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Section de GéoChimie / LAT

POTENTIELS REDOX DES COUPLES PuO_2^{2+}/PuO_2^{+} ET Pu^{4+}/Pu^{3+} A FORCE IONIQUE ET TEMPERATURE VARIABLES. ENTROPIE ET CAPACITE CALORIFIQUE

par

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Sommaire - Les potentiels E(T,I), des couples réversibles du plutonium sont mesurés par voltampérométrie cyclique à force ionique et température variables (0,5 M < I < 3 M et 5°C < T < 65°C). Les résultats expérimentaux sont extrapolés à I = 0 par la Théorie de l'Interaction Spécifique (SIT) : on détermine ainsi le coefficient d'interaction spécifique, Δε(T), et E(T,0) qui à 25°C correspond au potentiel standard. A 25°C tous les potentiels des couples du plutonium sont voisins de 1 Volt. Il est alors très difficile de détecter expérimentalement une erreur systématique due à la dismutation ou à l'existence d'une impureté rédox. Ceci pourrait par conséquent, expliquer certaines des différences observées parmi les valeurs de potentiels déjà publiées. Une analyse critique de la bibliographie est menée pour finalement, recommander des valeurs pour ces potentiels réversibles. Les variations de ces derniers avec la température peuvent être considérées linéaires en première approximation, ce qui signifie que l'influence de la température sur l'entropie est faible. Cependant, la prise en compte de la capacité calorifique, modélise les résultats, E(T,I) = f(T), de façon plus satisfaisante. Des développements limités au deuxième ordre en (T-T°), sur ε(T)et sur le terme de Debye et Huckel, D(T) permettent de proposer des équations, rendant compte de l'influence de la force ionique et de la température sur G, S, Cp, H et lg K. Parmi ces équations, celle modélisant les variations avec I de ΔS, ΔCp, et ΔH sont testées au préalable sur les coefficients d'activité moyens des électrolytes HCl et NaCl, qui sont des valeurs publiées, puis sur les valeurs expérimentales de potentiels du plutonium. Enfin, les valeurs numériques des entropies déterminées par voie électrochimique ou calorimétrique sont comparées et discutées.

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"REDOX POTENTIALS OF PuO_2^{2+}/PuO_2^+ AND $Pu^{4+}/Pu"^{3+}$ AT DIFFERENT IONIC STRENGTHS AND TEMPERATURES; ENTROPY AND HEAT CAPACITY

Summary - The reversible redox potentials of the Plutonium couples are measured by using cyclic voltammetry, in perchloric media at ionic strengtht, I, from 0?5 M to 3 M, and temperature, T, from 5°C to 65°C. At each T, the experimental results, E(T,I), are extrapolated to I = 0 by applying the Specific Interaction Theory (S.I.T.) to get interaction coefficients, Δε(T), and E(T,0) (e.g. standard potentials when T = 25°C). At T = 25°C the numerical values of the potentials of all the Pu couples are nearly the same. It is then not easy to detect a systematic error due to disproportionation or redox impurity. This can explain some discrepancy on numerical values already published.

We finally propose "recommended values" of the reversible redox potentials. As a first approximation, the variations of these potentials seem to be quite linear versus temperature : entropy variation versus T is small. But taking into account heat capacity that is involved in the E(T,I) second order derivative, usually improves the fitting. A second order expansion of ε(T) and of the Debye Huckel term, D(T) are used to propose equations that account for simultaneous ionic strength and temperature influences on G, S, Cp, H, and lg K. These equations, in particular those modelling the ionic strength influence on ΔS, ΔCp, and ΔH are first checked for published mean activity coefficients of HCl and NaCl. Small discrepancy between the numerical values of entropy changes of actinides redox couples, deduced from electrochemical and calorimetric techniques are discussed.

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Avant - propos

Ce rapport comprend deux parties :

- la première correspond au texte (en anglais) d'une publication écrite par H. Capdevila et P. Vitorge dont le titre est " Redox potentials of PuO_2^{2+} /PuO_2^+ and Pu^{4+} /Pu^{3+} at different temperatures and ionic strengths. Entropy and heat capacity". Ces travaux ont fait l'objet de discussions avec Ingmar Grenthe (Suède) et seront soumis très prochainement à publication.

- la deuxième partie reproduit de façon synthétique les calculs qui ont permis d'aboutir aux résultats et conclusions de la publication.

Le travail présenté dans ce rapport a deux objectifs:

- premièrement de proposer des "valeurs définitives" pour les potentiels rédox des couples réversibles du plutonium qui présentent encore aujourd'hui quelques incohérences.

- deuxièmement, de valider sur des mesures expérimentales faites au laboratoire ou publiées par d'autres auteurs, des équations déjà établies permettant de prédire les variations de température et de force ionique sur un bon nombre de grandeur thermodynamiques, comme l'enthalpie libre, le potentiel rédox, la constante de stabilité, l'entropie, l'enthalpie, ou la capacité calorifique.

Les études présentées ici font donc référence à des mesures de potentiels rédox qui sont issues de la thèse de H. Capdevila (Rapport CEA R-5643). L'interprétation et les calculs théoriques font notamment appel a une publication antérieure de E. Giffaut, P. Vitorge et H. Capdevila, qui a fait l'objet d'une présentation au congrès "Actinides 93" (Septembre 93, Santa Fe USA) et qui est acceptée pour publication dans le "Journal of Alloys and Compounds".

Redox potentials of PuO_2^{2+}/PuO_2^+ and Pu^{4+}/Pu^{3+} at different ionic strengths and temperatures.
Entropy and heat capacity.

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Summary

The reversible redox potentials of the plutonium couples are measured by using cyclic voltammetry, in perchloric media at ionic strength, I, from 0.5 M to 3 M, and temperature, T, from 5°C to 65°C. At each T, the experimental results, E(T,I), are extrapolated to I=0 by applying Specific Interaction Theory (S.I.T.) to get interaction coefficients, $\Delta\varepsilon(T)$, and E(0,T) (e.g, standard potentials when T=25°C). At T=25°C the numerical values of the potentials of all the Pu couples are nearly the same. It is therefore not easy to detect a systematic error due to disproportionation or redox impurities. This can explain some discrepancies observed between numerical values already published. As a first approximation, the variations of the reversible redox potentials seem to be linear with temperature: the entropy variation versus T is small. But taking into account the heat capacity term that is involved in the second order temperature derivative, experimental data usually fit better to the following series expansion about T° :

$$E(T) = E(T°) + \frac{\Delta S(T°)}{F}(T-T°) + \frac{\Delta Cp(T°)}{2T°F}(T-T°)^2 + ...$$

$\Delta\varepsilon$ variations with T are found to be small. A second order expansion of ε and of the Debye Hückel term are used to propose extended S.I.T. equations that account for both the ionic strength and the temperature influences on G, S, Cp, H, and lg K. These equations, in particular those modelling the ionic strength influence on ΔS, ΔCp and ΔH are first checked using published mean activity coefficients of HCl and NaCl. In addition, activity coefficients in chloride media are needed to calculate the Ag-AgCl reference electrode potential, and then for redox equilibria of plutonium. All the following data are given versus NHE:

for the PuO_2^{2+}/PuO_2^+ couple $E° = 938 \pm 10$ mV $\Delta\varepsilon(T°) = -0.22 \pm 0.03$ kg.mol^{-1}
$(\frac{\partial\Delta\varepsilon}{\partial T})_p = 0.001$ kg(mol.K)$^{-1}$ $\frac{\Delta S°}{F} = 0.34 \pm 0.04$ mV.K^{-1} $\frac{\Delta Cp°}{F} = -4.04 \pm 0.9$ mV.K^{-1}
and for the Pu^{4+}/Pu^{3+} couple $E° = 1044 \pm 10$ mV $\Delta\varepsilon(T°) = -0.33 \pm 0.05$ kg.mol^{-1}
$(\frac{\partial\Delta\varepsilon}{\partial T})_p = -0.002$ kg(mol.K)$^{-1}$ $\frac{\Delta S°}{F} = 1.67 \pm 0.14$ mV.K^{-1} $\frac{\Delta Cp°}{F} = 1.77 \pm 3.20$ mV.K^{-1}

The small discrepancy between the numerical values of entropy changes deduced from electrochemical and calorimetric techniques are discussed for actinides redox couples.

Introduction

In order to assess the safety of radioactive waste disposal in geological formations, one needs to predict the migration of radioelements, especially actinides, in groundwaters. This migration depends on chemical speciation which can be deduced from complexation constants and redox potentials when local equilibrium is achieved. Plutonium is one of the important elements to consider because of its high toxicity and long half life.

The plutonium redox system, and particularly reversible couples, have already been investigated [1 to 8]. We have measured these potentials at various ionic strengths, and reviewed [8] them in a previous study. However, the survey of published Pu^{4+}/Pu^{3+} and PuO_2^{2+}/PuO_2^{+} redox potentials (at $HClO_4$= 1M and T = 25°C) display small discrepancies We suggest [9] that the Specific Interaction Theory (S.I.T.) [10,11] can be used to compare data determined in different media, and to extrapolate them to the standard state (I=0). We expect similar numerical values of the specific interaction coefficient, ε, for chemical analogs; however $\Delta\varepsilon$ of the Pu reversible couples, differs significantly from the corresponding U and Np values [8,12].

Temperature is another important parameter when recalculating standard state data to the conditions in ground and surface water systems. The temperature influence on the U, Np and Pu redox potentials can be either directly measured with electrochemical techniques or deduced from calorimetric measurements. There are very few studies [2, 5] where plutonium redox potentials have been measured at different temperatures, and none have investigated a large enough range to allow precise determination of $(\frac{\partial E}{\partial T})_P$.

Hence, we measure redox potentials of reversible redox systems of plutonium at different ionic strengths and temperatures. We have chosen cyclic voltammetry as a suitable experimental method, based on previous experiences with this technique on uranium and neptunium [8, 13]. The method works well even in carbonate media where the couples are not completely reversible [13]. The results produced agree with those from other experimental methods like polarography. We have previously tested this technique from 5°C to 60°C for Uranium [13]. Before discussing the temperature effects, we will consider the observed discrepancies between the numerical values of reversible redox potentials measured at 25°C to propose finally "recommended" values for the standard potentials.

Extrapolation to I = 0 of entropy and enthalpy data of chemical reactions in aqueous solution is not always clearly explained in thermodynamic data bases: often no theory is used to perform these corrections, only rough approximations which may result in large uncertainty in the deduced values. In a previous study [14], we proposed some equations, based on S.I.T. and series expansions as a function of T, to calculate from few experimental results (redox potential or equilibrium constant measurements), numerical values of the thermodynamic functions (G, E, H, S, Cp) as functions of temperature and ionic strength at constant pressure. Therefore we would like to verify the validity of these equations. Firstly, we shall test the methodology on published mean activity coefficients of the electrolytes HCl and NaCl [15]. These calculations are in any case required to compute the Ag-AgCl reference electrode potential that is published [16] at $I = 0$ from 0°C to 70°C, and only at $T = 25°C$ when $I \neq 0$. Finally, we shall apply this data treatment on our plutonium redox potentials to estimate entropies, heat capacities changes and their ionic strength dependence.

Notations

ln, lg : natural and decimal logarithms, respectively
z_i : charge of the ion i
Δz^2 $= z^2_{Red} - z^2_{Ox}$
a_i , m_i : activity and concentration of the ion i (mol/kg), respectively
γ_i : activity coefficient of the ion i, $\gamma_i = a_i/m_i$
[i] : concentration of the ion i (mol/l) = molarity
$\varepsilon(i,j)(T)$: value of the specific interaction coefficient between the ions i and j at T (kg/mol)
$\Delta\varepsilon(T)$ $= \varepsilon(Red, ClO_4^-) - \varepsilon(Ox, ClO_4^-)$
$D(T,I)$ $= \dfrac{a(T)\sqrt{I}}{1 + a_j b(T)\sqrt{I}}$: Debye Hückel term, a(T) and b(T) values versus T [11], we assume a_j to be independent of T and equal to $a_j = 1.5/b(25°C)$
I : ionic strength (mol/kg)
T : temperature ; $\Delta T = T - T°$ where $T°$ = standard temperature, $\Delta 1/T = 1/T - 1/T°$
F : Faraday number
R : molar gas constant
r : Rln(10)
$A(T)$ $= \dfrac{RT\ln(10)}{F}$
$X(T,I)$: numerical value of the function X at T and I, where X is E , G, H, S, Cp, lnK or D
$X°$: $X(T°,0)$ is the standard value of X
$X'(T,I)$:$(\frac{\partial X}{\partial T})_p(T,I)$ numerical value at I and T of the first derivative of the function X at constant pressure
$X''(T,I)$ $= (X')'(T,I)$
ΔZ $=(Z_{Red} + Z_{H^+} - 0.5\, Z_{H_2} - Z_{Ox})$ is Z changes for the equilibrium $Ox + 0.5\, H_2 \rightleftharpoons Red + H^+$, Z is G, S, H or Cp.
$°H^+$, $°H_2$: We use these notations when these species are in the NHE conditions, *i.e.*, $a_{H^+} = \gamma_{H^+} = 1, P_{H_2} = 1$ atm, $\Delta_f G°_{(H^+ \text{ or } H_2)} = \Delta_f H°_{(H^+ \text{ or } H_2)} = S°_{H^+} = 0$ and $S°_{H_2} = 13.680$ J K^{-1} mol^{-1} [11]
$\Delta_f G°$, $\Delta_f H°$: standard Gibbs energy and enthalpy of formation
$S°$: standard molar entropy

Method

Ionic strength Influence on Redox Potential (S.I.T.)

According to the Nernst equation, it is possible to write the emf of the cell corresponding to the redox reaction:

$$\mathrm{Ox} + {}^{\circ}\mathrm{H_2} \rightarrow \mathrm{Red} + {}^{\circ}\mathrm{H^+}$$

$$E = E^{\circ} + A(T)\,\lg\frac{a_{Ox}}{a_{Red}} = E^{\circ} + A(T)\,\lg\frac{\gamma_{Ox}\, m_{Ox}}{\gamma_{Red}\, m_{Red}} \qquad (1)$$

where E° is the standard potential of the redox couple Ox/Red, a, γ, and m the activity, the activity coefficient and the molality of the oxidant (Ox) or the reducer (Red). We apply this equation for the redox reaction studied (reversible plutonium couples) and also for the redox reaction of our experimental reference electrode $Ag\downarrow, Cl^-/AgCl\downarrow$ (in this case $a_{red} = a_{ag\downarrow} * a_{Cl^-}$):

$$\mathrm{AgCl}\downarrow + {}^{\circ}\mathrm{H_2} \rightarrow \mathrm{Ag}\downarrow + \mathrm{Cl^-} + {}^{\circ}\mathrm{H^+}$$

The half wave potential, $E_{1/2}$, measured by cyclic voltammetry (the difference between the oxidation and reduction peaks divided by 2), is a good approximation of E, Eq.(1), when $m_{Ox} = m_{Red}$ [17]: this assumes that the diffusion coefficients of Ox and Red are the same. This approximation induces an error of about 0,5 mV (resp. 2mV) for PuO_2^{2+}/PuO_2^{+} (resp. Pu^{4+}/Pu^{3+}) system [12], which is well within our experimental uncertainty.

We use solutions of high ionic strength to perform accurate potential measurements. In order to compare our results, determined in perchlorate media at different ionic strengths with literature (see *Experimental Section*) we have to extrapolate them to the standard state, I = 0. According to the S.I.T. [11], the activity coefficient of a cation i, in a perchlorate medium is:

$$\lg\gamma_i = -z_i^2 D + \varepsilon(i, ClO_4^-)\, m_{ClO_4^-} \qquad (2)$$

Substituting for γ_i from Eq.(2) into Eq.(1) and taking into account the experimental conditions ($m_{Ox} = m_{Red}$ for plutonium redox couple and $a_{Ag\downarrow} = a_{AgCl\downarrow} = 1$ for the reference) gives :

$$E_{Ox/Red}(T,I) = E_{Ox/Red}(T,0) + A(T)\,[\Delta z^2 D(T,I) - \Delta\varepsilon(T)\, m_{ClO_4^-}] \qquad (3)$$

$$E_{Ref}(T,I) = E_{Ag/AgCl}(T,0) - A(T)\,[\lg m_{Cl^-} - D(T,I) + \mathcal{E}\,m] \qquad (4)$$

where $\Delta\varepsilon = \varepsilon(Red, ClO_4^-) - \varepsilon(Ox, ClO_4^-)$, $\Delta z^2 = z^2_{Red} - z^2_{Ox}$

$\mathcal{E}\,m = \varepsilon(Na^+,Cl^-)\, m_{Na^+}$ when measuring PuO_2^{2+}/PuO_2^{+} potential

or $\mathcal{E}\,m = \varepsilon(Na^+,Cl^-)\, m_{Na^+} + \varepsilon(H^+,Cl^-)\, m_{H^+}$ when measuring Pu^{4+}/Pu^{3+} potential

By subtracting Eq.(4) from Eq.(3), one obtains the expression of the potential of the Ox/Red couple versus Ag-AgCl, *i.e.*, the value directly measured, $E_{1/2}(T,I)$. From measured $E_{1/2}(T,I)$, tabulated $E_{Ag/AgCl}(T,0)$ vs NHE [16], and Eq.(4), we calculate the Ox/Red potential versus NHE,

$$E_{Ox/Red}(T,I) = E_{1/2}(T,I) + E_{Ref}(T,I) \qquad (5)$$

Based on Eq.(3), the plot of $Y(T,I) = \frac{E_{Ox/Red}(T,I)}{A(T)} - \Delta z^2\, D(T,I)$ (where $\Delta z^2 = -3$ for PuO_2^{2+}/PuO_2^{+} or -7 for Pu^{4+}/Pu^{3+}) versus $m_{ClO_4^-}$ is a straight line whose slope is $-\Delta\varepsilon(T)$, and intercept at I=0 is $Y(T,0) = \frac{E_{Ox/Red}(T,0)}{A(T)}$. We use the same data treatment at each temperature. For I corrections, all calculations are performed in molal unit.

Ag/AgCl Potential

We calculate the potential of the Ag/AgCl reference electrode, $E_{Ref}(T,I)$, using Eq.(4) for each experimental condition. $E_{Ag/AgCl}(T,0)$ [16] is tabulated using the old definition of the standard state, *i.e.*, standard pressure = 1atm instead of 1bar. We do not subtract from the tabulated $E_{Ag/AgCl}(T,0)$ *(or from our results) the 0.169 mV correction corresponding to the* change for 1 atm to 1bar, [11, 17] because this figure is much smaller than our experimental uncertainty. The interaction coefficients, $\varepsilon(Na^+,Cl^-)$ and $\varepsilon(H^+,Cl^-)$, are only published at 25°C [11]. From published mean activity coefficients $\gamma_\pm$ [15] measured by Robinson et al. from 0°C to 60°C and from 0.0001 for HCl (resp. 0.1 for NaCl) to 4 mol/kg, we calculate the interaction coefficient of both electrolytes, using the S.I.T. equation simplified for 1:1 electrolyte :

$$\lg\gamma_\pm(T,I) = - D(T,I) + \varepsilon(T)\, I \qquad (6)$$

A linear regression of $[\lg\gamma_\pm(T,I) + D(T,I)]$ versus I, leads to $\varepsilon(T)$ as the slope of the line. This treatment is performed at each experimental temperature for HCl and NaCl. We find that the variations of these $\varepsilon(T)$ are small and quite linear in this temperature range and at atmospheric pressure. But to be consistent with the second order Taylor's expansion, that we used to model the temperature influence on G and to estimate Cp, we prefer to calculate $E_{Ref}(T,I)$ (Eq.4) using smoothed values of $\varepsilon(T)$ deduced from quadratic regression Eqs. (7) and (8). However we verified that a calculation based on a linear regression could be accurate enough and the difference between the two sets of $E_{Ref}(T,I)$ results is less than 0,5 mV.

$$\varepsilon(Na^+,Cl^-) = 0.034 + 3.7\ 10^{-4}\,\Delta T - 6.2\ 10^{-6}\,\Delta T^2 \qquad (7)$$

$$\varepsilon(H^+,Cl^-)(T) = 0.122 - 5.4\ 10^{-4}\,\Delta T - 2.1\ 10^{-6}\,\Delta T^2 \qquad (8)$$

The values of $\varepsilon(25°C)$ calculated here agree fairly well with those usually tabulated at 25°C (0.12 ± 0.01 for $\varepsilon(H^+,Cl^-)$ respectively 0.03 ± 0.01 for $\varepsilon(Na^+,Cl^-)$) [11].

To calculate $E_{Ref}(T,I)$, we also need $E_{Ag/AgCl}(T,0)$. The variations of $E_{Ag/AgCl}(T,0)$ are given [16] as a polynomial function of temperature. These results [16], are based on the original measurements [18] of the electromotive force, ΔE, of the following cell:

Pt; H_2(g, 1atm), HCl (m), AgCl; Ag

which can be written according to Eq.(9) if we assume that H_2 is an ideal gas.

$$\Delta E = E_{Ag/AgCl}(T,0) + RT/F\ [\ \ln(\gamma\, m)_{Cl^-} + \ln(\gamma\, m)_{H^+}] \qquad (9)$$

The difference between ΔE and $E_{Ag/AgCl}(T,0)$, is that the first one is measured against a real hydrogen electrode and the second one is calculated against the NHE. In [18], the author used a Debye Hückel equation in extended form to model the activity coefficient versus m. They performed a linear regression of $[\Delta E - f(m)]$ versus m, and then deduced $E_{Ag/AgCl}(T,0)$ as the intercept at m = 0. This treatment is done at each T. The authors did not use the S.I.T. like us to model ionic strength influence on potential measurements, nevertheless we use their values.

Temperature Influence

We have proposed some formulae [14] to predict the temperature influence on the thermodynamic functions directly measured in solution chemistry such as Gibbs energy, G, stability constant, K and formal redox potential, E. We have expanded G(T), into series as a function of T Eq.(10), using Eqs.(11) and (12), to introduce entropy, S, and heat capacity, Cp in the successive derivatives:

$$G(T,I) = G(T^\circ,I) - S(T^\circ,I)\,\Delta T - C_p(T^\circ,I)\frac{\Delta T^2}{2T^\circ} + \left(\frac{C_p(T^\circ,I)}{T^\circ} - C'_p(T^\circ,I)\right)\frac{\Delta T^3}{6T^\circ} + \ldots \qquad (10)$$

$$G'(T,I) = \left(\frac{\partial G}{\partial T}\right)_p(T,I) = -S(T,I) \qquad (11)$$

$$S'(T,I) = \left(\frac{\partial S}{\partial T}\right)_p(T,I) = \frac{C_p}{T}(T,I) \qquad (12)$$

Expression (10) is valid at each ionic strength, I. The entropy is the first order temperature correction of -G and the heat capacity is involved in the second order term. From Eq.(10) and

$$\Delta G\,(T,I) = -n\,F\,E(T,I) \qquad (13)$$

we easily deduce a similar formula for E. E°, ΔG°, ΔH° and S° are tabulated using the NHE convention, so they account for the following redox reaction:

$$\mathrm{Ox} + 0.5\ {}^\circ H_2 \rightarrow \mathrm{Red} + {}^\circ H^+$$

where $^\circ H_2$ and $^\circ H^+$ are in NHE conditions. Applying this convention, the Gibbs energy, enthalpy and entropy changes of this hypothetical reaction are

$$\Delta G^\circ = \Delta_f G^\circ(\mathrm{Red}) - \Delta_f G^\circ(\mathrm{Ox})$$

$$\Delta H^\circ = \Delta_f H^\circ(\mathrm{Red}) - \Delta_f H^\circ(\mathrm{Ox})$$

$$\Delta S^\circ = S^\circ(\mathrm{Red}) - S^\circ(\mathrm{Ox}) + 0.5\,S^\circ(H_2) \quad (S^\circ(H^+) = 0 \text{ is a convention})$$

We compute both $\Delta S(T^\circ,I)$ and $\Delta C_p(T^\circ,I)$ by fitting the experimental values of $E_{Ox/Red}(T,I)$, to a second order polynomial versus temperature. In this work, we will always neglect the third order term and higher ones in Eq.(10), since we will see later that they do not improve the regression: the accuracy of the measurements is not high enough here, for the determination of the first derivative of the heat capacity.

We have also proposed an equation [14] where lnK is expanded into a series as a function of 1/T. Vant' Hoff's relation (15), shows that the enthalpy is the first term of (-RlnK) (14):

$$R\ln K(T,I) = R\ln K(T^\circ,I) - \Delta H(T^\circ,I)\,\Delta\frac{1}{T} + \frac{T^{\circ 2}\,\Delta C_p(T^\circ,I)}{2}\,\Delta\left(\frac{1}{T}\right)^2 - T^{\circ 3}\left(\frac{T^\circ\Delta C_p'(T^\circ,I) + 2\,\Delta C_p(T^\circ,I)}{6}\right)\Delta\left(\frac{1}{T}\right)^3 + \ldots \qquad (14)$$

$$R\left(\frac{\partial \ln K}{\partial 1/T}\right)_p (T,I) = -\Delta H(T,I) \qquad (15)$$

Therefore, there are two ways to determine $\Delta H(T^\circ,I)$. From experimental results of redox potentials we can deduce, $\Delta G(T,I)$ Eq.(13), fit $\Delta S(T^\circ,I)$ Eq.(10) and then calculate $\Delta H\,(T^\circ,I)$ using the classical thermodynamic relation (17). But we can also, from the same experimental results E(T,I), deduce lnK(T,I) Eqs.(13) and (16), and fit it directly using Eq.(14).

$$\Delta G(T,I) = -RT\ln K(T,I) \qquad (16)$$

$$= \Delta H\,(T,I) - T\,\Delta S(T,I) \qquad (17)$$

We will verify that both approaches give the same numerical results.

Ionic Strength and Temperature Influences

We have also proposed [14] various extended S.I.T. equations, to model the simultaneous influence of ionic strength and temperature on thermodynamic functions. Here we do not specify the steps of these developments. We only want to recall that the relations are based on series expansions around the standard temperature T° (e.g., Eq.(10) for G) and the Specific Interaction Theory Eq.(2). Among these equations, we here use Eqs.(18) to (20), that are extended S.I.T. equations, for ΔH, ΔS and ΔCp at T°.

$$\Delta H(T^\circ,I) = \Delta H^\circ + r\, T^{\circ 2}(\Delta z^2\, D'(T^\circ,I) - m\, \Delta\varepsilon'(T^\circ)) \quad (18)$$

$$\Delta S(T^\circ,I) = \Delta S^\circ + r\, (\Delta z^2\, (D(T^\circ,I) + T^\circ\, D'(T^\circ,I)) - m\, (\Delta\varepsilon(T^\circ) + T^\circ\, \Delta\varepsilon'(T^\circ)) \quad (19)$$

$$\Delta Cp(T^\circ,I) = \Delta Cp^\circ + r\, T^\circ(\Delta z^2\, (2D'(T^\circ,I) + T^\circ\, D''(T^\circ,I)) - m(2\Delta\varepsilon'(T^\circ) + T^\circ\, \Delta\varepsilon''(T^\circ)) \quad (20)$$

In the previous equations, ε and D derivatives come from thermodynamic relations, *i.e.*, H, S and Cp definitions, and not from Taylor's expansions. Note that if the variations of activity coefficients with T are neglected, G and S would still be I dependent, but H and Cp would not.

Experimental Section

A precise description of our experimental setup is already published [8,13,20]. We use a classical 3 electrode device. The working and counter electrodes are platinum wires. The silver-silver chloride reference electrode is put into a solution where m_{Cl^-} is fixed by adding NaCl to a perchlorate solution of known ionic strength: we then calculate its potential according to Eqs.(4) (7) and (8).

To study the Pu^{4+}/Pu^{3+} couple we start with a pure Pu^{3+} solution in different perchlorate media ($HClO_4$, $NaClO_4$) where $[H^+] = 1M$, $[ClO_4^-] = 1$, 2 or 3 M. We never study this couple at $[HClO_4] < 1M$ to avoid Pu^{4+} hydrolysis and disproportionation [19,20]. For these measurements, we also add NaCl in the working solution ($m_{Cl^-} = 0.02$ mol/kg), in order to use a junction free cell with a reference Ag-AgCl electrode. With this methodology, there is no junction potential. The temperature is regulated with a Haake F3 and controlled by a thermometer plunged into the solution. We record the voltammogram from E = 300 mV to E = 900 mV against Ag-AgCl and at different temperatures from 5°C to 70°C. We increase and decrease temperature by step of 5°C, waiting around 15 minutes between two measurements.

To study PuO_2^{2+}/PuO_2^+ couple we use a pure PuO_2^{2+} working solution. This solution is prepared by introducing a known quantity of the $PuO_2(CO_3)_3^{4-}$ stock solution in the studied perchlorate medium ($HClO_4$+ $NaClO_4$ where $[HClO_4] = 0.5$ or $[H^+] = 1M$, $[ClO_4^-] = 1$, 2 or 3 M). These conditions are too oxidant for the reference electrode, and we therefore have to put it into a separate compartment, filled with a ($NaClO_4$, NaCl) solution, of the same ionic strength as the working solution one, and where $m_{Cl^-} = 0.02$ mol/kg. We measure the junction potential for each ionic strength and verify that it is constant in the temperature range studied. Voltammograms are recorded for $0.5\ M \leq I \leq 3\ M$ and $5°C \leq T \leq 70°C$ from E = 800 to E = 200mV/Ag-AgCl and the temperature cycle carried out as for Pu^{4+}/Pu^{3+}.

Results

Interference, Potentials at 25°C

At 20°C we observe a classical recording for the PuO_2^{2+}/PuO_2^+ reversible couple. But sometimes, we notice a change in the shape of the voltammogram when increasing the temperature (Fig.1). From T = 25°C the oxidation wave becomes broader, and at 40°C it splits into two peaks. When we use freshly prepared PuO_2^{2+} solution this deformation does not appear at any temperature; we never see the second peak. Hence, we attribute the first peak at about 650 mV/Ag-AgCl, to the oxidation of PuO_2^+ into PuO_2^{2+} and the second one, to the oxidation of Pu^{3+} to Pu^{4+}. We shall now explain why we state this hypothesis and which experiments are performed to verify it.

