Lecture 13: Acid-Base equilibria (continued)

recall the K_a is the acid dissociation constant (or acidity constant)

Carbonate system – acid-base equilibria

water is naturally acidic due to dissolution of CO_2 gas in water

will now calc pH using 2 relevant equil

$CO_2(g) + H_2O \Leftrightarrow H_2CO_3(aq)$

$K_H = [H_2CO_3]/P_{CO2}$

given conc of CO_2 = 360 ppm (0.00036 atm) and $K_s = 3.2 \times 10^{-2}$ M/atm

$[H_2CO_3] = 1.1 \times 10^{-5}$ M

$H_2CO_3(aq) \Leftrightarrow H^+(aq) + HCO_3^-(aq)$

$K_a = [H^+][HCO_3^-]/[H_2CO_3]$

given $K_a = 4.45 \times 10^{-7}$ and $[H_2CO_3]$ from above can calc $[H^+]$:

$K_a = [H^+][HCO_3^-]/[H_2CO_3]$

$4.45 \times 10^{-7} = x^2/(1.1 \times 10^{-5}\ M)$

$[H^+] = 2.2 \times 10^{-6}$ and pH = 5.65

(assuming all other rxns irrelevant)

Carbonate system –equilibria and the solubility product constant (K_{sp})

water dissolves and solvates many inorganic salts, most alkali (Na, K, Cs) and halogen (F, Cl) salts are completely soluble, nearly all others are only slightly soluble

We can calculate the concentration of Ca^{2+} in equilibrium with solid calcite ($CaCO_3(s)$) by assuming all other reactions are irrelevant

$CaCO_3(s) \Leftrightarrow Ca^{2+}(aq) + CO_3^{2-}(aq)$

$K_{sp} = [Ca^{2+}]\,[CO_3^{2-}]$

given $K_{sp} = 4.6 \times 10^{-9}$

can calc $[Ca^{2+}] = 6.8 \times 10^{-5}$ M

Carbonate system –equilibria and the basicity constant (K_b)

The basicity constant (K_b) is used to describe the reaction of a base (A^-) with water to produce hydroxide ion:

$A^- + H_2O \Leftrightarrow HA + OH^-$ (A^- = weak base)

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$ (note we neglect $[H_2O]$

Important relationship:

$$K_w = K_a K_b = \frac{[H^+][A^-]}{[HA]}\frac{[HA][OH^-]}{[A^-]} = [H^+][OH^-] = 1.00\times10^{-14}$$ ALWAYS

Now apply the basicity constant (K_b) to the carbonate system:

$$CO_3^{2-}(aq) + H_2O \Leftrightarrow HCO_3^-(aq) + OH^-(aq)$$

$$K_b = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]}$$

$$K_w = K_a K_b = \left(\frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}\right)\left(\frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]}\right) = [H^+][OH^-] = 1.00\times10^{-14} \quad \text{ALWAYS}$$

The significance of this relationship is that it relates the acidity and basicity of the acid/base system to the solvent (water).

This relationship can be used as an additional tool for solving more complex equilibria involving many reactions (simultaneous equilibria).