CHAPTER 5
Isopoly and Heteropoly Acids and Salts:

- Isopoly and Heteropoly Acids and Salts of Mo and W: Structures of Isopoly and Heteropoly Anions

The term polymetalate acid or simply poly acid may be defined as the condensed or polymerized form of the weak acids of amphoteric metals like vanadium, niobium, tantalum (VB group metals) or chromium, molybdenum, and tungsten (VIB group metals) in the +5 and +6 oxidation states. The anions of these poly acids contain several molecules of the acid anhydride and the corresponding salts are called as polysalts.

Furthermore, if these polymerized acids contain only one type of acid anhydride, they are called as isopoly acids. However, these anhydrides can also condense with some other acids like phosphoric or silicic acid to form heteropoly acids. In other words, isopoly acids contain only one metal along with hydrogen and oxygen while heteropoly acids contain two elements other than hydrogen and oxygen. The corresponding salts of isopoly and heteropoly acids are called as isopoly and heteropoly salts, respectively.

Consider the polymerization of chromate ion to form different isopoly chromates anions. CrO₃ dissolves in an alkali to give yellow coloured CrO₄²⁻ ions solution. At very high pH, above 8, the chromate ions, CrO₄²⁻, exist as the discrete entities but as the pH is lowered down, the protonation and dimerization takes place. For instance:

\[ 2H_2CrO_4 \rightarrow H_2Cr_2O_7 - H_2O \]

and

\[ 3H_2CrO_4 \rightarrow H_2Cr_3O_{10} - 2H_2O \]

and

\[ 4H_2CrO_4 \rightarrow H_2Cr_4O_{13} - 3H_2O \]

The polymeric anions Cr₂O₇²⁻, Cr₃O₁₀²⁻ and Cr₅O₁₅²⁻ produced by the polyacids H₂Cr₂O₇, H₂Cr₃O₁₀ and H₂Cr₄O₁₃, can successfully be isolated from their aqueous as sodium or potassium polysalts like K₂Cr₂O₇, K₃Cr₃O₁₀ and K₂Cr₄O₁₃, respectively. Among the isopoly-anions of V⁵⁺, Nb⁵⁺, Ta⁵⁺, Cr⁶⁺, Mo⁶⁺ and W⁶⁻, only Cr⁶⁺ is found to have tetrahedral CrO₄²⁻ units joined through the corners. The other metal ions form isopolyanions by the sharing of edges of octahedral MO₆ units. This may be attribute to the small size of Cr⁶⁺ which can afford only four oxide ions around itself.
The tri-chromate and tetra-chromate anions can be crystallized as their alkali metal salts only from strongly acidic solution and no polymerization beyond tetrameric entity is observed. The Cr–O–Cr bond angle of all polychromates is approximately 120°.

Figure 1. The structure of chromate and isopoly anions of chromium.
Isopoly Acids and Salts of Mo and W

When molybdenum trioxide is dissolved in highly basic aqueous solutions of sodium hydroxide or potassium hydroxide (alkali solutions), molybdate ions with tetrahedral geometry are formed as:

\[ \text{MoO}_3 + 2\text{NaOH} \rightarrow \text{Na}_2\text{MoO}_4 + \text{H}_2\text{O} \]

These normal molybdates, Na\(_2\)Mo\(_4\), containing discrete Mo\(_4^{2-}\) units, can easily be crystallised out of them.

\[ \text{MoOO}_6 \quad \text{(tetrahedral)} \]

![Figure 2. The discrete MoO\(_4^{2-}\).](image)

When the pH of the solution is lowered down, the protonation of molybdate ions start followed by the condensation yielding the first major polyanion i.e. paramolybdate. The whole process of condensation can be depicted as follows:

\[ \text{MoO}_4^{2-} + \text{H}_3\text{O}^- \leftrightarrow [\text{HO}^-\text{MoO}_3]^- + \text{H}_2\text{O} \]

\[ [\text{HO}^-\text{MoO}_3]^- + \text{H}_2\text{O} + \text{H}_2\text{O} \leftrightarrow \text{Mo(OH)}_6 \]