The numerical values of the two reversible redox potentials at 25°C (Tab.1 and 2) are very close (106 mV difference at I = 0 and around 70 mV at classical experimental conditions). On the other hand, this difference increases with temperature (see below). This proves that the interference between the two couples is much more difficult to detect at low temperature. Furthermore in a PuO_2^{2+} perchloric solution, Pu^{3+} might be produced by radiolytic autoreduction. To test the assumption that the second peak is due to a Pu^{3+} impurity we increase $[Pu^{3+}]$ by reducing a part of the working solution, and we measure the concentrations by spectrophotometry. A voltammogram of this mixed solution shows an increase of the second peak. This can therefore explain a systematic error that results in an overestimation of PuO_2^{2+}/PuO_2^+ redox potential determination by a few tens of a mV. To avoid it, *i.e.*, the reduction to Pu^{3+} in our PuO_2^{2+} test solution, we prepare for almost each $E(PuO_2^{2+}/PuO_2^+)$ measurement, a fresh PuO_2^{2+} solution from the Pu(VI) carbonate stock solution and we check the purity of the acidic solution by spectrophotometry.

When measuring $E(Pu^{4+}/Pu^{3+})$, a similar interference could result in an underestimation of the potential, due to a PuO_2^{2+} impurity. We therefore start with a pure Pu^{3+} solution and not a Pu^{4+} one, since Pu^{4+} disproportionates slowly and partially in $HClO_4$ 1M [20].

Our results (Tab.1 and 2) are compared (Tab.3) with published ones in the *Discussion Section.*

Extrapolation of Redox Potentials to I=0

We use the S.I.T. equation, Eq.(3), at each T to extrapolate the experimental results $E_{Ox/Red}(T,I)$ to I = 0. The variation of $[\frac{E_{Ox/Red}(T,I)}{A(T)} - \Delta z^2 D(T,I)]$ versus $m_{ClO_4^-}$ is quite linear (Fig.2) and allow the determination of $E_{Ox/Red}(0,T)$ and the specific interaction coefficient, $\Delta\varepsilon(T)$ with rather good accuracy (Tab.1). We employ the linear form of the S.I.T. equation (Fig.2b) to fit the parameters, while Eq.(3) also accounts for the important variation of redox potential at low ionic strength (Fig.2a). The variations of E with T (Fig.3) are I dependent: I corrections on ΔS are then needed. The variations of $\Delta\varepsilon(T)$ are small and quite linear in our T conditions (Fig.4) and a second order polynomial regression versus T does not improve significantly the curve fitting of $\varepsilon = f(T)$. But we will see later that $\Delta\varepsilon''(T°)$ seems to be required for further calculations. Therefore we could fit $\Delta\varepsilon'(T^\circ)$ by using a linear regression, but for consistency with E(T,I) expansion we fit both $\Delta\varepsilon'(T^\circ)$ and $\Delta\varepsilon''(T^\circ)$ with a second order polynomial function. We employ the same treatment for the Debye Hückel term, D(T,I), whose numerical values are calculated at each I and T using its analytical expression, tabulated numerical values of a(T) and b(T) [11] and setting a_j to 1.5/b(25°C) for each ion and each temperature. However, in the *Discussion Section* we will compare the results of this data treatment and those we obtained assuming linear variations for $\Delta\varepsilon(T)$ and D(T).

Determination of Entropies, Heat Capacities and Enthalpies

We plot $E_{Ox/Red}(T,I)$ (Tab.1) versus T at each I, for the two reversible plutonium couples. Then we test Taylor's series expansion of different degrees, Eq.(10). We compare in Fig.3, linear and quadratic regressions on PuO_2^{2+}/PuO_2^{+} potentials measured at I = 3M and extrapolated to I = 0. A linear regression assumes that ΔS is constant, while a second degree polynomial regression takes into account ΔCp, *i.e.*, ΔS variations versus T Eq.(12). $E_{Ox/Red}(T,I)$ variations versus T are small but we can see (Fig.3) that experimental data fit better on a parabola than on a straight line. We have verified that the standard deviation is lower when using a second power function but that a third order function does not improve the curve fitting. Therefore, we will use only a second order regression, which determine the two fitted parameters $\Delta S(T^\circ,I)$ and $\Delta Cp(T^\circ,I)$ at each ionic strength I (Tab.2). We also fit $\Delta H(T^\circ,I)$ using Eq.(14) or calculate it according to Eq.(17). We have verified that the two ways to determine *the numerical values of $\Delta H(T^\circ,I)$, (see Method) are consistent* within our experimental uncertainties.

We have also performed the same treatment on published HCl and NaCl mean activity coefficients, $\gamma_\pm$ [15]. We apply Eq.(10) on excess Gibbs energy, ΔG^{ex}:

$$\Delta G^{ex} = RT\ln\gamma_\pm \tag{21}$$

where

$$X^{ex}(T,I) = X(T,I) - X(T^\circ,0) \tag{22}$$

and calculate in the same way $\Delta S^{ex}(T^\circ,I)$ and $\Delta C_p^{ex}(T^\circ,I)$.

Ionic Strength Influence on $\Delta S(T^\circ,I)$, $\Delta Cp(T^\circ,I)$ and $\Delta H(T^\circ,I)$

When comparing numerical values (Tab.5) of $\Delta S(T^\circ,I)$ fitted according to a second order polynomial function, we notice that $\Delta S(T^\circ,I)$ varies as a function of I. This is even more clear in Fig. 3, when comparing the slope (*i.e.*, entropy mean value when assuming $\Delta Cp = 0$) of the two straight lines. Inversely, the ionic strength influence on $\Delta Cp(T^\circ,I)$ does not seem to be very accurate and not clearly identified in Fig.3. Let us test Eqs.(18) to (20) for the prediction of ΔS, ΔCp and ΔH variations versus I.

In order to test these equations, we first focus on HCl and NaCl mean activity coefficient data. Note that Eqs.(18) to (20) written for excess functions are simpler: the standard numerical values ΔX° disappear and we only have the I and T terms. We plot versus I, $\Delta S^{ex}(T^\circ,I)$ and

$\Delta Cp^{ex}(T^\circ,I)$ previously fitted, and draw the curves using Eqs.(19) and (20). In Fig. 5 we compare a model taking into account $\varepsilon''(T^\circ,I)$ and $D''(T^\circ,I)$ (Model 2) and another one (Model 1) where these second derivatives are disregarded and the values at T° of the first derivatives are deduced from linear regressions. Numerical values fit better with Model 2 especially for $\Delta Cp^{ex}(T^\circ,I)$ (Fig. 5b) even though both Debye Hückel term and specific interaction coefficient variations seem to be linear (Fig.4): the $D''(T^\circ,I)$ contribution is more important at low ionic strength, and the $\varepsilon''(T^\circ,I)$ one at high I. Model 2 is also needed to model the ionic strength influence on entropy but only for values higher than 2 mol/kg (Fig. 5a).

For the plutonium redox couples the results are quite similar (Fig.6a and b) but here the difference between the two models is not so important. In the HCl and NaCl cases we have calculated and represented the excess functions, *i.e.*, only the terms depending on I. For plutonium these terms are only T corrections on small I corrections. So their relative importance is lower. We have also tested Eq.18 (Fig.6c).

Discussion

Formal and standard potentials

We have decided to measure reversible redox potentials of plutonium because of the discrepancy between the numerical values available in literature (Tab.3). We have chosen cyclic voltammetry technique to perform these measurements. We have previously validated this experimental method, on uranium system [13]: we found agreement with the values recommended by the NEA - OECD Thermodynamics Data Base, and even for couples not completely reversible, *i.e.*, $AnO_2(CO_3)_3^{4-}/AnO_2(CO_3)_3^{5-}$ (An = U or Pu) [12,13,20]. Our values are in accordance with some of those reported in literature for each plutonium system. We shall now describe, and justify why we reject the other results.

PuO_2^{2+}/PuO_2^{+} couple

We determine PuO_2^{2+}/PuO_2^{+} potentials (Tab.3 and Fig.2a) in agreement with the value reported in [5] at I = 1 M, but lower by up to 30 mV than all the other published values [1, 4, 8]. At I = 0 our value agrees with [7, 8] within the 10 or 25 mV uncertainty, but it is still the smallest published one. For Kraus's determination [1] the junction potential was included in the arbitrary uncertainty proposed by the author. Connick et al. [4] have not directly measured the PuO_2^{2+}/PuO_2^{+} potential; they calculated it from Pu^{4+}/Pu^{3+} potential determination [3] and Kasha's [21] determination of Pu^{4+} disproportionation corrected for Pu^{4+} hydrolysis. We think that Kasha's measurements are not very accurate because of the spectrophotometer performance, the reference spectra used to calculate the concentration of each species, and also because of the discrepancy found between his determinations performed at two different acidities. The uncertainty evaluated by Connick seems, therefore, too small; we estimate the precision of the disproportionation constant to be 0.5 (lg unit), as in our similar experiment [20]. Hence, the uncertainty is about 30 mV for the corresponding PuO_2^{2+}/PuO_2^{+} value. The value reported in [7] is not very precise and this is only due to the solubility technique employed by the author. In literature, typically in [8], all measurements have been performed only at one temperature, 25°C or 20°C. As we explained before (*see Section Results*), at these temperatures, it is difficult to detect pollution of the PuO_2^{2+} working solution with Pu^{3+}, which can induce an overestimation of the potential of PuO_2^{2+}/PuO_2^+. This systematic error (*see Section Results*) agrees with the sign of the observed difference between the results reported in [8] and those in present work. Furthermore we can suspect pollution in our previous work [8], since the plutonium redox composition of the solution was not checked at the end of the experiments. This systematic error can occur only for plutonium whose redox potentials of the two reversible couples are quite close to one another. For uranium and neptunium, redox impurity would not induce this type of error. We think that Rabideau's determination [5] is correct. In this work, the redox potential of a PuO_2^{2+} solution, reduced step by step either with I^- or Pu^{3+}, has been measured. The author considered the junction potential problem, verified the concentration of each redox species of plutonium by spectrophotometry, even though PuO_2^+ one could not be measured with good accuracy, and was also aware of the possible reduction due to radiolysis. Furthermore, his two determinations performed with the same methodology but with two different reductants, are in very good agreement.

Pu^{4+}/Pu^{3+} couple

We find a value of the Pu^{4+}/Pu^{3+} redox potential (Tab.3 and Fig.2b) in agreement with the one reported in [2,3] at 1 M within a 5 mV uncertainty, but higher by 12 mV than our previous determination [8]. Our extrapolation to $I = 0$ is also higher than previous ones [6, 8]. Schwabe et al [6] have calculated the standard potential from a measurement performed at $I = 0.1$ M. The ionic strength correction is not clearly explained and furthermore these experimental results are probably affected by Pu^{4+} hydrolysis. The uncertainty evaluated by the author is probably too low. For all these reasons we do not take this value into account. We can explain the too low value in our previous determination [8] from the experimental method used to prepare Pu^{3+}: Pu^{3+} was obtained by electroreduction of the initial PuO_2^{2+} solution for twelve hours and some PuO_2^{2+} might have remained in the working solution. This is the same kind of redox pollution error, as mentioned before. In this case the PuO_2^{2+} involved in the PuO_2^{2+}/PuO_2^+ system, whose potential is lower than the Pu^{4+}/Pu^{3+} one, results in an underestimation of the Pu^{4+}/Pu^{3+} redox potential.

Interaction coefficients

Our plutonium interaction coefficients $\Delta\varepsilon(25°C)$ are in agreement with the values previously published for similar uranium and neptunium redox couples (Tab.4). We have found before, that the variations of $\Delta\varepsilon$ versus T are small. Anyhow, we calculate the difference between the numerical values at 25°C and 20°C to compare correctly these data for plutonium. The systematic error in the potential measurements, which we have discussed before, might not be constant with ionic strength. It is strongly dependent on radiolysis, whose effects increase with I. Therefore, this could induce an error in the interaction coefficient determination. This is probably the origin of the discrepancy between the two plutonium Δε determinations (Tab.4) and the reason why we reject the previous one [8]. Finally Δε for AnO_2^{2+}/AnO_2^+ or An^{4+}/An^{3+} have the same value for An = U, Np and Pu.

ΔH, ΔS, ΔCp and their ionic strength influence

In a previous work [13], where we focused on the uranium system, we observed that the variations of the U^{4+}/U^{3+} potential versus T was more important than the UO_2^{2+}/UO_2^+ system; according to the present study the behavior of plutonium is similar.

There is no theory commonly applied to take into account ΔH and ΔS variation with I. In data bases, it is usually not clear how ΔH and ΔS experimental data were extrapolated to I=0 and whether the calculations are consistent or not. The treatment of our experiments gives the variation of E (or ΔG) versus T, and furthermore the ΔH and ΔS variations versus I. Here we verify that the formulae we proposed [14] are valid within the classical uncertainties found in solution chemical experiments. In the *Results* section, we always expand the functions (E, ε and D) up to the second order and show examples where these terms improve clearly the fitting. But, sometimes the treatment can be simplified. The Pu^{4+}/Pu^{3+} entropy change is much more important than for PuO_2^{2+}/PuO_2^+. Consequently the heat capacity change of Pu^{4+}/Pu^{3+} have less relative importance and a linear regression fits correctly E(T,I) results: the numerical values of ΔS, determined by either first or second order polynomial regressions versus T on E(T,I), are consistent. In Eq.(20) the second derivatives ε" and D" are only needed when one wants to model Cp. This is clear in Fig.5b for NaCl, but the difference between the two models is much less obvious in HCl case. Therefore, by using linear regressions we often determine ε' and D' with enough accuracy to model S correctly Eq.19. In the same way, ε" is not very useful in calculating the redox potential of Ag/AgCl reference electrode when using Eq.(4).

Comparison of ΔS and ΔCp with literature

In order to compare our ΔS determinations for redox processes, and the numerical value calculated using the individual entropies of metal or ionic species, we shall first focus on the Ag/AgCl system. The redox reaction involved is:

$$AgCl\downarrow + 0.5\ {}^{\circ}H_2 \rightarrow Ag\downarrow + Cl^- + {}^{\circ}H^+ \qquad (23)$$

and the corresponding standard entropy change:

$$\Delta S^\circ = S^\circ_{Ag} + S^\circ_{Cl^-} - S^\circ_{AgCl} - 0.5\, S^\circ_{H_2} \quad (S^\circ_{H^+} = 0 \text{ by convention}) \qquad (24)$$

We calculate this sum ($\Delta S^\circ = -62.4 \pm 0.35$ J mol^{-1} K^{-1}) using the standard entropies selected in the TDB [11] that agree fairly well with the ones tabulated by Bard *et al.* [16]. We also perform a second order regression polynomial of $E_{Ag/AgCl}(T,0) = f(T)$ [16] and we then estimate $\Delta S^\circ/F = -0.67$ mV K^{-1}, *i.e.*, $\Delta S^\circ = -64.6 \pm 0.1$ J K^{-1}. These two values are very close and this seems to be proof that the study of the temperature influence on the potential and the use of a series expansion about T° to model this influence, is also a way to measure entropy.

In Table 5 we report the plutonium entropy determinations of the present work and we also add the values of uranium, deduced from a previous work [13]. We treat the potential measurements of uranium with the methodology presented here, and we do not use our previous entropy determination [13] where we disregarded its T dependence. We compare now our numerical values with those already published, deduced from calorimetric measurements and calculations using thermodynamic cycles (Tab.5). These values show up some discrepancy. We think that this might be due to the methodology used to extrapolate calorimetric data to I=0. The calculations on thermodynamic cycles [11,22] (typically the determination of entropy) are performed with data (Gibb's energy and enthalpy) obtained from different works and measured in different media. But the theory of extrapolation to I = 0 is not clearly explained. Furthermore, when standard values are not available in literature, it is often assumed that $\Delta X(25°C,0) = \Delta X(25°C,1M)$ (typically on ΔH calorimetric measurements). Fig.6c shows that the influence of ionic strength on enthalpy is not negligible. When disregarding it, one makes a rough approximation, and this can induce significant error in the entropy result. We have reported in Tab.5, the values of the entropies that we have determined at different I, to point out the importance of these variations.

We also compare our determinations of the entropies with previous published values deduced from potential measurements. Rabideau et al. [5] have measured PuO_2^{2+}/PuO_2^+ redox potential at I = 1M and 6, 15 and 25°C. They deduced from these results a value of the entropy changes $\Delta S = -5.9$ cal K^{-1}, *i.e.*, $\Delta S/F = -0.26$ mV K^{-1}. This value, and above all its sign, are surprising. For this system the entropy change is very small and the temperature range investigated in this publication is perhaps too small to give an accurate result. Anyhow the author gives very little information about the measurements performed at low temperature and on the attainment of the equilibrium. Connick et al. [2] have determined the entropy change of the Pu^{4+}/Pu^{3+} redox reaction from potential measurements at I = 1M. They deduced first the enthalpy change and then $\Delta S/F = 1.33$ mV K^{-1}. If we assigned a reasonable uncertainty of about 0.1 mVK^{-1}, this determination agrees with our results. Based on this value, on the measurement of the heat of oxidation of Pu^{3+} to PuO_2^{2+} by Ce(IV) [23], and the estimated values of the entropy of Pu^{3+} [24,25] and PuO_2^+ [24], Connick [4] has also calculated $\Delta S/F = 0.69$ mVK^{-1} for the PuO_2^{2+}/PuO_2^+ redox system. This value does not agree with our result but it is not a direct measurement and it depends on several more or less accurate approximations.

We have also verified that our method of determining ΔS and ΔCp, *i.e.*, a second order expansion on redox potentials Eq.(10), yields similar results to those obtained with another method often used in literature and recommended by the T.D.B. [26]. This method assumes that heat capacity change does not depend on T and taking into account this assumption, equilibrium constant is developed versus temperature by integrating Van't Hoff's expression Eq.(15). One obtains the following equation for Gibb's energy:

$$\Delta G(T) = \Delta G(T°) - \Delta S(T°)(T - T°) + \Delta Cp(T°)[T - T° - T\ln(T / T°)] \qquad (25)$$

The two methods of determing $\Delta S(T^\circ)$ and $\Delta Cp(T^\circ)$ are in very good agreement for each plutonium system and at each ionic strength.

There are very few values available in literature on heat capacities of aqueous species and above all for actinides. Approximations are therefore often used to estimate these values and to calculate the dependence of the equilibrium constant with temperature. One approximation is to use $\Delta Cp = 0$, typically for the isoelectric reactions [27], *i.e.*, reactions where the sum of positive and the sum of negative charges are the same for reactants and products. We perform a polynomial regression on the plutonium potentials measured versus Ag-AgCl reference electrode and on the standard potentials. Now we can compare the heat capacities corresponding to reactions (26) and (27) :

$$PuO_2^{2+} + Ag\downarrow + Cl^- \rightarrow PuO_2^+ + AgCl\downarrow \qquad (26)$$

$$PuO_2^{2+} + 0.5^\circ H_2 \rightarrow PuO_2^+ + {}^\circ H^+ \qquad (27)$$

Reaction (27) is isoelectric but we calculate a heat capacity change higher than the one for reaction (26) which is not isoelectric. In fact the difference between these two reactions, (26) and (27), is exactly reaction (23). We verify that ΔCp of reaction (23), is quite constant when calculating it from the PuO_2^{2+}/PuO_2^+ measurements or the Pu^{4+}/Pu^{3+} ones, and consistent with the value directly determined from $E_{Ref}(T,I)$ (e.g, $\Delta Cp^\circ/2T^\circ = 3{,}8.\ 10^{-3}$ mVK^{-1}). In conclusion we observe that the approximation $\Delta Cp = 0$ is not valid for these redox isoelectric reactions. In fact, the isoelectric assumption seems to be used mainly for complexation reactions [26], where the electronic structure of the central cation is obviously less affected than in a redox reaction.

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Table 1: Redox potentials and interaction coefficients of Pu^{4+}/Pu^{3+} and PuO_2^{2+}/PuO_2^{+}.

$E_{1/2}(T,I)$ are measured in perchloric media against Ag-AgCl reference electrode. We calculate its potential according to Eq.(4) to get $E_{Ox/Red}(T,I)$ versus NHE that are tabulated here. For PuO_2^{2+}/PuO_2^{+}, junction potential, E_j, are measured for each I, and it is independent from T. E_j = 31, 28, 16 and 18mV for respectively I = 0.5, 1, 2, and 3M. Numerical values in this table are already corrected for E_j. By using the S.I.T. (Eq.3) at different T, we deduce $E_{Ox/Red}(0,T)$ and $\Delta\varepsilon(T)$ (2 last columns).

Tab 1a	$E(Pu^{4+}/Pu^{3+})(T,I)$(mV/NHE)				
T(°C)	I = 1 M	I = 2 M	I = 3 M	I = 0	$-\Delta\varepsilon$(kg/mol)
5	949.5	967	976	1011	0.319
10	954		980	1020	0.297
10	959		981		
10.5		972			
15	961	979	989	1029.5	0.304
15	970		991.5		
20	968		993	1034	0.310
20	971		992		
21			1002		
25	971	988.5	1011.5	1044	0.325
25	981	996.5	1001.5		
25			1004.5		
26		995			
30	984.5		1014.5	1053.5	0.300
31			1018		
35	988	1002.5	1022	1063	0.336
35	998	1014			
40	1007	1021	1039.5	1074	0.373
40			1044		
40.5			1046		
41			1046		
42			1028		
44		1016.5			
45	1005.5	1020	1049.5	1073.5	0.392
45	1009				
50	1017		1057	1086.5	0.390
50			1060		
50			1055		
54		1042.5	1055		
55	1024.5	1036.5	1061.5	1100	0.345
55	1024.5				
60	1029	1050		1098.5	0.451
65	1039		1067	1121	0.306

Tab 1b

T(°C)	$E(PuO_2^{2+}/PuO_2^{+})(T,I)$(mV/NHE)					
	I = 0.5 M	I = 1 M	I = 2 M	I = 3 M	I = 0	−Δε(kg/mol)
5	914.5	906	918	941.5	928	0.255
5	910.5	906	914	940		
10	912	912.5	920	943.5	931.5	0.249
10	916.5	908	917	943		
10			920			
15	920	912.5	918.5	944	936	0.227
15	914	913	918.5	941		
20	918	914.5	917	945.5	937	0.225
20	920.5	910	919	942.5		
20	916	913.5	919			
25	917.5	911	920.5	944	938.5	0.219
25	920.5	914.5	918	943		
25	919.5	911	919.5	944		
25	916	912				
30	919		922	942	939	0.219
30	916	914.5	919.5	943		
31		912				
35	916.5	916		943	942	0.197
35	919	915	920	941		
35	920	914	920.5			
36			919.5			
40	920	915	919	942	941.5	0.205
40	916	914	919.5	942.5		
45	919.5	914.5	918		942	0.196
45	916	912.5	919.5	939.5		
45			919.5	941.5		
48	916					
50	918	915	918	939.5	941	0.203
50		911.5	919	939		
50		911.5				
55		913.5	916		944.5	0.164
55	918	910.5	917			
55	920	910.5	918	938		
60	915	911	914.5	936.5	941	0.187
60		908.5				
60		910				
61			915.5			
64			915.5			
65	914.5	908	913.5	935	941.5	0.181

Table 2: Redox potentials, entropies, enthalpies, heat capacities, interaction coefficients and its derivatives versus T in standard conditions. $E_{Ox/Red}(0,T°)$ and $\Delta\varepsilon(T°)$ are calculated by using the S.I.T.. ΔS, and ΔCp (resp.$\Delta\varepsilon'(T°)$, and $\Delta\varepsilon''(T°)$) numerical values are fitted from $E_{Ox/Red}(0,T)$ (resp. $\Delta\varepsilon(T)$) tabulated in Table 1a and 1b according to a 2^{nd} order polynomial regression versus T, Eq.(10); the values in paranthesis are 1.5 s where s is the standard deviation, except for potentials whose uncertainty is evaluate including experimental errors.

	Pu^{4+}/Pu^{3+}	PuO_2^{2+}/PuO_2^{+}
$E_{Ox/Red}(0,T°)$ (mV)	1044 (10)	938 (10)
$\frac{\Delta S(0,T°)}{F}$ (mV K^{-1})	1.67 (0.14)	0.34 (0.04)
$\frac{\Delta H(0,T°)}{F}$ (mV)	-543 (35)	-839 (11)
$\frac{\Delta Cp(0,T°)}{F}$ (mV K^{-1})	1.77 (3.20)	-4.04 (0.97)
$\Delta\varepsilon(T°)$ (kg mol^{-1})	-0.33 (0.05)	-0.22 (0.03)
$\Delta\varepsilon'(T°)$ (kg mol^{-1}K^{-1})	-1.76 10^{-3} (1.42 10^{-3})	1.48 10^{-3} (0.34 10^{-3})
$\Delta\varepsilon''(T°)$ (kg mol^{-1}K^{-2})	3.34 10^{-5} (1.09 10^{-5})	-2.44 10^{-5} (2.6 10^{-5})

Table 3. Formal and standard potentials of Pu^{4+}/Pu^{3+} and PuO_2^{2+}/PuO_2^{+}.

We select numerical values of [2,3 and p.w] (resp. [5 and p.w]) for Pu^{4+}/Pu^{3+} (resp. for PuO_2^{2+}/PuO_2^{+}). We resume below why we reject the other ones; for further explanations see *Discussion Section*. [1]: junction potential, [4]: indirect and unprecised measurement, [6]: ionic strength correction, [7]: not rejected but unprecised experimental technique, [8]: systematic error due to interference.

Numerical values measured at 20°C (*) are recalculated at 25°C using numerical values of $\Delta S/F$ and $\Delta Cp/F$ (Tab.2) and printed in italic face.

Pu^{4+}/Pu^{3+}			PuO_2^{2+}/PuO_2^{+}		
E (1M) mV/NHE	E(0M) mV/NHE	Ref.	E (1M) mV/NHE	E(0M) mV/NHE	Ref.
982 ± 2		[2]	935 ± 15		[1]
982.1 ± 0.5		[3]	925 ± 4		[4]
	1006 ± 3	[6]	916.4 ± 0.2		[5]
				956 ± 25	[7]
959 ± 5*	1015 ± 10*	[8]	9..1 ± 5*	954 ± 10*	[8]
966 ± 5	*1023 ± 10*		*942 ± 5*	*956 ± 10*	
978 ± 5	1044 ± 10	p.w.	913 ± 5	938 ± 10	p.w.

Table 4. Interaction coefficients $-\Delta\varepsilon$ (kg/mol) of An^{4+}/An^{3+} and AnO_2^{2+}/AnO_2^{+}.

An = U, Np or Pu. Numerical values of present work are fitted from $E_{Ox/Red}(T,I)$ (Tab.1) and Eq(3). The original published values measured at 20°C are followed by *. We recalculated them at 25°C (italic face) using numerical values of first and second order derivatives of $\Delta\varepsilon$ (Tab.2), anyhow we reject these values (see *Discussion Section*).

	An^{4+}/An^{3+}	[Ref.]	AnO_2^{2+}/AnO_2^{+}	[Ref.]
U	0.35 ± 0.06	[12]	0.20 ± 0.06	[11]
Np	0.35 ± 0.03	[8]	0.21 ± 0.03*	[8]
Pu	0.54 ± 0.03* *0.53 ± 0.03*	[8]	0.29 ± 0.03* *0.30 ± 0.03*	[8]
Pu	0.33 ± 0.05	p.w.	0.22 ± 0.05	p.w.

Table 5. Temperature coefficients, ΔS/F (mV $K^{-1}mol^{-1}$), of An^{4+}/An^{3+} and AnO_2^{2+}/AnO_2^+. Δ S is the entropy changes of the reaction: Ox + 0.5 $°H_2 \rightarrow$ Red + $°H^+$. Our numerical values are fitted according to Eqs.(10) and (13) and the uncertainty is (1.5 s) where s is the standard deviation. For published ones we used individual entropy of each species. $S°_{H^+} = 0$ by convention and $S_{H_2} = 130.680 \pm 0.003$ J(mol K)$^{-1}$ [11]; the uncertainty is obtained based on the rules of error propagation.

I (mol/Kg)	Pu^{4+}/Pu^{3+}	U^{4+}/U^{3+}	PuO_2^{2+}/PuO_2^+	UO_2^{2+}/UO_2^+
0	1.44 ± 0.23 [22]	1.69 ± 0.19 [11]	0.017 ± 0.12 [22]	0.08 ± 0.09 [11]
0	1.67 ± 0.14	1.46 ± 0.05 *	0.34 ± 0.04	-0.06 ± 0.05 *
0.5			0.13 ± 0.05	
1.05			-0.26 [5]	
1.05	1.33 [2]		0.69 [4]	
1.05	1.47 ± 0.11	1.27 ± 0.02	0.16 ± 0.04	-0.24 ± 0.02
2.21	1.42 ± 0.15		0.07 ± 0.03	
3.5	1.90 ± 0.16		-0.02 ± 0.02	

when nothing is mentionned it means present work. * calculated from results measured at I = 1M and assuming that ΔS(1M) - ΔS(0) is the same for U and Pu. All these values are compared and criticized in *Discussion Section.*

Figures Captions

Fig. 1. : Temperature influence on the shape of the voltammogram of a PuO_2^{2+} solution containing 5% of Pu^{3+}. The interference between the two reversible couples (see the oxydation wave at T = 40°C) induces a systematic error.

Fig. 2. : Comparison of Pu redox potential determinations.

Redox potentials are measured in ClO_4^- media and extrapolated to I=0 by using the S.I.T. The rejected values (see caption of Tab.3) are plotted in this figure but not taken into account to perform the extrapolation.

