SOLUTIONS

Module - 6 / JEE-2021

In-Chapter Exercises	Chemistry	p-block Elements - II

EXERCISE- A

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)** $4NO \xrightarrow[50^\circ C]{2O_2} 4NO_2 \xrightarrow{2H_2O + O_2} \underset{(60\%)}{4HNO_3}$

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 :

$$\begin{array}{c} \quad OH \\ \quad | \\ O = P - H \\ \quad | \\ \quad OH \end{array}$$

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

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

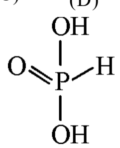
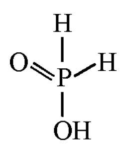
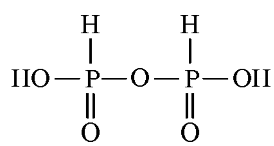
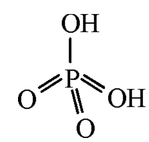
(d) $\underset{(A)}{NH_4NO_3} + NaOH \xrightarrow{\Delta} \underset{(B)}{NH_3(g)} + \underset{(C)}{NaNO_3}$

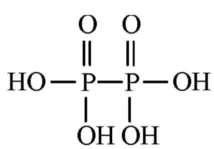
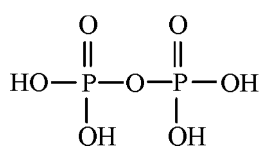
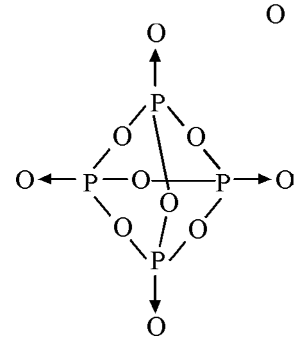
$NH_3 + HCl \longrightarrow NH_4Cl$ (white fumes)

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

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

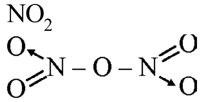
(b) This is because N_2 can form much stable triple bond than an unstable tetrahedral structure.

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 $CaCl_2$

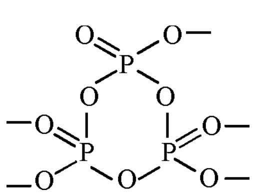
7.(A) Molar mass of NO is 31 and that of O_2 is 32.

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.

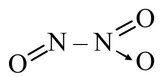
12.(A) P – bond causes reducing nature.

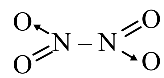
$O = P - O - H$ causes basicity.

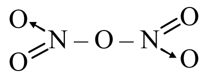
$$H_3PO_3 \text{ is } \quad \begin{array}{c} O \\ \| \\ H - P - O - H \\ | \\ O - H \end{array} \qquad H_3PO_3 \quad \begin{array}{c} O \\ \| \\ H - O - P - O - H \\ | \\ O - H \end{array}$$

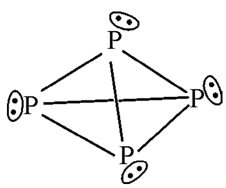
13.(B) X is limited supply of O_2. This is possible by mixing O_2 with N_2.

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) $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$; $NH_2OH + HNO_2 \xrightarrow{\Delta} N_2O + 2H_2o$

$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$

EXERCISE-B

1. **(a)** **(i)** Heat $KClO_3$ in the presence of manganese dioxide.

$$2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2$$

(ii) Passing carbon dioxide through oxone releases O_2.

$$Na_2O_2 + CO_2 \longrightarrow Na_2CO_3 + \frac{1}{2}O_2$$

(iii) $Pb(NO_3)_2 \xrightarrow{\Delta} PbO + NO_2 + O_2$

(b) **(i)** $5H_2O_2 + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$

(ii) $H_2O_2 + 2I^- + 2H^+ \longrightarrow 2H_2O + I_2$

2. **(a)** White lead on exposure to atmosphere oxidises to block plumbous oxide. This can be removed by a treatment with hydrogen peroxide.

