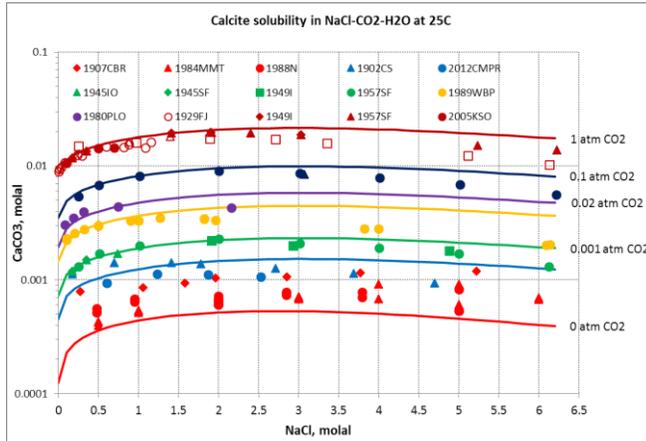


Aqueous (AQ) Thermodynamic Model

The OLI Aqueous (AQ) model is a mature electrolyte activity coefficient model that predicts the properties of solutions up to 30 molal ionic strength. Its accompanying database contains 6,000 species for 80+ elements (metals and non-metals) across multiple oxidation states.

This AQ model is suitable for applications involving electrolytes, gases, and hydrocarbons dissolved in water. Typical uses include:



- ✓ Corrosion rate calculations
- ✓ Mineral scaling during oil and gas production
- ✓ Flue gas scrubbing using lime, caustic, or limestone
- ✓ Sulfur oxidation
- ✓ Multiple effect evaporation of saline water
- ✓ Sour water (H₂S, NH₃, CO₂) stripping
- ✓ Transition metal hydrolysis and complexation reactions
- ✓ Water injection to deep wells
- ✓ Surface complexation of anions and cations onto hydrous ferric oxide
- ✓ Ion exchange reactions

The basis of this model can be described the following way: 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.

Activity coefficient model

The activity coefficient, γ_{ij} is computed using the Bromley-Zemaitis¹ activity model. This expression is a combination of the Debye-Hückel long-range electrostatic interactions and a semi-empirical expression for short-range interactions between cations and anions. The generalized form of the implemented activity coefficient is:

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

where A is the Debye-Hückel coefficient, *z_i* is the charge, I is the ionic strength, 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.

¹ L.A. Bromley. 1973. Thermodynamic properties of strong electrolytes in aqueous solutions. AIChE Journal. Vol. 19, No. 2, pp 313-320; J. F. Zemaitis, 1980, Predicting vapor-liquid-solid equilibria in multicomponent aqueous solutions of electrolytes, ACS Symposium Series, 133, (1980): p. 227-246.

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This model is restricted to cation-anion interactions. For ion-molecule and molecule-molecule interactions, the Pitzer model is used. To calculate gas-phase fugacities, 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.

Speciation and equilibrium constants

Each species is linked to other species through a chemical reaction. The final concentration of each species in solution, m_i , including ion pairs, complexes, and precipitates is obtained by solving the equilibrium equations for each chemical reaction in which it participates.



$$K_{intrinsic} = \frac{m_C m_D}{m_A m_B} \cdot \frac{\gamma_C \gamma_D}{\gamma_A \gamma_B}$$

The intrinsic equilibrium constant, $K_{intrinsic}$, for the reaction is obtained from the Gibbs free energy of reaction.

$$K_{intrinsic} = e^{\left(\frac{-\Delta_{Reaction} \bar{G}^0}{RT}\right)}$$

The Gibbs free energy of reaction is in turn, obtained from calculating the Gibbs energy of formation for each species in the reaction. This is done via the Helgeson-Kirkham-Flowers-Tanger equation of state (EOS).

$$\bar{G}_i^0 = \bar{G}_i^R - S_i^R(T - T_R) + f(a_i, a_2, a_3, a_4, c_1, c_2, \omega)$$

This EOS accurately quantifies a species' thermodynamic properties as a function of temperature and pressure. Other properties include total volume, enthalpy, heat capacity, and entropy. In its implemented form, this equation of state reproduces standard-state properties up to 1000 °C and 5 kbar.

Total species concentration

The final element for solving electrolyte systems is the total mass balance equation. Each element (e.g., Ca^{+2} , Fe^{+2} , Fe^{+3} , etc.) has an associated mass balance. For instance, in a calcium carbonate solution, the total calcium mass balance would be:

$$Ca_T(\text{moles}) = (m_{Ca^{+2}} + m_{CaOH^{+1}} + m_{CaHCO_3^{+1}} + m_{CaCO_3^0})V_{aq} + CaCO_3^{solid}$$

Combined model

Each variable in the equilibrium equation, K , γ , and m now has associated mathematical models. The number of equilibrium equations to be solved depends on the complexity of the solution. It is common to have several hundred equations in a given calculation to account for all the dissolved species, solid phases, gases, and organic components. All of equations are solved simultaneously using an advanced numerical solver. The output is the equilibrium composition and properties of the system.

