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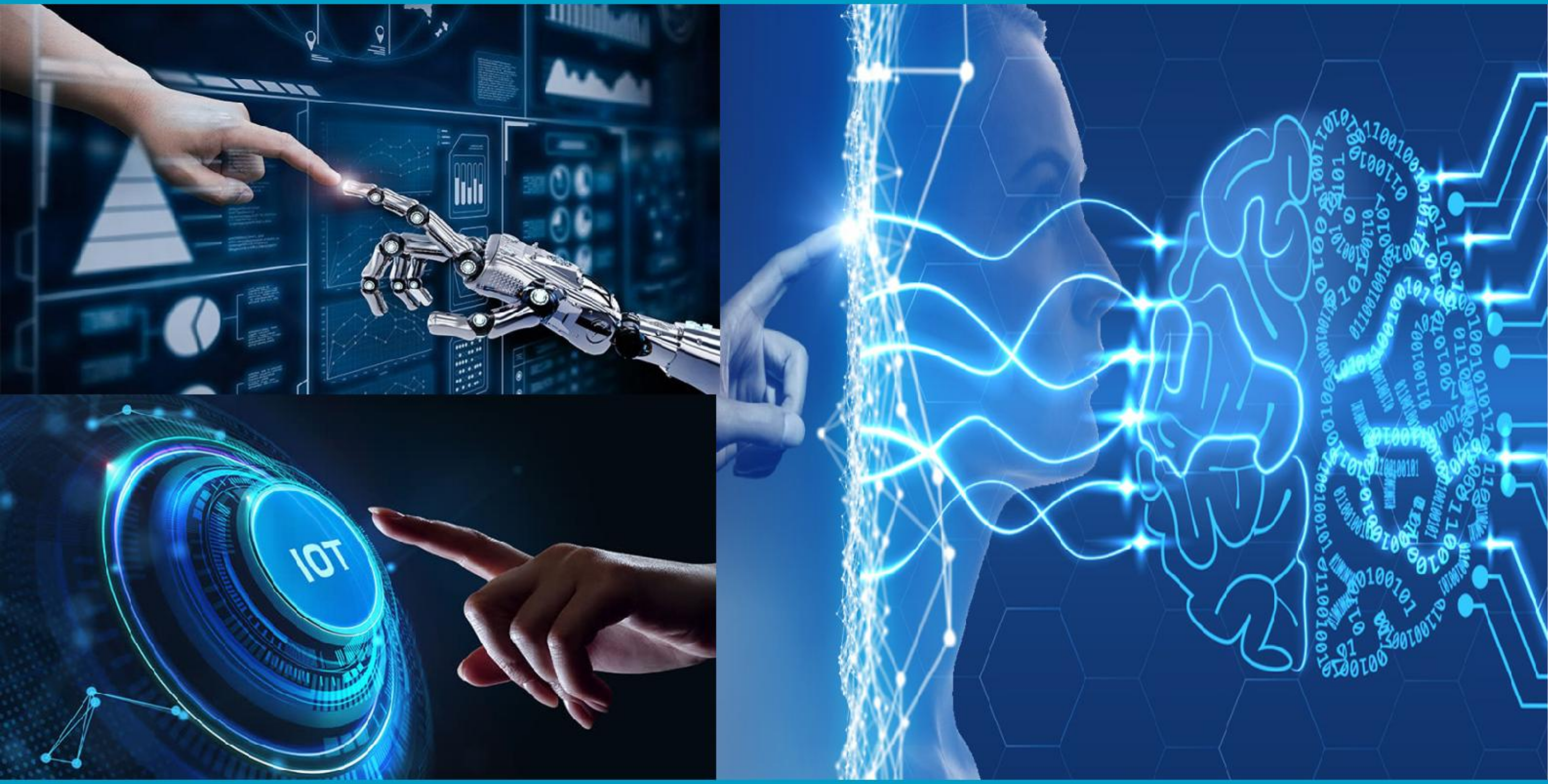

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Stability of Complexes- Degree of Association Between Metal Ion and Ligand

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ABSTRACT: The stability of a complex in solution means the degree of association between the metal ion and the ligands involved in the state of equilibrium.The magnitude of the (stability or formation) equilibrium constant for the association express quantitatively the stability.For example: The formation of $[Cu(NH_3)_4]^{2+}$ complex may be expressed as :
Cu^{2+} (aq) $+4NH_3$ (aq) ⇔ $[Cu(NH_3)_4]^{2+}$ (aq) The equilibrium constant for the reaction, is therefore, called the stability constant and is represented by K_s as

$$\text{Stability constant, } K_s = \frac{[Cu(NH_3)_4]^{2+}}{[Cu^{2+}][NH_3]^4}$$

The interaction between metal ion and ligand may be regarded as Lewis acid-base reaction. If the interaction is strong, the complex formed would be thermodynamically more stable and the value of stability constant (K_s) will be large.The larger the numerical value of K_s, the more thermodynamically stable is the complex.

