CHEM

UNIT - II

Chemical Bonding

Lattice Energy (U)

The stability of an ionic crystal is measured in terms of lattice energy

Defintion : by product of [illegible]

1Q Lattice energy of an ionic crystal is defined as the energy released when one mole of gaseous cations and one mole of gaseous anions separated from each other by an infinite distance are brought to their equilibrium distances to form one mole of the ionic crystal. 1Q

Explanation :

The formation of a mole of an ionic solid $A^+B^-_{(s)}$ from its constituent gaseous ions $A^+_{(g)}$ and $B^-_{(g)}$ may be represented as follows

$$\underset{\text{one mole}}{A^+_{(g)}} + \underset{\text{one mole}}{B^-_{(g)}} \longrightarrow \underset{\text{one mole}}{A^+B^-_{(s)}} + \text{Energy released}$$

The energy released is called lattic energy.

Another definition :

Lattic energy is the energy required to move the ions of one mole of the ionic crystal which are at an equilibrium distance from each other, to an infinite distance.

Explanation :

The lattic energy of an ionic cystal is the energy required to convert one mole of an ionic crystal $A^+B^-_{(s)}$ into gaseous A^+ and B^- i.e.,

$$\underset{\text{One mole}}{A^+B^-_{(s)}} + \text{Energy absorbed} \longrightarrow A^+_{(g)} + B^-_{(g)}$$

The energy absorbed is numerically equal to the lattice energy.

Lattice energy is represented by - U. The negative sign indicates that the formation of an ionic solid from its gaseous cations and anions is an *exothermic process.* ie., in the formation of the ionic solid, there is a release of energy and hence the energy of the system is lowered.

This is because of the decrease in energy, the ionic solid is more stable than the individual ions of which the ionic solid is made of. Greater the value of lattice energy of an ionic solid, greater will be the stability of the ionic solid.

Example :

The melting points of NaCl, KCl and CsCl decrease in the same order. This is because their lattice energies decrease in the same order (184, 163 and 151 k.cals/mole respecively)

Applications of lattice energy :

1. With the help of lattice energy we can estimate electron affinities, proton affinities and heats of formation.
2. It is applied in the discussion of the special properties of fluorine in relation to other halogens.
3. It is applied to account for the stabilities of metal chlorides, hydrides, poly halides, peroxides and super oxides.
4. It is applied in the derivation of crystal field stabisation energies.
5. It is applied to account for the occurrence of high oxidation states of metals in their fluorides and low oxidation states in their iodides.

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Born - Haber Cycle

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The direct determination of the lattice energy of an ionic crystal has been carried out for only a few compounds. In many cases it is not possible to measure the lattice energy directly. Born and Haber devised a cyclic process to find the lattice energy.

Born - Haber cycle can be explained taking the formation of sodium chloride from elementary solid sodium and elementary gaseous chlorine. Let us make the following assumptions.

1. Sodium metal is evaporated to sodium atom, $Na_{(g)}$. The energy of sublimation is +S.
2. The diatomic chlorine gas is dissociated to chlorine atom $Cl_{(g)}$. The energy of dissociation for Cl_2 is + D.
3. The sodium atoms are ionised to form Na^+. The ionisation energy of sodium atom is +I.
4. The electrons obtained from sodium atoms are transferred to chlorine atoms to form negative chloride ions Cl^-. The electron affinity of chlorine atom is - E.

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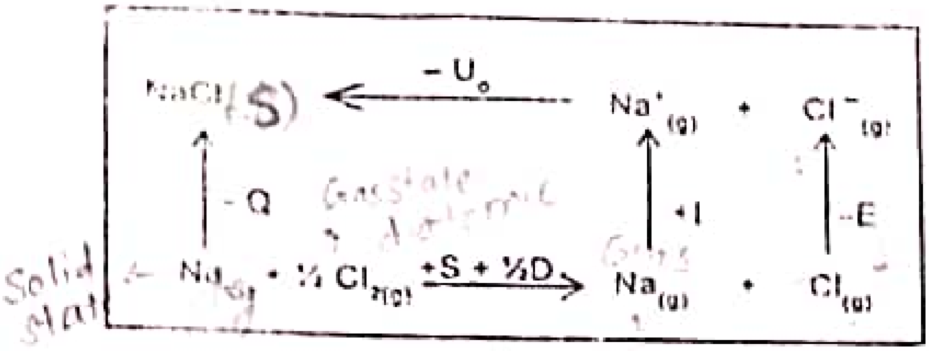
S - Sublimation
D - Decomposition

The lattice energy of sodium chloride is $-U_o$.

6. The heat of formation ?of the crystals from its element is $-Q$

All these changes can be represented by the Born - Haber cycle as follows



7. The total energy of formation of the crystal from is elementary components is given by the equation.

$$-Q = S + \tfrac{1}{2}D + I - E - U_o$$

So, $$U_o = Q + S + \tfrac{1}{2}D + I - E$$

The values of Q are accurately known for many substances. Knowing the other thermochemical values, it is possible to calculate the lattice energy U_o. 2a

3a 5

Pauling's scale of electronegativity

On the basis of bond energies, Pauling devised a scale for electronegativity. Bond energy of a compound A – B for pure covalency is geometric mean of the bond energies of A – A and B – B.

That is, $E_{A-B} = [E_{A-A} \times E_{B-B}]^{\frac{1}{2}}$

But actual experimental value is found to be greater than this expected value. Let the difference between the two be D.

i.e., $D = E_{A-B} - [E_{A-A} \times E_{B-B}]^{\frac{1}{2}}$

D is a measure of the polarity of the bond A – B. It depends on the difference in the electronegative character of A and B.

4a

Let X_A and X_B represent the electronegativity of A and B to Pauling. The relationship between Δ and the electronegativity is

$$X_A - X_B = 0.088\sqrt{\Delta}$$

The factor 0.088 converts Δ from kJ mole^{-1} to eV (electron volts) units

Pauling gave an arbitrary value of electronegativity to hydrogen as $X_H = 2.1$. This is used as reference standard for calculating the electronegativities of other elements 3Q

4Q

Mulliken scale of electronegativity

According to Mulliken, the electronegativity is related to its ionisation potential and its electron affinity. Ionisation potential measures an element's tendency to lose its valence electron while electron affinity measures its tendency to attract an extra electron. Thus elements having high values of ionisation potential and electron affinity will also have high value of electronegativity. Thus

$$\chi = \frac{IP + EA}{2}$$

Where χ = Electronegativity ; IP = ionisation potential in eV and EA = Electron affinity in eV.

Mulliken's value of electronegativities are about 2.8 times larger than Pauling's value. Hence to make both values approximately equal, Mulliken's value is divided by 2.8. Thus,

$$\chi = \frac{IP + EA}{2 \times 2.8} = \frac{IP + EA}{5.6}$$

The constant $\frac{1}{5.6}$ is called ***scale adjustment factor***. This factor is used when IP and EA are expressed in eV. If they are expressed in k.cals, the following scale is used.

Transition from ionic to covalent character and vice - versa

From the above discussion we come to know that a compound is neither 100% covalent nor 100% ionic. When there is a difference in electronegativities between two covalently bound atoms, the covalent bond present in it develops a partial ionic character. In an ionic compound, there may be ion polarisation causing a partial covalent character. Thus there is a transition between ionic and covalent characters.

ion polarising power
and ion polarizability

7Q

Fajan's Rules :

The various factors that affect the magnitude of the polarising power of a cation and the polarizability of the anion are suggested by Fajans. These are called Fajan's rules.

1. ***Size of cation :***

   If the cation is small, it will have greater polarising power on anion.

2. ***Size of anion :***

   If the anion is large, in will have greater tendency to get polarised by cations. When an anion is small, the valency electrons are nearer to the nucleus and hence the tendency to get polarised by the cation will be less. But when an anion is large, it is polarised easily.

