

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

2.1. Pressure corrections to condensed substances

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 °C), molar volumes of solids and liquids can be assumed constant, or $V_T = V_{298}^o$. This leads to the following simple corrections:

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

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:

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

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:

$$\begin{aligned} g_{T,P} &= g_T^o + \int_1^P V_T dP = g_T^o + V_{298}^o P \left[1 + A_0(T - T_r) + A_1(T - T_r)^2 + A_2(T - T_r)^3 + \right. \\ &\quad \left. + \frac{1}{2} B_0 P + \frac{1}{3} B_1 P^2 \right] \end{aligned} \quad (2-3).$$

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

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

and the molar enthalpy function as:

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

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:

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

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

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

$$V_{T,P} = V_T^o [1 + \alpha(T - T_r)] \cdot (1 - \beta \cdot P) \quad (2-8).$$

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:

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

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:

$$V_T^o = V_{T_r}^o [1 + a(T - T_r) - 20a(\sqrt{T} - \sqrt{T_r})] \quad (2-10).$$

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

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

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:

$$V_{T,P} = V_T^o \left[1 - \frac{4P}{\kappa_T + 4P} \right]^{1/4} \quad (2-12),$$

where V_T^o is given in eqn (2-10) and $\kappa_T = \kappa_{298} [1 - 1.5 \cdot 10^{-4}(T - T_r)]$ (Holland and Powell, 1998). Values of κ_T and κ_{298} 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 :

$$\begin{aligned} g_{T,P} &= g_T^o + \int_1^P V_T dP = \\ &= g_T^o + \frac{1}{3} V_{T_r}^o [1 + a(T - T_r) - 20a(\sqrt{T} - \sqrt{T_r})] \kappa_T \left[\left(1 + \frac{4P}{\kappa_T} \right)^{3/4} - 1 \right] \end{aligned} \quad (2-13).$$

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

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

For the molar enthalpy function at T, P , one then calculates:

$$\begin{aligned} i_{T,P} = i_T^o + \Delta_P G + T \Delta_P S = i_T^o - T V_{298}^o P \left(a - 10a/\sqrt{T} \right) \\ + \frac{1}{3} V_{T_r}^o [1 + a(T - T_r) - 20a(\sqrt{T} - \sqrt{T_r})] \kappa_T \left[\left(1 + \frac{4P}{\kappa_T} \right)^{3/4} - 1 \right] \end{aligned} \quad (2-15).$$

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 (Gottschalk, 1997) imported into GEM-Selektor DComp format (to be described in a separate document).

2.2. Pressure corrections to aqueous nonelectrolytes through properties of hydration

The most commonly used approach for calculating the standard state thermodynamic properties of aqueous species at elevated temperatures and pressures applies the revised Helgeson-Kirkham-Flowers (HKF) equation of state (Tanger and Helgeson, 1988). This model was originally developed for charged aqueous species and its extension to aqueous nonelectrolyte species (Shock and Helgeson, 1989) generally lacks a rigorous theoretical basis. Consequently, application of this model to aqueous nonelectrolytes faces intrinsic limitations. The performance of the HKF model at supercritical conditions and in the near-critical region of water is not very good, which has resulted in ongoing efforts to develop more adequate equations of state for aqueous nonelectrolytes (Plyasunov et al., 2000a; 2000b; Sedlbauer et al., 2000; Akinfiev and Diamond, 2003). These models are all based on the Gibbs energy (and other properties) of hydration of aqueous species, which is defined as follows:

$$G_{T,P} = G_{ig}^o + \Delta_{hyd} G^o \quad (2-16),$$

where G_{ig}^o is the Gibbs energy of the aqueous solute in the ideal gas state, and $\Delta_{hyd} G^o$ is the Gibbs energy of hydration. This accounts for the transfer of the aqueous solute from the ideal gas state to the solvated aqueous species. All other partial molal properties of the aqueous species are calculated through statements analogous to eq. (2-16). The only exception is the partial molal volume of species, which is calculated directly from the equation of state without reference to the volumetric properties of the ideal gas. The Akinfiev-Diamond model for aqueous nonelectrolytes was implemented into GEM-Selektor as a special case of pressure correction. The molal thermodynamic properties of the species in the ideal gas state are calculated through standard heat capacity integration, and the hydration properties are then added as a pressure correction. The Gibbs energy of hydration is calculated as (Akinfiev and Diamond, 2003):

$$\Delta_{hyd} G^\circ = -RT \ln N_w + (1 - \xi) RT \ln f_{H_2O}^\circ + RT \xi \ln \left(\frac{\bar{R}T}{M_w} \rho_{H_2O} \right) + R \left[T \rho_{H_2O} \left[a + b \left(\frac{10^3}{T} \right)^{0.5} \right] \right] \quad (2-17)$$

Here, N_w is the number of moles H_2O in 1 kg (55.51), $f_{H_2O}^\circ$ is the standard state fugacity of H_2O , $\rho_{H_2O}^\circ$ is water density, \bar{R} is equal to 83.1451. The parameters a , b and ξ are empirical coefficients of the EoS model. The partial molal volume, entropy and heat capacity are calculated as (Akinfiev and Diamond, 2003):

$$V^\circ = V_{H_2O}^\circ (1 - \xi) + \xi \bar{R} T \frac{1}{\rho_{H_2O}} \frac{\partial \rho_{H_2O}}{\partial P} + \bar{R} \frac{\partial}{\partial P} \left[T \rho_{H_2O} \left[a + b \frac{10^3}{T} \right]^{0.5} \right] \quad (2-18)$$

$$\Delta_{hyd} S^\circ = (1 - \xi) (S_{H_2O}^\circ - S_{H_2O,ig}^\circ) + R \ln N_w - R \left(\xi + \xi \ln \frac{\bar{R}T}{M_w} + \xi \ln \rho_{H_2O} + \xi T \frac{1}{\rho_{H_2O}} \frac{\partial \rho_{H_2O}}{\partial T} \right) - R \frac{\partial}{\partial T} \left[T \rho_{H_2O} \left[a + b \left(\frac{10^3}{T} \right)^{0.5} \right] \right] \quad (2-19)$$

$$\Delta_{hyd} Cp^\circ = (1 - \xi) (Cp_{H_2O}^\circ - Cp_{H_2O,ig}^\circ) - R \left[\xi + 2\xi T \frac{1}{\rho_{H_2O}} \frac{\partial \rho_{H_2O}}{\partial T} - \xi \frac{T^2}{(\rho_{H_2O})^2} \left(\frac{\partial \rho_{H_2O}}{\partial T} \right)^2 + \xi \frac{T^2}{\rho_{H_2O}} \frac{\partial^2 \rho_{H_2O}}{\partial T^2} \right] - RT \frac{\partial^2}{\partial T^2} \left[T \rho_{H_2O} \left[a + b \left(\frac{10^3}{T} \right)^{0.5} \right] \right] \quad (2-20)$$

Solutions for the partial derivatives given in eqs. (2-18), (2-19) and (2-20) are given in Akinfiev and Diamond (2003). The enthalpy of hydration is obtained from the standard relationship:

$$\Delta_{hyd} G^\circ = \Delta_{hyd} H^\circ - T S_{hyd} G^\circ \quad (2-21),$$

The model requires the ideal gas properties of the aqueous solute and three empirical parameters, which are available for a number of common solutes such as $CO_2(aq)$, $H_2(aq)$, $O_2(aq)$ and $H_2S(aq)$. These empirical parameters can also be estimated from standard state properties at T_r and P_r using correlation equations from (Akinfiev and Diamond, 2003).

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