

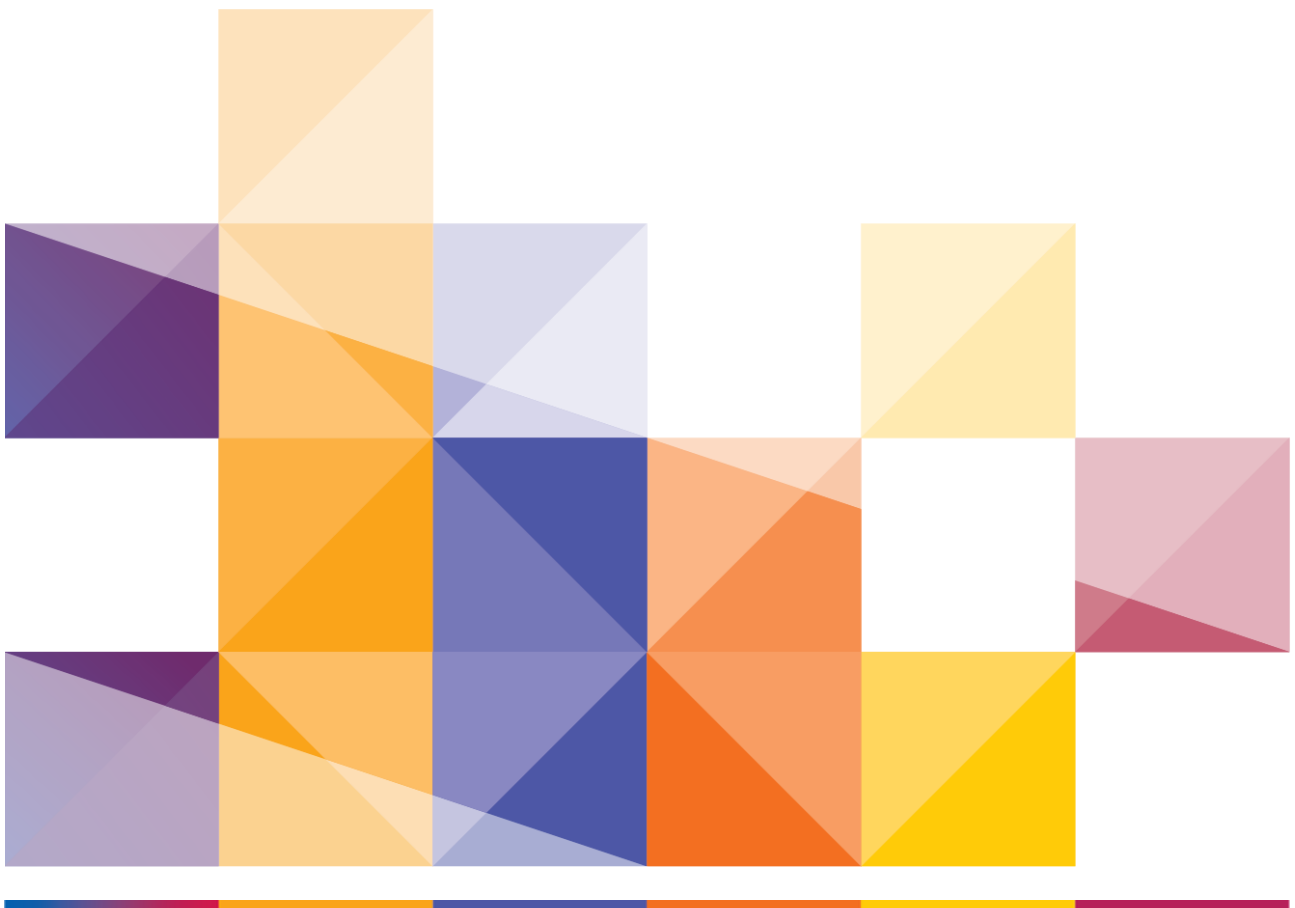
**ThermoChimie**

Technical report

# ThermoChimie guideline 2: Data integration and consistency

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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 5M, 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 is the second guideline for the ThermoChimie database. It details how the consistency of the database is maintained and how values within it are added, removed, or modified. This document also provides a template for data selection, which should be completed before any new values are added to the database.



# **ThermoChimie guideline 2: Data integration and consistency**

## **VERSION 3, APRIL 2022**

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## 1. Introduction

One of the main requirements of the ThermoChimie database is its consistency. The values within the database must be internally consistent and the model results it produces must be consistent and reproducible. To support this requirement, this second guideline describes processes for amending, eliminating, or modifying any value in the ThermoChimie database, while maintaining the database's consistency.

This document is structured as shown below:

- Section 2 briefly presents detail on the necessary requirements to ensure the consistency of a thermodynamic database.
- Section 3 summarises the processes that must be followed to maintain ThermoChimie's consistency when adding, removing or modifying values within the database. This section also describes the structure of the database and its associated tools (XCheck© and TCEExtract©).
- Appendix A contains a template to support the selection of new data.
- Appendix B contains a summary of the equations applied when performing internal calculations, following the standard calculation routes.

## 2. Consistency

The overall consistency of a thermodynamic database depends on its:

- Consistency with the fundamental laws of thermodynamics.
- Consistency with auxiliary data.
- Consistency within a chemical system.
- Consistency between estimated and experimental data.
- Consistency in data correction procedures.

Maintaining the consistency of a database also requires a detailed understanding of a large amount of primary information (Wanner, 1991), upon which the database is built.

This section provides a more detailed description of these different aspects, which together govern the overall consistency of ThermoChimie.

### 2.1 Consistency with the fundamental laws of thermodynamics

The first requirement of the ThermoChimie database is that it remain consistent with the fundamental laws of thermodynamics. All of the speciation reactions modelled by the database and all of the parameters within it rely on the thermodynamic values of Gibbs energy, enthalpy

and entropy. These values are closely related and when values have been selected for two of these three variables, the rest of the data must be internally calculated using Eq. 1 and Eq. 2.

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

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

Where

- $\Delta_f \mathbf{G}_m^0$  is the standard molar Gibbs energy of formation from the elements in their reference state ( $\text{J}\cdot\text{mol}^{-1}$ ),
- $\Delta_f \mathbf{H}_m^0$  is the standard molar enthalpy of formation from the elements in their reference state ( $\text{J}\cdot\text{mol}^{-1}$ ),
- $\mathbf{S}_m^0$  is the standard molar entropy ( $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ),
- $z$  is the charge of the species,
- $\nu$  is the stoichiometric coefficient of the elements in the formation reaction, and
- $\Delta_r \mathbf{G}_m^0$  is the molar Gibbs energy of reaction ( $\text{J}\cdot\text{mol}^{-1}$ ),
- $\Delta_r \mathbf{H}_m^0$  is the molar enthalpy of reaction ( $\text{J}\cdot\text{mol}^{-1}$ ), and
- $\Delta_r \mathbf{S}_m^0$  is the molar entropy of reaction ( $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ).

To ensure that ThermoChimie remains consistent with these basic principles, all of the parameters used in the database (where not directly input) are calculated using the appropriate equations following standard calculation routes (see appendix B). These equations are integrated into the XCheck©, one of the tools used to maintain the ThermoChimie database (see section 3.2).

## 2.2 Consistency with auxiliary data.

The reference states of elements and master species within the database are termed “auxiliary data”. These reference states are defined as the stable form of the element at ambient temperature (298.15 K) and at standard pressure (1 bar); for example, U(cr) is the reference state for uranium. By definition, the Gibbs energy of formation and the enthalpy of formation of an element in its reference state is zero.

The master species are the building blocks of the formation reactions for product species, either aqueous, solid or gas. There must be at least one master species for each element included in the database, this is the primary master species. For some elements, secondary master species (related to the primary master species by redox reactions) may also be included. This is the case of uranium (U);  $\text{UO}_2^{2+}$  (U(+VI)) is the primary master species in

ThermoChimie, and secondary master species defined in the database are  $U^{3+}$  (U(+III)),  $U^{4+}$  (U(+IV)), and  $UO_2^+$  (U(+V)).

As described in *Guideline 1: Data selection and uncertainties*, ThermoChimie relies on the CODATA recommendations (Cox et al. 1989) for reference states of the elements and for the primary master species where possible. Whenever the CODATA values or the auxiliary data published in the NEA TDB project are modified, these changes are incorporated into ThermoChimie. In all cases, data are reviewed and verified during the selection process, following the data selection criteria applied to all chemical species in the database.

In some specific cases, thermodynamic data selected for the master species in ThermoChimie may differ from the values recommended by CODATA. In these cases, the change must be fully justified and any practical consequences for the consistency of the database must be assessed. For example, the master species for Al and Si in ThermoChimie differ from those in CODATA and an exhaustive explanation for this is provided in Blanc et al. (2006).

