Board

from alcohol

↳ $3ROH + PX_3 \longrightarrow 3RX + H_3PO_3$

$ROH + PCl_5 \longrightarrow R\text{-}X + POX_3 + HX$ (~~HCl~~)

(PX_3, PX_5)

↳ PBr_3 & PI_3 ⇒ not stable @ room temp.

∴ produced in situ by action of red phosphorous on bromine or iodine

$2P + 3I_2 \longrightarrow 2PI_3$ or $2P + 3Br_2 \longrightarrow 2PBr_3$

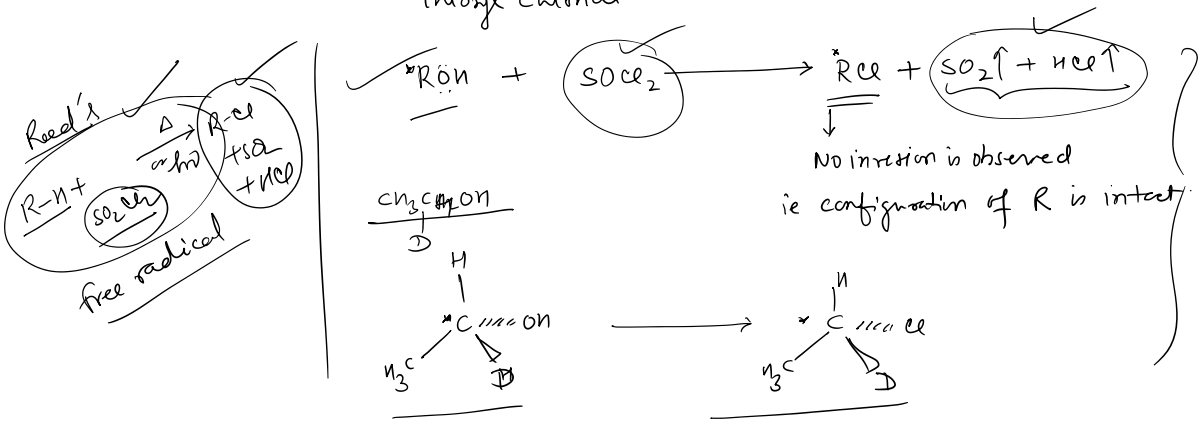
$R\text{-}OH \xrightarrow[(\equiv PI_3)]{P + I_2} R\text{-}I$; $P + OH \xrightarrow[(\equiv PBr_3)]{P + Br_2} R\text{-}Br$

↳ Alcohol

Rxn with $SOCl_2$ (Darzen's Method)

