p-block

Table of Contents

THEORY

Introduction :

Group 13 to 18 of the periodic table of elements constitute the p–block. The p–block contains metals, metalloids as well as non–metals.

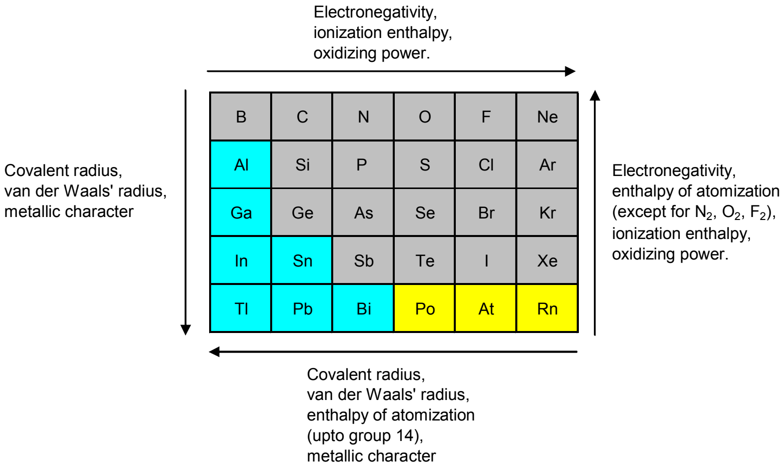
The p–block elements have general valence shell electronic configuration $ns^2 np^{1-6}$.

The first member of each group from 13–17 of the p–block elements differ in many respects from the other members of their respective groups because of small size, high electronegativity and absence of d–orbitals.

The first member of a gorup also has greater ability to form $p\pi$–$p\pi$ multiple bonds to itself (e.g. $C = C$, $C \equiv C$, $N \equiv N$) and to element of second row (e.g $C = O$, $C = N$, $C \equiv N$, $N = O$) compared to the other members of the same group.

The highest oxidation of p–block element is equal to the group number minus 10. Moving down the group, the oxidation state two less than the highest group oxidation state becomes more stable in groups 13 to 16 due to inert pair effect (reluctance of s-subshell electrons to participate in chemical bonding)

TRENDS IN PROPERTIES OF p-BLOCK ELEMENTS.



B	C	N	O	F	Ne
Al	Si	P	S	Cl	Ar
Ga	Ge	As	Se	Br	Kr
In	Sn	Sb	Te	I	Xe
Tl	Pb	Bi	Po	At	Rn

(A) GROUP 13 ELEMENTS : THE BORON FAMILY

Boron is a typical non-metal, aluminium is a metal but shows many chemical similarities to boron , and gallium, indium and thallium are almost exclusively metallic in character,

Electronic Configuration:

The outer electronic configuration of these elements is $ns^2 np^1$.

Atomic Radii :

On moving down the group, for each successive member one extra shell of electrons is added and therefore, atomic radius is expected to increases. Atomic radius of Ga is less than of Al. The presence of additional 10 d-electrons offer only poor screening effect for the outer electrons from the increased nuclear charge in gallium. Consequentlym, the atomic redius of gallium (135 pm) is less than that of aluminium (143 pm).

Ionization Enthalpy:

The ionisation enthalpy values as expected from the general trends do not decrease smoothly down the group . The decreases from B to Al is associated with increases in size. The observed discontinuity in the ionisation enthalpy values between Al and Ga, and between In and Tl are due to inability of d- and f electrons, which have low screening effect, to compensate the increase in nuclear charge. The sum of the first three ionisation enthalpies for each of the elements is very high .

Electronegativity:

Down the group, electronegativity first decreases from B to Al and then increases marginally. This is because of the discrepancies in atomic size of the elements.

Physical Properties

Boron is non-metallic in nature . It is extremely hard and black coloured solid. It exists in many allotropic forms. Due to very strong crystalline lattice, boron has unusually high melting point. Rest of the member are soft metals with low melting point and high electrical conductivity. Gallium with low melting point (303 K), could exist in liquid state during summer. Its high boiling point (2676 K) makes it a useful material for measuring high temperatures. Density of the elements increases down the group from boron to thallium.

Atomic & physical properties :

Element		B	Al	Ga	In	Tl
Atomic Number		5	13	31	49	81
Atomic Mass		10.81	26.98	69.72	114.82	204.38
Electronic configuration		$[He]\ 2s^2\ 2p^1$	$[Ne]\ 3s^2\ 3p^1$	$[Ar]\ 3d^{10}\ 4s^2 4p^1$	$[Kr]\ 4d^{10}\ 5s^2\ 5p^1$	$[Xe]\ 4f^{14}\ 5d^{10}\ 6s^2 6p^1$
Atomic Radius / pm		85	143	135	167	170
Ionic Radius M^{3+} / pm		–	53.5	62	80	88.5
Ionization enthalpy / ($kJ\ mol^{-1}$)	I	800	577	578	558	590
	II	2427	1816	1979	1820	1971
	III	3659	2744	2962	2704	2877
Electronegativity		2.0	1.5	1.6	1.7	1.8
Density/[$g\ cm^{-3}$ (293 K)]		2.35	2.70	5.90	7.31	11.85
Melting point / K		2453	933	303	430	576
Boiling point / K		3923	2740	2676	2353	1730

Chemical Properties :

Oxidation state and trends in chemical reactivity :

Due to small size of boron, the sum of its first three ionization enthalpies is very high. This prevents it to form + 3 ions and force it to form only covalent compounds. But as we move from B to Al, the sum of the first three ionisation enthalpies of Al considerably decreases, and is therefore able to form Al^{+3} ions. However, down the group, due to poor shielding, effective nuclear charge holds ns electrons tightly (responsible for inert pair effect) and thereby, restricting their participation in bonding. As a result of this only p-orbital electron may be involved in bonding. In fact in Ga, In and Tl, both + 1 and + 3 oxidations states are observed. The relative stability of + 1 oxidations state progressively increases for heavier elements: Al < Ga < In < Tl. In thallium +1 oxidation state is predominant and + 3 oxidation state highly oxidising in character. The compound in +1 oxidation state , as expected from energy considerations, are more ionic than those in + 3 oxidations state.

In trivalent state, the number of electrons around the central atom in a molecule of the compounds of these elements (e.g., boron in BF_3) will be only six.

Such **electron deficient** molecules have tendency to accept a pair of electrons to achieve stable electronic configuration and thus, behave as Lewis acids. The tendency to behave as Lewis acid decreases with the increases in the size down the group. BCl_3 easily accepts a lone pair of electrons from ammonia to form $BCl_3.NH_3$. In trivalent state most of the compounds being covalent are hydrolysed in water. The trichloride on hydrolysis in water form tetrahedral $[M(OH)_4]^-$ species; Aluminium chloride in acidified aqueous solution form octahedral $[Al(H_2O)_6]^{3+}$ ion.

(i) Reactivity towards air

Boron is unreactive in crystalline form. Aluminium forms a very thin oxide layer on the surface which protects the metal from further attack. Amorphous boron and aluminium metal on heating in air form B_2O_3 and Al_2O_3 respectively. With dinitrogen at high temperature they form nitrides.

$$2E(s) + 3\,O_2\,(g) \xrightarrow{\Delta} 2\,E_2O_3(s)\ ;\ 2E(s) + N_2(g) \xrightarrow{\Delta} 2\,EN\,(s).$$

The nature of these oxides varies down the group. Boron trioxide is acidic and reacts with basic (metallic) oxides forming metal borates. Aluminium and gallium oxides are amphoteric and those of indium and thallium are basic in their properties.

(ii) Reactivity towards acids and alkalies

Boron does not react with acids and alkalies even at moderate temperature; but aluminium dissolves in mineral acids and aqueous alkalies and thus shows amphoteric character.

Aluminimum dissolved in dilute HCl and liberates dihydrogen. However, concentrated nitric acid renders aluminium passive by forming protective oxide layer on the surface . Aluminium also reacts with aqueous alkali and liberates dihydrogen .

$$2\,Al(s) + 6\,HCl(aq) \longrightarrow 2\,Al^{3+}(aq) + 6\,Cl^{-}(aq) + 3\,H_2(g)$$

$$2Al(s) + 2NaOH\,(aq) + 6H_2O\,(1) \longrightarrow 2Na^{+}[Al(OH)_4]^{-}(aq) + 3H_2(g)$$

Sodium tetrahydroxoaluminate (III)

(iii) Reactivity towards halogens

These elements react with halogen to form trihalides (except TlI_3).

$$2E(s) + 3X_2(g) \rightarrow 2EX_3(s) \qquad (X = F, Cl\ Br, I)$$

IMPORTANT TRENDS AND ANOMALOUS PROPERTIES OF BORON

The tri-chlordes, bromides and iodies of all these elements being covalent in nature are hydrolysed in water. Species like tetrahedral $[M(OH)_4]^{-}$ and octahedral $[M(H_2O)_6]^{3+}$,except in boron, exist in aqueous medium.

It is due to the absence of d orbitals that the maximum covalence of boron is 4. Since the d-orbitals are available with Al and other elements, the maximum covalence can be expected beyond 4.

● BORON (B):

❍ OCCURRENCE :

Boron occurs in nature in the form of the following minerals:

(i) Borax $(Na^{+})_2B_4O_7^{2-}.10H_2O$.(Boron is part of an anionic complex), (ii) Boric acid H_3BO_3,
(iii) Kernite $Na_2B_4O_7 . 4H_2O$ & (iv) Colemanite $Ca_2B_6O_{11}. 5H_2O$

❍ EXTRACTION OF BORON :

(i) By the reduction of B_2O_3 with magnesium, sodium or potassium in the absence of air :

$$Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 4H_3BO_3 + 2NaCl$$

$$2H_3BO_3 \xrightarrow{\Delta} B_2O_3 + 3H_2O\ ; \qquad B_2O_3 + 3Mg \longrightarrow 2B + 3MgO$$

The product thus obtained is boiled with HCl and filtered when K_2O or MgO dissolves leaving behind elemental boron. It is thoroughly washed to remove HCl and then dried finally.

Brown amorphous powder of B is obtained in this way.

(ii) From potassium fluoroborate (KBF_4) by heating it with potassium metal.

$$KBF_4 + 3K \xrightarrow{\Delta} 4KF + B.$$

It is then treated with dilute HCl to remove KF and B is then washed and dried.

(iii) In small quantities in pure form (crystalline boron) by the

(i) Reduction of BBr_3 with H_2 on a heated titanium metal filament at 1275-1475 K

The vapours of Br_2 are absorbed in Cu and the residual vapours of boron are condensed.

(ii) Decomposition of BI_3 vapours by means of high tension arc (80 kV) through tungsten electrodes.

$$2BI_3 \longrightarrow 2B\uparrow + 3\,I_2\uparrow \qquad \text{(Van Arkel mehod).}$$

❍ PROPERTIES :

(i) It exists in five forms, four of which are crystalline and one is amorphous. All crystalline forms are very hard made up of clusters of B_{12} units. All crystalline forms are black in appearance and chemically inert. Melting points are around 2300°C. But amorphous form is brown and chemically active.

(ii) Reaction with air :

$$4B + 3O_2 \xrightarrow{700°C} 2B_2O_3$$

$$2B + N_2 \xrightarrow{700°C} 2BN \; ; \qquad BN + 3H_2O \xrightarrow{\text{High temperature, pressure}} H_3BO_3 + NH_3$$

(iii) Action of alkalies and acids :

$$2B + 2NaOH + 2H_2O \longrightarrow 2NaBO_2 + 3H_2$$

$$2B + 3H_2SO_4 \xrightarrow{\text{oxidation}} 2H_3BO_3 + 3SO_2$$

$$2B + 6HNO_3 \xrightarrow{\text{oxidation}} 2H_3BO_3 + 6NO_2$$

(iv) Reaction with Mg and Ca :

$$3Mg + 2B \longrightarrow Mg_3B_2$$

$$3Ca + 2B \longrightarrow Ca_3B_2$$

Mg_3B_2 on consequent hydrolysis gives diborane.

$$Mg_3B_2 + 6HCl \xrightarrow{\text{hydrolysis}} 3MgCl_2 + B_2H_6 \quad ; \qquad B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$$

(v) Reducing properties :

$$3SiO_2 + 4B \longrightarrow 2B_2O_3 + 3Si$$

$$3CO_2 + 4B \longrightarrow 2B_2O_3 + 3C$$

(vi) It decomposes steam liberating hydrogen gas.

$$2B + 3H_2O(\text{steam}) \longrightarrow B_2O_3 + 3H_2$$

❍ USES :

Boron is used in the construction of high impact-resistant steel and, since it absorbs neutrons, in reactor rods for controlling atomic reactions.

❍ COMPOUNDS OF BORON :

❍ BORON TRIOXIDE (B_2O_3) :

❍ PREPARATION :

$$\underset{\text{Boric acid}}{H_3BO_3} \xrightarrow{100°C} HBO_2 \xrightarrow{160°C} H_2B_4O_7 \xrightarrow{\text{red heat}} B_2O_3$$

❍ PROPERTIES :

It is a weakly acidic oxide and reacts with alkalies or bases to form borates.

$3Na_2O + B_2O_3 \rightarrow 2Na_3BO_3$ (sodium orthoborate).

It reacts with water slowly to form orthoboric acid. When heated with transition metal salts, it forms coloured compounds.

$$H_2O + B_2O_3 \rightarrow 2HBO_2 \; ; \qquad HBO_2 + H_2O \rightarrow H_3BO_3$$

$$3B_2O_3 + Cr_2(SO_4)_3 \xrightarrow{\Delta} 3SO_3\uparrow + 2Cr(BO_2)_3(\text{green})$$

$$2B_2O_3 + 2Cu(NO_3)_2 \xrightarrow{\Delta} 4NO_2\uparrow + O_2\uparrow + 2Cu(BO_2)_2 \text{ (blue)}$$

$$B_2O_3 + P_2O_5 \rightleftharpoons 2BPO_4$$

❍ ORTHOBORIC ACID (H_3BO_3) :

Among the oxyacids of boron are

❍ PREPARATION :

(i) It is precipitated by treating a concentrated solution of borax with sulphuric acid.
$Na_2B_4O_7 + H_2SO_4 + 5H_2O \rightarrow Na_2SO_4 + 4H_3BO_3 \downarrow$

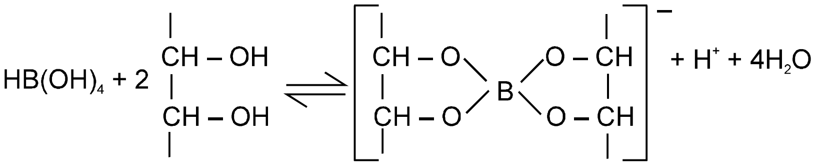
(ii) From Colemanite: Powdered colemanite is suspended in water and excess SO_2 is passed through it. On filtering and cooling the filtrate, white crystals of H_3BO_3 are obtained.
$Ca_2B_6O_{11} + 2SO_2 + 11H_2O \longrightarrow 2Ca(HSO_3)_2 + 6H_3BO_3$

❍ PROPERTIES:

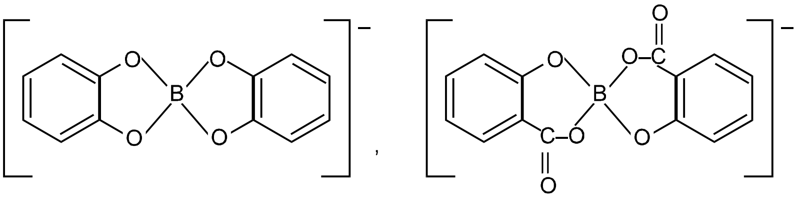
(i) It is a weak monobasic acid and in aqueous solution the boron atom completes its octet by removing OH^- from water molecules:

$$B(OH)_3(aq) + 2H_2O(\ell) \rightarrow B(OH)_4^-(aq) + H_3O^+(aq).$$

It, therefore, functions as a Lewis acid and not as a proton donor.
It behaves as strong acid when a polyhydroxy compound such as glycol or glycerol is added to its aqueous solution. The acidity is due to the high stability of the conjugate bone chelate complex.



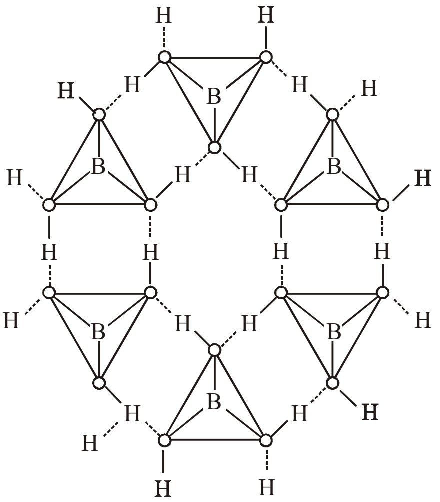
Ethanol does not form similar complex but catechol, salicylic acids form similar complexes.



When heated it first forms metaboric acid (HBO_2) and then boron trioxide.

$$\underset{\text{Boric acid}}{H_3BO_3} \xrightarrow{100^\circ C} HBO_2 \xrightarrow{160^\circ C} H_2B_4O_7 \xrightarrow{\text{red heat}} B_2O_3$$

Orthoboric acid is greasy to touch less soluble in cold water but more soluble in hot water. It has a layered structure in which planar BO_3 units are joined by hydrogen bonds.



❍ **TEST FOR BORATE RADICAL :**

When boric acid is heated with ethyl alcohol, the evolved gas is burned forming a green edged flame.

$$H_3BO_3 + 3C_2H_5OH \longrightarrow \underset{\text{ethyl borate (volatile)}}{B(OC_2H_5)_3} + 3H_2O$$

❍ **USES :**

It is an antiseptic and its water solution is used as an eyewash. It is also used in glass, enamel and pottery industry.

❍ **BORAX ($Na_2B_4O_7.10H_2O$) :**

❍ **PREPARATION:** It is found in nature but can also be prepared by the following methods.

(i) From Colemanite.

When colemanite powder is heated with Na_2CO_3 solution, the following reaction occurs with the precipitation of $CaCO_3$.

$$Ca_2B_6O_{11} + 2Na_2CO_3 \longrightarrow 2CaCO_3\downarrow + Na_2B_4O_7 + 2NaBO_2$$

The filterate is cooled when white crystals of borax are precipitated. The mother liquor on treatment with CO_2 converts $NaBO_2$ to $Na_2B_4O_7$ which precipitates out on crystallization.

$$4NaBO_2 + CO_2 \longrightarrow Na_2B_4O_7 + Na_2CO_3$$

(ii) From orthoboric acid.

