Thermochimica Acta, 126 (1988) 221–234
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

ELECTROCHEMISTRY AND CALORIMETRY COUPLING. IV. DETERMINATION OF ELECTROCHEMICAL PELTIER HEAT

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(Received 2 July 1987)

ABSTRACT

An adiabatic electrolysis cell is used for the determination of electrochemical Peltier heat Π, either by a direct method (measurement of the thermal power of the electrode reaction for different current intensities), or by a differential method (measurement of the thermal power of the electrode reaction for current intensities $+I$ and $-I$). In each experiment, irreversibility of the electrode reaction is taken into account by overvoltage corrections and a good agreement is observed between the individual values Π^{ox} and Π^{red} and the Π value deduced from the differential method.

The average values are $\Pi^{ox} = -45.35 \pm 1.75$ kJ mol^{-1} for $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ (0.1 M on Pt) and $\Pi^{ox} = +39.3 \pm 3$ kJ mol^{-1} for 0.5 M $CuSO_4/Cu$.

INTRODUCTION

The thermal effect developed at an electrode/solution interface crossed by an electric current is known as the Peltier effect. According to Conway, the knowledge of the thermal effects arising on the electrodes is essential to understand the thermochemistry of battery reactions and to foresee their energy efficiency [1]. Thus, a new interest in calorimetric studies of electrochemical reactions has recently occurred.

Two experimental techniques were successively developed to measure electrochemical Peltier heat by calorimetry. The oldest method [2–10] uses a calorimeter divided into two symmetrical compartments (anodic and cathodic) and the heating difference between the two compartments is measured. In the second technique, introduced by Holmes [11] and further improved by Graves [12], the thermistor probe is inserted inside the working electrode and the heating difference between the electrode and the bulk of the solution is measured.

0040-6031/88/$03.50

All recent works on electrochemical Peltier heat have used the second method [1,12–18].

These two techniques have advantages and disadvantages. The first method only allows a differential measurement of the electrochemical Peltier heat and requires the knowledge of important current densities. In the second method, the most important problem is the determination of the relative heat capacity of the electrode and its vicinity, the knowledge of which is necessary for conversion of temperature variations into heat variations.

In this paper we describe a technique which allows either direct or differential determination of electrochemical Peltier heat through a mathematical treatment of the temperature variations inside the anodic and cathodic compartments of an adiabatic electrolysis cell. This study is illustrated by the measurement of the molar electrochemical Peltier heat of Cu^{2+}/Cu and $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ on a Pt electrode.

THEORETICAL

The theoretical treatment of the electrochemical Peltier heat has been developed in the previously given references and more especially in refs. 4, 15 and 19–22.

When a redox reaction involving a metal M and the corresponding cation M^{z+}_{aq} occurs at an electrode interface, the molar electrochemical Peltier heat Π (that is to say the reversible thermal effect) is the sum of two terms. The first term is the entropy change $T\Delta S$ of the electrode reaction and the second term is the heat of transport $\Delta Q^\star$ of the ionic species migrating in solution

$$\Pi = \Pi^{ox} = -(T\Delta S^{ox} + \Delta Q^\star) = -\Pi^{red} = (T\Delta S^{red} - \Delta Q^\star) \tag{1}$$

with

$$\Delta S^{ox} = \bar{S}_{M^{z+}} + z\bar{S}_e - S_M = -\Delta S^{red} \tag{2}$$

and

$$\Delta Q^\star = z\left(\Sigma t_j Q^\star_j / z_j + Q^\star_e\right) \tag{3}$$

where $\bar{S}_{M^{z+}}$ is the partial molar entropy of the ion M^{z+}_{aq}, $\bar{S}_e$ is the entropy of the electron in the metal M, S_M is the entropy of the metal which can be identified as the standard entropy $S^{\ominus}_M$ and z is the number of electrons involved in the electrode reaction. The subscript j denotes all the ionic species that undergo migration in the electric field, t_j and z_j are the transport number and the algebraic charge of the ion j. $Q^\star_j$ and $Q^\star_e$ are the molar heat of transport of the ion j in solution and the electron in the electrode material, respectively. The heat of transport $Q^\star$ is linked up to the entropy of transport $S^\star$ (or Eastman entropy of transfer) by the relation $Q^\star_j = TS^\star_j$; values for some ionic species are given in refs. 22 and 23.

EXPERIMENTAL

Adiabatic electrolysis cell and measurement devices

The adiabatic electrolysis cell described in ref. 24 was built for a general purpose (analytical, thermodynamic and kinetic studies [24,25]).

