

Adjustment of activity coefficients as a function of changes in temperature, using the specific interaction theory*

Eric Giffaut, Pierre Vitorge** and H el ene Capdevila

CEA DCC-DESD-SCS-Section de G eoChimie LAT, Centre d'Etudes Nucl eaires, B.P. 6, 92265 Fontenay-aux-Roses Cedex (France)

Abstract

The aim of this work is to propose and to check approximations to calculate from only a few experimental measurements, ionic strength I and temperature T , influences on Gibbs' energy G , formal redox potential E and standard equilibrium constant K . Series expansions vs. T are first used: S and $C_p/2T^\circ$ are typically the first- and second-order terms in $-G$. In the same way, $-\Delta H$ and $T^2 \Delta C_p/2$ are the first- and second-order terms of $R \ln K$ expansions vs. $1/T$. This type of approximation is discussed for 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 ($M \equiv U$ or Pu) measured from 5 to 70 °C, for the standard ΔG of some solid U compounds, calculated from 17 to 117 °C, and for ΔC_p , ΔG and $\log K$ of the $CO_{2(aq)}/HCO_3^-$ equilibrium from 0 to 150 °C. Excess functions X^{ex} are then calculated from activity coefficients γ : enthalpy H or heat capacity C_p adjustment as a function of I changes is needed only when the γ adjustment as a function of T changes is needed. The variations in the specific interaction theory coefficient ϵ with T are small and roughly linear for the above redox equilibria and for the mean γ of chloride electrolytes: first-order expansion seems enough to deduce ϵ , and then the excess functions G^{ex} , S^{ex} and H^{ex} , in this T range; but second-order expansion is more consistent for estimation of C_p^{ex} .

1. Introduction

Chemical speciation in aqueous solutions is needed to understand and to predict the 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 accuracy only in high ionic strength I electrolytes, but in most groundwaters studied for radioactive waste disposal, I is lower and the temperature T is higher than in usual laboratory conditions. Activity coefficients γ are needed to calculate the influence of I on K and E , typically to extrapolate them to the standard state (infinite dilution). We focus on actinides. We will, in fact, use the specific interaction theory (SIT) for adjustment as a function of changes in I and we will test some approximations, namely Taylor's series expansion for adjustment as a function of T changes. This type of calculation with the first derivative of $\ln \gamma$ has already been made for the NaCl Pitzer parameters [1], but their T variations are not linear: empirical formulae similar to eqn. (1) are now proposed [2]. We find that the shapes of the curves

representing the T variations of the LiCl, KCl and SrCl₂ Pitzer parameters differ from the NaCl curve. In addition, the two second virial Pitzer parameters are correlated [3] and many experimental points are then needed to fit them: this leads to some difficulties [4, 5] for the complex ions whose predominance domain is small. There are even fewer data measured at different temperatures. We then prefer to calculate the γ of complex ions by using [6–10] the SIT [11], which needs only one fitted parameter ϵ . Many published data on changes in mean γ with T are measured at water-saturated pressure, but we here focus on the influence of T at (constant) atmospheric pressure and then at T less than 100 °C.

We here first evaluate the order of magnitude of the influence of T on E , $\log K$ and G , from E measurements and from some published C_p , ΔC_p and K values. We then propose and discuss formulae for adjustments of G , H , S , C_p and K with changes in T . We then examine the influences of T together with I on E measurements and on some published mean γ . Classical thermodynamic relations that we refer to in section 2 can then be used to adjust the excess contribution to G , H , S and C_p , as a function of changes in I and T , by using γ calculated from the ϵ value.

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**Author to whom correspondence should be addressed.

2. Working equations

2.1. Temperature variations of thermodynamic functions

The variations with T in solid compound heat capacity (eqn. (1a)) are typically calculated with empirical coefficients a , b , d , e in thermochemical data bases, e.g. ref. 11. We easily deduce similar expressions for the entropy S (eqn. (2)) and for the enthalpy H (eqn. (3)) from the classical thermodynamic relations (4a) and (5)

$$C_{pI,T} = a + bT + \frac{d}{T} + \frac{e}{T^2} \quad (1a)$$

$$S_{I,T} = S_{I,T^0} + a \ln \frac{T}{T^0} + b(T - T^0) - d \left(\frac{1}{T} - \frac{1}{T^0} \right) - \frac{e}{2} \left(\frac{1}{T^2} - \frac{1}{T^{02}} \right) \quad (2)$$

$$H_{I,T} = H_{I,T^0} + a(T - T^0) + \frac{b}{2} (T^2 - T^{02}) + d \ln \frac{T}{T^0} - e \left(\frac{1}{T} - \frac{1}{T^0} \right) \quad (3)$$