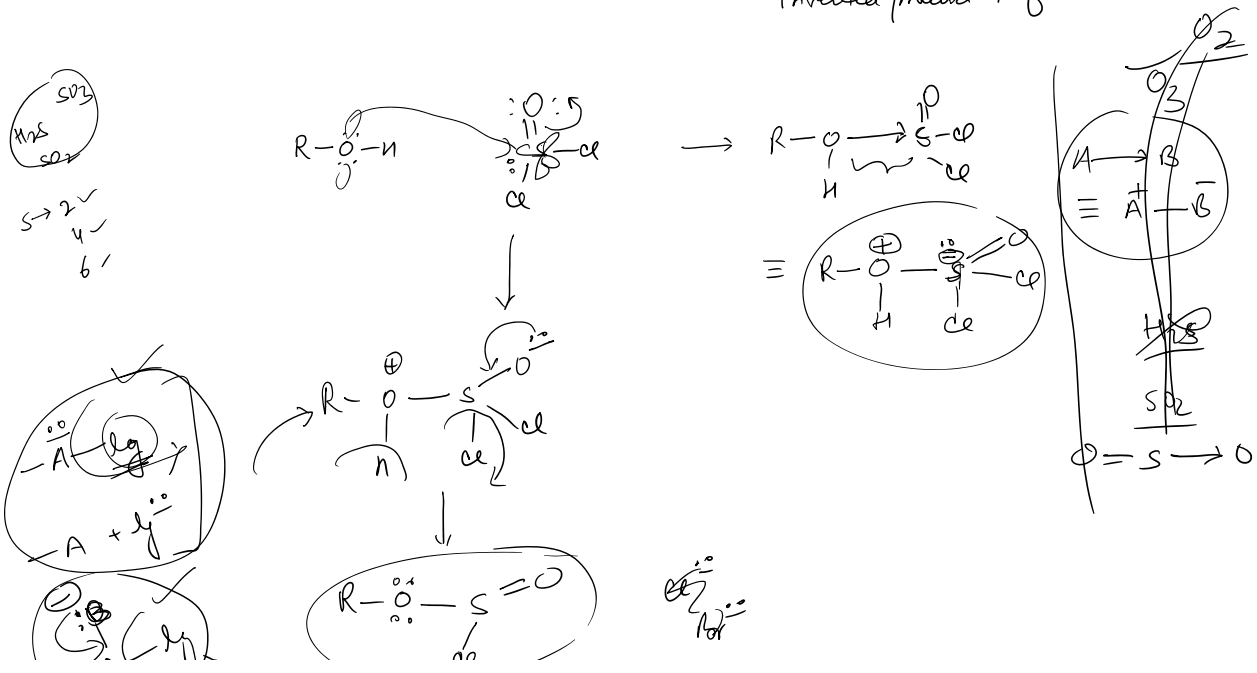
↓

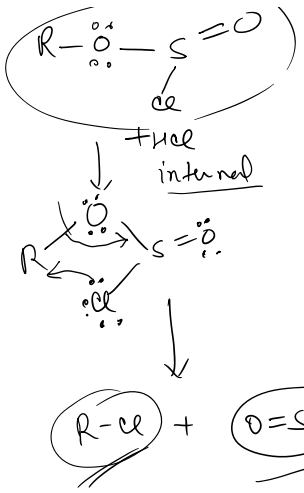
thionyl chloride

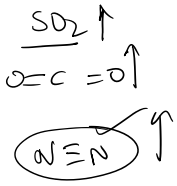


$ROH + SOCl_2 \xrightarrow{\text{Pyridine}} RCl + SO_2\uparrow + HCl\uparrow$

inverted product is formed



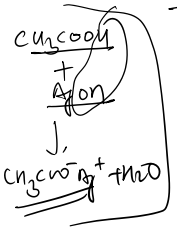




→ ROH $\xrightarrow{PCl_3}$ / $\xrightarrow{SOCl_2}$ ✓ better by product is $HCl_{(g)}$ & $SO_{2(g)}$ → easily removed

→ Darzen process cannot be used to prepare alkyl bromide and alkyl iodides. b'coz SO_2Br_2 → unstable
SOI_2 → does not exist

Preparation By Hunsdiecker Rxn: (fact)



$$Br_2 + \underbrace{RCOOAg}_{\text{Silver salt of fatty acid}} \xrightarrow{CCl_4} R\text{-}Br + CO_2\uparrow + AgBr\downarrow$$

| ° |

$\xrightarrow{\text{get}}$ (R-Br) $+ CO_2 + AgBr$

But

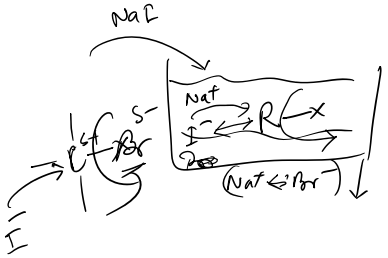
$$I_2 + 2RCOOAg \xrightarrow{\text{get}} \underset{\text{ester}}{RCOOR} + 2CO_2 + 2AgI$$ Major

→ **Preparation of alkyl iodide by halide exchange method** ⭐

"Finkelstein reaction"

$$\underbrace{RX}_{\substack{Cl\\Br\\*}} + NaI \xrightarrow{\text{acetone}^*} (RI) + NaCl\downarrow$$

In acetone NaCl, NaBr, NaF are insoluble ✓



(Nucleophilicity order in acetone $F^- > Cl^- > Br^- > I^-$)

→ **Alkyl fluoride by halogen exchange:** (Swarts reaction)

R–Cl / R–Br + Hg_2F_2 (or AgF) ⟶ R–F

↳ **Rydons Method:**

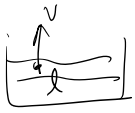
$R\text{–}OH + Br_2 + (C_6H_5O)_3PO \xrightarrow{\Delta} R\text{–}Br + C_6H_5OH + (C_6H_5O)_2POBr$

$(C_6H_5O)_3PO$: triphenyl phosphate

Properties of Alkyl halides:

Physical: ⟶ "insoluble in water" but soluble in organic solvent

⟶ **Beilstein test:** burn on copper wire with green edged flame.

