TEMPERATURE CORRECTIONS FOR ACTIVITY COEFFICIENTS CALCULATED BY USING THE SIT

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ABSTRACT

The aim of this work is to propose and verify approximations to calculate from only a few experimental measurements, ionic strength, I, and temperature, T, influences on Gibbs energy, G, enthalpy, H, heat capacity, Cp, redox normal potential, E, and standard equilibrium constant, K.

Series expansions are first used to calculate the T dependency of these functions: typically, S and Cp/2T° are the first and second order corrections on -G. This type of approximation is discussed for the E of the M^{4+}/M^{3+}, MO_2^{2+}/MO_2^{+} and $MO_2(CO_3)_3^{4-}/MO_2(CO_3)_3^{5-}$ couples (M = U or Pu) measured from 5 to 70°C, and for the standard K of some solid Uranium compounds, calculated from 17 to 117 °C.

Excess functions, X^{ex}, are then calculated from activity coefficients, γ: I corrections for H and Cp are needed only when the variations of γ with T cannot be ignored. The variations versus T, of ε, the SIT (Specific Interaction Theory) coefficient, are small and approximately linear, for the above redox equilibria and for published mean γ of some chloride electrolytes: first order (versus T) approximation of the SIT equation is then enough to deduce G^{ex}, S^{ex}, H^{ex}; but second order approximation seems more consistent to estimate Cp^{ex}.

INTRODUCTION

Chemical speciation in aqueous solutions is needed to understand and predict migration of radioelements in groundwaters, from waste disposal. Normal redox potentials, E, and equilibrium constants, K, are needed to predict speciation. They are usually measured with good precision only in high ionic strength, I, electrolytes ; but in most groundwaters studied for waste radioactive disposal, I is lower and the temperature, T, is higher than the usual laboratory conditions. Activity coefficients, γ, are needed to perform I corrections on K and E, typically to extrapolate them to the standard state (infinite dilution). We focus on Actinides. We will, in fact, use measured γ and some approximations, namely Taylor's series expansion, to take into account their T variations.

This type of calculation with first drivative, has been made for the NaCl Pitzer parameters [15], but their T variations are not linear: empirical formula similar to (1) are proposed [16] instead. Anyhow we find that the shapes of the curves representating the T variations of the LiCl, KCl or $SrCl_2$ Pitzer parameters differ from NaCl one: probably for this reason, we do not succeed to propose a simple anlaytical approximative formula. The two second virial Pitzer parameters are correlated [17], many experimental points are then needed to fit them: this leads to some difficulties [18][19] for the complex ions whose predominance domain is small. They are even less data measured at different temperatures.

We prefere to calculate the γ of complex ions, by using [1][2][3][4][5] the Specific Interaction Theory, SIT [6]. Specific interaction coefficient, ε, is empirical: it is measured [6]. We here first evaluate the order of magnitude of temperature corrections on thermodynamic functions, E, and on lg K, from some redox potential measurements and from some published mean γ. We then examine T together with I corrections for lg K, E, G, S, H and Cp. We finally propose formulae either to fit ε from experimental γ data, or to predict γ from tabulated ε values.

NOTATIONS

$X' = \left(\frac{\partial X}{\partial T}\right)_p = \left(\frac{\partial X}{\partial t}\right)_p$ $\quad$ $'X = \left(\frac{\partial X}{\partial (1/T)}\right)_p = \left(\frac{\partial X}{\partial f}\right)_p$

$X'' = (X')'$ $\quad$ $''X = '('X)$

$t = T - T°$ $\quad$ $f = \frac{1}{T} - \frac{1}{T°}$

$Y_{I,T}$ is Y value at ionic strength, I, and temperature, T, where Y can be X or X'...

$D_{I,T} = \frac{a_T \sqrt{I}}{1 + b_T \sqrt{I}}$ where $a_{25°C} = 0.5091$, $b_{25°C} = 1.5$ [6].

r = R ln(10) where R is the molar gas constant. F is the Faraday number

ΔX is the algebraic (with stoichiometric coefficients) summation of the X of each chemical species involved in the chemical equilibrium.

