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Redox Reactions

Multiple Choice Questions (MCQs)

Q. 1 Which of the following is not an example of redox reaction?

(a) $CuO + H_2 \longrightarrow Cu + H_2O$

(b) $Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$

(c) $2K + F_2 \longrightarrow 2KF$

(d) $BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HCl$

Thinking Process

Redox reactions represent those reactions which involve change in oxidation number of the interacting species. (i.e., oxidation and reduction)

Ans. *(d)* *Following are the examples of redox reaction*

(a) $CuO + H_2 \longrightarrow Cu + H_2O$

(b) $Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$

(c) $2K + F_2 \longrightarrow 2KF$

Option (d) is not an example of redox reaction.

Q. 2 The more positive the value of $E^\ominus$, the greater is the tendency of the species to get reduced. Using the standard electrode potential of redox couples given below find out which of the following is the strongest oxidising agent.

$$E^\ominus \text{ values: } Fe^{3+}/Fe^{2+} = +0.77$$
$$I_2(s)/I^- = +0.54;$$
$$Cu^{2+}/Cu = +0.34;\ Ag^+/Ag = 0.80\ V$$

(a) Fe^{3+} (b) $I_2(s)$ (c) Cu^{2+} (d) Ag^+

Ans. *(d)* Given that, $E°$ values of

$$Fe^{3+}/Fe^{2+} = +0.77\ V$$
$$I_2(s)/I^- = +0.54\ V$$
$$Cu^{2+}/Cu = +0.34\ V$$
$$Ag^+/Ag = +0.80\ V$$

Since, $E°$ of the redox couple Ag^+/Ag is the most positive, *i.e.,* 0.80 V, therefore, Ag^+ is the strongest oxidising a

Q. 3 $E^{\ominus}$ values of some redox couples are given below. On the basis of these values choose the correct option.

$$E^{\ominus} \text{ values: } Br_2/Br^- = +1.90$$
$$Ag^+/Ag(s) = +0.80$$
$$Cu^{2+}/Cu(s) = +0.34;\ I_2(s)/I^- = +0.54$$

(a) Cu will reduce Br^-
(b) Cu will reduce Ag
(c) Cu will reduce I^-
(d) Cu will reduce Br_2

Ans. *(d)* Given that $E°$ values of

$$Br_2/Br^- = +1.90\text{ V}$$
$$Ag/Ag^+ = -0.80\text{V}$$
$$Cu^{2+}/Cu(s) = +0.34\text{V}$$
$$I^-/I_2(s) = -0.54\text{V}$$
$$Br^-/Br_2 = -1.90\text{V}$$

The E° values show that copper will reduce Br_2, if the $E°$ of the following redox reaction is positive.

$$2Cu + Br_2 \rightarrow CuBr_2$$

Now,
$$Cu \rightarrow Cu^{2+} + 2e^-;\ E° = -0.34\text{ V}$$
$$Br_2 + 2e^- \rightarrow 2Br^-;\ E = +1.09\text{V}$$
$$\overline{Cu + Br_2 \rightarrow CuBr_2;\ E° = +0.75\text{ V}}$$

Since, $E°$ of this reaction is positive, therefore, Cu can reduce Br_2.
While other reaction will give negative value.

Q. 4 Using the standard electrode potential, find out the pair between which redox reaction is not feasible.

$$E^{\ominus} \text{ values: } Fe^{3+}/Fe^{2+} = +0.77;\ I_2/I^- = +0.54;$$
$$Cu^{2+}/Cu = +0.34;\ Ag^+/Ag = +0.80\text{ V}$$

(a) Fe^{3+} and I^-
(b) Ag^+ and Cu
(c) Fe^{3+} and Cu
(d) Ag and Fe^{3+}

Thinking Process

Calculate the $E°_{cell}$ of the four redox reactions. If $E°_{cell}$ of a reaction is negative, that reaction will not occur.

Ans. *(d)*

(a) $2Fe^{3+} + 2e^- \rightarrow 2Fe^{2+};\ E° = +0.77\text{V}$

$2I^- \rightarrow I_2 + 2e^-;\ E° = -0.54\text{ V}$ (sign of $E°$ is reversed)

$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2;\ E°_{cell} = +0.23\text{ V}$

This reaction is feasible since $E°_{cell}$ is positive.

(b) $Cu \rightarrow Cu^{2+} + 2e^-;\ E° = -0.34\text{V}$ (sign of $E°$ has been reversed)

$$2Ag^+ + 2e^- \rightarrow 2Ag;\ E° = +0.80\text{ V}$$
$$Cu + 2Ag^+ \rightarrow 2Cu^{2+} + 2Ag;\ E° = +0.46\text{V}$$

This reaction is feasible since $E°_{cell}$ is positive.

(c)
$$2Fe^{3+} + 2e^- \rightarrow 2Fe^{2+};\ E° = +0.77\ V$$
$$Cu \rightarrow Cu^{2+} + 2e^-;\ E° = -0.34\ V \qquad \text{(sign of } E° \text{ is reversed)}$$
$$\overline{2Fe^{3+} + Cu \rightarrow 2Fe^{2+} + Cu^{2+};\ E° = +0.43\ V}$$

This reaction is feasible since $E°_{cell}$ is positive.

(d)
$$Ag \rightarrow Ag^+ + e^-;\ E° = -0.80\ V \qquad \text{(sign of } E° \text{ is reversed)}$$
$$Fe^{3+} + e^- \rightarrow Fe^{2+};\ E° = +0.77\ V$$
$$Ag + Fe^{3+} \rightarrow Ag^+ + Fe^{2+};\ E° = -0.03\ V$$

This reaction is not feasible since $E°_{cell}$ is negative.

Q. 5 Thiosulphate reacts differently with iodine and bromine in the reactions given below

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$
$$S_2O_3^{2-} + 2Br_2 + 5H_2O \rightarrow 2SO_4^{2-} + 2Br^- + 10H^+$$

Which of the following statements justifies the above dual behaviour of thiosulphate?

(a) Bromine is a stronger oxidant than iodine

(b) Bromine is a weaker oxidant than iodine

(c) Thiosulphate undergoes oxidation by bromine and reduction by iodine in these reactions

(d) Bromine undergoes oxidation and iodine undergoes reduction in these reactions

Ans. ***(a)*** $2\overset{+2}{S_2}\overset{-2}{O_3^{2-}}(aq) + I_2^0(s) \rightarrow \overset{2.5}{S_4}O_6^{2-}(aq) + 2I^-(aq)$

$$\overset{+2}{S_2}\overset{-2}{O_3^{2-}}(aq) + 2\overset{0}{Br_2}(l) + 5H_2O(l) \rightarrow 2\overset{+6}{S}\overset{2-}{O_4^{2-}}(aq) + 4Br^-(aq) + 10H^+(aq)$$

Bromine being stronger oxidising agent than I_2, oxidises S of $S_2O_3^{2-}$ to SO_4^{2-} whereas I_2 oxidises it only into $S_4O_6^{2-}$ ion.

Q. 6 The oxidation number of an element in a compound is evaluated on the basis of certain rules. Which of the following is incorrect in this respect?

(a) The oxidation number of hydrogen is always +1

(b) The algebraic sum of all the oxidation numbers in a compound is zero

(c) An element in the free or the uncombined state bears oxidation number zero

(d) In all its compounds, the oxidation number of fluorine is –1

Ans. ***(a)*** Oxidation number of hydrogen is always +1 is a wrong rule since, it is +1 in hydrogen halides, –1 in hydrides and zero in H_2 molecule.

