CHEMISTRY

1. (A) There is irregular trend in the first ionisation enthalpy of the 3d metals.

	Se	Ti	V	Cr	Mn	F	Co	Ni	Cu	Zn
In kJ/mol :	631	656	650	653	717	762	758	736	745	906

3. $AgNO_3 \longrightarrow Ag + NO_2 + \frac{1}{2}O_2$; $Cu(NO_3)_2 \longrightarrow CuO + 2NO_2 + \frac{1}{2}O_2$

$Pb(NO_3)_2 \longrightarrow PbO + 2NO_2 + \frac{1}{2}O_2$; $2Al(NO_3)_2 \longrightarrow Al_2O_3 + 6NO_2 + \frac{3}{2}O_2$

4. $2MnO_4^- + 3Mn^{2+} + 2H_2O \longrightarrow 5MnO_2 + 4H^+$

5. $V_2O_5 + NaOH \longrightarrow 2Na_3VO_4 + 3H_2O$

6._ $Pb^{2+} + S^{2-} \longrightarrow PbS \downarrow$ (black)

$PbS + HNO_3 \longrightarrow Pb(NO_3)_2 + H_2S \uparrow$

$SO_4^{2-} + Pb(NO_3)_2 \longrightarrow PbSO_4 \downarrow$ (white precipitate)

7._ Pb^{2+} and Ag^+ —

→ $PbCl_2$ dissolves in hot water $\xrightarrow{\text{Cooled}}$ $PbCl_2$ white ppt.

→ AgCl does not dissolve in hot water $\xrightarrow{NH_3\ \text{Sol.}}$ $[Ag(NH_3)_2]Cl$ (soluble) Clear solution

8. $Ni^{2+} + S^{2-} \longrightarrow NiS \downarrow$ (black)

$NiS + HNO_3 + 3HCl \longrightarrow Ni^{2+} + S \downarrow + NOCl \uparrow + 2Cl^- + 2H_2O$

$$Ni^{2+} + 2\begin{array}{l} CH_3-C=N-OH \\ \quad\ \ | \\ CH_3-C=N-OH \end{array} \xrightarrow{NH_4OH} [Ni(dmg)_2] \downarrow \text{(red)} + 2H^+$$

9. Carbon monoxide is better reducing agent than carbon below 983 K.

10. (a) → van – Arkel method for Zr – Hg
→ Based on volatile nature of halides of methods.

12. **(A)** $Al_2O_3(s) + 3H_2O(\ell) + 2NaOH(aq) \xrightarrow{\text{Leaching}} 2Na[Al(OH)_4](aq)$

$2Na[Al(OH)_4](aq) + CO_2(g) \longrightarrow Al_2O_3 . xH_2O(s) + 2NaHCO_3(aq)$

$Al_2O_3 . xH_2O(s) \xrightarrow[\text{Calcination}]{1470\text{ K}} Al_2O_3(s) + xH_2O(g)$

Electrolytic reduction of molten pure Al_2O_3 mixed with Na_3AlF_6 or CaF_2
Method is known as Hall-Heroult process

Cathode : Al^{3+} (melt) + $3e^- \longrightarrow Al(l)$

Anode : $C(s) + O^{2-}$ (melt) $\longrightarrow CO(g) + 2e^-$

$C(s) + 2O^{2-}$ (melt) $\longrightarrow CO_2(g) + 4e^-$

(B) **Leaching :**

$$Ag_2S + 4NaCN \rightleftharpoons 2Na[Ag(CN)_2] + Na_2S$$

$$Na_2S + 2O_2 \longrightarrow Na_2SO_4$$

Displacement by zinc in aqueous solution :

$$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag\downarrow$$

(C) **Roasting :**

$$2PbS + 3O_2 \xrightarrow{\Delta} 2PbO + 2SO_2$$

Self reduction :

$$2PbO + PbS \longrightarrow 3Pb + SO_2$$

(D) **Calcination :**

$$MgCl_2.\,6H_2O \xrightarrow[\text{Dry HCl(g)}]{\Delta\text{(calcination)}} MgCl_2 + 6H_2O$$

It is not made anhydrous by simple heating because it gets hydrolysed

$$MgCl_2.\,6H_2O \xrightarrow{\Delta} MgO + 5H_2O + 2HCl$$

Electrolytic reduction :

Electrolytic reduction of molten anhydrous carnallite.

$$MgCl_2 \rightleftharpoons Mg^{2+} + 2Cl^-$$

At cathode : $Mg^{2+} + 2e^- \longrightarrow Mg$(99% pure) ;

At anode : $2Cl^- \longrightarrow Cl_2 + 2e^-$

13. $HgCl_2$ due to covalent characters, sufficient chloride ions are not obtained.