E is the normal potential of redox couple. K is equilibrium constant.

n is the number of electrons involved in redox equilibrium.

WORKING EQUATIONS

Temperature variations for thermodynamic functions

The variation with temperature of the heat capacity (1) of solid compound, is typically calculated with empirical coefficients (a, b, d, e) in thermochemical data bases [6]. We easily deduce similar expressions (2 and 3) for the entropy, S, and the enthalpy, H, from some of the classical thermodynamic relationships (4 and 5):

$$Cp = a + bT + \frac{d}{T} + \frac{e}{T^2} \tag{1}$$

$$S = S° + a \ln\frac{T}{T°} + b\,(T - T°) - d\left(\frac{1}{T} - \frac{1}{T°}\right) - \frac{e}{2}\left(\frac{1}{T^2} - \frac{1}{T°^2}\right) \tag{2}$$

$$H = H° + a\,(T - T°) + \frac{b}{2}(T^2 - T°^2) + d \ln\frac{T}{T°} - e\left(\frac{1}{T} - \frac{1}{T°}\right) \tag{3}$$

$$H'_{I,T} = Cp_{I,T} \tag{4}$$

$$'H_{I,T} = -T^2\, Cp_{I,T} \tag{'4}$$

$$S'_{I,T} = \frac{Cp_{I,T}}{T} \tag{5}$$

$$S''_{I,T} = \frac{Cp'_{I,T}}{T} - \frac{Cp_{I,T}}{T^2} \tag{6}$$

$$G'_{I,T} = -S_{I,T} \tag{7}$$

$$G_{I,T} = H_{I,T} - T\, S_{I,T} \tag{8}$$

The above (1) to (8) relations are valid at each I and T: we do not these parameters in the (1) to (3) relations since we shall use them only for T (not I) corrections.

From (4) to (7) differential relations and from (11) to (13) similar ln K ones, we also expand G, H, S, Cp, E (9) and ln K (10) into series as a function of T (or t, this is equivalent) about T = T° (1a), (24) and (table I). We also expand (24) and (last line of table I) ln K as a function of 1/T (or f, this is equivalent) by using Vant'Hoff ('4) and ('11) to ('13) differential relations:

$Cp_{I,T}$ ### $Cp_{I,T^\circ} + Cp'_{I,T^\circ}\, t + Cp''_{I,T^\circ}\, t^2 / 2$ (1a)
$\Delta G_{I,T} = -n\, F\, E_{I,T}$ (9)
$\Delta G_{I,T} = -R\, T \ln K_{I,T}$ (10)
$RT(\ln K_{I,T})' = \Delta H_{I,T} / T$ (11)
$RT^2(\ln K_{I,T})'' = \Delta Cp_{I,T} - 2\, \Delta H_{I,T} / T$ (12)
$RT^3(\ln K_{I,T})''' = T\, \Delta Cp'_{I,T} - 4\, \Delta Cp_{I,T} + 6\, \Delta H_{I,T} / T$ (13)
$R\, '(\ln K_{I,T}) = -\Delta H_{I,T}$ ('11)
$R\, ''(\ln K_{I,T}) = T^2\, \Delta Cp_{I,T}$ ('12)
$R\, '''(\ln K_{I,T}) = -T^3\, (2\Delta Cp_{I,T} + T\, \Delta Cp'_{I,T})$ ('13)

Temperature variations of activity SIT coefficients

We calculate activity coefficient, γ_i, of an ion, i, by using the SIT [6] :

$$\lg \gamma_{i_{I,T}} = -z_i^2\, D_{I,T} + \sum_j \varepsilon_{i,j_T}\, m_j \tag{14}$$

ε_{i,j_T} are fitted parameters for interactions between the ions i and j, with opposite charges; $D_{I,T}$ is a Debye-Hückel term [6]; z_i is the charge of the ion i, and m_j is the molality of the ion j. Note that $\varepsilon_{i,j_T}\, m_j$, can be neglected when m_j is low enough (typically when j is at trace level). We shall now omitte i and j notations, and we shall take into account only one major ion, j (since all equations are linear, generalisation is straightforward [5]).