All the other three statements (b), (c) and (d) are correct.

Q. 7 In which of the following compounds, an element exhibits two different oxidation states?

(a) NH_2OH (b) NH_4NO_3 (c) N_2H_4 (d) N_3H

Ans. ***(b)*** NH_4NO_3 is actually NH_4^+ and NO_3^-. It is an ionic compound.

The oxidation number of nitrogen in the two species is different as shown below

Let, oxidation number of N in $\overset{+}{N}H_4$ is x.

$\Rightarrow \qquad x + (4 \times 1) = +1$

or $\qquad x + 4 = +1$ or $x = -3$

Let, oxidation number of N in NO_3^- is x

$\Rightarrow \qquad x + (3 \times -2) = -1$ or $x - 6 = -1$ or $x = +5$

Q. 8 Which of the following arrangements represent increasing oxidation number of the central atom ?

(a) $CrO_2^-, ClO_3^-, CrO_4^{2-}, MnO_4^-$

(b) $ClO_3^-, CrO_4^{2-}, MnO_4^-, CrO_2^-$

(c) $CrO_2^-, ClO_3^-, MnO_4^-, CrO_4^{2-}$

(d) $CrO_4^{2-}, MnO_4^-, CrO_2^-, ClO_3^-$

Ans. ***(a)*** Writing the oxidation number (O.N.) of Cr, Cl and Mn on each species in the four set of ions, then,

(a) $\overset{+3}{Cr}O_2^-, \overset{+5}{Cl}O_3^-, \overset{+6}{Cr}O_4^{2-}, \overset{+7}{Mn}O_4^-$

(b) $\overset{+5}{Cl}O_3^-, \overset{+6}{Cr}O_4^{2-}, \overset{+7}{Mn}O_4^-, \overset{+3}{Cr}O_2^-$

(c) $\overset{+3}{Cr}O_2^-, \overset{+5}{Cl}O_3^-, \overset{+7}{Mn}O_4^-, \overset{+6}{Cr}O_4^{2-}$

(d) $\overset{+6}{Cr}O_4^{2-}, \overset{+7}{Mn}O_4^-, \overset{+3}{Cr}O_2^-, \overset{+5}{Cl}O_3^{3-}$

Only in the arrangement (a), the O.N. of central atom increases from left to right, therefore, option (a) is correct.

Q. 9 The largest oxidation number exhibited by an element depends on its outer electronic configuration. With which of the following outer electronic configurations the element will exhibit largest oxidation number?

(a) $3d^1 4s^2$ (b) $3d^3 4s^2$ (c) $3d^5 4s^1$ (d) $3d^5 4s^2$

Ans. ***(d)*** Highest oxidation number of any transition element = $(n-1)d$ electrons + ns electrons. Therefore, large the number of electrons in the $3d$-orbitals, higher is the maximum oxidation number.

(a) $3d^1 4s^2 = 3$

(b) $3d^3 4s^2 = 3 + 2 = 5$

(c) $3d^5 4s^1 = 5 + 1 = 6$ and

(d) $3d^5 4s^2 = 5 + 2 = 7$

Thus, option (d) is correct.

Q. 10 Identify disproportionation reaction

(a) $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

(b) $CH_4 + 4Cl_2 \longrightarrow CCl_4 + 4HCl$

(c) $2F_2 + 2OH^- \longrightarrow 2F^- + OF_2 + H_2O$

(d) $2NO_2 + 2OH^- \longrightarrow NO_2^- + NO_3^- + H_2O$

Ans. ***(d)*** Reactions in which the same substance is oxidised as well as reduced are called disproportionation reactions. Writing the O.N. of each element above its symbol in the given reactions

(a) $\overset{-4}{C}\overset{+1}{H_4} + 2\overset{\circ}{O_2} \longrightarrow \overset{+4}{C}\overset{-2}{O_2} + 2\overset{+1}{H_2}\overset{-2}{O}$

(b) $\overset{-4}{C}\overset{+1}{H_4} + 4\overset{0}{Cl_2} \longrightarrow \overset{+4}{C}\overset{-1}{Cl_4} + 4\overset{+1}{H}\overset{-1}{Cl}$

(c) $2\overset{0}{F_2} + 2\overset{-2}{O}\overset{+1}{H} \longrightarrow 2\overset{-1}{F^-} + \overset{+2}{O}\overset{-1}{F_2} + \overset{+1}{H_2}\overset{-2}{O}$

(d) $2\overset{+4}{N}\overset{-2}{O_2} + 2\overset{-2}{O}\overset{+1}{H^-} \longrightarrow \overset{+3}{N}\overset{-2}{O_2^-} + \overset{+5}{N}\overset{-2}{O_3^-} + \overset{+1}{H_2}\overset{-2}{O}$

Thus, in reaction (d), N is both oxidised as well as reduced since the O.N. of N increases from +4 in NO_2 to +5 in NO_3^- and decreases from +4 in NO_2 to +3 in NO_2^-.

Q. 11 Which of the following elements does not show disproportionation tendency ?

(a) Cl (b) Br (c) F (d) I

Ans. ***(c)*** Being the most electronegative element, F can only be reduced and hence it always shows an oxidation number of –1. Further, due to the absence of *d*-orbitals it cannot be oxidised and hence it does not show positive oxidation numbers.

In other words, F cannot be oxidised as well as reduced simultaneously and hence does not show disproportionation reactions.

Multiple Choice Questions (More Than One Options)

Q. 12 Which of the following statement(s) is/are **not** true about the following decomposition reaction?

$$2KClO_3 \longrightarrow 2KCl + 3O_2$$

(a) Potassium is undergoing oxidation

(b) Chlorine is undergoing oxidation

(c) Oxygen is reduced

(d) None of the species are undergoing oxidation or reduction

Ans. ***(a, b, c, d)***

Write the oxidation number of each element above its symbol, then

$$2\overset{+1}{K}\overset{+5}{Cl}\overset{-2}{O_3} \longrightarrow 2\overset{+1}{K}\overset{-1}{Cl} + 3\overset{0}{O_2}$$

(a) The O.N. of K does not change, K undergoes neither reduction nor oxidation. Thus, option (a) is not correct.

(b) The O.N. of chlorine decreases from +5 in $KClO_3$ to –1 in KCl, hence Cl undergoes reduction.

(c) Since, O.N. of oxygen increases from –2 in $KClO_3$ to 0 in O_2, oxygen is oxidised.

(d) This statement is not correct because Cl is undergoing reduction and O is undergoing oxidation.

Q. 13 Identify the correct statement (s) in relation to the following reaction.

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$

(a) Zinc is acting as an oxidant

(b) Chlorine is acting as a reductant

(c) Hydrogen ion is acting as an oxidant

(d) Zinc is acting as a reductant

Ans. ***(c, d)***

Writing the oxidation number of each element above its symbol, so that

$$\overset{0}{Zn} + 2\overset{+1}{H}\overset{-1}{Cl} \longrightarrow \overset{+2}{Zn}\overset{-1}{Cl_2} + \overset{0}{H_2}$$

(a) The oxidation number of Zn increases from 0 in Zn to +2 in $ZnCl_2$, therefore, Zn acts as a reductant. Thus, option (a) is incorrect.

(b) The oxidation number of chlorine does not change, therefore, it neither acts as a reductant nor an oxidant. Therefore, option (b) is incorrect.

(c) The oxidation number of hydrogen decreases from +1 in H^+ to 0 in H_2, therefore, H^+ acts as an oxidant. Thus, option (c) is correct.