3. ***Charge on ions :***

   As the ionic charge on cation increases the polarising capacity also increases. 7Q

Explanation with examples :

i. Let us consider Ag^+ and K^+. Whose ionic radii are 1.13Å and 1.33 Å respectively. Because of smaller size Ag^+ will have greater polarising power.

ii. Let us consider Na^+ and Al^{3+}. Since Al^{3+} has got more ionic charge, it will have greater polarising power.

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ii Ion polarisation accounts for variation of melting point in ionic crystals

Partial ionic character from electro negativity :

We have seen that a covalent bond is set up by sharing of electrons between atoms. If the electron pair is shared equaly the bond is non - polar. If the electron pair is shared unequally the bond is polar. For example, the covalent bonds in H_2 and Cl_2 are called non polar. In the case of hydrogen fluoride the bond is polar as the electron pair is unequaly shared. Fluorine has a greater attraction for electrons (higher electronegativity than hydrogen). So the shared pair of electrons is nearer to fluorine atom than hydrogen. This makes the covalent bond polar in nature. This is called the partial ionic character

Calculation of percent ionic nature from electronegativity :

Electronegativity can b used to calculate the percentage of ionic character in a polar covalent bond. If two atoms A and B are linked by a polar covalent bond A – B, the amount of ionic character in this bond depends on the difference of electronegativity values of A and B. If the differnce of electronegativity value is $X_A - X_B$, the greater the value of $X_A - X_B$ greater is the percentage of ionic character in A – ←B bond. Here the electronegativity of ionic atom A (X_A) is assumed to be greater than that of B(X_B). Pauling has estimated the percentage of ionic character in various polar covalent bonds from $X_A - X_B$ values and has derived the following conclusions.

Value of $X_A - X_B$	Percentage ionic Character	Nature of A – B bond
1.7	50%	50% covalent 50% ionic
< 1.7	< 50% Written as A – B	Predominantly covalent
> 1.7	> 50% Written as A – B.	Predominantly ionic

$$\chi = \frac{IP + EA}{2 \times 62.5}$$]4Q

Example :

Calculate the electronegativity value of chlorine on Mulliken's scale Given that $(IP)_{Cl}$ = 13 eV / atom and $(EA)_{Cl}$ = 4eV / atom.

Solution :

$$\chi_{Cl} = \frac{(IP)_{Cl} + (EA)_{Cl}}{5.6} = \frac{13 + 4}{5.6} = \frac{17}{5.6} = 3.03$$

$\therefore \chi_{Cl} = 3.03$

Disadvantages of Mulliken's scale :

1. Electron affinity values are accurately known for only a few elements.
2. The values of IP and EA refer to the transfer of electrons between the atomic orbitals. We do not know whether these can be rightly applied to the electrons is a bond.
3. The values of IP and EA vary with the nature of shell in which the concerned electrons are situated. So values on Mulliken scale will also vary accordingly.

Ability of cation to [illegible] and anion [illegible]

Polarising Power

6Q [The ability of a cation to polarize a nearby anion is called polarising power or polarising ability.] 6Q

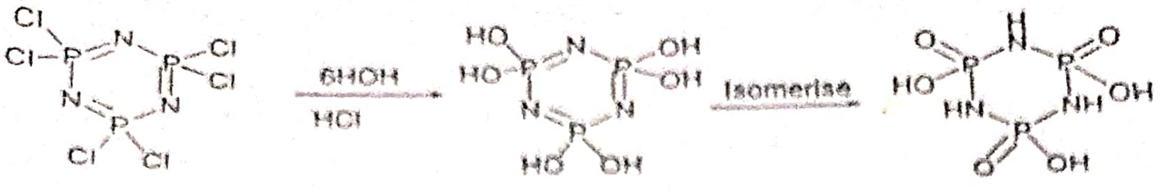
Polarizability

5Q [The tendency of an anion to get polarised or distorted by a cation is called its polarizability.] 5Q

Thus in ion polarisation, the role of cation is to distort the electronic cloud of the anion because of the its polorising power. The role of anion is to get distorted by the cation because of its nature of polarizability.

Effects of ion polarization :

i. Due to ion polarisation, some covalent character is introduced in an otherwise ionic bond.

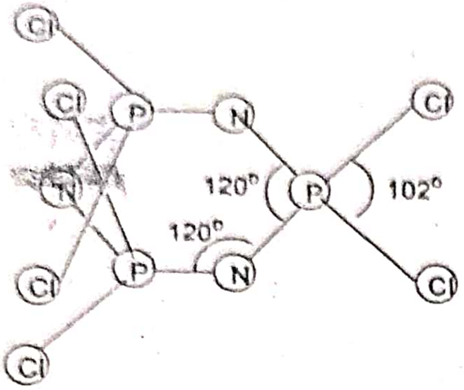


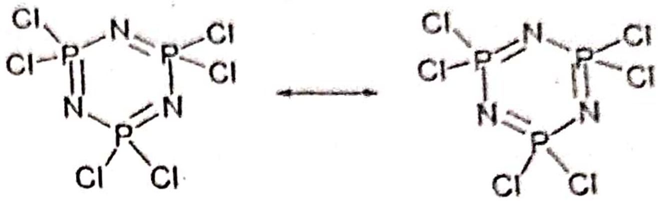
8) KSCN is acetone converts $[NPCl_2]_3$ to $[NP(SCN)_2]_3$.

Structure

1) They are either cyclic or linear.

The trimer consists of a planar six-membered ring.





The bond angles are consistent with sp^2 hybridization of nitrogen and sp^3 hybridization phosphorous. Resonance structures can be drawn analogue to those for benzene indicati aromaticity in the ring.

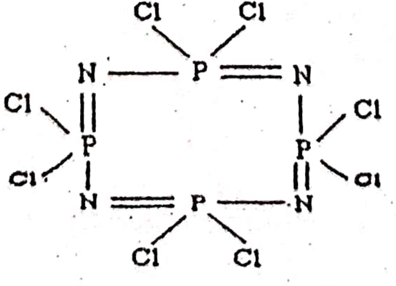
Unlike in benzene, π-bonding here involves d-p π-bonds. The dπ-pπ bonding in phosphonitri systems is explained based on two concepts.

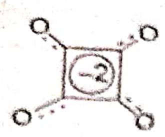
Craig and Paddock model: The d_{xz} orbital on each phosphorous overlaps with the p_z orbital nitrogen adjacent to it. As a result of the gerade symmetry of the d-orbital an inevitable mismatch the sign of the wave function occurs in the trimer. This node decreases the stability of the delocali molecular orbital.

Dewar model: Both the d_{xz} and d_{yz} orbitals participate in the π-bonding. They hybridize themselve form d_a and d_b directed towards the adjacent nitrogen atoms. This allows delocalized, three cent bonds to be formed about each N atom. This scheme results in delocalization over selected atoms segment of the ring but nodes are present on each P atom since the d_a and d_b orbitals mutually orthogonal.

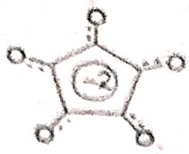
The structures of tetrameric forms are more flexible than those of the trimers. The rings are pla $[NPF_2]_4$ and $[NPCl_2]_5$. But chain and boat forms have been identified for $[NPCl_2]_4$ and for {NP

2) The structure of the tetramer has also been determined by the X-ray method.

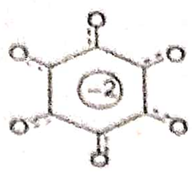




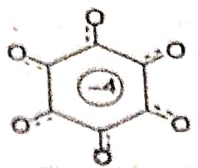
Squarrate



Croconate



Rhodizonate



Tetraanion of tetrahydroquinone

Carboranes

Carboranes are mixed hydrides of carbon and boron having both C and B atoms in an electron-deficient framework. There are two main types.