$$H'_{I,T} = C_{pI,T} \quad (4a)$$

$$H''_{I,T} = -T^2 C_{pI,T} \quad (4b)$$

$$S'_{I,T} = \frac{C_{pI,T}}{T} \quad (5)$$

$$S''_{I,T} = \frac{C'_{pI,T}}{T} - \frac{C_{pI,T}}{T^2} \quad (6)$$

$$G'_{I,T} = -S_{I,T} \quad (7)$$

$$G_{I,T} = H_{I,T} - TS_{I,T} \quad (8)$$

S , C_p and $\Delta H/T^2$ are the first-order terms of T series expansion of respectively $-G$ (eqn. (7)), H (eqn. (4a)) and $R \ln K$ (eqn. (11a)). G , H and $\log K$ can be directly measured. Relations (1a), (2), (3), (4a), (4b) and (5)–(8) are valid at each I and T : we write a , b , ... and not $a_{I,T}$, $b_{I,T}$, ... since we shall use eqns. (1a), (2) and (3) only for T adjustments. We shall use eqns. (1a), (2) and (3) together with eqns. (8) and (10) for discussion and to build Table 2. We shall see that Taylor's series expansions are also useful approximations in our T range in solution chemistry. For this, we shall use

$$C_{pI,T} \approx C_{pI,T^0} + C'_{pI,T^0}t + C''_{pI,T^0}t^2/2 \quad (1b)$$

instead of eqn. (1a). As for C_p (eqn. (1b)) from the differential relations (4a), (4b) and (5)–(7) and from similar $\ln K$ relations (eqns. (11a)–(13a)), we shall expand G , H , S , E (eqn. (9)) and $\ln K$ (eqn. (10)) into series as a function of T (or t ; this is equivalent) about $T = T^0$ (eqn. (24) and Table 1). We shall also expand (last line of Table 1) $\ln K$ as a function of $1/T$ (or f ;

this is equivalent) by using the Van't Hoff (eqn. (11a)), and differential (eqns. (4b), (12a) and (13a)) relations

$$\Delta G_{I,T} = -nFE_{I,T} \quad (9)$$

$$\Delta G_{I,T} = -RT \ln K_{I,T} \quad (10)$$

$$RT(\ln K_{I,T})' = \Delta H_{I,T}/T \quad (11a)$$

$$RT^2(\ln K_{I,T})'' = \Delta C_{pI,T} - 2 \Delta H_{I,T}/T \quad (12a)$$

$$RT^3(\ln K_{I,T})''' = T \Delta C'_{pI,T} - 4 \Delta C_{pI,T} + 6 \Delta H_{I,T}/T \quad (13a)$$

$$R'(\ln K_{I,T}) = -\Delta H_{I,T} \quad (11b)$$

$$R''(\ln K_{I,T}) = T^2 \Delta C_{pI,T} \quad (12b)$$

$$R'''(\ln K_{I,T}) = -T^3(2 \Delta C_{pI,T} + T \Delta C'_{pI,T}) \quad (13b)$$

2.2. Temperature variations of activity and specific interaction theory coefficients

We calculate the activity coefficient $\gamma(i)$ of an ion i by using the SIT [11]:

$$\log \gamma(i)_{I,T} = -z(i)^2 D_{I,T} + \sum_j \epsilon(i,j)_T m(j) \quad (14a)$$

$\epsilon(i,j)_T$ are fitted parameters related to the ions i and j , with opposite charges. $z(i)$ is the charge of the ion i . $m(j)$ is the molality of the ion j . $\epsilon(i,j)_T$ is supposed to be only T dependent: eqn. (14a) is then an approximation, but we still use the symbol “=” and not “ \approx ” that we are writing only for Taylor's series expansions as a function of T (or $1/T$). When $m(j)$ is low enough (typically when j is at trace level), we disregard the $\epsilon(i,j)_T m(j)$ term [11]. We shall now omit i and j , and we shall take into account only one major ion j (eqn. (14b)). Since all equations are linear, generalization is straightforward [10]. Excess functions [12], eqns. (17), (18a)–(21a), (22) and (23), account for the transformation from ideal ($I=0$) to real solution. They introduce new linear relations. We refer to the exact equations (16a), (17), (18a)–(21a), (22) and (23) before using the Taylor series expansion (15):

$$\log \gamma_{I,T} \approx -z^2(D_{I,T^0} + D'_{I,T^0}t + D''_{I,T^0}t^2/2) + m(\epsilon_{T^0} + \epsilon'_{T^0}t + \epsilon''_{T^0}t^2/2) \quad (15)$$

$$\log K_{0,T} = \log K_{I,T} + \Delta \log \gamma_{I,T} \quad (16a)$$

$$X_{I,T} = X_{0,T} + X_{I,T}^{\text{ex}} \quad (\text{where } X \equiv G \text{ or } H \text{ or } S \text{ or } C_p) \quad (17)$$

$$G_{I,T}^{\text{ex}} = RT \ln \gamma_{I,T} \quad (18a)$$

$$H_{I,T}^{\text{ex}} = -RT^2(\ln \gamma)'_{I,T} \quad (19a)$$

$$S_{I,T}^{\text{ex}} = -R[\ln \gamma_{I,T} + T(\ln \gamma)'_{I,T}] \quad (20a)$$

$$C_{pI,T}^{\text{ex}} = -RT[2(\ln \gamma)'_{I,T} + T(\ln \gamma)''_{I,T}] \quad (21a)$$

$$(C_p^{\text{ex}})'_{I,T} = -R[2(\ln \gamma)'_{I,T} + 4T(\ln \gamma)''_{I,T} + T^2(\ln \gamma)'''_{I,T}] \quad (22)$$

TABLE 1. Series expansion coefficients $X_{0,T^0}^{(q)}$, of thermodynamic functions $X_{I,T}$