(d) As explained in option (a), Zn acts as reductant, therefore, it cannot act as an oxidant. Thus, option (d) is correct.

Q. 14 The exhibition of various oxidation states by an element is also related to the outer orbital electronic configuration of its atom. Atom (s) having which of the following outermost electronic configurations will exhibit more than one oxidation state in its compounds.

(a) $3s^1$ (b) $3d^1 4s^2$ (c) $3d^2 4s^2$ (d) $3s^2 3p^3$

Ans. *(b, c, d)*

Elements which have only *s*-electrons in the valence shell do not show more than one oxidation state. Thus, element with $3s^1$ as outer electronic configuration shows only one oxidation state of +1.

Transition element such as elements (b), (c) having incompletely filled *d*-orbitals in the penultimate shell show variable oxidation states. Thus, element with outer electronic configuration as $3d^1 4s^2$ shows variable oxidation states of +2 and +3 and the element with outer electronic configuration as $3d^2 4s^2$ shows variable oxidation states of +2, +3 and +4.

***p* – Block elements** also show variable oxidation states due to a number of reason such as involvement of *d*-orbitals and inert pair effect *e.g.,* element (d) with $3s^2 3p^3$ as (*i.e.,* P) as the outer electronic configuration shows variable oxidation states of +3 and +5 due to involvement of *d*-orbitals.

Q. 15 Identify the correct statements with reference to the given reaction

$$P_4 + 3OH^- + 3H_2O \longrightarrow PH_3 + 3H_2PO_2^-$$

(a) Phosphorus is undergoing reduction only

(b) Phosphorus is undergoing oxidation only

(c) Phosphorus is undergoing oxidation as well as reduction

(d) Hydrogen is undergoing neither oxidation nor reduction

Ans. *(c, d)*

Write the O.N. of each element above its symbol, then

$$\overset{0}{P_4} + 3\overset{-2}{O}\overset{+1}{H^-} + 3\overset{+1}{H_2}\overset{-2}{O} \rightarrow \overset{-3}{P}\overset{+1}{H_3} + 3\overset{+1}{H_2}\overset{+1}{P}O_2^-$$

In this reaction, O.N. of P increases from 0 in P_4 to +1 in $H_2PO_2^-$ and decreases to – 3 in PH_3, therefore, P undergoes both oxidation as well as reduction. Thus, options (a) and (b) are wrong and option (c) is correct.

Further, O.N. of H remains +1 in all the compounds, *i.e.,* H neither undergoes oxidation nor reduction. Thus, option (d) is correct.

Q. 16 Which of the following electrodes will act as anodes, which connected to Standard Hydrogen Electrode ?

(a) Al/Al^{3+} $E^\ominus = -1.66$

(b) Fe/Fe^{2+} $E^\ominus = -0.44$

(c) Cu/Cu^{2+} $E^\ominus = +0.34$

(d) $F_2(g)/2F^-(aq)$ $E^\ominus = 02.87$

Ans. ***(a, b)***

All electrodes which have negative electrode potentials are stronger reducing agents than H_2 gas and hence acts as anodes when connected to standard hydrogen electrode. Thus, Al^{3+} / Al ($E^{\ominus}$ = – 1.66 V) and Fe^{2+} / Fe ($EE^{\ominus}$ = – 0.44 V) act as anode.

Short Answer Type Questions

Q. 17 **The reaction $Cl_2(g) + 2OH^-(aq) \rightarrow ClO^-(aq) + Cl^-(aq) + H_2O(l)$ represents the process of bleaching. Identify and name the species that bleaches the substances due to its oxidising action.**

Thinking Process

Write the oxidation number of each element above its symbol. and then identify the bleaching reagent by observing the change in oxidation number.

Ans. $\overset{0}{Cl_2}(g) + 2\overset{-2}{O}\overset{+1}{H^-}(aq) \rightarrow \overset{+1}{Cl}\overset{-2}{O^-}(aq) + \overset{-1}{Cl^-}(aq) + \overset{+1}{H_2}\overset{-2}{O}(l)$

In this reaction, O.N. of Cl increases from 0 (in Cl_2) to 1 (in ClO^-) as well as decreases from 0 (in Cl_2) to –1 (in Cl^-). So, it acts both reducing as well as oxidising agent. This is an example of disproportionation reaction. In this reaction, ClO^- species bleaches the substances due to its oxidising action. [In hypochlorite ion (ClO^-) Cl can decrease its oxidation number from +1 to 0 or –1.]

Note *Disproportionation reactions are a special type of redox reactions. In which an element in one oxidation state is simultaneously oxidised and reduced.*

Q. 18 **MnO_4^{2-} undergoes disproportionation reaction in acidic medium but MnO_4^- does not. Give reason.**

Ans. In MnO_4^{2-}, the oxidation number of Mn is +6. It can increase its oxidation number (to + 7) or decrease its oxidation number (to + 4, + 3, + 2, 0).

Hence, it undergoes disproportionation reaction in acidic medium.

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

O.N. increases by 1 per atom (oxidation)

O.N. decreases by 2 per atom (reduction)

In MnO_4^-, Mn is in its highest oxidation state, *i.e.,* +7. It can only decrease its oxidation number. Hence, it cannot undergo disproportionation reaction.

Q. 19 **PbO and PbO_2 react with HCl according to following chemical equations**

$$2PbO + 4HCl \longrightarrow 2PbCl_2 + 2H_2O$$
$$PbO_2 + 4HCl \longrightarrow PbCl_2 + Cl_2 + 2H_2O$$

Why do these compounds differ in their reactivity ?

Ans. *Writing the oxidation number of each element above its symbol in the following reactions*

(a) $\underset{\text{Basic oxide}}{2\overset{+2}{P}\overset{-2}{bO}} + \underset{\text{Acid}}{4\overset{+1}{H}\overset{-1}{Cl}} \longrightarrow 2\overset{+2}{Pb}\overset{-1}{Cl_2} + 2\overset{+1}{H_2}\overset{-2}{O}$

In this reaction, oxidation number of each element remains same hence, it is not a redox reaction. In fact, it is an example of **acid-base reaction.**

(b) $\overset{+4\ -2}{PbO_2} + 4\overset{+1-1}{HCl} \longrightarrow \overset{+2\ -1}{PbCl_2} + \overset{0}{Cl_2} + 2\overset{+1\ -2}{H_2O}$

In PbO_2, Pb is in +4 oxidation state. Due to inert pair effect Pb in +2 oxidation state is more stable. So, Pb in +4 oxidation state (PbO_2) acts as an oxidising agent. It oxidises Cl^- to Cl_2 and itself gets reduced to Pb^{2+}.

$$\underset{\text{O.A.}}{\overset{+4\ -2}{PbO_2}} + \underset{\text{R.A.}}{4\overset{+1-1}{HCl}} \longrightarrow \overset{+2-1}{PbCl_2} + \overset{0}{Cl_2} + 2\overset{+1\ -2}{H_2O}$$

O.N. decreases by 2 per atom

O.N. increases by 1 per atom

Q. 20 Nitric acid is an oxidising agent and reacts with PbO but it does not react with PbO_2. Explain why ?

Ans. PbO is a base. It reacts with nitric acid and forms soluble lead nitrate.

$$PbO + 2HNO_3 \longrightarrow \underset{\text{Soluble}}{Pb(NO_3)_2} + H_2O \qquad \text{(acid base reaction)}$$

Nitric acid does not react with PbO_2. Both of them are strong oxidising agents. In HNO_3, nitrogen is in its maximum oxidation state (+5) and in PbO_2, lead is in its maximum oxidation state (+ 4). Therefore, no reaction takes place.

