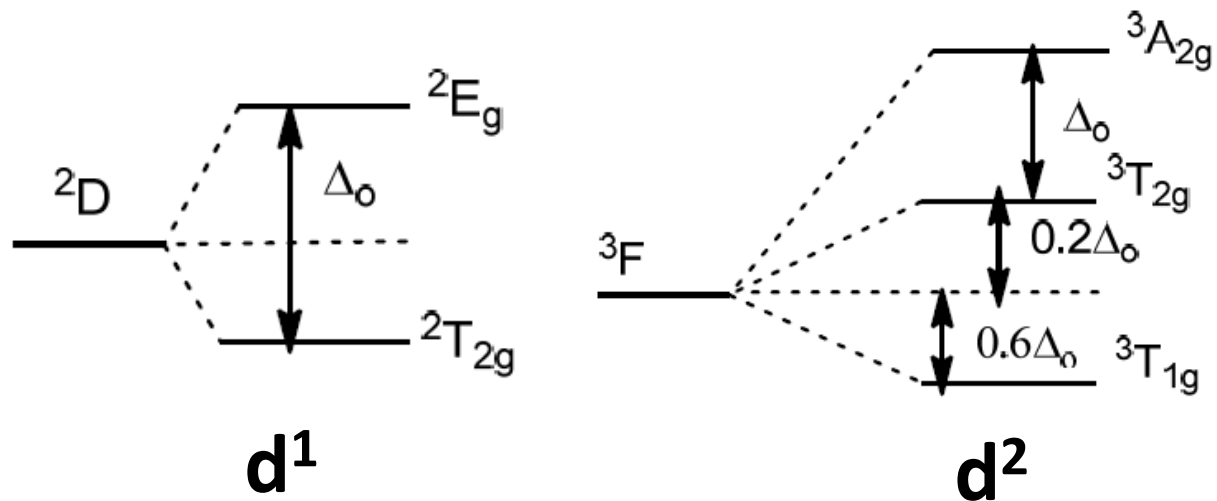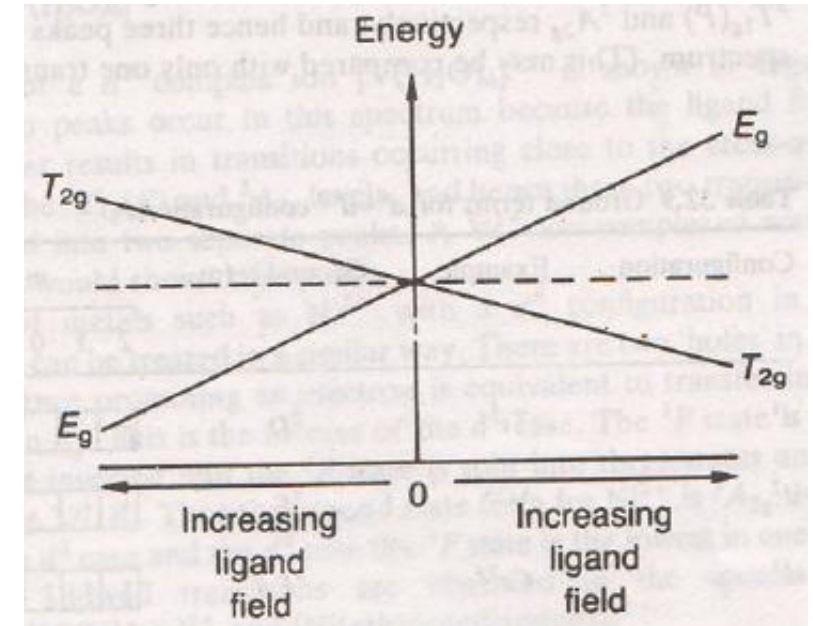# CHEM F111 : General Chemistry
Semester II: AY 2017-18
Lecture-28, 28-03-2018

