

7. **Crooke's glass.** This is a special type of glass used for optical purposes and contains cerium oxide.

8. **Bottle glass.** It is ordinary soda-lime glass containing MgO to the extent of 3.5 per cent and $\text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3$ to the extent of 0.5 per cent.

9. **Ground glass.** It is prepared by grinding ordinary soda (soft) glass by emery and turpentine oil or by *sand blasting*.

10. **Safety glass.** It is used in making wind screens of automobiles, aeroplanes, railway trains, etc. It is prepared by placing a layer of *transparent plastic* (usually a sheet of *vinyl acetate resin*) between two layers of glass by means of a suitable adhesive. The three layers are joined together tightly by the action of heat and pressure.

This glass does not break easily under ordinary impact. This is the reason for the name "safety glass" or "unbreakable glass" given to it. However, it does break under heavy impact. But the particles of glass do not shatter because they are held by the plastic.

Thermoplastics. The main disadvantage of using glass is that it is brittle and fragile. In recent years, it has been replaced, for a variety of purposes, by *transparent plastics*. A plastic consists of highly polymerised substances. It softens on heating and can be given any shape just like glass and is, therefore, sometimes called *thermoplastic*. The interlinking of the molecules in the polymerised materials gives it hardness as well as insolubility.

SILICATES

Silicates occur in earth's crust in abundance in the form of *silicate minerals* and *aluminosilicate clays*. Sodium silicate, Na_2SiO_3 , is the only common silicate which is soluble in water. It is prepared by fusing sodium carbonate with silica (SiO_2) at 1500°C . Most of the silicates are insoluble in water. This is due to the great strength of the Si-O bond. This bond can be broken only on treatment with strong reagents like hydrofluoric acid.

The electronegativity of oxygen is 3.5 and that of silicon is 1.9. The electronegativity difference of 1.6 suggests that Si-O bond, though covalent, has an appreciable degree of ionic character.

All silicates comprise of $(\text{SiO}_4)^{4-}$ units which are formed by sp^3 hybridisation of Si orbitals. The outer electronic configuration of silicon atom in the excited state is $3s^1 3p_x^1 3p_y^1 3p_z^1$. Thus, it forms four bonds with oxygen atoms by utilising its sp^3 hybrid orbitals and yielding $(\text{SiO}_4)^{4-}$ units. The oxygen atoms pick up one electron each from some metal in order to complete their octets. As expected, $(\text{SiO}_4)^{4-}$ unit has a **tetrahedral structure**, as shown in Fig. 6. The plane circles represent oxygen atoms and the small dots represents the silicon atoms.

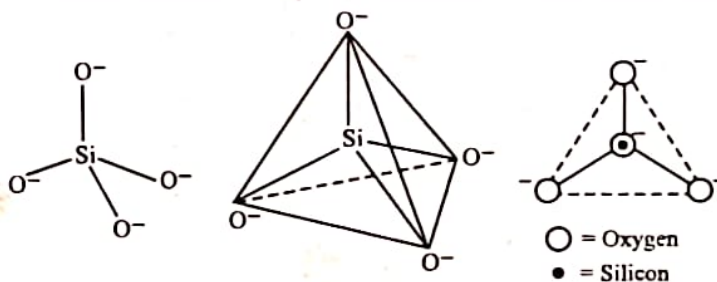


Fig. 6. Tetrahedral structure of $(\text{SiO}_4)^{4-}$ ion.

As already mentioned, all silicates contain the tetrahedral $(\text{SiO}_4)^{4-}$ units. They differ from one another only in the manner in which these units are linked together.

In some cases, several $(\text{SiO}_4)^{4-}$ tetrahedral units are bridged together through oxygen atoms of the units. The bridging oxygen atom is covalently bonded to the two Si atoms of the bridging $(\text{SiO}_4)^{4-}$ units. The number of oxygen atoms of an $(\text{SiO}_4)^{4-}$ unit which form bridges with other $(\text{SiO}_4)^{4-}$ units may be one, two, three or all the four. In this way, a number of complex silicates can be formed. The resulting silicate chains are negatively charged anions because any oxygen atom which is not a bridging

atom carries a unit negative charge. This negative charge is balanced by a metal cation. Thus, metal cations such as Li^+ , K^+ , Ca^{2+} , Al^{3+} are present in silicate minerals. These serve to hold the solid together by ionic attraction.

The structure of silicates has been understood recently with the development of X-ray diffraction techniques.

Different Types of Silicates

Depending upon the linkage of $(\text{SiO}_4)^{4-}$ tetrahedral units, the silicates may be classified into the following types.

1. **Ortho silicates.** These contain discrete $(\text{SiO}_4)^{4-}$ units. The common examples are *zircon* (ZrSiO_4), *willemitite* (Zn_2SiO_4), *phenacite* (Be_2SiO_4). Another important group of orthosilicates is the *garnets* having the general formula $[\text{M}_3^{\text{II}}\text{M}_2^{\text{III}}(\text{SiO}_4)_3]$, where M^{II} can be Ca^{2+} , Mg^{2+} or Fe^{2+} and M^{III} can be Al^{3+} , Fe^{3+} or Cr^{3+} .

2. **Pyrosilicates.** These contain disilicate anion, $(\text{Si}_2\text{O}_7)^{6-}$ units. The $(\text{Si}_2\text{O}_7)^{6-}$ units are formed by joining two tetrahedral units through one oxygen atom, as shown in Fig. 7.

It may be noted that any oxygen atom which does not form a bridge has to pick up an electron from some metal to complete its octet and thus acquire a negative charge. In the present case, there are 6 oxygen atoms which do not form bridges, as shown. Consequently, the Si_2O_7 unit is an anion carrying 6 negative charges and is written as $(\text{Si}_2\text{O}_7)^{6-}$.

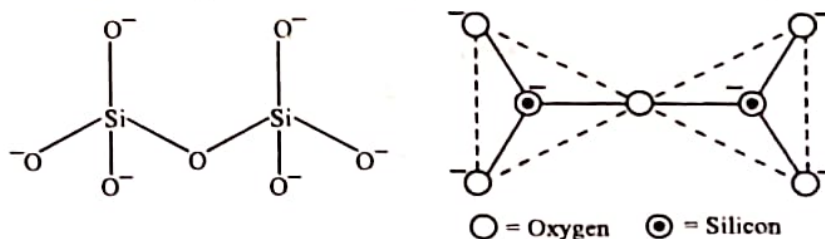


Fig. 7. Structure of $(\text{Si}_2\text{O}_7)^{6-}$ ion in pyrosilicates.

The metal atoms from which the electrons are picked up by the oxygen atoms are present in the silicate structure as cations. The number of cations is such that they balance the negative charge on the silicate anion. The most important pyrosilicate is of scandium known as *thortveitite* having the formula $\text{Sc}_2(\text{Si}_2\text{O}_7)$. The 6 negative charges on $(\text{Si}_2\text{O}_7)^{6-}$ anion are balanced by the same number of positive charges on the two Sc^{3+} ions. The other example of pyrosilicates is *hemimorphite* $[\text{Zn}_4(\text{OH})_2\text{Si}_2\text{O}_7]$.

3. **Chain Silicates.** If there are two bridging oxygens per silicon atom, i.e., there is sharing of two oxygen atoms by each SiO_4 tetrahedron, a simple chain structure, as shown in Fig. 8, results. The remaining two oxygens per silicon atom do not form bridges. The resulting silicate, therefore, is an anion carrying 2 negative charges per silicon atom. The structure given below, for example, contains 5 silicon atoms and, therefore, the silicate ion is an anion carrying 10 negative charges.

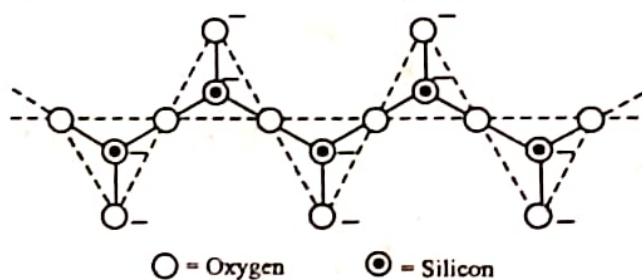


Fig. 8. Structure of chain silicates. The primary unit is $(\text{SiO}_3)^{2-}$.

It is evident from the above structure that there is a total of 3 oxygen atoms per silicon atom. Therefore, the chain silicates contain $(\text{SiO}_3)^{2-}$ as the primary units and the general formula of this type of silicates is $[\text{SiO}_3]^{2n-}$. These chains are found in minerals called *pyroxenes*. The common examples are *enstatite*, MgSiO_3 , *diopside*, $\text{CaMg}(\text{SiO}_3)_2$ and *spodumene*, $\text{LiAl}(\text{SiO}_3)_2$.

In certain minerals, double chain structures have been observed. These are formed by further

sharing of oxygen atoms by half the silicon atoms. The double chain structures (Fig. 9) have the basic unit $(\text{Si}_4\text{O}_{11})^{6-}$ and are represented by a class of minerals called *amphiboles*. Typical examples of this class are *tremolite*, $\text{Ca}_2\text{Mg}_5(\text{Si}_4\text{O}_{11})_2(\text{OH})_2$, *amosite*, $(\text{MgFe})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ and *crocidolite* $\text{Na}_2\text{Fe}_3^{\text{II}}\text{Fe}_2^{\text{III}}\text{Si}_5\text{O}_{22}(\text{OH})_2$.

4. **Cyclic Silicates.** These are formed by sharing of two oxygens per silicon atom resulting in the formation of a cyclic structure, as shown in Fig. 10. The primary unit in this case also is $(\text{SiO}_3)^{2-}$.

The cyclic ion, $(\text{Si}_3\text{O}_9)^{6-}$, shown in Fig. 10 (a), occurs in *wollastonite* ($\text{Ca}_2\text{Si}_3\text{O}_9$) and *bentonite* ($\text{BaTiSi}_3\text{O}_9$) while the cyclic ion $(\text{Si}_6\text{O}_{18})^{12-}$, shown in Fig. 10 (b), occurs in *beryl* ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$).

