Group IVA (Carbon family)
or 14th

C, Si, Ge, Sn, Pb

· General configuration:- ns^2np^2

→ Carbon is 17th no. element in occurence.

Isotope:- C^{12} C^{13} C^{14}
↳ Radiactive
↳ Half life = 5770 yrs.
↳ used in radio carbon dating.

Si → 2nd most abundant.

Ge → exist in very small traces.

$\boxed{\text{Abundance} \rightarrow O > Si > Al > Fe}$

→ lead mainly Galena (PbS) को form मा पाइन्छ।

Note: Ultra pure form of Ge & Si used to make transistor and semiconductor.

→ Tin mainly SnO_2 को form मा पाइन्छ।

→ All 14th group elements are solid.

C, Si → Non metal.

Ge → Metalloid

Sn, Pb → soft metal with low m.pt.

Abhishek

Radius:-

C, Si, Ge, Sn, Pb ↓ size ↑es radius ↑es

Pb को radius जति हुन पर्छ त्यति हुन्न due to lanthanide contraction but Sn भन्दा होर हुन्छ।

Ionization energy:-

$I.E \propto \frac{1}{size}$.

C > Si > Ge > Pb > Sn
↳ due to lanthanide contraction
or
due to poor shielding of GF subshe

Density:- $\rho = \frac{m}{V}$ (m: group, V: period) Top to bottom m↑es.

∴ $\boxed{\rho \rightarrow C < Si < Ge < Sn < Pb}$

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Melting point & Boiling point

Melting point → C > Si > Ge > Sn < Pb.

↳ Due to lanthanide contraction of 4f electron.

Electronegativity:-

Electronegativity → C > Si ≃ Ge ≃ Sn < Pb.

→ Carbon has maximum covalency as 4. No vacant d-orbital.
but silicon has maximum covalency as 6. vacant d-orbital.

→ Carbon has more tendency to form double & triple bond due to small size (more overlapping).

– Carbon has unique property to form long chain called catenation.

C > Si > Ge > Sn > Pb

→ silicon doesnot form π bond / double bond.

Oxidation state:

+2 / +4

C < +2 / +4

Si < +2 / +4

Ge < +2 / +4 — more stable.

Sn < +2 / +4

Pb < +2 (more stable because of inert pair effect.) / +4

stable: – $Si^{+2} < Sn^{+4}$.

– $Pb^{+2} > Pb^{+4}$

→ Pb^{+4} O.S is behaves as good oxidising agent.

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→ All the tetravalent compound of pb are strong oxidizing agent.
eg. PbO_2 (+4)

→ Stability of +4 O.S → $C^{+4} > Si^{+4} > Ge^{+4} > Sn^{+4} > Pb^{+4}$.

→ Stability of +2 O.S → $C^{+2} < Si^{+2} < Ge^{+2} < Si^{+2} < Pb^{+2}$.

Order of stability of di-halides

→ $CX_2 < SiX_2 < GeX_2 < SnX_2 < PbX_2$

Tetrahalides

$CX_4 > SiX_4 > GeX_4 > SnX_4 > PbX_4$

- M^{+4} is more covalent than M^{+2}. due to more polarizing power.

Reaction with oxygen

MO
monoxide
eg. CO
but SiO not form

MO_2
Dioxide.
eg. CO_2

Q. Which IVA does not form MO oxide?
(a) C (b) Ge (c) Si (d) Sn (e) Pb

C → CO neutral
Ge → GeO acidic
Sn → SnO, Pb → PbO → amphoteric.

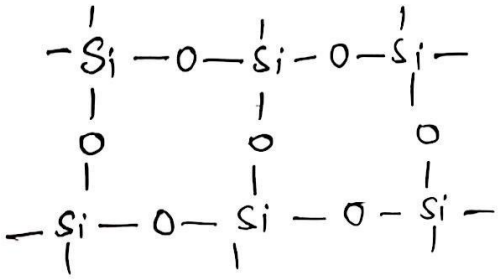
Dioxide
CO_2 SiO_2 GeO_2 SnO_2 PbO_2
acidic — amphoteric.

Trick of amphoteric

Pb Zn Be Al Ga Sn Cr^{+3} → oxide & hydroxide are amphoteric in nature

पैं गा बे अली Gana मुनाओ का मे.

$CO_2 \rightarrow O=C=O$

$SiO_2 \rightarrow$ 

3d structure
Non palanar.

→ CO_2 is gas but SiO_2 is covalent solid.

→ In SiO_2 each silicon is bonded with 4 oxygen & each oxygen is bonded with 2 silicon atom.

→ Solid CO_2 is also called dry ice.
└ molecular solid.

CO_2 ┬ CO_2
└ vander waals force of attraction.