Summary of lecture 27
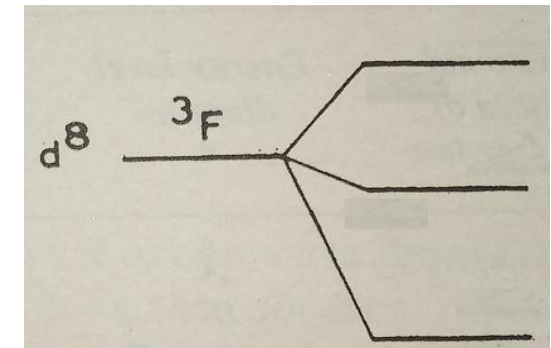
✓ Splitting of d^n terms, hole formulation

✓ Selection rule for electronic transition

✓ Spectra of d^1 and d^9 ions

Free ion	Splitting in an octahedral
S	A_{1g}
P	T_{1g}
D	$E_g + T_{2g}$
F	$A_{2g} + T_{1g} + T_{2g}$

Summary of lecture 27

Splitting of all d^n ions
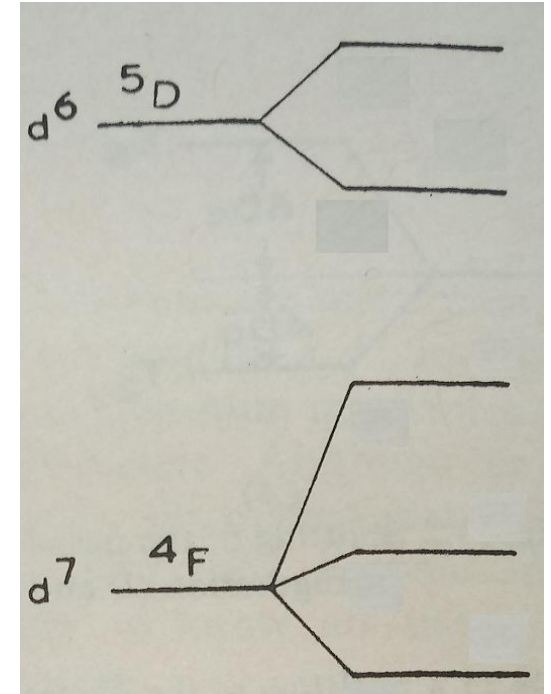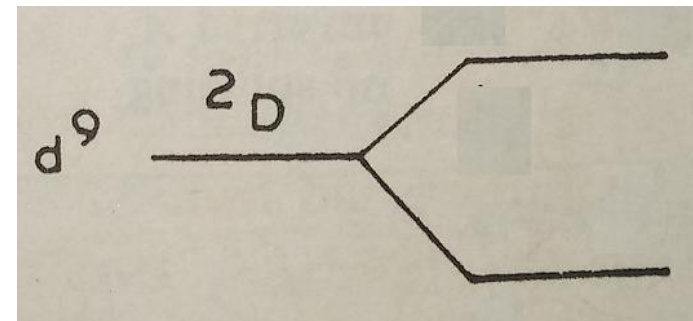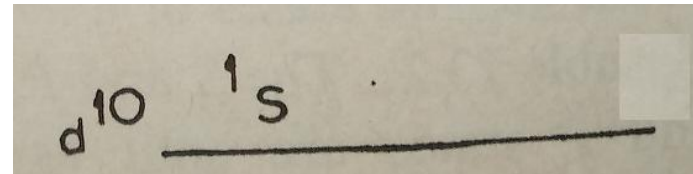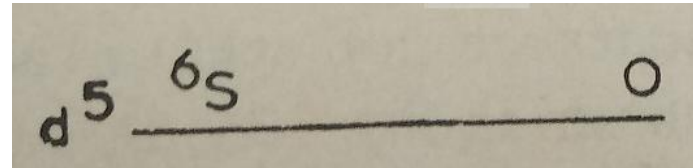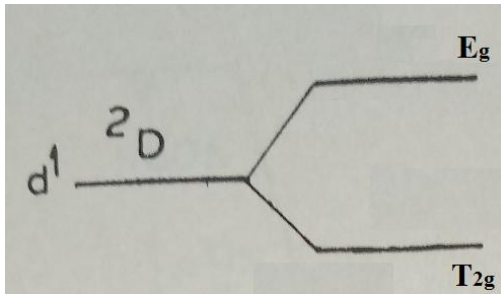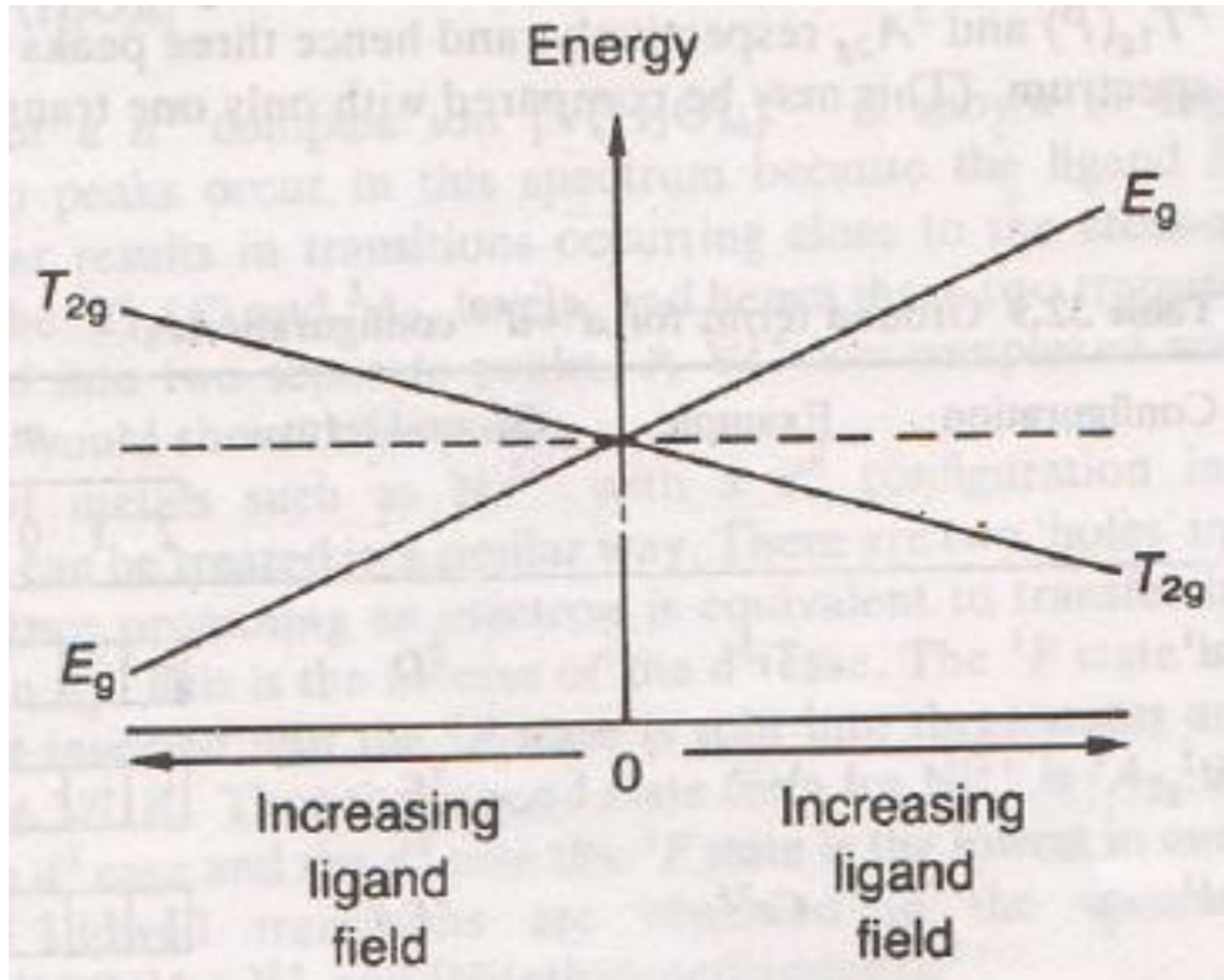
d^1 octahedral

