

CHAPTER 5

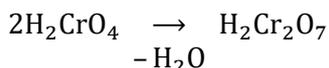
Isopoly and Heteropoly Acids and Salts:

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

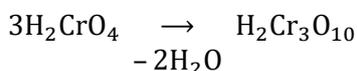
The term polymetalate acid or simply poly acid may be defined as the condensed or polymerized form of the weak acids of amphoteric metals like vanadium, niobium, tantalum (VB group metals) or chromium, molybdenum, and tungsten (VIB group metals) in the +5 and +6 oxidation states. The anions of these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

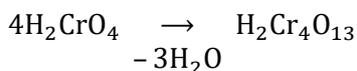
Consider the polymerization of chromate ion to form different isopoly chromates anions. CrO_3 dissolves in an alkali to give yellow colored CrO_4^{2-} ions solution. At very high pH, above 8, the chromate ions, CrO_4^{2-} , exist as the discrete entities but as the pH is lowered down, the protonation and dimerization take place. For instance:



and



and



The polymeric anions $\text{Cr}_2\text{O}_7^{2-}$, $\text{Cr}_3\text{O}_{10}^{2-}$ and $\text{Cr}_4\text{O}_{13}^{2-}$ produced by the polyacids $\text{H}_2\text{Cr}_2\text{O}_7$, $\text{H}_2\text{Cr}_3\text{O}_{10}$ and $\text{H}_2\text{Cr}_4\text{O}_{13}$, can successfully be isolated from their aqueous as sodium or potassium polysalts like $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{K}_2\text{Cr}_3\text{O}_{10}$ and $\text{K}_2\text{Cr}_4\text{O}_{13}$, respectively. Among the isopoly-anions of V^{5+} , Nb^{5+} , Ta^{5+} , Cr^{6+} , Mo^{6+} and W^{6+} , only Cr^{6+} is found to have tetrahedral CrO_4^{2-} units joined through the corners. The other metal ions form isopolyanions by the sharing of edges of octahedral MO_6 units. This may be attributable to the small size of Cr^{6+} which can afford only four oxide ions around itself.

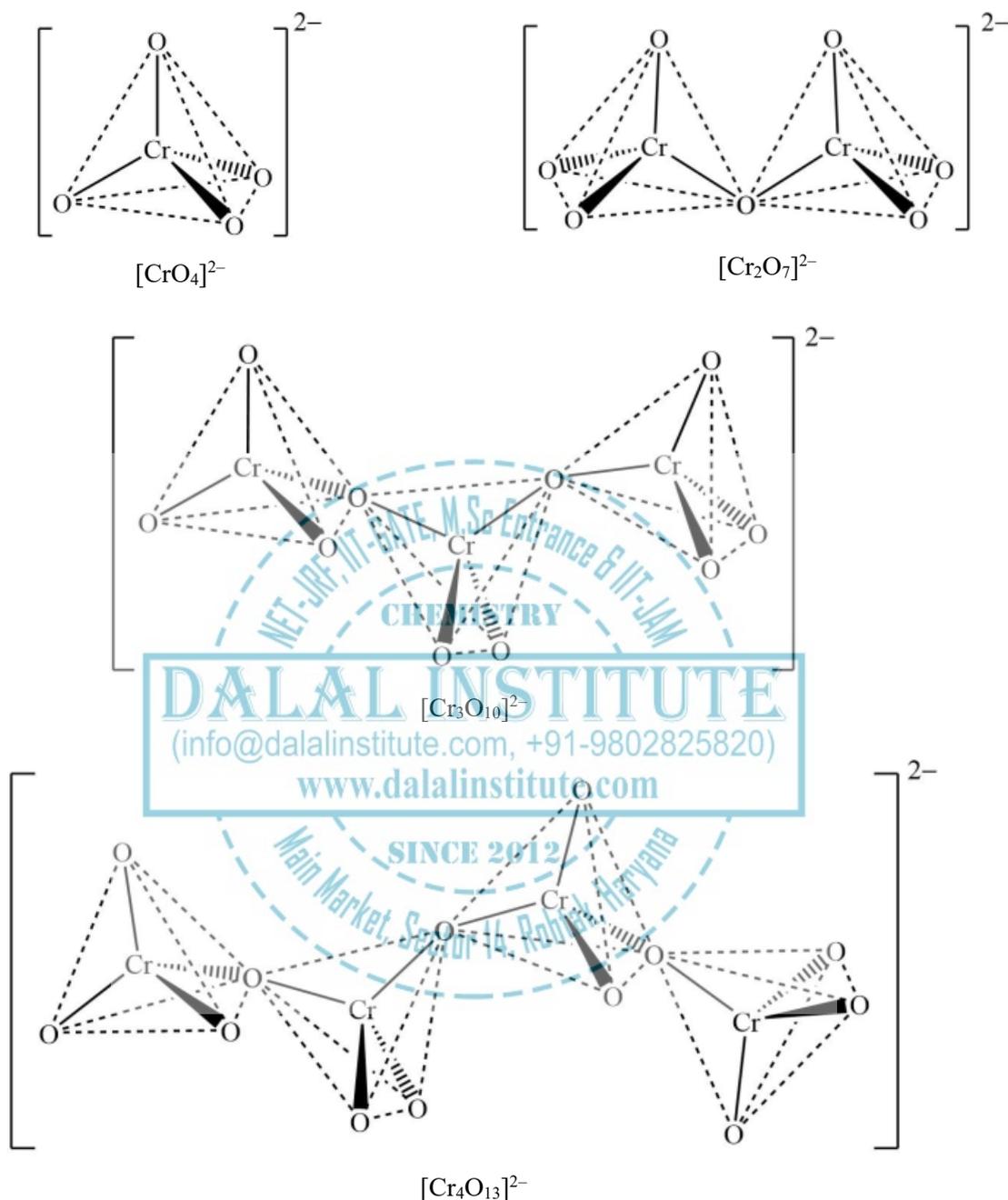
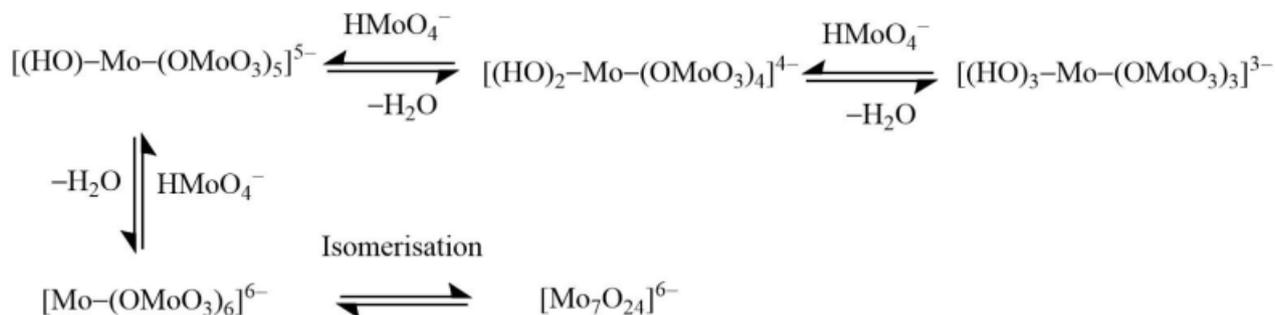
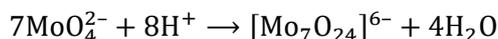


Figure 1. The structure of chromate and isopoly anions of chromium.

The tri-chromate and tetra-chromate anions can be crystallized as their alkali metal salts only from strongly acidic solution and no polymerization beyond the tetrameric entity is observed. The Cr–O–Cr bond angle of all polychromates is approximately 120°.



The complete reactions giving different isopoly molybdates can be written as:



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, $\text{Mo}_8\text{O}_{26}^{4-}$ is obtained. If the pH of the solution is dropped below 1, yellow colored, molybdic acid ($\text{MoO}_3 \cdot 2\text{H}_2\text{O}$) is formed which can be converted into monohydrate form just by warming it up.



It is worth noting that during the condensation process, from 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 the polyhedral entity becomes MoO_6 octahedron.

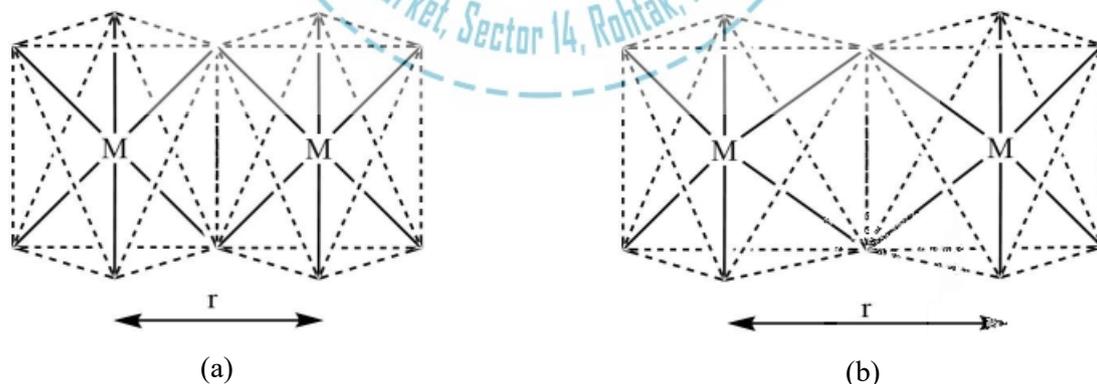


Figure 3. The structure of (a) ideal edge sharing octahedrons and (b) distorted edge sharing octahedrons.

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 centers can be explained in terms of reduced inter-metal ion repulsion.

Keeping in mind that electrostatic repulsion between metal centers 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 centers 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 types of sharing, face > edge > corner, suggests a face sharing of the octahedron units as the most favorable choice for the condensation but it is actually the least favored 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 $M_2O \cdot 2MoO_3 \cdot xH_2O$ ($M = Na, K$ or NH_4) and are observed in the pH range of 5-6.



$Na_2Mo_2O_7$ is not stable and hence dimolybdate systems do not contain $Mo_2O_7^{2-}$ ions. The compounds like $M_2Mo_2O_7$ 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_4^{2-}) and paramolybdate ($Mo_7O_{24}^{6-}$) ions in general. However, molybdate ions as a salt of tetrabutylammonium, $[(C_4H_9)_4N]_2Mo_2O_7$, is one of the very few compounds which is known to have discrete $Mo_2O_7^{2-}$ ions.

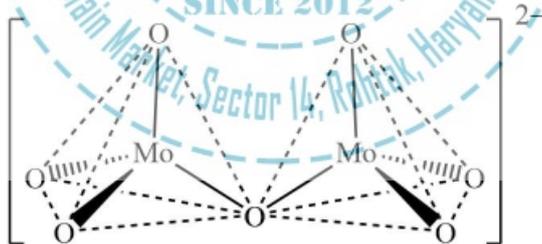


Figure 4. $Mo_2O_7^{2-}$ ion in tetrabutylammonium dimolybdate.

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



$Na_2Mo_3O_{10}$ 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 $M_2O \cdot 4MoO_3 \cdot xH_2O$ where M represents Na or K.



