

Part 3. Temperature corrections of standard molar (partial molal) thermodynamic properties of substances and reactions using data in ReacDC records of GEM-Selektor (version 2.2.3 and later)

3.1. General overview

The ReacDC record format can be used for defining thermodynamic properties of minerals (e.g. solid-solution end-members), aqueous or surface complexes, for which measured thermochemical data are not available; or predicted thermochemical data are too uncertain; or it is not possible to predict the HKF EoS parameters. In such cases, only $\log K$ of the dissolution, association or surface complexation reaction is usually known at 25 °C.

A chemical reaction involving any number of dependent components taken as reactants and products can be written as

$$\sum_{j=1}^L \nu_j M_j = 0, \quad j \in L_R \quad (3-1)$$

where L_R is a set of $n(L_R)$ dependent components (chemical species) involved in the reaction, M_j stands for a (formula of) chemical species and, ν_j represents the stoichiometric coefficients, negative for reactants and positive for products.

Because the GEM algorithm cannot use reactions and their equilibrium constants to calculate the equilibrium speciation in phases, each ReacDC record also provides a set of standard molar properties for a "new" species - the last one in eqn (3-1) having the greatest index L . It is called "new" in a sense that its standard molar properties are defined through properties of the reaction and that of other species involved (and provided as records in the database); the "new" species also gives a name to the reaction. Obviously, the "new" reaction-defined species can be either a product or a reactant given the sign of its stoichiometry coefficient.

Any molar property of the "new" species in the reaction at temperature T and pressure P of interest can be found algebraically from the respective property of the reaction and all but one of involved species. For instance, the standard Gibbs energy change in reaction $\Delta_r G_{T_r}^o$ (in $\text{J}\cdot\text{mol}^{-1}$; instead of Δ_r , Δ will be written everywhere below for brevity) at reference temperature T_r and pressure P_r is

$$\Delta G_{T_r}^o = \sum_{j=1}^L \nu_j G_{j,T_r}^o, \quad j \in L_R \quad (3-2),$$

where $R = 8.31451 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ is the universal gas constant and

$$\Delta G_{T_r}^o = -RT_r \ln K_{T_r} \quad (3-3),$$

where K_{T_r} is a thermodynamic equilibrium constant at T_r , P_r [cf. Anderson and Crerar, 1993]. From eqn (3-2), the value G_{L,T_r}^o of the new species can be found if K_{T_r} value is independently known, and standard molar Gibbs energies of other involved species are available:

$$G_{L,T_r}^o = \Delta G_{T_r}^o - \sum_{j=1}^{L-1} \nu_j G_{j,T_r}^o, \quad j \neq L \quad (3-4).$$

Using eqn (3-3), one can alternatively obtain G_{L,T_r}^o using the known equilibrium constant:

$$G_{L,T_r}^o = -RT_r \ln K_{T_r} - \sum_{j=1}^{L-1} \nu_j G_{j,T_r}^o, \quad j \neq L \quad (3-5).$$

Equations of the form (3-4) hold for other standard molar (or partial molal) properties:

$$H_{L,T_r}^o = \Delta H_{T_r}^o - \sum_{j=1}^{L-1} \nu_j H_{j,T_r}^o, \quad j \neq L \quad (3-6),$$

$$S_{L,T_r}^o = \Delta S_{T_r}^o - \sum_{j=1}^{L-1} \nu_j S_{j,T_r}^o, \quad j \neq L \quad (3-7),$$

$$V_{L,T_r}^o = \Delta V_{T_r}^o - \sum_{j=1}^{L-1} \nu_j V_{j,T_r}^o, \quad j \neq L \quad (3-8),$$

$$Cp_{L,T_r} = \Delta Cp_{T_r} - \sum_{j=1}^{L-1} \nu_j Cp_{j,T_r}, \quad j \neq L \quad (3-9),$$

where H , S , V , and Cp stand for enthalpy, third-law entropy, volume and isobaric heat capacity, respectively. If properties standing on the right side of eqns (3-4) to (3-9) are corrected to T,P of interest then respective properties of the new species can be found at T,P :

$$g_{L,T,P} = -RT \ln K_{T,P} - \sum_{j=1}^{L-1} \nu_j g_{j,T,P}, \quad j \neq L \quad (3-10).$$

$$g_{L,T,P} = \Delta G_{T,P} - \sum_{j=1}^{L-1} \nu_j g_{j,T,P}, \quad j \neq L \quad (3-11).$$

$$i_{L,T,P} = \Delta H_{T,P} - \sum_{j=1}^{L-1} \nu_j i_{j,T,P}, \quad j \neq L \quad (3-12).$$

$$S_{L,T,P} = \Delta S_{T,P} - \sum_{j=1}^{L-1} \nu_j S_{j,T,P}, \quad j \neq L \quad (3-13).$$

$$V_{L,T,P} = \Delta V_{T,P} - \sum_{j=1}^{L-1} \nu_j V_{j,T,P}, \quad j \neq L \quad (3-14).$$

$$Cp_{L,T} = \Delta Cp_T - \sum_{j=1}^{L-1} \nu_j Cp_{j,T}, \quad j \neq L \quad (3-15).$$