The auxiliary data used to calculate the thermodynamic values must be consistent with the auxiliary data included in ThermoChimie. In order to maintain the consistency of the database, the XCheck© tool (section 3.2) uses the values included in ThermoChimie for both master species and reference states when performing calculations.

## 2.3 Consistency within a chemical system

When using a geochemical model to reproduce experimental data, it is often possible to arrive at the correct value via multiple calculation routes, or with different starting parameters (Wanner, 1991).

In order to maintain the consistency of the database, it is therefore necessary to consider the chemical systems already included in ThermoChimie for the interpretation of the experimental data. When selecting new data for addition to ThermoChimie (see *Guideline 1: Data selection and uncertainties*) care is taken to ensure it remains consistent with the rest of the chemical system.

For example, the selection of data for organic complexation with radionuclides needs to take into account the protonation constants of organic ligands when evaluating the aqueous speciation of the system. These protonation constants must be consistent with the selected hydrolysis data for the organic complexes included in ThermoChimie, as described in *Guideline 1: Data selection and uncertainties*.

As another example, when selecting cementitious phases, the proposed values are used to draw predominance diagrams of the defined chemical subsystems before any modification is made to the database. These phase relationships are compared with the observations gathered from the literature to ensure they are consistent.



When performing kinetic calculations, the equilibrium constant term used in the rate equation must be consistent with the data included in ThermoChimie.

## 2.4 Consistency between estimated and experimental data.

As far as possible, values provided in the ThermoChimie database are based on original experimental data (see *Guideline 1: Data selection and uncertainties*). However, when reliable experimental data are not available, a number of methods can be used to estimate the missing values.

One of the most commonly used estimation methods relies on Linear Free-Energy Relationships (LFER). These LFERs can be used to establish a linear relationship between known, “well established” stability constants with different parameters, such as the charge density ( $z^2/r_i$ ), the reciprocal of the ionic radii ( $1/r_i$ ) or the Gibbs energy of formation ( $\Delta_f G^\circ$ ) of the aqueous metal cation. After the relationship is established, the known parameter ( $z^2/r_i$ ,  $1/r_i$  or  $\Delta_f G^\circ$ ) of the species can be used to calculate (estimate) the unknown stability constant.

LFER procedures are used in different ways within the ThermoChimie database. Where insufficient experimental data are available, LFERs are commonly used to estimate missing stability constants along a chemical series. To perform these calculations, “well established” stability constants (which must be taken from the ThermoChimie database in order to maintain consistency) are used to derive the LFER function. Therefore, if the “well established” stability data in ThermoChimie are changed, a new LFER must be derived, and all dependant data must be recalculated accordingly.

Furthermore, when different stability constants from a common chemical series are included in ThermoChimie, LFER correlations provide a good indication of the quality of the selected data and the level of consistency between the different values in the database. The LFER correlations also provide a good mechanism to verify the database contents within a particular chemical series.

## 2.5 Consistency in the data correction procedures.

The values in ThermoChimie are provided at standard chemical conditions (zero ionic strength) and reference temperature (25°C). However, it is not generally possible to perform experimental studies at these standard state conditions (i.e., at zero ionic strength). When equilibrium constants are determined experimentally, measurements are generally taken at constant (though non-zero) ionic strength (Grenthe et al. 2013). In some cases, the measurements may also be made at temperatures other than 25°C. Therefore, it is necessary to correct the experimental values to the standard state conditions before including them in the database.

### 2.5.1 Data correction to zero ionic strength

Ionic strength (I) is calculated as shown in Eq. 3, where  $m_i$  is the molality of each ion present in solution.

$$I = \frac{1}{2} \sum_i m_i z_i^2 \quad \text{Eq. 3}$$

When performing modelling using the ThermoChimie database, it is recommended that ionic strength corrections are made using the Specific Ion Interaction Theory (SIT). Therefore, in order to guarantee the consistency of the database, this same approach should be used to correct experimental values (obtained at  $I \neq 0$ ) to infinite dilution, ( $I=0$ ) when adding them to ThermoChimie.

The SIT equation (Eq. 4) calculates the activity coefficient  $\gamma_i$  of an ion ( $i$ ) of charge  $z_i$  in a solution of ionic strength I, where A and B are empirical constants for a given temperature,  $a_i$  is the effective ion diameter,  $\varepsilon(i,k,I_m)$  is the ionic interaction coefficient ( $\text{kg}\cdot\text{mol}^{-1}$ ), and  $m_k$  is the molality of the different ions ( $k$ ) present in the solution. The procedure for selecting these ion interaction coefficients  $\varepsilon(i,j,I_m)$  is described in *Guideline 1: Data selection and uncertainties*.

$$\log(\gamma_i) = -z_i^2 \left( \frac{A\sqrt{I_m}}{1 + Ba_i\sqrt{I_m}} \right) + \sum_k \varepsilon(i,k,I_m)m_k \quad \text{Eq. 4}$$

The SIT approach takes into account short-range non-electrostatic interactions by adding terms to the Debye-Hückel expression (Eq. 5). Thus, when it is not possible to use SIT for the correction (due to limited amount of data at different ionic strengths and/or the lack of appropriate ion interaction coefficients) the Debye-Hückel approach can be used as an alternative.

$$\log(\gamma_i) = -z_i^2 \left( \frac{A\sqrt{I_m}}{1 + Ba_i\sqrt{I_m}} \right) \quad \text{Eq. 5}$$

### 2.5.2 Data correction to the standard temperature

ThermoChimie contains a wide range of data, including thermodynamic values for major elements, radioactive and toxic elements, organic ligands, cementitious hydrates, clay minerals, zeolites, and kinetic data for some minerals. As some of this data is measured at values other than 25°C, to maintain the consistency of the database, these new values must

be corrected to this standard temperature. The process for doing this is dependent on the type of data used, and is described in more detail in *Guideline 1: Data selection and uncertainties*.

The equilibrium constants can be extrapolated to standard temperature using various modifications of the so-called second- and third-law methods. The application of these methods requires knowledge of the reaction enthalpy, entropy and/or heat capacity data.

The temperature dependence of the equilibrium constant can be written as a function of the enthalpy of reaction,  $\Delta_r H_m^\circ$  and the heat capacity of reaction,  $\Delta_r C_{p,m}^\circ$  (Eq. 6):

$$\log_{10} K^\circ(T) = \log_{10} K^\circ(T_0) - \frac{\Delta_r H_m^\circ(T_0)}{R \ln(10)} \left( \frac{1}{T} - \frac{1}{T_0} \right) - \frac{1}{RT \ln(10)} \int_{T_0}^T \Delta_r C_{p,m}^\circ dT + \frac{1}{R \ln(10)} \int_{T_0}^T \frac{\Delta_r C_{p,m}^\circ}{T} dT, \quad \text{Eq. 6}$$

When the change in the heat capacity of reaction with temperature is not known, it can be assumed to remain constant, and the constant heat capacity equation (Eq. 7) can be used.

$$\log_{10} K^\circ(T) = \log_{10} K^\circ(T_0) + \frac{\Delta_r H_m^\circ(T_0)}{R \ln(10)} \left( \frac{1}{T_0} - \frac{1}{T} \right) + \frac{\Delta_r C_{p,m}^\circ}{R \ln(10)} [(T_0/T) - 1 + \ln(T/T_0)] \quad \text{Eq. 7}$$

Unfortunately, experimentally measured  $C_{p,m}$  data are not available for many relevant aqueous species and solid phases present in ThermoChimie. Therefore, the simplest assumption to be made is that the heat capacity of reaction is zero at all temperatures. In that case, the Van't Hoff expression is obtained (Eq. 8).

$$\log_{10} K^\circ(T) = \log_{10} K^\circ(T_0) + \frac{\Delta_r H_m^\circ(T_0)}{R \ln(10)} \left( \frac{1}{T_0} - \frac{1}{T} \right) \quad \text{Eq. 8}$$

Wherever enthalpies of reaction (and in some cases  $C_{p,m}$  values) are included in ThermoChimie, temperature correction calculations can be performed in a consistent way. However, given limitations in the available data, presently temperature corrections are usually performed with the Van't Hoff approach.

### 3. Data integration procedure

Whenever new data is added to, modified in or deleted from the database, this must be done in a consistent and traceable manner. In order to achieve this, ThermoChimie is stored as a number of different types of files, supported by a set of tailored programs.

The database administrators must follow a specific procedure, when updating the database (data integration). Details on these procedures are provided in sections 3.1 and 3.2 and summarised in Figure 1.

