CHAPTER NO: 3

GROUP III-A AND GROUP IV-A ELEMENTS.

1. GROUP III-A ELEMENTS.

Elements of III-A group are included in p-block elements. This group include B, Al, Ga In, Tl. All elements of this group are metals except Boron, which is non metal.

NAME	ATOMIC NO.	ELECTRONIC CONFIGURATION.
Boron.	$_{5}B$	$1s^2, 2s^2, 2p^1$
Aluminium.	$_{13}Al$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^1$.
Gallium.	$_{31}Ga$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s\ 3d^{10}, 4p^1$.
Indium.	$_{49}In$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6$
		$5s^2, 5p^1$.
Thallium	$_{81}Tl$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}$
		$5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^1$.

So each element of third group contains three electrons in its outer most shell. Its general configuration is $ns^2 np^1$.

Table 3.1 Electronic Configurations and Physical Properties of Group IIIA Elements

Property	B	Al	Ga	In	Ti
Atomic Number	5	13	31	49	81
Electronic configuration	[He] $2s^2 2p^1$	[Ne] $3s^2 3p^1$	[Ar] $3d^{10} 4s^2 4p^1$	[Kr] $4d^{10} 5s^2$ 5	[Xe] $4f^{14} 5d^{10} 6s^2 6p^1$
Density g/cm^3	2.33	2.7	5.93	7.3	11.85
M.P °C	2300	660	30	157	304
Ist Ionization potential kJ/mol	801	577	579	558	589
Atomic Radius (pm)	80	125	126	144	148
Ionic Radius (pm)	20	52	60	81	95

PECULIAR BEHAVIOUR OF BORON.

Boron is the first member of the group III.
It differs from other members of its group due to

1. smaller size
2. high ionization energy.

Some important dissimilarities are as follows.

i - NON METALLIC CHARACTER.

Boron is non metallic in nature. ~~But~~ while all other members are metallic.

ii -

All elements having less than four electrons in outer most shell are metallic in nature Except boron which is non metal.

iii -

Boron always uses all three valence electrons for bonding purposes have common oxidation state +3 and -3.

iv - FORMATION OF ADDITION PRODUCT.

Boron form molecular addition product.

V - IONIC COMPOUNDS OF BORON.

Boron does not form ionic ~~addition~~ compounds with sulphate, nitrate or other anions because its cation is unstable.

vi OXIDE OF BORON

Boron form acidic oxides while other members form amphoteric or basic oxides.

vii - REACTION WITH DILUTE ACIDS & ALKALIES.

Boron does not react with dilute acid and alkalies but other members do so.

$$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2$$

$$B + HCl_{(dil)} \longrightarrow \text{No REACTION.}$$

VIII – CONDUCTANCE.
Boron is a semiconductor while other members are good conductors.

IX – HYDRIDES OF BORON.
Boron forms stable covalent hydrides called BORANES which are quite stable BH_3, B_2H_6 etc. while other members donot form stable hydrides.

X – MELTING AND BOILING POINTS.
due to very small size boron has exceptionally high M.P and B.P.

OCCURRENCE OF III-A GROUP ELEMENTS.

BORON is a rare element (0.00%). It does not occur free in nature. Boron always exist in nature in combined state with oxygen. Boron exists as salts of polyboric acid. It occurs in traces in most soils. Important minerals of boron are as follows.

NAME OF MINERALS.	CHEMICAL FORMULA.
BORAX or TINCAL.	$Na_2B_4O_7 \cdot 10H_2O$.
COLEMANITE.	$Ca_2B_6O_{11} \cdot 5H_2O$.
ORTHOBORIC ACID.	H_3BO_3.

ALUMINIUM is the third most abundant element in the earth's crust. It occurs as alumino silicate minerals found in rocks. Important minerals of aluminium are

Names of minerals of Al	Chemical formula.
Feldspar.	$KAlSi_3O_8$ or $K_2O \cdot Al_2O_3 \cdot 6SiO_2$
Mica (Muscovite).	$KH_2Al_3(SiO_4)_3$
Bauxite	$Al_2O_3 \cdot 2H_2O$
Cryolite.	Na_3AlF_6.
Corundum	Al_2O_3.
Kaoline	$H_2Al_2(SiO_4)_2 \cdot H_2O$ or $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$

other elements are rare and obtained as byproduct during processing of other

4 DISCUSS OCCURRENCE • EXTRACTION & REACTIONS OF BORON·

Boron is a rare element (0·001%) It does not occur free in nature. The important ores of Boron are :-

(i) BORAX. $Na_2B_4O_7 \cdot 10H_2O$

(ii) COLEMANIT $Ca_2B_6O_{11}$

(iii) BORIC ACID H_3BO_3.

EXTRACTION:- Boron is mostly obtained by reduction of Potassium flouroborate KBF_4 or Boric oxide by using Na, K or Mg as reducing agents.

