# RADIONUCLIDES AND CHEMOTOXICS

## 1. SELECTION PROCEDURE FOR INORGANIC COMPLEXATION

Each individual datum introduced in TermoChimie is the result of an exhaustive work of literature research, comparison and/or estimation of thermodynamic data values. The coherence and internal consistency of ThermoChimie is ensured.

The main sources of thermodynamic data are:

- Previous thermodynamic data compilations

- Open scientific literature

- Specific experimental programmes

- Estimations

ThermoChimie relies on CODATA recommendations (Cox et al. 1989) for the primary master species and the reference states of the elements. The selection process also includes a revision of the thermodynamic data reported in *previous thermodynamic data compilations* such as SUPCRT92 (Johnson et al. 1992), NBS (Wagman et al. 1982) or USGS Database (Robie and Hemingway, 1995) for major elements and the IAEA (Fuger and Oetting, 1976) or the NEA-TDB's for radionuclides. The results of the NEA-TDB project are particularly considered in the selection, given their high quality; the selection process adopted by the NEA involves peer review and ensures the adequacy of the selected data. They have been the basis of the selection for several of the elements included in ThermoChimie database, as shown in the figure below, and enlarged when considered necessary and when possible. Nevertheless, the high quality standard of these databases precludes the inclusion of other data that are perhaps necessary to explain the system of interest, but that are not so much validated.

*Periodic table showing the elements introduced in ThermoChimie (in grey). Selected thermodynamic data for the elements highlighted in green are based on the OCDE-NEA-TDB publications.*

ThermoChimie takes advantage on the results of the extensive *experimental program* on actinides and fission products developed by Andra.

Furthermore, the data selection process includes an exhaustive work of literature research, comparison and evaluation of different data in *open scientific literature*. Data extracted from scientific literature are analysed and tested in front of independent values.

Finally, in some cases data gaps exist and good quality data are not available in previous compilations or in open literature. In this case, *estimations* can be conducted to solve this problem.

Data for radionuclides and chemotoxics included in ThermoChimie have been selected according to the following procedure:

**1.** When possible, *aqueous stability constants and solubility equilibria* are selected as main data. In some cases these data allow the calculation of Gibbs free energy of formation of the species as far as the free energy of formation of the basic components is available. $log_{10}K^0$ and $\Delta_r G_m^0$ are thus the first parameters selected and $\Delta_f G_m^0$ is calculated accordingly.

In some cases, if this procedure cannot be applied, Gibbs free energies are calculated from $\Delta_f H_m^0$ and $S_m^0$ data. The process is sumamrized in the figure below.

Solubility equilibrium constants can be obtained by different ways:

a) Calculation of the solubility product ($\log K_s^o$) from solubility experiments. In those cases, the aqueous concentrations of solutes in equilibrium with the solid phase are used to obtain the equilibrium constant by means of the mass action law.

This means the assumption of an aqueous speciation scheme and associated stabilities of the aqueous complexes of the element of interest.

b) Calculation of $\log K_s^o$ from formation magnitudes obtained by calorimetric measurements, from where values of enthalpy and/or entropy can be measured.

Because of ThermoChimie is used in solubility and performance assessment of deep underground repositories, preference is given to the value obtained from solubility experiments. During solubility process, the mineral surface can suffer changes such as hydration, precipitation of amorphous minerals, ion exchange and adsorption, that affect the value of the $\log K_r^o$. The solubility constant obtained from classical solution experiments includes all these effects, whereas $\Delta G_r^\circ$, derived from calorimetric data, refers to a perfectly crystalline surface that may differ from the surface of the most amorphous solid phases, which is the one in contact with the groundwater and, therefore, the one controlling the concentration in solution.

It is important to highlight that solubility and aqueous speciation cannot be separated. The determination of the solubility of a solid is always dependent on the aqueous speciation model used.

c) In some cases, due to the lack of data or to the unaccuracy of the existing ones, estimations are needed. There are special scientific publications developing methods for data estimations, such as the ones of Shock et al., (1997) or Sverjensky et al., (1997). Even the now classical book of hydroxides stability, Baes and Mesmer (1976), includes some correlations.

The estimation procedure used depends on many factors (type of data, availability of the original values, studied element,...) and can be of different forms (analogies with other elements and complexes, empirical algorithms,...). The accuracy of the estimation must be individually evaluated.