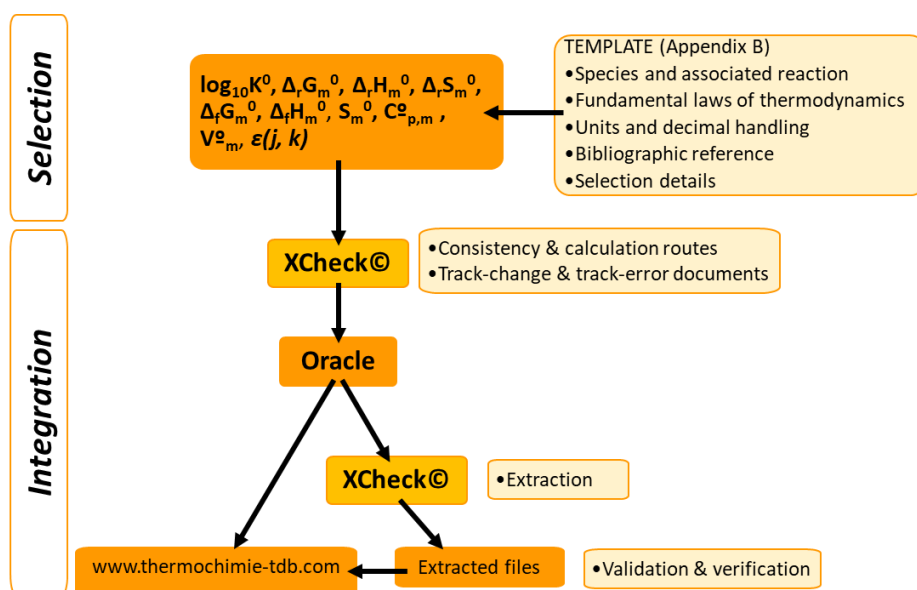


Figure 1. Summary of the ThermoChimie data integration procedure.

#### 3.1 Data requirements

The ThermoChimie database includes information on reference states, aqueous species (comprising primary master species, secondary master species, and product species), solids and gases. Product species are defined by reacting master species, with the appropriate stoichiometric coefficients. Data for product species may include all or some of the following:  $\text{Log}_{10}K^0, \Delta_r G_m^0, \Delta_r H_m^0, \Delta_r S_m^0, \Delta_f G_m^0, \Delta_f H_m^0, S_m^0, \epsilon(j, k), C_{p,m}^0$  and  $V_m^0$ . Further details are provided in *Guideline 1: Data selection and uncertainties*.

When adding new values to the database both the values themselves and a description of the processes leading to their selection must be sent to the database administrators. A template is provided in Appendix A to aid in this task. The following information must be provided:

- Information about the person performing the selection and the date.

- Details of the species being considered and its formation reaction.
- As the thermodynamic quantities Gibbs energy, enthalpy and entropy are closely related, when the value of two (or more) of these variables is edited, the rest of parameters must be internally (re)calculated using the calculation routes and equations shown in Appendix B. The (re)calculated values must then also be provided for inclusion in the database.
- Gibbs energy and enthalpy values must be provided in  $\text{kJ}\cdot\text{mol}^{-1}$ , entropy and heat capacity values in  $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , and molar volumes in  $\text{cm}^3\cdot\text{mol}^{-1}$
- Whenever possible, the values should be accompanied by their associated uncertainties (see *Guideline 1: Data selection and uncertainties*).
- Values for  $\Delta_r\mathbf{G}_m^0$ ,  $\Delta_r\mathbf{H}_m^0$ ,  $\Delta_r\mathbf{S}_m^0$ ,  $\Delta_f\mathbf{G}_m^0$ ,  $\Delta_f\mathbf{H}_m^0$  and  $\mathbf{S}_m^0$  must be provided with three decimal places while  $\log_{10}\mathbf{K}^0$ ,  $\boldsymbol{\varepsilon}(j, k)$ ,  $\mathbf{C}_{p,m}^0$  and  $\mathbf{V}_m^0$  data are provided with two decimal places. This is a database standard and should be adhered to regardless of the level of accuracy provided in the source data. Where the source data is less precise, zero can be added as a placeholder, while any extra precision (beyond three, or two decimal places) can be omitted.
- Despite these requirements, when performing the internal calculations and operations, these must use the most precise values available, in order to avoid loss of information. Only the final results should be rounded. Values should be rounded following the rules recommended by the NEA TDB guidelines (Wanner and Östhols, 1999):
  - When the digit following the last digit to be rounded is lower than 5, the last digit remains unchanged.
  - When the digit following the last digit to be rounded is 5 or higher, the last digit retained is increased by 1.
- To provide traceability, all the values selected in ThermoChimie must be accompanied by a bibliographic reference to its source.
  - If the data have been directly taken from a public<sup>1</sup> reference, without further data treatment, the complete bibliographic record of the original publication must be reported.
  - If data from the original reference have been recalculated or treated, it is necessary to provide the complete bibliographic record of the original publication and a brief description of the calculations performed to obtain the final value that will be included in the database.

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<sup>1</sup> Articles, Ph.D. technical reports or other technical documents available to the scientific community.

- If the data have been taken from a non-public<sup>2</sup> reference, it is necessary to provide the complete bibliographic citation of the original publication, a brief description of this publication and a brief description of the calculations performed to obtain the selected value.

### 3.2 Integration procedure (database administrators only)

*Note: This section specifically relates to ThermoChimie version 10d, procedures for earlier versions may differ.*

Once the information on selected data has been sent to database administrators, a data integration procedure is carried out:

- The bibliographic citation, the description of the publication and the description of the calculations performed are reviewed, to verify that enough detail is provided to guarantee traceability and to ensure that data selection requirements have been fulfilled.
- The internal calculations are verified and, if necessary, modified using the XCheck© tool. This tool is a VB.net based programme specifically developed to automate the verification procedure, avoiding “man-made” typos or incorrect assumptions, and ensuring consistency, both with the fundamental laws of thermodynamics and with auxiliary data (sections 2.1 and 2.2). The XCheck© tool is able to:
  - Automatically perform internal calculations for thermodynamic data, following the calculation routes detailed in Appendix B.
  - Automatically re-calculate the whole database when thermodynamic data for a master species or a reference state is changed.
  - Automatically modify the original ThermoChimie Access database.
  - Keep an automatic record of the changes and modifications.
- All ThermoChimie data are stored in a json file. These files store simple data structures and objects in JavaScript Object Notation (JSON) format, which is widely used for data storage and maintaining a reliable and consistent data structure.
- If the data passes the checks listed above, it is included, modified, or eliminated from the ThermoChimie json file using the XCheck© tool. In addition to the json file, the information is also stored in an Oracle database. Once a major update to the database is completed, intermediate or internal updates are removed from the Oracle database to ensure only the released versions are present.

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<sup>2</sup> Any document that is restricted to a limited number of readers and is not available to the whole scientific community.

- Track-changes documents are generated that describe the evolution of the database and highlight any differences between the versions of ThermoChimie (see *Guideline 4: Data traceability*).
- The TCExtract© tool is used to extract information contained in the ThermoChimie database into the different formats required for use with the various geochemical codes (e.g. PhreeqC, Crunch, ToughReact, CHESS, Geochemist Workbench, Spana, or Pflotran). This maximises the usability of the database.
- The data is then validated and verified following the procedures outlined in *Guideline 3: Validation and verification*. These procedures ensure that the selected thermodynamic data are accurate and consistent.

### 3.3 Data consultation

*Note: This section specifically relates to ThermoChimie version 10d, procedures for earlier versions may differ.*

The updated database with the revised values is made available to the wider scientific community through the ThermoChimie website (<https://www.thermochimie-tdb.com/>). Interested parties can then:

- consult the raw thermodynamic data contained in the different ThermoChimie versions,
- download the ThermoChimie database in the different formats compatible with different geochemical codes,
- consult the supporting documents and guidelines, and
- provide feedback on the database.

Furthermore, a XCheck© user tool for data consultation is also available for the public via a link on the ThermoChimie website; access to the user tool is granted following registration. The tool allows users to consult the data contained in the latest ThermoChimie version, applying different filters:

- Elements in ThermoChimie: This filter is presented as a periodic table and allows the user to select the elements for which data is to be consulted. It is also possible to discriminate between different oxidation states.
- Species by calculation routes: This filter returns species and data derived from a specified calculation route (Appendix B).
- Filter data by parameters: This allows the user to select a thermodynamic parameter (stability constant, enthalpy of reaction...) and then obtain all of the data for all the species in the database for which that parameter is included. The filter includes both selected and internally calculated data.

- Database statistics: This provides the user with a visual illustration of the data available in ThermoChimie.

The tool allows the user to export the filtered data in the CSV format, but it does not allow them to obtain files compatible with geochemical codes.

## **4. Summary**

This guideline has provided information on the processes for amending, eliminating, or modifying any value in the ThermoChimie database, while maintaining its consistency. In this regard, the different aspects that contribute to the overall consistency of a thermodynamic database are described, and the processes to be followed for the inclusion or modification of data in ThermoChimie are outlined. Furthermore, the two Appendices provide a template for data selection and information on the equations and routes used to internally calculate values.



