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# Unit-5 Isopoly & Heteropoly acids & salts

[By Dr. Birendra Kumar, Maharaja College]

## ⇒ Isopoly acids & Salts?

Any of a large group of Complex oxygen containing acids derived from a single inorganic acid by elimination of water from two or more molecules of acid anhydride, they are called isopoly acids. Isopoly acids contain only one metal (Group-5 or 6) along with hydrogen and oxygen. Amphoteric metals of Group-5 (V, Nb & Ta) and Group-6 (Cr, Mo & W) in the oxidation states +5 & +6 form weak acids, which readily condense or polymerize to form anions containing several molecules of the acid anhydride. Isopoly acids form from the combination of similar acids or anions.

Salts of isopoly acids are called isopoly salts. Molybdenum (Mo) and tungsten (W) form a large number of polymolybdate (VI) and polytungstate (VI) acids and their salts. Of the other transition metals only $V^{5+}$, $Nb^{5+}$, $Ta^{5+}$ and $U^{6+}$ show somewhat similar tendency. Comparatively little is known of these species and the extent to which they resemble the molybdenum and tungsten compounds.

General isopoly anions/salts have composition $[M_6O_{19}]^{n-}$, where M = Nb, Ta, Mo & W; n = valency or oxidation state of the metal. Cr forms polyanion of formula $Cr_2O_7^{2-}$. Some examples of isopoly acids & salts / anions are: (i) $[Mo_7O_{24}]^{6-}$: para or heptamolybdate (ii) $[Mo_8O_{26}]^{4-}$: octamolybdate (iii) $[H_2W_{12}O_{40}]^{6-}$: Metatungstate (iv) $[HW_6O_{21}]^{5-}$: paratungstate (v) $[Ta_6O_{18}]^{6-}$: Metatantalate (vi) $(NH_4)_4Mo_8O_{26}\cdot 5H_2O$: Ammonium octamolybdate. etc.

## ⇒ Heteropoly acids & salts?

When two or more different types of anions condense together, the poly acids formed are called heteropoly acids, and their salts are called heteropoly salts. Heteropoly acids and salts/anions contain one or two atoms of another element (Si, P, B etc.) in addition to Mo or W, oxygen and hydrogen. They form from the combination of different acids and anions. For example, molybdate ($MoO_4^{2-}$) or tungstate ($WO_4^{2-}$) combine with $SiO_3^{2-}$ (Silicate), $PO_4^{3-}$ (Phosphate), $CrO_4^{2-}$ (Chromate) etc. form heteropoly acids/anions $[SiW_{12}O_{40}]^{4-}$, $[Mo_{12}O_{36}(PO_4)]^{3-}$, $[CrMo_6O_{24}H_6]^{3-}$ etc. Some other examples of heteropoly acids & salts/anions are: (i) $Na_3[P^{+5}Mo_{12}O_{40}]$: sodium dodecamolybdophosphate. (ii) $H_3[P^{+5}Mo_{12}O_{40}]$: dodecamolybdophosphoric acid (iii) $Na_8[Ce^{+4}Mo_{12}O_{42}]$: sodium dodecamolybdocerate (IV). (iv) $K_8[Co_2^{+2}W_{12}O_{42}]$: dimeric potassium hexatungsto cobaltate (II) etc.

* All the polyanions contain octahedral $MoO_6$ or $WO_6$ groups so that the conversion of $MoO_4^{2-}$ or $WO_4^{2-}$ into polyanion (by lowering pH) requires an increase in coordination number.

e.g.; $[MoO_4]^{2-}$ (Molybdate anion) $\xrightarrow{pH=6}$ $[Mo_7O_{24}]^{6-}$ (Paramolybdate) $\xrightarrow{pH=1.5-2.9}$ $[Mo_8O_{26}]^{4-}$ (Octamolybdate) $\xrightarrow{pH<1}$ $MoO_3\cdot 2H_2O$ (Hydrated oxide)

$[WO_4]^{2-}$ (Tungstate anion) $\xrightarrow[\text{boil in } OH^-]{pH=6-7\,(fast)}$ $[HW_6O_{21}]^{5-}$ (Paratungstate-A) $\xrightarrow{pH=3.3}$ $[H_3W_6O_{21}]^{3-}$ (ψ-metatungstate) $\xrightarrow{pH<1}$ $WO_3\cdot 2H_2O$ (Hydrated oxide)