Reactions

→ $SnO + HCl \longrightarrow SnCl_2 + H_2O$

★ $SnO + NaOH \longrightarrow Na_2SnO_2$

→ $SnO_2 + HCl \longrightarrow SnCl_4 + H_2O$

★ $SnO_2 + NaOH \longrightarrow Na_2SnO_3$

→ $PbO_2 + NaOH \longrightarrow Na_2PbO_3$

★ $PbO_2 + 2HCl \longrightarrow PbCl_2 + H_2O$
└ $Cl_2 + PbO + H_2O$
⇕
$2HCl \rightarrow PbCl_2 + H_2O$

★ ∴ $PbO_2 \xrightarrow{4HCl} Cl_2 + PbCl_2 + 2H_2O$

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→ $MnO_2 \xrightarrow{2HCl} Cl_2 + MnCl_2 + H_2O$ ☆

$MnO_2 \xrightarrow[HCl]{NaCl + H_2SO_4} Cl_2 + MnCl_2 + H_2O$ ☆

Red lead (mixed oxide)

$Pb_3O_4 + HCl \longrightarrow PbCl_2 + H_2O$

$Pb_3O_4 \rightarrow 2PbO + PbO_2$

$PbO_2 + HCl \longrightarrow Cl_2 + PbCl_2 + H_2O$

☆ ∴ $Pb_3O_4 + HCl \longrightarrow 2PbCl_2 + Cl_2 + 2H_2O$

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

$PbO + PbO_2 + HNO_3 \longrightarrow$ No reaction (both are oxidising agent)

☆ ∴ $Pb_3O_4 + HNO_3 \longrightarrow Pb(NO_3)_2 + H_2O$

Q. $SnCl_4 \xrightarrow[NaOH]{excess} ?\ Na_2SnO_3$.

Sol

$SnCl_4 \xrightarrow{4NaOH} Sn(OH)_4 \xrightarrow{NaOH} Na_2[Sn(OH)_6]$ or Na_2SnO_3

$Sn(OH)_4$ amphoteric

Q. $SnCl_2 \xrightarrow[NaOH]{excess} Na_2SnO_2$.

→ $SnCl_2 \xrightarrow{2NaOH} Sn(OH)_2 \xrightarrow{NaOH} Na_2SnO_2$ or $Na_2[Sn(OH)_4]$

Q. $SnCl_2 \xrightarrow{HgCl_2}$ white ppt $\xrightarrow[excess]{SnCl_2}$ green ppt

white ppt: $Hg_2Cl_2 + SnCl_4$ (mercurous chloride)

green ppt: $Hg + SnCl_4$.

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Oxides of carbon

① CO :-

Q. In which reaction CO form :-

ⓐ $C \xrightarrow[\text{limited}]{O_2} CO$ ⓑ $C \xrightarrow[\Delta]{air} \underbrace{CO + N_2}_{\text{producer gas.}}$

☆ ⓒ $C \xrightarrow[\Delta, 1000°C]{H_2O} \underbrace{CO + H_2}_{\text{water gas. or syn gas}}$ ⓓ $HCOOH \xrightarrow[\Delta]{H_2SO_4} CO + H_2O$ ~~ⓔ~~ All

☆ Q. Pot. ferrocyanide when heated with conc. H_2SO_4 gas evolved is

ⓐ SO_2 ⓑ SO_3 ~~ⓒ~~ CO ⓓ CO_2

$$K_4[Fe(CN)_6] \xrightarrow[H_2SO_4]{conc} HCN$$

$$\downarrow HOH$$

$$HCOOH + NH_3$$

$$\downarrow H_2SO_4$$

$$CO + H_2O$$

property

- Neutral oxide, insoluble in water.
- colorless gas.
- Highly poisonous (forms stable complex with Hb).

→ CO estimated by I_2O_5 & liberated I_2 titrated with hypo solution. - (Iodometric titration)

$$\underset{R.A.}{5CO} + I_2O_5 \longrightarrow 5CO_2 + I_2$$

$$\downarrow \text{hypo} \quad \text{sod. thiosulphate.}$$

- $I_2 + \underset{\text{hypo}}{Na_2S_2O_3} \longrightarrow \underset{\text{sod, tetrathionate.}}{Na_2S_4O_6} + NaI$

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→ Act as reducing agent.

$$MO + \underset{R^1A.}{CO} \longrightarrow M + CO_2.$$

$$ZnO + CO \longrightarrow Zn + CO_2$$

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

$$I_2O_5 + CO \longrightarrow I_2 + 5CO_2$$

→ Uses:- used in purification of Nickel. (Mond's process).

