

Chemical weathering and secondary mineral formation

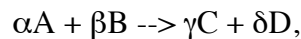
Construction of stability diagrams.

Equilibrium Processes

The change in concentration of any particular clay mineral phase occurs in response to the chemical state of the system. The primary processes that control the chemical states of a system include:

1. advection
2. diffusion
3. chemical reaction

The chemical reaction term is the driving force to compositional change and can be written in the general form:



where; A, B are the reactants and C, D are the products and α , β , γ and δ are the relative number of moles of each.

Example: Weathering of albite by carbonic acid to gibbsite



If the rate of chemical reaction is very rapid (in spite of advective and diffusive processes) and chemical equilibrium exists, then a thermodynamic approach to chemical reaction is possible.

Le chatelier's Principle – dynamic equilibrium adjust to “stress”.

In reality, NO net reaction can occur at equilibrium. However, the assumption is that there is so little kinetic impedance to the reaction that reactions occur at very small departures from equilibrium

How does one determine equilibrium concentrations?

This is expressed by way of the thermodynamic equilibrium constant, which is related to the Gibbs free energy (G) of the reactants and products.

$$\Delta G = \Delta H - T\Delta S$$

ΔH = change in enthalpy + exothermic (releases energy) - endothermic (absorbs energy)

ΔS = change in entropy (disorder in system)

+ ΔS more random (water)

- ΔS more ordered (ice)

T = temperature (Kelvin)

ΔG = change in reaction

+ ΔG endergonic (absorbs energy e.g. photosynthesis)

- ΔG exergonic (releases energy e.g. respiration).

Let: K = thermodynamic equilibrium constant

then one can write:

$$K = \frac{a_C^\gamma a_D^\delta}{a_A^\alpha a_B^\beta} \quad (\text{i.e., Products / Reactants})$$

Which can be stated as the activities (a) of the product over the reactants, each raised to the power of the relative molar abundance (at this point activities are assumed to be equal to molar concentrations, although this not generally the case; see below).

The difference in free energy of a reaction (ΔG_R) is a useful parameter to assess the tendency or likelihood for a given chemical reaction to proceed.

$$\Delta G_R = \Delta G^o_R + RT \ln \frac{a_C^\gamma a_D^\delta}{a_A^\alpha a_B^\beta}$$

For a chemical reaction to proceed spontaneously in the direction of the arrow, ΔG must be less than zero (there must be a decrease in free energy).

If $\Delta G_R = 0$, then the reaction will not proceed in either direction (at equilibrium state). In this case,

$$\Delta G^o_R = - RT \ln K_{eq}$$

Many calculations are done at 25° C (this is the form in which data are tabulated See Robie reference). R = gas constant = 8.3143 J K⁻¹ mol⁻¹

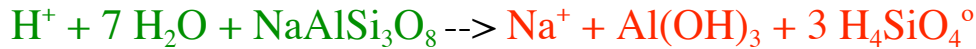
At T = 25° C (T = 298.2° Kelvin)

$$\Delta G_R^\circ = - 1.364 \log K_{eq} \text{ (log = base 10) kcal/mol}$$

$$\Delta G_R^\circ = - 5.708 \log K_{eq} \text{ (log = base 10) kJ/mol}$$

To adjust K for chemical reactions at different temperature and pressures, corrections can be made using appropriate thermodynamic data.

Example: $\Delta G_R = G_{\text{products}} - G_{\text{reactants}}$



$$0.0 \quad -237.14 \quad -3711.15 \quad -262.0 \quad -1154.86 \quad -1307.90$$

$$\Delta G_R^\circ = (-262.0 - 1154.86 - 3 * 1307.9) + (7 * 0237.14 + 3711.15) = 69.57 \text{ kJ/mol}$$

Activity - Once the equilibrium constant K is obtained from ΔG_R , the activities must be converted to concentrations (which is typically the measure that is made).

Activity Coefficients

The activity for dissolved species in solution can be expressed as

$$a = \gamma m$$

where:

γ = conventional molal activity coefficient (approaches one as solutions become more dilute).
 m = molality (moles per kg of H₂O).