Although the entropy (\(\Delta S\)) of the second reaction is negative yet it is as fast as the first reaction which may be attributed to the large negative enthalpy for second reaction, compensating the entropy loss. The Mo(OH)\(_6\), thus formed during the course of the second reaction, reacts with [MoO\(_3\)(OH)]\(^+\) ions present in the acidic media as:

\[ \text{Mo(OH)}_6 \quad \text{HMoO}_4^- \quad [\text{HO}_3\text{Mo}^-\text{(OMo}_3\text{)}]^- \quad \text{HMoO}_4^- \quad [(\text{HO})_4\text{Mo}^-\text{(OMo}_3\text{)}]^{2-} \]

\[ \text{HMoO}_4^- \quad [\text{HO}_3\text{Mo}^-\text{(OMo}_3\text{)}]^- \quad \text{HMoO}_4^- \quad [(\text{HO})_4\text{Mo}^-\text{(OMo}_3\text{)}]^{2-} \]

\[ \quad \text{HMoO}_4^- \quad [\text{HO}_3\text{Mo}^-\text{(OMo}_3\text{)}]^- \quad \text{HMoO}_4^- \quad [(\text{HO})_4\text{Mo}^-\text{(OMo}_3\text{)}]^{2-} \]

\[ \quad \text{HMoO}_4^- \quad [\text{HO}_3\text{Mo}^-\text{(OMo}_3\text{)}]^- \quad \text{HMoO}_4^- \quad [(\text{HO})_4\text{Mo}^-\text{(OMo}_3\text{)}]^{2-} \]
The complete reactions giving different isopoly molybdates can be written as:

\[ 7\text{MoO}_4^{2-} + 8\text{H}^+ \rightarrow [\text{Mo}_7\text{O}_{24}]^{6-} + 4\text{H}_2\text{O} \]
\[ 8\text{MoO}_4^{2-} + 12\text{H}^+ \rightarrow [\text{Mo}_8\text{O}_{26}]^{4+} + 6\text{H}_2\text{O} \]

It is worth noting that the hepta-molybdate or para-molybdate is the first stable form of isopoly-molybdates and when the acidification of the solution further continues, \([\text{Mo}_6\text{O}_{26}]^{4-}\) is obtained. If the pH of the solution is dropped below 1, yellow coloured, molybdc acid \((\text{MoO}_3\cdot2\text{H}_2\text{O})\) is formed which can be converted into monohydrate form just by warming it up.

\[
\begin{align*}
\text{pH} & \quad \text{from}\quad \text{to} \\
[\text{MoO}_4]^{2-} & \quad [\text{Mo}_7\text{O}_{24}]^{6-} & \quad [\text{Mo}_8\text{O}_{26}]^{6+} & \quad \text{MoO}_3 \cdot 2\text{H}_2\text{O} \\
6 & \quad 1.5 - 3.0 & \quad > 1
\end{align*}
\]

It is worth noting that during the condensation process, from \(\text{MoO}_4^{2-}\) to \([\text{Mo}_7\text{O}_{24}]^{6-}\), the coordination number of molybdenum ion changes from four to six and the building block unit of polyhedral entity becomes \(\text{MoO}_6\) octahedron.

Figure 3. The structure of (a) ideal edge sharing octahedrons and (b) distorted edge sharing octahedrons.

These octahedral units bind to each other by the sharing of corners or edges. Moreover, the terminal Mo–O bond lengths are less than that of Mo–O bond lengths in Mo–O–Mo bridge and hence the two joining
octahedra are somewhat more or less distorted. This increment in the distance between two metal centres can be explained in terms of reduced inter-metal ion repulsion.

Keeping in mind that electrostatic repulsion between metal centres is a governing factor in justifying the structures of isopoly and heteropoly anions and acids, corner sharing among octahedrons is expected more frequently than edge sharing as it separates the metal centres more profoundly. But in actual practice, edge sharing is preferred over the corner sharing because the edge sharing reduces the number of oxide ions required to pack the polyhedral units which in turn decreases the unwanted anionic charge from $O^{2-}$ ions. Therefore, the edge sharing stabilizes the polyanions to a greater extent than corner sharing. The order of removal of $O^{2-}$ anionic charge by different type of sharing, face $>$ edge $>$ corner, suggests a face sharing of the octahedron units as the most favourable choice for the condensation but it is actually the least favoured due to the incorporation of highest inter-metal ion repulsion.

The structure and properties of different types of isopoly-molybdate are discussed below.

1. **Dimolybdate**: The general formula for dimolybdates system is $M_2O.2MoO_3.xH_2O (M = Na, K or NH_4)$ and are observed in the pH range of 5-6.

\[
Na_2O.2MoO_3.xH_2O \rightleftharpoons Na_2Mo_2O_7
\]

$Na_2Mo_2O_7$ is not stable and hence dimolybdate systems do not contain $Mo_2O_7^{2-}$ ions. The compounds like $M_2MoO_7$ have been isolated from anhydrous melts or aqueous solutions but discrete ions like $Mo_2O_7^{2-}$ are found to be absent. These systems are the mixture of simple $(MoO_2)^2-$ and paramolybdate $(MoO_2_{246}^-)$ ions in general. However, molybdate ions as a salt of tetrabutylammonium, $[(C_4H_9)_4N]_2Mo_2O_7$, is one of very few compounds which is known to have discrete $Mo_2O_7^{2-}$ ions.