## 5. Bibliography

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## Appendix A: Template for data selection

This appendix provides a template to be used when proposing additional data to the administrators for inclusion in the database. When completing the template, the following items must be considered:

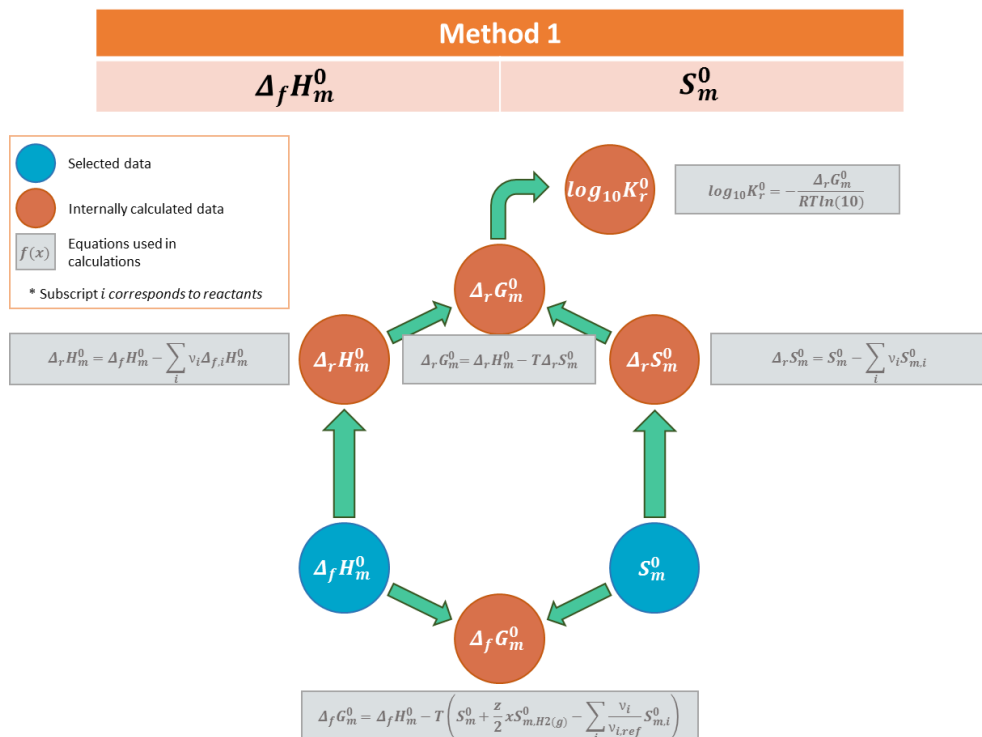
- Data selection procedures (see *Guideline 1: Data selection and uncertainties*) have to be followed.
- In the ThermoChimie database,  $\Delta_r\mathbf{G}_m^0$ ,  $\Delta_r\mathbf{H}_m^0$ ,  $\Delta_r\mathbf{S}_m^0$ ,  $\Delta_f\mathbf{G}_m^0$ ,  $\Delta_f\mathbf{H}_m^0$  and  $\mathbf{S}_m^0$  are provided to three decimal places while  $\log_{10}\mathbf{K}^0$ ,  $\boldsymbol{\varepsilon}(j, k)$ ,  $\mathbf{C}_{p,m}^0$  and  $\mathbf{V}_m^0$  are provided to two decimal places. However, all calculations and operations must be carried with the maximum possible precision, and only the final results are rounded.
- The thermodynamic quantities, Gibbs energy, enthalpy, and entropy, are closely related; only two of these parameters can be selected. Calculation routes and equations shown in Appendix B must be used to calculate the rest of the values.
- All the selected values must be accompanied by a complete bibliographic citation of the original publication. A brief description of this publication and of the calculations performed to obtain the selected value may be included under the “Selection details” heading.

SPECIES' NAME			
Date and version:			
Author/report:			
<input type="checkbox"/> New data <input type="checkbox"/> Updated/modified data <input type="checkbox"/> Eliminated data			
Species formula:			
Species name:			
Reaction:			
Selected data:			
Part 1: Data related through calculation routes			
	Value	Uncertainty	Reference
$\text{Log}_{10}K^0$			
$\Delta_r G_m^0$ (kJ·mol <sup>-1</sup> )			
$\Delta_r H_m^0$ (kJ·mol <sup>-1</sup> )			
$\Delta_r S_m^0$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )			
$\Delta_f G_m^0$ (kJ·mol <sup>-1</sup> )			
$\Delta_f H_m^0$ (kJ·mol <sup>-1</sup> )			
$S_m^0$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )			
Part 2: Other selected data			
$\varepsilon(j, k)$ (kg·mol <sup>-1</sup> )			
$C_{p,m}^0$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )			
$V_m^0$ (cm <sup>3</sup> ·mol <sup>-1</sup> )			
Selection details			
<ul style="list-style-type: none"> <li>• Details on the original publication (type of experiment, chemical conditions, analytical techniques, etc)</li> <li>• Data selection procedure and calculations (if applicable)</li> <li>• Comparison with other literature data</li> </ul>			
Notes (database administrators only)			

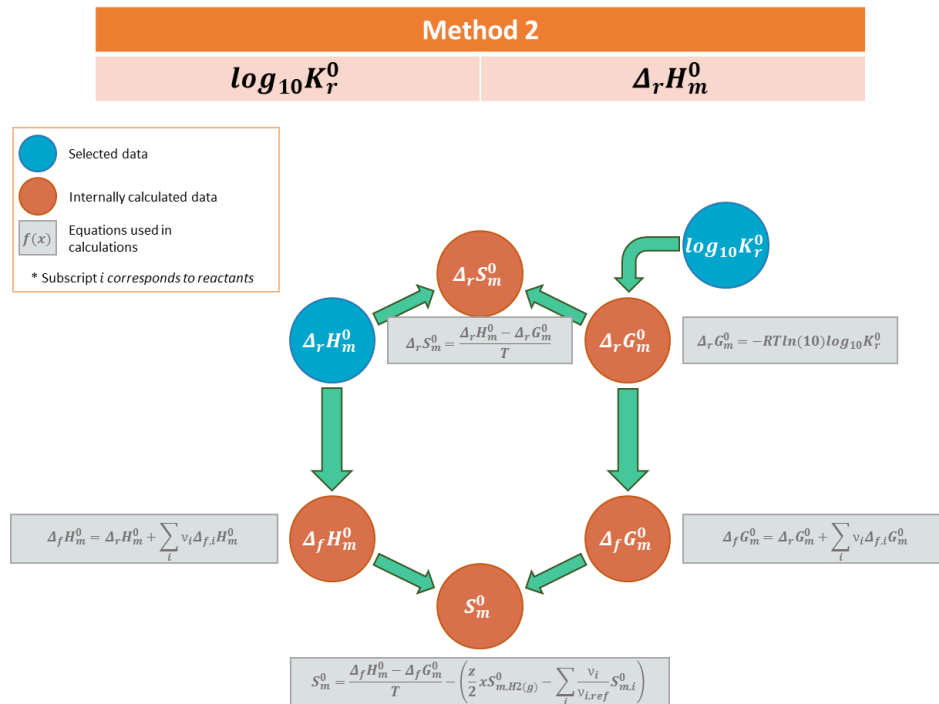
## Appendix B: Calculation routes

The thermodynamic values Gibbs energy, enthalpy and entropy are closely related. When values have been selected for two of these three variables, the rest of the data must be internally calculated. The following diagrams show the equations that must be used in order to perform those calculations, depending on which of them are selected.

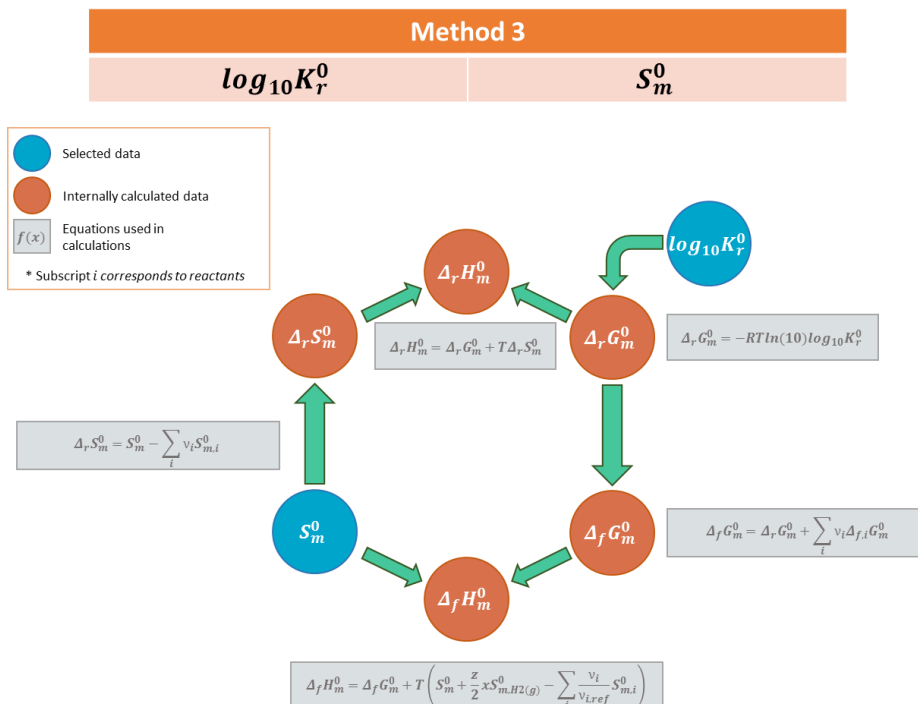
Method 1: Selected values are the standard enthalpy of formation and the standard entropy.