KEYWORDS: stability, complex, equilibrium, ligand, ion, thermodynamic, constant, magnitude, reaction

INTRODUCTION

Let us consider a general reaction:
$M+4L \Leftrightarrow ML_4$
The stability constant may be written as:[1]

$$K_B = \frac{[ML_4]}{[M][L]^4}$$

Larger the stability constant, the higher the proportion of ML_4 that exists in solution. Since free metal ions rarely exist in the solution so that metal ion (M) will usually be surrounded by solvent molecules which will complete with the ligand molecules, L and be successively represented as :

$[M(H_2O)_n] + 4L \Leftrightarrow [ML_4] + nH_2O$

The above overall reaction proceeds in steps with formation constant K_1, K_2, K_3 and K_4, for each step as represented below:[2]

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

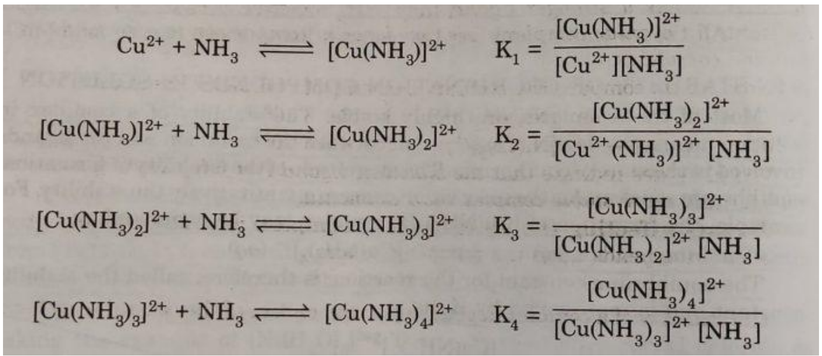
$$ML + L \rightleftharpoons ML_2 \qquad K_2 = \frac{[ML_2]}{[ML][L]}$$

$$ML_2 + L \rightleftharpoons ML_3 \qquad K_3 = \frac{[ML_3]}{[ML_2][L]}$$

$$ML_3 + L \rightleftharpoons ML_4 \qquad K_4 = \frac{[ML_4]}{[ML_3][L]}$$

where K_1, K_2, K_3 and K_4 are called **stepwise stability constants**

Alternatively, we may write the overall stability constant as
$M + 4L \Leftrightarrow ML_4$
$\beta_4 = [ML_4] / [M] [L]^4$
The stepwise and overall stability constants are therefore, related as:[3]
$\beta_4 = K_1 \times K_2 \times K_3 \times K_4$
$\beta_n = K_1 \times K_2 \times K_3 \times K_{4} \ldots\ldots\ldots\ldots K_n$
For example: The steps involved in the formation of the complex ion, tetraamminecopper(III) ion, we have the following:[4]



$$Cu^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)]^{2+} \qquad K_1 = \frac{[Cu(NH_3)]^{2+}}{[Cu^{2+}][NH_3]}$$

$$[Cu(NH_3)]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_2]^{2+} \qquad K_2 = \frac{[Cu(NH_3)_2]^{2+}}{[Cu^{2+}(NH_3)]^{2+}\,[NH_3]}$$

$$[Cu(NH_3)_2]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_3]^{2+} \qquad K_3 = \frac{[Cu(NH_3)_3]^{2+}}{[Cu(NH_3)_2]^{2+}\,[NH_3]}$$

$$[Cu(NH_3)_3]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} \qquad K_4 = \frac{[Cu(NH_3)_4]^{2+}}{[Cu(NH_3)_3]^{2+}\,[NH_3]}$$

$\beta_4 = [Cu(NH_3)_4]^{2+} / [Cu^{2+}][NH_3]^4$

Then, logβ may be used as a measure of stability of the complex.

For example:For $[Cu(NH_3)_4]^{2+}$, the four constants are :

$\log \beta_4 = \log K_1 + \log K_2 + \log K_3 + \log K_4$

$= 4.0 + 3.2 + 2.7 + 2.0$

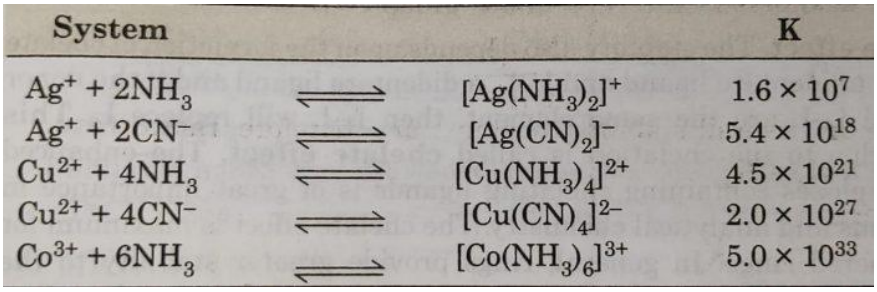
$\log \beta_4 = 11.9$

For example: for $[Cd(NH_3)_4]^{2+}$

$\log \beta_4 = 2.6 + 2.1 + 1.4 + 0.9 = 7.0$

Thus, the log β_4 value of $[Cu(NH_3)_4]^{2+}$ and $[Cd(NH_3)_4]^{2+}$ complexes indicate that $[Cd(NH_3)_4]^{2+}$ is more stable than $[Cd(NH_3)_4]^{2+}$ complex.In the second group of qualitative analysis of basic radicals, Cu^{2+} does not form precipitate as CuS when H_2S is passed through the solution containing $[Cd(NH_3)_4]^{2+}$ complex, while Cd^{2+} ions form precipitate as CdS because of instability of $[Cd(NH_3)_4]^{2+}$ complex ion.[5]

