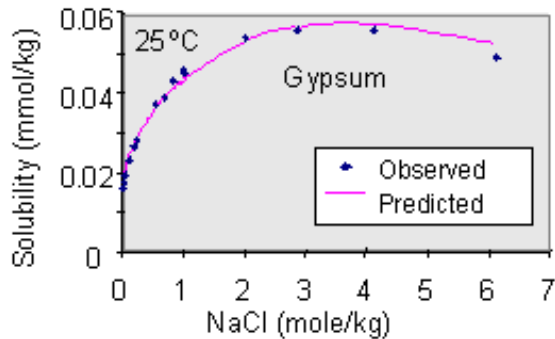


OLI Aqueous (AQ) Thermodynamic Model



In a multi-component system, the partial molal Gibbs energy of the *i*-th species is related to the molality (m_i) by $\bar{G}_i = \bar{G}_i^0 + RT \ln m_i \gamma_i$ where \bar{G}_i^0 is the standard-state partial Gibbs energy and γ_i is the activity coefficient. The thermodynamic properties of the system can be calculated if the standard-state Gibbs energies are available for all species as functions of temperature and pressure (i.e., $\bar{G}_i^0(T, P)$) and the activity coefficients are known as functions of the composition and temperature (i.e., $\gamma_i(\mathbf{m}, T)$).

STANDARD STATE : EQUATION OF STATE

The key to representing the standard-state properties over substantial temperature and pressure ranges is the accurate knowledge of the heat capacity and volume. For this purpose, the Helgeson-Kirkham-Flowers-Tanger (HKFT) equation of state is used. This equation accurately represents the standard-state thermodynamic functions for aqueous, ionic or neutral, species as functions of both temperature and pressure. In its revised form, the HKFT equation of state is capable of reproducing the standard-state properties up to 1000 °C and 5 kbar.

The HKFT equation is based on the solvation theory and expresses the standard-state thermodynamic functions as sums of structural and solvation contributions, the latter being dependent on the properties of the solvent (i.e., water). The standard partial molal volume (\bar{V}_p^0) and heat capacity (\bar{C}_p^0) are given by:

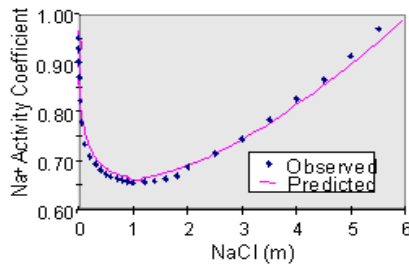
$$\bar{V}_p^0 = a_1 + \frac{a_2}{\Psi + P} + \left(a_3 + \frac{a_4}{\Psi + P} \right) \left(\frac{1}{T - \Theta} \right) - \omega Q + \left(\frac{1}{\varepsilon} - 1 \right) \left(\frac{\partial \omega}{\partial P} \right)_T$$

$$\bar{C}_p^0 = c_1 + \frac{c_2}{(T - \Theta)^2} - \left(\frac{2T}{(T - \Theta)^3} \right) \left(a_3(P - P_r) + a_4 \ln \frac{\Psi + P}{\Psi + P_r} \right) + \omega TX + 2TY \left(\frac{\partial \omega}{\partial T} \right)_p - T \left(\frac{1}{\varepsilon} - 1 \right) \left(\frac{\partial^2 \omega}{\partial T^2} \right)_p$$

where a_1, a_2, a_3, a_4, c_1 and c_2 represent species-dependent non-solvation parameters, T_r is the reference temperature of 298.15 K, P_r is the reference pressure of 1 bar, Ψ and Θ refer to solvent parameters equal to 2600 bars and 228 K, respectively. The variables $Q, X,$ and Y are functions of the pressure and temperature derivatives of the dielectric constant of water; the charge of the ionic species in water; and the electrostatic radius of the ion in water.

Thus, the HKF equation expresses the heat capacity and volume as functions of pure water properties and seven empirical parameters, which have been tabulated for large numbers of ions, complexes and neutral, both inorganic and organic, molecules.

AQUEOUS MODEL



The remaining thermodynamic properties are obtained by thermodynamic integration using the values of the Gibbs energy, enthalpy and entropy at reference temperature and pressure as integration constants.

ACTIVITY COEFFICIENT MODEL

The activity coefficient model used for representing the solution non-ideality is an extended form of an expression developed by Bromley. The Bromley equation is a combination of the Debye-Hückel term for long-range electrostatic interactions and a semi-empirical expression for short-range interactions between cations and anions. In a multi-component system, the activity coefficient of an ion i is given by

$$\log \gamma_i = \frac{-Az_i^2 I^{1/2}}{1 + I^{1/2}} + \sum_j^{NO} \left[\frac{|z_i| + |z_j|}{2} \right]^2 \left[\frac{(0.06 + 0.6B_{ij})|z_i z_j|}{\left(1 + \frac{1.5}{|z_i z_j|} I\right)^2} + B_{ij} + C_{ij} I + D_{ij} I^2 \right] m_j$$

where A is the Debye-Hückel coefficient which depends on temperature and solvent properties, z_i is the number of charges on ion i , I is the ionic strength (i.e., $I = 0.5 \sum z_i^2 m_i$), NO is the number of ions with charges opposite to that of ion i , and B_{ij} , C_{ij} and D_{ij} are empirical, temperature-dependent cation-anion interaction parameters. Bromley's original formulation contains only one interaction parameter, B_{ij} , which is sufficient for systems with moderate ionic strength. For concentrated systems, the two additional coefficients C_{ij} and D_{ij} usually become necessary. The three-parameter form of the Bromley model is capable of reproducing activity coefficients in solutions with ionic strength up to 30 mol/kg. The temperature dependence of the B_{ij} , C_{ij} and D_{ij} parameters is usually expressed using a simple quadratic function.

The Bromley model is restricted to interactions between cations and anions. For ion-molecule and molecule-molecule interactions, the well-known model of Pitzer is used. To calculate the fugacities of components in the gas phase, the Redlich-Kwong-Soave equation of state is used. In the absence of sufficient experimental data, reasonable predictions can be made using a method due to Meissner, which makes it possible to extrapolate the activity coefficients to higher ionic strengths based on only a single, experimental or predicted, data point.

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