1) *Closo carboranes* $C_2B_{n-2}H_n$ (n = 5 – 12)

2) *Nido carboranes* with open cage structure derived formally from one of either of several boranes and containing 1 to 4 C atoms in the skeleton.

In addition, there are a number of carboranes with an additional hetero atom such as phosphorous and a fairly numerous family of metallocarboranes some of which are similar to ferrocene.

Nomenclature: (i) The position of C-atoms is first indicated; (ii) the type of carborane (closo o nido), (iii) the name of borane from which formally derived and finally the number of hydroge atoms. For example: The three isomers of $C_2B_{10}H_{12}$ are (a) 1,2-dicarba-closododecaborane (12), (1,7-dicarba-closododecaborane (12), and (c) 1,12-dicarba-closododecaborane (12).

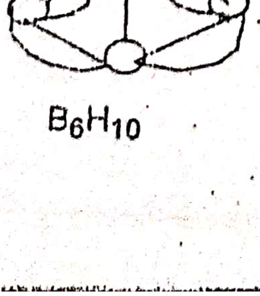
Similarly, CB_5H_9 can be named as monocarba-nidohexaborane (9).

Nidocarboranes: The small nidocarborane is usually prepared by the reaction of borane (B_4H B_5H_9, B_5H_{11}, etc.) with acetylene under mild conditions. The same reaction is drastic condition yield the closocarboranes. For example: B_5H_{11} and acetylene at 250 °C in the gas phase gives nidocarborane, 2,3-$C_2B_4H_8$ and at 450 °C gives the closocarboranes, 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$ and $C_2B_5H_7$.

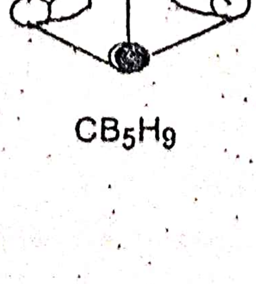
The nidocarborane 2,3-$C_2B_4H_8$ is converted into closocarboranes $C_2B_3H_5$, $C_2B_4H_6$ and C_2B_5H pyrolysis or UV radiation.

Structure: The structures of some nidocarboranes are shown below. The H-bridges are shown curved lines and terminal C-H and B-H bonds are omitted. The introduction of successive C-at the framework involves the elimination of one bridged H-atom and one B-H system, i.e. replacement of BH_2 group by isoelectronic CH group.

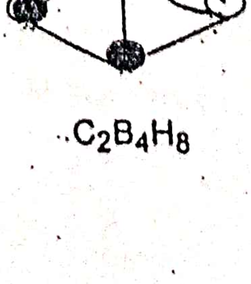
● C ○ B



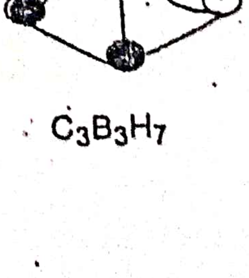
B_6H_{10}



CB_5H_9



$C_2B_4H_8$



$C_3B_3H_7$

All these compounds are electron deficient with multicentered bond and delocalization extending over the entire framework.

Closocarboranes: Members of $C_2B_{n-2}H_n$ series are isoelectronic with the corresponding $B_nH_n^{2-}$ ion and have the same closed polyhedral structure with one H-atom bonded to each C and B. They can be prepared by reacting boranes and acetylene at high temperatures.

$$B_5H_9 + C_2H_2 \xrightarrow{490^\circ} 1,5\text{-}C_2B_3H_5,\ 1,6\text{-}C_2B_4H_6,\ 2,4\text{-}C_2B_5H_7$$

$$B_2H_6 + C_2H_2 \xrightarrow{\text{Electric discharge}} 1,5\text{-}C_2B_3H_5,\ 1,6\text{-}C_2B_4H_6,\ 2,4\text{-}C_2B_5H_7$$

The closocarboranes $C_2B_6H_8$, $C_2B_7H_9$, $C_2B_8H_{10}$ and $C_2B_9H_{11}$ are best prepared by the partial degradation of $1,2\text{-}C_2B_{10}H_{12}$ with a strong base.

$C_2B_3H_5$ has a trigonal bipyramidal structure, $C_2B_4H_6$ an octahedral structure and $C_2B_5H_7$ a pentagonal bipyramidal structure.

The best known closocarborane is $C_2B_{10}H_{12}$ which is prepared by the reaction of $B_{10}H_{14}$ with C_2H_2 in presence of a Lewis base such as acetonitrile.

$$B_{10}H_{14} + 2L \rightarrow B_{10}H_{12}L_2 \xrightarrow{C_2H_2 \text{ when } L = CH_3CN} C_2B_{10}H_{12} + 2MeCN + H_2$$

hosphorous Cage Compounds

he simplest example is P_4. This is a tetrahedron of P atoms. Such a structure requires a bond angle f 60°. But the minimum bond angle available using only s and p orbitals is 90°. The smaller bond ngle in P_4 is accomplished either through involvement of d orbitals in bonding or through bent onds. In any event, the molecule is destabilized and quite reactive. It reacts readily with oxygen to orm a mixture of oxides.

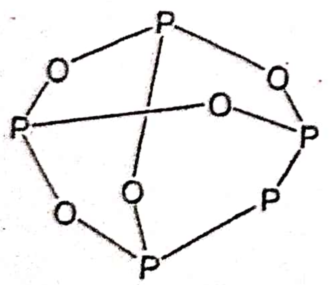
$$+ O_2 \rightarrow P_4O_6,\ P_4O_{10}$$

eaction of PCl_3 with methylamine produces a cage phosphorous imide, isoelectronic and ostructural with P_4O_6.

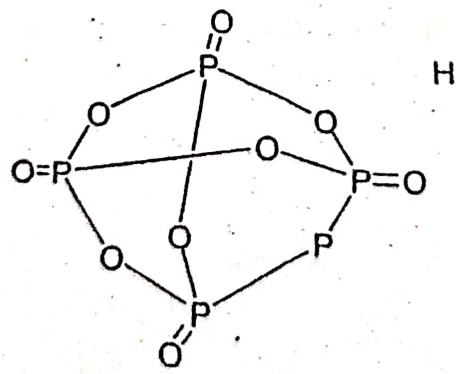
$$Cl_3 + 18CH_3NH_2 \rightarrow P_4(NCH_3)_6 + 12CH_3NH_3Cl$$

e structures of the cage compounds are given below:

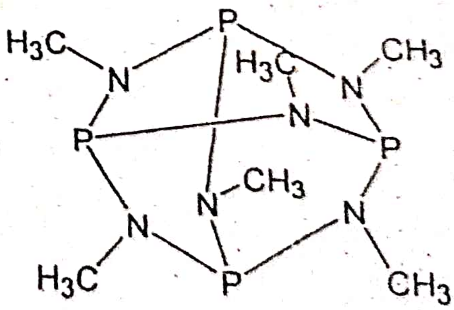
P_4O_6



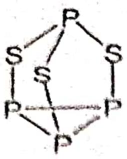
P_4O_{10}



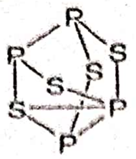
$P_4(NCH_3)_6$



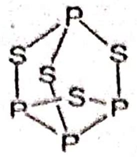
lar phosphorous cage compounds with sulphur also have been known. Few of them are P_4S_3, P_4S_7, P_4S_{10} have structures similar to the phosphorous oxide cage compounds.



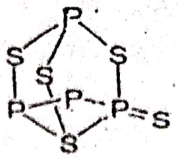
P_4S_3



α-P_4S_4 .



β-P_4S_4



P_4S_5

Boron Cage Compounds

Besides B_2H_6 several boranes possessing the general formulae B_nH_{n+4} and B_nH_{n+6} are known Example.: Pentaborane[11], B_5H_{11}; Pentaborane[9], B_5H_9; Hexaborane[10], B_6H_{10} an Hexaborane[12], B_6H_{12}

Diborane

It is prepared by the reduction of BCl_3 with $LiAlH_4$.

