Part 2. Pressure corrections for standard molar thermodynamic properties of condensed substances using data from DComp records of GEM-Selektor

After correction from reference temperature (T_r, usually 298.15 K) to temperature of interest T, the molar thermodynamic functions of substances can be corrected from reference pressure P_r (usually 1 bar) to elevated pressure of interest P using the standard molar volume V^o.

At moderate pressures and temperatures (100-200 ^{o}C), molar volumes of solids and liquids can be assumed constant, or $V_T = V^o_{298}$. This leads to the following simple corrections:

$$g_{T,P} = g_T^o + V_{298}^o (P - P_r);$$
$$S_{T,P} = S_T^o; \qquad\qquad\qquad (2\text{-}1a,b,c)$$
$$i_{T,P} = i_T^o + V_{298}^o (P - P_r);$$

At higher temperatures and pressures $P \gg 1$ bar (when $P \approx P - P_r$), molar volumes of condensed substances are no longer constant. There are several ways to describe the thermal expansion and the compressibility of minerals, melts and liquid water.

According to Dorogokupets et al. [1988], the dependence of molar volume V_T on T and P at $P \gg 1$ bar ($P \approx P - P_r$) is taken in the following form:

$$V_{T,P} = V_{298}^o + V_{298}^o \left(A_0(T - T_r) + A_1(T - T_r)^2 + A_2(T - T_r)^3 \right) + V_{298}^o \left(B_0 P + B_1 P^2 \right) \quad (2\text{-}2).$$

The above equation becomes equivalent to that given by Berman [1988] after setting $A_2=0$. Using eqn (2-2), the molar Gibbs energy function at T and P can be obtained as:

$$g_{T,P} = g_T^o + \int_1^P V_T dP = g_T^o + V_{298}^o P[1 + A_0(T - T_r) + A_1(T - T_r)^2 + A_2(T - T_r)^3 +$$
$$+ \tfrac{1}{2} B_0 P + \tfrac{1}{3} B_1 P^2] \qquad\qquad (2\text{-}3).$$

The molar entropy at T and P bar can be calculated as

$$S_{T,P} = S_T^o - \int_1^P \frac{\partial V}{\partial T} dP = S_T^o - V_{298}^o P\left[A_0 + 2A_1(T - T_r) + 3A_2(T - T_r)^2\right] \qquad (2\text{-}4),$$

and the molar enthalpy function – as

$$i_{T,P} = i_T^o + \int_1^P \left(V_T - T\frac{\partial V}{\partial T}\right) dP = i_T^o + V_{298}^o P[1 - T_r A_0 - A_1(T - T_r)(T + T_r) +$$
$$+ A_2(T - T_r)^2(2T + T_r) + \tfrac{1}{2} B_0 P + \tfrac{1}{3} B_1 P^2] \qquad (2\text{-}5).$$

These calculations are implemented in Selektor codes since 1988. From eqn (2-2), coefficients of thermal expansion α and compressibility β can be evaluated as:

$$\alpha = \frac{1}{V^o_{298}}\left(\frac{\partial V}{\partial T}\right)_P = A_0 + 2A_1(T - T_r) + 3A_2(T - T_r)^2 \qquad \text{(2-6);}$$

$$\beta = -\frac{1}{V^o_{298}}\left(\frac{\partial V}{\partial P}\right)_T = -B_0 - 2P \cdot B_1 \qquad \text{(2-7).}$$

Using thermal expansion and compressibility coefficients and assuming that both are constant, the molar volume at T, P can be alternatively calculated as:

$$V_{T,P} = V^o_T[1 + \alpha(T - T_r)] \cdot (1 - \beta \cdot P) \qquad \text{(2-8).}$$

Alternatively, instead of the empirical eqn (2-2) or the approximate eqn (2-8), one can consider using temperature-dependent isobaric thermal expansion and compressibility, as suggested by Holland and Powell [1998]. They defined the thermal expansion coefficient as

$$\alpha_T = a\left(1 - \frac{10}{\sqrt{T}}\right) \qquad \text{(2-9),}$$

where the input parameter a is a "limiting" thermal expansion value at high temperatures. This gives the following temperature correction for the standard molar volume:

$$V^o_T = V^o_{T_r}[1 + a(T - T_r) - 20a(\sqrt{T} - \sqrt{T_r})] \qquad \text{(2-10).}$$

Compressibility of solid phases as function of pressure is handled using the Murnaghan equation of state (EoS):

$$P = \frac{\kappa}{\kappa'}\left[\left(\frac{V_P}{V_{P_r}}\right)^{\kappa'} - 1\right], \qquad \text{(2-11),}$$

where κ is the bulk modulus (in units of pressure) and $\kappa' = 4$ is the pressure derivative of the bulk modulus. Upon rearranging, one obtains

$$V_{T,P} = V^o_T\left[1 - \frac{4P}{\kappa_T + 4P}\right]^{1/4} \qquad \text{(2-12),}$$

where V^o_T is given in eqn (2-10) and $\kappa_T = \kappa_{298}[1 - 1.5 \cdot 10^{-4}(T - T_r)]$ [Holland and Powell, 1998], both should be taken in kbar in eqns (2-11) to (2-13) and (2-15). This results in the following expression for the molar Gibbs energy at T,P:

$$g_{T,P} = g^o_T + \int_1^P V_T dP =$$

$$= g^o_T + \frac{1}{3}V^o_{T_r}[1 + a(T - T_r) - 20a(\sqrt{T} - \sqrt{T_r})]\kappa_T\left[\left(1 - \frac{4P}{\kappa_T}\right)^{3/4} - 1\right] \qquad \text{(2-13).}$$

It follows from eqn (2-10) and the definition $\alpha V_{298}^o = \left(\dfrac{\partial V}{\partial T}\right)_P$ that the molar entropy at *T,P* is

$$S_{T,P} = S_T^o - \int_1^P \frac{\partial V}{\partial T} dP = S_T^o - V_{298}^o P\left(a - \frac{10a}{\sqrt{T}}\right) \tag{2-14},$$

For the molar enthalpy function at *T,P*, one calculates

$$i_{T,P} = i_T^o + \Delta_P G + T\Delta_P S = i_T^o - TV_{298}^o P\left(a - \frac{10a}{\sqrt{T}}\right) +$$

$$+ \tfrac{1}{3}V_{T_r}^o [1 + a(T - T_r) - 20a(\sqrt{T} - \sqrt{T_r})]\kappa_T\left[\left(1 - \frac{4P}{\kappa_T}\right)^{3/4} - 1\right] \tag{2-15}.$$

Alternative pressure corrections (using a different approximation of the Birch-Murnaghan EoS and a different form of thermal expansion) are implemented for the data from M.Gottschalk's database [1997] imported into GEM-Selektor DComp format (described in a separate document).

References to Part 2

Berman R.G. (1988): Internally consistent thermodynamic data for minerals in the system Na_2O-K_2O-CaO-MgO-FeO-Fe_2O_3-Al_2O_3-SiO_2-TiO_2-H_2O-CO_2. *Journal of Petrology* **29**, 445-522.

Dorogokupets P.I., Karpov I.K., Lashkevich V.V., Naigebauer V.A. and 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).

Holland T.J.B. and Powell R. (1998): An internally consistent thermodynamic data set for phases of petrological interest. *Journal of Metamorphic Geology* **16**, 309-343.

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