

## Lecture 9 Chemical Equilibrium and Speciation

(1) Supersaturated solutions:

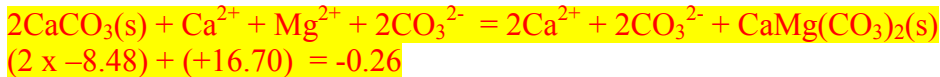
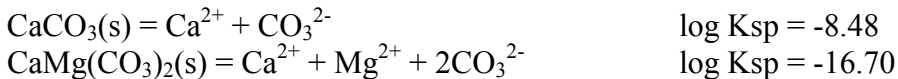
- (a) have more dissolved substances than predicted by solubility alone
- (b) prevent the spontaneous crystallization of dissolved chemicals
- (c) have much less dissolved substance than predicted by solubility
- (d) a and b but not c

(2) One way we can get the equilibrium constant for a reaction we are interested in is to combine other reactions for which we know the constants. Show how this is done by deriving the equilibrium constant for the reaction of calcite with  $Mg^{2+}$  to form the CaMg-carbonate mineral called dolomite as written below:



This is an important reaction used to describe the conversion of limestone to dolomite rock over geological time frames.

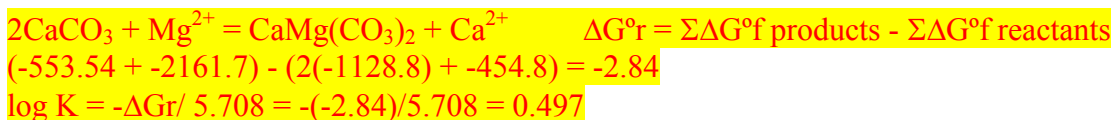
Combine (by addition or subtraction as necessary) the  $K_{eq}$  values for the following reactions (for 25°C) to get the  $K_{eq}$  (at 25°C) for the reaction of  $CaCO_3$  with  $Mg^{2+}$  to form dolomite as given above and derive an equation that expresses  $K_{eq}$  in terms of the  $K_{sp}$  listed above.



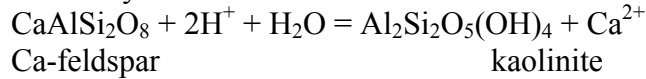
(3) The equilibrium constant for this reaction can also be calculated from the values of free energy of formation. From thermodynamic data tables (Stumm and Morgan, 1981) we obtain the following standard free energies of formation at 25°C.

- a) Calculate the standard free energy of reaction ( $\Delta G_r$ )
- b) Calculate the equilibrium constant  $K_{eq}$  at 25°C.

| Substance                                      | $\Delta G_f$ (kJ mol <sup>-1</sup> ) |
|--|--------------------------------------|
| CaCO <sub>3</sub> (calcite)                    | -1128.8                              |
| CaMg(CO <sub>3</sub> ) <sub>2</sub> (dolomite) | -2161.7                              |
| Ca <sup>2+</sup>                               | -553.54                              |
| Mg <sup>2+</sup>                               | -454.8                               |



(4) The breakdown of the silicate mineral Ca-feldspar (also called anorthite) to form kaolinite clay is an important weathering reaction, particularly in humid climate soils. The reaction may be written:



a). Calculate the equilibrium constant for this reaction given the following free energies of formation.

|                     |                |
|---------------------|----------------|
| Ca-feldspar         | -4001.4 kJ/mol |
| H <sup>+</sup>      | 0              |
| H <sub>2</sub> O(l) | -237.14 kJ/mol |
| kaolinite           | -3799.4 kJ/mol |
| Ca <sup>2+</sup>    | -553.54 kJ/mol |

$$\Delta G_r = (-3799.4 - 553.54) - (-4001.4 - 237.14) = -114.4$$

$$\log K = -\Delta G_r / 5.708 = 20.04 \quad K = 10^{20.04} = 1.1 \times 10^{20}$$

b) Assuming that soil moisture contains concentrations of [Ca<sup>2+</sup>] = 2 x 10<sup>-4</sup> mol/l, and behaves as an ideal solution (no activity corrections), at what pH would anorthite be in equilibrium with the kaolinite and, therefore not weather?