$Na_2Mo_4O_{13}$ is not stable and hence tetramolybdate systems do not contain $Mo_4O_{13}^{2-}$ ions. These systems are the mixture of simple (MoO_4^{2-}) and octamolybdate ($Mo_8O_{26}^{4-}$) ions in general.

4. Heptamolybdate or paramolybdate: The general formula for paramolybdates is $M_6Mo_7O_{24}$ where M represents Na, K or NH_4 . $M_6Mo_7O_{24}$ is quite stable and contains discrete $Mo_7O_{24}^{6-}$ ions.

The edge connections of seven ideal MoO_6 octahedrons in paramolybdate ion can be visualized in terms of one front unit (composed of four MoO_6) and one rear unit (composed of three 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 neighbors.

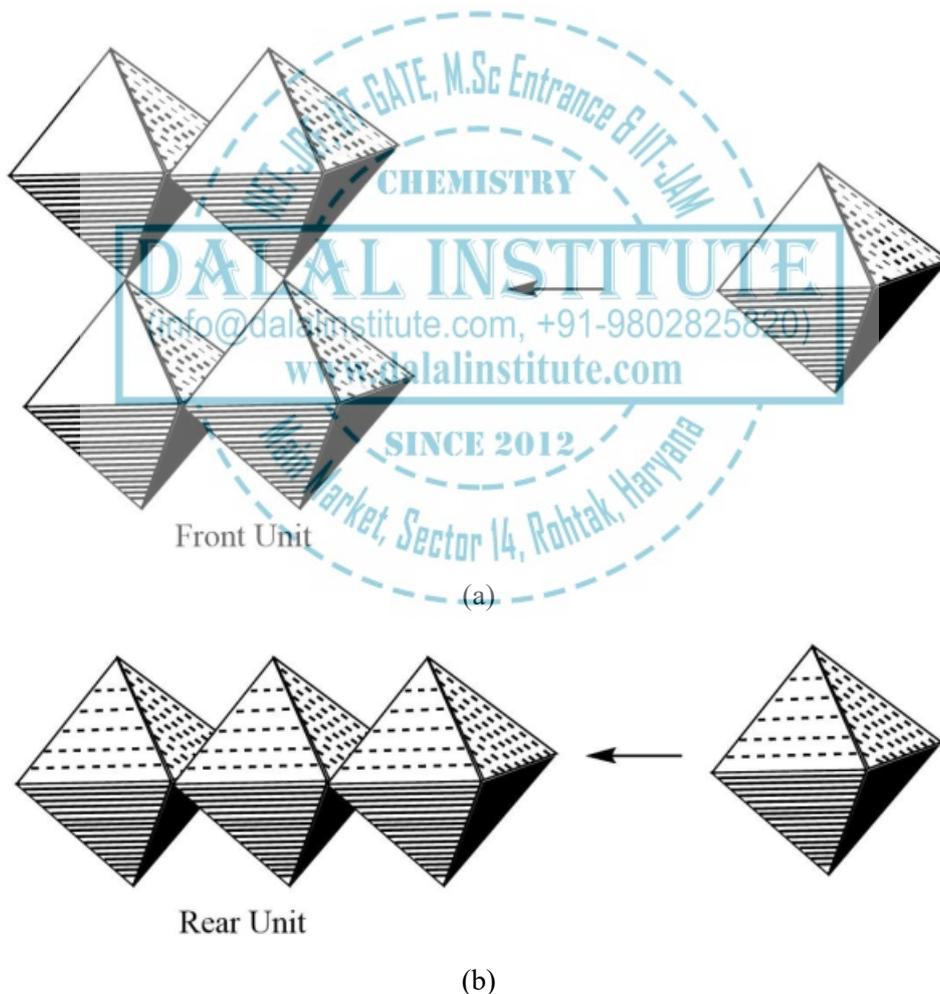
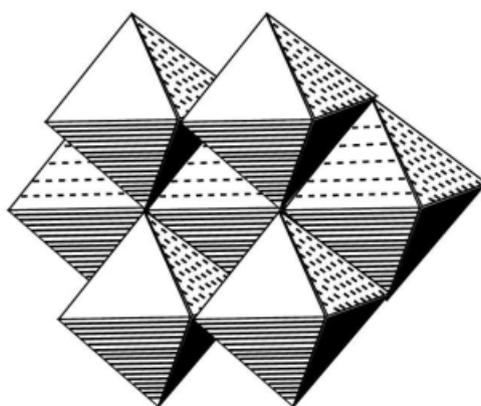


Figure 5. Continued on the next page...



(c)

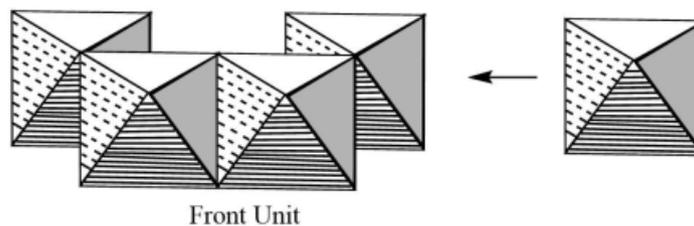
Figure 5. The (a) front unit and (b) rear unit are combined to produce the (c) overall structure of paramolybdate ion.

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 MoO_6 units.

5. Octamolybdate: The general formula for octamolybdates is $\text{M}_4\text{Mo}_8\text{O}_{24}$ where M represents Na, K or NH_4 . $\text{M}_4\text{Mo}_8\text{O}_{26}$ is quite stable and contains discrete $\text{Mo}_8\text{O}_{26}^{4-}$ 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.

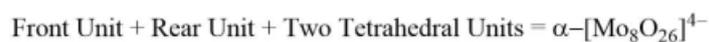
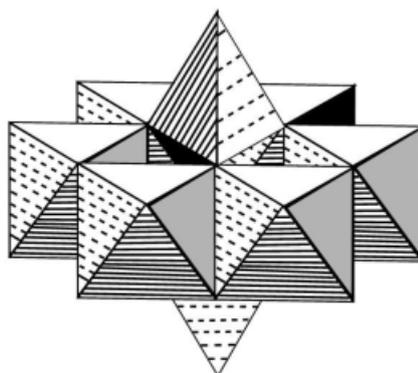


(a)



(b)

Figure 6. Continued on the next page...



(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 α -octamolybdate ion.

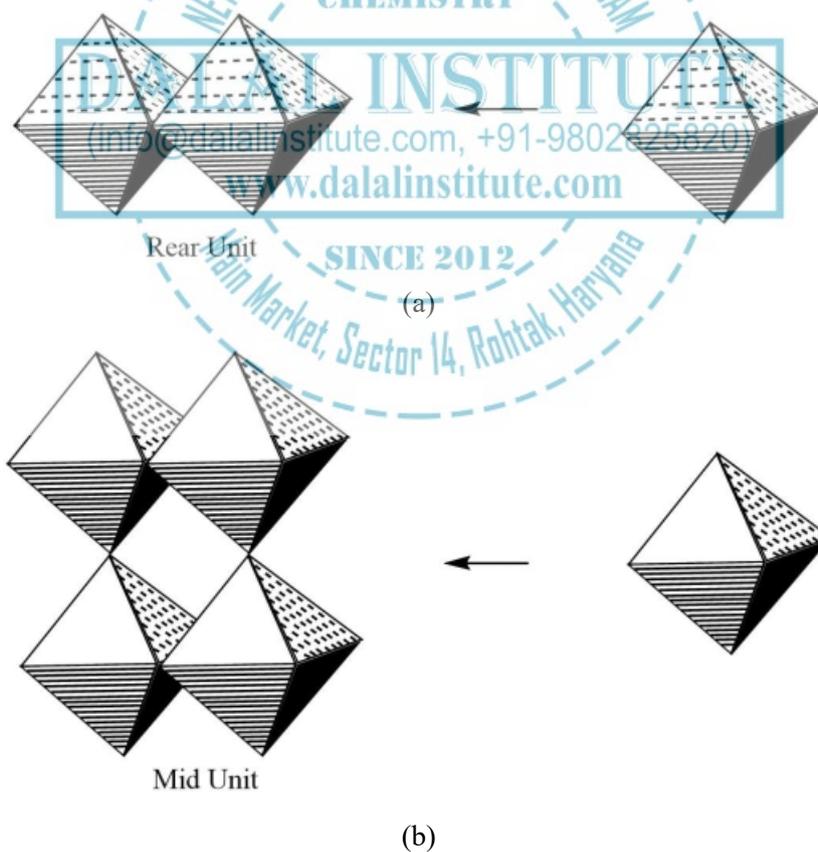
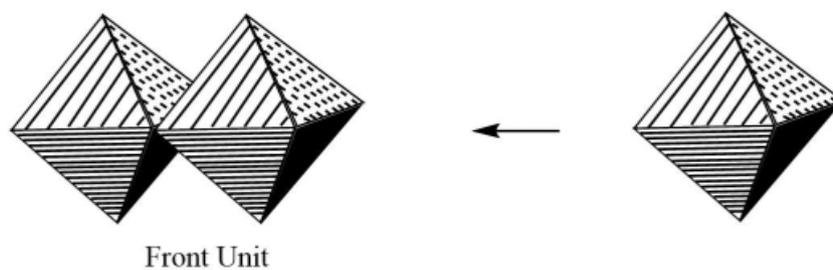
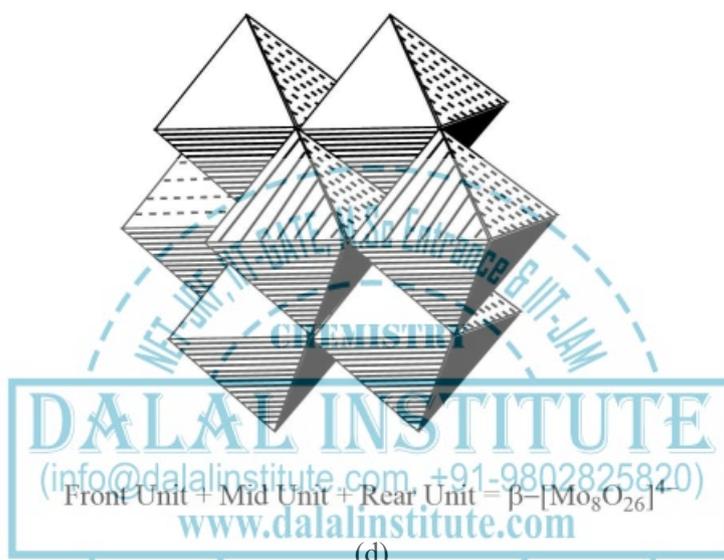


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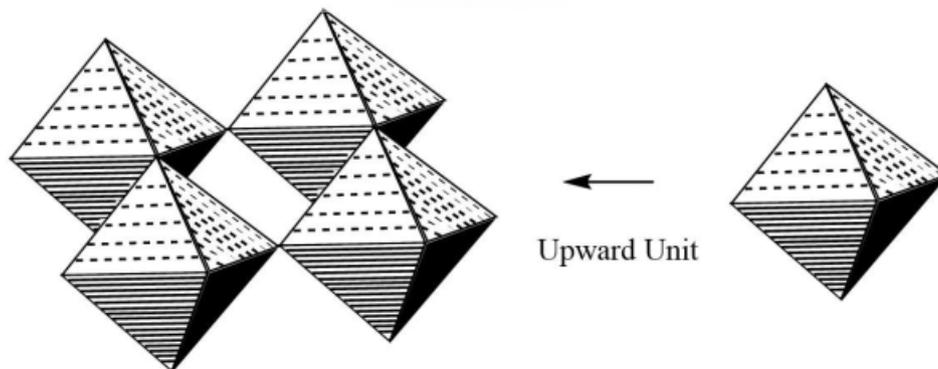


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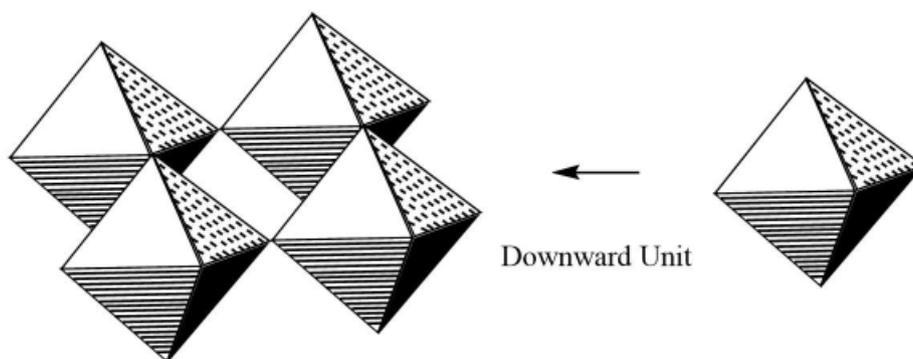
(d)

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.