Q. 21 Write balanced chemical equation for the following reactions.

(a) Permanganate ion (MnO_4^-) reacts with sulphur dioxide gas in acidic medium to produce Mn^{2+} and hydrogen sulphate ion.
(Balance by ion electron method)

(b) Reaction of liquid hydrazine (N_2H_4) with chlorate ion (ClO_3^-) in basic medium produces nitric oxide gas and chloride ion in gaseous state.
(Balance by oxidation number method)

(c) Dichlorine heptaoxide (Cl_2O_7) in gaseous state combines with an aqueous solution of hydrogen peroxide in acidic medium to give chlorite ion (ClO_2^-) and oxygen gas.
(Balance by ion electron method)

Ans. (a) **Ion electron method** Write the skeleton equation for the given reaction.

$MnO_4^- (aq) + SO_2(g) \longrightarrow Mn^{2+}(aq) + HSO_4^- (aq)$

Find out the elements which undergo change in O.N.

O.N. of Mn decreases by 5

$$2\overset{+7}{Mn}O_4^- (aq) + \overset{+4}{S}O_2 (g) \longrightarrow \overset{2+}{Mn} (aq) + H\overset{+6}{S}O_4^- (aq)$$

O.N. of S increases by 2

Divide the given skeleton into two half equations.

Reduction half equation : $MnO_4^-(aq) \longrightarrow Mn^{2+}(aq)$

Oxidation half equation : $SO_2(g) \longrightarrow HSO_4^-(aq)$

To balance reduction half equation

In acidic medium, balance H and O-atoms

$$MnO_4^- (aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + H_2O (l)$$

To balance the complete reaction

$$\begin{array}{l} 2MnO_4 \ (aq) + 16H^+(aq) + 10e^- \longrightarrow Mn^{2+}(aq) \ + \ 8H_2O \ (l) \\ \underline{5SO_2 \ (g) + 10 \ H_2O(l) \longrightarrow 5HSO_4^- (aq) \ + \ 15H^+(aq) + 10e^-} \end{array}$$

$$2MnO_4^-(aq) + 5SO_2(g) + 2H_2O(l) + H^+(aq) \rightarrow 2Mn^{2+}(aq) \ + 5HSO_4^-(aq)$$

(b) **Oxidation number method** Write the skeleton equation for the given reaction.

$$N_2H_4 \, (l) + ClO_3^- (aq) \longrightarrow NO(g) + Cl^- \ (g)$$

O.N. increases by 4 per N-atom

$$\overset{-2}{N_2}H_4(l) + \overset{+5}{Cl}O_3^- (aq) \longrightarrow \overset{+2}{N}O \ (g) + \overset{-1}{Cl}\ ^-(aq)$$

O.N. decreases by 6 per Cl-atom

Multiply NO by 2 because in N_2H_4 there are 2N atoms

$$N_2H_4(l) + ClO_3^-(aq) \longrightarrow 2NO(g) + Cl^-(aq)$$

Total increase in O.N. of N $= 2 \times 4 = 8$ ($8e^-$ lost)

Total decrease in O.N. of Cl $= 1 \times 6 = 6$ ($6e^-$ gain)

Therefore, to balance increase or decrease in O.N. multiply N_2H_4 by 3, 2NO by 3 and ClO_3^-, Cl^- by 4

$$3N_2H_4(l) + 4ClO_3^-(aq) \longrightarrow 6NO(g) + 4Cl^-(aq)$$

Balance O and H-atoms by adding $6H_2O$ to RHS

$$3N_2H_4(l) \ + \ 4ClO_3^-(aq) \longrightarrow 6NO(g) \ + \ 4Cl^-(aq) \ + \ 6H_2O(l)$$

(c) **Ion electron method** Write the skeleton equation for the given reaction.

$$Cl_2O_7(g) \ + H_2O_2(aq) \longrightarrow ClO_2^-(aq) + O_2(g)$$

Find out the elements which undergo a change in O.N.

O. N. of Cl decreases by 4 per Cl-atom

$$\overset{+7 \ -7}{Cl_2O_7}(g) \ + \ \overset{+1 \ -1}{H_2O_2} \ (aq) \longrightarrow \overset{+3 \ -2}{ClO_2^-}(aq) \ + \ O_2 \ (g)$$

O.N. of O increases by 1per O-atom

Divide the given skeleton equation into two half equations.

Reduction half equation : $Cl_2O_7 \longrightarrow ClO_2^-$

Oxidation half equation : $H_2O_2 \longrightarrow O_2$

To balance the reduction half equation

$$Cl_2O_7(g) + 6H^+(aq) + 8e^- \longrightarrow 2ClO_2^-(aq) + 3H_2O(l)$$

To balance the oxidation half equation

$$H_2O_2(aq) \longrightarrow O_2(g) + 2H^+ + 2e^-$$

To balance the complete reaction

$$\begin{array}{l} Cl_2O_7 \ (g) + \ 6H^+ \ (aq) + \ 8e^- \longrightarrow \ 2ClO_2^-(aq) + \ 3H_2O \ (l) \\ \underline{4H_2O_2(aq) \longrightarrow \ 4O_2(g) + \ 8H^+ \ (aq) + \ 8e^-} \end{array}$$

$$Cl_2O_7 \ (g) + \ 4H_2O_2 \ (aq) \ \longrightarrow 2ClO_2^- \ (aq) + \ 3H_2O \ (l) + \ 4O_2(g) + 2H^+ \ + (aq)$$

This represents the balanced redox reaction.

Q. 22 Calculate the oxidation number of phosphorus in the following species.

(a) HPO_3^{2-} (b) PO_4^{3-}

Ans. (a) Suppose that the O.N. of P in HPO_3^{2-} be x.

Then, $1 + x + 3(-2) = -2$

or, $x + 1 - 6 = -2$

or, $x = +3$

(b) Suppose that the O.N. of P in PO_4^{3-} be x.

Then, $x + 4(-2) = -3$

or, $x - 8 = -3$

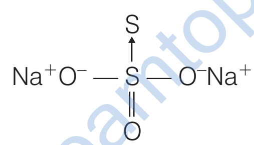
or, $x = +5$

Q. 23 Calculate the oxidation number of each sulphur atom in the following compounds.

(a) $Na_2S_2O_3$ (b) $Na_2S_4O_6$ (c) Na_2SO_3 (d) Na_2SO_4

Ans. *The oxidation number of each sulphur atom in the following compounds are given below*

(a) **$Na_2S_2O_3$** Let us consider the structure of $Na_2S_2O_3$.



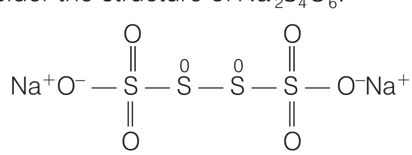
There is a coordinate bond between two sulphur atoms. The oxidation number of acceptor S-atom is –2. Let, the oxidation number of other S-atom be x.

$$\underset{\text{For Na}}{2(+1)} + \underset{\text{For O-atoms}}{3 \times (-2)} + x + \underset{\text{For coordinate S-atom}}{1(-2)} = 0$$

$$x = +6$$

Therefore, the two sulphur atoms in $Na_2S_2O_3$ have –2 and +6 oxidation number.

(b) **$Na_2S_4O_6$** Let us consider the structure of $Na_2S_4O_6$.



