ThermoChimie

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Technical report

ThermoChimie guideline 1: Data selection and uncertainties

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The ThermoChimie database was first developed in 1995 by Andra, the French national radioactive waste management agency. They have since been joined by Radioactive Waste Management (RWM) from the UK, and ONDRAF/NIRAS from Belgium.

ThermoChimie provides an accurate and consistent set of data, specifically chosen for use in modelling the behaviour of radionuclides in waste packages, engineered barriers, and both the near surface and deep geosphere. The database can be used to model the speciation and solubility of a wide range of stable and radioactive elements, organics, and solid phases including cements, clay minerals and degradation products (such as zeolites). The database is suitable for use within the range of conditions expected in both near-surface and geological disposal facilities: pH 6-14, ionic strength up to SIT, Eh within the stability fields of water, and temperatures from 15 to 80°C.

ThermoChimie is intended for use across the radioactive waste management community, to support repository performance assessment, research and development activities and decision making. To maximise their utility, the data are therefore provided in formats suitable for use with common geochemical modelling codes. The database can be viewed and downloaded from the project website: https://www.thermochimie-tdb.com/, where additional information and supporting documents are also available.

This document provides guidance on how the data included in ThermoChimie is selected for addition. This covers the choice of data source, the selection process and uncertainty estimation.

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ThermoChimie guidelines 1. Data selection and uncertainties

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2	Jul. 2019	Full revision to support the release of v10a
1	Jul. 2015	First version uploaded in ThermoChimie website

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1. Introduction

The ThermoChimie database contains thermodynamic data for major, radioactive and toxic elements as well as organic ligands and solid phases, including cement hydrates, clay minerals and zeolites. It also includes kinetic data for some minerals present in clay rich rocks and cements. Each of these datasets, though distinct, are jointly used in geochemical modelling calculations in support of Safety Assessment. All the data must be internally consistent and suited to the conditions for which ThermoChimie is designed (those expected in nuclear waste repositories[1]).

This guideline provides information on the data selection process. It details the data sources used and the steps taken to ensure consistency between them.

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[1] See the introduction to ThermoChimie guidelines for an exhaustive description of the systems for which ThermoChimie has been designed.

2. Selection process

ThermoChimie is continuously revised with additions or changes being made as new or improved data appears. The data included in ThermoChimie is taken from a wide range of sources:

- Previous thermodynamic data compilations
- The open scientific literature
- Targeted experimental programmes
- Estimations

2.1 Primary master species and reference states of the elements

Wherever possible, ThermoChimie relies on the **CODATA recommendations** (Cox et al. 1989) when selecting thermodynamic data for the **primary master species**[2] and **the reference states of the elements**[3] (Giffaut et al. 2014). Where there is disparity between the chosen master species (in the database) and the CODATA recommendation[4], a full justification for this is always provided.

2.2 Major species

Thermodynamic data for major species and solids are selected by the following method:

1. Data for the major elements is normally based on *previous compilations*, such as the CODATA key values for thermodynamics (Cox et al. 1989) or the Slop98 database (based on the works of Helgeson et al. 1978, Sverjensky et al. 1997 and Shock et al. 1997).

2. When selecting data, special care it taken to ensure **consistency** between the different aqueous and solid species (for example, the solubility of a solid must be calculated in agreement with the corresponding aqueous speciation). The influence of temperature is also taken into account.

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[2] Primary master species are the minimal set of aqueous species required to formulate product species; thus, they are the basic building blocks of formation reactions (see Guideline 0 for more details).

[3] The reference phase for an element is used as a base point in thermodynamic calculations; its $\Delta_f G_m^0$ and $\Delta_f H_m^0$ values are zero.

[4] In ThermoChimie, Al and Si master species do not agree with CODATA values; an exhausitive explanation for this is provided in Blanc et al. (2006).

3. Once an initial selection has been made this value is checked against the results of experimental work. Special attention is given to ***reference experimental publications*** (this is, well cited papers with a robust methodology) dealing with each system.