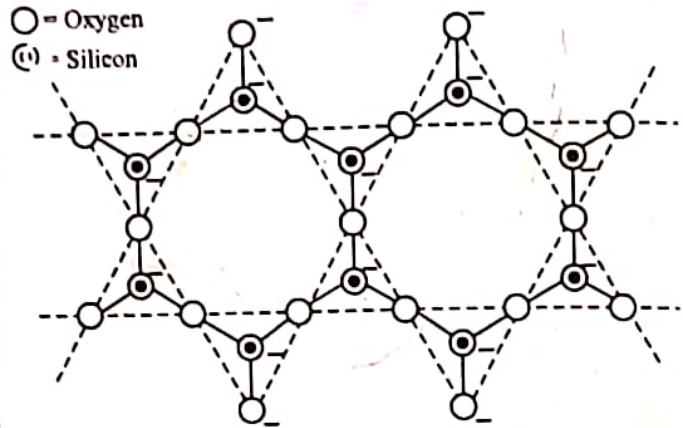


Fig. 9. Structure of double chain silicates. The basic unit is $(\text{Si}_4\text{O}_{11})^{6-}$.

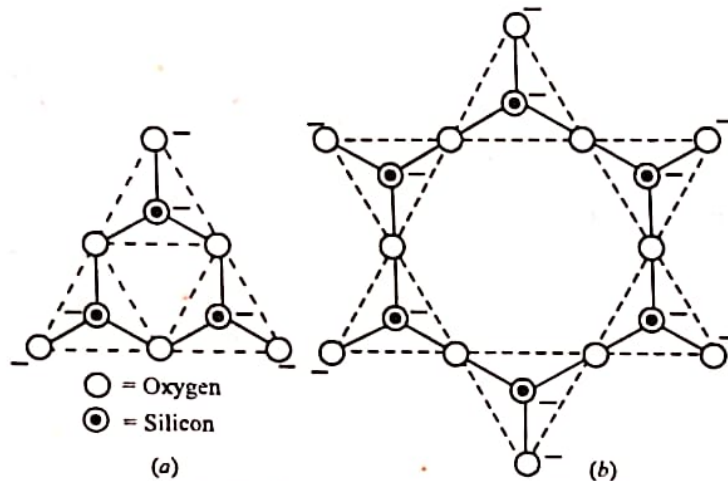


Fig. 10. Structure of cyclic silicates.

5. **Sheet Silicates.** These are formed by sharing of three bridging oxygens per silicon atom and result in the formation of infinite *two-dimensional sheets*. Each SiO_4 tetrahedron shares three corner oxygen atoms with other tetrahedra, as shown in Fig. 11. The oxygen atom shown around the silicon atom is the one that does not form the bridge and hence carries a negative charge. Actually, this oxygen lies below the plane of the paper. There is one negative charge per silicon atom in such structures. The negative charge on the sheets is neutralised by the positive charge of the 'binding' cations lying in between such sheets. Such substances cleave readily into thin sheets as in micas which are silicates or aluminosilicates of this type.

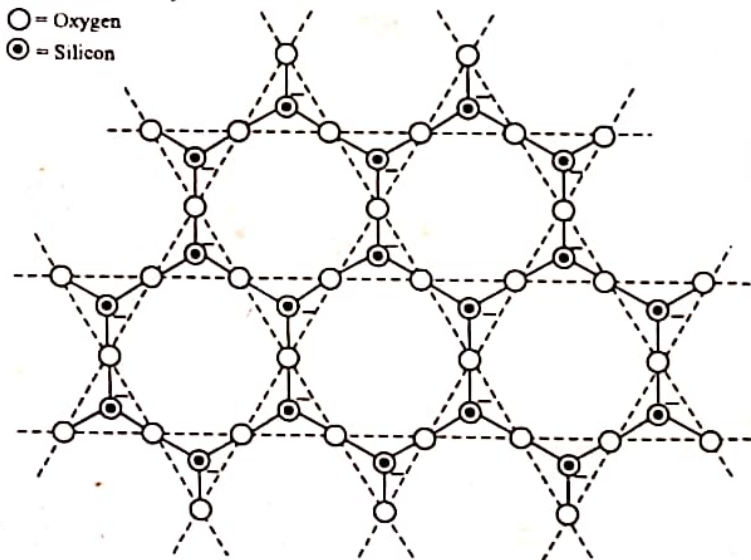


Fig. 11. Two-dimensional structure of sheet silicates.

Some common examples of sheet silicate are *kaolinite*, $\text{Al}(\text{OH})_4\text{SiO}_5$ and *talc*, $\text{Mg}_3(\text{OH})_3\text{Si}_4\text{O}_{16}$.

Sometimes in these silicates, silicon atoms are partially replaced by aluminium atoms. Examples are : *biotite* $\text{K}(\text{MgFe})_2(\text{OH})_2(\text{AlSi}_3\text{O}_{10})$ and *moscovite*, $\text{KAl}_2(\text{OH})_2(\text{AlSi}_3\text{O}_{10})$

6. **Three-Dimensional Silicates.** Lastly, there is the extreme case in which four oxygens per silicon atom are bridging atoms. In other words, all the four oxygens of the SiO_4 tetrahedron act as bridge atoms. This results in a *three-dimensional* structure. Since all the oxygens are the bridge atoms, the silicate is neutral. There are no metal cations in this structure. This silicate structure will have the general formula $(\text{SiO}_2)_n$, e.g., *quartz*, *tridymite*, *crystalite*.

However, sometimes, $(\text{SiO}_4)^{4-}$ unit is replaced by $(\text{AlO}_4)^{5-}$ unit in tetrahedral positions in the SiO_2 lattice. In such cases, the presence of an additional monovalent cation is necessary to maintain electrical neutrality. Such replacement results in minerals like *feldspar* (KAlSi_3O_8), *zeolite* ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$) etc.

When feldspar is acted upon by carbon dioxide and water of the atmosphere at room temperature it slowly forms potassium carbonate and the clay, *kaolin* [$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$]. The potassium carbonate, being soluble, becomes available in soil as plant food while kaolin is carried away by water streams to lower levels and is used in making pottery.

Replacement of $(\text{SiO}_4)^{4-}$ units with $(\text{AlO}_4)^{5-}$ units. Structure of aluminosilicates. The radius ratio $r_{\text{Al}^{3+}}/r_{\text{O}^{2-}}$ is about 0.43. This is close to the limiting ratio for coordination numbers 4 to 6. Accordingly, Al^{3+} ion would either fit into the space lattice of tetrahedral $(\text{AlO}_4)^{5-}$ ion or an octahedral $(\text{AlO}_6)^{9-}$ ion. The $(\text{AlO}_4)^{5-}$ ion has roughly the same size as the $(\text{SiO}_4)^{4-}$ ion and can thus replace the latter from silicates provided the electrical neutrality is maintained by the adjustment of positive charge elsewhere in the structure.

It is to be kept in mind that Al^{3+} ion can either be a part of $(\text{AlO}_4)^{5-}$ unit (in which its coordination number would always remain 4) or it can be present as cation used for binding the chains and sheets in the silicate structure by neutralising the negative charge of the chains or sheets. In the latter role, the coordination number of Al^{3+} cation is generally 6. Such a binding Al^{3+} cation can be replaced by other cations provided the principle of electroneutrality is maintained.

Some of the important aluminosilicates are described below.

Micas. Micas are *amphiboles* which are made up of *sheets* of $(\text{SiO}_4)^{4-}$ tetrahedra in which some of the $(\text{SiO}_4)^{4-}$ tetrahedra are replaced by $(\text{AlO}_4)^{5-}$ tetrahedra. In *moscovite*, the sheet composition is $(\text{Si}_3\text{AlO}_{10})^{5-}$. Two such sheets with their tetrahedral vertices inward are linked by the binding Al^{3+} ions whose octahedral coordination is completed by OH^- ions. The double sheets which have, in consequence, the composition $[\text{Al}_3\text{Si}_3\text{O}_{10}(\text{OH})_2]^-$ are stacked one upon another with sufficient number of K^+ ions between two such double sheets to maintain electrical neutrality. The cleavage of mica is due to the weakness along these layers of K^+ ions. A wide variety of replacement is possible. Thus, the binding Al^{3+} ions may be replaced by Mg^{2+} ions and the 'sandwiched' K^+ ions by Na^+ ions. Micas are tough, elastic and transparent.

They are chemically inert and thermally stable. They also have a high dielectric constant. Due to these characteristic properties micas are used in furnace windows and electrical appliances. The powdered mica is used as a filler for rubbers, plastics and in insulation boards.

Clay. Clays are produced by weathering and decomposition of igneous rocks. They are generally composed of very fine particles. China clay, i.e., *kaoline*, with formula $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, more correctly written as $\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5$, has a sheet structure in which the sheets are held together by the OH bridges.

When mixed with water, clay becomes plastic-soft and mouldable. The water of plasticity gets eliminated on heating at 100°C when the clay becomes rigid and brittle. Further heating removes structural water of crystallisation and results in oxidation of carbonaceous matter of the clay. At about 900°C , *multite*, $\text{Al}_6\text{Si}_2\text{O}_{13}$, begins to be formed. This has a *glassy appearance*.

Clay is widely used in making chinaware, fire bricks and many other useful materials.

Fuller's Earth. It is *montmorillonite* in which the principal exchangeable ion is Ca^{2+} . It has a high adsorptive power and pronounced cation exchange properties.

It is widely used as an adsorbent and a cation-exchanger.

Talc. Talc with the formula $\text{Mg}_3(\text{OH})_2\text{Si}_4\text{O}_{10}$ consists of electrically neutral sheets and there are no 'sandwich' type of cations between the sheets. It is soft and smooth and is used as a dry lubricant. It is chemically inert and is used in ceramics, paper manufacture and cosmetics.

Zeolites. Zeolites are aluminosilicates having a three-dimensional network with the general formula $\text{M}_{x/n}^{\text{n}+}(\text{Al}_x\text{Si}_y\text{O}_{2x+2y})^{x-} \cdot z\text{H}_2\text{O}$. They are characterised by their open structure which enables them to take up water and other small molecules in their interstices reversibly but not the complex or bigger molecules such as methane and ethane. In zeolites, the cations move freely through the open pore structure and can be exchanged reversibly with other cations. Sodium ions in zeolites, for instance, can be exchanged for calcium ions in hard waters. This explains the use of these materials in water softening operations.