REDUCTION OF B_2O_3

$$B_2O_3 + 6K \longrightarrow 3K_2O + 2B$$

$$B_2O_3 + Mg \longrightarrow 3MgO + 2B$$

REDUCTION OF KBF_4

$$KBF_4 + 3K \longrightarrow 4KF + B$$

$$2KBF_4 + 3Mg \longrightarrow 2B + 2KF + 3MgF_2$$

PHYSICAL & CHEMICAL PROPERTIES OF CRYSTALLINE BORON:-

Crystalline boron is hard and black solid with dull metallic lusture. It forms hexagonal crystals and is a bad conductor of electricity. Its density is 3·3 g/cm³

CHEMICAL PROPERTIES

(i) Crystalline boron is chemically quite inert.
(ii) It is not attacked by Conc HNO_3, H_2SO_4, HCl or HF.
(iii) It is not oxidized by Air.

AMORPHOUS BORON:- Amorphous boron is a brown powder with 2·45 g/cm³ density. It is volatile to some extent. Chemically it is more reactive than crystalline boron. It undergoes following reactions.

REACTIONS OF AMORPHOUS BORON

(i) It bursts into a flame at 700°C.

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

(ii) It reacts with halogens to form Boron halides.

$$2B + 3F_2 \longrightarrow 2BF_3$$

(iii) It forms BORIDES on heating with metals like Al. Mg

$$Al + B \xrightarrow{\Delta} AlB$$

$$3Mg + 2B \xrightarrow{\Delta} Mg_3B_2$$

(iv) It reacts with sulphur to form Boron sulphides

$$2B + 3S \xrightarrow{\Delta} B_2S_3$$

(v) On heating with carbon it forms Boron carbide

$$4B + 3C \xrightarrow{\Delta} C_3B_4$$

(vi) It is oxidized by conc. HNO_3 or H_2SO_4

$$B + 3HNO_3 \longrightarrow H_3BO_3 + 3NO_2$$

$$2B + 3H_2SO_4 \xrightarrow{600°C} 2H_3BO_3 + 3SO_2$$

(vii) On fusion with alkalies it forms Borates.

$$2B + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2$$

(viii) It is a good reducing agent. It can reduce SiO_2 and CO_2

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

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

WHAT IS BORAX? DISCUSS ITS PREPARATION & REACTIONS OF BORAX

It is a commonly occuring compound called TINCAL. It is prepared by following reactions:

COLEMANITE:- $Ca_2B_6O_{11}$. Colemanite on heating with an aqueous solution of Na_2CO_3 produces a precipitate of $CaCO_3$. The solution is filtered to separate residue of $CaCO_3$ and filterate containing Borax. The filterate is cooled to get crystals of $Na_2B_4O_7$.

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

FROM SODIUM METABORATE:- CO_2 is passed through aqueous solution of $NaBO_2$ (sodium metaborate) to get Borax.

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

FROM BORIC ACID:- Boric acid and an alkali like NaOH or Na_2CO_3 on heating produce Borax.

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

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

PHYSICAL PROPERTIES:- Borax is a colourless solid with M.P = 20°C. It is sparingly soluble in cold water but more soluble in hot water (99.3g/100g). On heating it loses H_2O and swells up.

CHEMICAL PROPERTIES:-

AQUEOUS SOLUTION OF BORAX IS ALKALINE:-

When borax is dissolved in water, produces H_3BO_3 and NaOH due to Hydrolysis

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

Since "NaOH" is a strong base and H_3BO_3 is a weak acid. Thus aqueous solution of Borax turns Red litmus paper blue.

EFFECT OF HEAT ON BORAX On heating it swells up and forms a transparent bead.

$$Na_2B_4O_7 \xrightarrow{HEAT} 2NaBO_2 + B_2O_3$$

REACTION WITH METAL OXIDES Borax reacts with some metal oxides to form coloured beads which makes bases of Borax Bead Test.

$$Na_2B_4O_7 + CoO \longrightarrow 2NaBO_2 + Co(BO_2)_2$$

Blue bead.

WRITE CHEMISTRY OF BORAX BEAD TEST.

Borax bead test is used to detect coloured ions like Cu^{2+}, Fe^{2+}, Fe^{3+}, Cr^{3+}, Mn^{2+}, Ni^{2+}, Co^{2+}.

In this test a platinum wire is drawn into a loop. It is heated in Bunsen flame then it is dipped in Borax and heated again. First it swells due to dehydration and then melts into a transparent mass of sodium metaborate

$$Na_2B_4O_7 \xrightarrow{Heat} 2NaBO_2 + B_2O_3$$

Then some salt is sprinkled on bead and heated again in flame. The salt form respective borate imparting characteristic colour to bead. For example cobalt imparts blue colour due to formation of cobalt metaborate.

$$B_2O_3 + CoO \xrightarrow{\Delta} Co(BO_2)_2 \text{ (Blue Coloured)}$$

The net reaction could be written as

$$Na_2B_4O_7 + CoO \xrightarrow{Heat} 2NaBO_2 + Co(BO_2)_2$$

WRITE USES OF BORAX:-

1) It is used in detection of coloured ions by borax bead test
(2) It is used in preparation of pyrex and jena glass which is heat resistant and not attacked by acids or bases
(3) It is used as an anticeptic.
(4) It is used as stiffening agent in laundries and candle wicks.
(5) It is used in making washing powders.
(6) It is used as a flux in soldering and welding.
(7) It is used as water softener.