$2Pb + O_2 \longrightarrow 2PbO \text{ (black)}$; $PbO + H_2O_2 \longrightarrow \underset{\text{(soluble)}}{PbO_2} + H_2O$

(b) Na_2O_2 gives H_2O_2 with dilute acids.

$$Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$$

However if water is used (or present), the NaOH formed being basic catalyses decomposition of H_2O_2 :

(c) In most reactions H_2O_2 acts as a strong oxidising agent (like with Fe^{2+}, SO_3^{2-}, $Cr_2O_7^{2-}$) but however with sronger oxidising agents it is forced to act as a reducing agent (like with MnO_4^-, IO_4^-).

(d) Hg in the presence of ozone is oxidied to suboxide and starts sticking to glass and loses its meniscus.

(e) Passing H_2S in aqueous solution of SO_2 precipitates sulphur which produces turbidity in the solution.

$$2H_2S + SO_2 \longrightarrow 2H_2O + 3S\downarrow$$

(f) NH_3 cannot be dried with H_2SO_4 as they neutralise each other. $NH_3 + H_2SO_4 \longrightarrow (NH_4)SO_4$. Ammonia is thus best dried with quick lime (CaO).

(g) Liquid oxygen is paramagnetic due to presence of unpaired electrons which liquid nitrogen being diamagnetic doesnot stick to a magnet.

(h) OF_6 cannot exist because their are no d orbital in an oxygen atom to accomodate incoming electrons from fluorine atoms.

3. Gaseous SO_3 has a planar triangular strucure with sp^2 hybridised s atom while solid SO_3 exists in a cyclic trimer form (or hetical chains)

4. $$H_2SO_4 + HNO_3 \longrightarrow HSO_4^- + H_2NO_3^-$$

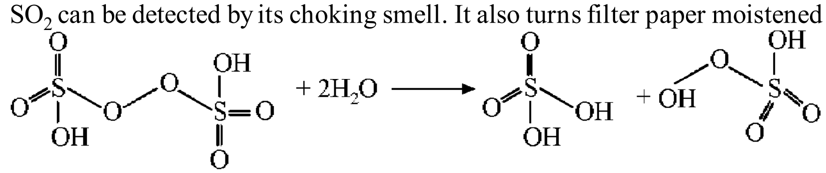
Thus H_2SO_4 is the stronger Bronsted acid.

5. **(a)** O_2 burns with a blue flame which serves as a test for it. **(b)** O_3 turns starch iodide paper blue.

(c) H_2S can be detected by its small of rotten eggs.

(d) SO_2 can be detected by its choking smell. It also turns filter paper moistened with $K_2Cr_2O_7/H^+$ green.

6.(C)



Peroxo disulphuric acid — Sulphuric acid — Peroxo mono sulphuric acid

7.(B) $KMnO_4$ already has Mn in its highest oxidation state of +7

8.(B) $$SO_3^{2-} + S \xrightarrow{OH^-} \underset{\text{(thiosulphate)}}{S_2O_3^{2-}}$$

Note that neutralisation of $H_2S_2O_3$ with NaOH produces a mixture of Na, S, SO_2, NO_2, SO_4, S and not $Na_2S_2O_3$.

9.(B) Fermentation of glucose involves the following reaction ; $C_6H_{12}O_6 \longrightarrow 2C_2H_5OH + 2CO_2$

EXERCISE-C

1. **(a)** There is hydrogen bonding among HF molecules which increases its viscosity and boiling point. Its existence as a dimer is also due to very strong hydrogen bond between two HF molecules (which is due to the larger electronegativity difference).

(b) HOCl is an acid [$H^+ + OCl^-$] which turns blue litmus red. HOCl is also an oxidising agent [HCl + O] and thus bleaches the colour of litmus solution. Thus this involves acidic as well as bleaching action of HOCl.

(c) $$NaI + H_2SO_4 \longrightarrow NaHSO_4 + HI$$

HI thus formed being a strong reducing agent reduces H_2SO_4 to SO_2.

$$2HI + H_2SO_4 + H_2SO_4 \longrightarrow SO_2 + I_2 + 2H_2O$$

H_3PO_4 is not reduced by HI.

(d) F_2 is better O.A. than Cl_2 because it has a very low value of bond dissociation energy (though its electron affinity is lower than Cl^-)

(e) $I^- \xrightarrow{NO_2^-} I_2 \xrightarrow{KI} I_3^-$ will lead to intensification of colour while,

$I_2 \xrightarrow{SO_3^{2-}} 2I^-$ will not.

