SOLUTIONS

Module - 3 / JEE-2022

IN-CHAPTER EXERCISES	Chemistry	p-Block Elements - I

EXERCISE-A

1. **(a)** Phosphoric acid is preferred to sulphuric acid in preparation of H_2O_2 from BaO_2 because H_3PO_4 acts as negative catalyst for H_2O_2 and prevents its decomposition.

(b) Red Phosphorous, due to steric strain is more reactive and has low B. pt. and thus it is more volatile.

(c) In B_2H_6 (diborane), B doesnot have enough valency electrons to form conventional two - electron bonds between all of the adjacent pairs of atoms and so it is termed as electron - deficient.

(d) $AlCl_3$ hydrolyses in moist air to give fumes of HCl.

$$AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HCl \text{ (white fumes)}$$

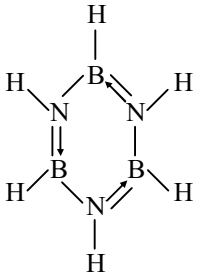
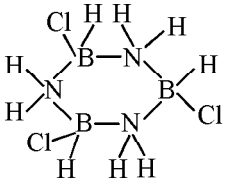
(e) NaOH reacts with Al and evolves hydrogen. The pressure of the evolved hydrogen opens up the clogged drain.

2. **(a)** $Na_2B_4O_7 + \text{conc. } H_2SO_4 \longrightarrow \underset{(A)}{H_3BO_3} \xrightarrow[2.\quad \text{Ignite}]{1.\ C_2H_5OH} \underset{(B)}{B(OC_2H_5)_3}$. The colour of flame produced is green.

(b) $BCl_3 + LiAlH_4 \longrightarrow B_2H_6 \xrightarrow{\text{excess } NH_3} [BH_2(NH_3)_2]^+ [BH_4]^-$

($B_2H_6 \xrightarrow{Cl_2} BCl_3$)

(c) $BCl_3 + NH_4Cl \xrightarrow{140°C} B_3N_3H_3Cl_3$

$B_3N_3H_3Cl_3 \longrightarrow$  $(B_3N_3H_6)$; $B_3N_3H_6 \xrightarrow{3HCl}$  $(B_3N_3H_9Cl_3)$

(d) $H_3BO_3 + HF \xrightarrow[\text{(non aqueous)}]{} BF_3 \xrightarrow{LiH} B_2H_6 \xrightarrow{\text{excess LiH}} Li[BH_4]$

3. AlF_3 is insoluble in the anhydrous HF because the F^- ions are not available in intermolecular hydrogen bonded HF but it becomes soluble in presence of KF due to formation of K_3AlF_6.

$$AlF_3 + 3KF \longrightarrow K_3[AlF_6]$$

4. $RCN \longrightarrow RCH_2NH_2$

$RNO_2 \longrightarrow RNH_2$

$RCHO \longrightarrow RCH_2OH$

5.(A) $B(OH)_3 + OH^- \longrightarrow [B(OH)_4]^-$

6.(AD) $Al_2O_3 + 6conc.HCl \longrightarrow 2AlCl_3 + 3H_2O$

$Al_2O_3 + C + Cl_2 \longrightarrow AlCl_3 + CO$

7.(BC) $Ca_2B_6O_{11} + 2Na_2CO_3 \longrightarrow 2CaCO_3 + Na_2B_4O_7 + 2NaBO_2$
(Colemanite)

8.(AB) BCl_3 is triangular planar $AlCl_3$ form dimer with 3-centre 4-electron bond while all others are electron - deficient compounds with 3-centre 2- elecron bond.

9.(A)

EXERCISE-B

1. **(i)** Pb **(ii)** C **(iii)** Si **(iv)** C

2. **(i)** Solid CO_2 is used as dry ice to maintain low temperatures

(ii) Carbon in the form of diamond is used as abrasive and in the form of graphite as a lubricant. This is due to the hardness of diamond and slipperiness of graphite.

