

Thermodynamic database: ThermoChimie
Database version: 12a (release version, from Data Source - Json file)
Database date: 22/08/2023
Software used for extraction: XCheck Tool v5.2.0

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ThermoChimie extracted files: supporting documentation

This document provides supporting information about the extracted database files for ThermoChimie.

The ThermoChimie database, while existing as a single entity, can be extracted into different formats for compatibility with several different geochemical codes. The language and formatting of the database are changed for each code, while the values remain the same. Calculations run using the database should then provide a consistent result, regardless of the geochemical model used to perform them.

There are currently several separate files available for ThermoChimie, allowing its use with six different geochemical codes (PhreeqC, ToughReact, Crunchflow, Chess, Geochemist's Workbench, Spana and Pflotran). Details of these extracted files are given in Table 1, and the succeeding text.

Table 1: Summary of extracted files for ThermoChimie using **XCheck Tool** v5.1.

| Extracted file format | Last code version ^{a)} | Ionic Strength Correction | Redox Pivot ^{b)} | File name | Last TC version revised ^{c)} |
|-----------------------|---------------------------------|---------------------------|---------------------------|--|---------------------------------------|
| PhreeqC | 3.7.0 | SIT | e ⁻ | PHREEQC_SIT_e-_ThermoChimie10d_ date.dat | 12a |
| | | Davies | e ⁻ | PHREEQC_Davies_e-_ThermoChimie10d_ date.dat | 12a |
| | | Extended Debye-Huckel | e ⁻ | PHREEQC_eDH_e-_ThermoChimievs_ date.dat | 12a |
| ToughReact | 1.2 | Helgeson-Kirkham-Flowers | O ₂ (aq) | THOUGHREACT_O2_ThermoChimievs_ date.dat | 10b |
| Crunchflow | 1.0 | Extended Debye-Huckel | O ₂ (aq) | CRUNCH_O2_ThermoChimievs_ date.dbs | 10b |
| Chess | 4.0.3 | d) | O ₂ (aq) | CHESS_O2_ThermoChimievs_ date.tdb | 9 |
| GWB | 16.0 | B-dot | O ₂ (aq) | GWB_eDH_O2_ThermoChimievs_ date.tdat | 12a |
| | | | e ⁻ | GWB_eDH_e-_ThermoChimievs_ date.tdat | 12a |
| | | SIT | O ₂ (aq) | GWB_SIT_O2_ThermoChimievs_ date.tdat | 12a |
| | | | e ⁻ | GWB_SIT_e-_ThermoChimievs_ date.tdat | 12a |
| Spana | 2020-June-08 | Davies | e ⁻ | SPANNA_Davies_e-_ThermoChimievs_ date.txt SPANNA_Davies_e-_ThermoChimievs_ date.elt | 11a |
| | | | e ⁻ | SPANNA_SIT_e-_ThermoChimievs_ date.txt SPANNA_SIT_e-_ThermoChimievs_ date.elt SIT-coefficients.dta | 11a |
| | | SIT | e ⁻ | | |
| Pflotran | 2 | B-dot | O ₂ (aq) | PFLOTRAN_O2_ThermoChimievs_ date.dat | 11a |

a) Last version of the geochemical code used for the verification

b) Indicates if redox reactions are written as a function of electrons or as a function of O₂(aq) in the database. Notice that only PhreeqC and GWB can work with both approaches; in the other geochemical software, redox reactions must be written as a function of O₂(aq).

c) Last ThermoChimie version that has been fully verified for its use with the geochemical code

d) Chess uses different models for ionic strength corrections (see text).

PhreeqC-format files: There are three different PhreeqC-format files available.

- SIT, Davies, or extended Debye-Huckel approaches can be used in PhreeqC for ionic strength corrections, with separate database files required for each approach.
 - ThermoChimie gives priority to SIT (Specific Ion Interaction Theory, see Grenthe et al. 2013) over other ionic strength corrections. However, the PhreeqC-format ThermoChimie files are also available with other correction approaches: Davies and extended Debye-Hückel (see Grenthe et al. 2013 and Parkhurst and Appelo 2013).
 - The Debye-Hückel parameter (a_i^0) for aqueous inorganic species is calculated as a function of the charge z of the species; $a_i^0=0.45z^2+0.2541z+3.41$. In the case of organic ligands, $a_i^0=5.5$.
- Redox equations in PhreeqC-format files can be written in terms of two different redox pivots: electrons (e-) and oxygen (O₂(aq)). Currently, ThermoChimie is extracted using electrons as the redox pivot.
- When reaction enthalpy values are available in ThermoChimie, the Van't Hoff approach has been used to derive the analytical expression for the log K dependency with temperature.
- Missing molar volumes for solid species are set to a default value of 0. In those cases, the keyword "-Vm" is commented with the hash symbol ("#-Vm 0") so this information is not read by the PhreeqC code.

