TCIII-2019-04E

ThermoChimie

Technical report

Introduction to the ThermoChimie guidelines

E. Colàs, O. Riba, I. Campos, L. Duro and Grivé, M. (Amphos 21)

A.J. Fuller (Galson Sciences Ltd)

03 July 2019

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 introduces the ThermoChimie database and summarises the content of the guidelines.

ONDRAF/NIRAS

ANDRA

Radioactive Waste Management

TCIII-2019-04E

Introduction to the ThermoChimie guidelines

VERSION 2, APRIL 2019

Written by: Amphos 21 (Colàs, E., Riba, O., Campos, I., Duro, L., Grivé, M.)

Revised by: Galson Sciences Ltd (Fuller, A.J.)

Approved by: ThermoChimie steering committee: Andra (Madé, B.); RWM (Hibberd, R.); ONDRAF/NIRAS (Brassinnes, S.).

TCIII-2019-04E

DOCUMENT VERSIONS

Version	***Date***	***Comment***
2	*Jul. 2019*	*Full revision to support the release of v10a*
1	*Jul. 2015*	*First version uploaded to the ThermoChimie website*

Index

1. The ThermoChimie database

ThermoChimie (TC) is a thermodynamic database, first developed in 1996 by Andra, the French National Radioactive Waste Management Agency. In September 2014, Andra and the UK's Radioactive Waste Management (RWM) jointly established the TC Project to work collaboratively on development of the database. They were joined in April 2018 by ONDRAF/NIRAS, the Belgian Agency for Radioactive Waste and Enriched Fissile Materials.

ThermoChimie was born from the need for a reliable and comprehensive thermodynamic database for use in modelling the performance of Nuclear Waste Repositories, including the migration and retention behaviour of radionuclides in engineered and natural barriers. The database can be applied from neutral to strongly alkaline pH, low to high ionic strength and Eh within the stability fields of water. It is therefore suitable for use within the range of conditions expected in near-surface, sub-surface and deep geological repositories.

The database was created with a requirement for the data to be as comprehensive and accurate as possible, while maintaining internal consistency. It contains data for numerous radionuclides and chemotoxic elements as well as organic and inorganic complexants. It also includes data on the major solid components expected in a geological repository, including clays, bentonites, concretes, and their associated secondary minerals. This allows the database to be used for modelling a wide range of wastes and repository concepts, at different stages of their lifecycle. The database also contains information to model the effects of temperature (of particular importance in the near field).

ThermoChimie is being continuously developed, with addition of new data, both from active experimental programs and reliable literature.

The ThermoChimie database, while existing as a single entity, can be extracted into different formats for compatibility with several different geochemical codes and activity correction models. The extraction procedure is designed in such a way that whilst the language and formatting of the database changes between codes, the values within it remain the same. Therefore, calculations run using ThermoChimie should provide a consistent result, regardless of the geochemical codes used to perform them.

The ThermoChimie database is available to view and download from the project website: http://www.thermochimie-tdb.com/. A general description of the database can be found in Giffaut et al. (2014) while specific information about radionuclides, minerals and kinetic data can be found in Grivé et al. (2015), Blanc et al. (2015) and Marty et al. (2015) respectively.

1.1 Requirements of the database

The ThermoChimie database was primarily developed for modelling radioactive waste repositories to support Safety Assessment. To achieve this, it must provide a number of technical and operational capabilities:

- Determination of the speciation and solubility of radioelements and chemotoxic elements in aqueous solution.
- Assessment of the geochemical evolution of both the near- and far-fields of the repository, covering the stability of clay minerals, bentonite clays, and aluminosilicates.
- Assessment of cement degradation processes, accounting for the stability of a wide range of cementitious phases.
- Assessment of the evolution of metallic components present in the containers, liners, reinforced waste packages, etc. with special emphasis on iron/steel corrosion processes and formation of secondary phases.
- Assessment of the role of simple organic ligands and their impact on the mobilisation of radionuclides, including: a) organic ligands present in wastes; b) organic ligands formed by degradation of organic materials present among the wastes or in the engineered barriers; c) those organic ligands derived from the degradation of Natural Organic Matter (NOM) present in the Callovo-Oxfordian claystone.
- Application of the data under different disposal scenarios (waste and packaging types, host rocks, etc.)