d^9 octahedral
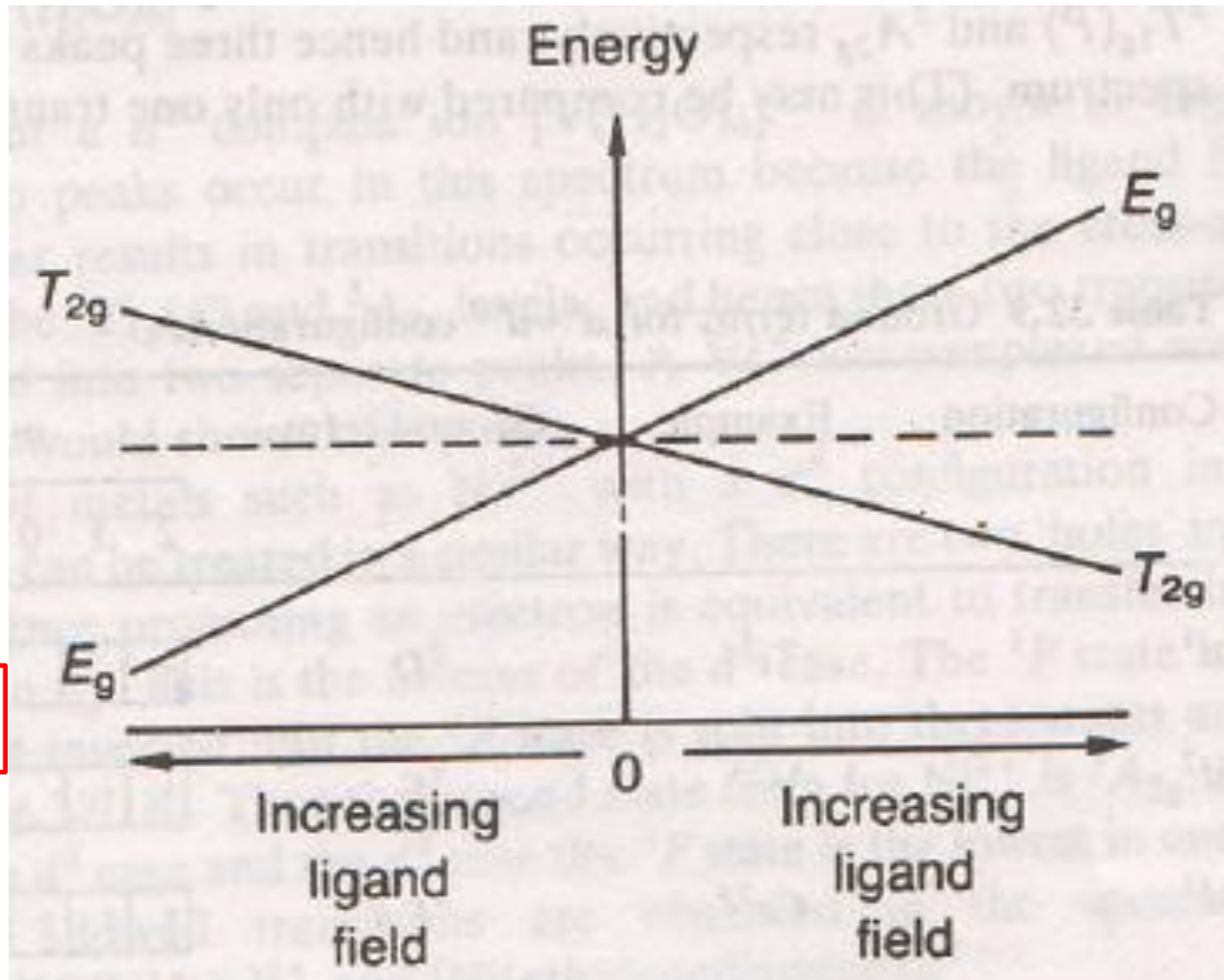
d⁶ octahedral

d⁴ octahedral

Stability of complexes

In studying the formation of complexes in solution, two kinds of stability of complexes come in mind:

