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Section de GéoChimie LAT

CORRECTIONS DE TEMPERATURE SUR LES COEFFICIENTS D'ACTIVITE CALCULES SELON LA TIS

par

Eric GIFFAUT, Pierre VITORGE, Hélène CAPDEVILA

- Novembre 1993 -

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"CORRECTIONS DE TEMPERATURE SUR LES COEFFICIENTS D'ACTIVITE CALCULES SELON LA TIS"

Sommaire - Le but de ce travail est de proposer et vérifier des approximations permettant de calculer, à partir de peu de mesures expérimentales, les corrections de force ionique, I, et de température, T, sur les enthalpies libres, G, les potentiels redox normaux apparents, E, et les constantes d'équilibres, K. Dans un premier temps, des développements limités en T sont utilisés : S et Cp/2T° sont ainsi les termes du premier et du second ordre pour -G. De même, -ΔH et $T^2\Delta Cp/2$ sont respectivement les termes du premier et du second ordre du développement limité de RlnK en 1/T. Ce type d'approximation est discutée pour le E des couples M^{4+}/M^{3+}, MO_2^{2+}/MO_2^{+} et $MO_2(CO_3)_3^{4-}/MO_2(CO_3)_3^{5-}$(M = U ou Pu), mesuré entre 5 et 70°C, pour le ΔG standard de plusieurs composés solides d'uranium calculés entre 17 et 117°C, et pour les ΔCp, ΔG et lgK de l'équilibre $CO_{2(aq)}/HCO_3^-$ entre 0 et 150°C. Les fonctions d'excès, X^{ex}, sont alors calculées à partir des coefficients d'activité, γ : les corrections de force ionique pour l'enthalpie, H, ou la capacité calorifique, Cp, sont uniquement nécessaires lorsque les variations de γ en fonction de T ne sont pas négligeables. Les variations en fonction de T du coefficient, ε, employé dans la théorie de l'interaction spécifique (TIS, SIT en anglais), sont faibles et approximativement linéaires pour les équilibres redox précédents et pour les coefficients d'activité moyens d'électrolytes chlorures. Un développement limité au premier ordre semble donc suffisant pour déterminer ε(T), et donc les fonctions d'excès G^{ex}, S^{ex} et H^{ex} dans le domaine de température étudié ; mais un développement au second ordre est plus cohérent pour estimer Cp^{ex}.

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"ADJUSTMENT OF ACTIVITY COEFFICIENTS AS A FUNCTION OF CHANGES IN TEMPERATURE, USING THE SIT"

Summary - 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, redox formal potential, E, and standard equilibrium constant, K. Series expansions versus T are first used ; S and Cp/2T° are typically the -G first and second order terms. In the same way, -ΔH and T^2 ΔCp/2 are the first and second order terms of R ln K expansions versus 1/T. 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, for the standard ΔG of some solid U compounds, calculated from 17 to 117°C, and for ΔCp, ΔG and lg 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, Cp, adjustment as a function of I changes is needed only when the γ adjustment as a function of T changes is needed. The SIT (Specific Interaction Theory) coefficient, ε, variations with T, are small and roughly linear for the above redox equilibria and for chloride electrolytes mean γ : 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 to estimate Cp^{ex}.

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Corrections de température sur les coefficients d'activité calculés selon la TIS.

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Ce travail fait partie de la thèse d'Eric Giffaut et a fait l'objet d'une communication orale présentée par Pierre Vitorge au congrès ACTINIDES-93. Nous présentons ici

- le **texte soumis à publication** (en angiais), écrit initialement par Eric Giffaut, assez profondément modifié par Pierre Vitorge en fonction des remarques et calculs en cours d'Hélène Capdevila ;

- des **figures ayant servi de base aux diapositives** dont l'élaboration, initialement par Hélène Capdevila, a été facilitée par les conseils, notamment linguistiques, de Sylvie Motellier et par l'aide de Patrick TranThe : qu'ils trouvent ici l'expression de nos remerciements ;

- un extrait d'une correspondance (en anglais) de Pierre Vitorge à Ingmar Grenthe sur l'utilisation de l'état standard pour les potentiels d'oxydo-réduction, l'entropie et les autres fonctions thermodynamiques.

Sommaire

Corrections de température sur les coefficients d'activité calculés selon la TIS

ADJUSTMENT OF ACTIVITY COEFFICIENTS AS A FUNCTION OF CHANGES IN TEMPERATURE, USING THE SIT.

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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 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 SIT for adjustment as a function of I changes and we will test some approximations, namely Taylor's series expansion for adjustment as a function of T changes. This type of calculation with ln γ first derivative, has already been made for the NaCl Pitzer parameters [1], but their T variations are not linear : empirical formulae similar to (1) are now proposed [2]. We find that the shapes of the curves representing the T variations of the LiCl, KCl and $SrCl_2$ Pitzer parameters, differ from the NaCl one. In addition, the two second virial Pitzer parameters are correlated [3], 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. They are even less data measured at different temperatures. We then prefer to calculate the γ of complex ions, by using [6][6a][7][8][9] the Specific Interaction Theory, SIT [10], which needs only one fitted parameter, ε. Many published data on T changes of mean γ are measured at water saturated pressure; but we here focus on T influence at (constant) atmospheric pressure and then at T less than 100°C.

We here first evaluate the order of magnitude of T influence on E, lg K and G, from E measurements and from some published Cp, ΔCp and K values. We then propose and discuss formulae for G, H, S, Cp and K adjustments with T changes. We then examine T together with I influences on E measurements and on some published mean γ. Classical thermodynamic relations that we remind in the working equation paragraph, can then be used to adjust the excess contribution to G, H, S and Cp, as a function of I and T changes, by using γ calculated from ε value.

2. Notations

X'	$= \left(\frac{\partial X}{\partial T}\right)_p$	$= \left(\frac{\partial X}{\partial t}\right)_p$	$'X$	$= \left(\frac{\partial X}{\partial (1/T)}\right)_p = \left(\frac{\partial X}{\partial f}\right)_p$
X''	$= (X')'$		$''X$	$= '('X)$
$\varepsilon^{*\prime}$	$= \left(\frac{\partial \varepsilon^*}{\partial T}\right)_{Psat}$	Psat , is saturated water pressure, and ε^* is at this pressure.		
t	$= T - T^\circ$	(T in Kelvin)	f	$= \frac{1}{T} - \frac{1}{T^\circ}$
r	$= R \ln(10)$	where R is the molar gas constant.		
$D_{I,T}$	$= \frac{a_T \sqrt{I}}{1 + b_T \sqrt{I}}$	where $a_{25°C} = 0.5091$,	$b_{25°C} = 1.5$	[10].

$Y_{I,T}$	is Y numerical value at ionic strength, I, and temperature, T, where Y is typically X or X'...
$<\Delta Y_{I,T^\circ}>$	is Y mean numerical value when T varies about T=T°.
$X^{\{q\}}$	is q^{th} order derivative of X with respect to T (or 1/T), hence $X'=X^{\{1\}}$ etc.
X	$= X^{\{0\}}$ is G, H, S, Cp, ln K or lg K where we usually omit $^{\{0\}}$.
$X^{\{q\}ex}$	is X excess function, (17) is its definition, we also usually omit $^{\{0\}}$.
ΔX	is the X algebraic summation with stoichiometric coefficients.
K	is equilibrium constant.
E	is normal redox potential.
F	is the Faraday number
n	is the number of electrons involved in redox equilibrium.

3. Working equations

3.1. Temperature variations of thermodynamic functions

The T variations of solid compound heat capacity (1), are typically calculated with empirical coefficients (a, b, d, e) in thermochemical data bases, e.g. [10]. We easily deduce similar expressions for the entropy, S (2), and for the enthalpy, H (3), from the (4) and (5) classical thermodynamic relations:

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

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

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

$$H'_{I,T} = Cp_{I,T} \quad (4)$$

$$'H_{I,T} = -T^2\, Cp_{I,T} \quad ('4)$$

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

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

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

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

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

$$Cp_{I,T} \approx Cp_{I,T^\circ} + Cp'_{I,T^\circ}\, t + Cp''_{I,T^\circ}\, t^2/2 \quad (1a)$$

instead of the equation (1). As for Cp (1a), from (4) to (7) differential relations and from ('11) to ('13) similar in K ones, we shall expand G, H, S, E (9) and ln K (10) into series as a function of T (or t, this is equivalent) about $T = T^\circ$, (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 Van't Hoff, ('11), and ('4), ('12) and ('13) differential relations:

$$\Delta G_{I,T} = -n\,F\,E_{I,T} \quad (9)$$

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

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

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

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

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

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

$$R\,T^2(\ln K_{I,T}) = -T^3\,(2\Delta Cp_{I,T} + T\,\Delta Cp'_{I,T}) \qquad (13)$$

3.2. Temperature variations of activity and SIT coefficients

We calculate activity coefficient, $\gamma(i)$, of an ion, i, by using the SIT [10] :

$$\lg \gamma(i)_{I,T} = -z(i)^2\,D_{I,T} + \sum_j \varepsilon(i,j)_T\,m(j) \qquad (14)$$

$\varepsilon(i,j)_T$ 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. $\varepsilon(i,j)_T$ is supposed to be only T dependent, (14) is then an approximation ; we still use = symbol and not ≈ one that we are writing only for Taylor's series expansion as a function of T (or 1/T). When $m(j)$ is low enough (typically when j is at trace level), we disregard the $\varepsilon(i,j)_T\,m(j)$ term [10]. We shall now omit i and j notations, and we shall take into account only one major ion, j, (14a). Since all equations are linear, generalisation is straightforward [9]. Excess functions [11], (17) to (23), account for the transformation from ideal (I = 0) to real solution. They introduce new linear relations. We write exact equations (16) to (23) before using the Taylor's series expansion, (15):

$$\lg \gamma_{I,T} \approx -z^2(D_{I,T^\circ} + D'_{I,T^\circ}\,t + D''_{I,T^\circ}\,t^2/2) + m\,(\varepsilon_{T^\circ} + \varepsilon'_{T^\circ}\,t + \varepsilon''_{T^\circ}\,t^2/2) \qquad (15)$$

$$\lg K_{0,T} = \lg K_{I,T} + \Delta \lg \gamma_{I,T} \qquad (16)$$

$$X_{I,T} = X_{0,T} + X^{ex}_{I,T} \qquad \text{(Where X = G or H or S or Cp)} \qquad (17)$$

$$G^{ex}_{I,T} = R\,T\,\ln \gamma_{I,T} \qquad (18)$$

$$H^{ex}_{I,T} = -R\,T^2\,(\ln \gamma)'_{I,T} \qquad (19)$$

$$S^{ex}_{I,T} = -R\,(\ln \gamma_{I,T} + T\,(\ln \gamma)'_{I,T}) \qquad (20)$$

$$Cp^{ex}_{I,T} = -RT(2(\ln \gamma)'_{I,T} + T\,(\ln \gamma)''_{I,T}) \qquad (21)$$

$$(Cp^{ex})'_{I,T} = -R(2(\ln \gamma)'_{I,T} + 4\,T(\ln \gamma)''_{I,T} + T^2\,(\ln \gamma)'''_{I,T}) \qquad (22)$$

$$(Cp^{ex})''_{I,T} = -R(6(\ln \gamma)'''_{I,T} + 6\,T(\ln \gamma)'''_{I,T} + T^2\,(\ln \gamma)''''_{I,T}) \qquad (23)$$