4. The validity of the data is then further **verified** by comparison with additional literature data.

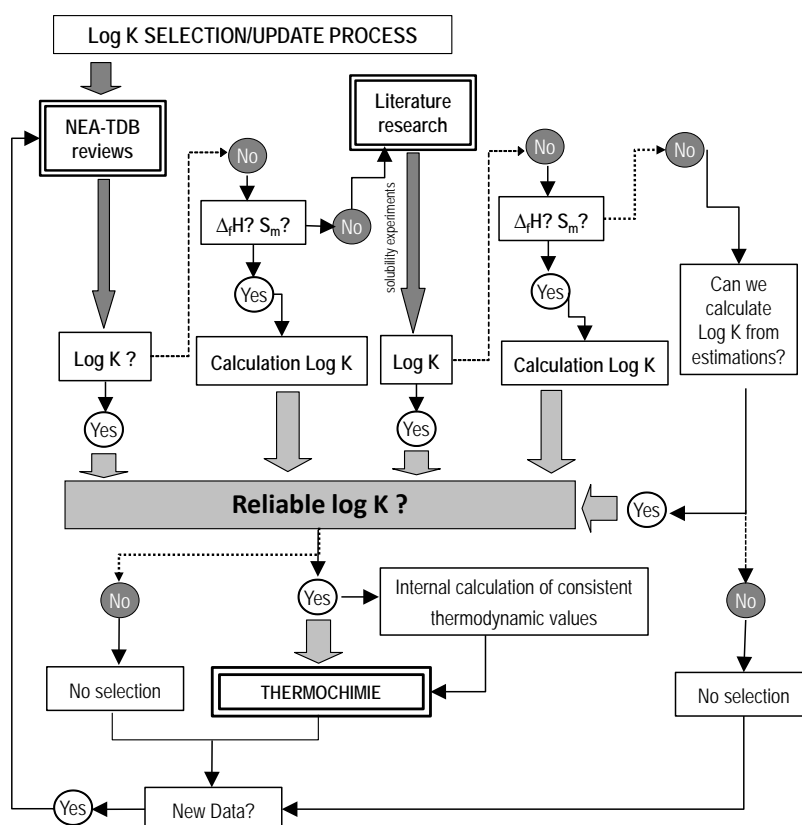## 2.3 Radioelements and chemotoxic elements

Each individual datum for the radionuclides and chemotoxic elements included in ThermoChimie is the result of exhaustive literature research, data intercomparison, estimation and, in some specific cases, development of a focused experimental programme to fill in important data gaps (Grivé et al. 2015).

The results of the **NEA-TDB project** are used as a primary data source for many radionuclides. However, the NEA data does not cover all the elements and conditions of interest to ThermoChimie. Therefore, the selection has to go beyond the limits of the NEA-TDB project. As one of the guiding principles of ThermoChimie is that it must be **exhaustive** enough to model the systems of interest, additional data not selected in other reviews is sometimes included in the database.

The data for radioelements and toxic elements included in ThermoChimie are selected according to the procedure described below:

1. Where available, ***aqueous stability constants and solubility equilibria ($log_{10}K^0$)*** are selected. The selection process is summarised in Figure 1. These values can then be used to calculate the species Gibbs energy of reaction and formation ($\Delta_r G_m^0$ and $\Delta_f G_m^0$), as long as the Gibbs energies of formation of the basic components are known.

Figure 1. Summary of the selection and update process for log K values of radionuclides and chemotoxic elements in ThermoChimie (Grivé et al. 2015).

Since ThermoChimie is intended for use in solubility calculations to support performance assessment of deep underground repositories, preference is given to values obtained directly from solubility experiments.

Data from these experiments are used to calculate the solubility product ($\log K_s^0$) from the equilibrium concentrations of the solid and aqueous phases. This requires some assumptions to be made about the element of interest, including its aqueous speciation and the stability of any solution complexes.

During the dissolution process, the mineral surface can undergo changes, including hydration, precipitation of amorphous minerals and adsorption that may affect the apparent equilibrium constants. The solubility constants obtained from classical dissolution experiments includes all these effects, whereas $\Delta_r G_m^0$ values derived from calorimetric data describe a perfectly crystalline surface. The surface of a crystalline solid may differ from the surface of an amorphous solid in contact with the groundwater. Therefore, data selection favours experiments where the solids have been fully characterised and the crystallinity accounted for.

Redox reactions may be an exception to this general rule, as solubility reactions where redox processes are involved may face experimental handicaps related to characteristaion of the solid and redox control. In this case, different methodologies (e.g., potentiometry) could be used to provide accurate thermodynamic data.

