## Part 1. Temperature corrections of standard molar thermodynamic properties of condensed substances and gases using data in DComp records of GEM-Selektor

This calculation is derived from integration of the heat capacity equation $Cp = f(T)$ which has the following form:

$$Cp = a_0 + \sum_i a_i T^{n_i}, \quad i = 1, \dots, 9 \tag{1-1}$$

where $a_i$ are the empirical coefficients, and power coefficients $n_i$ are: $n_0 = 0$; $n_1 = 1$; $n_2 = -2$; $n_3 = -0.5$; $n_4 = 2$; $n_5 = 3$; $n_6 = 4$; $n_7 = -3$; $n_8 = -1$; $n_9 = 0.5$. Some of these terms are used in most published databases. The corresponding isobaric heat capacity equation is:

$$Cp = a_0 + a_1 T + a_2 T^{-2} + a_3 T^{-0.5} + a_4 T^{2} + a_5 T^{3} + \\ + a_6 T^{4} + a_7 T^{-3} + a_8 T^{-1} + a_9 T^{0.5}. \tag{1-2}$$

As known from chemical thermodynamics (e.g., Anderson and Crerar, 1993), the increment of standard molar Gibbs energy $G^o$ at the reference pressure $P_r = 1$ bar from reference temperature $T_r$ to temperature of interest $T$ (in K) can be found by integrating the absolute molar entropy $S^o$ :

$$G_T^o - G_{T_r}^o = -\int_{T_r}^{T} S_T^o dT \tag{1-3}$$

where $S_T^o = \int_0^T {Cp}/{T}\, dT = S_{T_r}^o + \int_{T_r}^{T} {Cp}/{T}\, dT$ . Equation (1-3) can be transformed as follows:

$$G_T^o - G_{T_r}^o = -S_{T_r}^o (T - T_r) - \int_{T_r}^{T}\int_{T_r}^{T} {Cp}/{T}\, dTdT = -S_{T_r}^o (T - T_r) - T \sum_i M_{n_i} a_i \tag{1-4}$$

where the $M_{n_i}$ terms stand for the Temkin-Shwarzman functions of temperature (Dorogokupets et al., 1988):

$$M_{n_i} = \frac{T^{n_i}}{n_i(n_i+1)} + \frac{T_r^{n_i+1}}{T(n_i+1)} - \frac{T_r^{n_i}}{n_i}.$$

Using these functions and coefficients $n_i$ from eqn. (1-1), separate terms can be defined:

$$F_{G0} = TM_o = T \ln {T}/{T_r} - T + T_r;$$

$$F_{G1} = TM_1 = {1}/{2}(T - T_r)^2;$$

$$F_{G2} = TM_{-2} = (T - T_r)^2 / (2T \cdot T_r^2);$$

$$F_{G3} = TM_{-0.5} = 2\left(\sqrt{T} - \sqrt{T_r}\right)^2 / \sqrt{T_r};$$

$$F_{G4} = TM_2 = \left(T^3 + 2T_r^3 - 3T \cdot T_r^2\right)/6;$$

$$F_{G5} = TM_3 = \left(T^4 + 3T_r^4 - 4T \cdot T_r^3\right)/12;$$

$$F_{G6} = TM_4 = \left(T^5 + 4T_r^5 - 5T \cdot T_r^4\right)/20;$$

$$F_{G7} = TM_{-3} = \left(T_r^3 - 3T^2T_r + 2T^3\right)/\left(6T^2T_r^3\right);$$

$$F_{G8} = TM_{-1} = {}^{T}\!/_{T_r} - 1 - \ln {}^{T}\!/_{T_r};$$

$$F_{G9} = TM_{0.5} = {}^{2}\!/_{3}\left(2T\sqrt{T} - 3T\sqrt{T_r} + T_r\sqrt{T_r}\right).$$