(f) Water must be excluded otherwise F_2 produced will oxidize it to dioxygen and itself will get reduced to F^-. While anhydrous HF is only slightly ionized and therefore a poor conductor of electricity.

(g) A mixture of KF and HF is used to increase conductivity and lower the m.p.. The mixture exists in the ionic form $K^+[F-H-F]^-$

2. **(a)** **(i)** $2HF + CCl_4 \longrightarrow \underset{\text{(freon)}}{CC_2F_2} + 2HCl$ **(ii)** $4HF + SiO_2 \longrightarrow SiF_4 + 2H_2O$

(iii) $HF + KF \longrightarrow K^+[F-H-F]^-$

(b) **(i)** $Cl_2 + SO_2 \longrightarrow SO_2Cl_2$ **(ii)** $Cl_2 + H_2 \longrightarrow 2HCl$

(iii) $Cl_2 + 2NaOH \longrightarrow NaOCl + NaCl + H_2O$

3. **(a)** $MnO_2 + HCl \longrightarrow \underset{(A)}{Cl_2(g)} \xrightarrow{\text{hot NaOH}} \underset{(B)}{NaClO_3} + \underset{(C)}{NaCl}$

$\underset{(B)}{NaClO_3} \xrightarrow[\Delta]{OH^-} \underset{(C)}{NaCl} + \underset{(D)}{O_2}$

(b) $HCN + CuSO_4 \longrightarrow \underset{(B)}{Cu_2(CN)_2} + \underset{(A)}{(CN)_2(g)}$

$Cu_2(CN)_2 \xrightarrow{\text{excess } CN^-} \underset{(C)}{[(Cu(CN)_4]^{3-}}$

(c) $2P(\text{red}) \xrightarrow{3Br_2} \underset{(A)}{2PBr_3} \xrightarrow{6H_2O} \underset{(B)}{6HBr(g)} + 2H_3PO_3$

$HBr \xrightarrow{\text{conc. } H_2SO_4} Br_2$

(d) $CH_3-CH=CH_2 + ICl \longrightarrow CH_3-\underset{\displaystyle Cl}{\underset{|}{C}H}-\underset{\displaystyle I}{\underset{|}{C}H_2}$

(Iodination occurs : $ICl \longrightarrow I^+ + Cl^-$)

4. $NaCl + \underset{\text{(Weaker acid)}}{H_2SO_4} \longrightarrow NaHSO_4 + \underset{\text{(Stronger acid)}}{HCl(g)}$

This occurs because HCl gas escapes taking equilibrium tothe right.

5. H_2SO_4 oxidises HBr formed to Br_2 while this is not the case with HF.

6.(D) The reducing character increases in the following order.

HF < HCl < HBr < HI. **7.(B)**

8.(B) Chlorine water is good oxidising agent.

9.(B) $RCOO^-$ doesnot contain nitrogen atom.

10.(A) The stability order of respective conjugate base is :

$ClO^- > BrO^- > IO^-$

This is because electronegativity decreases down the group and thus the negative charge is stabilised most in ClO^- and least in IO^-.

11.(ABC)

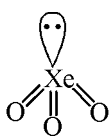
(1) $2ClO_2 + 2NaOH \longrightarrow NaClO_2 + NaClO_3 + H_2O$ **(2)** $\underset{(\equiv Cl_2O_6)}{2ClO_3} + 2NaOH \longrightarrow NaClO_3 + NaClO_4 + H_2O$

(3) $3ClO_2 + O_3 \longrightarrow 3ClO_3$ **(4)** Cl_2O is slightly acidic (being the anhydride of hypochlorous acid).

EXERCISE-D

1. By unpairing of one paired orbital,two singly occupied orbitals come into existence. Thus either two or four or six singly occupied orbitals can be formed instead of one or three or five singly occupied orbitals.

2.(A) Ar is unreactive (being a noble gas)

3.(C) 

is pyramidal

4.(A) All xenon fluroides are extremely strong oxidising and fluorinating agents.

5.(AB) 1. $XeF_2 \xrightarrow{H_2O} Xe + HF + O_2$

2. $XeF_4 \xrightarrow{H_2O} Xe + HF + O_2 + XeO_3$

3. $XeF_4 \xrightarrow[\text{(excess)}]{H_2O} HF + XeO_3$