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

The origin of Carbonate Rocks

- A quick review:
  - pH = \(-\log [H^+]) = -\log [\text{acidic}]^
  - a low pH value means: acidic, high concentration of $H^+$
  - a high pH value means: basic, low $H^+$ concentration

- Partial pressure - the pressure exerted by an individual gas in a mixture of gases

  Earth's atmosphere
  - $N_2$: 78.17%
  - $O_2$: 20.95%
  - $Ar$: 0.93%

  Other: $CO_2$, $NH_3$, etc. 0.17%

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

  $P_g = K_H \cdot C_g$

  partial pressure of gas
  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

- a A + b B $\rightleftharpoons$ c C + d D

  $K_eq = \frac{[C]_e^c [D]_e^d}{[A]_e^a [B]_e^b}$

  products
  Reactants

  What does this mean?
  - add more reactants $\rightarrow$ products must increase
  - reaction is driven to the right
  - add more products $\rightarrow$ amount of reactants must increase
  - reaction driven to left

  A few rules: for water in dilute solutions $[H_2O] = 1$
  - for solids, $[\text{solid}] = 1$

  Example:
  $CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) CO_3^{2-}$ $K_{eq} = 78 \times 10^{-9} 
  \Rightarrow 10^{-8.3}$

  $K_{eq} = 10^{-8.3} = \frac{[Ca^{2+}] [CO_3^{2-}]}{[CaCO_3(s)]}$

  "Solubility product"

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

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

  in acid or neutral water

  $[H^+] = [OH^-]$ $\Rightarrow K_{eq} = 10^{-14} = [H^+] [H^+] = [H^+]^2$

  $\Rightarrow [H^+] = 10^{-7}$, so $pH = -\log [H^+] = 7$
Acids and Bases

Acids = proton donor
Bases = proton acceptor

Strong acids dissociate completely

$\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$  
$K_a = 10^7$ Strong!

$\text{H}_2\text{SO}_4 \rightarrow \text{H}^+ + \text{HSO}_4^-$  
$K_a = 10^3$ Strong!

$\text{HSO}_4^- \rightarrow \text{H}^+ + \text{SO}_4^{2-}$  
$K_a = 10^{-1.99}$

$\text{H}_2\text{SO}_4 \rightarrow 2\text{H}^+ + \text{SO}_4^{2-}$

Weak acids only dissociate partially

$\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$  
$K_{a1} = 4.45 \times 10^{-7}$  
$K_{a2} = 4.69 \times 10^{-11}$

$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$  
$x = 10^{\log_{10}(4.45 \times 10^{-7})} = 10^{-6.35}$

Now, we're ready to consider a carbonate system in equilibrium with water and CO$_2$ gas:

$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$  
$K_{a1} = 10^{-1.5}$

$\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$  
$K_{a2} = 10^{-6.35}$

$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$  
$K_{a2} = 10^{-10.2}$

$\text{H}_2\text{O} + \text{CO}_2 + \text{CaCO}_3(\text{s}) \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-$  
$K_{eq} = \frac{[\text{Ca}^{2+}][2\text{HCO}_3^-]}{[\text{CaCO}_3(\text{s})][\text{CO}_2]}$

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?
   CO₂ escapes, carbonate precipitation is favored

B) the atmospheric pressure decreases?
   CO₂ evolves from solution → CaCO₃ precipitates

C) the water is agitated? (waves)
   lose CO₂ → reaction driven to left → CaCO₃ precip

D) the water pressure is decreased? (upwelling)
   CO₂ gas evolves → precipitation

E) the Salinity of the water is decreased?
   [Mg²⁺]↓ → favors CaCO₃ precip

Note: When T↑, the solubility product, K_{sp}, for CaCO₃ decreases

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CaCO₃ ⇌ Ca^{2+} + CO₃^{2-}
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K_{sp} = \frac{[Ca^{2+}][CO₃^{2-}]}{[CaCO₃]} = 10^{-8.34}
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What effect does this have on CaCO₃ solubility?
   lower solubility ⇒ precipitate