Now, the standard molar apparent Gibbs energy function $g^o{}_T$ of a substance can be calculated easily at reference pressure $P_r$ = 1 bar and temperature of interest $T \neq T_r$ (usually, reference temperature $T_r$ = 298.15 K):

$$\begin{aligned} g_T^o &= G_{T_r}^o - S_{T_r}^o\left(T - T_r\right) - T\sum_i M_{n_i} a_i = \\ &= G_{T_r}^o - S_{T_r}^o\left(T - T_r\right) - a_0F_{G0} - a_1F_{G1} - a_2F_{G2} - a_3F_{G3} - a_4F_{G4} - \\ &\quad - a_5F_{G5} - a_6F_{G6} - a_7F_{G7} - a_8F_{G8} - a_9F_{G9} \end{aligned} \qquad (1\text{-}5)$$

In a similar way, the standard molar entropy $S_T^o$ at $P_r$ and $T$ can be calculated

$$\begin{aligned} S_T^o &= \int_0^T {}^{Cp}\!/_{T}\, dT = S_{T_r}^o + \int_{T_r}^T {}^{Cp}\!/_{T}\, dT = S_{T_r}^o + a_0 \ln {}^{T}\!/_{T_r} + a_1\left(T - T_r\right) + \\ &+ {}^{1}\!/_{2} a_2\left({}^{1}\!/_{T_r^2} - {}^{1}\!/_{T^2}\right) + 2a_3\left({}^{1}\!/_{\sqrt{T_r}} - {}^{1}\!/_{\sqrt{T}}\right) + {}^{1}\!/_{2} a_4\left(T^2 - T_r^2\right) + \\ &+ {}^{1}\!/_{3} a_5\left(T^3 - T_r^3\right) + {}^{1}\!/_{4} a_6\left(T^4 - T_r^4\right) + {}^{1}\!/_{3} a_7\left({}^{1}\!/_{T_r^3} - {}^{1}\!/_{T^3}\right) + \\ &+ a_8\left({}^{1}\!/_{T_r} - {}^{1}\!/_{T}\right) + 2a_9\left(\sqrt{T} - \sqrt{T_r}\right) \end{aligned} \qquad (1\text{-}6),$$

as well as the standard molar apparent enthalpy function $i_T^o$:

$$\begin{aligned} i_T^o &= H_{T_r}^o + \int_{T_r}^T Cp\, dT = H_{T_r}^o + a_0\left(T - T_r\right) + {}^{1}\!/_{2} a_1\left(T^2 - T_r^2\right) + a_2\left({}^{1}\!/_{T_r} - {}^{1}\!/_{T}\right) + \\ &+ 2a_3\left(\sqrt{T} - \sqrt{T_r}\right) + {}^{1}\!/_{3} a_4\left(T^3 - T_r^3\right) + {}^{1}\!/_{4} a_5\left(T^4 - T_r^4\right) + {}^{1}\!/_{5} a_6\left(T^5 - T_r^5\right) + \\ &{}^{1}\!/_{2} a_7\left({}^{1}\!/_{T_r^2} - {}^{1}\!/_{T^2}\right) + a_8 \ln {}^{T}\!/_{T_r} + {}^{2}\!/_{3} a_9\left(T\sqrt{T} + T_r\sqrt{T_r}\right) \end{aligned} \qquad (1\text{-}7)$$

For any compound substance, the apparent molar $g_T^o$ and $i_T^o$ can be converted into standard molar Gibbs energy $G_{f,T}^o$ and enthalpy $H_{f,T}^o$ of formation from elements, respectively:

$$G_{f,T}^o = g_T^o(\text{compound}) - \sum g_T^o(\text{elements}); \qquad (1\text{-}8)$$