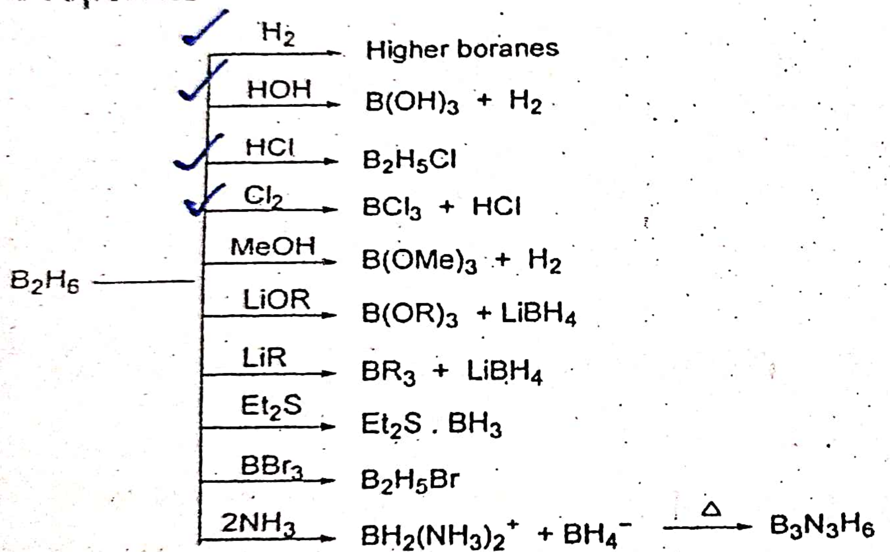
$$4BCl_3 + 3LiAlH_4 \xrightarrow{(C_2H_5)_2O} 3LiCl + 3AlCl_3 + 2B_2H_6$$

$$8BF_3 + 6NaH \xrightarrow{\text{Polyethers}} 6NaBF_4 + B_2H_6$$

$$4BF_3 + 3NaBH_4 \xrightarrow{(C_2H_5)_2O} 3NaBF_4 + 2B_2H_6$$

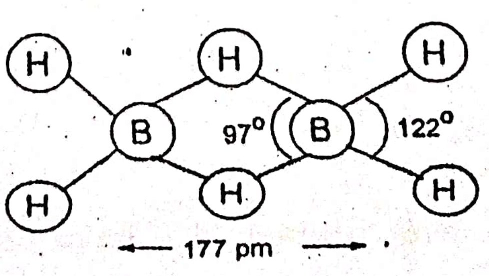
$$2NaBH_4 + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2 + B_2H_6$$

Properties



Structure

In diborane there are not enough electrons to permit the formation of conventional 2 electron (2e–2C) between all adjacent pairs of atoms. B_2H_6 requires 14 valency electrons for sever whereas it has only 12 such electrons. Electron diffraction studies have shown that B_2H_6 structure as

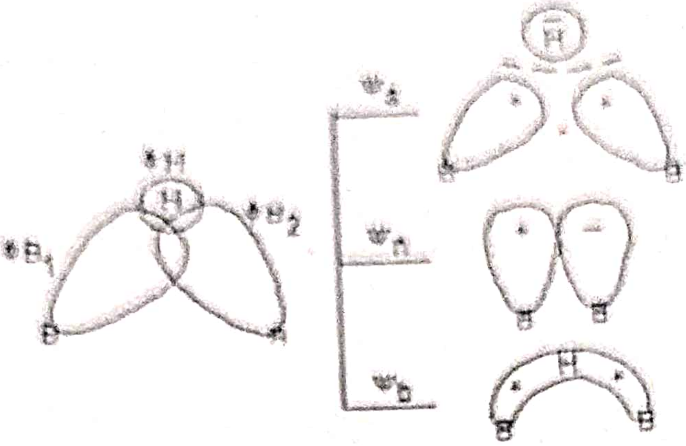


Banana bond structure: Each B atom is considered as sp^3 hybridised. The two terminal B-H bonds on each B atom are sigma bonds involving a pair of electrons each. This accounts for 8 of the 12 electrons available for bonding. Each of the bridging B-H-B linkages then involves a delocalized or 2e–3C bond as follows:

The approximate combinations of the three orbital wave functions ϕB_1, ϕB_2 and ϕH result in three molecular orbitals.

$\psi_b = \frac{1}{2}\phi B_1 + \frac{1}{2}\phi B_2 + \frac{1}{\sqrt{2}}\phi H$; $\psi_n = \frac{1}{2}\phi B_1 - \frac{1}{2}\phi B_2$; $\psi_a = \frac{1}{2}\phi B_1 + \frac{1}{2}\phi B_2 - \frac{1}{\sqrt{2}}\phi H$

where ψ_b, ψ_n and ψ_a are the bonding, non-bonding and anti-bonding molecular orbitals, respectively. The diagrammatic representation of molecular orbital formation is shown below:



ach bridging bond thus consists of a bonding MO containing two electrons. Although the onbonding orbital can accept an additional pair of electrons, this would not serve to stabilize the olecule beyond that achieved by ψ_b^2.

he second B – H – B bridge may likewise be considered as above and to have a configuration $\psi_b'^2$. his accounts for total 12 electrons and provide the existence of the dimer.

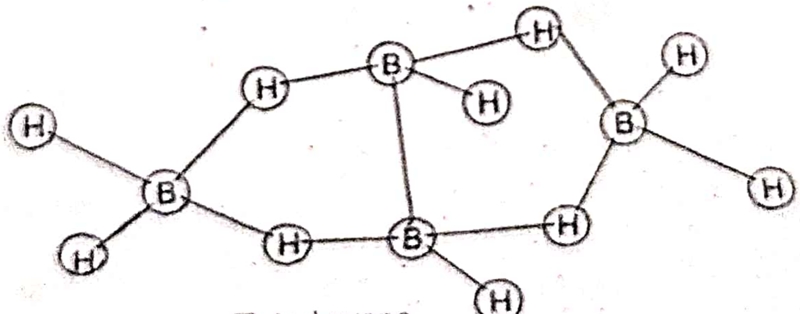
order to account for structure and bonding of higher boranes, in addition to 2e–2C B – H and 2e–C B – H – B groups, one has to consider 2e–3C B – B – B group and 2e–3C closed B – B – B roup.

etraborane

is formed by the slow decomposition of B_2H_6.

$_2H_6 \rightarrow B_4H_{10} + H_2$

etraborane has, in addition to the bridging B-H bonds, a direct B-B bond.

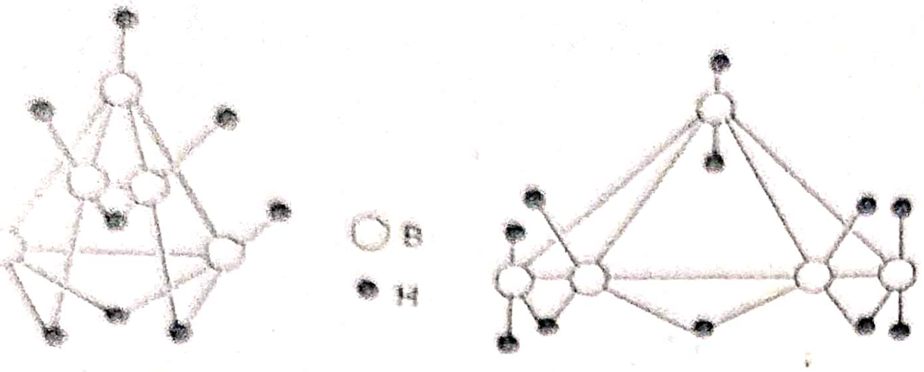


Tetraborane

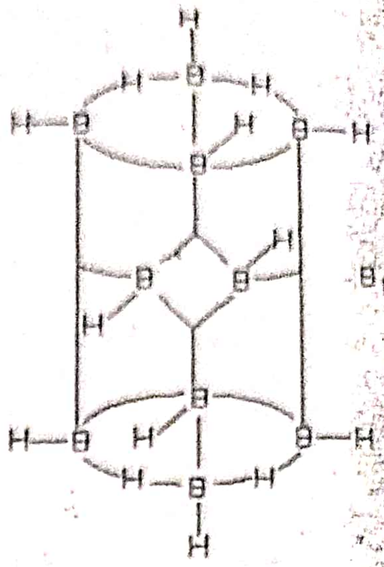
Pentaborane

Pentaborane[9] is prepared by circulating a mixture of B_2H_6 with excess H_2 through a tube at
50 °C.

