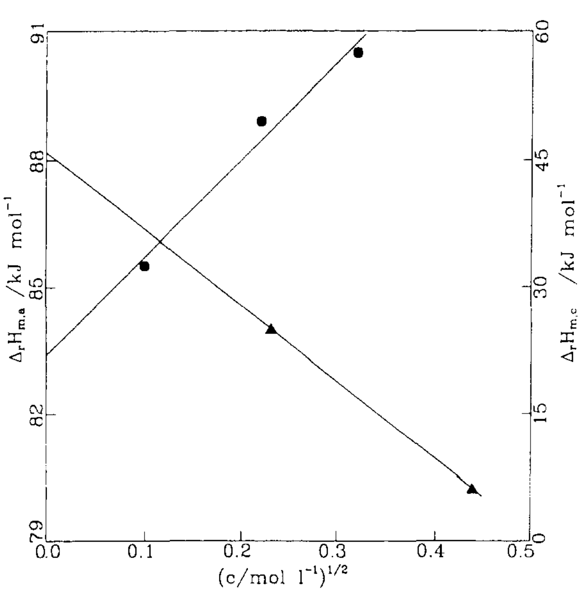

Fig. 3. A plot of apparent enthalpy change vs. the square root of active ion concentration, ● for anodic reaction (4), and ▲ for cathodic reaction (5)

[7]. Here we assume that the apparent enthalpy change of an electrode reaction changes linearly with the square root of the concentration of the electro-active ion. A plot of the former versus the latter is shown in Fig. 3. The apparent enthalpy change at infinite dilute concentration can be obtained by linear extrapolation: $\Delta_r H^{\infty}_{m,a} = 45.9$ kJ mol^{-1} for reaction (5).

In our previous research [2], the obtained enthalpy change of an electrode reaction can hardly be compared to the one calculated with the currently employed conventional thermodynamic data of aqueous ions. It was demonstrated that this difference can be bridged via the following equation [4]:

$$-\frac{\Delta_r H^{\infty}_{m,a} - \Delta_r H^{0}_{m,a}(\text{con.})}{z_a \cdot T} = \frac{\Delta_r H^{\infty}_{m,c} - \Delta_r H^{0}_{m,c}(\text{con.})}{z_c \cdot T} = K$$

where $\Delta_r H^0_{m,i}(\text{con.})$ is the standard enthalpy change of an electrode reaction calculated from conventional thermodynamic data, and K is a constant for any electrode reaction at a certain temperature. With data in reference [8], it was calculated that $\Delta_r H^0_{m,a}(\text{con.}) = 106.3$ KJ mol^{-1} at 298 K for reaction (4), and $\Delta_r H^0_{m,c}(\text{con.}) = 0$ KJ mol^{-1} for reaction (5). In consequence

$$-\frac{\Delta_r H^{\infty}_{m,a} - \Delta_r H^{0}_{m,a}(\text{con.})}{z_a \cdot T} = -\frac{(83.4 - 106.3) \times 1000}{1 \times 299} = 76.6\,\mathrm{J\,mol^{-1}\,K^{-1}} \tag{7}$$

$$-\frac{\Delta_r H^{\infty}_{m,c} - \Delta rH^{0}_{m,c}(\text{con.})}{z_c \cdot T} = -\frac{(45.9 - 0) \times 1000}{2 \times 301} = 76.2\,\mathrm{J\,mol^{-1}\,K^{-1}} \tag{8}$$

The results of Eq. (7) and Eq. (8) proved that K was a constant, it was also confirmed by other electrode systems [9]. With this constant the unknown standard enthalpy change of an electrode reaction can then be deduced from the apparent enthalpy change determined by electrochemical calorimetry.

4. Conclusions

A measurement system for electrochemical calorimetry by coupling a commercial microcalorimeter with usual electrochemical instruments was established. Because of the high quality of the commercial calorimeter, this system is of high heat flow sensitivity, high measurement precision, good reproducibility, and easy to operate. Calorimetric determination of two kinds of electrode systems were proceeded under constant current polarization. Determined apparent enthalpy changes can be related with the conventional thermodynamic data at a given temperature. This measurement system is valid for further determination of standard enthalpy changes of electrode reactions.

References

[1] J.M. Sherfey, J. Electrochem. Soc., 110 (1963) 214.
[2] P. Boudeville and J.L. Burgot, J. Thermal. Anal., 30 (1985) 5.
[3] P. Boudeville and A. Tallec, Thermochimica Acta, 126 (1988) 221.
[4] H. Zhang, P. Zhang and Z. Fang, The Inter. and 3rd Sino–Japn. Joint Sympo. on Thermal Measurements, Xi'an, China (1994), p. 152.
[5] H. Zhang, P. Zhang and Z. Fang , 6th Sympo. on Solu. Chem., Thermodynamics, Thermochem. and Thermal Anal., Chinese Chemical Society., Zhengzhou, China (1992) p. 253.
[6] H. Zhang, P. Zhang and Z. Fang, J. Thermal Anal., 45 (1995) 151.
[7] W. Zeng, Q. Chen and X. Chen, J. Chem. Thermodynamics, 26 (1994) 205.
[8] D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, I. Halow, S.M. Bailey, K.B. Churney and R.L. Nuttall, The NBS Tables of Chemical Thermodynamic Properties, J. Phy. Chem. Ref. Data, 11 (suppl 2) (1982) 2–38, 2–181.
[9] L. Guo, Master Thesis, Central South University of Technology, Changsha, China (1994) p. 53.