Chapter 2: Stability

1. Catalytic rxns -
2. photochemical rxns -
3. redox rxns -
4. direct rxns - dissolving metal salt in solvent

$$NiBr_2 + 6H_2O \rightleftharpoons [Ni(OH_2)_6]^{2+} 2Br^-$$

5. ligand substitution -
   ligand exchange process... lewis base is replaced by a second Lewis base

$$MX + Y \rightleftharpoons MY + X$$

Y: entering group; X: leaving group

kinetics - rate of product formation...

thermodynamics - strength of M-L bond forms, most stable product + degrees of freedom or entropy

K_f = formation constant

$$[M(H_2O)_n]_{aq} + L \rightleftharpoons [M(H_2O)_{n-1}L]_{aq} + H_2O$$

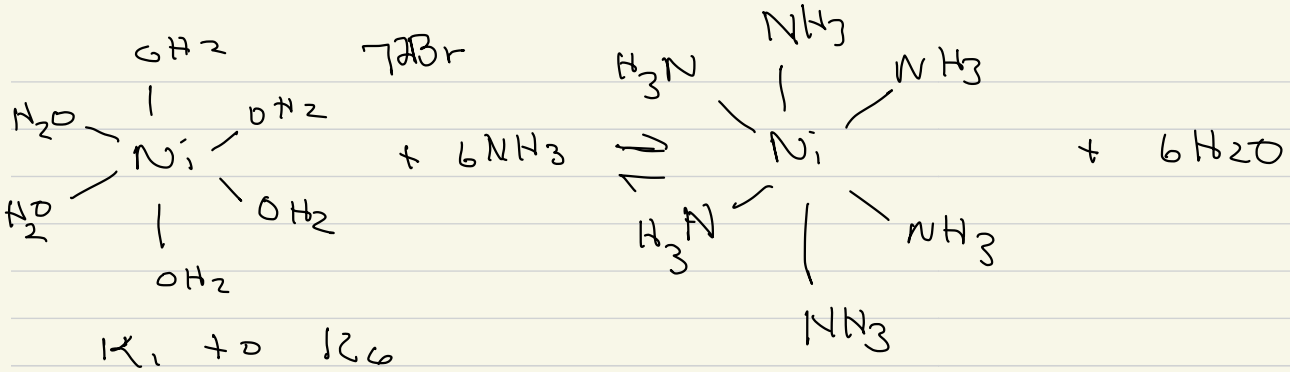
$$K_f = \frac{[Products]}{[Reactants]} = \frac{[M(H_2O)_{n-1}L][H_2O]}{[M(H_2O)_n][L]}$$

$$Molarity = \frac{mol\ solute}{L\ solvent}$$

$$M + L \rightleftharpoons ML \quad K_f = \frac{[ML]}{[M][L]}$$

$$[Fe(H_2O)_6]^{3+}(aq) + NCS^-(aq) \rightleftharpoons Fe(NCS)(H_2O)_5]^{2+} + H_2O(l)$$

$$K_f = \frac{[Fe(NCS)(H_2O)_5]^{2+}}{[Fe(H_2O)_6]^{3+}[NCS^-]} \qquad K_d = \frac{1}{K_f}$$



K_1 to K_6

$M + L \rightleftharpoons ML$

$ML + L \rightleftharpoons ML_2$

$ML_{n-1} + L \rightleftharpoons ML_n$

$M + nL \rightleftharpoons ML_n$

$K_1 = \frac{[ML]}{[M][L]}$

$K_2 = \frac{[ML_2]}{[ML][L]}$

Stepwise or successive formation constants

$\beta_n = \frac{[ML_n]}{[M][L]^n} = K_1 \cdot K_2 \cdot K_3 \cdots$

overall formation constant

$K_f > 1$ products are preferred

$K_f < 1$ reactants are preferred

stability constant

equilibrium constant

Gibbs free energy $\Delta G = -RT \ln K$

$R = 8.314\ J/K\,mol$

T = abs temperature (Kelvin)

