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

Eric Giffaut, Pierre Vitorge & Hélène Capdevila

CEA
DCC/DESD/SCS, Section de **GéoChimie** LAT
BP6, 92265 Fontenay aux Roses cedex, **France**

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:

Gibb's Energy, G(T).

Thermodynamic Equations:

❷ $G(I,T) = H(I,T) - T\,S(I,T)$.

❷ $-S(I,T) = \left(\frac{\partial G}{\partial T}\right)_p(I,T)$ first order adjustement.

❷ $\frac{Cp}{T}(I,T) = \left(\frac{\partial S}{\partial T}\right)_p(I,T)$ second order ...

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

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

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 $-\dfrac{Cp}{2T}$ (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 $\left(\dfrac{\partial Cp}{\partial T}\right)_p(I,T^\circ)$

Temperature Influence on Chemical Speciation:

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

$$X(I,T) \approx \sum_{q>=0} \left(X^{\{q\}}(0,T°) + X^{\{q\}ex}(I,T°)\right) x^{q} / q!$$

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

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

$X = X^{\{0\}}$	$X^{\{1\}}$	$X^{\{2\}}$	$X^{\{3\}}$
G	-S	$-\frac{Cp}{2\,T}$	$\frac{Cp - T\,Cp'}{6\,T^{2}}$
H	Cp	$\frac{Cp'}{2}$	**
S	$\frac{Cp}{T}$	$\frac{T\,Cp' - Cp}{2\,T^{2}}$	**
Cp	Cp'	**	**
R ln K	$\frac{\Delta H}{T2}$	Erreur !	$\frac{T^{2}\,\Delta Cp' - 4\,T\,\Delta Cp + 6\,\Delta H}{6\,T^{4}}$
*R ln K	$-\Delta H$	$T^{2}\,\frac{\Delta Cp}{2}$	$-\,T^{3}$ Erreur !

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

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

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

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

- 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.

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

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

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

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

S changes with I.

S.I.T.
at Constant Temperature.

- activity $= \gamma$. concentration

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

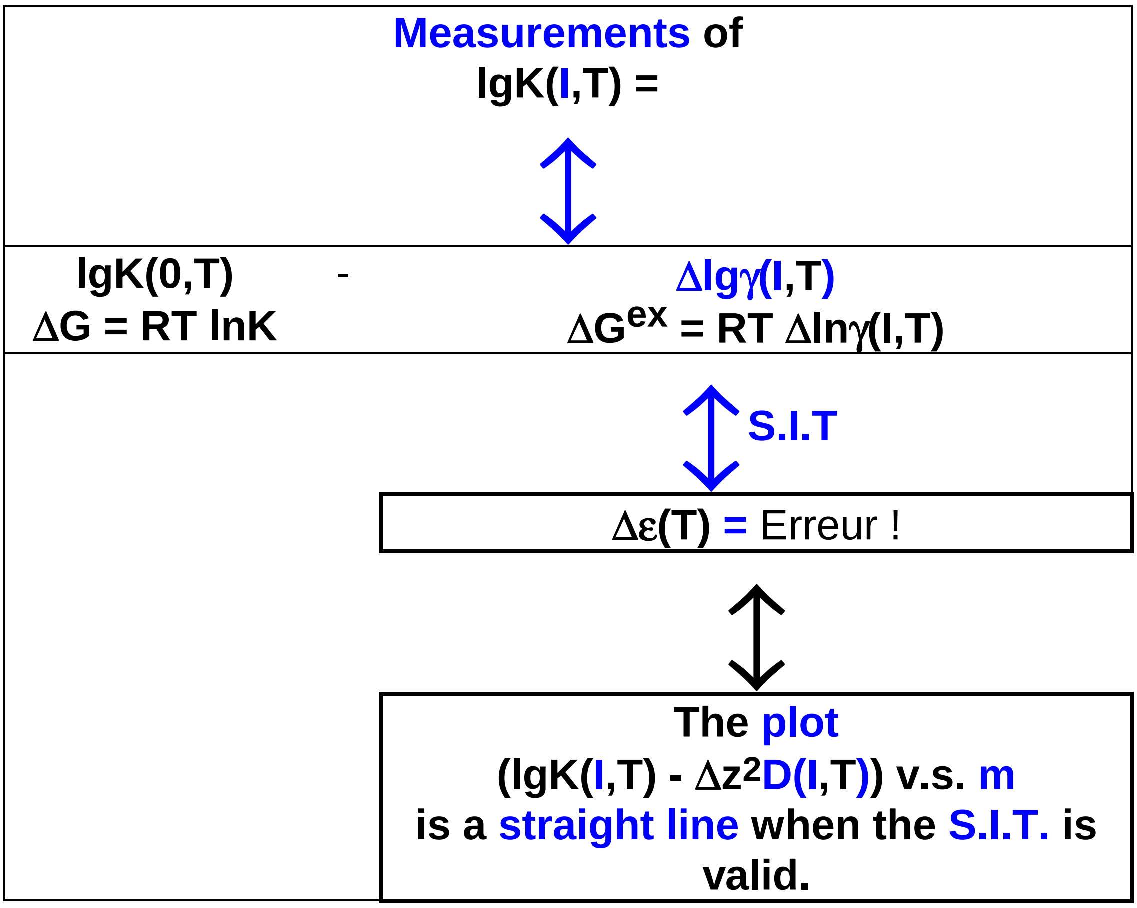
SIT for a trace element,
in an electrolyte whose concentration is m