Here, $g_{L,T,P}$ is the apparent molar Gibbs function and $i_{L,T,P}$ is the apparent molar enthalpy function of the L -th (new) species. Calculation of these (and other) functions at T,P for species available as DComp records in the GEMS database are described separately (see files `T-corrections.pdf`, `P-corrections.pdf` and `HKF-corrections.pdf`). Hence, the algorithm for calculating temperature and pressure corrections for the reaction-defined species consists of three steps:

- (i) Correct to T,P of interest the molar properties of all reaction species but the L -th one using independently the standard state data, parameter sets, and correction techniques defined in the DComp and ReacDC records available in the database;
- (ii) Correct to T,P of interest the corresponding effects of reaction ($\Delta G, \Delta H, \Delta S, \Delta V, \Delta Cp$);

- (iii) Apply eqns (3-11) to (3-15) to obtain molar properties of “new” L -th species at T, P .

Note that, if a link to the reaction-defined species (ReacDC data) is given for any of j -th species ($j < L$) in eqns (3-11) to (3-15), the above algorithm becomes recursive because it first has to be used for obtaining the molar properties at T, P for that j -th species. In the GEM-Selektor code, up to seven levels of such recursion are possible (see documentation for ReacDC module for details).

Now, it becomes clear that the whole problem is reduced to step (ii) of the above algorithm, i.e. to temperature and pressure corrections of the standard effects of reaction, based on the available equilibrium constants and other data. There seems to be no general solution but many specific ones, depending on the data and chemical species involved.

The most straightforward way is to provide equilibrium constants for the reaction as discrete $\log K$ values on a P, T grid Q having $n(Q) = n(Q_P) \cdot n(Q_T)$ nodes. Then, for any intermediate values of T, P between the nodes, the $\log K_{T,P}$ value can be found by interpolation. Historically, this method was implemented in the SOLMNEQ.88 code [Kharaka et al., 1988].

In GEMS implementation, an internal subroutine for Lagrange polynomial table interpolation is used for this purpose, similar to that in SOLMNEQ code. The drawback of this technique is that the variation of $K_{T,P}$ values cannot be analytically (functionally) connected to other properties of the reaction such that ΔH , ΔS , ΔV , ΔC_p (remember that only $g_{T,P}$ values are necessary for GEM calculations of equilibria). The advantage of the interpolation technique lies in its simplicity and universality.

A more theoretically sound thing is to use a power-series function of $\log K$ or $\ln K$ on temperature T . From theory (cf. [Anderson and Crerar, 1993]), it follows that

$$\frac{\partial}{\partial T}(R \ln K) = \frac{\partial}{\partial T} \left(-\Delta G^\circ / T \right) = \Delta H^\circ / T^2 \quad (3-16).$$

To integrate eqn (3-16), we need to know how ΔH° varies with temperature. Knowledge of this dependence is equivalent to knowledge of the $C_p^\circ = f(T)$ dependences (see document `T-corrections.pdf`) for all species involved in the reaction, or at least, the $\Delta C_p^\circ = f(T)$ dependence. For practical purposes, it is sufficient to limit the underlying $\Delta C_p^\circ = f(T)$ function (eqn 1-2 in `T-corrections.pdf`) to five terms corresponding to the Haas-Fisher equation:

$$\Delta C_{pT} = \Delta a_0 + \Delta a_1 T + \Delta a_2 T^{-2} + \Delta a_3 T^{-0.5} + \Delta a_4 T^2 \quad (3-17).$$

The integration [cf. Nordstrom and Munoz, 1988, Table 4-2; Anderson and Crerar, 1993, Appendix B] results in the following expression for $\log K_T$:

$$\log K_T = A_0 + A_1 T + A_2 T^{-1} + A_3 \ln T + A_4 T^{-2} + A_5 T^2 + A_6 T^{-0.5} \quad (3-18).$$

These seven coefficients can be directly entered into ReacDC records of GEM-Selektor (some or all can be zeros, of course). If not entered, they will be automatically computed from $\Delta C_p^\circ = f(T)$ coefficients (only the first five will be used according to eqn 3-17), $\Delta H_{T_r}^\circ$, and $\Delta S_{T_r}^\circ$ as follows. First, the standard “energy” properties of reaction are connected by the equation:

$$\Delta H_{T_r}^\circ = \Delta G_{T_r}^\circ + T_r \Delta S_{T_r}^\circ = -2.302585 RT \log K_{T_r} + T_r \Delta S_{T_r}^\circ \quad (3-19).$$

If all these parameters have been entered then their consistency will be checked; otherwise, a missing parameter(s) will be retrieved from eqn (3-19).