In this structure, two central sulphur atoms have zero oxidation number because electron pair forming the S—S bond remain in the centre. Let, the oxidation number of (remaining S-atoms) S-atom be x.

$$\underset{\text{For Na}}{2(+1)} + \underset{\text{For O}}{6(-2)} + 2x + 2(0) = 0$$

$$2 - 12 + 2x = 0 \text{ or } x = +\frac{10}{2} = +5$$

Therefore, the two central S-atoms have zero oxidation state and two terminal S-atoms have +5 oxidation state each.

(c) **Na_2SO_3** Let the oxidation number of S in Na_2SO_3 be x.

$$2(+1) + x + 3(-2) = 0 \text{ or } x = +4$$

(d) **Na_2SO_4** Let the oxidation number of S be x.

$$2(+1) + x + 4(-2) = 0 \text{ or } x = +6$$

Q. 24 Balance the following equations by the oxidation number method.

(a) $Fe^{2+} + H^{+} + Cr_2O_7^{-2} \longrightarrow Cr^{3+} + Fe^{3+} + H_2O$

(b) $I_2 + NO_3^{-} \longrightarrow NO_2 + IO_3^{-}$

(c) $I_2 + S_2O_3^{2-} \longrightarrow I^{-} + S_4O_6^{2-}$

(d) $MnO_2 + C_2O_4^{2-} \rightarrow Mn^{2+} + CO_2$

Ans. Oxidation number method

(a)

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

O.N. decreases by 3 per Cr-atom ($3 \times 2 = 6\,e^{-}$ gain)

O.N. increases by 1 per Fe-atom ($1\,e^{-}$ lose)

(Multiply Cr^{3+} by 2 because there are 2Cr atoms in $Cr_2O_7^{2-}$ ion.)

Balance increase and decrease in oxidation number.

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

Balance charge by multiplying H^{+} by 14.

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

Balance H and O-atoms by multiplying H_2O by 7.

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

This represents a balanced redox reaction.

(b)

$$\overset{0}{I_2} + \overset{+5}{NO_3^{-}} \longrightarrow \overset{+4}{NO_2} + \overset{+5}{2IO_3^{-}}$$

O.N. decreases by 1 per N-atom ($1\,e^{-}$ gain)

O.N. increases by 5 per I-atom (2×5 electrons lose)

Balance increase and decrease in oxidation number

$$I_2 + 10NO_3^{-} \longrightarrow 10NO_2 + 2IO_3^{-}$$

Balance charge by writing $8H^{+}$ in LHS of the equation.

$$I_2 + 10NO_3^{-} + 8H^{+} \longrightarrow 10NO_2 + 2IO_3^{-}$$

Balance H-atoms by writing $4H_2O$ in RHS of the equation.

$$I_2 + 10NO_3^{-} + 8H^{+} \longrightarrow 10NO_2 + 2IO_3^{-} + 4H_2O$$

Oxygen atoms are automatically balanced.

This represents a balanced redox reaction.

(c)

$$\overset{0}{I_2} + \overset{+2}{2S_2O_3^{2-}} \longrightarrow \overset{-1}{2I^{-}} + \overset{2.5}{S_4O_6^{2-}}$$

O.N. decreases by 1 per I-atom ($2 \times 1\,e^{-}$ gain)

O.N. increases by 0.5 per S-atom ($4 \times 0.5 = 2e^{-}$ lose)

(Multiply $S_2O_3^{2-}$ by 2 because there are 4 S-atoms in $S_4O_6^{2-}$ ion.)

Increase and decrease in oxidation number is already balanced. Charge and oxygen atoms are also balanced.

This represents a balanced redox reaction.

(d)

$$\overset{+4}{Mn}O_2 + \overset{+3}{C_2}O_4^{2-} \longrightarrow Mn^{2+} + 2\overset{+4}{C}O_2$$

O.N. decreases by 2 per Mn-atom ($2e^-$ gain)

O.N. increases by 1 per C-atom ($2 \times 1 = 2e^-$ lose)

Increase and decrease in oxidation number is already balanced.

Add $4H^+$ towards LHS of the equation to balance charge.

$$MnO_2 + C_2O_4^{2-} + 4H^+ \longrightarrow Mn^{2+} + 2CO_2$$

Add $2H_2O$ towards RHS of the equation to balance H-atoms

$$MnO_2 + C_2O_4^{2-} + 4H^+ \longrightarrow Mn^{2+} + 2CO_2 + 2H_2O$$

This represents a balanced redox reaction.

Q. 25 Identify the redox reaction out of the following reactions and identify the oxidising and reducing agents in them.

(a) $3HCl(aq) + HNO_3(aq) \longrightarrow Cl_2(g) + NOCl(g) + 2H_2O(l)$

(b) $HgCl_2(aq) + 2KI(aq) \longrightarrow HgI_2(s) + 2KCl(aq)$

(c) $Fe_2O_3(s) + 3CO(g) \xrightarrow{\Delta} 2Fe(s) + 3CO_2(g)$

(d) $PCl_3(l) + 3H_2O(l) \longrightarrow 3HCl(aq) + H_3PO_3(aq)$

(e) $4NH_3(aq) + 3O_2(g) \longrightarrow 2N_2(g) + 6H_2O(g)$

Ans. (a) Writing the O.N. on each atom above its symbol, then

$$3\overset{+1}{H}\overset{-1}{Cl}(aq) + \overset{+1}{H}\overset{+5}{N}\overset{-2}{O_3}(aq) \longrightarrow \overset{0}{Cl_2}(g) + \overset{+3}{N}\overset{-2}{O}\overset{-1}{Cl}(g) + 2\overset{+1}{H_2}\overset{-2}{O}(l)$$

Here, the O.N. of Cl increases from –1 in HCl to O in Cl_2, therefore, Cl^- is oxidised and hence HCl acts as the reducing agent.

The O.N. of N decreases from +5 in HNO_3 to +3 in NOCl, therefore, HNO_3 acts as the oxidising agent.

Thus, this reaction is a redox reaction.

(b) Writing the O.N. of each atom above its symbol, we have,

$$\overset{+2}{Hg}\overset{-1}{Cl_2}(aq) + 2\overset{+1}{K}\overset{-1}{I}(aq) \longrightarrow \overset{+2}{Hg}\overset{-1}{I_2}(s) + 2\overset{+1}{K}\overset{-1}{Cl^-}(aq)$$

Here, the O.N. of none of the atoms undergo a change, therefore, this reaction is not a redox reaction.

(c) $\overset{+3}{Fe_2}\overset{-2}{O_3}(s) + 3\overset{+2}{C}\overset{-2}{O}(g) \xrightarrow{\Delta} 2\overset{0}{Fe}(s) + 3\overset{+4}{C}\overset{-2}{O_2}(g)$

Here, O.N. of Fe decreases from +3 in Fe_2O_3 to 0 in Fe, therefore, Fe_2O_3 acts as an oxidising agent. Further, O.N. of C increases from +2 in CO to +4 in CO_2, therefore, CO acts as a reducing agent.

Thus, this reaction is an example of redox reaction.

(d) Writing the O.N. of each atom above its symbol, then

$$\overset{+3}{P}\overset{-1}{Cl_3}(l) + 3\overset{+1}{H_2}\overset{-2}{O}(l) \rightarrow 3\overset{+1}{H}\overset{-1}{Cl}(aq) + \overset{+1}{H_3}\overset{+3}{P}\overset{-2}{O_3}(aq)$$

Here, O.N. of none of the atoms undergo a change, therefore, this reaction is not a redox reaction.