Borax is obtained by the action of Na_2CO_3 on orthoboric acid.

$$4H_3BO_3 + Na_2CO_3 \longrightarrow Na_2B_4O_7 + 6H_2O + CO_2\uparrow$$

❍ **PROPERTIES:**

(i) Borax is a white powder, less soluble in cold water, more soluble in hot water.

(ii) Its aqueous solution is alkaline because of its hydrolysis to weak acid H_3BO_3 and strong alkali NaOH.

$$Na_2B_4O_7 + 7H_2O \longrightarrow 4H_3BO_3 + 2NaOH$$

(iii) Action of heat.

When borax powder is heated, it first swells due to loss of water in the form of steam but at 740ºC it becomes converted into colourless transparent borax bead.

$$Na_2B_4O_7.10H_2O + \xrightarrow{\Delta} Na_2B_4O_7 + 10\ H_2O\uparrow$$

$$Na_2B_4O_7 \xrightarrow{740^\circ C} 2NaBO_2 + B_2O_3 \text{ (borax bead)}$$

(iv) Action of acids :

$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + 4H_3BO_3 \text{ (boric acid)}$$

On cooking, the white flakes of boric acid are obtained

(v) $Na_2B_4O_7 \xrightarrow{NaOH} NaBO_2 \xrightarrow{H_2O_2} Na_2\ [(OH)_2\ B(O\text{–}O)_2\ B\ (OH)_2]\ 6H_2O$

☞ Correct formula of borax is $Na_2[B_4O_5(OH)_4]\ .\ 8H_2O$

❍ **BORAX-BEAD TEST :** Boric anhydride reacts with certain metal salts such as, Ni^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Mn^{2+} etc. to form coloured metaborates. The colour of the metaborates can be used to identify the metallic ions (cations) in salts.

$$Na_2B_4O_7.\ 10H_2O \xrightarrow[-10H_2O]{\Delta} Na_2B_4O_7 \xrightarrow{740°C} \underbrace{2NaBO_2 + B_2O_3}_{\text{glassy mass}} ;\ CuO + B_2O_3 \longrightarrow Cu(BO_2)_2 \text{ (blue bead)}$$

USES :

It is used

(i) in borax bead test, (ii) in purifying gold, (iii) as flux during welding of metals and (iv) in production of glass.

DIBORANE (B_2H_6) :

Binary compounds of B with H are called boron hydrides or boranes. These compounds form following two types of series :

B_nH_{n+4} - B_2H_6, B_5H_9, B_6H_{10}, $B_{10}H_{14}$
B_nH_{n+6} - B_4H_{10}, B_5H_{11}, B_6H_{12}, B_9H_{15}

The chemistry of diborane has aroused considerable interest because of its usefulness in many synthetic reactions and also because the elucidation of its structure helped to clarify the basic concepts about the structure of electron deficient compounds.

PREPARATION :

(i) $4BF_3 + 3LiAlH_4 \xrightarrow{\text{ether}} 2B_2H_6 + 3LiF + 3AlF_3$

(ii) $2BCl_3 + 6H_2 \text{ (excess)} \xrightarrow[\text{discharge}]{\text{silent electric}} B_2H_6 + 6HCl$

(iii) $8BF_3 + 6LiH \xrightarrow{\text{ether}} B_2H_6 + 6LiBF_4$

(iv) $2NaBH_4 + I_2 \xrightarrow{\text{ether}} B_2H_6 + 2NaI + H_2$

(v) $3NaBH_4 + 4BF_3 \xrightarrow[450\text{ K}]{\text{ether}} 3NaBF_4 + 2B_2H_6$

(vi) It can also be prepared by treating $NaBH_4$ with concentrated H_2SO_4 or H_3PO_4.

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

$2NaBH_4 + 2H_3PO_4 \longrightarrow B_2H_6 + 2H_2 + 2NaH_2PO_4$

(vii) $2BF_3 + 6NaH \xrightarrow{450\text{ K}} B_2H_6 + 6NaF$ (Industrial method)

PROPERTIES :

(i) Diborane is a colourless gas (boiling point 183 K).

(ii) It is rapidly decomposed by water with the formation of H_3BO_3 & H_2:

$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$

(iii) Mixtures of diborane with air or oxygen inflame spontaneously producing large amount of heat. Diborane has a higher heat of combustion per unit weight of fuel than most other fuels. It is therefore used as a rocket fuel.

$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O \quad \Delta H = -1976 \text{ kJ mol}^{-1}$

(iv) Pyrolysis of B_2H_6 in sealed vessels at temperatures above 375 K is an exceedingly complex process producing a mixture of various boranes, eg, B_4H_{10}, B_5H_9, B_6H_{12}, and $B_{10}H_{14}$.

(v) Diborane undergoes a facile addition reaction with alkenes and alkynes in ether solvents at room temperature to form organoboranes. This reaction is known as hydroboration reaction

(vi) $B_2H_6 + HCl \longrightarrow B_2H_5Cl + H_2$ (vii) $B_2H_6 + 6MeOH \longrightarrow 2B(OMe)_3 + 6H_2$

(vii) Cleavage reactions

(a) $B_2H_6 + 2Me_3N \longrightarrow 2Me_3NBH_3$ (b) $B_2H_6 + 2Me_3P \longrightarrow 2Me_3PBH_3$

(c) $B_2H_6 + 2CO \xrightarrow{200°C,\ 20\ atm} 2BH_3CO$ (borane carbonyl)

(viii) $B_2H_6 + 2Et_2S \longrightarrow 2Et_2SBH_3$

(ix) $3B_2H_6 + 6NH_3 \xrightarrow{\text{low temprature}} B_2H_6 . 2NH_3$ or $[BH_2(NH_3)_2]^+ BH_4^- \xrightarrow{200°C} B_3N_3H_6$ (borazole) $+ 12H_2$

(x) $B_2H_6 + 2KOH + 2H_2O \longrightarrow 2KBO_2 + 6H_2$ (xv) $B_2H_6 + 6Cl_2 \longrightarrow 2BCl_3 + 6HCl$

(xi) $B_2H_6 + 2LiH \longrightarrow 2LiBH_4$

● ALUMINIUM (Al) :

❍ EXTRACTION (HALL-HEROULT PROCESS):

The aluminium is extracted from ore bauxite ($Al_2O_3.2H_2O$). The ore is first purified by Bayere's process. The anhydrous Al_2O_3 is mixed with Na_3AlF_6 & CaF_2 & then fused. The fused mixture is subjected to electrolytic reduction when aluminium is obtained at cathode.

☞ Aluminium is purified by Hoope's process

❍ PROPERTIES:

(i) It is a silvery metal with a density of 2.7 g/cc, having a melting point of 660°C, and is a good conductor of heat and electricity. It is malleable and ductile.

(ii) Action of air: Dry air has no action on aluminium. But moist air forms a thin layer of Al_2O_3 on its surface and it loses its luster. At very high temperatures it burns to form Al_2O_3 and AlN.

(iii) Reaction with halogens: When gaseous halogens are passed over aluminium, its halide are formed in an anhydrous form. $2Al + 3Cl_2 \longrightarrow 2AlCl_3$

(iv) Action of alkalies: When warmed with concentrated NaOH, it liberates H_2 gas and a colourless solution of sodium aluminate is formed.

$2Al + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2 + 3H_2\uparrow$

(v) Action of acids: Aluminium reacts with dilute H_2SO_4 and dilute HCl but concentrated HNO_3 does not react with aluminium because aluminium becomes passive by the action of concentrated HNO_3 forming a protective oxide layer on the surface.

$2Al + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2\uparrow$; $2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2\uparrow$

(vi) Reaction with N_2: When N_2 gas is passed over heated aluminium, aluminium nitride is formed. Hot aluminium thus acts as an absorbing agent for N_2.

$2Al + N_2 \longrightarrow 2AlN$

AlN reacts with hot water to form $Al(OH)_3$ and NH_3

(vii) Reaction with water: Aluminium does not react with cold water. It is very slowly attacked by boiling water or steam.

$2Al + 3H_2O \longrightarrow Al(OH)_3 + 3H_2\uparrow$

(viii) Action of $HgCl_2$ solution: When aluminium is added to $HgCl_2$ solution mercury is liberated.

$3HgCl_2 + 2Al \longrightarrow 2AlCl_3 + 3Hg\downarrow$

(ix) Reduction of oxides of metals: When oxides of less reactive metal than aluminium is heated with aluminium, the other metal is liberated.

$3MnO_2 + 4Al + \xrightarrow{\Delta} 2Al_2O_3 + 3Mn$; $Cr_2O_3 + 2Al + \xrightarrow{\Delta} Al_2O_3 + 2Cr$

- **USES :**

It is extensively used

(i) for manufacture of cooking and household utencils.
(ii) as aluminium plating for tanks, pipes, iron bars and other steel objects to prevent corrosion.
(iii) for manufacture of aluminium cables.
(iv) for making precision instruments, surgical apparatus, aircraft bodies, rail coaches, motorboats, car

COMPOUNDS OF ALUMINIUM :

ALUMINIUM OXIDE (Al_2O_3) :

It is also called alumina. It occurs in nature in the form of bauxite and corundum. It is also found in the form of gems. Some important aluminium oxide gems are:

(A) Topaz-yellow, (B) Sapphire-blue, (C) Ruby-red, (D) Amethyst-violet, (E) Emerald-green

- **PREPARATION:**

Pure Al_2O_3 is obtained by igniting $Al_2(SO_4)_3$, $Al(OH)_3$ or ammonium alum.

$Al_2(SO_4)_3 + \xrightarrow{\Delta} Al_2O_3 + 3SO_3\uparrow$; $2Al(OH)_3 + \xrightarrow{\Delta} Al_2O_3 + 3H_2O\uparrow$

$(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O \xrightarrow{\Delta} 2NH_3\uparrow + Al_2O_3 + 4SO_2\uparrow + 25H_2O\uparrow$

- **PROPERTIES :**

It is a white amorphous powder insoluble in water but soluble in acids (forming eg., $AlCl_3$) as well as alkalies (forming $NaAlO_2$), Thus amphoteric in nature. It is a polar covalent compound.

- **USES :**

It is used

(i) for the extraction of aluminium.
(ii) for making artificial gems.
(iii) for the preparation of compounds of aluminium.
(iv) in making furnace linings. It is a refractory material.
(v) as a catalyst in organic reactions.

ALUMINIUM CHLORIDE ($AlCl_3.6H_2O$) :

It is a colourless crystalline solid, soluble in water. It is covalent. Anhydrous $AlCl_3$ is a deliquescent white solid.

- **PREPARATION :**

(i) By dissolving aluminium, Al_2O_3, or $Al(OH)_3$ in dilute HCl :

$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2\uparrow$; $Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$; $Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$

The solution obtained is filtered and crystallized when the crystals of $AlCl_3.6H_2O$ are obtained.

(ii) Anhydrous $AlCl_3$ is obtained by the action of Cl_2 on heated aluminium.

(iii) By heating a mixture of Al_2O_3 and coke and passing chlorine over it.

$Al_2O_3 + 3C + 3Cl_2 \longrightarrow 2AlCl_3$ (anhydrous) $+ 3CO\uparrow$

❍ PROPERTIES :

(i) Action of heat:

Hydrated salt when heated strongly is converted to Al_2O_3.

$$2AlCl_3.6H_2O \xrightarrow{\Delta} Al_2O_3 + 6HCl\uparrow + 9H_2O$$

(ii) Action of moisture on anhydrous $AlCl_3$:

When exposed to air, anhydrous $AlCl_3$ produces white fumes of HCl

$AlCl_3 + 3H_2O \Leftrightarrow Al(OH)_3 + 3HCl\uparrow$

(iii) Action of NH_3:

Anhydrous $AlCl_3$ absorbs NH_3 since the latter is a Lewis acid.

$AlCl_3 + 6NH_3 \rightarrow AlCl_3.6NH_3$ (white solid)

(iv) Action of NaOH solution:

When NaOH solution is added dropwise to an aqueous $AlCl_3$ solution, a gelatinous precipitate of $Al(OH)_3$ is first formed which dissolves in excess of NaOH solution to give a colourless solution of sodium aluminate.

$AlCl_3 + 3NaOH \rightarrow Al(OH)_3\downarrow + 3NaCl$; $\quad Al(OH)_3 + NaOH \rightarrow NaAlO_2 + 2H_2O$

This reaction is important as a test to distinguish between an aluminium salt from salts of Mg, Ca, Sr, and Ba. (When NaOH solution is added to their salt solutions, a white precipitate of hydroxide forms which does not dissolve in excess of NaOH).

(v) Action of NH_4OH solution:

When NH_4OH solution is added to a solution of $AlCl_3$, a white precipitate of $Al(OH)_3$ is formed which does not dissolve in excess of NH_4OH.

$AlCl_3 + 3NH_4OH \rightarrow Al(OH)_3\downarrow$ (white gelatinous) $+ 3NH_4Cl$

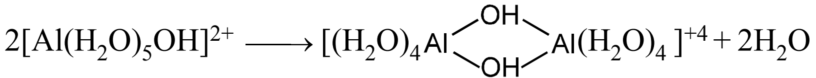
This reaction is important as a test to distinguish an Al salt from a Zn salt. (With a Zn salt a white precipitate of $Zn(OH)_2$ is formed which dissolves in excess of NH_4OH solution).

(vi) Hydrolysis with water:

When $AlCl_3$ is dissolved in water, it undergoes hydrolysis rapidly to produce $Al(OH)_3$ which is a weak base and HCl which is a strong acid. Hence the solution is acidic to litmus.

$[Al(H_2O)_6]^{3+} \rightleftharpoons [Al(H_2O)_5OH]^{+2} + H^+$

The complex cation has a high tendency to get dimerised.



$$2[Al(H_2O)_5OH]^{2+} \longrightarrow [(H_2O)_4Al(OH)_2Al(H_2O)_4]^{+4} + 2H_2O$$

(vii) $4LiH + AlCl_3 \longrightarrow LiAlH_4 + 3LiCl$

❍ USES :

It is used :

(i) as catalyst for cracking of petroleum.

(ii) as catalyst in Friedel-Crafts reactions.

(iii) for preparing aluminium compounds.

❍ ALUMS ; M_2SO_4. M'_2 $(SO_4)_3$. $24H_2O$ OR MM' $(SO_4)_2$. $12H_2O$

Alums are transparent crystalline solids having the above general formula where M is a univalent metal or positive radical and M′ is a trivalent metal. Some important alums are:

(i) Potash alum $K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$ (ii) Chrome alum $K_2SO_4 . Cr_2(SO_4)_3 . 24H_2O$

(iii) Ferric alum $K_2SO_4 . Fe_2(SO_4)_3 . 24H_2O$ (iv) Ammonium alum $(NH_4)_2SO_4 . Al_2(SO_4)_3 . 24H_2O$

Alums are double salts which when dissolved in water produce metal ions(or ammonium ions) and the sulphate ions.

❍ PREPARATION :

Alums can be prepared by fusing M_2SO_4 & $M'_2(SO_4)_3$ in 1 : 1 molar ratio & the resulting mass is dissolved into water. From the solution thus obtained, alums are crystallised.

❍ USES :

It is used

(i) as a mordant in dye industry
(ii) as a germicide for water purification
(iii) as a coagulating agent for precipitating colloidal impurities from water.

(B) GROUP 14 ELEMENTS : THE CARBON FAMILY

Carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb) are the members of group 14. Naturally occurring carbon contains two stable isotopes: ^{12}C and ^{13}C. In addition to these third isotopes, ^{14}C is also presents , it is a radioactive isotope with half-life 5770 years and used for radiocarbon dating. Silicon is a very important component of ceramices, glass and cement. Germanium exists only in traces. Tin occurs mainly as cassiterite, SnO_2 and lead as galena, PbS. Ultrapure form of germanium and silicon are used to make transistors and semiconductor devices.

Electronic Configuration :

The valence shell electronic configuration of these elements is $ns^2 np^2$.

Covalent Radius :

There is a considerable increase in covalent radius from C to Si, thereafter from Si to Pb a small increase in radius is observed. This is due to the presence of completey filled d and f orbitals in heavier members.

Ionization Enthalpy :

The first ionization enthalpy of group 14 members is higher than the corresponding members of group 13. The influence of inner core electron is visible here also. In general the ionisation enthalpy decreases down the group.Small decreases in $\Delta_i H$ from Si to Ge to Sn and slight increase in $\Delta_i H$ from Sn to Pb is the consequence of poor shielding effects of intervening d and f–orbitals and increases in size of the atom.

Electronegativity :

Due to small size, the elements of this group are slightly more electronegative than group 13 elements. The electronegativity value for elements from Si to Pb are almost the same.

Physical Properties :

All group 14 members are solids. Carbon and silicon are non-metals, germanium is metalloid whereas tin and lead are soft metals with low melting points. Melting points and boiling points of group 14 elements are much higher than those of corresponding elements of group 13.

ATOMIC & PHYSICAL PROPERTIES

Element		C	Si	Ge	Sn	Pb
Atomic Number		6	14	32	50	82
Atomic Mass		12.01	28.09	72.60	118.71	207.2
Electronic configuration		[He] $2s^2$ $2p^2$	[Ne] $3s^2$ $3p^2$	[Ar] $3d^{10}$ $4s^2$ $4p^2$	[Kr] $4d^{10}$ $5s^2$ $5p^2$	[Xe] $4f^{14}$ $5d^{10}$ $6s^2$ $6p^2$
Atomic Radius / pm		77	118	122	140	146
Ionic Radius M^{+4} / pm		–	40	53	69	78
Ionization enthalpy / (kJ mol^{-1})	I	1086	786	761	708	715
	II	2352	1577	1537	11411	1450
	III	4620	3228	3300	2942	3081
Electronegativity		2.5	1.8	1.8	1.8	1.9
Melting point / K		4373	1693	1218	505	600
Boiling point / K		–	3550	3123	2896	2024

Chemical Properties :

Oxidation states and trends in chemical reactivity :

The group 14 elements have four electrons in outermost shell. The common oxidation states exhibited by these elements are + 4 and + 2. Carbon also exhibits negative oxidation states.Since the sum of the first four ionization enthalpies is very high, compound in +4 oxidation state are generally covalent in nature. In heavier members the tendency to show +2 oxidation state increases in the sequence Ge < Sn < Pb. It is due to the inability of ns^2 electrons of valence shell to participate in bonding. The relative stabilities of these two oxidation states vary down the group. Carbon cannot exceed its covalence more than 4. Other elements of the group can do so. It is because of the presence of d orbital in them. Due to this, their halides undergo hydrolysis and have tendency to form complexes by accepting electron pairs from donor species. For example, the species like ,SiF_6^{2-} . $[GeCl_6]^{2-}$,$[Sn(OH)_6]^{2-}$ exist .

