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Thermometric determination of electrochemical Peltier heat (thermal effect associated with electron transfer) of some redox couples

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Abstract

The electrochemical Peltier heat Π is the thermal effect produced at an electrode/solution interface when an electric current passes through. It can be measured by thermometry. A thermistor probe inserted inside the working electrode allows the measurement of the temperature difference between the electrode and the bulk of the solution during a half-cell reaction. But the most important problem of this method is the determination of the relative heat capacity of the electrode and its vicinity, which is necessary for the temperature variation/heat variation conversion. Using the Π values: -45.1 kJ mol^{-1} for 0.1 mol l^{-1} $K_3Fe(CN)_6$/0.1 mol l^{-1} $K_4Fe(CN)_6$ on Pt and $+39.3$ kJ mol^{-1} for 0.5 mol l^{-1} $CuSO_4$/Cu determined with the aid of a two-compartment adiabatic electrolysis cell, a platinum plated thermistor-electrode was calibrated into heat. The quality of this calibration method was discussed and the experimental Π values found were compared with literature data when it was possible or with estimated values calculated from thermodynamic constants. The average values of the electrochemical Peltier heat (in kJ mol^{-1}) found were: $\Pi(Zn^{2+}/Zn) = +46.8 \pm 1.7$ (0.5 mol l^{-1} $ZnSO_4$); $\Pi(Ag^+/Ag) = -13.4 \pm 1.5$ (0.1 mol l^{-1} $AgNO_3$), $\Pi(Cl_2/Cl^-) = +21.2 \pm 2.3$ (0.012 mol l^{-1} Cl_2 + 0.1 mol l^{-1} KCl on Pt), $\Pi(Br_2/Br^-) = +22.4 \pm 1.3$ (0.028 mol l^{-1} Br_2 + 0.1 mol l^{-1} KBr on Pt) and $\Pi(I_3^-/I^-) = +44.2 \pm 3.0$ (0.1 mol l^{-1} I_3^-, K^+ + 0.1 mol l^{-1} KI on Pt).

Keywords: Electrochemical Peltier heat; Peltier effect; Thermometry; Calorimetry; Redox couples

1. Introduction

The electrochemical Peltier effect is the heat associated with the electron(s) transfer reaction. Vetter [1] and Agar [2] define the electrochemical Peltier effect as heat absorbed or evolved at the electrode/electrolyte interface when an electric charge unit passes through this interface at constant temperature and pressure. Thouvenin [3,4] gives a similar definition: the Peltier heat represents the heat amount occurring at an isothermal junction of two phases passed through an electric current when the irreversibility of the phenomenon is negligible and the molar electrochemical Peltier heat is the heat amount produced at the electrode from the reversible crossing from phase I to phase II of one mole of the electroactive species.

The electrochemical Peltier heat noted Π is due to a change in entropy ΔS as the time of the electrode reaction and in the entropy of ions transported by migration ΔS^* (entropy of transport or Eastman entropy [2,5]) and, by convention, it is positive when the anodic reaction is exothermic.

For a redox reaction:

$$x\ \mathrm{Red} \rightleftharpoons \mathrm{Ox} + ze^-$$

$$\Pi = \Pi_{ox} = -T(\Delta S_{ox} + \Delta S^*) = -\Pi_{red} = T(\Delta S_{red} - \Delta S^*) \qquad (1)$$

with

$$\Delta S_{ox} = \bar{S}_{ox} - x\bar{S}_{red} + z\bar{S}_e \qquad (2)$$

$$\bar{S}_i = \bar{S}^\circ_i - R \ln a_i - RT\ \mathrm{d} \ln a_i/\mathrm{d}T \qquad (3)$$

$$= \bar{S}^\circ_i - R \ln c_i - R \ln \gamma_i - RT\ \mathrm{d} \ln \gamma_i/\mathrm{d}T \qquad (4)$$

$$= \bar{S}^\circ_i - R \ln c_i + S_i^E \qquad (5)$$

$$S_i^E = -R \ln \gamma_i - RT\ \mathrm{d} \ln \gamma_i/\mathrm{d}T \qquad (6)$$

where i denotes the species which take place in the redox reaction, $\bar{S}^\circ_i$ is the absolute standard or partial molar entropy and S_i^E is the excess entropy of ion i at its concentration c_i, a_i is the activity of ion i and γ_i its activity coefficient. RT d ln γ_i/dT can be calculated

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from the relative partial molar enthalpy $\bar{L}_2$

$$d(\ln \gamma\pm)/dT = -\bar{L}_2/\nu RT^2 \qquad (7)$$

where ν is the number of ions produced per mole of salt.

$$\Delta S_{ox} = \bar{S}^{\circ}{}_{ox} - x\bar{S}^{\circ}{}_{red} - R \ln c_{ox} + xR \ln c_{red} + S^{E}{}_{ox} - xS^{E}{}_{red} + z\bar{S}_e \qquad (8)$$

the entropy of transport term ΔS^*:

$$\Delta S^* = z(\Sigma t_j S^*{}_j/z_j + S^*{}_e) \qquad (9)$$

where j denotes all the ionic species that undergo migration in the electric field, t_j and z_j are the transference number and the algebraic charge of ion j; $S^*{}_j$ is the Eastman entropy at the considered ionic strength

$$S^*{}_j = S^{*\circ}{}_j + S^{*E}{}_j \qquad (10)$$

where $S^{*\circ}{}_j$ is the absolute Eastman entropy at infinite dilution and $S^{*E}{}_j$ is the excess entropy of transport. $z\bar{S}_e + zS^*{}_e = z\bar{\bar{S}}_e$, $\bar{\bar{S}}_e$ is the transported entropy of the metallic electron.

The theoretical aspects of electrochemical Peltier heat have been presented and discussed in numerous papers [1–4,6–20], so they will not be developed. According to Subrahmanyam and Conway, the knowledge of the thermal effects arising on the electrodes is essential for understanding the thermochemistry of battery reactions and their energy efficiency [19]. In the same way, electrochemical Peltier heat could be an important tool for computing heat evolutions in electrochemical reactors and thus to foresee their compensation. Finally, electrochemical Peltier heat allows access to the individual thermodynamic properties of aqueous ions.

Two experimental techniques were successively developed to measure electrochemical Peltier heat by calorimetry. The oldest method [3,4,10,21–26] used a calorimeter divided into two symmetrical compartments (anodic and cathodic) and the temperature difference between the two compartments was measured. In the second technique, introduced by Holmes and Joncich [27] and further improved by Graves [28], a thermistor probe was inserted inside the working electrode and the temperature difference between the electrode and the bulk of the solution was measured.