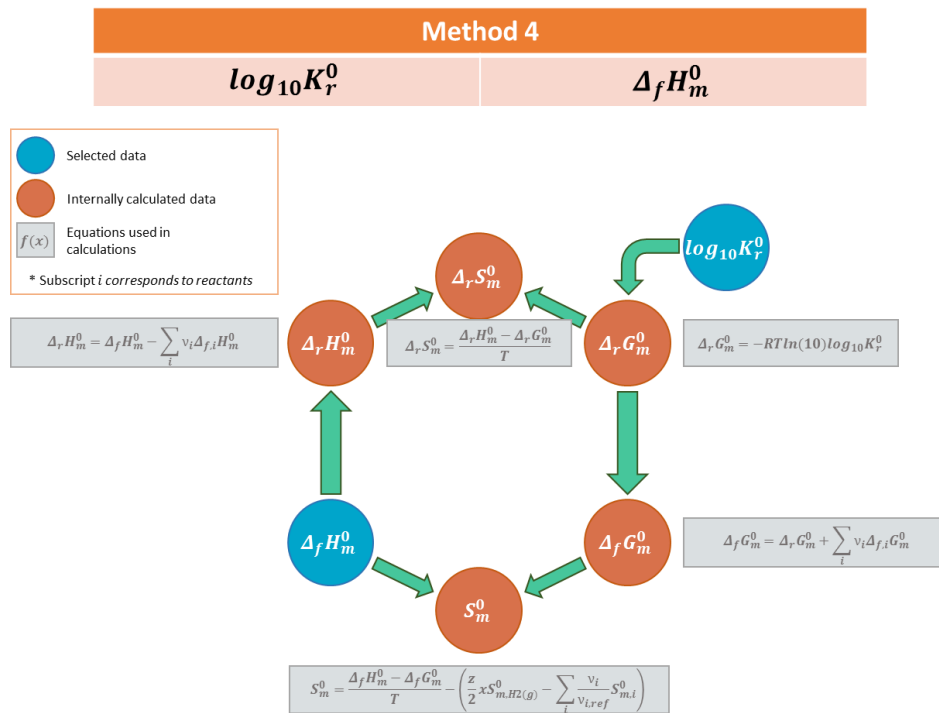
Method 2: Selected values are the equilibrium constant of the reaction and the enthalpy of reaction.



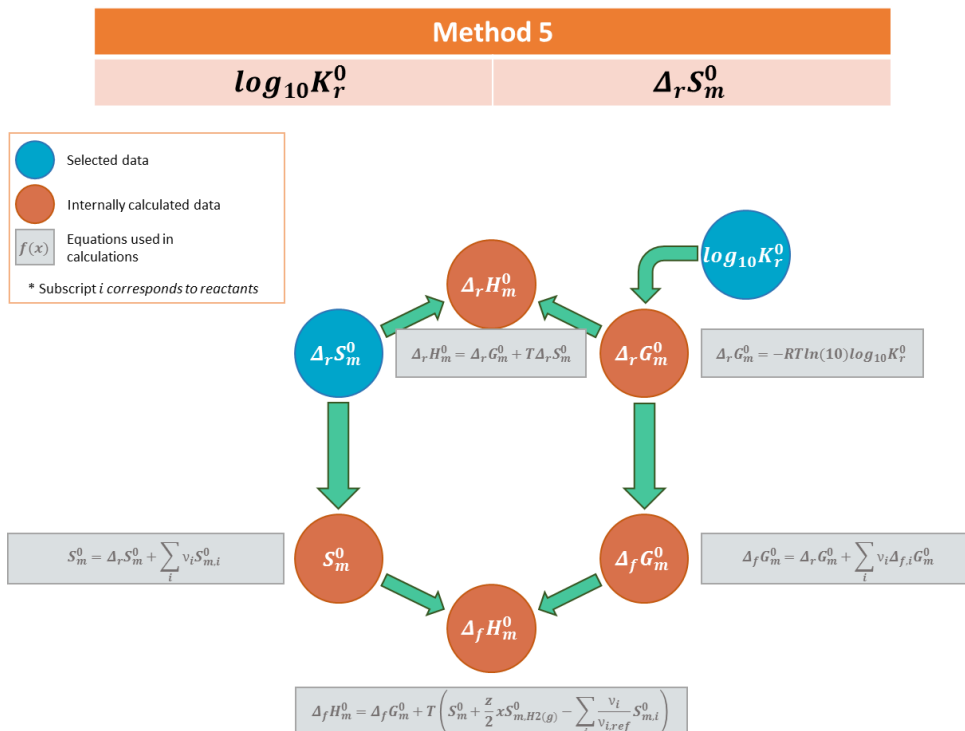
Method 3: Selected values are the equilibrium constant of the reaction and the standard entropy.



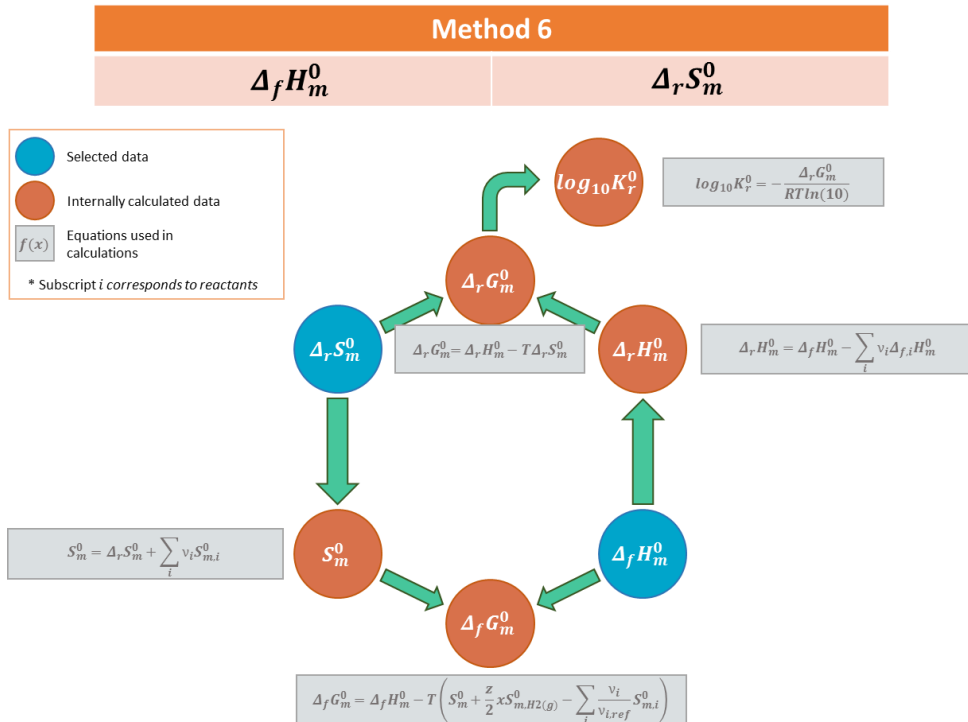
Method 4: Selected values are the equilibrium constant of the reaction and the standard enthalpy of formation.