The iterative behaviour of the selection process is always present because of the continuously appearing data in the open scientific literature, which implies the revision and final update of previously selected data or even the inclusion of new thermodynamic data.
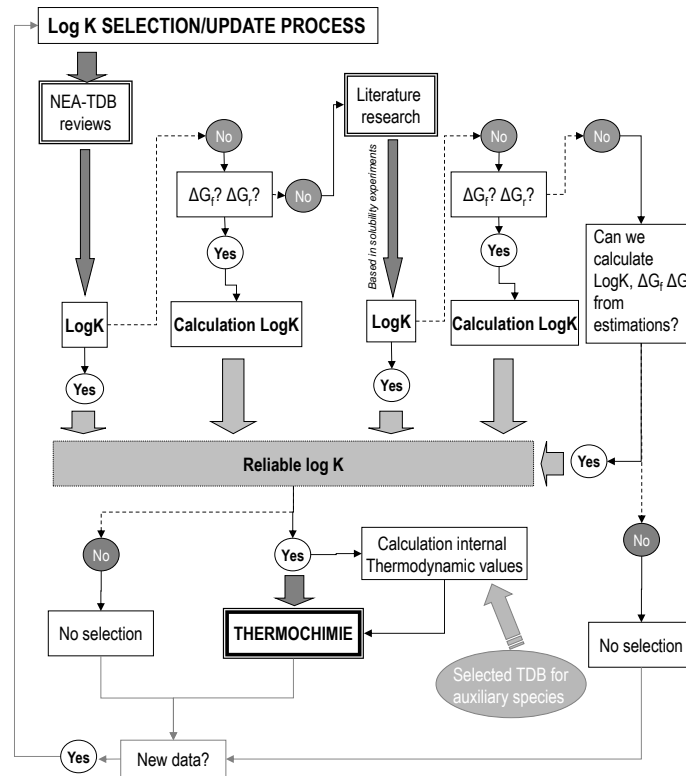
Diagram showing the general procedure used in the selection of log K values in ThermoChimie.

**2.** Secondly, *enthalpies or entropies* are selected. When a value has been selected for two of these three variables ($\Delta_r G_m^0$, $\Delta_f H_m^0$ and $S_m^0$), the rest of the data are internally calculated using Eq. 1-1 and Eq. 1-2.

$$\Delta_f G_m^0 = \Delta_f H_m^0 - T \sum_i S_{m,i}^0 \qquad \text{Eq. 1-1}$$

$$\Delta_r G_m^0 = \Delta_r H_m^0 - T \Delta_r S_m^0 \qquad \text{Eq. 1-2}$$

**3.** ThermoChimie primes *SIT (specific ion interaction theory)* for activity corrections to the derivation of the stability constants to the standard state.

The SIT approach (as described in Grenthe et al. (1997) and recommended by the NEA guidelines Grenthe and Wanner 2000) takes into account short-range non-electrostatic interactions by adding terms to the Debye-Hückel expression, as shown in Eq. 1-3. The use of SIT could provide adequate ionic strength corrections of data up to 6-10 mol/kg, depending on the particular system and the ionic media considered.

$$\log(\gamma_i) = -z_i^2 \left( \frac{A\sqrt{I_m}}{1 + Ba_i\sqrt{I_m}} \right) + \sum_k \varepsilon(i,k,I_m) m_k \qquad \text{Eq. 1-3}$$

Many interaction coefficients are already available in the NEA compilations, and others are available in the open literature. If individual, reliable and consistent interaction coefficients are available, it is possible to calculate $log_{10} K^0$ values accordingly.

If the individual interaction coefficients are not reported, it is possible to calculate $log_{10}K^0$ values using stability constants at different ionic strengths ($log_{10}K$), by interpolating $log_{10}K^0$ and Δε from a lineal regression.

## RELATIONSHIP OF LogK⁰ AND LogK FOLLOWING SIT

$$logK^0 = \log K - \Delta z^2 \times D + \Delta \varepsilon \times I$$

$$\Delta z^2 = \sum_{products} z_i^2 - \sum_{reactants} z_i^2$$

$$D = \frac{-0.5\sqrt{I}}{1+1.5\sqrt{I}}$$

$$\Delta \varepsilon = \sum_{products} \varepsilon_i - \sum_{reactants} \varepsilon_i$$

$z_i$: ionic charge; $I$: ionic strength; $\varepsilon$: interaction coefficients between ions

*SIT Relationship among SIT equations, $log_{10}K^0$ and Δε values.*

**4.** Sometimes, either because of the absolute lack of experimental data or because the inappropriateness of the existing ones, *estimations* are needed in order to fill in important data gaps. The estimation procedures can be applied to obtain different types of thermodynamic data, such as $log_{10}K^0$, $S_m^0$ or ε*(j,k)* values. The validity and the accuracy of the estimations depend on each particular case and must be individually evaluated.