The reciprocal of stability constant gives the instability constant or dissociation constant of coordination compound, Thus,Dissociation constant of complex = 1 / Stability constantThe overall stability constant, β_n is related to thermodynamic stability when the system has reached equilibrium. Most of the measurements are made from aqueous solutions, which means that the complex is formed by the ligand displacing water molecules from the aqua complex of the metal ion.The values indicate that CN^- ion ia a stronger ligand than NH_3 molecule because the stability constants for cyanide complexes are very large in comparison to corresponding ammine complexes.[6]



System			K
$Ag^+ + 2NH_3$	$\rightleftharpoons$	$[Ag(NH_3)_2]^+$	1.6×10^7
$Ag^+ + 2CN^-$	$\rightleftharpoons$	$[Ag(CN)_2]^-$	5.4×10^{18}
$Cu^{2+} + 4NH_3$	$\rightleftharpoons$	$[Cu(NH_3)_4]^{2+}$	4.5×10^{21}
$Cu^{2+} + 4CN^-$	$\rightleftharpoons$	$[Cu(CN)_4]^{2-}$	2.0×10^{27}
$Co^{3+} + 6NH_3$	$\rightleftharpoons$	$[Co(NH_3)_6]^{3+}$	5.0×10^{33}

Now, let us compare the stability constant of two nickel complexes:

$Ni^{2+} + 6\,NH_3 \rightarrow [Ni(NH_3)_6]^{2+}$ $K = 6.1 \times 10^8$
$Ni^{2+} + 3\,en \rightarrow [Ni(en)_3]^{2+}$ $K = 4.6 \times 10^{18}$

The K values indicate that the bidentate ligand $NH_2CH_2CH_2NH_2$ forms a considerably more stable complex than ammonia.[7]

Factors affecting the stability of a complex ion

The stability of the complex ion depends upon the following factors:[8]

(1) The nature of the central ion

The stability of a complex depend upon the nature of the central metal ion as:

(i) Charge on the central metal ion: In general, the greater the charge density on the central ion, the greater is the stability of its complexes.The greater the charge and the smaller the size of an ion, i.e., (the larger the charge/radius ratio of an ion), the greater is the stability of its complex. Fe^{3+} ion carries higher charge than Fe^{2+} ion but their size is about the same.

Hence charge density is higher on Fe^{3+} than on Fe^{2+} ion. The complexes of Fe^{3+} ion are, therefore more stable.[9]

$Fe^{3+} + 6CN^- \rightarrow [Fe(CN)_6]^{3-}$

$K = 1.2 \times 10^{31}$

$Fe^{2+} + 6CN^- \rightarrow [Fe(CN)_6]^{4-}$

$K = 1.8 \times 10^6$

(ii) Size of metal ion: As the size of the metal ion decreases, the stability of the complex increases. If we consider the bivalent metal ions, than the stability of their complexes (irrespective of the ligands) increases with increase in the ionic radius of the central metal ion as:[10]

Ion	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
Ionic Radius	91	83	82	78	69	64

Therefore, the order of stability is

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

This order is called Irving William's order of stability.[11]

(iii) Electronegativity or charge distribution of metal ion: The stability of complex ion is also related to the electron charge distribution on the metalion.

Metal ions may be classified into two types:

(a) Class 'a' acceptors: These are fairly electropositive metals and include the metals of groups 1 and 2, inner transition metals and the early members of the transition series (groups 3 to 6) which have relatively a few electrons beyond an inert gas core. These form most stable coordination entities with ligands containing N, O or F donor atoms.[12]

(b) Class 'b' acceptors: These are much less electropositive and include heavy metals such as Rh, Pd, Ag, Ir, Pt, Au, Hg, Pb, etc. having relatively full d-orbitals. These form most stable complexes with ligands whose donor atoms are the heavier members of the N, O and F groups.

(iv) Chelate effect: The stability also depends upon the formation of chelate rings. If L is an unidentate ligand and L-L, a bidentate ligand and if the donor atoms of L and L-L are the same element, then L-L will replace L.

This stabilisation due to the chelation is called **chelate effect.** The enhanced stability of complexes containing chelating ligands is of great importance in biological systems and analytical chemistry.

The chelate effect is maximum for 5- and 6-membered rings. In general, rings provide greater stability to the complex.[13]

(v) Macrocyclic effect: If a multidentate ligand is cyclic and there are no unfavourable stearic effects, the complexes formed are more stable than corresponding complexes without cyclic ligands. This is called macrocyclic effect.