Two hemispherical glass flasks (100 ml volume) were separated by a sintered glass disc of porosity 3 (3 cm diameter), fixed with epoxy resin glue (araldite) and covered with aluminium foil. This was then enclosed in a wooden box filled with polyurethane foam. The electrodes were 8 cm^2 platinum grids or copper plates. These were placed flat against the sintered glass. Solutions were vigorously stirred by four glass blades driven by "Tacussel-controvit" systems. This ensured the rapid establishment of a homogeneous temperature. The temperature inside each compartment was followed using standard equipment: thermistor (VECO I EA 31 A 6 2 B 9), voltage source, Wheatstone bridge and operational amplifier (MacKee Pedersen Instruments). The output voltages were recorded (Tacussel Ecoscript and EPL1) and stored in a Hewlett Packard HP 85 F computer. The potentiostat galvanostat was a P.A.R. 363 being able to regulate up to 1 A.

Determination of dissipated thermal effect

This equipment, in contrast with other equipment built for the same purpose, can easily separate interesting and non-interesting thermal effects dissipated inside each compartment of the electrolysis cell. A typical temperature/time curve recorded for each compartment is shown in Fig. 1. During the pre-period ($t_0 \leqslant t \leqslant t_\alpha$) and the post-period ($t \geqslant t_\beta$), only non-interesting thermal effects occur (e.g. from solution stirring, heat exchanges with the exterior or between the two compartments through the sintered glass junction, current flow in the thermistor and solvent evaporation). During the reaction period, the effects due to current crossing add to the previous effects. The method of correction for non-interesting effects, based on the slopes of the $T = \mathrm{f}(t)$ curves before and after the current flow in the two compartments, is described in ref. 26; it allows the evaluation of the thermal powers exclusively as a result of the current flow inside the anodic and/or the cathodic compartment.

Determination of electrochemical Peltier heat

When an electric current crosses a half cell, four different thermal effects arise: (a) the electronic Peltier effect at the level of the conductor/electrode junction, (b) the electrochemical Peltier effect at the electrode/solution interface, (c) the thermal effect due to the overvoltage related to the

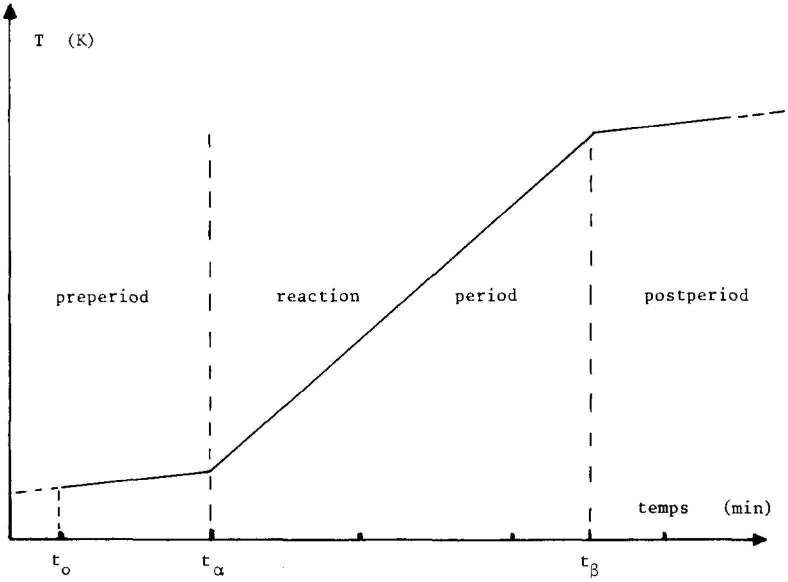

Fig. 1. Experimental thermogram recorded in anodic and cathodic compartments.

electrolysis current and (d) the Joule effect owing to the solution resistance. The first effect is much smaller than the others and can be neglected [22].

The thermal power q (J s^{-1}) dissipated inside a compartment of the electrolysis cell can thus be expressed as

$$q = -\frac{C_s \Delta T}{t} = -\frac{\Pi |I|}{zF} - \eta I - R_{in} I^2 \tag{4}$$

where C_s is the heat capacity of the compartment, ΔT the temperature variation, t the electrolysis time, Π the molar electrochemical Peltier heat (J mol^{-1}), z the number of electrons involved in the electrode reaction, F the Faraday constant, η the overvoltage (V), I the electrolysis current (A) and R_{in} the inner solution resistance between the electrode and the middle of the sintered glass junction.

As with an exothermic chemical reaction, the thermal power q is considered negative when the temperature of the solution rises. By convention, the reversible molar electrochemical Peltier heat is positive when the anodic reaction is exothermic; this explains the minus sign before the first term in eqn. (4) and the absolute value sign for the current intensity. The overvoltage η and the current I always have the same sign so their product is always positive like the product $R_{in}I^2$. These last two effects are irreversible, that is to say, whatever the current direction (anodic or cathodic) they heat the solution. Consequently, a minus sign is put before the last two terms of eqn. (4).