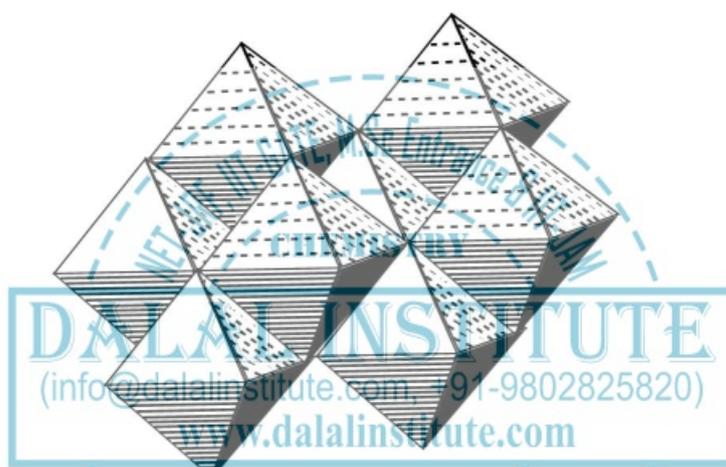


(a)

Figure 8. Continued on the next page...



(b)



(c)

Figure 8. The (a) upward unit and (b) downward units are combined to produce the (c) overall structure of the γ -octamolybdate ion.

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

The edge connections of eight ideal MoO_6 octahedrons in β -octamolybdate ion can be visualized in terms of one front unit (composed of two MoO_6), one mid-unit (composed of four MoO_6) and one rear 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 β -octamolybdate.

6. Hexamolybdate: The hexamolybdates are derived from discrete $\text{Mo}_6\text{O}_{19}^{2-}$ 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.

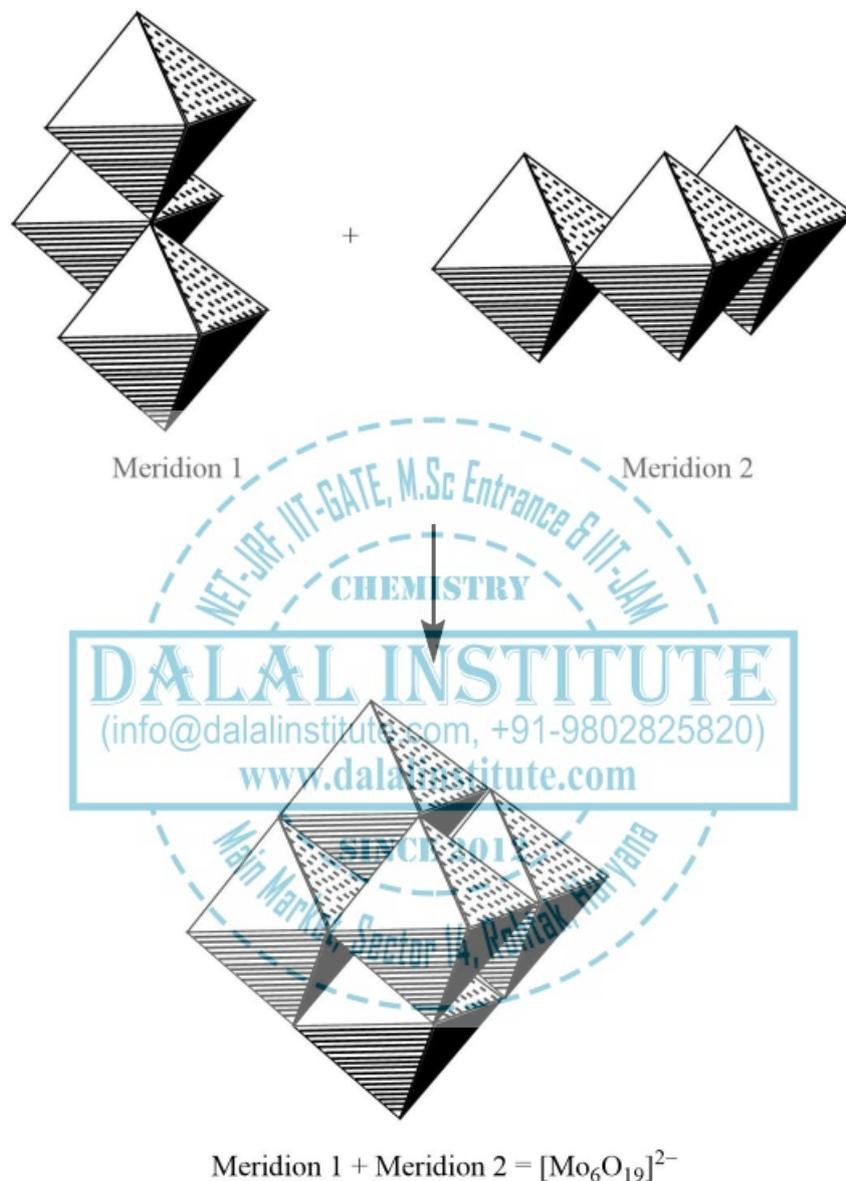


Figure 9. The hexamolybdate anion.

7. Decamolybdate: The decamolybdates are obtained as $(\text{NH}_4)_8\text{Mo}_{10}\text{O}_{34}$ and the corresponding molybdate ion $\text{Mo}_{10}\text{O}_{34}^{8-}$ are found to have one Mo_8O_{28} unit and two MoO_4 tetrahedral units attached at corners. The structure of decamolybdate can be visualized as an extension of $\gamma\text{-}[\text{Mo}_8\text{O}_{26}]^{8-}$ in which two additional tetrahedral units are attached at corners of two opposite octahedrons.

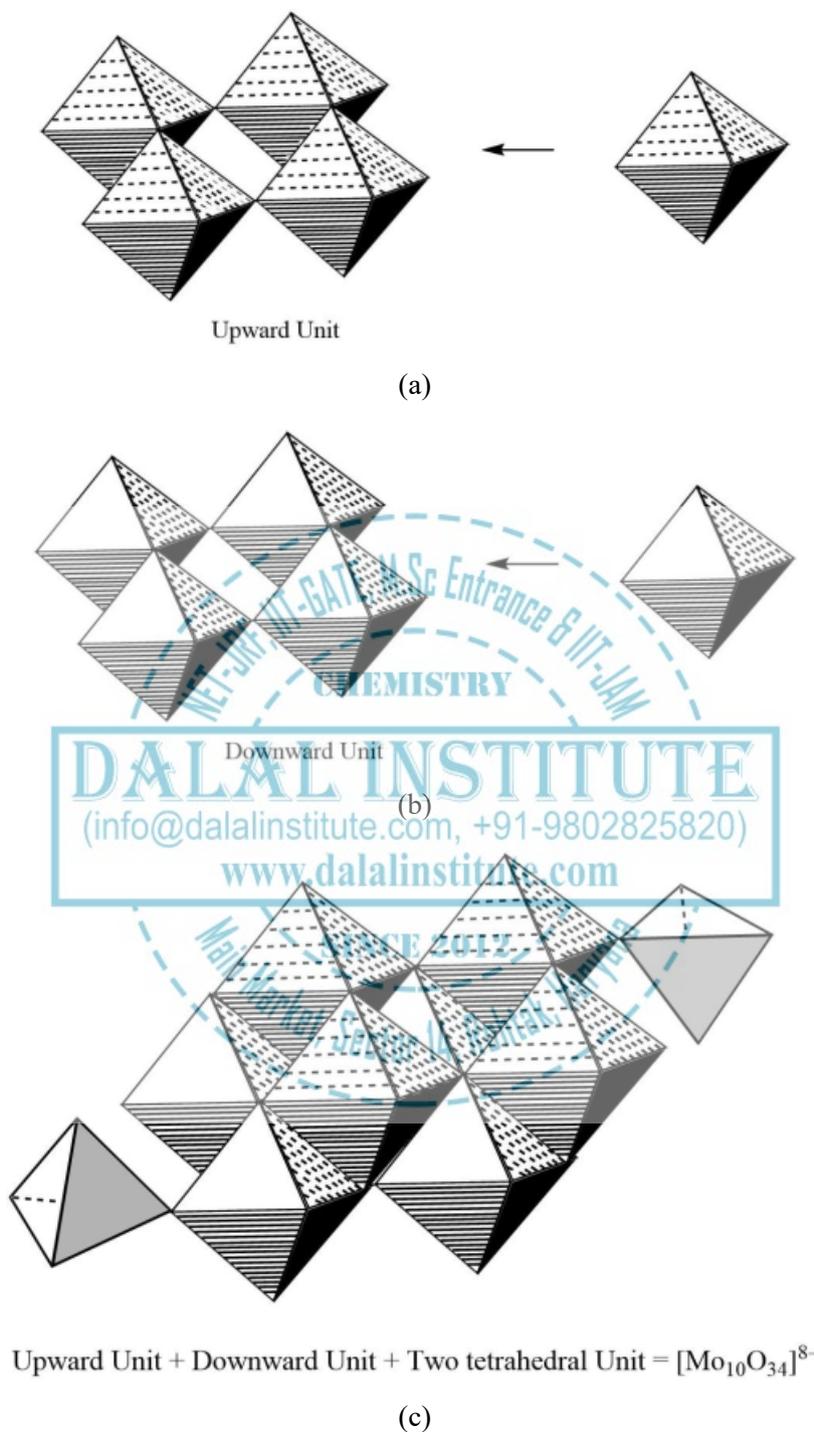
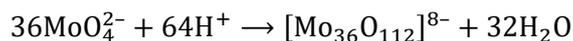


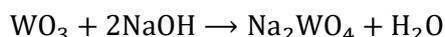
Figure 10. The (a) upward unit and (b) downward unit and two tetrahedral units are combined to produce the (c) overall structure of dacamolybdate ion.