$m = m_{ClO_4^-}$ in mol/kg and $D(I,T^\circ) = \frac{0.5091\sqrt{m}}{1+1.5\sqrt{m}}$;

a) PuO_2^{2+}/PuO_2^{+} $\quad E_{Ox/Red}(I,T^\circ) = E^\circ + 59.16(-3\,D(I,T^\circ) - \Delta\varepsilon(T^\circ)\,m)$

$E(0,T^\circ)$ and $\Delta\varepsilon(T^\circ)$ are deduced from linear regression similar to Fig.2b one.

b) Pu^{4+}/Pu^{3+} $\quad Y(I,T^\circ) = \frac{E_{Ox/Red}(I,T^\circ)}{59.16} + 7D(I,T^\circ) = \frac{E^\circ}{59.16} - \Delta\varepsilon(T^\circ)\,m$

The slope of the regression line $Y(I,T^\circ) = f(I)$ is $-\Delta\varepsilon(T^\circ)$ and the intercept at I = 0, is $\frac{E^\circ}{59.16}$.

Fig. 3. : Temperature influence on PuO_2^{2+}/PuO_2^{+} potential at I = 0 and 3 M.

$E_{Ox/Red}(I,T)$ are measured by cyclic voltammetry in perchlorate media at different ionic strengths (numerical values in Tab.1) and extrapolated by using S.I.T. to I = 0. Data are fitted according to Eq.(10) : when disregarding the second order derivative we determine a $\frac{\Delta S(I,T^\circ)}{F}$ mean value (linear regression,thin line) or both $\frac{\Delta S(I,T^\circ)}{F}$ and $\frac{\Delta Cp(I,T^\circ)}{2T^\circ F}$ (squared regression, thick line)(Tab.2) .

Fig. 4. : Temperature influence on the interaction coefficient, $\Delta\varepsilon(T)$, of the PuO_2^{2+}/PuO_2^{+} couple. When extrapolating $E_{Ox/Red}(I,T)$ at each T to determine $E_{Ox/Red}(0,T)$, (Fig.2), we also obtain $\Delta\varepsilon(T)$ that are plotted here.The curves are calculated according to a linear regression (thin line) or a quadratic regression (thick line).

Fig. 5. : Verification of the extended S.I.T. equations for $\Delta S^{ex}(I,T°)$ and $\frac{\Delta Cp^{ex}(I,T°)}{2T°}$ of strong electrolyte XCl (X = H or Na).

$\Delta G^{ex}(I,T) = RT\ln\gamma_{\pm}$ is computed from $\gamma_{\pm}$ numerical values [15]. The dots are calculated according to Eq.(10), as the 1rst and 2nd order terms of the curve fitting $\Delta G^{ex}(I,T) = f(T)$. The curves (see Fig. 6 caption) are calculated from Eqs.(19) and (20) where X° = 0.

Fig. 6. : $\frac{\Delta S(I,T°)}{F}$, $\frac{\Delta Cp(I,T°)}{2T°F}$ and $\frac{\Delta H(I,T°)}{F}$ variation versus ionic strength for the redox equilibrium : $PuO_2^{2+} + 0.5\ °H_2 \rightleftharpoons PuO_2^{+} + °H^{+}$

Experimental data in Fig.6a and in Fig.6b are numerical values of the 1rst order term, or the 2nd order one of the E (I,T) curve fitting versus (T-T°) (Eq.(10)) (e.g, Fig.3 at I = 3 and 0). In Fig.6c the dots are deduced from Eq.(12), the measured values of E(I,T°) and the fitted ΔS(I,T°) ones. The curves are calculated according to Eq.(18), (19) or (20) using the standard values in Tab.2. The thin line model involves only first order derivatives of $\Delta\varepsilon$ and D, and the thick line takes into account both 1rst and 2nd order derivatives.

Figure 1

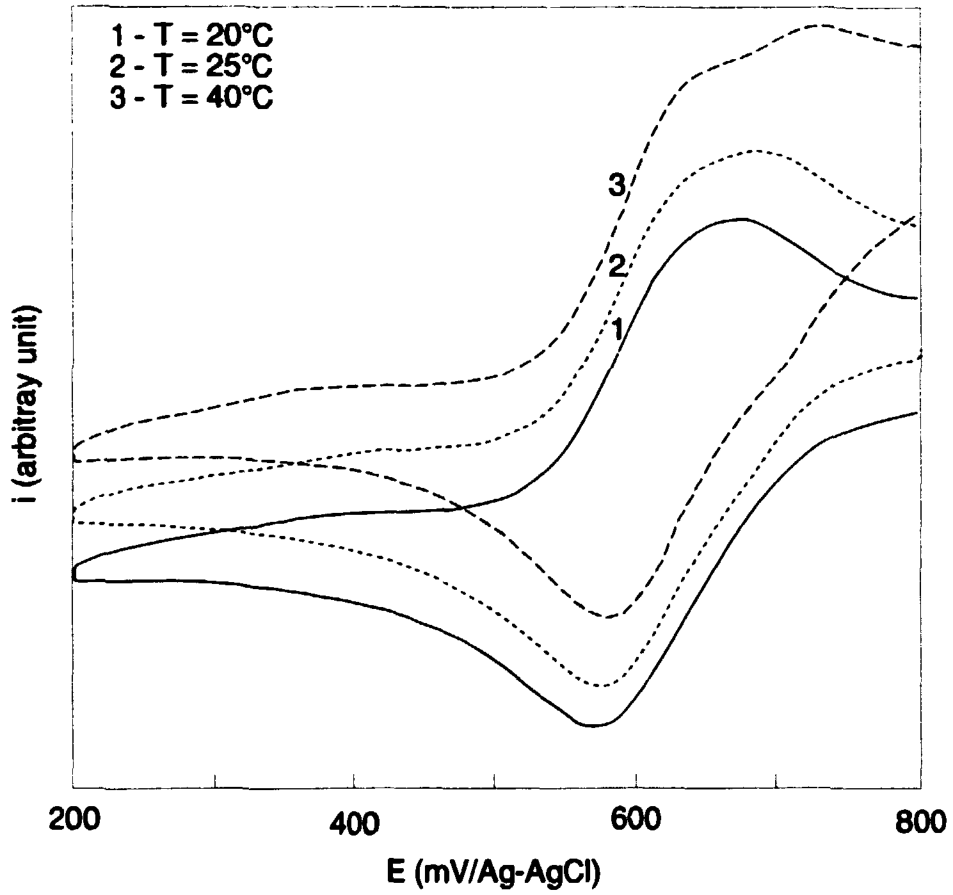

1 - T = 20°C
2 - T = 25°C
3 - T = 40°C
3
2
1
i (arbitray unit)
200
400
600
800
E (mV/Ag-AgCl)

Figure 2a

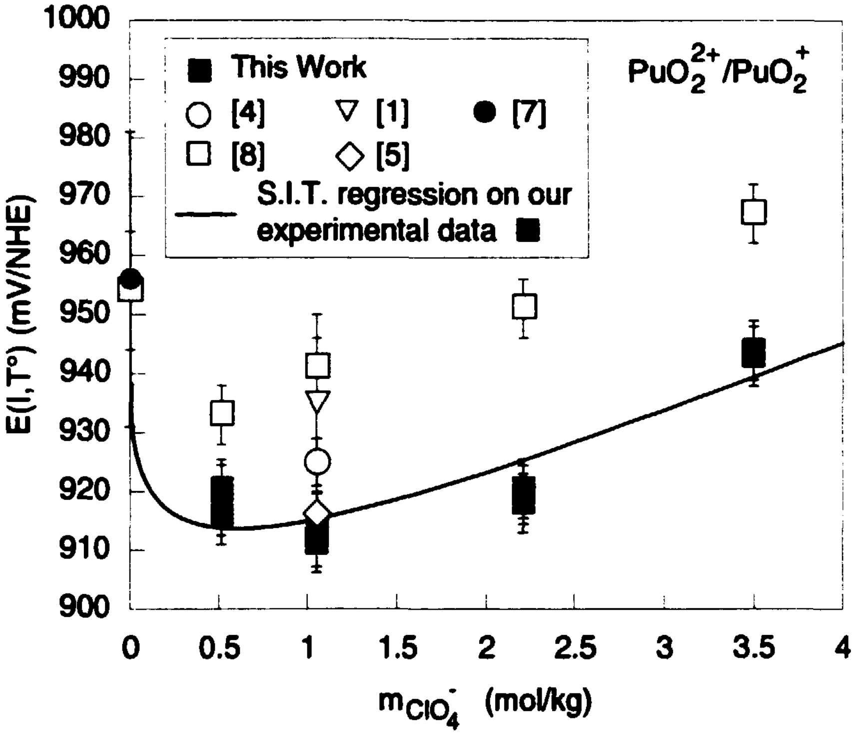


Figure 2b

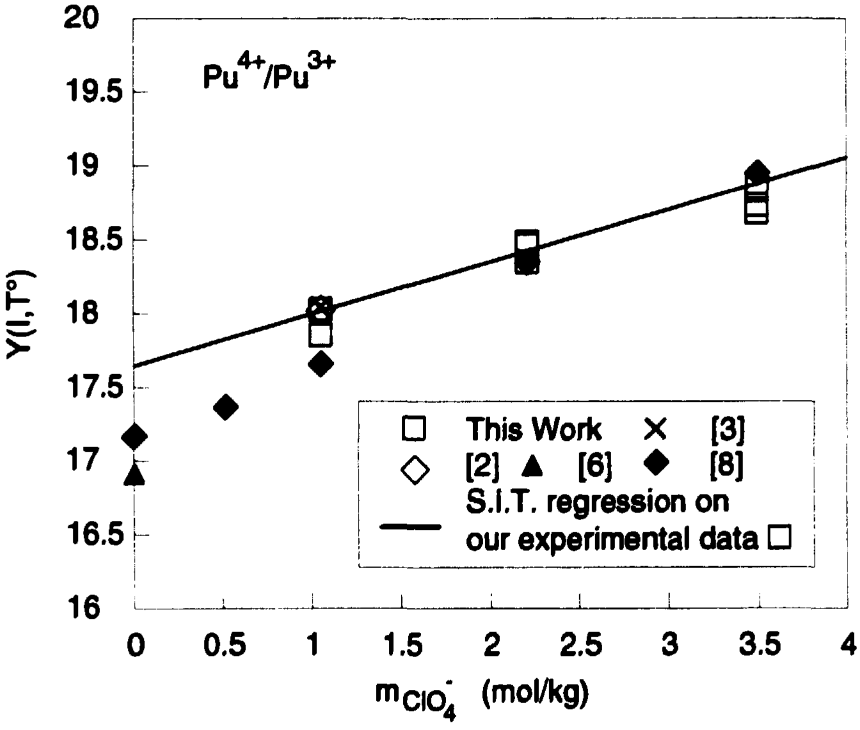


Figure 3

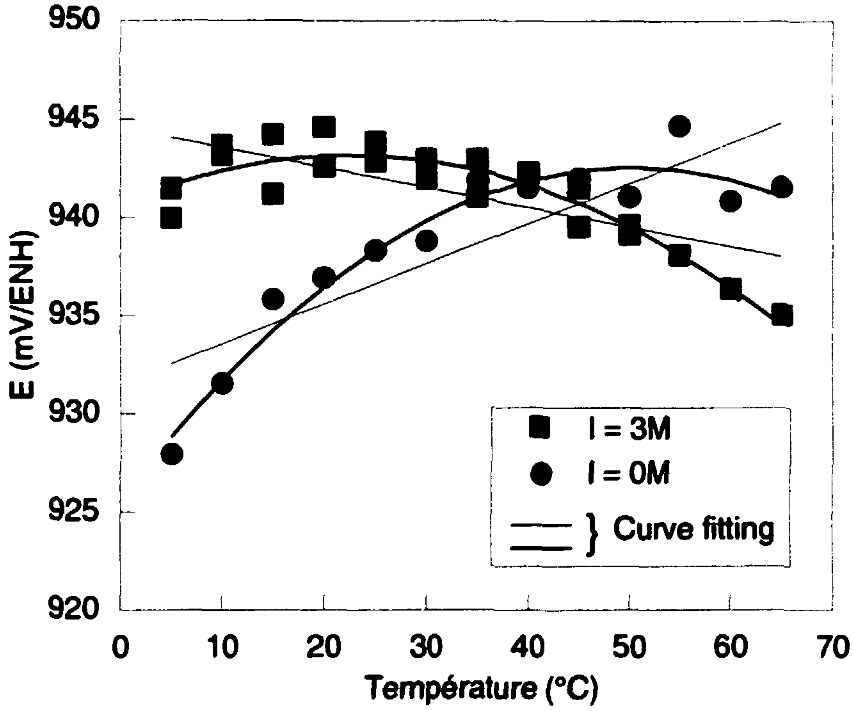


Figure 4

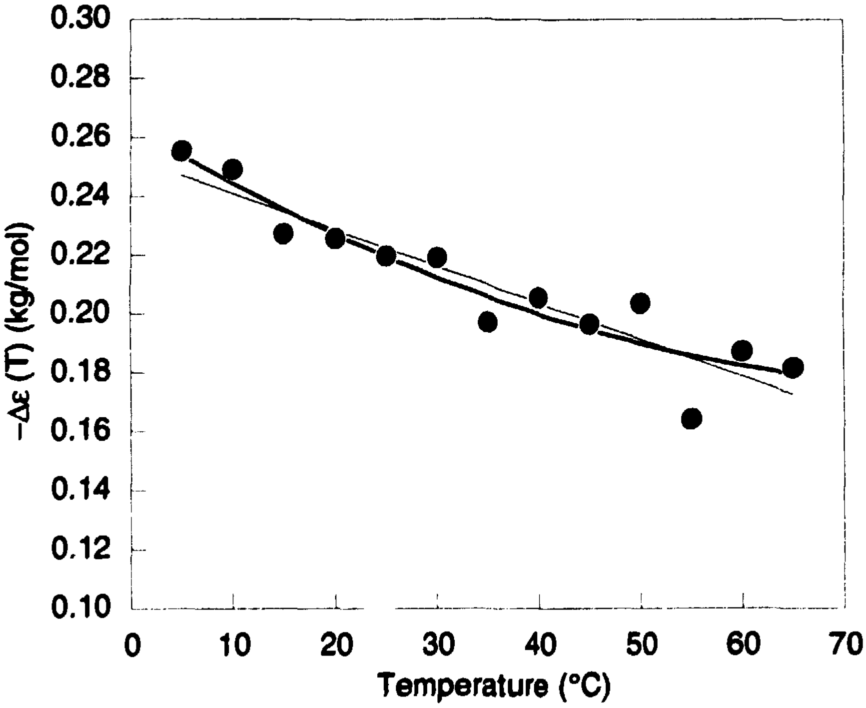


Figure 5a

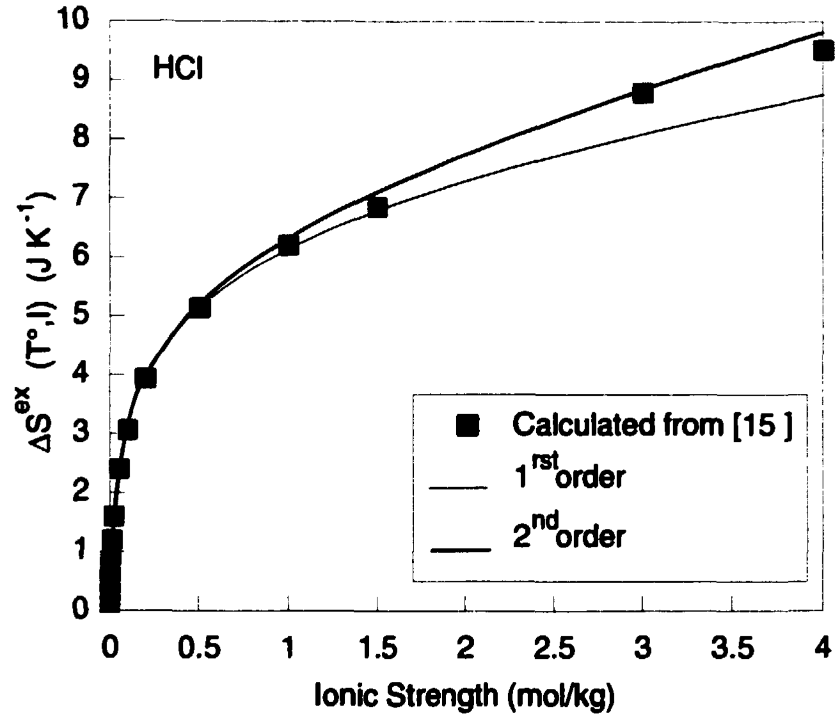


Figure 5b

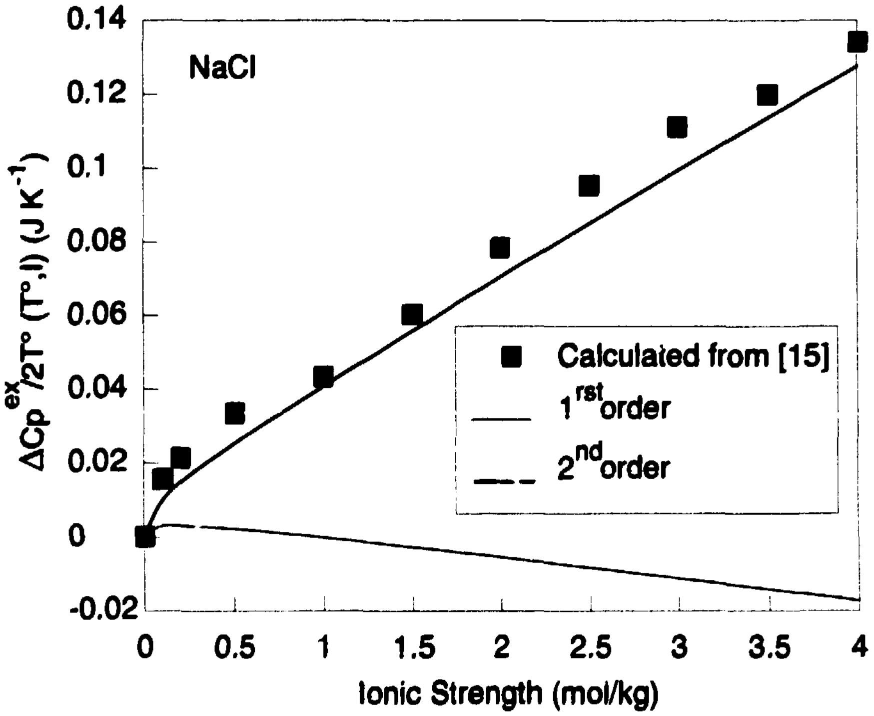


Figure 6a

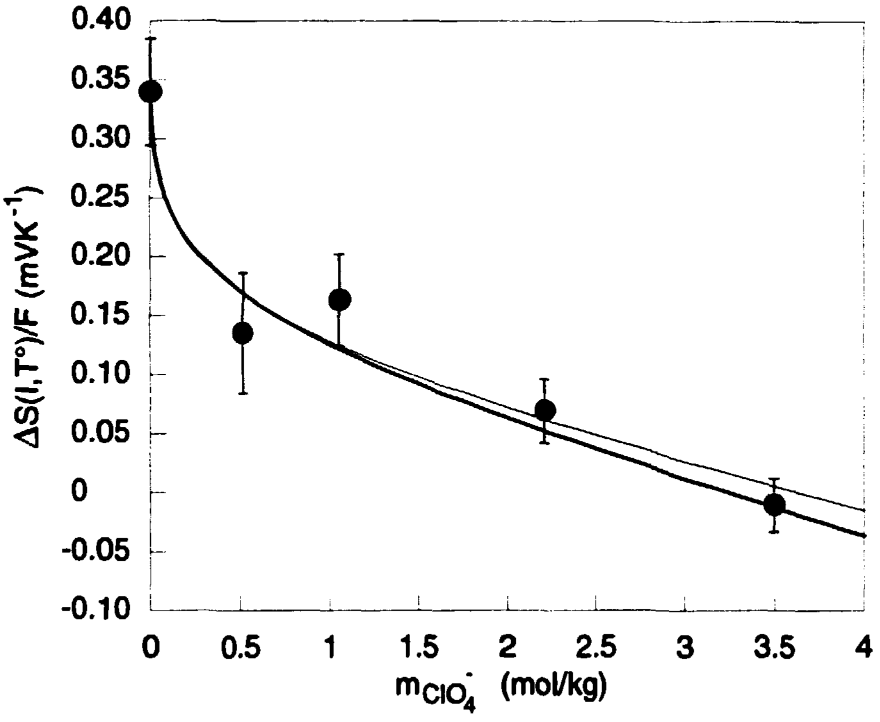


Figure 6b

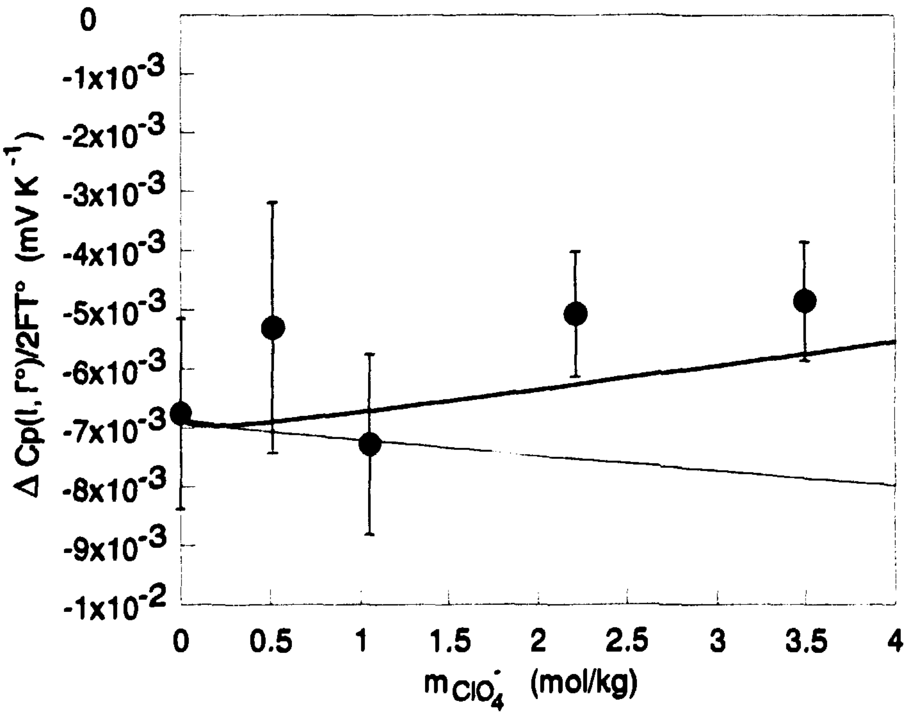
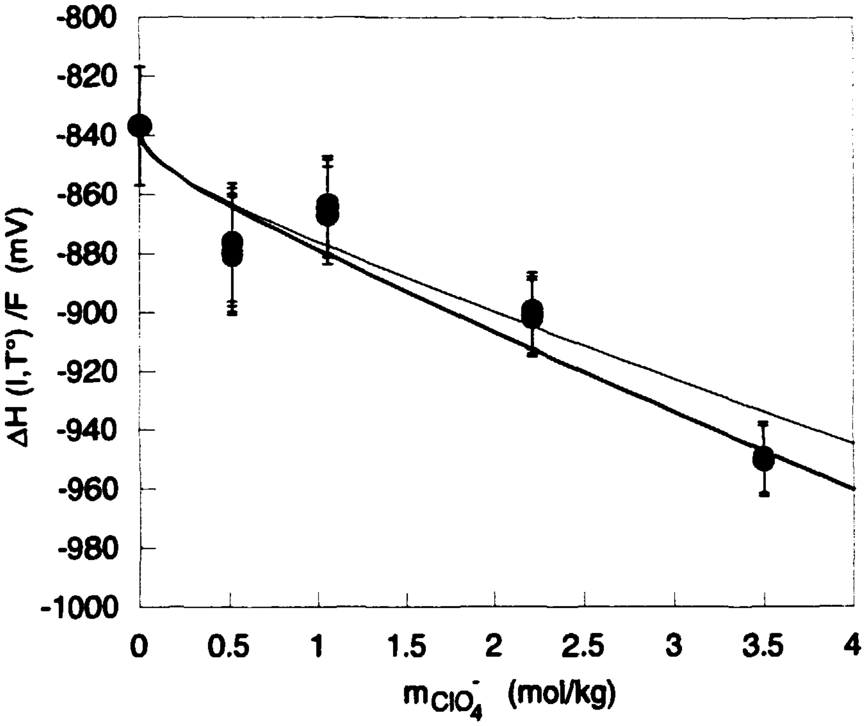


Figure 6c


-800
-820
-840
-860
-880
-900
-920
-940
-960
-980
-1000
ΔH (I,T°) /F (mV)
0
0.5
1
1.5
2
2.5
3
3.5
4
$m_{ClO_4^-}$ (mol/kg)

Présentation des calculs

Dans les pages suivantes sont regroupés les calculs intermédiaires et complémentaires aux résultats présentés dans la publication. Tous ces calculs ont été effectués sur tableur (Lotus 123 pour Macintosh). Nous résumons rapidement ci-dessous, les différentes étapes de calculs de chacun des 7 fichiers et les similitudes existant entre certains d'entre eux pour que la consultation en soit facilitée. Nous ne rappelons pas ici, les équations utilisées, car elles sont en général écrites en tête de fichier. Nous ne donnons pas non plus les références bibliographiques qui sont identiques à celles mentionnées dans la publication. Il s'agit de calculs dont la consultation permettra peut être d'approfondir certains points de la publication et qui permettent d'être exhaustifs, là où dans la publication nous avons été contraints de mentionner que certains exemples.

Dans le fichier **D=f(T)**, on calcule le coefficient de Debye et Huckel, par sa formule analytique, et on détermine sa première et deuxième dérivées par rapport à la température.

Le fichier **Eps(H,Na Cl)=f(T)** est découpé en deux parties structurées rigoureusement de la même façon, l'une concernant HCl, et l'autre NaCl. Dans chacune d'entre elles on applique la S.I.T. sur les valeurs publiées de coefficient d'activité moyens $\gamma_{\pm}$. Pour chaque température, on en déduit, $\varepsilon(T)$ ($\varepsilon(H^+,Cl^-)(T)$ ou $\varepsilon(Na^+,Cl^-)(T)$). A partir de ces valeurs de $\varepsilon(T)$, on calcule par régression polynomiale $\varepsilon'(T)$ et $\varepsilon''(T)$.

Dans le fichier **gHCl**, les points expérimentaux sont les mêmes que précédemment, à savoir les coefficients d'activité moyens. Dans un premier temps, on calcule l'enthalpie libre d'excès $\Delta G^{ex}=RT\ln\gamma_{\pm}$. C'est sur ces valeurs que l'on effectuera la plupart des calculs ultérieurs. Dans un deuxième temps, on détermine par ajustement à chaque force ionique, les paramètres G(I,T°), S(I,T°), Cp(I,T°) intervenant dans le développement au deuxième ordre en (T-T°) de G(I,T).

Ces valeurs "expérimentales" sont ensuite comparées, figures à l'appui, aux valeurs calculées par les formules théoriques dérivées de la SIT permettant de modéliser la variation de l'entropie et de la capacité calorifique avec la force ionique. Cette comparaison est tout d'abord faite avec un modèle simplifié ne faisant intervenir que les valeurs des dérivées premières $\varepsilon'(T)$ et $D'(T)$, calculées par régression linéaire dans Eps(H,Na Cl). Ensuite, nous faisons une comparaison avec un modèle où l'on tient compte des 4 paramètres $\varepsilon'(T)$, $D'(T)$, $\varepsilon''(T)$ et $D''(T)$ calculés par régression d'ordre 2 cette fois, toujours dans Eps(H,Na Cl).

Le fichier **gNaCl** est totalement similaire au précédent, mais concerne l'elevtrolyte NaCl.

Dans le fichier **RefAgCl(I,T)**, on calcule le potentiel de l'électrode de référence à toute force ionique et température, dans les deux milieux dans lesquels nous l'avons utilisée. Ce fichier fait appel aux résultats de Eps(H,Na Cl). Ces valeurs de potentiels permettront de calculer les potentiels expérimentaux du plutonium par rapport à l'ENH.

Dans les fichiers **E6/5** et **E4/3** les calculs sont similaires à ceux menés dans gHCl ou gNaCl. Dans le cas présent, le point de départ est constitué des valeurs expérimentales des potentiels rédox et non plus des coefficients d'activité moyens publiés. Toutefois quelques calculs supplémentaires ont été menés. Il s'agit de la détermination de $\Delta H(I,T°)$ par développement en $1/T$ sur $R\ln K$. Ensuite toutes les valeurs de $\Delta H(I,T°)$, $\Delta S(I,T°)$ et $\Delta Cp(I,T°)$ déterminées par ajustement sont comparées aux valeurs calculables par les équations que nous avons établies.

