Thermodynamic and Kinetic Aspects of Metal Complexes



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Outline

- Background/Importance of the study
- Definition/Types
- Factors affecting stability constants
- Kinetic aspects stability of metal complexes
- Determination of stability constant
- Reading materials

SEMESTER VI CHEMISTRY-C XIII: INORGANIC CHEMISTRY-IV

UNIT-IV

Thermodynamic & kinetic aspects and reaction mechanism of metal complexes

Thermodynamic and kinetic stability, Stepwise and overall formation constants and their relationship, factors affecting stability. Introduction to inorganic reaction mechanisms-types of reaction and classification of substitution reactions. Substitution reaction of square planar complexes, Trans effect and its applications, theories of trans-effect (electrostatic polarization and Static π -Bonding Theory). Kinetics of octahedral substitution (classification of metal ions based on water exchange rate), General mechanism of ligand substitution reactions in octahedral complexes (D, I, $I_{\rm d}$, $I_{\rm a}$).

Coordination Complex

Metal complex: $Fe(CN)_2 + 4 KCN \rightarrow K_4[Fe(CN)_6]$

- Composed of two or more components capable of independent existence
- Retains identity in solid as well as in solution
- May contain one or more units of complexes
 - * $[Co(NH_3)_6]Cl_3$
 - * [Cu(NH₃)₄][PtCl₄]
 - * $[Pt(NH_3)_2Cl_2]$
- Complexes: Have metal ion (can be zero oxidation state) bonded to number of ligands.
- Transition metals can act as Lewis acid while ligand acts Lewis base.

The term ligand (ligare [Latin], to bind) was first used by Alfred Stock in 1916 in relation to silicon chemistry.

The first use of the term in a British journal was by H. Irving and R.J.P. Williams in Nature, 1948, 162, 746.

Formation of Metal Complex

Metal ligand equilibria in solution:

■ In solution complexes results from the reversible association one or more metal ions (M) and ligands (L)

$$Ag^+ + 2NH_3 \leftrightarrows Ag(NH_3)_2^+$$

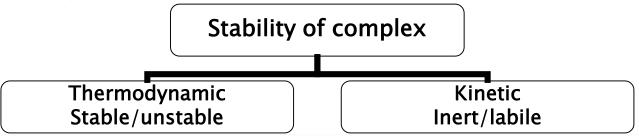
- The complex can be mononuclear, binuclear, polynuclear (mixed metal, mixed ligand)
- Equilibrium constant or stability constant for metal complex formation is an effective measure of the affinity of a ligand for metal ion in solution.
- Equilibrium Constant (K) = $[Ag(NH_3)_2^+] / [Ag^+][NH_3]^2$
- Conventions employed for expressing equilibrium constant:
 - Protonation/acid dissociation; step wise dissociation
 - Formation constant Stepwise / overall
 - Conditional formation constant (effect of pH)
 - Stability constant / Instability constant
 - Hydrolysis constant / displacement constnat

Stability of Metal Complexes

- The statement that a complex is stable is rather loose and misleading very often.
- Use of term stability without qualification means that a complex exists and under suitable/required conditions it can be stored for a long time but cannot be generalized to all complexes.
- One particular complex may be stable towards a reagent/condition and highly reactive towards another.
 - Aqueous solution of $[Co(NH_3)_5Cl]^{2+} \rightarrow No$ change even on boiling for days.
 - In presence of light ($\lambda = 350$ nm) it rapidly converts into $[Co(NH_3)_5OH_2]^{3+}$.

Stability of Metal Complexes

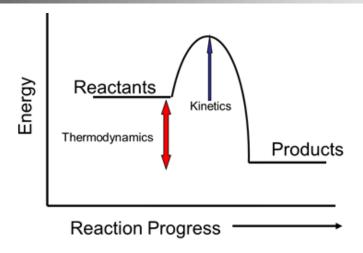
The stability of complex is commonly expressed in terms of thermodynamic and kinetic



There is **NO** connection between Thermodynamic Stability/Instability of a complex and its Lability/Inertness towards substitution.

The tremendous thermodynamic driving force of six basic ammonia molecules combining with six protons results in an equilibrium constant for the above reaction of value 10^{25} .