All recent works on electrochemical Peltier heat have used the second method [16–19,27–31]. A review has been presented by Kuhn and Shams El Din [32].

These two techniques have advantages and drawbacks. The first method only allows a differential measurement of the electrochemical Peltier heat and requires 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. Graves [28] plated the thermistor with a bimetal thermocouple (Pt–13% Rh/Pt), which, by electronic Peltier effect, was used to heat calibrate the thermistor. Ozeki et al. [16] used the electrochemical Peltier heat literature values of Cu^{2+}/Cu and Ag^+/Ag systems to calibrate their thermistor-electrodes and confirmed this calibration by the slope of the line $\Delta\Pi = f(\ln(Cu^{2+}))$ at constant ionic strength; they only studied these two systems. Subrahmanyam and Conway [19] used a calibrated resistance wire placed on the thermistor.

Kuz'minskii and Gorodyskii [20], using a different device, a 1 cm^2 platinum window in which a differential thermocouple was pressed, proposed an interesting approach to break away from the heat capacity determination. They used the linear relationship (11)

$$\Delta T_{st}/Ik_q = -\pi + \eta \qquad (11)$$

where ΔT_{st} is the steady temperature variation and k_q is the coefficient of heat emission from the electrode surface into the electrolyte under conditions of convective exchange, or the thermal conductivity coefficient for the system with allowance for heat transfer by conduction. The electrochemical Peltier coefficient can be determined graphically or from the relation $\Delta T_{st}/I = f(\eta)$ by the least-squares method: $\pi = \eta$ when $\Delta T_{st}/I = 0$ and $\Pi = zF\pi$. This method implies that k_q (which includes the heat capacity) is constant whatever ΔT_{st}; unfortunately we will see that it is not the case with the thermistor-electrodes.

In previous papers [33–36] we described an adiabatic two-compartment electrolysis cell [33,34] allowing either a direct or a differential determination of electrochemical Peltier heat [36] through a mathematical treatment [34,35] of the temperature variations inside the anodic and cathodic compartments. The molar electrochemical Peltier heat values Π we found [36] were: -45.1 ± 0.5 kJ mol^{-1} for 0.1 mol l^{-1} $[Fe(CN)_6]^{3-}$/0.1 mol l^{-1} $[Fe(CN)_6]^{4-}$ on Pt system and $+39.3 \pm 0.6$ kJ mol^{-1} for 0.5 mol l^{-1} $CuSO_4/Cu$ system. In the present paper, we show that these two redox systems can be efficiently used for the heat calibration of thermistor-electrodes. Molar electrochemical Peltier heats of I_3^-/I^-, Br_2/Br^-, Cl_2/Cl^- on Pt, Zn^{2+}/Zn and Ag^+/Ag redox couples were determined in this way.

2. Experimental

2.1. Thermistor-electrode

Two thermistor-electrodes were built. The thermistor (VECO IEA 31 A 62B9) was plated with either a copper foil (22 μm thick) or a platinum foil (10 μm thick) and inserted inside a glass tube (inner diameter 4 mm) and fixed with epoxy resin glue (araldite)

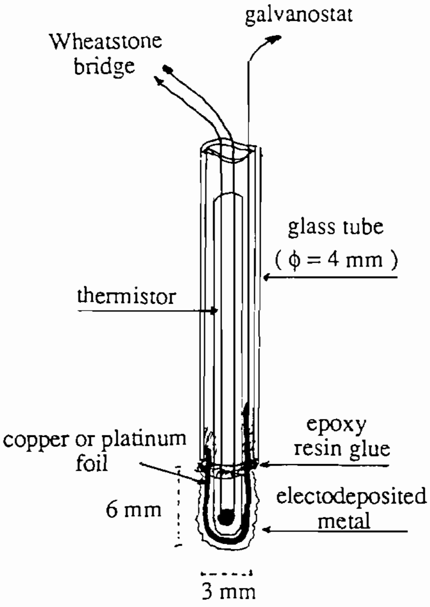

Fig. 1. The thermistor-electrode.

(Fig. 1). Then copper was electrochemically deposited on the copper-plated thermistor-electrode and the platinum-plated thermistor-electrode was used as a platinum electrode or electrochemically covered with copper, silver or zinc.

The thermistor-electrodes were temperature calibrated, which allowed the electrolyte temperature measurement to within about 0.01 K and conversion factors (K/mV) were also determined to convert the Wheatstone bridge disequilibrium voltage during the electrolysis into temperature change; for our thermistor-electrodes, 0.01 mV (millivoltmeter sensitivity) represented 5×10^{-5} K.

2.2. Measurement device

The electrode temperature was recorded using standard equipment: voltage source, Wheatstone bridge in which the thermistor was incorporated and operational amplifier (Mac Kee Pedersen Instruments). The output voltages were amplified and digitized with the aid of a highly sensitive (0.01 mV) millivoltmeter (Tacussel ISIS 20000) and accumulated and analyzed by a microcomputer HP 85F Hewlett Packard. To perform the constant current electrolyses, a potentiostat-galvanostat PAR 363 driven by a signal generator PAR 175 was used.

2.3. Electrolysis cell

The electrolysis cell was a dewar round flask (100 ml volume) immersed in a thermostated bath at ±0.01 K (Huber Unistat). The insert of the dewar flask was a 29–32 Teflon plug, through which were passed a glass stirrer, a joule heat calibrator (100 Ω), a gas delivery tube, a reference electrode (Ag/AgCl/KCl 3 M), the counter electrode (platinum plate, silver, copper or zinc 2 mm diameter wire) and the working thermistor-electrode.

2.4. Chemical reagent

Pure metals were supplied by Goodfellow Metals Ltd., and electrolytes were obtained by dissolving the corresponding salts (Prolabo, Merck or Carlo Erba, analytical reagent grade) in twice deionized water. The electrolytic baths used were $CuSO_4$ 0.5 mol l^{-1} + H_2SO_4 0.5 mol l^{-1} to deposit copper, $AgNO_3/KCN/K_2CO_3$ (50/90/25 g l^{-1}) to deposit silver and ZnO/KCN/NaOH (35/90/80 g l^{-1}) to deposit zinc. Iodine, bromine and chlorine solutions were obtained by dissolving iodine crystals, liquid bromine or gaseous chlorine (from MnO_2 + HCl) in their respective potassium salts. The final concentration of halogen was determined just after the experiments by the standard method (KI in excess and $Na_2S_2O_3$ 0.1 mol l^{-1}).