2. Secondly, ***enthalpies or entropies*** are selected. If available, experimental data obtained by calorimetric measurements are preferred. When reliable data are not available, these values are estimated (see point 5).

3. When values have 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 can be internally calculated using the following equations (Eq. 1, Eq. 2):

$$\Delta_f G_m^0 = \Delta_f H_m^0 - T\left(S_m^0 + \left(\frac{z}{2}\right)xS_{m,H2(g)}^0 - \sum_i \frac{\nu_i}{\nu_{i,ref}}S_{m,i}^0\right) \qquad \text{Eq. 1}$$

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

Here, $\Delta_f \mathbf{G_m^0}$ (KJ·mol^{-1}) and $\Delta_f \mathbf{H_m^0}$ are respectively molar Gibbs energy an enthalpy of formation, $\mathbf{S_m^0}$ is the molar entropy, $\Delta_r \mathbf{G_m^0}$, $\Delta_r \mathbf{H_m^0}$ and $\Delta_r \mathbf{S_m^0}$ are the molar Gibbs energy, enthalpy and entropy of reaction, z stands for the ion charge, and υ_i are the stoichiometric coefficients.

4. ThermoChimie primarily uses *SIT (Specific ion Interaction Theory)* for **activity corrections** of the stability constants to the standard state.

The SIT approach takes into account short-range non-electrostatic interactions by adding terms to the Debye-Hückel expression (Eq. 3):

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

Eq. 3 accounts for the activity coefficient γ_i of an ion of charge Z_i in a solution of ionic strength $I = \frac{1}{2}\sum_i m_i z_i^2$. A and B are empirical constants for a given temperature. The parameter a_i is the effective ion diameter, Z is the charge and $\varepsilon(i,k,I_m)$ is the ionic interaction coefficient (Kg·mol^{-1}).

The first part of the expression, in brackets, is the Debye-Hückel term that calculates the activity coefficients in dilute solutions and accounts for long-range electrostatic interactions.

At higher ionic strengths, short-range, non-electrostatic interactions between ions must be taken into account and the term $\varepsilon(i, j, I_m)$ is added to the Debye-Hückel expression.

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, by interpolating $\log_{10}K^0$ and $\Delta\varepsilon$ from a linear regression.

Whenever correction using the SIT approach is impossible, due to lack of available data, the extended Debye-Hückel expression is used for extrapolation to zero ionic strength.

5. In some cases, due to the lack of or inaccuracy in data, ***estimations*** are needed.

Three main data gaps are commonly identified in thermodynamic databases:

- gaps in stability constants;
- gaps in enthalpy and/or entropy values;
- and gaps in ionic strength correction interaction coefficients (SIT interaction coefficients).

Different estimation approaches can be used to fill these gaps. The choice of estimation procedure depends on many factors (type of data, availability of the original values, studied element, etc) and can be of different forms (analogies with other elements and complexes, correlations considering the charge (z) and the ionic radii (r) of different elements, empirical algorithms, etc). The validity and accuracy of the estimate must be individually evaluated, and consistency between estimated data with the rest of the database must be maintained (see Guideline 2).

6. **Verification** is carried out by comparison of selected values to additional independent data (when available), or with calculations including correlations or analogies (see Guideline 2 for further details).

2.4 Low molecular weight organic complexes

The selection of organic ligands is focused on stoichiometric, low molecular weight organic species likely to play a role under disposal conditions. These include[5]:

- bitumen degradation products (e.g., oxalate, acetate);
- analogues for cement additives or their degradation products (e.g., gluconate);

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[5] The type of organics and the level of information included in the database depends on the ThermoChimie version. Those examples are for version 9b0 onwards.

- chemicals used for decontamination and cleaning processes (e.g., EDTA, NTA);
- degradation and leaching products from plastics, filters or resins (e.g., adipate, phthalate);
- cellulose degradation products (e.g., isosaccharinate);
- low molecular weight organic species identified in natural clay systems in the presence of kerogen (e.g., malonic and succinic acids).

The methodology for selection of the relevant thermodynamic data for organic ligands is described below.

