The p-block elements

Q.1 complete the following reactions :-

a) $BrO_3^- + F_2 + 2OH^- \longrightarrow BrO_4^- + 2F^- + H_2O$

b) $Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$ (Phosphine)

c) $XeF_4 + SbF_5 \longrightarrow [XeF_3][SbF_6]$

d) $P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3$ (Potasium hypophosphite)

e) $Cu + (Conc.)2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$

f) $I_2 + 10HNO_3\ (conc.) \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$

g) $Cl_2 + 3F_2\ (excess) \xrightarrow{250^\circ C} 2ClF_3$.

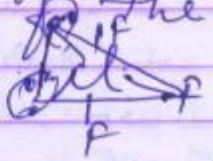
h) $2XeF_2 + 2H_2O \longrightarrow 2Xe + 2H_2F_2 + O_2$

i) $I_2 + 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2I^-$ (Tetrathionate ion.)

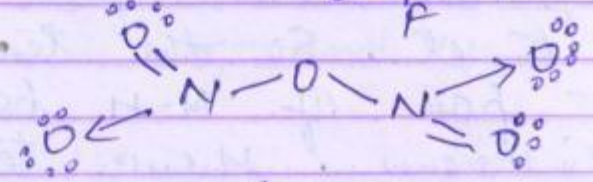
j) $P_4 + 10SO_2Cl_2 \longrightarrow 4PCl_5 + 10SO_2$

Q.2 Draw the structures of the following :-

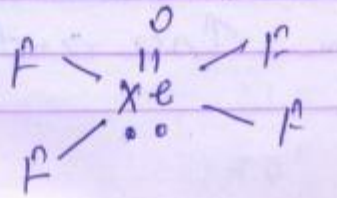
i) ClF_3



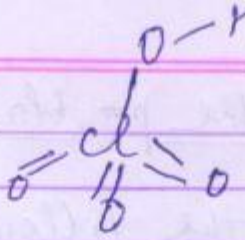
ii) N_2O_5



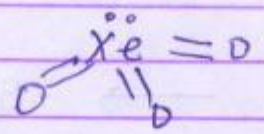
iii) $XeOF_4$



iv) $HClO_4$

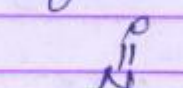


v) XeO_3.



Q.3. How would you account for the following?

⇒ N-O bond in NO_2^- is shorter than the N-O bond in NO_3^-

Ans:- NO_2^-  Bond order = $\frac{2+1}{2}$ = 1.5

NO_3^- ; Bond order = $\frac{2+1+1}{3}$ = 1.33

Bond order of NO in NO_2^- is 1.5 while bond order of NO in NO_3^- is 1.33 so bond (N-O) in NO_2^- is shorter than the N-O bond in NO_3^-

Q.4. The acidic strength of compounds increases in the order $PH_3 < H_2S < HCl$.

Ans. As we move in a period the electronegativity increases from P to S and from S to Cl. So the tendency to pull the e^- pair of M-H bond towards M increases. Hence tendency to loose H^+ ion ↑ses and acidic strength ↑ses.

Q.5 NF_3 is an exothermic compound NCl_3 is not?

Ans. The N-F bonds in NF_3 are stronger than F-F bond in F_2. The stronger the bonds in the compound indicate that the compound in its formation release energy. NCl_3 is not ~~stronger~~ stable compound as N-Cl bond is not strong.

Q.6 Structure of xenon fluorides cannot be explained by Valence bond approach.

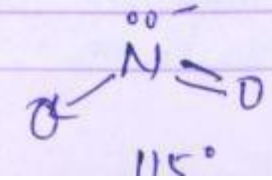
Ans According to VBT covalent bonds are formed by overlapping of half filled orbitals. But Xe has fully filled atomic orbitals.

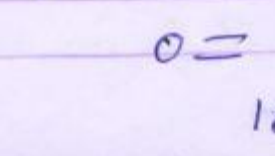
Q.7 Explain: The stability of +5 oxid^n state decreases down the group 15.

Ans:- Due to increase in inert pair effect i.e. reluctant to participate ns^2 e^- in compound formation.

Q.8 The bond angle (O-N-O) are not of same value in NO_2^- and NO_2^+. Explain

Ans. Due to difference in the its structure.





