

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:

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

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:

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

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 :

$$G_T^o - G_{T_r}^o = - \int_{T_r}^T S_T^o dT \quad (1-3),$$

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:

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

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:

$$\begin{aligned} F_{G0} &= TM_o = T \ln T/T_r - T + T_r; \\ F_{G1} &= TM_1 = 1/2 (T - T_r)^2; \\ F_{G2} &= TM_{-2} = (T - T_r)^2 / (2T \cdot T_r^2); \\ F_{G3} &= TM_{-0.5} = 2(\sqrt{T} - \sqrt{T_r})^2 / \sqrt{T_r}; \\ F_{G4} &= TM_2 = (T^3 + 2T_r^3 - 3T \cdot T_r^2) / 6; \end{aligned}$$

$$\begin{aligned}
F_{G5} &= TM_3 = (T^4 + 3T_r^4 - 4T \cdot T_r^3)/12; \\
F_{G6} &= TM_4 = (T^5 + 4T_r^5 - 5T \cdot T_r^4)/20; \\
F_{G7} &= TM_{-3} = (T_r^3 - 3T^2T_r + 2T^3)/(6T^2T_r^3); \\
F_{G8} &= TM_{-1} = T/T_r - 1 - \ln T/T_r; \\
F_{G9} &= TM_{0.5} = 2/3(2T\sqrt{T} - 3T\sqrt{T_r} + T_r\sqrt{T_r}).
\end{aligned}$$

Now, the standard molar apparent Gibbs energy function g_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):

$$\begin{aligned}
g_T^\circ &= G_{T_r}^\circ - S_{T_r}^\circ(T - T_r) - T \sum_i M_{n_i} a_i = \\
&= G_{T_r}^\circ - S_{T_r}^\circ(T - T_r) - a_0 F_{G0} - a_1 F_{G1} - a_2 F_{G2} - a_3 F_{G3} - a_4 F_{G4} - \\
&\quad - a_5 F_{G5} - a_6 F_{G6} - a_7 F_{G7} - a_8 F_{G8} - a_9 F_{G9}
\end{aligned} \tag{1-5}$$

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

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

as well as the standard molar apparent enthalpy function i_T° :

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

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

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

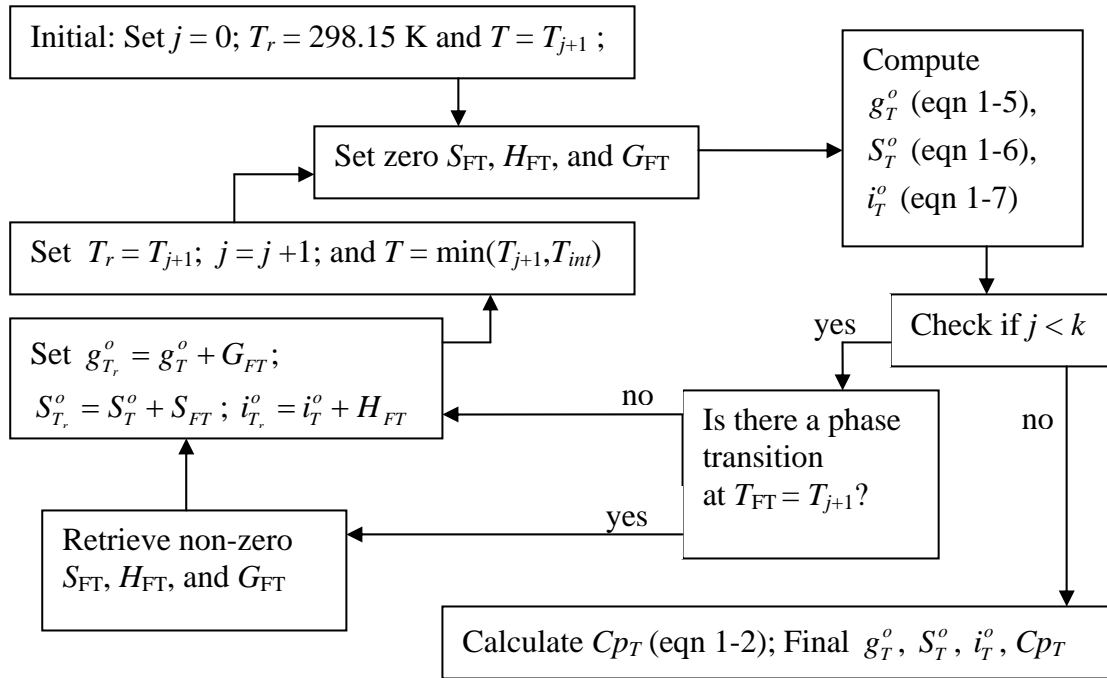
$$H_{f,T}^o = i_T^o(\text{compound}) - \sum i_T^o(\text{elements}). \quad (1-9)$$