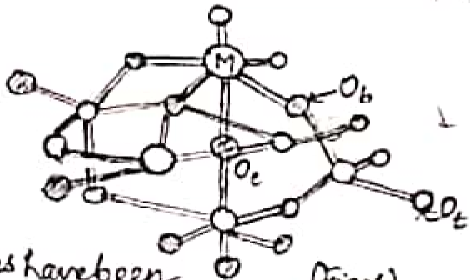
$[HW_6O_{21}]^{5-}$ (Paratungstate-A) $\overset{slow}{\rightleftharpoons}$ $[W_{12}O_{36}(OH)_{10}]^{10-}$ (paratungstate-B) $\xrightarrow{H^+}$ $[H_2W_{12}O_{40}]^{6-}$ (metatungstate) $\rightleftharpoons$ $[H_3W_6O_{21}]^{3-}$ (ψ-metatungstate)

⇒ **Structure of Iso- & Heteropoly anions:** (A) Isopoly anions structures have discussed in different Cases:

(a) The structure & bonding in $[M_6O_{19}]^{n-}$, isopoly anions of Nb, Ta, Mo & W have been investigated using density functional methods. The computational experimental agreements is good for the geometrical parameters of Mo & W species but less satisfactory for Nb & Ta Clusters. The electronic structure of the anions has been probed with molecular orbital Mulliken-Mayer, and bonding-energy approaches. The results have been indicated (Table-1) that M-O interactions are largely $M_d$-$O_p$ in character and that σ & π bonds link the metal Centres to terminal and bridging ($O_b$) oxygen atoms. Some M-$O_b$ bonds exhibit a $[M_4O_4]$ Closed loop structure, but this orbital-interaction mode has not been found to make a particularly outstanding contribution to the bonding stability of the molecules. Mayer indexes Correspond to (fractional) multiple, approx. single and low order character for terminal, bridging and internal bonds, respectively, and the valency analysis has yielded similar bonding capacities for the different oxygen atoms. A distribution of the negative change over all types of oxygen sites and metal charges considerably smaller than the formal oxidation states have been obtained from the Mulliken analysis. Minimal structural changes have been detected on reduction of molybdates & tungstates, in accordance with the general properties of the orbitals occupied by the added electron. The structure is shown in Fig. 1.

Table-1

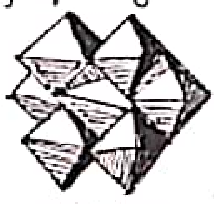
| Anion | $O_t$-M-$O_b$ | $O_b$-M-$O_b$ | $O_b$-M-$O_c$ | M-$O_b$-M |
|---|---|---|---|---|
| $[Nb_6O_{19}]^{8-}$ | 104 | 151 | 76 | 119 |
| $[Ta_6O_{19}]^{8-}$ | 104 | 152 | 76 | 118 |
| $[Mo_6O_{19}]^{2-}$ | 103 | 153 | 77 | 117 |
| $[W_6O_{19}]^{2-}$ | 104 | 153 | 76 | 117 |



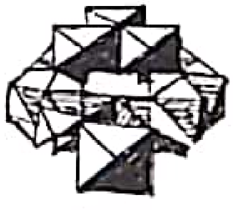
(Fig. 1)

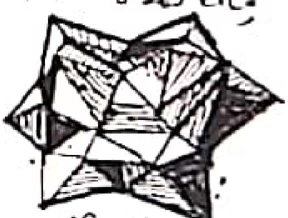
(b) The structure of isopoly molybdates & tungstate anions have been investigated by X-ray diffraction methods. In all the cases so far studied definitely by X-ray diffraction, the Mo & W atoms lie at the centre of octahedra of oxygen atoms (Fig. 2) and the structures are built up of these octahedra by means of shared corners and shared edges but not shared faces/planes. In the complete structures of the polyanions, $[Mo_7O_{24}]^{6-}$, $[Mo_8O_{26}]^{4-}$ etc. the octahedra are frequently distorted.