ThermoChimie is built to fulfil the following main requirements:

- Consistency: The thermodynamic functions included in ThermoChimie must be internally consistent with agreement between the different thermodynamic functions, covering the whole chemical system. Further details about consistency can be found in Guideline 2.
- Exhaustivity: The database must contain all the required data to represent the expected behaviour of the systems for which it has been developed (nuclear waste repositories). Details about the data selection procedures are provided in Guideline 1.
- Traceability: Each thermodynamic parameter has to be identified with its original source, and the calculations used to obtain the data must also be traceable. The history of the values included in the database has to be verifiable, keeping an appropriate track of the changes made. Further details can be found in Guideline 4.
- Usability: Data values and database organisation must be fully compatible with a range of geochemical codes. Further details can be found in Guideline 2.

As the ThermoChimie database was explicitly designed for modelling nuclear waste repositories it is optimised for use within the range of conditions expected in those systems. Its use is therefore constrained within the following limits:

- pH ranging from 6 to 14.
- Eh within the stability fields of water (in the pH range of interest).
- T range of 15 to 80 °C.
- Ionic strength up to the limit of the SIT corrections.

1.2 Contents of the database

ThermoChimie contains an extended dataset of elements, ligands, solid phases and minerals that are essential for geochemical modelling and performance assessment of Nuclear Waste Repositories. Specifically, it includes:

- Thermodynamic data for modelling the speciation and solubility of a large number of stable (including toxic) elements and radionuclides. These are highlighted in Figure 1.
- A large dataset covering the stability of cement hydrates, clay minerals and other aluminosilicate phases, such as zeolites.
- Data describing the stability of key organic ligands (Table 1) and their complexation with stable elements and with radionuclides.
- A compilation of kinetic parameters describing the dissolution and precipitation of some minerals present in clay rich rocks and cements (Table 2).

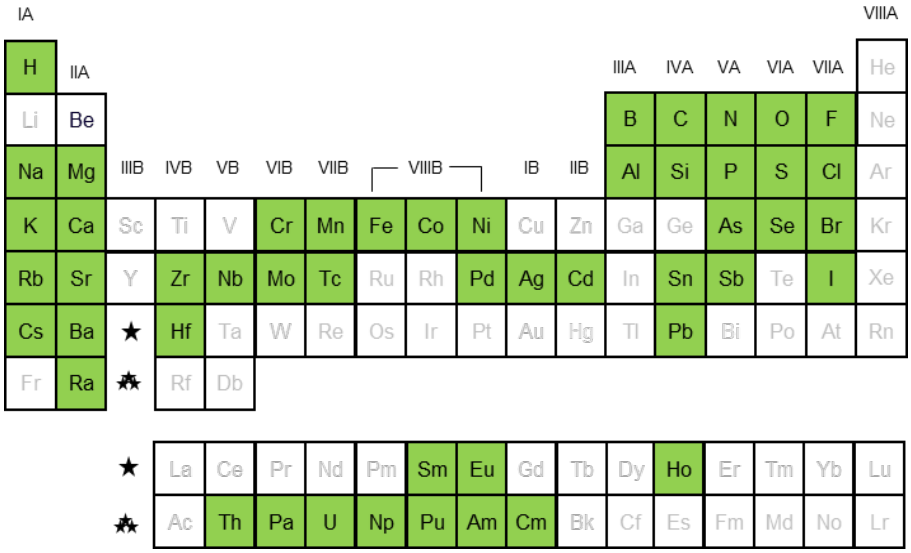


Figure 1. Periodic table highlighting the elements included in ThermoChimie (from version 9 onwards).

Table 1. Organic ligands included in ThermoChimie (from version 9b onwards).

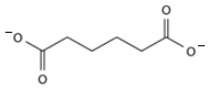
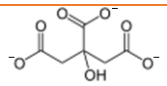
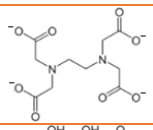
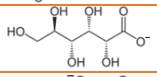
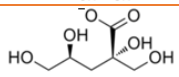
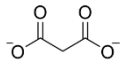
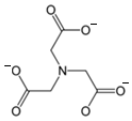
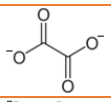
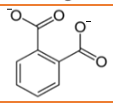
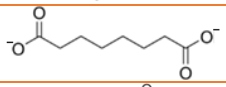
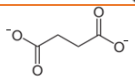
Species	Molecular formula	Structural formula
Acetate	$C_2H_3O_2^-$	
Adipate	$C_6H_8O_4^{2-}$	
Citrate	$C_6H_5O_7^{3-}$	
EDTA	$C_{10}H_{12}N_2O_8^-$	
Gluconate	$C_6H_{11}O_7^-$	
Isosaccharinate	$C_6H_{11}O_6^-$	
Malonate	$C_3H_2O_4^{2-}$	
NTA	$C_6H_6NO_6^{3-}$	
Oxalate	$C_2O_4^{2-}$	
Phthalate	$C_8H_4O_4^{2-}$	
Suberate	$C_8H_{12}O_4^{2-}$	
Succinate	$C_4H_4O_4^{2-}$	

Table 2. 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

1.2.1 Thermodynamic data

For each element in the database, a reference state and a basic component (master species) are defined.