(16) is an approximation: ε_{i,j_T} is supposed not to be I dependent; but we still use = symbol and not ### one that we are writting only for Taylor expansion versus T or 1/T. Excess functions [8], (17) to (23), noted with an ^{ex} subscript, account for the transformation from ideal (I = 0) to real solution. They introduce new linear relationships when correcting lg K for I (18) together with T; we write exact equations before using Taylor approximation (17):

$\lg \gamma_{I,T}$ ### $- z^2(D_{I,T^\circ} + D'_{I,T^\circ}\, t + D''_{I,T^\circ}\, t^2 / 2) + m\, (\varepsilon_{T^\circ} + \varepsilon'_{T^\circ}\, t + \varepsilon''_{T^\circ}\, t^2 / 2)$ (15)
$\lg K_{0,T} = \lg K_{I,T} + \Delta \lg \gamma_{I,T}$ (16)
$X_{I,T} = X_{0,T} + X^{ex}_{I,T}$ (Where X = G or H or S or Cp) (17)
$G^{ex}_{I,T} = R\, T \ln \gamma_{I,T}$ (18)
$H^{ex}_{I,T} = -R\, T^2\, (\ln \gamma)'_{I,T}$ (19)
$S^{ex}_{I,T} = -R\, (\ln \gamma_{I,T} + T\, (\ln \gamma)'_{I,T})$ (20)
$Cp^{ex}_{I,T} = -RT(2(\ln \gamma)'_{I,T} + T\, (\ln \gamma)''_{I,T})$ (21)
$(Cp^{ex})'_{I,T} = -R(2(\ln \gamma)'_{I,T} + 4\, T(\ln \gamma)''_{I,T} + T^2\, (\ln \gamma)'''_{I,T})$ (22)
$(Cp^{ex})''_{I,T} = -R(6(\ln \gamma)'''_{I,T} + 6\, T(\ln \gamma)'''_{I,T} + T^2\, (\ln \gamma)''''_{I,T})$ (23)

(19) is the definition of the excess functions, since it is linear, (4) to (8) are still valid for the excess functions: we obtain (20) from (18) and (10), (22) from (20) and (7), (21) from

(20), (22) and (8), (23) from (21) and (4). (20) [21], (21) [8], (22) [9][21][22] and (23) [9][16] have already more or less been proposed.

We substitute (16a) into (18) to (23') to write these equations for the SIT:

$$\lg \gamma = -z^2 D_{I,T} + m\, \varepsilon_T \tag{16a}$$

$$G^{ex}_{I,T} = r\, T(-z^2 D_{I,T} + m\, \varepsilon_T) \tag{20a}$$

$$H^{ex}_{I,T} = r\, T^2 (z^2 D'_{I,T} - m\, \varepsilon'_T) \tag{21a}$$

$$S^{ex}_{I,T} = r\, (z^2 (D_{I,T} + T\, D'_{I,T}) - m\, (\varepsilon_T + T\, \varepsilon'_T) \tag{22a}$$

$$Cp^{ex}_{I,T} = rT(z^2 (2\, D'_{I,T} + T\, D''_{I,T}) - m\, (2\, \varepsilon'_T + T\, \Delta\varepsilon''_T)) \tag{23a}$$

$$\lg K_{I,T} = \lg K_{0,T} + \Delta z^2 D_{I,T} - m\, \Delta\varepsilon_T \tag{18b}$$

$$G_{I,T} = G_{0,T} + G^{ex}_{I,T} \tag{20b}$$

$$H_{I,T} = H_{0,T} + H^{ex}_{I,T} \tag{21b}$$

$$S_{I,T} = S_{0,T} + S^{ex}_{I,T} \tag{22b}$$

$$Cp_{I,T} = Cp_{0,T} + Cp^{ex}_{I,T} \tag{23b}$$

We finaly write $X_{I,T}$ ($X = G$, H, Cp or $R \ln K$) Taylor approximations that we summarize the following way (these then includes previous equations) to use only standard tabulated values, X_{0,T° (25) and (table III), together with other parameters that account for ionic strength corrections, D_{I,T°, D'_{I,T°, D''_{I,T°... and ε_{T°, ε'_{T°, ε''_{T°... (table III):