Kinetic *Vs* Thermodynamic stability



- The difference between stability and inertness can be expressed thermodynamically.
- Stable complexes have a large POSITIVE ΔG^{o}_{React} for ligand substitution and Inert complexes have a large POSITIVE ΔG^{\dagger} (activation).
- The standard enthalpy change, ΔH^o for this reaction is related to the equilibrium constant, β_n by the well thermodynamic equation.

$$\Delta G^{o} = -RT \ln_{\beta}$$

$$\Delta G^{o} = \Delta H^{o} - T \Delta S^{o}$$

Thermodynamic Stability

- ➤ Thermodynamic stability measures the extent to which the complex will form or will be transform into another species under given set of condition at equilibrium.
- ➤ It depends on the strength of M-L bonds which vary widely.
- ➤ Complexes like [Co(SCN)₄]²⁺ ion the bond is very weak and on dilution, it breaks immediately and forms another compound.
- While, in case of $[Fe(CN)_6]^{3-}$, the bond is stronger in aqueous solution and in this complex Fe^{3+} cannot be detected by any sensitive reagent.
- ➤ So thermodynamic stability deals with metal-ligand bond energy (strength), stability constant and other thermodynamic parameters.

Thermodynamic Stability

- Thermodynamic Stability is measured in terms of the stability constant (eqbm. constant) of the complex formation process.
- Formation of complexes may take place overall or in step wise manner.

$$M + L \implies ML$$

$$ML + L \implies ML_{2}$$

$$ML_{2} + L \implies ML_{3}$$

$$M + L \implies ML$$

$$M + L \implies ML$$

$$M + 2L \implies ML_{2}$$

$$M + 3L \implies ML_{3}$$

$$\beta_{3} = \frac{[ML_{2}]}{[M][L]^{2}} = K_{1}K_{2}$$

$$\beta_{3} = \frac{[ML_{3}]}{[M][L]^{3}} = K_{1}K_{2}K_{3}$$

For **n** no. of ligand, the overall reaction:

$$M(H_2O)_n + nL \leftrightarrow ML_n + nH_2O$$

and $\beta_n = K_1K_2K_3.....K_n$.

$$\beta_n = \frac{[ML_n]}{[M(H_2O)_n][L]^n}$$

NB: Water is not included; its concentration can be regarded as 'constant' because of its high concentration (55.5 M).

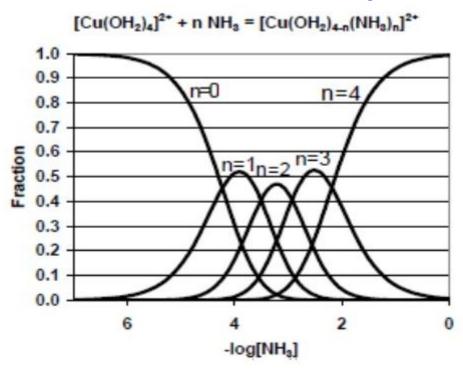
Thermodynamic Stability

Characteristics of K_i and β_i

- With a few exception, K_i values decrease progressively
 - Statistical factor
 - Steric hindrance (if entering ligand is bulkier than H₂O)
 - Coulombic factor (mainly with charged entering ligands)
- Higher the value of K or β , the greater its stability
- K_i and β_i are related each other
- The standard free energy is related to K/β
 - $\Delta G^{\circ} = -2.303 \text{ RT log K}, \Delta G^{\circ} = \Delta H^{\circ} T\Delta S^{\circ}$
 - By measuring β at several temp. one can get ΔH^o by graphical solution of $2.303 \text{ R log}\beta = (\Delta G^o \Delta G^o / T)$

Statistical factor

Plots of proportion of various complexes, $Cu(NH_3)_n^{2+}$, as a function of - $log[NH_3]$



- Entry of more and more ligand into the coordination sphere results in decrease of aqua ligands at metal centre which in turns reduces the probability of substitution of aqua ligand with a new ligand.
- Reflected as decreasing stepwise formation constant.

Conditional Formation Constant

■ Effect of pH on the free ligand concentration in a complexation reaction.

For a diprotic acid: oxalic acid H_2Ox H_2Ox , HOx^- , Ox^{2-}

$$C_{\rm T} = [{\rm H}_2{\rm Ox}] + [{\rm HOx}^-] + [{\rm Ox}^2]$$

$$\alpha_0 = \frac{[H_2Ox]}{C_T} = \frac{[H^+]^2}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}$$

$$\alpha_1 = \frac{[HOx^-]}{C_T} = \frac{K_{a1}[H^+]}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}$$

$$\alpha_2 = \frac{[Ox^{2-}]}{C_T} = \frac{K_{a1}K_{a2}}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}$$

■ Similarly metal ion can have different species depending on pH $Fe(OH_2)_6^{3+} \leftrightarrow Fe(OH_2)_5OH^{2+} + H^+$