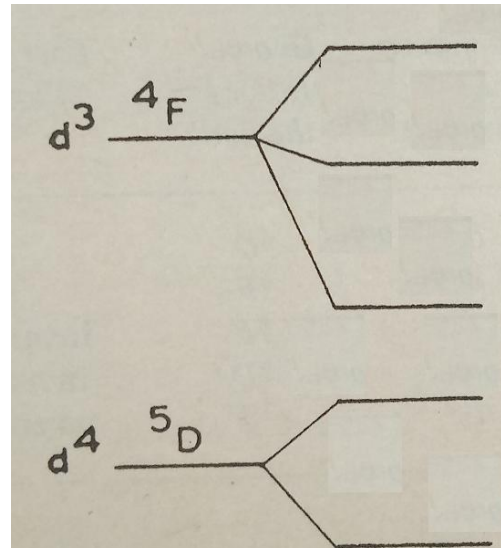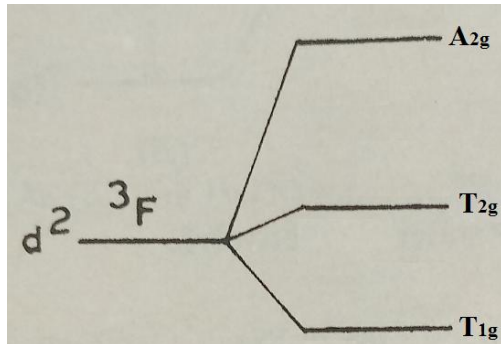1. Thermodynamic stability: This is a measure of the extent to which the complex will form or will be transformed into another species (*under certain conditions*), when the system has reached equilibrium. Here, metal-ligand bond energies, stability constant etc. are very important

2. Kinetic stability: Refers to the speed with which transformations leading to the attainment of equilibrium will occur. (faster rate of formation of the particular species)

Stability of complexes

Higher the value of equilibrium constant for a reaction, more stable is the product formed.

TYPES:

1. Stepwise formation constant
2. Overall formation constant

Stepwise formation constants

M = central metal atom, L = monodentate ligand, n = coordination number

Stepwise formation constants

$M + L \rightleftharpoons ML$; $K_1 = [ML]/[M][L]$

$ML + L \rightleftharpoons ML_2$; $K_2 = [ML_2]/[ML][L]$

$\cdot \quad \cdot \qquad \cdot$

$\cdot \quad \cdot \qquad \cdot$

$ML_{n-1} + L \rightleftharpoons ML_n$; $K_n = [ML_n]/[ML_{n-1}][L]$
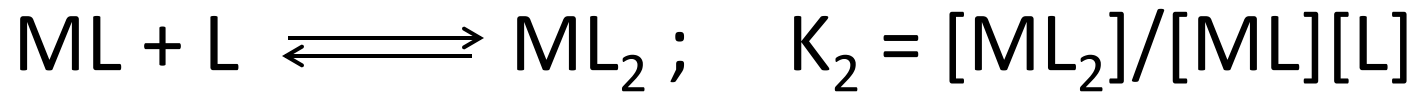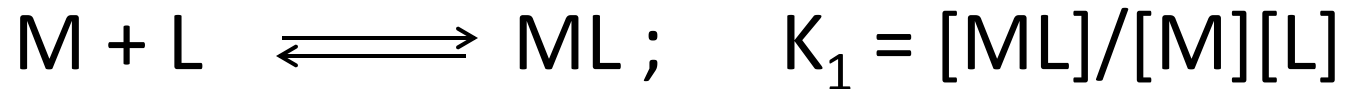
K_1, K_2, K_n are known as stepwise formation constants