$$X_{I,T} \#\#\# X_{0,T^\circ} + X^{ex}_{I,T^\circ} + \sum_i (X_{i0,T^\circ} + X^{ex}_{i0,T^\circ})t^i \tag{24}$$

where X_{0,T° ($X = A$, B, or C) are deduced (table III) from tabulated standard values of G, H, Cp; and X^{ex}_{I,T° are calculated by using the equations (20a) to (23a) or (24) where we set T to T°.

Table I Taylor expansion coefficients, $X_{i0,T°}$, of thermodynamic functions $X_{I,T}$. In the equation (25) $X_{I,T}$ ### $X_{0,T°} + X^{ex}_{I,T°} + \sum_i (X_{i0,T°} + X^{ex}_{i0,T°})t^i$, where t=T-T°, we get $Y_{0,T°}$ (here tabulated Y = X or X_i) formula from equations (12) to (15') where we set I to 0; we calculate its numerical value from typically [6] tabulated standard values of G, H or Cp. We also get (here tabulated) $Y^{ex}_{0,T°}$ formula this way; but we calculate its numerical values by using the equations (16a), (18b) or (20a) to (23a) where we calculate, $D'_{I,T°}$, $D''_{I,T°}$... from typically [6] tabulated $D_{I,T}$, and where we measure (see text) $\varepsilon_{T°}$, $\varepsilon'_{T°}$, $\varepsilon''_{T°}$... For consistency (see text), we do not writte the X_i terms that include Cp''' contribution.
*in the last line we also tabulate the coefficients of the R ln K Taylor expansion versus 1/T (and not T)

X	X_1	X_2	X_3	X_4
G	-S	$-\frac{Cp}{2\,T}$	$\frac{Cp - T\,Cp'}{6\,T^2}$	...
H	Cp	$\frac{Cp'}{2}$	$\frac{Cp''}{6}$	...
S	$\frac{Cp}{T}$	$\frac{T\,Cp' - Cp}{2\,T^2}$	...	
Cp	Cp'	$\frac{Cp''}{2}$	...	
R ln K	$\frac{\Delta H}{T^2}$	$\frac{T\,\Delta Cp - 2\,\Delta H}{2\,T^3}$	$\frac{T^2\,\Delta Cp' - 4\,T\,\Delta Cp + \Delta H}{6\,T^4}$	...
*R ln K	$-\Delta H$	$\frac{T^2\,\Delta Cp}{2}$	$-\frac{2\,T^3\,\Delta Cp + T^4\,\Delta Cp'}{6}$	...

TEMPERATURE CORRECTIONS FOR THERMODYNAMIC FUNCTIONS

Basic equations

S, Cp and $\Delta H/T^2$ are the first order correction versus T, for respectively (7) -G, (4) H and (11) R ln K that can be directly measured.

Numerical values

We have found [4][5] approximately linear variations from 5 to 70°C, for the reversible Uranium and Plutonium redox potentials in acidic and carbonate solutions: we then deduce ΔS mean value from the slope of E (versus T) measurements, and it is then quite difficult to detect (5 and 7) ΔCp influence on E (also G): it not straightforward to deduce ΔCp from curve fitting. The uncertainty of this ΔS determination includes ΔCp (see below). We can still estimate ΔCp: further interpretation in this direction is in course [7] (see also [5]).

