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

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 ^{o}C.

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

$$\sum_{j=1}^{L} v_j M_j = 0, \quad j \in L_R \tag{3-1}$$

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, v_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 J·mol^{-1}; instead of Δ_r, Δ will be written everywhere below for brevity) at reference temperature T_r and pressure P_r is

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

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

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

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:

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

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

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

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

$$H^o_{L,T_r} = \Delta H^o_{T_r} - \sum_{j=1}^{L-1} \nu_j H^o_{j,T_r}, \quad j \neq L \tag{3-6},$$

$$S^o_{L,T_r} = \Delta S^o_{T_r} - \sum_{j=1}^{L-1} \nu_j S^o_{j,T_r}, \quad j \neq L \tag{3-7},$$

$$V^o_{L,T_r} = \Delta V^o_{T_r} - \sum_{j=1}^{L-1} \nu_j V^o_{j,T_r}, \quad j \neq L \tag{3-8},$$

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

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:

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

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

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

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

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

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

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, ΔCp (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

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

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

$$\Delta Cp_T = \Delta a_0 + \Delta a_1 T + \Delta a_2 T^{-2} + \Delta a_3 T^{-0.5} + \Delta a_4 T^2 \tag{3-17}$$

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

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

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 $\Delta Cp^o = f(T)$ coefficients (only the first five will be used according to eqn 3-17), $\Delta H^o_{T_r}$, and $\Delta S^o_{T_r}$ as follows. First, the standard "energy" properties of reaction are connected by the equation:

$$\Delta H^o_{T_r} = \Delta G^o_{T_r} + T_r \Delta S^o_{T_r} = -2.302585RT\log K_{T_r} + T_r \Delta S^o_{T_r} \tag{3-19}$$

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:

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

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

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

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

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

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

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

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

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

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

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

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

The entropy change in reaction at T is found as

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

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

$$\Delta H_T^o = \Delta G_T^o + T\Delta S_T^o =$$
$$= h_{T_r} + \Delta a_0 T + \Delta a_1 \frac{T^2}{2} - \Delta a_2 \frac{1}{T} + \Delta a_3 \cdot 2\sqrt{T} + \Delta a_4 \frac{T^3}{3} \tag{3-31}.$$

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):

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

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

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

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

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

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

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

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

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):

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

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

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

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 $Cp_T = const$) 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, respecitvely) 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 seldomly used in low-temperature geochemistry.

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:

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

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

$$A_2 = -\frac{0.4343}{R} \cdot \left(\Delta H^o_{T_r} - \Delta Cp_{T_r} T_r \right) \tag{3-45};$$

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

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

$$\Delta S^o_T = \Delta S^o_{T_r} + \Delta Cp_{T_r} \ln T \big/ T_r \tag{3-48};$$

$$\Delta H^o_T = \Delta H^o_{T_r} + \Delta Cp_{T_r} \left(T - T_r \right) \tag{3-49};$$

$$\Delta G^o_T = \Delta H^o_T - T \Delta S^o_T \tag{3-50}.$$

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 ^{o}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 $\Delta Cp_T = \Delta Cp_{T_r} = \Delta a_0 = 0$:

$$\log K_T = A_0 + A_2 T^{-1} = \frac{0.4343}{R} \left(\Delta S^o_{T_r} - \frac{\Delta H^o_{T_r}}{T} \right) \tag{3-51};$$

$$\Delta S^o_T = \Delta S^o_{T_r} \tag{3-52};$$

$$\Delta H^o_T = \Delta H^o_{T_r} \tag{3-53};$$

$$\Delta G^o_T = \Delta G^o_T - T \Delta S^o_T \tag{3-54}.$$

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

$$\log K_T = A_2 T^{-1} = -\frac{0.4343 \Delta H^o_{T_r}}{RT} \tag{3-55};$$

$$\Delta G^o_T = \Delta H^o_T = \Delta G^o_{T_r} = \Delta H^o_{T_r} \tag{3-56}.$$

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

$$\log K_T = A_0 = \frac{0.4343}{R} \Delta S^o_{T_r} = \log K_{T_r} \tag{3-57};$$

$$\Delta S^o_T = \Delta S^o_{T_r} \tag{3-58};$$

$$\Delta G^o_T = -T \Delta S^o_{T_r} \tag{3-59}.$$

These one-term extrapolations should be applied to isocoulombic reactions, where they can produce good predictions up to 300 ^{o}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 $\Delta S^o_{T_r}$, $\Delta H^o_{T_r}$ and $\Delta Cp^o_{T_r}$ values, after all unnecessary coefficients have been zeroed off.

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

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

and the pressure correction to the equilibrium constant becomes

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

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

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

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