Overall formation constants

Overall formation constants

$$M + L \rightleftharpoons ML \; ; \qquad \beta_1 = [ML]/[M][L]$$

$$M + 2L \rightleftharpoons ML_2 \; ; \qquad \beta_2 = [ML_2]/[M][L]^2$$

$$. \qquad . \qquad .$$

$$. \qquad . \qquad .$$

$$M + nL \rightleftharpoons ML_n \; ; \qquad \beta_n = [ML_n]/[M][L]^n$$
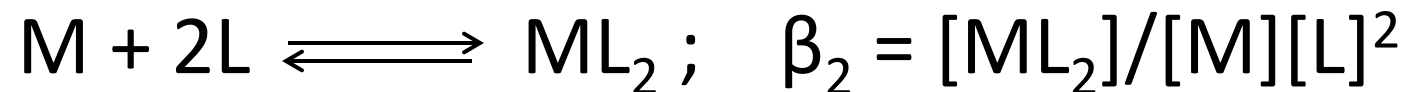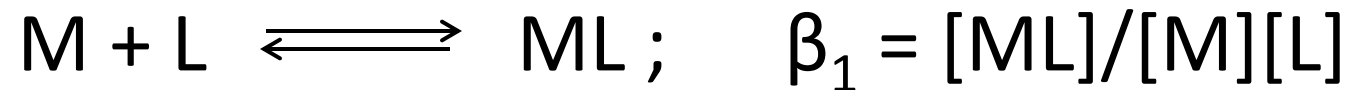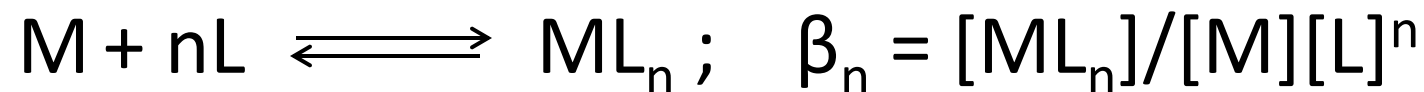
$\beta_1, \beta_2, \beta_n$ are known as overall formation constants.

Relationship between K and β

K's and β's are related to one another

$$\beta_1 = K_1$$

$$\beta_2 = K_1 . K_2$$

$$\beta_3 = [ML_3]/[M][L]^3 = [ML]/[M][L] . [ML_2]/[ML][L] . [ML_3]/[ML_2][L]$$

$$= K_1 . K_2 . K_3$$

$$\beta_n = K_1 . K_2 . K_3 .... K_n$$

$$\log \beta_n = \log K_1 + \log K_2 + \log K_3 + ... \log K_n$$

Thermodynamic parameters

$$\Delta G^0 = - 2.303 \, RT \log \beta_n$$

$$\text{Since, } \Delta G^0 = \Delta H^0 - T\Delta S^0$$

Where, ΔH^0 and ΔS^0 are the enthalpy and entropy changes during the reaction

Therefore, $- 2.303 \, R \log \beta_n = \Delta H^0 / T - \Delta S^0$

1. In aqueous solution, the enthalpy change is ±20 kJ/mol for ionic ligands, 0.20 kJ/mol for neutral monodentate and up to -85 kJ/mol for the polydentates.

2. ΔS^0 is usually positive (i) effect of the binding ligands to metal ion and (ii) charge neutralization on the metal ion

Factors determining stability of comp.

The stability constants (K) of the metal complexes depend upon the

A. Metal ion: (i) K increases with decreasing size of the metal ion, K α 1/r
(ii) K increases with the charge of the central ion [K for Fe(III) is higher than Fe(II)]
(iii) Electronegativity also parallels the polarizing power. Higher electronegativity gives stable complexes
(iv) Ionization energy: The electronegativity, covalent nature, and ionic radii can all be related to the ionization energies of the atoms

Factors determining stability of comp.