Zeolites as Molecular Sieves. Some crystalline aluminosilicates having open structure with apertures or holes of molecular dimensions can trap small molecules having size smaller than the size of the apertures and can thus act as 'molecular sieves' for separating such molecules from a mixture of molecules having different sizes. Since the apertures (holes) defined by the cage-like structures of aluminosilicates are highly regular and are of molecular dimensions, these 'molecular sieves' can trap molecules with greater selectivity than do solid adsorbents with large surface areas such as activated charcoal. One such class of compounds is zeolites which can trap cations in their tunnels or interstices of their open structure. Apart from acting as molecular sieves, they can also act as ion exchangers.

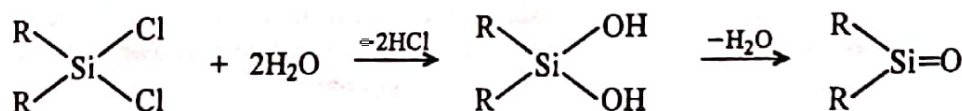
Zeolites are also used in **shape-selective heterogeneous catalysis**. For example, the zeolite ZSM-5 is used as a catalyst in the manufacture of ortho xylene selectively. Meta and para xylenes are not produced in the presence of this catalyst because the catalytic process is controlled by the shape (and size) of the tunnels existing in the structure of this zeolite which permits only the synthesis of ortho xylene.

Silicones

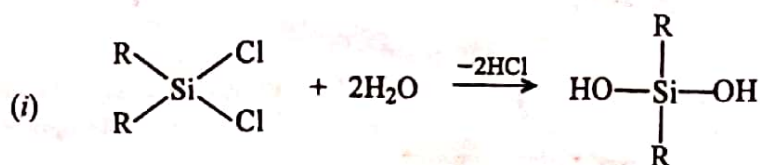
Silicon tetrachloride, SiCl_4 , when fully hydrolysed, gives silica, SiO_2 , which has a stable three-dimensional structure, as mentioned earlier.



However, when an alkyl substituted chlorosilane (which can be obtained from SiCl_4 by Grignard reaction) is subjected to similar hydrolysis, we do not get the alkyl silicon compound according to the following expected reaction :



On the contrary, **long chain polymers**, called **silicones**, are obtained in this process. For example, in the case of dialkyl dichlorosilane, the reaction proceeds as follows :



TRISILYLAMINE, N(SiH₃)₃

Trisilylamine is prepared by reacting monochlorosilane with ammonia.



Trisilylamine is a trigonal planar compound with N orbitals in sp^2 hybrid state, unlike trimethyl or triethylamine which is pyramidal and has N orbitals in sp^3 hybrid state. There is considerable $d\pi$ overlap between the p orbital (containing the lone pair) of N atom and the vacant $d\pi$ orbitals of Si atoms. The trigonal planar structure of $\text{N}(\text{SiH}_3)_3$ is, thus, strengthened due to $p\pi - d\pi$ bonding.

Since the lone pairs of electrons of N atom are engaged in $p\pi - p\pi$ bonding between N and Si, they are no longer available for donation to Lewis acids. Trisilylamine, therefore, behaves as a much weaker base compared to trimethylamine or triethylamine. Hence, trisilylamine does not form adducts with BH_3 even at low temperature whereas trimethylamine or triethylamine does so readily. Due to the same reason, $\text{N}(\text{SiH}_3)_3$ acts as a much weaker ligand compared to $\text{N}(\text{CH}_3)_3$ and $\text{N}(\text{C}_2\text{H}_5)_3$.

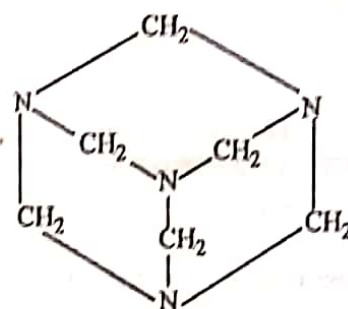
HEXAMETHYLENE TETRAMINE, HEXAMINE, UROTROPINE, (CH₂)₆N₄

Hexamethylene tetramine is prepared by reacting formaldehyde with concentrated ammonia solution.

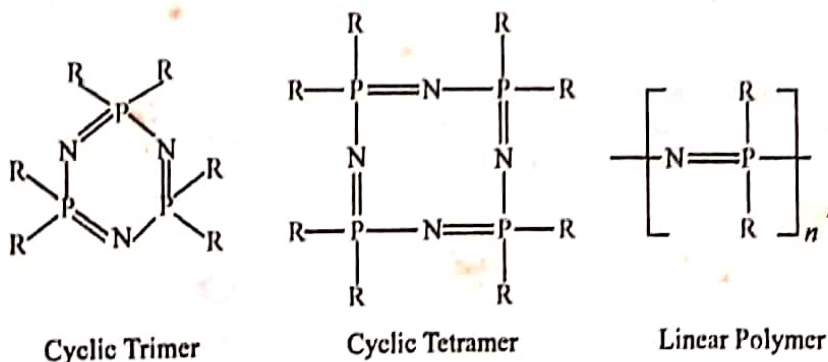


Hexamine has a complicated ring structure. The bonding (but not the exact orientations of the rings) in the compound is roughly as shown.

It is a white crystalline compound soluble in water. It is basic in nature and is used for adjusting the pH of aqueous solutions during pH-sensitive complexometric titrations. Hexamine is used for the treatment of gout and rheumatism.

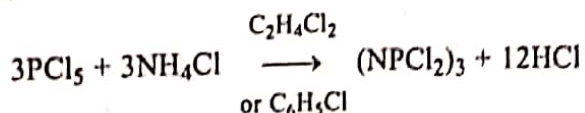
**PHOSPHAZINES, (NPR₂)_n**

Phosphazines are cyclic or chain polymers which contain $\text{-N}=\underset{\text{R}}{\text{P}}\text{-R}$ as the repeating unit. Common phosphazines exist as cyclic trimers, cyclic tetramers and also as linear polymers, as shown below.



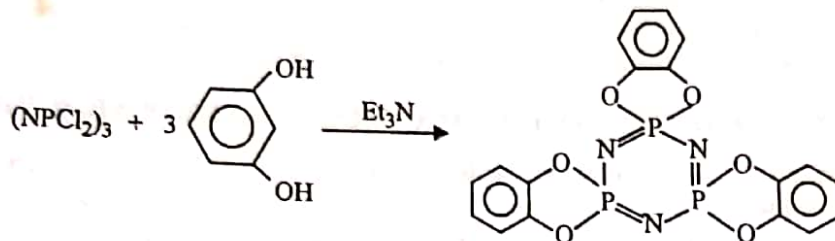
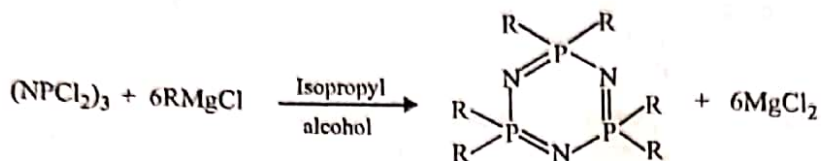
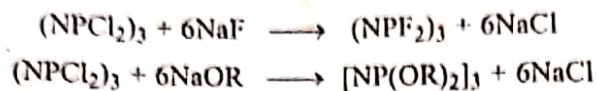
Chlorophosphazines. Two important chlorophosphazines are described here.

Hexachlorocyclotriphosphazine, (N₃PCl₂)₃. It is prepared by the reaction of PCl_5 with NH_4Cl in the presence of $\text{C}_2\text{H}_4\text{Cl}_2$ or $\text{C}_6\text{H}_5\text{Cl}$ under controlled conditions.



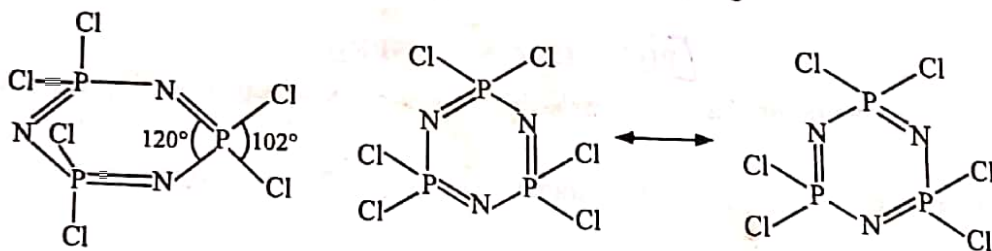
The above reaction produces a mixture of $(\text{N}_3\text{PCl}_2)_3$ and $(\text{N}_4\text{PCl}_2)_4$. Any tetramer produced along with the trimer can be easily separated since the trimer sublimes in vacuum at 50°C as a white crystalline solid whereas the tetramer does not do so under these conditions.

Hexachlorocyclotriphosphazine is the key material for the synthesis of a number of linear polymers. Thus,

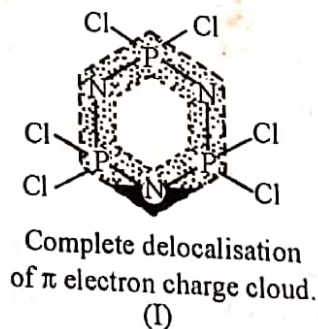


The mechanism of replacement of Cl by other nucleophiles is not well understood. However, it appears to involve S_{N}^2 attack on P atom.

Structure of Hexachlorocyclotriphosphazine. The trimer is known to be a planar six-membered ring (structure I) in which the bond angles are consistent with sp^2 hybridisation of N orbitals and an approximate sp^3 hybridisation of P orbitals of the ring. Resonance structures II and III can also be drawn, as in the case of benzene, indicating aromaticity in the ring.



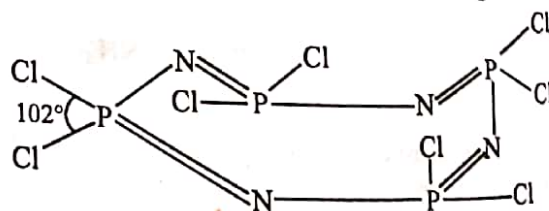
But unlike benzene which involves extensive $p\pi-p\pi$ bonding, phosphazine involves $p\pi-d\pi$ bonding. The extent of π bonding in phosphazine appears to be quite appreciable as the N-P distance (1.6 Å) is considerably shorter than the normal N-P single bond distance (1.75 - 1.8 Å). The main question about the π bonding is whether the π electron charge cloud is delocalised on all the ring atoms, as shown in (I) or there are more intensely localised islands within the NPN segments, as shown in (II).