$X \equiv X^{(0)}$	$X^{(1)}$	$X^{(2)}$	$X^{(3)}$	$X^{(4)}$
G	$-S$	$-\frac{C_p}{2T}$	$\frac{C_p - TC_p'}{6T^2}$	$-\frac{T^2 C_p'' + 2C_p}{24T^3}$
H	C_p	$\frac{C_p'}{2}$	$\frac{C_p''}{6}$	
S	$\frac{C_p}{T}$	$\frac{TC_p' - C_p}{2T^2}$	$\frac{T^2 C_p'' + 2C_p}{6T^3}$	
C_p	C_p'	$\frac{C_p''}{2}$		
$R \ln K$	$\frac{\Delta H}{T^2}$	$\frac{T \Delta C_p - 2 \Delta H}{2T^3}$	$\frac{T^2 \Delta C_p' - 4T \Delta C_p + 6 \Delta H}{6T^4}$	$\frac{T^3 \Delta C_p'' - 6T^2 \Delta C_p' + 18T \Delta C_p - 24 \Delta H}{24T^5}$
$R \ln K^*$	$-\Delta H$	$T^2 \frac{\Delta C_p}{2}$	$-T^3 \frac{T \Delta C_p' + 2 \Delta C_p}{6}$	$T^4 \frac{T^2 \Delta C_p'' + 6T \Delta C_p' + 6 \Delta C_p}{24}$

The expansion is eqn. (24): $X_{I,T} \approx \sum_{q \geq 0} (X_{0,T^0}^{(q)} + X_{I,T^0}^{(q)ex}) x^q$, $x = t = T - T^0$ except in the last line where $x = f = 1/T - 1/T^0$. $X \equiv G, H, S, C_p$ or $\ln K$ (first column). $X = X^{(0)}$ and $X^{(q+1)}$ is the derivative of $X^{(q)}/(q+1)$; typically the derivative value of $X \equiv X^{(0)}$ for $I=0$ and $T=T^0$ is $X_{0,T^0}^{(1)}$ and this corresponds to the exact thermodynamic relations (4a), (5) and (7). Typically, when $X \equiv G$ (first line), $-(S_{0,T^0} + S_{I,T^0}^{ex})t$ is first- (second column) order term of $G_{I,T}$. Numerical values of $X_{0,T^0}^{(q)}$ and $X_{I,T^0}^{(q)ex}$ are then needed to calculate $X_{I,T}$ by using eqn. (24). We calculate the numerical value of $X_{0,T^0}^{(q)}$ (typically $X_{0,T^0}^{(1)}$ is $-S_{0,T^0}$ when $X \equiv G$ from tabulated standard values of G_{0,T^0} , H_{0,T^0} or C_{p0,T^0} , e.g. ref. 11). Numerical values of neither $X_{I,T^0}^{(q)ex}$ nor $X_{0,T^0}^{(q)}$ are tabulated: we calculate them by using eqns. (16b) or (18b)–(21b). Numerical values of D_{I,T^0} , D'_{I,T^0} , D''_{I,T^0} , ..., ϵ_{T^0} , ϵ'_{T^0} , ϵ''_{T^0} , ... are needed for this. We calculate D'_{I,T^0} , D''_{I,T^0} , ... values from tabulated Debye–Hückel term values, $D_{I,T}$, and we measure (see text) the others. For consistency (see text), we do not write the $X^{(q)}$ terms that include a C_p'' contribution.

*We tabulate the coefficients of the $R \ln K$ Taylor expansion *vs.* $1/T$ (and not *vs.* T).

$$(C_p^{ex})_{I,T} = -R[6(\ln \gamma)''_{I,T} + 6T(\ln \gamma)'''_{I,T} + T^2(\ln \gamma)''''_{I,T}] \quad (23)$$

Equation (16a) is the definition of γ and eqn. (17) is the excess function definition; since they are linear, eqns. (4a) and (5)–(8) are still valid for the excess functions. We obtain eqn. (18a) from eqns. (16a) and (10), eqn. (20a) from eqns. (18a) and (7), eqn. (19a) from eqns. (18a), (20a) and (8), eqn. (21a) from eqns. (19a) and (4a), eqn. (22) from eqn. (21a), and eqn. (23) from eqn. (22). Equations (18a) [13], (19a) [12], (20a) [13, 14] and (21a) [2] have more or less already been proposed. ΔH (eqn. (19a)) and ΔC_p (eqn. (21a)) adjustments as a function of changes in I are needed only when γ adjustments as a function of changes in T are needed. The γ derivative in eqns. (19a)–(21a), (22) and (23) comes from differential thermodynamic equations (and not from series expansion): there are no approximations in these equations that can be used for any γ theory. To write them for the SIT, we substitute the SIT equation (14b) into eqns. (16a) and (18a)–(21a):

$$\log \gamma = -z^2 D_{I,T} + m \epsilon_T \quad (14b)$$

$$\log K_{I,T} = \log K_{0,T} + \Delta z^2 D_{I,T} - m \Delta \epsilon_T \quad (16b)$$

$$G_{I,T}^{ex} = rT(-z^2 D_{I,T} + m \epsilon_T) \quad (18b)$$

$$H_{I,T}^{ex} = rT^2(z^2 D'_{I,T} - m \epsilon'_T) \quad (19b)$$

$$S_{I,T}^{ex} = r[z^2(D_{I,T} + TD'_{I,T}) - m(\epsilon_T + T\epsilon'_T)] \quad (20b)$$

$$C_{pI,T}^{ex} = rT[z^2(2D'_{I,T} + TD''_{I,T}) - m(2\epsilon'_T + T\epsilon''_T)] \quad (21b)$$