B. <u>The nature of the ligand</u>: Basicity of the ligands, dipole moment and polarizability, π-bonding always increases the stability, and steric factors

C. <u>The chelate effect:</u>

$$[Co(NH_3)_6]^{3+} + 3en \rightleftharpoons [Co(en)_3]^{3+} + 6NH_3$$
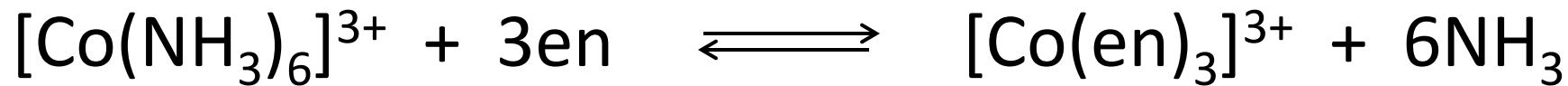
$\Delta H^0 = -13.0$ kJ/mol and log K = 8.7

$\Delta G^0 = -RT\ ln\ K = -70.4$ kJ/mol

$T\ \Delta S^0 = 57.4$ kJ/mol

An example

$$[Cu(NH_3)_4]^{2+} \quad < \quad [Cu(en)_2]^{2+} \quad < \quad [Cu(trien)]^{2+}$$

$$\text{Log } \beta = \quad 12.7 \quad < \quad 19.7 \quad < \quad 20.5$$
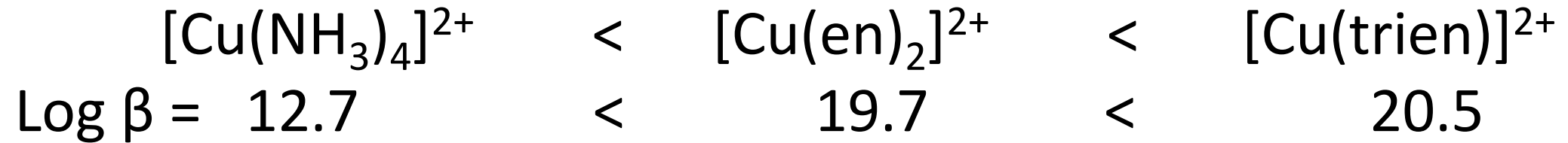
$$- RT \ln \beta = \Delta G^0 = \Delta H^0 - T\Delta S^0 \ (\Delta H^0 \text{ is negative})$$

(i) $Cd^{2+} + 2en \rightleftharpoons [Cd(en)_2]^{2+}$ with log β = 10.6

{ΔH^0 = -56.3 kJ/mol, ΔS^0 = +14.1 kJ/mol, - $T\Delta S^0$ = -4.2 kJ/mol and ΔG^0 = -60.7 kJ/mol}

Kinetic stability of complexes

Kinetic stability discusses rates and the mechanism of chemical reactions, formation of intermediate complexes, activation energies for the processes, etc.

Kinetic stability: Refers to the speed with which transformations leading to the attainment of equilibrium will occur. (faster rate of formation of the particular species)

Inert and labile complexes

❖ In the kinetic sense it is more proper to call the complexes inert or labile complexes rather than stable or unstable complexes

❖ The complexes in which the ligands are rapidly replaced by others are called **labile** or **non-inert complexes** while those in which substitution occurs slowly are termed **inert complexes**
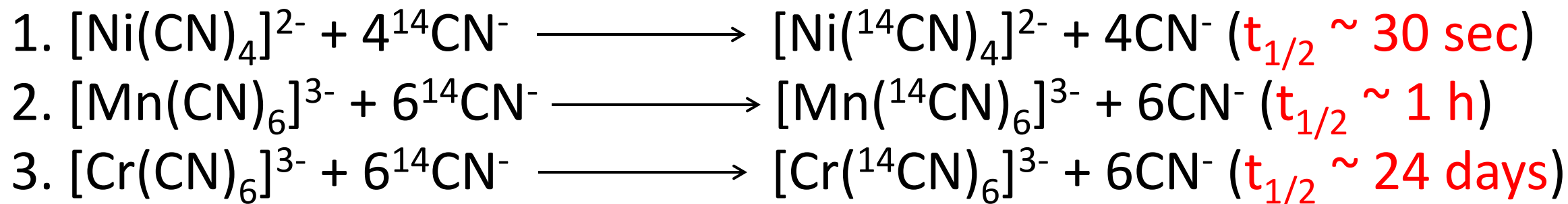
Not to be confused with