This question remains unanswered. However, considering the difference in the electronegativities of N and P and the location of a lone pair of electrons on each N atom of the ring, structure (II) appears to be more probable than structure (I).

Structure of Octachlorocyclotetraphosphazine. $(\text{NPCl}_2)_4$ has a 'tub-like' structure, as shown.

This structure is, evidently, non-planar.



Phosphazines of high molar masses have been discussed in details in Chapter 34 on 'Inorganic Polymers'.

Another polymeric nitrogen compound of phosphorus is $P_4(NR)_6$, the structure of this compound is analogous to P_4O_6 in which the bridging oxygens are replaced by bridging NR groups. Another polymeric nitrogen compound is $P(N(CH_3)_2)_3$ which is analogous to $P(OR)_3$ in which OR groups are replaced by $N(CH_3)_2$ groups.

Organometallic Compounds of Group 15 Elements

These have been discussed in details in Chapter 33 on Organometallic Compounds.

FERTILIZERS

Essential Nutrients for Plants. Plants require phosphorus, potassium, nitrogen, sulphur, calcium, iron and magnesium, besides traces of a few other elements such as copper, boron, zinc, manganese, molybdenum and cobalt for their growth and health. These elements are generally present in the soil to more or less extent in the form of minerals or otherwise. However, after a few years of continuous cropping, the soil becomes poorer and poorer in these materials and there is need to put back what has been taken out from the soil by successive crops. If the soil is not replenished by what it has lost, in time, it would become less productive and, in extreme cases, may become even infertile. In order to keep up soil fertility and to get good yields of various crops, it is necessary to add materials containing nitrogen, phosphorus and potassium in the form of *manures* which may be natural or artificial. The artificial manures are called **chemical fertilizers**. Nitrogen, phosphorus and potassium are regarded as essential plant nutrients.

Functions of Essential Nutrients

1. **Nitrogen.** Nitrogen is highly essential for rapid growth of plants and hence it improves the yields of crops. It also raises protein content of the crops and thus adds to their food value.

2. **Phosphorus.** Phosphates are highly valuable fertilizers. Experiments have shown that phosphates promote early growth as well as early maturity of plants. The addition of phosphates also increases resistance of plants to frost and disease and helps in formation of high yielding seeds.

3. **Potassium.** Potassium develops a healthy root system which helps the plants to get regular supply of nutrients from the soil. As a result, we get a healthy plant which develops sufficient resistance towards various diseases. It also helps in the formation of albuminoids and carbohydrates in the various plants.

Potassium compounds are generally used in mixed fertilizers containing nitrogen and phosphorus. Such materials are commonly referred to as **N.P.K. fertilizers**.

Types of Manures. There are two types of manures :

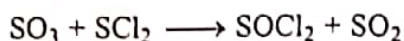
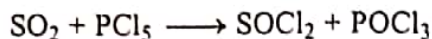
1. *Natural* and
2. *Artificial Manures (i.e., Chemical Fertilizers)*

Natural Manures. Natural manures generally added to soil include animal dung, blood, bones, horns, hair stock, leather waste, fish scrap, night soil, animal excreta, guano, sewage, sludge, etc. Manures prepared out of vegetable growth such as leaves, barks, seeds, ashes, etc., are also included in this category. Leguminous plants grown in the soil are also ploughed back into the soil for replenishing nitrogen content of the soil.

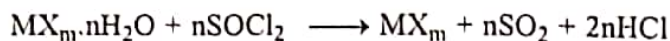
Artificial Manures or Fertilizers. Artificial manures are generally called **fertilizers**. These are chemical compounds containing nitrogen, phosphorus or potassium.

Every compound of nitrogen, phosphorus or potassium *cannot* be used as a fertilizer. A good fertilizer must be *soluble in water* and nitrogen, phosphorus or potassium contained in it should be in such a form that it can *readily be made available* to the plants. The common **nitrogenous fertilizers** are ammonium sulphate, ammonium nitrate, urea and nitrates of potassium and calcium. The most important **phosphatic manure** is calcium superphosphate. The most widely used compound of **potassium** is

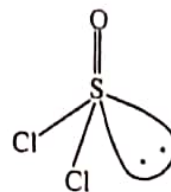
PCl_5 or by reacting SO_3 with SCl_2 .



Thionyl chloride vigorously reacts with water and is used for drying some inorganic halides.

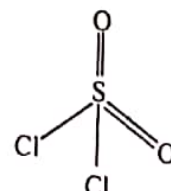


It is widely used as a nonaqueous solvent. S in SOCl_2 is sp^3 hybridised. It forms one S = O bond and two S - Cl bonds and has a lone pair, as shown.



Amongst the known sulphuryl dihalides, viz., SO_2F_2 , SO_2FCl , SO_2Cl_2 and SO_2FBr , the most important is sulphuryl dichloride which is prepared by reacting SO_2 with Cl_2 using activated charcoal as catalyst. S in SO_2Cl_2 is sp^3 hybridised and forms two S = O and two S - Cl bonds, as shown.

It is a useful chlorinating agent. It is also used for introducing - SO_2Cl group in organic compounds.



NITRIDES OF SULPHUR

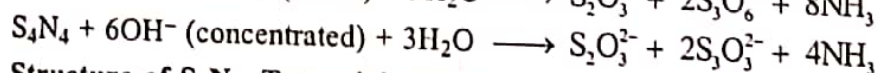
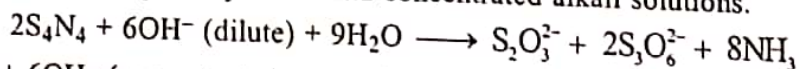
Tetrasulphur Tetranitride, S_4N_4 . This is the most important nitride of sulphur which can be prepared by any of the following reactions :

- $$16\text{NH}_3 + 6\text{S}_2\text{Cl}_2 \xrightarrow[\text{CCl}_4]{50^\circ\text{C}} \text{S}_4\text{N}_4 + 8\text{S} + 12\text{NH}_4\text{Cl}$$
- $$4\text{NH}_4\text{Cl} + 6\text{S}_2\text{Cl}_2 \xrightarrow{160^\circ\text{C}} \text{S}_4\text{N}_4 + 8\text{S} + 16\text{HCl}$$
- $$10\text{S} + 4\text{NH}_3 \longrightarrow \text{S}_4\text{N}_4 + 6\text{H}_2\text{S}$$

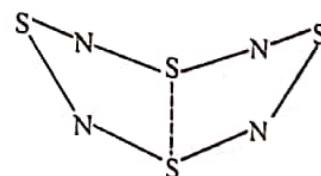
$$\text{H}_2\text{S} + 2\text{NH}_3 \longrightarrow (\text{NH}_4)_2\text{S}$$

S_4N_4 is an orange compound with a melting point of 178°C . It explodes to give S and N_2 when struck or heated. It forms adducts $\text{S}_4\text{N}_4 \cdot \text{BF}_3$ and $\text{S}_4\text{N}_4 \cdot \text{SbCl}_5$ with BF_3 and SbCl_5 , respectively.

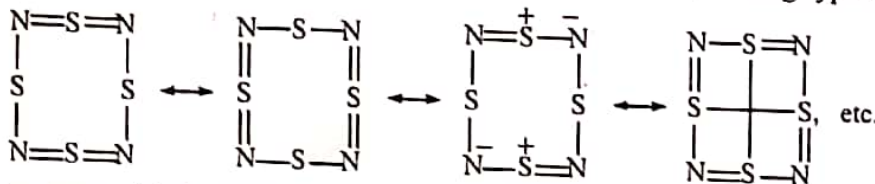
S_4N_4 gets hydrolysed by dilute and concentrated alkali solutions.



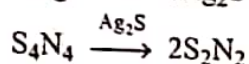
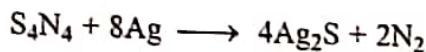
Structure of S_4N_4 . Tetrasulphur tetra-nitride has a cradle-like skeletal structure as shown.



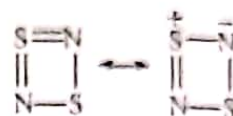
All the S-N bond distances are equal (i.e., 1.60 \AA) which are shorter than the calculated S - N single bond distance of 1.75 \AA . This indicates some double bond character in S - N bonds. The trans annular S - S distances are shorter than twice the van der Waals radius for S atom indicating that there may be a weak association between the trans annular S atoms. The actual structure of S_4N_4 appears to be a resonance hybrid of a number of the following types of structures :



Disulphur Dinitride, S_2N_2 . This compound is prepared by pumping vapours of S_4N_4 through silver wool.



S_2N_2 is a colourless crystalline compound which explodes on heating. On slow heating, it polymerises to $(SN)_x$. It has a square planar cyclic structure, as shown:

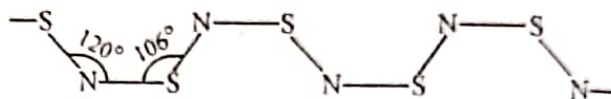


Polythiazyl, $(SN)_x$. It is prepared by heating pure S_4N_4 at $70^\circ C$ and condensing the vapour produced on glass surface at $10-30^\circ C$. It is also produced by slow heating of S_2N_2 , as mentioned above.

Polythiazyl shows optical anisotropy and electrical anisotropy. It is superconducting at $0.26 K$. $(SN)_x$ is a rare example of a superconducting compound obtained from a non-metal.

Its structure contains a zig-zag chain having SNS angle of 120° and NSN angle of 106° , as shown

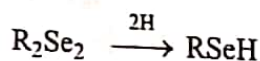
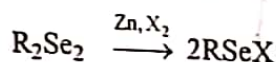
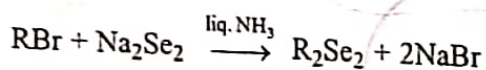
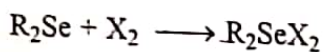
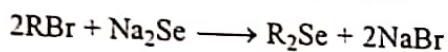
Other sulphur-nitrogen compounds known are S_4N_2 , $S_{11}N_2$ and S_5N_6 . A number of cationic and anionic species such as S_2N^+ , $S_3N_2^+$, $S_4N_3^+$, $S_4N_4^{2+}$, $S_4N_5^-$, $S_5N_5^-$, $S_4N_5^-$, $S_3N_3^-$, etc., are also known.