Fichier D=f(T)

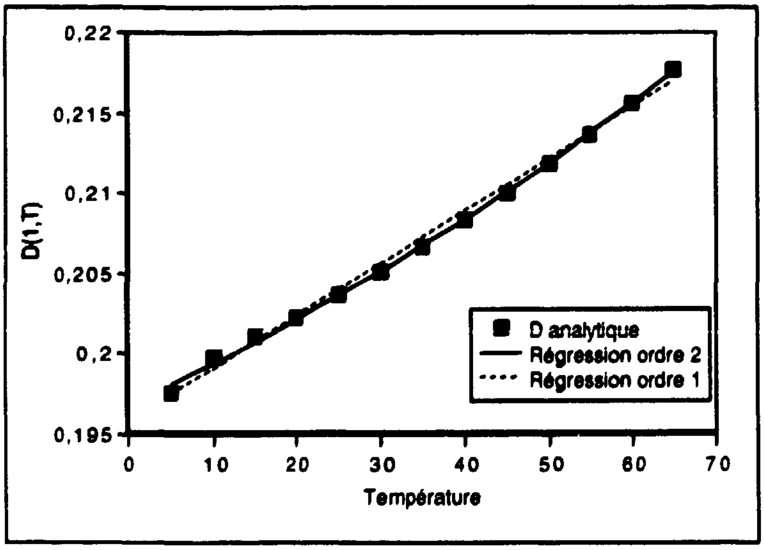
D(I,T) =(a*I^0,5)/(1+b*I^0,5) avec I en mol/kg

Régression d'ordre 1 sur D(I,T)
D(I,T) = D(I,T°)+D'(I,T°)DT

Régression d'ordre 2 sur D(I,T)
D(I,T) = D(I,T°)+D'(I,T°)DT+D''(I,T°)/2 DT^2

					ordre 1	ordre 2	
T	a	b	I	D(I,T°)	D'(I,T°)	D'(I,T°)	D''(I,T°)/2
5	0,4913	1,4867	0,0001	5,02E-03	9,50E-06	8,78E-06	3,64E-08
10	0,4976	1,4899	0,0002	7,05E-03	1,33E-05	1,23E-05	5,10E-08
15	0,5012	1,4931	0,0005	1,10E-02	2,08E-05	1,92E-05	7,94E-08
20	0,505	1,4968	0,001	1,54E-02	2,89E-05	2,67E-05	1,10E-07
25	0,5091	1,5	0,002	2,13E-02	3,99E-05	3,68E-05	1,52E-07
30	0,5135	1,5037	0,005	3,25E-02	6,03E-05	5,57E-05	2,30E-07
35	0,5182	1,5073	0,01	4,43E-02	8,12E-05	7,50E-05	3,09E-07
40	0,5231	1,511	0,02	5,94E-02	1,08E-04	9,94E-05	4,09E-07
45	0,5282	1,5151	0,05	8,52E-02	1,51E-04	1,40E-04	5,72E-07
50	0,5336	1,5192	0,1	1,09E-01	1,89E-04	1,75E-04	7,16E-07
55	0,5392	1,5233	0,2	1,36E-01	2,31E-04	2,13E-04	8,70E-07
60	0,545	1,5274	0,5	1,75E-01	2,86E-04	2,64E-04	1,07E-06
65	0,5511	1,5315	0,513	1,76E-01	2,87E-04	2,66E-04	1,08E-06
			1	2,04E-01	3,24E-04	3,00E-04	1,22E-06
			1,05	2,06E-01	3,27E-04	3,02E-04	1,23E-06
			1,5	2,20E-01	3,44E-04	3,19E-04	1,29E-06
			2	2,31E-01	3,58E-04	3,31E-04	1,34E-06
			2,21	2,34E-01	3,62E-04	3,35E-04	1,36E-06
			3	2,45E-01	3,75E-04	3,47E-04	1,40E-06
			3,4956	2,50E-01	3,81E-04	3,52E-04	1,43E-06
			4	2,55E-01	3,86E-04	3,57E-04	1,44E-06

Exemple pour I=1



Fichier Epa(H,Na Cl)=f(T)

HCl

Calcul du coefficient d'interaction spécifique Epa(H,Cl) à partir de valeurs de coefficients d'activité moyen, g±, tirées du "Handbook of electrolyte solutions" Pat A page 519-520 qui cite R.A. Robinson, H.S. Harned (Some aspects of the thermodynamics of strong electrolytes from electromotive force and vapor pressure measurements) Chem. Rev.28, 419 (1941)

y = lg(coeff d'activité) + D = epa(H,Cl) m (S.I.T)

ye = yexpérimental yc = y calculé par régression linéaire de la SIT

	T=0°C					T=5°C					T=10°C				
m	D(T,I)	coeff.activ	ye	yc	(ye-yc)^2	D(T,I)	coeff.activ	yexp	yc	(ye-yc)^2	D(T,I)	coeff.activ	yexp	yc	(ye-yc)^2
0,0001	0,0048	0,989	3,75E-05	1,34E-05	5,80E-10	0,0049	0,9886	-1,09E-04	1,32E-05	1,49E-08	0,0049	0,989	9,92E-05	1,29E-05	7,45E-09
0,0002	0,0068	0,9848	1,53E-04	2,68E-05	1,60E-08	0,0068	0,9847	1,50E-04	2,64E-05	1,54E-08	0,0069	0,9846	1,52E-04	2,59E-05	1,58E-08
0,0005	0,0106	0,9756	-9,51E-05	6,69E-05	2,63E-08	0,0107	0,9756	-3,10E-05	6,59E-05	9,38E-09	0,0108	0,9756	3,97E-05	6,47E-05	6,23E-10
0,001	0,0148	0,9668	1,77E-04	1,34E-04	1,84E-09	0,0149	0,9662	-3,73E-06	1,32E-04	1,84E-08	0,0150	0,9666	2,74E-04	1,29E-04	2,10E-08
0,002	0,0206	0,9541	1,98E-04	2,68E-04	4,79E-09	0,0207	0,9539	2,30E-04	2,64E-04	1,09E-09	0,0209	0,9544	5,94E-04	2,59E-04	1,12E-07
0,005	0,0314	0,9303	6,48E-05	6,69E-04	3,65E-07	0,0316	0,93	1,10E-04	6,59E-04	3,01E-07	0,0318	0,93	3,15E-04	6,47E-04	1,10E-07
0,01	0,0428	0,9065	1,51E-04	1,34E-03	1,41E-06	0,0430	0,9056	-3,14E-05	1,32E-03	1,82E-06	0,0433	0,9055	1,96E-04	1,29E-03	1,21E-06
0,02	0,0574	0,8774	6,29E-04	2,68E-03	4,20E-06	0,0578	0,8768	6,61E-04	2,64E-03	3,90E-06	0,0581	0,8773	1,27E-03	2,59E-03	1,73E-06
0,05	0,0825	0,8346	3,97E-03	6,69E-03	7,41E-06	0,0830	0,8344	4,33E-03	6,59E-03	5,12E-06	0,0835	0,8338	4,52E-03	6,47E-03	3,79E-06
0,1	0,1058	0,8027	1,03E-02	1,34E-02	9,49E-06	0,1063	0,8023	1,07E-02	1,32E-02	6,33E-06	0,1070	0,8016	1,09E-02	1,29E-02	4,06E-06
0,2	0,1321	0,7756	2,17E-02	2,68E-02	2,55E-05	0,1328	0,7756	2,24E-02	2,64E-02	1,55E-05	0,1335	0,774	2,23E-02	2,59E-02	1,29E-05
0,5	0,1695	0,7761	5,95E-02	6,69E-02	5,56E-05	0,1704	0,773	5,86E-02	6,59E-02	5,34E-05	0,1713	0,7694	5,75E-02	6,47E-02	5,18E-05
1	0,1978	0,8419	0,123	1,34E-01	1,16E-04	0,1988	0,8363	0,121	0,132	1,13E-04	0,1998	0,8295	0,119	0,129	1,15E-04
1,5	0,2136	0,9452	0,189	2,01E-01	1,35E-04	0,2146	0,9365	0,186	0,198	1,33E-04	0,2157	0,927	0,183	0,194	1,27E-04
2	0,2243	1,078	0,257	2,68E-01	1,17E-04	0,2253	1,068	0,254	0,264	9,27E-05	0,2265	1,053	0,249	0,259	9,72E-05
3	0,2384	1,452	0,400	4,02E-01	1,38E-06	0,2395	1,427	0,394	0,395	1,87E-06	0,2407	1,401	0,387	0,388	1,05E-06
4	0,2477	2,006	0,550	5,35E-01	2,14E-04	0,2488	1,96	0,541	0,527	1,97E-04	0,2501	1,911	0,531	0,518	1,89E-04
écart type					6,36E-03					6,06E-03					5,97E-03

	T=30°C					T=35°C					T=40°C				
m	D(T,I)	coeff.activ	yexp	yc	(ye-yc)^2	D(T,I)	coeff.activ	yexp	yc	(ye-yc)^2	D(T,I)	coeff.activ	yexp	yc	(ye-yc)^2
0,0001	0,0051	0,989	2,55E-04	1,13E-05	5,95E-08	0,0051	0,9886	1,26E-04	1,10E-05	1,31E-08	0,0052	0,9885	1,30E-04	1,07E-05	1,42E-08
0,0002	0,0071	0,9835	-1,15E-04	2,25E-05	1,89E-08	0,0072	0,9838	8,23E-05	2,20E-05	3,64E-09	0,0072	0,9833	-7,10E-05	2,14E-05	8,54E-09
0,0005	0,0111	0,9747	-2,03E-05	5,64E-05	5,88E-09	0,0112	0,9745	-8,66E-06	5,50E-05	4,05E-09	0,0113	0,9741	-8,19E-05	5,36E-05	1,83E-08
0,001	0,0155	0,965	2,85E-05	1,13E-04	7,09E-09	0,0156	0,9647	3,37E-05	1,10E-04	5,82E-09	0,0158	0,9643	-3,18E-07	1,07E-04	1,15E-08
0,002	0,0215	0,9515	-7,38E-05	2,25E-04	8,95E-08	0,0217	0,9513	2,86E-05	2,20E-04	3,66E-08	0,0219	0,9505	-1,35E-04	2,14E-04	1,22E-07
0,005	0,0328	0,9275	1,34E-04	5,64E-04	1,84E-07	0,0331	0,9268	9,90E-05	5,50E-04	2,03E-07	0,0334	0,9265	2,64E-04	5,36E-04	7,40E-08
0,01	0,0446	0,9034	5,18E-04	1,13E-03	3,71E-07	0,0450	0,9025	4,79E-04	1,10E-03	3,84E-07	0,0454	0,9016	4,57E-04	1,07E-03	3,77E-07
0,02	0,0599	0,8741	1,45E-03	2,25E-03	6,53E-07	0,0604	0,8731	1,47E-03	2,20E-03	5,29E-07	0,0610	0,8715	1,22E-03	2,14E-03	8,51E-07
0,05	0,0859	0,8285	4,22E-03	5,64E-03	2,00E-06	0,0867	0,8265	3,91E-03	5,50E-03	2,53E-06	0,0874	0,8246	3,67E-03	5,36E-03	2,84E-06
0,1	0,1101	0,794	9,87E-03	1,13E-02	1,96E-06	0,1110	0,7918	9,59E-03	1,10E-02	1,98E-06	0,1119	0,7891	9,07E-03	1,07E-02	2,71E-06
0,2	0,1373	0,763	1,98E-02	2,25E-02	7,34E-06	0,1384	0,7604	1,95E-02	2,20E-02	6,34E-06	0,1396	0,7569	1,86E-02	2,14E-02	7,76E-06
0,5	0,1760	0,7526	5,25E-02	5,64E-02	1,45E-05	0,1774	0,7477	5,11E-02	5,50E-02	1,50E-05	0,1788	0,7432	4,99E-02	5,36E-02	1,32E-05
1	0,2051	0,8018	0,109	0,113	1,26E-05	0,2067	0,7942	0,107	0,110	1,12E-05	0,2083	0,7865	0,104	0,107	9,67E-06
1,5	0,2213	0,8849	0,168	0,169	7,27E-07	0,2230	0,874	0,165	0,165	1,78E-07	0,2247	0,8601	0,159	0,161	1,96E-06
2	0,2323	0,9929	0,229	0,225	1,41E-05	0,2340	0,9755	0,223	0,220	1,11E-05	0,2358	0,9602	0,218	0,214	1,54E-05
écart type					1,91E-03					1,82E-03					1,92E-03

Fichier Eps(H,Na Cl)=f(T)
HCl suite

	T=15°C					T=20°C					T=25°C				
m	D(T,I)	coeff.activ	yexp	yc	(ye-yc)^2	D(T,I)	coeff.activ	yexp	yc	(ye-yc)^2	D(T,I)	coeff.activ	yexp	yc	(ye-yc)^2
0,0001	0,0049	0,989	1,35E-04	1,27E-05	1,49E-08	0,0050	0,9892	2,60E-04	1,24E-05	6,11E-08	0,0050	0,9891	2,56E-04	1,22E-05	5,94E-08
0,0002	0,0069	0,9844	1,13E-04	2,54E-05	7,69E-09	0,0070	0,9844	1,65E-04	2,49E-05	1,97E-08	0,0071	0,9842	1,34E-04	2,44E-05	1,19E-08
0,0005	0,0108	0,9757	1,61E-04	6,35E-05	9,59E-09	0,0109	0,9759	3,32E-04	6,22E-05	7,27E-08	0,0110	0,9752	1,08E-04	6,09E-05	2,22E-09
0,001	0,0151	0,9661	1,57E-04	1,27E-04	8,92E-10	0,0152	0,9661	2,70E-04	1,24E-04	2,12E-08	0,0154	0,9656	1,67E-04	1,22E-04	2,07E-09
0,002	0,0210	0,953	1,04E-04	2,54E-04	2,24E-08	0,0212	0,9527	1,24E-04	2,49E-04	1,57E-08	0,0213	0,9521	1,89E-05	2,44E-04	5,05E-08
0,005	0,0321	0,9297	3,99E-04	6,35E-04	5,58E-08	0,0323	0,9294	4,94E-04	6,22E-04	1,65E-08	0,0325	0,9285	3,29E-04	6,09E-04	7,88E-08
0,01	0,0436	0,9055	4,97E-04	1,27E-03	5,96E-07	0,0439	0,9052	6,70E-04	1,24E-03	3,30E-07	0,0443	0,9048	8,22E-04	1,22E-03	1,57E-07
0,02	0,0585	0,877	1,52E-03	2,54E-03	1,03E-06	0,0589	0,8768	1,84E-03	2,49E-03	4,18E-07	0,0594	0,8755	1,65E-03	2,44E-03	6,14E-07
0,05	0,0840	0,8329	4,61E-03	6,35E-03	3,01E-06	0,0846	0,8317	4,57E-03	6,22E-03	2,72E-06	0,0852	0,8304	4,53E-03	6,09E-03	2,43E-06
0,1	0,1077	0,8	1,07E-02	1,27E-02	3,78E-06	0,1084	0,7965	1,07E-02	1,24E-02	3,16E-06	0,1092	0,7964	1,03E-02	1,22E-02	3,45E-06
0,2	0,1344	0,7717	2,18E-02	2,54E-02	1,25E-05	0,1353	0,7694	2,14E-02	2,49E-02	1,19E-05	0,1363	0,7667	2,09E-02	2,44E-02	1,21E-05
0,5	0,1724	0,7658	5,65E-02	6,35E-02	4,85E-05	0,1735	0,7616	5,52E-02	6,22E-02	4,91E-05	0,1747	0,7571	5,38E-02	6,09E-02	5,01E-05
1	0,2010	0,8229	0,116	0,127	1,11E-04	0,2023	0,8162	0,114	0,124	1,08E-04	0,2036	0,809	0,112	0,122	1,05E-04
1,5	0,2170	0,9154	0,179	0,190	1,39E-04	0,2183	0,9065	0,178	0,187	1,20E-04	0,2198	0,8962	0,172	0,183	1,12E-04
2	0,2278	1,039	0,244	0,254	8,95E-05	0,2291	1,024	0,239	0,249	8,87E-05	0,2307	1,009	0,235	0,244	8,38E-05
3	0,2421	1,373	0,380	0,381	1,13E-06	0,2435	1,345	0,372	0,373	1,18E-06	0,2451	1,318	0,364	0,366	1,49E-06
4	0,2515	1,862	0,521	0,508	1,88E-04	0,2529	1,812	0,511	0,498	1,78E-04	0,2546	1,762	0,501	0,487	1,73E-04
écart type					5,93E-03					5,76E-03					5,66E-03

	T=45°C					T=50°C					T=55°C				
m	D(T,I)	coeff.activ	yexp	yc	(ye-yc)^2	D(T,I)	coeff.activ	yexp	yc	(ye-yc)^2	D(T,I)	coeff.activ	yexp	yc	(ye-yc)^2
0,0001	0.0052	0,9886	2,24E-04	1,05E-05	4,55E-08	0.0053	0,9879	-3,09E-05	1,03E-05	1,69E-09	0.0053	0.9879	2,39E-05	9,99E-06	1,95E-10
0,0002	0,0073	0,9835	8,75E-05	2,11E-05	4,42E-09	0,0074	0,9831	-1,48E-05	2,05E-05	1,25E-09	0,0075	0.9833	1,50E-04	2,00E-05	1,70E-08
0,0005	0,0114	0,9741	2,74E-05	5,26E-05	6,35E-10	0,0115	0,9738	9.42E-06	5,13E-05	1,75E-09	0,0117	0,9735	-5,01E-06	5,00E-05	3,02E-09
0,001	0,0159	0,9644	1,97E-04	1,05E-04	8,36E-09	0,0161	0,9639	1,32E-04	1,03E-04	8,89E-10	0,0163	0,9636	1,63E-04	9,99E-05	3,96E-09
0,002	0,0221	0,9504	2,93E-05	2,11E-04	3,28E-08	0,0223	0,95	6,88E-05	2,05E-04	1,86E-08	0,0226	0,9497	1,60E-04	2,00E-04	1,61E-09
0,005	0,0337	0,9261	3,93E-04	5,26E-04	1,77E-08	0,0341	0,925	2,13E-04	5,13E-04	9,01E-08	0,0344	0,924	8,57E-05	5,00E-04	1,71E-07
0,01	0,0459	0,9008	4,99E-04	1,05E-03	3,07E-07	0,0463	0,9	5,65E-04	1,03E-03	2,12E-07	0,0468	0.899	5,41E-04	9,99E-04	2,10E-07
0,02	0,0615	0,8704	1,24E-03	2,11E-03	7,54E-07	0,0621	0,869	1,14E-03	2,05E-03	8,38E-07	0,0827	0,868	1,24E-03	2,00E-03	5,77E-07
0,05	0,0882	0,8232	3,73E-03	5,26E-03	2,36E-06	0,0891	0,8211	3,46E-03	5,13E-03	2,80E-06	0,0899	0,8195	3,44E-03	5,00E-03	2,41E-06
0,1	0,1129	0,7872	9,01E-03	1,05E-02	2,29E-06	0,1140	0,785	8,85E-03	1,03E-02	1,99E-06	0,1150	0,7829	8,72E-03	9,99E-03	1,63E-06
0,2	0,1408	0,7538	1,81E-02	2,11E-02	8,91E-06	0,1421	0,7508	1,76E-02	2,05E-02	8,42E-06	0,1433	0,7474	1,69E-02	2,00E-02	9,64E-06
0,5	0,1803	0,7387	4,88E-02	5,26E-02	1,48E-05	0,1819	0,7344	4,78E-02	5,13E-02	1,20E-05	0,1834	0,7292	4,62E-02	5,00E-02	1,38E-05
1	0,2100	0,779	0,102	0,105	1,37E-05	0,2118	0,7697	0,098	0,103	1,99E-05	0,2135	0,7628	0,095867	0,0999054	1,63E-05
1,5	0,2265	0,8517	0,157	0,158	1,12E-06	0,2285	0,8404	0,153	0,154	9,12E-07	0,2302	0,8278	0,147998	0,1498581	3,48E-08
2	0,2377	0,9481	0,215	0,211	1,63E-05	0,2397	0,9327	0,209	0,205	1,79E-05	0,2415	0,9198	0,2045791	0,1998108	2,27E-05
écart type					2,01E-03					2,08E-03					2,18E-03

Fichier Eps(H,Na Cl)=f(T)
HCl suite

T	Eps (H,Cl)
0	0,1338436
5	0,1317559
10	0,1293896
15	0,1269332
20	0,124428
25	0,12185
30	0,1127097
35	0,1099531
40	0,1071316
45	0,1052579
50	0,1025969
55	0,0999054
60	0,0980755

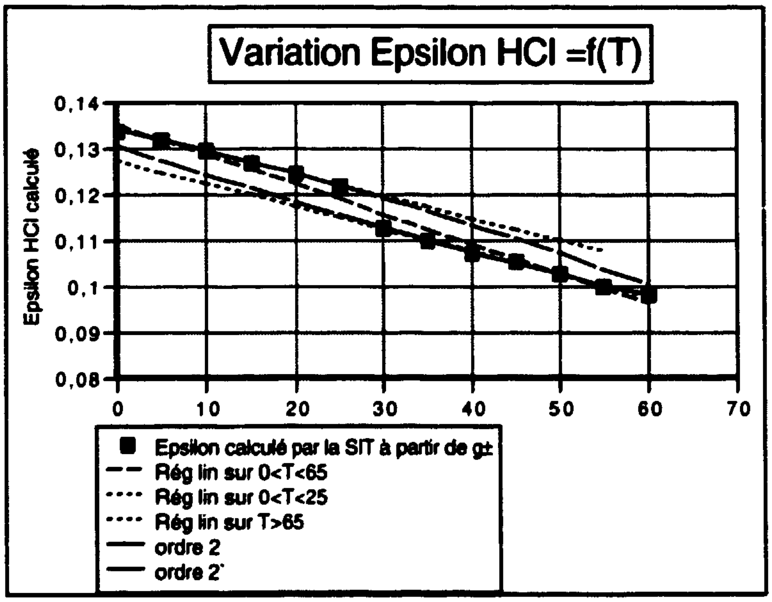
Régression linéaire
0<T<65°C
Epsilon HCl =0,118935-6,51E-4 *(T-T°)

0<T<25°C
Epsilon HCl =0,122004-4,82E-4 *(T-T°)

T>25°C
Epsilon HCl =0,111488-4,9E-4* (T-T°)

Régression d'ordre 2
0<T<25°C
Epsilon HCl =0,121825-5,36E-04 *(T-T°)-2,15E-06*(T-T°)^2

T>25°C
Epsilon HCl =0,115410-5,60E-04* (T-T°)+1,77E-06* (T-T°)^2



Fichier E[illegible]H,N[illegible](T)

NaCl

Calcul du coefficient d'interaction spécifique Eps(Na,Cl) à partir de valeurs de coefficients d'activité moyen, g±, tirées du "Handbook of electrolyte solutions" Pat A page 519-520 qui cite R.A. Robinson, H.S. Harned (Some aspects of the thermodynamics of strong electrolytes from electromotive force and vapor pressure measurements) Chem. Rev.28, 419 (1941)

y = lg(coeff d'activité) + D = eps(Na,Cl) m [S.I.T]

ye = yexpérimental yc = y calculé par régression linéaire de la SIT

	T=0°C					T=5°C					T=10°C				
m	D(T,I)	coeff.activ	ye	yc	(ye-yc)^2	D(T,I)	coeff.activ	yexp	yc	(ye-yc)^2	D(T,I)	coeff.activ	yexp	yc	(ye-yc)^2
0,1	0,1058	0,781	-1,60E-03	2,01E-03	1,30E-05	0,1063	0,781	-1,03E-03	2,43E-03	1,19E-05	0,1070	0,781	-3,88E-04	2,74E-03	9,76E-06
0,2	0,1321	0,731	-4,00E-03	4,03E-03	6,44E-05	0,1328	0,733	-2,12E-03	4,86E-03	4,87E-05	0,1335	0,734	-7,55E-04	5,47E-03	3,88E-05
0,5	0,1695	0,671	-3,73E-03	1,01E-02	1,90E-04	0,1704	0,675	-3,05E-04	1,21E-02	1,55E-04	0,1713	0,677	1,93E-03	1,37E-02	1,38E-04
1	0,1978	0,638	2,64E-03	2,01E-02	3,06E-04	0,1988	0,644	7,66E-03	2,43E-02	2,77E-04	0,1998	0,649	1,21E-02	2,74E-02	2,33E-04
1,5	0,2136	0,626	1,02E-02	3,02E-02	4,01E-04	0,2146	0,636	1,81E-02	3,64E-02	3,38E-04	0,2157	0,643	2,40E-02	4,10E-02	2,92E-04
2	0,2243	0,63	2,36E-02	4,03E-02	2,78E-04	0,2253	0,643	3,35E-02	4,86E-02	2,27E-04	0,2265	0,652	4,07E-02	5,47E-02	1,96E-04
2,5	0,2322	0,641	3,90E-02	5,03E-02	1,28E-04	0,2332	0,659	5,21E-02	6,07E-02	7,42E-05	0,2345	0,667	5,86E-02	6,84E-02	9,66E-05
[illegible]	0,2384	0,66	5,79E-02	6,04E-02	6,12E-06	0,2395	0,677	7,01E-02	7,29E-02	8,04E-06	0,2407	0,691	8,02E-02	8,21E-02	3,65E-06
3,5	[illegible]	0,687	8,04E-02	7,05E-02	9,86E-05	0,2445	0,706	9,34E-02	8,50E-02	6,90E-05	0,2458	0,721	1,04E-01	9,58E-02	6,33E-05
4	[illegible]	0,717	1,03E-01	8,05E-02	5,14E-04	0,2488	0,74	1,18E-01	9,72E-02	4,34E-04	0,2501	0,757	1,29E-01	1,09E-01	3,88E-04
écart type					1,41E-02					1,28E-02					1,21E-02

	T=15°C					T=20°C					T=25°C				
m	D(T,I)	coeff.activ	yexp	yc	(ye-yc)^2	D(T,I)	coeff.activ	yexp	yc	(ye-yc)^2	D(T,I)	coeff.activ	yexp	yc	(ye-yc)^2
0,1	0,1077	0,78	-2,46E-04	3,01E-03	1,06E-05	0,1084	0,779	-7,20E-05	3,30E-03	1,13E-05	0,1092	0,778	1,75E-04	3,42E-03	1,05E-05
0,2	0,1344	0,734	9,43E-05	6,03E-03	3,52E-05	0,1353	0,733	3,89E-04	6,59E-03	3,85E-05	0,1363	0,732	7,77E-04	6,84E-03	3,68E-05
0,5	0,1724	0,678	3,62E-03	1,51E-02	1,31E-04	0,1735	0,679	5,35E-03	1.65E-02	1,24E-04	0,1747	0,679	6,57E-03	1,71E-02	1,11E-04
1	0,2010	0,652	1,53E-02	3,01E-02	2,20E-04	0,2023	0,654	1,78E-02	3,30E-02	2,29E-04	0,2036	0,656	2,05E-02	3,42E-02	1,87E-04
1,5	0,2170	0,648	2,86E-02	4,52E-02	2,76E-04	0,2183	0,652	3,26E-02	4,95E-02	2,86E-04	0,2198	0,656	3,67E-02	5,13E-02	2,15E-04
2	0,2278	0,659	4,67E-02	6,03E-02	1,84E-04	0,2291	0,665	5,20E-02	6,59E-02	1,95E-04	0,2307	0,67	5,67E-02	6,84E-02	1.37E-04
2,5	0,2358	0,677	6,64E-02	7,53E-02	7,98E-05	0,2372	0,684	7,22E-02	8,24E-02	1,04E-04	0,2387	0,691	7,82E-02	8,55E-02	5,38E-05
3	0,2421	0,702	8,84E-02	9.04E-02	3,89E-06	0,2435	0,712	9,60E-02	9,89E-02	8,69E-06	0,2451	0,719	1,02E-01	1,03E-01	7,36E-07
3,5	0,2472	0,735	1,13E-01	1,05E-01	6,44E-05	0,2486	0,752	1,25E-01	1.15E-01	8,91E-05	0,2502	0,752	1,26E-01	1,20E-01	4,46E-05
4	0,2515	0,772	1,39E-01	1,21E-01	3,45E-04	0,2529	0,791	1,51E-01	1,32E-01	3,69E-04	0,2546	0,791	1,53E-01	1,37E-01	2,51E-04
écart type					1,16E-02					1,21E-02					1,02E-02

Fichier Eps(H,Na Cl)=f(T)
NaCl suite

	T=15°C					T=20°C					T=25°C				
m	D(T,I)	coeff.activ	yexp	yc	(ye-yc)^2	D(T,I)	coeff.activ	yexp	yc	(ye-yc)^2	D(T,I)	coeff.activ	yexp	yc	(ye-yc)^2
0,1	0,1077	0,78	-2,46E-04	3,01E-03	1,06E-05	0,1084	0,779	-7,20E-05	3,30E-03	1,13E-05	0,1092	0,778	1,75E-04	3,42E-03	1,05E-05
0,2	0,1344	0,734	9,43E-05	6,03E-03	3,52E-05	0,1353	0,733	3,89E-04	6,59E-03	3,85E-05	0,1363	0,732	7,77E-04	6,84E-03	3,68E-05
0,5	0,1724	0,678	3,62E-03	1,51E-02	1,31E-04	0,1735	0,679	5,35E-03	1,65E-02	1,24E-04	0,1747	0,679	6,57E-03	1,71E-02	1,11E-04
1	0,2010	0,652	1,53E-02	3,01E-02	2,20E-04	0,2023	0,654	1,78E-02	3,30E-02	2,29E-04	0,2036	0,656	2,05E-02	3,42E-02	1,87E-04
1,5	0,2170	0,648	2,86E-02	4,52E-02	2,76E-04	0,2183	0,652	3,26E-02	4,95E-02	2,86E-04	0,2198	0,656	3,67E-02	5,13E-02	2,15E-04
2	0,2278	0,659	4,67E-02	6,03E-02	1,84E-04	0,2291	0,665	5,20E-02	6,59E-02	1,95E-04	0,2307	0,67	5,67E-02	6,84E-02	1,37E-04
2,5	0,2358	0,677	6,64E-02	7,53E-02	7,98E-05	0,2372	0,684	7,22E-02	8,24E-02	1,04E-04	0,2387	0,691	7,82E-02	8,55E-02	5,38E-05
3	0,2421	0,702	8,84E-02	9,04E-02	3,89E-06	0,2435	0,712	9,60E-02	9,89E-02	8,69E-06	0,2451	0,719	1,02E-01	1,03E-01	7,36E-07
3,5	0,2472	0,735	1,13E-01	1,05E-01	6,44E-05	0,2486	0,752	1,25E-01	1,15E-01	8,91E-05	0,2502	0,752	1,26E-01	1,20E-01	4,46E-05
4	0,2515	0,772	1,39E-01	1,21E-01	3,45E-04	0,2529	0,791	1,51E-01	1,32E-01	3,69E-04	0,2546	0,791	1,53E-01	1,37E-01	2,51E-04
écart type					1,16E-02					1,21E-02					1,02E-02