(2) The nature of the ligand

(i) Basic strength: The more basic a ligand, the greater is the ease with which it can donate its lone pairs of electrons and, therefore, the greater is the stability of the complexes formed by it. Thus, CN^- and F^- ions and NH_3 molecules, which are strong bases, are also good ligands and form many stable complexes.[14]

(ii) Size and charge of ligands: For anionic ligands, the higher the charge and the smaller the size, the more stable is the complex formed. Thus, F^- ion gives more stable complexes than does Cl^- ion.

II.DISCUSSION

Stability of Coordination Compounds and reaction kinetics is an important aspect of coordination Chemistry and finds their application in all disciplines, from catalyst design to pharmaceutical studies of drug design and metabolism.

The study of stabilities and reaction mechanism of complexes is vital to determine the behaviour of metal complexes in different environments, including changes in temperature or changes in pHpH of the reaction medium. A higher equilibrium constant indicates the greater stability of a complex. Let's understand the different types of stabilities present in metal complexes and their effect on reaction mechanisms.

According to the J. Bjerrum, the formation of a metal complex in solution proceeds by the stepwise addition of the ligands to the central metal ion. Thus, the formation of complex MLnMLn by the stepwise formation method can be given as:[15]

$$\begin{array}{ll}
M + L \xrightleftharpoons{K_1} ML, & K_1 = \dfrac{[ML]}{[M][L]} \\
ML + 2L \xrightleftharpoons{K_2} ML_2, & K_2 = \dfrac{[ML_2]}{[ML][L]^2} \\
ML_2 + 3L \xrightleftharpoons{K_3} ML_3, & K_3 = \dfrac{[ML_3]}{[ML_2][L]^3} \\
\vdots \qquad \vdots \qquad \vdots & \vdots \qquad \vdots \\
ML_{n-1} + nL \xrightleftharpoons{K_n} ML_n, & K_n = \dfrac{[ML_n]}{[ML_{n-1}][L]^n}
\end{array}$$

Where K1,K2,K3,⋯.KnK1,K2,K3,⋯.Kn are stepwise formation or stability constant for the complexes formed in the corresponding steps.

The formation of complex MLnMLn may also proceed in a single step which can be given as:[16]

$$M + nL \rightleftharpoons ML_n \qquad \beta_n = \frac{[ML_n]}{[M][L]^n}$$

Where M represents the centre metal, n represents the number of ligands; L is the ligand type involved, and β represents the equilibrium constant for the whole process.

From the expression of βn we can conclude that the magnitude of βn is:

1. Proportional to the molar concentration of complex formed
2. A measure of the strength of the interaction between the ligands that come in close contact of the metal centre to form the metal complex

Hence, the equilibrium constant βn is also called the formation constant or stability constant of the metal complex.To define the stability of the complex compound formed in the solution, two types of the stability concept can be used, which are explained in the following section.[17]

Thermodynamic Stability Concept of Complexes

The thermodynamic stability of metal complexes is a function of the equilibrium constant and is defined by the thermodynamic parameters like bond energy, stability constant or formation constant of the metal complexes.According to the thermodynamic stability concept, a complex compound can be categorised into two different types, which are given below:

1. **Stable Complexes**: Metal complexes that exhibit very high formation constant in the solution are known as stable complexes.
2. **Unstable Complexes:** Metal complexes that exhibit low formation constant in the solution are known as unstable complexes

The stability of the complexes is a function of the rate constant of the metal complexes and is defined by the kinetic parameters. The reaction with a high rate constant is expected to proceed fast.According to the kinetic stability concept, complex compounds in the solution can be divided into two types:[18]

1**. Inert Complex:** Metal complexes that exhibit a very low or negligible replacement of ligands in the solution are known as inert complexes. This means the substitution of one or more ligands present in the coordination sphere of the complex takes place very slowly. The rate of substitution of inert complexes can be measured easily by conventional techniques.

2. **Labile Complex:** Metal complexes that exhibit a very high rate of replacement of one or more ligands in the solution are known as labile complexes. This means the substitution of one or more ligands present in the coordination sphere of the complex takes place quickly or rapidly.

Relationship between Thermodynamic and Kinetic Stability Concept

[Hg(CN)4]2–[Hg(CN)4]2– ion has a very high formation constant (1042)(1042) but it can easily undergo a replacement reaction in the solution. Therefore, this complex is thermodynamically stable but kinetically labile.