In the same way, ϵ' , ϵ'' , D' and D'' come from exact relations in eqns. (19b)–(21b). We finally write $X_{I,T}$ ($X \equiv G, H, C_p$ or $R \ln K$) Taylor's series expansions:

$$X_{I,T} \approx \sum_{q \geq 0} (X_{0,T^0}^{(q)} + X_{I,T^0}^{(q)ex}) x^q \quad (24)$$

$$X^{(q+1)} = \frac{(X^{(q)})'}{q+1}, \quad \text{when } x=t \quad (25a)$$

$$X^{(q+1)} = -T^2 \frac{(X^{(q)})'}{q+1}, \quad \text{when } x=f \quad (25b)$$

We first focus on the functions $X^{(q)}$ and $X^{(q)ex}$. We will then explain how to obtain their numerical values, $X_{0,T^0}^{(q)}$ and $X_{I,T^0}^{(q)ex}$ respectively. Since eqn. (24) is X , the series expansion of $X = X^{(0)}$. We obtain the definition of $X^{(1)}$ by deriving $X^{(0)}$: we set q to 0 in eqn. (25a) or (25b). We deduce in the same way the definition of $X^{(2)}$ from that of $X^{(1)}$, and so on (Table 1). Some of the above formulae explain eqn. (24) by giving more explicit relations: when we set q to 0 in eqn. (25a),

$(X^{(0)})' = X^{(1)}$ is the thermodynamic relation (4a) when $X \equiv H$, it is eqn. (5) one when $X \equiv S$, or it is eqn. (7) one when $X \equiv G$. In the same way, eqns. (25a) and (25b) summarize eqns. (6), (11a)–(13a), (4b) and (11b)–(13b), e.g. when $X \equiv G$, $X^{(1)}$ is $G' = -S$, and $-(S_{0,T^0} + S_{I,T^0}^{\text{ex}})t$ is first-order term of $G_{I,T}$ (eqn. (7a)). We shall see that numerical values of C_p^m are not very useful (and difficult to measure) for our purpose. For consistency (Table 1) when writing formula (24), we then do not write the $X^{(q)}$ terms that include any C_p^m contribution. We will test approximations with experimental data on C_p and other functions. We calculate numerical values of $X_{0,T^0}^{(q)}$ (typically $G_{0,T^0}^{(1)} = -S_{0,T^0}$) from tabulated G_{0,T^0} , H_{0,T^0} or C_{p0,T^0} standard values. Numerical values of $X_{I,T^0}^{(q)\text{ex}}$ are not tabulated. To calculate them, we propose to use D and ϵ Taylor's series expansions to obtain formulae such as eqn. (15) and to substitute them into eqns. (16), (18)–(21a), (22) and (23). The first-order terms of these formulae are eqns. (14b), (16b) or (18b) with (19b)–(21b) where we set T to T^0 . Explicit writing of eqn. (24) is now straightforward (some of them will be in Eric Giffaut's thesis). We then need numerical values of D_{I,T^0} , D'_{I,T^0} , D''_{I,T^0} , ..., ϵ_{T^0} , ϵ'_{T^0} , ϵ''_{T^0} We calculate D'_{I,T^0} , D''_{I,T^0} ... values from tabulated $D_{I,T}$ values, e.g. ref. 11. We measure ϵ_T as a function of T to deduce ϵ_{T^0} , ϵ'_{T^0} , ϵ''_{T^0} by curve fitting (see next section).

3. Results and discussion of numerical data and of equations

3.1. Influences of temperature on thermodynamic functions

3.1.1. Some U and Pu redox equilibria in acidic and carbonate media

We have found [9, 10] roughly linear variations from 5 to 70 °C for the reversible U and Pu redox potentials in acidic and carbonate solutions: by using eqns. (7) and (9), we deduce the mean value of $\langle \Delta S_{I,T^0} \rangle$ from the slope of $E_{I,T}$ (as a function of T) measurements, and we detect (eqn. (5)) the influence of ΔC_p on $E_{I,T}$ (also $\Delta G_{I,T}$), but it is not straightforward to deduce $\Delta C_{pI,T^0}$. We fit experimental $E_{I,T}$ data to the second-order (eqn. (24), where $X \equiv G$) power function as a function of T (constant I). The results are E_{I,T^0} , $\Delta S_{I,T^0}$, and inaccurate $\langle \Delta C_{pI,T^0} \rangle$ values. They are not much different from the previous interpretation [9, 10] where we disregarded ΔC_p . The potential $E(\text{Ag}/\text{AgCl})$ of the reference electrode that we are using in our measurements is tabulated only when $I=0$. Power functions formally equivalent to the Taylor series expansion (24) are typically proposed [15]. For consistency we treat the original experimental $E(\text{Ag}/\text{AgCl})$ values in the same way as our U and Pu data to obtain them

vs. the normal hydrogen electrode. We will give supplementary results of this data treatment elsewhere [16].