![Figure 4. Mo$_2$O$_7^{2-}$ ion in tetrabutylammonium dimolybdate.](image_url)

2. **Trimolybdate**: The general formula for trimolybdate system is $M_2O.3MoO_3.xH_2O$ where $M$ represents Na or K.

\[
Na_2O.3MoO_3.xH_2O \rightleftharpoons Na_2Mo_3O_{10}
\]

$Na_2Mo_3O_{10}$ is not stable and hence trimolybdate systems do not contain $Mo_3O_{10}^{2-}$ ions. These systems are prepared by crystallising paramolybdate in the presence acetic acid or by saturating molybdenum oxide in the presence of alkali.
3. **Tetramolybdate or metamolybdate**: The general formula for tetramolybdate system is \( \text{M}_2\text{O}_4\text{MoO}_4\text{xH}_2\text{O} \) where \( \text{M} \) represents Na or K.

\[
\text{Na}_2\text{O}_4\text{.4MoO}_4\text{xH}_2\text{O} \rightleftharpoons \text{Na}_2\text{Mo}_4\text{O}_{13}
\]

\( \text{Na}_2\text{Mo}_4\text{O}_{13} \) is not stable and hence tetramolybdate systems do not contain \( \text{Mo}_4\text{O}_{13}^{5-} \) ions. These systems are the mixture of simple \( \text{MoO}_4^{2-} \) and octamolybdate \( \text{Mo}_8\text{O}_{26}^{4+} \) ions in general.

4. **Heptamolybdate or paramolybdate**: The general formula for paramolybdates is \( \text{M}_6\text{Mo}_7\text{O}_{24} \) where \( \text{M} \) represents Na, K or \( \text{NH}_4 \). \( \text{M}_6\text{Mo}_7\text{O}_{24} \) is quite stable and contains discrete \( \text{Mo}_7\text{O}_{24}^{6-} \) ions.

The edge connections of seven ideal \( \text{MoO}_6 \) octahedrons in paramolybdate ion can be visualized in term of one front unit (composed of four \( \text{MoO}_6 \)) and one rear unit (composed of three \( \text{MoO}_6 \)). As the name suggests, the front unit is placed above the rear unit in such a way that each octahedron shares three edges with its neighbours.

*Figure 5. continued on next page...*
The structure shown (Figure 5) is an idealized one with perfect octahedrons; but in actual practice, the distortions play its role giving a range of Mo–O bond lengths in MoO₆ units.

5. Octamolybdate: The general formula for octamolybdates is \( M_4Mo_8O_{24} \) where \( M \) represents Na, K or \( NH_4 \). \( M_4Mo_8O_{24} \) is quite stable and contain discrete \( Mo_8O_{24}^{6+} \) ions. These molybdates can be synthesized by adding stoichiometric amount of \( MoO_3 \) in paramolybdate solution or by treating alkali molybdate solutions with 1.75 molar hydrochloric acid. These molybdates exist in three forms.
Front Unit + Rear Unit + Two Tetrahedral Units = $\alpha$-[Mo$_8$O$_{24}$]$^{4-}$

(c)

Figure 6. The (a) front unit and (b) rear unit and two tetrahedral units as capping are combined to produce the (c) overall structure of $\alpha$-octamolybdate ion.

Rear Unit

(a)

Mid Unit

(b)

Figure 7. continued on next page...
Figure 7. The (a) rear unit and (b) mid unit and (c) front unit are combined to produce the (d) overall structure of the β-octamolybdate ion.

Figure 8. continued on next page...
Figure 8. The (a) upward unit and (b) downward units are combined to produce the (c) overall structure of the $\gamma$-octamolybdate ion.

The first two isomeric forms of octamolybdate anion, $\alpha$-$[\text{Mo}_8\text{O}_{26}]^{4-}$ and $\beta$-$[\text{Mo}_8\text{O}_{26}]^{4+}$, are in equilibrium with each other in solution phase. $\alpha$- and $\beta$- isomers have been obtained from non-aqueous and aqueous solutions respectively. A $\gamma$- form has also been suggested as an intermediate between $\alpha$- and $\beta$- isomers.

