Example 5: Chemical Reactions and Equilibrium Constants – Surgical Strike and Perturbation

The origin of Carbonate Rocks

A quick review: activity $\{i\} = \gamma_i [C_i]$ (activity coefficient; concentration)

- $pH = -\log\{H^+\} = -\log[H^+]$

a low pH value means: acidic, high concentration of H^+

a high pH value means: basic, low H^+ concentration, high OH^- conc.

- partial pressure – the pressure exerted by an individual gas in a mixture of gasses

Earth's atmosphere	N_2	78.1%
	O_2	20.9%
	Ar	0.9%
Other: CO_2, NH_4, etc.		0.1%

- Henry's Law – the [partial] pressure of a gas above a solution is proportional to the concentration of the gas in the solution

$$P_g = K_H C_g$$

P_g: partial pressure of gas; K_H: Henry's Law Constant; C_g: molar concentration of gas in solution

$$\frac{P_g}{C_g} = K_H$$

What does this mean? if the pressure goes up, so does the concentration

Chemical Reactions and Equilibrium Constants

$$aA + bB \rightleftharpoons cC + dD$$

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad \frac{\text{products}}{\text{reactants}}$$

What does this mean?

add more reactants → products must increase, reaction is driven to the right

add more products → amount of reactants must increase, reaction driven to left

A few rules: for water in dilute solutions, $[H_2O] = 1$

for solids, $[solid] = 1$

example: $CaCO_{3(s)} \rightleftharpoons Ca^{2+}_{(aq)} + CO_{3\,(aq)}^{2-}$ $\quad K_{eq} = 4.8\times10^{-9} \approx 10^{-8.3}$

$$K_{eq} = 10^{-8.34} = \frac{[Ca^{2+}][CO_3^{2-}]}{[\cancel{CaCO_{3(s)}}]^1} = [Ca^{2+}][CO_3^{2-}] = K_{sp}$$

"solubility product"

example: $H_2O \rightleftharpoons H^+ + OH^-$ $\quad K_{eq} = 10^{-14}$

$$K_{eq} = 10^{-14} = \frac{[H^+][OH^-]}{[\cancel{H_2O}]^1} = [H^+][OH^-]$$

in acid nuetral water $[H^+] = [OH^-]$ so, $K_{eq} = 10^{-14} = [H^+][H^+] = [H^+]^2$

$$\Rightarrow [H^+] = 10^{-7} \quad \text{so } pH = -\log[H^+] = 7$$

Acids and Bases

Acids = proton donor

Bases = proton acceptor

Strong acids dissociate completely

$HCl \longrightarrow H^+ + Cl^-$ $K_A =$ 10^7 Strong!

$H_2SO_4 \longrightarrow H^+ + HSO_4^-$ $K_A =$ 10^3 Strong!

$HSO_4^- \longrightarrow H^+ + SO_4^{2-}$ $K_A =$ $10^{-1.99}$

$H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$

Weak acids only dissociate partially

$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$ $K_{A1} = 4.45 \times 10^{-7} = 10^{-6.35}$

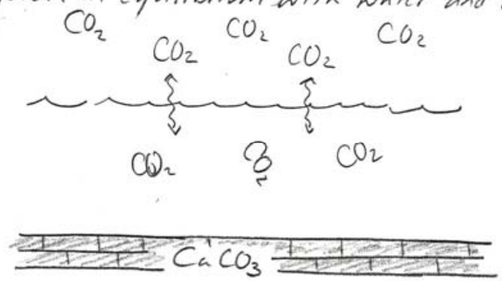
$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$ $K_{A2} = 4.69 \times 10^{-11} = 10^{-10.3}$

$10^x = 4.45 \times 10^{-7}$

$\log_{10}(10^x) = \log_{10}(4.45 \times 10^{-7})$

$x = \log_{10}(4.45 \times 10^{-7}) = 10^{-6.35}$

Now, we're ready to consider a carbonate system in equilibrium with water and CO_2 gas:



$CO_{2(g)} + H_2O \rightleftharpoons H_2CO_3$ $K_{eq} = 10^{-1.5}$

$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$ $K_{A_1} = 10^{-6.35}$

$HCO_3^- \rightleftharpoons H^+ + CO_3^{-2}$ $K_{A2} = 10^{-10.3}$

$\boxed{H_2O + CO_2 + \underset{\uparrow}{CaCO_{3(s)}} \rightleftharpoons Ca^{2+} + 2HCO_3^-}$ $K_{eq} =$

calcite or aragonite

What happens if we add more CO_2 to the atmosphere?

The reaction is driven to the right.
$CaCO_3$ is dissolved.

What happens if CO_2 gas escapes from the water?

The reaction is driven to the left.
$CaCO_3$ is precipitated.

What will happen if:

A) the water temperature increases?

CO_2 escapes, Carbonate precipitation is favored

B) the atmospheric pressure decreases?

CO_2 evolves from solution → $CaCO_3$ precipitates

C) the water is agitated? (waves)

lose CO_2 → reaction driven to left → $CaCO_3$ precip

D) the water pressure is decreased? (upwelling)

CO_2 gas evolves → precipitation

E) the salinity of the water is decreased?

$[Mg^{2+}]\downarrow$ → favors $CaCO_3$ precip

Note; When $T\uparrow$, the solubility product, K_{sp}, for $CaCO_3$ decreases

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$$

$$K_{sp} = \frac{[Ca^{2+}][CO_3^{2-}]}{[CaCO_3]} = 10^{-8.34}$$

$10^{-7} > 10^{-8.34}$

favors dissolution

$10^{-5.65} > 10^{-8.34}$

What effect does this have on $CaCO_3$ solubility?

lower solubility ⇒ precipitate