8. Mo₃₆-polymolybdate: The largest polymolybdate under non-reducing conditions known till recent times is [Mo₃₆O₁₁₂(H₂O)₁₆]⁸⁻ and can be synthesized at a pH of 1.8 as:



The structure of Mo₃₆-polymolybdate contains the [(Mo)Mo₅]-type unit comprising a central MoO₇ pentagonal bipyramid sharing edges with five MoO₆ 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:

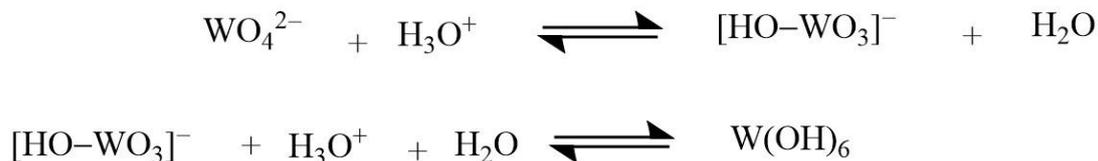


These normal tungstates, Na₂WO₄, containing discrete WO₄²⁻ units, can easily be crystallized out of aqueous solution. The normal tungstate of other metals can be synthesized from sodium tungstate via double decomposition.

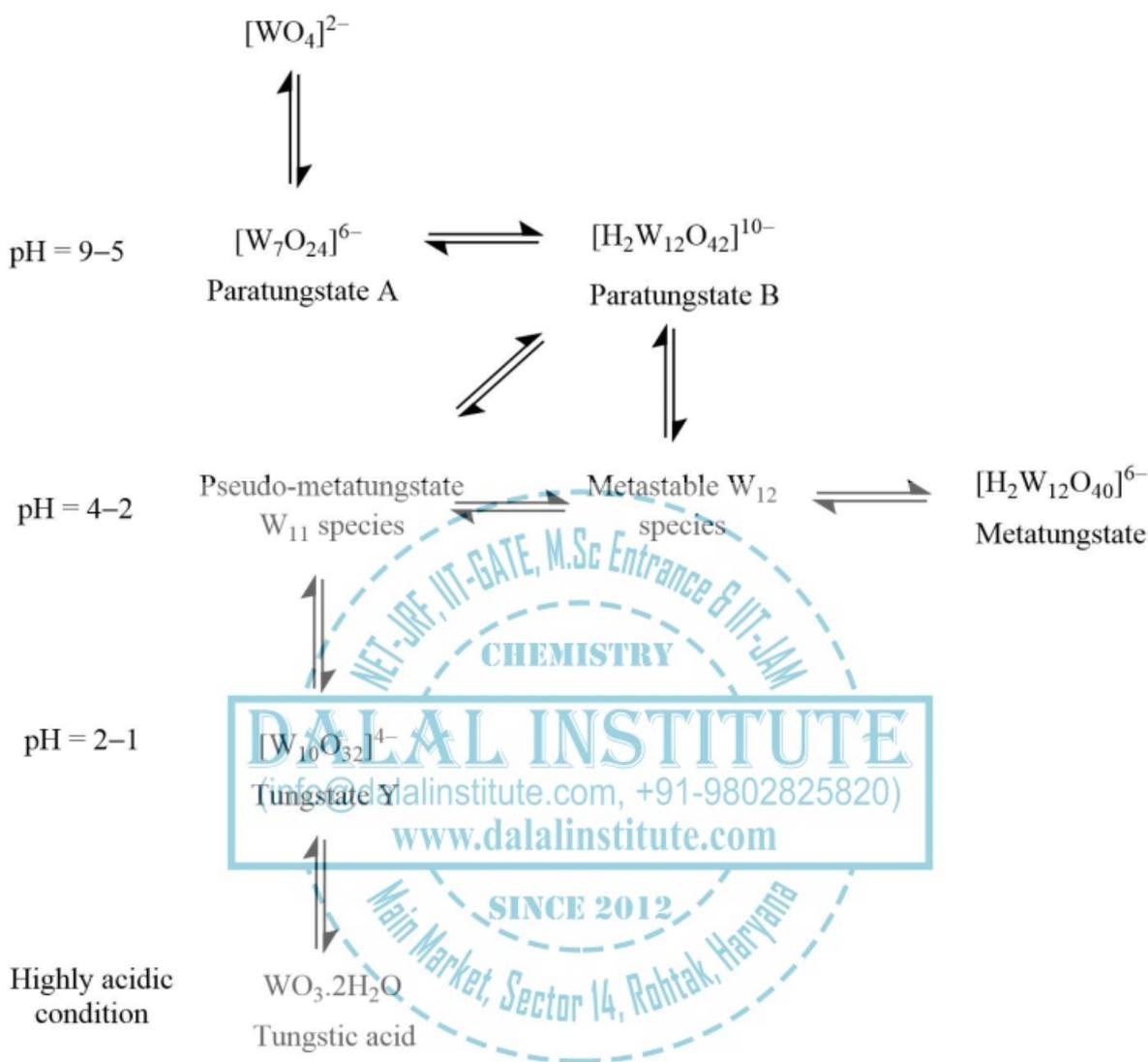


Figure 11. The discrete WO₄²⁻.

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 W₇O₂₄⁶⁻ i.e. paratungstate A. The whole process of condensation can be depicted as follows:



Although the entropy (ΔS) 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 the second reaction, compensating the entropy loss. The W(OH)₆, thus formed during the course of the second reaction, reacts with [WO₃(OH)]⁻ ions present in the acidic media as:



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 $\text{M}_6\text{W}_7\text{O}_{24}$ where M is normally Na, K or NH_4 and contains discrete $\text{W}_7\text{O}_{24}^{6-}$ ions. The edge connections of seven ideal WO_6 octahedrons in paratungstate-A ion can be visualized in terms 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 neighbors. It should be noted that $\text{W}_6\text{O}_{24}^{6-}$ is isostructural with $\text{Mo}_6\text{O}_{24}^{6-}$.

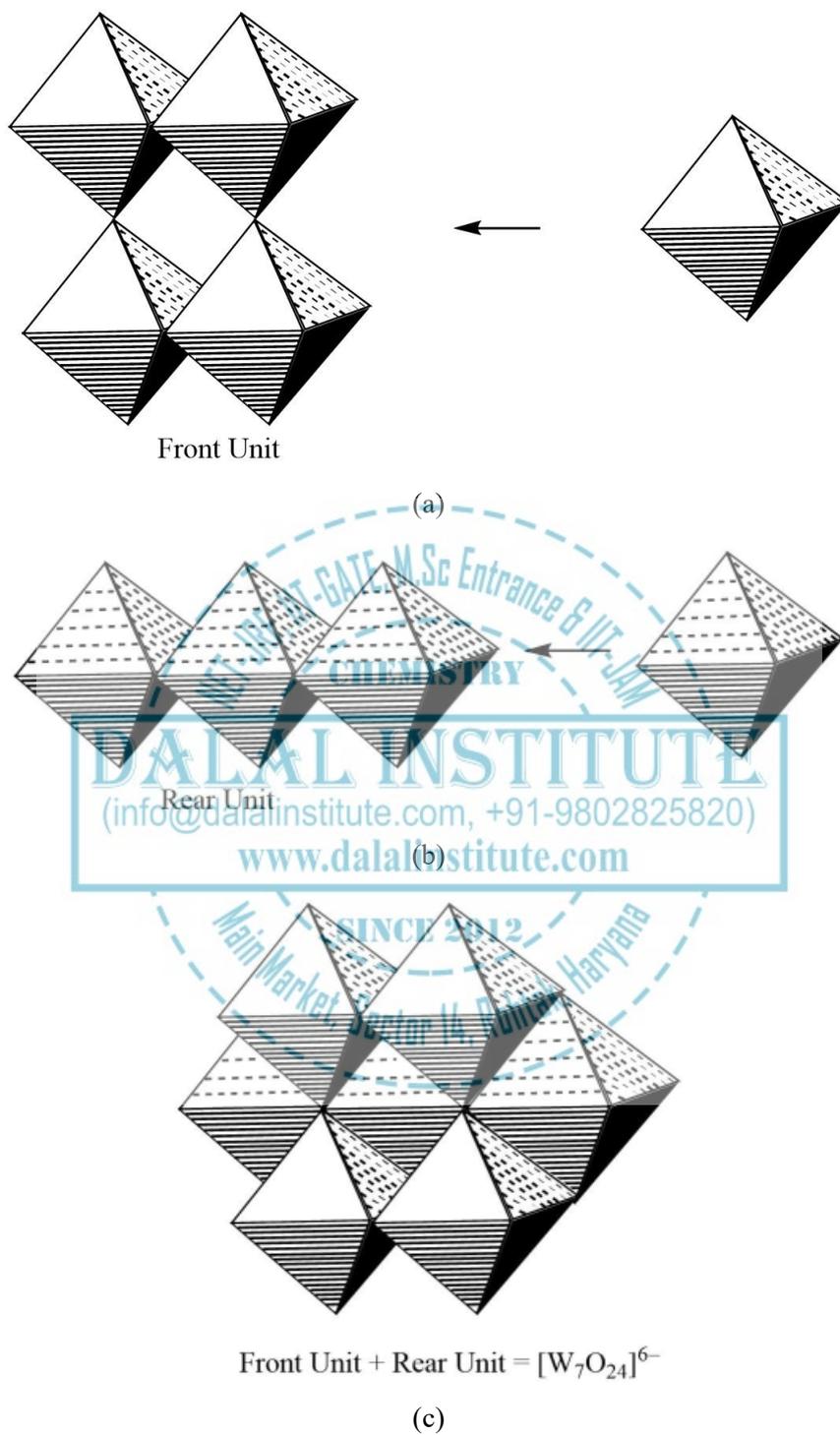


Figure 12. The (a) front unit and (b) rear unit are combined to produce the (c) overall structure of the paratungstate A ion.

2. Paratungstate B: The paratungstate B is derived as the alkali metal salts of dodecameric anions, $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$, from the acidification of normal tungstate aqueous solutions. The protons reside in the polyhedral cavity and are involved in rapid exchange solvent water.