(16) is the γ definition and (17) is the excess function one; since they are linear, (4) to (8) are still valid for the excess functions. We obtain (18) from (16) and (10); (20) from (18) and (7); (19) from (18), (20) and (8); (21) from (19) and (4); (22) from (21); (23) from (22). (18) [12], (19) [11], (20) [12][13] and (21) [2] have more or less already been proposed. ΔH (19) and ΔCp (21) 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 (19) to (23) equations come 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 (14a) SIT equation into (16) and (18) to (21).

$$\lg \gamma = -z^2\,D_{I,T} + m\,\varepsilon_T \qquad (14a)$$

$$\lg K_{I,T} = \lg K_{0,T} + \Delta z^2\,D_{I,T} - m\,\Delta\varepsilon_T \qquad (16a)$$

$$G^{ex}_{I,T} = r\,T(-z^2\,D_{I,T} + m\,\varepsilon_T) \qquad (18a)$$

$$H^{ex}_{I,T} = r\,T^2\,(z^2\,D'_{I,T} - m\,\varepsilon'_T) \qquad (19a)$$

$$S^{ex}_{I,T} = r\,(z^2\,(D_{I,T} + T\,D'_{I,T}) - m\,(\varepsilon_T + T\,\varepsilon'_T)) \qquad (20a)$$

$$Cp^{ex}_{I,T} = rT(z^2\,(2\,D'_{I,T} + T\,D''_{I,T}) - m\,(2\,\varepsilon'_T + T\,\varepsilon''_T)) \qquad (21a)$$

In the same way, ε', ε'', D' and D'' come from exact relations in (19a) to (21a). We finally write $X_{I,T}$ (X = G, H, Cp or R ln K) Taylor's series expansion:

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

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

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

We first focus on $X^{\{q\}}$ and $X^{\{q\}ex}$ functions. We will then explain how to get their numerical values, $X^{\{q\}ex}_{0,T^\circ}$ and $X^{\{q\}ex}_{I,T^\circ}$ respectively. Since (24) is X series expansion $X = X^{\{0\}}$. We obtain $X^{\{1\}}$ definition by deriving $X^{\{0\}}$: we set q to 0 in equation (25) or '(25). We deduce the same way $X^{\{2\}}$ definition from $X^{\{1\}}$ one, and so on (table 1). Some above formulae explain the (24) equation by giving more explicit relations: when we set q to 0 in equation (25), $(X^{\{0\}})' = X^{\{1\}}$ is the thermodynamic relation (4) when X = H; it is (5) one when X = S; or it is (7) one when X = G. In the same way, (25) and '(25) summarise (6), (11) to (13), '(4) and '(11) to '(13), e.g. : when X = G, $X^{\{1\}}$ is G' = -S, and $-(S_{0,T^\circ} + S^{ex}_{I,T^\circ})t$ is $G_{I,T}$ first order term (7). We shall see that Cp'" numerical values are not much useful (and it is difficult to measure) for our purpose. For consistency when (table 1) writing formula (24), we then do not write the $X^{\{q\}}$ terms that include any Cp'" contribution. We will test approximations with experimental data on Cp and other functions. We calculate $X^{\{q\}}_{0,T^\circ}$ (typically $G^{\{1\}}_{0,T^\circ} = -S_{0,T^\circ}$) numerical value from tabulated, e.g. [10], G_{0,T°, H_{0,T° or Cp_{0,T° standard values. $X^{\{q\}ex}_{I,T^\circ}$ numerical values are not tabulated. To calculate them, we propose to use D and ε Taylor's series expansions to get formulae such as (15) and to substitute them into (16), (18) to (23). The first order terms of these formulae are equations (14a), (16a) or (18a) to (21a) where we set T to T°. Explicit writings of the equation (24) is now straightforward (some of them will be in Eric Giffaut's thesis). We then need D_{I,T°, D'_{I,T°, D''_{I,T°... ε_{T°, ε'_{T°, ε''_{T°... numerical values. We calculate D'_{I,T°, D''_{I,T°... ones from tabulated $D_{I,T}$ values, e.g. [10]. We measure ε_T as a function of T to deduce ε_{T°, ε'_{T°, ε''_{T° by curve fitting (see next paragraph).

4. Results and discussion of numerical data and of equations

4.1. Temperature influence on thermodynamic functions

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

We have found [8][9] roughly linear variations from 5 to 70°C, for the reversible U and Pu redox potentials in acidic and carbonate solutions : by using (7) and (9), we deduce $<\Delta S_{I,T^\circ}>$ mean value from the slope of $E_{I,T}$ (as a function of T) measurements, and we detect (5) ΔCp influence on $E_{I,T}$ (also $\Delta G_{I,T}$); but it is not straightforward to deduce $\Delta Cp_{I,T^\circ}$. We fit $E_{I,T}$ experimental data to the second order (24, where X = G) power function as a function of T (constant I). The results are E_{I,T°, $\Delta S_{I,T^\circ}$, and inaccurate $<\Delta Cp_{I,T^\circ}>$ values. They are not much different from previous interpretation [8][9] where we disregarded ΔCp. The potential, E(Ag/AgCl), of the reference electrode that we are using in our measurements is tabulated only when I = 0. Power functions formally equivalent to (24) Taylor's series expansion, are typically proposed [17]. For consistency we treat the original experimental E(Ag/AgCl) values the same way as our U and Pu data to get them versus NHE. We will give supplementary results of this data treatment elsewhere [14].

4.1.2. $CO_{2(aq)}$-bicarbonate equilibrium

There are few published measurements of the heat capacities of soluble actinide complexes [15]. The ΔCp value of $CO_{2(aq)}$ bicarbonate equilibrium [16] varies between -400 and -50 J/(mol. K) in NaCl (0 to 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 table 1 equations to take into account pressure influence, we believe that Cp value at (constant) atmospheric pressure is not much different. In pure water or at low I, ΔCp increases with T (up to 70°C) and then decreases, but at I more than 3 no ΔCp decrease is observed at least up to 150°C. This last (at high I) shape of the curve representing ΔCp variations with T, is usually also observed for solids compounds (see below). The ΔG variations with T seem to be roughly linear, this means that the first order term, $-\Delta S_{I,T^\circ}$, is the predominating one and consequently the second, $\Delta Cp_{I,T^\circ}/2T$, and further terms (table 1) have small or negligible influence in these conditions. lg K variations with T are classically interpreted with Van't Hoff

equation, ('11). We have then plotted the carbonate equilibrium lg K variations as a function of T or as a function of 1/T. These representations are roughly strait lines : $\Delta Cp_{I,T^\circ}$ and further terms have again small or negligible influence on lg K variations with T, the main contribution is due to H_{I,T°. Van't Hoff representation is the better lg K one in this case. For consistency with usual data bases, we only fit $\Delta Cp'_{TI^\circ}$ and we use published [16] $\Delta G_{I,T^\circ}$, $\Delta S_{I,T^\circ}$ and $\Delta Cp_{I,T^\circ}$. ΔG and lg K representations are then predictions and not curve fitting. Anyhow lg K and ΔG changes as a function of T, are relatively small, typically lg K varies by less than 0,4 unit, at I=0.

4.1.3. Formation of some U compounds

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

4.1.4. Discussion of formulae

We previously [9] disregarded $\Delta Cp_{I,T}$ influence on $E_{I,T}$ variations with T. This attributes to $\Delta S_{I,T^\circ}$, the estimated mean value, $<\Delta S_{I,T^\circ}>$, which includes (disregarded) $\Delta Cp_{I,T^\circ}$ contributions. $<\Delta S_{I,T^\circ}>$ is indeed a little different from $\Delta S_{I,T^\circ}$. In the same way, when disregarding $\Delta Cp'_{I,T^\circ}$ we fit E_{I,T°, $\Delta S_{I,T^\circ}$ and we estimate $<\Delta Cp_{I,T^\circ}>$ which might include (disregarded) $\Delta Cp'_{I,T^\circ}$ contribution etc. First order rough approximation on ΔCp is enough to account for $\Delta G_{I,T}$ or lg $K_{I,T}$ results but not for $\Delta Cp_{I,T}$ ones. Interpretation deduced either from the (1) approximation or from the (1a) one should both be just as good (table 1) in our T range since (table 2) $a \approx Cp_{I,T^\circ}$ and $Cp'_{I,T^\circ} \approx b$-2.$T^{-3}$. The first formula, (1), 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 (1a) Taylor's series expansion of Cp to the second order and then, at the most, the corresponding ones (24) for G, H, S and ln K (table 1). Chemical speciation predictions only need E and lg K thermodynamic functions : anyhow Cp variations induce only small variations on them (figures 1).

In solution chemistry around 10 to 100°C, "zero" (disregarding S), "first" (disregarding Cp, hence S and H are not T dependent) or "second" (not T dependent Cp) order estimate can be used to predict chemical speciation depending on the needed accuracy. The validity domain of these approximations is correlated to T°. T° could also be chosen in the middle of the working T range to minimise uncertainties. We do not do it for consistency with classical thermodynamic data base.

Taylor's series expansions are approximations, hence, classical thermodynamic relations, typically (4) to (8), are valid only within the same order of approximation : we always disregard the third or forth order and further terms in (24) since they should also include Cp'''_{I,T° that we disregard, even when there is also Cp_{I,T°, Cp'_{I,T° or Cp''_{I,T° contributions to these higher terms. For many solids, and in the above example in high I electrolyte, $Cp_{I,T}$ 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 $Cp_{I,T}$ 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 $Cp_{I,T}$ variations with T, in any 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 Cp, is no

longer much smaller than the energy of chemical bounds. Since activity coefficients and excess functions (17) are related to weak interactions (and not chemical bound) there is no reason to find the same temperature behaviour for excess and ideal functions.

4.2. Temperature Variations of Activity and SIT Coefficients

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

In the same way, by using classical methodology [10], we can treat our redox measurements [8][9] by first using the SIT for I influence and by then using Taylor's series expansion for T influence: we first fit $E_{0,T}$ and $\Delta\varepsilon_T$ values at each T, from $E_{I,T}$ data, by using (9) and (18a). We then fit the standard values, E_{0,T° and at least $\Delta S_{0,T^\circ}$, by using (9) and (24), from $E_{0,T}$ data fitted at the first step. We finally use $\Delta\varepsilon$ Taylor's series expansion to fit $\Delta\varepsilon_{T^\circ}$ and at least $\Delta\varepsilon'_{T^\circ}$ from $\Delta\varepsilon_T$ fitted at the first step. We can also treat the data the other way round. At first step, by using (9) and (24) at each I, we fit E_{I,T° and at least $\Delta S_{I,T^\circ}$ (that we do not directly calculate with the previous methodology) as a function of T changes. We can then fit again E_{0,T° and $\Delta\varepsilon_{T^\circ}$ by using the (18a) classical SIT equation on the first step results, E_{I,T°. We then fit $\Delta\varepsilon'_{T^\circ}$ by using the (20a) new SIT equation for entropy, on the first step results, $\Delta S_{I,T^\circ}$ etc. Treating experimental data by using any of these procedures should be consistent : the link between these two data treatments are the new SIT formulae including T influence (14a) (16a) (18a) to (21a). We can also fit the parameters of equation (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 ε_T or $\Delta\varepsilon_T$ variations with T, seem to be linear (figure 1). We have also checked from $D_{I,T}$ tabulated values [10], that $D'_{I,T}$ is neither much T dependent. A first order expansion (as a function of T) of (14a) seems a reasonable estimate, in the present work (figure 1).