3.1.2. $\text{CO}_2(\text{aq})$ –bicarbonate equilibrium

There are few published measurements of the heat capacities of soluble actinide complexes [17]. The ΔC_p value of $\text{CO}_2(\text{aq})$ –bicarbonate equilibrium [18] varies between -400 and $-50 \text{ J mol}^{-1} \text{ K}^{-1}$ in NaCl (0–5 M) from 0 to 150 °C. Some data were measured at saturated water pressure which varies with T . Hence, we should use other terms in the equations of Table 1 to take into account the influence of pressure; we believe that the C_p value at (constant) atmospheric pressure is not much different. In pure water or at low I , ΔC_p increases with T (up to 70 °C) and then decreases, but at $I > 3$ no ΔC_p decrease is observed at least up to 150 °C. This last (at high I) shape of the curve representing ΔC_p variations with T is usually also observed for solid compounds (see below). The ΔG variations with T seem to be roughly linear; this means that the first-order term $-\Delta S_{I,T^0}$ predominates and consequently the second, $\Delta C_{pI,T^0}/2T$, and further terms (Table 1) have small or negligible influence in these conditions. $\log K$ variations with T are classically interpreted with the Van't Hoff equation (11b). We have then plotted the carbonate equilibrium $\log K$ variations as a function of T or as a function of $1/T$. These representations are roughly straight lines: $\Delta C_{pI,T^0}$ and further terms have again a small or negligible influence on $\log K$ variations with T ; the main contribution is due to H_{I,T^0} . Van't Hoff representation is the better $\log K$ representation in this case. For consistency with the usual databases, we only fit $\Delta C'_{pI,T^0}$ and we use published [18] $\Delta G_{I,T^0}$, $\Delta S_{I,T^0}$ and $\Delta C_{pI,T^0}$. ΔG and $\log K$ representations are then predictions and not curve fitting. Anyhow, $\log K$ and ΔG changes as a function of T are relatively small; typically $\log K$ varies by less than 0.4 unit, at $I=0$.

3.1.3. Formation of some U compounds

We calculate the variations in the thermodynamic functions from 290 to 390 K for some solid U compounds (Table 2) by using eqns. (1a), (2), (3), (8) and (10). We find (in this T range) that C_p variations are usually lower than $20 \text{ J K}^{-1} \text{ mol}^{-1}$ and S variations are lower than $60 \text{ J K}^{-1} \text{ mol}^{-1}$; this induces less than 50 kJ mol^{-1} variations in G (Table 2). The a term of these developments (eqns. (1a), (2) and (3)) is then always the most important term. This means that C_p is roughly constant in this T range. Still, for further discussion about solubility, heat capacity data for soluble species are lacking.

TABLE 2. Influence of T on formation enthalpy and entropy of some U compounds

	T_{ea}	T_{min}	T_{ab}	T_{max}	T_{ab}	$S_{T_{max}} - S_{T_{min}}$ (J K ⁻¹ mol ⁻¹)	$G_{T_{max}} - G_{T_{min}}$ (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
β -UO ₂ (OH) ₂	291	298		473		41.8	43.5
β -UO ₃	113	298		678	3450	25.1	25.1
UO ₃ ·2H ₂ O(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 ₂ Cl(cr.)	93	298		1000	4050	26.9	24.3
UO ₂ Cl ₂ (cr.)	100	298		650	6311	32.9	31.4
U ₂ O ₂ Cl ₅ (cr.)	98	298		700	6588	66.9	50.8
(UO ₂) ₂ Cl ₃ (cr.)	114	298		900	6353	62.7	54.3

$X_{T_{max}}$ (or $X_{T_{min}}$) is the maximum (or minimum) value of X (S or G) from 290 to 390 K. We calculate these values from Grenthe *et al.* [11] by using eqns. (1a), (2), (3) and (9). $C_p \approx a$ when $T_{ea} < T < T_{ab}$, but eqn. (1a) is only valid between T_{min} and T_{max} , so this estimate is valid only in the corresponding temperature domain. $T_{ea} = |e/a|^{0.5}$ and $T_{ab} = |a/b|$. $C_p \approx e/T^2$ when $T < T_{ea}$ and $C_p \approx bT$ when $T_{ab} < T$. Typically, the heat capacity of U(cr.) is nearly constant from 298 to 923 K and its variations with T are linear from 923 to 941 K, but the heat capacity of UO₂(cr.) is nearly constant from 250 to 600 K, since the fitted parameters b and e have negligible influence in the temperature range where the formula (1a) is valid.