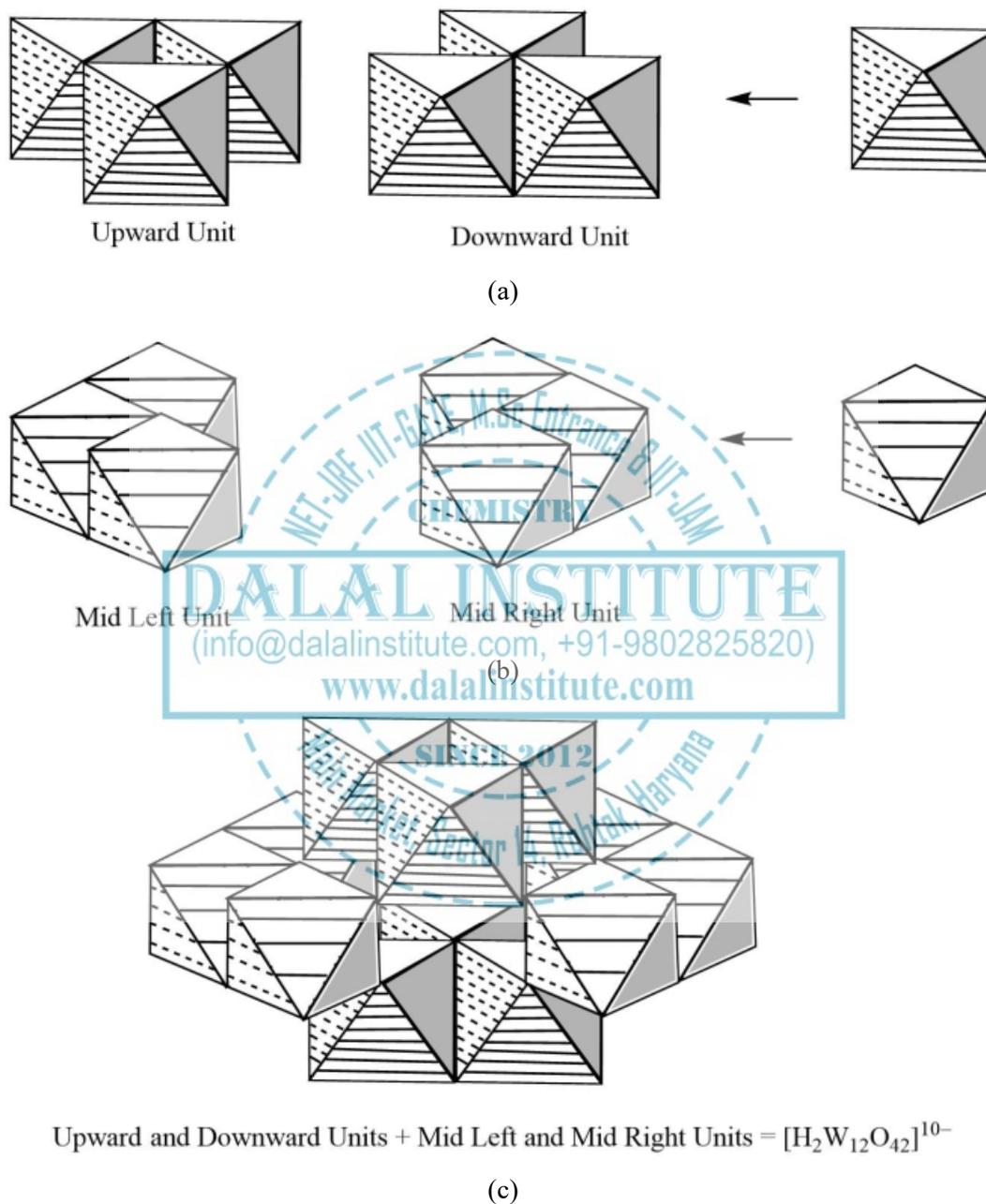


Figure 12. The (a) upward - downward units and (b) mid left - mid units are combined to produce the (c) overall structure of the metatungstate anion.

3. Metatungstate: The metatungstates are derived as the alkali metal salts of dodecameric anions, $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$, 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.

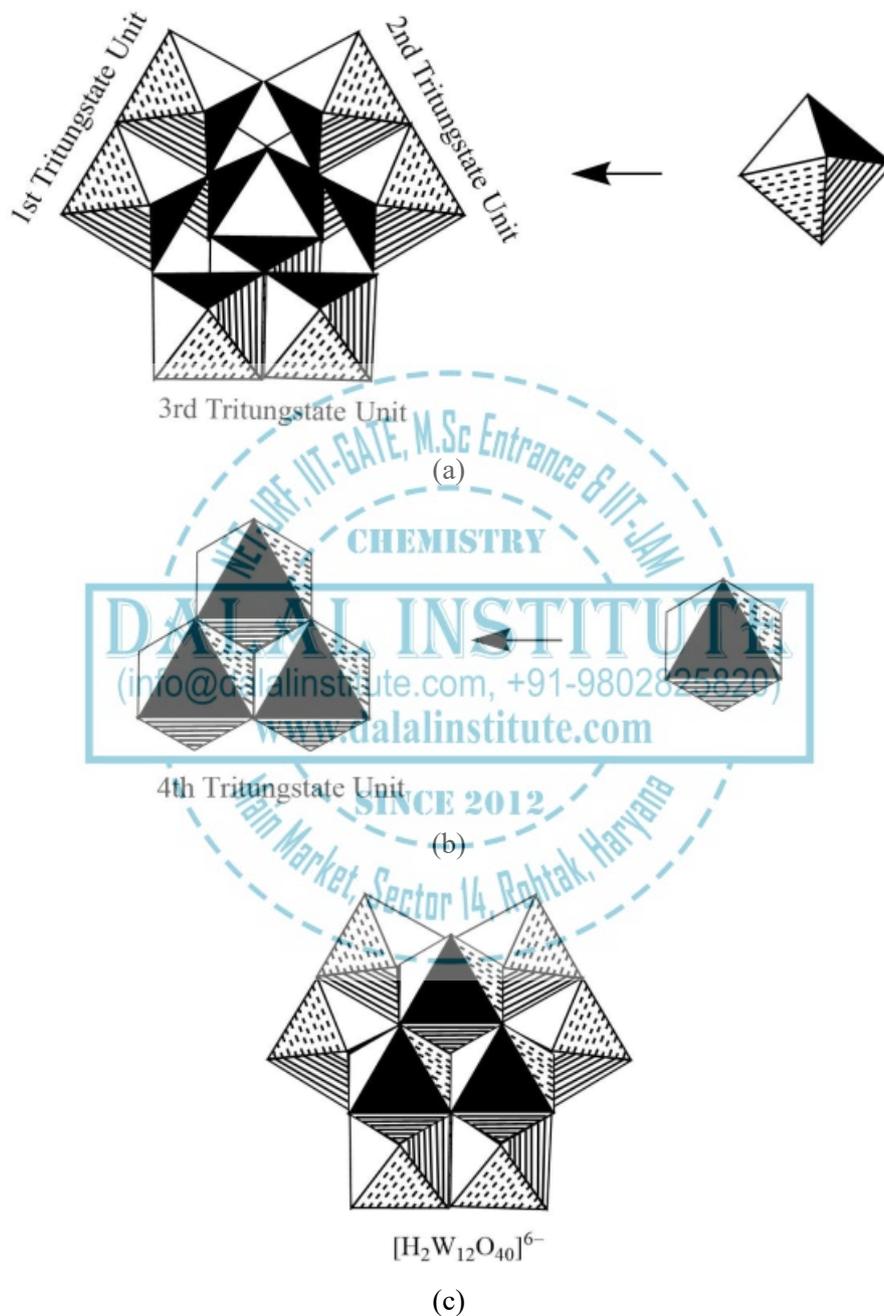


Figure 13. The structure of metatungstate anion is obtained by joining four equivalent tritungstate units along tetrahedral faces.

4. Tungstate Y: These isopoly tungstates are derived as the alkali metal salts of $[\text{W}_{10}\text{O}_{32}]^{4-}$ anions and are yellow in color. The discrete $[\text{W}_{10}\text{O}_{32}]^{4-}$ anions are found to be present in both solution and crystallized form.