⟶ 

for a given alkyl grp:

$RI > RBr > RCl > RF$ } Boiling point

for a give halide & isomeric alkyl halide

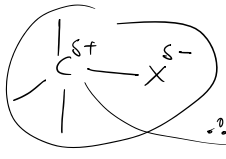
$CH_3\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}Cl > CH_3CH_2\underset{H}{\underset{|}{C}}(CH_3)\text{–}Cl > CH_3\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}\text{–}Cl$

$1^\circ > 2^\circ > 3^\circ$

as branching ⇒ ↓ in surface area

Chemical Properties:

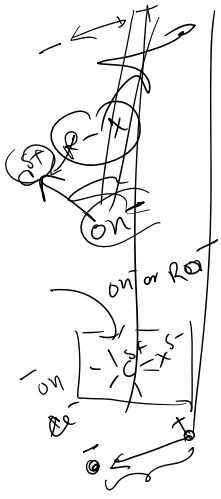
R–X

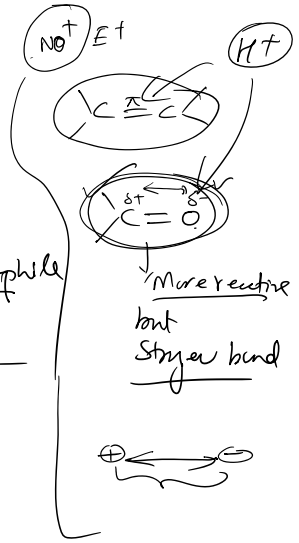


EN(X) > EN(C)

⟶ polar

⟶ centre for incoming nucleophile



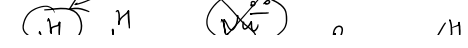


More reactive but Stronger bond

⟶

Two kind of rxn is possible

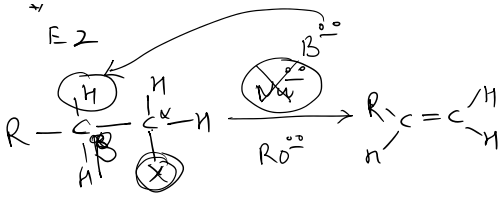
- **Nucleophilic substitution (SN)**
  - Two type
    - SN1
- **Elimination reaction (E)**
  - E1
  - E2
  - β-H must



SN1

SN2

E1 E2



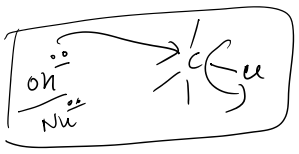
$Nu^{:}$ + R-X → Nu-R + $X^{:}$

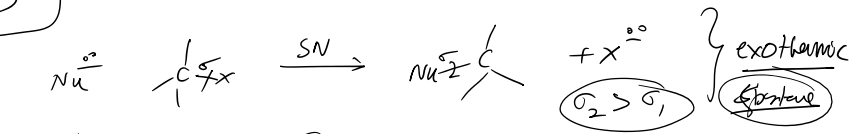
Nucleophile (eg: $:OH^-$, $RO^{:}$ etc.)

Halide ion (leaving gp)