1. *Identification* of the available thermodynamic data for the organic ligands of interest, including open literature data and previous compilations. The results of the **NEA-TDB project** are also taken into account in the selection. However, the NEA review for organic ligands (Hummel et al. 2005) only contains data for complexation of a limited number of ions by citrate, oxalate, EDTA and isosaccharinate. Therefore, data included in ThermoChimie extends beyond this limited scope and uses other sources.

2. Selection of reliable *experimental* data (*stability constants, $log_{10}K$)* available for each system and extrapolation to I = 0 using the specific-ion interaction theory (SIT). Data from experimental programmes conducted within the ThermoChimie project are especially useful.

In order to maintain the consistency of the database, the selection is carried out in three successive steps:

- 2.a) selection of hydrolysis data for the organic complexes;
- 2.b) selection of organic complexation data with the alkaline-earth elements Ca and Mg, in agreement with the hydrolysis data selected in step 2.a;
- 2.c) selection of organic complexation data for the radionuclides of interest included in ThermoChimie, in agreement with the hydrolysis and complexation data selected with data in steps 2.a and 2.b.

3. There is limited experimental data available for the organic ligands of interest. When possible, relevant data gaps for stability constants are filled with *estimations* based on analogies or correlations.

4. Finally, *entropy or enthalpy* data are selected to evaluate the influence of temperature. However, it should be noted that information on these parameters, for organic species, in the open literature is extemely limited. Therefore, only very limited information is included in ThermoChimie. This is not forseen to be a significant issue though as, according to different waste inventories, organic species are not expected to be a significant component of exothermic wastes.

5. *Verification* is carried out by comparison of selected values with additional independent data available in the literature (e.g., estimations or values reported in other thermodynamic data compilations), or with calculations including correlations or analogies. These verification exercises increase confidence in the selected values and any uncertainty associated with them.

2.5 Clay minerals

Thermodynamic data for the clay minerals are obtained using three different approaches (Blanc et al. 2015):

- critical selection from literature data;
- dedicated experimental measurements (e .g Blanc et al. 2014);
- estimation by predictive models. These predictive models play a key role in thermodynamic data selection for clays: estimating missing values, verifying the consistency of data selection and providing guidance for the critical data selection and dedicated experiments.

A scheme summarising the process of data selection for clay minerals is shown in Figure 2; the methodology is described below.
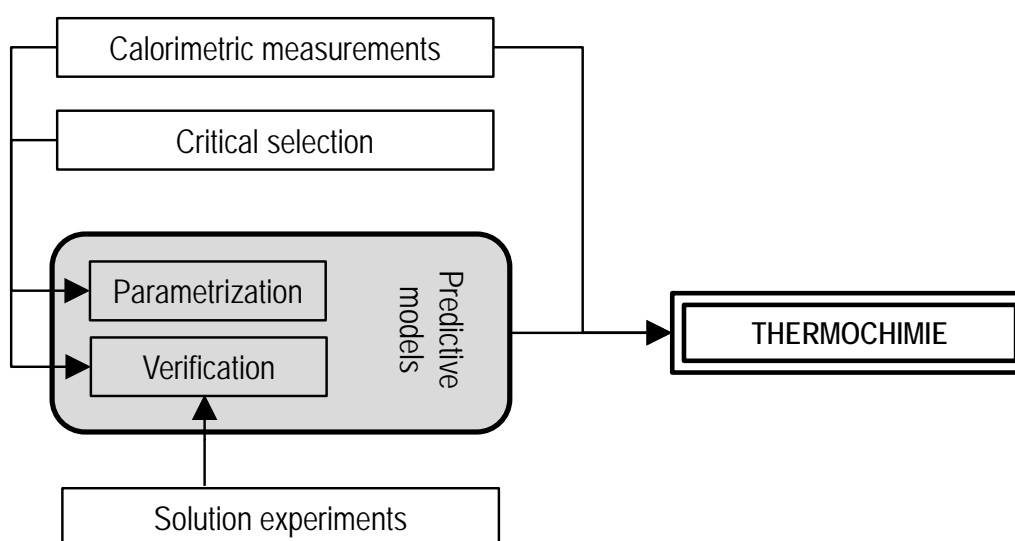
Figure 2. Selection of thermodynamic datasets for clay minerals (from Blanc et al. 2015).