Then, coefficients A_0 to A_6 of eqn (3-18) will be calculated:

$$A_0 = \frac{0.4343}{R} \cdot (s_{T_r} - \Delta a_0) \quad (3-20).$$

$$A_1 = \frac{0.4343}{R} \cdot \frac{\Delta a_1}{2} \quad (3-21).$$

$$A_2 = -\frac{0.4343}{R} \cdot h_{T_r} \quad (3-22).$$

$$A_3 = \frac{0.4343}{R} \cdot \Delta a_0 \quad (3-23).$$

$$A_4 = \frac{0.4343}{R} \cdot \frac{\Delta a_2}{2} \quad (3-24).$$

$$A_5 = \frac{0.4343}{R} \cdot \frac{\Delta a_4}{6} \quad (3-25).$$

$$A_6 = -\frac{0.4343}{R} \cdot 4\Delta a_3 \quad (3-26).$$

Here, the entropy and enthalpy terms at T_r , respectively, are:

$$s_{T_r} = \Delta S_{T_r}^o - \Delta a_0 \ln T_r - \Delta a_1 T_r + \Delta a_2 \frac{1}{2T_r^2} + \Delta a_3 \frac{2}{\sqrt{T_r}} - \Delta a_4 \frac{T_r^2}{2} \quad (3-27);$$

$$h_{T_r} = \Delta H_{T_r}^o - \Delta a_0 T_r - \Delta a_1 \frac{T_r^2}{2} + \Delta a_2 \frac{1}{T_r} - 2\Delta a_3 \sqrt{T_r} - \Delta a_4 \frac{T_r^3}{3} \quad (3-28).$$

Combining eqns (3-13) to (3-28) yields an equation to calculate ΔG_T^o :

$$\begin{aligned} \Delta G_T^o &= -2.302585RT \log K_T = \\ &= h_{T_r} - s_{T_r} T + \Delta a_0 T(1 - \ln T) - \Delta a_1 \frac{T^2}{2} - \Delta a_2 \frac{1}{2T} + \Delta a_3 \cdot 4\sqrt{T} - \Delta a_4 \frac{T^3}{6} \end{aligned} \quad (3-29).$$

The entropy change in reaction at T is found as

$$\Delta S_T^o = s_{T_r} + \Delta a_0 \ln T + \Delta a_1 T - \Delta a_2 \frac{1}{2T^2} - \Delta a_3 \cdot \frac{2}{\sqrt{T}} + \Delta a_4 \frac{T^2}{2} \quad (3-30),$$

and the enthalpy of reaction is corrected to temperature of interest as follows:

$$\begin{aligned} \Delta H_T^o &= \Delta G_T^o + T\Delta S_T^o = \\ &= h_{T_r} + \Delta a_0 T + \Delta a_1 \frac{T^2}{2} - \Delta a_2 \frac{1}{T} + \Delta a_3 \cdot 2\sqrt{T} + \Delta a_4 \frac{T^3}{3} \end{aligned} \quad (3-31).$$

Conversely, coefficients of eqn (3-17), as well as $\Delta G_{T_r}^o$, $\Delta H_{T_r}^o$ and $\Delta S_{T_r}^o$, if unknown, can be calculated from known coefficients of eqn (3-18):

$$\Delta a_0 = \frac{R}{0.4343} \cdot A_3 \quad (3-32).$$

$$\Delta a_1 = \frac{R}{0.4343} \cdot 2A_1 \quad (3-33).$$

$$\Delta a_2 = \frac{R}{0.4343} \cdot 2A_4 \quad (3-34).$$

$$\Delta a_3 = -\frac{R}{0.4343} \cdot \frac{A_6}{4} \quad (3-35).$$

$$\Delta a_4 = \frac{R}{0.4343} \cdot 6A_5 \quad (3-36).$$

$$\log K_{T_r} = A_0 + A_1 T_r + \frac{A_2}{T_r} + A_3 \ln T_r + \frac{A_4}{T_r^2} + A_5 T_r^2 + \frac{A_6}{\sqrt{T_r}} \quad (3-37).$$

$$\Delta H_{T_r}^o = \frac{R}{0.4343} [-A_2 + A_3 T_r + A_1 T_r^2 - \frac{2A_4}{T_r} - \frac{A_6 \sqrt{T_r}}{2} + 2A_5 T_r^3] \quad (3-38).$$

$$\Delta S_{T_r}^o = \frac{R}{0.4343} [A_0 + A_3(1 + \ln T_r) + 2A_1 T_r - \frac{A_4}{T_r^2} + \frac{A_6}{2\sqrt{T_r}} + 3A_5 T_r^2] \quad (3-39).$$