ToughReact-format files: There is one ToughReact-format file available.

- ToughReact uses the Helgeson-Kirkham-Flowers approach for ionic strength correction.
 - The effective ionic radii ($r_{e,i}$) for aqueous species used in the Helgeson-Kirkham-Flowers are calculated as a function of the charge of the species (see Xu et al. 2008).
- Redox equations are written in terms of oxygen (O₂(aq)).
- When reaction enthalpy values are available in ThermoChimie, the Van't Hoff approach has been used to derive the array of log K values at different temperatures.
- Missing molar volumes for solid species are set to a default value of 500, which is the usual default value for this code.

Crunchflow-format files: There is one Crunchflow-format file available.

- Crunchflow uses the extended Debye-Huckel approach for ionic strength correction.
 - The Debye-Hückel parameter (a_i^0) for inorganic aqueous species is calculated as a function of the charge z of the species; $a_i^0=0.45z^2+0.2541z+3.41$. In the case of organic ligands, $a_i^0=5.5$.
- Redox equations are written in terms of oxygen (O₂(aq)).
- When reaction enthalpy values are available in ThermoChimie, the Van't Hoff approach has been used to derive the array of Log K values at different temperatures in the extracted file. When the reaction enthalpy is not available, Log K values at

temperatures, other than 25°C, are written as “500” in the array (“500” is the default value used in Crunchflow for “null” values).

- Missing molar volumes for solid species are set to a default value of 500, which is the default value used in this code for “null” values.
- For all minerals, the kinetic database entries have been set to default values:
 - type = tst ; rate(25C) = -3.00 ; activation = 0.0 (kcal / mole)

Chess-format files: There is one Chess-format file available.

- Chess uses different approaches to ionic strength corrections. The information needed for these corrections is not provided in the database but in the geochemical software itself. Thus, only one Chess-format file is available on the web page.
 - The ThermoChimie extracted file in the Chess format has only been verified for use with the Davies or B-dot ionic strength correction approaches.
 - The Debye-Hückel parameter (a_i^0) for aqueous inorganic species is calculated as a function of the charge z of the species; $a_i^0=0.45z^2+0.2541z+3.41$. In the case of organic ligands, $a_i^0=5.5$.
- Redox equations are written in terms of oxygen ($O_2(aq)$).
- When reaction enthalpy values are available in ThermoChimie, the Van’t Hoff approach has been used to derive the array of log K values at different temperatures in the extracted file.
- Missing molar volumes for solid species are set to a default value of 1000.

GWB-format files: There are two Geochemist’s Workbench-format files available.

- GWB can use two methods for ionic strength corrections; the “B-dot” equation, which is an extended form of the Debye-Hückel equation, and SIT. However, the ThermoChimie database can only be used in GWB with the “B-dot” equation.
 - The Debye-Hückel parameter (a_i^0) for aqueous inorganic species, is calculated as a function of the charge z of the species; $a_i^0=0.45z^2+0.2541z+3.41$. In the case of organic ligands, $a_i^0=5.5$.
 - ThermoChimie gives priority to SIT (Specific Ion Interaction Theory, see Grenthe et al. 2013) over other ionic strength corrections.
- Redox equations in the latest versions of GWB files can be written in terms of two different redox pivots: electrons (e^-) and oxygen ($O_2(aq)$). The choice of approach, however, can be made independently of the redox pivot used in the database, and no differences in the results of the calculations should be observed.
- When reaction enthalpy values are available in ThermoChimie, the Van’t Hoff approach has been used to derive the array of log K values at different temperatures.
- Missing molar volumes for solid species are set to a default value of 0.