1. Where possible, $log_{10}K(T)$ functions are calculated from **calorimetric data**, either obtained from literature or from targeted experiments. Calorimetry is especially well suited to this purpose as results do not depend on the attainment of equilibrium, something that is difficult to prove for clay materials, especially in low-temperature solution experiments (Blanc et al. 2013). To increase data traceability fitting of $log_{10}K(T)$ functions and averaging of equilibrium constants is avoided as far as possible. .

2. Literature data are limited to micas and chlorites, as trying to acquire thermodynamic datasets for all possible clay minerals is not realistic. To solve this problem, **predictive models** have been developed to estimate the thermodynamic properties of most common clay minerals.

In these predictive models, the thermodynamic properties of formation of anhydrous phases are first calculated. Hydrated phase are then parameterised by addition of the properties of hydration.

> **2.a)** Predictive models for the properties of formation of the anhydrous clay minerals. For anhydrous clay minerals, formation enthalpy is calculated following the approach of Vieillard (1994a and b). This method relies on the difference in electronegativity between two cations around a common oxygen atom. The thermodynamic functions are completed using the polyhedral decomposition model (Blanc et al. 2013). The combination of both models calculates an estimated Gibbs energy for anhydrous phyllosilicates.

> **2.b)** Predictive models of the thermodynamic properties of the hydration of clay minerals. The hydration properties are modelled using an improved version of the original Ransom and Helgeson (1994) model, described in Vieillard et al. (2011). This thermodynamic model was initially developed considering an asymmetric subregular binary solid solution between a fully hydrated and an anhydrous smectite. It calculates the effective amount of hydration water as the difference between the so-called gravimetric water and the surface covering water.

> The thermodynamic properties of the hydrated clay mineral end members are first calculated from the properties of the anhydrous end members. Then, the hydration model from Vieillard et al. (2011) is used to calculate the number of H_2O moles, the enthalpies and entropies of hydration, for $P/P0 = 1$ (water saturation). For the moment, the hydration model does not account for the charge on the H_2O molecule or its location in the TOT sheet.

3. The calculations are then processed in the following way:

- first, formation enthalpies, entropies, heat capacities and volumes are calculated for different clay minerals;

- then, formation enthalpies and entropies are combined to provide the Gibbs energy;
- finally, the equilibrium constant, $log_{10}K(T)$, is calculated as a function of temperature, from primary species in the ThermoChimie database.

4. ***Verification*** is carried out by generating activity diagrams for the minerals of interest in the chemical subsystems of concern and comparing these phase relationships with observations gathered from the literature. This process ensures that data generated by the different approaches, outlined above, gives a consistent result. It also allows identification of gaps and weaknesses in the database.

The $log_{10}K$ values calculated from calorimetric data and the results of predictive models are further verified by comparison with results of solution experiments (Blanc et al. 2015). Taking into account the specific pitfalls of these types of experiments (compositional variability, presence of impurities, difficulties in confirming equilibrium, etc) the application of this verification procedure is limited.

2.6 Cement minerals

The data selection process for C-S-H phases is different than for the other cementitious phases, as described in Blanc et al. (2015).

1.   For ***C-S-H phases***, the selection of thermodynamic properties involves the following steps (Blanc et al. 2010a):

- The experimental data available for the solubility or calorimetry of C–S–H phases at T ≥25 °C are compiled and analysed.
- Equilibrium constants for nanocrystalline C–S–H and their corresponding compositions are extracted from a set of experimental data.
- For crystalline C–S–H, there is some inconsistency within the available values.   To overcome this, the datasets are completed by manual refinement of the resulting phase diagram..
- The missing properties (formation enthalpy and heat capacity) are obtained by using a polyhedral decomposition method applied to the system SiO_2–CaO-H_2O. This method is derived from the oxide summation method.

2.   For ***other cement phases***, the selection process entails the following steps (Blanc et al. 2010b):

- For each phase, the equilibrium constant at 25 °C is selected from a single experimental source. For equilibration experiments in aqueous media, only the aqueous solutions displaying a low ionic charge imbalance (smaller than 5% when

possible) are retained. The duration and reversibility of the experiments, in addition to the electroneutrality of the solutions, are also considered in the selection and analysis of the experimental works.