After that, $\Delta G_{T_r}^o$ can be found from eqn (3-19). Calculation of the properties of reaction at T of interest can be performed using eqns (3-17), (3-18), and (3-29) to (3-31). Alternatively (as done in the GEM-Selektor code), ΔS_T^o and ΔH_T^o at temperature of interest T are computed using the equations analogous to (3-18), (3-38) and (3-39):

$$\begin{aligned} \Delta G_T^o &= -\frac{RT}{0.4343} \log K_T = \\ &= -\frac{R}{0.4343} [A_0 T + A_1 T^2 + A_2 + A_3 T \ln T + \frac{A_4}{T} + A_5 T^3 + A_6 \sqrt{T}] \end{aligned} \quad (3-40).$$

$$\Delta H_T^o = \frac{R}{0.4343} [A_1 T^2 - A_2 + A_3 T - \frac{2A_4}{T} + 2A_5 T^3 - 0.5A_6 \sqrt{T}] \quad (3-41).$$

$$\Delta S_T^o = \frac{R}{0.4343} [A_0 + 2A_1 T + A_3(1 + \ln T) - \frac{A_4}{T^2} + 3A_5 T^2 + \frac{A_6}{2\sqrt{T}}] \quad (3-42).$$

Depending on how many non-zero coefficients of eqn (3-18) are known, different temperature extrapolations of reaction properties can be distinguished. The most practically important ones are: zero-term (all effects of reaction are zeros at all temperatures); two kinds of one-term (at $\Delta H_T^o = 0$ and at $\Delta S_T^o = 0$); two-term (Van't Hoff extrapolation, at $Cp_T = 0$); and three-term (at non-zero $Cp_T = \text{const}$) extrapolations. These simple dependencies are especially useful for the so-called *isocoulombic* or *isoelectric* reactions (having equal number of species with equal charges or having equal sum of charges on both sides, respectively) involving colloidal minerals, aqueous or surface species [cf. Gu et al., 1994; Puigdomenech et al., 1997; Kulik, 2000, 2002].

Extrapolations of higher order may be appropriate for the mineral-mineral or mineral-fluid reactions, though rarely used in low-temperature geochemistry.

3.2. Special cases of simple temperature extrapolations

Equations for three-term temperature extrapolations of $\log K$ can be obtained by zeroing off the coefficients Δa_1 to Δa_4 in eqn (3-17), yielding:

$$\Delta Cp_T = \Delta Cp_{T_r} = \Delta a_0 \neq 0 \quad (3-43);$$

$$A_0 = \frac{0.4343}{R} \cdot [\Delta S_{T_r}^o - \Delta Cp_{T_r} (\ln T_r + 1)] \quad (3-44);$$

$$A_2 = -\frac{0.4343}{R} \cdot (\Delta H_{T_r}^o - \Delta Cp_{T_r} T_r) \quad (3-45);$$

$$A_3 = \frac{0.4343}{R} \cdot \Delta Cp_{T_r} \quad (3-46);$$

$$\log K_T = A_0 + A_2 T^{-1} + A_3 \ln T \quad (3-47);$$

$$\Delta S_T^o = \Delta S_{T_r}^o + \Delta Cp_{T_r} \ln T / T_r \quad (3-48);$$

$$\Delta H_T^o = \Delta H_{T_r}^o + \Delta Cp_{T_r} (T - T_r) \quad (3-49);$$

$$\Delta G_T^o = \Delta H_T^o - T \Delta S_T^o \quad (3-50).$$

The three-term extrapolation (eqns 3-43 to 3-50) is best suited for isoelectric reactions, and it appears to be still good for non-isoelectric reactions up to T around 150 °C. The two-term (Van't Hoff) extrapolation (eqns 3-51 to 3-54), the use of which should be limited to isoelectric cases, is obtained further by zeroing Δa_0 and A_3 off, or $\Delta Cp_T = \Delta Cp_{T_r} = \Delta a_0 = 0$:

$$\log K_T = A_0 + A_2 T^{-1} = \frac{0.4343}{R} \left(\Delta S_{T_r}^o - \frac{\Delta H_{T_r}^o}{T} \right) \quad (3-51);$$

$$\Delta S_T^o = \Delta S_{T_r}^o \quad (3-52);$$

$$\Delta H_T^o = \Delta H_{T_r}^o \quad (3-53);$$

$$\Delta G_T^o = \Delta G_{T_r}^o - T \Delta S_{T_r}^o \quad (3-54).$$

The one-term extrapolation (eqns 3-55 and 3-56) at $\Delta S_T^o = \Delta S_{T_r}^o = 0$ has the only non-zero A_2 coefficient, which leads to $\Delta G_T = \Delta H_T = \text{const}$ (independent of temperature):

$$\log K_T = A_2 T^{-1} = -\frac{0.4343 \Delta H_{T_r}^o}{RT} \quad (3-55);$$

$$\Delta G_T^o = \Delta H_T^o = \Delta G_{T_r}^o = \Delta H_{T_r}^o \quad (3-56).$$