(e) Writing the O.N. of each atom above its symbol, then

$$4\overset{-3}{N}\overset{+1}{H_3}(aq) + 3\overset{0}{O_2}(g) \longrightarrow 2\overset{0}{N_2}(g) + 6\overset{+1}{H_2}\overset{-2}{O}(l)$$

Here, O.N. of N increases from –3 to 0 in N_2, therefore, NH_3 acts as a reducing agent. Further, O.N. of O decreases from 0 in O_2 to –2 in H_2O, therefore, O_2 acts as a oxidising agent. Thus, this reaction is a redox reaction.

Q. 26 Balance the following ionic equations.

(a) $Cr_2O_7^{2-} + H^+ + I^- \longrightarrow Cr^{3+} + I_2 + H_2O$

(b) $Cr_2O_7^{2-} + Fe^{2+} + H^+ \longrightarrow Cr^{3+} + Fe^{3+} + H_2O$

(c) $MnO_4^- + SO_3^{2-} + H^+ \longrightarrow Mn^{2+} + SO_4^{2-} + H_2O$

(d) $MnO_4^- + H^+ + Br^- \longrightarrow Mn^{2+} + Br_2 + H_2O$

Ans. (a) Write the O. N. of all atoms above their respective symbols.

O. N. decreases by, 3 per Cr-atom

O.N. decreases by 3 per Cr-atom

$$\overset{+6\ -2}{Cr_2O_7} + H^+ + I^- \longrightarrow \overset{+3}{Cr} + \overset{0}{I_2} + \overset{+1-2}{H_2O}$$

O.N. increases by 1 per I-atom

Divide the given equation into two half reactions

Reduction half reaction : $Cr_2O_7 \rightarrow Cr^{3+}$

Oxidation half reaction : $I^- \rightarrow I_2$

To balance reduction half reaction.

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

To balance oxidation half reaction

$$2I^- \longrightarrow I_2 + 2e^-$$

To balance the reaction by electrons gained and lost

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

$$6I^- \longrightarrow 3I_2 + 6e^-$$

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

This gives the final balanced ionic equations.

(b) Write the skeletal equation of the given reaction

$$Cr_2O_7^{2-}(aq) + Fe^{2+}(aq) \longrightarrow Cr^{3+}(aq) + Fe^{3+}(aq)$$

Write the O. N. of all the elements above their respective symbols.

O.N. decreases by 3 per Cr-atom

$$\overset{+6\ -2}{Cr_2O_7}(aq) + Fe^{2+}(aq) \longrightarrow Cr^{3+}(aq) + Fe^{3+}(aq)$$

O.N. increases by 1 per Fe-atom

Divide the given equation into two half reactions

Oxidation half reaction : $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$

reduction half reaction : $Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)$

To balance oxidation half reaction

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$$

To balance reduction half reaction

$$Cr_2O_7^{2-}(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq)$$

Balance charge by adding H^+ ions.

$$Cr_2O_7^{2-}(aq) + 14H^+ (aq) + 6e^- \longrightarrow 2Cr^{3+}(aq)$$

Balance O atoms by adding H_2O molecules

$$Cr_2O_7^{2-} (aq) + 14H^+ (aq) + 6e^- \longrightarrow 2Cr^{3+} (aq) + 7H_2O (l)$$

To balance the reaction

$$6Fe^{2+}(aq) \longrightarrow 6Fe^{3+}(aq) + 6e^-$$

$$\underline{Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)}$$

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

(c) Write the O. N. of all atoms above their respective symbols.

O.N. decreases by 5 per Mn-atom

$$\overset{+7\,-2}{MnO_4^-} + \overset{+4\,-2}{SO_3^{2-}} \longrightarrow Mn^{2+} + \overset{+6\,-2}{SO_4^{2-}} + H_2O$$

O.N. increases by 2 per S-atom

Divide the skeleton equation into two half-reactions.

Reduction half reaction: $MnO_4^- \longrightarrow Mn^{2+}$

Oxidation half reaction : $SO_3^{2-} \longrightarrow SO_4^{2-}$

To balance reduction half reaction

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

To balance oxidation half reaction

$$SO_3^{2-} \longrightarrow SO_4^{2-} + 2e^-$$

Balance charge by adding H^+ ions.

$$SO_3^{2-} \longrightarrow SO_4^{2-} + 2H^+ + 2e^-$$

Balance O-atoms by adding H_2O molecules

$$SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2e^-$$

To balance the reaction

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

$$\underline{5SO_3^{2-} + 5H_2O \longrightarrow 5SO_4^{2-} + 10H^+ + 10e^-}$$

$$2MnO_4^- + 5SO_3^{2-} + 6H^+ \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$$

This represents the correct balanced redox equation.

(d) Write the O. N. of all the atoms above their respective symbols.

O.N. decreases by 5 per Mn-atom

$$\overset{+7-2}{MnO_4^-} + H^+ + Br^- \longrightarrow Mn^{2+} + \overset{0}{Br_2} + \overset{+2-1}{H_2O}$$

O.N. increases by 1 per Br-atom

Divide skeleton equation into two half reactions

Reduction half reaction $MnO_4^- \rightarrow Mn^{2+}$

Oxidation half reaction $Br^- \rightarrow Br_2$

To balance reduction half reaction

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

To balance oxidation half reaction

$$2Br^- \longrightarrow Br_2 + 2e^-$$

To balance the reaction

$$2MnO_4^- + 16H^+ + 10e^- \longrightarrow 2Mn^{2+} + 8H_2O$$
$$10Br^- \longrightarrow 5Br_2 + 10e^-$$
$$2MnO_4^- + 10Br^- + 16H^+ \longrightarrow 2Mn^{2+} + 5Br_2 + 8H_2O$$

This represents the correct balanced ionic equation.

Matching The Columns

Q. 27 Match Column I with Column II for the oxidation states of the central atoms.

	Column I		Column II
A.	$Cr_2O_7^{2-}$	1.	+3
B.	MnO_4^-	2.	+4
C	VO_3^-	3.	+5
D.	FeF_6^{3-}	5.	+6
		6.	+7

Ans. **A.** → (4) **B.** → (5) **C.** → (3) **D.** → (1)

Suppose that x be the oxidation states of central atoms.

A. Oxidation number of Cr in $Cr_2O_7^{2-}$

$$2x + 7(-2) = -2$$
$$2x - 14 = -2$$
$$2x = +12$$
$$x = +6$$

B. Oxidation number of Mn in MnO_4^-

$$x + 4(-2) = -1$$
$$x - 8 = -1$$
$$x = +7$$

C. Oxidation number of V in VO_3^-

$$x + 3(-2) = -1$$
$$x - 6 = -1$$
$$x = +5$$

D. Oxidation number of Fe in FeF_6^{3-}

$$x + 6(-1) = -3$$
$$x - 6 = -3$$

or $$x = +3$$

Q. 28 Match the items in Column I with relevant items in Column II.

	Column I		Column II
A.	Ions having positive charge	1.	+7
B.	The sum of oxidation number of all atoms in a neutral molecule	2.	−1
C.	Oxidation number of hydrogen ion (H^+)	3.	+1
D.	Oxidation number of fluorine in NaF	4.	0
E.	Ions having negative charge	5.	Cation
		6.	Anion

Ans. **A.** → (5) **B.** → (4) **C.** → (3) **D.** → (2) **E.** → (6)

A. Ions having positive charge — Cation

B. The sum of oxidation number of all atoms in a neutral molecule — Zero

C. Oxidation number of hydrogen ion (H^+) — +1

D. Oxidation number of fluorine in NaF — −1

E. Ions having negative charge — Anion

Assertion and Reason

In the following questions a statement of assertion (A) *followed by a statement of reason* (R) *is given. Choose the correct option out of the choices given below in each question.*

Q. 29 Assertion (A) Among halogens fluorine is the best oxidant.

Reason (R) Fluorine is the most electronegative atom.