DISCUSS METHODS OF PREPARATION OF BORIC ACID. HOW DOES IT REACT WITH FOLLOWING (i) ETHANOL (ii) ACETIC ANHYDRIDE (iii) NaOH

ANS:- There are three common acids of Boron.

(i) Orthoboric acid H_3BO_3

(ii) Metaboric acid HBO_2

(iii) Pyroboric acid. $H_2B_4O_7$

The most common of these is Orthoboric acid

Let us discuss its methods of preparation.

ACTION OF H_2SO_4 ON BORAX:- When hot concentrated solution of Borax ($Na_2B_4O_7$) is treated with conc H_2SO_4 Calculated quantity of conc. H_2SO_4, Boric acid is produced.

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3$$

The crystals of boric acid are obtained on cooling solution.

FROM COLEMANITE:- When SO_2 is passed through hot aqueous suspension of Colemanite boric acid is produced

$$Ca_2B_6O_{11} + 9H_2O + 2SO_2 \longrightarrow 2CaSO_3 + 6H_3BO_3$$

FROM BORIC OXIDE:- The aqueous solution of boric oxide on cooling produce crystals of orthoboric acid.

$$B_2O_3 + 3H_2O \longrightarrow 2H_3BO_3$$

PHYSICAL PROPERTIES:-

(1) Boric acid forms white, flaky transparent crystals.

(2) It is slightly soluble in cold water and reasonably soluble in hot water. At 100°C its solubility is 34 g/100g of water.

(3) It is volatile in steam.

CHEMICAL PROPERTIES:- It is a very weak monobasic acid with $K_a = 6 \times 10^{-10}$. It behaves like acid not by giving its proton but by accepting hydroxyl ion from water.

$$B(OH)_3 + H^{+}OH^{-} \rightleftharpoons B(OH)_4^{\ominus} + H^{\oplus}$$

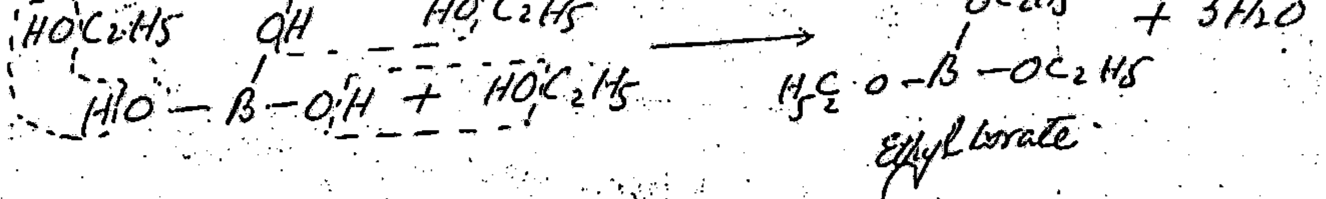
REACTION WITH NaOH:- Boric acid reacts with NaOH on boiling to produce Borax.

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

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

REACTION WITH C_2H_5OH:- Boric acid produce ethyl borate (an ester of boric acid) when treated with ethyl alcohol.

$$H_3BO_3 + 3C_2H_5OH \longrightarrow B(OC_2H_5)_3 + 3H_2O$$



REACTION WITH ACETIC ANHYDRIDE:-
Boric acid reacts with acetic anhydride to form boron acetate

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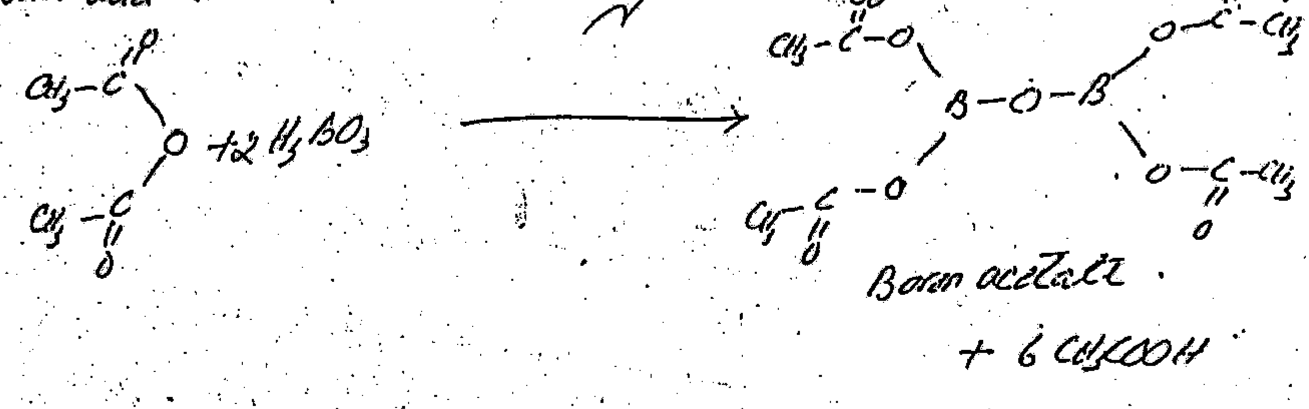