Factors contributing to metal complex stability

Factors affecting stability w.r.t.:

- Metal ions: charge/size/Charge to size ratio, CFSE,
 Hard acid-soft base (HSAB) concept (class a or class b or boarder line metal)/electronegativity etc.
- Ligands: size, charge, nature of donor atom (HSAB concept), stability of conjugate base, chelate effect ring size, steric effect, (entropy factor); Macrocyclic effect.
- Shape of the complex.
- Solvation effects

Nature of Central Metal Ion:

- *Ionic Size:* Stability of decreases with increase in size of metal ion. Zn²⁺ (0.74 Å) forms more stable complexes than Cd²⁺ (0.97 Å).
- *Ionic Charge:* In general, the small and highly charged cation can form more stable complexes because of most stable coordinate bonds.

 Stability increases with increase of Ionic potential (ratio effective cationic charge to effective cationic radius)

Complex ion	Charge on the ion	Ionic radii (A°)	Value of B	stability
[Be"(OH)] +	+2	0.31	107	
[Mg ^{II} (OH)] ⁺	+2	0.65	120	Stability increases
[Ca (OH)] +	+2	0.99	30	bility in
[Ba"(OH)] +	+2	1.35	4	Sta

Nature of the Ligand:

- Size and Charge: Ligands with less charge and more size are less stable and form less stable complexes. Ligands with higher charge have small size and form more stable complex.
- **Basic Character:** Higher basic character or strength of the ligand, higher will be the stability of complexes because of its donating tendency of electron to central metal ion is higher.

Ex: Aromatic diamines form unstable complexes while aliphatic diamines form stable complexes.

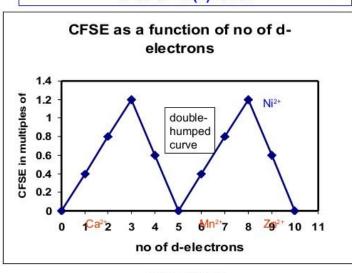
Crystal Field Effects: Irving-William Order

Stabilities of high spin complexes of divalent metal ion of 3d series usually follow the order:

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

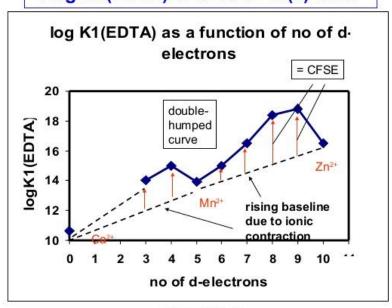
- The order is called Irving-William order and is also consistent with charge to radius ratio.
- The discrepancy with Cu²⁺ is due to Jahn-Teller distortion.

Crystal Field Stabilization Energy (CFSE) of do to do M(II) ions:



santhanam SCSVMV

Log K1(EDTA) of do to do M(II) ions:



Ligand Concentration: Some coordination complexes exist in aqueous solution only in presence of higher conc. of ligands. In some cases H_2O shows greater coordinating tendency than the ligand which is originally present.

■ **Ex-1:** in presence of high [SCN⁻], Co^{2+} forms a stable blue coloured complex but on dilution in aq. medium the blue complex is destroyed and a pink aqua complex $[Co(H_2O)_6]^{2+}$ is formed.

$$[Co(SCN)_4]^{2-} + H_2O \leftrightarrows [Co(H_2O)_6]_{2+} + 4SCN^{-}$$

Blue Pink

■ Ex-2: In the synthesis of tetra amine cupric sulphate complex at lower conc. of ammonia forms copper hydroxide, while at higher concentration of ligand form following complex.

 $CuSO_4 + NH_4OH \rightarrow Cu(OH)_2$ (Low concentration of NH_3) $Cu(OH)_2 \rightarrow [Cu(NH_4)_2SO_4.H_2O$ (High conc. of ligand, NH_3)

Hard-Soft Acid-Base Classification of Metals & Ligands

- Hard metals & ligands. Hard cations have high positive charges, not easily polarized. *e.g.* Fe³⁺. Hard ligands usually have electronegative non-polarizable donor atoms (O, N). The metal-ligand bonding is more ionic
- Soft metals and ligands. Soft cations (e.g. Hg²+, Cd²+, Cu+) have low charge densities, easily polarized. Soft ligands usually have larger, more polarizable (S, P) donor atoms or unsaturated molecules or ions. The metal-ligand bonding is more covalent
- Hard metals like to bond to hard ligands, Soft metals like to bond to soft ligands