Pentaborane[11] is prepared by heating B_2H_6 with H_2 at 100 °C.



B_5H_9 B_5H_{11}



B_{10}

Hexaborane[10]

It is prepared by the decomposition of B_5H_{11} in the presence of weak Lewis bases such as dim ether.

$$2B_5H_{11} \xrightarrow{(CH_3)_2O} B_6H_{10} + 2B_2H_6$$

It is stable at room temperature. In this compound, B atoms are found to form a pentagonal pyr with one H atom bonded to each B by a 2-electron terminal bond. In addition, there are four B - B bridge bonds in this structure.

Decaborane[14]

It is prepared by heating B_2H_6 in a flow system at 100 °C to 150 °C in the presence of a catalyst as dimethyl ether. B_5H_9 is formed as the precursor.

$$2B_5H_9 + 5B_2H_6 \rightarrow 2B_{10}H_{14} + 10H_2$$

$B_{10}H_{14}$ behaves as a strong monoprotic acid and can be titrated with bases such as amine. The so salt $NaB_{10}H_{13}$ is formed in the reaction with NaH in diethyl ether. Reaction with CH_3MgBr in yields Grignard type compound, $B_{10}H_{13}MgI$.

Compounds with Metal-Metal Bonds

i) The term M-M bond is exclusively used for the bond between the homo or hetero ato covalent compounds.

ii) The existence of M-M bond in a compound can be, in general, inferred from (a) the shorter distance, and (b) the lower paramagnetic susceptibility value than the calculated value for the is metal ion.

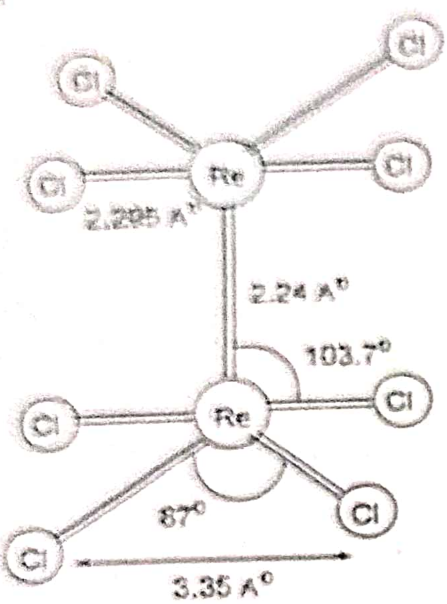
The conditions favourable for M-M bond is the lower-than-three oxidation state of the metal ion hen the charge is low, the metal orbitals are able to overlap sufficiently without the metal atoms ming near to each other to experience the coulombic repulsion).

Compounds containing M-M bonds are classified into two: (i) compounds with 2-centered M-M nd and (ii) metal atom clusters. For compounds containing 2-centered M-M bonds, the examples e $Re_2Cl_8^{2-}$, $Mo_2Cl_8^{4-}$, $Re_2Br_8^{2-}$, etc.

e best studied species are $Re_2X_8^{2-}$ ions, prepared by reducing perrhenate in presence of acid.

$$ReO_4^- \xrightarrow[HX]{H_3PO_2} Re_2X_8^{2-} \quad (X = Cl, Br)$$

$Re_2Cl_8^{2-}$, two square $ReCl_4$ groups are joined through the Re atom without any bridging group. he structure possesses two unusual features, viz., (i) The Re-Re bond distance is extremely short 24 Å) compared to an average Re-Re distance 2.75 Å in Re metal and 2.48 Å in Re_3Cl_9; (ii) The alogen atoms have eclipsed configuration.



These unusual features and the diamagnetic nature of $Re_2Cl_8^{2-}$ are explained in terms of quadruple bond between the Re atoms.

The bond is made up of a σ bond, two π bonds and a δ bond. The formation of quadruple bond is explained as follows:

The z-axis is taken as the line joining the Re atoms. Each Re atom is bonded to four Cl atoms almost in a square planar array. The Re-Cl bonds can be considered to be approximately dsp^2 hybrids utilizing the $d_{x^2-y^2}$ orbital. The d_{z^2} and p_z orbitals lie along the bond axis and one orbital directed in the opposite direction. The former can overlap with the similar orbital on the second Re atom to form a σ bond while the second hybrid orbital forms an approximately non-bonding orbital.

he d_{xz} and d_{yz} orbitals of each Re atom will overlap to form d-d π bonds. This results in two π onds, one in the xz plane and one in the yz plane. A fourth (δ) bond is formed by the sidewise verlap of the remaining d orbitals, the d_{xy}. Overlap can only occur if the Cl atoms are eclipsed. If the l atoms are staggered, the two d_{xy} orbitals will likewise be staggered resulting in zero overlap.

e(III) is a d^4 species. The Re-Cl bonds may be considered to be dative bonds from Cl^- ions to Re^{3+} ns. The formation of one σ bond, two π bonds and one δ bond causes the pairing of the four ectrons in the quadruple bond. Hence the complex is diamagnetic.

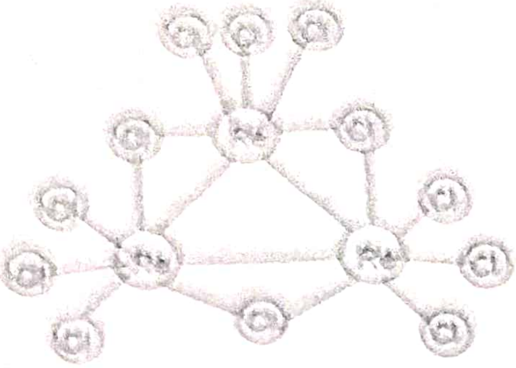
etal Atom Clusters

hese contain three or more metal atoms (like or alike) arranged in a polygonal or polyhedron array ith delocalization of electrons. Examples: $Fe_2(CO)_9$ and $Mn_2(CO)_{10}$

rinuclear clusters

he best known example of cluster containing three metal atoms are the derivatives of rhenium alide where rhenium atom is bonded to other two Re atoms directly by M-M bond and indirectly by bridging halide ion. In addition to each Re atom in a triangular array, it is coordinated by two or more halide ions above and below the plane defined by three Re atoms. Example: $Re_3Cl_{12}^{3-}$.

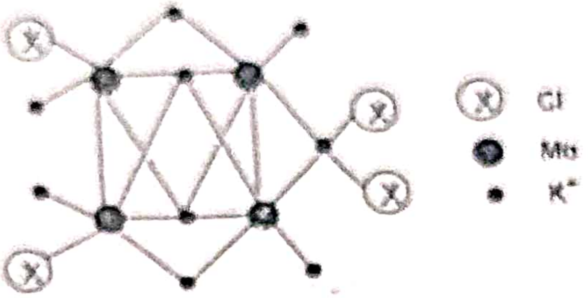
Dissolving $ReCl_3$ in HCl results in the formation of $Re_3Cl_{12}^{3-}$ ion. The bond length is 2.4 – 2.5 A which is indicative of strong bonding.