2.5. Experimental operation

The dewar flask was filled with 100 ml electrolyte solution at approximately 298 K, closed with the Teflon plug and immersed in the thermostated bath. The solution was deoxygenated by nitrogen bubbling for 10 min under stirring and the temperature was adjusted to 298±0.01 K with the aid of the joule heat calibrator. Then, in order to have a stable signal, the system was not stirred for 2–3 h until the temperature change did not exceed 2×10^{-4} K per min (0.04 mV min^{-1}). The electrolysis currents used ranged from ±0.05 to ±5 mA, according to the electrochemical system studied and the electrolyte concentration.

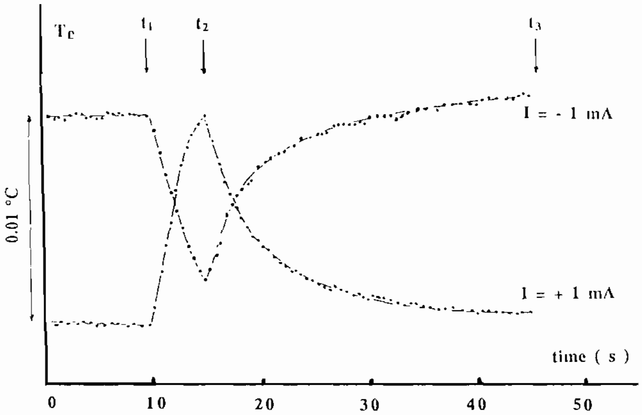

Fig. 2. Thermograms (electrode temperature $T_e=f(t)$) corresponding to the Cu oxidation ($I=+1$ mA) and the Cu^{2+} reduction ($I=-1$ mA) on the copper-deposited/copper-plated thermistor-electrode. Preperiod = 10 s ($t_0=0$ to t_1), electrolysis period = 5 s (t_1 to t_2) and postperiod = 30 s (t_2 to t_3).

The thermograms (electrode temperature versus time curves) showed three stages (Fig. 2): (i) the preperiod (from time t_0 to t_1) which allowed us to correct the thermogram of the possible temperature drift; (ii) the electrolysis period (from time t_1 to t_2); (iii) the postperiod (from time t_2 to t_3) which allowed the Newton exchange modulus χ determination. Regularly, a thermogram was recorded without electrolysis to check the temperature stability and the temperature drift correction efficiency. The temperature variation after 100 s did not exceed $\pm 2\times10^{-4}$ K (it was generally inferior to $\pm 10^{-4}$ K).

3. Results and discussion

3.1. Heat evolution and electrode temperature change on the copper-deposited/copper-plated thermistor-electrode

When an electric current passes through a half-cell, in addition to the electrochemical Peltier effect, three other thermal effects take place: (i) the electronic Peltier effect at the level of the conductor/electrode junction, which is generally neglected [2]; (ii) the thermal effect due to the overvoltage η related to the electrolysis current; (iii) the joule effect resulting from the electrode and solution resistance R. Thus the thermal power W (in watt) dissipated at the electrode can be expressed as:

$$W = -\Pi I/zF - \eta I - RI^2 \qquad (12)$$

where Π is the molar electrochemical Peltier heat (J mol^{-1}), I is the electrolysis current (A), z is the number of electrons involved in the electrode reaction, F is the Faraday (96493 C) and η the overvoltage (V). In this work the heat dissipated by Joule effect (RI^2) in the electrode and the solution, which is very small considering the low electrolysis currents used (≈ 1 mA) and the thinness of the solution layer concerned by heat evolution, is neglected. Thus Eq. (12) becomes:

$$W = -\Pi I/zF - \eta I \qquad (13)$$

The thermal evolution of the electrode during the electrolysis period ($t_1 < t < t_2$) is given by the following relationship:

$$C\,\mathrm{d}T_e/\mathrm{d}t = -(W - C\chi(T_e - T_b)) \qquad (14)$$

where C is the heat capacity of the system (thermistor + electrode + solution layer), χ is the Newton exchange modulus, T_e is the electrode temperature and T_b is the bulk solution temperature, which is taken as reference and equal to zero.

By integration, relationship (14) gives

$$T_e = -W(1 - \exp(-\chi t))/C\chi \qquad (15)$$

During the postperiod ($t > t_2$), the electrode temperature changes with time according to

$$\ln T_e = -\chi t + \ln T_{t2} \qquad (16)$$

where T_{t2} is the electrode temperature when the electrolysis current is switched off. Experimentally we only observed a good linear relation ($r > 0.99$) between ln T_e and t during the first ten seconds. The slope of this straight line gives the Newton exchange modulus χ.

Attempts to determine the thermal power dissipated from the data obtained at the beginning of the electrolysis (first five seconds corresponding to the curves in Fig. 2) were unsuccessful.

So, Eq. (15) can be rewritten as

$$W/C = -T_e\chi/(1 - \exp(-\chi t)) \qquad (17)$$

and if the time t is important, the exponential term is negligible and Eq. (17) is simplified

$$t \longrightarrow \infty \Rightarrow W/C = -T_{st}\chi \quad \text{or}$$

$$T_{st} = -W/C\chi = \text{constant} \qquad (18)$$

where T_{st} is the maximum temperature of the electrode, for a given electrolysis current, when the electrolysis time is important (i.e. when a steady state is reached). This is effectively observed with a 50-s electrolysis time (Fig. 3).

The value of the ratio W/C was determined, using Eq. (17), throughout the electrolysis period (Fig. 4). As can be seen in Fig. 4, this ratio decreases with time at the beginning of the electrolysis and remains constant after 30 s. As the thermal power W is constant, there is an increase in the heat capacity due to an increase in the thermal diffusion volume until a steady state is reached when the heat provided by the electrode reaction is equal to the heat lost by conduction.

We tested the reproducibility of T_{st} obtained for different electrolysis currents. Results with the copper thermistor-electrode in $CuSO_4$ 0.5 mol l^{-1} are summarized in Table 1. Reproducibility is below 1.5% when T_{st} is superior to 4×10^{-3} K but is only 10% when T_{st}

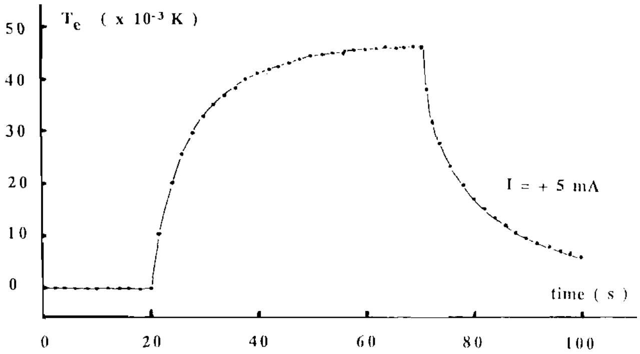

Fig. 3. Thermogram corresponding to the Cu oxidation ($I = +5$ mA) with a 50 s electrolysis time (preperiod = 20 s and postperiod = 30 s).