USES OF BORIC ACID:-

- It is used as mild disinfectant in medicine
- It is used in the manufacture of glazes and enamels for pottery.
- The aqueous solution of boric acid is used for washing eyes

10 DISCUSS EFFECT OF HEAT ON BORIC ACID.

Boric acid on heating undergoes dehydration through following steps:

(i) On heating to 100°C or little above it loses a water molecule to form metaboric acid.

$$H_3BO_3 \xrightarrow{100°C} HBO_2 + H_2O$$

(ii) On heating to 160°C tetraboric acid is formed.

$$4HBO_2 \xrightarrow{160°C} H_2B_4O_7 + H_2O$$

It can also be written as

$$4H_3BO_3 \xrightarrow{160°C} H_2B_4O_7 + 5H_2O$$

At temperature of 300°C it swells and loses all of its water molecules and form boric oxide.

$$2H_3BO_3 \longrightarrow B_2O_3 + 3H_2O$$

The reaction can be summarized as follows.

$$4H_3BO_3 \xrightarrow{100°C} 4HBO_2 + 4H_2O$$

$$4HBO_2 \xrightarrow{160°C} H_2B_4O_7 + H_2O$$

$$H_2B_4O_7 \xrightarrow{300°C} 2B_2O_3 + H_2O$$

$$4H_3BO_3 \longrightarrow 2B_2O_3 + 6H_2O$$

OR

$$2H_3BO_3 \longrightarrow B_2O_3 + 3H_2O$$

REACTIONS OF ALUMINIUM:-

(i) ACTION OF AIR:- Aluminium is quite resistant to air. It does not undergo corrosion process because a thin film of Al_2O_3 is formed on its surface which prevents further attack of environmental conditions.

REACTION WITH OXYGEN:- Finely divided aluminium burns vigorously in oxygen. The reaction is highly exothermic.

$$4Al + 3O_2 \longrightarrow 2Al_2O_3 + 760\ Kcal$$

The reaction is used in photoflash tubes where "Al" foil is sealed in atmosphere of oxygen. The energy liberated in this reaction is mostly available as light.

REDUCING ACTION Aluminium has great affinity for oxygen. Thus it reduces metal oxides to metals

$$Fe_2O_3 + 2Al \longrightarrow 2Fe + Al_2O_3 + 207\ KCal$$

The reaction is so exothermic that iron is obtained in molten state. This reaction is used in thermite process.

THERMITE PROCESS:- The reaction of metal oxide using aluminium as reducing agent is called Thermite process. In this process metal oxide (Fe_2O_3) is mixed with aluminium powder. This mixture is called Thermite mixture. It is heated to form Al_2O_3 and metal. The reaction is so exothermic that metal and Al_2O_3 are obtained in molten state. The reaction creates a temperature of 3000—3500°C.

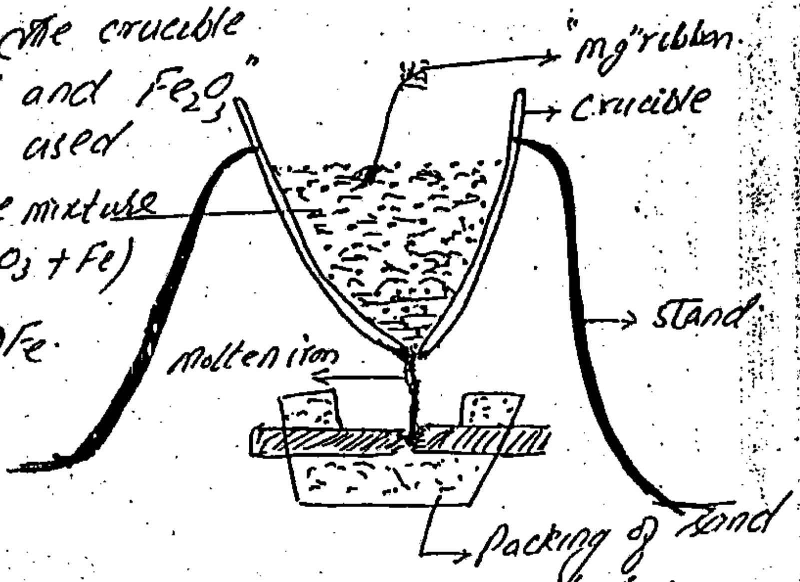
The heavy metal settles to the bottom and can easily be separated.