3.1.4. Discussion of formulae

We previously [10] disregarded the influence of $\Delta C_{p_i, T}$ on $E_{I, T}$ variations with T . This is attributed to $\Delta S_{I, T^0}$, the estimated mean value $\langle \Delta S_{I, T^0} \rangle$ which includes (disregarded) $\Delta C_{p_i, T^0}$ contributions. $\langle \Delta S_{I, T^0} \rangle$ is indeed a little different from $\Delta S_{I, T^0}$. In the same way, when disregarding $\Delta C'_{p_i, T^0}$ we fit E_{I, T^0} , $\Delta S_{I, T^0}$ and we estimate $\langle \Delta C'_{p_i, T^0} \rangle$ which might include a (disregarded) $\Delta C'_{p_i, T^0}$ contribution etc. A first-order rough approximation on ΔC_p is enough to account for $\Delta G_{I, T}$ or $\log K_{I, T}$ results but not for $\Delta C_{p_i, T}$ results. Interpretations deduced either from approximation (1a) or from approximation (1b) should both be just as good (Table 1) in our T range since (Table 2) $a \approx C_{p_i, T^0}$ and $C'_{p_i, T^0} \approx b - 2e/T^{0.5}$. The first formula (1a) is supposed to be valid in a wider T range but the above discussion on numerical values suggests that, in aqueous solution conditions at atmospheric pressure, it is equivalent to the Taylor series expansion (1b) of C_p to the second order and then, at the most, the corresponding equations (24) for G , H , S and $\ln K$ (Table 1). Chemical speciation predictions only need E and $\log K$ thermodynamic functions: anyhow, C_p variations induce only small variations on them (Fig. 1).

In solution chemistry around 10–100 °C, “zero” (disregarding S), “first” (disregarding C_p , and hence S and H are not T dependent) or “second” (C_p not T dependent) order estimates can be used to predict chemical speciation depending on the needed accuracy. The

validity domain of these approximations is correlated to T^0 . T^0 could also be chosen in the middle of the working T range to minimize uncertainties. We do not do it for consistency with the classical thermodynamic database.

Taylor's series expansions are approximations; hence classical thermodynamic relations, typically eqns. (4a), (4b) and (5)–(8), are valid only within the same order of approximation: we always disregard the third- or fourth-order and further terms in eqn. (24) since they should also include C'''_{p_i, T^0} which we disregard, even when there are also C_{p_i, T^0} , C'_{p_i, T^0} or C''_{p_i, T^0} contributions to these higher terms. For many solids, and in the above example in high I electrolyte, $C_{p_i, T}$ increases with T and is then constant in the T range that we are discussing. In pure water and in low I electrolyte for the above example, the shape of the curve representing $C_{p_i, T}$ variations with T is different: this type of behaviour might be related to physical properties of electrolytes. It is then not straightforward to propose a general simple analytical formula that would account for $C_{p_i, T}$ variations with T in all cases. Anyhow, this has little practical consequence for chemical speciation. These approximations are certainly no longer valid at higher T , where the thermal energy involved in the physical phenomena related to C_p is no longer much smaller than the energy of chemical bonds. Since activity coefficients and excess functions (17) are related to weak interactions (and not chemical bonds) there

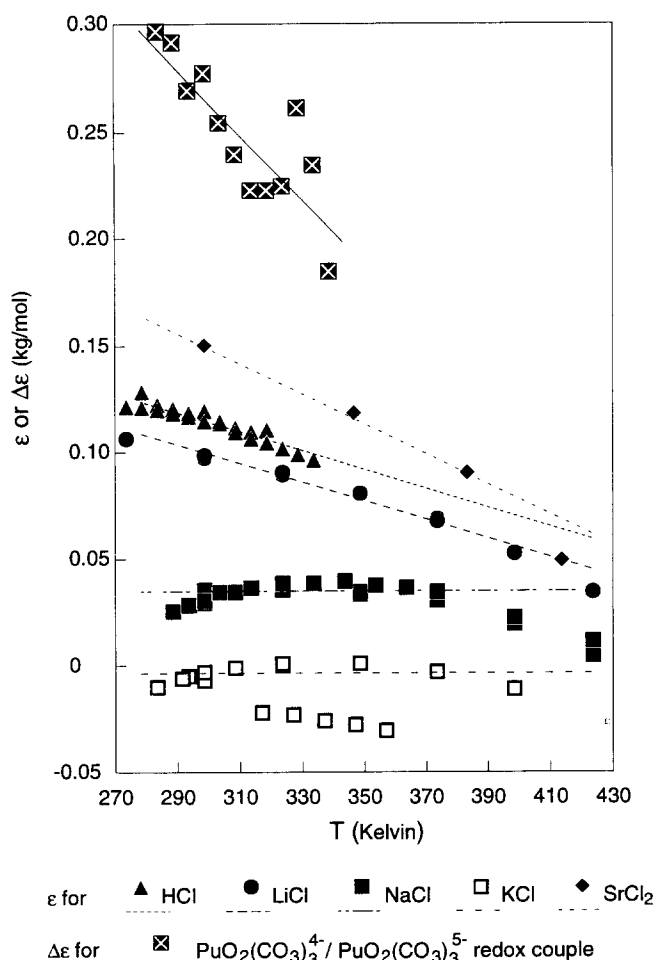


Fig. 1. Specific interaction coefficients ϵ as a function of temperature. We draw the lines with the equation $\epsilon_T = \epsilon_{T^0} + \epsilon'_{T^0} (T - T^0)$, where ϵ_T is the value of ϵ at temperature T and $T^0 = 298.15$ K. We calculate ϵ_T from mean γ_T data of the MCl electrolyte, and we then fit ϵ_{T^0} and ϵ'_{T^0} . We fit $\Delta\epsilon_{T^0}$ and $\Delta\epsilon'_{T^0}$ from $\Delta\epsilon_T$ data. $\text{Pu(VI)} \equiv \text{PuO}_2(\text{CO}_3)_3^{4-}$; $\text{Pu(V)} \equiv \text{PuO}_2(\text{CO}_3)_3^{5-}$. We plot $\epsilon = \epsilon(\text{M}^{n+}, \text{Cl}^-)$ and $\Delta\epsilon = \epsilon[\text{Pu(VI)}, \text{ClO}_4^-] - \epsilon[\text{Pu(V)}, \text{ClO}_4^-] + \epsilon(\text{Na}^+, \text{Cl}^-)$. See Table 3 for references, numerical values and other examples.

is no reason to find the same temperature behaviour for excess and ideal functions.