Our ε_{T° and $\Delta\varepsilon_{T^\circ}$ determinations (table 3) are in accordance with published ones [6][6a][7][9][10]. We cannot compare our ε'_{T° or $\Delta\varepsilon'_{T^\circ}$ determinations with other ones, since we do not find any published ones (excepted recently in [9] by one of us). As usual [10] similar ions have similar ε_{T° numerical values e.g. : $\varepsilon(HCl) \approx \varepsilon(LiCl)$ and $\varepsilon(NaCl) \approx \varepsilon(KCl)$. ε decreases with atomic number among the alkaline metals. We now observe (table 3) the same analogies for ε'. As we already observed [9] $\Delta\varepsilon(M(VI)/M(V))$ is an exception, probably due to ion pairing. Published ε numerical values of 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 [9][10].

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. $\Delta S_{I,T}$ and $\Delta Cp_{I,T}$ can then be deduced from them. When typically measuring lg $K_{I,T}$ or $\Delta G_{I,T}$, we calculate $\Delta\varepsilon_T$ and control that it is not I dependent, by [10] plotting ($\lg K_{I,T} - \Delta z^2 D_{I,T}$) versus m (16a) : it must be a straight line with slope $-\Delta\varepsilon_{T^\circ}$. Using (18a) for E (9) measurements is equivalent [6] to [10]. One could, in the same way, plot (19a) ($\Delta H_{I,T} - r\,T^2\,\Delta z^2\,D'_{I,T}$) as a function of m, to calculate $\Delta\varepsilon'_T$ from calorimetric experiments. For verification one should also plot as a function of m (20a) $[\Delta S_{I,T} - r\,\Delta z^2(D_{I,T} + T\,D'_{I,T})]$; or (21a) $[\Delta Cp_{I,T} - r\,T\,\Delta z^2\,(2\,D'_{I,T} + T\,D''_{I,T})]$. These data treatments can be performed at any (constant) T. It is also possible to fit all the parameters $X^{(q)}_{0,T^\circ}$, ε_{T°, ε'_{T° and eventually ε''_{T° together by using (15), (16a) to (21a) and (24).

Acknowledgements.

This work receives some financial support from ANDRA.

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Table 1 Series expansion coefficients, $X^{\{q\}}_{0,T^\circ}$, of thermodynamic functions $X_{I,T}$. The expansion is equation (24): $X_{I,T} = \sum_{q\geq 0}(X^{\{q\}}_{0,T^\circ} + X^{\{q\}ex}_{I,T^\circ})x^q$, $x = t = T-T^\circ$ except in the last line where $x = f = 1/T - 1/T^\circ$. X = G, H, S, Cp or ln K (first column). $X = X^{\{0\}}$ and $X^{\{q+1\}}$ is $X^{\{q\}}/(q+1)$ derivative, typically $X (= X^{\{0\}})$ derivative value for I =0 and T = T° is $X^{\{1\}}_{0,T^\circ}$ and this correspond to the exact (4), (5) and (7) thermodynamic relations. Typically, when X = G (first line), $-(S_{0,T^\circ} + S^{ex}_{I,T^\circ})t$ is $G_{I,T}$ first (second column) order term. $X^{\{q\}}_{0,T^\circ}$ and $X^{\{q\}ex}_{I,T^\circ}$ numerical values are then needed to calculate $X_{I,T}$ by using (24). We calculate $X^{\{q\}}_{0,T^\circ}$ (typically $X^{\{1\}}_{0,T^\circ}$ is $-S_{0,T^\circ}$ when X = G) numerical value from tabulated G_{0,T°, H_{0,T° or Cp_{0,T° standard values e.g. [10]. Neither $X^{\{q\}ex}_{I,T}$ nor $X^{\{q\}ex}_{0,T^\circ}$ numerical values are tabulated : we calculate them by using the equations (16a) or (18a) to (21a). D_{I,T°, D'_{I,T°, D''_{I,T°... ε_{T°, ε'_{T°, ε''_{T°... numerical are needed for this. We calculate D'_{I,T°, D''_{I,T°... ones from tabulated Debye-Hückel term values, $D_{I,T}$, and we measure (see text) the other ones. For consistency (see text), we do not write the $X^{\{q\}}$ terms that include Cp'" contribution.

* in the last line we tabulate the coefficients of the R ln K Taylor expansion versus 1/T (and not versus T)

$X = X^{\{0\}}$	$X^{\{1\}}$	$X^{\{2\}}$	$X^{\{3\}}$	$X^{\{4\}}$
G	-S	$-\frac{Cp}{2T}$	$\frac{Cp - T\,Cp'}{6T^2}$	$-\frac{T^2\,Cp'' + 2\,Cp}{24\,T^3}$
H	Cp	$\frac{Cp'}{2}$	$\frac{Cp''}{6}$	
S	$\frac{Cp}{T}$	$\frac{T\,Cp' - Cp}{2T^2}$	$\frac{T^2\,Cp'' + 2\,Cp}{6T^3}$	
Cp	Cp'	$\frac{Cp''}{2}$		
R ln K	$\frac{\Delta H}{T^2}$	$\frac{T\,\Delta Cp - 2\,\Delta H}{2T^3}$	$\frac{T^2\,\Delta Cp' - 4\,T\,\Delta Cp + 6\,\Delta H}{6T^4}$	$\frac{T^3\,\Delta Cp'' - 6\,T^2\,\Delta Cp' + 18\,T\,\Delta Cp - 24\,\Delta H}{24\,T^5}$
*R ln K	$-\Delta H$	$T^2\frac{\Delta Cp}{2}$	$-T^3\frac{T\,\Delta Cp' + 2\,\Delta Cp}{6}$	$T^4\frac{T^2\,\Delta Cp'' + 6\,T\,\Delta Cp' + 6\,\Delta Cp}{24}$

Table 2: T influence on formation enthalpy and entropy of some U compounds. $X_T max$ (or min) is X (S or G) maximum (or minimum) value from 290 to 390 Kelvin. We calculate these values from Grenthe et al. [10] by using equations (1) to (3) and (9). $Cp \approx a$ when $T_{ea} < T < T_{ab}$, but (1) is only valid between T_{min} and T_{max}, so this estimate is valid only in the grey temperature domain. $T_{ea} = \left|\frac{e}{a}\right|^{0.5}$ and $T_{ab} = \left|\frac{a}{b}\right|$. $Cp \approx \frac{e}{T^2}$ when $T < T_{ea}$; $Cp \approx b\,T$ when $T_{ab} < T$. Typically, the $U^{(cr.)}$ heat capacity is nearly constant from 298 to 923 Kelvin and its variations with T are linear from 923 to 941 Kelvin; but $UO_{2(cr.)}$ heat capacity is nearly constant from 250 to 600 Kelvin, since the b and e fitted parameters have negligible influence in the temperature range where the formula (1) is valid.

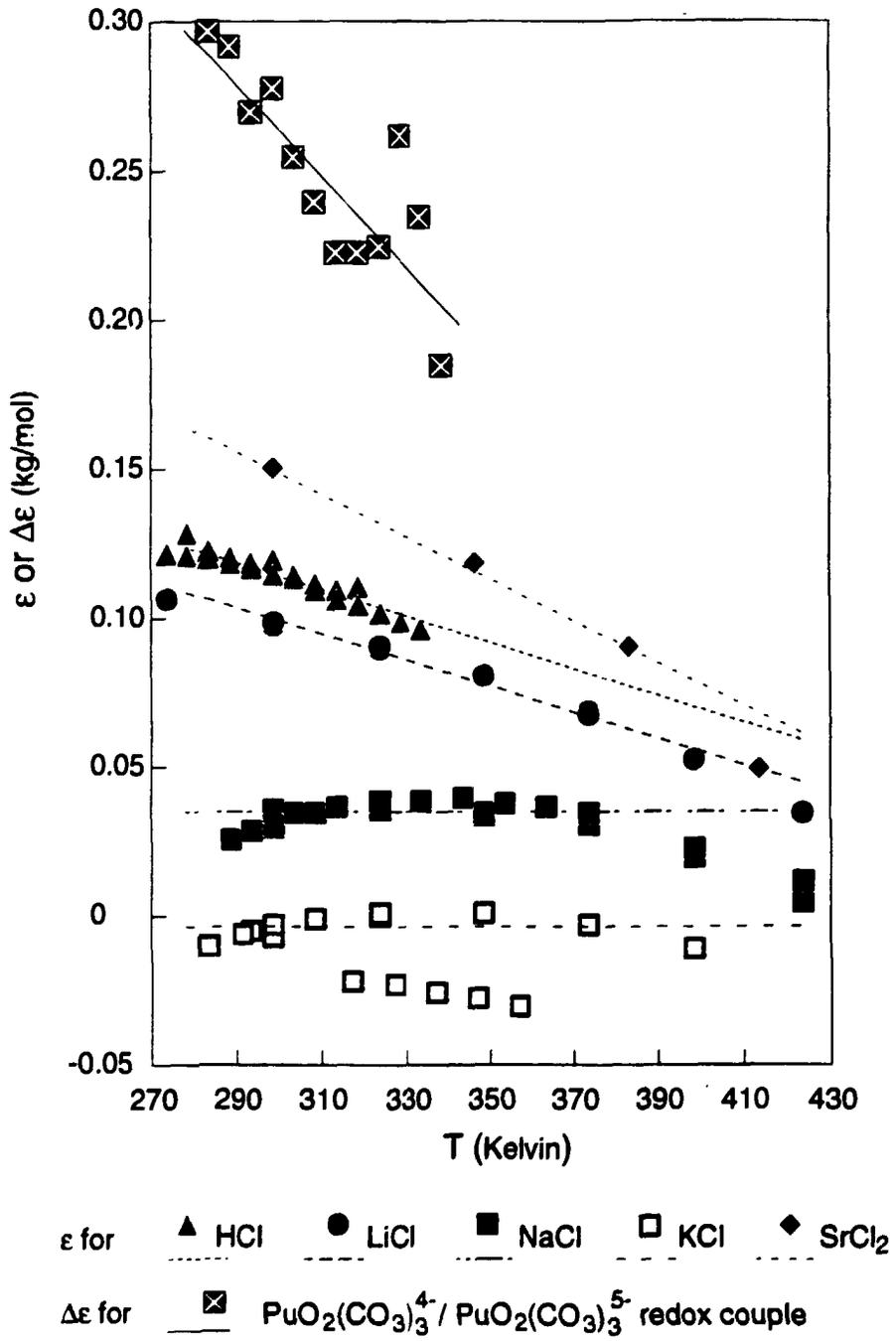
	T_{ea}	T_{min}	T_{ab}	T_{max}	T_{ab}	$S_T max - S_T min$ (J.Kelvin^{-1}.mol^{-1})	$G_T max - G_T min$ (kJ.mol^{-1})
U(cr.)		298	923	941		8.5	0
$UO_{2(cr.)}$	111	250		600	1978	19.7	17.0
$UO_{2.6667(cr.)}$	119	298		900	3938	24.8	21.9
$\beta.UO_2(OH)_2$	291	298		773		41.8	43.5
$\beta.UO_3$	113	298		773	3450	25.1	25.1
$UO_3.2H_2O_{(cr.)}$		298	298	400		54.4	61.3
$UCl_{3(cr.)}$	74	298		1100	1128	28.1	21.5
$UCl_{4(cr.)}$	29	298		591	2197	36.3	30.1
$UCl_{5(cr.)}$		298		600	3940	45.1	34.6
$UCl_{6(cr.)}$	65	298		425	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 3 : Specific Interaction Coefficients, ε, as function of Temperature : $\varepsilon_T = (\varepsilon_{T°} + \varepsilon'_{T°}(T-T°))$, where ε_T is ε value at temperature, T, and T° = 298.15 Kelvin, T range is *usually within 0 to 70°C. We calculate ε_T from mean γ_T data of MCl electrolyte, we then fit $\varepsilon_{T°}$ and $\varepsilon'_{T°}$. We fit $\Delta\varepsilon_{T°}$ and $\Delta\varepsilon'_{T°}$ from $\Delta\varepsilon_T$ data. M(VI) = $MO_2(CO_3)_3^{4-}$; M(V) = $MO_2(CO_3)_3^{5-}$. $\Delta\varepsilon$(ox/red) = ε(ox,N)-ε(red,N)+ε(Na^+,Cl^-), N is Na^+ when ox and red are anionic carbonate complexes, it is ClO_4^- when ox and red are the aquo cations. $\varepsilon(ox,N)_{T°}$ is ε(ox,N) value at T = T°. ε unit is (kg/mol.), ε' unit is (kg/mol./Kelvin).

