

# *The conversion of thermal energy into electrical energy using cells having a reversal of potential with temperature*

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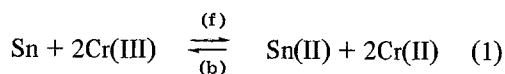
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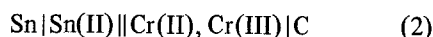
The e.m.f. of the galvanic cell Sn/Sn(II)//Cr(II), Cr(III)/C changes sign between 25–95° C. Its possibilities for electrochemical conversion of thermal energy have been considered. The redox potentials of the systems Sn/Sn(II) and Cr(II)/Cr(III) have been determined as a function of the temperature and the concentration of chloride ions. By choosing the appropriate CaCl<sub>2</sub> concentration the inversion may be made to occur at any temperature. The temperature coefficient of the cell has been found to be 1.42 mV/° C. An experimental cell has been designed and the causes of the phenomenon are discussed.

## 1. Introduction

In 1886, Case [1] observed that hot aqueous solutions of chromic chloride attacked metallic tin but on cooling the resulting chromous and stannous chlorides reacted together to regenerate tin and Cr(III). These two oxido-reduction reactions may be represented by the following equilibrium:



reaction (f) occurring at high temperature and reaction (b) at low temperature. This phenomenon could be used to convert directly thermal energy into electrical energy, by means of the following cell:



where both redox couples are confined in separate compartments by a convenient diaphragm to avoid any direct recombination following one of the reactions of Equilibrium 1. When the cell is cold, tin(II) is reduced and the tin electrode acts as the positive terminal of a battery. On the other hand, when the cell is hot, the carbon electrode becomes the positive terminal. Hence the device can transform heat energy into electric power.

The purpose of the present work was to see if such an aqueous cell could allow a reasonable conversion of energy. The e.m.f. of the cell was studied as a function of two parameters, the temperature and the calcium chloride concentration, the latter being a good parameter to fix the 'reversal temperature', i.e. the temperature at which the direction of the spontaneous change is reversed.

## 2. Experimental

### 2.1. Techniques

Polarography allows a fast determination of the half-wave potential of a redox system (close to the apparent redox potential). Moreover, only one component of the pair is required, for example Cr(III) (avoiding difficulties related to the reactivity of Cr(II) to oxygen), and it indicates the reversibility of the system. Polarography has been used under the tass polarography conditions, allowing a high potential scanning rate (apparatus used: Tacussel PRG5 polarograph).

Potentiometry necessitates more care, especially in the preparation and storage of chromous chloride. An air-tight thermoregulated all glass electrochemical cell has been designed,

allowing the reduction of chromic chloride into chromous chloride on a mercury pool. Oxygen was eliminated with a flow of argon.

All the potentials were measured versus the Ag/AgCl/KCl(1 M) electrode.

## 2.2. Chemicals and solutions

**2.2.1. Prolabo RP SnCl<sub>2</sub> · 6H<sub>2</sub>O.** For 1 M solutions, the precipitation of Sn(OH)<sub>2</sub> occurs at pH > 1. Therefore, solutions have been prepared in 1 M acidic solution.

**2.2.2. Prolabo RP CrCl<sub>3</sub> · 6H<sub>2</sub>O and CaCl<sub>2</sub> · 2H<sub>2</sub>O.** When the calcium chloride concentration is less than 4 M, the colour of a freshly prepared CrCl<sub>3</sub> solution is different from that of an older one. Furthermore, polarograms obtained with the two solutions are different. A fresh solution may be artificially aged either by heating or by reduction into Cr(II) and reoxidation by air. All determinations were made using aged solutions.

For concentrations less than 0.1 M chromous chloride was prepared by cathodic reduction and for greater concentrations, by chemical reduction using zinc amalgam.

## 2.3. Experimental cell

The cell was a glass tube ( $\phi = 5$  cm) internally lined with graphite felt (apparent area: 70 cm<sup>2</sup>). It contains the chromium solution and a porous alumina container (thickness: 0.4 cm, diameter: 2.6 cm) for the stannous chloride solution and the tin electrode. The two compartments are air tight. The device is heated by a water jacket and the temperature is controlled by a thermocouple placed inside the chromium compartment.