Different procedures aiming at testing and validating the selected data have been used. Among those procedures, the most significant ones are:

a) The continuous comparison of measured solubilities recently reported in scientific publications, to those calculated by using values included in ThermoChimie

b) The comparison with other thermodynamic databases developed by other organisms.

c) The comparison with natural systems

The consistency and reliability of a thermodynamic database is often judged in front of its capability of reproducing experimental data gathered from either laboratory experiments or field observations. To this aim, it is very relevant to compare the theoretical results obtained from a solubility calculation of a given element by using the thermodynamic database with concentrations of this element measured in natural systems. In nuclear waste management the natural environments that present resemblances with what would be a repository of nuclear wastes are called natural analogues.

Natural analogue studies have become excellent occasions to test the conceptual geochemical models, the associated thermodynamic databases and the required numerical codes to describe radionuclides migration under repository conditions. Poços de Caldas (Brazil), Cigar Lake (Canada), Maqarin (Jordan), El Berrocal (Spain), Oklo (Gabon) or Palmottu (Finland) are some of the natural analogues used to test different aspects of the thermodynamic databases (Bruno et al. 2002).
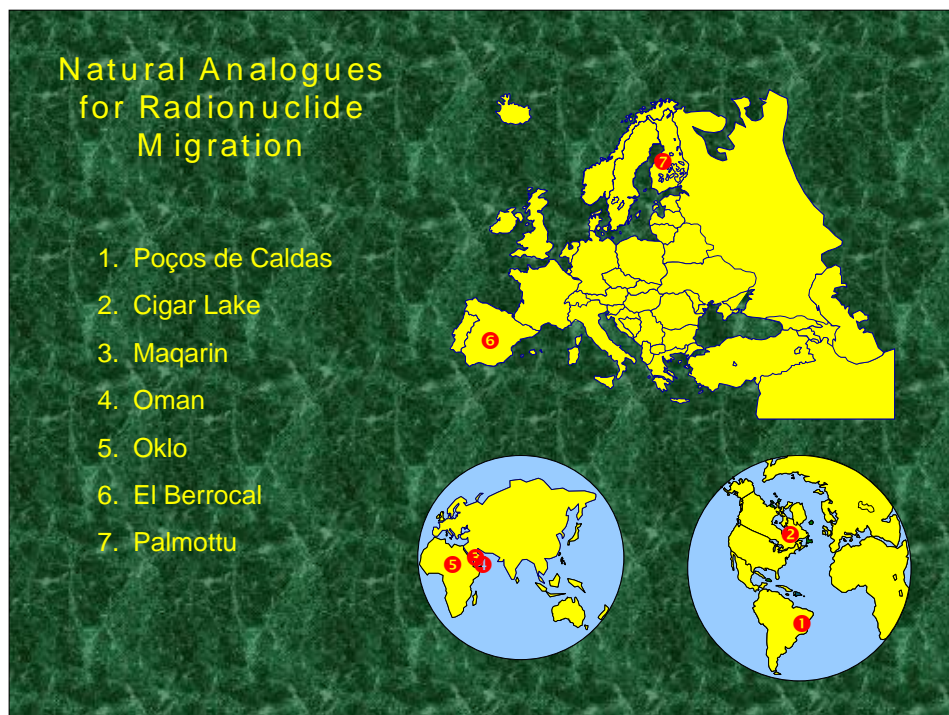
*Some of the Natural Analogues used for studies for radionuclide migration.*

The results obtained from analyses of trace metals in the mentioned natural analogue studies in combination with the mineralogical characterisation helps to the validation of the database. The comparison of the solubility calculations conducted with the database under the groundwater compositions of the natural sites with the analysed concentrations provides further confidence in the selected values incorporated in ThermoChimie.

# 2. TEMPERATURE CORRECTIONS

Temperature variations are expected to significantly affect radionuclide behaviour especially in the near of a HLNW repository. It is therefore a parameter to consider when defining the disposal concepts: temperature elevation must be limited to a reasonable domain where radionuclide behaviour can be properly predicted.