* $\varepsilon^*_{T°}$ and $\varepsilon^{*\prime}_{T°}$ 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.

ox / red	$\Delta\varepsilon_{T°}$ this work	$\Delta\varepsilon_{T°}$ [10]	$\Delta\varepsilon'_{T°}$	Reference of γ_T or $\Delta\varepsilon_T$ original data.
U(VI)/U(V)	0.95	0.77	-0.006	[8][9]
Pu(VI)/Pu(V)	0.28		-0.001_5	[9]
PuO_2^{2+}/ PuO_2^+	0.25	0.32	-0.001	[9]
Pu^{4+}/ Pu^{3+}	0.36	0.55	0.002	[9]
MCl	$\varepsilon_{T°}$ (or ε^*)		$\varepsilon'_{T°}$ (or $\varepsilon^{*\prime}$)	
HCl	0.11_5	0.12	-0.0005	[21][22]
LiCl	*(0.09)	0.10	-0.0000	*([19][20][23])
NaCl	0.03 *(0.03_5)	0.03	0.0001 *(-0.0002)	[18][23] *([13][23])
KCl	-0.01 *(-0.00)	0.00	-0.0002 *(-0.0000)	[21][23][24] *([23][25])
$SrCl_2$	0.15		-0.0010	[20]

Figure 1 : **Specific Interaction Coefficients, ε, as a function of Temperature.** We draw the lines with $\varepsilon_T = (\varepsilon_{T^\circ} + \varepsilon'_{T^\circ}(T-T^\circ))$ equation, where ε_T is ε value at temperature, T, and T° = 298.15 Kelvin. We calculate ε_T from mean γ_T data of MCl electrolyte, we then fit ε_{T° and ε'_{T°. We fit $\Delta\varepsilon_{T^\circ}$ and $\Delta\varepsilon'_{T^\circ}$ from $\Delta\varepsilon_T$ data. Pu(VI) = $PuO_2(CO_3)_3^{4-}$; Pu(V) = $PuO_2(CO_3)_3^{5-}$. We plot $\varepsilon = \varepsilon(M^{Z+},Cl^-)$ and $\Delta\varepsilon = \varepsilon(Pu(VI),ClO_4^-) - \varepsilon(Pu(V),ClO_4^-) + \varepsilon(Na^+,Cl^-)$. See table 3 for references, numerical values and other examples.



Figures ayant servi de base à l'élaboration des diapositives.

Les diapositives effectivement projetées sont les 13 premières : jusqu'aux deux intitulées conclusion.

Adjustment of Activity Coefficients as a Function of Changes in Temperature. using the S.I.T.

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Purpose :

Influence of ionic strength and temperature on speciation and on prediction of the migration of radioelements in environmental conditions.

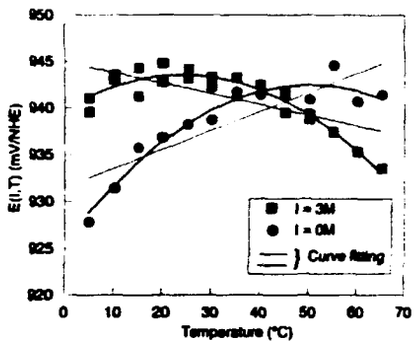
Data required :

Thermodynamic functions.

Determination of thermodynamic functions from few experimental measurements.

This work receives financial support from **ANDRA.**

Temperature Influence on Chemical Speciation: $PuO_2^{2+} + e^- \rightarrow PuO_2^+$ Redox Potential.



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

$$G(I,T) = G(I,T^\circ) - S(I,T^\circ)\,\Delta T - \frac{Cp}{2T}(I,T^\circ)\,\Delta T^2$$

- linear regression → $E(I,T^\circ)$ and $S(I,T^\circ)$
- Curve fitting with second order expansion → also $\Delta Cp(I,T^\circ)$
- ΔCp changes with T; this can be disregarded when calculating E variations with T.

S changes with I.

S.I.T. Verification at Constant Temperature.

Measurements of $\lg K(I,T)$ =

$\lg K(0,T)$ — $\Delta G = RT \ln K$

$\Delta \lg\gamma(I,T)$ — $\Delta G^{ex} = RT \ln\gamma(I,T)$

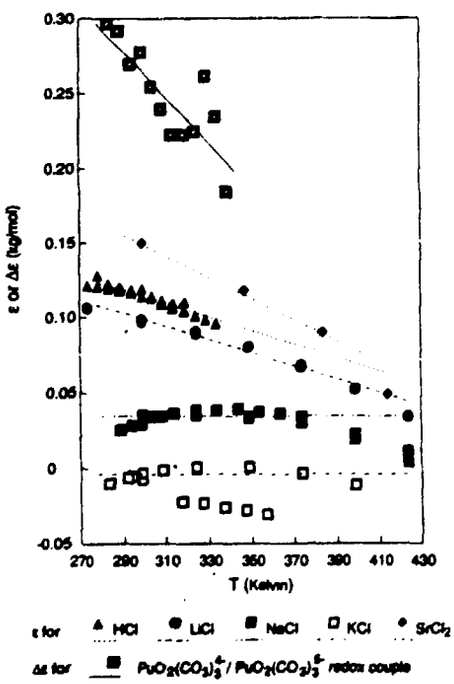
S.I.T

$$\Delta\varepsilon(T) = \frac{\Delta \lg\gamma(I,T) + z^2\,\Delta D(I,T)}{m}$$

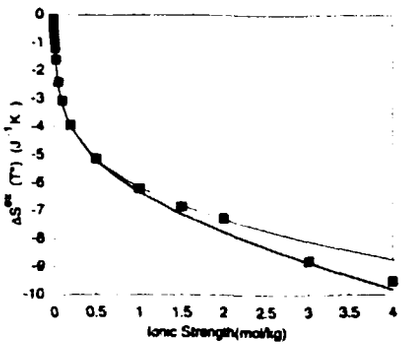
The plot $(\lg K(I,T) - \Delta z^2 D(I,T))$ v.s. m is a straight line when the S.I.T. is valid.

The S.I.T. is used in the same way for measurements of $E(I,T) = -\Delta G(I,T) / nF$

Temperature Influence on S.I.T. Coefficients: Some Data.



Temperature influence on ΔS^{ex} deduced from the HCl Mean Activity Coefficient, $\gamma_{\pm}$, [41ROB].



The S.I.T. is not used to plot the points:

$$\Delta G^{ex}(I,T) = R\,T\,\Delta \ln\gamma_{\pm}(I,T)$$

$$= \Delta G^{ex}(I,T^\circ) - \Delta S^{ex}(I,T^\circ)\Delta T - \frac{\Delta Cp^{ex}}{2\,T}(I,T^\circ)\,\Delta T^2$$

The S.I.T is used to draw the curve:

$$S^{ex}(I,T) = -R\left(\ln\gamma(I,T) + T\frac{\partial \ln\gamma}{\partial T}(I,T)\right)$$

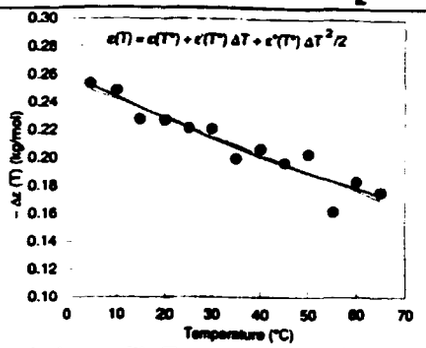
$$= R\ln(10)[z^2(D(I,T)TD'(I,T)) - m(\varepsilon(T) + T\varepsilon'(T))]$$

Temperature influence on PuO_2^{2+}/PuO_2^{+} Redox Couple:

SIT coefficient.

E(I,T) data	SIT →	E(0,T) and Δε(T)
$\lg\gamma(I,T) = -z^2 D(I,T) + \varepsilon(T)\,m$		
Δε(T)	→ Series expansion	Δε(T°), Δε'(T°), Δε"(T°)

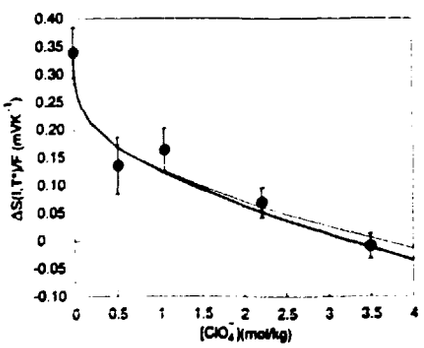
$$\varepsilon(T) = \varepsilon(T^\circ) + \varepsilon'(T^\circ)(T-T^\circ) + \frac{\varepsilon''(T^\circ)(T-T^\circ)^2}{2}$$



Δε variations with T are small and they seem to be roughly linear; but the second order expansion about T = T° is more consistent when deducing the entropy and heat capacity variations with I, from these data.

Temperature influence on PuO_2^{2+}/PuO_2^{+} Redox Couple:

Entropy Changes with I



The S.I.T. is not used to calculate the points:
ΔS(I,T°) is fitted from E(I,T) data

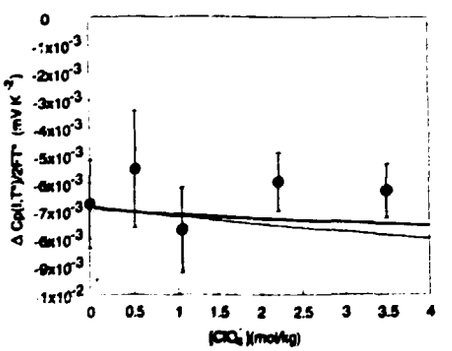
The S.I.T is used to draw the curve:

E(I,T)	→ SIT →	E(0,T) and Δε(T)
E(0,T)	→ regression →	ΔS(0,T°), ΔCp(0,T°)
Δε(T)	→ regression →	Δε(T°), Δε'(T°), Δε"(T°)

Entropy changes with I are deduced from (only) two fitted parameters, Δε(T°), Δε'(T°) These changes > measurement uncertainty

Temperature influence on PuO_2^{2+}/PuO_2^{+} Redox Couple:

Heat Capacity Changes with I.