16.* (D) Oxidation state of iron in Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$ is +2

17.* (A) $2Cu^{2+} + 5I^- \longrightarrow Cu_2I_2$ (white) + I_3^- ; $Pb^{2+} + 2I^- \longrightarrow PbI_2\downarrow$ (yellow)

(B) $Cu^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{2+}$ (deep blue solution)

$Pb^{2+} + 2NH_3 + 2H_2O \longrightarrow Pb(OH)_2\downarrow$ (white) + $2NH_4^+$ (Pb^{2+} does not form soluble complex)

(C) $Cu^{2+} + 2OH^- \longrightarrow Cu(OH)_2\downarrow$ (blue) ; $Pb^{2+} + 2OH^- \longrightarrow Pb(OH)_2\downarrow$ (white)

$Pb(OH)_2\downarrow + 2OH^- \longrightarrow [Pb(OH)_4]$ soluble complex.

(D) $Pb^{2+} + 2Cl^- \longrightarrow PbCl_2\downarrow$ (white) ; $Cu^{2+} + 2Cl^- \longrightarrow CuCl_2$ (green solution).

18.* $Na_3[AlF_6] \longrightarrow 3NaF + AlF_3$

NaF and AlF_3 both are ionic compounds and so ionise to give ions. This increases the electrical conductivity and lowers the melting point of Al_2O_3 .

At cathode : Al^{3+} (melt) + $3e^- \longrightarrow Al$.

At anode : $C(s) + O^{2-}$ (melt) $\longrightarrow CO\,(g) + 2e^-$; $C(s) + 2O^{2-}$ (melt) $\longrightarrow CO_2\,(g) + 4e^-$.

19.* $\underset{\text{(white)}}{ZnCO_3} \xrightarrow[\Delta]{} ZnO + CO_2\uparrow$. ZnO is yellow when hot.

$$Co(NO_3)_2.6H_2O \xrightarrow[\Delta]{} CoO\text{ (black)} + 2NO_2\uparrow + \frac{1}{2}O_2\uparrow + 6H_2O\uparrow$$

$$2FeSO_4.6H_2O \xrightarrow[\Delta]{} Fe_2O_3\text{ (brown)} + SO_2\uparrow + SO_3\uparrow + 6H_2O\uparrow$$

$$\underset{\text{(faint pink)}}{3MnSO_4} \xrightarrow[\Delta]{} \underset{\text{(black)}}{Mn_3O_4} + 2SO_2\uparrow + SO_3\uparrow$$

20.*– Cyanide process used for Au and Ag comlexes formed in this, are : $Na[Au(CN)_2]$, $Na[Ag(CN)_2]$, $Na_2[Zn(CN)_4]$.

23. Due to common ion effect the concentrations of OH^- ions is just sufficient to precipitate the cations of III group as their hydroxides. (As they have low K_{sp} values).

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

NO_2^- gives brown vapours of NO_2 with dil H_2SO_4

31. $2MnO_4^-\ (Y) + 3Mn^{2+}\ (Z) + 2H_2O \longrightarrow 5MnO_2 + 4H^+$

This reaction is Vohhard method for estimation of manganese carried out in presence of $ZnSO_4$ or suspended ZnO which catalyses the oxidation.

32. $3\overset{+6}{Mn}O_4^{2-} + H^+ \longrightarrow 2\overset{+7}{Mn}O_4^- + \overset{+4}{Mn}O_2 + 2H_2O$

33. $2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \longrightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$

Mn(VII) – $[Ar]^{18}\ 3d^0$. No unpaired electron so 'spin only' magnetic moment of compound is .

34. $Ti^{3+} - 3d^1$ (purple) ; $V^{4+}\ 3d^1$ (blue) ; Cr^{3+} — $3d^3$ (Green), Pb^{2+} – (colourless) ; $Fe^{2+} - 3d^6$ (green) ; $Zn^{2+} - 3d^{10}$ (colourless) ; $Ni^{2+} - 3d^8$ (green) ; $Sc^{3+} - 3d^0$ (colourless) ; Hg^{2+} (colourless).

35. All except $BaCl_2$

36._ $X \equiv \overset{VI}{Cr}O_2Cl_2$ "sp^3"

37. $K_2Cr_2O_7 \xrightarrow{H_2O_2} CrO_5 \xrightarrow[H_2O]{H^+} Cr^{3+} + O_2\uparrow$

$\xrightarrow{KOH} KCrO_2$ (green)

So the answer is 3.