	T=35°C					T=40°C					T=50°C				
m	D(T,I)	coeff.activ	yexp	yc	(ye-yc)^2	D(T,I)	coeff.activ	yexp	yc	(ye-yc)^2	D(T,I)	coeff.activ	yexp	yc	(ye-yc)^2
0,1	0,1110	0,776	8,35E-04	4,39E-07	6,97E-07	0,1119	0,774	6,75E-04	3,78E-03	9,61E-06	0,1140	0,77	4,72E-04	3,92E-03	1,19E-05
0,2	0,1384	0,73	1,75E-03	1,79E-06	3,07E-06	0,1396	0,728	1,73E-03	7,55E-03	3,38E-05	0,1421	0,725	2,43E-03	7,84E-03	2,93E-05
0,5	0,1774	0,679	9,24E-03	5,70E-06	8,53E-05	0,1788	0,678	1,01E-02	1,89E-02	7,79E-05	0,1819	0,675	1,12E-02	1,96E-02	7,05E-05
1	0,2067	0,657	2,42E-02	1,02E-05	5,87E-04	0,2083	0,657	2,59E-02	3,78E-02	1,41E-04	0,2118	0,656	2,87E-02	3,92E-02	1,10E-04
1,5	0,2230	0,66	4,25E-02	1,24E-05	1,81E-03	0,2247	0,661	4,49E-02	5,66E-02	1,37E-04	0,2285	0,662	4,93E-02	5,88E-02	9,03E-05
2	0,2340	0,676	6,40E-02	8,36E-06	4,09E-03	0,2358	0,678	6,71E-02	7,55E-02	7,15E-05	0,2397	0,678	7,09E-02	7,84E-02	5,64E-05
2,5	0,2422	0,697	8,54E-02	[illegible]	7,29E-03	0,2440	0,696	8,79E-02	9,44E-02	4,22E-05	0,2480	0,699	9,25E-02	9,80E-02	3,09E-05
3	0,2486	0,726	1,10E-01	2,96E-07	1,20E-02	0,2505	0,728	1,13E-01	1,13E-01	4,33E-07	0,2545	0,728	1,17E-01	1,18E-01	9,77E-07
3,5	0,2538	0,759	1,34E-01	2,54E-06	1,80E-02	0,2557	0,761	1,37E-01	1,32E-01	2,46E-05	0,2598	0,762	1,42E-01	1,37E-01	2,06E-05
4	0,2582	0,8	1,61E-01	1,60E-05	2,60E-02	0,2601	0,802	1,64E-01	1,51E-01	1,76E-04	0,2643	0,802	1,68E-01	1,57E-01	1,34E-04
écart type					8,36E-02					8,45E-03					7,45E-03

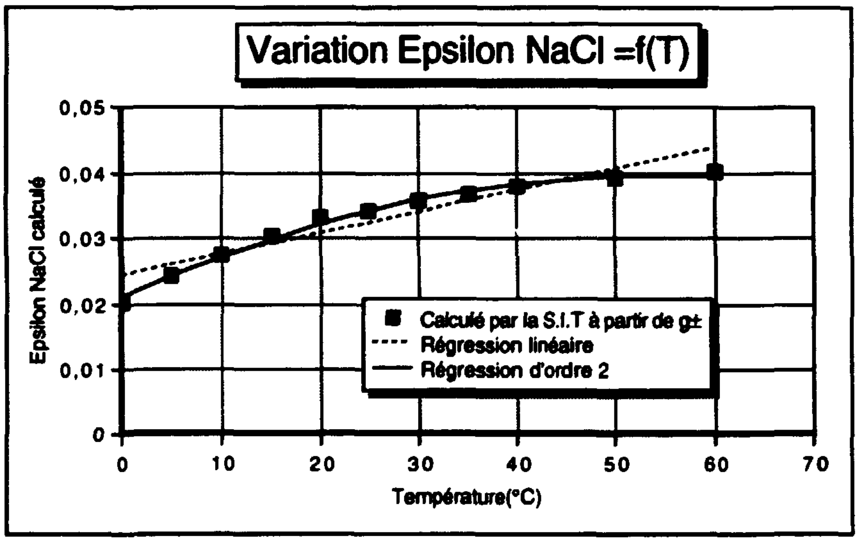
	T=30°C					T=60°C				
m	D(T,I)	coeff.activ	yexp	yc	(ye-yc)^2	D(T,I)	coeff.activ	yexp	yc	(ye-yc)^2
0,1	0,1101	0,777	4,73E-04	4,65E-07	2,23E-07	0,1162	0,766	4,41E-04	4,02E-03	1,28E-05
0,2	0,1373	0,731	1,23E-03	2,30E-06	1,50E-06	0,1448	0,721	2,75E-03	8,04E-03	2,80E-05
0,5	0,1760	0,679	7,85E-03	6,79E-06	6,15E-05	0,1853	0,671	1,20E-02	2,01E-02	6,58E-05
1	0,2051	0,657	2,27E-02	1,09E-05	5,13E-04	0,2156	0,654	3,12E-02	4,02E-02	8,10E-05
1,5	0,2213	0,658	3,95E-02	1,43E-05	1,56E-03	0,2325	0,659	5,14E-02	6,03E-02	7,95E-05
2	0,2323	0,674	6,09E-02	9,90E-06	3,71E-03	0,2429	0,676	7,38E-02	8,04E-02	4,33E-05
2,5	0,2404	0,695	8,24E-02	4,55E-06	6,78E-03	0,2523	0,696	9,49E-02	1,01E-01	3,13E-05
3	0,2468	0,724	1,06E-01	2,18E-07	1,13E-02	0,2589	0,726	1,20E-01	1,21E-01	5,95E-07
3,5	0,2519	0,756	1,30E-01	3,52E-06	1,70E-02	0,2643	0,76	1,45E-01	1,41E-01	1,92E-05
4	0,2563	0,797	1,58E-01	1,83E-05	2,49E-02	0,2688	0,799	1,71E-01	1,61E-01	1,10E-04
écart type					8,12E-02					6,87E-03

Fichier Eps(H,Na Cl)=f(T)
HCl suite

T	Eps(Na,Cl)
0	0,0201
5	0,0243
10	0,0274
15	0,0301
20	0,0330
25	0,0342
30	0,0357
35	0,0368
40	0,0378
50	0,0392
60	0,0402

Régression linéaire
Epsilon NaCl =0,0323+3,22E-4 *(T-T°)

Régression d'ordre 2
Epsilon NaCl =0,0341+7,07E-3,74E-04 *(T-T°)-6,19*(T-T°)^2



Fichier gHCl

Calcul de Gex(I,T)= R*T*ln(g±)=f(I,T)
Pour les valeurs de coefficients d'activité moyen, g±, cf Fichier Eps(H,NaCl)=f(T)

T/m	0,0001	0,0002	0,0005	0,0010	0,0020	0,01	0,01	0,02	0,05
0	-25,12	-34,78	-56,10	-76,68	-106,71	-164,07	-222,93	-297,03	-410,60
5	-26,51	-35,66	-57,13	-79,52	-109,14	-167,82	-229,31	-304,04	-418,67
10	-26,04	-36,54	-58,15	-79,97	-109,87	-170,84	-233,69	-308,17	-427,89
15	-26,50	-37,67	-58,93	-82,62	-115,33	-174,63	-237,81	-314,43	-438,03
20	-26,47	-38,32	-59,46	-84,06	-118,10	-178,45	-242,75	-320,44	-449,14
25	-27,17	-39,48	-62,25	-86,77	-121,67	-183,89	-247,98	-329,58	-460,68
30	-27,88	-41,93	-64,59	-89,79	-125,30	-189,69	-256,05	-339,14	-474,18
35	-29,37	-41,84	-66,18	-92,07	-127,91	-194,75	-262,82	-347,67	-488,20
40	-30,11	-43,85	-68,32	-94,65	-132,17	-198,76	-269,68	-358,09	-502,11
45	-30,33	-44,01	-69,41	-95,88	-134,56	-203,07	-276,34	-367,15	-514,62
50	-32,71	-45,79	-71,33	-98,78	-137,81	-209,46	-283,07	-377,24	-529,57
55	-33,21	-45,95	-73,27	-101,16	-140,80	-215,65	-290,48	-386,22	-543,09
60	-33,72	-47,21	-74,67	-103,85	-144,70	-220,43	-295,83	-396,58	-560,50

T/m	0,10	0,20	0,50	1,00	1,50	2,00	3,00	4,00
0	-499,10	-577,09	-575,63	-390,82	-127,99	170,57	846,94	1580,92
5	-509,39	-587,66	-595,42	-413,41	-151,72	152,14	822,28	1556,21
10	-520,60	-603,08	-617,12	-440,06	-178,45	121,57	793,77	1524,58
15	-534,58	-620,86	-639,25	-466,97	-211,76	91,66	759,43	1489,28
20	-548,43	-638,91	-663,75	-495,00	-239,25	57,80	722,39	1448,78
25	-564,31	-658,52	-689,76	-525,40	-271,66	22,21	680,68	1404,13
30	-581,38	-681,76	-716,35	-556,74	-308,19	-17,96		
35	-598,08	-701,75	-744,90	-590,33	-345,03	-63,55		
40	-616,68	-725,15	-772,70	-625,27	-392,37	-105,74		
45	-632,90	-747,58	-801,10	-660,60	-424,59	-140,97		
50	-650,37	-770,04	-829,38	-703,25	-467,15	-187,18		
55	-667,74	-794,34	-861,60	-738,70	-516,25	-231,64		
60	-683,58	-820,19	-895,70	-781,72	-557,11	-269,76		

Fichier gHCl suite

Comparaison entre G(I,T°), -S(I,T°) et-Cp(I,T°)/2T° "expérimentaux", obtenus per régression d'ordre 2 en (T-T°) sur RTlng± à I= cte selon:
RTlng±(I,T) = a +b*(T-T°)+c*(T-T°)^2
a(I) = Gex(I,T°)
b(I) = -Sex(I,T°)
c(I) = -Cpex(I,T°)/2T°

et les valeurs calculées à partir de D(I,T°) et eps(T°) et leurs dérivées successsives
D G(I,T°)/F = r(D(I,T°)+T°D'(I,T°)-m(De(T°)+T°De'(T°)))
D S(I,T°)/F = RT°ln(10)(D(I,T°)-me(T°))
D Cp(I,T°)/2T°F = r(D'(I,T°)+T°D"(I,T°)/2)- m(De'(T°)+T°e"(T°)/2))
r=R*ln10*1000/F

Pour les valeurs de D, eps et leurs dérivées cf les fichiers précédents
D=f(T) et Eps(H,Na Cl) =f(T)

Une première comparaison est faite en ne prenant en compte
que De' et D' : les modèles qui s'y réfèrent sont notés Reg1

Une deuxième comparaison est faite en prenant en compte
De', De", D' et D" : les modèles qui s'y réfèrent sont notés Reg2

Fichier gHCl suite

		Reg 1	**Reg 2**
(De)(T°)	0,12185		
(De)'(T°)		-4,82E-04	-5,36E-04
(De)"(T°)/2			-2,15E-06

m	**D(I,25°C)**	**D'(I,25°C**	**Gexp**	**Gcalc**	**Sexp**	**Scalc**	**(Cp/2T°)exp**	**(Cp/2T°)cal**
0,0001	0,0050	9,50E-06	27,52	28,56	0,13	0,15	1,87E-03	1,83E-04
0,0002	0,0071	1,33E-05	39,98	40,10	0,22	0,21	-1,63E-04	2,57E-04
0,0005	0,0110	2,08E-05	62,46	62,52	0,31	0,33	1,54E-03	4,02E-04
0,001	0,0154	2,89E-05	87,05	87,03	0,44	0,46	1,10E-03	5,62E-04
0,002	0,0213	3,99E-05	121,53	120,39	0,64	0,64	4,93E-04	7,82E-04
0,005	0,0325	6,03E-05	184,05	182,29	0,91	0,97	3,98E-03	1,20E-03
0,01	0,0443	8,12E-05	249,83	245,72	1,19	1,32	4,87E-03	1,65E-03
0,02	0,0594	1,08E-04	330,44	325,11	1,59	1,76	9,54E-03	2,24E-03
0,05	0,0852	1,51E-04	461,71	451,78	2,40	2,52	1,22E-02	3,35E-03
0,1	0,1092	1,89E-04	565,62	553,71	3,05	3,21	1,14E-02	4,55E-03
0,2	0,1363	2,31E-04	659,70	638,67	3,93	4,01	1,95E-02	6,27E-03
0,5	0,1747	2,86E-04	689,81	649,37	5,13	5,19	2,09E-02	1,01E-02
1	0,2036	3,24E-04	525,24	466,83	6,19	6,17	3,23E-02	1,54E-02
1,5	0,2198	3,44E-04	274,11	211,17	6,84	6,80	3,76E-02	2,04E-02
2	0,2307	3,58E-04	-17,98	-74,40	7,26	7,30	3,34E-02	2,53E-02
3	0,2451	3,75E-04	-680,57	-687,65	8,79	8,09	8,53E-02	3,49E-02
4	0,2546	3,86E-04	-1403,92	-1329,03	9,51	8,76	9,66E-02	4,43E-02

m	**D(I,25°C)**	**D'(I,T°)**	**D"(I,T°)/2**	**Sexp**	**Scalc**	**(Cp/2T°)e**	**(Cp/2T°)calc**
0,0001	0,0050	8,78E-06	3,64E-08	0,13	0,1461876	1,87E-03	2,94E-04
0,0002	0,0071	1,23E-05	5,10E-08	0,22	0,2054113	-1,63E-04	4,14E-04
0,0005	0,0110	1,92E-05	7,94E-08	0,31	0,3206976	1,54E-03	6,48E-04
0,001	0,0154	2,67E-05	1,10E-07	0,44	0,4472046	1,10E-03	9,08E-04
0,002	0,0213	3,68E-05	1,52E-07	0,64	0,6202265	4,93E-04	1,27E-03
0,005	0,0325	5,57E-05	2,30E-07	0,91	0,9446048	3,98E-03	1,96E-03
0,01	0,0443	7,50E-05	3,09E-07	1,19	1,2830218	4,87E-03	2,71E-03
0,02	0,0594	9,94E-05	4,09E-07	1,59	1,7190748	9,54E-03	3,73E-03
0,05	0,0852	1,40E-04	5,72E-07	2,40	2,4650765	1,22E-02	5,73E-03
0,1	0,1092	1,75E-04	7,16E-07	3,05	3,1629106	1,14E-02	8,02E-03
0,2	0,1363	2,13E-04	8,70E-07	3,93	3,9722856	1,95E-02	1,15E-02
0,5	0,1747	2,64E-04	1,07E-06	5,13	5,2161041	2,09E-02	1,99E-02
1	0,2036	3,00E-04	1,22E-06	6,19	6,3366398	3,23E-02	3,23E-02
1,5	0,2198	3,19E-04	1,29E-06	6,84	7,1162756	3,76E-02	4,42E-02
2	0,2307	3,31E-04	1,34E-06	7,26	7,7584263	3,34E-02	5,59E-02
3	0,2451	3,47E-04	1,40E-06	8,79	8,8511251	8,53E-02	7,89E-02
4	0,2546	3,57E-04	1,44E-06	9,51	9,8169167	9,66E-02	1,02E-01

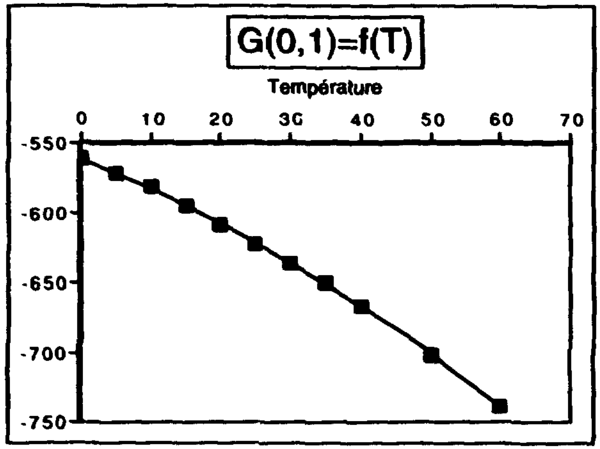
Fichier gNaCl=f(T)

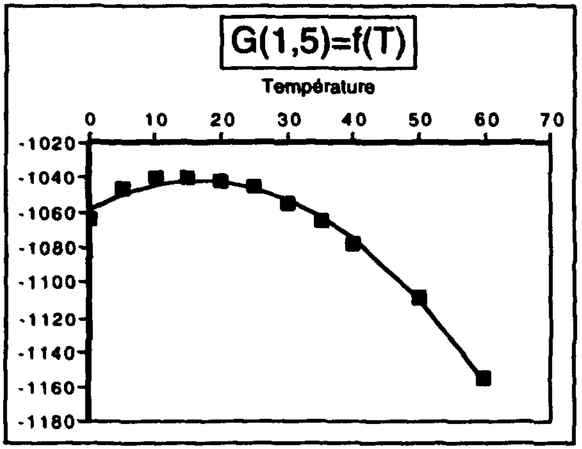
Calcul de Gex(I,T)= R*T*ln(g±)=f(I,T)
Pour les valeurs de coefficients d'activité moyen, cf Eps(H,Na Cl) =f(T)

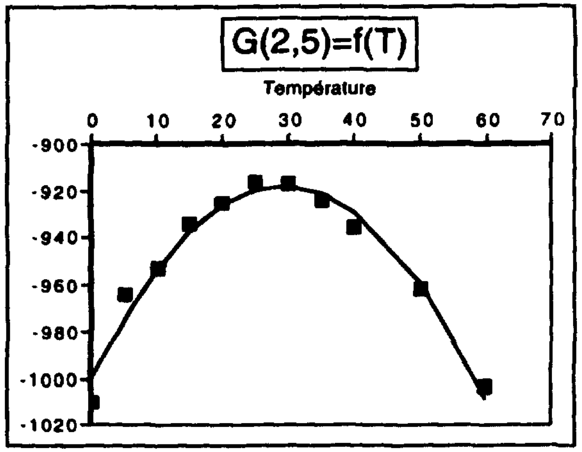
m/T	0	5	10	15	20	25	30	35	40	50	60
0,1	-561,34	-571,61	-581,89	-595,23	-608,69	-622,25	-635,93	-649,72	-666,98	-702,20	-738,36
0,2	-711,59	-718,30	-728,00	-740,85	-757,03	-773,33	-789,74	-806,28	-826,50	-863,99	-906,05
0,5	-906,09	-908,93	-918,30	-930,98	-943,54	-959,64	-975,73	-991,82	-1011,75	-1055,98	-1105,12
1	-1020,61	-1017,65	-1017,73	-1024,66	-1034,97	-1045,06	-1058,74	-1076,21	-1093,67	-1132,68	-1176,19
1,5	-1063,73	-1046,56	-1039,60	-1039,40	-1042,44	-1045,06	-1054,91	-1064,53	-1077,86	-1108,22	-1155,10
2	-1049,27	-1021,24	-1006,88	-999,07	-994,32	-992,71	-994,36	-1003,17	-1011,75	-1044,06	-1084,55
2,5	-1009,96	-964,40	-953,33	-934,52	-925,66	-916,21	-917,03	-924,79	-936,06	-962,11	-1003,79
3	-943,62	-902,08	-870,12	-847,64	-827,88	-817,75	-813,99	-820,35	-826,50	-852,89	-886,91
3,5	-852,57	-805,09	-770,07	-737,59	-694,66	-706,51	-704,99	-706,47	-711,08	-730,26	-760,14
4	-755,50	-696,32	-655,37	-619,93	-571,43	-581,18	-571,88	-571,68	-574,46	-592,80	-621,53

Régression d'ordre 2 en (T-T°) sur RTlng± à I= cte selon
RTlng±(I,T) = a +b*(T-T°)+c*(T-T°)^2
a(I) = Gex(I,T°)
b(I) = -Sex(I,T°)
c(I) = -Cpex(I,T°)/2T°

Quelques exemples de comparaisons entre points expérimentaux et courbe ajustées







Fichier gNaCl suite

Comparaison entre G(I,T°), -S(I,T°) et-Cp(I,T°)/2T° expérimentaux
(régression sur RTlng(I,T) d'ordre 2 en T-T° cf page précédente pour calculs et figures)
et les valeurs calculées à partir de D(I,T°) eps(T°) et leur dérivées
(Régression d'ordre 1ou 2 sur eps(T) et D(I,T) cf les fichiers D=f(T) et Eps(H,Na Cl)=f(T))

D S(I,T°)/F = r(D(I,T°)+T°D'(I,T°)-m(De(T°)+T°De'(T°)))
D G(I,T°)/F = RT°ln(10)(D(I,T°)-me(T°))
D Cp(I,T°)/2T°F = r(D'(I,T°)+T°D"(I,T°)/2)- m(De'(T°)+T°e"(T°)/2))
r=R*ln10*1000/F

Modèle Reg1

eps(T°)
0,03422
eps'(T°)
3,22E-04

D(I,25°C)	D'(I,25°C)	m	Gexp	Gcalc	-Sexp	-Scalc	(-Cp/2T°)exp	(-Cp/2T°)calc
0	0	0						0
0,1092	1,89E-04	0,1	-621,53	-603,72	-2,80	-2,92	-0,0155	-0,0030
0,1363	2,31E-04	0,2	-772,65	-738,70	-3,11	-3,43	-0,0212	-0,0032
0,1747	2,86E-04	0,5	-958,45	-899,45	-3,04	-3,73	-0,0334	-0,0024
0,2036	3,24E-04	1	-1046,31	-967,00	-2,29	-3,26	-0,0432	-0,0000
0,2198	3,44E-04	1,5	-1046,02	-961,42	-1,04	-2,44	-0,0603	0,0026
0,2307	3,58E-04	2	-992,86	-925,93	0,03	-1,48	-0,0784	0,0055
0,2387	3,67E-04	2,5	-919,94	-874,36	0,80	-0,44	-0,0953	0,0084
0,2451	3,75E-04	3	-821,80	-812,85	1,81	0,64	-0,1111	0,0113
0,2502	3,81E-04	3,5	-707,87	-744,64	2,38	1,75	-0,1199	0,0143
0,2546	3,86E-04	4	-580,02	-671,63	3,16	2,89	-0,1341	0,0172

Modèle Reg2

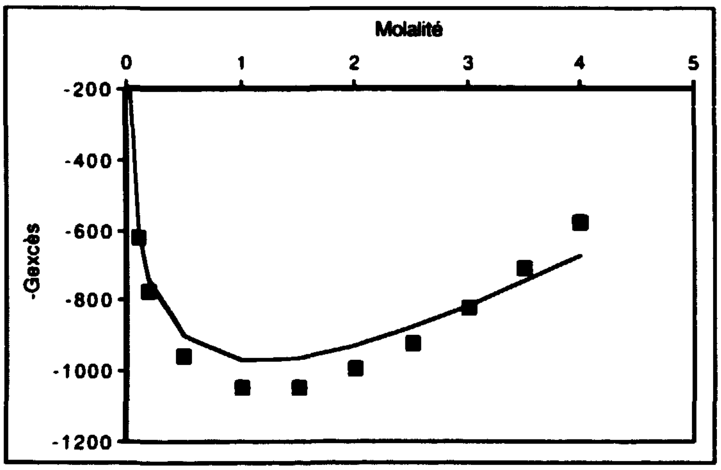
eps(T°)
0,03422
eps'(T°)
3,74E-04
eps"(T°)/2
-6,20E-06

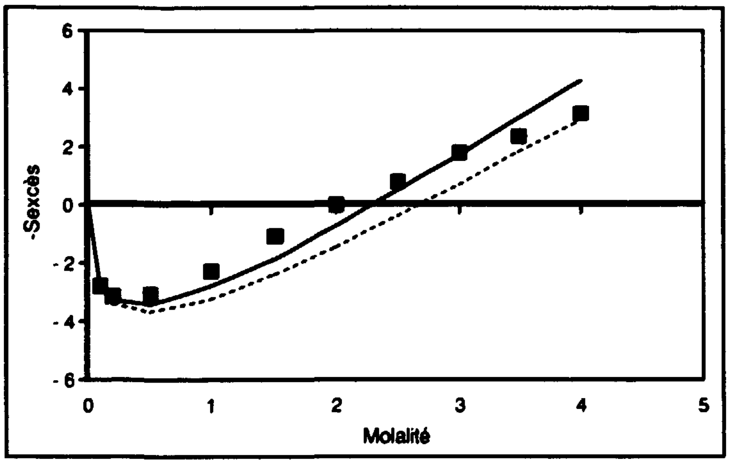
D(I,25°C)	D'(I,25°C)	D"(I,25°C)/2	m	Gexp	Gcalc	-Sexp	-Scalc	(-Cp/2T°)exp	(-Cp/2T°)calc
0	0	0	0		0,00		0,00		0,0000
0,1092	1,75E-04	7,16E-07	0,1	-621,53	-603,72	-2,80	-2,81	-0,0155	-0,0103
0,1363	2,13E-04	8,70E-07	0,2	-772,65	-738,70	-3,11	-3,27	-0,0212	-0,0147
0,1747	2,64E-04	1,07E-06	0,5	-958,45	-899,45	-3,04	-3,46	-0,0334	-0,0253
0,2036	3,00E-04	1,22E-06	1	-1046,31	-967,00	-2,29	-2,82	-0,0432	-0,0409
0,2198	3,19E-04	1,29E-06	1,5	-1046,02	-961,42	-1,04	-1,84	-0,0603	-0,0558
0,2307	3,31E-04	1,34E-06	2	-992,86	-925,93	0,03	-0,72	-0,0784	-0,0704
0,2387	3,40E-04	1,38E-06	2,5	-919,94	-874,36	0,80	0,47	-0,0953	-0,0848
0,2451	3,47E-04	1,40E-06	3	-821,80	-812,85	1,81	1,71	-0,1111	-0,0992
0,2502	3,52E-04	1,43E-06	3,5	-707,87	-744,64	2,38	2,97	-0,1199	-0,1136
0,2546	3,57E-04	1,44E-06	4	-580,02	-671,63	3,16	4,26	-0,1341	-0,1279

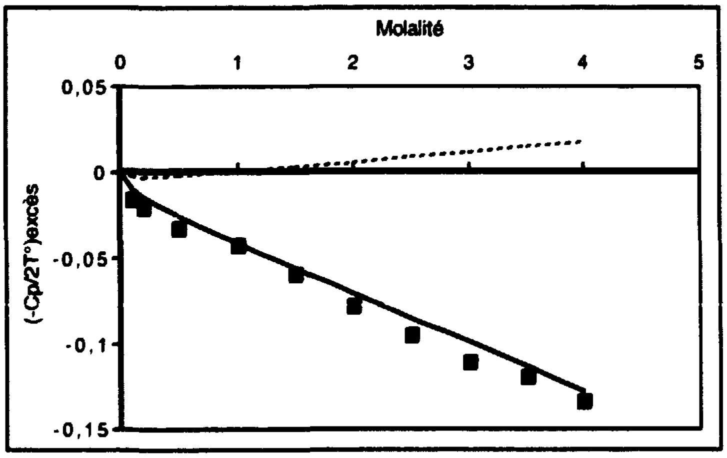
Fichier gNaCl suite

Illustration des 2 tableaux précédents

Comparaison sur S et Cp entre les modèles prenant en compte l'ordre 2 (trait plein) ou l'ordre 1 (pointillés)sur epsilon et D







Fichier RefAgCl(I,T)
Calcul du potentiel de l'électrode de référence pour toute force ionique et température
dans le cas du couple 6/5 : Milieu NaClO4, NaCl
et celui du couple 4/3 : Milieu NaClO4, HClO4, NaCl

Eps(H,Cl) = f(T) et Eps(Na,Cl) = f(T) = Résultats du fichier Eps(H,Na Cl)=f(T)

E(T,I) = E(T,0) -A(T) [lg mCl- - D(T,I) +Eps(Na,Cl) mNa+ + Eps(H,Cl) mH+] [SIT]
E(T,0) est tabulé sous la forme d'un polynôme par Bard et col.