It follows that at $T_r = 298.15$ K, $g_{298}^o = G_{f,298}^o$ and $i_{298}^o = H_{f,298}^o$ because, for any element at its standard state, $g_{T_r}^o = G_{f,T_r}^o = 0$ and $i_{T_r}^o = H_{f,T_r}^o = 0$ by convention. Note that in Selektor codes (as well as in SUPCRT92 [Johnson et al., 1992]), apparent molar functions g_T^o and i_T^o , but not the formation functions $G_{f,T}^o$ and $H_{f,T}^o$ 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. $T_{min}^{(q)} = T_{max}^{(q-1)}$, $q > 0, q = 0, 1, \dots, n(Q)$.

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 $T_0 \leq T_r < T_1$ then $T_0 \leq T_{int} \leq T_1$ 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 $T_k \leq T_{int} \leq T_{k+1}$ is still found from eqn (1-2) applied directly to the k -th set of Cp coefficients. However, the values of g_T^o , i_T^o and S_T^o must be calculated incrementally in k loops, as shown in the flow chart below, which also includes accounting for optional molar increments S_{FT} , H_{FT} , G_{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 to Part 1

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* (eds. Kiselev A.I. and Karpov I.K.), 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 °C. *Computers and Geosciences* **18**, 899-947.

Appendix 1-1a. 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.2.2.3 PSI).

| Code | Model | Input parameters |
|------------|---|---|
| CSC | integration of heat capacity, constant molar volume | empirical C_p 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 C_p 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 C_p 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 C_p coefficients (a_0 to a_9) entered into aiCpT array; isothermal compressibility and isobaric expansibility into BetAlp fields; S_{max} and T_{crit} of Lambda transition into LamST fields; V_{max} into ab[0] field |
| CSB | integration of heat capacity, molar volume from Birch-Murnaghan equation | empirical C_p 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 C_p 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 C_p coefficients (a_0 to a_9) entered into aiCpT array; coefficients of PRSV fluid EoS ($T_c, P_c, \omega, k1, k2, k3$) into CritPg array |
| CST | integration of ideal gas heat capacity, VdP contribution from Soave-Redlich-Kwong (SRK) fluid EoS | empirical C_p coefficients (a_0 to a_9) entered into aiCpT array; coefficients of SRK fluid EoS (T_c, P_c, ω) into CritPg array |

Appendix 1-1b. 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.2.2.3 PSI).

| Code | Model | Input parameters |
|------------|---|--|
| CSA | integration of heat capacity, hydration properties of aqueous species from the Akinfiyev-Diamond nonelectrolyte model | empirical Cp coefficients (a_0 to a_9) entered into aiCpT array; 3 coefficients of the Akinfiyev-Diamond nonelectrolyte model (x_i , a , b) into aiNES array |
| HWF | water properties from Haar-Gallagher-Kell (HGK) model | only standard state data need to be provided; parameters 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 , ω_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 . |