By dividing eqn. (4) by the absolute value of the current, we obtain a linear relation

$$\frac{q}{|I|} + |\eta| = -\frac{\Pi}{zF} - R_{\text{in}}|I| \tag{5}$$

Sometimes, when the electrochemical system is reversible and electrolysis currents are low, the overvoltage is a linear function of the current intensity and the product ηI becomes similar to a Joule effect $R_{\text{o}}I^2$ where R_{o} is called the overvoltage resistance. Equation (5) then becomes

$$\frac{q}{|I|} = -\frac{\Pi}{zF} - (R_{\text{o}} + R_{\text{in}})|I| \tag{6}$$

Two possibilities of determination of the molar electrochemical Peltier heat result from eqn. (5):

(i) a direct method by determining the thermal power of the electrode reaction for different values of electrolysis current: the slope of the line $[q/|I| + |\eta|]$ vs. $|I|$ gives the solution resistance and the intercept allows the calculation of the anodic Π^{ox} or cathodic Π^{red} molar Peltier heat according to the sign of I.

(ii) A differential method by determining the thermal power of the electrode reaction for two current values $+I$ and $-I$: for current $+I$ we have

$$\frac{q^{\text{ox}}}{|I|} + \eta_{\text{a}} = -\frac{\Pi^{\text{ox}}}{zF} - R_{\text{in}}|I| \tag{7}$$

and for current $-I$ we have

$$\frac{q^{\text{red}}}{|I|} + |\eta_{\text{c}}| = -\frac{\Pi^{\text{red}}}{zF} - R_{\text{in}}|I| \tag{8}$$

The two measurements are performed in the same compartment with the same electrode and with the same solution. R_{in} is the same whatever the sign of I. Subtraction of eqn. (8) from eqn. (7) leads to

$$\frac{q^{\text{ox}} - q^{\text{red}}}{|I|} + (\eta_{\text{a}} - |\eta_{\text{c}}|) = -\frac{\Pi^{\text{ox}} - \Pi^{\text{red}}}{zF} \tag{9}$$

As the electrochemical Peltier heat is reversible $(\Pi^{\text{ox}} = -\Pi^{\text{red}})$

$$\Pi = \Pi^{\text{ox}} = -\frac{zF}{2}\left[\frac{q^{\text{ox}} - q^{\text{red}}}{|I|} + \eta_{\text{a}} - |\eta_{\text{c}}|\right] \tag{10}$$

For reversible systems and low current intensities $\eta_{\text{a}} = |\eta_{\text{c}}|$ and

$$\Pi = \Pi^{\text{ox}} = -\frac{zF}{2|I|}(q^{\text{ox}} - q^{\text{red}}) \tag{11}$$

This second method is equivalent to the differential measurement of the heating of anodic and cathodic compartments previously used [1–10,19]

$$Q^{\mathrm{ox}} - Q^{\mathrm{red}} = 2\Pi \frac{It}{zF} \qquad \text{with } Q^{\mathrm{ox}} = q^{\mathrm{ox}} t \tag{12}$$

Of course Π determined with the differential method will have to be equal to Π^{ox} and $-\Pi^{\mathrm{red}}$ determined from the direct method; comparison of these three values allows us to check the reliability of the measurement.

RESULTS AND DISCUSSION

The two compartments of the electrolysis cell are not perfectly symmetrical and therefore we only consider the results obtained in the one compartment (called the "working compartment" in refs. 24–26).

Solutions used were 0.5 M $CuSO_4$ for the Cu^{2+}/Cu system and 0.1 M $[Fe(CN)_6]^{3-}$ and 0.1 M $[Fe(CN)_6]^{4-}$ for the hexacyanoferrate III/II system. All experiments were started at 298 ± 0.2 K.

The electrolyses were performed for 150 s with 0.05, 0.1, 0.15, 0.2, 0.25 and 0.3 A anodic and cathodic current intensities. The thermal power q of the electrode reaction was calculated for each experiment, after correction of non-interesting thermal effects, by a least-squares method taking into account 30 points. The slope and the intercept of the lines $[q/|I| + |\eta|] = \mathrm{f}(|I|)$ were also determined by a least-squares method.

Estimation of the variations in overvoltage with the electrolysis current is rather inaccurate; we prefer to measure the electrode potential during each experiment. The curves $I = \mathrm{f}(E)$ for the two systems are shown in Fig. 2. The Cu^{2+}/Cu system is not very fast, especially for the cathodic reaction; according to Mattson and Bockris [27] the reduction of Cu^{2+} ions is limited by the rate of the reaction: $Cu^{2+} + e^- \rightleftharpoons Cu^+$. Except for the equilibrium potential ($E_{\mathrm{eq}} = 102 \pm 2$ mV (Ag/AgCl)), the measured potential for a given current is not reproducible from one experiment to another. The hexacyanoferrate III/II system is fast but the solution used was a dilute one and current intensity was rapidly limited by the mass transfer rate.