## 3. Results

### 3.1. Sn/Sn(II) couple

The logarithmic analysis of the polarographic waves showed the charge transfer reaction to be reversible, at all temperatures and CaCl<sub>2</sub> concentrations. The standard cell potentials,  $E^0$ , were determined by plotting the equilibrium potential of a tin electrode against the log of the Sn(II) concentration. In HClO<sub>4</sub> (1 M) solution, at 25° C

the value obtained ( $E^0 = -0.448$  V) agrees well with the corresponding half-wave potential ( $E_{1/2} = -0.442$  V) confirming the reversibility of the couple. In chloride solutions, however, the Nernst relation was not observed because of the formation of chloro-complexes and the comparison between  $E^0$  and  $E_{1/2}$  is no longer possible. The results of the polarographic study are plotted in Fig. 1; the data corresponding to the intermediate concentrations at  $T > 25^\circ$  C were obtained by interpolation. The calcium chloride addition increases the reducing power of metallic tin, by complex formation between Sn<sup>2+</sup> cations and Cl<sup>-</sup> anions. At constant chloride concentration the increase in temperature shifts the observed redox to less negative values. This shift includes a possible contribution from a variation of the Ag/AgCl electrode potential with temperature. These values, obtained using dilute Sn(II) solutions (10<sup>-2</sup> M) were confirmed by potentiometric determinations at more realistic concentrations (Sn(II) = 1 M). At 25° C the equilibrium potentials are about equal to the half-wave potentials (Table 1). When the temperature was increased, the equilibrium potentials are practically unchanged although the  $E_{1/2}$  changed by about 40 mV (Fig. 2).

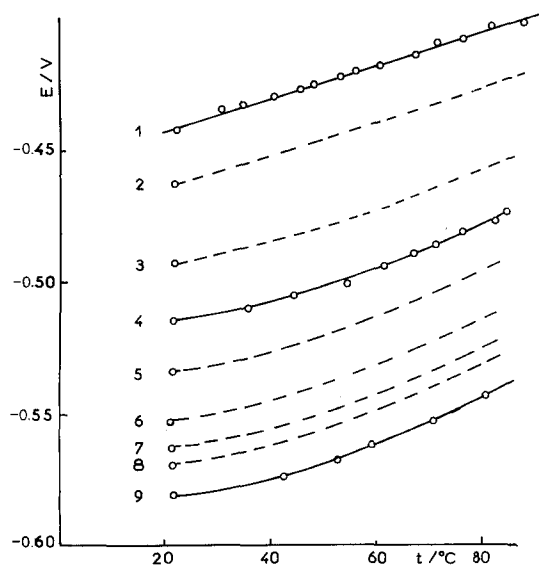


Fig. 1. Variation of the half-wave potential with temperature and electrolyte composition for the Sn/Sn(II) couple. Tin(II) concentration 10<sup>-2</sup> M. Electrolyte composition: 1, HClO<sub>4</sub> 1 M; 2, HCl 1 M. HCl: CaCl ratios (M:M): 3, 1:1; 4, 1:2; 5, 1:3; 6, 1:4; 7, 1:5; 8, 1:6; 9, 1:7. Dashed curves are interpolated.

Table 1. Comparison between half-wave potentials ( $E_{1/2}$ ) and equilibrium potential as a function of the electrolyte composition (25° C) for the Sn/Sn(II) couple

HCl: CaCl <sub>2</sub> (M: M)	$E_{1/2}$	$E_{eq}$
1:0	-0.463	-0.454
1:1	-0.493	-0.497
1:2	-0.515	-0.519
1:3	-0.534	-0.540
1:4	-0.556	-0.557
1:5	-0.563	-0.571
1:6	-0.570	-0.577

### 3.2. Cr(II)/Cr(III) couple

The polarograms follow the equation for reversible systems when the CaCl<sub>2</sub> concentration is greater than 4 M. The  $E_{1/2}$  variations against temperature are plotted in Fig. 3. Chloride addition makes the redox potential less negative and the temperature influence is greater for chromium than for tin: 0.15 V instead of 0.040 V.