Fig. 2 ($MoO_6$ or $WO_6$)
[• : Mo or W atom
O : O-atom]


(Fig. 3)


(Fig. 4)


(Fig. 5)


(Fig. 6)

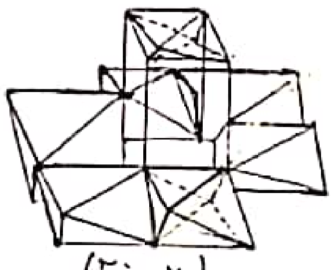
The isopoly anion structures definitely known from X-ray studies of their crystals are the paramolybdate ion, $[Mo_7O_{24}]^{6-}$ in $(NH_4)_6Mo_7O_{24}4H_2O$ and the octamolybdate ion, $[Mo_8O_{26}]^{4-}$ in $(NH_4)_4Mo_8O_{26}5H_2O$. Their structures are shown in fig. 3 & 4. The metatungstate ion, $[W_{12}O_{40}]^{8-}$ in $Na_6[H_2W_{12}O_{40}]\cdot 3H_2O$, has the same structure as the 12-tungsto and 12-molybdohetero anion (fig. 5). The paratungstate ion, $[W_{10}O_{41}]^{10-}$ or, $[W_{12}O_{36}(OH)_{10}]^{10-}$ in $Na_{10}[W_{12}O_{36}(OH)_{10}]\cdot 23H_2O$ is given in the fig. 6.

(B) **Structures of heteropoly anions:** (3) Heteropoly anions are formed by acidify the molybdate or tungstate ($MO_4^{2-}$) solution in the presence of phosphate ($PO_4^{3-}$), silicate ($SiO_3^{2-}$), borate ($BO_3^{3-}$) or metal ions. The second anion provides a centre round which the $MoO_6$ or $WO_6$ octahedra condense, by sharing oxygen atoms with other octahedra and with the central group/anion (e.g. $PO_4^{3-}$, $SiO_3^{2-}$). The ratio of $MoO_6$ or $WO_6$ octahedra to other central atom (P, Si, B..) is usually 12:1, 9:1 or 6:1. A well known example of heteropolyacid formation is test for $PO_4^{3-}$ ion. A phosphate salt is warmed with ammonium molybdate and $HNO_3$, a yellow precipitate of ammonium phosphomolybdate, $(NH_4)_3[PO_4 \cdot Mo_{12}O_{36}]$ is formed. The structures of a number of heteropoly anions have been established by x-ray diffraction method. In the 12 heteropoly acids, e.g; 12 phosphotungstic acid, twelve $WO_6$ octahedra surraund a $PO_4^{3-}$ tetrahedron. This ion may be considered as four groups of three $WO_6$ octahedra (fig.5). The heteropoly acids accommodate larger central atoms, which have a coordination number of 6.

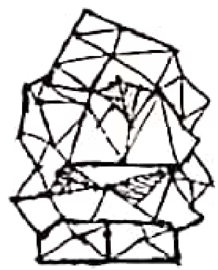
The structure of the $[TeMo_6O_{24}]^{6-}$ anion is shown in (fig.7). Six $MoO_6$ octahedra share edges in such a way as to create a ring with a central octahedron of oxygen atoms which is occupied by the Te (tellurium) atom. Although, the paramolybdate ion, $[Mo_7O_{24}]^{6-}$, might be formally regarded as a 6-molybdomolybdate ion, $[MoMo_6O_{24}]^{6-}$, it is structurally different in detail from the $[TeMo_6O_{24}]^{6-}$ ion.

The various dimeric 9-molybdo & 9-tungsto heteropolyanions of general formula/composition $[X_2Mo_{18}O_{62}]^{6-}$ have the same structure as the $[P_2W_{18}O_{62}]^{6-}$ ion (shown in fig. 8). This structure consists of two half units, each of which is derived from 12-molybdo heteropoly anion structure (fig.5) by removal of three $MoO_6$ anions.

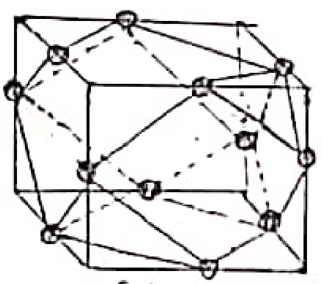
The 11-molybdo & 10-molybdo heteropoly anions may also be dimeric and consist of appropriate fragments of the 12-molybdo structure. As for the isopoly acids, there have been extensive studies of heteropoly anions in solutions. X-rays studies of solutions of $12WO_3 SiO_2 2H_2O$ have demostrated the ion $[SiW_{12}O_{40}]^{4-}$ with the structure shown in fig. 9. This structure is consistent with the crystal structure of the compound.



(Fig. 7)



(Fig. 8)



(Fig. 9)