3.2. Temperature variations of activity and specific interaction theory coefficients

At each T , we fit ϵ_T values of some chloride electrolytes from published mean γ data (Table 3, Fig. 1), by using the SIT for I changes at constant T . Some of the γ data were measured at $T > 100$ °C, at saturated water vapour pressure. We select the data only up to 150 °C. We fit ϵ_{T^0} and ϵ'_{T^0} (Table 3) on the data at atmospheric pressure and we fit $\epsilon_{T^0}^*$ and $\epsilon'_{T^0}^*$ from those at higher pressure: we find negligible difference between the results of the two fittings.

In the same way, by using classical methodology [11], we can treat our redox measurements [9, 10] by first

TABLE 3. Specific interaction coefficients ϵ as a function of temperature

ox/red couple	$\Delta\epsilon_{T^0}$		$\Delta\epsilon'_{T^0}$	Reference for original γ_T or $\Delta\epsilon_T$ data
	This work	Ref. 11		
U(VI)/U(V)	0.95	0.77	-0.006	9, 10
Pu(VI)/Pu(V)	0.28		-0.001 ₅	10
$\text{PuO}_2^{2+}/\text{PuO}_2^+$	0.25	0.32	-0.001	10
$\text{Pu}^{4+}/\text{Pu}^{3+}$	0.36	0.55	0.002	10
MCl	ϵ_{T^0} (or ϵ^*)		ϵ'_{T^0} (or ϵ'^*)	
HCl	0.11 ₅	0.12	-0.0005	19, 20
LiCl	(0.09) ^a	0.10	-0.0000	21–23
NaCl	0.03	0.03	0.0001	23, 24,
	(0.03 ₅) ^a		(-0.0002) ^a	14, 23 ^a
KCl	-0.01	0.00	-0.0002	19, 23, 25,
	(-0.00) ^a		(-0.0000) ^a	23, 26 ^a
SrCl ₂	0.15		-0.0010	22

$\epsilon_T = \epsilon_{T^0} + \epsilon'_{T^0} (T - T^0)$, where ϵ_T is the value of ϵ at temperature T and $T^0 = 298.15$ K; the range of T is usually a 0–70 °C. We calculate ϵ_T from mean γ_T data of the MCl electrolyte, and we then fit ϵ_{T^0} and ϵ'_{T^0} . We fit $\Delta\epsilon_{T^0}$ and $\Delta\epsilon'_{T^0}$ from $\Delta\epsilon_T$ data. $\text{M(VI)} \equiv \text{MO}_2(\text{CO}_3)_3^{4-}$; $\text{M(V)} \equiv \text{MO}_2(\text{CO}_3)_3^{5-}$. $\Delta\epsilon(\text{ox/red}) = \epsilon(\text{ox}, \text{N}) - \epsilon(\text{red}, \text{N}) + \epsilon(\text{Na}^+, \text{Cl}^-)$; N is Na^+ when ox and red are anionic carbonate complexes, and it is ClO_4^- when ox and red are the aquo cations. $\epsilon(\text{ox}, \text{N})_{T^0}$ is the value of $\epsilon(\text{ox}, \text{N})$ at $T = T^0$. ϵ has units of kilograms per mole and ϵ' has units of kilograms per mole per kelvin.

^a $\epsilon_{T^0}^*$ and $\epsilon'_{T^0}^*$ are fitted from γ measurements up to 150 °C, at saturated water vapour pressure for LiCl and the second lines of NaCl and KCl results.

using the SIT for the influence of I and by then using a Taylor's series expansion for the influence of T : we first fit $E_{0,T}$ and $\Delta\epsilon_T$ values at each T , from $E_{I,T}$ data, by using eqns. (9) and (18b). We then fit the standard values E_{0,T^0} and at least $\Delta S_{0,T^0}$, by using eqns. (9) and (24) from $E_{0,T}$ data fitted at the first step. We finally use a Taylor's series expansion for $\Delta\epsilon$ to fit $\Delta\epsilon_{T^0}$ and at least $\Delta\epsilon'_{T^0}$ from $\Delta\epsilon_T$ fitted at the first step. We can also treat the data the other way around. At the first step, by using eqns. (9) and (24) at each I , we fit E_{I,T^0} and at least $\Delta S_{I,T^0}$ (which we do not directly calculate with the previous methodology) as a function of changes in T . We can then fit again E_{0,T^0} and $\Delta\epsilon_{T^0}$ by using the classical SIT equation (18b) on the first step results E_{I,T^0} . We then fit $\Delta\epsilon'_{T^0}$ by using the new SIT equation (20b) for entropy on the first step results $\Delta S_{I,T^0}$ etc. Treatment of experimental data by any of these procedures should be consistent: the link between these two data treatments is the new SIT formulae (14b), (16b) and (18b)–(21b) including the influence of T . We can also fit the parameters of eqn. (24) altogether and then calculate $S_{I,T}$, $H_{I,T}$ etc. by using again this equation (Table 1), but two-step data

treatments are needed to validate these equations, *i.e.* to control consistency.