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

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

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

S.I.T.
Verification at Constant Temperature.



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

$\lg K(0,T)$ - $\Delta \lg \gamma(I,T)$
$\Delta G = RT \ln K$ $\Delta G^{ex} = RT\,\Delta \ln \gamma(I,T)$

S.I.T

$\Delta\varepsilon(T)$ = Erreur !

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

Temperature Influence on Activity Coefficients:

Excess Functions.

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

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

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

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

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

Temperature Influence on S.I.T. Coefficients:

Excess Functions for the S.I.T.

Classical S.I.T. equations:

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

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

New S.I.T. equations:

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

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

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

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.

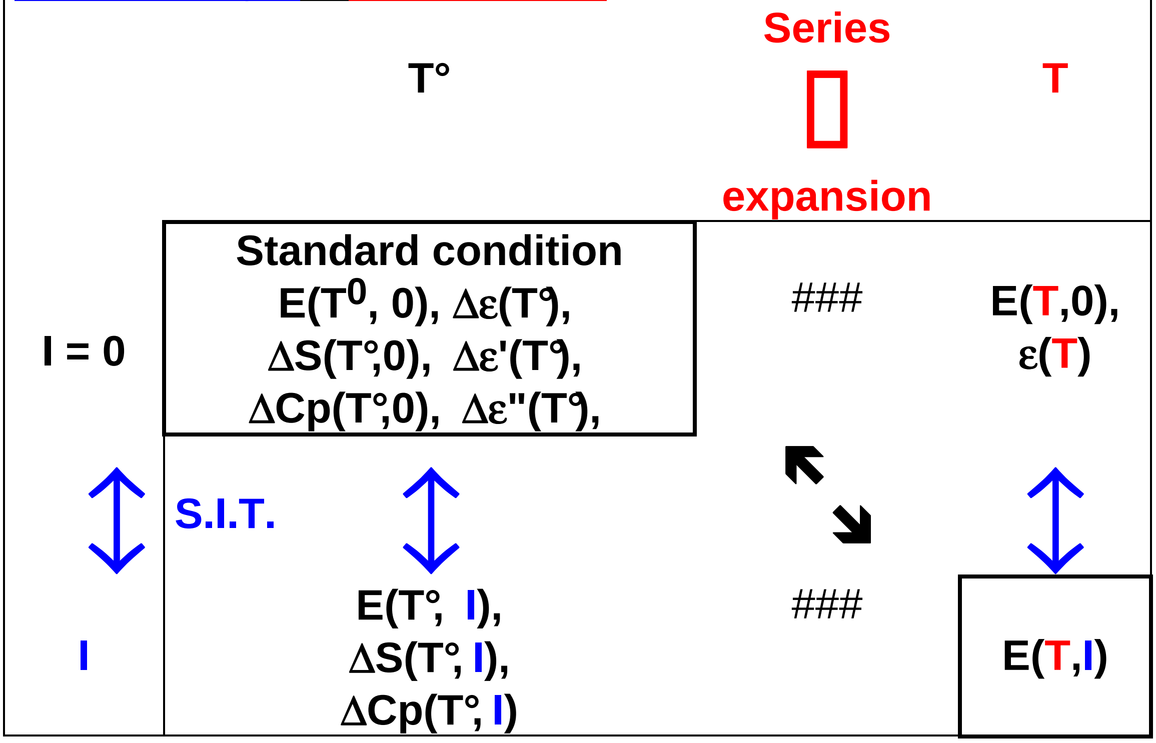
Temperature Influence on S.I.T. Coefficients: Some Data.