ORGANOMETALLIC COMPOUNDS

Amongst the elements of Group 16, only selenium and tellurium are known to form organometallic compounds. A detailed discussion of these compounds is beyond the scope of the book. Only a brief description is given below.

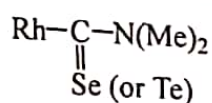
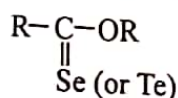
Organometallic Compounds of Selenium and Tellurium. The common organoselenium compounds are $RSeX$, R_2SeX_2 , R_2Se and $RSeH$. These are prepared by the following reactions:



(R is alkyl or aryl group ; X is the halogen)

Selenium and tellurium also form compounds which are analogous to carbonyl compounds and the amides.

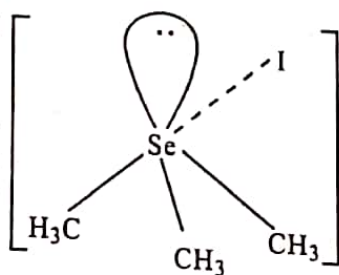
The structures of derivatives of seleno and tellurocarbonyls and amides are given below:



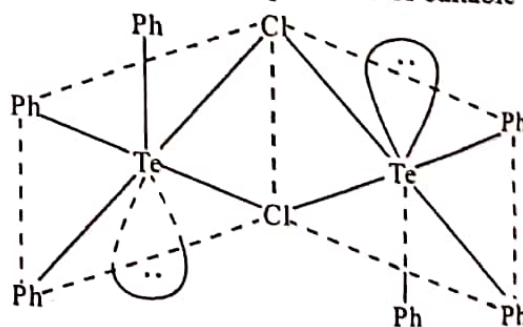
Telluro derivatives are more reactive than the corresponding seleno derivatives.

Both Se and Te have a tendency to increase their coordination numbers in the presence of suitable ions. Thus, the compound

$[Se(CH_3)_3]^+I^-$ has I^- ion associated with Se as shown.



Similarly, the compound, commonly written as $[Ph_3Te]^+Cl^-$, is a dimer with the structure as shown.



Isopoly Acids and Heteropoly Acids

34.1 INTRODUCTION TO POLY ACIDS

(The weak acids formed from the amphoteric metals of groups VB and VIB of the periodic classification are characterised by the ease with which they condense to form anions containing several molecules of the acid anhydride. These are known as polyacids. For example, the formulae of molybdates in alkaline solutions are represented by R_2MoO_4 whereas in acid solution the formation of more complex anions takes place which are represented by $R_2O \cdot nMoO_3$ aq. where $n = 1, 2, 3, 4, 8, 10$ and 16 depending upon the pH of solutions.)

34.2 TYPES OF POLY ACIDS

There are two types of poly acids :

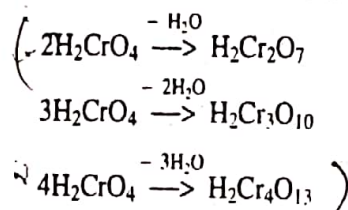
(a) **Isopoly acids**—(These are the poly acids containing only one type of acid anhydrides.) The polychromic acids, $H_2O \cdot yCrO_3$ ($y > 1$) may be cited examples of this class.

(b) **Heteropoly acids**— These are the poly acids containing more than a single type of anhydrides. It means that they contain different series of anhydrides. For example, polymolybdophosphoric acids, $mH_2O \cdot P_2O_5 \cdot yMoO_3$, $y = 12$ or 24 , are most common heteropolyacids.

34.3 ISOPOLY ACIDS

(These acids are formed if the oxygen atoms in any oxyacid are replaced by radicals of the same acid.) For example, the introduction of one or more CrO_4^{2-} radicals in H_2CrO_4 acid gives rise to various isopoly acids like H_2CrO_3 , CrO_4 , H_2CrO_2 , $2CrO_4$, H_2CrO , $3CrO_4$.

(Isopolyacids may also be defined in another way in which these acids are derived from a single acid by the elimination of water from two or more molecules of the same acid.)



The important isopolyacids are isopolymolybdates, isopolytungstates and isopolyvanadates. These acids are discussed one by one.

1. **Isopolymolybdates**— These are of the following types :

(a) **Dimolybdates**— Their composition is $R_2O \cdot 2MoO_3 \cdot nH_2O$. They are formed when the pH of a solution containing sodium molybdate is adjusted to 6. On crystallisation, dimolybdates crystallise out. These crystals are not pure but form a mixture of normal molybdates and paramolybdates.

(b) **Paramolybdates**—(These are the most stable polymolybdates in solution. These are obtained by crystallising a solution containing sodium molybdate at a pH 4.5.) The formula of paramolybdate ion is $Mo_7O_{24}^{6-}$. The structure of this ion has been confirmed by X-ray measurements of the cell dimensions and density of sodium paramolybdate. It still remains to be shown that the anion $(Mo_7O_{24})^{6-}$ exists as such in the solution.

(c) **Trimolybdates**— Their composition is $R_2O \cdot 3MoO_3 \cdot nH_2O$. They are prepared by saturating molybdic oxide with alkali or by crystallising paramolybdates in the presence of acetic acid.

The various trimolybdates of general formula $R_2O \cdot 3MoO_3 \cdot nH_2O$ appear to contain acid paramolyb-

date ions or other ions with seven or more molybdenum atoms.

(d) **Tetramolybdates or metamolybdates**—Their composition is $R_2O \cdot 4MoO_3 \cdot nH_2O$. These can be prepared by treating concentrated solution of alkali molybdates with 1.5 moles of hydrochloric acid. These acids are derived from the ion $[Mo_8O_{26}]^{4-}$.

(e) **Octamolybdates**— Their general composition is $R_2O \cdot 8MoO_3 \cdot nH_2O$. These are prepared by treating concentrated solutions of alkali molybdates with 1.75 moles of hydrochloric acid per mole of normal molybdate.

These molybdates are derived from the ion $[Mo_8O_{26}]^{4-}$.

From the above types of isopolymolybdates it is evident that these are obtained at various pH of alkali molybdates. Their formation can be explained as follows :

- The simple molybdate ion, MoO_4^{2-} is stable at high pH. Thus, sodium molybdate and ammonium molybdate are quite stable compounds.
- At pH 4 to 5, $Mo_7O_{24}^{6-}$ which is either called the heptamolybdate or paramolybdate ion (Fig. 34.1 (a)) is in equilibrium with the simple molybdate ion, MoO_4^{2-} .
- In more acidic solutions octamolybdate ion, $Mo_8O_{26}^{4-}$ is produced (Fig. 34.1 (b)). It is likely that higher polymers are formed. They have not been studied because they do not attain equilibria due to low rates of reaction. The structures depicted in Fig. 34.1 have been confirmed by X-Ray crystallographic studies.

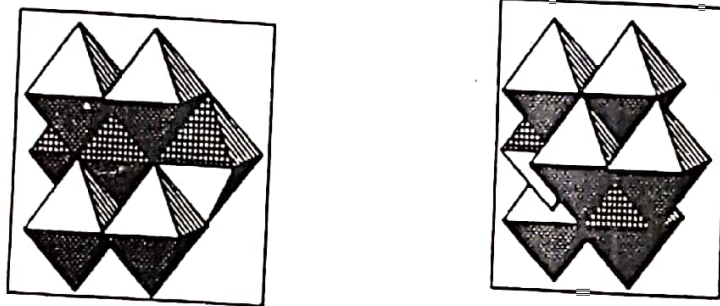
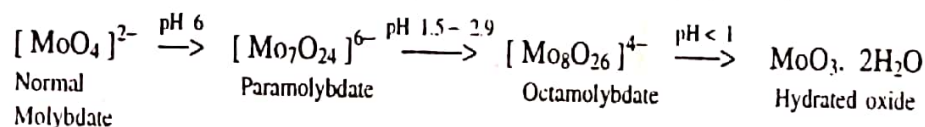


Fig. 34.1 (a). Paramolybdate ion, $[Mo_7O_{24}]^{6-}$.

(b) Octamolybdate ion, $[Mo_8O_{26}]^{4-}$.

The relationship between the various stable species is summarized as follows :



2. Isopoly tungstates— Like molybdates numerous tungstates of the metals have been described differing in their $R_2O : WO_3$ ratio. Of these, however, three types of isopolytungstates are of great importance.

(a) **Normal tungstates**— The general formula of normal tungstates is $M_m(WO_4)_n$ where M is a metal. Examples of this type of tungstates are Na_2WO_4 and $Na_2W_2O_7$.

Na_2WO_4 is prepared by dissolving tungsten trioxide in sodium hydroxide solution and crystallising the solution. The normal tungstates of metals other than sodium may be prepared from the sodium salt by double decomposition. Sodium tungstate is water soluble whereas tungstates other than alkali metals and magnesium are insoluble.

$Na_2W_2O_7$ is prepared by fusing the oxide in the correct proportions. It is important to note that ion $[W_2O_7]^{2-}$ does not exist in solution.

(b) **Paratungstates**— An example of paratungstates is $Na_5[HW_6O_{21}] \cdot 13\frac{1}{2}H_2O$ which is prepared by adding hydrochloric acid to boiling solution of Na_2WO_4 . Sodium paratungstate separates out on cooling.

All paratungstates (including ammonium paratungstates) except alkali metals and magnesium are not soluble in water.

(c) **Metatungstates**— An interesting example is $K_6(H_2W_{12}O_{40}) \cdot 18H_2O$. This can be prepared by boiling solution of the normal tungstates with tungstic acid. If the solution is acidified, soluble metatungstic acid is formed which may be extracted with ether and form large colourless crystals. The metatungstates are isomorphous with the phosphotungstates and the silicotungstates.

Alkali metatungstates are more soluble than the normal tungstates or the paratungstates.

When an alkaline solution containing the $[WO_4]^{2-}$ ion is acidified, various isopolytungstates are obtained at different pH. This can be seen from the following discussion :

(i) On addition of mineral acid, the process of polymerization commences with polymers being built up from WO_6 groups which are octahedral in shape. pH is one of the factors which determines the nature of the polymer that is produced. An interesting feature of this process is that the history of the sample also determines the nature of the polymer. This means that some kind of building up takes place very slowly but steadily among WO_4^{2-} ions. Thus when an aged sample of sodium tungstate is acidified, it does not undergo conversion into higher polymeric forms very easily.