Q.9 Why is Bi(V) a stronger oxidant than Sb(V)?

Ans +3 oxidation state become more stable than +5 as we move from top to bottom due to inert pair effect. So Bi(V) accepts e⁻ easily and changes into Bi(III) and thus behaves as an oxidant.

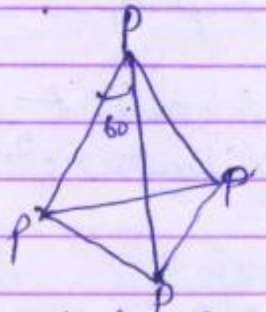
Q.10 SF_6 is not hydrolysed while SF_4 is hydrolysed?

Ans. In SF_4 d-orbital is available for bonding or saturation but not in case of SF_6. So SF_4 easily hydrolysed into SOF_2.

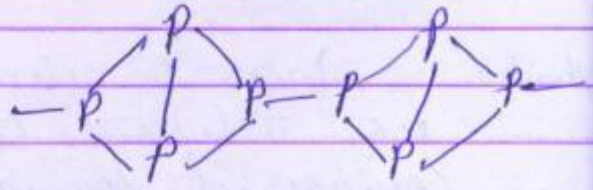
$$SF_4 + H_2O \longrightarrow SOF_2 + H_2F_2$$

Q.11 Draw structures of white phosphorus and red phosphorus. Which one is more reactive and why?

Ans.



White Phosphorus.



Red P.

P_4 tetrahedra linked together to form Polymer.

White phosphorus is more reactive due to angular strain.

Q12. Arrange the following in increasing acid strength: H_2O, H_2S, H_2Se, H_2Te.

Ans. $H_2O < H_2S < H_2Se < H_2Te$

Q.13 Arrange following in increasing bond dissociation enthalpy. HF, HCl, HBr, HI.

Ans. $HI < HBr < HCl < HF$

Q.14 Sodium salt of an acid (A) is formed on boiling white phosphorus with NaOH sol^n.

Ans. $P_4 + 3NaOH + 3H_2O \longrightarrow \underset{\text{(A) Sod. hypophosphite}}{3NaH_2PO_2} + PH_3$

Q.15 (A) on treatment with a sol^n of $HgCl_2$ first gives a white ppt of compound (B) and then a grey ppt of (E). Identify (A) to (E) and write balanced eq^n for the rx^n.

Ans $H_3PO_2 + 2H_2O \longrightarrow H_3PO_4 + 4H$

$HgCl_2 + 2H \longrightarrow \underset{\text{(B) white PPt.}}{Hg_2Cl_2} + 2HCl$

$Hg_2Cl_2 + 2H \longrightarrow \underset{\text{(E) grey PPt.}}{2Hg} + 2HCl$

Q.16 A pale yellow substance (A) when heated with conc. HNO_3 evolves a brown coloured gas (B). (A) also dissolves in sodium sol^n on heating

a clear sol^n (C) is formed which on acidification gives a turbid sol^n and a pungent smelling gas (D) which is formed by the substance (A) in air. The sol^n (C) decolourises iodide sol^n. Identify (A) to (D),

Ans $\underset{(A)}{S} + 6HNO_3 \rightarrow H_2SO_4 + 2H_2O + \underset{(B)}{6NO_2}$

$S + Na_2SO_3 \rightarrow \underset{(C)}{Na_2S_2O_3}$

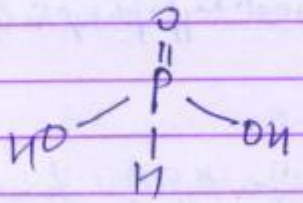
$Na_2S_2O_3 + H_2SO_4 \rightarrow Na_2SO_4 + SO_2 + S + H_2O$

D) Turbidity

$2\,Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$

colourless sol^n.

Q.17. What is the basicity of H_3PO_3 and why?

Ans 

Basicity: 2 due to two replaceable ~~H atom~~ Hydrogen.

Q.18. Why do noble gases have very low boiling pt.

Ans Due to weak van der waal's forces of attraction.

Q.19. Why does fluorine not play the role of a central atom in interhalogen compound?

