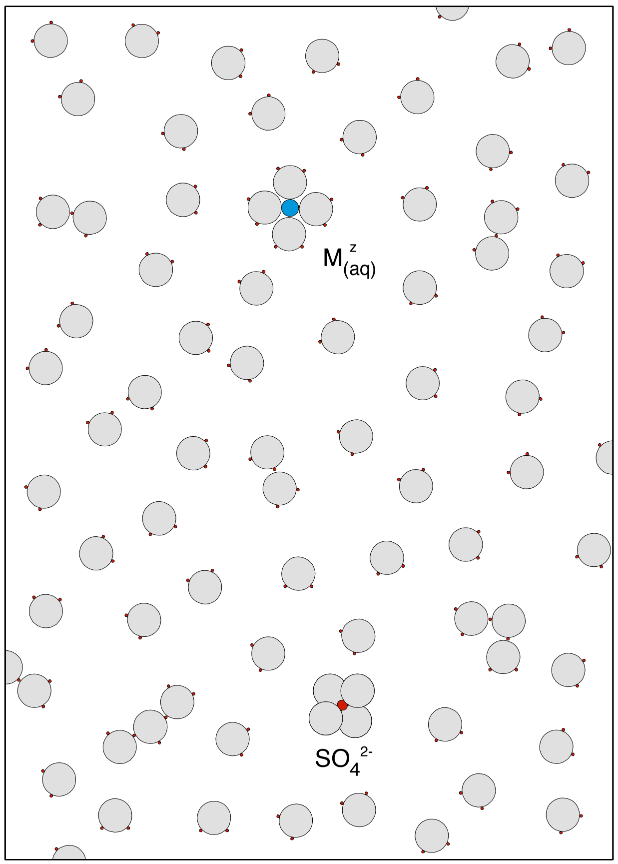
Railsback's *Some Fundamentals of Mineralogy and Geochemistry*

Activity and activity coefficients V: from infinitely dilute solutions to brines

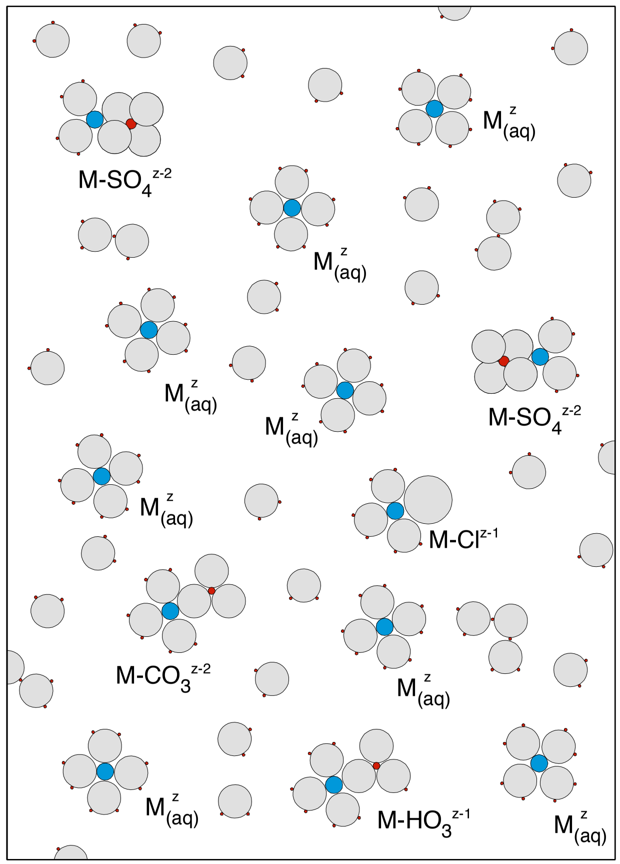
In previous pages of this series, two of the sketches below were used to illustrate the concepts of activity (*a*) and the activity coefficient (γ). This page adds the sketch at left, which shows a dilute solution that approximates an infinitely dilute solution. An infinitely dilute solution, despite being oxymoronic, is the condition wherein activity and the activity coefficient are defined. Consideration of that defining condition where $\gamma = 1$, wherein solutes are "fully" hydrated, explains how γ can be greater than 1 in a solution with fewer free H_2O molecules, like the brine at right.

an infinitely dilute solution



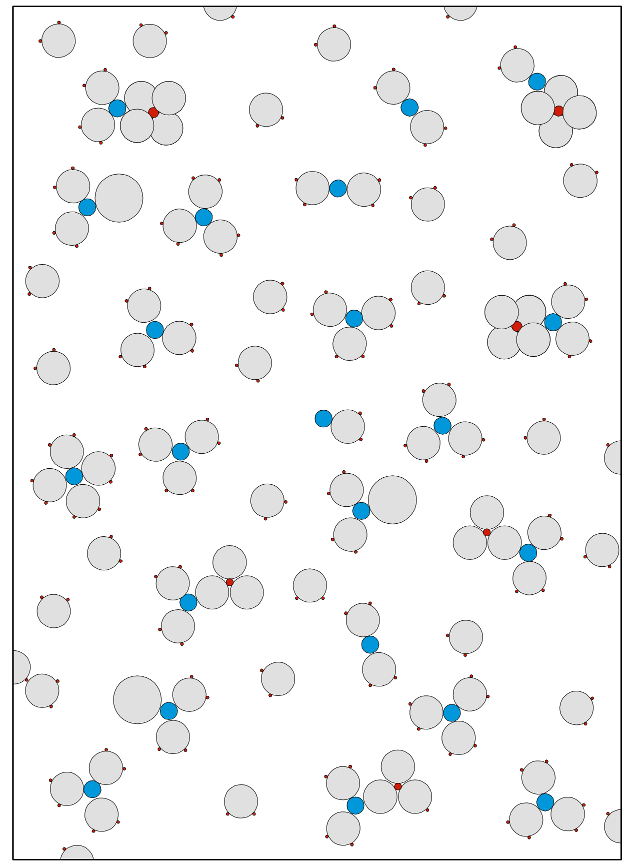
$a_i = m_i \quad \gamma_i = 1.0 \quad a_{H_2O} = 1.0$

a concentrated solution



$a_i < m_i \quad \gamma_i < 1.0 \quad a_{H_2O} > 0.99$

a very concentrated solution (a brine)



$a_i > m_i \quad \gamma_i > 1.0 \quad a_{H_2O} < 0.9$

The three sketches above have the same number of water molecules. However, they *are* schematic. In reality, cations would commonly be more extensively hydrated in ther inner sphere, cations would commonly have outer hydration spheres, the overall ratio of water molecules to solute entities would be much greater, and total charge of solutes would balance, rather than yield net positive charge.

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