Ionic Strength

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

i = species of interest, m = concentration, z = charge of species

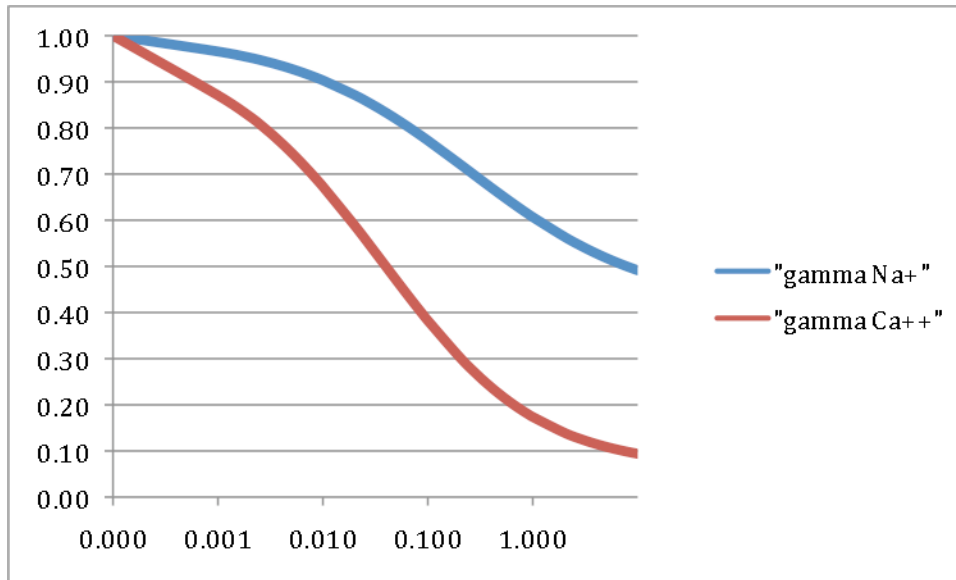
Activity coefficient as predicted by Debye-Huckel equation

$$\log \gamma_i = \frac{-Az_i^2 \sqrt{I}}{1 + Ba_o \sqrt{I}}$$

A, B = Temperature dependent parameters

a_o = ionic radius dependent parameter

The plot below is Debye-Huckel γ (y axis) versus ionic strength (x axis). $I_{\text{seawater}} \sim 0.7$



In terms of concentration of per unit volume of pore solution (C):

$$a = (\gamma / \rho_w^*) C$$

where ρ_w^* = mass of water per unit volume of interstitial solution.

In near surface conditions $\rho_w^* = 1$ therefore,

$$a = \gamma m$$

The solid solutions can be expressed as

$$a = \lambda X$$

where:

λ = rational molal activity coefficient (for major components as X approaches one so does λ).
 X = mole fraction of an end-member in a solid solution.

In most sedimentary systems we deal with end-members therefore, $X = 1$ and $\lambda = 1$.

Hence: $a = 1$ for solids.

Also, most pore waters are sufficiently dilute, that the activity of H_2O can be considered to be one.

$$a_{\text{H}_2\text{O}} = 1$$

For surface species adsorbed onto the surface of a clay mineral, there is a special convention adopted where:

$$a = \psi C$$

where:

ψ = surface activity coefficient

C = mass absorbed per unit mass of total sedimentary solids.

Graphical representation of mineral phases and the effect of aqueous fluid composition and temperature on their stability's.

Recall Gibb's phase rule.

$$f = c - p + 2$$

where:

- f = number of degrees of freedom
- c = number of components in the system
- p = number of phases in the system

variables include; $T, P, \mu_i, \mu_j \dots$

Example: $\text{K}_2\text{O} - \text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O}$ system

In a five-component system at constant T and P , description of a single phase requires 4 degrees of freedom

$$f = 5 - 1 + 2 = 6 - 2 (T,P) = 4$$

If the 4 variables are taken to be activities and 2 are held constant then we can make a 2 dimensional coordinate system where any reaction between any two pair of phases will produce univariant curve. It follows then that any reaction between three phases will be invariant.

The specific choice of variables is both dictated and represented by the formulas of the reacting species.

In the above system we might choose the aqueous species: $a_{\text{K}^+}, a_{\text{Na}^+}, a_{\text{H}^+}, a_{\text{H}_4\text{SiO}_4^0}$