The S.I.T. is not used to calculate the points:
ΔCp(I,T°) is fitted from E(I,T) data

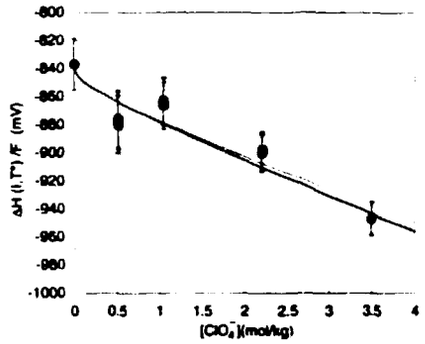
The S.I.T is used to draw the curve:

E(I,T)	→ SIT →	E(0,T) and Δε(T)
E(0,T)	→ regression →	ΔS(0,T°), ΔCp(0,T°)
Δε(T)	→ regression →	Δε(T°), Δε'(T°), Δε"(T°)

Measurements are not accurate enough to detect ionic strength influence on ΔCp.

Temperature Influence on PuO_2^{2+}/PuO_2^{+} Redox Couple:

Enthalpy Changes with I.



H can be deduced from G and S by using
$H = G + T S$
or
by curve fitting on lgK data:

$$R \ln K(I,T) = R \ln K(I,T^\circ) - \Delta H(I,T^\circ)\left(\frac{1}{T} - \frac{1}{T^\circ}\right) + T^{\circ 2}\frac{\Delta Cp(I,T^\circ)}{2}\left(\frac{1}{T} - \frac{1}{T^\circ}\right)^2$$

From I = 0 to 4 m, $\Delta H(I,T^\circ)$ varies by 12%, only due to $D'(I,T^\circ)$ and $\Delta\varepsilon'(T^\circ)$ but not due to $D(I,T^\circ)$ and $\Delta\varepsilon(T^\circ)$

Temperature Influence on Chemical Speciation:

G, H, S, Cp and lnK Taylor's Series Expansion.

$$X(I,T) = \sum_{q\geq 0}(X^{(q)}(0,T^\circ) + X^{(q)ex}(I,T^\circ))x^q / q!$$

$$x = T - T^\circ \quad \text{or} \quad {}^*\left(\frac{1}{T} - \frac{1}{T^\circ}\right)$$

$Cp' = \left(\frac{\partial Cp}{\partial T}\right)_p$ **"terms with Cp" are not written

$X = X^{(0)}$	$X^{(1)}$	$X^{(2)}$	$X^{(3)}$
G	-S	$-\frac{Cp}{2T}$	$\frac{Cp - T\,Cp'}{6\,T^2}$
H	Cp	$\frac{Cp'}{2}$	**
S	$\frac{Cp}{T}$	$\frac{T\,Cp' - Cp}{2\,T^2}$	**
Cp	Cp'	**	**
R ln K	$\frac{\Delta H}{T^2}$	$\frac{T\,\Delta Cp - 2\,\Delta H}{2\,T^3}$	$\frac{T^2\,\Delta Cp' - 4\,T\,\Delta Cp + 6\,\Delta H}{6\,T^4}$
*R ln K	$-\Delta H$	$T^2\frac{\Delta Cp}{2}$	$-T^3\frac{T\,\Delta Cp' + 2\,\Delta Cp}{6}$

* expansion versus 1/T (for the last line only).

Temperature Influence on S.I.T. Coefficients:

Excess Functions for the S.I.T.

Classical S.I.T. equations:

$\lg\gamma = -z^2 D + m\,\varepsilon$

$G^{ex} = r\,T\,(-z^2 D + m\,\varepsilon)$ where $r = R \ln 10$

New S.I.T. equations:

$H^{ex} = r\,T^2\,(z^2\,(\frac{\partial D}{\partial T})_p - m\,(\frac{\partial \varepsilon}{\partial T})_p)$

$S^{ex} = r\,(z^2\,(D + T\,(\frac{\partial D}{\partial T})_p) - m\,(\varepsilon + T\,(\frac{\partial \varepsilon}{\partial T})_p))$

$Cp^{ex} = r\,T\,(z^2\,(2\,(\frac{\partial D}{\partial T})_p + T\,(\frac{\partial^2 D}{\partial T^2})_p) - m\,(2\,(\frac{\partial \varepsilon}{\partial T})_p + T\,(\frac{\partial^2 \varepsilon}{\partial T^2})_p))$

Verification of S.I.T. equations:

The plot (X^{ex} - D terms) v.s. m, is a straight line when the S.I.T. is valid.

Conclusion.

- **We use** $X(I,T) = X(0,T) + X^{ex}(I,T)$

  where X = G (*ln*K or E), S, Cp, H

  for $0 \leq I \leq 4$ mol./kg and $0 \leq T \leq 70°C$ at atmospheric pressure

G(I,T) is needed for speciation:

- 2 or 3 measured parameters, *e.g.* G(I,T°), S(I,T°) and Cp(I,T°), are enough to predict G variations with T (at each I).
- 1 fitted parameter, ε(T), is needed to calculate $G^{ex}(I,T)$ at each T: S.I.T. requires at least 1 measurement to predict changes with I.
- 1 or 2 extra measured parameters, ε'(T°) and ε"(T°), are enough to predict G^{ex}, S^{ex} and Cp^{ex} variations with I and T.

Hence 4 to 6 parameters are needed.

Conclusion.

Equations tested on

- published $\gamma_{\pm}$ of HCl
- PuO_2^{2+}/PuO_2^{2+} and Pu^{4+}/Pu^{3+} redox potential measurements.

We also have some data in carbonate media and on Uranium. There are not enough published experimental measurements studying T and I simultaneous variations. There are very few of them for actinides.

Results :

- E variations with Temperature are quadratic, hence $\Delta S(T)$ is linear and $\Delta Cp(T)$ influence is small.
- $\Delta S(I)$, $\Delta H(I)$ and $\Delta Cp(I)$ are correctly predicted by using new S.I.T. equations with $D(I,T°)$, $D'(I,T°)$, $D''(I,T°)$, $\varepsilon(T°)$, $\varepsilon'(T°)$, $\varepsilon''(T°)$.

Comparison with calorimetric data...

Correlation (prediction?) of the thermodynamic function numerical values with physical and chemical properties.

Temperature Influence on Chemical Speciation:

Gibb's Energy, G(T)

Thermodynamic Equations:

- $G(I,T) = H(I,T) - T\,S(I,T)$.
- $-S(I,T) = (\frac{\partial G}{\partial T})_p(I,T)$ first order adjustement.
- $\frac{Cp}{T}(I,T) = (\frac{\partial S}{\partial T})_p(I,T)$ second order ...

Expansion of G(T) into a series about T=T°

- $G(I,T) = G(I,T°) - S(I,T°)\Delta T - \frac{Cp}{2T}(I,T°)\,\Delta T^2$

Temperature Influence on Chemical Speciation:

G, H, S, Cp... determinations.

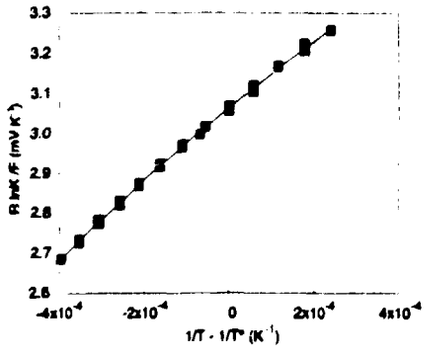
G(I,T) from lgK(I,T) or E(I,T) measurements

- curve fitting with first order G expansion
  → G(I,T°) and - S(I,T°)
- with second order expansion
  → also $-\frac{Cp}{2T}(I,T°)$ → Cp(I,T°)

Calorimetric measurements

- mean value → H(I,T°)
- linear regression → also Cp(I,T°)
- curve fitting with second order H expansion
  → also $(\frac{\partial Cp}{\partial T})_p(I,T°)$

Temperature Influence on Chemical Speciation:
Equilibrium Constant of $PuO_2^{2+} + e^- \rightleftharpoons PuO_2^+$.



$\Delta G(T) = -F\,E(T) = -R\,T\,\ln K(T)$

$R\,\ln K(T) = R\,\ln K(T°) - \Delta H(T°)\,(\frac{1}{T} - \frac{1}{T°}) + T°^2\,\frac{\Delta Cp(T°)}{2}\,(\frac{1}{T} - \frac{1}{T°})^2$

- E(T) measurements → lgK(T)
- Linear regression → lgK(T°) and ΔH(T°)
- Curve fitting with second order expansion
  → also ΔCp(T°)
- *ΔCp changes with T; this can be disregarded when calculating lg K variations with T.*

S.I.T.
at Constant Temperature.

- activity = γ . concentration

  $\lg K(0,T) = \lg K(I,T) + \Delta \lg \gamma(I,T)$

SIT for a trace element,
in an electrolyte whose concentration is m

- $\lg \gamma = -z^2 D + \varepsilon\, m$

  $D = \frac{a\sqrt{I}}{1+b\sqrt{I}}$

  ε fitted parameter, accounts for the the interaction between the trace ion and the electrolyte conter-ion.

Temperature Influence on Activity Coefficients:

Excess Functions.

$$X(I,T) = X(0,T) + X^{ex}(I,T)$$

$$G^{ex} = R\,T\,\ln\gamma$$

$$H^{ex} = -R\,T^2\left(\frac{\partial \ln\gamma}{\partial T}\right)_p$$

$$S^{ex} = -R\left(\ln\gamma + T\left(\frac{\partial \ln\gamma}{\partial T}\right)_p\right)$$

$$Cp^{ex} = -R\,T\left(2\left(\frac{\partial \ln\gamma}{\partial T}\right)_p + T\left(\frac{\partial^2 \ln\gamma}{\partial T^2}\right)_p\right)$$

Ionic Strength and Temperature Influences on Redox Potential.

Ionic Strength : S.I.T.
validated on U, Np and Pu in acidic and carbonate Media.

Temperature : Linear or quadratic variations with T found for U and Pu.

Ionic Strength + Temperature :

	T°	Series expansion	T
I = 0	Standard condition $E(T^0, 0)$, $\Delta\varepsilon(T°)$, $\Delta S(T°,0)$, $\Delta\varepsilon'(T°)$, $\Delta Cp(T°,0)$, $\Delta\varepsilon''(T°)$,	↔	$E(T,0)$, $\varepsilon(T)$
↕	S.I.T. ↕	↖ ↘	↕
I	$E(T°, I)$, $\Delta S(T°,I)$, $\Delta Cp(T°,I)$	↔	$E(T,I)$

Temperature Influence on ΔS^{ex} and ΔCp^{ex} deduced from Mean Activity Coefficients, $\gamma\pm$.