Molar Peltier heat of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ on platinum

In comparison with the Cu^{2+}/Cu system, the hexacyanoferrate III/II system is interesting in several ways: (i) the electrode reaction is fast on platinum and only one electron is transferred; (ii) the two ions are weakly solvated, e.g. only water molecules occurring in the second solvation sphere are less strongly held than in $[Fe(H_2O)_6]^{2+}$; (iii) the two ions do not decoordinate during the electron transfer; (iv) there is no change in the physical state during the electron transfer.

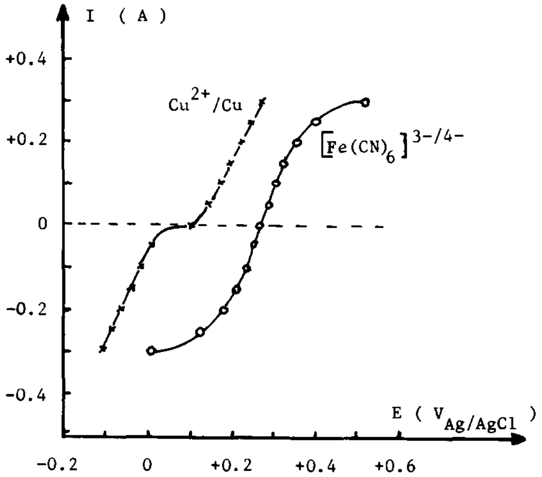

Fig. 2. I–E curves for a Cu electrode in 0.5 M $CuSO_4$ and for a Pt electrode in 0.1 M $[Fe(CN)_6]^{3-}$ and 0.1 M $[Fe(CN)_6]^{4-}$ (solutions stirred at 298 K).

After electrolyses with + and − 0.05, 0.1, 0.15, 0.20, 0.25 and 0.3 A current intensities and correction of the T/t curves, correct linear drawings were obtained according to eqn. (5) for anodic and cathodic experiments (Fig. 3). The molar electrochemical Peltier heat values deduced from direct and differential methods are given in Table 1.

Good agreement is observed between the individual values of Π^{ox} and Π^{red} and with the Π value obtained from the differential method. Gododyskii et al. [28] give a lower value of -31.9 kJ mol^{-1} at 298 K, but comparison is difficult because the experimental conditions are probably not the same.

Accurate values of the partial molar entropy (absolute or conventional) of hexacyanoferrate III and II ions are not known [23,29]. However, electrochemical Peltier heat allows the evaluation of their difference

$$\Pi^{ox} = -(T\Delta S^{ox} + \Delta Q^{\star}) \tag{13}$$

$$\Delta S^{ox} = \bar{S}_{ox} + \bar{S}_{e} - \bar{S}_{red} \tag{14}$$

$$\Delta Q^{\star} = T\left(\frac{t_{red}S^{\star}_{red}}{z_{red}} + \frac{t_{ox}S^{\star}_{ox}}{z_{ox}} + \frac{t_{K}S^{\star}_{K}}{z_{K}} + S^{\star}_{e}\right) \tag{15}$$

where the subscripts ox, red, K and e designate $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, K^+ ions and the electron, respectively. Breck and Lin [23] give the following values for an equimolecular solution: transport numbers, $t_{red} = 0.353$, $t_{ox} = 0.238$ and $t_K = 0.409$; absolute entropies of transport, $S^{\star}_{red} = 81.5$, $S^{\star}_{ox} = 58.9$ and $S^{\star}_{K} = 6.3$ J mol^{-1} K^{-1}. These latter values are for an infinitely dilute solution, but as the variation with ionic strength is unknown, we take these as approximate values.

