

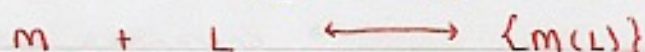
Macrocyclic and Supramolecular Chemistry

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)



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

STEPWISE STABILITY CONSTANTS

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

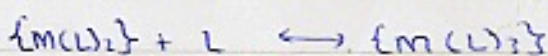
Stepwise Stability Constants:



$$K_1 = \frac{[\{M(L)\}]}{[M][L]}$$



$$K_2 = \frac{[\{M(L)_2\}]}{[\{M(L)\}][L]}$$



$$K_3 = \frac{[\{M(L)_3\}]}{[\{M(L)_2\}][L]}$$

Overall Stability Constant β : $M + 3L \rightleftharpoons \{M(L)_3\}$

$$\beta = \frac{[\{M(L)_3\}]}{[M][L]^3} = K_1 \cdot K_2 \cdot K_3$$

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

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

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

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

MULTI-DENTATE LIGANDS - THE CHELATE EFFECT

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