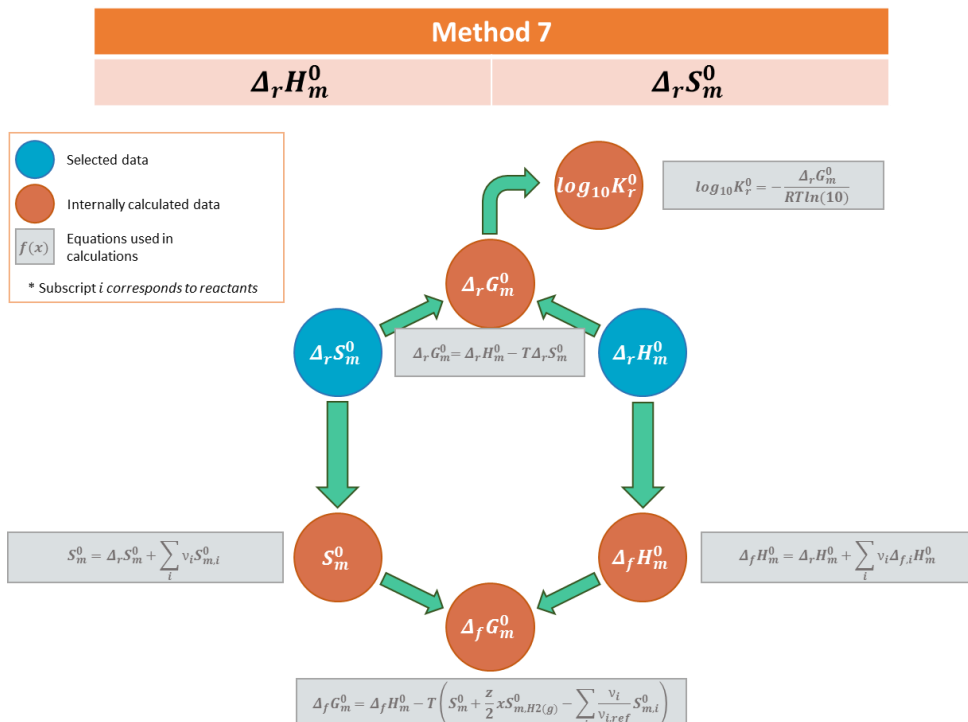
Method 5: Selected values are the equilibrium constant of the reaction and the entropy of reaction.



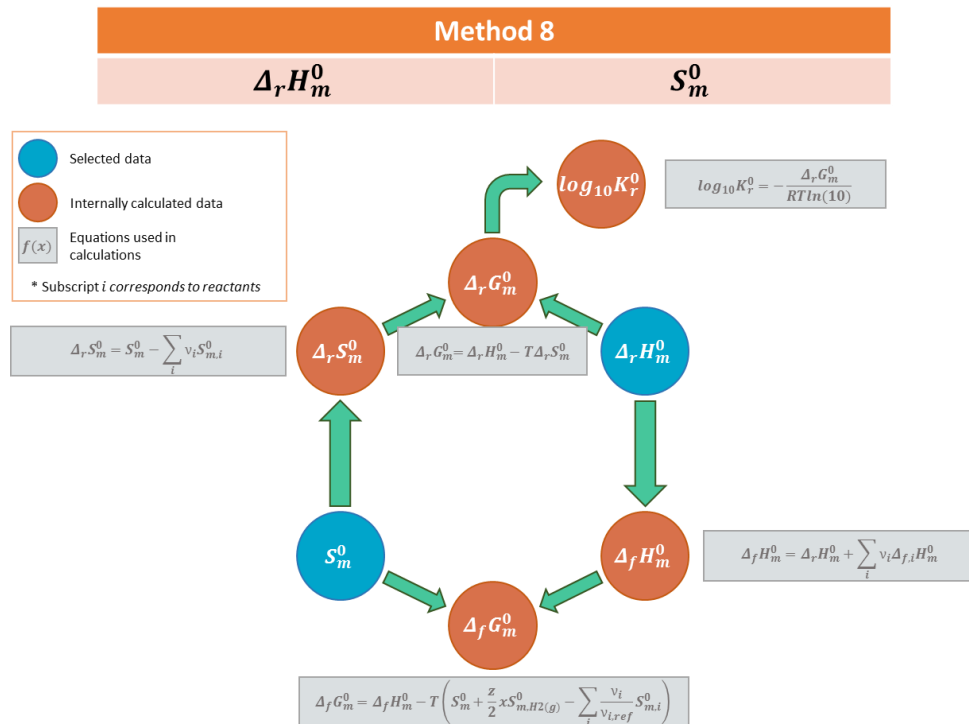
Method 6: Selected values are the standard enthalpy of formation and the entropy of reaction.



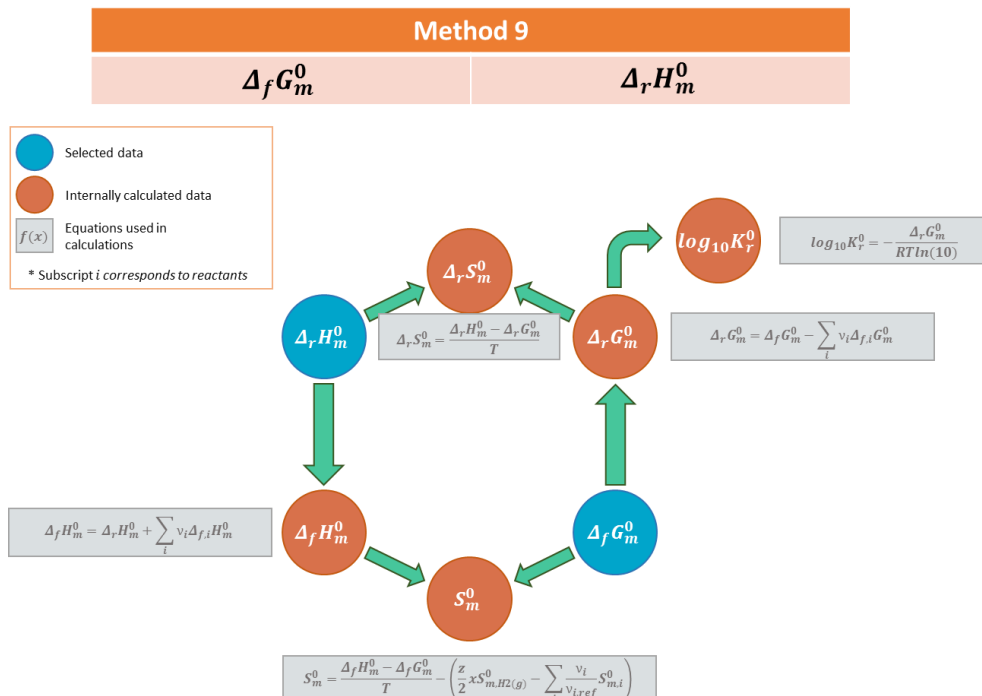
Method 7: Selected values are the enthalpy of reaction and the entropy of reaction.



Method 8: Selected values are the enthalpy of reaction and the standard entropy.

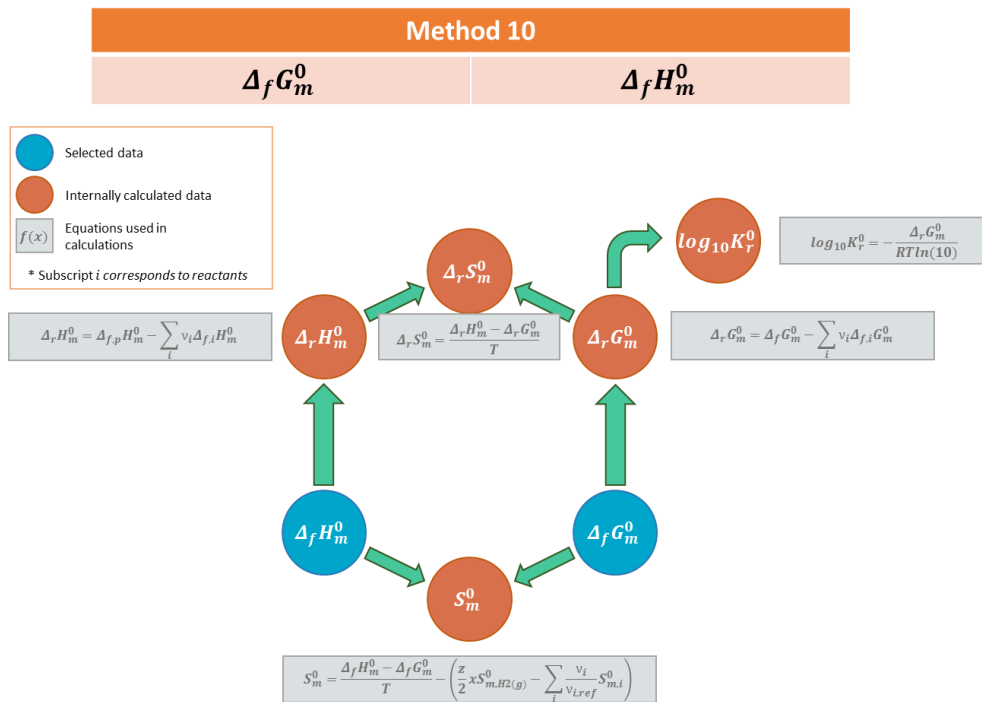


Method 9: Selected values are the standard Gibbs energy of formation and the enthalpy of reaction.