(iii) NaOH reacts with glass (SiO_2) forming silicates which block the stopper of the bottle.

(iv) Although thermodynamically it is favourable for diamonds to turn into graphite but this doesnot happen because there is a high energy of activation required for the process. If this energy is available, the change occurs.

(v) Carbon halides cannot hydrolyse because they donot have d orbitals and cannot form a hydrolysis intermediate while silicon halides readily hydrolyse.

(vi) $SnCl_4$ forms hydrates in moisture : -

$SnCl_4 \xrightarrow[(limite)]{H_2O} SnCl_4.3H_2O$ (fumes)

3. **(a)** $CO + Cl_2 \longrightarrow \underset{\downarrow H_2O}{COCl_2} \xrightarrow{NH_3} \underset{urea}{(NH_2)_2CO} \xleftarrow{NH_3(E)} \underset{(D)}{CO_2}$

$\underset{(D)}{HCl + CO_2}$

(b) $Si \xrightarrow{HNO_3|HF} SiF_4 \xrightarrow{HF} [SiF_6]^{2-}$

$SiF_4 \xrightarrow{H_2O} Si(OH)_4 + H_2SiF_6$

(c) $Na_2CO_3 + Si(fused) \longrightarrow Na_2SiO_3 + CO_2$

(d) $Sn(C_2O_4) \xrightarrow{\Delta} SnO + CO\uparrow + CO_2\uparrow$

$\underset{(A)}{SnO} \xrightarrow{dil.\ HCl} SnCl_2$

Among CO and CO_2 ; CO is measured quantitatively by I_2O_5 solution. Thus (B) is CO and (C) is CO_2.

4. CO_2 being an acidic oxide decreases the pH of water and thus makes the soil acidic.

5. **(i)** $2SiCl_4 + 4Al \longrightarrow 4AlCl_3 + 3Si$

$SiCl_4 + 3Mg \longrightarrow Si + 2MgCl_2$

(ii) $SiCl_4 + CH_3MgCl \longrightarrow CH_3SiCl_3 + MgCl_2$

$CH_3SiCl_3 + CH_3MgCl \longrightarrow (CH_3)_2SiCl_2 + MgCl_2$

$(CH_3)_2SiCl_2 \xrightarrow{2H_2O} (CH_3)_2Si(OH)_2$

$$n[Si(CH_3)_2(OH)_2] \xrightarrow{-H_2O} \left[-O-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{Si}}}}-O- \right]_n$$

(iii) $3SiCl_4 + 4Al \longrightarrow 3Si + 4AlCl_3$

$Si + O_2 \longrightarrow SiO_2$

$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$

6. **(i)** CO is detected by flame test. It burns with a blue flame.

(ii) CO_2 is detected by lime water test. It turns lime water milky.

(iii) Silicates are detected by first dissolving them in HF to form SiF_4 which when comes in contact with a water droplet forms silicic acid (seen as floating white solid)

(iv) $PbCl_2$ forms a yellow precipitate of $PbCrO_4$ in presence of K_2CrO_4 which dissolves in NaOH forming a yellow solution.

7.(B) Graphite shows conductivity due to electrons.

8.(B)

Silicate	No. of oxygen atom shared per tetrahedra
Pyrosilicate	1
Sheet silicate	3
Linear chain	2
3-D silicate	4

9.(D) PbI_4 does not exist - stable oxidation state of Pb is +2. It is due to Inert pair effect.