We calculate the variations of the thermodynamic functions from 290 to 390 K, for some solid Uranium compounds (table I), using (1) to (3), (8), (10): we find (in this T range) that Cp variations are usually lower than 20 $J.K^{-1}.mol^{-1}$, S ones lower than 60 $J.K^{-1}.mol^{-1}$; this induces variations on G included in a 50 $kJ.mol^{-1}$ range (table I). The "a" term of these developments (1 to 3) is then always the most important one at room temperature. Hence G series expansion (14) is meaningful: here $-S_{I,T°}$ and $-Cp_{I,T°}/T°$ can indeed be considered as the first and the second order corrections (versus T) of G. Still, for further discussion about solubility, soluble species heat capacitie data are lacking. There are few published measurements of the heat capacities of soluble actinide complexes [13]. The ΔCp value of carbonate bicarbonate equilibrium [] is between -400 and -50 J/(mol. K) in NaCl (0 to 5 M) from -30 to 150 °C. This again induces small correction on ΔG, typically less than 0,4 unit on lg K at I=0. In pure water or at low I, ΔCp increases (figure) with T (up to 70°C) and then decreases, but at I more than 3 no ΔCp decrease is observed up to 150°C as for many solid Cp (table I). This type of behaviour might be related to physical properties of pure water and electrolyte: it should then be the same for some other solutes.

To interpret this type of data in this T range, a second order (at least) Cp approximation:

is needed, but since Cp variations induces only small variations on E or lg K we shall always neglect $Cp''_{I,T}$ and sometimes $Cp'_{I,T}$ or even $Cp_{I,T}$ when using the corresponding approximation for the other thermodynamic functions. To compare (1) and (1a), note that (table I) a ### Cp_{I,T° and Cp'_{I,T° ### $b-2e/T^{\circ 3}$. These approximations are certainly no longer valid at higher T, where the thermal energy involved in the physical phenomena related to Cp (rotations and vibrations of atoms and bounds), is no longer much smaller than the energy of chemical bounds. Since activity coefficients and excess functions (19) are related to weak interactions (and not chemical bound) there is no reason to find the same temperature behaviour for excess and ideal functions.

Taylor expansion of the thermodynamic functions, versus T.

Around T° (typically the standard temperature), from the equations (4) to (8) and (11):

These equations (12 to 15) are approximations, hence, classical thermodynamic relationships (typically 4 to 8), are verified only within the same order of approximation: we are neglecting the third or forth order and further terms since they should also include Cp''_{I,T° that we are neglecting (1a), even when there is also Cp_{I,T° or Cp'_{I,T° contributions to these higher terms: this might induce some difficulties or inconsistency when fitting experimental data with polynomial formula (see below and [7]).

Instead of using (1) as we are doing above (table I), E (9) temperature coefficients are often tabulated as polynomial expressions [14] analogue to (14). Approximations deduced either from (1) or from (1a) should both be just as good (table I) in our T range. We find that it is difficult to deduce Cp'_{I,T° from E measurements, we then set Cp'_{I,T° to 0 and we neglect the third and further order terms: the results are not straightforward to interpret, they will be dicussed later [7] and we are here only using (14) first order approximation (Table II).

The validity domain of (12) to (15') is correlated to T°. Finally, in solution chemistry around 20 to 100°C, "zero" (neglecting S), "first" (neglecting Cp, hence S and H are constant) or "second" (constant Cp) order approximation can be used to estimate G, (also E and theoretically K), depending on the needed precision, using (14) or (15) formula. lg K variations with T are classically interpreted with Van't Hoff equation: typically, the carbonate equilibrium $\lg K_1$ variations with T or 1/T [20] are not realy linear (figure) wich means that neither S (15) nor H (15') is constant in this T range, Cp_{I,T° cannot then be neglected. Neglecting ΔCp to interpret E measurements, attributes to ΔS a mean value that includes (neglected) ΔCp contribution; in the same way, the interpretation of ΔCp measurement with the "second" approximation also includes ΔCp' contribution and so on...

TEMPERATURE VARIATIONS OF ACTIVITY AND SIT COEFFICIENTS.