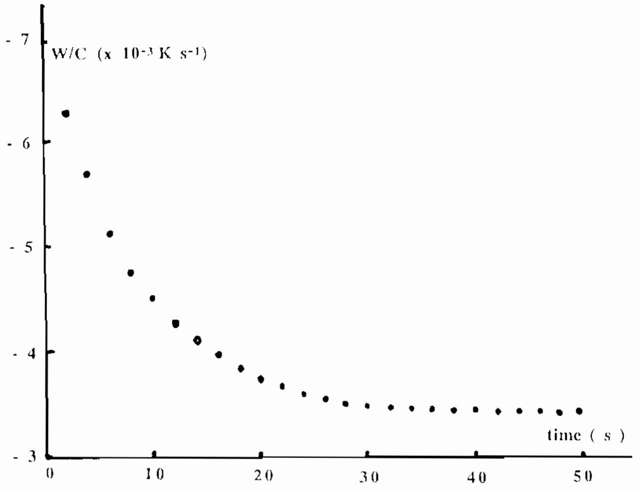

Fig. 4. Variation of the ratio W/C throughout the electrolysis period corresponding to the experiment showed in Fig. 3.

Table 1
Reproducibility of T_{st} for different electrolysis currents after 50 s of electrolysis with the copper-deposited/copper-plated thermistor-electrode (n = number of experiments; σ = standard deviation)

i (mA)	n	T_{st} ($\times 10^{-3}$ K)	σ ($\times 10^{-3}$ K)	%
0.5	4	4.40	0.065	1.5
1.0	3	8.78	0.14	1.6
1.5	3	13.32	0.17	1.3
2.0	5	17.68	0.26	1.4
3.0	3	27.17	0.12	0.4
4.0	3	37.13	0.23	0.6
5.0	6	47.53	0.53	1.1

is about 10^{-3} K. Similar results were obtained with the platinum thermistor-electrode in 0.1 mol l^{-1} $K_3Fe(CN)_6/K_4Fe(CN)_6$. Each set of experiments was carried out on two days with a new solution each day and no significant difference was noted.

For each electrolysis current, the theoretical thermal power W, dissipated by the electrode reaction was calculated according to Eq. (13) using $\Pi = +39.3$ kJ mol l^{-1} for 0.5 mol l^{-1} Cu^2/Cu and overvoltage was measured during each experiment. These values were correlated with the corresponding T_{st} (Fig. 5). There is no linear correlation and with the aid of a non-linear regression least-squares method, we found, for the Cu oxidation ($n = 27$ experimental data):

$$W_{ox} = -0.0250T_{st} - 0.1502T_{st}^2 \qquad (19)$$

and for the Cu^{2+} reduction ($n = 21$)

$$W_{red} = -0.0237T_{st} - 0.186T_{st}^2 \qquad (20)$$

and taking into account all the experimental data ($n = 48$)

$$W = -0.0246T_{st} - 0.161T_{st}^2 \qquad (21)$$

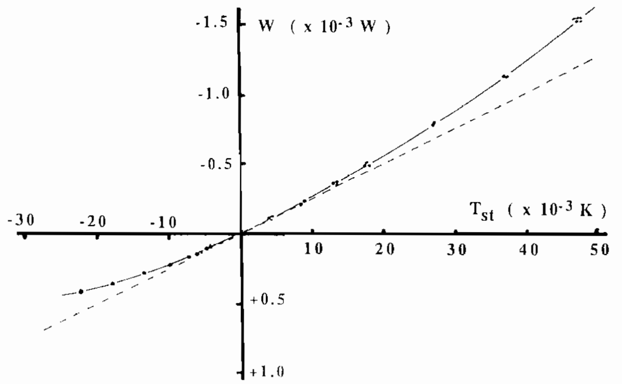

Fig. 5. Thermal power/steady state electrode temperature curve ($W = f(T_{st})$) for the Cu-deposited/Cu-plated thermistor-electrode in 0.5 mol l^{-1} $CuSO_4$ with a 50 s electrolysis time. ●, Experimental points; - - -, $W = -0.0246T_{st}$; ——, Eq. (21).

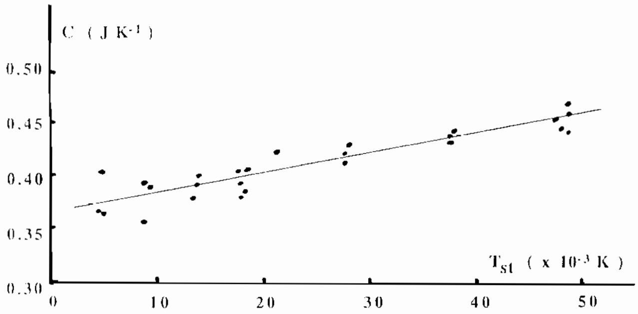

Fig. 6. Heat capacity C increase with the steady state electrode temperature T_{st} (Cu-deposited/Cu-plated thermistor electrode).

The heat capacity C was calculated from Eq. (18) for each experiment (Fig. 6) and it rises with T_{st}. The volume of electrode and solution layer around the electrode concerned by heat diffusion logically increases with the electrode temperature. At 2.5×10^{-2} K, the heat capacity was 0.42 J K^{-1} and represented a 0.1 ml water volume equivalent. It is difficult to take into account the respective contributions of the thermistor material, the electrode metal and the solution layer to the total heat capacity but, considering a 50 mm^3 electrode volume, and a 65 mm^2 electrode surface, we can estimate that the solution layer concerned by heat evolution is no more than 1 mm thick, and presents little electrical resistance.

3.2. Heat evolution and electrode temperature change on the platinum-plated thermistor-electrode

The hexacyanoferrate III/II redox couple (noted Fe III/Fe II) is interesting in several ways: (i) the electron transfer reaction is fast on platinum and only one electron is transferred; (ii) the two ions are weakly solvated, i.e. water molecules, only occurring in the second solvation sphere, are less strongly held than in $[Fe(H_2O)_6]^{2+/3+}$; (iii) the two ions do not decoordinate during the electron transfer; (iv) there is no change in the physical state during the electron transfer contrary to Cu^{2+}/Cu.