+ B-H

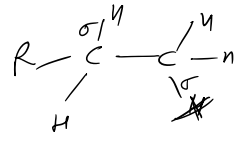
+ $X^{:}$



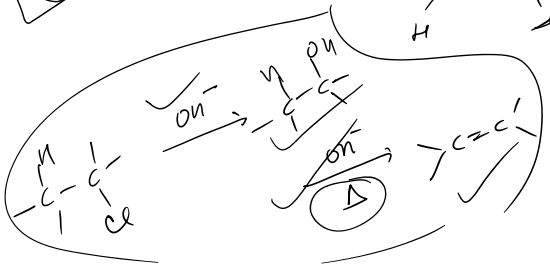


exothermic

Spontaneous

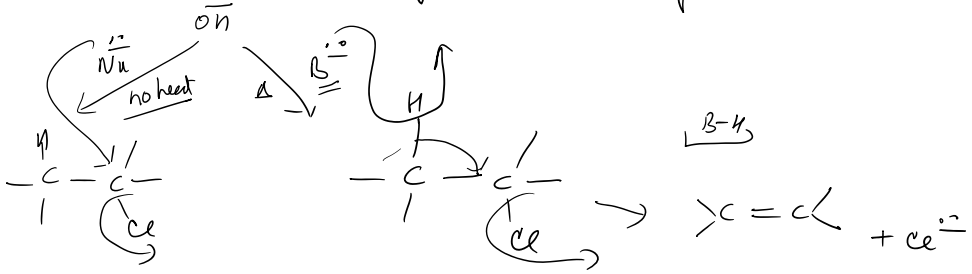


always endothermic



$:^{:}$ elimination process is non-Spontaneous

↳ Any Nucleophilicity Vs Basicity



In water:

$F^- > Cl^- > Br^- > I^-$ — Base

$F^- < Cl^- < Br^- < I^-$ — Nucleophile (Mobility)

↓ heavily hydrated : moves slow

In acetone:

$F^- > Cl^- > Br^- > I^-$ — Base

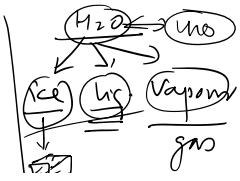
Not solvated

$F^- > Cl^- > Br^- > I^-$ — Nucleophile

"Solid State"

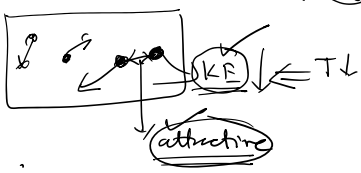
What solid :

↳ Characteristic : fixed mass, volume & shape



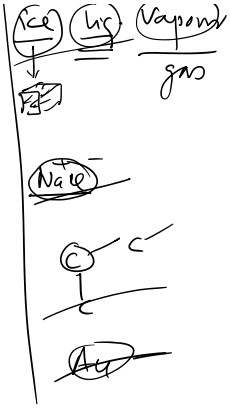
→ Characteristic : fixed mass, volume & shape

→ forces betⁿ constituent particle is very strg



→ position of constituent particle is fixed

→ constituent particle are closer to each other



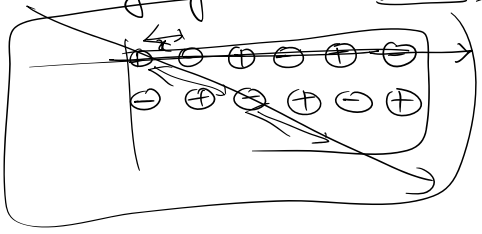
Type of solid : (on the basis of presence of order in constituent particle)

Solid

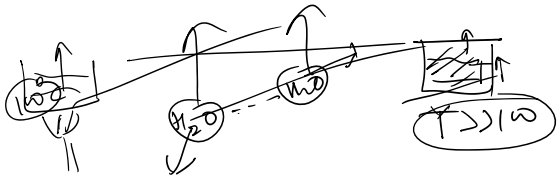
Crystalline solid
("solid state")
eg: salt (NaCl), etc

→ consist of smallest repeating geometrical shape (Unit cell)

→ constituent particle has long range order - (throughout solid)

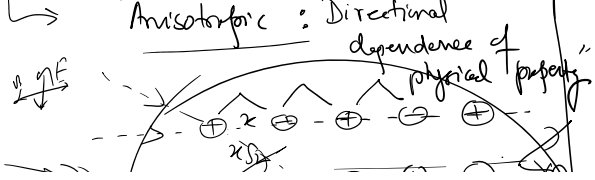


→ Melting point is defined



or have sharp melting point

→ "Anisotropic" : "Directional dependence of physical property"

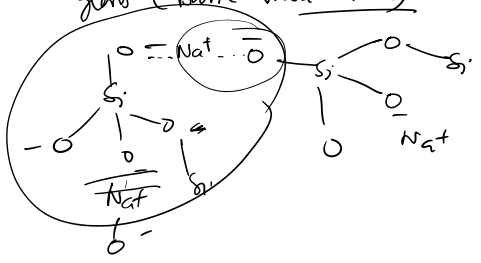


Amorphous solid
(Not true solid or supercooled liquid)
eg: glass etc.