Another one-term extrapolation is obtained from the Van't Hoff equation (3-51) by setting $\Delta H_T^o = \Delta H_{T_r}^o = 0$, resulting in the equilibrium constant K independent of temperature:

$$\log K_T = A_0 = \frac{0.4343}{R} \Delta S_{T_r}^o = \log K_{T_r} \quad (3-57);$$

$$\Delta S_T^o = \Delta S_{T_r}^o \quad (3-58);$$

$$\Delta G_T^o = -T \Delta S_{T_r}^o \quad (3-59).$$

These one-term extrapolations should be applied to isocoulombic reactions, where they can produce good predictions up to 300 °C [Gu et al., 1994; Kulik, 2002]. The above four specific cases are implemented in GEM-Selektor code separately. If one of them is specified then the

necessary A_i and Δa_i coefficients will be computed from $\Delta S_{T_r}^o$, $\Delta H_{T_r}^o$ and $\Delta C p_{T_r}^o$ values, after all unnecessary coefficients have been zeroed off.

3.3. Pressure corrections of $\log K$

Pressure corrections require that at least the volume change $\Delta V_{T_r}^o$ in the reaction is known. In the GEM-Selektor ReacDC format, only the constant volume approximation is used, i.e. it is assumed that $\Delta V_{T,P} = \Delta V_{T_r}^o$ at any P and T of interest. This is a good approximation for “new” substances since molar volumes and fugacities of pure gases that participate in the reaction are automatically corrected to T, P using EoS or another appropriate technique; the molar volumes of minerals are corrected as well from thermal expansion/compressibility data; and the partial molar volumes of aqueous species are corrected using the HKF EoS coefficients. At constant $\Delta V_{T,P}$, the pressure correction to ΔG is

$$\Delta G_{T,P} - \Delta G_T^o = \int_{P_r}^P \Delta V_{T,P} dP = \Delta V_{T_r}^o \int_{P_r}^P dP = \Delta V_{T_r}^o (P - P_r) \quad (3-60),$$

and the pressure correction to the equilibrium constant becomes

$$\log K_{T,P} = \log K_T - \frac{0.4343}{RT} \Delta V_{T_r}^o (P - P_r) \quad (3-61).$$

As in this case $\Delta S_{T,P} = \Delta S_{T_r}^o$ then, analogous to eqn (3-57),

$$\Delta H_{T,P} = \Delta H_T^o + \Delta V_{T_r}^o (P - P_r) \quad (3-62).$$

3.4. TP-corrections applying electrostatic and density models

(added by Th. Wagner and D.Kulik to GEM-Selektor v. 2.2.0 on August 10, 2007)

The *modified Ryzhenko-Bryzgalin (MRB)* model is based on earlier electrostatic models that were developed to extrapolate equilibrium constants of aqueous complexes to elevated temperatures and pressures. The original model formulation included an explicit dependence of the equilibrium constants (or pK , the negative logarithm of the equilibrium constant) on water density and dielectrical constant [Ryzhenko and Bryzgalin, 1985; Bryzgalin, 1986; 1989]

$$pK_{T,P} = pK_{298,1} + \frac{298}{T} + \frac{e^2 N z^+ z^-}{\ln(10) RT a} \left(\frac{1}{\epsilon_{T,P}} - \frac{1}{\epsilon_{298,1}} \right) \quad (3-63)$$

Here, e is the electron charge, N is the Avogadro number, z^+ and z^- are the ionic charges, and ϵ is the dielectrical constant of water at P and T of interest. The term a stands for $a = r_{\text{Cation}} + r_{\text{Anion}}$, i.e. the sum of the crystallographic radii of the ions. By comparing the model predictions with experimental data, it was found that the parameter a would differ from the sum of the crystallographic radii. Therefore, this parameter was combined with the ionic charges into the adjustable parameter (zz/a) , similar to the effective electrostatic radii in the HKF model. From this, the new basic model equation would become [Shvarov and Bastrakov, 1999]

$$pK_{T,P} = pK_{298,1} \frac{298}{T} + \bar{B}_{T,P}(zz/a) \quad (3-64)$$

The parameter $\bar{B}_{T,P}$ does not depend on the complex type, but only on pressure and temperature. It would be calculated from the dissociation constant of water as given by Marshall and Franck (1981)

$$\log K_{T,P}^W = a + \frac{b}{T} + \frac{c}{T^2} + \frac{d}{T^3} + \left(e + \frac{f}{T} + \frac{g}{T^2} \right) \log \rho \quad (3-65)$$

This would result in a best-fit value of 1.0107 for $(zz/a)_W$ [Shvarov and Bastrakov, 1999]. The function $\bar{B}_{T,P}$ can now be calculated at any pressure and temperature

$$\bar{B}_{T,P} = \frac{pK_{T,P}^W - pK_{298,1}^W \frac{298}{T}}{(zz/a)_W} \quad (3-66)$$