The variation with temperature of the potential of a vitreous carbon electrode and a mercury electrode were compared. The electrodes were immersed in a solution of CrCl<sub>2</sub> (0.5 M) and CrCl<sub>3</sub> (0.5 M) in the electrolyte HCl: CaCl<sub>2</sub> = 1:5 (M: M). The potential of the mercury electrode is always close to the  $E_{1/2}$  value but that for the

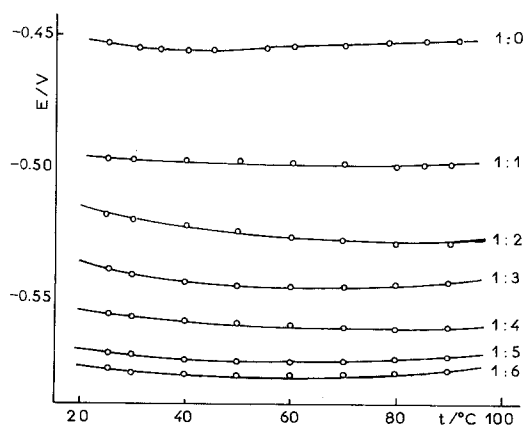


Fig. 2. Variation of the equilibrium potential of a tin electrode in a SnCl<sub>2</sub> 1 M solution in various electrolytes at various temperatures for the Sn/Sn(II) couple. The figures indicated are for HCl: CaCl<sub>2</sub> ratio values.

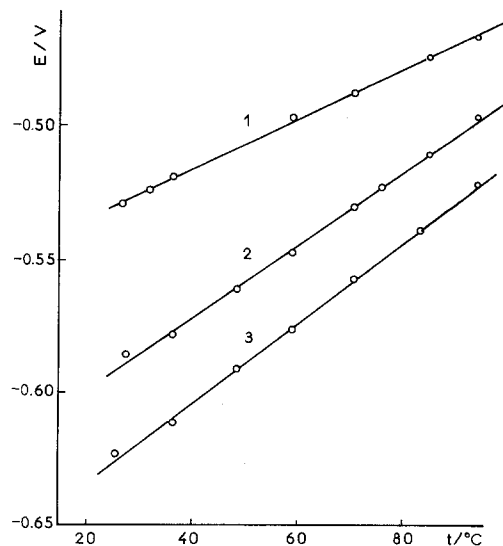


Fig. 3. Variation of the half-wave potential with temperature for the Cr(II)/Cr(III) couple. Electrolyte composition: 1, HCl: CaCl<sub>2</sub> = 1:7; 2, HCl: CaCl<sub>2</sub> = 1:5; 3, HCl: CaCl<sub>2</sub> = 1:4.

vitreous carbon electrode is always more negative by about 30 mV (Table 2).

### 3.3. Study of a cell

The choice of the calcium chloride concentration determines the inversion temperature of the cell. The electrolyte HCl: CaCl<sub>2</sub> = 1:5 appears to be the most favourable since it leads to a reversal of

Table 2. Comparison between half-wave potential ( $E_{1/2}$ ) obtained in Cr(III) dilute solution, and equilibrium potentials of a vitreous carbon electrode ( $E_C$ ) and a mercury electrode ( $E_{Hg}$ ) obtained in a solution of CrCl<sub>2</sub>: CrCl<sub>3</sub>: HCl: CaCl<sub>2</sub> = 0.5: 0.5: 1:5 at various temperatures for the Cr(II)/Cr(III) couple.