Thermodynamic stable and unstable (a thermodynamic concept $\Delta G_f < 0$)

Thermodynamic and kinetic stability

$[Ni(CN)_4]^{2-}$, $[Mn(CN)_6]^{3-}$, and $[Cr(CN)_6]^{3-}$
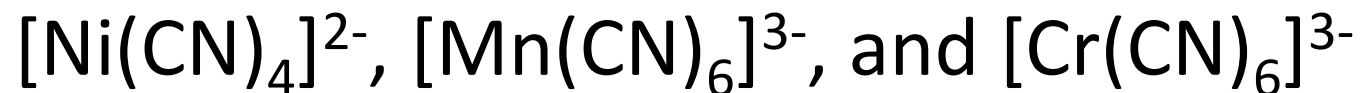
All of these complexes are extremely stable from a thermodynamic point of view; yet kinetically they are quite different.

One of these complexes exchanges cyanide ligand very rapidly (is labile), a second is moderately labile, and only $[Cr(CN)_6]^{3-}$ can be considered to be inert:

1. $[Ni(CN)_4]^{2-} + 4\,^{14}CN^- \longrightarrow [Ni(^{14}CN)_4]^{2-} + 4CN^-$ ($t_{1/2} \sim 30$ sec)
2. $[Mn(CN)_6]^{3-} + 6\,^{14}CN^- \longrightarrow [Mn(^{14}CN)_6]^{3-} + 6CN^-$ ($t_{1/2} \sim 1$ h)
3. $[Cr(CN)_6]^{3-} + 6\,^{14}CN^- \longrightarrow [Cr(^{14}CN)_6]^{3-} + 6CN^-$ ($t_{1/2} \sim 24$ days)

Thermodynamic and kinetic stability

An example of kinetically inert and thermodynamically unstable complex:

$$[Co(NH_3)_6]^{3+} + 6H^+ \rightleftharpoons Co^{3+}(aq.) + 6NH_4^+$$
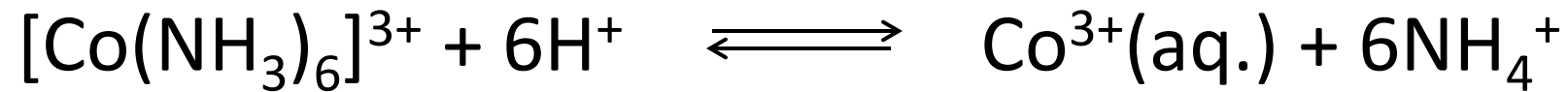
The tremendous thermodynamic driving force of six basic ammonia molecules combining with six protons results in an equilibrium constants for the reaction of 10^{25}

At room temperature several days are required for degradation of the complex

What is/are the driving force (s) behind the conversion of complex II to complex III? Calculate the overall formation constant (β) in "$\log_{10}$" form for complex III at 40 °C, if the standard enthalpy and entropy changes are -8.1 kJ/mol and 0.152 kJ/mol, respectively [R = 8.314 J/(mol.K)]?

$$[Cr(H_2O)_6]^{2+} \xrightarrow{\textbf{2 en}} [Cr(en)_2(H_2O)_2]^{2+}$$

Complex II   Complex III
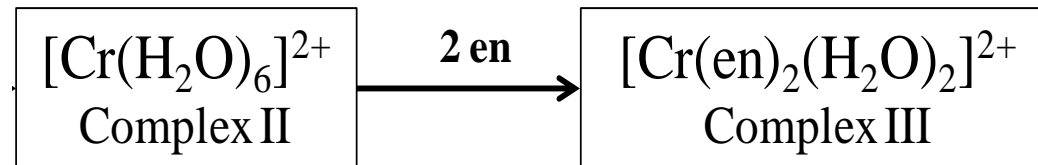
Discussed topics……

- ✓ Thermodynamic and kinetic stability

- ✓ Factors determining stability of complexes

- ✓ Labile and inert complexes