To improve the representation of experimentally determined complex dissociation constants, the parameter (zz/a) would become temperature dependent [Shvarov and Bastrakov, 1999]

$$(zz/a) = A + B/T \quad (3-67)$$

By noting the relationship between $\Delta_r G_{T,P}^\circ$ and the equilibrium constant

$$pK_{T,P} = \frac{\Delta_r G_{T,P}^\circ}{RT \ln(10)} \quad (3-68)$$

the full expression for the $\Delta_r G_{T,P}^\circ$ can be obtained through combination of eqns (3-64), (3-65), (3-67) and (3-68). The analytical expressions for $\Delta_r S_{T,P}^\circ$, $\Delta_r Cp_{T,P}^\circ$ and $\Delta_r V_{T,P}^\circ$ are then obtained from the temperature and pressure derivatives of the $\Delta_r G_{T,P}^\circ$ function. These equations are not given in the literature and were developed for a consistent implementation of the MRB model into the GEM-Selektor code. The enthalpy of reaction, $\Delta_r H_{T,P}^\circ$, is calculated from entropy and Gibbs energy by difference. The full derivation of these equations is given in Appendix 1. Implementation of the modified Ryzhenko-Bryzgalin (MRB) model in GEM-Selektor is realized as a special case of the ReacDC database module, i.e. reaction-defined dependent components.

The *Marshall-Franck density model* [Marshall and Franck, 1981; Mesmer et al., 1991] allows calculation of the dissociation constants of aqueous electrolytes at elevated temperatures and pressures from the empirical equation:

$$\log K = a + \frac{b}{T} + \frac{c}{T^2} + \frac{d}{T^3} + \left(e + \frac{f}{T} + \frac{g}{T^2} \right) \log \rho \quad (3-69)$$

The analytical expressions for $\Delta_r S_{T,P}^\circ$, $\Delta_r C p_{T,P}^\circ$ and $\Delta_r V_{T,P}^\circ$ are readily obtained from the temperature and pressure derivatives of the $\Delta_r G_{T,P}^\circ$ function, and are similar to those for the modified Ryzhenko-Bryzgalin model. Fit coefficients for this model are available for a number of common electrolytes such as NaCl, KCl, NaOH and KOH [Ho et al., 1994; Ho and Palmer, 1996; 1997]. The density model would potentially allow to extrapolate equilibrium constants beyond the current 5 kbar pressure limit of the HKF model, if an appropriate equation of state for the thermodynamic properties of aqueous ions at high pressures would become available.

3.5. References

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Appendix 3-1. Derivative reaction properties calculated from the MRB model.

The full expression for the $\Delta_r G_{T,P}^\circ$ is given by

$$(3.A1) \quad \Delta_r G_{T,P}^\circ = \Delta_r G_{298,1}^\circ - \frac{R \ln(10)}{1.0107} [\log K_{T,P}^W T - \log K_{298,1}^W (298)] \left(A + \frac{B}{T} \right)$$

Rearranging and substituting the expression for the dissociation constant of water from Marshall and Franck (1981) results in

$$(3.A2) \quad \Delta_r G_{T,P}^\circ = \Delta_r G_{298,1}^\circ - \frac{R \ln(10)}{1.0107} \left[aT + b + \frac{c}{T} + \frac{d}{T^2} + \left(eT + f + \frac{g}{T} \right) \log \rho - \log K_{298,1}^W (298) \right] \left(A + \frac{B}{T} \right)$$

Now we define the following terms

$$(3.A3) \quad i = aT + b + \frac{c}{T} + \frac{d}{T^2} + \left(eT + f + \frac{g}{T} \right) \log \rho - \log K_{298,1}^W (298)$$

$$(3.A4) \quad j = A + \frac{B}{T}$$

The derivative thermodynamic properties are then obtained as

$$(3.A5) \quad \Delta_r S_{T,P}^\circ = \frac{R \ln(10)}{1.0107} \left[\frac{\partial i}{\partial T} j + \frac{\partial j}{\partial T} i \right]$$

$$(3.A6) \quad \Delta_r CP_{T,P}^\circ = \frac{R \ln(10)}{1.0107} T \left[\frac{\partial^2 i}{\partial T^2} j + 2 \frac{\partial i}{\partial T} \frac{\partial j}{\partial T} + \frac{\partial^2 j}{\partial T^2} i \right]$$

$$(3.A7) \quad \Delta_r V_{T,P}^\circ = - \frac{R \ln(10)}{1.0107} \left(eT + f + \frac{g}{T} \right) \frac{1}{\rho \ln(10)} \left(\frac{\partial \rho}{\partial P} \right)_T \left(A + \frac{B}{T} \right)$$

with the partial derivatives of i and j given by

$$(3.A8) \quad \left(\frac{\partial i}{\partial T} \right)_P = a - \frac{c}{T^2} - \frac{2d}{T^3} + \left(e - \frac{g}{T^2} \right) \log \rho + \left(eT + f + \frac{g}{T} \right) \frac{1}{\rho \ln(10)} \left(\frac{\partial \rho}{\partial T} \right)_P$$