→ No such unit

→ short range order
(Molecular level)

glass (basic unit silica)



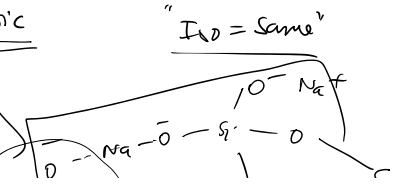
Melting point is not defined
(Range of temperature during which solid soften & finally melt)

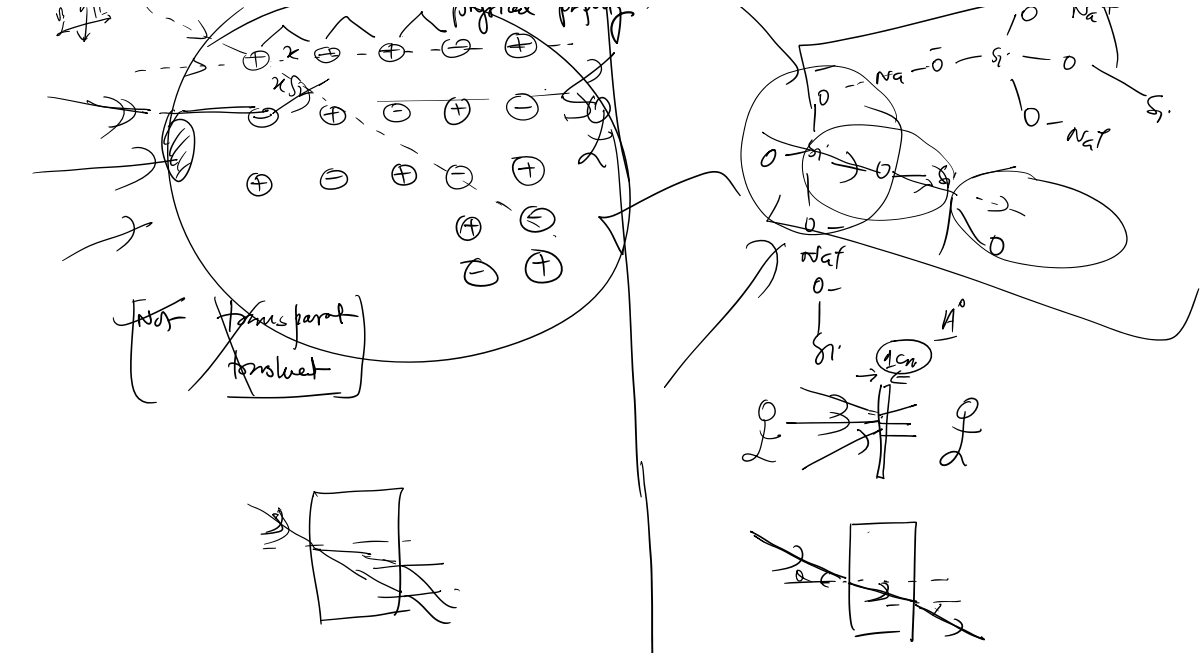
700° – 900 °C

or Range of temp.

"Isotropic"

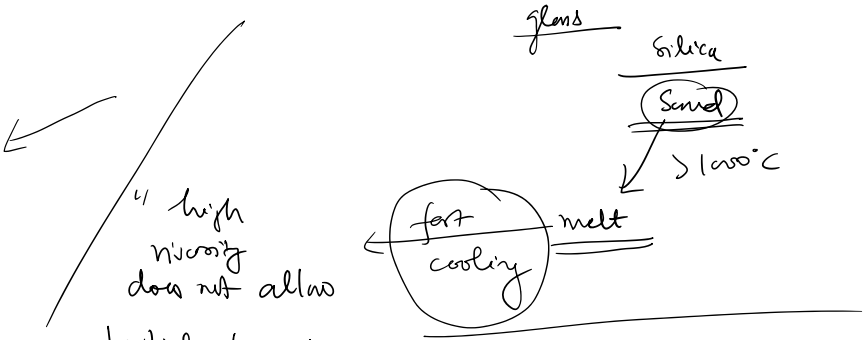
"Iso = same"





↳ " They are in solid state (phase) due to very strong force of attraction between constituent particle"