Numerical values

At each T, we fit ε_T values of some strong chloride electrolytes from published mean γ data (table II, figure 1). In the same way, by using classical methodology [6], we deduce $\Delta\varepsilon_T$ at each T for the redox equilibria (figure 2). Hence, we fit $\Delta\varepsilon_T$ and $E_{0,T}$ by using the SIT for I correction at each T, we then fit $E_{0,T°}$ and at least $\Delta S_{0,T°}$ by using (9) and (14) for T corrections. We also treat of the data the other way round: we first fit $E_{I,T°}$ and at least $\Delta S_{I,T°}$ by using (9) and (14) at each I, and we then fit $\Delta\varepsilon_{T°}$ and $E_{0,T°}$ by using the SIT. Interpretating experimental data by using both procedure should be consistent: we shall show in the next paragraph that the link between these two data treatments are the theoritical SIT formulae with T corrections to, typically, deduce $\Delta S_{I,T°}$ from $\Delta\varepsilon_{T°}$ and $\Delta\varepsilon'_{T°}$.

The variations of ε_T or $\Delta\varepsilon_T$ versus T, seem to be linear (figures 1 and 2) : ε'_T is not much T dependent. We have also verified from $D_{I,T}$ tabulated values [6], that $D'_{I,T}$ is neither much T dependent. A first order expansion (versus t) of (16) seems a reasonable approximation, in the present work, we calculate most of the numerical values by using a first order approximation, but further interpretation is in course [7] to estimate Cp by using (9) and the second order term of (14); for consistency and further [7] calculations, we then write the second order approximation:

Basic equations for activity coefficient T corrections and excess functions.

In the second or third order developments (versus T) of thermodynamic functions or lg K (12) to (15), we will now substitute the SIT second order approximation (17); this could decrease the precision. We shall then use the approximation on activity coefficient, only at the end of the calculations. Activity coefficients are used to take into account the influence of the ionic medium on equilibrium constants [6] :

Note that ionic strength corrections on ΔH (21) and ΔCp (23) are needed only when the variations of the activity coefficients with T are taken into account. These equations (20) to (23) do not include any approximation. They are valid for any activity coefficient theory.

SIT equations for the treatment of experimental data.

In order to explicitely mix T and I corrections by using the SIT, we substitute (16) into (20) to (23) to calculate the excess (20a) to (23a) that we sustitute (20b) to(23b) into (19):

Note that in these formulae ε', ε'', D' and D'' come from exact relationships (20) to (23) and not from Taylor expansions.

$\lg K_{I,T}$, $\Delta G_{I,T}$ or $\Delta H_{I,T}$ can be directly measured from solution chemistry, electrochemical or calorimetric techniques at fixed T and I in each experiment, $S_{I,T}$ and $Cp_{I,T}$ can then be deduced by curve fitting (15), (14) or (13): we find that it is usually more precise to perform first this data treatment versus T wich fit $X_{I,T°}$ (X= G, H, S, eventually Cp, Cp'...). We then typically measure $\Delta\varepsilon_{T°}$ and controls that it is not I dependent, by [6] plotting ($\lg K_{I,T} - \Delta z^2 D_{I,T}$) versus m (24): it is a straight line with slope $-\Delta\varepsilon_{T°}$. Using (20a and b) for E (9) measurements is equivalent. One could, in the same way, plot (21a) ($H_{I,T}$ - r T^2 z^2 $D'_{I,T}$) versus m to measure $\Delta\varepsilon'_T$ from calorimetric experiments. For verification we shall also plot [7] versus m (22a) [$S_{I,T}$ - r z^2($D_{I,T}$ + T $D'_{I,T}$)], or (23a) [$Cp_{I,T}$ - 2 r T z^2 ($D'_{I,T}$ + T $D''_{I,T}$)]. Note that this data treatment can be performed at any (constant) T since we set T to T° in the SIT formulae (20a) to (23b) and (24) that we use for linearisation of I influence. It is also possible to together all the parameters $X_{0,T°}$, $\varepsilon_{T°}$, $\varepsilon'_{T°}$ and eventually $\varepsilon''_{T°}$, but one must be carreful in interpretating the results, specially the uncertainties since they come from two independant Taylor expansions versus T: one for $X_{0,T}$ and one for ε_T (or γ_T). This overall type of data treatment is easier by using explicit substituion of (20b) to (24) into (12) to (15'). These big formulae (table III) are straightforward and they are also needed for speciation predictions.