$PbI_4 \xrightarrow{\Delta} PbI_2 + I_2$

10.(C) $(CH_3)_2SiCl_2 \xrightarrow{2H_2O} (CH_3)_2Si(OH)_2$

$$n[Si(CH_3)_2(OH)_2] \xrightarrow{-H_2O} \left[-O-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{Si}}}}-O- \right]_n$$

11.(ABC) $Pb(NO_3)_2 \xrightarrow{\Delta} PbO + 2NO_2 + \frac{1}{2}O_2$

EXERCISE-C

1. **(a)** **(i)** $2NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2$ **(ii)** $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$

(iii) $NH_4Cl + NaNO_2 \xrightarrow{\Delta} N_2 + 2H_2O + NaCl$

(b) **(i)** $Li_3N + H_2O \longrightarrow Li$ **(ii)** $AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3\uparrow$

(iii) $NCl_3 + 4H_2O \longrightarrow NH_4OH + 3HOCl$ **(iv)** $2NO_2 + H_2O \longrightarrow HNO_3 + HNO_2$

(c) **(i)** $8HNO_3 + 3Cu \longrightarrow 2NO + 3Cu(NO_3)_2 + 4H_2O$

(Laboratory preparation)

(ii) Serpeck's process :

$Al_2O_3 + 3C + N_2 \longrightarrow 2AlN + CO$; $AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3 \uparrow$

(iii) Using Ostwalds Process :

(a) $4NH_3(g) + 5O_2 \xrightarrow{Pt} 4NO + 6H_2O$ **(b)** $4NO \underset{50°C}{\overset{2O_2}{\rightleftharpoons}} 4NO_2 \xrightarrow[(60\%)]{2H_2O + O_2} 4HNO_3$

2. **(i)** NF_3 is more stable than NCl_3 due to higher bond dissociation enthalpy. Thus it is not readily hydrolysed.

(ii) NH_3 has higher b.p. than PH_3 molecules due to hydrogen bonding present among NH_3 molecules. This makes it difficult to evaporate solid NH_3 than solid PH_3.

(iii) conc. $HNO_3 \xrightarrow{light} NO_2 + O_2 + H_2O$

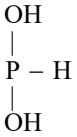
The brown colour of NO_2 produced makes it look yellow in solution.

(iv) $(CH_3)_3N$ is pyramidal while $(SiH_3)_3N$ is planar because in $(SiH_3)_3N$[trisilyamine] three sp^2 orbitals are used for σ - bonding. The lp of e– occupy a p orbital at right angles to the plane triangle. This overlaps with empty d orbitals on each of the three silicon atoms resulting in $p\pi - d\pi$ bonding. This is impossible in $(CH_3)_3N$ because C does not posses d orbitals.

(v) NF_5 cannot exist because there are no d-orbitals to accomodate the 5 electrons coming from five fluorine atoms. This however can occur in PF_5.

(vi) NH_3 cannot be dried with H_2SO_4 for else they will neutralise each other. Similarly P_2O_5 will react with CaO.

(vii) H_3PO_3 has the structure :



Which shows that it is dibasic due to only 2 OH groups.

3. **(a)** $P_4 + \text{conc. } HNO_3 \longrightarrow H_3PO_4 + NO_2$

(b) $PCl_5 + SO_2 \longrightarrow \underset{(A)}{POCl_3} + SOCl_2$

$6PCl_5 + P_4O_{10} \longrightarrow \underset{(B)}{10POCl_3}$

$\underset{(A)}{SOCl_2} + P_4 \longrightarrow SO_2 + \underset{(C)}{PCl_3}$

(c) $NH_3 + O_2 \xrightarrow{Pt} \underset{(A)}{NO(g)} \xrightarrow{O_2} \underset{(B)}{NO_2} \xrightarrow{H_2O} \underset{(C)}{HNO_2} + \underset{(D)}{HNO_3}$

$\underset{(C)}{HNO_2} + I^- \longrightarrow \underset{(E)}{I_2}$

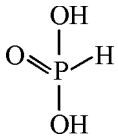
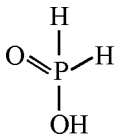
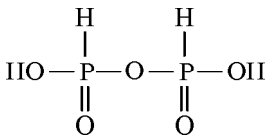
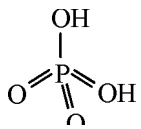
(d) $\underset{(A)}{NH_4NO_3} + NaOH \xrightarrow{\Delta} \underset{(B)}{NH_3(g)} + \underset{(C)}{NaNO_3}$