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A

(c) A is true but R is false

(d) Both A and R are false

Ans. *(b)* Both assertion and reason are true but reason is not the correct explanation of assertion. Among halogen F_2 is the best oxidant because it has the highest $E°$ value.

Q. 30 Assertion (A) In the reaction between potassium permanganate and potassium iodide, permanganate ions act as oxidising agent.

Reason (R) Oxidation state of manganese changes from +2 to +7 during the reaction.

(a) Both A and R are true and R is the correct explanation of A

(b) Both A and R are true but R is not the correct explanation of A

(c) A is true but R is false

(d) Both A and R are false

Ans. ***(c)*** Assertion is true but reason is false.

$$10KI + 2K\overset{+7}{Mn}O_4 + 8H_2SO_4 \longrightarrow 2\overset{+2}{Mn}SO_4 + 6K_2SO_4 + 8H_2O + 5I_2$$

Oxidation state of Mn decreases from +7 to +2.

Q. 31 Assertion (A) The decomposition of hydrogen peroxide to form water and oxygen is an example of disproportionation reaction.

Reason (R) The oxygen of peroxide is in −1 oxidation state and it is converted to zero oxidation state in O_2 and −2 oxidation state in H_2O.

(a) Both A and R are true and R is the correct explanation of A
(b) Both A and R are true but R is not the correct explanation of A
(c) A is true but R is false
(d) Both A and R are false

Ans. ***(a)*** Both assertion and reason are true and reason is the correct explanation of assertion.

Oxidation

$$2H_2\overset{-1}{O_2} \longrightarrow 2H_2\overset{-2}{O} + \overset{0}{O_2}$$

Reduction

Thus, the above reaction is an example of disproportionation reaction.

Q. 32 Assertion (A) Redox couple is the combination of oxidised and reduced form of a substance involved in an oxidation or reduction half cell.

Reason (R) In the representation $E^{\ominus}_{Fe^{3+}/Fe^{2+}}$ and $E^{\ominus}_{Cu^{2+}/Cu}$, Fe^{3+}/Fe^{2+} and Cu^{2+}/Cu are redox couples.

(a) Both A and R are true and R is the correct explanation of A
(b) Both A and R are true but R is not the correct explanation of A
(c) A is true but R is false
(d) Both A and R are false

Ans. ***(a)*** Both assertion and reason are true reason is the correct explanation of assertion.

Redox couple is the combination of oxidised and reduced form of substance. In the representation $E^{\ominus}_{Fe^{3+}/Fe^{2+}}$ and $E^{\ominus}_{Cu^{2+}/Cu}$, Fe^{3+}/Fe^{2+} and Cu^{2+}/Cu are redox couples.

Long Answer Type Questions

Q. 33 Explain redox reaction on the basis of electron transfer. Given suitable examples.

Ans. As we know that, the reactions

$$2Na\,(s) + Cl_2(g) \longrightarrow 2NaCl\,(s)$$
$$4Na\,(s) + O_2(g) \longrightarrow 2Na_2O\,(s)$$

are redox reactions because in each of these reactions sodium is oxidised due to the addition of either oxygen or more electronegative element to sodium. Simultaneously, chlorine and oxygen are reduced because of each of these, the electropositive element sodium has been added.

From our knowledge of chemical bonding we also know that, sodium chloride and sodium oxide are ionic compounds and perhaps better written as $Na^+Cl^-(s)$ and $(Na^+)_2O^{2-}(s)$. Development of charges on the species produced suggests us to rewrite the above reaction in the following manner

Loss of $2e^-$

$$2Na\,(s) + Cl_2\,(g) \longrightarrow 2Na^+Cl^-\,(s)$$

Gain of $2e^-$

Loss of $2e^-$

$$2Na(s) + O_2\,(g) \longrightarrow [Na^+]_2\,O^{2-}\,(s)$$

Gain of $2e^-$

For convenience, each of the above processes can be considered as two separate steps, one involving the loss of electrons and other the gain of electrons. As an illustration, we may further elaborate one of these, say, the formation of sodium chloride.

$$2Na\,(s) \longrightarrow 2Na^+\,(g) + 2e^-$$
$$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(g)$$

Each of the above steps is called a half reaction, which explicitly shows involvement of electrons. Sum of the half reactions gives the overall reaction:

$$2Na\,(s) + Cl_2(g) \longrightarrow 2Na^+Cl^-\,(s) \text{ or } 2NaCl\,(s)$$

The given reactions suggest that half reactions that involved loss of electrons are oxidation reactions. Similarly, the half reactions that involve gain of electrons are called reduction reactions.

It may not be out of context to mention here that the new way of defining oxidation and reduction has been achieved only by establishing a correlation between the behaviour of species as per the classical idea and their interplay in electron-transfer change.

In the given reactions, sodium, which is oxidised, acts as a reducing agent because it donates electron to each of the elements interacting with it and thus helps in reducing them. Chlorine and oxygen are reduced and act as oxidising agents because these accept electrons from sodium.

To summarise, we may mention that

Oxidation Loss of electron(s) by any species.

Reduction Gain of electron(s) by any species.

Oxidising agent Acceptor of electron(s).

Reducing agent Donor of electron(s).

Q. 34 On the basis of standard electrode potential values, suggest which of the following reactions would take place? (Consult the book for $E^\ominus$ value)

(a) $Cu + Zn^{2+} \longrightarrow Cu^{2+} + Zn$

(b) $Mg + Fe^{2+} \longrightarrow Mg^{2+} + Fe$

(c) $Br_2 + 2Cl^- \longrightarrow Cl_2 + 2Br^-$

(d) $Fe + Cd^{2+} \longrightarrow Cd + Fe^{2+}$

Ans. As we know that,

$$E^\circ_{Cu^{2+}/Cu} = 0.34\text{ V},\ E^\circ_{Zn^{2+}/Zn} = -0.76\text{ V},$$
$$E^\circ_{Mg^{2+}/Mg} = -2.37\text{ V},\ E^\circ_{Fe^{2+}/Fe} = -0.74\text{ V},$$
$$E^\circ_{Br_2/Br^-} = +\ 1.08\text{ V},\ E^\circ_{Cl_2/Cl^-} = +1.36\text{ V}$$
$$E^\circ_{Cd^{2+}/Cd} = -\ 0.44\text{ V}$$

(a) $E°_{Cu^{2+}/Cu} = +\ 0.34\ V$ and $E°_{Zn^{2+}/Zn} = -0.76\ V$

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

In the given cell reaction, Cu is oxidised to Cu^{2+}, therefore, Cu^{2+}/Cu couple acts as anode and Zn^{2+} is reduced to Zn, therefore, Zn^{2+}/Zn couple acts as cathode.

$$E°_{cell} = E°_{cathode} - E°_{anode}$$
$$E°_{cell} = -0.76 - (+0.34) = -1.10V$$

Negative value of E°_{cell} indicates that the reaction will not occur.