Data enthalpies of formation of reactants and products make possible to estimate the enthalpy of raction and the influence of temperature on stability. Formation/reaction entropy and enthalpy of solid phases are normally calorimetrically determined. But reliable data are sometimes scarce and the thermodynamic data gap is consequence of the inherent difficulties in determining experimental data associated with the temperature effect, thus, requiring the use of estimation methodologies commonly based on empirical observations.

One of ANDRA's main concerns is related to the lack of enthalpy data for radionuclide species, which limits the reliable assessment of temperature variations effect on radionuclide behaviour. For this reason one of the specific tasks of this project has been to extend the enthalpy data available in ThermoChimie, for the main aqueous species and solid compounds expected to exist under the conditions outlined by ANDRA: cementitious and Callovo-Oxfordian environments. For such a purpose, a specific methodology has been developed for estimating enthalpy (and/or entropy). In principle, the enthalpy has been considered as independent of the Temperature (Van't Hoff approach), although Cp data have been considered when available.

The assessment has been focused on aqueous species and solid compounds of Se, Th, Pa, U, Np, Pu, Am and Cm. In the case of aqueous species, priority has been given to aqueous species accounting for more than a $\geq 10\%$ of the total aqueous concentration of a radionuclide under Callovo-Oxfordian and cement groundwater compositions. The solid phases considered had been those likely to precipitate and control the concentration of radionuclides under either the conditions prevailing in the Callovo-Oxfordian formation or the hyperalkaline conditions defined by the cementitious barriers. The calculations conducted to select the species and solids of interest can be found in Domènech et al., (2007) and Gaona et al., (2008a,b).

The general methodology followed for this specific issue is schematized below.
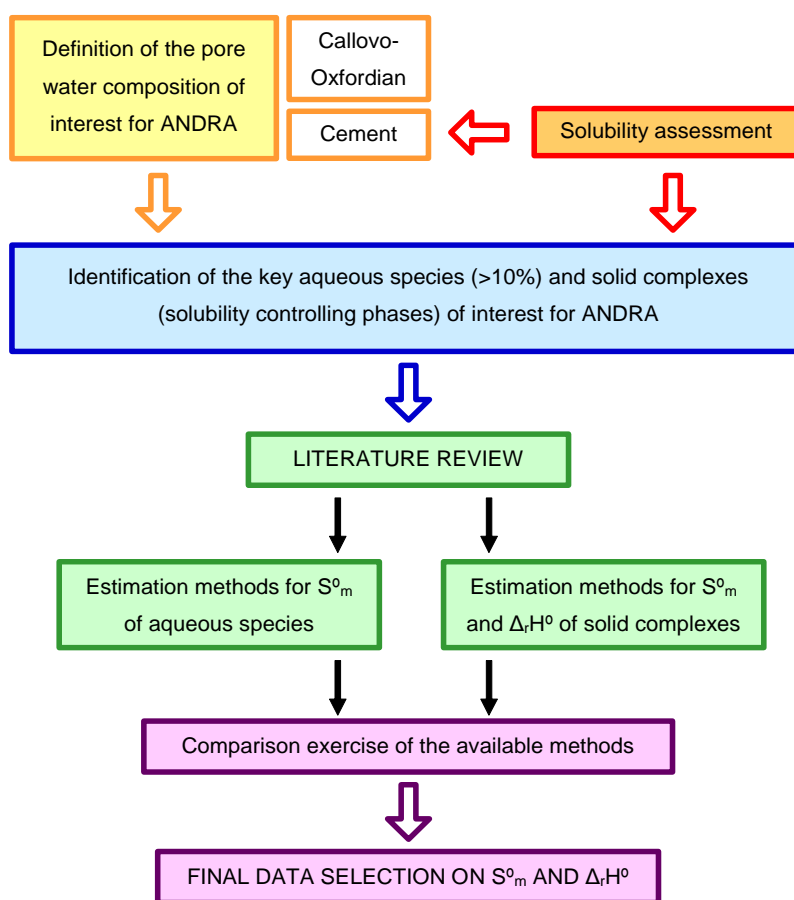


*Methodology followed to calculate unknown enthalpy values to be included in ThermoChimie database*

## 2.1     Aqueous species

Several methods are described in the literature to estimate formation entropies of aqueous species and reaction entropies at 298.15 K. These methods use correlations between entropies of analogous complexes and a combination of crystallographic radii, molar volumes, masses, electrical charge, etc. The estimation works developed by Powell and Latimer, (1951) and Couture and Laidler, (1957) set the basis to demonstrate that entropies of very different types of ions could be correlated using ionic mass, charge and simple structural features.