$$(3.A9) \quad \left(\frac{\partial j}{\partial T} \right)_P = - \frac{B}{T^2}$$

$$(3.A10) \quad \left(\frac{\partial^2 i}{\partial T^2} \right)_P = \frac{2c}{T^3} + \frac{6d}{T^4} + \frac{2g}{T^3} \log \rho + 2 \left(e - \frac{g}{T^2} \right) \frac{1}{\rho \ln(10)} \left(\frac{\partial \rho}{\partial T} \right)_P$$

$$\begin{aligned}
& -\left(eT + f + \frac{g}{T}\right) \frac{1}{\rho^2 \ln(10)} \left(\frac{\partial \rho}{\partial T}\right)_P \left(\frac{\partial \rho}{\partial T}\right)_P + \left(eT + f + \frac{g}{T}\right) \frac{1}{\rho \ln(10)} \left(\frac{\partial^2 \rho}{\partial T^2}\right)_P \\
(3.A11) \quad & \left(\frac{\partial^2 j}{\partial T^2}\right)_P = \frac{2B}{T^3}
\end{aligned}$$

Appendix 3-2. Built-in options for calculation of temperature and pressure correction to standard molar (partial molal) properties of substances and reactions using data in ReacDC records (GEM-Selektor v.2.2.3 PSI).

Code	Model	Input parameters
KZZ	Langrangian interpolation of discrete $\log K$ values	table with experimental $\log K$ values (up to 20 temperatures and 10 pressures), entered into logKTP array
K3C	3-term extrapolation with constant reaction volume	$\log K$ of reaction at at 25 °C and 1 bar, constant heat capacity and volume of reaction
K2C	2-term extrapolation with constant reaction volume	$\log K$ of reaction at at 25 °C and 1 bar, constant entropy ($dC_{pr} = 0$) and volume of reaction
K1C	1-term extrapolation with constant reaction volume	$\log K$ of reaction at at 25 °C and 1 bar, constant Gibbs energy and volume of reaction
K0C	1-term extrapolation with constant reaction volume	$\log K$ of reaction at at 25 °C and 1 bar, constant $\log K$ ($dH_r = 0$) and volume of reaction
KLC	empirical function $\log K = f(T)$ with constant reaction volume	$\log K$ of reaction at at 25 °C and 1 bar, up to 7 empirical coefficients (a_0 to a_6), entered into aiLgKr array
KXC	empirical function $dC_{pr} = f(T)$ with constant reaction volume	$\log K$ of reaction at at 25 °C and 1 bar, up to 5 empirical coefficients (a_0 to a_4), entered into adCpT array
KY0	modified Ryzhenko-Bryzgalin (MRB) model	$\log K$ of reaction at at 25 °C and 1 bar, MRB coefficients (pK_{298} , A , B) entered into a_dST array
KR0	Marshall-Franck density model	$\log K$ of reaction at at 25 °C and 1 bar, up to 7 empirical coefficients (a to g) entered into a_dST array
K3P	prediction of S° , C_p° and V° of aqueous complexes using Pronsprep97 algorithm from Sverjensky et al. (1997)	$\log K$ of dissociation reaction at at 25 °C and 1 bar (see Appendix 3.3)
KEP	prediction of S° , C_p° and V° of aqueous hydroxide complexes using an algorithm from Shock et al. (1997)	$\log K$ of dissociation reaction at at 25 °C and 1 bar (see Appendix 3.3)

Note: alternative to assuming constant molar volume of reaction (as set by the third letter 'C' in the code), the molar volume can also be calculated from five empirical coefficients. This option is invoked by setting the third letter to 'K' (e.g., **K3K** instead of **K3C**) and entering the empirical coefficients for $V=f(T,P)$ into **advTP** array.

Appendix 3.3. Using Pronsprep, Pronsprep-OH and Parcor algorithms for prediction of standard state and HKF equation of state parameters in GEM-Selektor

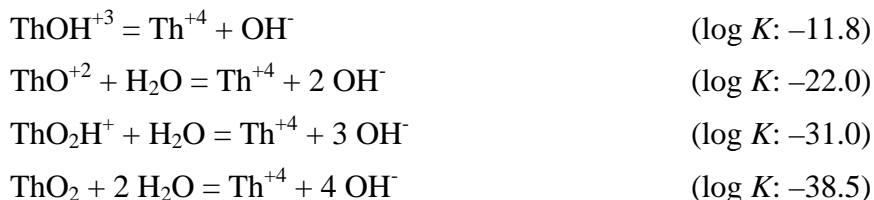
These methods for estimation of standard state and HKF (Helgeson-Kirkham-Flowers equation of state) parameters for aqueous species were developed by E.L.Shock and D.A.Sverjensky as supporting tools for the extension of SUPCRT92 data base. The algorithms are now built into the GEM-Selektor code; they only work for two specific classes of species where empirical correlations between properties have been found (Sverjensky et al., 1997; Shock et al., 1997; Shock and Helgeson, 1988). These include (1) simple mononuclear metal complexes with simple ligands (Sverjensky et al., 1997), and (2) mononuclear hydroxide complexes (Shock et al., 1997), both with ligand numbers up to 4. Possible ligands for the metal complexes are halides (F^- , Cl^- , Br^- , I^-), carbonates (CO_3^{2-} and HCO_3^-), sulfates and bisulfides (SO_4^{2-} , HSO_4^- , HS^-), with possible extension to phosphates ($H_2PO_4^-$, HPO_4^{2-} , PO_4^{3-}) and nitrates (NO_3^-).

