Chapter 13. Chemical Equilibrium

Definition: Equilibrium is the state where the concentrations of all reactants and products remain constant with time.

Note that this implies stability, not simply slow kinetics.
For example, the system will spontaneously return to the equilibrium state following a fluctuation.

Stability of Equilibrium

The following two experiments start with different initial conditions, yet the final equilibrium concentrations are the same.

Forward and Reverse Rxn Rates

The Approach to Equilibrium

Assume you are given initial conditions. Is the system at equilibrium? If not, which direction will the reaction go to reach equilibrium?

- Calculate the instantaneous value of the reaction quotient, Q (i.e. the value of the equilibrium constant expression using the given conditions).
- If Q = K, the system is already at equilibrium.
- If Q < K, the system shift to the right to increase product concentrations.
- If Q > K, the system shifts to the left to increase reactant concentrations.

Demo: Shift Equilibrium

Le Chatelier’s Principle

- **Le Chatelier’s principle**: If an external stress is applied to a system at equilibrium, the system adjusts in such a way that the stress is partially offset.

  - Stress may be changes in concentration, pressure, volume, or temperature that removes the system from equilibrium.
Adjustment to Increased Concentration

\[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \quad K_c = 0.291 \text{ at 700K} \]

- Add \( \text{N}_2 \) to the system at equilibrium.

Temperature Changes

- Changes in temperature can change the equilibrium constant.
- Endothermic processes are favored when temperature increases.
- Exothermic processes are favored when temperature decreases.

K vs. T

- Consider the reaction \( \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \) which is exothermic by 92.2kJ.

Hess’s Law

- \( K \) of a net reaction is the product of the reactions that are added.

\[ \begin{align*}
(1) \quad & \text{S(s)} + \text{O}_2(g) \rightleftharpoons \text{SO}_2(g) \quad K_1 = \frac{[\text{SO}_2]}{[\text{O}_2]} \\
(2) \quad & \text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) \rightleftharpoons \text{SO}_3(g) \quad K_2 = \frac{[\text{SO}_3]}{[\text{SO}_2][\text{O}_2]^{1/2}} \\
\text{net:} \quad & \text{S(s)} + \frac{3}{2}\text{O}_2(g) \rightleftharpoons \text{SO}_3(g) \quad K_{\text{net}} = \frac{[\text{SO}_3]}{[\text{O}_2]^{3/2}} = K_1 K_2 \\
\text{note that} \quad & K_1 K_2 = \frac{[\text{SO}_2][\text{SO}_3]}{[\text{O}_2][\text{O}_2]^{3/2}} = \frac{[\text{SO}_3]}{[\text{O}_2]^{3/2}} = K_{\text{net}}
\end{align*} \]

Weak Acid Equilibrium

\[ \text{HCN(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CN}^-(aq) \]

System initially contains 0.10 M HCN. What is final [\( \text{H}_3\text{O}^+ \)]?

\[
\begin{array}{c|c|c}
\text{HCN} & \text{[H}_3\text{O}^+] & \text{[CN}^-] \\
\hline
\text{Initial} & 0.10 & 0 \\
\text{Change} & -x & +x \\
\text{Equilibrium} & 0.10-x & x \\
\end{array}
\]

\[ K_c = 4.9 \times 10^{-10} = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]} \]

\[ x = [\text{H}_3\text{O}^+] = 7 \times 10^{-4} \]

Small \( x \).