USES:- The process can be used for extraction of metals from their oxides. For example Fe_2O_3, Mn_2O_3, BaO, CaO are easily reduced by this process.

$Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + Cr$

WELDING PURPOSES:- Thermite process is used commercially to weld rail tracks and heavy machinary. The equipment consists of a cone shaped crucible with an opening at the bottom. The crucible contains a mixture of "Al and Fe_2O_3". A magnesium ribbon is used for ignition of reaction.

$Fe_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Fe$



INCENDIARY BOMBS. — The thermite process is not effected by water thus it is used in wars for incendiary Bombs.

2) **REACTION WITH NITROGEN:-** Aluminium reacts with nitrogen on heating forming Aluminium nitride.

$$2Al + N_2 \xrightarrow{\Delta} 2AlN$$

3) **REACTION WITH HALOGENS:-** Aluminium reacts with halogens on heating producing corresponding halides

$$2Al + 3X_2 \xrightarrow[Heat]{\Delta} 2AlX_3$$

$$2Al + 3Cl_2 \xrightarrow{\Delta} 2AlCl_3$$

REACTION WITH SULPHUR :- Sulphur in molten state combines with aluminium forming aluminium sulphide.

$$2Al + 3S \xrightarrow{\Delta} Al_2S_3$$

REACTION WITH ACIDS / Aluminium reacts with concentrated "HCl" to liberate hydrogen gas.

$$2Al + 6HCl \xrightarrow{Heat} 2AlCl_3 + 3H_2$$

Hot concentrated sulphuric acid reacts with Aluminium to form SO_2 gas.

$$2Al + 6H_2SO_4 \xrightarrow[Heat]{\Delta} Al_2(SO_4)_3 + 3SO_2 + 6H_2O$$

REACTION WITH CARBON / Aluminium reacts with carbon on heating forming Aluminium Carbide

$$4Al + 3C \xrightarrow[Heat]{\Delta} Al_4C_3$$

REACTION WITH ALKALIES / Aluminium dissolves rapidly in aqueous caustic alkali forming aluminates, liberating H_2.

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

GROUP IV-A ELEMENTS.

Give the names, electronic configuration and occurrence of IV-A group elements.

Group IV-A consist of free elements
(1) Carbon (2) Silicon (3) Germanium
(4) Tin (5) lead.
This group is present in the middle of periodic table and serves as a link between metals and non metals. Their properties are intermediate between metals and non metals.

Electronic configurations of IV-A group elements are as follow

NAME	ATOMIC No.	ELECTRONIC CONFIGURATION
Carbon.	$_{6}C$	$[He]\ 2s^2, 2p^2$.
Silicon.	$_{14}Si$	$[Ne]\ 3s^2, 3p^2$.
Germanium	$_{32}Ge$	$[Ar]\ 3d^{10}, 4s^2, 4p^2$.
Tin	$_{50}Sn$	$[Kr]\ 4d^{10}, 5s^2, 5p^2$.
Lead.	$_{82}Pb$	$[Xn]\ 5d^{10}, 6s^2, 6p^2$.

OCCURRENCE OF CARBON:

Carbon exist in free state as well as in combined state. in free state it is found as diamond Graphite. Minerals of carbon are as

LIME STONE.	$CaCO_3$
DOLOMITE.	$MgCO_3 \cdot CaCO_3$
MAGNESITE.	$MgCO_3$

OCCURRENCE OF SILICON:-

Silicon is not found in free state: it is very ~~ofte~~ abundant in earth crust (25%)

Silicon exist as silica or silicates in rocks. As oxide it is found as quartz in the following forms:

- Rock crystals
- Amethyst quartz
- Smoky quartz
- ~~Milgy~~ Milky quartz
- Rose quartz

Sand is largely silicon dioxide (silica). Important minerals of silicon are

MINERAL OF SILICON.	CHEMICAL FORMULA.
ANALCITE (a zeolite)	$NaAl(SiO_3)_2 \cdot H_2O$
ASBESTOS	$CaMg_3(SiO_3)_4$
KAOLINE	$H_2Al_2(SiO_4)_2 \cdot H_2O$
ZIRCON	$ZrSiO_4$
TALC (or soapstone)	$H_2Mg_3(SiO_3)_4$

COMMON PROPERTIES OF IV-A ELEMENTS.

Table 3.2 Electronic Configurations and Physical Properties of Group IVA Elements.

Property	C	Si	Ge	Sn	Pb
Atomic Number	6	14	32	50	82
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] $4f^{14} 5d^{10} 6s^2 6p^2$
Density (g/cm^3)	2.33	2.7	5.93	7.3	11.85
M.P (^oC)	3930	1420	937	232	323
Ist Ionization energy (kJ/mol)	1086	736	760	707	715
Atomic Radius (pm)	77	117	122	140	154
Ionic Radius (pm)	20	39	53	71	84

PECULIAR BEHAVIOUR OF CARBON.