(ii) An important species is the dodecatungstate ion, $W_{12}O_{42}^{12-}$ which was earlier known as paratungstate Z. It is also known as 12- isopolytungstate. Fig 34.2. (a) gives the structure of this ion.

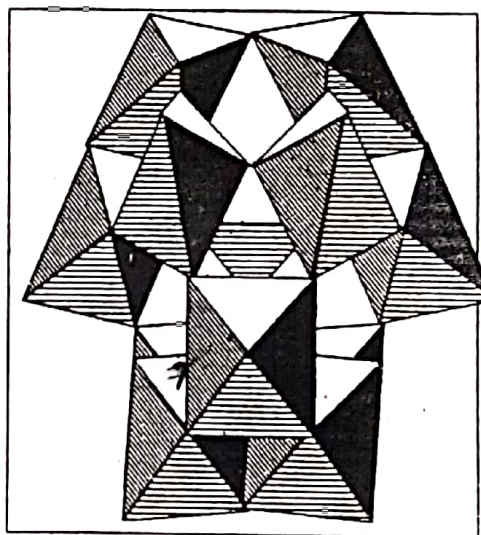
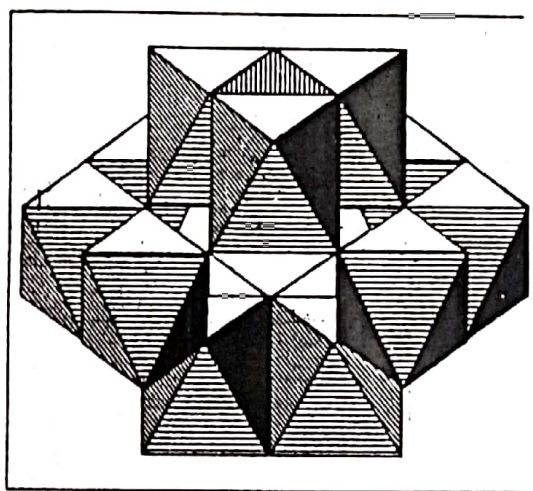


Fig. 34.2. Dodecatungstate isopolyanion, $W_{12}O_{42}^{12-}$.

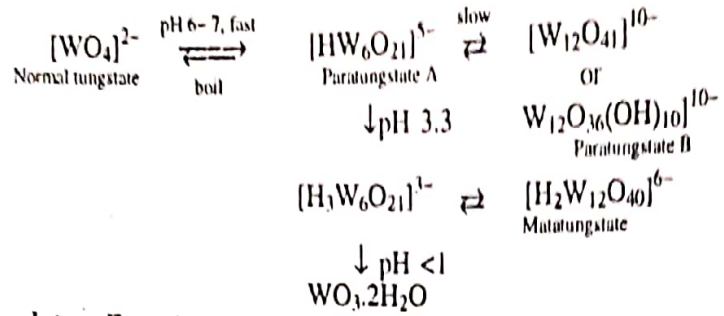
(b) Dodecatungstate isopolyanion $[H_2(W_{12}O_{40})]^{6-}$.

(iii) When the solution is highly acidic, it is possible to crystallize from the solution a second dodecatungstate ion, $[H_2(W_{12}O_{40})]^{6-}$ which was earlier designated as the metatungstate ion. The structure of this ion is depicted in Fig. 34.2 (b). In this structure also there are WO_6 octahedra present as in Fig. 34.2 (a). Here the arrangement of the octahedra is more symmetrical, so that there is a cavity in the centre of the ion.

(iv) Other isopolytungstate anions like $HW_6O_{21}^{5-}$ called paratungstate A, exist in solution but their exact nature is unknown. It should be remembered that the labels A, B and Z are purely arbitrary and were given earlier to distinguish these species.

(v) If the pH of a solution containing $[WO_4]^{2-}$ is adjusted at one, tungsten oxide (WO_3) is precipitated.

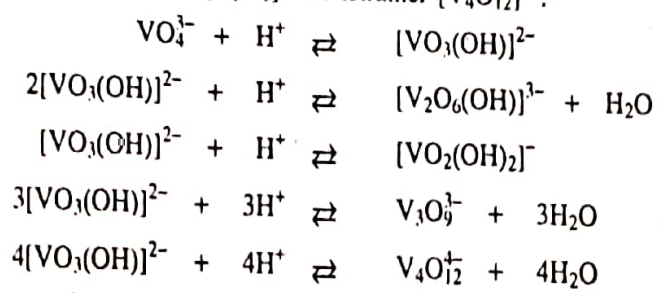
The relationships between the various stable species are summarized below :



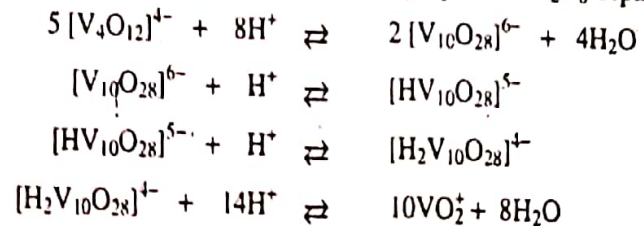
3. Isopoly vanadates- For a long time, it was known that there existed vanadates of alkali metal and of silver with the ratio R₂O : V₂O₅ = 3 : 1, 2 : 1 and 1 : 1 analogous to the ortho, pyro and metaphosphates.

A solution of sodium vanadate is colourless. When an acid is added to this solution, a brownish red colour is developed which immediately converts into a yellow orange colour. As the pH of this acidified solution takes enough time to attain a steady value, it means that the reaction proceeds by way of some unstable intermediates. Actually, salts with various ratios R₂O : V₂O₅ have been recovered from this acidified solution. This reaction has been studied by a large number of methods including Raman spectra but the nature of the species has been still doubtful. However, the available data are in agreement to some extent, with the following explanation.

The solution of sodium vanadate has high pH and it only contains VO₄³⁻ ions. When the pH of the solution is changed from 13 to 8, condensation to [V₂O₆(OH)]³⁻ occurs. When the pH is further reduced to 7.2, metavanadate ion is formed. The name metavanadate is derived from the fact that the same ion is produced if a crystalline metavanadate with the M₂O : V₂O₅ ratio of unity is dissolved in water. The metavanadate ion in solution is a trimer [V₃O₉]³⁻ or tetramer [V₄O₁₂]⁴⁻.



If the pH of the solution ion is reduced still further, decavanadate is formed at pH 6. This ion, then, gets protonated in turn to [HV₁₀O₂₈]⁵⁻ and [H₂V₁₀O₂₈]⁴⁻ if the pH is decreased to about 3.5. However, when the pH becomes 2, [VO₂]⁺ ions are formed and finally hydrated V₂O₆ separate out.



When various efforts were employed to isolate vanadates from solutions containing isopolyvanadates at various pH, crystalline vanadates were obtained but the stoichiometries did not give any information about the nature of species in solution. However, the yellow orange solutions deposit orange crystals which are evidently the hydrates of the orange species [Na₃V₁₀O₂₈ · 16H₂O] in solution. If the solution of orange crystals is warmed, the sparingly soluble vanadates like Na₃V₅O₁₄ and NaV₃O₉ separate out. Similarly, crystalline salts like the NaVO₃ and Na₂V₄O₇ · 18 H₂O can be isolated.

34.3 ISOPOLYANIONS OF NIOBIUM AND TANTALUM

Niobate and tantalate isopolyanions can be obtained by fusing the oxides in an excess of alkali

hydroxide or carbonate and dissolving the melts in water. The solutions are stable only at higher pH. precipitation occurs below pH ~ 7 for niobates and ~ 10 for tantalates. The only species that appear to be present in solution are the $[H_xM_6O_{19}]^{(8-x)-}$ ions ($x = 0, 1, \text{ or } 2$) despite frequent claims for others. The structure of the $M_6O_{19}^{8-}$ ions, found in crystals and believed to persist in solutions, is shown in Fig. 34.3.

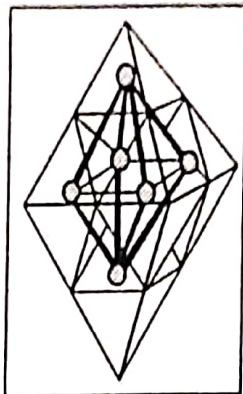


Fig. 34.3. The structure of the $M_6O_{19}^{8-}$ ions ($M = Nb \text{ or } Ta$). The central oxygen atom is shared by all six octahedra.

34.5 STRUCTURE OF ISOPOLYACIDS

Relatively little work has been done on the structures of isopolymolybdates and isopolytungstates. In both these types, there occurs the union of MoO_6 or WO_6 octahedra. These combine by sharing of corners or edges, but not of faces. For example, the $[Mo_7O_{24}]^{6-}$ anion in ammonium para-molybdate possesses the structure similar to Fig. 34.4.

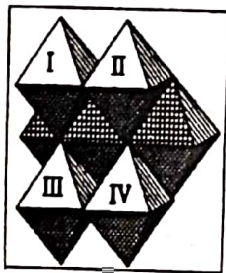


Fig. 34.4.

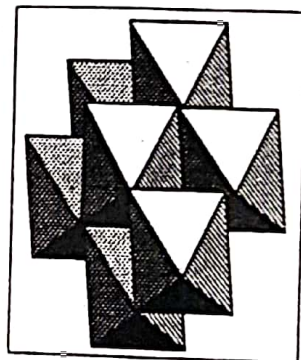


Fig. 34.5.

In Fig. 34.4, it is evident that the octahedra are so placed in $[Mo_7O_{24}]^{6-}$ that they share their edges with their nearest neighbours. However, the octamolybdate ion possesses a structure as shown in Fig. 34.5. This structure is more complicated in which six of the MoO_6 octahedra are arranged in the same way as in $Mo_7O_{24}^{6-}$ and two remaining MoO_6 octahedra are arranged in a different manner. The similar type of structure is found in the paratungstate and metatungstate ions.

The structure of $[V_{10}O_{28}]^{6-}$ in two decavandates $Ca_3V_{10}O_{28} \cdot 16H_2O$ and $K_2Zn_2V_{10}O_{28} \cdot 16H_2O$ has been determined by X-Ray studies. The structure of this anion consists of ten VO_6 octahedra which are joined by sharing edges.