Similarly, [Co(NH3)6]+3[Co(NH3)6]+3 ion is kinetically inert but thermodynamically unstable.Hence, a thermodynamically stable complex may be kinetically labile (fast-reacting complex) and a thermodynamically unstable complex may be kinetically inert (slow reacting complex).[19]

III.RESULTS

Relationship between Stepwise Formation Constant and Overall Formation Constant

To give the relationship between stepwise formation constants and overall formation constant, let us consider the formation of ML3 complex by the stepwise formation method and overall formation method. According to the stepwise formation method:

$$M + L \overset{K_1}{\rightleftharpoons} ML, \quad K_1 = \frac{[ML]}{[M][L]} \quad \text{---------} (1)$$

$$ML + L \overset{K_2}{\rightleftharpoons} ML_2, \quad K_2 = \frac{[ML_2]}{[ML][L]} \quad \text{---------} (2)$$

$$ML_2 + L \overset{K_3}{\rightleftharpoons} ML_3, \quad K_3 = \frac{[ML_3]}{[ML_2][L]} \quad \text{---------} (3)$$

According to the overall formation method-[20]

$$M + 3L \rightleftharpoons ML_3 \quad \beta_3 = \frac{[ML_3]}{[M][L]^3} \ldots\ldots(4)$$

Dividing and multiplying Eqn (4)(4) with [ML2][ML][ML2][ML], we get-

β3=[ML3][M][L]3×[ML2][ML2]×[ML][ML]3=[ML3][M][L]3×[ML2][ML2]×[ML][ML]

β3=[ML3][ML2][L]×[ML2][ML][L]×[ML][M][L]3=[ML3][ML2][L]×[ML2][ML][L]×[ML][M][L]

From Eqn (1),(2),(3)(1),(2),(3) and (4)(4), we get-

β3=K3×K2×K13=K3×K2×K1

βn=Kn…………K3×K2×K1n=Kn…………K3×K2×K1

Thus, from the above equation, it is observed that the product of the stepwise formation constant is always equal to the overall formation constant for any particular complex.
The overall stability constant is generally reported in the logarithmic scale as logβlog shown below.

logβn=log(Kn…………K3×K2×K1)logn=log(Kn…………K3×K2×K1)

logβn=logKn+…………..+logK3+logK2+logK1logn=logKn+…………..+logK3+logK2+logK1)

Or, logβn=∑i=1i=nlogKilogn=∑i=1i=nlogKi

If the value of the logβlog is more than 88 the complex is considered thermodynamically stable.[21]

Relationship between Dissociation (or instability) Constant and Overall Formation Constant
In an aqueous solution, a complex ion dissociates, and an equilibrium exists between the undissociated complex ion and the species obtained by the dissociation of the complex ion.For example, The dissociation of [Cu(NH3)4]2+[Cu(NH3)4]2+ ion in solution is represented by the equilibrium:

$$\left[\mathrm{Cu}\left(\mathrm{NH}_3\right)_4\right]^{2+} \rightleftharpoons \mathrm{Cu}^{2+} + 4\mathrm{NH}_3$$

The dissociation (or instability) constant KiKi of the above equilibrium is given by:
Ki=[Cu2+][NH3]4[Cu(NH3)4]2+………………..eqn(i)Ki=[Cu2+][NH3]4[Cu(NH3)4]2+………………..eqn(i)The formation of [Cu(NH3)4]2+[Cu(NH3)4]2+ ion in a solution can be represented by the equilibrium given below:[22]

$$\mathrm{Cu}^{2+} + 4\mathrm{NH}_3 \rightleftharpoons \left[\mathrm{Cu}\left(\mathrm{NH}_3\right)_4\right]^{2+}$$

The formation (or stability) constant for the above reaction, which is represented by β is given by:

β=[Cu(NH3)4]2+[Cu2+][NH3]4……………………eqn(ii)=[Cu(NH3)4]2+[Cu2+][NH3]4……………………eqn(ii)

On comparing eqn (i)(i) and (ii)(ii), we get-

Thus, the formation constant (or stability constant), β is reciprocal of dissociation constant (or instability constant), KiKi.
β=1Ki=1Ki
Higher is the value of the stability constant, β (formation constant) for a complex ion, greater is the stability of the complex ion. Now since βα1Ki1Ki, we can say that smaller is the value of instability constant, KiKi (dissociation constant) of a complex ion, greater is the stability of the complex ion.[23]

IV.CONCLUSIONS

The different factors that affect the stability of complexes formed in the solution are given as below:

1. Nature of the central metal atom/ion
2. Nature of the ligands
3. Amount of Metal-Ligand Covalent Characters Present in Complexes

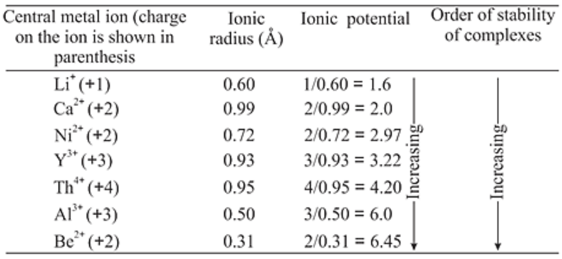
A. Nature of the Central Metal Atom/Ion
i) Size of the Central Metal Atom: As the size of metal ions decreases, the stability of the complex increases; thus, the stability of isovalent complexes decreases down the group and increases along the period as the size varies in the reverse order.
If we consider the divalent metal ions Mn2+,Fe2+,Co2+,Ni2+,Cu2+,Zn2+Mn2+,Fe2+,Co2+,Ni2+,Cu2+,Zn2+ then the stability of their complexes increases with a decrease in the ionic radius of the central metal as given below:

