Phosphorus

Electronic Configuration: $1s^2$; $2s^2p^6$; $3s^2p^3$.

Non-metal ~ no carbonate due to hydrolysis

Occurrence :-

$Ca\,F_2 . Ca_3(PO_4)_2$ ~ fluorapatite

$Ca_3(PO_4)_2$ ~ apatite or phosphorite

Also $AlPO_4$, $Fe_3(PO_4)_2 . 8H_2O$, Bones etc.

Extraction : $2Ca_3(PO_4)_2 + 6SiO_2 + 10C \xrightarrow{1400-1500^\circ c.}$

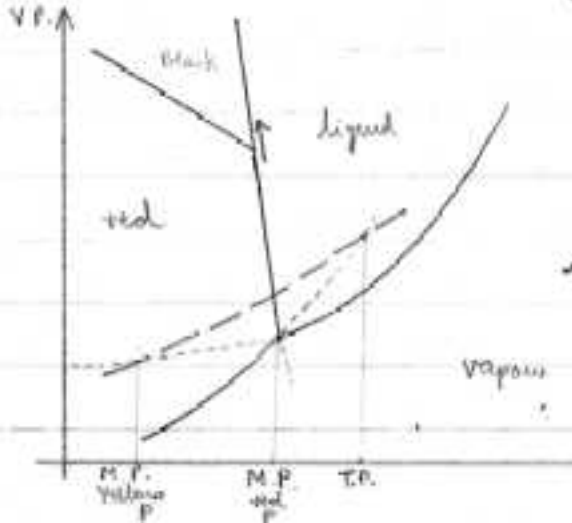
$6CaSiO_3 + 10CO\uparrow + P_4\uparrow$

[YELLOW ALLOTROPE]

$CO + H_2O \xrightarrow{catalyst} CO_2 + H_2\uparrow$ (BOSCH)

(If Al_2O_3, Fe_2O_3 mixed with SiO_2 cement clinker obtained).

Metastable allotrope (having greater intrinsic energy than red P) is obtained by condensation.



Volatile, in steam, → v. pure phosphorus.

To prepare red allotrope, heat yellow to 250°c. in inert atmosphere (no catalyst necessary) light catalyses change

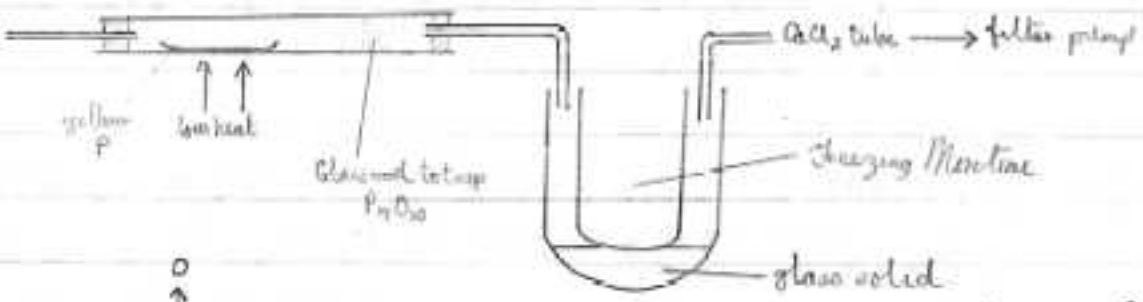
Yellow removed by aq. NaOH $\rightarrow PH_3$

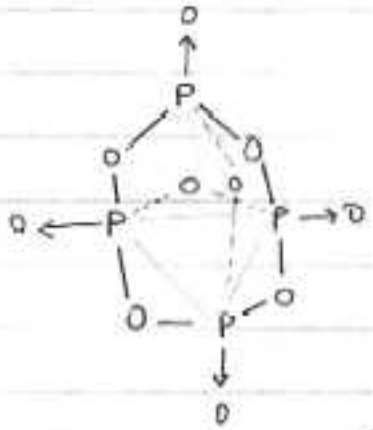
Allotropes are monotropic, yellow only formed via the vapour phase.
Red phosphorus is insoluble in NaOH, CS_2, is non-luminous, non-poisonous.
Black phosphorus obtained (at 200°c, 12,000 atmos).
It has a small electrical conductivity.

$\rho_{yellow} = 1.8$; $\rho_{RED} = 2.2$; $\rho_{BLACK} = 2.7$

Properties

(a) $P_4 + 3O_2 \xrightarrow[\text{air}]{\text{deficiency}}$ P_4O_6 (unstable waxy solid $\rightarrow P_4O_{10}$)





$P_4O_6 + 6H_2O \xrightarrow{\text{slowly}} 4H_3PO_3$ (ortho-ous)

$P_4 + 5O_2 \rightarrow P_4O_{10}$

$P_4O_{10} + 2H_2O \rightarrow 4HPO_3$ (meta-ic)

$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$ (ortho-ic)

$P_4O_{10} + 4H_2O \rightarrow 2H_4P_2O_7$ (pyro-ic)

$2H_3PO_4 \xrightarrow[220°c]{\text{heat}} H_4P_2O_7 + H_2O$

(b) yellow P is chemiluminescent.

Intra-Group Separation.