34.6 HETEROPOLY ACIDS

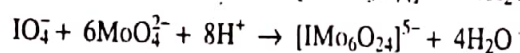
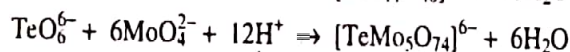
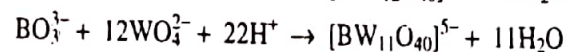
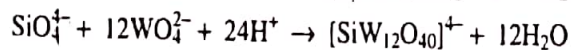
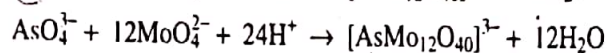
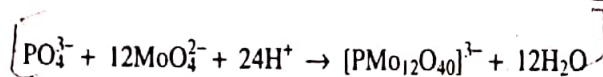
These acids are obtained by the union of varying number of acid anhydride molecules (generally WO_3, MoO_3, V_2O_5) with some other acid which could furnish the central atom of central ion of the

whole complex anion.

The ability to act as the central atom in heteropolyacids is found amongst the acid forming elements as well as among the metals of the transition series (Table 34.1).

Group I	H, Cu
Group II	Be
Group III	B, Al, Ce
Group IV	C, Si, Ge, Sn, Ti, Zr, Th
Group V	N, P, As, Sb, V, Nb, Ta
Group VI	Cr, Mo, W, U, S, Se, Te
Group VII	Mn, I
Group VIII	Fe, Co, Ni, Rh, Os, Ir, Pt

Preparation— Heteropolyacids are formed by the union of varying number of acid anhydride molecules most commonly WO_3 , MoO_3 or V_2O_5 , with some acid which must furnish the central atom of central ion of whole complex anion. Then, the salts of polyacids are obtained by acidifying this solution to an appropriate hydrogen ion concentration. A variety of different types of heteropolyanions may, therefore, be formed by taking different ratios of acid anhydride molecules and such acids which furnish central atom of central ion. For example heteropolymolybdates and tungstates are produced when alkaline solution of normal molybdates or tungstates are acidified in the presence of PO_4^{3-} , AsO_4^{3-} , SiO_4^{4-} , BO_3^{3-} , IO_4^- and TeO_6^{6-} ions.



The heteropolyacids are generally extracted from aqueous solutions by ethers and esters. Purification of these materials is usually done by crystallisation from water or organic solvents. Whenever heteropolyacids are prepared, certain precautions should be kept in mind which are :

- (i) Exact quantities of acid anhydride molecules and the acid which furnish central atom of central ion must be taken.
- (ii) Exact pH must be maintained.
- (iii) Equilibrium has to be established which is indicated by the fact that pH remains constant throughout the reaction.
- (iv) Most of the heteropolyacids have to be prepared at room temperature because at high temperature evaporation and concentration cause hydrolysis and change the pH of the solution.

The preparation of heteropolyacids belonging to the unsaturated series is very difficult. However, these compounds are obtained by the decomposition of co-ordinated compounds by hydrolytic reaction with OH^- ions.

Table 34.2, gives the list of principal known species of heteropolymolybdates. The heteropolytungstates are similar to heteropolymolybdates in their structures but no reliable information is available about the heteropolyvanadates.

Number of atoms	Principal hetero atoms	Typical formulae	Comment
1 : 12	Series A : P(V), As(V), Si(IV) Ge(IV), Ti(IV), Zr(IV) Series B : Ce(IV), Th(IV), P(V)	$[X^{n+} Mo_{12}O_{40}]^{(8-n)-}$ $[X^{n+} Mo_{12}O_{42}]^{(12-n)-}$	possibly dimeric possibly dimeric
1 : 11	As(V), Ge(IV)	$[X^{n+} Mo_{11}O_{39}]^{(12-n)-}$	
1 : 10	P(V), As(V), Pt(IV)	$[X^{n+} Mo_{10}O_x]^{(2x-60-n)-}$	
1 : 9	Mn(IV), Ni(IV)	$[X^{n+} Mo_9O_{32}]^{(10-n)-}$	
1 : 6	Te(VI), I(VII), Co(III), Al(III), Cr(III), Fe(III), Rh(III)	$[X^{n+} Mo_6O_{24}]^{(12-n)-}$	
2 : 8	P(V), As(V)	$[X_2^{n+} Mo_{18}O_{62}]^{(16-n)-}$	
2 : 17	P(V), As(V)	$[X_2^{n+} Mo_{17}O_x]^{(2x-102-2n)-}$	
1m : m	Ni(II), Co(II), Mn(II), Cu(II)	$[X^{n+} Mo_6O_x]^{n, (2x-36-n)-}$	

From Table 34.2, it follows that there are two types of 12- polyacids, i.e.,

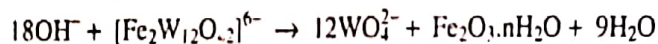
(a) 12 Polyacids type A. This type of heteropolyacids is formed by P(V), As(V), Si(IV), Ge(IV), Ti(IV), Cr(IV) and its general formula is $[X^{n+} Mo_{12}O_{40}]^{(8-n)-}$.

(b) Polyacids types B. This type of heteropolyacids is formed by Ce(IV), Th(IV) and Sn(IV). Its general formula is $[X^{n+} Mo_{12}O_{42}]^{(12-n)-}$.

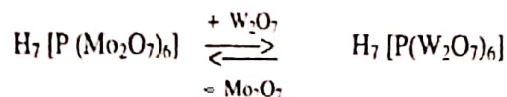
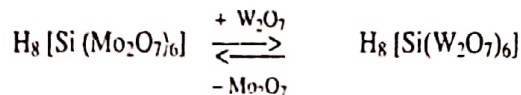
Properties of Heteropolyacids and its Salts

1. In general, heteropolyacids are soluble in water and ether. Heteropoly molybdates and tungstates of small alkali metal ions are water soluble whereas large metal ions are insoluble in water. For example, heteropolyacids of Pb^{2+} , Ba^{2+} , Cs^+ are insoluble in water.

2. Heteropolyacids are generally attacked by hydroxyl ions. These are completely decomposed by strong alkalis.



3. Heteropolyacids exhibit isomorphism. In these compounds, the co-ordinating radicals Mo_2O_7 could replace W_2O_7 or vice versa without bringing any change in the crystalline form. In some cases, the shape of the crystal is not changed provided the basicity of the acid is maintained same. Examples, showing isomorphism, are given below :



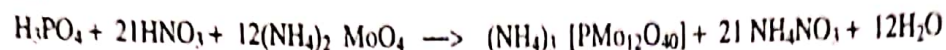
4. The heteropolyacids exhibit very high basicity but the maximum permitted basicity is never reached.

5. These acids form insoluble precipitates with many complex organic compounds such as albumin and various alkaloids.

Heteropoly Acids of Molybdenum

If a molybdate like sodium molybdate is made to react with an acid in the presence of phosphate, silicate and metal ions, heteropoly anions are produced.

(1) 12-molybdo heteropoly acids (Series A)– The phosphomolybdate test for the phosphate anion in qualitative analysis is an example of heteropoly anion formation. In this test a solution containing phosphate is treated with an excess of ammonium molybdate solution and the resulting mixture is strongly acidified with concentrated nitric acid and warmed when a canary yellow ammonium phosphomolybdate is precipitated.



Similarly, a yellow precipitate of ammonium molybdo-arsenate, $(\text{NH}_4)_3[\text{AsMo}_{12}\text{O}_{40}]$ is obtained. These anions $(\text{PMo}_{12}\text{O}_{40})^{3-}$ and $(\text{AsMo}_{12}\text{O}_{40})^{3-}$ are known as 12-molybdoheteropoly anions and they have the general formula, $[\text{X}^{n+}\text{Mo}_{12}\text{O}_{40}]^{(8-n)-}$.

Structure– The structure of such anions is shown in Fig. 34.6. The cavity which is the centre of the anion is surrounded by a tetrahedron of four oxygen atoms. This cavity is sufficiently big to contain a relatively small atom such as P^{5+} (0.52 Å), As^{5+} (0.60), Si^{4+} (0.54 Å), Ge^{4+} (0.67 Å), Ti^{4+} (0.74 Å) or Zr^{4+} (0.86 Å). Nearly 35 – 40 atoms form heteropoly acids. In Fig. 34.6 (a), the structure of 12-molybdophosphate and 12-tungstophosphate is given.

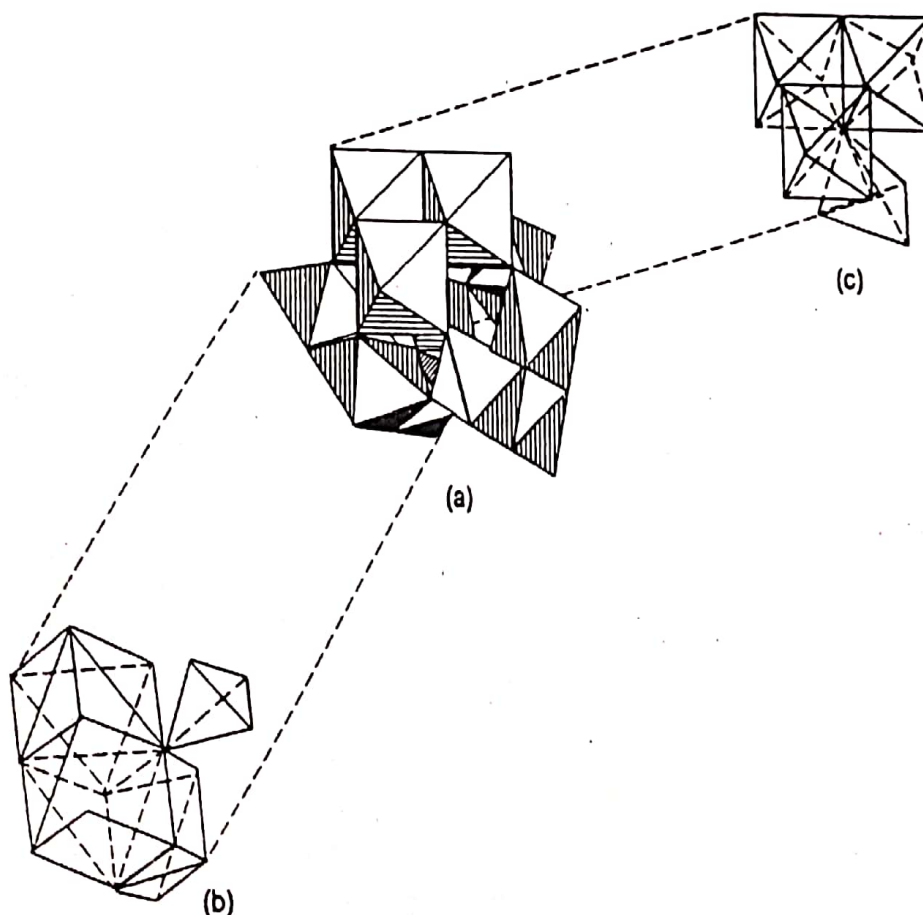


Fig. 34.6 (a). Structure of 12-molybdophosphate or 12-tungstophosphate. (b) and (c) show structure (a) severed in such a way to show the tetrahedral cavity attached apically to three octahedra.