Ans:- Fluorine is most electronegative and due to absence of d-orbital it can not accomodate more than one e^-.

Q.20 Why conc. H_2SO_4 cannot be used for drying H_2S gas?

Ans- Conc. H_2SO_4 is an oxidising agent it oxidises H_2S gas.

$H_2SO_4 \rightarrow H_2O + SO_2 + [O]$

$H_2S + [O] \rightarrow H_2O + S$.

d & f block elements

Q.1 Which ions of first transition series show highest paramagnetism?

Ans Mn^{2+} $(3d^5)$, Fe^{3+} $(3d^5)$

Q.2 Out of Mn^{3+} and Cr^{3+} which is more paramagnetic and why?

Ans. Mn^{3+} ; $3d^4$; Cr^{3+} ; $3d^3$
Mn^{3+} is more paramagnetic.

Q.3 Though copper, Ag and Au atoms have completely filled sets of d-orbitals, yet they are considered as transition metals, why?

Ans:- common oxidn states have only partially filled sets of d-orbitals.

Q.4 Why is the third ionisation energy of manganese (Z=25) unexpectedly high?

Ans Third e^- is to be removed from a stable configuration M^{2+} $(3d^5)$. It requires higher energy.

Q.5 What is the effect of increasing pH on $K_2Cr_2O_7$ soln?

Ans:- On increasing pH $K_2Cr_2O_7$ (orange soln) is converted to potassium chromate (yellow soln).

$$Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$$

Q.6. Why is hydrochloric acid not used to acidify a permanganate soln in volumetric estimation of Fe^{2+} and $C_2O_4^{2-}$?

Ans HCl is a reducing agent and chlorine gas is evolved

$$2MnO_4^- + 10Cl^- + 16H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5Cl_2$$

Q7 Why do the transition elements exhibit complex formation? Explain with suitable ex?

Ans:- i) Smaller size of metal ion ii) High charge on metal ion iii) Empty d-orbital present with almost equivalent energy.

Q.8 $La(OH)_3$ is more basic than $Lu(OH)_3$. Why?

Ans As the size of lanthanoid ions decreases from La^{3+} to Lu^{3+} the covalent character of M-OH bond increased and hence basic strength decreases.

Q.9 Iron on reⁿ with HCl forms $FeCl_2$ and not $FeCl_3$. Why?

Ans:- Iron reacts with HCl to liberate Hydrogen gas as $Fe + 2HCl \rightarrow FeCl_2 + H_2$.
Fe^{2+} easily oxidised to Fe^{3+} even in presence of air but liberated hydrogen prevents its oxidⁿ and itself combine with Oxygen.

Q.10. a) Of these ions Ag^+, Co^{2+} and Ti^{4+}, which one will be coloured in aq. solⁿ?

Ans:- Co^{2+} $(3d^7)$

b) If each one of the above ionic species in turn is placed in a mag-field, How will they respond and why?

Ans:- Ag^+ $(4d^{10})$ Ti^{4+} $(3d^0)$ — diamagnetic.
Co^{2+} $(3d^7)$ / Paramagnetic.

Q.11 Write eqn for the following:-

a) Manganate to permanganate

Ans $K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$.

b) Chromate to dichromate

Ans $2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$

Q.12 Indicate the steps in the prep^n of :-
$K_2Cr_2O_7$ from chromite ore.

Ans:- $FeO.Cr_2O_3$ (Chromite ore) $+ Na_2CO_3$

↓ Fused in presence of air

$Na_2CrO_4 + Fe_2O_3 + CO_2\uparrow$ (Mass is extracted with H_2O)

↓

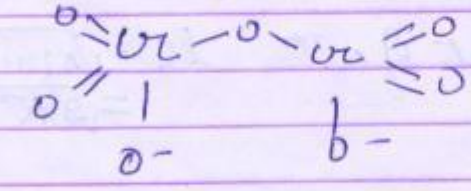
H_2SO_4 (dil.) $\rightarrow Na_2CrO_4$ sol^n

sol^n is concentrated when less soluble $Na_2SO_4 \cdot 10H_2O$ is crystallised out ↓

KCl sol^n $\rightarrow$ $Na_2Cr_2O_7$ sol^n $\rightarrow K_2Cr_2O_7$.