The edge connections of eight ideal MoO$_6$ octahedrons in $\beta$-octamolybdate ion can be visualized in term of one front unit (composed of two MoO$_6$), one mid unit (composed of four MoO$_6$) and one front unit (composed of two MoO$_6$). It must be noted down that one octahedra of the rear unit is completely hidden in the overall idealized structure of $\beta$-octamolybdate.

6. Hexamolybdate: The hexamolybdates are derived from discreate Mo$_{6}$O$_{19}^{2-}$ ions and are not as conventional as hepta or octamolybdates. Crystallographic studies have shown that these isopoly anions are formed by
molybdenum ions in octahedral pattern and each ion is further surrounded by six oxide ions. Each MoO$_6$ unit has only one terminal O$^{2-}$ ion.

\[ \text{Meridion 1} + \text{Meridion 2} = [\text{Mo}_6\text{O}_{19}]^{2-} \]

Figure 9. The hexamolybdate anion.

7. Decamolybdate: The decamolybdates are obtained as (NH$_4$)$_8$Mo$_{10}$O$_{34}$ and the corresponding molybdate ion Mo$_{10}$O$_{34}^{8-}$ are found to have one Mo$_8$O$_{28}$ unit and two MoO$_4$ tetrahedral units attached at corners. The structure of decamolybdate can be visualised as an extension of $\gamma$-[Mo$_8$O$_{28}$]$^{8-}$ in which two additional tetrahedral units are attached at corners of two opposite octahedrons.
Figure 10. The (a) upward unit and (b) downward unit and two tetrahedral units are combined to produce the (c) overall structure of dacamolybdate ion.
8. **Mo\(_{36}\)-polymolybdate**: The largest polymolybdate under non-reducing conditions known till recent times is \([\text{Mo}_{36}\text{O}_{112}(\text{H}_2\text{O})_{16}]^{8-}\) and can be synthesized at a pH of 1.8 as:

\[
36\text{MoO}_4^{2-} + 64\text{H}^+ \rightarrow [\text{Mo}_{36}\text{O}_{112}]^{8-} + 32\text{H}_2\text{O}
\]

The structure of Mo\(_{36}\)-polymolybdate contain the \([(\text{Mo})\text{Mo}_5]\)-type unit comprising a central Mo\(_7\) pentagonal bipyramid sharing edges with five MoO\(_6\) octahedra.

When tungsten trioxide is dissolved in highly basic aqueous solutions of sodium hydroxide or potassium hydroxide (alkali solutions), tungstate ions with tetrahedral geometry are formed as:

\[
\text{WO}_3^2^- + 2\text{NaOH} \rightarrow \text{Na}_2\text{WO}_4 + \text{H}_2\text{O}
\]

These normal tungstate, Na\(_2\)WO\(_4\), containing discreate WO\(_4\)^2− units, can easily be crystallised out of aqueous solution. The normal tungstate of other metals can be synthesised from sodium tungstate via double decomposition.

![Figure 11. The discreate WO\(_4\)^2−](image)

When the pH of the solution is lowered down in the range of 9–5, the protonation of tungstate ions starts followed by the condensation yielding the W\(_7\)O\(_{24}\)^6, i.e. paratungstate A. The whole process of condensation can be depicted as follows:

\[
\text{WO}_4^{2-} + \text{H}_3\text{O}^+ \rightleftharpoons [\text{HO-WO}_3]^- + \text{H}_2\text{O}
\]

\[
[\text{HO-WO}_3]^- + \text{H}_3\text{O}^+ + \text{H}_2\text{O} \rightleftharpoons \text{W(OH)}_6
\]

Although the entropy (\(\Delta S\)) of the second reaction is negative yet it is as fast as the first reaction which may be attributed to the large negative enthalpy for second reaction, compensating the entropy loss. The W(OH)\(_6\), thus formed during the course of the second reaction, reacts with [WO\(_3\)(OH)]\(^−\) ions present in the acidic media as:
In the early times, it was believed that the paratungstate $A$ is formed as a hexamer in solution but later studies showed that it is actually an heptamer. If the acidification of the solution further continues, metatungstate, $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$, is obtained. Metatungstate is more soluble than paratungstate and can be crystallized out by prolong heating of the solution or by standing for a long time.

If the pH of the solution is maintained in the range of 2–1, a yellow coloured tungstate $[\text{W}_{10}\text{O}_{32}]^{4-}$, tungstate $Y$, is obtained. Moreover, if pH is lowered down below 1, yellow coloured, tungstic acid ($\text{WO}_3\cdot 2\text{H}_2\text{O}$) is formed which can be converted into monohydrate form just by warming it up.