(i) Reactivity towards oxygen :

All members when heated in oxygen form oxides. There are mainly two types of oxides, i.e. monoxide and dioxide of formula MO and MO_2 respectively. SiO only exists at high temperature. Oxides in higher oxidation states of elements are generally more acidic than those in lower oxidation state. The dioxides – CO_2, SiO_2 and GeO_2 are acidic, whereas SnO_2 and PbO_2 are amphoteric in nature. Among monoxides, CO is neutral, GeO is distinctly acidic whereas SnO and PbO are amphoteric .

(ii) Reactivity towards water :

Carbon , silicon and germanium are not affected by water . Tin decomposes steam to form dioxide and dihydrogen gas. Lead is unaffected by water, probably becauses of a protective oxide film formation.

(iii) Reactivity towards halogen :

These elements can form halides of formula MX_2 and MX_4 (where X = F, Cl Br, I). Except carbon all other members react directly with halogen under suitable condition to make halides. Most of the MX_4 are covalent in nature. Exceptions are SnF_4 and PbF_4, which are ionic in nature . PbI_4 does not exist because Pb–I bond initially formed during the reaction does not release enough energy to unpair $6s^2$ electrons and excite one of them to higher orbital to have four unpaired electrons around lead atom. Heavier members Ge to Pb are able to make halides of formula MX_2 . Stability of dihalides increases down the group. Except CCl_4 other tetrachlorides are easily hydrolysed by water because the central atom can accommodate the lone pair of electrons from oxygen atom of water molecules in d orbital.

IMPORTANT TRENDS AND ANOMALOUS BEHAVIOUR OF CARBON

Like first member of other groups, carbon also differs from rest of the members of its group. It is due to its smaller size, higher electronegativity, higher ionisation enthalpy and unavailability of d orbitals. Accommodate only four pairs of electrons around it. This would limit the maximum covalence to four whereas other members can expand their covalence due to the presence of d orbitals, Carbon also has unique ability to form $p\pi$-$p\pi$ multiple bonds with itself and with other atoms of small size and high electronegativity. Few example of multiple bonding are $C = C$, $C \equiv C$, $C = O$ $C = S$ and $C \equiv N$. Heavier elements do not form $p\pi$-$p\pi$ bonds because their atomic orbital are too large and diffuse to have effective overlapping .

Carbon atoms have the tendency to link with one another through covalent bonds to form chains and rings. This property is called catenation. This is becauses C–C bonds are very strong. Down the group the size increases tendency to show catenation decreases. This can be clearly seen from bond enthalpies values. The order of catenation is C > > Si > Ge ≈ Sn. Lead does not show catenation. Due to the property of catenation and $p\pi$-$p\pi$ bonds formation, carbon is able to show allotropic forms.

ALLOTROPES OF CARBON

Carbon exhibits many allotropic forms; both crystallic as well as amorphous. Diamond and graphite are two well-known crystalline forms of carbon. In 1985 third form of carbon known as **fullerenes** was discovered by H.W. Kroto, E Smalley and R.F.Curl.

Diamond :

It has a crystalline lattice. In diamond each carbon atom undergoes sp^3 hybridisation and linked to four other carbon atoms by using hybridised orbitals in tetrahedral fashion. The C–C bond length is 154 pm. The structure extends in space and produces a rigid three dimensional network of carbon atoms .In this structure directional covalent bonds are presents throughout the lattice.

It is very difficult to break extended covalent bonding and therefore, diamond is a hardest substance on the earth. It is used as an abrasive for sharpening hard tools in making dyes and in the manufacture of tungsten filament for electric light bulbs.

Graphite :

Graphite has layered structure. Layers are held by van der Waal's forces and distance between two layers is 340 pm. Each layer is composed of planar hexagonal rings of carbon atoms. C – C bond length within the layer is 141.5 pm Each carbon atom in hexagonal ring undergoes sp^2 hybridisation and make three sigma bonds with three neighbouring carbon atoms. Fourth electron forms a π bond. The electrons are delocalised over the whole sheet. Electrons are mobile and , therefore graphite conducts electricity along the sheet. Graphite cleaves easily between the layers and therefore, it is very soft and slippery. For this reason graphite is used as a dry lubricant in machines running at high temperature, where oil cannot be used as a lubricant.

Fullerenes :

Fullerenes are made by the heating of graphite in an electrical arc in the presence of inert gases such as helium or argon. Fullerences are the only pure form of carbon becauses they have smooth structure without having 'dangling' bonds. Fulleren are cage like molecules. C_{60} molecule has a shape like soccer ball and called **Buckminsterfullerene.** It contains twenty six -membered rings and twelve five membered rings. A six membered ring is fused with six or five membered rings but a five membered ring can only fuse with six membered rings. All the carbon atoms are equal and they undergo sp^2 hybridisation. Each carbon atom forms three sigma bonds with other three carbon atoms. The remaining electron at each carbon atom is delocalised in molecular orbitals, which in turn give aromatic character to molecule. This ball shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C – C distance of 143.5 pm and 138.3 pm respectively. Spherical fullerenes are also called bucky balls in short. It is very important to know that graphite is thermodynamically most stable allotrope of carbon and, therefore, $\Delta_f H^{(-)}$ values of diamond and fullerene, C_{60} are 1.90 and 38.1 kJ mol^{-1}, respectively. Carbon black is obtained by burning hydrocarbons in a limited supply of air.

Uses of carbon :

Graphite fibres embedded in plastic material form high strength, lightweight composites. The composites are used in products such as tennis rackets, fishing rods, aircrafts and canoes. Being good conductor, graphite is used for electrodes in batteries and industrial electrolysis. Crucibles made from graphite are inert to dilute acids and alkalies. Being highly porous, activated charcoal is used in adsorbing poisonous gases; also used in water filters to remove organic contaminators and in air conditioning system to control odour. Carbon black is used as black pigment in black ink and as filler in automobile tyres. Coke is used as a fuel and largely as a reducing agent in metallurgy. Diamond is a precious stone and used in jewellery. It is measured in carats (1 carat = 200 mg.).

❍ PROPERTIES OF CARBON :

(i) Carbon in any form will react with oxygen at a sufficiently high temperature to give carbon dioxide; in a deficiency of oxygen, carbon monoxide is formed as well.

(ii) $C(s) + 2S(s) \longrightarrow CS_2(l)$ (iii) $Ca(s) + 2C(s) \longrightarrow CaC_2(s)$

(iii) $C(s) + 2F_2(g) \longrightarrow CF_4(g)$

(iv) It will reduce steam, forming water gas, and many oxides of metals; these reductions are of industrial importance.

$$C + H_2O(g) \xrightarrow{\Delta} CO + H_2 \ ; \ Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$

(v) It is not attacked by dilute acids, but concentrated nitric acid and sulphuric acid are reduced if warmed with carbon according to the equations:

$$C(s) + 4HNO_3(aq) \longrightarrow 2H_2O(l) + 4NO_2(g) + CO_2(g) \quad ; \quad C(s) + 2H_2SO_4(l) \longrightarrow 2H_2O(l) + 2SO_2(g) + CO_2(g)$$

● OXIDES OF CARBON :

❍ CARBON DIOXIDE (CO_2) :

❍ PREPARATION :

(i) In the laboratory it can be conveniently made by the action of dilute hydrochloric acid on marble chips:

$$CO_3^{2-}(aq) + 2H^+(aq) \longrightarrow CO_2(g) + H_2O(l)$$

(ii) Industrially it is produced as a by-product during the manufacture of quicklime and in fermentation processes:

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g) \ ; \ C_6H_{12}O_6(aq)\{glucose\} \rightarrow 2C_2H_5OH(aq) + 2CO_2(g)$$

❍ PROPERTIES:

(i) It is a colourless, odourless and heavy gas which dissolves in its own volume of water at ordinary temperature and pressure. Like all gases, it dissolves much more readily in water when the pressure is increased and this principle is used in the manufacture of soda water and fizzy drinks.

(ii) CO_2 is easily liquefied (critical temperature = 31.1°C) and a cylinder of the gas under pressure is a convenient fire extinguisher. When the highly compressed gas is allowed to expand rapidly solid carbon dioxide ('dry ice') is formed. Solid carbon dioxide sublimes at –78°C and, since no massy liquid is produced, it is a convenient means of producing low temperatures.

(iii) Carbon dioxide is the acid anhydride of carbonic acid, which is a weak dibasic acid and ionises in to steps as follows :

$H_2CO_3(aq) + H_2O\ (l)$ **(reversible)** $HCO_3^-(aq) + H_3O^+\ (aq)$

$HCO_3^-\ (aq) + H_2O\ (l)$ **(reversible)** $CO_3^{2-}\ (aq) + H_3O^+\ (aq)$

H_2CO_3 / HCO_3^- buffer system helps to maintain pH of blood between 7.26 to 7.42.

A solution of carbonic acid in water will slowly turn blue litmus red and when the solution is boiled, all the CO_2 is evolved.

(iv) Carbon dioxide readily reacts with alkalies forming the carbonate and, if CO_2 is in excess, the hydrogen carbonate. This is the basis of the lime-water test for CO_2 gas.

$Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(liq)$;

$CaCO_3(s) + H_2O(liq) + CO_2(g) \rightarrow Ca(HCO_3)_2(aq)$

The above reaction accounts for the formation of temporarily hard water.

(v) Carbon dioxide, which is normally present to the extent of ~ 0.03% by volume in the atmosphere, is removed from it by the process known as photosynthesis. It is the process by which green plants convert atmospheric CO_2 into carbohydrates such as glucose. The overall chemical change can be expressed as :

$$6\ CO_2 + 12\ H_2O \xrightarrow[\text{Chlorphyll}]{hv} C_6H_{12}O_6 + 6\ O_2 + 6\ H_2O$$

By this process plants make food for themselves as well as for animals and human beings.But the increase in combustion of fossil fuels and decomposition of limestone for cement manufacture in recent years seem to increase the CO_2 content of the atmosphere. This may lead to increase in green house effect and thus, raise the temperature of the atmosphere which might have serious consequences.

(vi) Gaseous CO_2 is extensively used to carbonate soft drinks. Being heavy and non–supporter of combustion it is used as fire extinguisher. A substantial amount of CO_2 is used to manufacture urea.

❍ CARBON MONOXIDE (CO) :

❍ PREPARATION:

(i) It forms together with CO_2, when carbon or carbonaceous matter is oxidized by air or oxygen. It is also produced when CO_2 is reduced by red- hot carbon; this reaction is of importance in metal extractions.

$$C(s) + CO_2(g) \longrightarrow 2CO(g)$$

(ii) In the laboratory it can be prepared by dehydrating methanoic acid with concentrated sulphuric acid:

$$HCOOH\ (liq) \xrightarrow[\text{conc.}H_2SO_4]{373K} CO(g) + H_2O$$

(iii) If oxalic acid is dehydrated in the same way, CO_2 is formed as well.

$$H_2C_2O_4 \xrightarrow[-H_2O]{\text{conc. }H_2SO_4,\Delta} CO + CO_2$$

(iv) On commercial scale it is prepared by the passage of steam over hot coke. The mixture of CO and H_2 thus produced is known as water gas or synthesis gas.sss

$C\ (s) + H_2O\ (g) \xrightarrow{473-1273K} CO\ (g) + H_2(g)$ (water gas).
When air is used instead of steam, a mixture of CO and N_2 is produced, which is called producer gas.

$2\ C\ (s) + O_2\ (g) + 4\ N_2\ (g) \xrightarrow{1273K} 2\ CO\ (g) + 4\ N_2\ (g)$ (Producer gas).
Water gas and producer gas are very important industrial fuels. Carbon monoxide in water gas or producer gas can undergo further combustion forming carbon dioxide with the liberation of heat.

(v) $Zn + CO_2 \longrightarrow ZnO + CO$

(vi) $K_4Fe(CN)_6 + 6H_2SO_4\ (conc.) + 6H_2O \xrightarrow{\Delta} 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$

(vii) $HCN + 2H_2O \longrightarrow HCOOH + 2NH_3$ (absorbed by H_2SO_4)

$HCOOH \xrightarrow{\Delta} H_2O + CO$

❍ **PROPERTIES :**

(i) Carbon monoxide is a colourless, odourless gas which burns in air with a blue flame, forming CO_2. It is exceedingly poisonous, combining with the haemoglobin in the blood more readily than oxygen, so that normal respiration is impeded very quickly. Ordinary gas masks are no protection against the gas, since it is not readily adsorbed on active charcoal. In the presence of air, a mixture of manganese (IV) oxide and copper(II) oxide catalytically oxidizes it to CO_2, and this mixed catalyst is used in the breathing apparatus worn by rescue teams in mine disasters.

(ii) Carbon monoxide is a powerful reducing agent, being employed industrially in the extraction of iron and nickel:

$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 2CO_2(g)$; $NiO(s) + CO(g) \longrightarrow Ni(s) + CO_2(g)$

(iii) It reacts with many transition metals, forming volatile carbonyls; the formation of nickel carbonyl followed by its decomposition is the basis of the Mond's process for obtaining very pure nickel:

$Ni(s) + 4CO(g) \xrightarrow{90°C} Ni(CO)_4(liq) \xrightarrow{180°C} Ni(s) + 4CO(g)$

(iv) In addition to reacting with oxygen, carbon monoxide combines with sulphur to give carbonyl sulphide and with chlorine in the presence of light to give carbonyl chloride (phosgene), used in the production of polyurethane foam plastics. Phosgene is an exceedingly poisonous gas.
$CO(g) + S(s) \longrightarrow COS(s)$ (carbonyl sulphide) ; $CO(g) + Cl_2(g) \longrightarrow COCl_2(g)$ (carbonyl chloride)

(v) Although carbon monoxide is not a true acid anhydride since it does not react with water to produce an acid, it reacts under pressure with fused sodium hydroxide to give sodium methanoate:

$NaOH(liq) + CO(g) \longrightarrow HCOONa(s) \xrightarrow{dil.\ HCl} HCOOH(aq)$

(vi) With hydrogen under pressure and in the presence of zinc oxide or chromium (III) oxide catalyst it reacts to give methanol; this reaction is of industrial importance.

$CO(g) + 2H_2(g) \longrightarrow CH_3OH(liq)$

(vii) CO is readily absorbed by an ammoniacal solution of copper (I) chloride to give $CuCl.CO.2H_2O$. It reduces an ammonical solution of silver nitrate to silver (black) and, in the absence of other gaseous reducing agents, this serves as a test for the gas. It can be estimated by reaction with iodine pentoxide, the iodine which is produced quantitatively being titrated with standard sodium thiosulphate solution.
$5CO(g) + I_2O_5(s) \longrightarrow I_2(s) + 5CO_2(g)$

❍ CARBON SUBOXIDE (C_3O_2) :

This is an evil-smelling gas and can be made by dehydrating propanedioic acid (malonic acid), of which it is the anhydride, with phosphorus pentoxide:

$$3\ CH_2(COOH)_2 + P_4O_{10} \longrightarrow 3C_3O_2 + 4H_3PO_4$$

When heated to about 200°C, it decomposes into CO_2 and C:

$$C_3O_2(g) \longrightarrow CO_2(g) + 2C(s)$$

The molecule is thought to have a linear structure: O=C=C=C=O.

❍ CARBONATES (CO_3^{2-}) AND BICARBONATES (HCO_3^{-})

Carbonic acid is a dibasic acids giving rise to two series of salts, carbonates (normal salts) and bicarbonates (acid salts) due to successive removal of the replaceable hydrogens from H_2CO_3.

$$H_2CO_3 + NaOH \longrightarrow NaHCO_3 + H_2O\ ; \quad NaHCO_3 + NaOH \longrightarrow Na_2CO_3 + H_2O$$

❍ PREPARATION :

(i) With NaOH :

$$2NaOH + CO_2 \longrightarrow Na_2CO_3\ ; \quad Na_2CO_3 + H_2O + CO_2 \longrightarrow 2NaHCO_3$$

(ii) By precipitation :

$$BaCl_2 + Na_2CO_3 \longrightarrow BaCO_3 \downarrow + 2NaCl$$

❍ CARBIDES :

The binary compounds of carbon with other elements (less electronegative or of similar electronegativity) are called carbides. They are classified into following 3 categories :

(i) Ionic (ii) Covalent (iii) Interstitial (or metallic)

(i) Ionic carbides (or salt like carbides) : Generally formed by elements of I, II & III group (Boron is exception). Based on the product obtained on hydrolysis, they are further sub-classified into three types.

(a) Methanides

These give CH_4 on reaction with H_2O.

$$Al_4C_3 + 12H_2O \longrightarrow 4Al\ (OH)_3 + 3CH_4\ ; \quad Be_2C + 4H_2O \longrightarrow 2Be\ (OH)_2 + CH_4$$

These carbides contain C^{4-} ions in their constitution.

(b) Acetylides

These give C_2H_2 on reaction with H_2O.

$$CaC_2 + 2H_2O \longrightarrow Ca\ (OH)_2 + C_2H_2\ ; \quad Al_2\ (C_2)_3 + 6H_2O \longrightarrow 2Al\ (OH)_3 + 3C_2H_2$$

$$SrC_2 + 2H_2O \longrightarrow Sr\ (OH)_2 + C_2H_2$$

Such compounds contain C_2^{2-} $[:C\equiv C:]^{2-}$ ions.

(c) Allylides

These give 1-propyne on reaction with H_2O.

$$Mg_2C_3 + 4H_2O \longrightarrow 2Mg\ (OH)_2 + CH_3-C \equiv CH$$

Such compounds contain C_3^{4-} $[:\overset{..}{\underset{..}{C}}-C\equiv C:]^{4-}$ ions.

(ii) Covalent carbides

Compounds like CH_4, CO_2, CS_2 can be considered to be covalent carbides. Besides these, some giant molecules like SiC are also examples of covalent carbides.

(iii) Interstitial or metallic carbides

Such carbides are formed by transition metals in which carbon atoms occupy interstitials in the crystal structure of metals.

❍ **CARBORUNDUM (SiC) :**

❍ **PREPARATION:**

$$SiO_2 + 3C \xrightarrow[\text{furnace } 2000°C]{\text{elect.}} SiC + 2CO$$

❍ **PROPERTIES :**

(i) It is a very hard substance (Hardness = 9.5 Moh)

(ii) On heating it does not melt rather decomposes into elements.

(iii) Not attacked by acids. However, it gives the following two reactions at high temperature.

$$SiC + 2NaOH + 2O_2 \xrightarrow{\Delta} Na_2SiO_3 + CO_2 + H_2O \; ; \; SiC + 4Cl_2 \xrightarrow{\Delta} SiCl_4 + CCl_4$$

☞ It has a diamond like structure in which each atom is sp^3 hybridized. Therefore each atom is tetrahedrally surrounded by 4 atoms of other type.