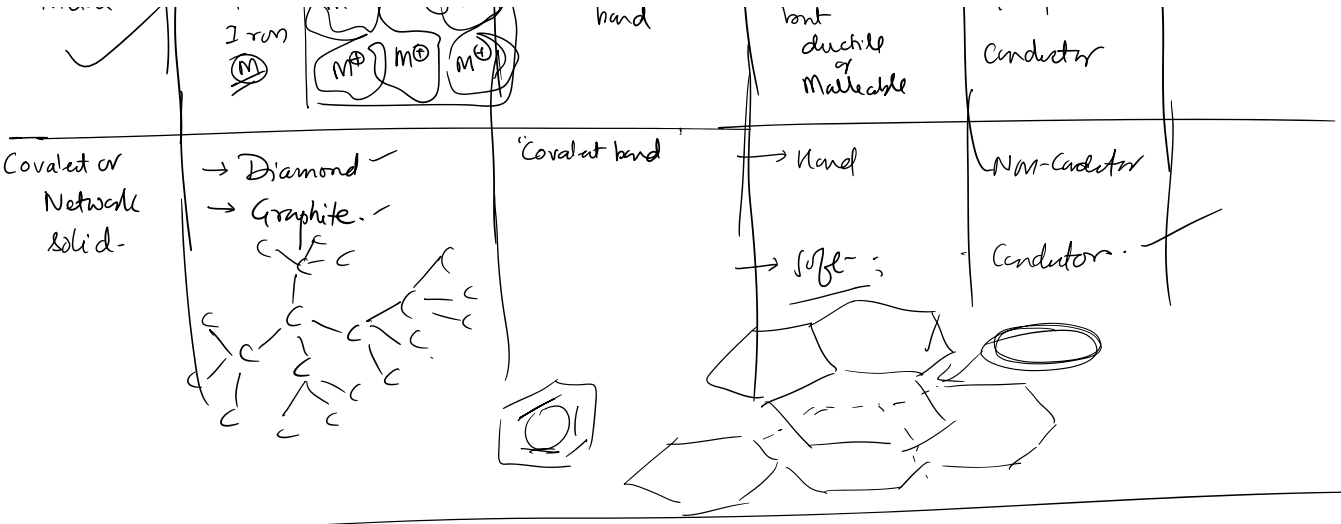
↳ Solid because of very high viscosity of the medium. Constituent particles are trapped in high viscous fluid.



" high viscosity does not allow particle to get ordered"

Type of solid (On the basis of bonding between constituent particle).

		type of force	physical prop.	Conductivity
Molecular solid	Solid ~~Solid~~ N_2	→ vander wall forces	very soft	Non-Conductor
	Solid HCl	→ dipole - dipole	soft	"
	Solid H_2O (ice)	→ H-bonding	Hard	"
Ionic	Salt Na^+Cl^-	→ electrostatic attraction.	→ Hard but brittle	Non conductor in solid but conductor in molten state.
Metal	Gold, Iron, M	→ Metallic bond	→ Hard but ductile or Malleable	Good Conductor