SIT equations for predictions.

Numerical values of the thermodynamic functions in real (not only standard) conditions are often needed: typically $E_{I,T}$ and lg $K_{I,T}$ for speciation prediction in real aqueous solution. Their standard values, $X_{0,T°}$ (X=G, H, S or Cp, see also (1)) are usually tabulated. $E_{0,T°}$ and lg $K_{0,T°}$ are then calculated by using (9) and (10). T corrections (to get $E_{0,T}$ and lg $K_{0,T}$) are then performed by using (12) to (15) or (15') where I is set to 0. They are finally corrected for I, by using (20) to (24) wich also require to get $\varepsilon_{T°}$, $\varepsilon'_{T°}$, $\varepsilon''_{T°}$, $D_{I,T°}$, $D'_{I,T°}$ and $D'''_{I,T°}$ tabulated values. All these parameters can indeed be measured and then used in the following formula:

where $X_{0,T°}$ (X = A, B, or C) are deduced (table III) from tabulated standard values of G, H, Cp; and $X^{ex}_{I,T°}$ are calculated by using the equations (20a) to (23a) or (24) where we set T to T°.

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Table I: **Predominating terms of heat capacity** deduced from the formula (1) :

$Cp \approx Cp° \approx a$ when $T_{ea} < T < T_{ab}$, but (1) is only valid between T_{min} and T_{max}, so this approximation is valid only in the grey temperatures (K) domain.

$T_{ea} = \left|\frac{e}{a}\right|^{0.5}$ and $T_{ab} = \left|\frac{a}{b}\right|$, $Cp \_ -\frac{e}{T^2}$ when $T < T_{ea}$, C b T when $T_{ab} < T$.

Typically, the U(cr) heat capacity is nearly constant from 298 to 923 K and its variations with temperature are linear from 923 to 941 K; but UO_2(cr) heat capacity is nearly constant from 250 to 600 K, since the b and e fitted parameters have negligible influence in the temperature range where the formula (1) is valid.

$X_{Tmax\ (or\ min)}$ is X (S or G) maximum (or minimum) value from 290 to 390 K.

	T_{ea}	T_{min}	T_{ab}	T_{max}	T_{ab}		S_{Tmax}-S_{Tmin} ($J.K^{-1}.mol^{-1}$)	G_{Tmax}-G_{Tmin} ($kJ.mol^{-1}$)
U(cr)		298	923	941			8.5	0
UO_2(cr)	111	250		600	1978		19.7	17.0
$UO_{2.6667}$(cr)	119	233		600	3938		24.8	21.9
$\beta.UO_2(OH)_2$	291	298		473			41.8	43.5
$\beta.UO_3$	113	298		678	3450		25.1	25.1
$UO_3.2H_2O$(cr)		298	286	400			54.4	61.3
UCl_3(cr)	74	298		1000	1128		28.1	21.5
UCl_4(cr)	29	298		800	2197		36.3	30.1
UCl_5(cr)		298		600	3940		45.1	34.6
UCl_6(cr)	65	298		452	4946		52.9	41.1
UOCl(cr)	105	298		900	5283		21.7	15.3
$UOCl_2$(cr)	97	298		700	4449		29.0	22.5
$UOCl_3$(cr)	14	298		900	2640		35.1	30.2
UO_2Cl(cr)	93	298		1000	4050		26.9	24.3
UO_2Cl_2(cr)	100	298		650	6311		32.9	31.4
$U_2O_2Cl_5$(cr)	98	298		700	6588		66.9	50.8
$(UO_2)_2Cl_3$(cr)	114	298		900	6353		62.7	54.3

Table II : Specific Interaction Coefficients, ε, as function of Temperature

$\varepsilon_T = (\varepsilon_{T^\circ} + \varepsilon'_{T^\circ}\, t)$, where ε_T is ε value at temperature, T, $\Delta T = T - T^\circ$, $T^\circ = 25°C$.