$$Ni \xrightarrow[\Delta]{4CO} Ni(CO_4)$$

(2) CO_2

Q. In which reaction, CO_2 not formed :-

(a) $C + O_2 \xrightarrow{excess} CO_2$

(b) $\underset{R^1A.\ water\ gas}{CO + H_2} + H_2O \longrightarrow CO_2 + 2H_2$

(c) $CaCO_3 \xrightarrow{\Delta} CaO + CO_2$

(d) $CuCO_3 \xrightarrow{\Delta} CuO + CO_2$

(e) $Ag_2CO_3 \xrightarrow{\Delta} \underset{Unstable}{Ag_2O} + CO_2 \longrightarrow 2Ag + CO_2 + \frac{1}{2}O_2.$

(f) $Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2.$

(g) $Na_2CO_3 \xrightarrow{\Delta}$ No effect

(h) $2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2.$
(baking soda)

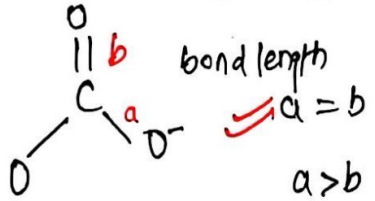
Property

→ Acidic oxide & soluble in water. & equilibrium mix. contain H_2CO_3, HCO_3^-, CO_3^{--} & CO_2.

Q. When CO_2 dissolved in H_2O. eqm mix contains:-

(a) H_2CO_3 (b) HCO_3^- (c) CO_3^{--} (d) CO_2 ~~(e)~~ All

Q.



bond length

a = b

a > b

b > a

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③ C_3O_2 (carbon suboxide)

↳ Heating malonic acid with P_2O_5



$$\boxed{O=C=C=C=O}$$

- All carbon are sp & molecules is linear.
- bond angle 180°.
- dipole moment → zero (Non polar).

Q. Which oxide is polar?

(a) CO (b) CO_2 (c) C_3O_2 (d) None

contain dipole moment.

Allotropes of Carbon

② Graphite :- Natural allotrope.

① Diamond :- Hardest natural substance.

→ pure carbon.
→ each carbon connected to 4 C atom.
→ every carbon are sp^3.
→ Giant molecules.
→ 3D covalent network. so, it has high B.pt & m.pt.
→ Bond length in C–C :- 154 picometre.
→ Bad conductor of electricity. but good conductor of heat.
→ Graphite ⇌ Diamond $\Delta H = +ve$

stable.

Diamond ↓ density high, vol. less

endothermic, high tempr. so, pressure high

→ At high tempr & high pressure, graphite to diamond.
→

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2) Graphite:-

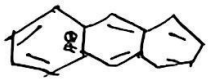
→ soft, low density.

$$SiC \xrightarrow{\Delta} Si + C_{\text{graphite}}$$

→ Graphite is thermodynamically more stable than diamond.

ΔH_f° (graphite) = 0

↳ standard enthalpy of formation

-  → vanderwaals force of attraction.
  - → Hexagonal planar ring.
  - → each carbon → sp^2 hybridized.
  - → πe^- delocalized.
  - → good conductor of electricity because of free electron.
  - → uses as dry lubricant as layer can slide each other due to low vanderwaal's force of attraction.

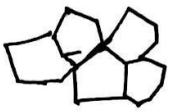
→ Along the plane, electrical conductivity is high but perpendicular to the plane, electrical conductivity is low. This phenomena is called anisotropism. (dif phy. properties in dif. direction).

→ When tempr ↑es, conductivity ↓es along the layer.
but conductivity ↑es across the layer.

→ So, graphite behaves as both metal & ~~non-metal~~ semi conductor.

3) Fullerene:- artificial allotrope of carbon by electric spark of carbon electrode. e.g. C_{70}, C_{48}, C_{60}.

C_{60} → like soccer ball shape.
→ Most symmetrical
↳ bucky ball / Buck buckminister fullerene



Pentagon → 12 nos
↳ 5 membered ring
Hexagon → 20 nos
↳ 6 membered ring

→ pentagon is always connected with Hexagon.