38. $\overset{+2}{\cancel{Fe}}S_2$, $\overset{+3}{\cancel{Fe_2}}O_3$, Fe_3O_4 ($\overset{+2}{\cancel{Fe}}O + Fe_2O_3$), $[\overset{+1}{\cancel{Fe}}(H_2O)_5(NO)]^{2+}$, $Na_2[\overset{+2}{\cancel{Fe}}(CN)_5(NO)]$, $\overset{+3}{\cancel{Fe}}[\overset{+3}{\cancel{Fe}}(CN)_6]$,

$K_2\overset{+2}{\cancel{Fe}}[\overset{+2}{\cancel{Fe}}(CN)_6]$, $\overset{+2}{\cancel{Fe}}(C_5H_5)_2$, $\overset{+2}{\cancel{Fe}}WO_4$

39. $2I^- + Pb^{2+} \longrightarrow PbI_2\downarrow$ (yellow) $+ 2K^+$

$2NH_3 + 2H_2O + Pb^{2+} \longrightarrow Pb(OH)_2\downarrow$ (white) $+ 2NH_4^+$

$2Pb^{2+} + 2CO_3^{2-} + H_2O \longrightarrow Pb(OH)_2\downarrow$ (white) $+ PbCO_3\downarrow$ (white) $+ CO_2\uparrow$

$Pb^{2+} + CrO_4^{2-} \longrightarrow PbCrO_4\downarrow$ (yellow)

$Pb^{2+} + 2Cl^- \longrightarrow PbCl_2\downarrow$ (white)

$Pb^{2+} + SO_3^{2-} \longrightarrow PbSO_3\downarrow$ (white)

$Pb^{2+} + S^{2-} \longrightarrow PbS\downarrow$ (black)

$Pb^{2+} + KNO_3 \longrightarrow$ No precipitate is formed.

$Pb(ClO_4)_2$ is water soluble.

40. $Al_2O_3 + 2NaOH + 2H_2O \xrightarrow{\Delta} 2NaAlO_2 + 3H_2O$; $Ag_2S + 2CN^- \longrightarrow [Ag(CN)_2]^- + S^{2-}$

$Au + 2CN^- + 2H_2O + O_2 \longrightarrow [Au(CN)_2]^- + 4OH^-$; $CuFeS_2 \longrightarrow$ No leaching

$PbS \longrightarrow$ No leaching ; $MgCl_2 \longrightarrow$ No leaching ; $FeCO_3 \longrightarrow$ No leaching

$2Cu_2O\ (s) + 4H_2SO_4\ (aq) + O_2\ (g) \longrightarrow 4CuSO_4\ (aq) + 4H_2O\ (\ell)$; $HgS \longrightarrow$ No leaching

41. At 500 – 800 K (lower temperature range in the blast furnace)

$$3\,Fe_2O_3 + CO \longrightarrow 2\,Fe_3O_4 + CO_2$$

$$Fe_3O_4 + CO \longrightarrow 3Fe + 4\,CO_2$$

$$Fe_2O_3 + CO \longrightarrow 2FeO + CO_2$$

At 900 – 1500 K (higher temperature range in the blast furnace):

$$C + CO_2 \longrightarrow 2\,CO\,; \qquad FeO + CO \longrightarrow Fe + CO_2$$

42. (A) $FeSO_4 \longrightarrow Fe_2O_3 + SO_2 + SO_3$

(B) $NH_4NO_3 \longrightarrow N_2O + 2H_2O$

(C) $Ba(N_3)_2 \longrightarrow N_2 + Ba$

(D) $MgCl_2 . 6H_2O \longrightarrow MgO + 2HCl + 5H_2O$

43. (A) $S_2O_3^{2-} + H^+ \longrightarrow S + SO_2$

(B) $2Cu^{2+} + 4I^- \xrightarrow{\Delta} Cu_2I_2 \downarrow + I_2$

(C) $2\,CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$

(D) $2\,Mg(NH_4)VO_4 \longrightarrow Mg_2V_2O_7 + 2NH_3\uparrow + H_2O\uparrow$

44. (A) $Pb^{2+} + CrO_4^{2-} \longrightarrow PbCrO_4 \downarrow$ (yellow) ; $Pb^{2+} + 2I^- \longrightarrow PbI_2$ (yellow)

(B) $Zn^{2+} + 2OH^- \longrightarrow Zn(OH)_2 \downarrow$ (White) ; $Zn(OH)_2 \downarrow + 2OH^- \longrightarrow [Zn(OH)_4]^{2-}$ soluble

$Zn^{2+} + 2NH_3 + 2H_2O \longrightarrow Zn(OH)_2 \downarrow$ (White) $+ 2NH_4^+$

(C) $Ni^{2+} + 2OH^- \longrightarrow Ni(OH)_2 \downarrow$ (Green) ; $Ni^{2+} + 2NH_3 + 2H_2O \longrightarrow Ni(OH)_2 \downarrow$ (Green) $+ 2NH_4^+$

$Ni^{2+} + 2CN^- \longrightarrow Ni(CN)_2 \downarrow$ (Green)

(D) $Cu^{2+} + 2OH^- \longrightarrow Cu(OH)_2 \downarrow$ (blue)

$Cu^{2+} + 2NH_3 + 2H_2O \longrightarrow Cu(OH)_2 \downarrow$ (blue) $+ 2NH_4^+$