Some of the revisited methods can be applied to the whole range of aqueous species, whereas others are only appropriate to specific groups, e.g. hydroxides, halides, *etc*. Despite the published methods can be grouped in nine sets, only six out of the nine have been considered appropriate to estimate the entropy data of the aqueous species under the conditions of interest for ANDRA. A summary of the methods used to estimate entropies and enthalpies is given below. For more information on the methodology to fill in the enthalpy data gaps, the reader is referred to Gaona et al., (2008a,b).

## 2.2    Solid compounds

Several methods to calculate both enthalpy and entropy data of solid compounds are available in the literature. Most of these methods are based on empiric observations and are usually focused on particular groups of elements. One of the key limitations identified on the reviewed methodologies is the lack of knowledge on estimation procedures for amorphous solid compounds.

One of the most widespread approaches for the estimation of entropies is the methodology developed by Latimer (Latimer, 1951). Latimer indicated that the apparent entropy contribution of an anion to the entropy of the compound was related to the charge of the cation in the salt, therefore, the entropy of an ionic solid depends upon the magnitude of the ionic charges. In agreement with these observations, Latimer indicated entropy contributions of cations and anions (the latter depending on the charge of the cation in the ionic compound) and suggested that the enthalpy of solid complexes could be estimated according to Eq. 2-1. Furthermore, Latimer also suggested that each hydration water contributed 9.4 cal· K$^{-1}$ to that of the solid.

$$S_f^\circ = \Delta S_{LAT,C} \cdot n_C + \Delta S_{LAT,A} \cdot n_A$$

Eq. 2-1

$\Delta S_{LAT,i}$: contribution of the ion to the entropy of the compound
$n_i$: moles of ions in the correspondent solid compound

Latimer's method (Latimer, 1951) was updated by Mills (Mills, 1974) from the analysis of experimental data for *ca*. 300 compounds. Although Latimer initially devised the method for ionic compounds, Mills demonstrated its usefulness to estimate entropies of non-ionic compounds. Langmuir (Langmuir, 1978) provided with some improved parameters to estimate entropies of solid compounds containing the $UO_2^{2+}$ moiety. Kumok (Kumok, 1987) improved the estimation approach in Latimer (1951) by considering a larger set of available experimental data. Grenthe (Grenthe et al., 1992) considered the method developed by Latimer, (1951) to estimate the entropies of some uranium compounds taking advantage of the contribution coefficients improved in Naumov et al., (1971). The thermodynamic data selection on U(VI) compounds indicated in Grenthe et al., (1992) was used to provide a more accurate value of $UO_2^{2+}$ in U(VI) solids, determined as 94.7 J· K$^{-1}$· mol$^{-1}$.

We have complemented the Latimer´s method to fill in remaining gaps. For more and specific information on the methodologies and procedures followed the reader is referred to Gaona et al. (2008b) and Duro et al. (2010).

The figure below shows a scheme of the methodology followed for entropy estimations.
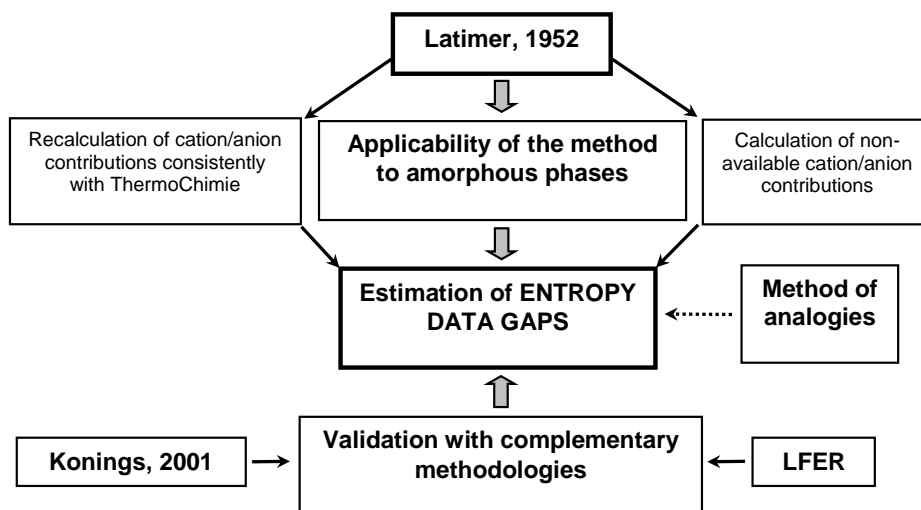
Scheme of the followed approach to estimate the unknown entropy/enthalpy data

Special care has been taken when analysing the uncertainty, as estimations might introduce too large uncertainties in calculations. Therefore, estimations must be taken with caution and tested in front of experimental data for analogue species when available.