			Milieu NaClO4 où NaCl = 0,02mol/kg **Utilisation de la S.I.T et de eNaCl =f(T)**					**Milieu NaClO4, HClO4 où NaCl = 0,02mol/kg** **Utilisation de la S.I.T de eNaCl et eHCl =f(T)**			
T	**A**	**E(T,0)**	**e(Na,Cl)**	**E(T,0,5)**	**E(T,1)**	**E(T,2)**	**E(T,3)**	**e(H,Cl)**	**E(T,1)**	**E(T,2)**	**E(T,3)**
5	55,19	234,44	0,0241	336,93	337,82	337,82	336,96	0,1317	329,98	328,11	326,04
10	56,18	231,75	0,0271	336,11	336,94	336,76	335,68	0,1294	329,25	327,17	324,87
10,5	56,28	231,47	0,0274	336,01	336,84	336,64	335,54	0,1291	329,17	327,06	324,74
15	57,18	228,88	0,0298	335,06	335,84	335,49	334,20	0,1270	328,31	326,03	323,51
20	58,17	225,82	0,0321	333,84	334,57	334,06	332,58	0,1245	327,20	324,74	322,02
21	58,37	225,19	0,0325	333,58	334,29	333,76	332,24	0,1239	326,96	324,46	321,70
25	59,16	222,58	0,0341	332,45	333,14	332,49	330,84	0,1218	325,92	323,30	320,39
26	59,36	221,91	0,0345	332,16	332,83	332,16	330,47	0,1213	325,65	322,99	320,05
30	60,15	219,14	0,0358	330,89	331,53	330,77	328,96	0,1191	324,47	321,69	318,62
31	60,35	218,43	0,0361	330,55	331,19	330,41	328,56	0,1185	324,16	321,35	318,25
35	61,14	215,51	0,0372	329,14	329,76	328,90	326,95	0,1162	322,84	319,94	316,72
36	61,34	214,76	0,0375	328,77	329,39	328,50	326,53	0,1157	322,50	319,56	316,32
40	62,14	211,68	0,0383	327,20	327,81	326,86	324,80	0,1133	321,03	318,01	314,67
40,5	62,24	211,28	0,0384	327,00	327,61	326,65	324,58	0,1130	320,84	317,81	314,46
41	62,33	210,88	0,0385	326,79	327,40	326,44	324,36	0,1127	320,65	317,61	314,24
42	62,53	210,08	0,0387	326,37	326,98	326,01	323,91	0,1121	320,26	317,20	313,81
44	62,93	208,46	0,0390	325,52	326,12	325,12	322,99	0,1109	319,45	316,35	312,93
45	63,13	207,63	0,0391	325,07	325,68	324,67	322,52	0,1102	319,03	315,92	312,48
48	63,72	205,11	0,0395	323,71	324,32	323,28	321,09	0,1084	317,75	314,59	311,09
50	64,12	203,38	0,0396	322,76	323,37	322,32	320,10	0,1071	316,85	313,66	310,14
54	64,91	199,83	0,0398	320,76	321,38	320,32	318,07	0,1045	314,96	311,74	308,16
55	65,11	198,92	0,0398	320,24	320,87	319,81	317,55	0,1038	314,47	311,24	307,66
60	66,10	194,23	0,0396	317,52	318,18	317,13	314,85	0,1004	311,89	308,63	305,02
61	66,30	193,27	0,0396	316,95	317,62	316,57	314,30	0,0997	311,35	308,09	304,48
64	66,90	190,32	0,0393	315,20	315,90	314,87	312,60	0,0976	309,69	306,42	302,81
65	67,10	189,32	0,0392	314,60	315,30	314,28	312,02	0,0969	309,12	305,85	302,24

Fichier E6/5

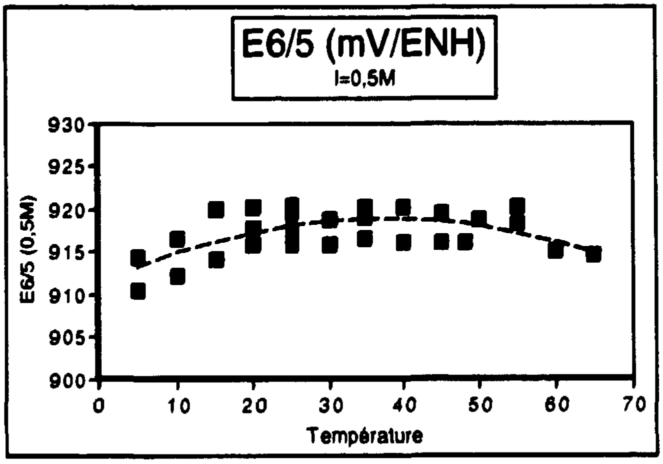
Détermination des entropies, des capacités calorifiques
directement sur le potentiel E6/5 /ENH à différentes force ioniques

(pour le calcul de ERef(T,I) cf fichier RefAgCl(T,I); E1/2 = potentiel mesuré /AgAgCl)

EO/R= E1/2 + Eref

T	T-T0	(T-T0)^2	E1/2(0,5)	ERef(T,0,5)	EO/R(0,5)	Ecalculé
5	-20	400	577,5	336,93	914,43	913,17
5	-20	400	573,5	336,93	910,43	913,17
10	-15	225	576	336,11	912,11	914,77
10	-15	225	580,5	336,11	916,61	914,77
15	-10	100	585	335,06	920,06	916,10
15	-10	100	579	335,06	914,06	916,10
20	-5	25	584	333,84	917,84	917,17
20	-5	25	586,5	333,84	920,34	917,17
20	-5	25	582	333,84	915,84	917,17
25	0	0	585	332,45	917,45	917,97
25	0	0	588	332,45	920,45	917,97
25	0	0	587	332,45	919,45	917,97
25	0	0	583,5	332,45	915,95	917,97
30	5	25	588	330,89	918,89	918,50
30	5	25	585	330,89	915,89	918,50
35	10	100	587,5	329,14	916,64	918,77
35	10	100	590	329,14	919,14	918,77
35	10	100	591	329,14	920,14	918,77
40	15	225	593	327,20	920,20	918,77
40	15	225	589	327,20	916,20	918,77
45	20	400	594,5	325,07	919,57	918,51
45	20	400	591	325,07	916,07	918,51
48	23	529	592,5	323,71	916,21	918,22
50	25	625	596	322,76	918,76	917,98
55	30	900	598	320,24	918,24	917,19
55	30	900	600	320,24	920,24	917,19
60	35	1225	597,5	317,52	915,02	916,13
65	40	1600	600	314,60	914,60	914,80

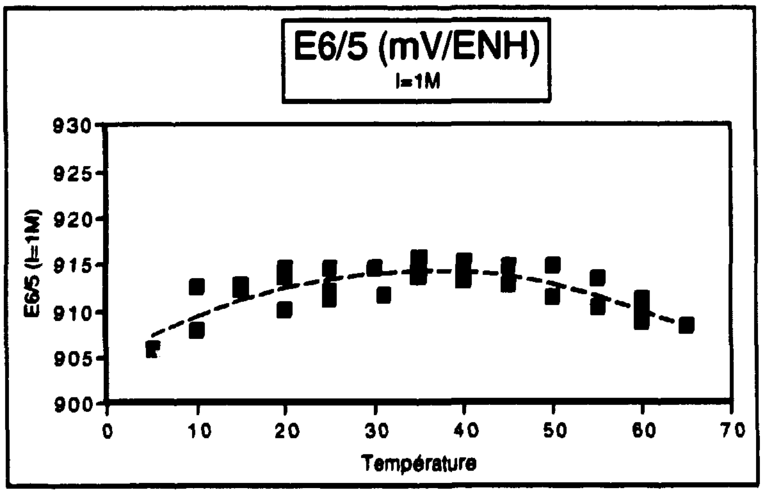
Sortie régression polynomiale d'ordre 2:		
Constante		**918,0**
R au carré		0,41
Nombre d'observations		28
Degrés de liberté		25
Coefficient(s) X	**0,133**	-5,31E-03
Ecart type de coef.	3,39E-02	1,41E-03



Fichier E6/5 suite

T	T-T0	(T-T0)^2	E1/2(1M)	ERef(T,1)	EO/R(1M)	Ecalculé
5	-20	400	568	337,82	905,82	907,18
5	-20	400	568	337,82	905,82	907,18
10	-15	225	575,5	336,94	912,44	909,25
10	-15	225	571	336,94	907,94	909,25
15	-10	100	576,5	335,84	912,34	910,96
15	-10	100	577	335,84	912,84	910,96
20	-5	25	580	334,57	914,57	912,31
20	-5	25	575,5	334,57	910,07	912,31
20	-5	25	579	334,57	913,57	912,31
25	0	0	578	333,14	911,14	913,29
25	0	0	581,5	333,14	914,64	913,29
25	0	0	578	333,14	911,14	913,29
25	0	0	579	333,14	912,14	913,29
30	5	25	583	331,53	914,53	913,90
31	6	36	580,5	331,19	911,69	913,98
35	10	100	586	329,76	915,76	914,16
35	10	100	585	329,76	914,76	914,16
35	10	100	584	329,76	913,76	914,16
40	15	225	587,5	327,81	915,31	914,04
40	15	225	585,5	327,81	913,31	914,04
45	20	400	589	325,68	914,68	913,56
45	20	400	587	325,68	912,68	913,56
50	25	625	591,5	323,37	914,87	912,72
50	25	625	588	323,37	911,37	912,72
50	25	625	588	323,37	911,37	912,72
55	30	900	592,5	320,87	913,37	911,52
55	30	900	589,5	320,87	910,37	911,52
55	30	900	589,5	320,87	910,37	911,52
60	35	1225	593	318,18	911,18	909,94
60	35	1225	590,5	318,18	908,68	909,94
60	35	1225	592	318,18	910,18	909,94
65	40	1600	593	315,30	908,30	908,01

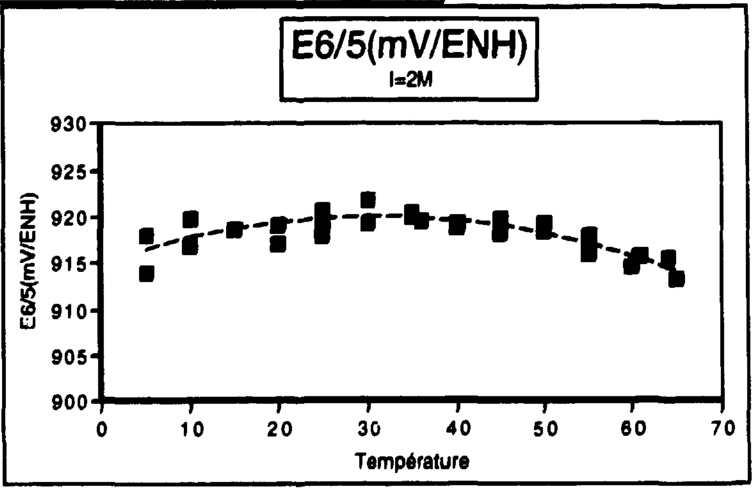
Sortie régression polynomiale d'ordre 2:		
Constante		**913,3**
R au carré		0,64
Nombre d'observations		32
Degrés de liberté		29
Coefficient(s) X	**1,60E-01**	**-7,29E-03**
Ecart type de coef.	2,58E-02	1,02E-03



Fichier E6/5 suite

T	T-T0	(T-T0)^2	E1/2(2M)	ERef(T,2)	E0/R(2M)	Ecalcul
5	-20	400	580	337,82	917,82	916,44
5	-20	400	576	337,82	913,82	916,44
10	-15	225	583	336,76	919,76	917,64
10	-15	225	580	336,76	916,76	917,64
10	-15	225	583	336,76	919,76	917,64
15	-10	100	583	335,49	918,49	918,58
15	-10	100	583	335,49	918,49	918,58
20	-5	25	583	334,06	917,06	919,27
20	-5	25	585	334,06	919,06	919,27
20	-5	25	585	334,06	919,06	919,27
25	0	0	588	332,49	920,49	919,71
25	0	0	585,5	332,49	917,99	919,71
25	0	0	587	332,49	919,49	919,71
30	5	25	591	330,77	921,77	919,90
30	5	25	588,5	330,77	919,27	919,90
35	10	100	591	328,90	919,90	919,82
35	10	100	591,5	328,90	920,40	919,82
36	11	121	591	328,50	919,50	919,78
40	15	225	592	326,86	918,86	919,50
40	15	225	592,5	326,86	919,36	919,50
45	20	400	593,5	324,67	918,17	918,92
45	20	400	595	324,67	919,67	918,92
45	20	400	595	324,67	919,67	918,92
50	25	625	596	322,32	918,32	918,09
50	25	625	597	322,32	919,32	918,09
55	30	900	596	319,81	915,81	917,00
55	30	900	597	319,81	916,81	917,00
55	30	900	598	319,81	917,81	917,00
60	35	1225	597,5	317,13	914,63	915,66
61	36	1296	599	316,57	915,57	915,36
64	39	1521	600,5	314,87	915,37	914,40
65	40	1600	599	314,28	913,28	914,06

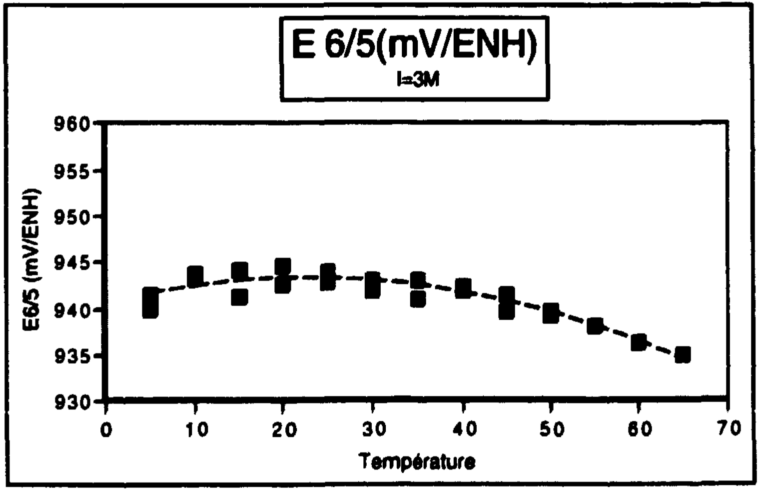
Sortie régression polynomiale d'ordre 2:		
Constante		**919,7**
R au carré		0,68
Nombre d'observations		32
Degrés de liberté		29
Coefficient(s) X	**0,06**	-5,08E-03
Ecart type de coef.	1,78E-02	7,02E-04



Fichier E6/5 suite

T	T-T0	(T-T0)^2	E1/2(3M)	ERef(T,3)	EO/R(3M)	Ecalculé
5	-20	400	604,5	336,96	941,46	941,66
5	-20	400	603	336,96	939,96	941,66
10	-15	225	608	335,68	943,68	942,40
10	-15	225	607,5	335,68	943,18	942,40
15	-10	100	610	334,20	944,20	942,90
15	-10	100	607	334,20	941,20	942,90
20	-5	25	612	332,58	944,58	943,15
20	-5	25	610	332,58	942,58	943,15
25	0	0	613	330,84	943,84	943,16
25	0	0	612	330,84	942,84	943,16
25	0	0	613	330,84	943,84	943,16
30	5	25	613	328,96	941,96	942,92
30	5	25	614	328,96	942,96	942,92
35	10	100	616	326,95	942,95	942,45
35	10	100	614,5	326,53	941,03	942,45
40	15	225	617	324,80	941,80	941,73
40	15	225	617,5	324,80	942,30	941,73
45	20	400	617	322,52	939,52	940,76
45	20	400	619	322,52	941,52	940,76
50	25	625	619,5	320,10	939,60	939,56
50	25	625	619	320,10	939,10	939,56
55	30	900	620,5	317,55	938,05	938,11
60	35	1225	621,5	314,85	936,35	936,42
65	40	1600	623	312,02	935,02	934,48

Sortie régression polynomiale d'ordre 2:		
Constante		943,2
R au carré		0,86
Nombre d'observations		24
Degrés de liberté		21
Coefficient(s) X	-0,02	-4,86E-03
Ecart type de coef.	1,59E-02	6,73E-04



Fichier E6/5 suite

T	T-T0	T-T0^2	EO/R(0M)	Ec(1)	Ec(2)	Delta eps	Deltaeps(1)	Deltaeps(2)
5	-20	400	927,90	932,52	928,79	0,2551	0,2471	0,2538
10	-15	225	931,49	933,54	931,68	0,2488	0,2409	0,2443
15	-10	100	935,80	934,56	934,23	0,2269	0,2347	0,2353
20	-5	25	936,91	935,59	936,44	0,2253	0,2285	0,2270
25	0	0	938,30	936,61	938,31	0,2195	0,2223	0,2193
30	5	25	938,78	937,64	939,84	0,2189	0,2161	0,2121
35	10	100	941,88	938,66	941,03	0,1968	0,2099	0,2056
40	15	225	941,51	939,69	941,89	0,2053	0,2037	0,1997
45	20	400	941,99	940,71	942,40	0,1962	0,1975	0,1944
50	25	625	941,03	941,73	942,58	0,2035	0,1913	0,1897
55	30	900	944,67	942,76	942,42	0,1639	0,1851	0,1857
60	35	1225	940,82	943,78	941,92	0,1869	0,1789	0,1822
65	40	1600	941,53	944,81	941,08	0,1814	0,1726	0,1793

Régression d'ordre 2 sur E(0)

Constante		**938,31**
R au carré		0,94462905
Nombre d'observations		13
Degrés de liberté		10
Coefficient(s) X	**0,340**	**-6,77E-03**
Ecart type de coef.	0,02802024	1,08E-03

Régression linéaire sur E(0)

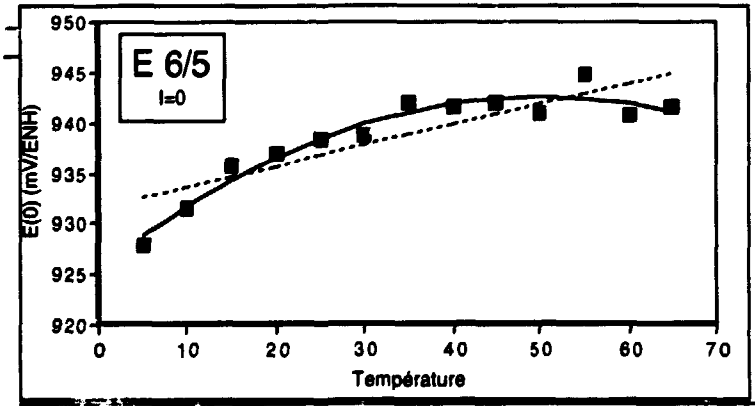
Constante		**936,61**
R au carré		0,72642079
Nombre d'observations		13
Degrés de liberté		11
Coefficient(s) X	0,205	
Ecart type de coef.	0,03790448	

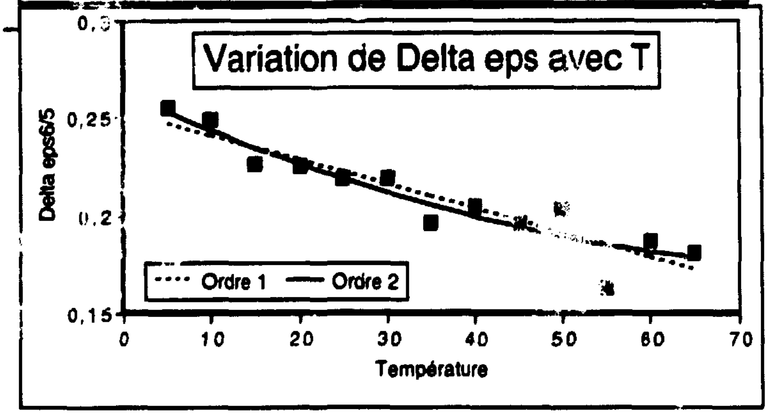
Régression linéaire sur Delta eps

Constante		**0,2223**
R au carré		0,86158295
Nombre d'observations		13
Degrés de liberté		11
Coefficient(s) X	-1,24E-03	
Ecart type de coef.	1,50E-04	

Régression d'ordre 2 sur Delta eps

Constante		**0,2193**
R au carré		0,88431854
Nombre d'observations		13
Degrés de liberté		10
Coefficient(s) X	**-1,48E-03**	**1,22E-05**
Ecart type de coef.	0,00022535	8,67E-06





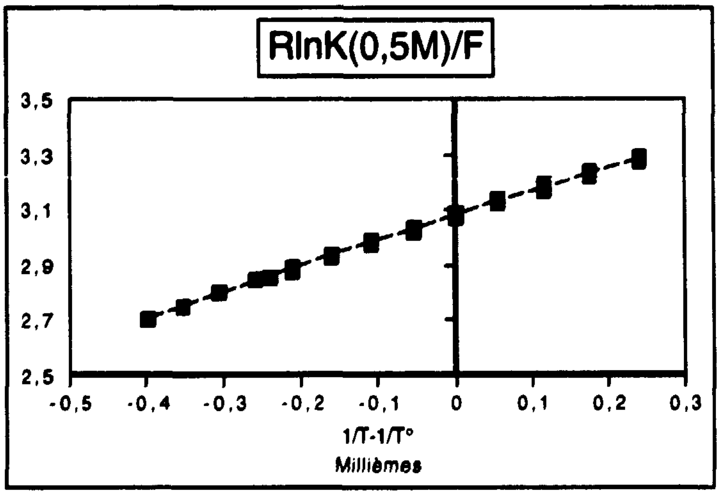
Détermination des enthalpies par développement d'ordre 2
en (1/T-1/T°) sur RlnK/F=E/T

Terme d'ordre 1	-DH(I,T°)/F
Terme d'ordre 2	DCp(I,T°)T°^2/2F
1/T0	0,003354

T	1/T-1/T0	(1/T-1/T0)^2	EO/R(0,5M)	RlnKexp/F	RlnKcal/F
5	2,41E-04	5,82E-08	914,43	3,288	3,282
5	2,41E-04	5,82E-08	910,43	3,273	3,282
10	1,78E-04	3,16E-08	912,11	3,221	3,231
10	1,78E-04	3,16E-08	916,61	3,237	3,231
15	1,16E-04	1,35E-08	920,06	3,193	3,179
15	1,16E-04	1,35E-08	914,06	3,172	3,179
20	5,72E-05	3,27E-09	917,84	3,131	3,129
20	5,72E-05	3,27E-09	920,34	3,139	3,129
20	5,72E-05	3,27E-09	915,84	3,124	3,129
25	0,00E+00	0,00E+00	917,45	3,077	3,079
25	0,00E+00	0,00E+00	920,45	3,087	3,079
25	0,00E+00	0,00E+00	919,45	3,084	3,079
25	0,00E+00	0,00E+00	915,95	3,072	3,079
30	-5,53E-05	3,06E-09	918,89	3,031	3,030
30	-5,53E-05	3,06E-09	915,89	3,021	3,030
35	-1,09E-04	1,18E-08	916,64	2,975	2,982
35	-1,09E-04	1,18E-08	919,14	2,983	2,982
35	-1,09E-04	1,18E-08	920,14	2,986	2,982
40	-1,61E-04	2,58E-08	920,20	2,939	2,934
40	-1,61E-04	2,58E-08	916,20	2,926	2,934
45	-2,11E-04	4,45E-08	919,57	2,890	2,887
45	-2,11E-04	4,45E-08	916,07	2,879	2,887
48	-2,40E-04	5,77E-08	916,21	2,853	2,859
50	-2,59E-04	6,73E-08	918,76	2,843	2,840
55	-3,07E-04	9,40E-08	918,24	2,798	2,795
55	-3,07E-04	9,40E-08	920,24	2,804	2,795
60	-3,52E-04	1,24E-07	915,02	2,747	2,750
65	-3,97E-04	1,57E-07	914,60	2,705	2,706

Sortie régression :

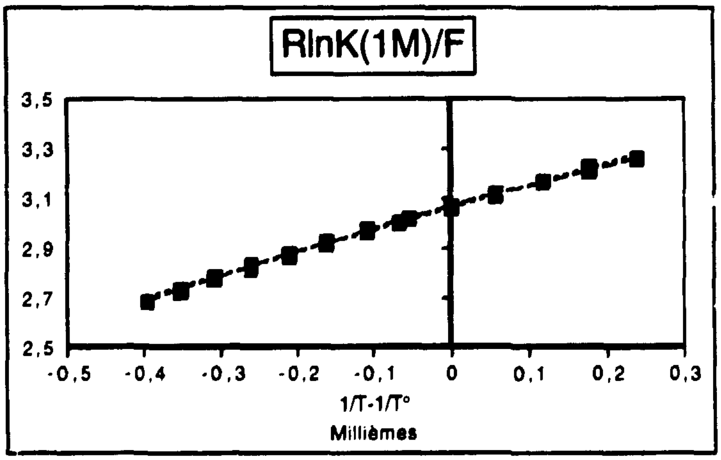
Constante		**3,079**
R au carré		0,998298126
Nombre d'observations		28
Degrés de liberté		25
Coefficient(s) X	**8,80E+02**	**-1,56E+05**
Ecart type de coef.	9,30E+00	4,09E+04



Fichier E6/5 suite

T	1/T-1/T0	(1/T-1/T0)^2	EO/R(1M)	RlnKexp/F	RlnKcal/F(2)	RlnKcal/F
5	2,41E-04	5,82E-08	905,82	3,257	3,261	3,275
5	2,41E-04	5,82E-08	905,82	3,257	3,261	3,275
10	1,78E-04	3,16E-08	912,44	3,222	3,211	3,218
10	1,78E-04	3,16E-08	907,94	3,207	3,211	3,218
15	1,16E-04	1,35E-08	912,34	3,166	3,162	3,163
15	1,16E-04	1,35E-08	912,84	3,168	3,162	3,163
20	5,72E-05	3,27E-09	914,57	3,120	3,113	3,109
20	5,72E-05	3,27E-09	910,07	3,104	3,113	3,109
20	5,72E-05	3,27E-09	913,57	3,116	3,113	3,109
25	0,00E+00	0,00E+00	911,14	3,056	3,064	3,058
25	0,00E+00	0,00E+00	914,64	3,068	3,064	3,058
25	0,00E+00	0,00E+00	911,14	3,056	3,064	3,058
25	0,00E+00	0,00E+00	912,14	3,059	3,064	3,058
30	-5,53E-05	3,06E-09	914,53	3,017	3,015	3,008
31	-6,62E-05	4,38E-09	911,69	2,998	3,005	2,998
35	-1,09E-04	1,18E-08	915,76	2,972	2,967	2,959
35	-1,09E-04	1,18E-08	914,76	2,969	2,967	2,959
35	-1,09E-04	1,18E-08	913,76	2,965	2,967	2,959
40	-1,61E-04	2,58E-08	915,31	2,923	2,919	2,913
40	-1,61E-04	2,58E-08	913,31	2,917	2,919	2,913
45	-2,11E-04	4,45E-08	914,68	2,875	2,871	2,867
45	-2,11E-04	4,45E-08	912,68	2,869	2,871	2,867
50	-2,59E-04	6,73E-08	914,87	2,831	2,824	2,823
50	-2,59E-04	6,73E-08	911,37	2,820	2,824	2,823
50	-2,59E-04	6,73E-08	911,37	2,820	2,824	2,823
55	-3,07E-04	9,40E-08	913,37	2,783	2,778	2,781
55	-3,07E-04	9,40E-08	910,37	2,774	2,778	2,781
55	-3,07E-04	9,40E-08	910,37	2,774	2,778	2,781
60	-3,52E-04	1,24E-07	911,18	2,735	2,731	2,739
60	-3,52E-04	1,24E-07	908,68	2,728	2,731	2,739
60	-3,52E-04	1,24E-07	910,18	2,732	2,731	2,739
65	-3,97E-04	1,57E-07	908,30	2,686	2,686	2,699

Régression d'ordre 2			**Régression linéaire**	
Constante		**3,064**	Constante	
R au carré		0,999093	R au carré	
Nombre d'observations		32	Nombre d'observations	
Degrés de liberté		29	Degrés de liberté	
Coefficient(s) X	**8,68E+02**	**-2,11E+05**	Coefficient(s) X	**9,03E+02**
Ecart type de coef.	7,00	2,93E+04	Ecart type de coef.	8,30

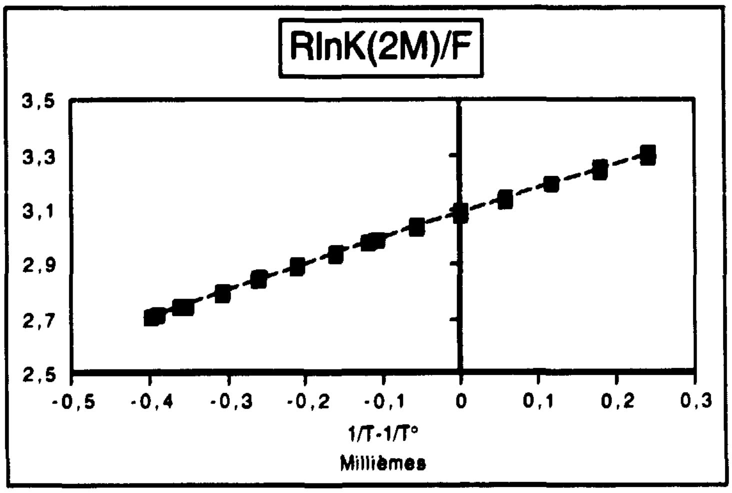


Fichier E6/5 suite

T	1/T-1/T0	(1/T-1/T0)^2	E0/R(2M)	RlnKexp/F	RlnKcal/F
5	2,41E-04	5,82E-08	917,82	3,300	3,294
5	2,41E-04	5,82E-08	913,82	3,285	3,294
10	1,78E-04	3,16E-08	919,76	3,248	3,241
10	1,78E-04	3,16E-08	916,76	3,238	3,241
10	1,78E-04	3,16E-08	919,76	3,248	3,241
15	1,16E-04	1,35E-08	918,49	3,188	3,188
15	1,16E-04	1,35E-08	918,49	3,188	3,188
20	5,72E-05	3,27E-09	917,06	3,128	3,136
20	5,72E-05	3,27E-09	919,06	3,135	3,136
20	5,72E-05	3,27E-09	919,06	3,135	3,136
25	0,00E+00	0,00E+00	920,49	3,087	3,085
25	0,00E+00	0,00E+00	917,99	3,079	3,085
25	0,00E+00	0,00E+00	919,49	3,084	3,085
30	-5,53E-05	3,06E-09	921,77	3,041	3,034
30	-5,53E-05	3,06E-09	919,27	3,032	3,034
35	-1,09E-04	1,18E-08	919,90	2,985	2,985
35	-1,09E-04	1,18E-08	920,40	2,987	2,985
36	-1,19E-04	1,42E-08	919,50	2,974	2,975
40	-1,61E-04	2,58E-08	918,86	2,934	2,936
40	-1,61E-04	2,58E-08	919,36	2,936	2,936
45	-2,11E-04	4,45E-08	918,17	2,886	2,888
45	-2,11E-04	4,45E-08	919,67	2,891	2,888
45	-2,11E-04	4,45E-08	919,67	2,891	2,888
50	-2,59E-04	6,73E-08	918,32	2,842	2,841
50	-2,59E-04	6,73E-08	919,32	2,845	2,841
55	-3,07E-04	9,40E-08	915,81	2,791	2,794
55	-3,07E-04	9,40E-08	916,81	2,794	2,794
55	-3,07E-04	9,40E-08	917,81	2,797	2,794
60	-3,52E-04	1,24E-07	914,63	2,745	2,749
61	-3,61E-04	1,31E-07	915,57	2,740	2,740
64	-3,88E-04	1,51E-07	915,37	2,715	2,713
65	-3,97E-04	1,57E-07	913,28	2,701	2,704

Sortie régression :

Constante		**3,085**
R au carré		0,99954341
Nombre d'observations		32
Degrés de liberté		29
Coefficient(s) X	**9,03E+02**	**-1,44E+05**
Ecart type de coef.	5,03E+00	2,12E+04

