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CHEMISTRY

TARGET : JEE Advanced – 2021

CAPS – 12

p-block (Group 15-18)

Answer Key

1.	(A)	**2.**	(B)	**3.**	(A)	**4.**	(A)	**5.**	(D)
6.	(B)	**7.**	(A)	**8.**	(B)	**9.**	(D)	**10.**	(C)
11.	(ABD)	**12.**	(AC)	**13.**	(ABC)	**14.**	(AB)	**15.**	(ABD)
16.	(A)	**17.**	(D)	**18.**	(D)	**19.**	(C)	**20.**	(B)
21.	(7.00)	**22.**	(16.00)						
23.	((A) - (p, r, s, t); (B) - (p, q, r, s, t); (C) - (t); (D) - (p, r, s))								
24.	(B)	**25.**	(A)	**26.**	(B)				

Solution

1. $Na + NH_3(g) \xrightarrow{\Delta} \underset{[x]}{NaNH_2} \xrightarrow{N_2O} \underset{[Y]}{NaN_3} \xrightarrow{\Delta} \underset{[Z]}{N_2}\uparrow$

2. $\underset{(A)}{PCl_5} + H_2O \rightarrow \underset{(B)}{POCl_3} + 2HCl$

$\underset{(B)}{POCl_3} + 3H_2O \rightarrow \underset{(C)}{H_3PO_4} + 3HCl$

3. If the nitric acid is dilute, the copper will be oxidized to form copper nitrate with nitric oxide as a byproduct.

$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

4. a : $2OF \xrightarrow{\text{Dimerisation}} F-\overset{+1}{O}-\overset{+1}{O}-F$

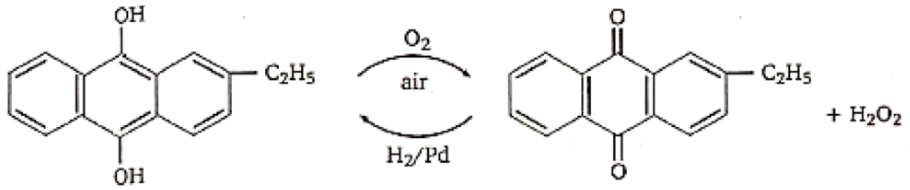
b : $H_4P_2O_8 \xrightarrow{+H_2O} 2H_3PO_4 + H-\overset{-1}{O}-\overset{-1}{O}-H$

c : $2Na \xrightarrow{\text{excess}\,O_2,\,\Delta} Na^+O^- - O^-Na^+$

5. In SF_6, S sterically hindered by six fluorine atoms hence, attack of H_2O molecule will not occur.
NF_3 is not hydrolysed due to absence of vacant orbital either on N or F atom.
TeF_6 is hydrolysed due to large size of Te.

6. * $H_2SO_4 + PbO_2 \rightarrow PbSO_4\downarrow + \frac{1}{2}O_2 + H_2O$ (PbO_2 is not peroxy compound)

* $H_2SO_4 + BaO_2 \rightarrow BaSO_4\downarrow + H_2O_2$

* 

* $(NH_4)_2SO_4 \rightleftharpoons 2NH_4^+ + SO_4^{2-}$

At anode: $2SO_4^{2-} \xrightarrow{\text{Electrolysis}} S_2O_8^{2-} + 2e^-$

Peroxo sulphate on hydrolysis, produces H_2O_2.

7. When Cl_2 is passed through $H-\overset{18}{O}-\overset{18}{O}-H$,

It produces $H^+ + Cl^- + O_2$ (both oxygen having 18)

8. $$6Cl_2 + 2Ba(OH)_2 \rightarrow \underset{(x)}{Ba(ClO_3)_2} + 5BaCl_2 + 6H_2O$$

$$Ba(ClO_3)_2 + H_2SO_4 \rightarrow \underset{(Y)}{2HClO_3} + BaSO_4 \downarrow$$