In those cases where more than one method has been used to estimate the entropy values, the resulting data have been obtained by averaging the different estimations. The methods proven to be unreliable have not been considered to average the entropy estimation.

The combination of different estimation methods has allowed to significantly decreasing the uncertainty associated to the final entropy selection. The most accurate results have been achieved for hydroxo-complexes, whereas silicates and mixed complexes (aqueous hydroxo-carbonates of Np and Th) hold larger uncertainties, mainly due to the limited number of estimation methods applying to these chemical groups. A specific statistical exercise (the 'Paired t-test') has led to the conclusion that, with a confidence level of 95%, no important differences arise between the experimental data and entropies estimated in this exercise.

A comparison between the available experimental entropies and those estimated by following the methodology presented here is shown in the figure below.
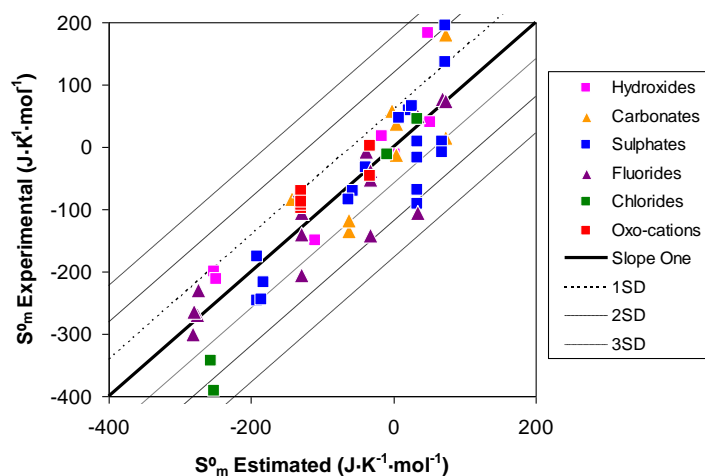


Comparison between experimental and estimated $S^o_m$ for different type of complexes. SD stands for standard deviation.

# 3.    IONIC STRENGTH CORRECTIONS

## 3.1    SIT use for generic data selection

Thermodynamic data are usually determined in the laboratory under different conditions, far from standard state conditions. The activity coefficient $\varepsilon_i$ of the species *i* is the factor that accounts for the difference of the behaviour of the solute from ideality. It depends on the temperature, pressure, solvent properties and especially on the concentrations of other solutes.

To subtract the effect of the ionic strength and obtain the value of $log_{10}K^0$ at infinite

dilution several models, that allow the estimation of the activity coefficients of solutes, have been established. Some of these models are Debye-Hückel, Extended Debye-Hückel, Davies, Pitzer and SIT.

The Debye-Hückel term, which is the dominant term in the expression for the activity coefficients in dilute solutions, accounts for electrostatic long-range interactions. At higher concentrations short-range non-electrostatic interactions have to be taken into account, as well. This is usually done by adding terms to the Debye-Hückel expression as in the case of the Specific Interaction Theory, SIT, as described in Grenthe et al. (1997) and recommended by the NEA guidelines. The use of SIT could provide adequate ionic strength corrections of data up to 6-10 mol/kg, depending on the particular system and the ionic media considered.

*Equations for activity coefficients calculation. The SIT approach is the one primary used in ThermoChimie*

$$\log(\gamma_i) = -Az_i^2\sqrt{I_m} \qquad \text{DEBYE-HÜCKEL}$$

$$\log(\gamma_i) = \frac{-Az_i^2\sqrt{I_m}}{1 + Ba_i\sqrt{I_m}} \qquad \text{EXTENDED DEBYE-HÜCKEL}$$

$$\log(\gamma_i) = -Az_i^2\left(\frac{\sqrt{I_m}}{1 + \sqrt{I_m}} - 0.3I_m\right) \qquad \text{DAVIES}$$