The complete reactions giving different isopoly molybdates can written as

$$7\text{WO}_4^{2-} + 8\text{H}^+ \rightarrow [\text{W}_7\text{O}_{24}]^{6-} + 4\text{H}_2\text{O}$$

$$12\text{WO}_4^{2-} + 14\text{H}^+ \rightarrow [\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-} + 6\text{H}_2\text{O}$$

$$12\text{WO}_4^{2-} + 18\text{H}^+ \rightarrow [\text{H}_2\text{W}_{12}\text{O}_{42}]^{6-} + 8\text{H}_2\text{O}$$

The has been proven that $\text{W}_2\text{O}_7^{2-}$ never exists in solution phase and no discreate $\text{W}_2\text{O}_7^{2-}$ ions in crystal phase are obtained. However, Na2W2O7 can be prepared by fusing tungsten oxide with sodium oxide in required stoichiometry. Recent studies have shown that no $W_6$ is obtained in solution phase but discrete salts with $[\text{W}_6\text{O}_{19}]^{6-}$ ions can be crystallized out.

The reaction scheme for the condensation of tungstate ions in aqueous solutions (along with the pH range required) is given below:
Just like in isopoly-molybdates, the condensation process changes the coordination number of tungsten ion from four to six and the building block unit of polyhedral entity becomes WO$_6$ octahedron. These WO$_6$ octahedrons are joined together by the sharing of edges and corners rather than the faces which we have already discussed in isopoly anions of molybdenum.

The structure and properties of different types of isopoly-molybdate are discussed below.

1. **Paratungstate A**: The general formula for paratungstate A is $M_6W_{12}O_{24}$ where $M$ is normally Na, K or NH$_4$ and contains discrete W$_{12}$O$_{24}^{6-}$ ions. The edge connections of seven ideal WO$_6$ octahedrons in paratungstate-A ion can be visualized in term of one front unit (composed of four WO$_6$) and one rear unit (composed of three WO$_6$). As the name suggests, the front unit is placed above the rear unit in such a way that each octahedron shares three edges with its neighbours. It should be noted that W$_{12}$O$_{24}^{6-}$ is isostructural with Mo$_6$O$_{24}^{6-}$.
Figure 12. The (a) front unit and (b) rear unit are combined to produce the (c) overall structure of the paratungstate A ion.
2. Paratungstate B: The paratungstate B are derived as the alkali metal salts of dodecameric anions, \([H_2W_{12}O_{42}]^{10-}\), from the acidification of normal tungstate aqueous solutions. The protons reside in the polyhedral cavity and are involved in rapid exchange solvent water.

![Upward Unit](image1)

![Downward Unit](image2)

(a)

![Mid Left Unit](image3)

![Mid Right Unit](image4)

(b)

![Upward and Downward Units + Mid Left and Mid Right Units](image5)

(c)

Figure 12. The (a) upward - downward units and (b) mid left - mid units are combined to produce the (c) overall structure of the metatungstate anion.
3. **Metatungstate:** The metatungstates are derived as the alkali metal salts of dodecameric anions, \([H_2W_{12}O_{40}]^6^-\), from the acidification of normal tungstate aqueous solutions. The protons reside in the polyhedral cavity and are not involved in rapid exchange with solvent water as in peratungstate B.

![Diagram of metatungstate](image)

**Figure 13.** The structure of metatungstate anion is obtained by joining four equivalent tritungstate units along tetrahedral faces.
4. **Tungstate Y**: These isopoly tungstates are derived as the alkali metal salts of $[W_{10}O_{32}]^{4-}$ anions and are yellow in colour. The discrete $[W_{10}O_{32}]^{4-}$ anions are found to be present in both solution and crystallized form.

![Diagram of Meridions 1 and 2](image)

*Figure 14. continued on next page...*
The structure of tungstate Y can be visualized from hexa-tungstate systems in which two meridians, composed of WO₆ octahedral units are joined to form W₆-polyhedra. When one octahedron from each [W₆O₁₀]²⁻ unit is removed, the resulting structural units can be combined through the corners to form the overall geometry of decameric isopoly anion.

Figure 14. The structure of tungstate Y.
5. Hexatungstate: These isopoly hexatungstates are obtained from methanolic solutions and contains discrete \([\text{W}_6\text{O}_{19}]^{2-}\) ions both in solution and in crystallized form.

\[
\text{Meridion 1} + \text{Meridion 2} = [\text{W}_6\text{O}_{19}]^{2-}
\]

Figure 15. The hexatungstate anion.