To draw curves:

$\ln\gamma\pm$ data —SIT→ $\Delta\varepsilon(T)$

$\Delta\varepsilon(T)$ —Series expansion→ $\Delta\varepsilon(T°)$, $\Delta\varepsilon'(T°)$, $\Delta\varepsilon''(T°)$

$$\varepsilon(T) = \varepsilon(T°) + \varepsilon'(T°)\,(T-T°) + \frac{\varepsilon''(T°)\,(T-T°)^2}{2}$$

$$S^{ex}(I,T) = -R\left(\ln\gamma(I,T) + T\,\frac{\partial \ln\gamma}{\partial T}(I,T)\right)$$
$$= r\,[z^2\,(D(I,T) + T\,D'(I,T)) - m\,(\varepsilon(T) + T\,\varepsilon'(T))]$$

$$Cp^{ex}(I,T) = -R\,T\left(2\,\frac{\partial \ln\gamma}{\partial T}(I,T) + T\,\frac{\partial^2 \ln\gamma}{\partial T^2}(I,T)\right)$$
$$= rT[z^2(2D'(I,T)+TD''(I,T)) - m(2\varepsilon'(T)+T\varepsilon''(T))]$$

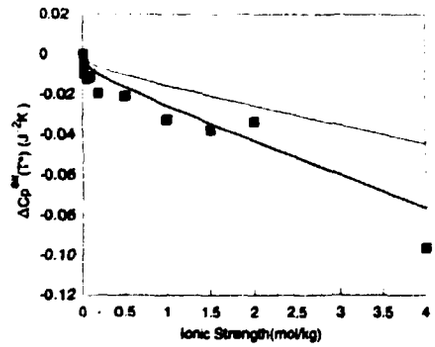
$$\varepsilon' = \frac{\partial \varepsilon}{\partial T} \qquad \varepsilon'' = (\varepsilon')' \qquad r = R\ln 10$$

To get data:

$\ln\gamma\pm$ data —Series expansion→ $\Delta S^{ex}(I,T°)$, $\Delta Cp^{ex}(I,T°)$

$$\Delta G^{ex}(I,T) = R\,T\,\Delta\ln\gamma\pm(I,T)$$
$$= \Delta G^{ex}(I,T°) - \Delta S^{ex}(I,T°)\,\Delta T - \frac{\Delta Cp^{ex}}{2\,T}(I,T°)\,\Delta T^2$$

Temperature Influence on ΔCp^{ex} deduced from the HCl Mean Activity Coefficient, $\gamma\pm$, [41ROB].



The S.I.T. is not used to calculate the points:

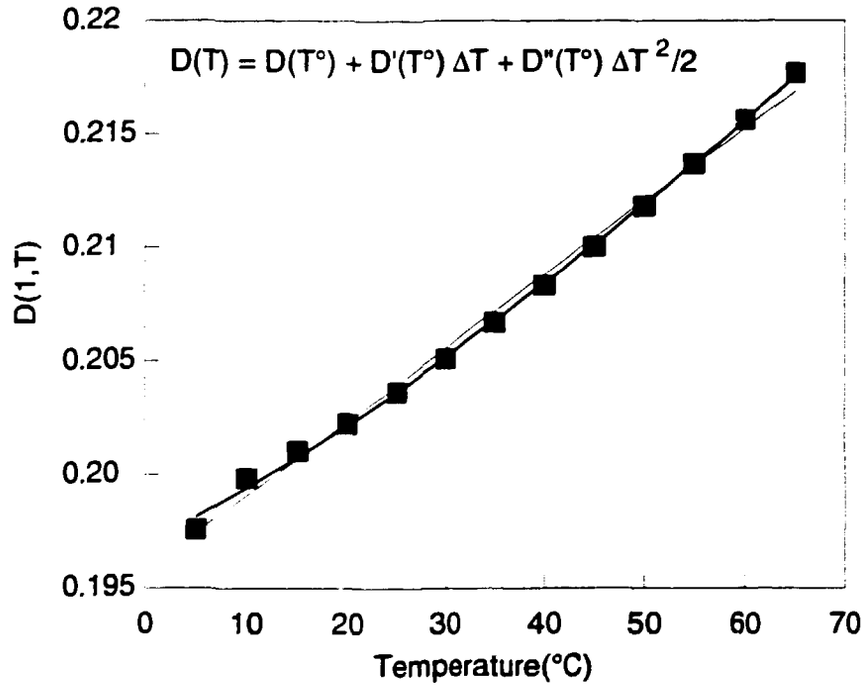
$$\Delta G^{ex}(I,T) = R\,T\,\ln\gamma\pm(I,T)$$
$$= \Delta G^{ex}(I,T°) - \Delta S^{ex}(I,T°)\,\Delta T - \frac{\Delta Cp^{ex}}{2\,T}(I,T°)\,\Delta T^2$$

The S.I.T. is used to draw the curve:

$$Cp^{ex}(I,T) = -R\,T\left(2\,\frac{\partial \ln\gamma}{\partial T}(I,T) + T\,\frac{\partial^2 \ln\gamma}{\partial T^2}(I,T)\right)$$
$$= rT[z^2(2D'(I,T)+TD''(I,T)) - m(2\varepsilon'(T)+T\varepsilon''(T))]$$

Temperature Influence on PuO_2^{2+}/PuO_2^{+} Redox Couple:

Debye-Hückel Term.



D variations with T are small and they seem to be roughly linear; second order polynomial regression can still be used to calculate

$$D' = \frac{\partial D}{\partial T} \text{ and } D'' = (D')'$$

A propos de l'utilisation de l'état standard pour les potentiels d'oxydo-réduction, l'entropie et les autres fonctions thermodynamiques.

Cet extrait d'une correspondance (on y rajoute des sous-titre) de Pierre Vitorge à Ingmar Grenthe se réfère notamment au livre Chemical Thermodynamics of Uranium par Ingmar Grenthe et al. et au travail en cours au sein de la Thermodynamic Data Base (AEN-OCDE) pour compléter cet ouvrage par les volumes sur Np, Pu, Am.

3.1. Introduction.

In the U book, on the Figure V.1 page 91, $\Delta\varepsilon = -0.20 = 0.46-0.26$ (Table B.3 p 693 and 694) = $\varepsilon(UO_2^{2+}) - \varepsilon(UO_2^{+})$ which is not consistent with the equilibrium written in the legend, just above the figure, that involves H^+ : H^+ should be suppressed (in my opinion, see below). This is also not much consistent with Appendix B where the only redox example (B.27, p 691) involves again H^+. Figure V.2 is OK. Still this has no influence on numerical values since the SIT is correctly used in all these examples.

There are several ways to use the SIT for redox equilibria, only one of them is explained in Appendix B. I already pointed out this type of problem twice, first time when Jean Fuger reviewed our paper, second time when I suggested to add new examples in appendix B. I still think that appendix B should first give :

- an example for a **real equilibrium** (not involving the reference state assumption and problems...) this is done for real hydrogen electrode, an example with another one could be added, typically AgCl-Ag, because the SIT can be used with any electrode (not only real or standard hydrogen electrode). Primary experimental measurement cannot depend on the (arbitrary chosen) standard state. The standard electrode does not exist (it is a concept that (see below) is equivalent to the half cell concept) at least because when H^+ activity is 1, its activity coefficient cannot be 1 in real solution,
- then an (the same) example using the **standard electrode**,
- then an (the same) example using **half cells**,

and then the link among the 3 treatments that I will now explain.

3.2. Half cell.

3.2.1. First example: U(VI)/U(V).

The **electrochemists** do not always use the standard state, just because they do not always need it. It is then more convenient to use **half cells**. I am doing it now for the following example: the working electrode is

$$UO_2^{2+} + e^- \Leftrightarrow UO_2^{+} \qquad (1)$$

its potential is:

$E_1 = E'^{\circ}_1 + A\,\Delta lg\gamma_1$ (1e)

$E'^{c}_1 = E^{\circ}_1 + A\,lg(m(VI)/m(V))$ (1e')

$\Delta lg\gamma_1 = lg(\gamma(VI)/\gamma(V))$ (1ac)

$\Delta\varepsilon_1 = \varepsilon(V) - \varepsilon(VI)$ (1sc)

for this reaction, the thermodynamic function, X (= G or S...), is :

$\Delta G_1 = -\mathcal{F} E_1$ (1g)

$\Delta X_1 = X(V) - X(VI) - X(e^-)$ (1x)

where VI is UO_2^{2+} and V is UO_2^{+}.

I am adding extra equations that I will use below and I will always write as an indice, the equilibrium number which the parameter is related to.

X° (X = E, G, S...) is (usually tabulated) standard value. E'° is formal potential. For X = G, (1x) can be obtained from (1e) to 1(e') with the chemical potentials $\mu(M) = G(M) = \mu^\circ(M) + A \lg(m(M)\,\gamma(M))$, where M = V or VI but not e^- because this would mean that $G(e^-)$ is set to 0 (which I am not doing in (1x)) and this would implicitly be standard state definition. One must first verify that the usual standard state does not already set a value for $X(e^-)$: I will do it below (I will then have to come back to these equations). I know that one can introduce the electrochemical potential and so on; but this introduces new (extra-thermodynamical) physical hypothesis (double layer and so on): it is not my point here, I just want to use the classical thermodynamical cycles to write explicitly the links between the different classical ways to handle redox equilibria. Cutting redox equilibrium into two half equilibria is arbitrary: the exact place of the boundary is arbitrary or is set with standard state definition (see below). The fundamental reason for this, is that one have to handle the exchange of a particle, e^-, that is never free (even in hydrated form) in aqueous solution, hence, for this individual particle, one cannot measure any physical entity: $X(e^-)$ and then ΔX_1, E_1, and so on cannot be measured directly, one can typically measure E_1 only versus a real reference system, typically the AgCl/Ag reference electrode.

3.2.2. Second example: AgCl/Ag.

$$AgCl + e^- \quad \Leftrightarrow \quad Ag + Cl^- \qquad (2)$$

$$E_2 = E'^\circ_2 - A\,\Delta lg\gamma_2 \qquad (2e)$$

$$E'^\circ_2 = E^\circ_2 - A\,lg(m(Cl^-)) \qquad (2e')$$

$$\Delta lg\gamma_2 = -lg\gamma(Cl^-) \qquad (2ac)$$

$$\Delta\varepsilon_2 = \varepsilon(Cl^-) \qquad (2sc)$$

$$\Delta X_2 = X(Ag) + X(Cl^-) - X(AgCl) - X(e^-) \qquad (2x)$$

Again the same type of remarks as for (1) are valid and will be valid for all half cell equilibria used below.