- The formation enthalpy and the Cp(T) function are taken from the literature or estimated. The estimation technique of Helgeson et al. (1978) is usually applied. This technique involves imagining a solid–solid transformation reaction in which the thermodynamic properties of all the solids involved (except one) are known. The unknown properties of this solid can then be estimated based on the the assumption that $\Delta_r Cp(298) = 0$.

- Finally the $log_{10}K(T)$ function is calculated by combination of the $log_{10}K$ at 25 °C, enthalpy data and heat capacity data.

3. ***Verification*** is initially carried out by comparing the $log_{10}K\ (T)$ function with the reaction quotient $log_{10}Q$ from the literature, at different temperatures. An important step in the verification procedure is to draw speciation/predominance diagrams corresponding to defined chemical subsystems. Phase relationships are compared with observations gathered from the literature. These diagrams allow verification of the predicted phase relationships and the consistency of the data set. Furthermore, they may identify data gaps and weak points. This is, therefore, a key step in the process, guaranteeing consistency of the different approaches used in development of the system. These verification tests, involving the C-S-H phases and the other cementitious phases, are done before the data are integrated into ThemoChimie.

A summary of the processes are shown in Figure 3.
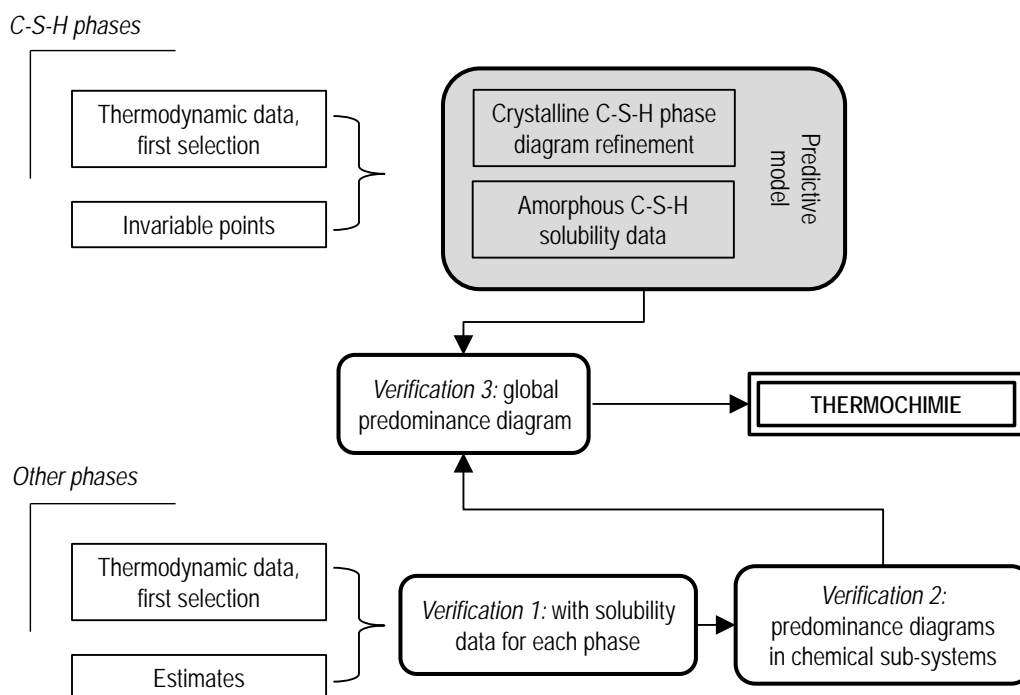
Figure 3. Process for the selection of thermodynamic datasets for cement minerals (reproduced from Blanc et al. 2015).

2.7 Zeolites

The selection for zeolites is limited to those phases that can be formed at temperatures below 90 °C and that are likely to play a role during cement/clay interaction in deep disposal systems.

Details on the selection process (Blanc et al. 2015) can be summarised as follows:

1. Where possible, the thermodynamic properties of zeolites are obtained from *literature data.*

- Calorimetric data are preferred over solution equilibria; solution data are used mainly for comparison and verification purposes.
- If it is necessary to use solution data, these are accurately selected according to the electroneutrality condition, the duration of the experiment, the analysis of the final solid products and the experimental protocol used in the original work.
- The selection of thermodynamic properties is focused on using direct and traceable measurements. Therefore, the fitting of $log_{10}K(T)$ functions, as well as averaging equilibrium constants, is avoided as far as possible.