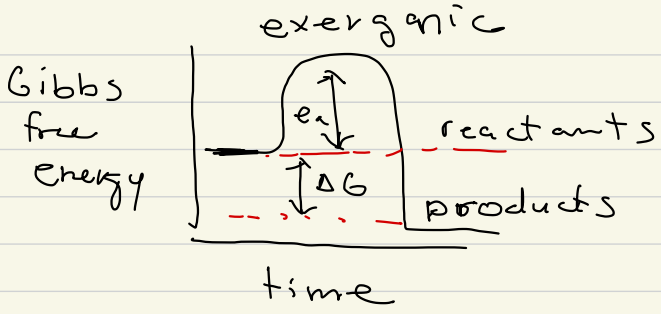
$\Delta G = \Delta H - T\Delta S$

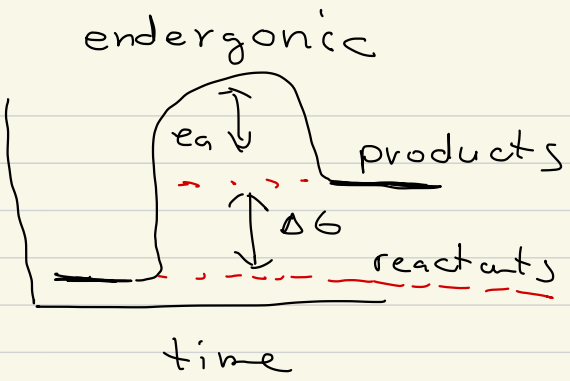
ΔH = reflects the binding strength

ΔS = reflects structured degrees of freedom

$\Delta G < 0$

1. $\Delta H << 0$ enthalpically stabilized
2. $\Delta S >> 0$ entropically stabilized
3. $\Delta H < 0$, $\Delta S > 0$

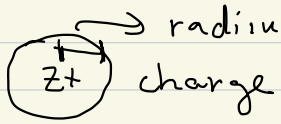




Stability tool box...

1. electrostatics... consider the size + charge of ions
2. Irving williams series -
3 hard. soft acid base theory -
4. Strength of ligands as a bronsted base...
5. Structural aspects of our ligands
   - i chelate effects
   - ii size of the chelate ring
   - iii sterics of ligads
   - iv Macrocyclic effect.

electrostatics - charge density z^2/r_i



general rule: $\uparrow z^2/r_i \uparrow K_f$

charge is dominate

	Fe^{3+}/F^-	Fe^{3+}/Cl^-
	1.33 pm	1.81 pm
	$\log K_f = 6$	$\log K_f = 1.3$

ionic radius $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$

$Mn^{2+} > Fe^{2+} > Co^{2+} > Ni^{2+} < Cu^{2+} < Zn^{2+}$

stabilities

$Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$

→ Irving Williams Series.

Hard soft acid base theory.
Classify metal + ligads as hard or soft

Exercise ① CO + NH_3 + Fe(0)
which ligad will preferentially bind

② CO + NH_3 Fe(III)

③ $[CH_3Hg(H_2O)]^+ + HCl \rightarrow CH_3HgCl + H_2O$ $\log K_f = 12.25$

$[CH_3Hg(H_2O)]^+ \; HF \rightleftharpoons CH_3HgF + H_2O$

one rxn prefers products + one rxn prefers reactants..