The same procedure as for the copper-deposited/copper-plated thermistor-electrode was performed.

Using the -45.1 kJ mol^{-1} Π value and the overvoltage measured during each electrolysis the theoretical thermal power W was calculated and correlated to T_{st} measured after a 100 s electrolysis (Fig. 7).

For the oxidation of $[Fe(CN)_6]^{4-}$ we obtained negative electrode temperatures, which confirmed that the oxidation was endothermic and relation (22) was calculated ($n=35$).

$$W_{ox} = -0.0240T_{st} - 0.0428T_{st}^2 \quad (22)$$

For the reduction of $[Fe(CN)_6]^{3-}$ wc obtained relation (23) ($n=34$).

$$W_{red} = -0.0242T_{st} - 0.0456T_{st}^2 \quad (23)$$

These relations are quite equivalent and taking into account all the experimental data ($n=69$) we obtained:

$$W = -0.02414T_{st} - 0.0484T_{st}^2 \quad (24)$$

This last relation (24) was used to determine the electrochemical Peltier heat of other redox couples.

3.3. Heat evolution and electrode temperature change on the copper-deposited/platinum-plated thermistor-electrode

To verify the accuracy of the molar electrochemical Peltier heats determined using Eq. (24), copper was electrochemically deposited on the platinum-plated thermistor-electrode. The electrochemical Peltier heat average value found using electrolysis current intensities up to 1 mA (0.25, 0.5, 0.75 and 1 mA) was 38.6±1.4 kJ mol^{-1} ($n=18$), which agrees well with the reference value 39.3±0.6 kJ mol^{-1}. But, when the electrolysis current intensities were more important than 1 mA, a regular decrease of the Π value was obscrvcd.

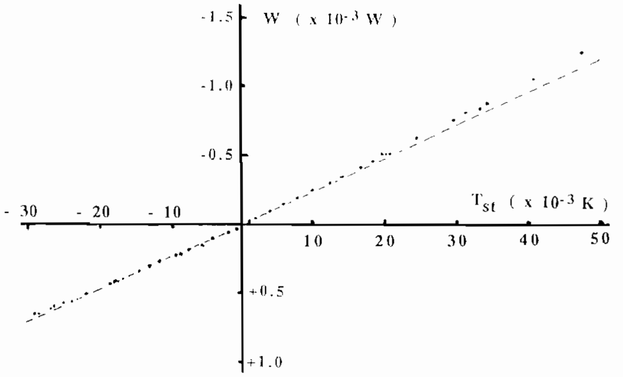

Fig. 7. Thermal power/steady state electrode temperature curve ($W=f(T_{st})$) for the Pt-plated thermistor-electrode in 0.1 mol l^{-1} Fe III/Fe II with a 100 s electrolysis time. ●, Experimental points, – – –, $W = -0.02412\ T_{st}$.

The correlation between the theoretical thermal power W, using the reference value $\Pi = 39.3$ kJ mol^{-1} and the measured overvoltage and the respective T_{st} gave

for the Cu oxidation ($n=36$)

$$W_{ox} = -0.02422T_{st} - 0.1396T_{st}^2 \quad (25)$$

for the Cu^{2+} reduction ($n=16$)

$$W_{red} = -0.02387T_{st} - 0.1356T_{st}^2 \quad (26)$$

and for all the experimental data ($n=52$)

$$W = -0.02395T_{st} - 0.1387T_{st}^2 \quad (27)$$

3.4. Heat evolution and electrode temperature change on the zinc-deposited/platinum-plated thermistor-electrode

Zinc was deposited on the platinum-plated thermistor-electrode and the 0.5 mol l^{-1} $ZnSO_4/Zn$ redox couple was studied with current intensities between -3.5 and $+3.5$ mA. The T_{st} obtained were treated using Eq. (24), and an average Π value of $+46.85 \pm 1.7$ kJ mol^{-1} was obtained ($n=42$). This value agrees well with the literature data for a Zn^{2+}/Zn system with comparable ionic strength: 44.4 (0.1 mol l^{-1} $ZnBr_2$) and 49.5 (1 mol l^{-1} $ZnBr_2$) kJ mol^{-1} [19]; 42.0±6 kJ mol^{-1} (mean value of the rcsults rcviewed by Lange and Monheim [10] for 1 mol l^{-1} $ZnSO_4$).

However we observed the same evolution of Π with the electrolysis current I (Fig. 8(a)) as for the Cu^{2+}/Cu redox couple. So, the experimental data were treated

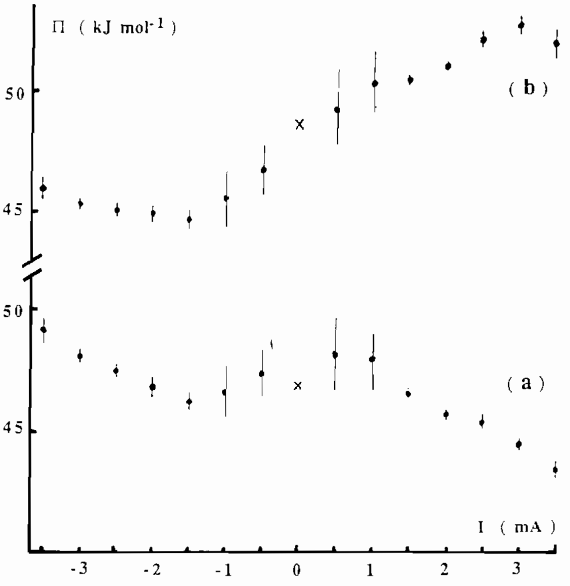

Fig. 8. Evolution of Π with the electrolysis current for the Zn^{2+}/Zn redox couple on the Zn-deposited/Pt-plated thermistor-electrode. Π values were calculated from experimental T_{st} using (a) Eq. (24) and (b) Eq. (27). ●, Average experimental value for each current intensity; |, standard deviation; ×, mean Π value.

with Eq. (27) and an average value of 48.6 ± 3.0 was found, which also agrees with literature data, but the standard deviation is more important and the curve $\Pi = f(I)$ is not better than previously (Fig. 8(b)).