Group I : To Distinguish between Pb^{++}, Ag^{+}, Hg_2^{++}.

a) To p.p. add soln of KI or K_2CrO_4 in HNO_3 :- [First add ¾ t.t. d.w. warm] [Cfg. warm]
Yellow p.p. PbI confirms presence of Pb^{++}.

b) Centrifuge, to residue, repeat addition of d.w. and test for Pb^{++} until no more yellow p.p. [all Pb^{++} removed].

c) To residue add ¼ t.t. dil. NH_3. Mix. Centrifuge.
Acidify filtrate with HNO_3
White p.p. confirms presence of Ag^{+} (of AgCl)

$$\left[\begin{array}{l} \underset{(insol)}{AgCl} + 2NH_3 \rightarrow \underset{(sol)}{Ag(NH_3)_2Cl} \\ 2H^{+} + Ag(NH_3)_2Cl \rightarrow AgCl + 2NH_4^{+} \end{array}\right]$$

d) Repeat extraction of Ag^{+} from residue, which is now black

$$Hg_2Cl_2 + NH_3 \rightarrow Hg(NH_2)Cl + Hg + HCl$$

Dissolve in aqua regia

$$Hg + Cl_2 \rightarrow HgCl_2$$

$$2Hg(NH_2)Cl + 6Cl \rightarrow 2HgCl_2 + N_2 + 4HCl$$

Add 1 dr. $SnCl_2$

White, grey, black p.p. shows Hg_2^{++}

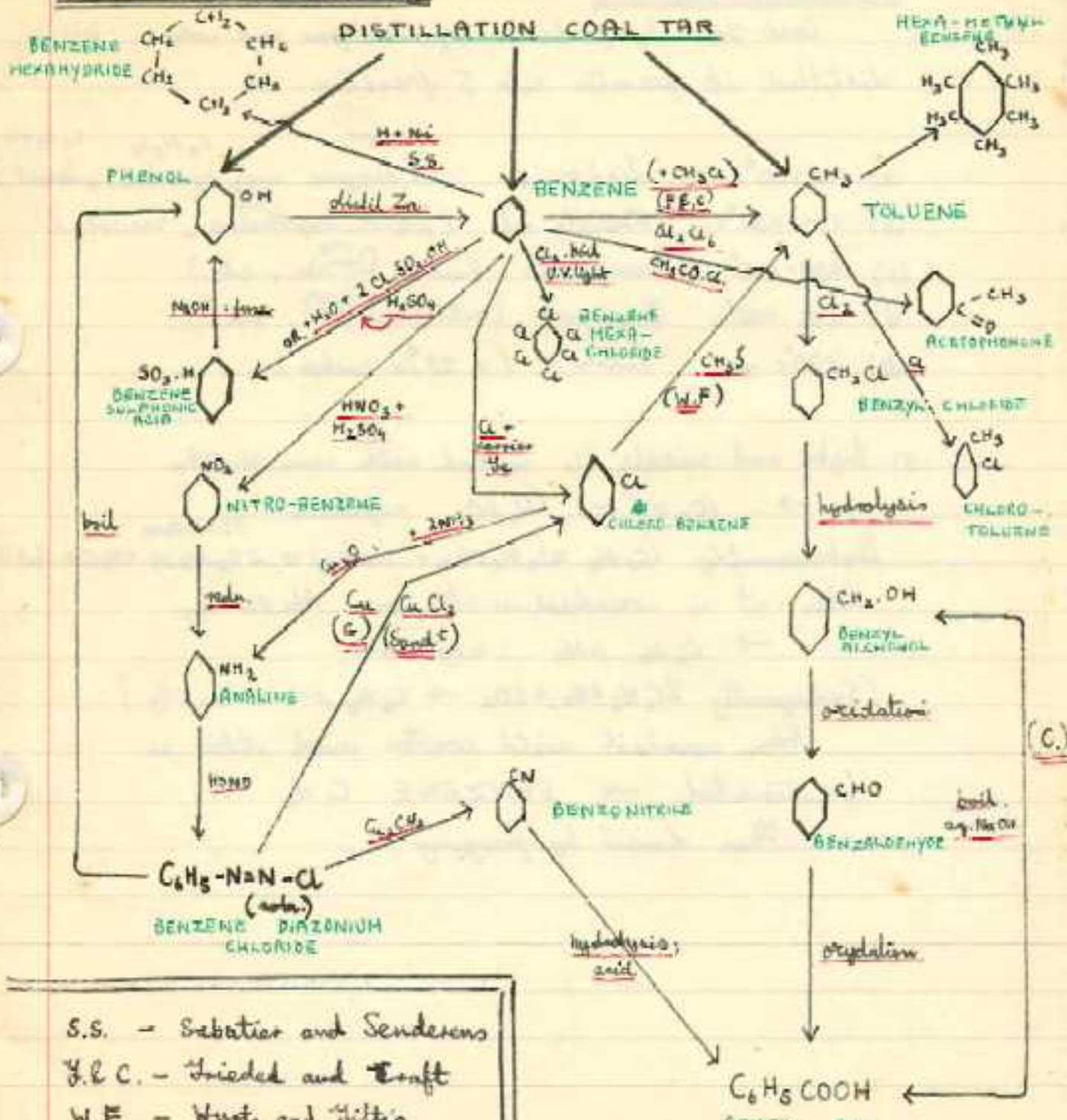
$$Sn^{++} + 2Hg^{++} \rightarrow Sn^{4+} + Hg_2^{++} \downarrow$$

$$(SnCl_2 + HgCl_2 \rightarrow SnCl_4 + Hg \downarrow \text{ (black)}$$

$$\text{OR. } 2HgCl_2 \rightarrow SnCl_4 + Hg_2Cl_2 \text{ (white)})$$

[Or for Ag^{+}, Hg_2^{++} ~ add soln K_2CrO_4 – brick red p.p. [mercurous silver chromate (soluble in dil. HNO_3 ~ cf. lead chromate).]

Aromatic Chemistry



S.S. – Sabatier and Senderens
F.R.C. – Frieded and Craft
W.F – Wurtz and Fittig
Sandt – Sandmeyer
C. – Cannizzaro
G. – Gattermann