Hard acids	Hard bases
H+, Li+, Na+, K+,	F-, Cl-, H ₂ O, OH-, O ^{2-,} NO ₃ -,
Mg ²⁺ , Ca ²⁺ , Mn ²⁺ ,	RCO ₂ -, ROH, RO-, phenolate
Al ³⁺ , Cr ³⁺ , Co ³⁺ , Fe ³⁺ ,	CO ₃ -, SO ₄ ²⁻ , PO ₄ ³⁻ , NH ₃ , RNH ₂
Borderline acids	Borderline bases
Fe ²⁺ , Co ²⁺ , Ni ²⁺ , Cu ²⁺ , Zn ²⁺ , Sn ²⁺	NO ₂ -, Br-, SO ₃ ²⁻ , N ₃ -
Pb ²⁺ , Ru ³⁺	Pyridine, imidazole,
Soft acids	Soft acids
Cu+, Ag+, Au+, Cd2+, Hg2+, Pt2+	I ⁻ , H ₂ S, HS ⁻ , RSH, RS ⁻ , R ₂ S, CN ⁻ , CO, R ₃ P

Effect and consequences of HSAB concept on stability

Stability constant trends for Fe(III) and Hg(II) halides

 $\log K_1$

	X = F	X = CI	X = Br	X = I
$Fe^{3+} + X^{-} \longrightarrow FeX ^{2+}$	6.0	1.4	0.5	
$Hg^{2+} + X^{-} \longrightarrow [HgX]^{+}$	1.0	6.7	8.9	12.9

• Hard metal formation constants (K_f)

$$F \gg Cl \gg Br \gg I$$
 and $O \gg S \gg Se \gg I$

• Soft metal formation constants (K_f)

$$F \ll Cl \ll Br \ll I$$
 and $0 \ll S \approx Se \approx Te$

HSAB Concept in Geochemistry

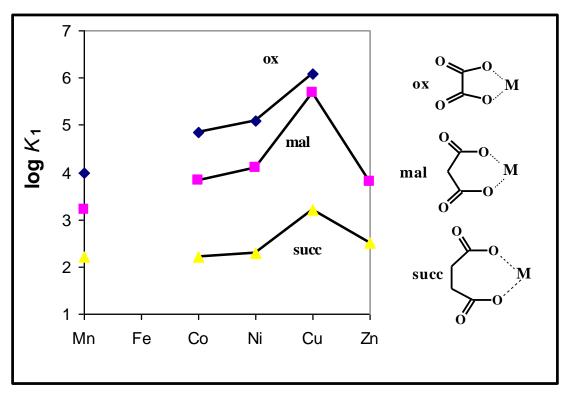
- Common ore of Al is alumina, Al₂O₃ (bauxite) while most common ore of Ca is CaCO₃ (limestone, calcite, marble). Both are hard acid hard base combinations.
- Zn is found mostly as ZnS (wurtzite) and mercury as HgS (cinnabar).
 Both involve soft acid soft base interactions.

- A *chelate* [derived from the great claw or chela (chely Greek) of the lobster], is produced when a metal ion coordinates with two or more donor groups of a single ligand to form a five or six membered heterocyclic ring. Ex- Cu(II) complex with glycine.
- The higher stability (more K_f values) due to formation of chelate is called chelate effect of chelon effect.

System	Stab. Contst.
$[Ni(H_2O)_6]^{+2} + 2NH_3 \rightarrow [Ni(NH_3)_6]^{2+} + 2H_2O$	$\log K = 7.5$
$[Ni(H_2O)_6]^{+2} + NH_2CH_2CH_2NH_2 (en) \rightarrow [Ni(H_2O)_4 (en)]^{2+} + 2H_2O$	log K = 18.3
$[Ni(H_2O)_6]^{+2} + 6NH_3 \rightarrow [Ni(NH_3)_6]^{2+} + 6H_2O$	$\log \beta = 8.6$
$[Ni(H_2O)_6]^{+2} + 3 \text{ en } \rightarrow [Ni(en)_3]^{2+} + 6H_2O$	$\log \beta = 18.3$

Chelation effects on stability

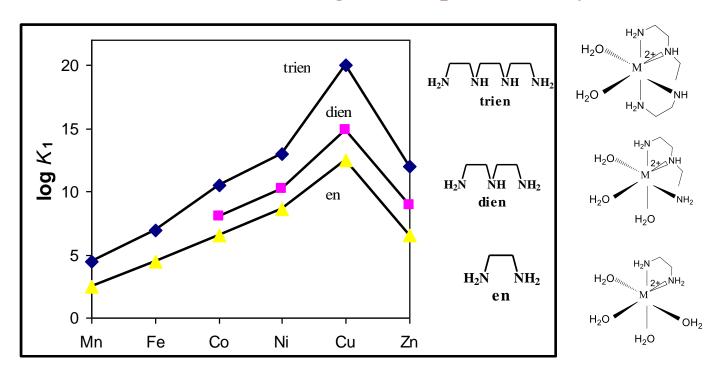
Chelate Ring Size and Complex Stability



Four-membered rings are unstable and rare than five-membered rings which are common and stable. For chelate (saturated chelate) rings, the stability of metal complexes decrease with increasing ring size.