Q.13 Draw structure of ~~chromite~~ potassium dichromate ($Cr_2O_7^{2-}$)

Ans.



Q.14 Describe with an example each of the oxidising action of permanganate ion in alkaline and acidic media.

Ans Acidic medium

$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \longrightarrow 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$

Basic medium or Alkaline medium.

$2KMnO_4 + KI + H_2O \longrightarrow 2MnO_2 + 2KOH + KIO_3$

Q.15 complete the following eqn.

i) $2MnO_2 + KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$

ii) $KMnO_4 \xrightarrow{Heat} K_2MnO_4 + MnO_2 + O_2$

Q.16 Write complete eqn for.

i) Oxidn of Fe^{2+} by $Cr_2O_7^{2-}$ in acidic medium.

Ans. $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7$

ii) $Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$

Q.17 Of the ions Co^{2+}, Sc^{3+} and Cr^{3+} which one will give coloured aq soln and how will eqn of them respond to magnetic field and why?

Ans :- Co^{2+} $(3d^7)$ and Cr^{3+} $(3d^4)$ are coloured and paramagnetic while Sc^{3+} $(3d^0)$ colourless and diamagnetic.

Magnetic moment of Co^{2+} $\mu = \sqrt{n(n+2)}$

$= \sqrt{3 \times 5} = \sqrt{15}$

Q.18 Name an important alloy which contains some of lanthanoids metal?

Ans. Misch metal is an alloy of many metals including lanthanoids.

Q.19 Out of Cr^{3+} and Mn^{3+} which is stronger oxidising agent and why?

Ans. Mn^{3+} as it readily accept an e^- to achieve stable configuration.

Q.20

Q20 copper (I) has d^{10} configuration while copper (II) has d^9 configuration. Still Cu(II) is more stable than Cu(I) in aq. soln

Ans. In Cu(I) it has not any valent d-orbital so water cannot form coordinate bonds. Hydration energy is responsible for greater stability of Cu(II) in aq soln. Cu(I) undergoes disproportionation in aq. soln as

$$2Cu^{+} \longrightarrow Cu^{2+} + Cu.$$

Coordination compound

1. What is coordination no. of central metal atom in $[Fe(EDTA)]^-$

Ans 6.

2. Which of the following is more stable complex? Why? $[Co(NH_3)_6]Cl_3$ and $[Co(en)_3]Cl_3$

Ans $[Co(en)_3]Cl_3$ due to formation of chelate ring

3. Write IUPAC name of the following complex

i) $K_3[Co(NO_3)_6]$:- Potassium hexanitrocobaltate (III).

ii) $[Co(en)_3]Cl_3$:- Tris (ethylenediamine) cobalt (III) chlor

4. Name the ionisation isomer of $[Cr(H_2O)_5Br]SO_4$

Ans. $[Cr(H_2O)_5SO_4]Br$ – Pentaaquasulphatochromium(III) bromide

5. What type of isomerism is shown by the complex $Cr(H_2O)_6Cl_3$?

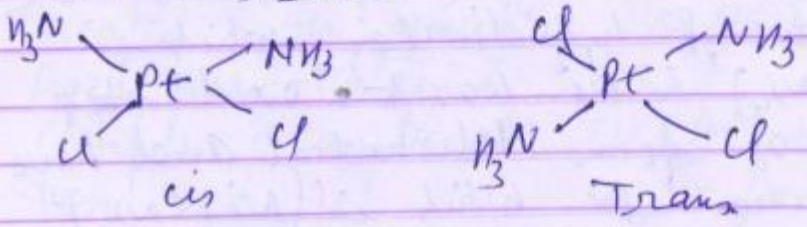
Ans Hydrate or solvate isomer.

(i) $[Cr(H_2O)_6]Cl_3$ (ii) $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$

iii) $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$.

6. Draw geometrical ~~isomerism~~ isomers of complex $[Pt(NH_3)_2Cl_2]$.

Ans.



Q.7 Predict the geometry and magnetic behaviour of $[NiCl_4]^{2-}$

Ans: Paramagnetic and tetrahedral complex with two unpaired e^-.