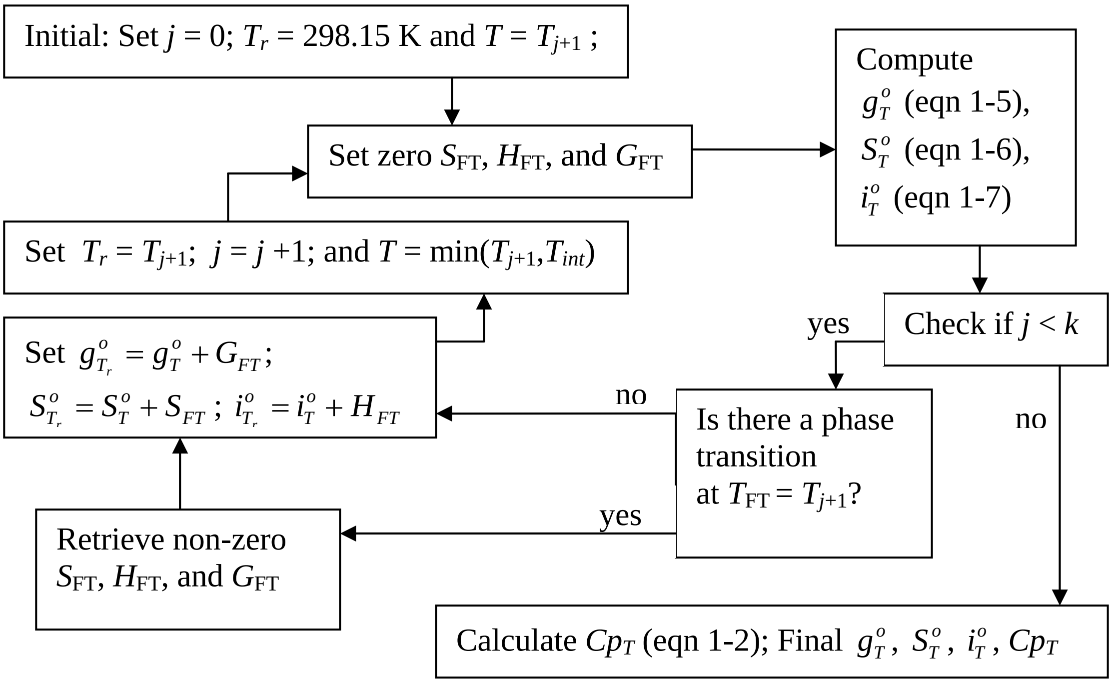
$$H^o_{f,T} = i^o_T(\text{compound}) - \sum i^o_T(\text{elements}) \,. \tag{1-9}$$

It follows that at $T_r$ =298.15 K, $g^o_{298} = G^o_{f,298}$ and $i^o_{298} = H^o_{f,298}$ because, for any element at its standard state, $g^o_{T_r} = G^o_{f,T_r} = 0$ and $i^o_{T_r} = H^o_{f,T_r} = 0$ by convention. Note that in Selektor codes (as well as in SUPCRT92; Johnson et al., 1992), apparent molar functions $g^o_T$ and $i^o_T$, but not the formation functions $G^o_{f,T}$ and $H^o_{f,T}$ are calculated throughout at elevated temperatures.

It is possible that, within a wide temperature range, the heat capacity function $Cp = f(T)$ is approximated by more than one set of coefficients of the form eqns (1-1) and (1-2). In the DComp data format, up to 10 such sets are allowed, and each set of coefficients must be supplied with a temperature applicability interval [$T_{min}$; $T_{max}$]. No break is allowed within the whole temperature range covered by $n(Q)$ sets; i.e. $T^{(q)}_{\min} = T^{(q-1)}_{\max}$, $q > 0$, $q = 0, 1, ..., n(Q)$.

For simplicity, let $T_0$ be the lowest temperature for the first $Cp$ approximation interval; $T_1$ be the upper temperature for the latter ($T_0$ to $T_1$) and at the same time – the lower boundary for the next interval ($T_1$ to $T_2$), and so on. Usually, $T_0$ equals 273.15 or 298.15 K, and some of the intermediate temperature boundaries refer also to temperatures of phase transitions at $P = P_r$.