SPANA-format files: There are different SPANA-MEDUSA format files available, in agreement with the different types of files needed by SPANA program:

- Database file (Reactions.db): Where reactions, $\log K^0$ values and enthalpy of reaction are included. This file has the extension “.txt”
- Elements file (equivalent to the Reactions.elb): Where the elements are related with their respective master and secondary species. This file has the extension “.elt”.
- Epsilon file (SIT-coefficients.dta): This file contains specific ion interaction parameters (ϵ) needed for the SIT equation This file has the extension “.dta”.
- SPANA can use three different approaches for ionic strength corrections; the Davies approach, the SIT approach and the HKF approach. The ThermoChimie database has been extracted for its use in SPANA with the Davies and the SIT approaches.
 - For the Davies approach, two files are available: the database file and the elements file (no epsilon file is needed).
 - For the SIT approach, three files are available: the database file, the elements file and the epsilon file (SIT-coefficients.dta).
- Redox equations are written in terms of electrons (e^-).
- When reaction enthalpy values are available in ThermoChimie, they have been extracted to the SPANA-format files. The Van't Hoff approach will be used by SPANA to calculate $\log K$ variations with temperature.

Pflotran-format files: There is one Pflotran format file available

- Pflotran uses the “B-dot” equation, which is an extended form of the Debye-Hückel equation, for ionic strength correction.
 - The Debye-Hückel parameter (a_i^0) for inorganic aqueous species is calculated as a function of the charge z of the species; $a_i^0=0.45z^2+0.2541z+3.41$. In the case of organic ligands, $a_i^0=5.5$.
- Redox equations are written in terms of oxygen ($O_2(aq)$).
- When reaction enthalpy values are available in ThermoChimie, the Van't Hoff approach has been used to derive the array of $\log K$ values at different temperatures.
- Missing molar volumes for solid species are set to a default value of 500.

Organic species and some inorganic ligands have special names in the ThermoChimie database. These names have been chosen to fulfil specific nomenclature requirements (for example, limitation of the number of characters, use of capital letters, etc) in each geochemical code. *Table 2* provides a summary of these names, their corresponding molecular and structural formula, and details on specific nomenclature in geochemical codes with specific requirements (i.e. PhreeqC and GWB).

Table 2: Summary of organic compounds files for ThermoChimie available

| Species | Molecular formula | Name in the extracted files | element field (PhreeqC format) | Chemical symbol (GWB format) | Structural formula |
|--------------------|------------------------|-----------------------------|--------------------------------|------------------------------|--------------------|
| Acetate | $C_2H_3O_2^-$ | Acetate- | Acetate | Ae | |
| Adipate | $C_6H_8O_4^{2-}$ | Adipate-2 | Adipate | Ad | |
| Citrate | $C_6H_5O_7^{3-}$ | Cit-3 | Cit | Ci | |
| EDTA ^{a)} | $C_{10}H_{12}N_2O_8^-$ | Edta-4 | Edta | Ed | |
| Gluconate | $C_6H_{11}O_7^-$ | HGlu- | Glu | Gl | |
| Isosaccharinate | $C_6H_{11}O_6^-$ | Hlsa- | Isa | Is | |
| Malonate | $C_3H_2O_4^{2-}$ | Malonate-2 | Malonate | Ma | |
| NTA ^{b)} | $C_6H_6NO_6^{3-}$ | Nta-3 | Nta | Nt | |
| Oxalate | $C_2O_4^{2-}$ | Ox-2 | Ox | Ox | |
| Phthalate | $C_8H_4O_4^{2-}$ | Phthalat-2 | Phtalat | Ph | |
| Pyrophosphate | $P_2O_7^{4-}$ | Pyrophos-4 | Pyrophos | Py | |
| Thiocyanate | SCN^- | Scn- | Scn | Ty | $S-C\equiv N$ |
| Suberate | $C_8H_{12}O_4^{2-}$ | Suberate-2 | Suberate | Su | |
| Succinate | $C_4H_4O_4^{2-}$ | Succinat-2 | Succinat | St | |
| Cyanide | CN^- | Cn- | Cn | Cn | $C\equiv N^-$ |

a) Ethylenediaminetetraacetate

b) Nitriloacetate

Additional information regarding use of the extracted data can be found in the ThermoChimie guidelines (available on the web page) and in Giffaut et al. (2014) and Grivé et al. (2015).

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