3.3. Real redox equilibrium in aqueous solution: AgCl oxydates U(V).

One **measures the potential** of (1) - (2) = (3) equilibrium. With the above notations, I can now use (3i) = (1i) - (2i) (i is none, e, e', ac, x or sc):

$$UO_2^{2+} + Ag + Cl^- \quad \Leftrightarrow \quad UO_2^{+} + AgCl \qquad (3)$$

$$E_3 = E'^\circ_3 + A\,\Delta lg\gamma_3 \qquad (3e)$$

$$E'^\circ_3 = E^\circ_1 - E^\circ_2 + A\,lg(m(Cl^-)\,m(VI)/m(V)) \qquad (3e')$$

$$\Delta lg\gamma_3 = lg(\gamma(Cl^-)\,\gamma(VI)/\gamma(V)) \qquad (3ac)$$

$$\Delta\varepsilon_3 = \varepsilon(V) - \varepsilon(VI) - \varepsilon(Cl^-) \qquad (3sc)$$

$$\Delta X_3 = X(V) - X(VI) - X(Ag) - X(Cl^-) + X(AgCl) \qquad (3x)$$

(3e') and (3e) equations also indicate that

$$E^\circ_3 = E^\circ_1 - E^\circ_2 \qquad (3')$$

$X(e^-)$ term now cancels which is consistent, because (3) is a real equilibrium, and E_3 and ΔX_3 are now measurable parameters. My notations are then not very good because they do not make any **difference between measurable parameters and (conventional) not measurable ones**; I have then written in italic face the non measurable parameters, and the corresponding equilibria and equations. Also typically G(Ag) is 0 because the metal phase is the Ag standard state but I am presently ignoring this convention (I will discuss it below): one can set it to 0, to get the usual equations.

(3sc) indicates that **SIT regression** gives $\Delta\varepsilon_3$, the slope is $-\Delta\varepsilon$ (3ac): sign must then be changed or (3x) directly used.

It is the SIT data treatment that I prefer since it does not need any assumption on the standard state during the data treatment (I do not have to verify wether the tabulated values of my reference electrode potential are obtained by using a data treatment that is SIT consistent); but the (non standard) parameters (at least E) calculated by using this treatment, cannot be compared (used) when different reference electrodes are used : they must then be recalculated (after the above data treatment) in standard conditions (by using reference electrode tabulated values).

(3e), (3e') and (3ac) indicate how to calculate the standard value of the (VI/V) couple, $E°_3 = E°_2 - E°_1$, from m(Cl^-), the activity (or SIT) coefficients for the equilibrium (3), and the tabulated $E°_2$ value (see below).

None of these formulae involve explicitly H^+ or H_2 (including the case X = S); but it was involved when tabulating $E°_2$.

(3x) can typically be used for X = S (see below).

3.4. Hydrogene electrodes.

3.4.1. H^+/H_2 half cell.

When **using tabulated $E°_2$ values**, I am making a difference between the standard electrode and the real hydrogen electrode that have been used to measure the AgCl/Ag electrode potential, E_5 (that had then been extrapolated to $E°_2$). For this, we can subtract from the (2) equilibrium, the real hydrogen electrode half reaction

$$H^+ + e^- \Leftrightarrow 0.5\ H_2 \qquad (4)$$

$E_4 = E'°_4 + A\ \Delta lg\gamma_4$ (4e)

$E'°_4 = E°_4 + A\ lg(m(H^+)/P(H_2)^{0.5})$ (4e')

$\Delta lg\gamma_4 = A\ lg(\gamma(H^+)/f(H_2)^{0.5})$ (4ac)

$\Delta\varepsilon_4 = -\varepsilon(H^+)$ (4sc)

$\Delta X_4 = 0.5\ X(H_2) - X(H^+) - X(e^-)$ (4x)

where at I = 0 and T = 298.15 K, E_4 is $E_4° = 0$,
to get the real equilibrium (5) used to measure E_5.

3.4.2. AgCl/Ag vs a hydrogene electrode.

$$AgCl + 0.5\ H_2 \Leftrightarrow Ag + Cl^- + H^+ \qquad (2) - (4) = (5)$$

$E_5 = E'°_5 + A\ \Delta lg\gamma_5$ (5e)

$E'°_5 = E°_2 - E°_4 + A\ lg(P(H_2)^{0.5}/m(H^+)/m(Cl^-))$ (5e')

$\Delta lg\gamma_5 = lg(f(H_2)^{0.5}/\gamma(H^+)/\gamma(Cl^-))$ (5ac)

$\Delta\varepsilon_5 = \varepsilon(H^+) + \varepsilon(Cl^-)$ (5sc)

$\Delta X_5 = X(Ag) + X(Cl^-) - X(AgCl) - 0.5\ X(H_2) + X(H^+)$ (5x)

where (5i) = (2i) - 4(i) (i is none, e, e', ac, x or sc).

(5e') and (5e) equations also indicate that

$$E°_5 = E°_2 - E°_4 \qquad (5')$$

(5e') indicates that the HCl mean activity coefficient should be used to deduce the standard value $E°_2$: with a SIT treatment one would hence measure (assuming that H_2 is a perfect gas above the solution), $\Delta\varepsilon_5$.

(5e') and (5e) indicate how to use these activity coefficients to calculate $E°_2$ from the experimental measurements, E_5.

I have again written $X(H_2)$ and $X(H^+)$ to point out that these terms do not cancel; but they are set to 0 when the standard state definition states so. When X = G, the standard state states these terms to 0. $G(H_2)° = 0$ (in fact $\Delta_f G(H_2)°$, but I am not using this notation : see just below) since dihydrogen gas is the hydrogen reference state (as metal U is U reference state); but when X = S, "absolute" entropy at 298.15 K, S°, is not 0, since S is 0 at 0 K.

(5x) can typically be used for entropy calculation (see below).

3.4.3. Standard and absolute states.

2 different notations, S° and $\Delta_f G°$, are typically used in the TDB tables:

* **S°** (so X°) is the ("absolute") entropy (S is 0 at 0 K and tabulated S° is S value at 298.15 K).
* **$\Delta_f G°$ or $\Delta_f H°$ (so $\Delta_f S°$)** refers to the usual standard state (metal or gas phase at 298.15 K).

I am not using these notations here. This type of problem is discussed in the first two chapters of A. Bard, R. Parson and J. Jordan's Book (Standard Potentials in Aqueous Solution, IUPAC, Marcel Dekker, New York 1985). In both books one finally gets tables where 2 different standard states are used, this is only indicated in the notation (Δ for G° and H°, but not for S°), this could be reminded in the caption of the tables and more clearly explained in the Chapter 1 and in the Appendix B of TDB book.

$G(H^+) = 0$ (hence the standard hydrogen electrode is the standard reference electrode) is an extra convention that cannot account for H_2 ionisation energy or any pathway that includes this reaction. Again, one measures ΔX only for real reactions and (more or less implicitly) state X to 0 in the reference state, but there are in fact 4 (more or less reference) states or assumptions:

* **Pure water activity is 1** for solution chemistry (infinite dilution and so on).
* **Standard hydrogen electrode is 0** to use standard potential.. Since this electrode does not exist, *it is not consistent to write a chemical equilibrium* with the usual writing conventions (see below), and for which $\Delta G(=-FE)=0$.
* **Gas or metal phase is the reference state** (only one phase per element... except for hydrogen: H_2 and H^+ for the usual standard hydrogen electrode). Physical properties of these (reference) phases change with T. Water must now be taken into account.
* **S is 0 at 0 K**... where measurements are not so easy!..

3.4.4. U(VI/V) redox couple vs a real hydrogene electrode.

Now to give the E_1 **versus a real hydrogen electrode** one can either use (1) and (4) half cell or (3) and (5) chemical equilibria to get (6) = *(1) - (4)* = (3) + (5), the *half cell equilibria and equations are subtracted*; but the chemical redox equilibria and equations are added:

$$UO_2^{2+} + 0.5\ H_2 \quad \Leftrightarrow \quad UO_2^{+} + H^+ \qquad (6)$$

$$E_6 = E'°_6 + A\ \Delta lg\gamma_6 \qquad (6e)$$

$$E'°_6 = E°_1 - E°_4 + A\ lg(P(H_2)^{0.5}\ m(VI)/m(V)/m(H^+)) \qquad (6e')$$
$$= E°_3 + E°_5 + A\ lg(P(H_2)^{0.5}\ m(VI)/m(V)/m(H^+))$$

$$\Delta lg\gamma_6 = lg(\gamma(VI)\ f(H_2)^{0.5}/\gamma(V)/\gamma(H^+)) \qquad (6ac)$$

$$\Delta\varepsilon_6 = \varepsilon(V) - \varepsilon(VI) + \varepsilon(H^+) \qquad (6sc)$$

$$\Delta X_6 = X(V) - X(VI) - 0.5\ X(H_2) + X(H^+) \qquad (6x)$$

(6e') and (6e) equations also indicate that

$E°_6 = E°_1 - E°_4$ (6')

$= E°_3 + E°_5$

This, and specially the equation (6sc), explains the figure V.1 problem. (6) equilibrium is the usual way used in the TDB book to write redox reactions; but (in the TDB book), from primary data, E_3, one first calculates the formal potential E(VI,V) vs ENH, and then tabulates it. E(VI,V) is not E_6. SIT treatment is supposed to be performed on E(VI,V) and not on E_6: this SIT regression does not use the (6) equilibrium and corresponding SIT equations.

Hence the way the SIT figures are presented in the book, is not much consistent for the redox reactions.

3.4.5. U(VI/V) redox couple vs the standard hydrogene electrode, E(VI/V) formal potential vs NHE.

E_6 is now measured. The VI/V (formal) redox potential vs the standard electrode, **E(VI/V), is E_6 potential when the hydrogen electrode is in standard condition**, i.e. it is E_6 when all the activities of the hydrogen electrode components are 1, i.e. when all the concentrations and all the activity coefficients of the hydrogen electrode components are 1:

$P°(H_2) = m°(H^+) = f°(H_2) = \gamma°(H^+) = 1$ (7s)

In the same way, I should use (but I am not using it)

$X°(H_2) = X°(H^+) = S°(H^+) = 0$ when X is not S (7s)

$E_6 = E'°_6 + A\,\Delta lg\gamma_6$ *(6e)*

$E'°_6 = E°_6 + A\,lg(P(H_2)^{0.5}\, m(VI)/m(V)/m(H^+))$ *(6e')*

$\Delta lg\gamma_6 = lg(\gamma(VI)\, f(H_2)^{0.5}/\gamma(V)/\gamma(H^+))$ *(6ac)*

$\Delta\varepsilon_6 = \varepsilon(V) - \varepsilon(VI) + \varepsilon(H^+)$ *(6sc)*

$\Delta X_6 = X(V) - X(VI) - 0.5\,X(H_2) + X(H^+)$ *(6x)*

then

$E(VI/V) = E°_6 + A\,lg(m(VI)\,\gamma(VI)/\gamma(V)\,m(V))$

and so one... With the above notations, this gives

E(VI/V) = E7

$E_7 = E'°_7 + A\,\Delta lg\gamma_7$ *(1e) = (7e)*

$E'°_7 = E°_6 + A\,lg(m(VI)/m(V))$ *(1e') = (7e')*

$\Delta lg\gamma_7 = lg(\gamma(VI)/\gamma(V))$ *(1ac) = (7ac)*

$\Delta\varepsilon_7 = \varepsilon(V) - \varepsilon(VI)$ *(1sc) = (7sc)*

$\Delta X_7 = X(V) - X(VI) - 0.5\,X(H_2) + X(H^+)$ *(1x) is not (7x)*

where (7s) I have substituted $P(H_2)$, $m(H^+)$, $f(H_2)$, $m(H^+)$ for 0 in all the (6) equations. (7e') equation also indicates that

$E°_7 = E°_6$ (7')

$= E°_1 - E°_4 = E°_1$ since $E°_4 = 0$ (standard electrode E°) (6')

$= E°_3 + E°_5$

I have also noted that (1ac) = (7ac) and (1sc) = (7sc): they are just the same equations. First (6') equation shows that (1e') = (7e') and then (1e) = (7e). *This would again induce to write (1) equilibrium for Figure V.1;* but this is not yet completely consistence because (1x) is not (7x). **To make it consistent one has to state**

$X(e^-) = 0.5\,X°(H_2)$ ***(4nhe)***

This convention (or standard state definition) is possible since, as I stated above, $X(e^-)$ value was not needed up to now.