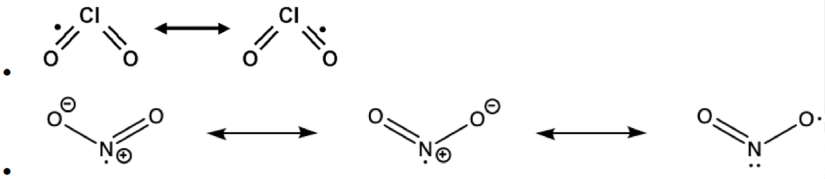
$$2HClO_3 \xrightarrow{\Delta,\ T>365K} 2ClO_2 + H_2O + \frac{1}{2}O_2$$

9. All are correct.

10. Hydrogen atom bonded to phosphorus are readily available as nascent hydrogen to carry out reduction. Thus, the more the number of such bonds the stronger is the reducing action of the compound.

Name	Formula	Oxidation state of phosphorus	Characteristic bonds and their number
Hypophosphorous	H_3PO_2	+ 1	One P – OH Two P – H One P = O
Orthophosphorous	H_3PO_3	+ 3	Two P – OH One P – H One P = O
Hypophosphoric	$H_4P_2O_6$	+ 4	Four P – OH Two P = O One P – P
Pyrophosphoric	$H_4P_2O_7$	+ 5	Four P – OH Two P = O One P – O – P

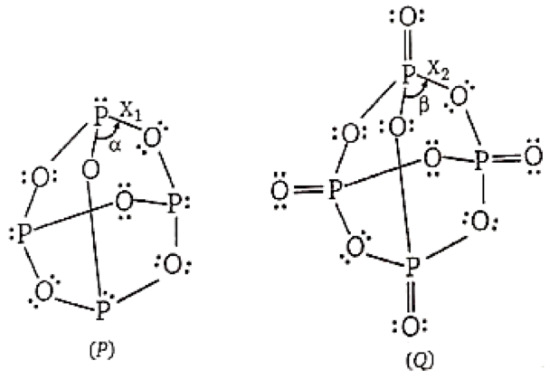
11.



12. Argon is the most abundant of the noble gases. Order is Ar > Ne > Kr > He > Xe

Melting point order of Xenon Fluorides is: $XeF_2 > XeF_4 > XeF_6$

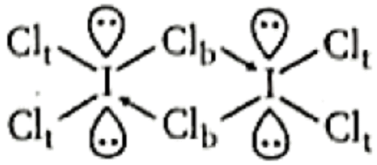
13. $$\underset{A_x}{P_4} + \underset{(yB_z)}{3O_2} \xrightarrow[\text{supply of air}]{\text{Limited}} \underset{(P)}{P_4O_6} \xrightarrow[\text{excess air}]{2O_2} \underset{(Q)}{P_4O_{10}}$$



(P) (Q)

According to Bent's rule: $x_1 > x_2$, $\alpha < \beta$

x + y + z = 4 + 3 + 2 = 9

14.  ($I–Cl_t$) and bridge bond are in same plane.

15. $H_3PO_4 \xrightarrow{520K,-H_2O} H_4P_2O_7 \xrightarrow{870K,-H_2O} (HPO_3)_n$

$(HPO_3)_4 \xrightarrow{\Delta,-2H_2O} P_4O_{10}$

Solution: 16 – (b), 17 – (d), 18 – (d)

(A) is PH_4I. The given changes are:

(i) $PH_4I + KOH \longrightarrow KI + PH_3 + H_2O$

(A) (B)

(ii) $4PH_3 + 8O_2 \longrightarrow P_4O_{10} + 6H_2O$

(B) (C)

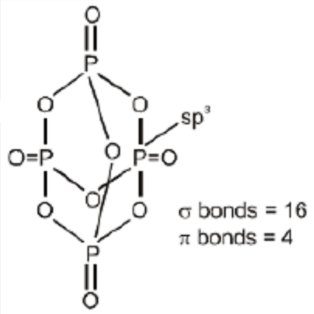
$3AgNO_3 + PH_3 \longrightarrow Ag_3P \downarrow + 3HNO_3$

$Ag_3P + 3AgNO_3 + 3H_2O \longrightarrow 6Ag \downarrow (black) + 3HNO_3 + H_3PO_3$

or

$6Ag^+ + PH_3 + 3H_2O \longrightarrow 3H_3PO_3 + 6Ag \downarrow (black) + 6H^+$

In P_4O_{10} there are 16 σ-bonds, and all central atoms have sp^3 hybridization.