$t$ (° C)	$E_C$ (V)	$E_{Hg}$ (V)	$E_{1/2}$ (V)
25	-0.630	-0.590	-0.588
37	-0.614	-0.580	-0.575
40	-0.609	-0.575	-0.571
45	-0.597	-0.566	-0.567
49	-0.592	-0.561	-0.562
55	-0.581	-0.552	-0.554
60	-0.570	-0.545	-0.548
70	-0.553	-0.526	-0.532
75	-0.544	-0.517	-0.524
80	-0.534	-0.504	-0.517
85	-0.524	-0.497	-0.510
90	-0.517	-0.490	-0.500

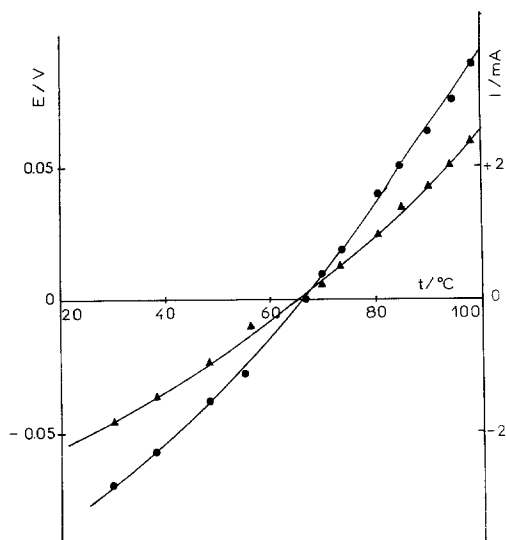


Fig. 4. Variation of the e.m.f. with temperature ( $\blacktriangle$ ) and of the short-circuit current with temperature ( $\bullet$ ) of Case's cell.

the cell potential at  $60^\circ\text{C}$ , in the middle of the temperature range. The difference between the redox potentials of the couples Cr(II)/Cr(III) and Sn/Sn(II) is, in this case,  $-0.050\text{ V}$  at  $25^\circ\text{C}$  and  $+0.050\text{ V}$  at  $95^\circ\text{C}$ .

In one compartment was placed a solution of  $\text{CrCl}_3$  ( $0.5\text{ M}$ ) and  $\text{CrCl}_2$  ( $0.5\text{ M}$ ) and in the Sn compartment  $\text{SnCl}_2$  solution ( $1\text{ M}$ ). From these values, the e.m.f. values of the hot cell ( $+0.065\text{ V}$ ) and of the cold cell ( $-0.060\text{ V}$ ) may be calculated. A current-voltage curve for the cell was obtained at  $25^\circ\text{C}$ . It is a straight line, corresponding to an open-circuit voltage (e.m.f.) equal to  $-0.060\text{ V}$  and an internal resistance of  $8\ \Omega$ , corresponding to a diaphragm specific resistance of about  $250\ \Omega\text{ cm}^2$ .

The variation of the cell e.m.f. versus temperature is plotted on Fig. 4. The fit to the theoretical curve is good: the e.m.f. varies from  $-0.060\text{ V}$  to  $+0.058\text{ V}$  and is zero at  $67^\circ\text{C}$ .

#### 4. Discussion

The good agreement between the e.m.f. observed with the experimental cell and the e.m.f. derived using the previously determined standard cell potential allows their use for a consideration of the possibilities of the cell. The highest e.m.f. available when the cell works in ordinary

conditions, that is for instance between  $25$ – $95^\circ\text{C}$  may be estimated. The greatest e.m.f. at a given temperature depends on the concentrations obtained at the other temperature. If the standard potential of the Sn/Sn(II) couple is chosen as the reference potential at the two temperatures the e.m.f. of the cell is related to concentrations by the expression

$$E = E_t^0 + (2.3RT/F) \log \frac{[\text{Cr(III)}]}{[\text{Cr(II)}][\text{Sn(II)}]^{1/2}} \quad (3)$$

with, at  $25^\circ\text{C}$ :  $2.3RT/F = 0.060\text{ V}$  and  $E_{25}^0 = -0.050\text{ V}$ ,  
and, at  $95^\circ\text{C}$ :  $2.3RT/F = 0.073\text{ V}$  and  $E_{95}^0 = +0.050\text{ V}$ .