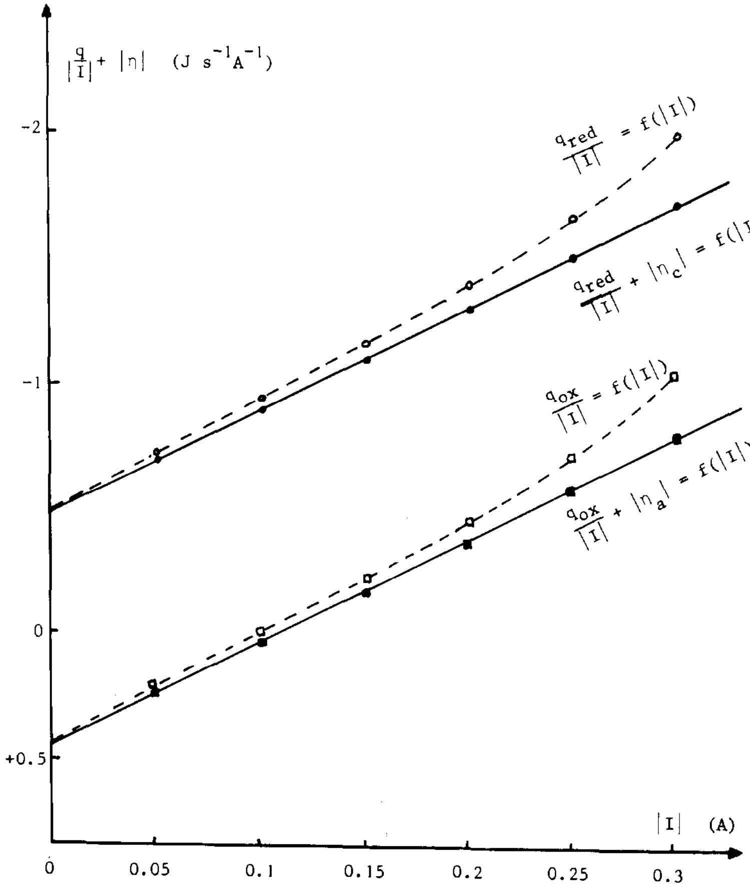

Fig. 3. $q/|I| = f(|I|)$ and $[q/|I| + |\eta|] = f(|I|)$ curves for the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ system on Pt.

Finally, the transported entropy of the electron in platinum is $\bar{\bar{S}}_e = \bar{S}_e + S_e^\star = 0.43$ J mol^{-1} K^{-1} [22]. Taking an average value, $\overline{\Pi}^{ox} = -45350 \pm 1750$ J mol^{-1}, we obtain for the difference of absolute entropies $\bar{S}_{ox} - \bar{S}_{red} = 161.2$

TABLE 1

Molar Peltier heat of the hexacyanoferrate III/II system on Pt at 298 K (R_{in} = solution resistance in ohms, r = correlation coefficient of the linear regression)

	Direct method		Differential method
	Oxidation	Reduction	$\Pi = \Pi^{ox}$
Π (kJ mol^{-1})	−43.6	+47.1	-45.1 ± 0.5 [a]
R_{in} (Ω)	4.17	4.14	
r	0.9998	0.9998	

[a] Standard deviation of the six data points corresponding to the different current intensities.

± 5.8 J mol^{-1} K^{-1}. To calculate the standard difference in entropies, deviation from ideal behaviour must be taken into account

$$\bar{S}_{\mathrm{ox}} - \bar{S}_{\mathrm{red}} = \bar{S}^{0}_{\mathrm{ox}} - \bar{S}^{0}_{\mathrm{red}} - R \ln \frac{\gamma_{\mathrm{ox}}}{\gamma_{\mathrm{red}}} - R \ln \frac{C_{\mathrm{ox}}}{C_{\mathrm{red}}} + \frac{\bar{L}_{2\mathrm{ox}}}{4T} - \frac{\bar{L}_{2\mathrm{red}}}{5T} \tag{16}$$

from $\mathrm{d}(\ln \gamma_{\pm})/\mathrm{d}T = -\bar{L}_2/\nu R T^2$, where $\bar{L}_2$ is the relative partial molar enthalpy of the substance and ν the number of ions formed by ionisation of one mole of substrate. The $\bar{L}_2$ values for 0.1 M $K_3Fe(CN)_6$ and 0.1 M $K_4Fe(CN)_6$ are not known but they are probably very close, and their difference $(\bar{L}_{2\mathrm{ox}}/4T - \bar{L}_{2\mathrm{red}}/5T)$ can be neglected. The ratio $\gamma_{\mathrm{ox}}/\gamma_{\mathrm{red}}$ can be evaluated from the Davies relation [30] although this relation is only usable for ionic strength up to 0.5 M; taking $\gamma_{\mathrm{ox}}/\gamma_{\mathrm{red}} = 7.1$ and with $C_{\mathrm{ox}} = C_{\mathrm{red}} = 0.1$ the above equation leads to $\Delta S^{\ominus} = (\bar{S}^{\ominus}_{\mathrm{ox}} - \bar{S}^{\ominus}_{\mathrm{red}})_{\mathrm{abs}} = 177.5 \pm 5.8$ J mol^{-1} K^{-1}. This value is in good agreement with the result of Breck and Lin [23], ($\Delta S^{\ominus} = 181.8$ J mol^{-1} K^{-1}) from potentiometric measurements of initial and stationary thermoelectric powers for the same system on platinum.

Molar electrochemical Peltier heat of the Cu^{2+}/Cu system

The "depositing–dissolving" cycle of a metal by electrolysis has been studied frequently. The Cu^{2+}/Cu system has been selected because many reference values can be found in the literature; moreover, copper is (with silver) one of the few common metals which have a positive standard potential. This enables studies to be carried out in acidic media.