$$\log(\gamma_i) = -z_i^2\left(\frac{A\sqrt{I_m}}{1+b\sqrt{I_m}} + \frac{2}{b}\ln\left(1+b\sqrt{I_m}\right)\right) + \sum_c\sum_a m_c m_a B'_{ac} + \sum_c\sum_{c'} m_c m_{c'}\phi'_{cc'}$$
$$+ \sum_a\sum_{a'} m_a m_{a'}\phi'_{aa'} + \sum_a m_a\left(2B_{ia} + ZC_{ia}\right) + \sum_c m_c\left(2\phi_{ic} + \sum_a m_a\psi_{ica}\right) \qquad \text{PITZER}$$
$$+ \sum_a\sum_{a'} m_a m_{a'}\psi_{iaa'} + |z_i|\sum_c\sum_a m_c m_a C_{ac} + 2\sum_n m_n\lambda_{ni}$$

$$\log(\gamma_i) = -z_i^2\left(\frac{A\sqrt{I_m}}{1+Ba_i\sqrt{I_m}}\right) + \sum_k \varepsilon(i,k,I_m)m_k \qquad \text{SIT}$$

In the SIT approach, the activity coefficient $\varepsilon_i$ of the species i of charge $z_i$ in the solution of ionic strength $I_m$ may be described by the SIT equation. A and B are constants which are temperature and pressure dependent, and $a_i$ is an ion size parameter for the hydrated ion. The Debye-Hückel limiting slope, A, has a value of $(0.509 \pm 0.001)$ kg$^{1/2} \cdot$ mol$^{-1/2}$. The term $Ba_i$ has been assigned a value of 1.5 kg$^{1/2} \cdot$ mol$^{-1/2}$ at 25°C and 1 bar (Grenthe et al. 1997).

The ion interaction coefficients $\varepsilon(j,k)$($kg \cdot mol^{-1}$) depend on each species and each ionic medium. The main ionic species present in the groundwaters of interest for Andra are $Na^+$ and $Cl^-$, therefore the SIT activity coefficients for $\varepsilon(Na^+,anion)$ and $\varepsilon(cation,Cl^-)$ are included in ThermoChimie database. The interaction coefficients for the species $\varepsilon(cation,ClO_4^-)$ and $\varepsilon(cation,NO_3^-)$ are also included when available. Interaction coefficients with $ClO_4^-$ are necessary in order to maintain the consistence of the database, as most of the experimental data are obtained in $NaClO_4(aq)$ media in the laboratory. Nitrate interaction coefficients are included to improve the modelling of waste packages where high nitrate concentrations are present.

Many interaction coefficients are already available in the NEA compilations, and some other are also available from literature. If individual $\varepsilon$ are available, it is possible to calculate $log_{10}K^0$ values accordingly. If the individual interaction coefficients are not reported, it is

possible to calculate $log_{10}K^0$ values if stability constants at different ionic strengths ($log_{10}K$)

are available, by interpolating $log_{10}K^0$ and $\Delta\varepsilon$ from a lineal regression

In some cases individual interaction coefficients are estimated based on well-founded correlations. For example, there is a very good correlation between interaction coefficients in chloride and in perchlorate and nitrate medium for mono and divalent cations, what allows the calculation of a regression line to estimate interaction coefficients in chloride solutions. It is also possible to get analogies among similar species with identical charge $z_i$. For instance, the interaction coefficient for $NpO_2^{2+}$ with perchlorate, $\varepsilon(NpO_2^{2+},ClO_4^-)$, can be obtained in analogy with the corresponding interaction coefficient of U(VI) cation, $\varepsilon(UO_2^{2+},ClO_4^-)$.

If activity coefficients are not available in the NEA compilations neither in the literature, and the estimation of interaction coefficients is not possible, the extended Debye-Hückel equations is used to obtain infinite dilution log K values in ThermoChimie.


## 3.2 Specific development regarding soluble salts from waste packages

Some type of radioactive wastes can contain significant amounts of salts (e.g. nitrates, sulphates…). The evaluation of the behaviour of these wastes entails handling calculations at high ionic strength values.

Pitzer approach has frequently been suggested as the most appropriate model when dealing with corrections at high ionic strength. Nevertheless, when using the Pitzer approach, it is necessary to include all the appropriate interaction parameters. Those parameters are hardly available for heavy metals and radionuclides, resulting in large deviations from experimental results. Thus, the Pitzer approach may not always provide a satisfactory solution for calculations where radionuclides are involved.