❍ **SILICON :**

Silicon is the second most abundant element occurring in the earth's crust (about 28 per cent by weight) as the oxide, silica, in a variety of forms, e.g., sand, quartz and flint, and as silicates in rocks and clays.

❍ **PREPARATION :**

(i) The element is obtained from silica by reduction with carbon in an electric furnace:

$$SiO_2(s) + 2C(s) \longrightarrow Si(s) + 2CO(g)$$

Extremely pure silicon is obtained from 'chemically' pure silicon by the method of zone refining.

(ii) $SiO_2 + 2Mg \xrightarrow{\Delta} 2MgO + Si$

❍ **PROPERTIES :**

Silicon is a very high melting-point solid with the same structure as diamond. The non-existence of an allotrope with the graphite structure clearly shows the inability of silicon atoms to multiple bond with themselves. In the massive form, silicon is chemically rather unreactive but powdered silicon is attacked by the halogens and alkalies:

(i) $Si(powdered) + 2Cl_2(g) \longrightarrow SiCl_4(liq)$

(ii) $Si(powdered) + 2OH^-(aq) + H_2O(liq) \longrightarrow SiO_3^{2-}(aq) + 2H_2(g)$

(iii) It is not attacked by acids except hydrofluoric acid, with which it forms hexafluorosilicic acid:

$Si(s) + 6HF(g) \longrightarrow H_2SiF_6(aq) + 2H_2(g)$

(iv) $Si + 2KOH + H_2O \longrightarrow K_2SiO_3 + 2H_2$ (v) $Na_2CO_3 + Si \xrightarrow{\Delta} Na_2SiO_3 + C$

(vi) $2Mg + Si \xrightarrow{\Delta} Mg_2Si$ (Magnesium silicide)

- **COMPOUNDS OF SILICON:**

Silicon Dioxide SiO_2

Silicon dioxide, commonly known as silica, occurs in several crystallographic forms. Quartz, cristobalite and tridymite are some of the crystalline forms of silica, and they are interconvertable at suitable temperature. Silicon dioxide is a covalent, three-dimensional network solid in which each silicon atom is covalently bonded in a tetrahedral manner to four oxygen atoms. Each oxygen atom in turn covalently bonded to another silicon atoms. Each corner is shared with another tetrahedron. The entire crystal may be considered as giant molecule in which eight membered rings are formed with alternates silicon and oxygen atoms. Silica in its normal form is almost non-reactive because of very high Si – O bond enthalpy. It resists the attack by halogens, dihydrogen and most of the acids and metals even at elevated temperatures. Howevers it is attacked by HF and NaOH.

$$SiO_2 + 2\,NaOH \longrightarrow Na_2SiO_3 + H_2O$$
$$SiO_2 + 4\,HF \longrightarrow SiF_4 + 2\,H_2O$$

Quartz is extensively used as a piezoelectric material ; it has made possible to develop extremely accurate clocks, modern radio and television broadcasting and mobile radio communications. Silica gel used as a drying agent and as a support for chromatographic materials and catalysts. Kieselghur, an amorphous form of silica is used in filtration plants.

❍ SILICATES :

Binary compouds of silicon with oxygen are called silicates but they contain other metals also in their structures.

(i) Since the negativity difference b/w O & Si is about 1.7, so Si–O bond can be considered 50% ionic & 50% covalent.

(ii) If we caluclate the radius ratio $\frac{r_{Si^{+4}}}{r_{O^{2-}}} = 0.29$

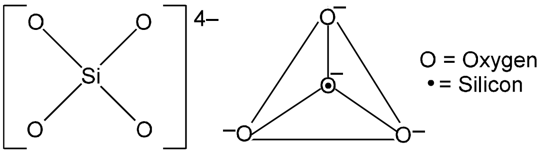
It suggests that the co-ordination no. of silicon must be 4 and from VBT point of view we can say that Si is sp^3 hybridized. Therefore silicate structures must be based upon SiO_4^{-4} tetrahedral units

(iii) SiO_4^{-4} tetrahedral units may exist as discrete units or may polymerise into larger units by sharing corners.

● CLASSIFICATION OF SILICATES :

(A) Orthosilicates :

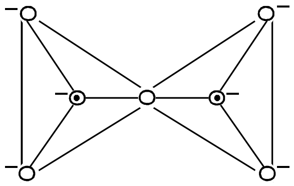
These contain discrete $[SiO_4]^{4-}$ units i.e., there is no sharing of corners with one another as shown is figure.



e.g. Zircon ($ZrSiO_4$), Forsterite of Olivine (Mg_2SiO_4), Willemite (Zn_2SiO_4)

(B) Pyrosilicate :

In these silicates two tetrahedral units are joined by sharing oxygen at one corner thereby giving $[Si_2O_7]^{6-}$ units.

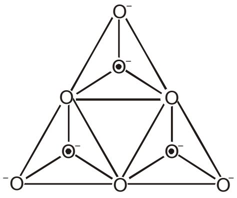


☞ (–) charge will be present on the oxygen atoms which is bonded with one Si atom.

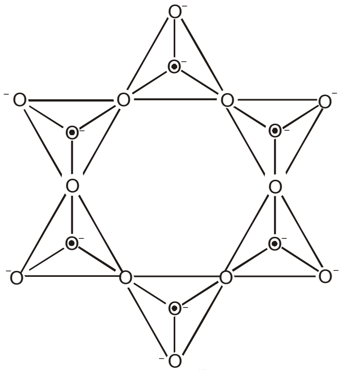
e.g. Thorteveitite ($Sc_2Si_2O_7$), Hemimorphite ($Zn_3(Si_2O_7)\,Zn(OH)_2H_2O$)

(C) Cyclic silicates :

If two oxygen atoms per tetrahedron are shared to form closed rings such that the structure with general formula $(SiO_3^{2-})_n$ or $(SiO_3)_n^{2n-}$ is obtained, the silicates containing these anions are called cyclic silicates. $Si_3O_9^{6-}$ and $Si_6O_{18}^{12-}$ anions are the typical examples of cyclic silicates.



$Si_3O_9^{6-}$

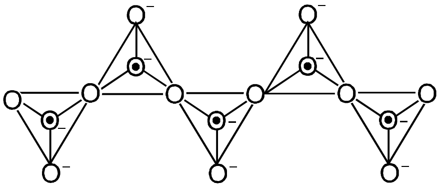


$Si_6O_{18}^{12-}$

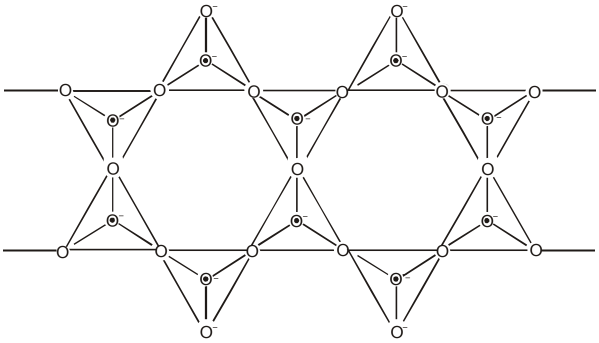
(D) Chain silicates :

Chain silicates may be further classified into simple chain & double chain compounds.

In case of simple chains two corners of each tetrahedron are shared & they form a long chain of tetrahedron. Their general formula is also same as the cyclic silicates i.e. $(SiO_3)_n^{2n-}$



Similarly, double chain silicates can be drawn in which two simple chains are joined together by shared oxygen. Such compounds are also known as amphiboles. The asbestos mineral is a well known example of double chain silicates. The anions of double chain silicates have general formula $(Si_4O_{11})_n^{6n-}$.



e.g., Synthetic silicates (Li_2SiO_3, Na_2SiO_3), Spondumene ($LiAl(SiO_3)_2$), Enstatite ($MgSiO_3$), Diopside ($CaMg(SiO_3)_2$), Tremolite ($Ca_2Mg_5(Si_4O_{11})_2(OH)_2$), etc.

(E) Two dimensional sheet silicates :

In such silicates, three oxygen atoms of each tetrahedral are shared with adjacent SiO_4^{4-} tetrahedrals. Such sharing forms two dimension sheet structure with general formula $(Si_2O_5)_n^{2n-}$

e.g. Talc ($(Mg(Si_2O_5)_2\,Mg(OH)_2$, Kaolin $Al_2(OH)_4(Si_2O_5)$

(F) Three dimensional sheet silicates :

These silicates involve all four oxygen atom in sharing with adjacent SiO_4^{4-} tetrahedral units.

e.g. Quartz, Tridymite, Crystobalite, Feldspar, Zeolite and Ultramarines.

- **SILICONES :**

Silicones are synthetic organosilicon compounds having repeated R_2SiO units held by Si – O – Si linkages. These compounds have the general formula $(R_2SiO)_n$ where R = alkyl or aryl group.

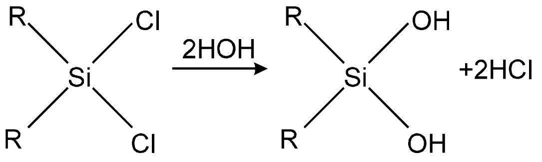
The silicones are formed by the hydrolysis of alkyl or aryl substituted chlorosilanes and their subsequent polymerisation. The alkyl or aryl substituted chlorosilanes are prepared by the following reactions.

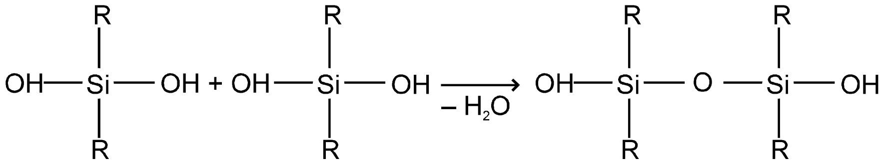
(a) $RCl + Si \xrightarrow[300°C]{Cu} R_3SiCl + R_2SiCl_2 + RSiCl_3$

(b) $RMgCl + SiCl_4 \longrightarrow RSiCl_3 + MgCl_2$

$2RMgCl + SiCl_4 \longrightarrow R_2SiCl_2 + 2MgCl_2$; $3RMgCl + SiCl_4 \longrightarrow R_3SiCl + 3MgCl_2$

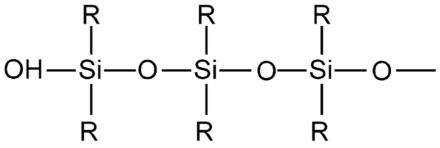
After fractional distillation, the silane derivatives are hydrolysed and the 'hydroxides' immediately condense by intermolecular elimination of water. The final product depends upon the number of hydroxyl groups originally bonded to the silicon atom:





$$OH{-}\overset{R}{\underset{R}{Si}}{-}OH + OH{-}\overset{R}{\underset{R}{Si}}{-}OH \xrightarrow[-\,H_2O]{} OH{-}\overset{R}{\underset{R}{Si}}{-}O{-}\overset{R}{\underset{R}{Si}}{-}OH$$

In this manner several molcules may combine to form a long chain polymer whose both the ends will be occupied by –OH groups. Such compounds are generally represented from the following formula.



$$OH{-}\overset{R}{\underset{R}{Si}}{-}O{-}\overset{R}{\underset{R}{Si}}{-}O{-}\overset{R}{\underset{R}{Si}}{-}O{-}$$

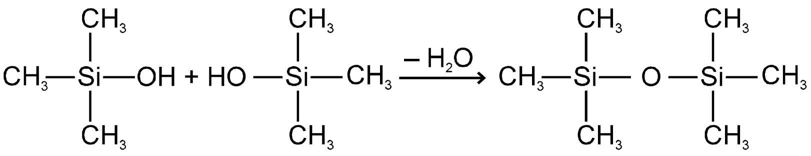
The polymer chain depicted above is terminated by incorporating a small quantity of the monochlorosilane derivative into the hydrolysis mixture.

☞ Silicones can be prepared from the following types of compounds only.

(i) R_3SiCl (ii) R_2SiCl_2 (iii) $RSiCl_3$

☞ Silicones from the hydrolysis of $(CH_3)_3$ SiCl

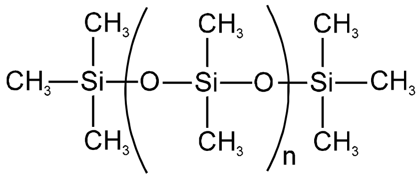
$(CH_3)_3\ SiCl \xrightarrow{H_2O} (CH_3)_3\ Si\ (OH)$



$$CH_3{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}OH + HO{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}CH_3 \xrightarrow{-\,H_2O} CH_3{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}O{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}CH_3$$

☞ Silicones from the hydrolysis of a mixture of $(CH_3)_3$ SiCl & $(CH_3)_2$ $SiCl_2$

The dichloro derivative will form a long chain polymer as usual. But the growth of this polymer can be blocked at any stage by the hydrolysis product of mono-chloro derivative.



$CH_3-\overset{CH_3}{\underset{CH_3}{Si}}\left(O-\overset{CH_3}{\underset{CH_3}{Si}}-O\right)_n\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$

☞ Silicones from the hydrolysis of trichloro derivative

When a compound like CH_3SiCl_3 undergoes hydrolysis, a complex cross-linked polymer is obtained.

☞ The hydrocarbon layer along the silicon-oxygen chain makes silicones water-repellent.

Products having the physical properties of oils, rubbers, and resins can be produced using silicones. Silicone fluids (say as hydraulic systems of planes) are thermally stable and their viscosity alters very little with temperature, and silicone rubbers retain their elasticity at much lower temperatures than ordinary rubber. Silicone varnishes are such excellent insulators and so heat-resistant that insulating wiring with them enabled motors to work over-loads that would have set fire to the insulation formerly used. A whole new field of chemistry and technology, civilian as well as military, has been opened up by the development of silicones.

TIN AND LEAD :

❍ COMPOUNDS OF TIN :

❍ STANNOUS OXIDE (SnO) :

❍ PREPARATION:

(i) By heating stannous hydroxide, $Sn(OH)_2$, in absence of air.

$Sn(OH)_2 \longrightarrow SnO + H_2O\uparrow$

(ii) By heating stannous oxalate, SnC_2O_4 in absence of air.

$SnC_2O_4 \longrightarrow SnO + CO\uparrow + CO_2\uparrow$

❍ PROPERTIES:

(i) SnO is an amphoteric dark grey or black solid oxide, insolulbe in water. It dissolves in acids to form stannous salts.

$SnO + 2HCl \longrightarrow SnCl_2 + H_2O$; $SnO + H_2SO_4 \longrightarrow SnSO_4 + H_2O$

(ii) SnO dissolves in hot NaOH solution to form (soluble) sodium stannite and water.

$SnO + 2NaOH \longrightarrow Na_2SnO_2 + H_2O$

stannites are only known in aqueous solutions. Stannites absorb oxygen from air and are oxidised to stannate which are stable in nature.

$2\ Na_2SnO_2 + O_2 \longrightarrow 2\ Na_2SnO_3$

❍ USES :

For the preparation of stannous chloride and stannous sulphate.

❍ STANNOUS CHLORIDE ($SnCl_2\cdot 2H_2O$) :

It is a colourless solid soluble in water. Its solution becomes milky on standing due to its hydrolysis to $Sn(OH)_2$ and HCl. It aqueous solution is acidic to litmus. It is a strong reducing agent. It is soluble in alcohol and ether also.

- PREPARATION :

(i) $Sn + 2HCl(concentrated) \longrightarrow SnCl_2(aq) + H_2\uparrow$
(ii) $SnO + 2HCl \longrightarrow SnCl_2(aq) + H_2O$
The solution on crystallization gives colourless crystals of $SnCl_2 \cdot 2H_2O$.

- PROPERTIES :

(i) Reaction with Hg_2Cl_2 solution: When $SnCl_2$ solution is added to an aqueous solution of mercuric chloride, a silky white precipitate of mercurous chloride, Hg_2Cl_2 is formed which turns black due to further reduction of Hg_2Cl_2 to black mercury.

$$2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2\downarrow + SnCl_4; \qquad Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg\downarrow + SnCl_4$$

(ii) It reduces ferric chloride, $FeCl_3$ to ferrous chloride, $FeCl_2$.
$2FeCl_3(brown\ solution) + SnCl_2 \longrightarrow 2FeCl_2\ (colourless\ solution) + SnCl_4$

(iii) It is hydrolysed with water to produce white precipitate of $Sn(OH)_2$

$$SnCl_2 + 2H_2O \Leftrightarrow Sn(OH)_2\ (white)\downarrow + 2HCl$$

As it produces a weak base and strong acid its aqueous solution is acidic. Its hydrolysis can be prevented by adding concentrated HCl to it during the process of its preparation.

- USES :

(i) In dye industry as a reducing agent.
(ii) For the test of mercuric salt.
(iii) For the preparation of other stannous compounds.

STANNIC OXIDE (SnO_2) :

- PREPARATION:

(i) By burning Sn in air

$$Sn + O_2 \longrightarrow SnO_2$$

(ii) By heating Sn with concentrated HNO_3

$$Sn + 4HNO_3 \longrightarrow H_2SnO_3 + 4NO_2\uparrow + H_2O\ ; H_2SnO_3 \xrightarrow{\Delta} H_2O\uparrow + SnO_2$$

- PROPERTIES :

(i) It is a white solid insoluble in water. It is weakly acidic

(ii) It dissolves in conc. H_2SO_4 to form stannic sulphate.
$SnO_2 + 2H_2SO_4 \longrightarrow Sn(SO_4)_2 + 2H_2O$

(iii) It also dissolves in conc. Alkalies to form alkali metal stannate solution.
$SnO_2 + 2NaOH \longrightarrow Na_2SnO_3\ (sodium\ stannate) + H_2O$

STANNIC CHLORIDE ($SnCl_4$) :

- PREPARATION:

(i) By the action of Cl_2 gas on heated Sn
$Sn + 2Cl_2 \longrightarrow SnCl_4$

(ii) By the action of Cl_2 on stannous chloride
$SnCl_2 + Cl_2 \longrightarrow SnCl_4$

❍ **PROPERTIES :**

(i) It is a colourless fuming liquid, Bp = 114°C. It is covalent.

(ii) Action of moisture: It absorbs moisture and becomes converted into hydrated stannic chlorides, $SnCl_4{\cdot}3H_2O$, $SnCl_4{\cdot}5H_2O$, $SnCl_4{\cdot}6H_2O$, and $SnCl_4{\cdot}8H_2O$. $SnCl_4 . 5\,H_2O$ is known as "butter of tin" or "oxymercurate of tin".