The reference phases are identified by the fact that $\Delta_f\mathbf{G_m^0}$ and $\Delta_f\mathbf{H_m^0}$ are 0. Standard molar entropy values ($\mathbf{S_m^0}$) for reference phases are included in the database.

For each of the **basic components** ThermoChimie includes values for:

- $\Delta_f\mathbf{G_m^0}$ (KJ·mol^{-1}) at 25 °C: Standard molar Gibbs energy of formation.
- $\Delta_f\mathbf{H_m^0}$ (KJ·mol^{-1}) at 25 °C: Standard molar enthalpy of formation
- $\mathbf{S_m^0}$ (J·K^{-1}·mol^{-1}) at 25 °C: Standard molar entropy.
- **Ion interaction coefficients *ε(j, k)*** (Kg·mol^{-1}) for the interaction of the species with Na^+, Cl^-, ClO_4^- and/or NO_3^-, when available, at 25 °C.

The basic component is usually a free cation of the element of interest (e.g., Sr^{2+} for strontium), an oxycation (e.g., UO_2^{2+} for uranium) or an oxyanion (e.g., SeO_4^{2-} for selenium).

These basic components (together with e^- and H^+) are used as building blocks for the formation of all the remaining species and solid phases in the database.

In ThermoChimie, aqueous species are defined through chemical reactions of the basic components. The thermodynamic data included in the database for **aqueous species** are:

- $\mathbf{Log_{10}K^0}$ at 25 °C: Equilibrium constant of the reaction.
- $\Delta_r\mathbf{G_m^0}$ (KJ·mol^{-1}) at 25 °C: Molar Gibbs energy of reaction.
- $\Delta_r\mathbf{H_m^0}$ (KJ·mol^{-1}) at 25 °C: Molar enthalpy of reaction.
- $\Delta_r\mathbf{S_m^0}$ (J·K^{-1}·mol^{-1}) at 25 °C: Molar entropy of reaction.
- $\Delta_f\mathbf{G_m^0}$ (KJ·mol^{-1}) at 25 °C: Standard molar Gibbs energy of formation.
- $\Delta_f\mathbf{H_m^0}$ (KJ·mol^{-1}) at 25 °C: Standard enthalpy of formation.
- $\mathbf{S_m^0}$ (J·K^{-1}·mol^{-1}) at 25 °C: Standard molar entropy.
- $\mathbf{C^o_{p,m}}$ (J·K^{-1}·mol^{-1}): Standard molar heat capacity at constant pressure.
- **Ion interaction coefficients *ε(j, k)*** (Kg·mol^{-1}) for the interaction of the species with Na^+, Cl^-, ClO_4^- and/or NO_3^-, when available, at 25 °C.

For **solid compounds**, in addition to the variables for aqueous species (listed above) ThermoChimie also includes values, when known, for:

- $\mathbf{V^o_m}$ (cm^3·mol^{-1}): Molar volume.

All the values included in ThermoChimie are accompanied, when possible, with their associated uncertainties. All the data sources are also given, with full a bibliographic reference for each parameter.

1.2.2 Kinetic data

Although a compilation of kinetic parameters is included in ThermoChimie, this is currently limited to a number of mineral phases present in clay rich rocks and cements (see Table 2). The selected data are written to follow Transition State Theory (TST). The exact variables depend on the mineral, but in general the parameters $\mathbf{k_n}$ (the kinetic constant), **θ** and **η** (parameters describing the dependence between the reaction velocity and the saturation index) are provided.

1.3 Database formats

The full set of thermodynamic and kinetic data available for each species in ThermoChimie can be viewed on the project web page: http://www.thermochimie-tdb.com/.

To maximise its usability, ThermoChimie has also been extracted into data formats compatible with several common geochemical codes (see Table 3).

Table 3. Geochemical codes compatible with ThermoChimie.