5-membered > 6-membered > 7-membered

Number of chelate rings & complex stability



- Increase in the number of rings increase the stability of compounds.
- Ex-1: Value of logK₁ for Ni complexes with ethylenediamine is
 7.9 and with trine is 14.0 and with penten 19.3.
- logK₁ for Zn with ethylenediamine is 6.0 and with trine is 12.1 and with penten 16.2.

$$\Delta G^{o} = -2.303 \text{ RT log K}, \Delta G^{o} = \Delta H^{o} - T\Delta S^{o}$$

$$Cd(H_2O)_4^{2+} + 4 CH_3NH_2$$
 $= [Cd(NH_2CH_3)_4]^{2+} + 4 H_2O$
 $\Delta G^0 = -37.2 \text{ kJ/mol},$
 $\log \beta = 6.52$
 $\Delta H^0 = -57.3 \text{ kJ/mol},$
 No chelation

 $-T\Delta S^0 = 20.1 \text{ kJ/mol},$
 No chelation

 $Cd(H_2O)_4^{2+} + 2 \text{ en}$
 $= [Cd(en)_2]^{2+} + 4 H_2O$
 $\Delta G^0 = -60.7 \text{ kJ/mol},$
 $\log \beta = 10.6$
 $\Delta S^0 = +14.1 \text{ J./mol. K}$
 chelation

 $-T\Delta S^0 = -4.2 \text{ kJ/mol}$

- The replacement of monodentate ligands by one bidentate ligands is thermodynamically favoured since it generates more particles (*increase in disorder*) in the solution.
- The chelate effect is an entropy effect *i.e.* ΔS is positive.

Chelate Formation: Entropy Gain

 $Cd^{2+} + 4 NH_3 \leftrightarrow [Cd(NH_3)_4]^{2+}$

Cd²⁺ + 4 MeNH₂ ↔ [Cd(MeNH₂)₄]²⁺

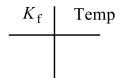
Cd2+ + 2 en ↔ [Cd(en),]2+

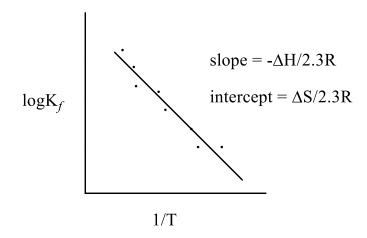
Ligands	log β	∆G kJmol ⁻¹	∆H kJmol⁴	∆S JK-¹mol-¹
4 NH ₃	7.44	-42.5	- 53.2	- 35.5
4 MeNH ₂	6.52	-37.2	-57.3	- 67.3
2 en	10.62	-60.7	-56.5	+13.8

Chelate effect - Thermodynamic consideration

$$\Delta G = -2.3RT \log K_f = \Delta H - T\Delta S$$

$$\log K_{\rm f} = \frac{-\Delta H}{2.3RT} + \frac{\Delta S}{2.3R}$$





 ΔH reflects strength of metal-ligand interaction

ΔS reflects change in "disorder"accompanying complexation

Stability constants (K_2 and K_1) at least in two temperature is required for determination thermodynamic parameters.

Solvation Effects

Reaction enthalpy (ΔH) and entropy (ΔS) for complexation of M²⁺ ions by ethylenediamine, glycinate and malonate.

 M^{2+} (solv)+ L^{n-} (solv) = ML^{2-n} (solv) (in kJ/mol and ΔS in J/mol. K.)

		Mn ²⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺
NH ₂	ΔH	-11.7	-28.8	-37.2	-54.3	-28.0
NH_2	ΔS	12.5	16.7	23.0	22.6	16.7
\sim NH ₂	ΔH	-1.3	-11.7	-20.5	-25.9	-13.8
0 0	ΔS	56.4	57.2	49.7	76.9	53.1
0	ΔH	15.4	12.1	7.9	11.9	13.1
	ΔS	115	113	104	148	117

Enthalpy changes ($\Delta H_{\rm solv}$) and entropy changes ($\Delta S_{\rm solv}$) arising from solvation of metal, ligand and complex contribute to the overall reaction enthalpy and entropy of the complexation process.

