CHEM30311 LECTURE 2

Macrocyclic and Supramolecular Chemistry

Thermodynamic and Kinetic Considerations in Metal Binding by Chelate and Macrocyclic Ligands.

STABILITY CONSTANTS

Stability or formation constants quantify affinity between a metal (M) and a ligand (L)

$$M + L \longleftrightarrow \{ML\}$$

Eqm Constant $K_{\{ML\}}$ = Conc^n of products / Conc^n of reactants = $[\{ML\}] / ([M][L])$

STEPWISE STABILITY CONSTANTS

M-L complexes are not all 1:1 M:L.

Stepwise Stability Constants:

$$M + L \longleftrightarrow \{ML\} \qquad K_1 = [\{ML\}] / ([M][L])$$

$$\{ML\} + L \longleftrightarrow \{ML_2\} \qquad K_2 = [\{ML_2\}] / ([\{ML\}][L])$$

$$\{ML_2\} + L \longleftrightarrow \{ML_3\} \qquad K_3 = [\{ML_3\}] / ([\{ML_2\}][L])$$

Overall Stability Constant β:

$$M + 3L \longleftrightarrow \{ML_3\} \qquad \beta = [\{ML_3\}] / ([M][L]^3) = K_1 \cdot K_2 \cdot K_3$$

- can be extremely large values - expressed as $\log_{10}\beta$ or $\log_{10}K$

$$\log_{10}K = \log_{10}K_1 + \log_{10}K_2 + \log_{10}K_3 + \ldots$$

- Typical $\log_{10}K$ for binding to macrocycles: 4 to 50

$\log_{10}K = 4$ is 10 times more stable than $\log_{10}K = 3$

MULTIDENTATE LIGANDS - THE CHELATE EFFECT

Complexes of chelate ligands are thermodynamically more stable than complexes of equivalent monodentate ligands - the chelate effect.

1. $[Ni(H_2O)_6]^{2+} + 6NH_3 \longrightarrow [Ni(NH_3)_6]^{2+} + 6H_2O \rightarrow \log_{10}K = 8.6$
2. $[Ni(H_2O)_6]^{2+} + 3\,en \longrightarrow [Ni(en)_3]^{2+} + 6H_2O \rightarrow \log_{10}K = 18.3$