2. Obtaining a complete thermodynamic dataset for a chosen zeolite from the literature is often problematic as, in many cases, values are only available for minerals with a slightly different composition than the phase used in TC. To complete the thermodynamic datasets, missing heat capacities for a specific zeolite are estimated using the ***predictive model*** developed by Vieillard (2010). This estimation method, based on a multiple linear regression approach, uses similar zeolitic minerals for calibration.

3. Finally, the selected data is subjected to a ***verification*** process:

- Additional experimental or field studies for individual phases are used for verification. This process is limited by the availability of data, as mineralogical determinations based on XRD alone do not provide precise enough information to determine the chemical composition and degree of hydration. Errors can also be introduced when trying to derive thermodynamic properties from experiments performed in supersaturated conditions, if they did not reach equilibrium.
- Verification is also carried out by drawing predominance diagrams and comparing these to the literature.
- An alternative verification procedure is carried out by comparing experimental data from the literature with model predictions.

2.8 Kinetic data

ThermoChimie includes a compilation of kinetic parameters (see Marty et al. 2015) currently limited to relevant minerals present in clay rich rocks and cements.

Table 1. List of minerals for which kinetic data are available in ThermoChimie (from version 9 onwards).

albite	biotite	calcite	celestite	chlorite	CSH	dolomite
gibbsite	illite	kaolinite	portlandite	quartz	siderite	smectite

The kinetic data in ThermoChimie follows transition state theory (TST), as described by Lasaga (1981) (Eq. 4).

$$r_n = \pm k_n S_n \left| 1 \right. \qquad \text{Eq. 4}$$

Where **k_n** is the kinetic dissolution or precipitation rate constant, **S_n** is the reactive surface area, and **Ω** is the saturation ratio. The two parameters **θ** and **η** empirically describe the dependence of the reaction rate on the saturation ratio.

The kinetic parameters are compiled into individual sheets (one for each mineral phase). Rather than providing a full description of the dissolution/precipitation processes, these sheets provide the data required by geochemical codes. This allows the end user to model these kinetic processes instead of requiring an assumption of instantaneous equilibrium.

The selection process is summarised below (see Marty et al. 2015).

1. The *data selection* focuses on the pressure and temperature ranges considered in ThermoChimie. Three parameters are considered for the development of kinetic data:

- dependence on **pH**, with the selected data covering a pH range as large as possible;
- dependence on **temperature**, preferentially selecting data that also incorporate the effect of pH;
- dependence on the **saturation ratio**.

Data is preferenentially taken from stirred flow-through reactor experiments as these allow a good control of reaction conditions.

2. To ensure the internal *consistency* of the database, reaction rates are defined with respect to given reactions and equilibrium constants already present in the database. Kinetic rates also depend on the structural formula considered, therefore, the same structural formala is used for both kinetic and equilibrium reactions.

3. Although some data for the *reactive surface area* of each mineral is provided in the individual sheets this parameter is system specific. Therefore, it must be selected by the modeller when defining the geochemical/reactive transport system.

4. The selected data are written in accordance with the *formalism* implemented in the geochemical code ToughReact (Xu et al., 2011). This form is used as it can be easily transformed into the equations needed by other geochemical codes such as PhreeqC (Parkhurst and Appelo, 2013) or Crunch (Steefel, 2009).

5. The models are *compared* with data available from the literature. This approach allows assessment of uncertainties in the selected rates.

3. Uncertainties

When assessing the geochemical evolution of a repository, several phenomena (e.g. solubility, speciation, ion exchange, adsorption, mineral dissolution and precipitation, transport paths, etc) must be taken into account. Uncertainties associated with these phenomena may affect PA calculations (Ekberg and Emrén, 2001). One source of uncertainty is the thermodynamic data used to parameterise the model. Therefore, data included in ThermoChimie must, where possible, have associated uncertainties. The procedure for assigning uncertainty in ThermoChimie varies between data sources:

- Data obtained from dedicated experimental programmes,
- Data obtained from the open literature (original experimental sources or thermodynamic data compilations),
- Data derived from estimations,
- Data internally calculated.

Uncertainties in thermodynamic values should ideally cover the range within which the corresponding data can be reproduced with 95% probability (Wanner and Östhols 1999). However, in many cases implememtation of a complete statistical procedure for the selection of uncertainty is not possible due to the limited availability of data.