Solvation Effects

$$M^{2+}(solv) + L(solv) \rightarrow ML(solv)$$

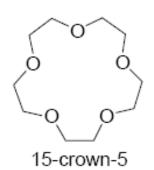
- Complexation with N-donor ligand (en) is more enthalpy driven than entropy driven (i.e. large negative ΔH and small positive ΔS).
- Complexation with mixed O- and N-donor ligand (glycinate) has less negative ΔH , and larger positive ΔS indicates that solvation entropy becomes more important with O-donors.
- Complexation with O-donor ligand (malonate) has small positive ΔH and large positive ΔS values indicates that the complexation is entropy driven.
- O-donor ligands are more strongly solvated by water molecules.
- Desolvation of O-donor ligands, prior to complexation with metal, reduces the overall ΔH for the complexation reaction. *i.e.* energy is used to remove solvent water from the O donor atoms before they can bond to the metal. This process also adds to the reaction entropy, when the water molecules are released to the solvent.

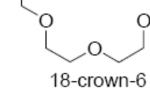
Macrocyclic Effects

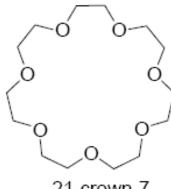
Macrocylic Ligands

Large ring compounds most commonly containing or O, N and/or S atoms

crown ether:

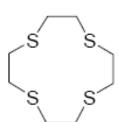




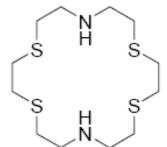


21-crown-7

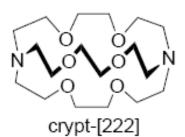
thia-crown ether:

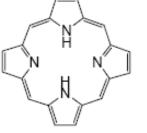


aza-thia-crown:



cryptand:

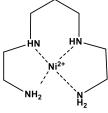


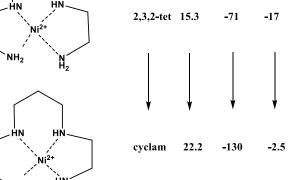


porphyrin



Macrocyclic Effects





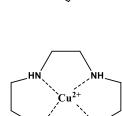
Ligand logK

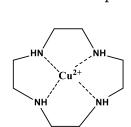
-TAS

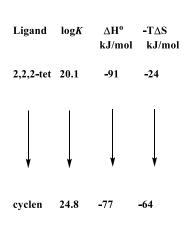
kJ/mol

kJ/mol

enthalpy difference opposed by entropy difference







entopy difference opposed by ethalpy difference

Macrocyclic chelate complexes are up 10⁷ times more stable than non-cyclic chelates with the same number of donors

Ni(trien)²⁺ + H⁺
$$\leftrightarrows$$
 Ni²⁺ + H₄trien⁴⁺ $t_{\frac{1}{2}} = 2 \text{ s}$
Ni(cyclam)²⁺ + H⁺ \leftrightarrows Ni²⁺ + H₄cyclam⁴⁺ $t_{\frac{1}{2}} = 2 \text{ yrs}$

- Entropy & enthalpy changes provide driving force for the macrocyclic effect but the balance betⁿ the two is complex.
- M-L bonding is optimized when the size of the macrocyclic cavity and metal ion radius is closely matched. This promotes a favorable negative ΔH for complexation
- For macrocycles, there is minimal reorganization required of the polydentate ligand structure before coordination to M. This promotes a more negative ΔH for complexation in macrocycles compared to corresponding acyclic open chain ligands.
- More extensive desolvation of ligand donor atoms may also be involved for acyclic ligands, which detracts from the overall ΔH for complexation.

Determination of Thermodynamic Stability

- Direct method (potentiometric/solubility)
- Indirect methods (pH, optical density)
- Bjerrum function (ń)
- Potentiometric titration
- Spectrophotometry

Methods Based on Study of Heterogeneous Equilibria:

- (i) Solubility Methods:
- (ii) Distribution Method:
- (iii) Ion-Exchange Method:

Electrometric Techniques:

- (i) Potentiometric Methods
- (ii) Polarographic method

Kinetic Stability

- ➤ Kinetic stability refers to the rate or speed at which a complex formation or transformation reaction proceeds at equilibrium. Time factors play an important role in deciding the kinetic stability of the complex.
- ➤ It deals with the rate and mechanism of a chemical reaction.
- ➤ In kinetic stability, the complexes are referred as "inert" or "labile". (Earlier Taube had used term "Inert" for thermodynamically stable complexes and "labile" for reactive complexes).