It is worth noting that hexatungstate is isostructural with hexamolybdate anion in which the coordination number of the oxide ion situated at the centre of the \([\text{W}_6\text{O}_{19}]^{2-}\) anion is six.
6. **Tetratungstate**: The crystallized form of Li$_{14}$(WO$_4$)$_3$(W$_4$O$_{16}$)$_4$H$_2$O, obtained from aqueous solution, is found to have discrete W$_4$O$_{16}$$^8$-. However, the presence of this isopoly anion in solution phase is still unknown.

![Upward Unit](image1.png) ![Downward Unit](image2.png)

(a)

![Upward Unit + Downward Unit](image3.png)

(b)

Figure 16. The (a) upward and downward units are combined to produce the (b) overall structure of [W$_4$O$_{16}$]$^8$ anion.

> **Heteropoly Acids and Salts of Mo and W**

One of the founder of modern chemistry, a Swedish chemist, Jacob Berzelius found that the acidification of the solution containing phosphate and molybdate results in a yellow coloured precipitate. This crystalline substance was actually the first example of a heteropoly anion, [PMo$_{12}$O$_{40}$]$^{3-}$, which has been frequently used in the quantitative estimation phosphates. A large number of heteropoly anions with a wide range of hetero atoms, metal as well as non-metal, have been prepared in the following years. The thermal stability of heteropoly salts is found to be greater than their isopoly analogues. One of the major application of these heteropoly anions is in the petrochemical industry where they are used as a catalyst, as flame retardants and as precipitants for dyes.

The hetero atoms of these polymetallates generally reside in the baskets or cavities formed by the parent MO$_6$ octahedron units. The hetero atoms are bonded to the neighbouring oxygens of surrounding...
octahedrons. The shape of the cavity, generally decided by the ratio of hetero to parent atoms, greatly influences the stereochemistry of heteroatom. The acidification of simple monomeric anions can yield condensed heteropoly systems as:

\[
\text{HPO}_4^{2-} + 12\text{MoO}_4^{2-} + 23\text{H}^+ \rightarrow [\text{PMo}_{12}\text{O}_{40}]^{3-} + 12\text{H}_2\text{O}
\]

\[
\text{HPO}_4^{2-} + 12\text{WO}_4^{2-} + 23\text{H}^+ \rightarrow [\text{PW}_{12}\text{O}_{40}]^{3-} + 12\text{H}_2\text{O}
\]

The structure and properties of different types of heteropoly-metallates are discussed below.

1. **1:12 (Tetrahedral heteroatom):** The general formula for these type of heteropolyanions is \([X^{n+}\text{M}_{12}\text{O}_{40}]^{(8-n)^-}\), where M is Mo or W and X represents the heteroatom which is generally P, Si, As, Ge or Ti. The labelling of this category of polyanions is justified on the basis of the number ratio of heteroatom to the parent atom which is one to twelve. The small heteroatom is present in the inner tetrahedral cavity of the polyanion and hence is surrounded by six oxygen atoms of different MO₆ octahedron units.

The structure of this type of heteropolyanions is of either \(T_d\) symmetry (Keggin structure) or a \(C_{3v}\) one which can be obtained as a derivative of Keggin structure by rotating one of the four set of trimetallate (composed of three MO₆) units through 60°. The first structure is perfect tetrahedral with four three-fold axis of rotation but the second structure contains only one three-fold axis of rotation. The stability of both the structures is same. \([X\text{M}_{12}\text{O}_{40}]^{n+}\), with X as Ge⁴⁺ or Si⁴⁺, is found to be present in both of the isomeric forms.

![Figure 17. continued on next page...](image_url)
One of the most common examples of these types of heteropoly anions is $[\text{Co}^{2+}\text{W}_{12}\text{O}_{40}]^{6-}$, which can be oxidised to $[\text{Co}^{3+}\text{W}_{12}\text{O}_{40}]^{5-}$. In both of the anions, the heteroatom is present in the tetrahedral void and is surrounded by four oxygen atoms of nearby MoO$_6$ octahedrons.