$\log K_f = -1.35$

Strength of a ligad as a bronsted base.
B.A. = H^+ donor
B.B = H^+ acceptor

$HA \rightarrow H^+ + A^-$ $\quad pK_a = -\log \frac{[H^+][A^-]}{[HA]}$

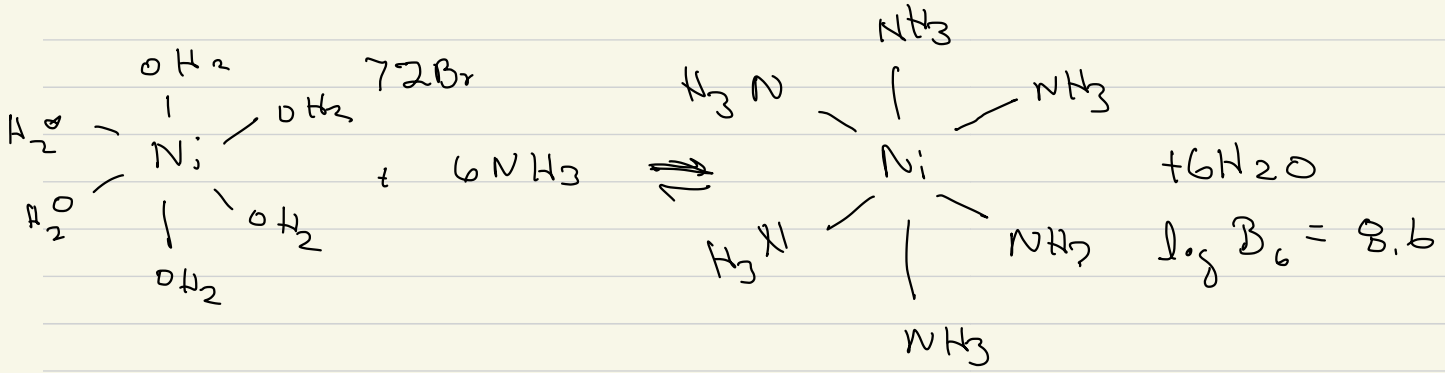
metal ↓ ligand

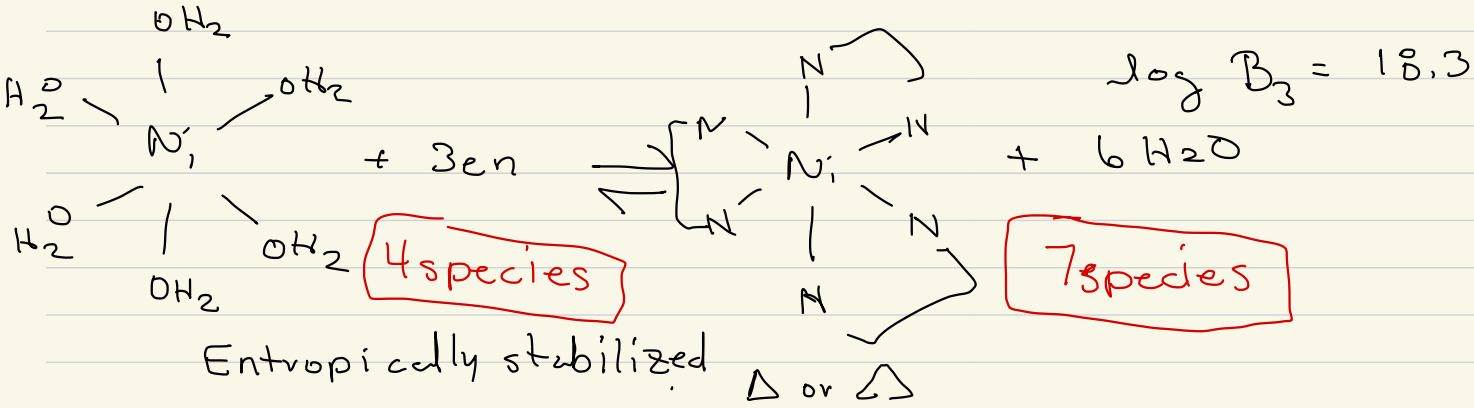
low pka → stronger + weaker conjugate base
higher pka → weaker acid + stronger conjugate

Rule: high Pka ligad then it form strong complexes w/ hard metals

Structural aspects

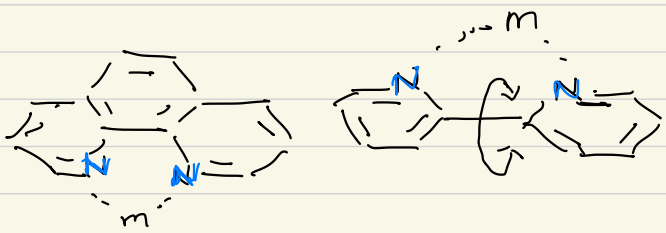
① Chelate — chelates they often form more stable complexes then non-chelates





Entropically stabilized

Δ or Δ



reorientation decreases lk of bipy relative to phen

chelate ring size

5 membered > 6 memb. > 7 memb ≈ 4 memb.

Exercise: Mixing Co^{3+} with ① en, ② malonato, ③ glycinato, & ④ succinato ... rank the stability of the complexes

1 > 3 > 2 > 4

Consider size of chelate ring. 5-membered is more stable than 6 is more stable than 7
Also consider ligand Pkas.