Six series of measurements were performed, corresponding to different electrode preparations. In the first series, copper was electrodeposited on the working electrode (8 cm^2 metallic copper plate) for 80 min under a current intensity of 0.5 A without bubbling nitrogen. Copper was essentially deposited on the side of the electrode in front of the counter electrode. In the second series, electrodes were "metallic" copper plates without metal electrodeposition. The unfaced sides were covered with epoxy resin (araldite). The copper sulphate solution was made oxygen free by bubbling nitrogen during all the measurements. In the third to the sixth series, copper was electrodeposited on the preceding copper plates using a current intensity of only 0.05 A for 24 h with bubbling N_2. The copper deposit was thinner, more regular and shiny than in the first series. The other experimental conditions were the same as in the study of the hexacyanoferrate III/II system. (+ and −0.05, 0.1, 0.15, 0.20, 0.25 and 0.3 A current intensity for 150 s at 298.0 ± 0.2 K).

The results obtained by the direct method (Π^{ox} and Π^{red}) and by the differential method (Π) are given in Table 2. The first six columns correspond to the individual results of each series and the seventh to average values of these six series.

TABLE 2

Molar electrochemical Peltier heat for the Cu^{2+}/Cu system obtained with direct and differential methods

	1	2	3	4	5	6	Average
Π^{ox} (kJ mol^{-1})	41.2	43.8	37.22	39.86	36.47	41.13	39.95 ±2.70
Π^{red} (kJ mol^{-1})	−35.17	−38.93	−43.07	−36.63	−37.03	−40.57	−38.57 ±2.90
Π (kJ mol^{-1})	39.31 ±2.22	39.73 ±1.84	38.44 ±1.86	38.48 ±1.20	39.84 ±2.66	39.44 ±2.80	39.31 ±0.61
R_{ox} (Ω)	7.06	6.85	6.92	7.01	7.46	7.02	7.05
r	0.9984	0.9999	0.9997	0.9997	0.9997	0.9998	±0.21
R_{red} (Ω)	6.97	6.94	7.02	6.99	7.35	7.11	7.06
r	0.9978	0.9999	0.9998	0.9998	0.9998	0.9999	±0.15

R_{ox} and R_{red}, solution resistance calculated from the slope of the lines; r, correlation coefficient.

A rather good reproducibility is reached whatever the electrode preparation; however, a large scattering is observed between Π^{ox} and Π^{red} in the first to the third series.

Moreover, good correlations are obtained for the linear representation $[q/|I| + |\eta|] = f(|I|)$ as shown by the correlation coefficients and in Fig. 4. The molar electrochemical Peltier heat of the Cu^{2+}/Cu system in 0.5 M copper sulphate solution is a reasonable $\Pi = 39.3 \pm 3.0$ kJ mol^{-1}. (It is worth noting the importance of overvoltage corrections. If this effect is not taken into account, average values would be $\Pi^{ox} = 44.7$, $\Pi^{red} = -26.2$ and $\Pi = 36.0$ kJ mol^{-1}. These values are very different.)

The electrochemical Peltier heat value is dependent on experimental conditions and it is not always easy to compare one value with other data. However, if we consider the previous published values obtained for the Cu^{2+}/Cu system in solution with (a) a Cu^{2+} concentration higher than 0.2 M, (b) an ionic strength, with or without supporting electrolyte, higher than 0.5 M for which activity coefficients are quasi-invariant and (c) a proton concentration lower than 0.01 M (the presence of protons induces a sharp decrease in the molar Peltier heat through their entropy of transport), then an average value of 40 ± 4 kJ mol^{-1} [8,10,14,19] in good agreement with our experimental result, can be evaluated.

The entropy of transport corresponding to copper sulphate $\Delta S^\star = t_{Cu^{2+}} S^\star_{Cu^{2+}} - t_{SO_4^{2-}} S^\star_{SO_4^{2-}}$ can be determined from eqn. (1) written as

$$\frac{\Pi^{ox}}{T} = \frac{39300}{298} = 131.9 \text{ J mol}^{-1}\text{ K}^{-1} = -\left(\bar{S}_{Cu^{2+}} - S^\ominus_{Cu}\right) - 2\bar{\bar{S}}_{e(Cu)} - \Delta S^\star \tag{17}$$

The first term of eqn. (17) can be calculated from the standard absolute entropies of Cu ($S^\ominus_{Cu} = 33.2$ J mol^{-1} K^{-1}) and Cu^{2+} ($\bar{S}^\ominus_{Cu^{2+}} = -141.5$ J