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 :



Series ▯ expansion

T°

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 $\Delta\varepsilon(T^\circ)$, $\Delta\varepsilon'(T^\circ)$, $\Delta\varepsilon''(T^\circ)$

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

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

$$= r\,[z^2\,(D(I,T) + T\,D'(I,T)) - m\,(\varepsilon(T) + T\,\varepsilon'(T))]$$

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

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

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

To get data:

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

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

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

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:

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

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

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

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

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

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

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

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

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

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:

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) $\xrightarrow[\text{expansion}]{\text{Series}}$ Δε(T°), Δε'(T°), Δε"(T°)

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

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:

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

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

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:
$\Delta S(I,T^\circ)$ 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 $\Delta\varepsilon(T)$
$E(0,T)$ → regression → $\Delta S(0,T^\circ)$, $\Delta Cp(0,T^\circ)$
$\Delta\varepsilon(T)$ → regression → $\Delta\varepsilon(T^\circ)$, $\Delta\varepsilon'(T^\circ)$, $\Delta\varepsilon''(T^\circ)$

Entropy changes with I are deduced from (only) two fitted parameters, $\Delta\varepsilon(T^\circ)$, $\Delta\varepsilon'(T^\circ)$
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:
$\Delta Cp(I,T°)$ 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 $\Delta\varepsilon(T)$
$E(0,T)$ ➔regression➔ $\Delta S(0,T°)$, $\Delta Cp(0,T°)$
$\Delta\varepsilon(T)$ ➔regression➔ $\Delta\varepsilon(T°)$, $\Delta\varepsilon'(T°)$, $\Delta\varepsilon''(T°)$

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:

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

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 $\Delta\varepsilon(T^\circ)$

Conclusion.

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

where X = G (lnK or E), S, Cp, H

for $0 < I < 4$ mol./kg and $0 < T < 70$℃
at atmospheric pressure

G(I,T) is needed for speciation:

- **2 or 3 measured parameters,**
  e.g. $G(I,T^\circ)$, $S(I,T^\circ)$ and $Cp(I,T^\circ)$,
  are enough to predict G variations with T (at each I).

- **1 fitted parameter,**
  $\varepsilon(T)$,
  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,**
  $\varepsilon'(T^\circ)$ and $\varepsilon''(T^\circ)$,
  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 ΔS(T) is linear and ΔCp(T) influence is small.
- ΔS(I), ΔH(I) and ΔCp(I) are correctly predicted by using new S.I.T. equations with D(I,T°), D'(I,T°), D''(I,T°), ε(T°), ε'(T°), ε''(T°).

Comparison with calorimetric data...

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