19. $2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 \uparrow + O_2 \uparrow$

$\underset{(B)}{NO_2} + \underset{(H)}{NO} \xrightarrow[\text{temp.}]{\text{low}} \underset{\text{(Blue colour liquid)}}{N_2O_3}$

$\underset{(C)}{N_2O_3} + H_2O \longrightarrow \underset{(D)}{2HNO_2}$

$2HNO_2 + 2FeSO_4 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2NO + 2H_2O$

$FeSO_4(aq) + NO \longrightarrow \underset{(E)}{\left[Fe(H_2O)_5 NO\right]} SO_4$

$Pb(NO_3)_2 + H_2S \longrightarrow \underset{\text{Black ppt.}}{\underset{(G)}{PbS} \downarrow} \longrightarrow Pb(NO_3)_2 + S + \underset{(H)}{NO} \uparrow + \underset{(G)}{H_2O}$

$Pb(NO_3)_2 + K_2CrO_4 \longrightarrow \underset{\text{(yellow ppt.)}}{\underset{(I)}{PbCrO_4} \downarrow} + 2K^+ + 2NO_3^-$

$\underset{(D)}{NO_2^-} + 2H^+ + I^- \longrightarrow I_2 \uparrow \underset{(gas)}{NO} \uparrow + H_2O$

20. $2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 \uparrow + O_2 \uparrow$

$\underset{(B)}{NO_2} + \underset{(H)}{NO} \xrightarrow[\text{temp.}]{\text{low}} \underset{\text{(Blue colour liquid)}}{N_2O_3}$

$\underset{(C)}{N_2O_3} + H_2O \longrightarrow \underset{(D)}{2HNO_2}$

$2HNO_2 + 2FeSO_4 + H_2SO_4 \longrightarrow Fe(SO_3)_3 + 2NO + 2H_2O$

$FeSO_4(aq) + NO \longrightarrow \underset{(E)}{\left[Fe(H_2O)_5 NO\right]} SO_4$

$Pb(NO_3)_2 + H_2S \longrightarrow \underset{\text{Black ppt.}}{\underset{(G)}{PbS} \downarrow} \longrightarrow Pb(NO_3)_2 + S + \underset{(H)}{NO} \uparrow + \underset{(G)}{H_2O}$

$Pb(NO_3)_2 + K_2CrO_4 \longrightarrow \underset{\text{(yellow ppt.)}}{\underset{(I)}{PbCrO_4} \downarrow} + 2K^+ + 2NO_3^-$

$PbCrO_4 + 4OH^- \longrightarrow \underset{\text{soluble}}{[Pb(OH)_4]^{2-}} + CrO_4^{--}$

$2PbCrO_4 + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + H_2Cr_2O_7 + H_2O$

21. (ii) $CuSO_4 + PH_3 \longrightarrow \underset{\text{(Black)}}{Cu_3P_2}$

(viii) $SbF_5 + XeF_4 \longrightarrow [XeF_3]^+ [SbF_6]^-$

22. Correct order is:

(1) $H_2SO_4 > H_2SO_3$: Boiling point

(2) $H_2O >$ HF: Extent of H-bond

(6) Ethylene glycol > Phenol: Viscosity

(7) 1, 3-Dichlorobenzene > 1, 3, 5-Trichlorobenzene: Strength of molecular force

23.