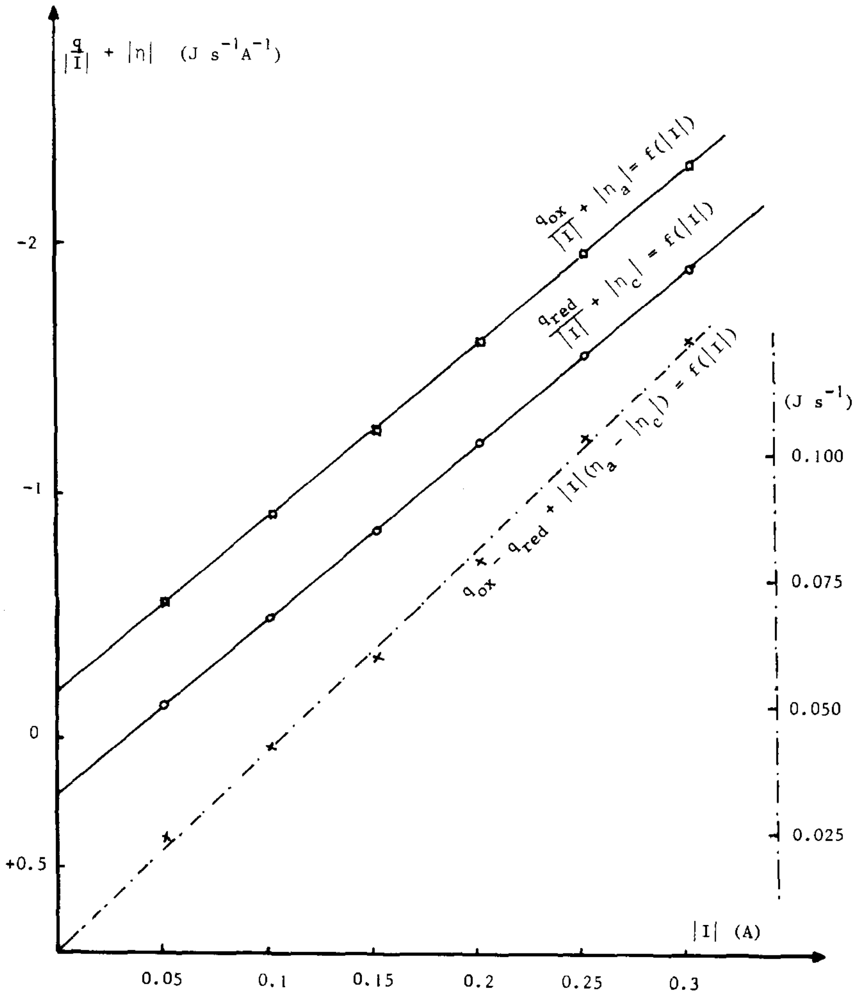

Fig. 4. $[q/|I| + |\eta|] = f(|I|)$ curves for the oxidation of Cu and the reduction of Cu^{2+} at 298 K. The slope of the line $[q_{ox} - q_{red} + |I|(\eta_a - |\eta_c|)] = f(|I|)$ is Π/F.

mol^{-1} K^{-1} [29], taking $\bar{S}^{\ominus}_{H^+} = -22.2$ J mol^{-1} K^{-1} [31]) and the excess ionic entropy term $S^{E}_{Cu^{2+}} = -R \ln \gamma_{Cu^{2+}} - RT \, d \ln \gamma_{Cu^{2+}}/dT$. In dilute solution $\gamma_{Cu^{2+}}$ is calculable from the Davies equation [30] but in solution with strong ionic strength, only the mean activity coefficient $\gamma_{\pm}$ and the relative partial molar enthalpy $\bar{L}_2$ are available ($\gamma_{\pm} = 0.067$ [32] and $\bar{L}_2 = 6763$ J mol^{-1} [33] with $\nu = 2$ for 0.5 M $CuSO_4$ solution). Then $\bar{S}_{Cu^{2+}} - S^{\ominus}_{Cu} = -174.7 - R \ln(Cu^{2+}) - R \ln \gamma_{\pm} + \bar{L}_2/2T = -135.1$ J mol^{-1} K^{-1}. The transported entropy of the electron in copper is $\bar{S}_{e(Cu)} = 0.16$ J mol^{-1} K^{-1} [22], so we calculate the transport term $\Delta S^{\star} = 2.9$ J mol^{-1} K^{-1}.

The absolute entropies of transport of some ions at infinite dilution are known [22,23]: $S^{\star\ominus}_{SO_4^{2-}} = 32.6$ J mol^{-1} K^{-1} [23] and $S^{\star\ominus}_{Cu^{2+}} = 25.0$ J mol^{-1} K^{-1}