Q.8. Using V.B. approach, predict the shape and magnetic character of:

i) $[Fe(CN)_6]^{3-}$ ion — octahedral and weakly paramagnetic.

ii) $[Cr(CO)_6]$:- Octahedral diamagnetic.

Q.9 On the basis of CFT, write electronic configuration of d^4 in terms of t_{2g} and e_g in an octahedral field when:

i) $\Delta_o > P$ ii) $\Delta_o < P$

Ans i) $t_{2g}^4 e_g^0$ ii) $t_{2g}^3 e_g^1$

Q.10 Compare the magnetic behaviour of the complex entities

$[Fe(CN)_4]^{4-}$ and $[FeF_6]^{3-}$

Ans $[Fe(CN)_6]^{4-}$ Diamagnetic

$[FeF_6]^{3-}$ - Paramagnetic 5.92 BM.

Q.11 Why $Ni(CO)_4$ has tetrahedral geometry whereas $[Ni(CN)_4]^{2-}$ has square planar

Oxidation stat

Ans. ~~Valency~~ of Ni in $Ni(CO)_4$ is zero so ($4s^2 3d^8$) it show sp^3 hybridisation which in $[Ni(CN)_4]^{2-}$ Ni has +2 oxid^n stat

So $Ni(CO)_4$ forms tetrahedral and have hybridisation sp^3. Which in $[Ni(CN)_4]^{2-}$ has dsp^2 hybridisation and square planar structure. Ni ($3d^8 4s^0$).

12 Give name of two complexes which are used in medicines.

Ans EDTA used in lead poisoning and cis platin $[Pt(NH_3)_2Cl_2]$ used in treatment of cancer.

13 How many geometrical isomers are possible for the complex, $Ni(CO)_4$?

Ans Nil. No isomer (geometrical) is shown by tetrahedral complex.

14 The spin only magnetic moment of $[MnBr_4]^{2-}$ is 5.9 BM. Predict geometry of complex ion.

Ans. $\mu = \sqrt{n(n+2)}$

$5.9 = \sqrt{n(n+2)}$ BM. , $n = 5$

In $[Mn Br_4]^{2-}$ oxid^n state of Mn is +2

$Mn^{+2} = 3d^5\ 4s^0\ 4p^0$

Hybridisation = sp^3. and geometry tetrahedral.

15 When 0.1 mole $CoCl_3(NH_3)_5$ is treated with excess of $AgNO_3$, 0.2 mole of AgCl are obtained what is conductivity of sol^n?

Ans. 1:2 electrolyte.

Q.16. When 1 mole of $CrCl_3 \cdot 6H_2O$ is treated with excess of $AgNO_3$, 3 mole of AgCl are obtained. What is formula of complex? Write its IUPAC name.

Ans. $[Cr(H_2O)_6]Cl_3$

Hexaaquachromium(III) chloride

Q.17. A coordination compound $CrCl_3 \cdot 4H_2O$ precipitates silver chloride when treated with silver nitrate. Molar conductance of its soln is due to two ion. Write structural formula of the compound. Name it.

Ans. $CrCl_3 \cdot 4H_2O + AgNO_3 \longrightarrow AgCl$.

$[Cr(H_2O)_4Cl_2]Cl \rightleftharpoons [Cr(H_2O)_4Cl_2]^+ + Cl^-$

Two ions

$\downarrow AgNO_3$

$[Cr(H_2O)_4Cl_2]NO_3 + AgCl \downarrow$

Name:- Tetraaquadichloridochromium(III) chloride

Q.18. $CuSO_4 \cdot 5H_2O$ is blue in colour while $CuSO_4$ is colourless. Why?

Ans. $CuSO_4 \cdot 5H_2O$ is a coordination compound $[Cu(H_2O)_4]SO_4 \cdot H_2O$ and show colour due to d-d transition while $CuSO_4$ doesnot contain any water molecule thus colourless.

Q.19 Why are low spin tetrahedral complexes are not formed?

Ans For tetrahedral complexes, CFSE is lower than pairing energy.

Q.20 Give oxidn state, d-orbital occupation and coordination metal ion in $K_3[Co(C_2O_4)_3]$

Ans Oxidn No. of Co = +3

coordination no. = 6

configuration $3d^6$ $t_{2g}^6 e_g^0$