$$K = [\text{Ca}^{2+}] / [\text{H}^+]^2$$

$$[\text{H}^+]^2 = [\text{Ca}^{2+}] / K; \quad [\text{H}^+] = (2 \times 10^{-4} / 1.1 \times 10^{20})^{1/2}; \quad [\text{H}^+] = 1.348 \times 10^{-12} \quad \text{pH} = -\log [\text{H}^+] = 11.8$$

(5) Gypsum solubility is written as:



a) If we added gypsum to distilled water (with no other salts present) and let it come to equilibrium, what would the equilibrium concentration of total Ca be?

$$K_{sp} = [\text{Ca}^{2+}] \times [\text{SO}_4^{2-}]; \quad [\text{Ca}^{2+}] = [\text{SO}_4^{2-}]; \quad [\text{Ca}^{2+}] = K_{sp}/2 = 5.12 \times 10^{-3}$$

b) If the total sulfate concentration of seawater is 25.0 x 10<sup>-3</sup> mol kg<sup>-1</sup>, what would be the concentration of total Ca if gypsum was at solubility equilibrium? How does this compare with the actual concentration of seawater?

Is seawater saturated with respect to gypsum?

Concentrations and activity coefficients for seawater are:

$$[\text{Ca}^{2+}] = 10.28 \times 10^{-3} \quad \gamma_{\text{Ca}} = 0.28; \quad [\text{SO}_4^{2-}] = 28.00 \times 10^{-3} \quad \gamma_{\text{SO}_4} = 0.12$$

If the sulfate concentration is 25.0 x 10<sup>-3</sup> mol kg<sup>-1</sup> and the seawater is at solubility equilibrium then the concentration of Ca<sup>2+</sup> is:

$$K_{sp} = [\text{Ca}^{2+}] \gamma_{\text{Ca}} \times [\text{SO}_4^{2-}] \gamma_{\text{SO}_4} = [\text{Ca}] \times 0.28 \times 25.0 \times 10^{-3} \times 0.12 = 2.62 \times 10^{-5}$$

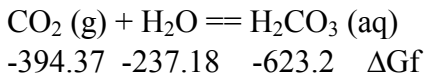
[Ca] = 31 x 10<sup>-3</sup> mol kg<sup>-1</sup>. The actual Ca concentration is less than that but the sulfate concentration in seawater is 28 x 10<sup>-3</sup> mol kg<sup>-1</sup>.

To calculate saturation we need to use the seawater concentrations and activity coefficients and compare to K<sub>sp</sub>.

$$K_{sp} = [\text{Ca}^{2+}] \gamma_{\text{Ca}} \times [\text{SO}_4^{2-}] \gamma_{\text{SO}_4} = 10.28 \times 10^{-3} \times 0.28 \times 28.0 \times 10^{-3} \times 0.12 = 9.67 \times 10^{-6}$$

This is less than 2.62 x 10<sup>-5</sup> so seawater is undersaturated.

(6) Calculate the solubility (K) of CO<sub>2</sub> in seawater using the ΔGf values and the relation between ΔGr and K

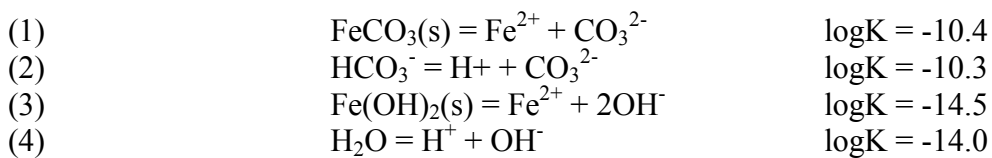


$$\Delta G_r = (-623.2) - (-394.37 + -237.18) = 8.35$$

$$\log K = -8.35/5.708 = 1.46 \quad K = 10^{1.46} = 29$$

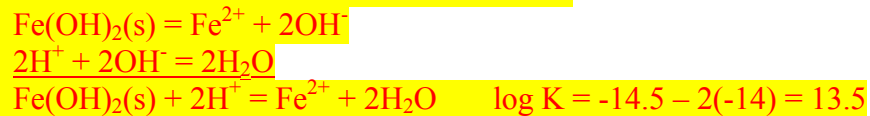
(7) One way we can get the equilibrium constant for a reaction we are interested in is to combine other reactions for which we know the constants. In anoxic water like the Black Sea dissolved iron can be present as either Fe(OH)<sub>2</sub>(s) or FeCO<sub>3</sub>(s).