$[Re_3Cl_{12}]^{3-}$

Tetranuclear clusters

Quadruple bonded binuclear compounds can dimerize through a cyclic addition reaction to give a tetranuclear cluster.



The resulting four-membered ring is not square-planar. There are alternative single and triple Mo- bonds as evidenced by bond length measurements.

Octahedral clusters

Clusters of six molybdenum, niobium or tantalum atoms have been known. They are of two kinds.

In the first, an octahedron of six Mo(II) atoms is coordinated by six chloride ions one on each fac the octahedron. This is found in Mo_6Cl_{12} (formulated as $[Mo_6Cl_8]Cl_4$). The micro environment a each Mo atom is approximately a square antiprism with four chloride ions above and four Mo a below. The Mo(II) atom can use its four electrons to form four bonds with the adjacent Mo a and receive dative bonds from four chloride ions.

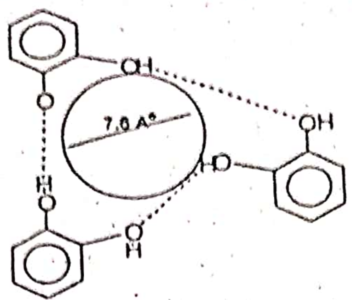
The second class also contains an octahedron of metal atoms but coordinated by twelve chlorid along the edges. Niobium and Tantalum form these clusters. Here the bonding situation is som more complicated. The metal atoms are surrounded by a very distorted square prism of four atoms and four chloride ions.

Metal-only clusters

There is a small group of ions that do not fall neatly into any classification. They are exempli Bi_9^{5+}, Ge_9^{2-}, Ge_9^{4-}, Sn_9^{4-}, Pb_5^{2-}, Pb_9^{4-} and Sb_7^{3-}. They exist as regular polyhedra, but ther obvious relation between their geometries and electronic structures.

Clathrates

A compound in which a molecule is trapped in a cage of crystal lattices is called clathrate compound. If an aqueous solution of hydroquinone is cooled under a pressure of several atmospheres of a noble gas (X = Ar, Kr, or Xe), a crystalline solid of approximate composition $[C_6H_4(OH)_2]_3X$ is obtained. These solids are β-hydroquinone clathrates with noble gas atoms filling most of the cavities. These



clathrates are of some importance since they provide a stable, solid source of the noble gases, especially the radioactive forms. They have also been used to effect separation of the noble gases since there is a certain selectivity exhibited by the clathrates.

Helium and neon fail to form clathrates presumably due to smaller size of the atom which enables to escape from quinol lattice.

In the quinol lattice all the OH groups are tied together through hydrogen bonding as in figure. The interlocating of all hydroquinone molecules forms an infinite three dimensional work. the void of which has a diameter of 7.6 Å.

An ammoniacal solution of nickel cyanide produces pale colour clathrate when shaken vigorously with benzene. This is benzene ammine nickel clathrate $Ni(CN)_6(NH_3)(C_6H_6)$.

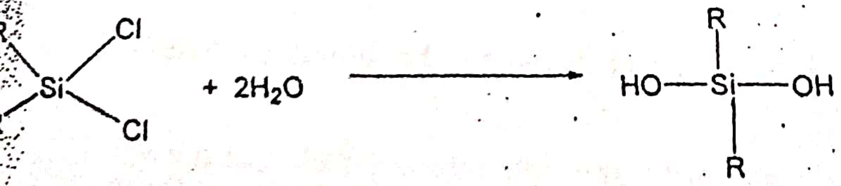
Compounds of the formula $6X.46H_2O$ where X = Ar, Kr, Xe, Cl2, CH4, etc. are the other examples of clathrates. The basic building block for this type of structure is a dodecahedron formed from 20 molecules of H_2O. Each water molecule is bonded to three others by hydrogen bonds. Half of the oxygen atoms have their fourth coordination position occupied by a hydrogen atom that can hydrogen bond to adjacent polyhedron and the other half have a lone pair at the fourth position which can accept a hydrogen bond from an adjacent polyhedron. When these dodecahedra pack together to form larger units relatively large voids are formed in the structure and it is in these spaces that the host molecules reside.

Silicon Polymers

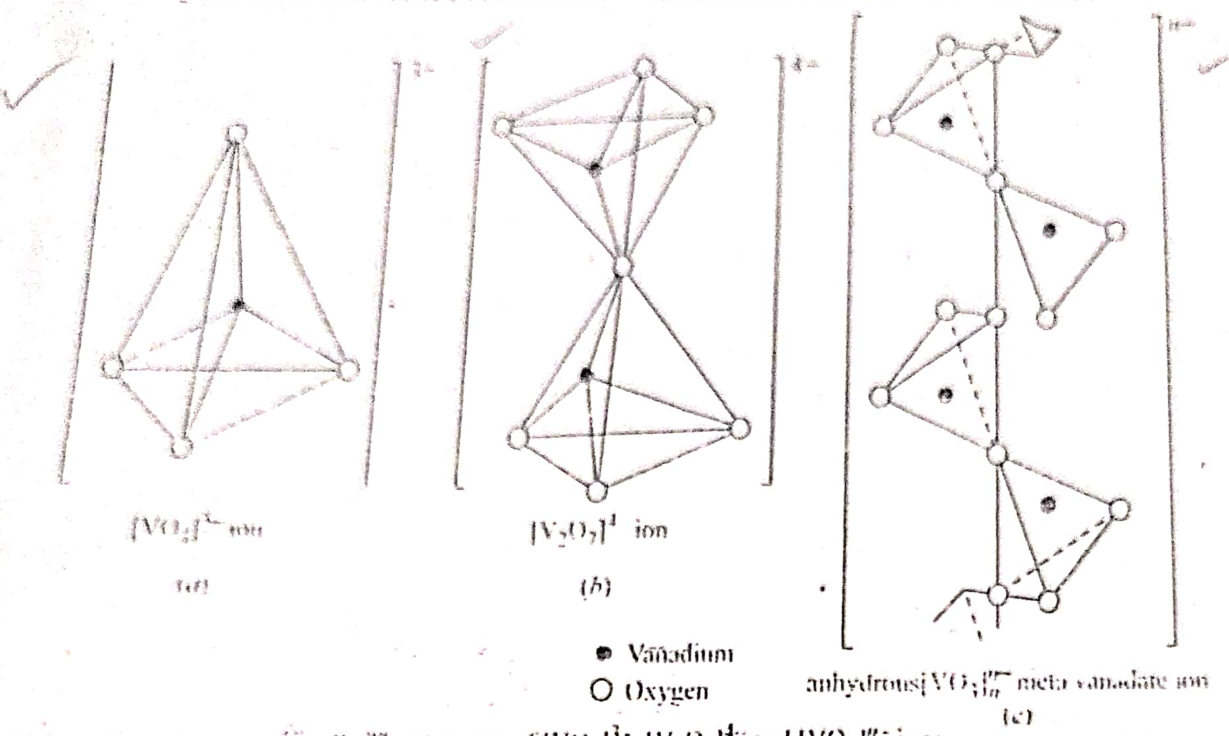
Silicon tetrachloride is fully hydrolyzed giving SiO_2 which has a stable three dimensional structure.

$$SiCl_4 + 4H_2O \rightarrow Si(OH)_4 \rightarrow SiO_2 + 2H_2O$$

When alkyl substituted chlorosilicon is subjected to hydrolysis, it gives silicones



(iv) Isopoly Vanadates, Isopoly Niobates and Isopoly Tantalates. When V_2O_5 is dissolved in strong alkaline solutions, monovanadate ion, VO_4^{3-} (also called orthovanadate ion) is predominantly formed. The gradual acidification of the alkaline solution of monovanadate ions, till neutralisation, produces pyrovanadate $V_2O_7^{4-}$ and metavanadate $[VO_3]_n^{n-}$. The structure of pyrovanadate ion contains two VO_4^{3-} tetrahedra linked through a vertex. The structures of $[VO_4]^{3-}$, $[V_2O_7]^{4-}$ and polymeric metavanadate are shown in Figures 8a, 8b and 8c. The lines between V and O do not show the exact bond order.