(b) $Mg + Fe^{2+} \longrightarrow Mg^{2+} + Fe$

$$E°_{Mg^{2+}/Mg} = -2.37V \text{ and } E°_{Fe^{2+}/Fe} = -0.74\ V$$

In the given cell reaction, Mg is oxidised to Mg^{2+} hence, Mg^{2+}/Mg couple acts as anode and Fe^{2+} is reduced to Fe hence, Fe^{2+}/Fe couple acts as cathode.

$$E°_{cell} = E°_{cathode} - E°_{anode}$$
$$E°_{cell} = -0.74 - (-2.37) = +1.63V$$

Positive value of $E°_{cell}$ 5 indicates that the reaction will occur.

(c)
$$Br_2 + 2Cl^- \longrightarrow Cl_2 + 2Br^-$$

$$E°_{Br^-/Br_2} = +\ 1.08\ V \text{ and } E°_{Cl^-/Cl_2} = +1.36\ V$$

In the given cell reaction, Cl^- is oxidised to Cl_2 hence, Cl^-/Cl_2 couple acts as anode and Br_2 is reduced to Br^- hence; Br^-/Br_2 couple acts as cathode.

$$E°_{cell} = E°_{cathode} - E°_{anode}$$
$$E°_{cell} = +1.08 - (+1.36) = -0.28\ V$$

Negative value of $E°_{cell}$ indicates that the reaction will occur.

(d)
$$Fe + Cd^{2+} \longrightarrow Cd + Fe^{2+}$$

$$E°_{Fe^{2+}/Fe} = -0.74\ V. \text{ and } E°_{Cd^{2+}/Cd} = -0.44\ V$$

In the given cell reaction, Fe is oxidised to Fe^{2+} hence, Fe^{2+}/Fe couple acts as anode and Cd^{2+} is reduced to Cd hence, Cd^{2+}/Cd couple acts as cathode.

$$E°_{cell} = E°_{cathode} - E°_{anode}$$
$$E°_{cell} = -0.44 - (-0.74) = +0.30\ V.$$

Positive value $E°_{cell}$ indicates that the reaction will occur.

Q. 35 Why does fluorine not show disproportionation reaction?

Ans. In a disproportionation reaction, the same species is simultaneously oxidised as well as reduced. Therefore, for such a redox reaction to occur, the reacting species must contain an element which has atleast three oxidation states.

The element, in reacting species, is present in an intermediate state while lower and higher oxidation states are available for reduction and oxidation to occur (respectively).

Fluorine is the strongest oxidising agent. It does not show positive oxidation state. That's why fluorine does not show disproportionation reaction.

Q. 36 Write redox couples involved in the reactions (a) to (d) given in question 34.

Thinking Process

A redox couple represents the oxidised and reduced forms of a substance together taking part in an oxidation or reduction half reaction.

Ans. Given that,

$$Cu + Zn^{2+} \longrightarrow Cu^{2+} + Zn$$
$$Mg + Fe^{2+} \longrightarrow Mg^{2+} + Fe$$
$$Br_2 + 2Cl^- \longrightarrow Cl_2 + 2Br$$
$$Fe + Cd^{2+} \longrightarrow Cd + Fe^{2+}$$

(a) Cu^{2+}/Cu and Zn^{2+}/Zn

(b) Mg^{2+}/Mg and Fe^{2+}/Fe

(c) Br_2/Br^- and Cl_2/Cl^-

(d) Fe^{2+}/Fe and Cd^{2+}/Cd

Q. 37 Find out the oxidation number of chlorine in the following compounds and arrange them in increasing order of oxidation number of chlorine.
$NaClO_4, NaClO_3, NaClO, KClO_2, Cl_2O_7, ClO_3, Cl_2O, NaCl, Cl_2, ClO_2$.
Which oxidation state is not present in any of the above compounds?

Ans. Suppose that the oxidation number of chlorine in these compounds be x.

O.N. of Cl in $NaClO_4$ $\therefore$ $+1 + x + 4(-2) = 0$ or, $x = +7$

O.N. of Cl in $NaClO_3$ $\therefore$ $+1 + x + 3(-2) = 0$ or, $x = +5$

O.N. of Cl in NaClO $\therefore$ $+1 + x + 1(-2) = 0$ or, $x = +1$

O.N. of Cl in $KClO_2$ $\therefore$ $+1 + x + 2(-2) = 0$ or, $x = +3$

O.N. of Cl in Cl_2O_7 $\therefore$ $+2x + 7(-2) = 0$ or, $x = +7$

O.N. of Cl in ClO_3 $\therefore$ $x + 3(-2) = 0$ or, $x = +6$

O.N. of Cl in Cl_2O $\therefore$ $2x + 1(-2) = 0$ or, $x = +1$

O. N. of Cl in NaCl $\therefore$ $+1 + x = 0$ or, $x = -1$

O. N. of Cl in Cl_2 $\therefore$ $2x = 0$ or, $x = 0$

O. N. of Cl in ClO_2 $\therefore$ $x + 2(-2) = 0$ or, $x = +4$

None of these compounds have an oxidation number of +2.

Increasing order of oxidation number of chlorine is : –1, 0, +1, +3, +4, +5, +6, +7

Therefore, the increasing order of oxidation number of Cl in compounds is

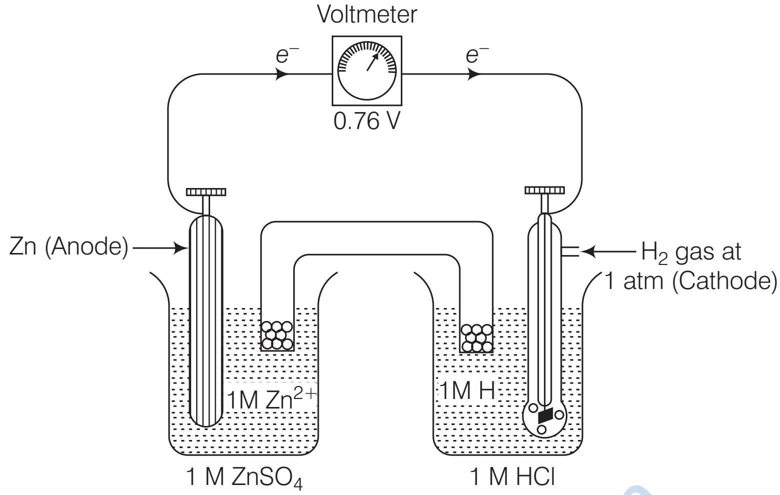
$$NaCl < Cl_2 < NaClO < KClO_2 < ClO_2 < NaClO_3 < ClO_3 < Cl_2O_7$$

Q. 38 Which method can be used to find out strength of reductant/oxidant in a solution? Explain with an example.

Ans. Measure the electrode potential of the given species by connecting the redox couple of the given species with standard hydrogen electrode. If it is positive, the electrode of the given species acts as reductant and if it is negative, it acts as an oxidant.

Find the electrode potentials of the other given species in the same way, compare the values and determine their comparative strength as an reductant or oxidant.

e.g., measurement of standard electrode potential of Zn^{2+}/Zn electrode using SHE as a reference electrode.



The EMF of the cell comes out to be 0.76 V. (reading of voltmeter is 0.76 V). Zn^{2+}/Zn couple acts as anode and SHE acts as cathode.

$$\therefore \quad E^\circ_{cell} = 0.76 = E^\circ_{cathode} - E^\circ_{anode}$$

$$0.76 = 0 - E^\circ_{anode}$$

$$E^\circ_{anode} = -0.76\text{ V}$$

$$E^\circ_{Zn^{2+}/Zn} = -0.76\text{V}.$$