2. 2:18 (Tetrahedral heteroatom): The general formula for this type of heteropoly anions is $[\text{X}^{n+}\text{M}_{12}\text{O}_{40}]^{(8-n)-}$, where M is Mo or W and X represents the heteroatom which is generally P or As. The labelling of this category of polyanions is justified on the basis of the number ratio of heteroatom to the parent atom which is two to eighteen. The potassium or ammonium salts of these polyanions can be crystallized out by standing a mixture of salts of 1:12 $[\text{X}^{n+}\text{M}_{12}\text{O}_{40}]^{(8-n)-}$ heteropoly anions.
Figure 18. The (a) upward and downward units are combined to produce the (b) overall structure of \([X_{25}^{5+}M_{18}O_{62}]^{6-}\) anion.

The structure is generally referred as the “Dawson structure” and can be visualized from Keggin structure easily. The \([X_{25}^{5+}M_{18}O_{62}]^{6-}\) can be considered as a fusion of two \(M_9\)-units each of which is derived from the Keggin structure by the removal of three corner linked \(Mo_6\) octahedrons. Both of the heteroatoms are present in the inner cavity of the polyanion made by different \(Mo_6\) octahedron units.

**3. 1:6 (Octahedral heteroatom):** The general formula for this type of heteropolyanions is \([X^{n+}M_6O_{24}]^{(12-n)-}\), where \(M\) is Mo or W and X represents the heteroatom which is generally Te, Co, I or Al. The labelling of this category of polyanions is justified on the basis of the number ratio of heteroatom to the parent atom which is one to six. The tendency form 1:6 heteropoly anions is found to be greater in case of Mo than in W. The heteroatoms are generally larger in size and are surrounded by six oxygen atoms of edge-sharing \(Mo_6\) octahedron units. It is worth noting down that all the six \(Mo_6\) octahedron units are parallel to each other.

Figure 19. continued on next page...
Figure 19. The (a) left and right units are combined to produce the (b) overall structure of \([X^{n+}\text{Mo}_6\text{O}_{26}]^{(12-n)-}\) heteropoly anion.

4. 1:9 (Octahedral heteroatom): The general formula for this type of heteropolyanions is \([X^{n+}\text{Mo}_9\text{O}_{32}]^{(10-n)-}\), where M is Mo or W and X represents the heteroatom which is generally Mn or Ni. The labelling of this category of polyanions is justified on the basis of the number ratio of heteroatom to the parent atom which is one to nine.

The nine \(\text{Mo}_6\) octahedron units are joined through the edges to form an octahedral cavity for the heteroatom present. Two of the most studied examples of these type of heteropoly anions are \([\text{NiMo}_9\text{O}_{32}]^{6-}\) and \([\text{MnMo}_9\text{O}_{32}]^{6-}\). It must also be noted down that Ni and Mn are present in +4 oxidation state which is highly unusual.
Figure 20. The (a) upward and (b) downward units are combined to produce the (c) overall structure of $[X^{m+}M_9O_{32}]^{(10-n)-}$ anion.
5. 1:12 (Icosahedral heteroatom): The general formula for this type of heteropolyanions is \([X^{n+}M_{12}O_{40}]^{(12-n)-}\), where \(M\) is Mo or W and \(X\) represents the heteroatom which is generally Ce, Th or U. The labelling of this category of polyanions is justified on the basis of the number ratio of heteroatom to the parent atom which is one to twelve. The heteroatom is present in an icosahedral void and is surrounded by 12 oxygen atom of nearby polyhedral unit of the parent atoms.
Figure 21. (a) Five $M_2O_{10}$ units are fused to create (b) $M_{10}O_{30}$ fragment which in turn cover by the sixth $M_2O_{10}$ unit resulting the (c) overall structure of $[X^{\text{an}}M_{12}O_{42}]^{(12-n)^-}$ anion.

In the recent years, bigger heteropoly anions with crown i.e. $[\text{Mo}_{16}O_{110}(\text{NO})_4(\text{H}_2\text{O})_4]$ and double crown i.e. structure $[\text{NaP}_3\text{W}_{36}O_{110}]^{14^-}$, $[\text{H}_2\text{P}_2\text{W}_{48}O_{184}]^{33^-}$, have also been prepared.
Problems

Q 1. Define isopoly and heteropoly metallates.

Q 2. Explain the condensation process involved in formation of paramolybdates.

Q 3. Draw and discuss the structure of paramolybdate anion, \( \text{MoO}_4^{2-} \), in detail.

Q 4. Draw and discuss the structure of octaamolybdate anion.

Q 5. Write down the reaction scheme giving the tungstic acid from normal tungstate with special reference to paramolybdate A.

Q 6. Explain the structure of metatungstate, \([\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}\), in detail.

Q 7. How can a Keggin structure with \( T_d \) symmetry be changed into a \( C_{3v} \) isomer?