Geochemical code	ThermoChimie version
PhreeqC	From TC version 8 onwards
Crunchflow	From TC version 8 onwards
ToughReact	From TC version 8 onwards
Chess	From TC version 8 onwards
Geochemist´s Workbench	From TC version 10a onwards
Spana	From TC version 10a onwards

Notes: PhreeqC: Parkhurst and Appelo (2013); Crunchflow: Steefel (2009); ToughReact: Xu et al. (2008); Chess: Van der Lee and De Windt (2002); Geochemist´s Workbench (Bethke and Yeakel, 2015); SPANA: Puigdomènech (2009).

Kinetic parameters are written with the formalisms implemented in ToughReact, but can be easily applied to other codes.

2. The ThermoChimie guidelines

In order to guarantee that the requirements of ThermoChimie (consistency, exhaustivity, traceability, and usability) are fulfilled, a number of procedures have to be clearly defined. These are outlined in a series of guidelines that govern the development of the database:

- **Guideline 1: Data selection and uncertainties.** This document describes how the data selection process must be carried out. This guideline guarantees consistency in the selection process between the different groups of experts involved in the development of ThermoChimie, while accounting for the differences between each dataset.
- **Guideline 2: Data integration and consistency.** This guideline describes the processes governing addition, elimination or modification of any value in ThermoChimie. These processes guarantee the consistency of the database.
- **Guideline 3: Validation exercises.** This document outlines the validation and verification tests that must be applied to data included in ThermoChimie. These tests must take into account the diversity of systems in which the database could be used.
- **Guideline 4: Data traceability.** This guideline describes the production of the documents that track the changes and updates in the database, and describes the different ThermoChimie versions and releases.
- **Guideline 5: Bibliographic reference recording process:** This document defines how the bibliographic references must be cited (style) and which reference management system is used to guarantee consistency in the bibliographic citations for all ThermoChimie developers.

These guidelines are available for all ThermoChimie developers and users. This ensures that the database is developed and maintained in such a way that all the ThermoChimie requirements are, and continue to be, fulfilled.

3. Bibliography

Bethke, C. M., Yeakel, S. 2016 The Geochemist's Workbench® Release 11: GWB Essentials Guide. Aqueous Solutions, LLC Champaign, Illinois.

Bethke, C. M., Yeakel, S. 2015. The Geochemist's Workbench: GWB Essentials Guide. Aqueous Solutions, LLC

Blanc, P., Vieillard, P., Gailhanou, H., Gaboreau, S., Marty, N., Claret, F., Madé, B., Giffaut, E. 2015. ThermoChimie database developments in the framework of cement/clay interactions. Applied Geochemistry 55, 95-107.

Giffaut, E., Grivé, M., Blanc, P., Vieillard, P., Colàs, E., Gailhanou, H., Gaboreau, S., Marty, N., Madé, B., Duro, L. 2014. Andra thermodynamic database for performance assessment: ThermoChimie. Applied Geochemistry, 49, 225-236.

Grivé, M., Duro, L., Colàs, E., Giffaut, E. 2015. Thermodynamic data selection applied to radionuclides and chemotoxic elements: An overview of the ThermoChimie-TDB. Applied Geochemistry 55, 85-94.

Marty, N. C., Claret, F., Lassin, A., Tremosa, J., Blanc, P., Madé, B., Giffaut, E., Cochepin, B., Tournassat, C. 2015. A database of dissolution and precipitation rates for clay-rocks minerals. Applied Geochemistry 55, 108–118.

Parkhurst, D.L., Appelo, C.A.J. 2013. Description of input and Examples for PHREEQC Version 3 — A Computer Program for Speciation, Batch-reaction, Onedimensional Transport, and Inverse Geochemical Calculations. U.S. Geological Survey Techniques and Methods, book 6, Chap. A43.

Puigdomènech, I. 2009. Medusa: Make equilibrium diagrams using sophisticated algorithms. Chemical equilibrium software. https://sites.google.com/site/chemdiagr/home.

Steefel C.I., 2009. Software for Modeling Multicomponent Reactive Flow and Transport. Rapport technique Lawrence Berkeley National Laboratory.

Van der Lee, J., De Windt, L. 2002. CHESS Tutorial and Cookbook. Updated for Version 3.0. Users Manual Nr. LHM/RD/02/13, Ecole des Mines de Paris, Fontainebleau, France.

Xu, T., Sonnenthal, E., Spycher, N., Pruess, K. 2008. TOUGHREACT user's guide: a simulation program for non-isothermal multiphase reactive geochemical transport in variably saturated geologic media, V1.2.1. Lawrence Berkeley National Laboratory.