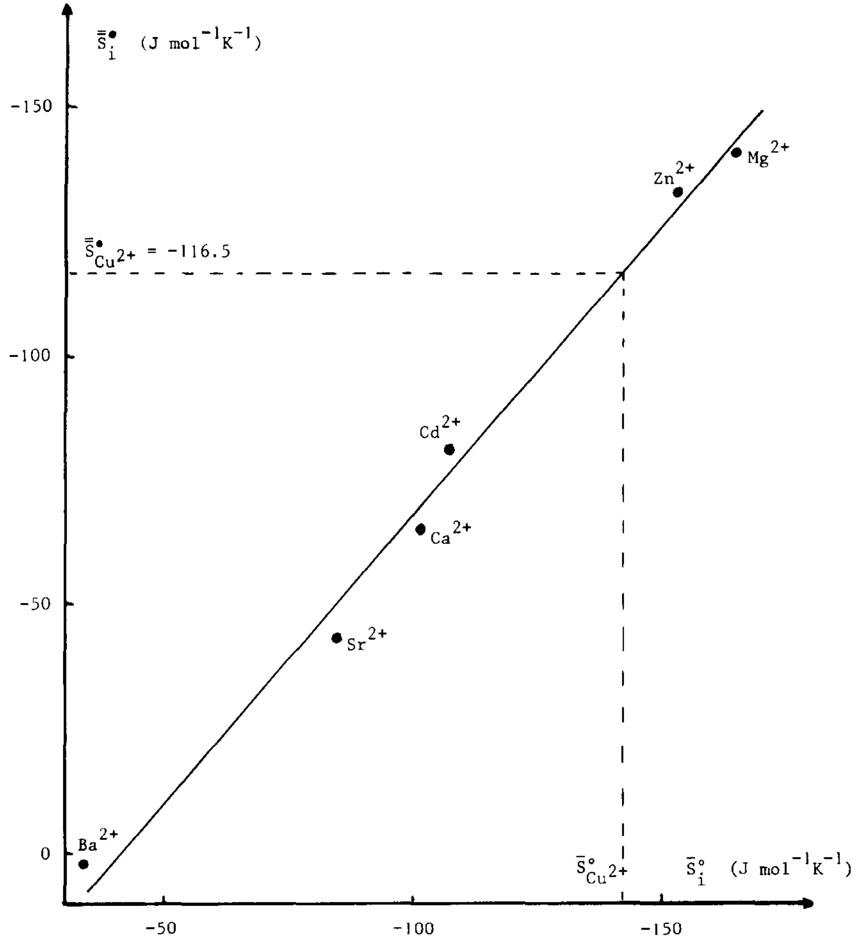

Fig. 5. $\bar{\bar{S}}_i^{\ominus} = f(\bar{S}_{i,abs}^{\ominus})$ curve for divalent cations from the values given in ref. 23.

(by extrapolation from the $\bar{\bar{S}}_i^{\ominus} = f(\bar{S}_i^{\ominus})$ curves given by Breck and Lin [23] *); then taking $t_{Cu^{2+}} = 0.327$ and $t_{SO_4^{2-}} = 0.673$ [32] we obtain $\Delta S^{\star\ominus} = -13.8$ J mol^{-1} K^{-1}. According to Agar [22] and Ozeki et al. [15] $S_i^{\star} = S_i^{\star\ominus} + S_i^{\star E}$ where $S_i^{\star E}$ is called the excess entropy of transport of the ionic species i. Then, the excess entropy of transport of 0.5 M $CuSO_4$ solution can be estimated, writing $\Delta S^{\star E} = t_{Cu^{2+}} S^{\star E}_{Cu^{2+}} - t_{SO_4^{2-}} S^{\star E}_{SO_4^{2-}} = \Delta S^{\star} - \Delta S^{\star\ominus} = 16.7$ J mol^{-1} K^{-1}.

It is worth noting the importance of this value, compared with $\Delta S^{\star\ominus}$ and $\Delta S^{\star}$: transported entropy appears to be strongly dependent on the ionic strength. Moreover, further experiments will be necessary for a better

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* We prefer this value to that given by Ozeki ($S^{\star\ominus}_{Cu^{2+}} = -1.79$ J mol^{-1} K^{-1}) [15] by comparison with entropies of transport of other divalent cations (Fig. 5).

understanding of these relations. For instance the sum $S^{\star E}_{\mathrm{Cu}^{2+}} + S^{\star E}_{\mathrm{SO}_4^{2-}}$ can be determined from measurements of the Soret coefficient σ [22] at the considered concentration and at infinite dilution ($S^{\star E}_{\mathrm{Cu}^{2+}} + S^{\star E}_{\mathrm{SO}_4^{2-}} = S^{\star}_{\mathrm{CuSO}_4} - S^{\star \ominus}_{\mathrm{CuSO}_4}$); this, combined with the estimation of $\Delta S^{\star E}$ would allow the determination of individual values $S^{\star E}_{\mathrm{Cu}^{2+}}$ and $S^{\star E}_{\mathrm{SO}_4^{2-}}$.

CONCLUSION

An adiabatic electrolysis cell (with the aid of a mathematical treatment of the temperature/time curves) allows a correct determination of the heat dissipated by an electrode reaction and of the corresponding absolute entropy variation. Furthermore, according to the available data, either the ionic entropy variation ΔS or the entropy of transport $\Delta S^{\star}$ can be estimated. In the case of the latter term, the interpretation of the experimental results is hazardous at present, due to the lack of information on the dependence of $\Delta S^{\star}$ on the ionic strength.

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