Let $k$ be the index of the temperature interval containing the temperature of interest $T_{int}$. Obviously, if $k = 0$ and $T_0 \le T_r < T_1$ then $T_0 \le T_{int} \le T_1$ and eqns (1-2) and (1-5) to (1-7) apply directly using the first set of $Cp=f(T)$ coefficients. If $k > 0$ then the value of molar $Cp$ at $T = T_{int}$ where $T_k \le T_{int} \le T_{k+1}$ is still found from eqn (1-2) applied directly to the $k$-th set of $Cp$ coefficients. However, the values of $g^o_T$, $i^o_T$ and $S^o_T$ must be calculated incrementally in $k$ loops, as shown in the flow chart below, which also includes accounting for optional molar increments $S_{\mathrm{FT}}$, $H_{\mathrm{FT}}$, $G_{\mathrm{FT}}$ at phase transitions. It is required that the temperature of any phase transition $T_{FT}$ (at $P_r$) always co-insides with one of the boundary temperatures $T_{j+1}$.



Note that usage of GEM solvers of equilibria does not really require representing phase transitions in a single DComp record as for a single dependent component. Polymorph modifications, as well as solid, liquid and gaseous states of a substance can be represented as different phases or phase components (i.e. separate DComp records), because GEM will always select the most stable one at *T,P* of interest. Besides, this also allows circumventing the problem of pressure dependence of the phase transition temperature.

## References

Anderson G.M., Crerar D.A. (1993) *Thermodynamics in geochemistry: The equilibrium model.* Oxford Univ. Press, N.Y.,Oxford.

Dorogokupets P.I., Karpov I.K., Lashkevich V.V., Naigebauer V.A., Kazmin L.A. (1988) Isobaric-isothermal potentials of minerals, gases and aqueous species in the “Selektor” program package. In: *Physicochemical models in geochemistry* (Kiselev A.I., Karpov I.K., eds.), Nauka Publ., Novosibirsk, p. 124-147 (in Russian).

Johnson J.W., Oelkers E., Helgeson H.C. (1992) SUPCRT92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bar and 0 to 1000 $^{o}$C. *Comp. Geosci.*, **18**, 899-947.

**Appendix 1.1.** Built-in options for calculation of temperature and pressure correction to standard molar (partial molal) properties of condensed substances and fluids (gases) using data in DComp records (GEM-Selektor v. 3.0).