$[VO_4]^{3-}$ ion

(a)

$[V_2O_7]^{4-}$ ion

(b)

anhydrous $[VO_3]_n^{n-}$ meta vanadate ion

(c)

Fig. 8. The structure of $[VO_4]^{3-}$, $[V_2O_7]^{4-}$ and $[VO_3]_n^{n-}$ ions

The metavanadate ions do not involve the discrete VO_3^- ions. The anhydrous metavanadate such as NH_4VO_3 contains infinite chains of corner linked VO_4 tetrahedra (Fig. 8c).

The ortho, pyro and meta vanadates are all based on tetrahedral VO_4 units in which the coordination number of V remains 4.

Further acidification of the vanadate solution, after the neutralisation, produces $[V_{10}O_{28}]^{6-}$.

The structure of $[V_{10}O_{28}]^{6-}$ is made up of ten edge sharing VO_6 octahedra in which vanadium aquires coordination number of 6. Its structure is shown in Fig. 9.

[PMo

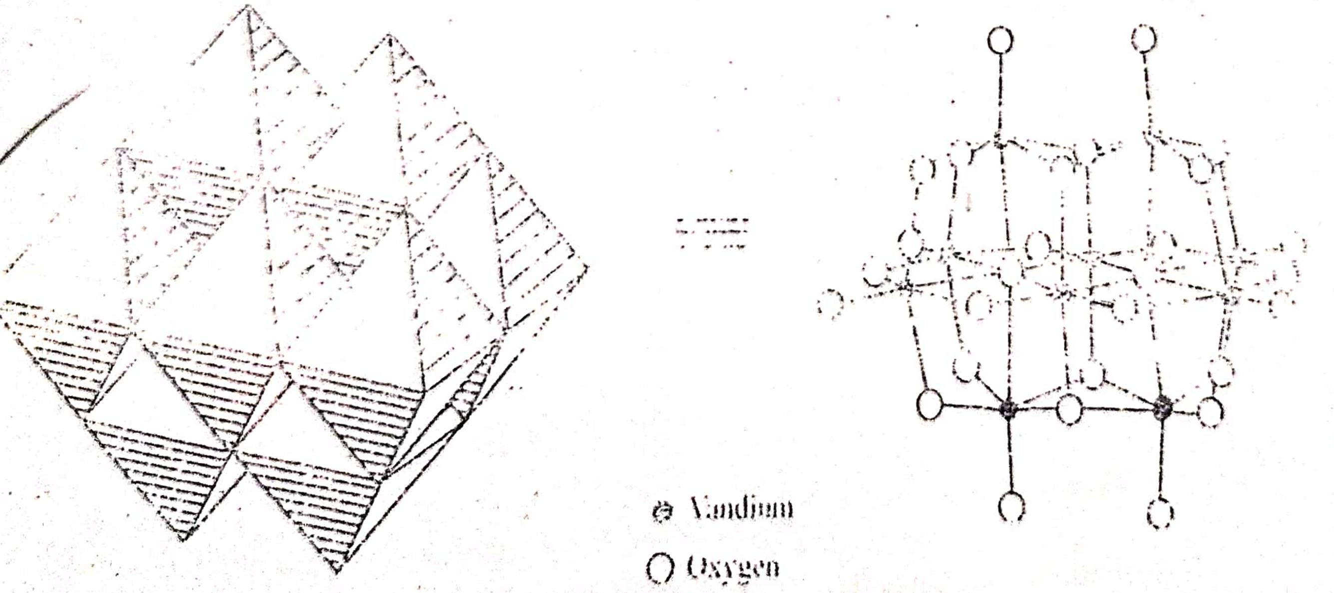


Fig. 9. The structure of $[V_{10}O_{28}]^{6-}$ ion

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When $[n\text{-}Bu_4N]_3[H_3V_{10}O_{28}]$ is dissolved in acetonitrile, the tetrabutyl ammonium salt of $[V_5O_{14}]^{3-}$ anion is formed. This anion is the first example of the transition metal polyoxyanion which has a cage structure that is built entirely from corner shared MO_4 tetrahedra instead of edge shared or corner shared MO_6 octahedra. (Fig. 10)

The same isopolyvanadate ion $[V_5O_{14}]^{3-}$ is also formed when $n\text{-}Bu_4NOH$ and $[H_3V_{10}O_{28}]^{3-}$ are dissolved in a non-aqueous solvent. Thus,

$$[H_3V_{10}O_{28}]^{3-} + 3OH^- \longrightarrow 2[V_5O_{14}]^{3-} + 3H_2O$$

When the tetrabutyl ammonium salt of $[H_3V_{10}O_{28}]^{3-}$ is refluxed in acetonitrile, the anion $[H_3C\ CNV_{12}O_{32}]$ is obtained in small quantity in which CH_3CN is suspended in the basket-like structure of $[V_{12}O_{32}]^{4-}$ ion.

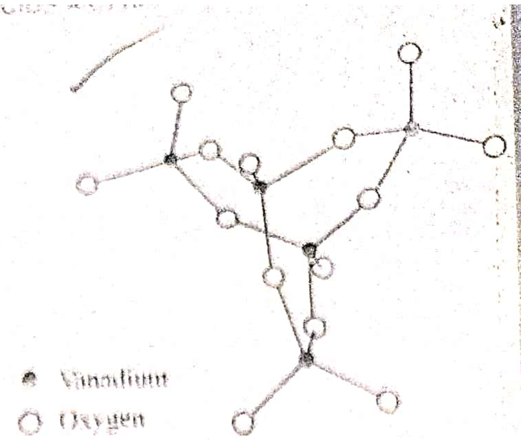

Fig. 10. The structure of $[V_5O_{14}]^{3-}$ made fr corner sharing of VO_4 tetrahedra

Fusing Nb_2O_5 and Ta_2O_5 with excess of alkali hydroxide followed by dissolution in water pr solutions of their isopolyanions. The isopolyanion $[M_6O_{19}]^{8-}$ (M = Nb and Ta) predominantly e solution upto pH 11. These polyanions have edge sharing distorted MO_6 octahedra as the structure b unit and have the same structure as $[Mo_6O_{19}]^{2-}$ and $[W_6O_{19}]^{2-}$ already discussed. Below pH protonation of this anion starts giving $[HM_6O_{19}]^{7-}$, $[H_2M_6O_{19}]^{6-}$ and $[H_3M_6O_{19}]^{5-}$ (M = Nb and the pH is lowered to less than 10, the hydrous oxides $V_2O_5.xH_2O$ and $Nb_2O_5.xH_2O$ start precipitati

3. **Heteropoly Anions and Heteropoly Acids.** The first heteropolyanion, $[PMo_{12}O_{40}]^{3-}$, was by J.J. Berzelius. This anion is now used for the quantitative estimation of PO_4^{3-} in its solution then, a large number of heteropolyanions of Mo and W have been prepared with a large nu heteroatoms of both metals and non-metals. The salts of hetropolyanions are thermally more sta the corresponding salts of isopolyanions. The heteropoly anions are extensively used as cat petrochemical industry, as precipitants for dyes with which they form lakes and as flame retarda heteroatoms in heteropolyanions are situated inside the "cavities" formed by MO_6 octahedra (M W) and are bonded to O atoms of MO_6 units of condensing MO_6 octahedra.

Heteropolyanions can be prepared by acidifying the solutions of simple monomeric anions.

$[PMo_{12}O_{40}]^{3-}$

$$HPO_4^{2-} + 12MoO_4^{2-} + 23H^+ \longrightarrow [PMo_{12}O_{40}]^{3-} + 12H_2O$$

Many of the heteropolyanions are quite stable in acidic solutions.