In all cases, the consistency and traceability requirements of ThermoChimie (see Guideline 2 and Guideline 4) also apply to the uncertainty data. A discussion of the possible sources of uncertainty and the appropriate quantification procedure must be reported together with the discussion on the thermodynamic data itself.

3.1 Uncertainties in data from dedicated experimental programs

Data obtained from experimental sources may have uncertainties due to both systematic and random errors. Systematic errors are introduced by inaccuracy inherent to the system (in either the observation or measurement process). These errors can be reduced and avoided by improving the accuracy of the experiment. However, all experiments are prone to unavoidable random error. Random errors are unpredictable and are scattered about the true value; these errors can be estimated and quantified.

The quantification of random errors requires close examination of all the possible sources of uncertainty and this kind of detailed study may require considerable effort. Nevertheless, several procedures can help to quantify the uncertainty introduced by random errors:

- A good estimation of the uncertainty can be made if the largest contribution to the total uncertainty is identified and quantified (EURACHEM, 2012). For example: in solubility experiments, uncertainty related to calibration of the balance used to weigh the solid could be of minor importance compared to the uncertainty related to the solid homogenisation procedure.

- Replicate measurements made under the same conditions are always advisable as they provide indications on the variability associated with the experimental procedure (Olofsson et al. 1981). These include, for example, heterogeneity of the samples, random errors in analytical determinations, uncertainty associated to volumetric and weight procedures.

- Comparison between results obtained from complementary/alternative techniques can also be used to provide an indication on the uncertainty associated with a particular method.

When data are obtained from original experimental sources in dedicated experimental programs, whereever possible, the uncertainty should be estimated by someone familiar with the experimental method (EURACHEM, 2012). The possible sources of uncertainty and their values must be reported with the data.

3.2 Uncertainties in data from open literature

The criteria used to assign uncertainty to data obtained from the open literature depends on the data source:

- When data are selected from one of the NEA TDB compilations, the uncertainty provided in the NEA review is used.

- When data are derived from compilations other than the NEA TDB, a review of the selection process and also of the original sources is conducted. This review provides information to assign the most appropriate uncertainty.

- When data are obtained from different experimental sources, the uncertainty range should include all reliable data reported in the literature.

- When data are obtained from a single experimental source, it is sometimes possible to provide an estimation of the uncertainty based on the original publication. If this is not possible (because the uncertainty is not provided, or because the uncertainty

assignment in the original work seems inadequate[6]) an appropriate value may be assigned based on similar species present in the database.

In all cases the procedure used to quantify uncertainty must be reported together with the thermodynamic data itself.

3.3 Uncertainties in estimated data

The uncertainty assigned to an estimated value can be determined by comparison with analogous systems for which experimental data are available. In order to do this, experimental data with similar characteristics to those of the estimated values are identified. Then, the same estimation approaches are applied to those comparable systems, and the observed deviations between the estimated and the experimental values are quantified. Those deviations provide a reasonable uncertainty for the estimated values.

3.4 Internally calculed values

For internally calculated values, an error propagation is applied in agreement with the NEA recommended procedures for the propagation of errors specified in the NEA TDB guidelines (Wanner and Östhols, 1999).

Using error propagation theory, the uncertainty of S, ΔS, can be derived from uncertainties in input parameters, ΔZ_i, as shown in Eq. 5.

In agreement with the NEA recommended procedures for the propagation of errors specified in the NEA TDB guidelines (Wanner and Östhols, 1999).

$$\Delta S = \sqrt{\left(\frac{\partial S}{\partial Z_1}\right)^2 \Delta Z_1{}^2 + \left(\frac{\partial S}{\partial Z_2}\right)^2 \Delta Z_2{}^2 + ... + \left(\frac{\partial S}{\partial Z_n}\right)^2 \Delta Z_n{}^2} \qquad \text{Eq. 5}$$

Internal calculation of thermodynamic parameters (and their associated uncertainties) have to be carried out by the XCheck tool. Further detail on this process is given in Guideline 2.

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[6] In some cases, uncertainty values reported in original works may seem small in comparison with the complexity of the system studied. This may indicate that the autor has not correctly identified the largest contribution to the total uncertainty.

4. Bibliography

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