The variations in ϵ_T or $\Delta\epsilon_T$ with T seem to be linear (Fig. 1). We have also checked from tabulated $D_{I,T}$ values [11] that $D'_{I,T}$ is not very T dependent. A first-order expansion (as a function of T) of eqn. (14b) seems a reasonable estimate, in the present work (Fig. 1).

Our ϵ_{T^0} and $\Delta\epsilon_{T^0}$ determinations (Table 3) are in accordance with published results [6–8, 10, 11]. We cannot compare our ϵ'_{T^0} or $\Delta\epsilon'_{T^0}$ determinations with others, since we cannot find any published results (except recently in ref. 10 by one of us). As usual [11] similar ions have similar numerical values of ϵ_{T^0} , *e.g.* $\epsilon(\text{HCl}) \approx \epsilon(\text{LiCl})$ and $\epsilon(\text{NaCl}) \approx \epsilon(\text{KCl})$. ϵ decreases with atomic number among the alkaline metals. We now observe (Table 3) the same analogies for ϵ' . As we already observed [10] $\Delta\epsilon[\text{M(VI)/M(V)}]$ is an exception, probably as a result of ion pairing. Published numerical values of ϵ for most complexes with charge more negative than -5 are surprising, *e.g.* the limiting carbonate complexes of M(IV) and M(V) and the trinuclear M(VI) carbonate complex [10, 11].

$\log K_{I,T}$, $\Delta G_{I,T}$ or $\Delta H_{I,T}$ can be directly measured from solution chemistry, electrochemical or calorimetric techniques at fixed T and I in each experiment. $\Delta S_{I,T}$ and $\Delta C_{pr,T}$ can then be deduced from them. When typically measuring $\log K_{I,T}$ or $\Delta G_{I,T}$, we calculate $\Delta\epsilon_T$ and check that it is not I dependent by [11] plotting $\log K_{I,T} - \Delta z^2 D_{I,T}$ *vs.* m (eqn. (16b)): it must be a straight line with slope $-\Delta\epsilon_T$. Using eqn. (18b) for E (eqn. (9)) measurements is equivalent [6–11]. One could, in the same way, plot (eqn. (19b)) $\Delta H_{I,T} - rT^2 \Delta z^2 D'_{I,T}$ as a function of m , to calculate $\Delta\epsilon_T$ from calorimetric experiments. For verification one should also plot $\Delta S_{I,T} - r \Delta z^2 (D_{I,T} + TD'_{I,T})$ (eqn. (20b)) or $\Delta C_{pr,T} - rT \Delta z^2 (2D'_{I,T} + TD''_{I,T})$ (eqn. (21b)) as a function of m . These data treatments can be performed at any (constant) T . It is also possible to fit all the parameters $X_{0,T^0}^{(q)}$, ϵ_{T^0} , ϵ'_{T^0} and eventually ϵ''_{T^0} together by using eqns. (15), (16b)–(21b) and (24).

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Appendix A: Nomenclature

$D_{I,T}$	$a_T I^{1/2} / (1 + b_T I^{1/2})$, where $a_{25^\circ\text{C}} = 0.5091$, $b_{25^\circ\text{C}} = 1.5$ [A1]
$b_T = B_n$	where B is taken from ref. A1 and n is assumed to be constant
E	normal redox potential
F	Faraday number
f	$1/T - 1/T^\circ$
K	equilibrium constant
n	number of electrons involved in redox equilibrium
r	$R \ln(10)$, where R is the molar gas constant

t	$T - T^\circ$ (K)	ΔX	algebraic summation of X with stoichiometric coefficients
ϵ^{*}	$(\partial \epsilon^* / \partial T)_{P_{\text{sat}}}$, where P_{sat} is the saturated water pressure, and ϵ^* is at this pressure	$Y_{I, T}$	numerical value of Y at ionic strength I and temperature T , where Y is typically X or X' ,
X	$X^{(0)}$, G , H , S , C_p , $\ln K$ or $\log K$ where we usually omit ⁽⁰⁾	\dots	
X'	$(\partial X / \partial T)_p = (\partial X / \partial t)_p$	$\langle \Delta Y_{I, T^\circ} \rangle$	mean numerical value of Y when T varies about $T = T^\circ$
X''	$(X')'$		
$'X$	$[\partial X / \partial (1/T)]_p = (\partial X / \partial f)_p$		
$''X$	$'(X)$		
$X^{(q)}$	q th-order derivative of X with respect to T (or $1/T$), hence $X' = X^{(1)}$ etc.		
$X^{(0)\text{ex}}$	excess function of X , defined by eqn. (17); we also usually omit ⁽⁰⁾		

Reference for Appendix A

A1 I. Grenthe, J. Fuger, R. Konings, R. Lemire, A. Muller, C. Nguyen-Trung and H. Wanner, *Chemical Thermodynamics of Uranium*, NEA-OECD, Elsevier, Amsterdam, 1992.