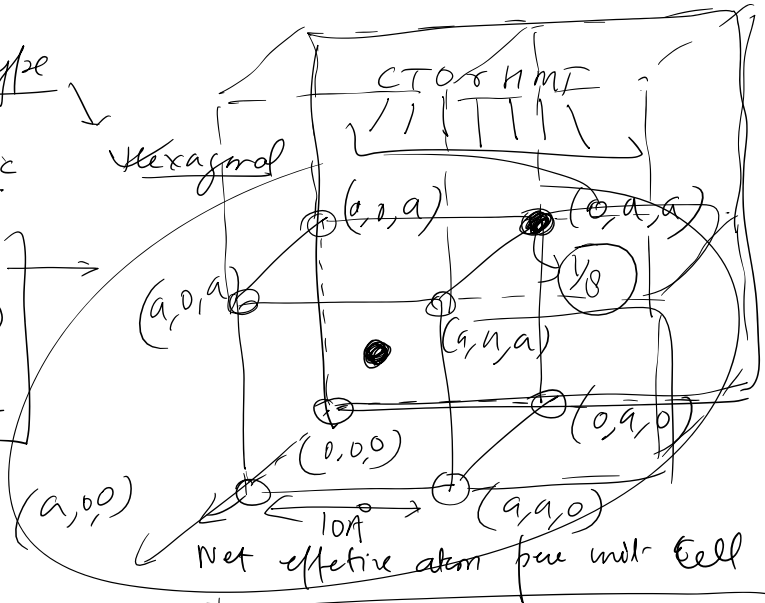


Unit Cell : ⇒ 7 type

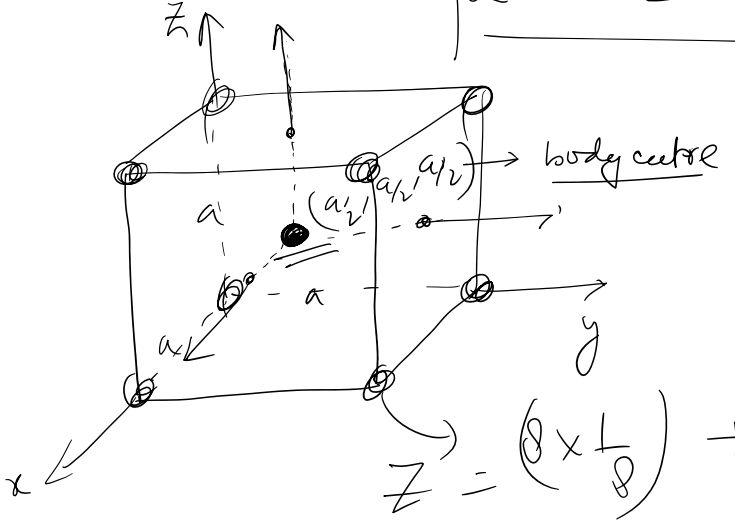
Cubic

Hexagonal

- Simple Cubic
- Body centred
- Face centre

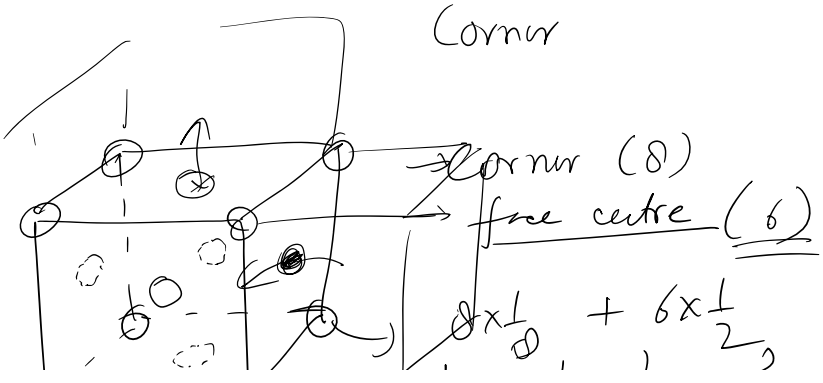


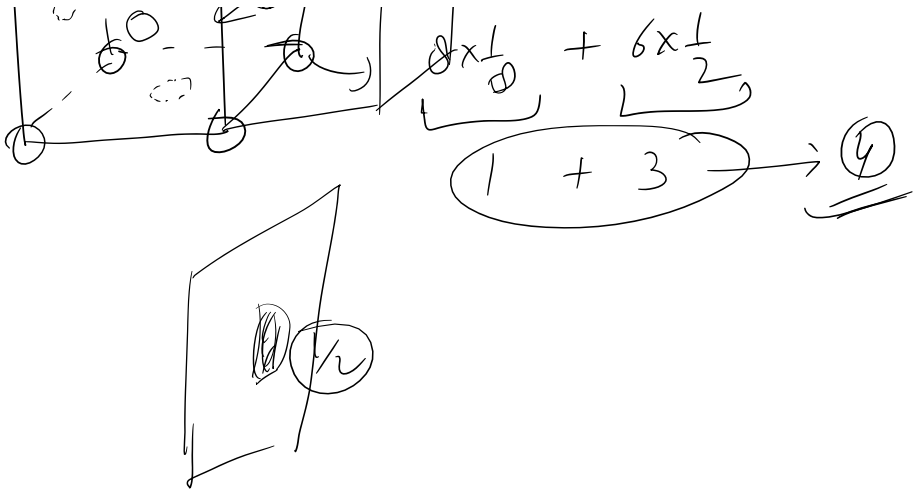
$$Z = 8 \times \frac{1}{8} = 1$$



$$Z = \left(8 \times \frac{1}{8}\right) + 1 = 2$$

Corner




8 x 1/10 + 6 x 1/2
1 + 3
4

1/2