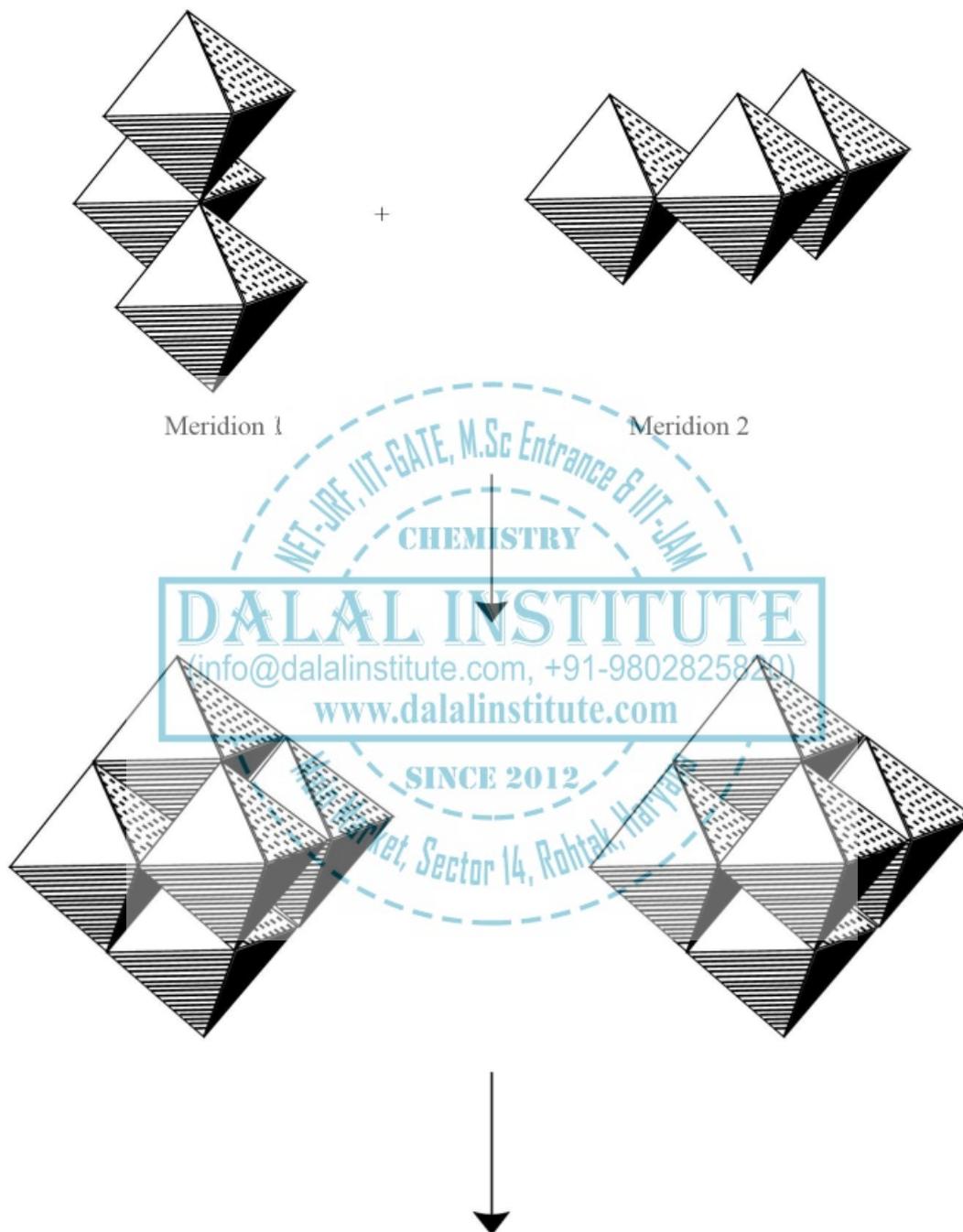


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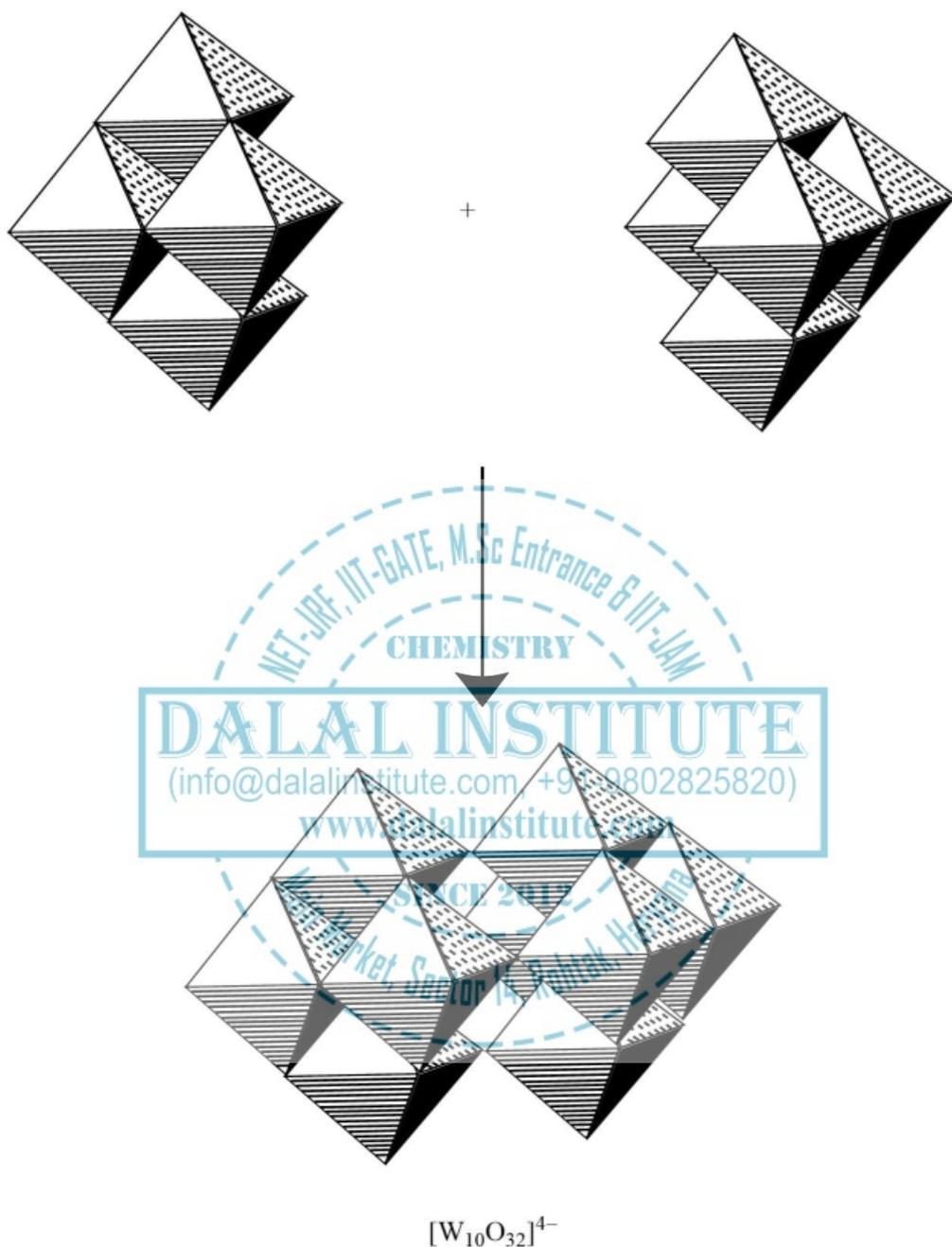


Figure 14. The structure of tungstate Y.

The structure of tungstate Y can be visualized from hexa-tungstate systems in which two meridians, composed of WO_6 octahedral units are joined to form W_6 -polyhedra. When one octahedron from each $[W_6O_{10}]^{2-}$ unit is removed, the resulting structural units can be combined through the corners to form the overall geometry of decameric isopoly anion.

5. Hexatungstate: These isopoly hexatungstates are obtained from methanolic solutions and contain discrete $[\text{W}_6\text{O}_{19}]^{2-}$ ions both in solution and in crystallized form.

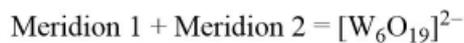
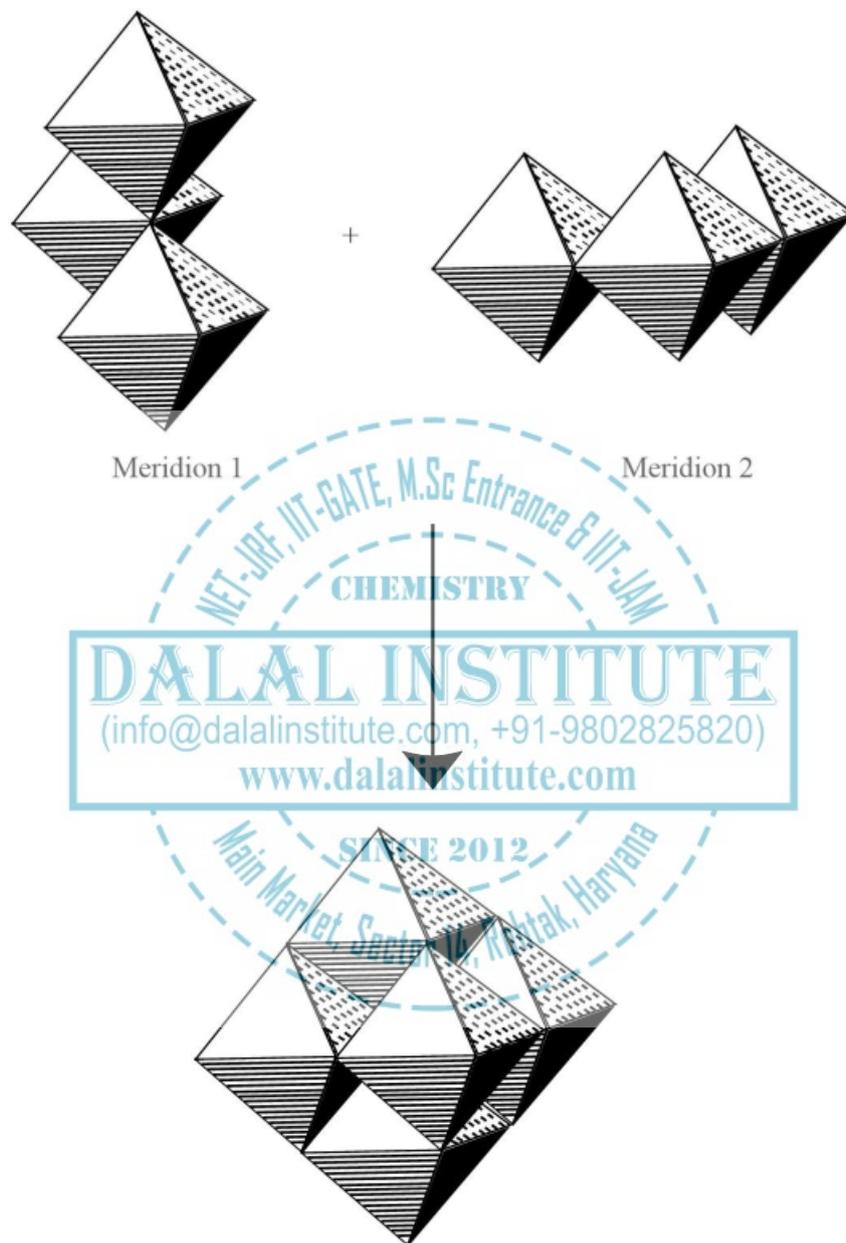


Figure 15. The hexatungstate anion.

It is worth noting that hexatungstate is isostructural with hexamolybdate anion in which the coordination number of the oxide ion situated at the center of the $[\text{W}_6\text{O}_{19}]^{2-}$ anion is six.

6. Tetratungstate: The crystal form of $\text{Li}_{14}(\text{WO}_4)_3(\text{W}_4\text{O}_{16}) \cdot 4\text{H}_2\text{O}$, obtained from aqueous solution, is found to have discrete $\text{W}_4\text{O}_{16}^{8-}$. However, the presence of this isopoly anion in the solution phase is still unknown.

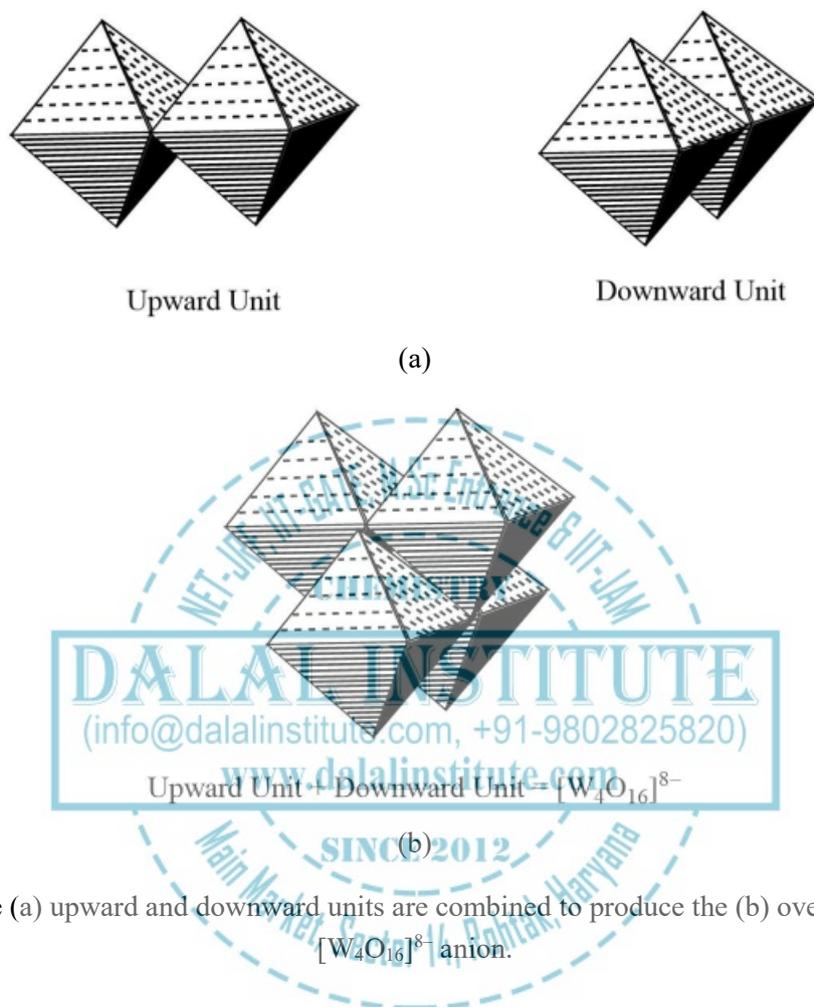


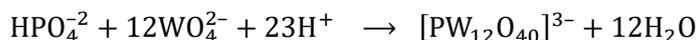
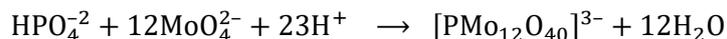
Figure 16. The (a) upward and downward units are combined to produce the (b) overall structure of $[\text{W}_4\text{O}_{16}]^{8-}$ anion.