Ion	Mn2+Mn2+	Fe2+Fe2+	Co2+Co2+	Ni2+Ni2+	Cu2+Cu2+	Zn2+Zn2+
Ionic radius pmpm	91 91	83 83	82 82	78 78	73 73	7474

Therefore, the order of the stability is: Mn2+<Fe2+<Co2+<Ni2+<Cu2+>Zn2+Mn2+<Fe2+<Co2+<Ni2+<Cu2+>Zn2+
This order is called the natural order of stability or Irving William's order, which is due to the regular decrease in size from Mn2+Mn2+ to Cu2+Cu2+ and increase in size from Cu2+Cu2+ to Zn2+Zn2+ ion.

ii) Charge on the Central Metal Atom: A smaller, more highly charged ion allows a closer and faster approach of the ligands and greater force of attraction. This results in the formation of a stable complex. In general, the greater the charge on the central metal ion, the greater the complex's stability.
Stability α+ve oxidation state of Central Metal ion

iii) Charge to size ratio: Metal ions having high charge density forms stable complexes. Charge density means the ratio of the charge to the radius of the ion. Thus, the smaller the size and higher the charge of the metal ion, i.e. larger is the charge/radius ratio of a metal ion, the greater is the stability of its complex.[24]
For example, the stability of hydroxide complexes of Li+,Ca2+,Ni2+,….Be2+Li+,Ca2+,Ni2+,….Be2+ ions whose charge density increases from Li+Li+ to Be2+Be2+ ions also increase in the same direction as shown below.



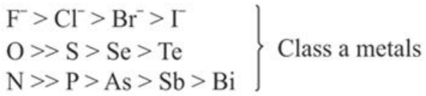
Central metal ion (charge on the ion is shown in parenthesis	Ionic radius (Å)	Ionic potential	Order of stability of complexes
Li^{+} (+1)	0.60	1/0.60 = 1.6	Increasing
Ca^{2+} (+2)	0.99	2/0.99 = 2.0	
Ni^{2+} (+2)	0.72	2/0.72 = 2.97	
Y^{3+} (+3)	0.93	3/0.93 = 3.22	
Th^{4+} (+4)	0.95	4/0.95 = 4.20	
Al^{3+} (+3)	0.50	3/0.50 = 6.0	
Be^{2+} (+2)	0.31	2/0.31 = 6.45	

iv) Electronegativity: Electronegativity of the central ion also influences the stability of its complexes. This is because the bonding between a central ion and ligand is due to the donation of electron pairs by the ligands. Hence, a strongly electron-attracting central ion will give stable complexes. Hence, the greater the positive charge density (i.e., charge/size ratio) and greater the central ion's electronegativity, the higher the stability of the complex formed by it.[25]

v) Class of the Metal Ion: Chatt and Ahrland have classified metals into three categories: a,ba,b and borderline, based on their electron-acceptor properties. This classification is shown below:

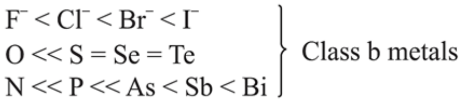
1. Class 'aa' metals: HH, the alkali and alkaline earth metals, the element Sc→Cr,Al→Cl,Zn→Br,ln,Sn,SbSc→Cr,Al→Cl,Zn→Br,ln,Sn,Sb and ll, the lanthanides and actinides.
2. Class 'bb' metals: Rh,Pd,Ag,Ir,Pt,Au,HgRh,Pd,Ag,Ir,Pt,Au,Hg.
3. Borderline metals: The elements Mn→Cu,Ti→Po,Mo,Te,Ru,W,Re,Os,CdMn→Cu,Ti→Po,Mo,Te,Ru,W,Re,Os,Cd.

Class 'aa' metals form more stable complexes with ligands having the coordinating atoms from the second-period elements (e.g., N,O,FN,O,F) than those of an analogous ligand in which the donor atom is from the third or later period (e.g., P,S,ClP,S,Cl). Class bb metals have the relative stabilities reversed.
For class 'aa' metals, the stability of metal complexes with different ligands follows the order:[22]



$$\left.\begin{array}{l} F^- > Cl^- > Br^- > I^- \\ O >> S > Se > Te \\ N >> P > As > Sb > Bi \end{array}\right\} \text{Class a metals}$$

For class ‘bb’ metals, the stability of metal complexes with different ligands follow the order:



$$\left.\begin{array}{l} F^- < Cl^- < Br^- < I^- \\ O << S = Se = Te \\ N << P << As < Sb < Bi \end{array}\right\} \text{Class b metals}$$

Class ‘b′‘b′ metals form more stable complexes due to the presence of a number of d-electrons beyond an inert gas core. The transfer of these dd-electrons is used to form π-bond with ligand atoms. The most stable complexes of class ‘b′‘b′ metals are formed with ligands like PMe3,S2–,I–PMe3,S2–,I– which have vacant dd-orbitals or like CO,CN–CO,CN– which have vacant molecular orbitals of low energy.
For borderline metals, the stability constants do not display either class ‘a′‘a′ or class ‘b′‘b′ behaviour uniquely[23].

vi) Polarising Power: With the increase in the polarising power of Central Metal Atom, the stability of complexes also increases. Stability α Polarising power of Central Metal atom

B. Nature of Ligand

i) Size and Charge of the Ligands: Cationic ligands with higher positive charges have small sizes and form more stable compounds. Though the size of the anion increases with an increase in the –ve–ve charge, the stability of complexes decreases with the increase in the –ve–ve charge value of the anionic ligands.

