

Notes 10: Liquid and solid solutions and K

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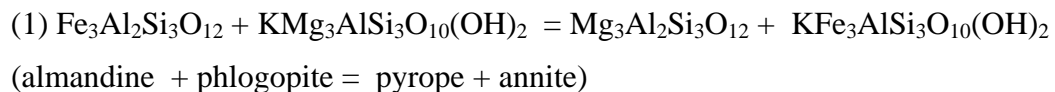
K as a function of P and T

For any reaction (easier with solid-solid reactions if the assumption of constant V_R and S_R can be made) one can calculate K-values at equilibrium as a function of P and T with a single value for G_R at a given T and P and V and S data. Inspection of any such plot, considering the equation for K, shows that dilution increases the range of conditions over which a particular set of products or reactants is stable (i.e. dilution extends stability). Common examples of this general phenomenon include melting point depression and boiling point elevation, with wet (vs. dry) melting being a good geologic example of melting point depression. It also follows that an increase in concentration will tend to decrease stability (i.e. increase in mole fraction or molality is coupled to a tendency for that endmember or solute to react).

Exchange reactions

Exchange reactions are reactions that involve two phases each of which has substitution of the same two elements in a single site. Common exchange reactions involve substitution of Fe and Mg in two Fe/Mg silicate minerals. Other examples are K and Na substituting in K/Na silicates, Ca and Mg substituting in Ca/Mg carbonates, and Sr and Ca dissolved in carbonate and sea water.

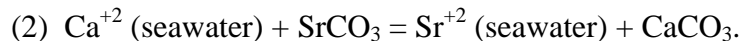
Examples:



The two phases are $(\text{Fe}, \text{Mg})_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (garnet) and $\text{K}(\text{Mg}, \text{Fe})_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ (biotite). Exchange reactions typically have very small V_R . Whereas S_R is also small, it is generally large compared to V_R so that S_R/V_R is large. For this reason exchange reactions make good thermometers.

For the reaction as written, $K = (a_{\text{pyr}})(a_{\text{ann}})/(a_{\text{alm}})(a_{\text{phl}})$.

If the solid solutions are ideal, then $K = (X_{\text{Mg}}^{\text{GAR}})(X_{\text{Fe}}^{\text{BIO}})/(X_{\text{Fe}}^{\text{GAR}})(X_{\text{Mg}}^{\text{BIO}})$.



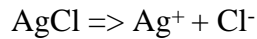
The two phases are seawater and $(\text{Ca}, \text{Sr})\text{CO}_3$ (aragonite). This exchange reaction is the basis for Sr/Ca thermometry in coral skeletons.

Solubility, solubility product, and ion activity product

Solubility is the maximum amount of a substance that can be dissolved in a solution that is in chemical equilibrium with a solid source of the solute. A solution in that state is called a 'saturated solution'

Solubility product, K_{sp} , is K , but for a system with a solid in equilibrium with its ions in dissolved form.

Example 1(assume STP).



$$K_{sp} = (a_{\text{Ag}^+})(a_{\text{Cl}^-})/a_{\text{AgCl}}$$

Since AgCl is a pure solid, its activity is 1. If the dissolved ions behave ideally then their activities are numerically equal to their molalities:

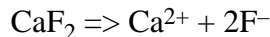
$$K_{sp} = (m_{\text{Ag}^+})(m_{\text{Cl}^-}) = 10^{-9.8}$$

$$m_{\text{Ag}^+} = m_{\text{Cl}^-} = 10^{-4.9} \text{ moles/kg}$$

Solids are not necessarily at equilibrium with the solutes in nature (you can have undersaturated and supersaturated solutions). We can define an IAP or ion activity product as an actual measured quantity

$$\text{IAP} = (m_{\text{Ag}^+})(m_{\text{Cl}^-}) \text{ where an IAP can be } =, < \text{ or } > K_{sp}$$

Example (mix of valences)



$$K_{sp} = 10^{-10.4} = (m_{\text{Ca}^{2+}})(m_{\text{F}^-})^2$$

If no other solutes, $K_{sp} = 10^{-10.4} = (m_{\text{Ca}^{2+}})(m_{\text{F}^-})^2 = (m_{\text{Ca}^{2+}})(2m_{\text{Ca}^{2+}})^2 = 4(m_{\text{Ca}^{2+}})^3$

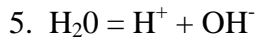
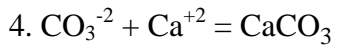
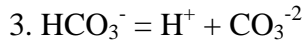
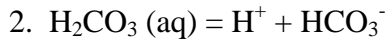
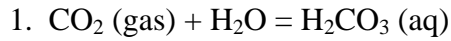
The substitution of $2m_{\text{Ca}^{2+}}$ for m_{F^-} is possible because there are twice as many F^- ions as Ca^{2+} ions in the solution.

We obtain $m_{\text{Ca}^{2+}} = 0.5 m_{\text{F}^-} = 2.2 \cdot 10^{-4} \text{ moles/kg}$

Carbonate equilibria, CO₂, and weathering

Imagine a system at STP with CaCO_3 solid in equilibrium with water and air with a fixed P_{CO_2} . The following ions/compounds will be present: CaCO_3 , CO_2 , H_2O , Ca^{2+} , HCO_3^- , CO_3^{2-} , H_2CO_3 , H^+ , OH^- . We know the activities of CaCO_3 (1 because it is a pure solid), H_2O (essentially 1 because the concentrations of the aqueous species are very low), and CO_2 (3×10^{-4} bars in the atmosphere). That leaves 6 concentrations of species that are not known. With 6 equations (largely $K = \dots$ equations), we can solve for these species.

The reactions among these species are as follows:



We know the equilibrium constants for these 5 equations at STP, leaving us with one additional equation needed to solve for the six species. The 6th equation comes from the requirement of electrical neutrality:

$$2 m_{\text{Ca}^{+2}} + m_{\text{H}^+} = 2m_{\text{CO}_3^{-2}} + m_{\text{HCO}_3^-} + m_{\text{OH}^-}.$$

With these equations we can solve for concentrations of all species. The concentrations are in the range of 10^{-3} to 10^{-8} m, with HCO_3^- having the highest concentration and H^+ having the lowest concentration. pH is about 8.3.