(iii) Hydrolysis with water: It easily gets hydrolysed in water and produces strong acid HCl. Hence its aqueous solution is acidic to litmus. It hydrolyses more rapidly than $SnCl_2$
$SnCl_4 + 4H_2O \longrightarrow H_4SnO_4$(colloidal white precipitate) + 4HCl

(iv) $SnCl_4$ is a Lewis acid. Hence it has a tendency to accept lone pair of electrons from NH_3, PH_3 etc and form adducts such as $SnCl_4{\cdot}4NH_3$

(v) It dissolves in concentrated HCl forming H_2SnCl_6 and in presence of ammonium chloride, it forms ammonium salts of this acid.
$SnCl_4 + 2\,HCl \longrightarrow H_2SnCl_6$
$SnCl_4 + 2\,NH_4Cl \longrightarrow (NH_4)_2SnCl_6$

❍ **USES :** For the preparation of stannic compounds.

❍ **COMPOUNDS OF LEAD :**

❍ **LITHARGE (PbO) :**

PbO is prepared by heating Pb at 180°C. It is a volatile yellow compound. $2Pb + O_2 \xrightarrow{\Delta} 2PbO$
It is an amphoteric oxide and dissolves in acids as well as in alkalis

$PbO + 2HNO_3 \xrightarrow{\Delta} Pb(NO_3)_2 + H_2O$; $PbO + 2NaOH \xrightarrow{\Delta} Na_2PbO_2$ (sodium plumbate) + H_2O
It is used in rubber industry and in the manufacture of flint glasses, enamels, and storage batteries.

❍ **LEAD DIOXIDE (PbO_2) :**

The fact that it does not liberate H_2O_2 by the action of dilute HCl suggest the above formula (It is a dioxide not a peroxide)

❍ **PREPARATION :**

(i) $PbO + NaOCl \xrightarrow{\Delta} PbO_2$ (insoluble) + NaCl

(ii) $Pb_3O_4 + 4HNO_3$ (dilute $\longrightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$

❍ **PROPERTIES :**

(i) It is a chocolate coloured insoluble powder. On heating at 440°C it gives the monoxide:
$2PbO_2 \xrightarrow{440°C} 2PbO + O_2$

(ii) It oxidizes HCl to Cl_2:
$PbO_2 + 4HCl \longrightarrow PbCl_2 + 2H_2O + Cl_2\uparrow$

(iii) It dissolves in conc. NaOH solution:
$PbO_2 + 2NaOH \longrightarrow Na_2PbO_3$(sodium plumbate) + H_2O

(iv) It oxidises Mn salt to permanganic acid:
$2MnSO_4 + 5PbO_2 + 6HNO_3 \longrightarrow 2HMnO_4 + 2PbSO_4 + 3Pb(NO_3)_2 + 2H_2O$

(v) It reacts with SO_2 at red heat to form lead sulphate:

$$PbO_2 + SO_2 \xrightarrow{\Delta} PbSO_4$$

(vi) It reacts with conc. HNO_3 to evolve oxygen gas.

$$PbO_2 + 2HNO_3 \longrightarrow Pb(NO_3)_2 + 1/2O_2 + H_2O$$

- **USES :**

It is used in match industry for making ignition surface of match boxes and in the preparation of $KMnO_4$.

RED LEAD (Pb_3O_4) :

- **PREPARATION:**

It is prepared by heating PbO at 450°C for a long time.

$$6PbO + O_2 \xrightarrow{450°C} 2Pb_3O_4$$

- **PROPERTIES :**

(i) It is a red powder insoluble in water but when heated with conc. HNO_3 it gives a red precipitate of PbO_2

$$Pb_3O_4 + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + PbO_2\downarrow + 6H_2O$$

(ii) When heated above 550°C, it decomposes into PbO

$$Pb_3O_4 \xrightarrow{\Delta} 6PbO + O2\uparrow$$

(iii) It oxidizes conc. HCl to chlorine

$$Pb_3O_4 + 8HCl \longrightarrow 3PbCl_2 + 4H_2O + Cl_2\uparrow$$

(iv) When heated with conc. H_2SO_4 it evolves oxygen

$$2Pb_3O_4 + 6H_2SO_4 \longrightarrow 6PbSO_4 + 6H_2O + O_2\uparrow$$

- **USES :**

It is used as an oxidizing agent, for making red paint, for making special lead cement and for making flint glass.

LEAD CHLORIDE ($PbCl_2$) :

- **PREPARATION:**

(i) $Pb(NO_3)_2 + 2HCl \longrightarrow PbCl_2\downarrow + 2HNO_3$

(ii) $Pb(NO_3)_2 + 2NaCl \longrightarrow PbCl_2\downarrow + 2NaNO_3$

(iii) $Pb(CH_3COO)_2 + 2HCl \longrightarrow PbCl_2\downarrow + 2CH_3COOH$

(iv) $PbO + 2HCl \longrightarrow PbCl_2\downarrow + H_2O$

(v) $Pb(OH)_2 + 2HCl \longrightarrow PbCl_2\downarrow + 2H_2O$

(vi) $Pb(OH)_2 \cdot PbCO_3$ (basic lead carbonate) $+ 4HCl \longrightarrow 2PbCl_2\downarrow + CO_2\uparrow + 3H_2O$

- **PROPERTIES :**

It is a white crystalline solid, insoluble in cold water but soluble in boiling water.It dissolves in concentrated HCl forming a complex ion.

$2\ HCl + PbCl_2$ **(reversible)** H_2PbCl_4 (chloroplumbous acid)

- **USES :**

It is used for making pigments for paints.

❍ LEAD TETRACHLORIDE ($PbCl_4$) :

❍ PREPARATION:

It is prepared by the following methods:

(i) By dissolving PbO_2 in cold conc. HCl

$PbO_2 + 4HCl \longrightarrow PbCl_4 + 2H_2O$

$PbCl_4$ dissolves in excess of HCl to form a stable solution of H_2PbCl_6.

$PbCl_4 + 2HCl \longrightarrow H_2PbCl_6$

☞ When NH_4Cl is added to a solution of chloroplumbic acid, a yellow precipitate of ammonium chloroplumbate is formed.

$$H_2PbCl_6 + 2NH_4Cl \longrightarrow (NH_4)_2PbCl_6\downarrow + 2HCl$$

☞ When crystals of ammonium chloroplumbate is added to ice cold conc. H_2SO_4, lead tetrachloride is formed and separates as a yellow oily liquid.

$$(NH_4)_2PbCl_6 + H_2SO_4 \longrightarrow PbCl_4 + (NH_4)_2SO_4 + 2HCl$$

(ii) By the action of Cl_2 on a solution of $PbCl_2$ in conc. HCl

$$PbCl_2 + Cl_2 \longrightarrow PbCl_4$$

❍ PROPERTIES :

(i) It is a yellow oily liquid which solidifies at –10°C and is soluble in organic solvents like ethanol and benzene.

(ii) Rapid hydrolysis with water forms PbO_2 precipitate

$$PbCl_4 + 2H_2O \longrightarrow PbO_2\downarrow + 4HCl$$

❍ USES :

It is used for making stannic compounds.

EXERCISE - 1 : BASIC OBJECTIVE QUESTIONS

Group - 13

1. Boric acid H_3BO_3 and BF_3 have the same number of electrons. The former is a solid and the latter is a gas. The reason is:

(a) BF_3 is a Lewis acid while $B(OH)_3$ is not

(b) they have different geometrics

(c) In BF_3, F^- is smaller in size than OH^- in $B(OH)_3$

(d) No molecular association is possible in BF_3 while it is possible in $B(OH)_3$ due to hydrogen bonding

2. Ionisation enthalphy (Δ_1H_1 in kJ mol^{-1}) for the elements of group 13 follows the order:

(a) $B > Al > Ga > In > Tl$ (b) $B < Al < Ga < In < Tl$

(c) $B < Al > Ga < In > Tl$ (d) $B > Al \approx Ga > In < Tl$

3. On the addition of mineral acid to an aqueous solution of borax, the following compound is formed:

(a) boron hydride (b) orthoboric acid

(c) metaboric acid (d) pyroboric acid

4. Which of the following compounds is formed when boron trichloride is treated with water?

(a) $H_3BO_3 + HCl$ (b) $B_2H_6 + HCl$

(c) $B_2O_3 + HCl$ (d) None of these

5. The hardest compound of boron is:

(a) boric acid (b) boron nitride

(c) boron carbide (d) boron hydride

6. When strongly heated, orthoboric acid leaves a residue of:

(a) metaboric acid (b) tetraboric acid

(c) boric anhydride (d) boron

7. Boric acid is prepared from borax by the action of :

(a) Hydrochloric acid (b) sodium hydroxide

(c) carbon dioxide (d) sodium carbonate

8. Borax bead test is responded by:

(a) divalent metals (b) heavy metals

(c) light metals

(d) metals which form coloured metaborates

9. Borazole, $B_3N_3H_6$ is related to benzene as:

(a) isoelectronic (b) isostructural

(c) both (a) and (b) (d) none of these

10. Reactivity of borazole is higher than that of benzene because:

(a) borazole is a polar compound

(b) borazole is a non-polar compound

(c) borazole is electron deficient compound

(d) of localised electrons in it

[**Note**: In benzene, π-electrons are delocalised over the ring which give stability to benzene ring.]

11. In diborane:

(a) 4 bridged hydrogens and two terminal hydrogens are present

(b) 2 bridged hydrogens and four terminal hydrogens are present

(c) 3 bridged hydrogens and three terminal hydrogens are present

(d) none of the above

12. The bonds present in borazole are:

(a) $9\sigma, 9\pi$ (b) $6\sigma, 6\pi$

(c) $9\sigma, 6\pi$ (d) $12\sigma, 3\pi$

13. BCl_3 does not exist as a dimer but BH_3 exists as B_2H_6 because

(a) Cl_2 is more electronegative than hydrogen

(b) large size of chlorine atom does not fit between small sized boron atoms, while small-sized hydrogen atoms occupy the space between boron atoms

(c) there is $p\pi$-$d\pi$ back bonding in BCl_3

(d) both (b) and (c)

14. The main factor responsible for weak acidic nature of B—F bonds in BF_3 is:

(a) high electronegativity of F

(b) three centred two electron bonds in BF_3

(c) pπ—dπ back bonding

(d) pπ—pπ back bonding

15. Which one of the following statements regarding BF_3 is not correct?

(a) It is a Lewis acid

(b) It is an ionic compound

(c) It is an electron deficient compound

(d) It forms adducts

16. The number of OH units directly linked to boron atoms in $Na_2B_4O_7.10H_2O$ is:

(a) 2 (b) 3

(c) 4 (d) 10

17. From B_2H_6, all the following can be prepared except:

(a) B_2O_3 (b) H_3BO_3

(c) $B_2(CH_3)_6$ (d) $NaBH_4$

18. The power of halides of boron to act as Lewis acids decreases in the order:

(a) $BF_3 > BCl_3 > BBr_3$ (b) $BBr_3 > BCl_3 > BF_3$

(c) $BCl_3 > BF_3 > BBr_3$ (d) $BCl_3 > BBr_3 > BF_3$

19. Which of the following is a false statement ?

(a) BH_3 is not a stable compound

(b) Boron hydrides are formed when dil. HCl reacts with Mg_3B_2

(c) All the B—H bond distances in B_2H_6 are equal

(d) The boron hydrides are readily hydrolysed

20. In B_2H_6:

(a) there is direct boron-boron bond

(b) the boron atoms are linked through hydrogen bridges

(c) the structure is similar to C_2H_6

(d) all the atoms are in one plane

21. BF_3 is used as catalyst in several industrial processes due to its:

(a) strong reducing nature

(b) weak reducing action

(c) strong Lewis acid nature

(d) weak Lewis acid character

22. Specify the coordination geometry around and hybridization of N and B atoms in 1:1 complex of BF_3 and NH_3:

(a) N: tetrahedral, sp^3 ; B:tetrahedral, sp^3

(b) N: pyramidal, sp^3 ; B:pyramidal , sp^3

(c) N:pyramidal, sp^3 ; B:planar, sp^3

(d) N:pyramidal, sp^3 ; B:tetrahedral, sp^3

23. H_3BO_3 is:

(a) monobasic and weak Lewis acid

(b) monobasic and weak Bronsted acid

(c) monobasic acid and strong Lewis acid

(d) tribasic acid and weak Bronsted acid

24. Which of the following compounds is known as inorganic benzene?

(a) B_6H_6 (b) C_5H_5B

(c) $C_3N_3H_3$ (d) $B_3N_3H_6$

25. A mixture of boron trichloride and hydrogen is subjected to silent electric discharge to form 'A' and HCl. 'A' is mixed with NH_3 and heated to 200°C to form 'B'. The formula of 'B' is:

(a) H_3BO_3 (b) B_2O_3

(c) B_2H_6 (d) $B_3N_3H_6$

26. Diborane reacts with ammonia under different conditions to give a variety of products. Which one among the following is not fomed in these conditions?

(a) $B_2H_6.2NH_3$ (b) $B_{12}H_{12}$

(c) $B_3N_3H_6$ (d) $(BN)_n$

27. Boron cannot form which one of the following anions?

(a) BF_6^- (b) BH_4^-

(c) $[B(OH)_4]^-$ (d) BO_2^-

[Hint: Due to non-availability of d-orbitals, boron is unable to expand its octet. The maximum covalency of boron is 4.]

28. Which one is the wrong statement ?

(a) Aluminium is the most abundant metal in the earth's crust

(b) Aluminium is not affected by strong alkalies

(c) Aluminium becomes passive with conc. HNO_3

(d) Aluminium when heated in the atmosphere of nitrogen forms a nitride of the formula AIN.

[Hint: Al is affected by strong alkalies with evolution of hydrogen.]

29. Alumina is:

(a) acidic (b) basic

(c) neutral (d) amphoteric

30. The element which exists in liquid state for a wide range of temperature and can be used for measuring high temperature is:

(a) B (b) Al

(c) In (d) Ga

31. When alumina is heated with carbon in nitrogen atmosphere, the products are:

(a) $Al + CO$ (b) $Al + CO_2$

(c) $Al + CO + CO_2$ (d) $AlN + CO$

32. Aluminium does not react with:

(a) NaOH (b) HCl

(c) N_2 (d) HNO_3

33. Alumina may be converted into anhydrous aluminium chloride by:

(a) heating it with conc. HCl

(b) heating in a current of dry chlorine

(c) heating it with rock salt

(d) mixing it with carbon and heating the mixture in a current of dry chlorine

34. Which of the following statements about anhydrous aluminium chloride is correct?

(a) It exists as $AlCl_3$ molecule

(b) It is a strong Lewis base

(c) It sublimes at 100°C under vaccum

(d) It is not easily hydrolysed

35. When a solution of sodium hydroxide is added in excess to the solution of potash alum, we obtain:

(a) a white precipitate (b) bluish white precipitate

(c) a clear solution (d) a crystalline mass

36. Which one of the statements is incorrect for aluminium metals?

(a) It is a good conductor of heat and electricity

(b) It is malleable and ductile

(c) It can be welded and cast but difficult to solder

(d) Its alloys are heavy

37. When excess of NaOH solution is added in potash alum, the product is:

(a) a bluish white precipitate

(b) clear solution

(c) a white precipitate (d) a greenish precipitate

[**Hint**: Alum consists $Al_2(SO_4)_3$ reacts with NaOH.

$$Al_2(SO_4)_3 + 6NaOH \rightarrow 2Al(OH)_3 + 3Na_2SO_4$$

$$Al(OH)_3 + NaOH \rightarrow \underset{\text{Soluble}}{NaAlO_2} + 2H_2O$$

The other sulphates K_2SO_4 and Na_2SO_4 are also soluble in water. Thus, a clear solution is obtained.]

38. Aluminium vessels should not be washed with materials containing washing soda since :

(a) washing soda reacts with aluminium to form soluble aluminate

(b) washing soda is expensive

(c) washing soda is easily decomposed

(d) washing soda reacts with aluminium to form insoluble aluminium oxide

39. Aluminium is more reactive than iron. But aluminium is less easily corroded than iron because:

(a) oxygen forms a protective oxide layer on aluminium

(b) aluminium is a noble metal

(c) iron undergoes reaction easily with water

(d) iron forms mono and divalent ions

40. Al_2O_3 formation from aluminium and oxygen involves evolution of a large quantity of heat, which makes aluminium used in:

(a) deoxidiser (b) confectionary

(c) indoor photography (d) thermite welding

41. The main factor responsible for weak acidic nature of B—F bonds in BF_3 is:

(a) high electronegativity of F

(b) three centred two electron bonds in BF_3

(c) $p\pi$—$d\pi$ back bonding

(d) $p\pi$—$p\pi$ back bonding

42. When aluminium is heated with conc. H_2SO_4

(a) aluminium becomes passive

(b) hydrogen is liberated

(c) oxygen is liberated

(d) sulphur dioxide is liberated

43. When aluminium hydroxide dissolves in NaOH solution, the product is:

(a) $[Al(H_2O)_3(OH)_3]$ (b) $[Al(H_2O)_4(OH)_2]^+$

(c) $[Al(H_2O)_2(OH)_4]^-$ (d) $[Al(H_2O)_5(OH)]^{2+}$

44. $AlCl_3$ on hydrolysis gives:

(a) $Al_2O_3 . H_2O$ (b) $Al(OH)_3$

(c) Al_2O_3 (d) $AlCl_3.6H_2O$

45. The stability of +1 oxidation state increases in the sequence:

(a) Tl < In < Ga < Al (b) In < Tl < Ga < Al

(c) Ga < In < Al < Tl (d) Al < Ga < In < Tl

46. Group 13 elements show +1 and +3 oxidation states. Relative stability of +3 oxidation state may be given as

(a) $Tl^{3+} > In^{3+} > Ga^{3+} > Al^{3+} > B^{3+}$

(b) $B^{3+} > Al^{3+} > Ga^{3+} > In^{3+} > Tl^{3+}$

(c) $Al^{3+} > Ga^{3+} > Tl^{3+} > In^{3+} > B^{3+}$

(d) $Al^{3+} > B^{3+} > Ga^{3+} > Tl^{3+} > In^{3+}$

47. Which of the following is not true regarding the nature of halides of boron ?

(a) Boron trihalides are covalent.

(b) Boron trihalides are planar triangular with sp^2 hybridisation

(c) Boron trihalides act as Lewis acids.

(d) Boron trihalides cannot be hydrolysed easily.

48. Which of the following does not show similarity between boron and aluminium ?

(a) Both form oxides of type M_2O_3 when heated with oxygen at high temperature.

(b) Both dissolve in alkalies and evolve hydrogen.

(c) Hydroxides of both the elements are basic in nature.