Below are some needed reactions:

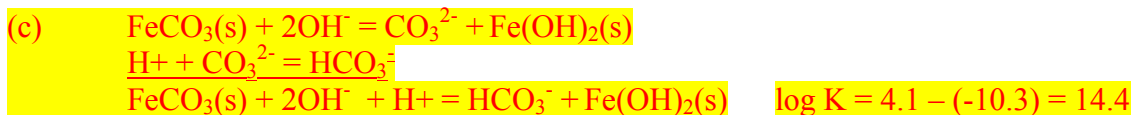
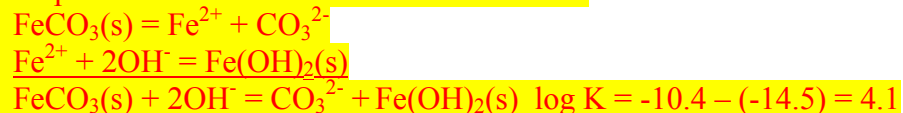


- (a) Write the reaction and give the equilibrium constant for the solubility of Fe(OH)<sub>2</sub>(s) in terms of H<sup>+</sup>.
- (b) Write the reaction and give the equilibrium constant for the conversion of FeCO<sub>3</sub> to Fe(OH)<sub>2</sub>
- (c) In seawater at pH 8 with HCO<sub>3</sub><sup>-</sup> = 2.0 x 10<sup>-3</sup>M, which phase of iron is more stable. Ignore activity corrections.

(a) This could be expressed as reaction # 3 minus 2 x reaction # 4:



(b) This could be expressed as reaction # 1 minus reaction # 3



$$K = 10^{14.4}$$

pH = 8                      H<sup>+</sup> = 10<sup>-8</sup>                      OH<sup>-</sup> = 10<sup>-6</sup>

$$K = \text{HCO}_3^- / [\text{H}^+] [\text{OH}]^2 = 2.0 \times 10^{-3} / 10^{-8} \times 10^{-12} = 2 \times 10^{17}$$

$$\log K = -\Delta G_r / 5.708; \quad \Delta G = -17.3 \times 5.708 = -98.74$$

Since ΔG is < 0 for the reaction, Fe(OH)<sub>2</sub>(s) is more stable.

(8) The precipitation and dissolution of  $\text{CaCO}_3$  is one of the important solubility reactions in seawater. The reaction can be written as:  $\text{CaCO}_3(\text{s}) = \text{Ca}^{2+} + \text{CO}_3^{2-}$

a) Calculate  $\Delta G_r$  for this reaction given the following  $\Delta G_f$

species  $\Delta G_f$

|                           |                               |
|---------------------------|-------------------------------|
| $\text{CaCO}_3(\text{s})$ | -1128.79 $\text{kJ mol}^{-1}$ |
| $\text{Ca}^{2+}$          | -553.58                       |
| $\text{CO}_3^{2-}$        | -527.81                       |

$$(-553.58 + -527.81) - (-1128.79) = 47.4 \text{ kJ mol}^{-1}$$

b) Calculate the equilibrium constant for this solubility reaction at  $25^\circ\text{C}$ .

$$\begin{aligned}\log K &= -\Delta G_r / 5.708 \\ -(47.4) / 5.708 &= -8.3 \\ K &= 5 \times 10^{-9}\end{aligned}$$

$[\text{CO}_3^{2-}]$  in surface water is about  $260 \mu\text{M}$  Ca is  $10.28 \text{ mM}$ , is the water at saturation with respect to  $\text{CaCO}_3$ ?

$$K = [\text{Ca}] \times [\text{CO}_3] = 260 \times 10^{-6} \times 10.28 \times 10^{-3} = 2.67 \times 10^{-6}$$

$$2.67 \times 10^{-6} > 5 \times 10^{-9} \text{ surface water is supersaturated}$$

In deep water at 4,500 meters in the Pacific  $[\text{CO}_3^{2-}]$  is about  $80 \mu\text{M}$ ;  $K_{sp}$  at  $4^\circ\text{C}$  and in-situ pressure is  $10^{-5.95}$ ; is the deep water at saturation with respect to  $\text{CaCO}_3$ ?

$$K = [\text{Ca}] \times [\text{CO}_3] = 80 \times 10^{-6} \times 10.28 \times 10^{-3} = 0.822 \times 10^{-6}$$

$$0.822 \times 10^{-6} < 10^{-5.95} \text{ so deep waters in the Pacific are undersaturated.}$$