For example: F–F– forms more stable complexes with Fe+3Fe+3 than Cl–,Br–Cl–,Br– or I–I– . Thus, a small fluoride F–F– ion forms more stable Fe+3Fe+3 complex as compared to the large Cl–Cl– ion. This is due to the easy approach of the ligand towards metal ions. Similarly, a small dinegative anion O2–O2– forms more stable complexes than does the large S2–S2– ion.

For class ‘a′‘a′ metals: The stability of the complexes of a given metal ion with halide ion used as ligands is in the order:
F–>Cl–>Br–>I–F–>Cl–>Br–>I–

For class ‘a′‘a′ metals (e.g. Pd,Ag,Pt,HgPd,Ag,Pt,Hg etc.): The stability of the complexes of a given metal ion with halide ion used as ligands is reversed:

F–<Cl–<Br–<I–F–<Cl–<Br–<I–

ii) Basic Character: Higher the basic character or strength of the ligand, the higher will be the stability of coordination compounds. This is because the electron-donating tendency of ligands to the central metal ion is higher. The more basic is the ligand, the more easily it can donate electron pairs to the central ion, and hence more easily it can form complexes of greater stability.[24] The ligand that binds H+H+ firmly form stable complexes with metal ions.

Thus, F–F– should form more stable complexes than Cl–,Br–Cl–,Br–, and I–I– and NH3,NH3, should be better ligand than H2OH2O which in turn should be better than HFHF. (NH3>H2O>HF)(NH3>H2O>HF). This behaviour is observed for alkali, alkaline earth and other electropositive metals like first row transition elements, lanthanides and actinides.

Stability α Basic character of the ligand
iii) The Dipole Moment of Ligands: For neutral ligands, the larger the magnitude of permanent dipole moment, the greater the complexes' stability. For example, the order of stability of complexes formed by some neutral ligands is ammonia >> ethylamine >> diethylamine >> triethylamine.

iv) π- Bonding Capacity of Ligands: The ligands like CN–,CO,PR3,AsR3CN–,CO,PR3,AsR3, alkenes, alkynes, which are capable of forming π-bonds with transition metal ions, give more stable complexes.

v) Steric Hindrance due to Bulky Ligands: When a bulky group is linked to or present near a ligand's donor atom, repulsion occurs between the ligand's donor atom and the bulky group, weakening the metal-ligand interaction. As a result, the complex becomes less stable.
For example, The complex of Ni2+Ni2+ ion with 22-methyl-88-hydroxy quinoline (log10β=17.8)(log10=17.8) is less stable than that with 88-hydroxy quinoline (log10β=17.8)(log10=17.8). The effect of the presence of a bulky group on the stability of a complex is commonly called a steric hindrance.
2,2′2,2′-bipyridine (also called 2,2′2,2′-dipyridyl) forms complexes with metal ions which are stable, but the substitution of an alkyl group in 4,4′4,4′ or 5,5′5,5′ positions gives less stable complexes. This is because the substituents crowd the metal ion, mutual repulsion occurs, and consequently, the complexes formed are of lower stability.

vi) Chelate Effect: The ligands which can form five or six-membered ring structures with the metal centre usually form more stable complexes than the others. This effect is called chelation, and the ligands are called chelating ligands.[25]

For example: The complex formation of Ni2+Ni2+ with ammonia and 1,21,2-diaminoethane can be expressed by the following equations:[Ni(H2O)6]2++6NH3→[Ni(NH3)6]2++6H2Oβ6=108.76[Ni(H2O)6]2++6NH3→[Ni(NH3)6]2++6H2O6=108.76

[Ni(H2O)6]2++3en→[Ni(en)3]2++6H2Oβ6=1018.28[Ni(H2O)6]2++3en→[Ni(en)3]2++6H2O6=1018.28

The overall stability constant value for the Ni2+Ni2+ complex with three chelate rings (en)(en) is about 10101010 greater than that formed with six monodentate ligands (NH3)(NH3).