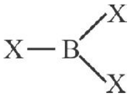
(d) Both form nitrides of MN type when heated with N_2.

49. The decreasing order of power of boron halides to act as Lewis acids is

(a) $BF_3 > BCl_3 > BBr_3$ (b) $BBr_3 > BCl_3 > BF_3$

(c) $BCl_3 > BF_3 > BBr_3$ (d) $BCl_3 > BBr_3 > BF_3$

50. In BX_3, B – X distance is shorter than what is expected theoretically because (X = F, Cl, Br, I)



(a) sp^3 hybridisation of B is responsible for shorter B – X distance.

(b) B – X has a double bond character due to back-bonding.

(c) Dimerisation takes place in BX_3 which is responsible for shorter B – X distance.

(d) Due to large size of X, B – X distance decreases.

51. Aluminium exhibits +3 oxidation state. As we move down the group, +1 oxidation state gets more stable. This is a consequence of

(a) increasing size of the atom

(b) inert pair effect

(c) electron deficient nature

(d) pπ - pπ bonding.

52. The shapes and hybridisation of BF_3 and BH_4^- respectively are

(a) BF_3 - Trigonal, sp^2 hybridisation ;
BH_4^- - Square planar, sp^3 hybridisation

(b) BF_3 - Triangular, sp^3 hybridisation ;
BH_4^- - Hexagonal, sp^3d hybridisation

(c) BF_3 - Trigonal, sp^2 hybridisation ;
BH_4^- - Tetrahedral, sp^3 hybridisation

(d) BF_3 - Tetrahedral, sp^3 hybridisation ;
BH_4^- - Tetrahedral, sp^3 hybridisation.

53. Electropositive charcter for the elements of group 13 follows the order

(a) B > Al > Ga > In > Tl (b) B < Al < Ga < In < Tl

(c) B < Al > Ga < In > Tl (d) B < Al > Ga > In > Tl

54. The reason behind the lower atomic radius of Ga as compared to Al is

(a) poor screening effect of d-electrons for the outer electrons from increased nuclear charge

(b) increased force of attraction of increased nuclear charge on electrons

(c) increased ionisation enthalpy of Ga as compared to Al

(d) anomalous behaviour of Ga.

55. Which of the following hydroxides is acidic ?

(a) $Al(OH)_3$ (b) $Ga(OH)_3$

(c) $Tl(OH)_3$ (d) $B(OH)_3$

56. Thermite is a mixture of iron oxide and

(a) aluminium powder (b) zinc powder

(c) iron turnings (d) copper turnings.

57. A metal M reacts with sodium hydroxide to give a white precipitate X which is soluble in excess of NaOH to give Y. Compound X is soluble in HCl to form a compound Z. Identify M, X, Y and Z.

	M	X	Y	Z
(a)	Si	SiO_2	Na_2SiO_3	$SiCl_4$
(b)	Al	$Al(OH)_3$	$NaAlO_2$	$AlCl_3$
(c)	Mg	$Mg(OH)_3$	$NaMgO_3$	$MgCl_2$
(d)	Ca	$Ca(OH)_2$	Na_2CO_3	$NaHCO_3$

58. Boron is unable to form BF_6^{3-} ions due to

(a) non-availability of d-orbitals

(b) small size of boron atom

(c) non-metallic nature

(d) it is a strong Lewis acid.

59. $Na_2B_4O_7.10H_2O \xrightarrow{\Delta} X \xrightarrow{\Delta} Y + Z$

X, Y and Z in the reaction are

(a) $X = Na_2B_4O_7, Y = NaBO_2, Z = H_3BO_3$

(b) $X = Na_2B_4O_7, Y = B_2O_3, Z = H_3BO_3$

(c) $X = B_2O_3, Y = NaBO_2, Z = B(OH)_3$

(d) $X = NaBO_2, Y = B_2O_3, Z = B(OH)_3$

60. $Na_2B_4O_7 + X \rightarrow H_3BO_3$. What is X in the reaction ?

(a) Aqueous solution of NaOH

(b) Dilute nitric acid

(c) Conc. H_2SO_4 or HCl

(d) Water

61. Which of the following compounds is formed in borax bead test ?

(a) Metaborate (b) Tetraborate

(c) Triborate (d) Orthoborate

62. Boric acid has a polymeric layer structure in which planar BO_3 units are joined by

(a) covalent bonds

(b) two centre - two electron bonds

(c) coordinate bonds

(d) hydrogen bonds.

63. What happens when a mixture of cobalt oxide and borax is heated in a flame on a loop of platinum wire ?

(a) A transparent white bead is formed.

(b) A bright pink coloured $NaBO_2$ bead is formed.

(c) A blue coloured $Co(BO_2)_2$ bead is formed.

(d) A red coloured $Co(BO_2)_2$ bead is formed.

64. In diborane,

(a) four bridged hydrogen atoms and two terminal hydrogen atoms are present

(b) two bridged hydrogen atoms and four terminal hydrogen atoms are present

(c) three bridged hydrogen atoms and three terminal hydrogen atoms are present

(d) there are no bridged hydrogen atoms in diborane, only hydrogen bonds are present.

65. Match the column I with column II and mark the appropriate choice.

Column I	**Column II**
(A) Borax	(i) Na_3AlF_6
(B) Inorganic benzene	(ii) $Na_2B_4O_7.10H_2O$
(C) Cryolite	(iii) $Al_2O_3.2H_2O$
(D) Bauxite	(iv) $B_3N_3H_6$

(a) (A) → (ii), (B) → (iv), (C) → (i), ((D)) → (iii)

(b) (A) → (i), (B) → (ii), (C) → (iii), (D) → (iv)

(c) (A) → (ii), (B) → (iii), (C) → (i), (D) → (iv)

(d) (A) → (iii), (B) → (i), (C) → (ii), (D) → (iv)

66. The type of hybridization of boron in bidorane is

(a) sp-hybridization (b) sp^2-hybridization

(c) sp^3-hybridization (d) sp^3d^2-hybridication.

67. An aqueous solution of boric acid is found to be weakly acidic in nature. This acidic character arises due to the following reasons.

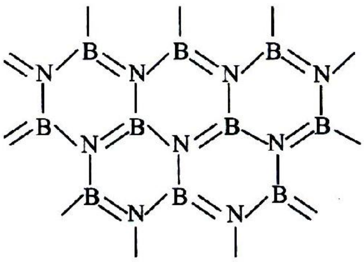
(a) It is a protic acid which donates protons in aqueous solution.

(b) It is a Lewis acid which abstracts OH^- from water and leaves H^+ to make the solution acidic.

(c) It gives metaboric acid when dissolved in water.

(d) It is prepared by reaction of borax with sulphuric acid hence it behaves as an acid.

68. Boron nitride can be represented by the given structure.



The structure of BN is similar to

(a) graphite (b) diamond

(c) benzene (d) pyridine.

69. $NaBH_4 + I_2 \rightarrow X + Y + Z$

$BF_3 + NaH \xrightarrow{450\ K} X + P$

$BF_3 + LiAlH_4 \rightarrow X + Q + R$

X, Y, Z, P, Q and R in the reactions are

	X	Y	Z	P	Q	R
(a)	$Na_4B_4O_7$	NaI	HI	HF	LiF	AlF_3
(b)	B_2H_6	NaI	H_2	NaF	LiF	AlF_3
(c)	B_2H_6	BH_3	NaI	$B_3N_3H_6$	Al_2F_6	AlF_3
(d)	BH_3	B_2H_6	H_2	$B_3N_3H_6$	LiF	AlF_3

70. Which of the following compounds are formed when BCl_3 is treated with water ?

(a) H_3BO_3
(b) B_2H_6
(c) B_2O_3
(d) HBO_2

71. Which is the hardest compound of boron ?

(a) B_2O_3
(b) BN
(c) B_4C
(d) B_2H_6

72. What are X and Y in the reaction ?

$$3B_2H_6 + 6X \rightarrow 3\,[BH_2(X)_2]^+[BH_4]^- \xrightarrow{heat} Y + 12H_2$$

(a) $X = NH_3, Y = B_3N_3H_6$
(b) $X = CO, Y = BH_3CO$
(c) $X = NaH, Y = NaF$
(d) $X = NF_3, Y = B_3N_3$

73. On hydroloysis, diborane produces

(a) $H_3BO_2 + H_2O_2$
(b) $H_3BO_3 + H_2$
(c) $B_2O_3 + O_2$
(d) $H_3BO_3 + H_2O_2$

74. What happens when diborane reacts with Lewis bases ?

(a) It forms boron trihydride (BH_3) due to cleavage.

(b) It undergoes cleaveage to give borane adduct BH_3L (where, L = Lewis base).

(c) It oxidises to give B_2O_3.

(d) It does not react with Lewis bases.

75. Which is not the use of orthoboric acid ?

(a) As an antiseptic and eye wash.

(b) In glass industry.

(c) In glazes for pottery.

(d) In borax - bead test.

76. Borax is not used

(a) as a styptic to stop bleeding

(b) in making enamel and pottergy glazes

(c) as a flux in soldering

(d) in making optical glasses.

77. The element which exists in liquid state for a wide range of temperature and can be used for measuring high temperature is

(a) B
(b) Al
(c) Ga
(d) In

78. Which of the following is a Lewis acid ?

(a) $AlCl_3$
(b) $MgCl_2$
(c) $CaCl_2$
(d) $BaCl_2$

79. The geometry of a complex species can be understood from the knowledge of type of hybridisation of orbitals of central atom. The hybridisation of orbitals of central atom in $[B(OH)_4]^-$ and the geometry of the complex are respectively

(a) sp^3, tetrahedral
(b) sp3, square planar
(c) sp^3d^2, octahedral
(d) dsp^2, square planar.

80. Which of the following oxides is acidic in nature ?

(a) B_2O_3
(b) Al_2O_3
(c) Ga_2O_3
(d) In_2O_3

81. The exhibition of highest co-ordination number depends on the availability of vacant orbitals in the central atom. Which of the following elements is not likely to act as central atom in MF_6^{3-} ?

(a) B
(b) Al
(c) Ga
(d) In

82. Ionisation enthalpy ($\Delta_i H_1$ kJ mol^{-1}) for the elements of Group 13 follows the order

(a) $B > Al > Ga > In > Tl$
(b) $B < Al < Ga < In < Tl$
(c) $B < Al > Ga > In > Tl$
(d) $B > Al < Ga > In < Tl$

83. In the structure of diborane

(a) all hydrogen atoms lie in one plane and boron atoms lie in a plane perpendicular to this plane

(b) 2 boron atoms and 4 terminal hydrogen atoms lie in the same plane and 2 bridging hydrogen atoms lie in the perpendicular plane

(c) 4 bridging hydrogen atoms and boron atoms lie in one plane and two terminal hydrogen atoms lie in a plane perpendicular to this plane

(d) all the atoms are in the same plane.

84. A compound X, of boron reacts with NH_3 on heating to give another compound Y which is called inorganic benzene. The compound X can be prepared by treating BF_3 with lithium aluminium hydride. The compounds X and Y are represented by the formulas

(a) B_2H_6, $B_3N_3H_6$ (b) B_2O_3, $B_3N_3H_6$

(c) BF_3, $B_3N_3H_6$ (d) $B_3N_3H_6$, B_2H_6

85. Which of the following ions is the most stable ?

(a) Sn^{2+} (b) Ge^{2+}

(c) Si^{2+} (d) Pb^{2+}

Group-14

86. The tendency of group 14 elements to show +2 oxidation state increases in the order of

(a) $C < Si < Sn < Pb < Ge$ (b) $C < Si < Ge < Sn < Pb$

(c) $Ge < Sn < Pb < C < Si$ (d) $Pb < Sn < Ge < C < Si$

87. An element of group 14 forms two oxides one of which is highly poisonous and neutral. Other oxide can be easily liquefied and compressed to give a solid which is used as a refrigerant under the name of drikold. The element and the oxides are

(a) Si, SiO, SiO_2 (b) Pb, PbO, PbO_2

(c) C, CO, CO_2 (d) Sn, SnO, SnO_2

88. The members of group 14 form tetrahalides of the type MX_4. Which of the following halides cannot be readily hydrolysed by water ?

(a) CX_4 (b) SiX_4

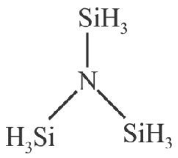
(c) GeX_4 (d) SnX_4

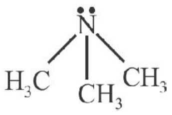
89. Which of the following hydrides is least stable to hydrolysis ?

(a) CH_4 (b) SiH_4

(c) SnH_4 (d) PbH_4

90. Trimethylammonia is pyramidal whereas trisilylammonia is a planar molecule. Why ?





(a) In silicon atom, the electron pair of nitrogen is involved in pπ - dπ bonding.

(b) In nitrogen, lone pair of electrons is present at nitrogen hence it has pyramidal shape.

(c) Both (a) and (b) are correct.

(d) Both (a) and (b) are wrong.

91. Identify X in the reaction :

$$X + \underset{\text{(steam)}}{2H_2O} \xrightarrow{\Delta} XO_2 + 2H_2$$

(a) C (b) Si

(c) Ge (d) Sn

92. All members of group 14 when heated in oxygen form oxides. Which of the following is the correct trend of oxides ?

(a) Dioxides CO_2, SiO_2 and GeO_2 are acidic while SnO_2 and PbO_2 are amphoteric.

(b) CO, GeO, SnO and PbO are amphoteric.

(c) Monoxides react with haemoglobin to form toxic compounds.

(d) All oxides burn with blue flame.

93. In which of the following the inert pair effect is most prominent ?

(a) C (b) Ge

(c) Si (d) Pb

94. Identify the wrong example from the following for the group 14 elements.

(a) Element which forms most acidic dioxide-Carbon

(b) Element which is affected by water - Lead

(c) Commonly found in +2 oxidation state - Lead

(d) Element used as semiconductor - Silicon

95. Maximum ability of catenation is shown by

(a) silicon (b) lead

(c) germanium (d) carbon.

96. Which one of the following is not the characteristic property of carbon ?

(a) It exhibits catenation.

(b) It forms compounds with multiple bonds.

(c) Its melting point and boiling point are exceptionally high.

(d) It shows semi-metallic character.

97. There is a large number of carbon compounds due to

(a) tetravalency of carbon

(b) strong catenation property of carbon

(c) allotropic property of carbon

(d) non-metallic character of carbon.

98. Carbon shows a maximum covalency of four whereas other members can expand their covalence due to

(a) absence of d-orbitals in carbon

(b) ability of carbon to form $p\pi$ - $p\pi$ multiple bonds

(c) small size of carbon

(d) catenation of carbon.

99. Which of the following is not true about structure of diamond and graphite ?

(a) In diamond, each carbon in sp^3 hybridised while in graphite each carbon is sp^2 hybridised.

(b) In diamond, carbon atoms are closely packed in crystal lattice while graphite has layer structure.

(c) Diamond is a hard substance while graphite is a soft substance.

(d) Graphite is thermodynamically very less stable as compared to diamond and is amorphous form of carbon.

100. Buckminsterfullerence is

(a) graphite (b) diamond

(c) C-60 (d) quartz.

101. In graphite, C atom is in .... state.

(a) sp^3 (b) sp

(c) sp^2 (d) None of these

102. In graphite, the layers of carbon atoms are held by

(a) covalent bonds (b) coordinate bonds

(c) van der Waals forces (d) ionic bonds.

103. Identify the incorrect statement.

(a) Graphite is thermodynamically most stable allotrope of carbon.

(b) Other forms of elemental carbon like coke, carbon black, charcoal are impure forms of graphite.

(c) All allotropes of carbon have thermodynamically same stability.

(d) Charcoal and coke are obtained by heating wood in absence of air.

104. Which of the following does not depict properties of fullerenes ?

(a) Fullerenes are made by heating graphite.

(b) Fullerenes are pure forms of carbon.

(c) Fullerenes have open cage structure like ice.

(d) C_{60} is called Buckminsterfullerene.

105. The most stable form of carbon at high temperature is X. The C – C bond length in diamond is Y while C – C bond length in graphite is Z.

What are X, Y and Z respectively ?

(a) Graphite, 1.42 Å, 1.54 Å

(b) Coke, 1.54 Å, 1.84 Å

(c) Diamond, 1.54 Å, 1.42 Å

(d) Fullerene, 1.54 Å, 1.54 Å

106. Which of the following is not a use of graphite ?

(a) For electrodes in batteries.

(b) Crucibles made from graphite are used for its inertness to dilute acids and alkalies.

(c) For adsorbing poisonous gases.

(d) Lubricant at high temperature.

107. Silicon is an important constituent of

(a) sand (b) atmosphere

(c) plants (d) water bodies

108. Match the column I with column II and mark the appropriate choice.

	Column I	Column II
(A)	Coal gas	(i) $CO + H_2$
(B)	Synthesis gas	(ii) CH_4
(C)	Producer gas	(iii) $H_2 + CH_4 + CO$
(D)	Natural gas	(iv) $CO + N_2$

(a) (A) → (i), (B) → (ii), (C) → (iii), (D) → (iv)

(b) (A) → (iii), (B) → (i), (C) → (iv), (D) → (ii)

(c) (A) → (iv), (B) → (iii), (C) → (ii), (D) → (i)

(d) (A) → (i), (B) → (iii), (C) → (ii), (D) → (iv)

109. In SiO_4^{4-}, the tetrahedral molecule, two oxygen atoms are shared in

(a) sheet silicates

(b) double-chain silicates

(c) chain silicates

(d) three-dimensional silicates.

110. Complete the following reactions :

(i) $SiO_2 + 2NaOH \rightarrow X + H_2O$

(ii) $SiO_2 + 4HF \rightarrow Y + 2H_2O$

(iii) $Si + 2CH_3Cl \xrightarrow[570\,K]{Cu\ powder} Z$

	X	Y	Z
(a)	Na_2SiO_3	SiF_4	$(CH_3)_2SiCl_2$
(b)	H_2SiO_3	SiF_2	CH_3SiCl_3
(c)	Na_2SiO_3	H_2SiO_3	$(CH_3)_3SiCl$
(d)	Na_2SiO_3	H_2SiF_4	$(CH_3)_2SiCl_2$

111. When excesss of carbon dioxide is passed through lime water, the milkiness first formed disappears due to

(a) the reversible reaction taking place

(b) formation of water soluble calcium bicarbonate

(c) huge amount of heat evolved during the reaction

(b) formation of water soluble complex of calcium.

112. Which of the following is the correct statement about silicones ?

(a) They are made up of SiO_4^{4-} units.

(b) They are polymers made up of R_2SiO units.

(c) They are water soluble compounds.

(d) They are hydrophillic in nature.