When the e.m.f. of the hot cell is zero the Cr(II) and Sn(II) concentrations have their maximal values and the Cr(III) concentration is at its lowest. These concentrations are related by

$$\log \frac{[\text{Cr(III)}]}{[\text{Cr(II)}][\text{Sn(II)}]^{1/2}} = -50/73.$$

Now if the cell is cooled at constant composition, its e.m.f. at  $25^\circ\text{C}$ ,  $E_{25}^m$ , is

$$E_{25}^m = -0.050 - 0.06 \times 50/73 = -0.091\text{ V}.$$

$E_{25}^m$  is the highest available e.m.f. for the cold cell. Similarly, the highest for the hot cell is

$$E_{95}^m = +0.111\text{ V}.$$

The concentrations are derived using balanced conditions. If, for instance, the initial concentrations in a cold cell are  $[\text{Cr(II)}] = 1\text{ M}$  and  $[\text{Cr(III)}] = [\text{Sn(II)}] = 0$  the relations between concentrations are

$$[\text{Cr(III)}] + [\text{Cr(II)}] = 1$$

$$[\text{Cr(II)}] = 2[\text{Sn(II)}]$$

and the corresponding extreme values are:

$$\text{at } 25^\circ\text{C}: [\text{Sn(II)}] = 0.14\text{ M}; [\text{Cr(II)}] = 0.28\text{ M};$$

$$[\text{Cr(III)}] = 0.72\text{ M}$$

$$\text{at } 95^\circ\text{C}: [\text{Sn(II)}] = 0.44\text{ M}; [\text{Cr(II)}] = 0.88\text{ M};$$

$$[\text{Cr(III)}] = 0.12\text{ M}.$$

Thus at  $25^\circ\text{C}$ , during the change of the e.m.f. from  $-0.091\text{ V}$  to  $0\text{ V}$ , the tin (II) concentration decreases from  $0.44\text{ M}$  to  $0.14\text{ M}$ . The quantity of electricity involved in that half-cycle is, for two litres of solution (one of tin and one of chromium)

$$Q = 2F(0.44 - 0.14) = 57900 \text{ C} = 16.1 \text{ A h.}$$

These values are too low to be of practical interest. Furthermore, they are maximum values derived by supposing that the e.m.f. cell is allowed to decay to zero at each temperature, but this is technically unacceptable. Is an improvement possible? In other words, is the observed phenomenon peculiar to Case's cell (caused, for instance by a particular instability of the Cr(II) complexes with temperature) or is it more general and are the involved species replaceable by others leading to a larger variation of potential with temperature?

The stability of the complexes is measured by the difference between half-wave potentials in the presence and absence of chloride ions. This difference, for both tin and chromium varies little with temperature. It does not seem therefore that a specific influence of temperature upon the stability of a particular complex is the cause of the observed phenomenon. It may also be noted that Case's cell consists of two half-cells with redox couples of a different nature: the first one is of the type metal/metal ion and the second is of the type metal ion/metal ion. The entropies of solids and ions being different, the observed shift could be attributed to a difference in behaviour of the two half-cells with temperature.

The variation of the e.m.f. with temperature of the cell may be estimated using the correspondence principle from Criss and Cobble [2], which allows an evaluation of the mean heat capacities of solutes in water.

The e.m.f.  $E^0$  of the cell is related to the Gibbs energy variation corresponding to Reaction 1(f) by

$$\Delta G^0 = -2FE^0$$

itself related to the standard chemical potentials of the species appearing in the reaction

$$\Delta G^0 = \mu^0 [\text{Sn(II)}] + 2\mu^0 [\text{Cr(III)}] - \mu^* (\text{Sn}) - 2\mu^0 [\text{Cr(III)}]. \quad (4)$$

The variation of  $\mu^0$  (for a solute) or  $\mu^*$  (for a solid) between the temperatures  $T_0$ - $T_1$  is

$$\mu_1^0 - \mu_0^0 = \int_{T_0}^{T_1} C_p \, dT - (T_1 - T_0)S_0^0 - T \int_{T_0}^{T_1} (C_p/T) \, dT \quad (5)$$

where  $S_0^0$  is the entropy of the species at the reference temperature  $T_0$ , and  $C_p$  the molar heat capacity of the solute or the solid.