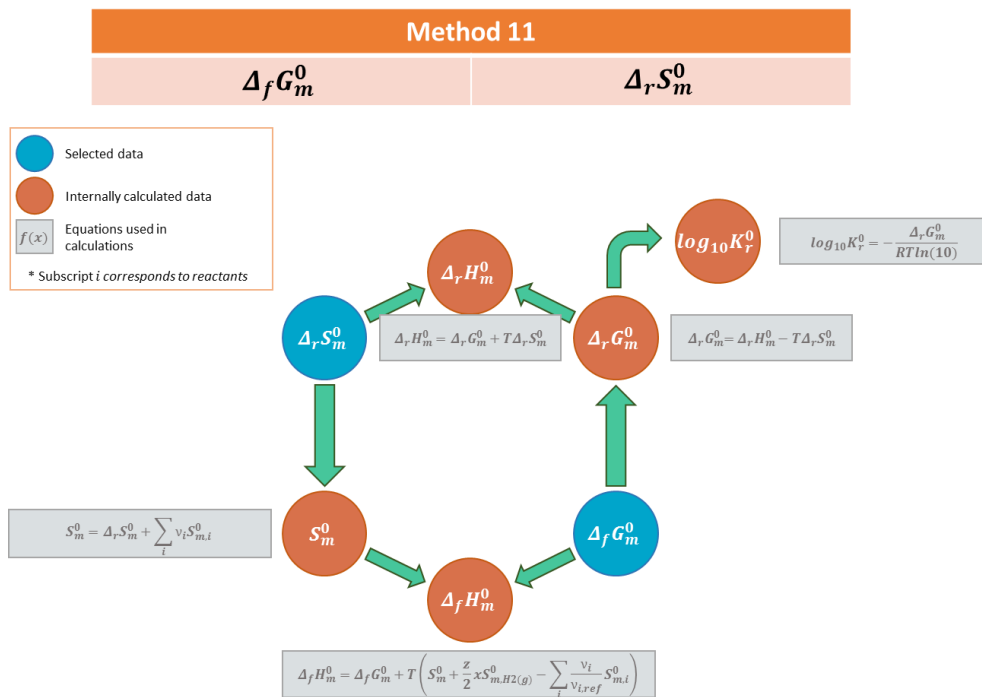




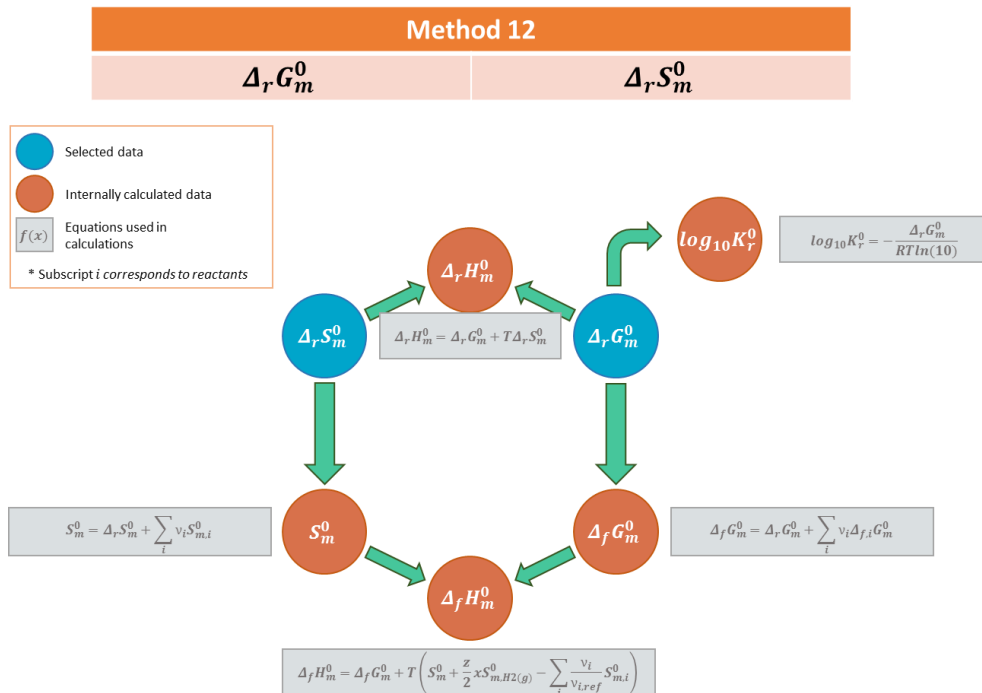
Method 10: Selected values are the standard Gibbs energy of formation and the standard enthalpy of formation.



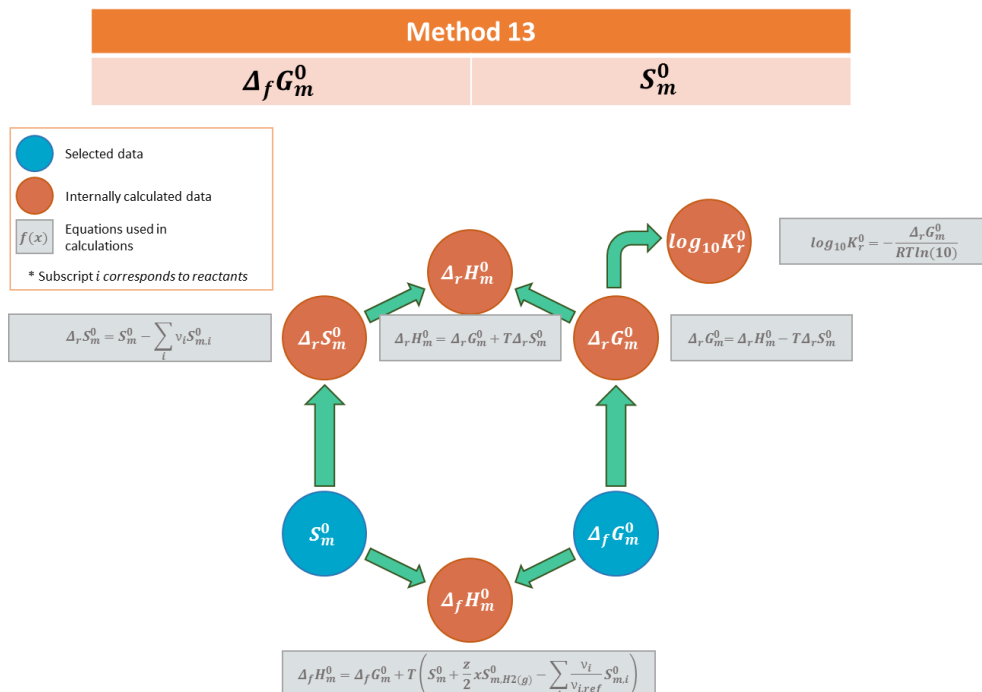
Method 11: Selected values are the standard Gibbs energy of formation and the entropy of reaction.



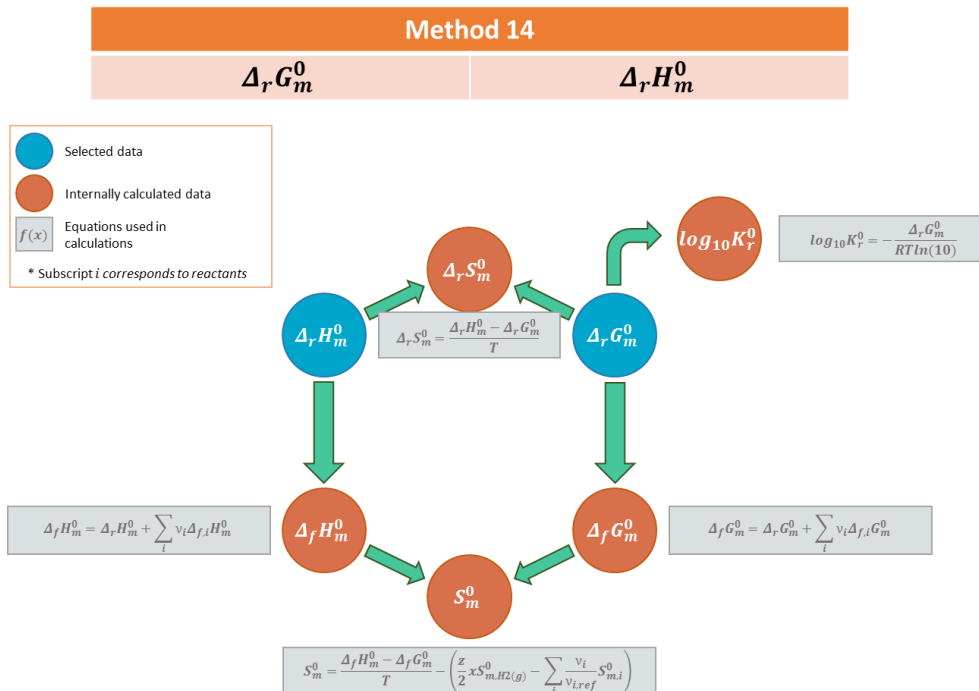
Method 12: Selected values are the Gibbs energy of reaction and the entropy of reaction.