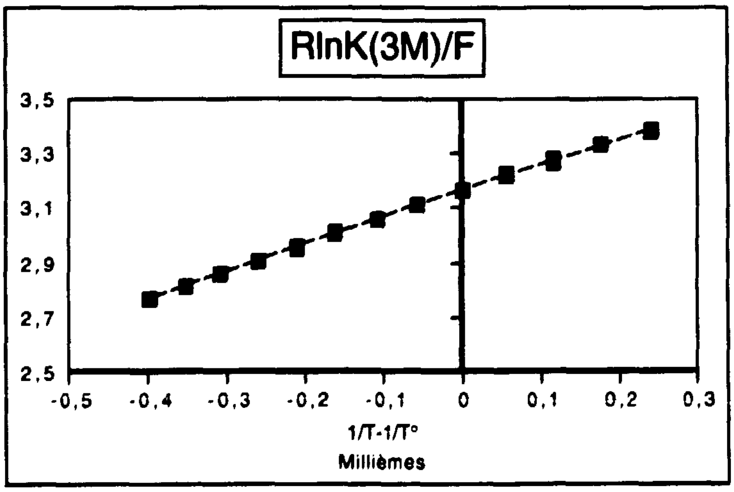


Fichier E6/5 suite

T	1/T-1/T0	(1/T-1/T0)^2	EO/R(3M)	RlnKexp/F	RlnKcal/F
5	2,41E-04	5,82E-08	941,46	3,385	3,385
5	2,41E-04	5,82E-08	939,96	3,379	3,385
10	1,78E-04	3,16E-08	943,68	3,333	3,328
10	1,78E-04	3,16E-08	943,18	3,331	3,328
15	1,16E-04	1,35E-08	944,20	3,277	3,272
15	1,16E-04	1,35E-08	941,20	3,266	3,272
20	5,72E-05	3,27E-09	944,58	3,222	3,218
20	5,72E-05	3,27E-09	942,58	3,215	3,218
25	0,00E+00	0,00E+00	943,84	3,166	3,164
25	0,00E+00	0,00E+00	942,84	3,162	3,164
25	0,00E+00	0,00E+00	943,84	3,166	3,164
30	-5,53E-05	3,06E-09	941,96	3,107	3,111
30	-5,53E-05	3,06E-09	942,96	3,111	3,111
35	-1,09E-04	1,18E-08	942,95	3,060	3,058
35	-1,09E-04	1,18E-08	941,03	3,054	3,058
40	-1,61E-04	2,58E-08	941,80	3,008	3,007
40	-1,61E-04	2,58E-08	942,30	3,009	3,007
45	-2,11E-04	4,45E-08	939,52	2,953	2,957
45	-2,11E-04	4,45E-08	941,52	2,959	2,957
50	-2,59E-04	6,73E-08	939,60	2,908	2,907
50	-2,59E-04	6,73E-08	939,10	2,906	2,907
55	-3,07E-04	9,40E-08	938,05	2,859	2,859
60	-3,52E-04	1,24E-07	936,35	2,811	2,811
65	-3,97E-04	1,57E-07	935,02	2,765	2,764

Sortie régression :

Constante		**3,1637**
R au carré		0,99971782
Nombre d'observations		24
Degrés de liberté		21
Coefficient(s) X	**9,51E+02**	**-1,43E+05**
Ecart type de coef.	4,35E+00	1,96E+04

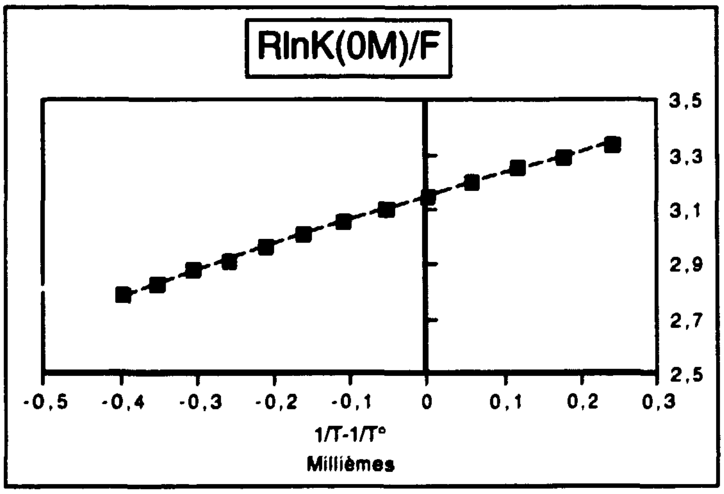


Fichier E6/5 suite

T	1/T-1/T0	(1/T-1/T0)^2	EO/R(0M)	RlnKexp/F	RlnKcal/F
5	2,41E-04	5,82E-08	927,896759	3,336	3,338
10	1,78E-04	3,16E-08	931,493919	3,290	3,290
15	1,16E-04	1,35E-08	935,79731	3,248	3,243
20	5,72E-05	3,27E-09	936,907567	3,196	3,195
25	0,00E+00	0,00E+00	938,297024	3,147	3,148
30	-5,53E-05	3,06E-09	938,782372	3,097	3,101
35	-1,09E-04	1,18E-08	941,875666	3,057	3,054
40	-1,61E-04	2,58E-08	941,512192	3,007	3,008
45	-2,11E-04	4,45E-08	941,989357	2,961	2,962
50	-2,59E-04	6,73E-08	941,032334	2,912	2,916
55	-3,07E-04	9,40E-08	944,671983	2,879	2,872
60	-3,52E-04	1,24E-07	940,817086	2,824	2,827
65	-3,97E-04	1,57E-07	941,532041	2,784	2,783

Sortie régression :

Constante		**3,148**
R au carré		0,99964383
Nombre d'observations		13
Degrés de liberté		10
Coefficient(s) X	**8,39E+02**	**-2,00E+05**
Ecart type de coef.	7,13E+00	2,95E+04



Fichier E6/5 suite

Corrections de force ionique sur l'entropie et la capacité calorifique à T°

Comparaison entre points expérimentaux et courbe théorique déduite de la S.I.T et de développements limités

DeltaS(T°)/F et DeltaCp(T°)2T°F sont les termes d'ordre1 et 2 de la régression polynomiale en T-T° sur E

DS(I,T°)/F = DS(0,T°)/F + r(Dz^2(D(I,T°)+T°D'(I,T°))-m(De(T°)+T°De'(T°)))

DCp(I,T°)/2T°F = DCp(0,T°)/2T°F + r(Dz^2(D'(I,T°)+T°D"(I,T°)/2))-m(De'(T°)+T°e"(T°)/2))

Valeurs numériques utilisées (cf p. précédentes)		
r=R*ln10*1000/F	0,1984	
Deltaeps(T°)	0,222	0,219
(Delta eps)'(T°)	-1,24E-03	-1,48E-03
(Delta eps)"(T°)/2		1,22E-05

D inscrit devant une grandeur (S,Cp,H, z ou e) signifie delta; D(I,T) est le terme de Debye Huckel; e signifie epsilon

(1) : Les variations de De et D avec Tsont considérées linéaires

(2) : Le calcul est fait avec les formules ci-dessus où les variations de De et D sont modélisées par un polynôme d'ordre 2

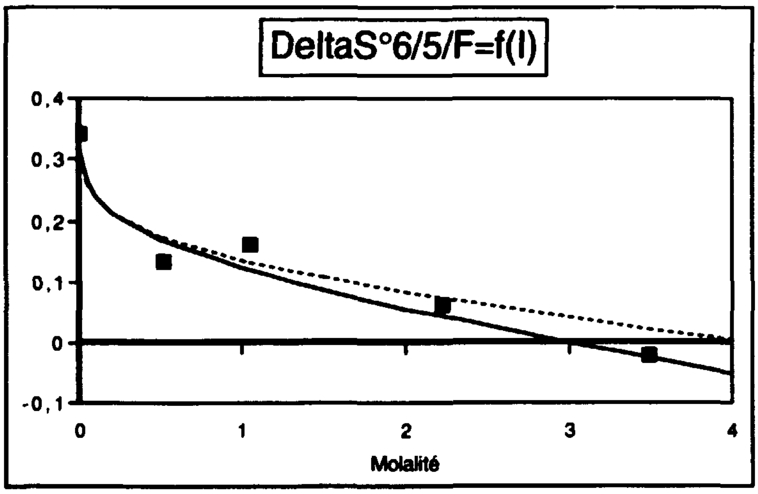
th : signifie théorique c.a.d valeur calculée

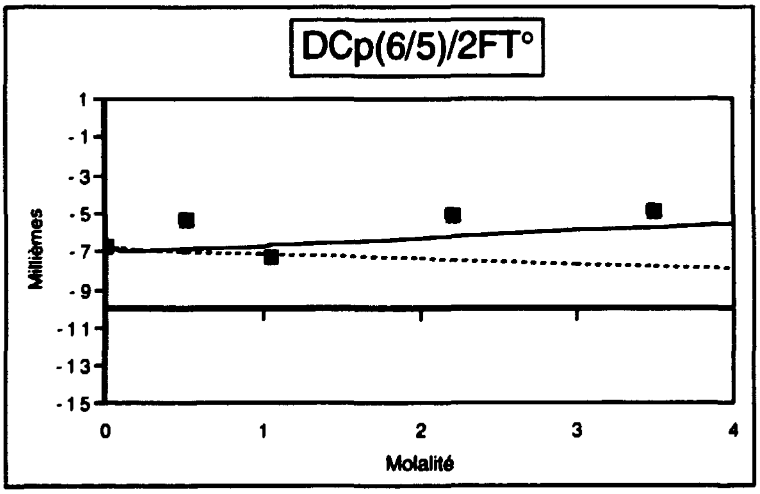
m	D(I,T°)	D'(I,T°)	D'(I,T°)	D"(I,T°)/2	DS(T°)/F	DCp(T°)/2FT°	DSth°/F(1)	DCpth°/2FT°(1)	DSth°/F(2)	DCpth°/2FT°(2)
0	0	0	0	0	0,3403	-6,77E-03	0,3403	-6,77E-03	0,3403	-6,77E-03
0,0001	5,02E-03	9,50E-06	8,78E-06	3,64E-08			0,3356	-6,78E-03	0,3357	-6,78E-03
0,0002	7,05E-03	1,33E-05	1,23E-05	5,10E-08			0,3337	-6,78E-03	0,3339	-6,79E-03
0,0005	1,10E-02	2,08E-05	1,92E-05	7,94E-08			0,3300	-6,78E-03	0,3303	-6,80E-03
0,001	1,54E-02	2,89E-05	2,67E-05	1,10E-07			0,3260	-6,79E-03	0,3263	-6,81E-03
0,002	2,13E-02	3,99E-05	3,68E-05	1,52E-07			0,3204	-6,79E-03	0,3209	-6,82E-03
0,005	3,25E-02	6,03E-05	5,57E-05	2,30E-07			0,3100	-6,81E-03	0,3108	-6,84E-03
0,01	4,43E-02	8,12E-05	7,50E-05	3,09E-07			0,2992	-6,82E-03	0,3002	-6,87E-03
0,02	5,94E-02	1,08E-04	9,94E-05	4,09E-07			0,2852	-6,84E-03	0,2864	-6,89E-03
0,05	8,52E-02	1,51E-04	1,40E-04	5,72E-07			0,2613	-6,87E-03	0,2625	-6,93E-03
0,1	1,09E-01	1,89E-04	1,75E-04	7,16E-07			0,2387	-6,91E-03	0,2398	-6,96E-03
0,2	1,36E-01	2,31E-04	2,13E-04	8,70E-07			0,2123	-6,96E-03	0,2124	-6,97E-03
0,5	1,75E-01	2,86E-04	2,64E-04	1,07E-06			0,1709	-7,06E-03	0,1672	-6,91E-03
0,513	1,76E-01	2,87E-04	2,66E-04	1,08E-06	0,1334	-5,31E-03	0,1696	-7,07E-03	0,1658	-6,90E-03
0,513	1,76E-01	2,87E-04	2,66E-04	1,08E-06			0,1696	-7,07E-03	0,1658	-6,90E-03
0,513	1,76E-01	2,87E-04	2,66E-04	1,08E-06			0,1696	-7,07E-03	0,1658	-6,90E-03
0,513	1,76E-01	2,87E-04	2,66E-04	1,08E-06			0,1696	-7,07E-03	0,1658	-6,90E-03
1	2,04E-01	3,24E-04	3,00E-04	1,22E-06			0,1322	-7,21E-03	0,1216	-6,74E-03
1,05	2,06E-01	3,27E-04	3,02E-04	1,23E-06	0,1596	-7,29E-03	0,1291	-7,22E-03	0,1177	-6,72E-03
1,05	2,06E-01	3,27E-04	3,02E-04	1,23E-06			0,1291	-7,22E-03	0,1177	-6,72E-03
1,05	2,06E-01	3,27E-04	3,02E-04	1,23E-06			0,1291	-7,22E-03	0,1177	-6,72E-03
1,05	2,06E-01	3,27E-04	3,02E-04	1,23E-06			0,1291	-7,22E-03	0,1177	-6,72E-03
1,5	2,20E-01	3,44E-04	3,19E-04	1,29E-06			0,1044	-7,34E-03	0,0865	-6,55E-03
2	2,31E-01	3,58E-04	3,31E-04	1,34E-06			0,0809	-7,48E-03	0,0557	-6,36E-03
2,21	2,34E-01	3,62E-04	3,35E-04	1,36E-06	0,0620	-5,08E-03	0,0718	-7,53E-03	0,0435	-6,27E-03
2,21	2,34E-01	3,62E-04	3,35E-04	1,36E-06			0,0718	-7,53E-03	0,0435	-6,27E-03
2,21	2,34E-01	3,62E-04	3,35E-04	1,36E-06			0,0718	-7,53E-03	0,0435	-6,27E-03
3	2,45E-01	3,75E-04	3,47E-04	1,40E-06			0,0400	-7,73E-03	-0,0000	-5,95E-03
3,4956	2,50E-01	3,81E-04	3,52E-04	1,43E-06	-0,0224	-4,86E-03	0,0213	-7,86E-03	-0,0260	-5,75E-03
3,4956	2,50E-01	3,81E-04	3,52E-04	1,43E-06			0,0213	-7,86E-03	-0,0260	-5,75E-03
3,4956	2,50E-01	3,81E-04	3,52E-04	1,43E-06			0,0213	-7,86E-03	-0,0260	-5,75E-03
4	2,55E-01	3,86E-04	3,57E-04	1,44E-06			0,0031	-7,98E-03	-0,0517	-5,54E-03

Fichier E6/5 Suite

Illustration du tableau précédent

Les traits pleins représentent les calculs (2) tandis que les pointillés correspondent aux (1)





Fichier E6/5 Suite

Corrections de force ionique sur l'enthalpie et la capacité calorifique à T°

Comparaison entre points expérimentaux et courbe théorique déduite de la S.I.T et de développements limités

DCp(I,T°)/2T°F = DCp(0,T°)/2T°F + r(Dz^2(D'(I,T°)+T°D"(I,T°)/2))-m(De'(T°)+T°e"(T°)/2))

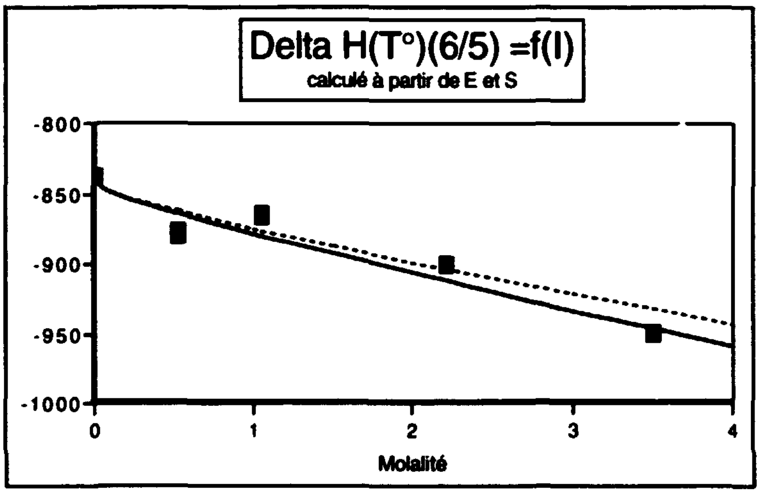
DH(I,T°)/F=-E(I,T°)+T°DS(I,T°)/F = DH(0,T°)/F + rT^2*(Dz^2D'(I,T°)-mDe'(T°))

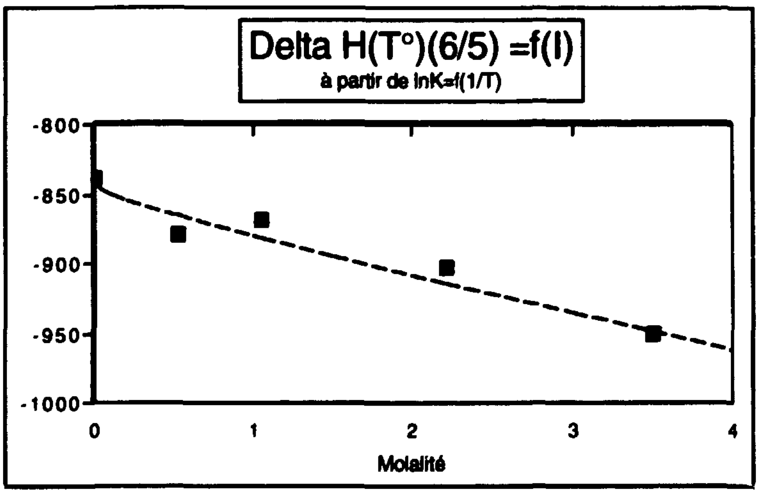
	Calcul de DH°/F = -E° + T*DS°/F			-DH(T°)/F et T°^2DCpth°/F sont les résultats de la régression d'ordre 2 en D(1/T) sur -G/FT ou E/T			
m	DH(T°)/F	DH°th/F(1)	DH°th/F(2)	DH(T°)/F	DCpth°/2FT°	DH°th/F(2)	DCpth°/2FT°(2)
0	-836,85	-836,85	-836,85	-838,81	-7,53E-03	-838,81	-7,53E-03
0,0001		-837,35	-837,32			-839,27	-7,55E-03
0,0002		-837,56	-837,51			-839,46	-7,55E-03
0,0005		-837,96	-837,88			-839,83	-7,56E-03
0,001		-838,40	-838,29			-840,24	-7,57E-03
0,002		-839,00	-838,85			-840,81	-7,58E-03
0,005		-840,15	-839,93			-841,88	-7,61E-03
0,01		-841,36	-841,08			-843,04	-7,63E-03
0,02		-842,98	-842,63			-844,59	-7,66E-03
0,05		-845,93	-845,54			-847,50	-7,70E-03
0,1		-849,06	-848,73			-850,69	-7,72E-03
0,2		-853,44	-853,38			-855,33	-7,73E-03
0,5		-862,91	-863,92			-865,88	-7,67E-03
0,513	-877,68	-863,27	-864,33	-879,64	-5,89E-03	-866,29	-7,67E-03
0,513	-880,68	-863,27	-864,33			-866,29	-7,67E-03
0,513	-879,68	-863,27	-864,33			-866,29	-7,67E-03
0,513	-876,18	-863,27	-864,33			-866,29	-7,67E-03
1		-875,89	-878,89			-880,85	-7,50E-03
1,05	-863,55	-877,11	-880,32	-868,10	-7,96E-03	-882,28	-7,49E-03
1,05	-867,05	-877,11	-880,32			-882,28	-7,49E-03
1,05	-863,55	-877,11	-880,32			-882,28	-7,49E-03
1,05	-864,55	-877,11	-880,32			-882,28	-7,49E-03
1,5		-887,91	-892,97			-894,93	-7,32E-03
2		-899,55	-906,71			-908,67	-7,12E-03
2,21	-902,00	-904,38	-912,42	-903,49	-5,45E-03	-914,38	-7,04E-03
2,21	-899,50	-904,38	-912,42			-914,38	-7,04E-03
2,21	-901,00	-904,38	-912,42			-914,38	-7,04E-03
3		-922,34	-933,72			-935,68	-6,72E-03
3,4956	-950,51	-933,50	-946,99	-951,29	-5,39E-03	-948,94	-6,51E-03
3,4956	-949,51	-933,50	-946,99			-948,94	-6,51E-03
3,4956	-950,51	-933,50	-946,99			-948,94	-6,51E-03
4		-944,81	-960,43			-962,39	-6,30E-03

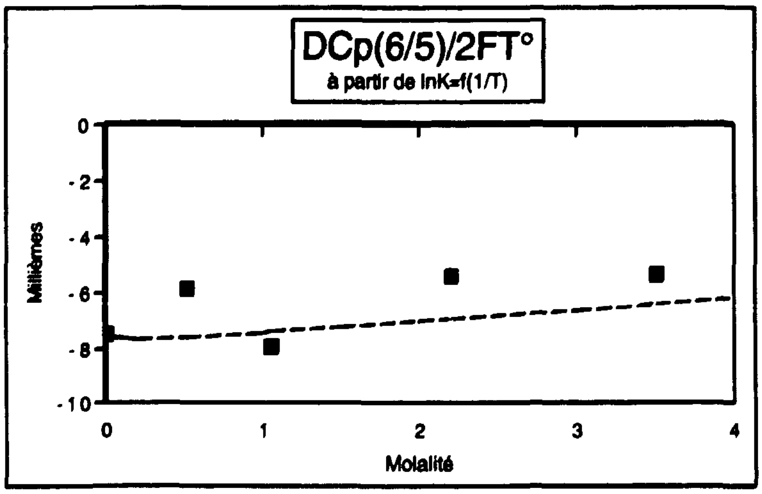
Fichier E6/5 Suite

Illustration du tableau précédent

Les traits pleins représentent les calculs (2) tandis que les pointillés correspondent aux (1)





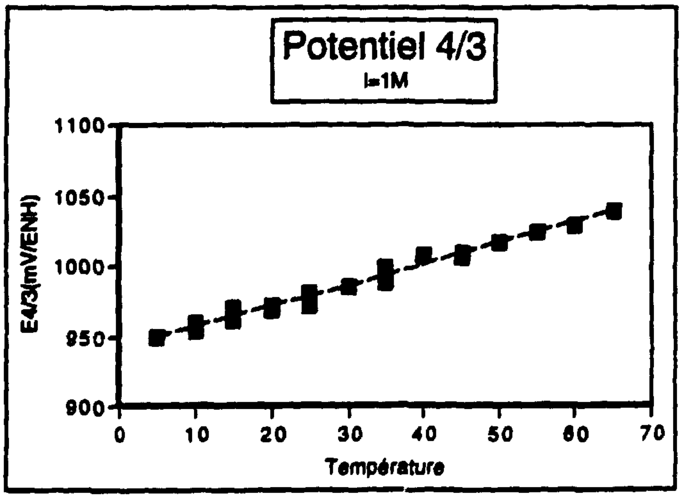


Fichier E4/3

Détermination des entropies, des capacités calorifiques
directement sur le potentiel E6/5 /ENH à différentes force ioniques
par régression polynomiale d'ordre 2
ordre 1 : DS/F; ordre 2 = DCp/2T*F
(pour le calcul de ERef(T,I) cf fichier RefAgCl(T,I); E1/2 = potentiel mesuré /AgAgCl)
EO/R= E1/2 + Eref

T	T-T0	(T-T0)^2	E1/2(1M)	ERef(T,1)	EO/R(1M)	Ecalculé
5	-20	400	619,5	329,98	949,48	949,31
10	-15	225	630	329,25	959,25	956,44
10	-15	225	625	329,17	954,17	956,44
15	-10	100	632,5	328,31	960,81	963,64
15	-10	100	641,5	328,31	969,81	963,64
20	-5	25	641	327,20	968,20	970,91
20	-5	25	644	327,20	971,20	970,91
25	0	0	645	325,92	970,92	978,23
25	0	0	655	325,92	980,92	978,23
30	5	25	660	324,47	984,47	985,63
35	10	100	665	322,84	987,84	993,09
35	10	100	675	322,84	997,84	993,09
40	15	225	686	321,03	1007,03	1000,62
45	20	400	686,5	319,03	1005,53	1008,21
45	20	400	690	319,03	1009,03	1008,21
50	25	625	700	316,85	1016,85	1015,87
55	30	900	710	314,47	1024,47	1023,60
55	30	900	710	314,47	1024,47	1023,60
60	35	1225	717	311,89	1028,89	1031,39
65	40	1600	730	309,12	1039,12	1039,25

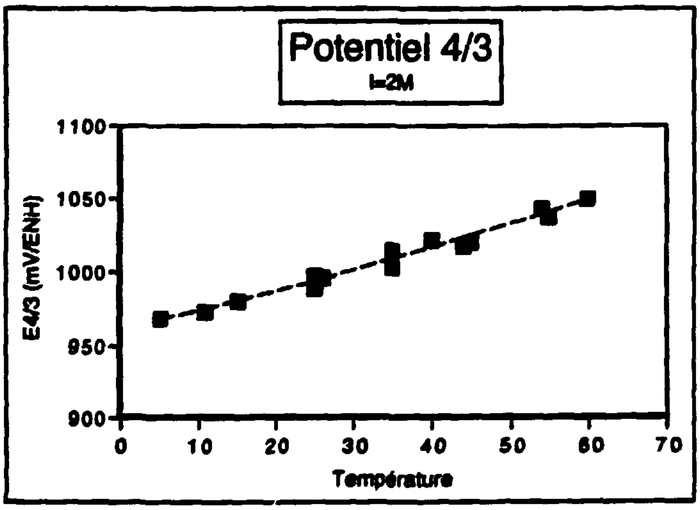
Sortie régression polynomiale d'ordre 2:		
Constante		978,23
R au carré		0,98
Nombre d'observations		20
Degrés de liberté		17
Coefficient(s) X	1,47	1,32E-03
Ecart type de coef.	7,35E-02	2,98E-03



Fichier E4/3 suite

T	T-T0	(T-T0)^2	E1/2(2M)	ERef(T,2)	EO/R(2M)	Ecalculé
5	-20	400	639	328,11	967,11	966,46
10,5	-14,5	210,25	645	327,06	972,06	973,27
15	-10	100	653	326,03	979,03	979,08
25	0	0	665	323,30	988,30	992,74
25	0	0	673	323,30	996,30	992,74
26	1	1	672	322,99	994,99	994,17
35	10	100	682,5	319,94	1002,44	1007,46
35	10	100	694	319,94	1013,94	1007,46
40	15	225	703	318,01	1021,01	1015,21
44	19	361	700	316,35	1016,35	1021,60
45	20	400	704	315,92	1019,92	1023,22
54	29	841	731	311,74	1042,74	1038,30
55	30	900	725,5	311,24	1036,74	1040,03
60	35	1225	741	308,63	1049,63	1048,83

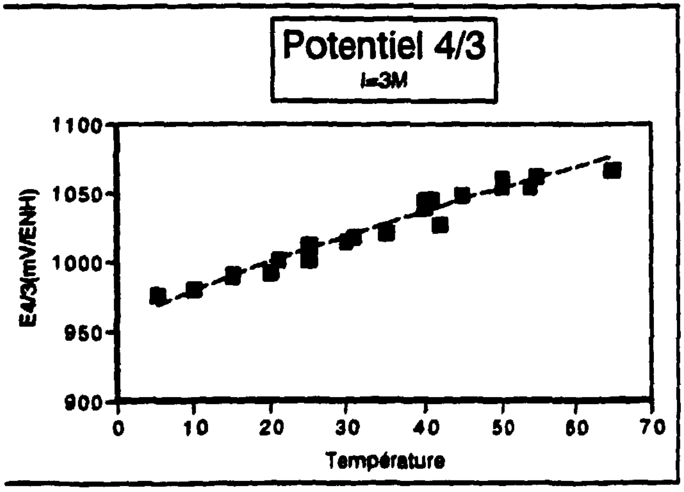
Sortie régression polynomiale d'ordre 2:		
Constante		992,74
R au carré		0,98
Nombre d'observations		14
Degrés de liberté		11
Coefficient(s) X	1,42	5,24E-03
Ecart type de coef.	9,87E-02	4,39E-03



Fichier E4/3 suite

T	T-T0	(T-T0)^2	E1/2(3M)	ERef(T,3)	EO/R(3M)	Ecalculé
5	-20	400	650	326,04	976,04	968,56
10	-15	225	655	324,87	979,87	979,12
10	-15	225	656	324,87	980,87	979,12
15	-10	100	665,5	323,51	989,01	989,38
15	-10	100	668	323,51	991,51	989,38
20	-5	25	671	322,02	993,02	999,35
20	-5	25	670	322,02	992,02	999,35
21	-4	16	680,5	321,70	1002,20	1001,31
25	0	0	691	320,39	1011,39	1009,02
25	0	0	681	320,39	1001,39	1009,02
25	0	0	684	320,39	1004,39	1009,02
30	5	25	696	318,62	1014,62	1018,39
31	6	36	700	318,25	1018,25	1020,23
35	10	100	705	316,72	1021,72	1027,46
40	15	225	725	314,67	1039,67	1036,24
40	15	225	729,5	314,67	1044,17	1036,24
40,5	15,5	240,25	731,5	314,46	1045,96	1037,10
41	16	256	731,5	314,24	1045,74	1037,96
42	17	289	714	313,81	1027,81	1039,67
45	20	400	736,5	312,48	1048,98	1044,72
50	25	625	747	310,14	1057,14	1052,91
50	25	625	750	310,14	1060,14	1052,91
50	25	625	745	310,14	1055,14	1052,91
54	29	841	747	308,16	1055,16	1059,24
55	30	900	754	307,66	1061,66	1060,80
65	40	1600	765	302,24	1067,24	1075,68

Sortie régression polynomiale d'ordre 2:		
Constante		1009,02
R au carré		0,96
Nombre d'observations		26
Degrés de liberté		23
Coefficient(s) X	1,90	-5,93E-03
Ecart type de coef.	1,09E-01	4,69E-03