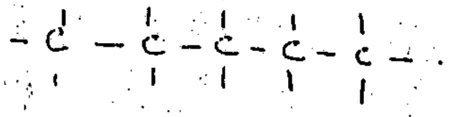
Carbon differs from other members of the group in following respects.

i- NON-METALLIC NATURE.

Carbon is non metal while other members of the family are metalloids or metals except silicon, silicon is also a non metal.

ii- CATENATION.

Carbon has tendency to form long chains of identical atoms. This type of linkage of identical atoms with each other is called CATENATION or SELF-LINKAGE. Property of catenation decreases down the group from carbon to lead. Carbon has max. tendency of catenation.



carbon and carbon linkages.

COMPOUNDS OF CARBON AND SILICON.

1- OXIDES OF CARBON.

Carbon forms three type of oxides, namely

Carbon monoxide. CO.
Carbon dioxide. CO_2.
Carbon suboxide. C_3O_2.

Structure of Carbon monoxide "CO"

Carbon monoxide is a diatomic molecule. CO molecule have triple bond b/w the two atoms. It is slightly polar.
Electronic structure of carbon monoxide can be represented as

:C⁝⁝:O:

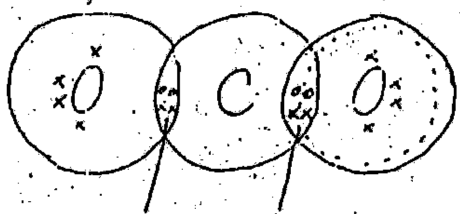
it is usually written as :C≡O:

from the structure it seems that molecule should have a large dipole moment, but the molecule actually have small dipole moment (0.112D)

$$\overset{-\delta}{C}=\overset{+\delta}{O}$$

Structure of carbon dioxide "CO_2"

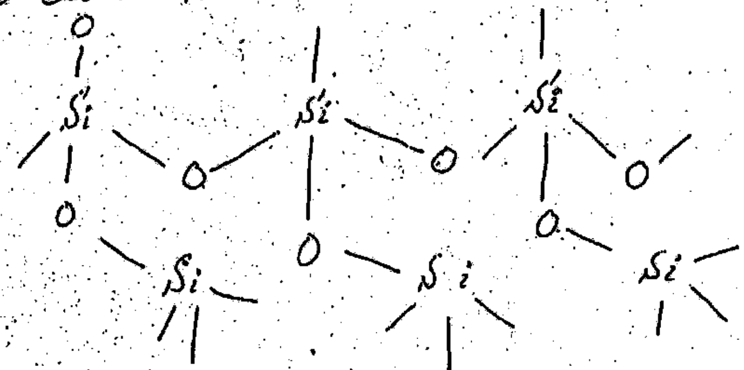
Carbon dioxide exists in gaseous state.
It is a linear molecule.
Being linear molecule its dipole moment is zero.
Solid CO_2 has a face-centered cubic structure.
The observed C-O bond distance is 115 pm and is in agreement with the following structure.



2. OXIDES OF SILICON.

SILICON DIOXIDE. (SILICA.)

Silicon dioxide is usually known as "SILICA". It is the most common and the most important compound of silicon.
In silica each silicon atom is tetrahedrally attached to four oxygen atoms and each oxygen has two close silicon atoms.



Silicon dioxide (SiO_2)

PROPERTIES OF SILICON DIOXIDE.

i – TRANSPARENCY TO LIGHT.
Vitreous silica is completely transparent to light.

ii – INSULATOR.
Silica is used as insulator. It is an excellent insulating material.

iii – EFFECT OF TEMPERATURE.
It is not much effected by temp. changes. It has very low thermal expansion.

iv – SOLUBILITY IN WATER.
Silica is insoluble in water and inert towards many reagents.

v – REACTIVITY TO ACIDS.
It is resistant towards all acids except HF.

vi – PHYSICAL PROPERTIES.
Silica is hard, brittle and elastic.

QUARTZ.
Crystalline form of silicon dioxide is called "QUARTZ."
It is hard, Brittle solid.
Quartz is a colourless solid.

WHY IS CO_2 A GAS WHILE SiO_2 IS A SOLID.

It is due to following reasons.
" Silicon atoms are much larger than carbon atoms. Each silicon is surrounded by four oxygen atoms, while carbon has smaller size which cannot be surrounded by four oxygen atoms.

Please consult Page No 66 - of TEXT ALSO

SILICATES AND THEIR USES.

Derivatives of silicic acid (H_2SiO_3) are called "SILICATES".