- $2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$
- $6XeF_4 + 12H_2O \longrightarrow 4Xe + 2\,XeO_3 + 24\,HF + 3O_2$
- $XeF_6 + 6H_2O \longrightarrow XeO_3 + 6HF$
- $XeO_3 + NaOH \longrightarrow Na^+\,[HXeO_4]^-$ (sodium xenate)

  $2[HXeO_4]^- + 2OH^- \longrightarrow [XeO_4]^{4-} + Xe + O_2 + 2H_2O$

24. (A) $P_4O_6 + 6H_2O(hot) \rightarrow 3H_3PO_4 + PH_3$

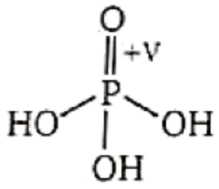
(B) $P_4 + 6NaOH + 3H_2O \rightarrow 2NaH_2PO_2 + PH_3$

(C) $4H_3PO_3 \xrightarrow{\Delta} 3H_3PO_4 + PH_3$

(D) $PH_4I + NaOH \rightarrow H_2O + PH_3 + NaI$

25.

- All halogens react with NaOH. Fluorine reacts with NaOH in a different way.
- F_2 with conc. NaOH gives off O_2 while with dil. NaOH it gives off OF_2 gas.
- Similarly, with hot and conc. NaOH, Cl_2, Br_2 and I_2 give $NaXO_3$ & NaX and with cold and dil. NaOH they give NaX and NaOX.
- Fluorine does not form F_3^- due to absence of vacant d-orbital, other halogens do.
- F_2 gas is pale yellow, Cl_2 is greenish, Br_2 is reddish brown and I_2 is dark violet in colour.

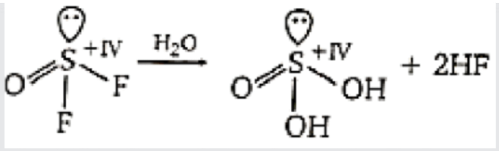
26. **(a)** $\overset{+V}{POCl_3} \xrightarrow{H_2O}$  $+ \ 3HCl$

$\Rightarrow$ Complete hydrolysis

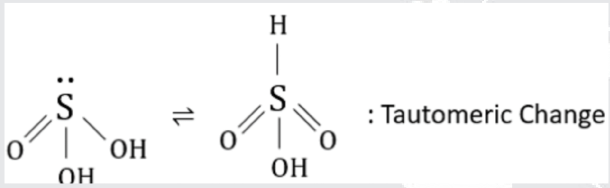
$\Rightarrow$ Hybridization of P in $POCl_3$: sp^3

$\Rightarrow$ Hybridization of P in H_3PO_4: sp^3

$\Rightarrow$ H3PO4 does not undergo Tautomeric change due to absence of lone pair at P-atom.

(b) 

$\Rightarrow$ Complete hydrolysis



$\Rightarrow$ HF reacts with glass

$\Rightarrow$ $SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$

$\Rightarrow$ Hybridization of S-atom remains sp^3

(c) $\overset{+VI}{Xe}\,OF_4 \xrightarrow[-2HF]{H_2O} XeO_2F_2 \xrightarrow{H_2O} \overset{+VI}{Xe}O_3 + 2HF$

$\Rightarrow$ $XeOF_4$ can be partially hydrolysed to XeO_2F_2

$\Rightarrow$ HF forms which reacts with glass

$\Rightarrow$ Hybridization Xe in $XeOF_4$ is sp^3d^2 while in XeO_3 it is sp^3

(d) $H_2\overset{+VI}{S_2}O_8 \xrightarrow{H_2O} H_2\overset{+VI}{S}O_5 + H_2\overset{+VI}{S}O_4 \xrightarrow{H_2O} 2H_2\overset{+VI}{S}O_4 + H-O-O-H$

$\Rightarrow$ $H_2S_2O_8$ can be partially hydrolysed to H_2SO_5

$\Rightarrow$ Hybridization S-atom in $H_2S_2O_8$ as well as in H_2SO_4 remains: sp^3

27. (A) NH_4NO_3 (B) NH_3 (C) ($NaNO_3$ +NaOH) (D) N_2O (E) H_2O