Some important [illegible] heteropolyanions are given [illegible]

(i) 1 : 12 (Tetrahedral heteroatoms): [illegible] of heteropolyanions, the is relatively small in size and is situated in a tetrahedral [illegible] heteroatom inside the polyanion is tetrahedrally [illegible] sharing units of the heteropolyanion. Common heteroatoms are [illegible] The gene for such heteropolyanions is $[X^{n+}M_{12}O_{40}]^{(8-n)-}$ [illegible] of heteropolyanions has either full tetrahedral (Td) symmetry (Keggin structure) (Fig. 11) or has which can be derived from Keggin structure by rotating one of the four sets of three cond octahedra of Keggin structure by 60°. The resulting structure no more has a fully tetrahedral s it contains only one three-fold axis of symmetry against four three-fold axes of symmetry o Keggin structure. This 'isomeric Keggin structure' is as stable as regular Keggin struc

The bombardment of boron with alpha particles yields a radioactive isotope of nitrogen with mass number 13. It has a short half-life period and disintegrates, as represented below :

$$^{10}_{5}B + ^{4}_{2}He \longrightarrow \underset{\text{(Radioactive)}}{^{13}_{7}N} + ^{1}_{0}n$$

$$^{13}_{7}N \longrightarrow \underset{\text{Stable isotope of carbon}}{^{13}_{6}C} + \underset{\text{Positron}}{^{0}_{+1}e}$$

Preparation of Transuranic Elements. It was found by Seaborg at the University of California that when uranium is bombarded with neutrons of a *certain critical velocity*, one neutron is captured per atom of uranium giving rise to an element of a higher mass number.

$$^{238}_{92}U + ^{1}_{0}n \longrightarrow ^{239}_{92}U + \gamma \text{ rays}$$

This new isotope of uranium is much more radioactive than the natural uranium. It emits a beta particle and gives a new element of atomic number 93 which does not occur in nature. This element was named neptunium (Np).

$$^{239}_{92}U \longrightarrow ^{239}_{93}Np + ^{0}_{-1}e$$

Neptunium is also radioactive and emits a beta particle giving another new element of atomic number 94, known as plutonium (Pu).

$$^{239}_{93}Np \longrightarrow ^{239}_{94}Pu + ^{0}_{-1}e$$

Plutonium (half-life period about 24000 years) is much more stable than ^{239}U (half-life period 23 minutes) and ^{239}Np (half-life period 2·6 days). However, it undergoes a further beta-ray change. In this way, by appropriate nuclear reactions, elements of atomic numbers 95 (americium), 96 (curium), 97 (berkelium), 98 (californium), 99 (einsteinium), 100 (fermium), 101 (mendelevium), 102 (nobelium), 103 (lawrencium), 104 (kurchatovium) and 105 (hahnium) have been prepared artificially. Three more elements of atomic numbers 106, 107 and 108 are also reported to have been discovered. The transuranic elements with atomic numbers beyond 100 are now named according to the IUPAC convention, as already described in Chapter 2.

✓ **Q Values of Nuclear Reactions.** The complete equation for a nuclear reaction should include *the energy change of the reaction* as well. This is usually denoted by *Q*. Thus, the complete equation for Rutherford's transmutation reaction described earlier should be

$$^{14}_{7}N + ^{4}_{2}He \longrightarrow ^{17}_{8}O + ^{1}_{1}H + Q$$

Q is called the *nuclear reaction energy*.

The value of *Q* may be *positive* when the reaction is said to be **exoergic** or *negative* when the reaction is said to be **endoergic**.

The value of *Q* for the above reaction can be calculated from the masses of the reactants and products. Thus,

Sum of masses of reactants = 14·0031 + 4·0026 = 18·0057 a.m.u.

Sum of masses of products = 16·9991 + 1·0078 = 18·0069 a.m.u.

ΔM = Masses of products − Masses of reactants

= 18·0069 − 18·0057 = + 0·0012 a.m.u.

The reaction, evidently, involves *increase of mass* by 0·0012 a.m.u. An equivalent amount of energy is therefore, *absorbed* in this case. Hence, the *Q* value, by convention, is *negative*.

Since 1 a.m.u. ≡ 931·5 MeV of energy

∴ $Q = -0{\cdot}0012 \text{ a.m.u.} \times 931{\cdot}5 \text{ MeV/a.m.u.} = -1{\cdot}118 \text{ MeV}$

The reaction is, evidently, *endoergic*.

Example 15. Calculate Q value of the following nuclear reaction :

$$^{27}_{13}\text{Al} + {}^4_2\text{He} \longrightarrow {}^{30}_{14}\text{Si} + {}^1_1\text{H} + Q$$

The exact mass of $^{27}_{13}Al$ isotope may be taken as 26·9815 a.m.u. and that of $^{30}_{14}Si$ as 29·9738 a.m.u.

Solution :

Sum of the masses of reactants = 26·9815 + 4·0026 = 30·9841 a.m.u.

Sum of the masses of products = 29·9738 + 1·0078 = 30·9816 a.m.u.

ΔM = Masses of the products − Masses of the reactants

= 30·9816 − 30·9841 = − 0·0025 a.m.u.

The reaction evidently involves *decrease* of mass and hence *release of energy*. The Q value is, therefore, *positive*.

$$Q = +0.0025 \text{ a.m.u.} \times 931.5 \text{ MeV/a.m.u.} = 2.329 \text{ MeV}$$

The Q values for most of the nuclear reactions are within 10 MeV. But in the reaction

$$^7_3\text{Li} + {}^1_1\text{H} \longrightarrow 2\,{}^4_2\text{He}$$

the value is quite high, as shown below :

Sum of the masses of reactants = 7·01601 + 1·00783 = 8·02384 a.m.u.

Mass of the product = 2×4·00260 = 8·00520 a.m.u.

∴ ΔM = Mass of the product − Masses of the reactants = 8·00520 − 8·02384 = − 0·01864 a.m.u.

There is a decrease of mass and hence the energy is *released*. The Q value is, therefore, *positive*. Thus,

$$Q = 0.01864 \text{ a.m.u.} \times 931.5 \text{ MeV/a.m.u.} = 17.36 \text{ MeV}$$

Nuclear Coulombic Barrier. When a positively charged particle such as an alpha particle approaches a nucleus, it is repelled by the nucleus. The repulsive force between the nucleus and the approaching positively charged particle is called the **nuclear coulombic barrier**. The energy of repulsion V is given by

$$V = (Ze)_1(Ze)_2/d = Z_1Z_2e^2/d \qquad \text{..(7)}$$

where Z is atomic number, e is the unit of protonic charge = 4.8×10^{-10} e.s.u. and d is the distance between the nucleus and the positively charged particle.

Example 16. Consider an alpha particle just in contact with a $^{238}_{92}U$ nucleus. Calculate the coulombic repulsion energy (*i.e.*, the height of the coulombic barrier between ^{238}U and alpha particle) assuming that the distance between them is equal to the sum of their radii.

Solution : According to Eq. 1, radius r of a nucleus is given by $r = R_0 A^{1/3}$ where A is mass number and R_0 is a constant = 1.4×10^{-13} cm

[illegible]

[illegible]

[illegible]

[illegible]

We may convert the result from erg to MeV, recalling that 1·602 × 10 [illegible] erg = [illegible] 1 MeV. Thus,

$$\text{Coulombic barrier, } V = \frac{3.88 \times 10^{-5} \text{ erg}}{1.602 \times 10^{-12} \times 10^{6} \text{ erg/Mev}} = 24.2 \text{ MeV}$$

The above result shows that an alpha particle would require a kinetic energy of at least 24·2 MeV to approach close enough to make a contact with the ^{238}U nucleus. If its kinetic energy is less than this value, it would not be able to overcome the coulombic barrier and would be repulsed before coming in contact with ^{238}U nucleus.