Kinetic Stability

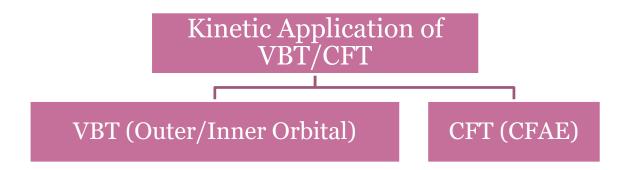
- ➤ Kinetic stability refers to the speed at which the transformation leading to equilibrium is attained. Deals with rates and mechanism.
- As a **'rule of thumb'** labile complexes refer to those undergoing substitution with $t_{1/2} < 1$ min (reaction almost completes within 1 min)
- Lability is generally a function of the metal ion, not the ligands

```
\begin{split} & [Fe(H_2O)_5(OH)]^{2+} + H^+ \rightarrow [Fe(H_2O)_6]^{3+} \\ & [Fe(H_2O)_6]^{3+} + Cl^- \rightarrow [Fe(H_2O)_5Cl]^{2+} \\ & [Fe(H_2O)_5Cl]^{2+} + PO_4^{3-} \rightarrow Fe(H_2O)_5PO_4 \\ & Fe(H_2O)_5PO_4 + SCN^- \rightarrow [Fe(H_2O)_5(SCN)]^{2+} \\ & [Fe(H_2O)_5(SCN)]^{2+} + F^- \rightarrow [Fe(H_2O)_5F]^{2+} \end{split}
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- \triangleright Often, the reaction happens at the diffusion limit = as soon as the reactants are mixed, they are done reacting. Diffusion = 10^{11} s⁻¹
- Labile Metal ions = those with small or zero LFSE: d^1 , d^2 , d^7 , d^9 , d^{10} /HS d^4 - d^6

Kinetic Applications of VBT and CFT

➤ Besides many other applications, VBT and CFT have also been used to predict the lability of octahedral metal complexes.



Structure	Inert Complexes	Labile Complexes	
Octahedral	d ³ and LS d ⁴ ,d ⁵ ,d ⁶	d ¹ ,d ² ,d ⁷ , d ⁸ ,d ⁹ ,d ¹⁰ / HS d ⁴ ,d ⁵ ,d ⁶	
Sqr. Planar	d ⁸ Pt ²⁺	Ni ²⁺	
	Pd ²⁺ (intermediate)		

Kinetic Applications of VBT

Analysis of large body of reaction rates of different complexes, the following general conclusions are made.

VBT (H. Taube): All Outer orbital complexes are labile while inner orbital complexes with at least one vacant low lying d-orbital (t_{2g}) is also labile.

- \gt Accordingly, the octahedral complexes of Cr(III) (t_{2g}^3) [Cr(NH₃)₆]³⁺, LS Co(III) (t_{2g}^6) [Co(NH₃)₅H₂O]³⁺, Fe(II) (t_{2g}^6) and Fe(III) (t_{2g}^6), and the low spin complexes of the second- and thirdrow TM ion with more than two d electrons are inert.
- ▶ Provide an explanation why complexes of V(III) (t_{2g}^2) are more labile than those of V(II) (t_{2g}^3) ; whereas complexes of Cr(III) (t_{2g}^3) are inert and those of Cr(II) (t_{2g}^3) are labile.
- ➤ Drawbacks: Qualitative as it does not explain the wide range of reactivities (w.r.t. d electron), especially of the labile systems. Why Ni(II) 10² times slower than that for Co(II) and >10⁴ times slower than that for Cu(II)? Same bond strength of IO and OO complex.

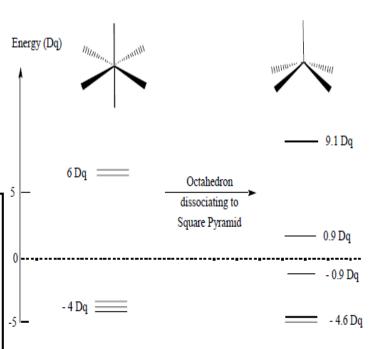
Kinetic Applications of CFT

- CFT: Basolo & Pearson used CFSE of starting and activated complex to calculate CFAE (CFAE = $CFSE_{sq\ py}$ $CFSE_{oct}$) to predict the lability of octahedral metal complexes.
- ➤ Complexes where there is a large loss of CFSE or more positive value of CFAE are of less lability compare to those having less positive CFAE or zero.

Structure	$d_{x^2-y^2}$	d_{z^2}	d_{xy}	$d_{_{RZ}}$	d_n
Octahedron	6.00	6.00	-4.00	-4.00	-4.00
Trigonal bipyramid (T.B.)	-0.82	7.07	-0.82	-2.72	-2.72
Square pyramid (S.P.)	9.14	0.86	-0.86	-4.57	-4.57
Pentagonal bipyramid (P.B.)	2.82	4.93	2.82	-5.28	-5.28
Octahedral wedge (O.W.)	8.79	1.39	-1.51	-2.60	-6.08
Square planar	12.28	-4.28	2.28	-5.14	-5.14

Table 3.15. Crystal Field Activation Energies for Two Transition States with High-Spin Configurations in Units of Dq

	CFSE			CFAE	
No. d Electrons	Octahedron	S. P.	O. W.	S. P.	O. W.
0, 10	0.0	0.0	0.0	0.0	0.0
1,6	4.00	4.57	6.08	0.57	-2.08
2, 7	8.00	9.14	8.68	-1.14	-0.68
3, 8	12.00	10.00	10.20	2.00	1.80
4, 9	6.00	9.14	8.79	-3.14	-2.79
5, 10	0.0	0.0	0.0	0.0	0.0



Simple problems

Ag(I) ion forms a stable 1:1 complex with trien. Calculate the Ag(I) conc. at equilibrium when 25 mL of 0.010 M silver nitrate is added to 50 mL of 0.015 M trien. Given $K_f = 5.0 \times 10^{7}$.

Solution