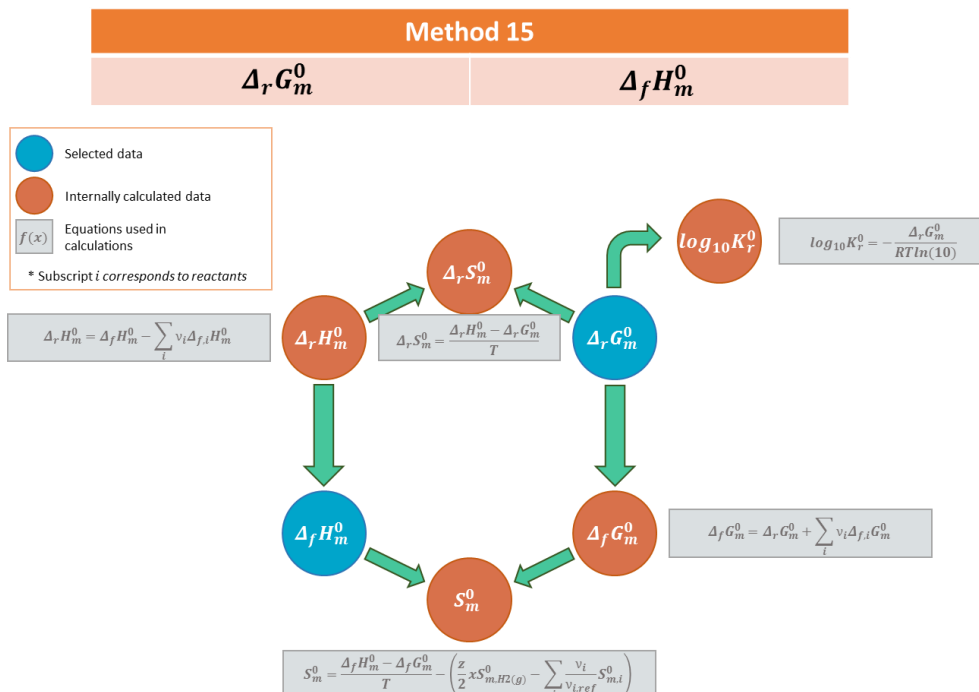
Method 13: Selected values are the standard Gibbs energy of formation and the standard entropy.



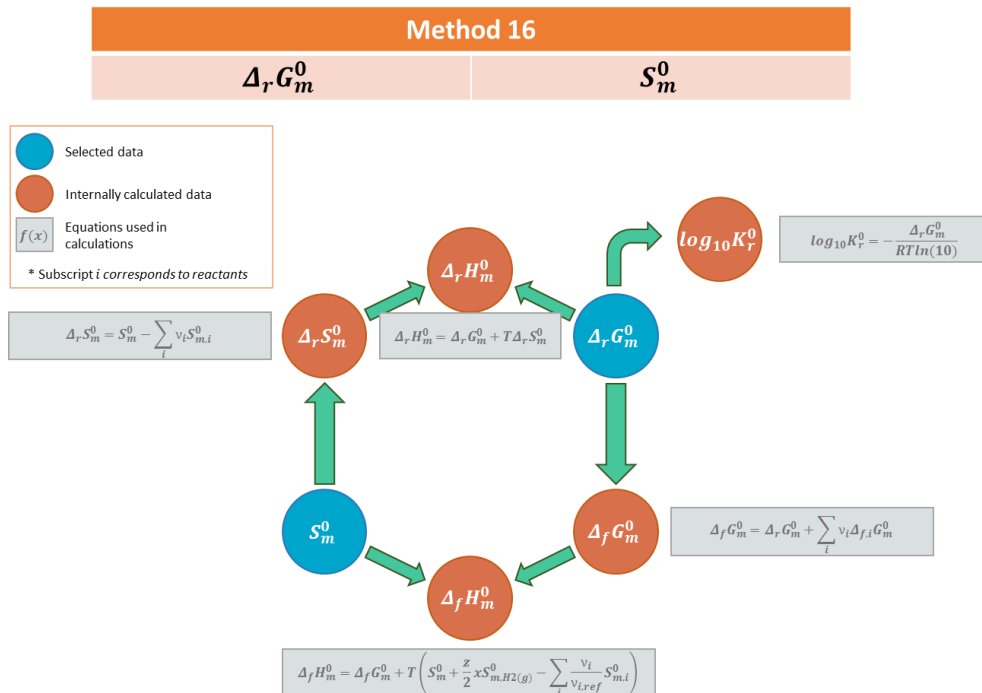
Method 14: Selected values are the Gibbs energy of reaction and the enthalpy of reaction.



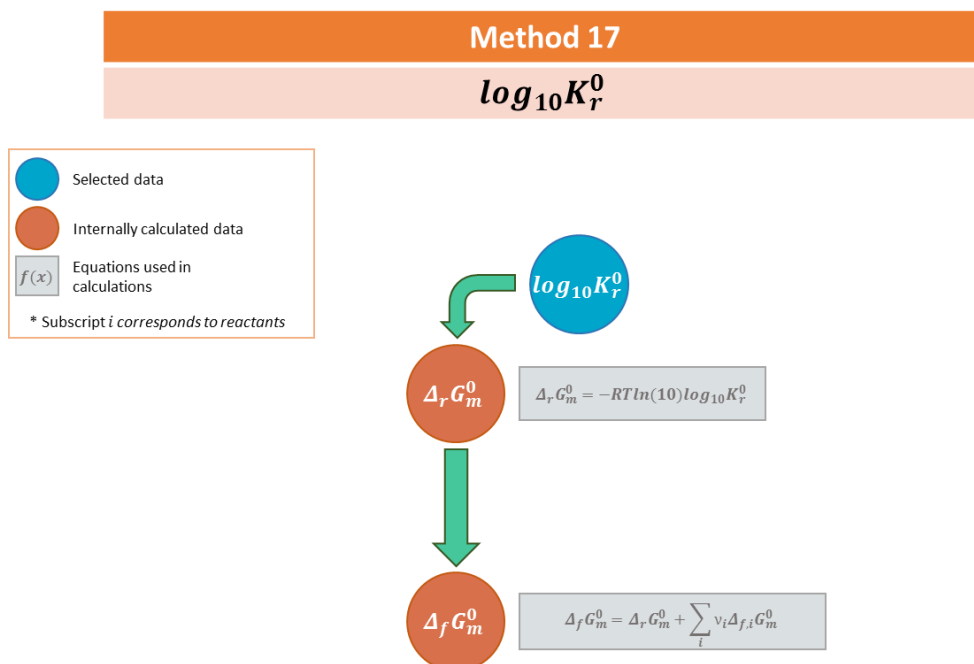
Method 15: Selected values are the Gibbs energy of reaction and the standard enthalpy of formation.



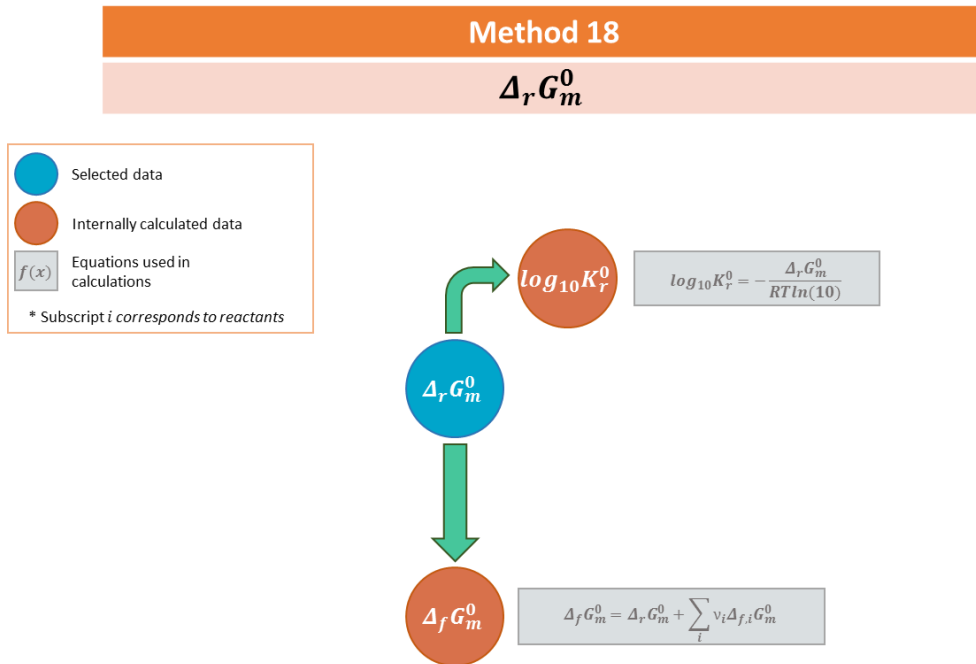
Method 16: Selected values are the Gibbs energy of reaction and the standard entropy.



Method 17: Selected value is the equilibrium constant of the reaction.



Method 18: Selected value is the Gibbs energy of the reaction.



Method 19: Selected value is the standard Gibbs energy of formation.