On the other hand, the amount and accuracy of the data related to interaction coefficients have significantly increased in the last years; this improvement is especially significant in the last NEA update (Rand et al. 2009). However, in the cases where no highly charged metal ions are present, it is sometimes difficult to distinguish between real complexes with a weak interaction or strong specific ion interaction effects. This may result in the inclusion of both interaction coefficients and complexes in the thermodynamic database, leading to inconsistencies in the selection and to an excessive correction of the medium effects when the database is used in calculations in high ionic strength media.

Taking that into account, a significant effort has been done to test and improve the behaviour of the database in high ionic strength calculations.

The general methodology used in order to attain this objective is summarized below:

- Weak complexes in the database have been identified. It is not easy to clearly define the frontier between strong specific ion interaction effects and weak species. However, in Hummel et al. (2005) the authors define a "weak complex" as a complex with K<10 (log K<1).

- Those weak complexes have been eliminated from the database, and the appropriate interaction coefficients have been introduced. The auxiliary data related to SIT calculations reported in the NEA reviews was revised and updated during this exercise.

- Changes have been evaluated by both benchmarking exercises (comparisons with other databases) and modelling of experimental data obtained at high ionic strength values.

The experimental data used in the validation was mainly solubility data for gypsum, portlandite, barite, and thorium, uranium and americium hydroxides in highly concentrated NaCl, KCl, $CaCl_2$ or $Na_2SO_4$ solutions (e.g. Azimi, 2010, Christov and Moller, 2004, Fanghänel and Kim, 1998, Felmy et al. 1991, Monnin and Galinier 1988, Rai at al. 1997).

The databases used for comparison, a part from ThermoChimie itself, were:

- Pitzer.dat, a database developed using the Pitzer approach for ionic strength corrections (Plummer et al. 1988).

- The Yucca Mountain Project dataset data0.ypf.R2, (YMP), developed with the Pitzer approach for the Yucca Mountain Project (Jove-Colon et al. 2007).

- Phreeqc.dat, a database file included in PHREEQC (Parkhurst and Appelo, 1999) that uses Debye-Huckel equations modified according to the WATEQ model for ionic strength corrections.

- Thermoddem database (Blanc et al. 2007). The version of the database used in the calculations was created in 25/08/2009 and uses Debye-Huckel equations, modified according to LLNL model, to perform ionic strength corrections.

The results of this validation exercise helped to confirm that the improvements in the database increase the performance of ThermoChimie when dealing with systems at high ionic strength concentrations.

# 4.    OUTCOME

The validation of the more than 2,000 aqueous complexes and solid phases included in ThermoChimie is not an easy task and despite the great effort made, the degree of confidence varies significantly depending on the studied system. The uncertainty value expressed for each selected data shows the confidence degree in the particular selection.

Several tasks have been carried out in the context of the ThermoChimie project in the period 2006-2013:

i)    Update of the data for radionuclides and chemotoxics using in the NEA TDB publications and new open literature available

ii)    Completion of missing data needed to asses the effect of the temperature on the behaviour of radionuclides. Efforts have focused on means of revisiting the experimental data (which is very scarce) and proposing estimation procedures to investigate and produce a sensible way of estimating temperature effects.

iii)    Testing and improvement of the behaviour of the database in high ionic strength calculations.

iv) Use of solid solution approaches to weigh how reliable is using the pure solid phases to estimate the concentration limits of different radionuclides in the vicinity of the repository.

v) Update of the data for organic ligands present in the wastes and their degradation products, including both extensive literature review and specific experimental and modelling studies.

vi) Theoretical and experimental study of the role of natural organic matter (NOM) on the migration of radionuclides in and around the Callovo-Oxfordian.

vii) Validation and application of ThermoChimie through the comparison with other databases, the calculation of solubility limits for radionuclides, application of the solid solution approaches and the study of the effect of organics in the mobility of radionuclides

A list of the systems related with radionuclides and chemotoxics that have been added or updated in the period 2006-2013 is provided below.

*Added or updated systems:*

- Transition elements: Cr, Fe, Co, Ni, Zr, Nb, Mo, Tc, Pd, Ag, Cd, Hf.
- Group IV: B and Al.
- Group V: Sn and Pb.
- Group VI: N, P, As, Sb
- Group VII: S and Se.
- Lanthanides: Sm, Eu, Ho
- Actinides: Th, Pa, U, Np, Pu, Am and Cm.
- Organics ligands: citrate, oxalate, EDTA, NTA, gluconate, isosaccharinate, acetate, phthalate and adipate.
- SIT coefficients and weak complexes