➤ *Heteropoly Acids and Salts of Mo and W*

One of the founders of modern chemistry, a Swedish chemist, Jacob Berzelius found that the acidification of the solution containing phosphate and molybdate results in a yellow-colored precipitate. This crystalline substance was actually the first example of a heteropoly anion, $[\text{PMo}_{12}\text{O}_{40}]^{3-}$, 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 analogs. 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 neighboring 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:



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

1. 1:12 (Tetrahedral heteroatom): The general formula for these types of heteropolyanions is $[\text{X}^{\text{n}+}\text{M}_{12}\text{O}_{40}]^{(8-\text{n})-}$, where M is Mo or W and X represents the heteroatom which is generally P, Si, As, Ge or Ti. The labeling 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 MO_6 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 sets of trimetallate (composed of three MO_6) units through 60° . The first structure is perfect tetrahedral with four three-fold axes of rotation but the second structure contains only one three-fold axis of rotation. The stability of both the structures is the same. $[\text{XM}_{12}\text{O}_{40}]^{4-}$, with X as Ge^{4+} or Si^{4+} , is found to be present in both of the isomeric forms.

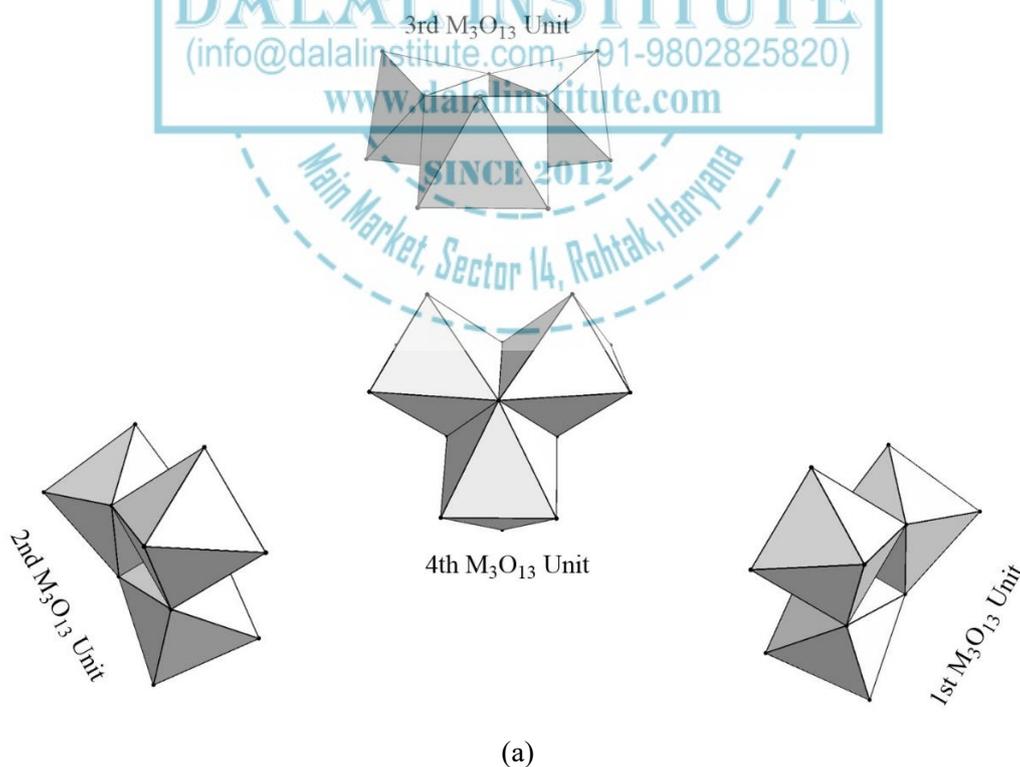
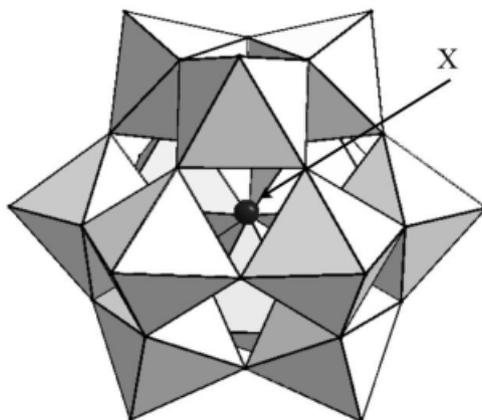


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The Keggin Structure of $[X^{n+}M_{12}O_{40}]^{(8-n)-}$

(b)

Figure 17. (a) Four M_3O_{13} units are combined to produce a tetrahedral cavity occupied by the heteroatom.

(b) The overall structure of $[X^{n+}M_{12}O_{40}]^{(8-n)-}$ anion.

One of the most common examples of these types of heteropoly anions is $[Co^{2+}W_{12}O_{40}]^{6-}$, which can be oxidized to $[Co^{3+}W_{12}O_{40}]^{5-}$. In both of the anions, the heteroatom is present in the tetrahedral void and is surrounded by four oxygen atoms of nearby MO_6 octahedrons.

2. 2:18 (Tetrahedral heteroatom): The general formula for this type of heteropolyanions is $[X_2^{5+}M_{18}O_{62}]^{6-}$, where M is Mo or W and X represents the heteroatom which is generally P or As. The labeling 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 $[X^{n+}M_{12}O_{40}]^{(8-n)-}$ heteropoly anions.

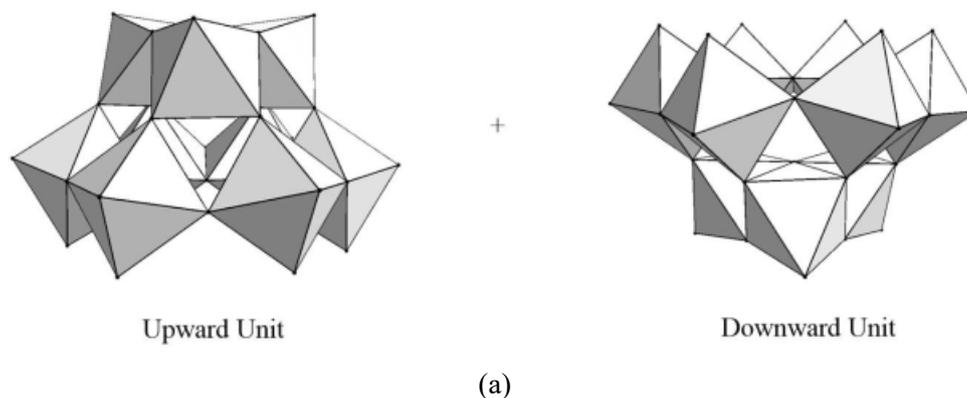
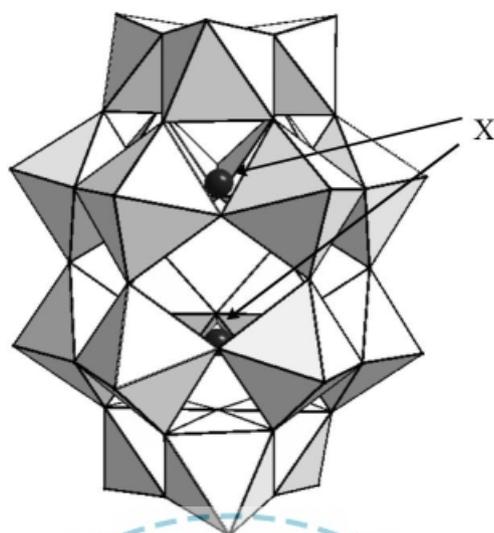


Figure 18. Continued on the next page...

The Dawson Structure of $[X_2^{5+}M_{18}O_{62}]^{6-}$

(b)

Figure 18. The (a) upward and downward units are combined to produce the (b) overall structure of $[X_2^{5+}M_{18}O_{62}]^{6-}$ anion.

The structure is generally referred to as the "Dawson structure" and can be visualized from the Keggin structure easily. The $[X_2^{5+}M_{18}O_{62}]^{6-}$ can be considered as a fusion of two M_6 units, each of which is derived from the Keggin structure by the removal of three corner-linked MO_6 octahedra. Both heteroatoms are present in the inner cavity of the polyanion, formed by different MO_6 octahedron units.

3. 1:6 (Octahedral heteroatom): The general formula for this type of heteropolyanion 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 labeling 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 for 1:6 heteropolyanions is found to be greater in the 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 that all the six MO_6 octahedron units are parallel to each other.

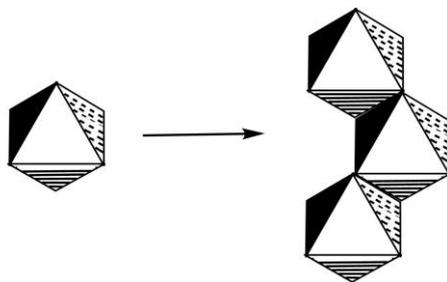


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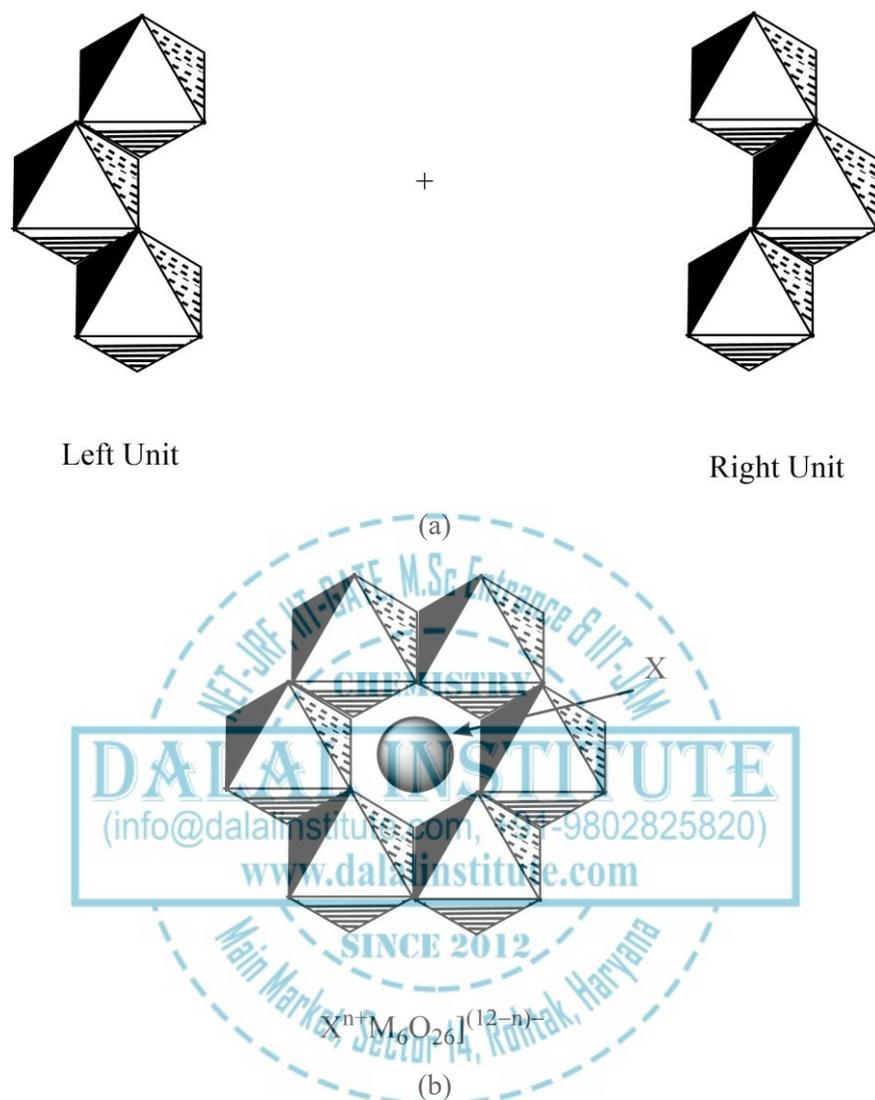


Figure 19. The (a) left and right units are combined to produce the (b) overall structure of $[X^{n+}M_6O_{26}]^{(12-n)-}$ heteropoly anion.