$\varepsilon' = \left(\frac{\partial \varepsilon}{\partial T}\right)_p$, ε'_T is ε' value at T°, $\Delta\varepsilon = \varepsilon_{ox} - \varepsilon_{red} + \varepsilon_{Na^+,Cl^-}$, $M(VI) = MO_2(CO_3)_3^{4-}$;

$M(V) = MO_2(CO_3)_3^{5-}$

	$\Delta\varepsilon_{T^\circ}$ or ε_{T° (kg.mol^{-1})	$\Delta\varepsilon'_{T^\circ}$ or ε'_{T° (kg.mol^{-1}.T^{-1})	Reference
Pu^{4+}/ Pu^{3+}	0.39	2	[5]
PuO_2^{2+}/ PuO_2^{+}	0.25	-1	
U(VI)/U(V)	0.98	-6	
Pu(VI)/Pu(V)	0.27	-1.5	
NaCl	0.035	2.3	[10]
LiCl	0.11	-3.3	[11][12]
$SrCl_2$	0.15	-9.7	[12]

Figure 1 : Variations with temperature of the Specific Interaction Coefficient, ε, of chloride strong electrolytes.

ε is deduced from mean activity coefficient measurements.

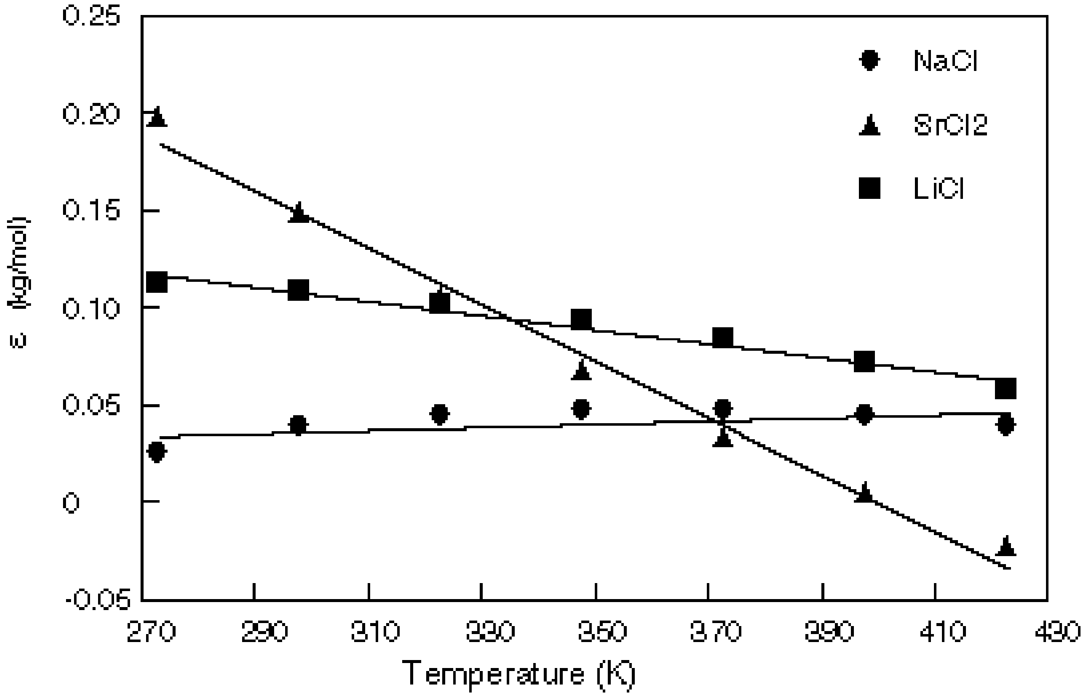

Figure 2 : Variations with temperature of the Specific Interaction Coefficient, Δε, of $PuO_2(CO_3)_3^{4-}/PuO_2(CO_3)_3^{5-}$ redox couple.

$\Delta\varepsilon = \varepsilon(PuO_2(CO_3)_3^{4-}, Na^+) - \varepsilon(PuO_2(CO_3)_3^{5-}, Na^+) + \varepsilon(Na^+, Cl^-)$