In both Pronsprep and Pronsprep-OH variants, the procedure includes two principal steps. In step one, the standard state properties (S° , Cp° , V°) are predicted using the Pronsprep (simple metal complexes) or Pronsprep-OH (hydroxide complexes) algorithm. This part is done in ReacDC module in Thermodynamic Database Management group. Execution of either Pronsprep or Pronsprep-OH will automatically create a new DComp record. The prediction of HKF parameters from the standard state properties is then done through the Parcor algorithm (Shock and Helgeson, 1988) by recalculating that record in the DComp module. It is very important that definition of the metal complex species (including hydroxides) is (1) always done in terms of dissociation and (2) that stepwise formation constants (that are commonly reported in experimental papers) are recalculated to give cumulative formation constants. Examples for typical reaction stoichiometries for Th fluoride and hydroxide species are given below.

Th fluoride complexes:

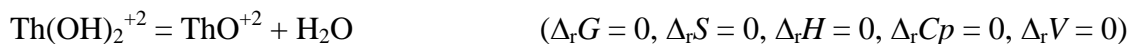


Th hydroxide complexes



Note that for hydroxide species, non-conventional (dehydrated) stoichiometries must be used, and that the reactions need to be written exactly according to the scheme that is listed above. Otherwise the correlation algorithm will either produce incorrect results or reaction properties of those reactions that involve H_2O will not be correct. After both Pronsprep calculations are completed, properties of species with conventional stoichiometry can be obtained by simply adding the appropriate properties of water. This has to be done before the Parcor algorithm in DComp is used to obtain HKF parameters from standard state properties. This utilizes the

convention that all thermodynamic properties for reactions between non-conventional and conventional hydroxide species are zero. For the Th hydroxide complexes in the example above, properties for conventional species are obtained from the relationships:



Practically, using the Pronsprep and Parcor algorithms requires that first a new ReacDC record is created (using ReacDC wizard), where the new complex is defined as given in the examples above. It is important to set the **RecMod** codes (step 1 of the wizard) to **K3P** for normal Pronsprep and to **KEP** for Pronsprep-OH. After completing steps 1 - 3 of the wizard, a dialog box appears that allows selecting the component species (cation and ligands, in addition water in case of Pronsprep-OH). Now Page1 of the new ReacDC record should be visible. Next you need to set up the stoichiometric coefficients for the reaction in the **SC_DC** field. Remember that the reaction has to be written as dissociation, so the new complex always gets a coefficient of -1 (reactant side), whereas cation and ligand have positive values (product side). Then you need to fill the remaining entries on Page1 of ReacDC. Essentially all values are set to 0 or unknown value (---) except the equilibrium constant ($\log K$) of the reaction that is placed in the **logKr[1]** field. For filling these fields correctly, simply follow the list below:

V0r[0]	molar volume effect of the reaction: set to 0
logKr[0]	K of the reaction: set to unknown value (---)
G0r[0]	Gibbs free energy of reaction: set to (---)
H0r[0]	enthalpy of the reaction: set to (---)
S0r[0]	entropy of the reaction: set to 0
Cpr[0]	heat capacity of the reaction: set to 0
V0r[1]	molar volume of the new complex: set to (---)
logKr[1]	$\log K$ of the reaction at 298.15 K and 1 bar: put here $\log K$ of the dissociation reaction
G0r[1]	Gibbs free energy of the new complex: set to (---)
H0r[1]	enthalpy of the new complex: set to (---)
S0r[1]	entropy of the new complex: set to (---)
Cpr[1]	heat capacity of the new complex: set to (---)

Save the record and recalculate it. Answer all the appearing questions with yes. The properties will be calculated and a new DComp record with estimated HKF parameters for the new complex automatically created. Now you have to change to the DComp module. Find the newly-created Dcomp record with your complex, and go to Page2 of the DComp window. There the **TPcMod** flags should be already set automatically to the code combination **HKP** to activate the Parcor estimation procedure. For some hydroxide complexes this currently does not work correctly, so one need to do remake of the DComp record and set the **TPcMod** codes to **HKP** manually on step 1 of the DComp wizard. Recalculate the record and you will see that the flags on Page2 will change to **HKF**. Recalculate the record once more (to get correct C_p° , V° and H° of the complex), and your new estimated data are ready for use in modeling.