Different types of silicates are:

1. SODIUM SILICATE. Na_2SiO_3.
2. ALUMINIUM SILICATE. $Al_2O_3 \cdot (SiO_2)_2 \cdot 2H_2O$
3. TALC. or SOAPSTONE. $Mg_3H_2(SiO_3)_4$.
4. ASBESTOS... $CaMg_3(SiO_3)_4$.

1. SODIUM SILICATE. Na_2SiO_3

The Sodium salt of meta silicic acid is called sodium silicate. It is also known as "SOLUBLE GLASS" or "WATER GLASS". Sod. silicate is prepared by fusing sodium carbonate with pure sand.

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2.$$

process is carried out in furnace called REVERBERATORY FURNACE.

PROPERTIES:..

i – It is soluble in water.

ii – Its solution is strongly alkaline due to the hydrolysis.

USES OF SOD. SILICATE.

1 – IN SOAP INDUSTRY.

It is used as a filler for soap in soap industry.

2 – IN TEXTILE.

It is used in textile as a fire proof.

3 – AS A POLISH.

It is used as furniture polish.

4. ________

It is also used in calico printing.

ALUMINIUM SILICATE. $Al_2O_3 \cdot (SiO_2)_2 \cdot 2H_2O$.

Many silica rocks contain aluminium. Due to weathering of these rocks complex silicates are disintegrated. Action of water and carbon dioxide convert these complex Potassium silicates into pot. carbonate sand and aluminium silicate (clay).

Consider following reaction to explain weathering of potassium feldspar.

$$K_2O \cdot Al_2O_3 \cdot 6SiO_2 + H_2CO_3 + H_2O \longrightarrow K_2CO_3 + 4SiO_2 + \underbrace{Al_2O_3 \cdot (SiO_2)_2 \cdot 2H_2O}_{\text{clay}}$$

pure clay is white and is called KAOLIN. Ordinary clay, contain ~~oxides~~ compounds of iron and other metals, It is yellow in colour or reddish yellow.

USES:-

IN BRICKS MAKING.

Impure clay is used in making bricks and tiles and stonewares. This clay contain oxides of iron, Ca, Mg and other metals which form fusable silicates with sand.

Due to the presence of ferric oxide, the article of this clay turn red when heated.

IN PORCELAIN AND CHINA WARES.

pure clay is white and is used to make porcelain and china wares.

MAKING WATER PROOF COATING.

Stone wares are usually glazed with ~~[illegible] aluminium~~ clay, when hot ~~[illegible]~~. clay make the surface of stoneware less porous.

This treatment produces sod. silicate and sod. aluminium silicates, which melt and covers entire surface. On cooling covering solidified and produce smooth water proof surface.

IN MAKING POTTERY.

Clay is used in making pottery and other ceramic articles. This depend upon the plasticity of the paste of clay.

Clay is hydrated in water and form paste. On heating water of hydration is lost and a hard rock like mass is formed.

3. TALC or SOAP STONE.

Magnesium silicate $Mg_3H_2(SiO_3)_4$ is called talc or soapstone. It is greasy to touch. Hence it is used in making cosmetics.
It is also used in making household articles.

4 ASBESTOS:-

Hydrated calcium magnesium silicate $[CaMg_3(SiO_3)_4]$ is called ASBESTOS.

USES:-

It is commonly used in making hardboard.
It is used in making incombustible fabric.

USES OF LEAD COMPOUNDS IN PAINTS.

Certain lead compounds are coloured. These compounds are used in paints as pigments. lead compounds used in paint industry are
1. Some oxides of lead,
2 - lead carbonates.
3 - lead chromate. etc.

1 - OXIDES OF LEAD.

lead oxides used as pigment in paints are.

a - lead suboxide (Pb_2O)
b - lead monoxide (PbO)
c - Triplumbic tetra oxide (Pb_3O_4)
d - lead dioxide (PbO_2)

a. LEAD SUBOXIDE. Pb_2O.

It is black powder. It is obtained on heating plumbous oxalate in absence of air.

$$2PbC_2O_4 \xrightarrow{HEAT} Pb_2O + 3CO_2 + CO.$$

On heating Pb_2O decompose into Pb and PbO. Lead suboxide is also used in the manufacture of lead storage batteries.

b. LEAD MONOXIDE. PbO.

(LITHARGE, MASSICOT.)

It varies in colour from pale yellow to reddish yellow. It exist in two forms rhombic (yellow) and a tetragonal (red).
It is slightly soluble in water. It is used in preparing flint glass and paints.
If PbO is boiled with water and olive oil it produce sticky mass lead oleate.
PbO is used in preparing oils.
Varnishes.
flint glass.

c. TRIPLUMBIC TETRA-OXIDE. Pb_3O_4

(RED LEAD, MINIUM)

Pb_3O_4 is also known as "red lead" or "minium". When white lead (Pb) is heated in air at 340°C it absorb oxygen and form bright scarlet crystalline powder of red lead.

$$3Pb + 2O_2 \longrightarrow Pb_3O_4 \text{ (red lead)}$$

it decomposes at 470°C

$$2Pb_3O_4 \longrightarrow 6PbO + O_2$$

USES:-

It is used for a variety of purposes.