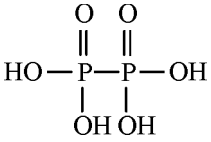
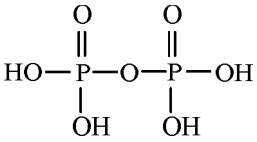
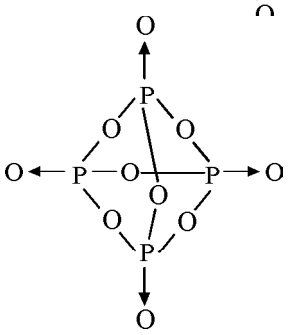
$NH_3 + HCl \longrightarrow NH_4Cl$ (white fumes)

$NH_4NO_3 \xrightarrow{\Delta} \underset{(D)}{N_2O(g)} + \underset{(E)}{H_2O(\ell)}$

(f) $\underset{(A)}{N_2O} + P_4 \longrightarrow P_4O_{10} + \underset{(B)}{N_2} \xrightarrow[\text{electric arc}]{O_2} \underset{(C)}{NO} \xrightarrow{O_2} \underset{(D)}{NO_2} \xrightarrow{H_2O} \underset{(F)}{HNO_3} \xrightarrow{P_4O_{10}} \underset{(G)}{H_3PO_4}$

$\underset{(C)}{NO} + \underset{(D)}{NO_2} \xrightarrow{cool} \underset{(E)}{N_2O_3}$ (blue)

4. **(a)**  **(b)**  **(c)**  **(d)** 

(e)  **(f)**  **(g)** 

5. **(a)** $3Ca_3(PO_4).CaF_2 + 14H_3PO_4 \longrightarrow \underset{\text{Triple Phosphate}}{10Ca(HPO_4)_2} + 2HF$

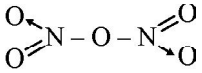
(b) This is because N_2 can form much stable triple bond than an unstable tetrahedral structure.

6.(D) NH_3 is basic reacts with H_2SO_4 and P_2O_5

NH_3 is lewis base as well so forms complex with $CaCl_2$

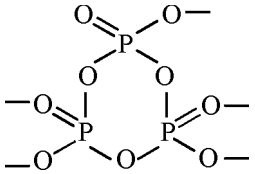
7.(A) Molar mass of NO is 31 and that of O_2 is 32.

8.(D) NO_2

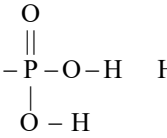
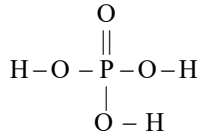
9.(B) 

10.(A) $NF_3 < NCl_3 < NBr_3 < NI_3$ (basic strength)

F being most electronegative so, will decrease e-density at N. Therefore NF_3 become less basic.

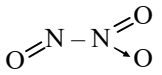
11.(C)  There 3 P – O – P bonds.

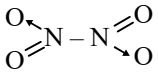
12.(A) P – bond causes reducing nature. ; O = P – O – H causes basicity.

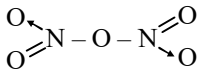
H_3PO_3 is  H_3PO_3 

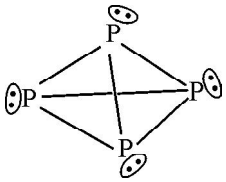
13.(B) X is limited supply of O_2. This is possible by mixing O_2 with N_2.

14.(ABC) N_2O is $N \equiv N \rightarrow O$

N_2O_3 is 

N_2O_4 is 

N_2O_5 is 

15.(ACD) 

16.(AD) $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$; $NH_2OH + HNO_2 \xrightarrow{\Delta} N_2O + 2H_2o$; $NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$