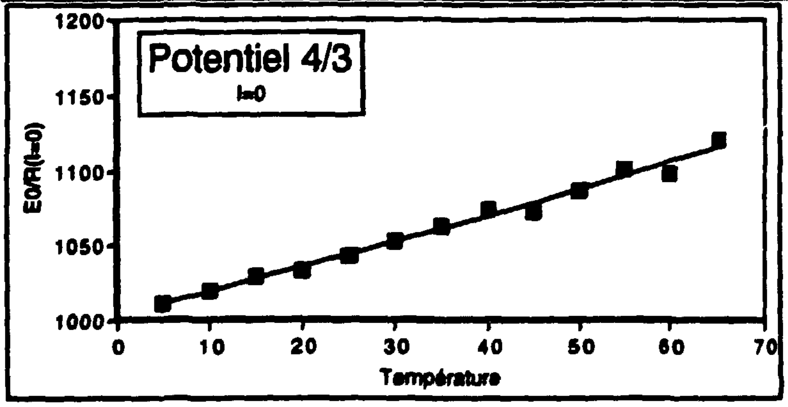
Fichier E4/3 suite

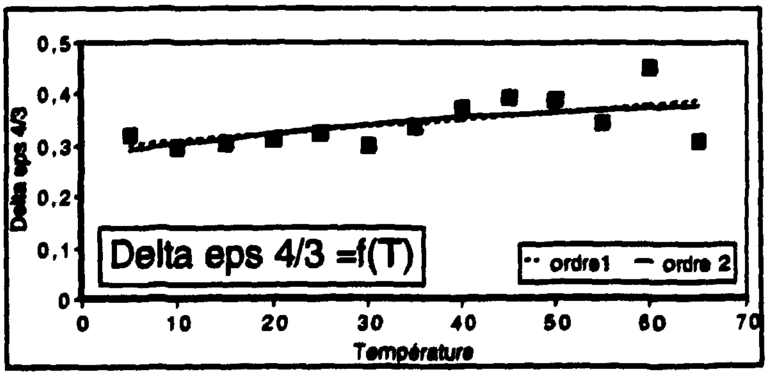
T	T-T*	(T-T*)^2	E0/R(0M)	Ecalculé	Deps	Depsc(1)	Depsc(2)
5	-20	400	1010,81	1011,87	0,3193	0,2993	0,2901
10	-15	225	1020,04	1019,69	0,2969	0,3064	0,3018
15	-10	100	1029,33	1027,67	0,3041	0,3136	0,3127
20	-5	25	1033,93	1035,79	0,3100	0,3207	0,3228
25	0	0	1043,89	1044,07	0,3252	0,3279	0,3320
30	5	25	1052,73	1052,49	0,2999	0,3350	0,3405
35	10	100	1063,15	1061,05	0,3358	0,3422	0,3480
40	15	225	1074,15	1069,77	0,3726	0,3493	0,3548
45	20	400	1073,33	1078,64	0,3919	0,3565	0,3607
50	25	625	1086,55	1087,65	0,3905	0,3636	0,3657
55	30	900	1100,19	1096,81	0,3449	0,3708	0,3700
60	35	1225	1098,29	1106,12	0,4515	0,3779	0,3734
65	40	1600	1120,81	1115,58	0,3057	0,3851	0,3759

Régression polynomiale d'ordre 2 sur E(0)		
Constante		1044,07
R au carré		0,9883381
Nombre d'observations		13
Degrés de liberté		10
Coefficient(s) X	1,67	2,96E-03
Ecart type de coef.	9,31E-02	3,58E-03

Régression linéaire (1) sur Deltaeps	
Constante	0,327874
R au carré	0,3553209
Nombre d'observations	13
Degrés de liberté	11
Coefficient(s) X	1,43E-03
Ecart type de coef.	5,81E-04

Régression d'ordre2 (2) sur Deltaeps		
Constante		0,3320488
R au carré		0,36863811
Nombre d'observations		13
Degrés de liberté		10
Coefficient(s) X	1,76E-03	-1,67E-05
Ecart type de coef.	9,45E-04	3,64E-05





Fichier E4/3 suite

Détermination des enthalpies par développement d'ordre 2 en 1/T sur RlnK/F=E/T

dans ces calculs T est exprimé en °K

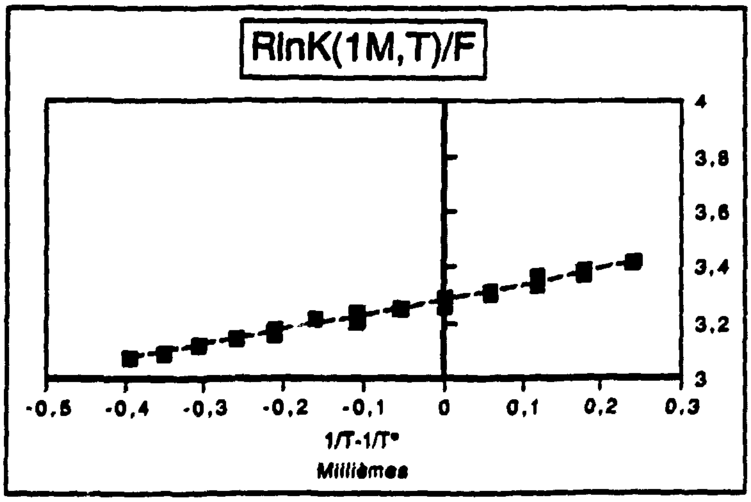
Terme d'ordre 1	-DH(I,T°)/F
Terme d'ordre 2	DCp(I,T°)T°^2/2F

1/T0 0,003354

T	1/T-1/T0	(1/T-1/T0)^2	EO/R(1M)	RlnKexp/F	RlnKcal/F
5	2,41E-04	5,82E-08	949,48	3,414	3,414
10	1,78E-04	3,16E-08	959,25	3,388	3,378
10	1,78E-04	3,16E-08	954,17	3,370	3,378
15	1,16E-04	1,35E-08	960,81	3,334	3,344
15	1,16E-04	1,35E-08	969,81	3,366	3,344
20	5,72E-05	3,27E-09	968,20	3,303	3,312
20	5,72E-05	3,27E-09	971,20	3,313	3,312
25	0,00E+00	0,00E+00	970,92	3,256	3,281
25	0,00E+00	0,00E+00	980,92	3,290	3,281
30	-5,53E-05	3,06E-09	984,47	3,247	3,251
35	-1,09E-04	1,18E-08	987,84	3,206	3,222
35	-1,09E-04	1,18E-08	997,84	3,238	3,222
40	-1,61E-04	2,58E-08	1007,03	3,216	3,195
45	-2,11E-04	4,45E-08	1005,53	3,161	3,169
45	-2,11E-04	4,45E-08	1009,03	3,172	3,169
50	-2,59E-04	6,73E-08	1016,85	3,147	3,144
55	-3,07E-04	9,40E-08	1024,47	3,122	3,119
55	-3,07E-04	9,40E-08	1024,47	3,122	3,119
60	-3,52E-04	1,24E-07	1028,89	3,088	3,096
65	-3,97E-04	1,57E-07	1039,12	3,073	3,074

Sortie régression polynomiale d'ordre 2:

Constante		3,281
R au carré		0,9873667
Nombre d'observations		20
Degrés de liberté		17
Coefficient(s) X	540	47082
Ecart type de coef.	20	87225

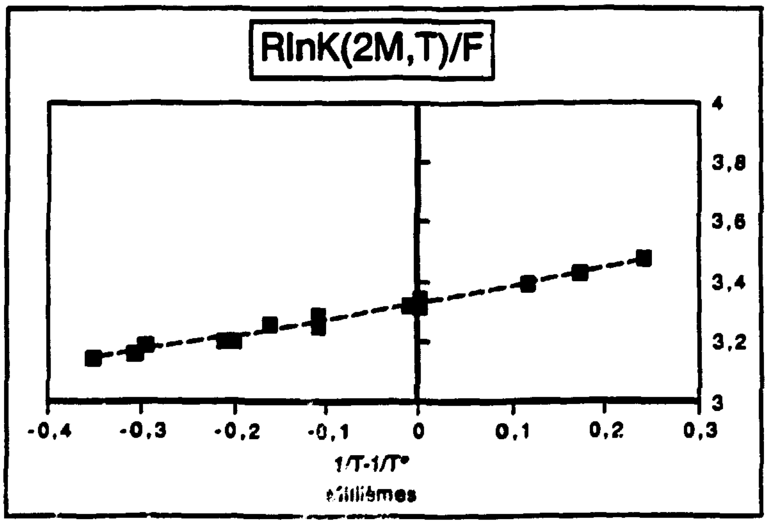


Fichier E4/3 suite

T	1/T-1/T0	(1/T-1/T0)^2	E0/R(2M)	RlnKexp/F	RlnKcal/F
5	2,41E-04	5,82E-08	967,11	3,477	3,475
10,5	*1,71E-04*	2,94E-08	972,06	3,427	3,431
15	1,16E-04	1,35E-08	979,03	3,398	3,398
25	0,00E+00	0,00E+00	988,30	3,315	3,330
25	0,00E+00	0,00E+00	996,30	3,342	3,330
26	-1,12E-05	1,26E-10	994,99	3,326	3,323
35	-1,09E-04	1,18E-08	1002,44	3,253	3,270
35	-1,09E-04	1,18E-08	1013,94	3,290	3,270
40	-1,61E-04	2,58E-08	1021,01	3,260	3,242
44	-2,01E-04	4,04E-08	1016,35	3,205	3,221
45	-2,11E-04	4,45E-08	1019,92	3,206	3,216
54	-2,97E-04	8,84E-08	1042,74	3,187	3,174
55	-3,07E-04	9,40E-08	1036,74	3,159	3,169
60	-3,52E-04	1,24E-07	1049,63	3,151	3,148

Sortie régression polynomiale d'ordre 2:

Constante		3,330
R au carré		0,9840837
Nombre d'observations		14
Degrés de liberté		11
Coefficient(s) X	5,67E+02	1,45E+05
Ecart type de coef.	2,60E+01	1,21E+05

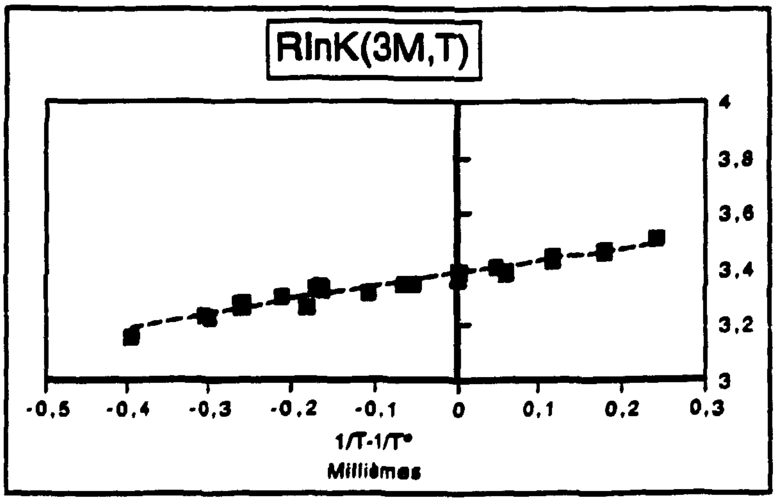


Fichier E4/3 suite

T	1/T-1/T0	(1/T-1/T0)^2	EO/R(3M)	RlnKexp/F	RlnKcal/F
5	2,41E-04	5,82E-08	976,04	3,509	3,486
10	1,78E-04	3,16E-08	979,87	3,461	3,460
10	1,78E-04	3,16E-08	980,87	3,464	3,460
15	1,16E-04	1,35E-08	989,01	3,432	3,434
15	1,16E-04	1,35E-08	991,51	3,441	3,434
20	5,72E-05	3,27E-09	993,02	3,387	3,409
20	5,72E-05	3,27E-09	992,02	3,384	3,409
21	4,56E-05	2,08E-09	1002,20	3,407	3,403
25	0,00E+00	0,00E+00	1011,39	3,392	3,383
25	0,00E+00	0,00E+00	1001,39	3,359	3,383
25	0,00E+00	0,00E+00	1004,39	3,369	3,383
30	-5,53E-05	3,06E-09	1014,62	3,347	3,358
31	-6,62E-05	4,38E-09	1018,25	3,348	3,353
35	-1,09E-04	1,18E-08	1021,72	3,316	3,332
40	-1,61E-04	2,58E-08	1039,67	3,320	3,307
40	-1,61E-04	2,58E-08	1044,17	3,334	3,307
40,5	-1,66E-04	2,75E-08	1045,96	3,335	3,305
41	-1,71E-04	2,92E-08	1045,74	3,329	3,303
42	-1,81E-04	3,27E-08	1027,81	3,261	3,298
45	-2,11E-04	4,45E-08	1048,96	3,297	3,283
50	-2,59E-04	6,73E-08	1057,14	3,271	3,258
50	-2,59E-04	6,73E-08	1060,14	3,281	3,258
50	-2,59E-04	6,73E-08	1055,14	3,265	3,258
54	-2,97E-04	8,84E-08	1055,16	3,225	3,239
55	-3,07E-04	9,40E-08	1061,66	3,235	3,234
65	-3,97E-04	1,57E-07	1067,24	3,156	3,187

Sortie régression polynomiale d'ordre 2:

Constante		3,383
R au carré		0,94863271
Nombre d'observations		26
Degrés de liberté		23
Coefficient(s) X	4,53E+02	-1,02E+05
Ecart type de coef.	2,96E+01	1,35E+05

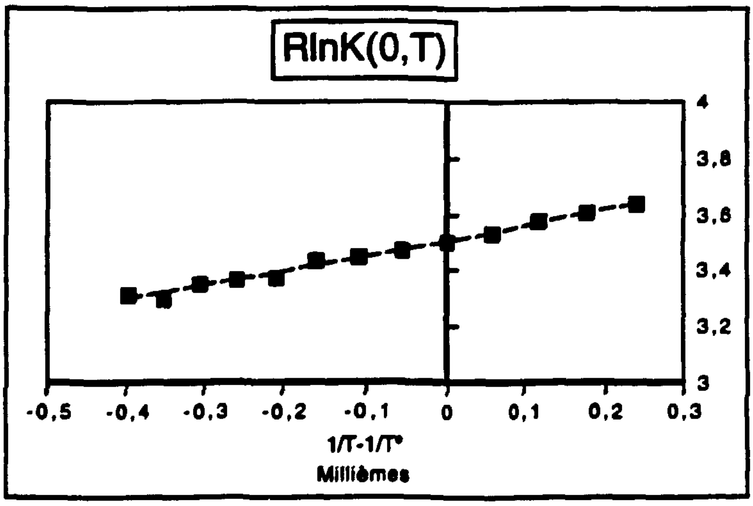


Fichier E4/3 suite

T	1/T-1/T0	(1/T-1/T0)^2	E0/R(0M)	RlnKexp/F	RlnKcal/F
5	2,41E-04	5,82E-08	1010,81	3,634	3,637
10	1,78E-04	3,16E-08	1020,04	3,602	3,601
15	1,16E-04	1,35E-08	1029,33	3,572	3,566
20	5,72E-05	3,27E-09	1033,93	3,527	3,533
25	0,00E+00	0,00E+00	1043,89	3,501	3,502
30	-5,53E-05	3,06E-09	1052,73	3,473	3,472
35	-1,09E-04	1,18E-08	1063,15	3,450	3,444
40	-1,61E-04	2,58E-08	1074,15	3,430	3,417
45	-2,11E-04	4,45E-08	1073,33	3,374	3,391
50	-2,59E-04	6,73E-08	1086,55	3,362	3,366
55	-3,07E-04	9,40E-08	1100,19	3,353	3,342
60	-3,52E-04	1,24E-07	1098,29	3,297	3,320
65	-3,97E-04	1,57E-07	1120,81	3,315	3,298

Sortie régression polynomiale d'ordre 2:

Constante		3,502
R au carré		0,9895568
Nombre d'observations		13
Degrés de liberté		10
Coefficient(s) X	5,43E+02	7,45E+04
Ecart type de coef.	2,36E+01	9,78E+04



Corrections de force ionique sur l'entropie et la capacité calorifique à T°

Comparaison entre points expérimentaux et courbe théorique déduite de la S.I.T et de développements limités
DeltaS(T°)/F et DeltaCp(T°)2T°F sont les termes d'ordre1 et 2 de la régression polynomiale en T-T° sur E
th : signifie théorique c.a.d valeur calculée selon les formules suivantes

D S(I,T°)/F = D S(0,T°)/F + r(Dz^2(D(I,T°)+T°D'(I,T°))-m(De(T°)+T°De'(T°)))
D Cp(I,T°)/2T°F = D Cp(0,T°)/2T°F + r(Dz^2D'(I,T°)+T° D"(I,T°)/2)-m(De'(T°)+T°De"(T°)/2)

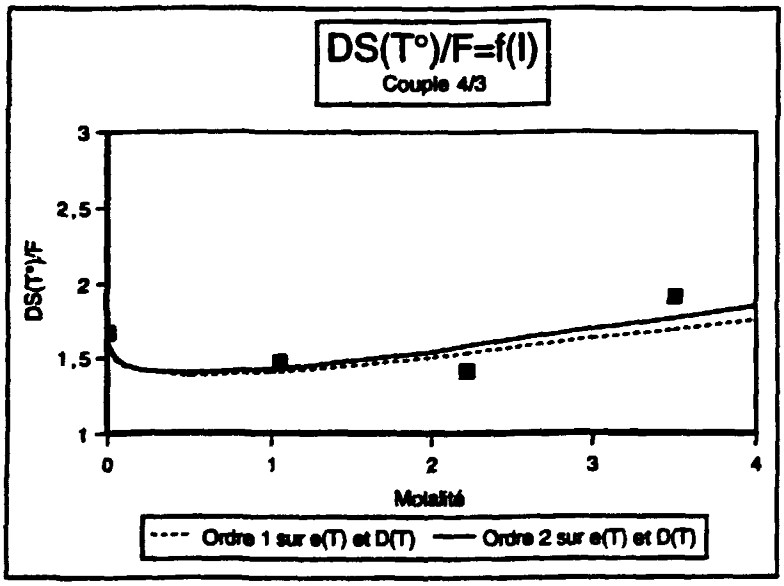
D inscrit devant une grandeur (S,Cp,H, z ou e) signifie delta; D(I,T) est le terme de Debye Huckel; e signifie epsilon
(1) : Les variations de De et D avec T sont considérées linéaires
(2) : Le calcul est fait avec les formules ci-dessus où les variations de De et D sont modélisées par un polynôme d'ordre 2

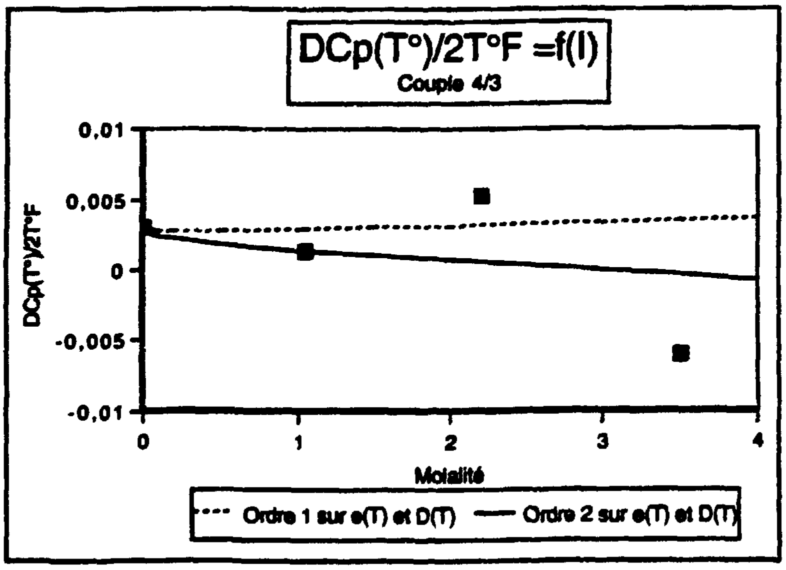
Valeurs numériques utilisées (cf p. précédentes)		
r=R*ln10*1000/F		0,1984
De(T°)	0,327873517076	0,332048799157
De'(T°)	1,43E-03	1,76E-03
De"(T°)/2		-1,67E-05

m	D(I,T°)	D'(I,T°)	D'(I,T°)	D"(I,T°)/2	DS(T°)/F	DSth/F(1)	DSth/F(2)	DCp/2FT°	DCpth/2FT°(1)	DCpth/2FT°(2)
0	0	0	0	0	1,67	1,67	1,67	2,96E-03	2,96E-03	2,96E-03
0,0001	5,02E-03	9,50E-06	8,78E-06	3,64E-08		1,66	1,66		2,95E-03	2,94E-03
0,0002	7,05E-03	1,33E-05	1,23E-05	5,10E-08		1,65	1,65		2,94E-03	2,92E-03
0,0005	1,10E-02	2,08E-05	1,92E-05	7,94E-08		1,65	1,65		2,93E-03	2,90E-03
0,001	1,54E-02	2,89E-05	2,67E-05	1,10E-07		1,64	1,64		2,92E-03	2,88E-03
0,002	2,13E-02	3,99E-05	3,68E-05	1,52E-07		1,62	1,62		2,91E-03	2,85E-03
0,005	3,25E-02	6,03E-05	5,57E-05	2,30E-07		1,60	1,60		2,88E-03	2,79E-03
0,01	4,43E-02	8,12E-05	7,50E-05	3,09E-07		1,58	1,58		2,85E-03	2,72E-03
0,02	5,94E-02	1,08E-04	9,94E-05	4,09E-07		1,55	1,55		2,82E-03	2,64E-03
0,05	8,52E-02	1,51E-04	1,40E-04	5,72E-07		1,50	1,50		2,77E-03	2,50E-03
0,1	1,09E-01	1,89E-04	1,75E-04	7,16E-07		1,45	1,46		2,73E-03	2,36E-03
0,2	1,36E-01	2,31E-04	2,13E-04	8,70E-07		1,41	1,43		2,70E-03	2,18E-03
0,5	1,75E-01	2,86E-04	2,64E-04	1,07E-06		1,38	1,40		2,71E-03	1,83E-03
0,513	1,76E-01	2,87E-04	2,66E-04	1,08E-06		1,38	1,40		2,71E-03	1,82E-03
1	2,04E-01	3,24E-04	3,00E-04	1,22E-06		1,40	1,43		2,80E-03	1,41E-03
1,05	2,06E-01	3,27E-04	3,02E-04	1,23E-06	1,47	1,41	1,44	1,32E-03	2,81E-03	1,37E-03
1,05	2,06E-01	3,27E-04	3,02E-04	1,23E-06		1,41	1,44		2,81E-03	1,37E-03
1,5	2,20E-01	3,44E-04	3,19E-04	1,29E-06		1,45	1,49		2,91E-03	1,03E-03
2	2,31E-01	3,58E-04	3,31E-04	1,34E-06		1,50	1,55		3,03E-03	6,73E-04
2,21	2,34E-01	3,62E-04	3,35E-04	1,36E-06	1,42	1,52	1,58	5,24E-03	3,09E-03	5,27E-04
2,21	2,34E-01	3,62E-04	3,35E-04	1,36E-06		1,52	1,58		3,09E-03	5,27E-04
3	2,45E-01	3,75E-04	3,47E-04	1,40E-06		1,62	1,70		3,29E-03	-1,28E-05
3,4956	2,50E-01	3,81E-04	3,52E-04	1,43E-06	1,90	1,69	1,77	-5,93E-03	3,43E-03	-3,46E-04
3,4956	2,50E-01	3,81E-04	3,52E-04	1,43E-06		1,69	1,77		3,43E-03	-3,46E-04

Fichier E4/3 Suite

Illustration du tableau précédent
Les traits pleins représentent les calculs (2) tandis que les pointillés correspondent aux (1)





Fichier E4/3 Suite

Corrections de force ionique sur l'enthalpie et la capacité calorifique à T°

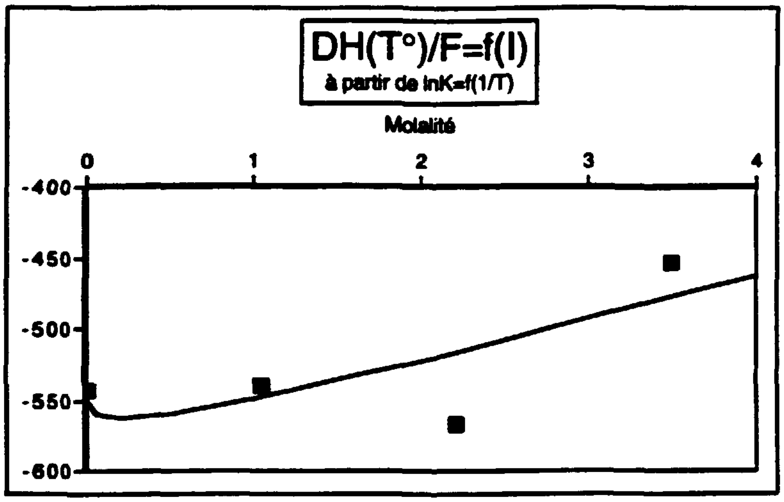
Comparaison entre points expérimentaux et courbe théorique déduite de la S.I.T et de développements limités
th : signifie théorique c.a.d valeur calculée selon les formules suivantes

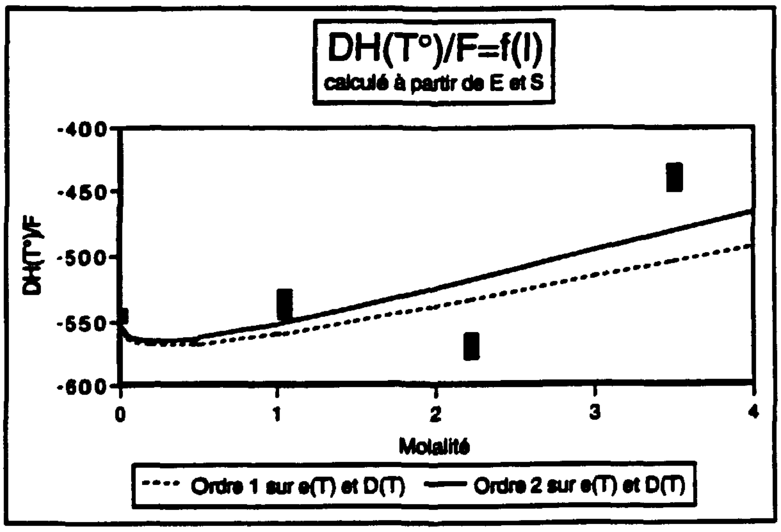
DH(I,T°)/F=-E(I,T°)+T°DS(I,T°)/F = DH(0,T°)/F + rT^2°(Dz^2D'(I,T°)-mDe'(T°))
D Cp(I,T°)/2T°F = D Cp(0,T°)/2T°F + r(Dz^2D'(I,T°)+T° D"(I,T°)/2)-m(De'(T°)+T°De"(T°)/2)

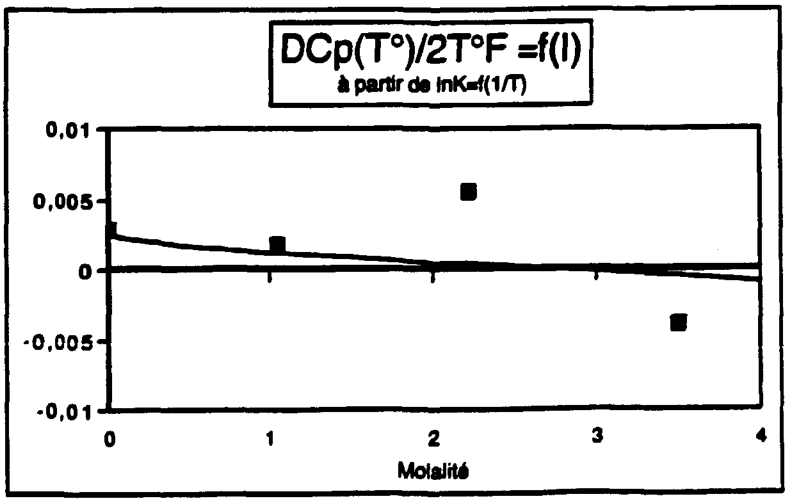
	Calcul de DH°/F = -E° + T°DS°/F			-DH(T°)/F et T°^2DCpth°/F sont les résultats de la régression d'ordre 2 en (1/T-1/T°) sur -G/FT ou E/T				
m	**DH(T°)/F**	**DHth/F(1)**	**DHth/F(2)**	**DH(I,T°)/F**	**DCp(I,T°)T°^2/2F**	**DHth/F(2**	**DCp/2FT°**	**DCpth/2FT°(2)**
0	-546,21	-546,21	-546,21	-543,28	7,45E+04	-543,28	2,81E-03	2,81E-03
0,0001		-547,38	-547,29			-544,36		2,78E-03
0,0002		-547,85	-547,73			-544,80		2,77E-03
0,0005		-548,76	-548,56			-545,64		2,75E-03
0,001		-549,75	-549,47			-546,55		2,73E-03
0,002		-551,09	-550,70			-547,77		2,70E-03
0,005		-553,53	-552,93			-550,00		2,64E-03
0,01		-555,98	-555,16			-552,23		2,57E-03
0,02		-558,99	-557,86			-554,93		2,49E-03
0,05		-563,59	-561,89			-558,96		2,35E-03
0,1		-567,08	-564,72			-561,79		2,21E-03
0,2		-569,66	-566,33			-563,41		2,03E-03
0,5		-568,87	-563,27			-560,34		1,68E-03
0,513		-568,72	-563,04			-560,11		1,67E-03
1		-560,99	-552,10			-549,17		1,25E-03
1,05	-531,91	-560,05	-550,83	-540,29	4,71E+04	-547,91	1,78E-03	1,21E-03
1,05	-541,91	-560,05	-550,83			-547,91		1,21E-03
1,5		-550,89	-538,86			-535,93		8,77E-04
2		-539,91	-524,82			-521,89		5,21E-04
2,21	-565,21	-535,15	-518,78	-567,19	1,45E+05	-515,86	5,49E-03	3,75E-04
2,21	-573,21	-535,15	-518,78			-515,86		3,75E-04
3		-516,78	-495,64			-492,72		-1,65E-04
3,4958	-443,72	-505,00	-480,89	-453,34	-1,02E+05	-477,97	-3,8[illegible]E-03	-4,98E-04
3,4958	-433,72	-505,00	-480,89			-477,97		-4,98E-04
3,4958	-438,72	-505,00	-480,89			-477,97		-4,98E-04
4		-492,89	-465,76			-462,84		-8,3[illegible]E-04

Fichier E4/3 suite

Illustration du tableau précédent


DH(T°)/F=f(I)
à partir de lnK=f(1/T)


DH(T°)/F=f(I)
calculé à partir de E et S


DCp(T°)/2T°F =f(I)
à partir de lnK=f(1/T)