```
Ag^+ + trien \leftrightarrows Ag(trien)^+
mmol Ag^{+} added = 25x0.01 = 0.25
mmol trien added = 50 \times 0.015 = 0.75
The reaction occurs in a 1:1 ratio
mmol trien excess = 0.75 - 0.25 = 0.50
[Trien] = 0.5/75 \,\mathrm{M} and [Ag(trien)<sup>+</sup>] = 0.25/75 \,\mathrm{M}
Let x be the concentration of free Ag^+ ion, [Ag^+]_{free}
So K_f = (0.25/75 - x)/(x * 0.50/75 + x)
Assume 0.25/75 >> x, since K_f is very large
       5.0 \times 10^7 = (0.25/75)/(x * 0.50/75)
Or. x = 1.0 \times 10^{-8}
Relative error = (1.0 \times 10^{-8} / (0.25 / 75)) \times 100 = 3.0 \times 10^{-4} \%
Hence, the assumption is valid and [Ag^+] = 1.0 \times 10^{-8} M
```

TABLE 17-1

Typical Inorganic Complex-Forming Titrations

Titrant	Analyte	Remarks
Hg(NO ₃) ₂	Br ⁻ , Cl ⁻ , SCN ⁻ , CN ⁻ , thiourea	Products are neutral Hg(II) complexes: various indicators used
AgNO ₃	CN-	Product is Ag(CN) ₂ ; indicator is I ⁻ ; titrate to first turbidity of AgI
NiSO ₄	CN-	Product is Ni(CN) ₄ ²⁻ ; indicator is I ⁻ ; titrate to first turbidity of AgI
KCN	Cu ²⁺ , Hg ²⁺ , Ni ²⁺	Products are $Cu(CN)_4^{2-}$, $Hg(CN)_2$, and $Ni(CN)_4^{2-}$; various indicators used

and Controls

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TABLE 17-2

Organic Reagents for Extracting Metals					
Reagent	Metal Ions Extracted	Solvents			
8-Hydroxyquinoline	Zn ²⁺ , Cu ²⁺ , Ni ²⁺ , Al ³⁺ , many others	Water → Chloroform (CHCl ₃)			
Diphenylthiocarbazone (dithizone)	Cd ²⁺ , Co ²⁺ , Cu ²⁺ , Pb ²⁺ , many others	Water \rightarrow CHCl ₃ , or CCl ₄			
Acetylacetone	Fe ³⁺ , Cu ²⁺ , Zn ²⁺ , U(VI), many others	Water \rightarrow CHCl ₃ , CCl ₄ , or C ₆ H ₆			
Ammonium pyrrolidine dithiocarbamate	Transition metals	Water → Methyl isobutyl ketone			
Tenoyltrifluoroacetone	Ca ²⁺ , Sr ²⁺ , La ³⁺ , Pr ³⁺ , other rare earths	Water → Benzene			
Dibenzo-18-crown-6	Alkali metals, some alkaline earths	Water \rightarrow Benzene			

Thank you