Generally, the variation of  $C_p^*$  (for the solid) with temperature may be written as

$$C_p^* = a + b 10^{-3} T + \dots$$

so that, the mean heat capacity between  $T_0$ - $T_1$  is

$$\bar{C}_{p_1}^* = \frac{\int_{T_0}^{T_1} C_p^* \, dT}{T_1 - T_0} = a + \frac{1}{2} b 10^{-3} (T_1 + T_0). \quad (6)$$

From Equation 4, one obtains

$$\mu_1^* - \mu_0^* = -S_0^*(T_1 - T_0) + \bar{C}_{p_1}^* F(T_1) - F(T_1) = (T_1 - T_0) - T_1 \ln(T_1 - T_0). \quad (7)$$

Similar expressions are derivable for solutes if their mean heat capacities are known.

By choosing, at each temperature, a convenient reference state (defined by the entropy of aqueous  $\text{H}^+$ ), Criss and Cobble showed that the partial molal entropy  $S_1^0$  of one ion at the temperature  $T_1$  is related to the partial molal entropy  $S_0^0$  of the same ion at the reference temperature  $T_0$  by an expression like

$$\bar{S}_1^0 = a_1 + b_1 \bar{S}_0^0 \quad (8)$$

where  $a_1$  and  $b_1$  are adjustable parameters depending on  $T_1$ ,  $T_0$ , and the 'class' of the ion (either 'simple cation', or 'simple anion' or 'oxyanion', etc.). For the simple cation class, with  $T_1 = 100^\circ \text{C}$ , the  $a_1$  and  $b_1$  values are, respectively 10.3 and 0.876. Defining the mean heat capacity by the expression

$$\bar{S}_1^0 = S_0^0 + \int_{T_0}^{T_1} (\bar{C}_p^0/T) \, dT \quad (9)$$

it may be shown that

$$\begin{aligned} \bar{C}_{p_1}^0 &= \alpha_1 + \beta_1 \bar{S}_0^0 \\ \text{with } \alpha_1 &= a_1 / (\ln T_1 / T_0) \\ \beta_1 &= (b_1 - 1) / (\ln T_1 / T_0) \end{aligned} \quad (10)$$

(Note: the choice of an entropy value of aqueous  $\text{H}^+$  different from zero requires the ionic entropies to be expressed in an 'absolute scale' and not in the 'conventional scale' [3].)

For the cell

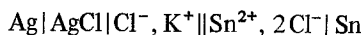


Table 3.

Species	$S_0^*$ or $\bar{S}_0^0$ (cal mol <sup>-1</sup> K <sup>-1</sup> )	$\bar{C}_{p_1}^*$ or $\bar{C}_{p_1}^0$ (cal mol <sup>-1</sup> )
AgCl	22.97	15.2
Sn	10.7	6.5
Ag	10.206	5.43
Cl <sup>-</sup>	18.17	-61.6
Sn <sup>2+</sup>	-15.9	+58.16

Table 4.

Species	$S_0^*$ or $\bar{S}_0^0$ (cal mol <sup>-1</sup> K <sup>-1</sup> )	$\bar{C}_{p_1}^*$ or $\bar{C}_{p_1}^0$ (cal mol <sup>-1</sup> )
Fe <sup>2+</sup>	-37.1	70.6
Fe <sup>3+</sup>	-85.1	98.82
Sn <sup>2+</sup>	-15.9	58.16
Sn	10.7	6.51

one obtains

$$\begin{aligned}
 (\Delta G^0)_1 - (\Delta G^0)_0 &= (T_1 - T_0)[-2S_0^*(\text{AgCl}) \\
 &\quad - S_0^*(\text{Sn}) + 2\bar{S}_0^0(\text{Cl}^-) + \bar{S}_0^0(\text{Sn}^{2+})] \\
 &\quad + 2S_0^*(\text{Ag}) + F(T_1)[2\bar{C}_{p_1}^*(\text{AgCl}) \\
 &\quad + \bar{C}_{p_1}^*(\text{Sn}) - 2\bar{C}_{p_1}(\text{Cl}^-) \\
 &\quad - \bar{C}_{p_1}^0(\text{Sn}^{2+}) - 2\bar{C}_{p_1}^*(\text{Ag})]
 \end{aligned}$$