Thermal stability:- Graphite > Diamond > Fullerene

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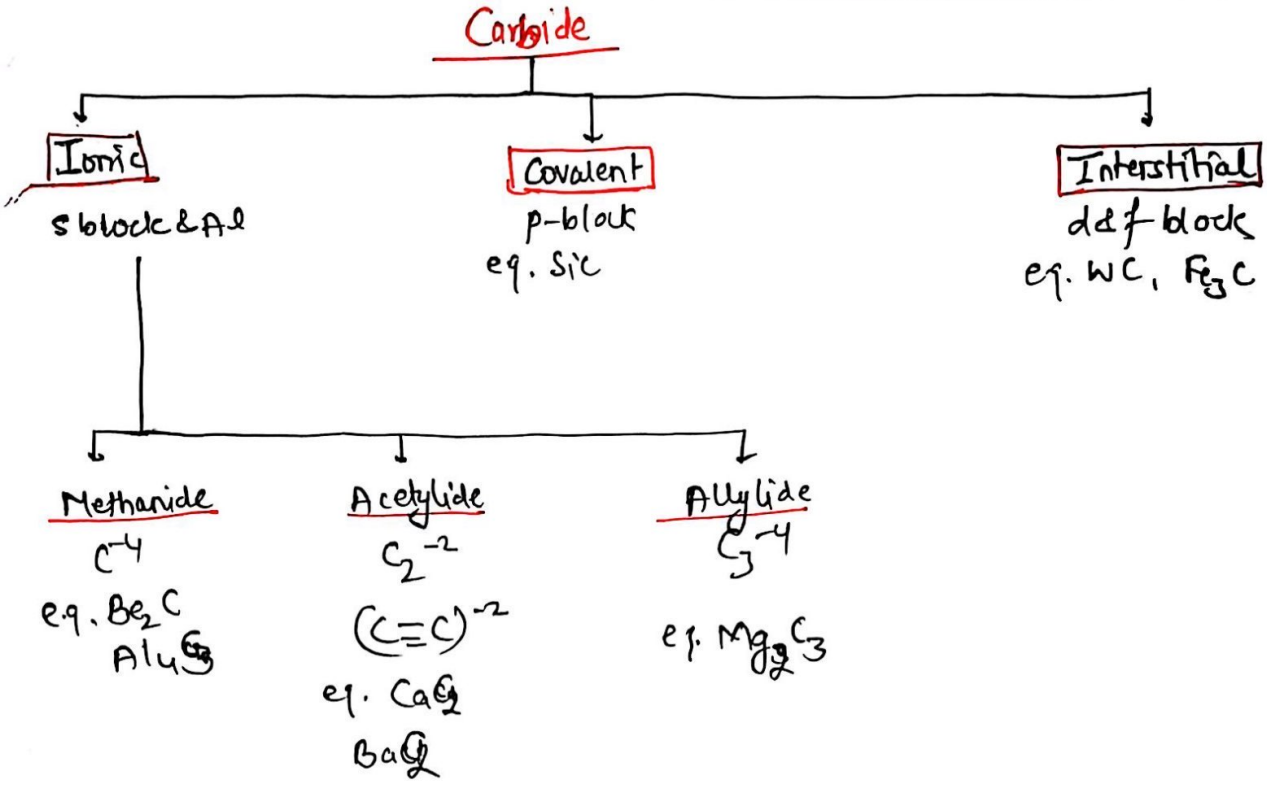

☆ → $Be_2C + HOH \longrightarrow Be(OH)_2 + CH_4$

$Al_4C_3 + HOH \longrightarrow Al(OH)_3 + CH_4$

→ $CaC_2 + HOH \longrightarrow Ca(OH)_4 + CH\equiv CH$

$BaC_2 + HOH \longrightarrow Ba(OH)_2 + CH\equiv CH$

→ $Mg_2C_3 + HOH \longrightarrow Mg(OH)_2 + CH_3-C\equiv CH$.

Covalent carbide

SiC → silicon carbide

→ also called carborandum.

→ sp^3, non-planar, 3D network like str.

prep $SiO_2 + C \xrightarrow{2000^\circ C} SiC + CO\uparrow$

$Si + C \xrightarrow{2000^\circ C} SiC$.

→ SiC has diamond like structure.

→ 2nd hardest after diamond.

→ SiC often dark purple | black | dark green due to impurities of traces of Fe & other impurities but pure SiC is pale yellow or colorless.

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Interstial carbide - also called metallic carbide. eg. Tungsten carbide (WC)
→ Hard & packing best.

The absorber of CO is Cu_2Cl_2.

→ $SnCl_4.5H_2O$ → Butter of tin.
└ used as Mordant.

→ $(NH_4)_2.SnCl_6$ → pink salt.
└ ↳ used in calico printing.
└ It is colorless.

Pb → PbO, PbO_2

Pb_2O_3
mixed
Sesqui oxide.
PbO + PbO_2
1 1

Pb_3O_4
red lead
PbO + PbO_2
2 1

Sesqui oxide → oxygen per atom 1 1/2.
eq. Pb_2O_3, Al_2O_3, B_2O_3, Fe_2O_3.

$Pb(C_2H_5)_4$ → anti knock.
└ Tetra ethyl lead.

$Pb^{+2} > Pb^{+4}$ ← Stability
$Sn^{+2} < Sn^{+4}$

$PbO_2 + HNO_3 \longrightarrow$

$PbO + HNO_3 \longrightarrow$

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