1- it is mainly used in the manufacture of storage batteries

2 — as a pigment in paint. Paints used for steel and iron to retard corrosion are made of red lead.

3 — Used in manufacture of flint glass.

4 — Used in manufacture of ceramic glazes. Matches

d. LEAD DIOXIDE. PbO_2

Red lead on treatment with HNO_3 (concentrated) produce lead dioxide

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

It is reddish brown powder.
It is not very soluble in water.
Soluble in alkaline water and produce soluble plumbates.
It is not affected by dilute acids.

2. LEAD CARBONATE. ($2PbCO_3 \cdot Pb(OH)_2$)

Basic lead carbonate is called white lead. It is an amorphous white pigment.
White lead is not suitable for use as good pigment. Because it is darkened by hydrogen sulphide present in atmosphere.
Lead carbonate mixes readily with linseed oil and has a good covering power.

3- LEAD CHROMATE. ($PbCrO_4$).

It is used as a pigment. It is called "CHROME YELLOW".
When lead chromate is boiled with dilute alkali hydroxide it gives orange and red basic lead chromates. These are also used as pigments.
Yellow lead chromate is monoclinic.
Other mixture of compounds are also used as yellow pigment e.g. lead chromate with lead sulphate or barium sulphate is used as yellow pigment.

FOR SILICONES & SEMICONDUCTORS SEE TEXT BOOK

COVALENT SOLIDS. (ATOMIC SOLIDS)

These are also called ATOMIC SOLIDS because they are composed of atoms of one two or more different elements. These atoms are held together by covalent bond.

COVALENT SOLIDS ARE OF TWO TYPES.

(a) which consist of giant molecules like diamond

(b) when atoms join to form covalent bonds. Separate layers of atoms are produced due to these covalent bonds. For example graphite, Cadmium iodide, Boron nitride

PROPERTIES:-

OPEN STRUCTURE:- Covalent bonds are directional. These bonds are formed in a specific direction and an open net work like structure is produced

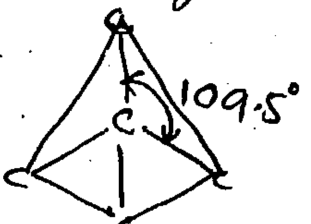
HIGH M.P. These crystals are hard and large amount of energy is required to break them. They have high M.p. and their volatility is quite low.

CONDUCTIVITY Due to absence of free electrons and ions they are bad conductors of electricity. Graphite has layered structure. The electrons are available between these layers. Thus graphite is a good conductor of electricity

SOLUBILITY These are insoluble in polar solvents but they are soluble in non polar solvents like Benzene, CCl_4 etc. Covalent crystals like diamond are giant molecules which are insoluble in all solvents. Due to big size they ~~are~~ donot interact with solvent molecules.

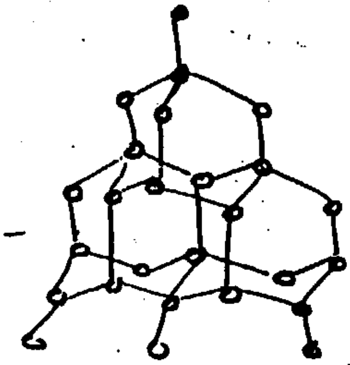
REACTIONS:- The chemical reactions of such covalent crystals are very slow.

STRUCTURE OF DIAMOND:- Diamond is an allotropic form of carbon. Carbon has four electrons in outermost shell. Each carbon is sp^3 hybridized. Four hybrid orbitals are produced. These four hybrid orbitals are located at an angle of 109.5°. A tetrahedral structure is produced. Each unit cell is ~~four~~ formed by five carbon atoms. Each C—C bond is formed by overlap of $sp^3 - sp^3$ orbitals. Each bond length is 1.54 A



This type of structure runs throughout the crystal. The entire structure behaves like a huge molecule. This is called MACROMOLECULE OR giant molecule. The overall structure is face centered cubic.

MOLECULER SOLIDS:



These are solids whose crystals are formed by polar or non polar atoms or molecules. Two type of intermolecular forces hold them together.

1- DIPOLE - DIPOLE FORCES
2- VANDER-WAALS FORCES.

These forces are much weaker than covalent and ionic bond. For example noble gases can be solidified due to London forces. They consist of non polar atoms. Iodine Phosphorus, CO_2 form molecules crystal containing non polar molecules. These moleculer crystals have low M.P and B.P. Ice and glucose are moleculer crystal which consist of polar molecules. They have relatively high M.P. B.P.

PROPERTIES OF MOLECULER CRYSTAL

1) These are soft and easily compressable.
2) They are mostly volatile and have low M.P, B.P.
3) They have low densities and poor conducter of electricity.
4) They may be transparent to light