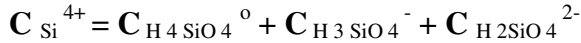


Determination of activity coefficients - primary concern is with the determination of γ for dissolved species in interstitial solutions.

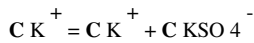
Several simplifying assumptions:

Assume that concentration (**C**) represents the sum of free ions plus ion pairs and complexes.

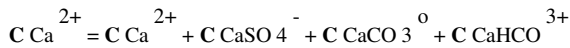
For example for dissolved silica species:



Case for dissolved potassium species:



Case for dissolved calcium species:



Using this convention, the activity coefficient γ becomes the total activity coefficient γ_T , where:

$$\gamma_T = a / C_T$$

This effect is important under conditions of high concentrations of dissolved ions, such as in sea water.

* see Table below from Berner 1980. Total activity coefficients for the major ions in seawater. T = 25°C, P = 1 atm., Salinity = 35 parts per thousand.

Ion	γ_T
Cl ⁻	0.681
Na ⁺	0.652
Mg ²⁺	0.215
SO ₄ ²⁻	0.121
Ca ²⁺	0.201
K ⁺	0.618
HCO ₃ ⁻	0.500
CO ₃ ²⁻	0.030

The activity is therefore, going to be a function of the ionic strength of the solution.

For ground water with total dissolved solids (i.e., salinity) up to the levels of sea water the γ_T is determined using the relationship

$$\gamma_T = (m / m_T) \gamma^*$$

where:

- m_T = total molality for a given element
- m = molality of the free ion
- γ^* = activity given by the Debye-Hückel limiting law

The molality of the free ion is calculated from mass balance expressions and ion-pair equilibrium expressions using an iterative method.

The value of γ^* is determined using the Debye-Hückel equation:

$$-\log \gamma_i^* = \frac{AZ_i^2 \sqrt{I}}{1 + a_i^0 B \sqrt{I}}$$

where:

- A, B = constants that are $f(T)$.
- a_i^0 = ion size parameter for ion i
- Z_i = valence of the ion i
- I = ionic strength

Ionic strength is defined as:

$$I = \frac{1}{2} \sum m_i Z_i^2$$

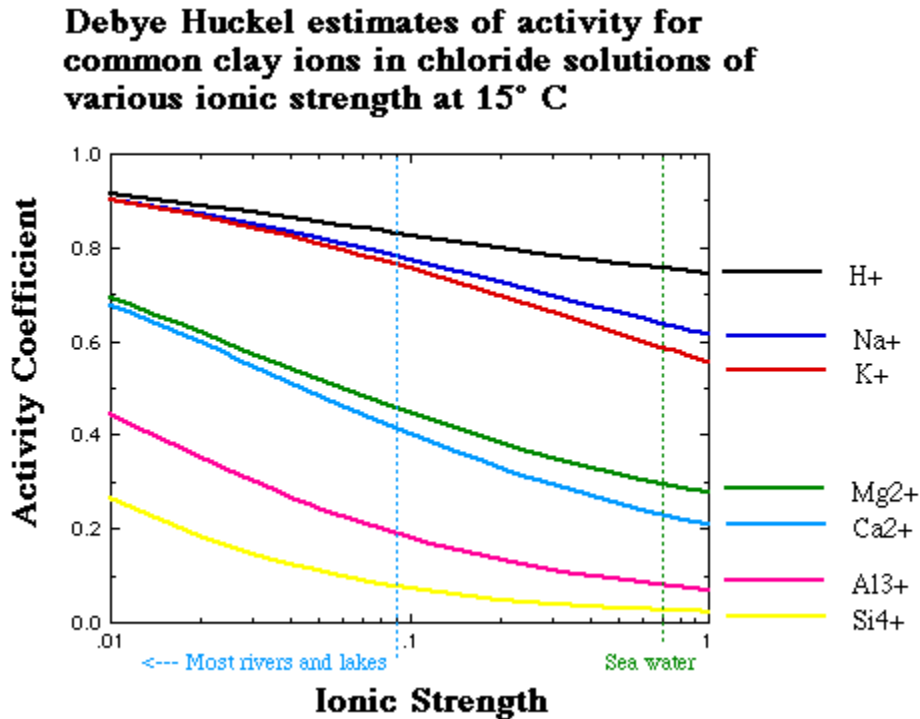
where,

m_i = molality of the i th species (mol . kg⁻¹)

A 1 m solution of CaCl₂ will have an ionic strength of

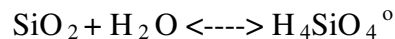
$$I = 1/2 [(1)(2)^2 + (2)(1)^2] = 3 m$$

A general plot of activity coefficient versus ionic strength for some common ion species in clays is shown below.



A common reaction that occurs in soils and sediments is that between solid SiO_2 and its ion complexes in solution. At pH values below 8 the only effective form of dissolve silica is orthosilicic acid.

Consider the reaction involving amorphous SiO_2 :



At 25° C:

$$K = a_{\text{H}_4\text{SiO}_4^0} = 2 \times 10^{-3}$$

where:

K = equilibrium solubility product.

recall that activity can be expressed in terms of concentration by the expression:

$$a_{\text{H}_4\text{SiO}_4^{\circ}} = \frac{\gamma_{\text{H}_4\text{SiO}_4^{\circ}}}{\rho_w^*} C_{\text{H}_4\text{SiO}_4^{\circ}}$$

recall ρ_w^* is the mass of water per volume of interstitial solution.

Therefore,

$$K = \frac{\gamma_{\text{H}_4\text{SiO}_4^{\circ}}}{\rho_w^*} C_{\text{H}_4\text{SiO}_4^{\circ}}$$

which simplifies the activity equation and introduces the concentration solubility product. Be careful to note the differences between the various forms of activity coefficients that are used in the literature.

$$K_c = \frac{\rho_w^*}{\gamma_{\text{H}_4\text{SiO}_4^{\circ}}} K = C_{\text{H}_4\text{SiO}_4^{\circ}}$$

Saturation index

Once the ion activity product is known, then the actual ion activity product can be used to create a dimensionless parameter called the saturation index (Ω) such that,

$$\Omega = \text{IAP}/K = \text{ICP}/K_c$$

where:

IAP = actual ion activity product

ICP = actual ion concentration product

K = equilibrium ion activity product (solubility product)

K_c = equilibrium ion concentration product.

It is now possible to express the state of saturation for a particular reaction by Ω , where:

if $\Omega > 1$, then the solution is supersaturated.

if $\Omega = 1$, then the solution is saturated.

if $\Omega < 1$, then the solution is undersaturated.