Using $\Pi = 46.85$ kJ mol^{-1}, the theoretical thermal power W was calculated and correlated with the corresponding T_{st}. We obtained Eq. (28) ($n = 42$)

$$W = -0.0238 T_{st} - 0.0841 T_{st}^2 \qquad (28)$$

3.5. *Molar electrochemical Peltier heat of the Cl_2/Cl^-, Br_2/Br^- and I_3^-/I^- redox couples on the platinum-plated thermistor-electrode*

The experimental conditions and the Π values obtained using Eq. (24) are given in Table 2. The current intensities used for the X_2/X^- redox couples were less important than those used for the previous redox couples and we did not observe any significant discrepancy between Π and I as Fig. 9 shows for the Br_2/Br^- system. For the I_3^-/I^- and Br_2/Br^- redox couples the overvoltage was low whatever the current intensity (Fig. 10). For the Cl_2/Cl^- redox couple the overvoltage was rapidly important ($\eta > 400$ mV when $i > 0.2$ mA) but, in spite of these high overvoltages, reproducible Π values were obtained.

For these systems, there are no reference values. So, they were compared with the estimated values calculated according to Eqs. (1) to (10) and using the following values: absolute standard entropies and partial molar entropies (in J mol^{-1} K^{-1}): $S°_{Cl_2\,aq} = 121.4$, $S°_{Br_2\,aq} = 130.6$, $\bar{S}°_{I_3^-\,aq} = 261.6$ ([37] and taking $\bar{S}°_{H^+\,aq} = -22.2$ [38]), $\bar{S}°_{Cl^-\,aq} = 78.2$, $\bar{S}°_{Br^-\,aq} = 103.6$ and $\bar{S}°_{I^-\,aq} = 132.1$; the activity coefficients: $\gamma_{Cl^-} = 0.772$, $\gamma_{Br^-} = 0.772$, $\gamma_{I_3^-} = 0.730$ and $\gamma_{I^-} = 0.730$ (calculated from the Davies equation); the relative partial molar enthalpies (in J mol^{-1}) $\bar{L}_2$: fo· 0.1 mol l^{-1} KCl $= 380.4$, for 0.1 mol l^{-1} KBr $= 293$ [39] (values for I_3^-, K^+ and KI were not found); the transference numbers calculated from the limiting equivalent conductances: $t_{K^+} = 0.485$ and $t_{Br^-} = 0.515$ (for KBr), $t_{K^+} = 0.491$ and $t_{Cl^-} = 0.509$ (for KCl), $t_{K^+} = 0.528$, $t_{I_3^-} = 0.196$ and $t_{I^-} = 0.276$ (for KI + K^+, $I_{I_3^-}$); the absolute entropies of transfer (in J mol^{-1} K^{-1}) at infinite dilution: $S^{*o}_{K^+} = 6.7$, $S^{*o}_{Cl^-} = 2.5$, $S^{*o}_{Br^-} = 2.4$ and $S^{*o}_{I^-} = -4.5$ (mean values of S^{*o}_i given in Table I, Ref. [40] and Table VIII, Ref. [2]).

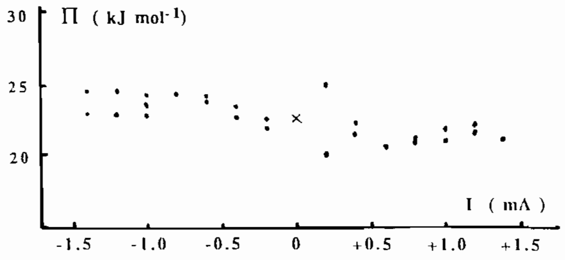

Fig. 9. Evolution of Π with the electrolysis current for the Br_2/Br^- redox couple on the Pt-plated thermistor-electrode. Π values were calculated from experimental T_{st} using Eq. (24). ●, Experimental value for each current intensity; ×, mean Π value.

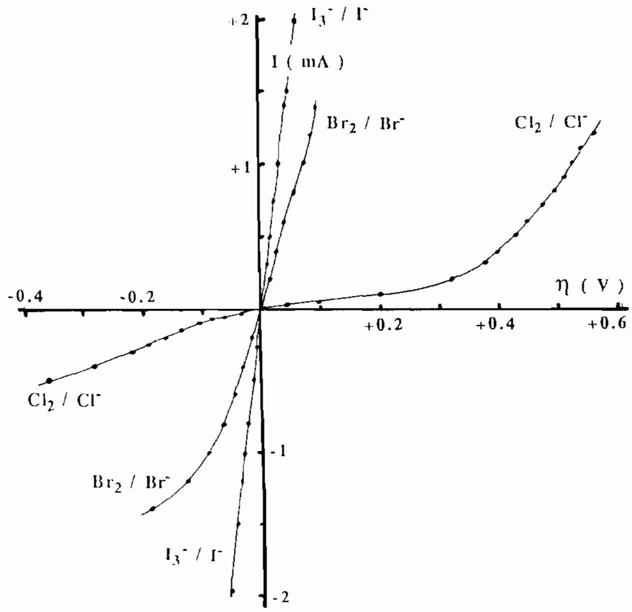

Fig. 10. $\eta = f(I)$ curves on the Pt-plated thermistor-electrode of the X_2/X^- redox couples.

For the Br_2/Br^- system: $S^E_{Br^-} = 2.64$ and $\bar{\bar{S}}_e(Pt) = 0.43$ J mol^{-1} K^{-1}; $S_{Br_2\,aq} - 2\bar{S}_{Br^-\,aq} + 2\bar{\bar{S}}_e = 130.6 - 207.2 - 8.32 \ln 0.028 + 2 \times 8.32 \ln 0.1 - 2 \times 2.64 + 0.86 = -89.79$ J mol^{-1} K^{-1}; $-\Pi/T = -22400/298 = -75.16 = -89.79 + \Delta S^*$.

Π and $T\Delta S_{ox}$ are not very different, which confirms the experimental Π value. ΔS^* cannot be theoretically calculated because the excess entropies of transport of ions S^{*E}_i are not known but from these experimental results ΔS^* and thus S^{*E}_i can be determined.

$$\Delta S^* = -\Pi/T - \Delta S_{ox} = +14.63 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta S^* = z[(t_{K^+} S^{*o}_{K^+} - t_{Br^-} S^{*o}_{Br^-}) + (t_{K^+} S^{*E}_{K^+} - t_{Br^-} S^{*E}_{Br^-})]$$

$$t_{K^+} S^{*o}_{K^+} - t_{Br^-} S^{*o}_{Br^-} = 2.01 \text{ J mol}^{-1} \text{ K}^{-1}$$

so

$$t_{K^+} S^{*E}_{K^+} - t_{Br^-} S^{*E}_{Br^-} = 14.63/2 - 2.01 = 5.31 \text{ J mol}^{-1} \text{ K}^{-1} \qquad (29)$$