Using the convenient values of entropies [4, 5] and coefficients the values shown in Table 3 are obtained (1 cal = 4.18 J). Thus

$$\begin{aligned}
 (\Delta G^0)_1 - (\Delta G^0)_2 &= -1105 - 692 \\
 &= -1797 \text{ cal mol}^{-1}
 \end{aligned}$$

and

$$E_1^0 - E_0^0 = 0.039 \text{ V.}$$

This value is in good agreement with the value obtained from polarographic data. For the tin-chromium cell, the thermodynamics of Cr(II) and Cr(III) are unknown. Nevertheless the temperature variation of the e.m.f. of the cell



very similar to Case's cell, may be calculated. The corresponding thermodynamic values are shown in Table 4. Using the difference

$$\begin{aligned}
 &(\Delta G^0)_1 - (\Delta G^0)_0 \\
 &= (T_1 - T_0)[-2\bar{S}_0^0(\text{Fe}^{2+}) - \bar{S}_0^0(\text{Sn}^{2+}) \\
 &\quad + 2\bar{S}_0^0(\text{Fe}^{3+}) + S_0^*(\text{Sn})] \\
 &\quad + F(T_1)[2\bar{C}_{p_1}^0(\text{Fe}^{3+}) + \bar{C}_{p_1}^0(\text{Sn}^{2+}) \\
 &\quad - 2\bar{C}_{p_1}^0(\text{Fe}^{2+}) - C_{p_1}^*(\text{Sn})] \\
 &= -8030 \text{ cal}
 \end{aligned}$$

and

$$E_0^1 - E_0^0 = 0.174 \text{ V}$$

The corresponding, and observed, difference for the Case cell is equal to about 0.105 V, and is of the same order of magnitude.

The differences  $(\Delta G^0)_1 - (\Delta G^0)_0$  are the sum of an entropic term and of an enthalpic term. The calculated values in the above examples are (1 cal = 4.18 J) shown in Table 5. The enthalpic term is about the same for the two cases, and about equal to the entropic term of the first cell. The e.m.f. shift of the second cell is then directly related to the contribution of its entropic term which depends strongly on the difference between the absolute ionic entropies  $\bar{S}_0^0(\text{Fe}^{3+}) - \bar{S}_0^0(\text{Fe}^{2+})$ . Now, the greater the ionic charge, the greater is the absolute ionic entropy. For instance, some absolute entropies are (in cal mol<sup>-1</sup> K<sup>-1</sup>): Gd<sup>3+</sup>, -60; Fe<sup>3+</sup>, -85.1; Al<sup>3+</sup>, -91; Fe<sup>2+</sup>, -37; Cu<sup>2+</sup>, -36.5; Cd<sup>2+</sup>, -25; H<sup>+</sup>, -5, etc. So the difference  $\bar{S}_0^0(\text{M}^{n+}) - \bar{S}_0^0[\text{M}^{(n-1)+}]$  increases with an increasing  $n$ . In addition, the effect is increased by the exchange of two electrons in the tin redox system leading to double the difference.

So, the reversal of the cell e.m.f. with temperature may be ascribed to a difference in the influence of temperature upon the two half-cells. This influence depends on the nature of the two

Table 5.

Cell	Entropic term	Enthalpic term
Ag AgCl K <sup>+</sup> , Cl <sup>-</sup>   Sn <sup>2+</sup> , 2Cl <sup>-</sup>  Sn	-1105 cal	-692 cal
Sn Sn <sup>2+</sup>   Fe <sup>3+</sup> , Fe <sup>2+</sup>  C	-7315 cal	-714 cal

redox couples involved, i.e., solid-solute and solute-solute. A galvanic cell will show a reversal of polarity with temperature if:

- (a) one of the redox couple is of the type  $M/M^{m+}$ , with  $m$  at least equal to 2;
- (b) the other one is of the type  $M^{n+}/M^{(n-1)+}$ , with  $n$  as high as possible;
- (c) their potentials are sufficiently close together to observe the change of sign.

These conditions are rather restrictive and it does not seem that other systems are likely to give larger values of e.m.f. Furthermore, the performance of this kind of cell is limited by the available temperature range and the stability of the solvent.

#### Acknowledgement

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