31. Upon reaction between KIO_3 and KI, I_2 is liberated

$$KIO_3 + 5KI \longrightarrow 3K_2O + 3I_2$$

This liberated I_2 reacts with $Na_2S_2O_3$

$$2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$$

One mole KIO_3 liberated three moles of I_2

Moles of $KIO_3 = \dfrac{0.10\,g}{\text{mol. wt.}(214)} = 0.000467$

Liberated moles of $I_2 = 3 \times 0.000467$

One mole of I_2 requires two moles of $Na_2S_2O_3$ for complete decolourisation of I_2

$\therefore$ Moles of $Na_2S_2O_3 = 2(3 \times 0.000467)$

Molarity of $Na_2S_2O_3 = \dfrac{\text{moles}}{\text{volume in litre}} = \dfrac{2 \times (3 \times 0.000467)}{45.0 \times 10^{-3}} = 0.0623\,M$

32.(A) **(i)** Oxidation state of element in its free state is zero

(ii) Sum of oxidation states of all atoms in compound is zero

O.N. of S in $S_8 = 0$; O.N. of S in $S_2F_2 = +1$; O.N. of S in $H_2S = -2$

33.(D) **(i)** In an ion sum of oxidation states of all atoms is equal to charge on ion and in a compound sum of oxidation states of all atoms is always zero.

Oxidation state of Mn in $MnO_4^- = +7$

Oxidation state of Cr in $Cr(CN)_6^{3-} = +3$

Oxidation state of Ni in $NiF_6^{2-} = +4$

Oxidation state of Cr in $CrO_2Cl_2 = +6$

34. $2KMnO_4 + 3H_2SO_4 + 5H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O$

$2KMnO_4 + 3MnSO_4 + 2H_2O \longrightarrow MnO_2 + 2H_2SO_4 + K_2SO_4$

$MnO_2 + Na_2C_2O_4 + 2H_2SO_4 \longrightarrow MnSO_4 + Na_2SO_4 + 2H_2O + 2CO_2$

Millimoles of $Na_2C_2O_4 = 10 \times 0.2 = 2$

mEq of $Na_2C_2O_4 = 4$

mEq of $MnO_2 = 4$

mEq of $KMnO_2 = 4$

mEq of $H_2O_2 = 4$

millimoles of $H_2O_2 = 2$

millimoles of H_2O_2 = Molarity $\times$ V mL

or $2 = \text{Molarity} \times 20$ or molarity $= 0.1$

35.(C) **(i)** In a disproportionation reaction same element undergoes oxidation as well as reduction during the reaction

(ii) In decomposition reaction a molecule breaks down to more than one atoms or molecules

$$3\overset{+1}{Cl}O^-(aq) \rightarrow \overset{+5}{Cl}O_3^- + 2\overset{-1}{Cl}^-(aq)$$

It is disproportionation reaction because Cl is both oxidised (+1 to +5) and reduced (+1 to −1) during reaction.

36.(B) In this reaction $Cr_2O_7^{2-}$ is changed into Cr^{3+} ion

So, equivalent weight of

$$K_2Cr_2O_7 = \frac{\text{molecular weight}}{\text{decrease of oxidation number} \times n} \quad \text{(where n = Number of atoms of Cr)}$$

$$= \frac{\text{molecular weight}}{3 \times 2} = \frac{\text{molecular weight}}{6}$$

37.(B) The highest O.S. of an elements is equal to the number of its valence electrons

(i) $[Fe(CN)_6]^{3-}$, O.N. of Fe $= +3$

$[Co(CN)_6]^{3-}$, O.N. of Co $= +3$

(ii) CrO_2Cl_2, O.N. of Cr $= +6$ (Highest O.S. of Cr)

$[MnO_4]^-$ O.N. of Mn $= +7$ (Highest O.S. of Mn)

(iii) TiO_3, O.N. of Ti $= +6$,

MnO_2 O.N. of Mn $= +4$

(iv) $[Co(CN)_6]^{3-}$, O.N. of Co $= +3$,

MnO_3, O.N. of Mn $= +6$

38.(D) The following reaction occurs :

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

From the above equation, we find that Mohr's salt $(FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O)$ and dichromate reacts in 6 : 1 molar ratio.

39. **[A-1, 4] [B-3] [C-1, 2] [D-1]**

$$2O_2^- \longrightarrow O_2 + O_2^{2-}$$

Oxidation state $-\frac{1}{2}$ 0 -1 Redox reaction & disproportionation

$$2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$$ Non-redox reaction

Oxidation state +6 +6

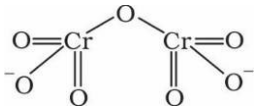
$$2MnO_4^- + 5NO_2^- + 6H^+ \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$$ Redox reaction

Oxidation state +7 +3 +2 +5

$$NO_3^- + 3Fe^{2+} + 4H^+ \longrightarrow NO + 3Fe^{3+} + 2H_2O$$ Redox reaction

Oxidation state +5 +2 +2 +3

NO_3^- has trigonal planar structure and $Cr_2O_7^{2-}$ has dimeric bridged tetrahedral structure as shown below.

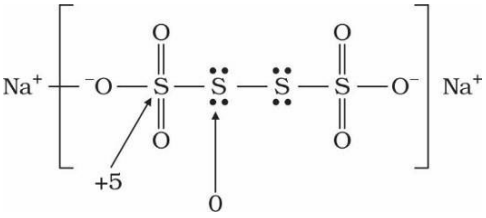


40.(2) O, Cl, F, N, P, Sn, Tl, Na, Ti

Na shows only +1

F shows only -1

41.(5)



Difference in oxidation number $= 5 - 0 = 5$

42.(A) $\left[Cr(H_2O)_6\right]Cl_3$

$x + 0 - 3 = 0$

$x = +3$

$\left[Cr(C_6H_6)_2\right]$

$x + 0 = 0$

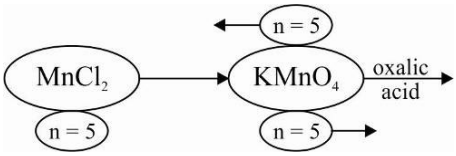
$x = 0$

$K_2\left[Cr(CN)_2(O)_2(O_2)(NH_3)\right]$

$2 + x - 2 - 4 - 2 + 0 = 0$

$x = +6$

43.(126.00)



Eq. of $MnCl_2$ = Eq.of oxalic acid

$$\frac{w \times 5}{126} = \frac{225}{90} \times 2 \quad \Rightarrow \quad w = \frac{225 \times 2}{90} \times \frac{126}{5} = 126 \text{ mg}$$