113. A type of zeolite used to convert alcohols directly into gasoline is

(a) zeolite A

(b) zeolite L

(c) zeolite Beta

(d) ZSM-5

114. Which of the following properties correctly explain SiO_2 ?

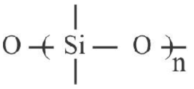
(a) Linear, basic

(b) Tetrahedral, acidic

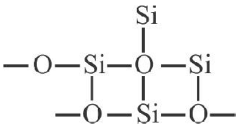
(c) Tetrahedral, basic

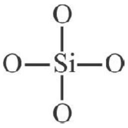
(d) Linear, acidic

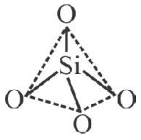
115. Which of the following bonds is shown in silicones ?

(a) 

$O \left(-\underset{|}{\overset{|}{Si}}-O \right)_n$

(b) 

(c) 

(d) 

116. Which of the following is not true about structure of carbon dioxide ?

(a) In CO_2, carbon is sp - hybridised.

(b) C forms two sigma bonds one with each oxygen atom and two $p\pi - p\pi$ bonds.

(c) CO_2 is a linear covalent compound

(d) It is a polar molecule.

117. Carbon monoxide acts as a donor and reacts with certain metals to give metal carbonyls. This is due to

(a) presence of one sigma and two pi bonds between C and $(:C \equiv O:)$

(b) presence of a lone pair on carbon atom in CO molecule

(c) presence of lone pair on oxygen atom in CO molecule

(d) poisonous nature of CO.

118. Mark the example which is not correct.

(a) Non-combustible heavy liquid used as fire extinguisher - CCl_4

(b) Blocks used to shield radioactive materials - Lead

(c) Element which has property of leaving mark on paper-Graphite

(d) A gas in solid form used as a refrigerant - Carbon monoxide.

119. Which of the following oxides can act as a reducing agent ?

(a) CO (b) CO_2

(c) SnO_2 (d) PbO_2

120. Glass and cement are two important examples of

(a) man-made silicates (b) silicones

(c) zeolites (d) organic polymers.

121. Match the column I with column II and mark the appropriate choice.

Column I	**Column II**
(A) Used as lubricant	(i) Carbon dioxide
(B) Oxide with three- dimensional structure	(ii) Graphite
(C) Used in solar cells	(iii) Silica
(D) Anhydride of carbonic acid	(iv) Silicone

(a) (A) → (iv), (B) → (iii), (C) → (ii), (D) → (i)

(b) (A) → (iv), (B) → (i), (C) → (iii), (D) → (ii)

(c) (A) → (iii), (B) → (ii), (C) → (i), (D) → (iv)

(d) (A) → (ii), (B) → (iii), (C) → (iv), (D) → (i)

122. Which of the following acids cannot be stored in glass ?

(a) HF (b) HCl

(c) H_2SO_4 (d) HI

123. Which property of CO_2 makes it of biological and geochemical importance ?

(a) Its acidic nature.

(b) Its colourless and odourless nature.

(c) Its low solubility in water.

(d) Its high compressibility.

124. CO_2 is not a poisonous gas but there is increase in concentration of CO_2 in the atmosphere due to burning of fossil fuels and decompostion of limestone. The increase in concentration of CO_2 may lead to

(a) increase in photosynthesis in plants

(b) higher concentration of CO_2 in water

(c) increase in greenhouse effect, thus raising the temperature

(d) increase in formation of metal carbonates.

125. An oxide X in its normal form is almost non-reactive due to very high X – O bond enthalpy. It resists the attack by halogens, hydrogen and most of acids and metals even at elevated temperatures. It is only attacked by HF and NaOH. The oxide X is

(a) SiO_2 (b) CO_2

(c) SnO_2 (d) PbO_2

126. Which is not a method of preparing carbon monoxide on a commercial scale ?

(a) $C_{(s)} + H_2O_{(g)} \xrightarrow{473-1273\text{ K}} CO_{(g)} + H_{2(g)}$

(b) $2C_{(s)} + O_{2(g)} + 4N_{2(g)} \xrightarrow{1273\text{ K}} 2CO_{(g)} + 4N_{2(g)}$

(c) $2C_{(s)} + O_{2(g)} \xrightarrow{\Delta} 2CO_{(g)}$

(d) $HCOOH \xrightarrow[\text{conc. } H_2SO_4]{373\text{ K}} H_2O + CO$

127. What happens when silicon is heated with methyl chloride in presence of copper as a catalyst at 573 K ?

(a) Methyl substituted chlorosilanes are formed.

(b) Only Me_4Si is formed.

(c) Polymerised chains of $(CH_3)_3SiCl$ are formed.

(d) Silicones are formed.

128. Catenation i.e., linking of similar atoms depends on size and electronic configuration of atoms. The tendency of catenation in Group 14 elements follows the order

(a) $C > Si > Ge > Sn$ (b) $C >> Si > Ge \approx Sn$

(c) $Si > C > Sn > Ge$ (d) $Ge > Sn > Si > C$

129. Silicon has a strong tendency to form polymers like silicones. The chain length of silicone polymer can be controlled by adding

(a) $MeSiCl_3$ (b) Me_2SiCl_2

(c) Me_3SiCl (d) Me_4Si

130. The most commonly used reducing agent is

(a) $AlCl_3$ (b) $PbCl_2$

(c) $SnCl_4$ (d) $SnCl_2$

131. Dry ice is

(a) solid NH_3 (b) solid SO_2

(c) solid CO_2 (d) solid N_2.

132. Cement, the important building material is a mixture of oxides of several elements. Besides calcium, iron and sulphur, oxides of elements of which of the group(s) are present in the mixture ?

(a) Group 2 (b) Groups 2, 13 and 14

(c) Groups 2 and 13 (d) Groups 2 and 14

EXERCISE - 2 : PREVIOUS YEAR JEE MAINS QUESTION

1. The soldiers of Napolean army while at Alps during freezing winter suffered a serious problem as regards to the tin buttons of their uniforms. White metallic tin buttons got converted to grey powder. This transformation is related to **(2003)**

(a) A change in the partial pressure of oxygen in the air

(b) A change in the crystalline structure of tin

(c) An interaction with nitrogen of the air at very low to temperatrure

(d) An interaction with water vapour contained in the humid air.

2. Aluminium chloride exists as dimer, Al_2Cl_6 in solid state as well as in solution of non-polar solvents such as benzene. When dissolved in water, it gives **(2004)**

(a) $[Al(OH)_6]^{3-} + 3HCl$

(b) $[Al(H_2O)_6]^{3+} + 3Cl^-$

(c) $Al^{3+} + 3Cl^-$

(d) $Al_2O_3 + 6HCl$

3. The structure of diborane (B_2H_6) contains **(2005)**

(a) Four 2c-2e bonds and two 3c-2e bonds

(b) Two 2c-2e bonds and four 3c-2e bonds

(c) Two 2c-2e bonds and two 3c-3e bonds

(d) Four 2c-2e bonds and four 3c-2e bonds

4. Heating an aqueous solution of aluminium chloride to dryness will give **(2006)**

(a) $AlCl_3$ (b) Al_2Cl_6

(c) Al_2O_3 (d) $Al(OH)Cl_2$

5. In silicon dioxide **(2008)**

(a) Each silicon atom is surrounded by four oxygen atoms and each oxygen atom is bonded to two silicon atoms

(b) Each silicon atom is surrounded by two oxygen atoms and each oxygen atom is bonded to two silicon atoms

(c) Silicon atom is bonded to two oxygen atoms

(d) There are double bonds between silicon and oxygen atoms

6. Which one of the following alkaline earth metal sulphates has its hydration enthalpy greater than its lattice enthalpy? **(2015)**

(a) $BaSO_4$ (b) $SrSO_4$

(c) $CaSO_4$ (d) $BeSO_4$

7. When metal 'M' is treated with NaOH, a white gelatinous precipitate 'X' is obtained, which is soluble in excess of NaOH. Compound 'X' when heated strongly gives an oxide which is used in chromatography as an adsorbent. The metal 'M' is: **(2018)**

(a) Fe (b) Zn

(c) Ca (d) Al

JEE MAINS ONLINE QUESTION

1. The gas evolved on heating CaF_2 and SiO_2 with concentrated H_2SO_4, on hydrolysis gives a white gelatinous precipitate. The precipitate is:

Online 2014 SET (3)

(a) hydrofluosilicic acid (b) silica gel

(c) silicic acid (d) calciumfluorosilicate

2. Example of a three-dimensional silicate is

Online 2014 SET (4)

(a) Ultramarines (b) Beryls

(c) Zeolites (d) Feldspars

3. Boron cannot form which one of the following anions

Online 2016 SET (1)

(a) BF_6^{3-} (b) BH_4^-

(c) $B(OH)_4^-$ (d) BO_2^-

4. **Assertion :** Among the carbon allotropes, diamond is an insulator, whereas, graphite is a good conductor of electricity.

Reason : Hybridization of carbon in diamond and graphite are sp^3 and sp^2, respectively.

Online 2016 SET (2)

(a) Both assertion and reason are correct, and the reason is the correct explanation for the assertion.

(b) Both assertion and reason are correct, but the reason is not the correct explanation for the assertion.

(c) Assertion is incorrect statement, but the reason is correct.

(d) Both assertion and reason are incorrect.

5. Consider the following standard electrode potentials (E° in volts) in aqueous solution : **Online 2017 SET (1)**

Element	**M^{3+}/M**	**M^{+}/M**
Al	–1.66	+0.55
TI	+1.26	–0.34

Based on these data, which of the following statements is **correct** ?

(a) TI^+ is more stable than Al^{3+}

(b) Al^+ is more stable than Al^{3+}

(c) TI^+ is more stable than Al^+

(d) TI^{3+} is more stable than Al^{3+}

6. In graphite and diamond, the percentage of p-characters of the hybrid orbitals in hybridisation are respectively :

Online 2018 SET (1)

(a) 33 and 25 (b) 33 and 75

(c) 50 and 75 (d) 67 and 75

7. Lithium aluminium hydride reacts with silicon tetrachloride to form : **Online 2018 SET (2)**

(a) LiCl, AlH_3 and SiH_4

(b) LiCl, $AlCl_3$ and SiH_4

(c) LiH, $AlCl_3$ and $SiCl_2$

(d) LiH, AlH_3 and SiH_4

EXERCISE - 3 : ADVANCED OBJECTIVE QUESTIONS

1. All questions marked **"S"** are single choice questions
2. All questions marked **"M"** are multiple choice questions
3. All questions marked **"C"** are comprehension based questions
4. All questions marked **"A"** are assertion–reason type questions

   (A) If both assertion and reason are correct and reason is the correct explanation of assertion.

   (B) If both assertion and reason are true but reason is not the correct explanation of assertion.

   (C) If assertion is true but reason is false.

   (D) If reason is true but assertion is false.
5. All questions marked **"X"** are matrix–match type questions
6. All questions marked **"I"** are integer type questions

---

1. (S) Which of the following is correct?

(a) The members of B_nH_{n+6} are less stable than B_nH_{n+4} series

(b) Diborane is coloured and unstable at room temperature

(c) The reaction of diborane with oxygen is endothermic

(d) All of the above

2. (S) In which of the following, a salt of the type KMO_2 is obtained?

(a) $B_2H_6 + KOH(aq.) \rightarrow$

(b) $Al + KOH(aq.) \rightarrow$

(c) Both

(d) None of these

3. (S) Which of the following compounds is formed in borax bead test?

(a) Metaborate (b) tetraborate

(c) Double oxide (d) Orthoborate

4. (S) Borax is used as a cleansing agent because on dissolving in water, it gives:

(a) alkaline solution (b) acidic solution

(c) bleaching solution (d) neutral solution

5. (S) Boric acid is used in carrom boards for smooth gliding of pawns because:

(a) H_3BO_3 molecules are loosely chemically bonded and hence soft

(b) its low density makes it fluffy

(c) it is chemically inert with the plywood

(d) H-bonding in H_3BO_3 gives it a layered structure

6. (S) $H_3BO_3 \xrightarrow{100^\circ C} X \xrightarrow{160^\circ C} Y \xrightarrow{\text{Red hot}} B_2O_3$;

X and Y respectively are:

(a) X = Metaboric acid ; Y = Tetraboric acid

(b) X = Borax; Y = Metaboric acid

(c) X = Tetraboric acid ; Y = Metaboric acid

(d) X = Tetraboric acid ; Y = Borax

7. (S) A gas other than HCl is obtained in :

(a) $BCl_3 + H_2 \xrightarrow[\text{discharge}]{\text{Silent electric}}$

(b) $LiAlH_4 + BF_3 \rightarrow$

(c) Both (d) None of these

8. (S) Hydride of boron occurs as B_2H_6 but B_2Cl_6 does not exist. This is because :

(a) $p\pi$-$d\pi$ back bonding is possible in B_2H_6 but not in B_2Cl_6

(b) boron and hydrogen have almost equal values of electronegativity

(c) boron and chlorine have almost equal atomic sizes

(d) small hydrogen atoms can easily fit in between boron atoms but large chlorine atoms do not

9. (S) When an inorganic compound (X) having 3C—2e as well as 2e—2e bonds reacts with ammonia gas at a certain temperature, gives a compound (Y), isostructural with benzene. Compound (X) with ammonia at a high temperature produces a substance (Z). Which of the following is not correct?

(a) (X) is B_2H_6

(b) (Z) is known as inorganic graphite

(c) (Y) is $B_3N_3H_6$ (d) (Z) is soft like graphite

10. (S) Boron does not form B^{3+} cation easily. It is due to:

(a) energy required to form B^{3+} ion is very high which will not be compensated by lattice energies or hydration energies of such ion

(b) boron is non-metal

(c) boron is semi-metal

(d) none of the above

11. (S) $Na_2B_4O_7.10H_2O$ is correctly represented as:

(a) $2NaBO_2.Na_2B_2O_3.10H_2O$

(b) $Na_2[B_4O_5(OH)_4].8H_2O$

(c) $Na_2[B_4(H_2O)_4O_7].6H_2O$

(d) all of these

12. (S) Orthoboric acid behaves as a weak monobasic acid giving H_3O^+ and

(a) $[B(OH)_4]^+$ (b) $H_2BO_2^+$

(c) $[B(OH)_4]^-$ (d) $H_2BO_2^-$

13. (S) Amorphous boron is extracted from borax by following steps:

$$\text{Borax} \xrightarrow{(A)} H_3BO_3 \xrightarrow{\text{Heat}} B_2O_3 \xrightarrow{(B)} \text{Boron.}$$

(A) and (B) are:

(a) H_2SO_4, Al (b) HCl, carbon

(c) H_2SO_4, Mg (d) HCl, Fe

14. (S) Aqueous solution of borax acts as a buffer because:

(a) it contains weak acid and its salt with strong base

(b) it contains tribasic acid and strong base

(c) it contains number of neutral water molecules

(d) none of the above

15. (S)

$$\begin{tikzcd} B \arrow[r, "Z"] & X \arrow[r, "LiH"] & Y + LiBH_4 \arrow[ll, bend left, "Heat"] \end{tikzcd}$$

Which of the statement is true for the above sequence of reactions?

(a) Z is hydrogen (b) X is B_2H_6

(c) Z and Y are F_2 and B_2H_6 respectively

(d) Z is potassium hydroxide

16. (S) The structure of diborane (B_2H_6) contains :

(a) four 2C-2e bonds and two 3C-2e bonds

(b) two 2C-2e bonds and four 3C-2e bonds

(c) two 2C-2e bonds and two 3C-3e bonds

(d) four 2C-2e bonds and four 3C-2e bonds

17. (S) Alumina is:

(a) acidic (b) basic

(c) neutral (d) amphoteric

18. (S) In the purification of bauxite by Hall's process:

(a) bauxite is heated with lime

(b) bauxite is heated with NaOH solution at 150°C

(c) bauxite is heated with Na_2CO_3 solution

(d) bauxite is heated at 1800°C in an atmosphere of N_2

19. (S) Which of the following minerals does not contain aluminium?

(a) Cryolite (b) Mica

(c) Feldspar (d) Fluorspar

20. (S) The function of fluorspar in the electrolytic reduction of alumina dissolved in fused cryolite (Na_3AlF_6) is:

(a) as a catalyst

(b) to lower the temperature of melt and to make the fused mixture very conducting

(c) to decrease the rate of oxidation of carbon anode

(d) none of the above

21. (S) Al_2O_3 can be converted to anhydrous $AlCl_3$ by heating:

(a) a mixture of Al_2O_3 and carbon in dry Cl_2 gas

(b) Al_2O_3 with Cl_2 gas

(c) Al_2O_3 with HCl gas

(d) Al_2O_3 with NaCl in solid state

22. (M) Orthoboric acid (H_3BO_3) and metaboric acid (HBO_2) differ in respect of:

(a) basicity (b) structure

(c) melting point (d) oxidation

23. (M) Select the correct statements about diborane

(a) B_2H_6 has three centred bond

(b) Each boron atom lies in sp^3 hybrid state

(c) H_b......B........H_b bond angle is 122°

(d) All hydrogens in B_2H_6 lie in the same plane

24. (M) Which of the following statements are true for H_3BO_3?

(a) It is mainly monobasic acid and a Lewis acid

(b) It does not act as a proton donor but acts as an acid by accepting hydroxyl ions

(c) It has a layer structure in which BO_3 units are joined by hydrogen bonds

(d) It is obtained by treating borax with conc. H_2SO_4

25. (M) In the reaction

$$2X + B_2H_6 \rightarrow [BH_2X_2]^+[BH_4]^-$$

the amine(s) X is (are) :

(a) NH_3 (b) CH_3NH_2

(c) $(CH_3)_2NH$ (d) $(CH_3)_3N$

26. (M) In Al_2Cl_6 which statement(s) is (are) incorrect?

(a) Four Al—Cl bonds are of the same length and two of different length

(b) Six Al—Cl bonds are of same length

(c) The angle Cl—Al—Cl is 110° and 93°

(d) The angle Cl—Al—Cl is 87°

Passage (Ques 27 to 32)

Aluminium is stable in air and water in sipite of the fact that it is reactive metal. The reason is that a thin film of its oxide is formed on its surface which it passive for further attack. The layer is so useful that in industry, it is purposely deposited by an electrolytic process called anodising

Reaction of aluminium with oxygen is highly exothermic and is called thermite reaction.

$$2Al(s) + \frac{3}{2}O_2(g) \rightarrow Al_2O_3(s); \quad \Delta H = -1670\,kJ$$

Thermite reaction finds applications in the metallurgical extraction of many metals from their oxides and for welding of metals. The drawback is that to start the reaction, high temperature is required for which an ignition mixture is used.