| Code | Model | Input parameters |
|---|---|---|
| **`CSC`** | integration of heat capacity, constant molar volume | empirical *Cp* coefficients ($a_0$ to $a_9$) entered into **`aiCpT`** array; optional phase transition parameters entered into **`FT_p`** array |
| **`CSK`** | integration of heat capacity, molar volume from empirical $V = f(T,P)$ function | empirical *Cp* coefficients ($a_0$ to $a_9$) entered into **`aiCpT`** array; 5 empirical coefficients for molar volume ($a_0$, $a_1$, $a_3$, $b_0$, $b_1$) entered into **`aiVTP`** array; optional phase transition parameters entered into **`FT_p`** array |
| **`CSE`** | integration of heat capacity, molar volume from HP Birch-Murnaghan equation | empirical *Cp* coefficients ($a_0$ to $a_9$) entered into **`aiCpT`** array; isothermal compressibility and isobaric expansibility into **`BetAlp`** fields |
| **`CHE`** | integration of heat capacity with Landau contribution, molar volume from HP Birch-Murnaghan equation | empirical *Cp* coefficients ($a_0$ to $a_9$) entered into **`aiCpT`** array; isothermal compressibility and isobaric expansibility into **`BetAlp`** fields; *Smax* and *Tcrit* of Lambda transition into **`LamST`** fields; *Vmax* into **`ab[0]`** field |
| **`CSB`** | integration of heat capacity, molar volume from Birch-Murnaghan equation | empirical *Cp* coefficients ($a_0$ to $a_9$) entered into **`aiCpT`** array; coefficients of BM equation into **`ai0Dc`** array |
| **`CSS`** | integration of ideal gas heat capacity, *VdP* contribution from Churakov-Gottschalk (CG) fluid EoS | empirical *Cp* coefficients ($a_0$ to $a_9$)entered into **`aiCpT`** array; coefficients of CG fluid EoS (*sig*, *eps*, *mu*, *alp*) into **`Cemp_s`** array |
| **`CSR`** | integration of ideal gas heat capacity, *VdP* contribution from Peng-Robinson-Stryjek-Vera (PRSV) fluid EoS | empirical *Cp* coefficients ($a_0$ to $a_9$) entered into **`aiCpT`** array; coefficients of PRSV fluid EoS (*Tc*, *Pc*, $\omega$, *k1*, *k2*, *k3*) into **`CritPg`** array |
| **`CS7`** | integration of ideal gas heat capacity, *VdP* contribution from Peng-Robinson (PR78) fluid EoS | empirical *Cp* coefficients ($a_0$ to $a_9$) entered into **`aiCpT`** array; coefficients of PR78 fluid EoS (*Tc*, *Pc*, $\omega$) into **`CritPg`** array |
| **`CS8`** | integration of ideal gas heat capacity, *VdP* contribution from compensated Redlich-Kwong (CORK) fluid EoS | empirical *Cp* coefficients ($a_0$ to $a_9$) entered into **`aiCpT`** array; coefficients of CORK fluid EoS (*Tc*, *Pc*) into **`CritPg`** array; for $H_2O$ and $CO_2$ special built-in routines are used that are activated through the DComp species codes V ($H_2O$) and C ($CO_2$) |
| **`CST`** | integration of ideal gas heat capacity, *VdP* contribution from Soave-Redlich-Kwong (SRK) fluid EoS | empirical *Cp* coefficients ($a_0$ to $a_9$) entered into **`aiCpT`** array; coefficients of SRK fluid EoS (*Tc*, *Pc*, $\omega$) into **`CritPg`** array |

**Appendix 1.2.** Built-in options for calculation of temperature and pressure correction to standard molar (partial molal) properties of aqueous species (and water) using data in DComp records (GEM-Selektor v. 3.0).

| Code | Model | Input parameters |
|---|---|---|
| **`CSA`** | integration of heat capacity, hydration properties of aqueous species from the Akinfiev-Diamond nonelectrolyte model | empirical Cp coefficients ($a_0$ to $a_9$) entered into **`aiCpT`** array; 3 coefficients of the Akinfiev-Diamond nonelectrolyte model (*xi*, *a*, *b*) into **`aiNEs`** array |
| **`HWF`** | water properties (stable state in single-phase fields, liquid properties on two-phase curve) from Haar-Gallagher-Kell (HGK) model | only standard state data need to be provided; paramters of HKF model in **`aiHKF`** array are all set to zero |
| **`HWG`** | properties of water vapor (on two-phase curve) from Haar-Gallagher-Kell (HGK) model | only standard state data need to be provided; paramters of HKF model in **`aiHKF`** array are all set to zero |
| **`HKF`** | aqueous species properties from revised Helgeson-Kirkham-Flowers (HKF) model | coefficients of revised HKF model ($a_1$, $a_2$, $a_3$, $a_4$, $c_1$, $c_2$, $\omega_0$) into **`aiHKF`** array (in their original calorie-based units) |
| **`HKP`** | prediction of HKF parameters of aqueous complexes using Parcor correlation algorithm | DComp record is automatically created from ReacDC calculation in PRONSPREP/Parcor mode. Only recalculation of DComp is required to obtain correct standard state properties. Upon this, the code will be automatically changed to **`HKF`**. |