The absolute entropy of transport of KBr at infinite dilution is $S^{*o}_{KBr} = 9.1$ J mol^{-1} K^{-1}. At ionic strength $m = 0.1$ mol l^{-1}, S^*_{KBr} can be determined with the aid

Table 2
Experimental conditions and Π values obtained for X_2/X^- redox couples couples on the platinum-plated thermistor-electrode according to Eq. (24)

Couple (X_2/X^-)	(X_2) (mol l^{-1})	(KX) (mol l^{-1})	I (mA)	$\Delta I^{*\,a}$ (mA)	n	Π (kJ mol^{-1}/X_2)
Cl_2/Cl^-	0.012	0.1	$0.4<i<1.2$	0.1	22	21.2 ± 2.3
Br_2^-/Br^-	0.04	0.1	$-1.4<i<1.4$	0.2	30	22.4 ± 1.3
I_3^-/I^-	0.1	0.1	$-2<i<2$	0.25	20	44.2 ± 3.0

[a] $^*\Delta I$ is the current increment.

of the slope of the line $S^* = f(\sqrt{m}/(1+\sqrt{m}))$ which is -28 J mol^{-1} K^{-1} [2]: $S^*_{KBr} = 2.38$ J mol^{-1} K^{-1} and

$$S^*_{KBr} - S^{*o}_{KBr} = -6.72 = S^{*E}_{Br^-} + S^{*E}_{K^+} \tag{30}$$

From these two relations (29) and (30): $S^{*E}_{K^+} = -15.29$ and $S^{*E}_{Br^-} = 8.57$ J mol^{-1} K^{-1} were calculated. These values seem important compared with those at infinite dilution but there is no other reference for comparison.

For the Cl_2/Cl^- redox couple (0.012 mol l^{-1} Cl_2 and 0.1 mol l^{-1} KCl): $S^E_i = 2.79$ J mol^{-1} K^{-1}; $S_{Cl_2\,aq} - 2\bar{S}_{Cl^-\,aq} + 2\bar{\bar{S}}_e = 121.4 - 156.4 + 36.8 - 38.32 - 2 \times 2.79 + 0.86 = -41.26$ J mol^{-1} K^{-1}; $-\Pi/T = -71.14 = -41.24 + \Delta S^*$ that gives $\Delta S^* = -29.9$ J mol^{-1} K^{-1}. This ΔS^* value and that, obtained for Br_2/Br^- (+14.13 J mol^{-1} K^{-1}), definitely diverge considering that their $S^{*\circ}$ are quite equivalent.

In neutral medium, Cl_2 is in equilibrium with ClO^- ($K = 1.45 \times 10^{-2}$ [41]). If all Cl_2 were as ClO^-, ΔS_{ox} ($Cl^- + H_2O \rightarrow ClO^- + 2H^+ + 2e^-$) would be -175.2 J mol^{-1} K^{-1}. In our experimental conditions, only 15% Cl_2 would be ClO^- and an approximate $\Delta S_{ox} = -61.36$ J mol^{-1} K^{-1} was calculated, a result which is closer to the experimental result (-71.14 J mol^{-1} K^{-1}). Further experiments in acidic and basic media will be necessary to confirm this hypothesis.

For the I_3^-/I^- redox couple (0.1 mol l^{-1} I_3^- + 0.1 mol l^{-1} I^-) a theoretical $\Delta S_{ox} = -173.0$ J mol^{-1} K^{-1} and a reasonable $\Delta S^* = -\Pi/T - \Delta S^*_{ox} = 24.6$ J mol^{-1} K^{-1} were calculated. $S^{*o}_{I_3^-}$ and $S^*_{KI_3}$ being unknown, no other explanation can be given.

3.6. Comparison between Eqs. (21), (24), (27) and (28)

Thermal power W varies with T_{st} as:

$$W = -aT_{st} - bT_{st}^2 \tag{31}$$

The coefficients of Eq. (27) (copper-deposited/platinum-plated thermistor-electrode) are smaller than those of Eq. (21) (copper-deposited/copper-plated thermistor-electrode) but with the same rough estimate. The difference can be explained by the construction of the thermistor-electrodes which were not quite identical but also by the electrolysis times which were 100 and 50 s, respectively, and T_{st} (100 s) $\approx 1.05 \times T_{st}$ (50 s).

The comparisons between Eqs. (24), (27) and (28) (Pt, Cu/Pt and Zn/Pt electrodes) are interesting: the polynomial coefficient a of the T_{st} term is roughly the same and would be representative of the basic heat capacity (C_0) of the electrode and solution layer $a = C_0\chi$. For each experiment, the Newton exchange modulus χ was determined and χ average values are given in Table 3. Considering the standard deviations, the differences between the average χ whatever the electrolyte and the metal the electrode is made of are not significant and $\bar{\chi} = \Sigma n\chi/\Sigma n = 0.0868$ s^{-1} was calculated. Linear correlations $\chi = f(T_{st})$ show that χ is independent of T_{st} (correlation coefficient $r = 0.05$ for hexacyanoferrate III/II on Pt). χ, among other things is in connection with the thermal conductivity λ of the electrolyte which was calculated from

$$\lambda = f(0.515 + \Sigma\alpha_i c_i)/(86.042 \times 10^4)$$

where $f = 1.012$ at 25 °C, α_i is a constant characteristic of the ion i and c_i its concentration in mol l^{-1} [42]. The values found for the different electrolytes do not differ more than ±1% whatever the electrolyte and this can explain the χ constancy.

The polynomial coefficient b of the T_{st}^2 term is very different according to the electrode metal. Eq. (31), taking $k = b/a$ can be rewritten as:

$$W = -T_{st}\chi C_0(1 + kT_{st}) \tag{32}$$

Table 3
Average values of the Newton exchange modulus χ obtained for different electrolytes

Conc. (mol l^{-1})	Redox couples	χ (s^{-1})	σ	n
0.1	FeIII/FeII/Pt	0.089 ±	0.007	63
	Cu^{2+}/Cu/Pt	0.088 ±	0.007	54
	Zn^{2+}/Zn/Pt	0.087 ±	0.008	42
	Br^2/Br^-/Pt	0.085 ±	0.009	22
	Cl^2/Cl^-/Pt	0.082 ±	0.006	20
	I_3^-/I^-/Pt	0.088 ±	0.010	22
0.25	FeIII/FeII/Pt	0.083 ±	0.012	16
0.025	FeIII/FeII/Pt	0.085 ±	0.015	19

and $k = 2.0$, 3.53 and 5.79 was calculated for Pt, Zn/Pt and Cu/Pt thermistor-electrodes, respectively. These k values can be compared with the thermal conductivities λ of the metals the electrode is made of: 71.6 (Pt), 116 (Zn) and 401 (Cu) W m^{-1} K^{-1}. The coefficient k represents the increase of the heat capacity with T_{st} and is a combination of the electrolyte, thermistor material and electrode metal thermal conductivities (the first two terms being constant). Three experimental data are not sufficient and other metals will have to be studied to solve this point.