Q 8. Draw and explain the structure of \([\text{NiMo}_9\text{O}_{32}]^{6-}\) and \([\text{MnMo}_9\text{O}_{32}]^{6-}\).

Q 9. Why do the isopoly and heteropoly acids of molybdenum and tungsten prefer edge sharing over the corner connection? Also explain the highly unusual face sharing.

Q 10. Write down the general formula for 1:12 and 2:18 heteropoly anions.
CHAPTER 5 Isopoly and Heteropoly Acids and Salts:

![Bibliography](image)


# Table of Contents

## CHAPTER 1
Stereochemistry and Bonding in Main Group Compounds:
- VSEPR Theory ................................................................................................................................ 11
- $d\pi-p\pi$ Bonds ................................................................................................................................ 23
- Bent Rule and Energetic of Hybridization ....................................................................................... 28
- Problems .......................................................................................................................................... 42
- Bibliography .................................................................................................................................... 43

## CHAPTER 2
Metal-Ligand Equilibria in Solution:
- Stepwise and Overall Formation Constants and Their Interactions ........................................ 44
- Trends in Stepwise Constants ......................................................................................................... 46
- Factors Affecting Stability of Metal Complexes with Reference to the Nature of Metal Ion and Ligand........................................................................................................... 49
- Chelate Effect and Its Thermodynamic Origin ............................................................................ 56
- Determination of Binary Formation Constants by pH-metry and Spectrophotometry .......... 63
- Problems .......................................................................................................................................... 68
- Bibliography .................................................................................................................................... 69

## CHAPTER 3
Reaction Mechanism of Transition Metal Complexes-I:
- Inert and Labile Complexes ........................................................................................................... 70
- Mechanisms for Ligand Replacement Reactions ....................................................................... 77
- Formation of Complexes from Aqua Ions ................................................................................... 82
- Ligand Displacement Reactions in Octahedral Complexes- Acid Hydrolysis, Base Hydrolysis .... 86
- Racemization of Tris Chelate Complexes ..................................................................................... 89
- Electrophilic Attack on Ligands .................................................................................................... 92
- Problems .......................................................................................................................................... 94
- Bibliography .................................................................................................................................... 95
CHAPTER 8 .......................................................... 214

Electronic Spectra of Transition Metal Complexes: ...................................................... 214

- Spectroscopic Ground States ......................................................................................... 214
- Correlation and Spin-Orbit Coupling in Free Ions for 1st Series of Transition Metals ... 243
- Orgel and Tanabe-Sugano Diagrams for Transition Metal Complexes (d^1 – d^6 States) 248
- Calculation of Dq, B and β Parameters ........................................................................... 280
- Effect of Distortion on the d-Orbital Energy Levels ...................................................... 300
- Structural Evidence from Electronic Spectrum ......................................................... 307
- Jahn-Tellor Effect ............................................................................................................ 312
- Spectrochemical and Nephelauxetic Series ................................................................. 324
- Charge Transfer Spectra ................................................................................................. 328
- Electronic Spectra of Molecular Addition Compounds ............................................... 336
- Problems .......................................................................................................................... 340
- Bibliography .................................................................................................................... 341

CHAPTER 9 ........................................................ 342

Magnetic Properties of Transition Metal Complexes: .................................................... 342

- Elementary Theory of Magneto-Chemistry ................................................................. 342
- Guoy’s Method for Determination of Magnetic Susceptibility ..................................... 351
- Calculation of Magnetic Moments ................................................................................ 354
- Magnetic Properties of Free Ions ................................................................................ 359
- Orbital Contribution: Effect of Ligand-Field ............................................................... 362
- Application of Magneto-Chemistry in Structure Determination .................................. 370
- Magnetic Exchange Coupling and Spin State Cross Over .......................................... 375
- Problems .......................................................................................................................... 384
- Bibliography .................................................................................................................... 385

CHAPTER 10 ..................................................... 386

Metal Clusters: ................................................................................................................ 386

- Structure and Bonding in Higher Boranes ................................................................. 386
- Wade’s Rules .................................................................................................................... 401
Mandeep Dalal is an Indian research scholar who is primarily working in the field of Science and Philosophy. He received his Ph.D in Chemistry from Maharshi Dayanand University, Rohtak, in 2018. He is also the Founder and Director of "Dalal Institute", a non-profit private educational organization in India which is trying to revolutionize the mode of higher education in Chemistry. He has published more than 25 research papers in various international scientific journals, including mostly from Elsevier (USA) and Springer (Europe).