The MoO_6 octahedra share their apices with neighbouring octahedra. This gives a tetrahedral cavity in the centre which accommodates a small atom like phosphorus or arsenic.

(2) **12-molybdoheteropoly acids (Series B)**— In this type the heteroatom is larger in size, e.g. Ce^{4+} (1.28 Å) and Th^{4+} (1.35 Å). The structure of $(\text{NH}_4)_2\text{H}_6\text{CeMo}_{12}\text{O}_{42}$ is shown in Fig. 34.7. In this structure there is a distinctive feature which is unique. This feature is, that there are pairs of MoO_6 octahedra that share faces to form MoO_9 groups. These MoO_9 groups coordinate around the cerium atom. We have said earlier that in the polyacid structures, octahedra share generally edges or apices and rarely faces.

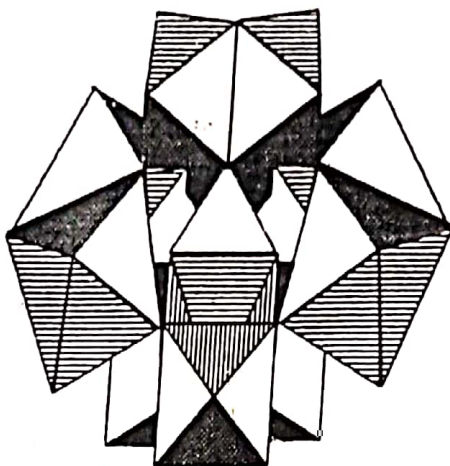


Fig. 34.7. Structure of $(\text{CeMo}_{12}\text{O}_{42})^{8-}$ anion.

(3) **6-molybdoheteropoly acids**— These acids are produced with heteroatoms Te^{6+} (0.70 Å), I^{7+} (0.67 Å) and Rh^{3+} (0.80 Å). In these structures the heteroatom is coordinated in an octahedral cavity which is formed by a ring of six MoO_6 octahedra which are joined at the edges. Fig. 34.8 gives the structure of the 6-molybdotellurate anion, $[\text{TeMo}_6\text{O}_{24}]^{6-}$.

If the position of the heteroatom in Fig. 34.8 is taken up by a MoO_6 octahedron, we get another type of polyanion which is the heptamolybdate. In this anion a MoO_6 octahedron is surrounded by six

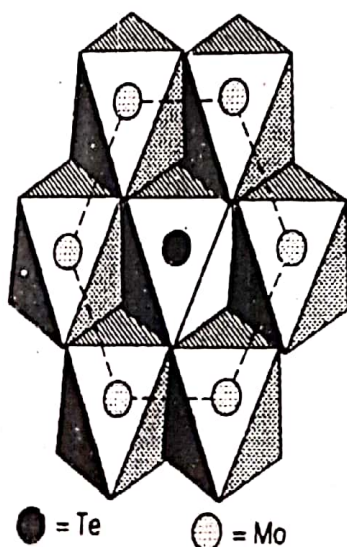


Fig. 34.8. Structure of 6-molybdotellurate anion.

MoO_6 octahedra. However, the structure of the heptamolybdate is not isomorphous with the 6-molybdate species.

In the 6-heteropoly acids (Fig. 34.8), the heteroatom is surrounded by a *planar* ring as shown in Fig. 34.9 (a). In the heptamolybdate the seventh MoO_6 octahedron—which is occupying the position of the hetero atom, is surrounded by a *puckered* ring of atoms Fig. 34.9 (b).



Fig. 34.9 (a). Planar ring of Mo atoms around heteroatom (6-heteropoly acids)
(b) Puckered ring of Mo atoms around the 7th Mo atom in $[\text{Mo}_7\text{O}_{24}]^{6-}$.

Just as complex isopoly acids are produced by changing the pH, it is possible to identify a sequence of a simple discrete heteropoly species giving rise to complex species on progressive acidification. The reverse situation is obtained when the pH is gradually raised. For example, if $\text{Na}_2\text{SiO}_3 - (\text{NH}_4)_2\text{MoO}_4$ solution is progressively acidified, we get 1-2-, 6- and 12- silicomolybdate ions being formed in turn. If the pH is gradually decreased, the highly condensed heteropoly anions break down into smaller species. These changes can be followed by analytical techniques like paper chromatography and pH titration.

Heteropoly Acids of Tungsten

In general the heteropoly acids of tungsten are similar to those of molybdenum.

(1) **12-tungstoheteropoly acids (Series A)**— These acids have the general formula $[\text{X}^{n+} \text{W}_{12}\text{O}_{40}]^{-(8-n)}$. The heteropoly anions are formed if a tungstate solution is acidified in the presence of phosphate, silicate or metal ions. The second anion provides a centre around which the WO_6 octahedra condense by sharing oxygen atoms with other neighbouring octahedra and with phosphate, silicate or borate ions which are in the centre. It may be mentioned here that the first study of the structure of a heteropoly acid was made by Keggin on a crystalline hydrate of 12-phosphotungstic acid having the formula $\text{P}_2\text{O}_5 \cdot 24\text{WO}_3 \cdot 9\text{H}_2\text{O}$. Here twelve WO_6 octahedra surround a PO_4^{3-} tetrahedron (Fig. 34.10). In the figure we can see a tetrahedron (PO_4^{3-}) which is surrounded by four groups of three octahedra (WO_6).

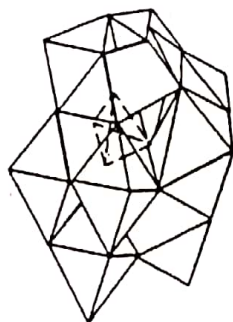


Fig. 34.10. Structure of 12-tungstoheteropoly acid, $\text{H}_3(\text{PO}_4\text{W}_{12}\text{O}_{36})$.

(2) **6-tungstoheteropoly acids**— These acids can accommodate larger central atoms inside their structure so that the coordination number is six. The structure of these acids is comparable to the 6-molybdate heteropoly acids (Fig. 34.8).

(3) **9-tungsto heteropoly acids**— Very little is known about the structures of these acids. In Fig. 34.11 the structure of the $(\text{P}_{12}\text{W}_{18}\text{O}_{62})^{6-}$ anion is shown in which there are two PO_4^{3-} tetrahedra enclosed with in WO_6 octahedra.

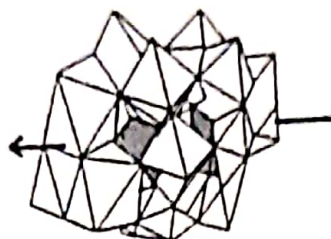


Fig. 34.11. Structure of $(P_2W_{18}O_{62})^{6-}$ anion

Complex heteropoly acids— Acids of greater complexity have been prepared in which the heteroatom is not completely surrounded by MoO_6 or WO_6 octahedra. In such cases, the fourth oxygen of the PO_4^{3-} tetrahedron is not coordinated to any octahedra but is attached to an organic molecule.

Heteropoly Anions of Niobium and Tantalum

Heteropoly niobates and tantalates are not well known, but a few of the former have been prepared and characterized.

34.7 STRUCTURE OF HETEROPOLYACIDS

The various theories have been put forward to explain the structure of heteropolyacids. These have been described below :

I. Miolati, Copaux and Rosenheim's Theory— This theory was based on the Werner's co-ordination theory. They considered the heteropolyacids as *co-ordination compounds* in which the acid *anhydride molecules* (WO_3 , MoO_3 and V_2O_5) were considered to be ligands whereas the acid with which these combined to form heteropolyacids furnished the central atom or central ion. It was also postulated that the polyacids formed from an element X (of valency n) as central atom was derived from a hypothetical form $H_{12-n}[XO_6]$ of the parent acid. The oxygen atoms of this complex may be substituted partially or wholly by acid radicals like MoO_4 or by pyroacid radicals Mo_2O_7 . In this way, two limiting series may be obtained : viz, $H_{12-n}[X(MoO_4)_6]$ and $H_{12-n}[X(Mo_2O_7)_6]$. The first is known as 6-polyacids whereas the latter 12-polyacids.

The 6-polyacids are formed when X is I, Te, Fe, Cr, Al, Co, Ni, Rh, Cu, Mn and H ; 1-polyacids by P, As, Si, Ti, Ge, Sn, Zr, Th, Ce, B and H ; Table 34.3 illustrates the formation of some typical heteropolyacids.

Central atom	Valency	Parent acid	Heteropolyacids
I	7	$H_5[IO_6]$	$H_5[I(MoO_4)_6]$
Te	6	$H_6[TeO_6]$	$H_6[Te(MoO_4)_6]$
P	5	$H_7[PO_6]$	$H_7[P(Mo_2O_7)_6]$
Si	4	$H_8[SiO_6]$	$H_8[Si(Mo_2O_7)_6]$
B	3	$H_9[BO_6]$	$H_9[B(W_2O_7)_6]$

This theory was quite successful in offering an explanation of the structure of many polyacids but there was no direct proof of correctness of many of the formulae.

Limitations— Although this theory explained the structures of various heteropolyacids, yet there are certain facts which could not be explained. Some of the main defects are :

- (i) According to this theory, the heteropolyacids must exhibit very high basicities although the maximum permitted basicity is very low. It means that salts of heteropolyacids can be fitted