4. 1:9 (Octahedral heteroatom): The general formula for this type of heteropolyanions is $[X^{n+}M_9O_{32}]^{(10-n)-}$, where M is Mo or W and X represents the heteroatom which is generally Mn or Ni. The labeling 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 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 types of heteropoly anions are $[NiMo_9O_{32}]^{6-}$ and $[MnMo_9O_{32}]^{6-}$. It must also be noted down that Ni and Mn are present in +4 oxidation state which is highly unusual.

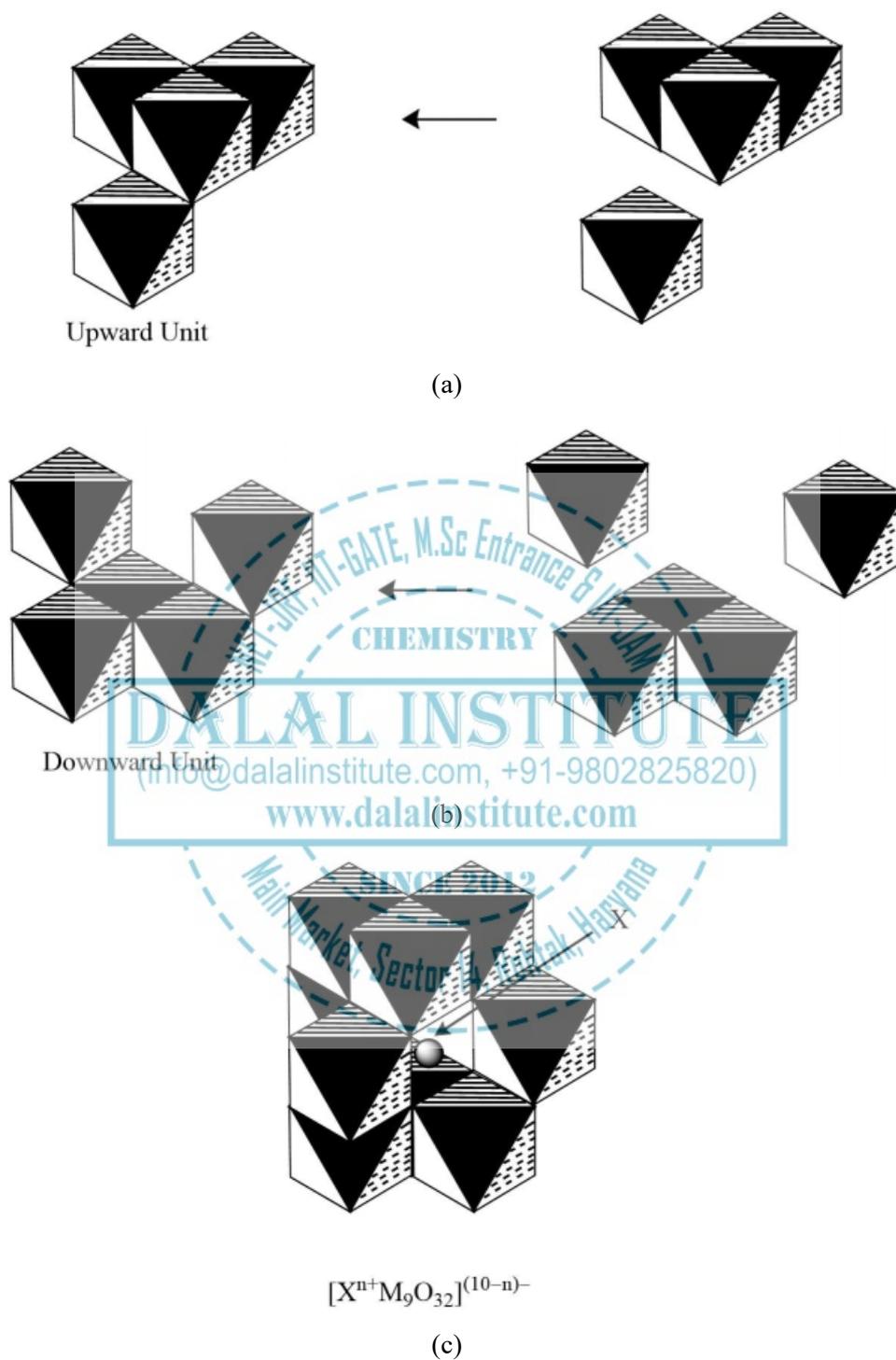


Figure 20. The (a) upward and (b) downward units are combined to produce the (c) overall structure of $[X^{n+}M_9O_{32}]^{(10-n)-}$ anion.

5. 1:12 (Icosahedral heteroatom): The general formula for this type of heteropolyanions is $[X^{n+}M_{12}O_{42}]^{(12-n)-}$, where M is Mo or W and X represents the heteroatom which is generally Ce, Th or U. The labeling 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 atoms of the nearby polyhedral unit of the parent atoms.

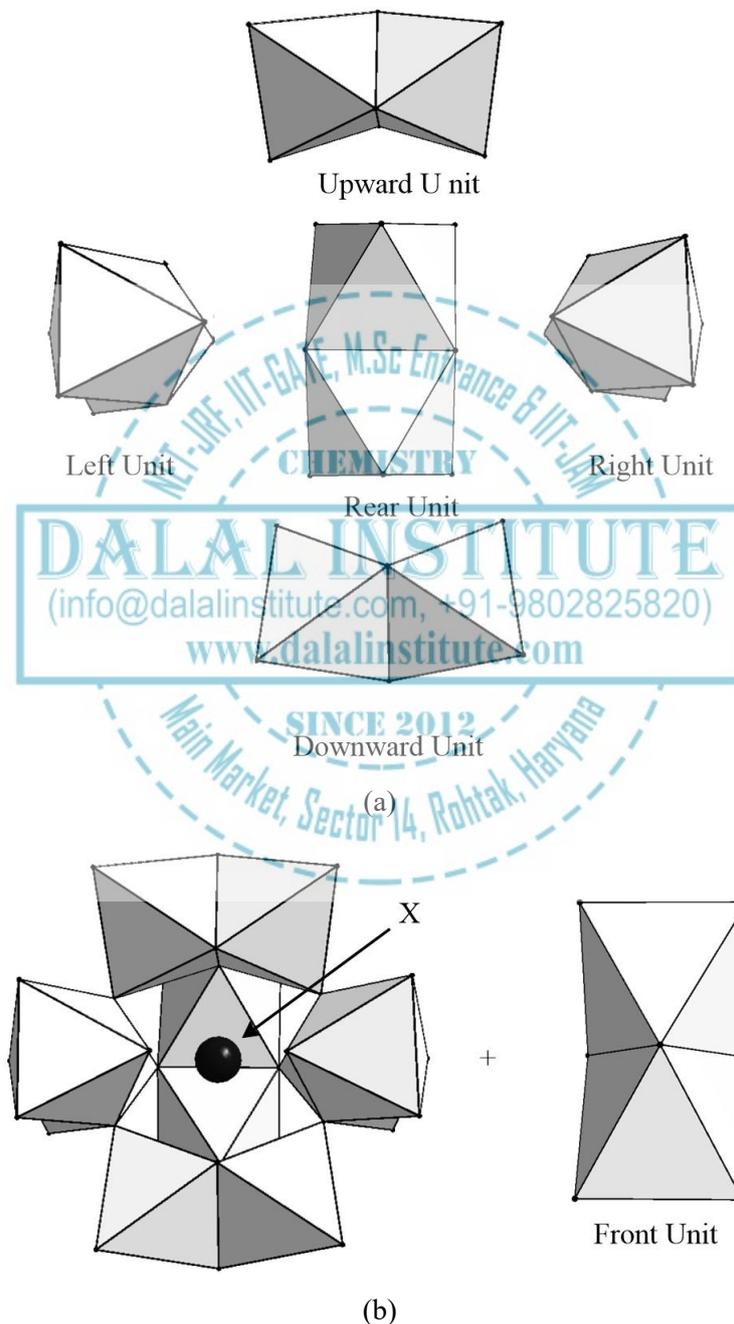
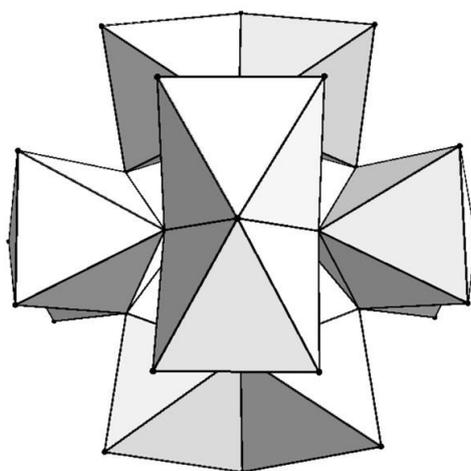


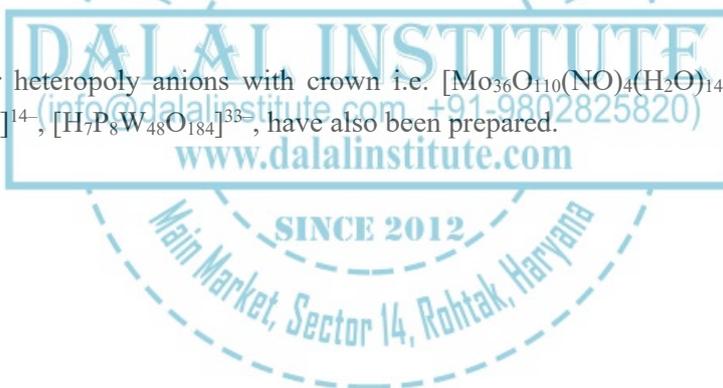
Figure 21. Continued on the next page...



(c)

Figure 21. (a) Five M_2O_{10} units are fused to create (b) $M_{10}O_{30}$ fragment which, in turn, covers by the sixth M_2O_{10} unit resulting in the (c) overall structure of $[X^{n+}M_{12}O_{42}]^{(12-n)-}$ anion.

In recent years, bigger heteropoly anions with crown i.e. $[Mo_{36}O_{110}(NO)_4(H_2O)_{14}]$ and double crown i.e. structure $[NaP_5W_{36}O_{110}]^{14-}$, $[H_7P_8W_{48}O_{184}]^{33-}$, have also been prepared.



❖ Problems

- Q 1. Define isopoly and heteropoly metallates.
- Q 2. Explain the condensation process involved in the formation of paramolybdates.
- Q 3. Draw and discuss the structure of paramolybdate anion, $\text{Mo}_7\text{O}_{24}^{6-}$, in detail.
- Q 4. Draw and discuss the structure of octamolybdate 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.

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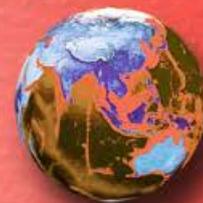
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