3.7. Heat evolution and electrode temperature change on the silver-deposited/platinum-plated thermistor-electrode

The T_{st} values obtained during the oxidation ($0 < I \leqslant 2$ mA) of Ag in 0.1 mol l^{-1} $AgNO_3$ were not reproducible but, in the same way, the Newton exchange modulus χ changed. Correcting the T_{st}:$T_{st\,corr} = T_{st} \times \chi/0.0868$ and using Eq. (24) we found an average value $\Pi = -13.4 \pm 1.5$ kJ mol^{-1} which agrees with literature data: -12.8 kJ mol^{-1} [11,17].

3.8. Treatment of the experimental results with the method of Kuz'minskii and Gorodyskii [20]

The experimental results were treated using Eq. (11). The curves $T_{st}/I = f(\eta)$ corresponding to 0.1 mol l^{-1} Fe III/II on Pt and 0.5 mol l^{-1} Cu^{2+}/Cu redox couples are shown in Figs. 11 and 12, respectively. A fairly good Π value was only obtained for the Fe III/II on Pt system: -48.3 and -56.9 kJ mol^{-1} (when $i > 0$ and $i < 0$, respectively) close to our reference value -45.1 kJ mol^{-1}. But this value differs from that of Kuz'minskii and Gorodyskii: -31.9 ± 1.4 kJ mol l^{-1} in 0.25 mol l^{-1} Fe III/II on Pt [20].

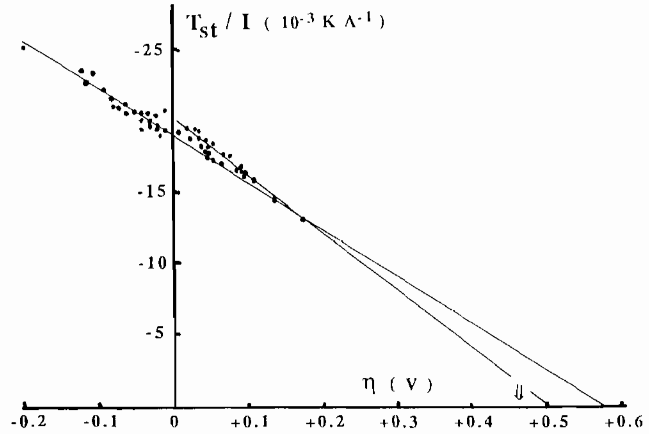

Fig. 11. $T_{st}/I = f(\eta)$ curves (Kuz'minskii's method) corresponding to the 0.1 mol l^{-1} Fe III/Fe II redox couple on the Pt-plated thermistor-electrode. ●, Experimental points; ⇓, our reference Π value (0.467 V = 45100 J mol^{-1} K^{-1}/96493 C).

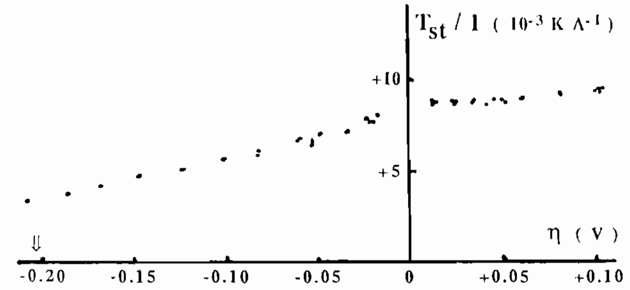

Fig. 12. $T_{st}/I = f(\eta)$ curves (Kuz'minskii's method) corresponding to the 0.5 mol l^{-1} Cu^{2+}/Cu redox couple on the Cu-deposited/Pt-plated thermistor-electrode. ●, Experimental points; ⇓, our reference Π value (0.204 V = 39300 J mol^{-1} K^{-1}/2×96493 C). No result was obtained for this redox couple.

So, the electrochemical Peltier heat of hexacyanoferrate III/II on Pt was determined at two other concentrations of electrolytes 0.25 and 0.025 mol l^{-1}. We found -45.2 ± 0.9 ($n = 15$) and -51.8 ± 2.7 ($n = 18$) kJ mol^{-1}, respectively, values always different from Kuz'minskii's. The Π value when the electrolyte concentration was 0.25 mol l^{-1} was the same as for 0.1 mol l^{-1} but, when concentration is important, $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ are not completely dissociated [43].

Breck and Lin [40] give: $\bar{S}^{\circ}_{FeIII} = 558.0$ and $\bar{S}^{\circ}_{FeII} = 376.2$ J mol^{-1} K^{-1}, $S^{*\circ}_{FeIII} = 58.9$ and $S^{*\circ}_{FeII} = 81.5$ J mol^{-1} K^{-1}; the ionic strength for 0.025 mol l^{-1} FeIII + 0.025 mol l^{-1} FeII is 0.4 mol l^{-1} and from the Davies equation we calculated $\gamma_{FeIII} = 0.0392$ and $\gamma_{FeII} = 0.00316$; the transference numbers are $t_{K^+} = 0.409$, $t_{FeIII} = 0.238$ and $t_{FeII} = 0.353$. From these values, $\Delta S_{ox} = 160.8$ J mol^{-1} K^{-1} was calculated which agrees better with our value ($-\Pi/T = 174.0 \pm 9$ J mol^{-1} K^{-1}) than with Kuz'minskii's ($-\Pi/T = 107.0 \pm 5$ J mol^{-1} K^{-1}). $\Delta S^* = 13.2 \pm 9$ J mol^{-1} K^{-1} is obtained for a calculated $\Delta S^{*\circ} = -9.12$ J mol^{-1} K^{-1}.

4. Conclusions

The electrochemical Peltier heats, determined for different redox couples, with a thermistor-electrode heat calibrated using the Π value -45.1 kJ mol^{-1} (for 0.1 mol l^{-1} $K_3Fe(CN)_6$/0.1 mol l^{-1} $K_4Fe(CN)_6$/Pt system) are in agreement with the literature data and those estimated from the thermodynamic constants that exist, but we must however point out that such constants for particularly entropies and excess entropies of transport do not exist. This calibration technique is suitable but needs to be further studied for a better understanding of all the phenomena occurring at the electrode/solution interface.

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