vii) Macrocyclic Ligands and Macrocyclic Effect: A macrocyclic ligand is a nine or more membered cyclic molecule having 33 or more potential donor atoms that can bind to a metal atom inside the cavity of the macrocycle. Some macrocyclic ligands have conjugated π system. The stability of a complex of a particular metal ion with a macrocyclic ligand is several times greater than that of an open-ended multidentate ligand (chelating ligand) containing an equal number of equivalent donor atoms.The increase in stability due to the presence of multidentate cyclic ligands is called the macrocyclic effect. Thus, if ligands are multidentate and cyclic without any steric effects, the stability of the complexes is increased.The cyclic crown polyether complexes are far more stable than those of their corresponding open-chain analogues.[25]

C. Amount of Metal-Ligand Covalent Characters Present in Complexes

In some complexes, the stability of the complex is influenced by the amount of metal-ligand covalent character present in the complex. This is more pronounced in complexes of the metals like those of copper and zinc family, Sb,PbSb,Pb. For example, the stability of [AgX2][AgX2] and [AgX3][AgX3] are found to be in the following order:

AgI2>AgBr2>AgCl2>AgF2>AgI3>AgBr3>AgCl3≥AgF3AgI2>AgBr2>AgCl2>AgF2>AgI3>AgBr3>AgCl3≥AgF3

This is due to the increase in the covalent character of the Ag–XAg–X bond as we move from Ag–FAg–F to Ag–IAg–I.

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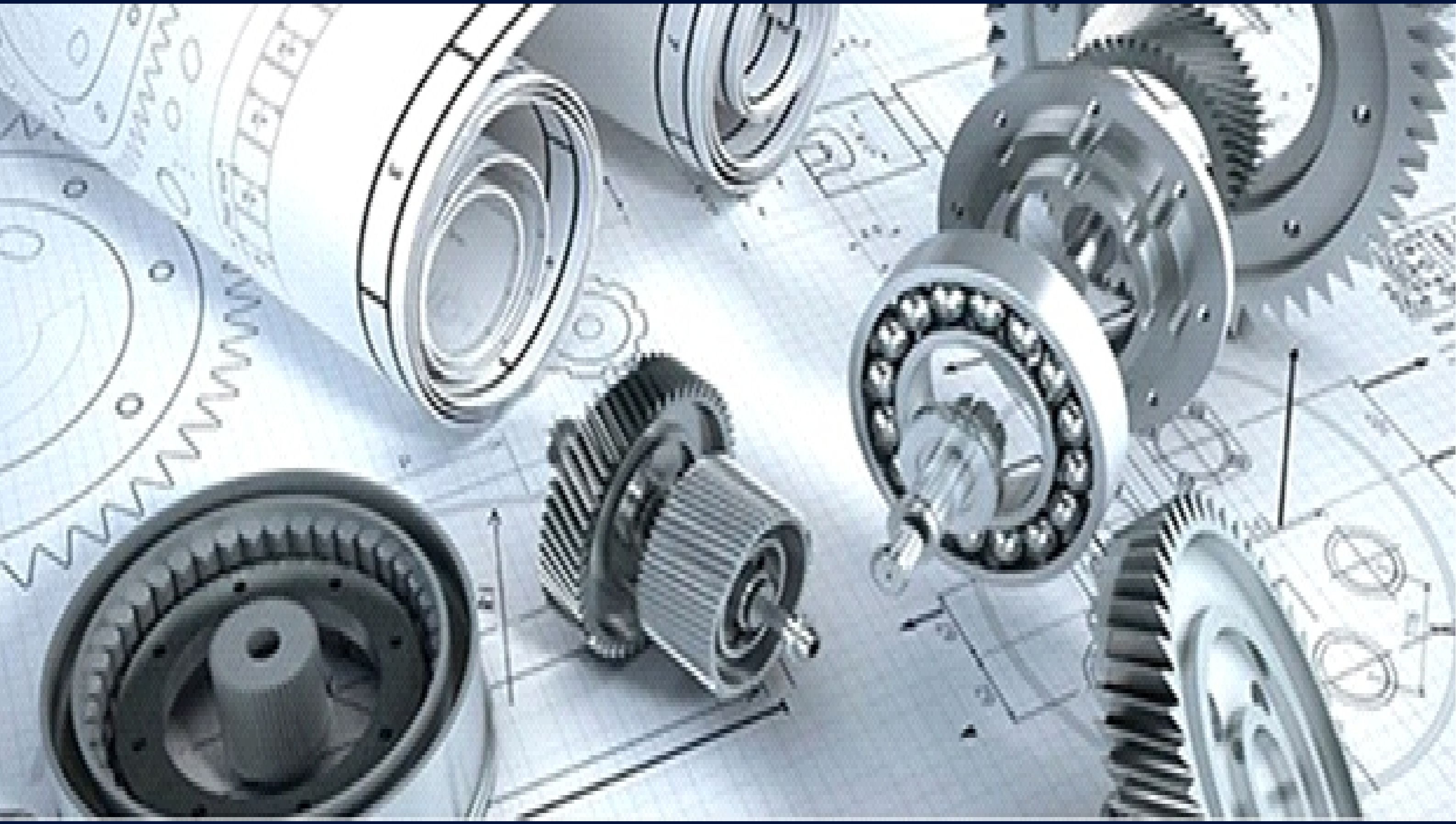

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