27. (C) Anodising can be done by electrolysing dilute H_2SO_4 with aluminium as anode. This results in :

(a) the formation of $Al_2(SO_4)_3$ on the surface of aluminium anode

(b) the formation of oxide film (Al_2O_3) on the surface of aluminium anode

(c) the formation of polymeric aluminium hydride film on the surface of aluminium anode

(d) none of the above

28. (C) The reaction which is not involved in thermite process:

(a) $3Mn_3O_4 + 8Al \longrightarrow 9Mn + 4Al_2O_3$

(b) $Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3$

(c) $2Fe + Al_2O_3 \longrightarrow Fe_2O_3 + 2Al$

(d) $B_2O_3 + 2Al \longrightarrow 2B + Al_2O_3$

29. (C) Thermite a mixture used for welding is:

(a) Fe and Al

(b) BaO and Mg powder

(c) Cu and Al

(d) Fe_2O_3 and Al powder

30. (C) Anodised aluminium is :

(a) Al obtained at anode

(b) Al prepared electrolytically

(c) alloy of Al containing 95% Al

(d) Al electrolytically coated with aluminium oxide

31. (C) Which one of the following metals cannot be extracted by using Al as a reducing agent?

(a) Na from Na_2O (b) Cr from Cr_2O_3

(c) W from WO_3 (d) Mn from Mn_3O_4

32. (C) Aluminium becomes passive in:

(a) conc. HNO_3 (b) H_2CrO_4

(c) $HClO_4$ (d) all of these

Passage (Ques. 33 to 37)

$$Ca_2B_6O_{11} + Na_2CO_3 \xrightarrow{\text{Fused}} (A) + (B) + CaCO_3$$

$$\underset{\text{Solution}}{(A)} + CO_2 \longrightarrow (B) + Na_2CO_3$$

$$(B) + \text{Conc.}\,HCl \longrightarrow NaCl + \text{Acid} \xrightarrow{H_2O} \text{Acid}\,(C)$$

$$(C) \xrightarrow[\text{heated}]{\text{Strongly}} (D)$$

$$(D) + CuSO_4 \xrightarrow[\text{inflame}]{\text{Heated}} \text{Blue coloured (E) compound}$$

33. (C) Compound (A) is:

(a) $NaBO_2$ (b) $Na_2B_4O_7$

(c) Na_3BO_3 (d) NaOH

34. (C) Compound (B) is:

(a) $NaBO_2$ (b) $Na_2B_4O_7$

(c) Na_3BO_3 (d) NaOH

35. (C) Compound (C) is:

(a) $H_2B_4O_7$ (b) HBO_2

(c) H_3BO_3 (d) HB_3O_5

36. (C) Compound (D) is:

(a) H_3BO_3 (b) B_2O_3

(c) B (d) none of these

37.(C) Compound (E) is:

(a) Cu_2O (b) CuS

(c) $CuSO_3$ (d) $Cu(BO_2)_2$

Passage (Ques. 38 to 45)

(i) $\text{Boron} + O_2 \xrightarrow{700^\circ C} (X)$

(ii) $(X) + C(\text{carbon}) + Cl_2 \rightarrow (Y) + CO$

(iii) $(Y) + LiAlH_4 \rightarrow (Z) + LiCl + AlCl_3$

(iv) $(Z) + NH_3 \rightarrow (A) \xrightarrow{\text{Heat}} (B)$

(v) $(Z) + NaH \rightarrow (D)$

38. (C) Compound (Z) is:

(a) an ionic compound

(b) an electron deficient compound

(c) 3C—2e compound

(d) having ethane like structure

39. (C) Compounds (X) and (Y) are:

(a) $(X) = BO_2, (Y) = BCl_2$

(b) $(X) = BO_3, (Y) = BCl_4$

(c) $(X) = B_2O_3, (Y) = BCl_3$

(d) $(X) = BO_3, (Y) = B_4C$

40. (C) Compound (B) is:

(a) borazole (b) inorganic benzene

(c) borazon (d) boron nitride

41. (C) Compound (D) is used as a/an :

(a) oxidising agent (b) complexing agent

(c) buffer agent (d) reducing agent

42. (C) Compound Y:

(a) has boron in sp^2 hybridized state

(b) is a planar molecule

(c) has zero dipole moment

(d) is a Lewis base

Passage (Ques. 43 to 45)

(i) $P + C(\text{carbon}) + Cl_2 \rightarrow Q + CO \uparrow$

(ii) $Q + H_2O \rightarrow R + HCl$

(iii) $BN + H_2O \rightarrow R + NH_3 \uparrow$

(iv) $Q + LiAlH_4 \rightarrow S + LiCl + AlCl_3$

(v) $S + H_2 \rightarrow R + H_2 \uparrow$

(vi) $S + NaH \rightarrow T$

(P, Q, R, S and T do not represent their chemical symbols)

43. (C) Compound Q has:

(I) Zero dipole moment

(II) a planar trigonal structure

(III) an electron deficient compound

(IV) a Lewis base

Choose the correct code:

(a) I, IV (b) I, II, IV

(c) I, II, III (d) I, II, III, IV

44. (C) Compound T is used as a/an :

(a) oxidising agent (b) complexing agent

(c) bleaching agent (d) reducing agent

45. (C) Compound S is:

(I) an odd-e^- compound

(II) (2c-3e^-) compound

(III) a electron deficient compound

(IV) a sp^2 hybridized compound

Choose the correct code:

(a) III (b) I, III

(c) II, III, IV (d) I, II, IV

46. (A) **Assertion :** Borax bead test is not suitable for Al (III)

Reason : Al_2O_3 is insoluble in water.

(a) A (b) B

(c) C (d) D

47. (A) **Assertion :** BF_3 is a weaker Lewis acid than BCl_3.

Reason : BF_3 molecule is stabilized to a greater extent than BCl_3 by B—F π-bonding.

(a) A (b) B

(c) C (d) D

48. (A) **Assertion :** In water, orthoboric acid behaves as a weak monobasic acid.

Reason : In water, othoboric acid acts as a proton donor.

(a) A (b) B

(c) C (d) D

49. (A) **Assertion :** Boron always forms covalent bond.

Reason : The small size of B^{3+} favours formation of covalent bond.

(a) A (b) B

(c) C (d) D

50. (A) **Assertion :** If aluminium atoms replace a few silicon atoms in three dimensional network of silicon dioxide, the overall structure acquires a negative charge.

Reason : Aluminium is trivalent while silicon is tetravalent.

(a) A (b) B

(c) C (d) D

51. (A) **Assertion :** AlF_3 is soluble in KF but addition of BF_3 brings its precipitation.

Reason BF_3 is more acidic than AlF_3.

(a) A (b) B

(c) C (d) D

52. (I) Consider the structure of Al_2Me_6 compound and find the vale of $\frac{x-y}{z}$.

Where x = Maximum number of atoms that can lie in plane having terminal (Al-Me) bonds.

y = Total number of 3c-2e$^-$ bonds.

z = Total number of atoms that are sp^3 hybridized.

53. (I) Find the value of x in the termolite abestos:

$$Ca_2Mg_x(Si_4O_{11})_2(OH)_2$$

54. (I) Consider $Al_2(OH)_6$ compound and calculate the value of $(X+Y) \div Z$

Where X = Total number of (2c—2e$^-$) bond.

Y = Total number of (3c—2e$^-$) bond.

Z = Total number of (3c—4e$^-$) bond.

55. (I) When B_2H_6 is allowed to react with following lewis bases, then how many given lewis bases form adduct through symmetrical cleavage of B_2H_6?

NH_3, $MeNH_2$, Pyridine, CO, T.H.F, PH_3, PF_3, Me_3N, Me_2NH

EXERCISE - 4 : PREVIOUS YEAR JEE ADVANCED QUESTIONS

Only One Correct Option

1. Moderate electrical conductivity is shown by **(1982)**

(a) silica (b) graphite

(c) diamond (d) None of these

2. Which of the following halides is least stable and has doubtful existence ? **(1996)**

(a) CCl_4 (b) GeI_4

(c) SnI_4 (d) PbI_4

3. Which one of the following oxides is neutral ? **(1996)**

(a) CO (b) SnO_2

(c) ZnO (d) SiO_2

4. In compounds of type ECl_3, where E = B, P, As or Bi, the angles Cl—E—Cl for different E are in the order **(1999)**

(a) $B > P = As = Bi$ (b) $B > P > As > Bi$

(c) $B < P = As = Bi$ (d) $B < P < As < Bi$

5. Identify the correct order of acidic strength of CO_2, CuO, CaO, H_2O. **(2002)**

(a) $CaO < CuO < H_2O < CO_2$

(b) $H_2O < CuO < CaO < CO_2$

(c) $CaO < H_2O < CuO < CO_2$

(d) $H_2O < CO_2 < CaO < CuO$

6. H_3BO_3 is **(2003)**

(a) monobasic acid and weak Lewis acid

(b) monobasic and weak Bronsted acid

(c) monobasic and strong Lewis acid

(d) tribasic and weak Bronsted acid

7. $(Me)_2\,SiCl_2$ on hydrolysis will produce **(2003)**

(a) $(Me)_2\,Si(OH)_2$ (b) $(Me)_2\,Si = O$

(c) $[\text{—O—}(Me)_2\,Si\text{—O—}]_n$

(d) $Me_2SiCl(OH)$

8. Name the structure of silicates in which three oxygen atoms of $[SiO_4]^{4-}$ are shared is **(2005)**

(a) pyrosilicate (b) sheet silicate

(c) linear chain silicate (d) three dimensional silicate

9. $B(OH)_3 + NaOH \rightleftharpoons NaBO_2 + Na[B(OH)_4] + H_2O$

How can this reaction is made to proceed in forward direction ? **(2006)**

(a) Addition of cis 1, 2 diol

(b) Addition of borax

(c) Addition of trans 1, 2 diol

(d) Addition of Na_2HPO_4

One or More than One Correct Option

10. In the reaction,

$$2X + B_2H_6 \rightarrow [BH_2(X)_2]^+ [BH_4]^-$$

the amine(s) X is (are) **(2009)**

(a) NH_3 (b) CH_3NH_2

(c) $(CH_3)_2\,NH$ (d) $(CH_3)_3\,N$

11. The crystalline form of borax has **(2016)**

(a) tetranuclear $[B_4O_5(OH)_4]^{2-}$ unit

(b) all boron atoms in the same plane

(c) equal number of sp^2 and sp^3 hybridized boron atoms

(d) one terminal hydroxide per boron atom

12. The correct statement(s) for orthoboric acid is/are **(2017)**

(a) It behaves as a weak acid in water due to self ionization.

(b) Acidity of its aqueous solution increases upon addition of ethylene glycol.

(c) It has a three dimensional structure due to hydrogen bonding.

(d) It is a weak electro in water

Assertion and Reason

Read the following question and answer as per the direction given below :

(a) Statement I is true; Statement II is true; Statement II is the correct explanation of Statement I.

(b) Statement I is true; Statement II is true; Statement II is not the correct explanation of Statement I.

(c) Statement I is true; Statement II is false.

(d) Statement I is false; Statement II is true.

13. **Statement I :** $Al(OH)_3$ is amphoteric in nature.

Statement II : Al—O and O—H bonds can be broken with equal ease in $Al(OH)_3$. **(1998)**

14. **Statement I :** Between $SiCl_4$ and CCl_4, only $SiCl_4$ reacts with water.

Statement II : $SiCl_4$ is ionic and CCl_4 is covalent.

15. **Statement I :** Boron always forms covalent bond.

Statement II : The small size of B^{3+} favours formation of covalent bond.

16. **Statement I :** In water, orthoboric acid behaves as a weak monobasic acid.

Statement II : In water, orthoboric acid acts as a proton donor.

17. **Statement I :** Pb^{4+} compounds are stronger oxidising agents than Sn^{2+} compounds.

Statement II : The higher oxidation states for the group 14 elements are more stable for the heavier members of the group due to 'inert pair effect'. **(2008)**

Match the Columns

18. Match the following :

Column I	**Column II**
(A) $Bi^{3+} \rightarrow (BiO)^+$	(p) Heat
(B) $[AlO_2]^- \rightarrow Al(OH)_3$	(q) Hydrolysis
(C) $SiO_4^{4-} \rightarrow Si_2O_7^{6-}$	(r) Acidification
(D) $(B_4O_7^{2-}) \rightarrow [B(OH)3]$	(s) Dilution by water

Subjective Questions

19. Carbon acts as an abrasive and also as a lubricant, explain **(1981)**

20. Give reason for the following in one or two sentences :

"Solid carbon dioxide is known as dry ice." **(1983)**

21. Give reasons for the following in one or two sentences :

"Graphite is used as a solid lubricant." **(1985)**

22. Each entry in column X is in some way related to the entries in columns Y and Z. Match the appropriate entries.

X	Y	Z
Yeast	Fermentation	Ethanol
Mica	Graphite	Abrasive
Superphosphate	Crystalline cubic	Insulator
Carbon fibres	Layer structure	Fertilizer
Rock salt	Diamond structure	Reinforced plastics
Carborundum	Bone ash	Preservative

(1989)

23. Write the balanced equation for the prepartion of crystalline silicon from $SiCl_4$. **(1990)**

24. Anhydrous $AlCl_3$ is covalent. From the data given below, predict whether it would remain covalent or become ionic in aqueous solution.

(Ionization energy for Al = 5137 kJ mol^{-1}

$\Delta H_{hydration}$ for $Al^{3+} = -4665$ kJ mol^{-1}

$\Delta H_{hydration}$ for $Cl^- = -381$ kJ mol^{-1}

25. Aluminium sulphide gives a foul odour when it becomes damp. Write a balanced chemical equation for the reaction. **(1997)**

26. Draw the structure of a cyclic silicate, $(Si_3O_9)^{6-}$ with proper labelling.

27. Compound X on reduction with $LiAlH_4$ gives a hydride Y containing 21.72% hydrogen alongwith other products. The compound Y reacts with air explosively resulting in boron trioxide. Identify X and Y. Give balanced reactions involved in the formation of Y and its reaction with air. Draw the structure of Y. **(2001)**

28. Starting from $SiCl_4$, prepare the following in steps not exceeding the number given in parenthesis (give reactions only)

(i) Silicon

(ii) Linear silicon containing methyl group only

(iii) Na_2SiO_3 **(2001)**

29. (i) How is boron obtained from borax ? Give chemical equations with reaction conditions.

(ii) Write the structure of B_2H_6 and its reaction with HCl

(2002)

30. AlF_3 is insoluble in anhydrous HF but when little KF is added to the compound it becomes soluble. On addition of BF_3, AlF_3 is precipitated. Write the balanced chemical equations. **(2004)**

ANSWER KEY

Exercise-1 (Basic Objective Questions)

1. (d) **2.** (d) **3.** (b) **4.** (a) **5.** (b) **6** (c) **7.** (a) **8.** (d) **9.** (b) **10.** (d)

11. (b) **12.** (d) **13.** (b) **14.** (d) **15.** (b) **16.** (c) **17.** (c) **18.** (b) **19.** (c) **20.** (b)

21. (c) **22.** (a) **23.** (a) **24.** (d) **25.** (d) **26.** (b) **27.** (a) **28.** (b) **29.** (d) **30.** (d)

31. (d) **32.** (d) **33.** (d) **34.** (c) **35.** (c) **36.** (d) **37.** (d) **38.** (a) **39.** (a) **45.** (d)

41. (d) **42.** (d) **43.** (c) **44.** (a) **45.** (d) **46.** (b) **47.** (d) **48.** (c) **49.** (b) **50.** (b)

51. (b) **52.** (c) **53.** (d) **54.** (a) **55.** (d) **56.** (b) **57.** (b) **58.** (a) **59.** (a) **60.** (c)

61. (a) **62.** (d) **63.** (c) **64.** (b) **65.** (a) **66.** (b) **67.** (b) **68.** (a) **69.** (b) **70.** (a)

71. (c) **72.** (a) **73.** (b) **74.** (b) **75.** (d) **76.** (a) **77.** (c) **78.** (a) **79.** (a) **80.** (a)

81. (a) **82.** (d) **83.** (b) **84.** (a) **85.** (d) **86.** (b) **87.** (c) **88.** (a) **89.** (b) **90.** (c)

91. (d) **92.** (a) **93.** (d) **94.** (b) **95.** (d) **96.** (d) **97.** (b) **98.** (d) **99.** (d) **100.** (c)

101. (c) **102.** (c) **103.** (d) **104.** (c) **105.** (c) **106.** (c) **107.** (a) **108.** (b) **109.** (c) **110.** (a)

111. (b) **112.** (b) **113.** (d) **114.** (b) **115.** (a) **116.** (d) **117.** (b) **118.** (d) **119.** (a) **120.** (a)

121. (d) **122.** (a) **123.** (c) **124.** (c) **125.** (a) **126.** (d) **127.** (a) **128.** (b) **129.** (c) **130.** (d)

131. (c) **132.** (b)

Exercise-2 (Previous Year JEE Mains Questions)

1. (b) **2.** (a) **3.** (a) **4.** (c) **5.** (a) **6.** (d) **7.** (d)

JEE Mains Online

1. (c) **2.** (c) **3.** (a) **4.** (b) **5.** (c) **6.** (d) **7.** (b)

Exercise-3 (Advanced Objective Questions)

1. (a) **2.** (c) **3.** (a) **4.** (a) **5.** (d) **6.** (a) **7.** (c) **8.** (d) **9.** (d) **10.** (a)
11. (b) **12.** (c) **13.** (c) **14.** (a) **15.** (c) **16.** (a) **17.** (d) **18.** (c) **19.** (d) **20.** (b)
21. (a) **22.** (abc) **23.** (abc) **24.** (abcd) **25.** (abc) **26.** (bcd) **27.** (b) **28.** (c) **29.** (d) **30.** (d)
31. (a) **32.** (d) **33.** (a) **34.** (b) **35.** (c) **36.** (b) **37.** (d) **38.** (bc) **39.** (c) **40.** (ab)
41. (d) **42.** (abc) **43.** (c) **44.** (d) **45.** (a) **46.** (b) **47.** (a) **48.** (c) **49.** (a) **50.** (a)
51. (a) **52.** (0001) **53.** (0005) **54.** (0005) **55.** (0006)

Exercise-4 (Previous Year JEE Advanced Questions)

1. (b) **2.** (d) **3.** (a) **4.** (b) **5.** (a) **6.** (a) **7.** (c) **8.** (b) **9.** (a) **10.** (abc)
11. (a,c,d) **12.** (b,d) **13.** (a) **14.** (c) **15.** (a) **16.** (c) **17.** (a) **18.** A – q; B – r; C – p; D – q, r

Dream on !!