3.4.6. Conclusion: thermodynamic functions for hydrated e^-.

I can "demonstrate" this convention by rewriting equation (4x) this way:

$$X(e^-) = 0.5\,X(H_2) - X(H^+) - \Delta X_4 \qquad (4x)$$

since ΔX_4 is X function change for a real hydrogen electrode, $\Delta X°_4$ is X° function change for the standard electrode it is then 0. Hence, with the usual conventions (4nhe)

$$G°(e^-) = H°(e^-) = 0 \qquad (4nhe)$$
$$S°(e^-) = 0.5\,S°(H_2) \qquad (4nhe)$$

Now X_1 and (1) equilibrium correspond to the (VI/V) potential vs NHE, and then to the legend of the figure V.1. This explain what I was meaning just above when saying "the way the SIT figures are presented in the book, is not much consistent for the redox reactions". This also means that it is more consistent to present half cell reaction, (1), in figure V.1 and not the chemical equilibrium with hydrogen as a reductant, (6). This is also, in my opinion, a good reason to give a half cell example in appendix B. Half cells are explained in Bard's book.

3.5. Usual ways to handle potential vs NHE.

When using real AgCl/Ag reference electrode to measure the (VI/V) redox potential (it is then E_3) we can use these primary data, E_3, to calculate the formal (VI/V) redox potential vs the standard electrode (NHE), E(VI/V). We then use tabulated standard potential (vs NHE) of the AgCl/Ag reference electrode, to subtract the real AgCl/Ag reference electrode potential (vs NHE), E(AgCl/Ag), from E_3:

$E(VI/V) = E_3 + E(AgCl/Ag)$

I am simulating this treatment of data, to check again consistency (it is not necessary; but it is just to be convinced again that the usual data treatment is consistent).

3.5.1. Calculating AgCl/Ag potential vs NHE, E(AgCl/Ag), from measurement vs real hydrogen electrode.

Equilibrium (5) must be used to deduce the real AgCl/Ag reference electrode potential (vs NHE), E(AgCl/Ag), just in the same way, (6) was used for $E(VI/V) = E_7$. It is the same type of demonstration, I am then only writing equations without justifications.

$E_5 = E'°_5 + A\,\Delta lg\gamma_5$ (5e)

$E'°_5 = E°_5 + A\,lg(P(H_2)^{0.5}/m(H^+)/m(Cl^-))$ (5e')

$\Delta lg\gamma_5 = lg\{f(H_2)^{0.5}/\gamma(H^+)/\gamma(Cl^-))$ (5ac)

$\Delta\varepsilon_5 = \varepsilon(H^+) + \varepsilon(Cl^-)$ (5sc)

$\Delta X_5 = X(Ag) + X(Cl^-) - X(AgCl) - 0.5\,X(H_2) + X(H^+)$ (5x)

$E°_5 = E°_2 - E°_4$ (5')

E_8 = E(AgCl/Ag),
it is E_5 when all the activities of the hydrogen electrode components are 1, i.e. when all the concentrations and all the activity coefficients of the hydrogen electrode components are 1. I am then using (7s) in the (5i) equations.

$P°(H_2) = m°(H^+) = f°(H_2) = \gamma°(H^+) = 1$ (7s)

$X°(H_2) = X°(H^+) = S°(H^+) = 0$ when X is not S (7s)

$E_8 = E'°_8 + A\,\Delta lg\gamma_8$ (8e)

$E'°_8 = E°_5 - A\,lg(m(Cl^-))$ (8e')

$E°_5 = E°_8$ from (8e')

$= E°_2 - E°_4$ (5')

$= E^\circ_2 (= E^\circ_8)$ *since* $E^\circ_4 = 0$ *(standard electrode E°)*

$\Delta lg\gamma_8 = -lg(\gamma(Cl^-))$ *(8ac)*

$\Delta\varepsilon_8 = \varepsilon(Cl^-)$ *(8sc)*

$\Delta X_8 = X(Ag) + X(Cl^-) - X(AgCl) - 0.5\, X(H_2) + X(H^+)$ *(8x)*

3.5.2. Calculating U(VI/V) potential vs NHE, E(VI/V), from measurement vs real AgCl/Ag electrode by using its standard potential, E(AgCl/Ag).

$E^\circ_9 = E^\circ_3 + E^\circ_8$

E(VI/V) $= E_9$

$E_3 = E'^\circ_3 + A\,\Delta lg\gamma_3$ (3e)

$E'^\circ_3 = E^\circ_3 + A\,lg(m(Cl^-)\, m(VI)/m(V))$ (3e')

$E^\circ_3 = E^\circ_1 - E^\circ_2$

$\Delta lg\gamma_3 = lg(\gamma(Cl^-)\, \gamma(VI)/\gamma(V))$ (3ac)

$\Delta\varepsilon_3 = \varepsilon(V) - \varepsilon(VI) - \varepsilon(Cl^-)$ (3sc)

$\Delta X_3 = X(V) - X(VI) - X(Ag) - X(Cl^-) + X(AgCl)$ (3x)

$E_9 = E_3 + E_8$

$= E'^\circ_9 + A\,\Delta lg\gamma_9$ *(9e)*

$E'^\circ_9 = E^\circ_9 + A\,lg(m(VI)/m(V))$ from (3e')*+(8e')* *(9e')*

$E^\circ_9 = (E^\circ_1 - E^\circ_2) + E^\circ_2 - E^\circ_4$

$= E^\circ_1 - E^\circ_4$ *since* $E^\circ_4 = 0$ *(standard electrode E°)*

$= E^\circ_1$ hence *(1e') = (9e')*

$= E^\circ_1 = E^\circ_7 = E^\circ_6$ *(6')* and *(7')*

$\Delta lg\gamma_9 = lg(\gamma(VI)/\gamma(V))$ from (3ac)*+(8ac), (1ac) = (9ac)*

$\Delta\varepsilon_9 = \varepsilon(V) - \varepsilon(VI)$ from (3sc)*+(8sc), (1sc) = (9sc)*

$\Delta X_9 = X(V) - X(VI) - 0.5\, X(H_2) + X(H^+)$ *from (3x)+(8x), (9x)*

Equations and equilibria (7i) and (9i) are indeed identical.

$\varepsilon(H^+)$ finally also cancel in (9sc) because it has already been used when calculating E°_2 from measurements. In other words, the (virtual) components of the standard electrode do not require any activity coefficient. I already pointed out this type of problem when checking the consistency of the tabulated water ionic product or carbonate equilibrium constants and also when working in Na_2CO_3 media where it is quite difficult to imagine an $\varepsilon(H^+, CO_3^{2-})$!.: One can always use some constants where some of the components are concentrations (the macroscopic ones used to control the chemical reactions) and other are activity (the theoretical or trace ones whose influence on mass balance can be disregarded, typically H^+ in basic media, or H^+ and H_2 in a redox reaction where neither H^+ is the real oxidant, nor H_2 is the real reductant).

Finally, the only consistent way to write (7) or (9) equilibria is **either**

$$UO_2^{2+} + e^- \quad \Leftrightarrow \quad UO_2^+ \qquad (1)$$

since we are quite free to give the needed signification to *e⁻*,

or

$$UO_2^{2+} + 0.5\, H_2 \quad \Leftrightarrow \quad UO_2^+ + H^+ \qquad (6)$$

where I have written H_2 and H^+ in italic face to say that they are not only components (I do not like to have notation with several meanings): the notation also includes concentration and activity.

3.6. Entropy.

I am now focusing on entropy, because we are working on temperature influence. All the treatment is already implicitly above ; there are several ways to treat the data :

3.6.1. Real equilibrium.

$$UO_2^{2+} + Ag + Cl^- \Leftrightarrow UO_2^+ + AgCl \quad (3)$$

the X change

$$\Delta X_3 = X(V) - X(VI) - X(Ag) - X(Cl^-) + X(AgCl) \quad (3x)$$

does not need any convention.

3.6.2. Real hydrogen electrode.

A real hydrogen electrode can be used in the same way :

$$UO_2^{2+} + 0.5\,H_2 \Leftrightarrow UO_2^+ + H^+ \quad (6)$$

$$\Delta X_6 = X(V) - X(VI) - 0.5\,X(H_2) + X(H^+) \quad (6x)$$

or might have been used before studying (3) to measure the AgCl/Ag real electrode potential with the following equilibrium :

$$AgCl + 0.5\,H_2 \Leftrightarrow Ag + Cl^- + H^+ \quad (5)$$

$$\Delta X_5 = X(Ag) + X(Cl^-) - X(AgCl) - 0.5\,X(H_2) + X(H^+) \quad (5x)$$

to deduce (6) = (3) + (5). In this procedure, (- 0.5 $X(H_2)$ + $X(H^+)$) term is used twice; one just have to verify that he is using the numerical value that was used to tabulate ΔX_5. When, in (5x), X is $\Delta_f Y°$ (Y = G, H or S) each term is 0 :

$\Delta_f G(H_2)° = \Delta_f G(H^+)° = \Delta_f H(H_2)° = \Delta_f H(H^+)° = \Delta_f S(H_2)° = \Delta_f S(H^+)° = 0$

when, in (5x), X is S (not $\Delta_f S$)

$S(H^+)° = 0$, but $S(H_2)°$ is not 0.

Reference state has then been chosen. It is H_2 gas at 298.15 K (or U metal etc.). $\Delta_f G(A)$ of a compound, A, at T, is calculated with a cycle that includes typically H_2 gas at 298.15 K (and not T) and heating up A from T° to T: only $\Delta_f X(H_2)°$ is needed, it is then consistent (with thermodynamical differential equations) to set it to 0 (for any X).

3.6.3. Potentials first recalculated vs NHE.

We have seen that no real chemical equilibrium is consistent with this treatment : half cell reactions must be used.

$$UO_2^{2+} + e^- \Leftrightarrow UO_2^+ \quad (1)$$

$$\Delta X_1 = X(V) - X(VI) - X(e^-) \quad (1x)$$

And this is again consistent with tabulated values for the AgCl/Ag electrode :

$$AgCl + e^- \Leftrightarrow Ag + Cl^- \quad (2)$$

$$\Delta X_2 = X(Ag) + X(Cl^-) - X(AgCl) - X(e^-) \quad (2x)$$

Now one can choose any value for $X(e^-)°$. It is usually sometime implicitly set to 0; but when one wants to be consistent with thermodynamic reference state and standard electrode definition

$$X(e^-) = 0.5\,X(H_2) - X(H^+) - \Delta X_4 \quad (4x)$$

where $\Delta X_4° = 0$..: this is the standard electrode and this gives the (4nhe) equations. Ouf ! This is consistent !

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