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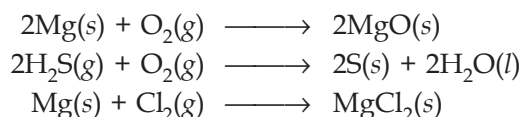
Redox Reactions

Facts that Matter

● Oxidation

Oxidation is defined as the addition of oxygen/electronegative element to a substance or removal of hydrogen/electropositive element from a substance.

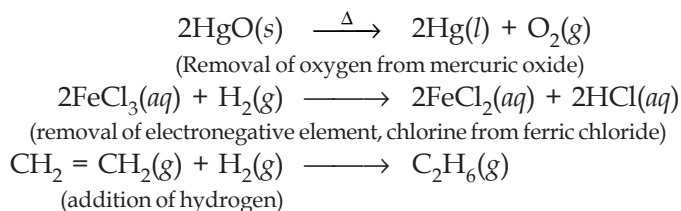
For example,



● Reduction

Reduction is defined as the removal of oxygen/electronegative element from a substance or addition of hydrogen or electropositive element to a substance.

For example,



● Redox Reaction in Terms of Electron Transfer Reaction

A few examples of redox reaction on the basis of electronic concept are given below:

According to electronic concept every redox reaction consists of two steps known as half reactions.

(i) **Oxidation reaction:** Half reactions that involve loss of electrons are called oxidation reactions.

(ii) **Reduction reaction:** Half reactions that involve gain of electrons are called reduction reactions.

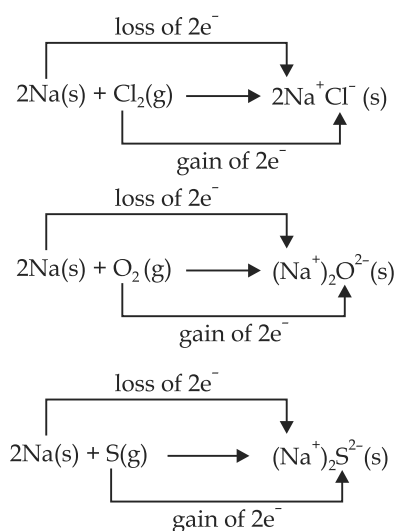
Oxidising agent: Acceptor of electrons.

Reducing agent: Donor of electrons.

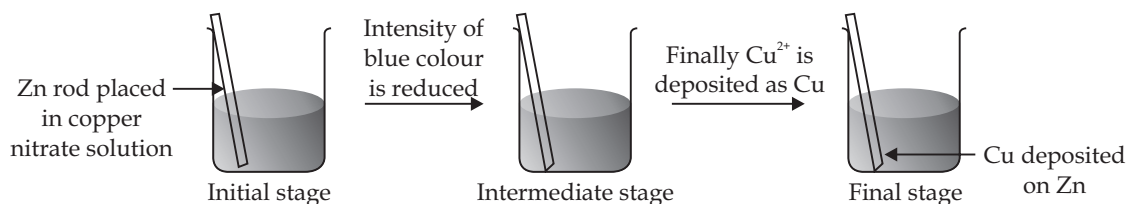
● Competitive Electron Transfer Reactions

To understand this concept let us do an experiment.

Place a strip of metallic zinc in an aqueous solution of copper nitrate as shown in Fig. After one hour following changes will be noticed.

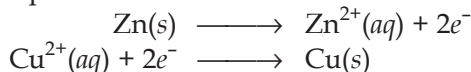


- (i) Strips becomes coated with reddish metallic copper.
- (ii) Blue colour of the solution disappears.
- (iii) If hydrogen sulphide gas is passed through the solution appearance of white ZnS can be seen on making the solution alkaline with ammonia.



Redox reaction between zinc and aqueous solution of copper nitrate occurring in a beaker.

Reaction takes place in the aqueous solution can be shown as



● Oxidation Number

It is the oxidation state of an element in a compound which is the charge assigned to an atom of a compound is equal to the number of electrons in the valence shell of an atom that are gained or lost completely or to a large extent by that atom while forming a bond in a compound.

● Rules for Assigning Oxidation Numbers

- (i) The oxidation number of an element in its elementary form is zero.
For example, H_2 , O_2 , N_2 etc. have oxidation number equal to zero.
- (ii) In a single monoatomic ion, the oxidation number is equal to the charge on the ion.
For example, Na^+ ion has oxidation number of +1 and Mg^{2+} ion has +2.
- (iii) Oxygen has oxidation number -2 in its compounds. However, there are some exceptions.
Compounds such as peroxides. Na_2O_2 , H_2O_2 oxidation number of oxygen = -1
In OF_2 O.N. of oxygen = +2
 O_2F_2 O.N. of oxygen = +1
- (iv) In non-metallic compounds of hydrogen like HCl , H_2S , H_2O oxidation number of hydrogen = +1 but in metal hydrides oxidation number of hydrogen = -1
[LiH , NaH , CaH_2 etc.]
- (v) In compounds of metals and non-metals metals have positive oxidation number while non-metals have negative oxidation number. For example, In NaCl . Na has +1 oxidation number while chlorine has -1.
- (vi) If in a compound there are two non-metallic atoms the atoms with high electronegativity is assigned negative oxidation number while other atoms have positive oxidation number.
- (vii) The algebraic sum of the oxidation number of all atoms in a compound is equal to zero.
- (viii) In poly atomic ion the sum of the oxidation no. of all the atoms in the ion is equal to the net charge on the ion.
For example, in $(\text{CO}_3)^{2-}$ —Sum of carbon atoms and three oxygen atoms is equal to -2.

● Redox Reactions in Terms of Oxidation Number

Oxidation. It is a chemical change in which an element undergoes increase in oxidation number.

Reduction. It is a chemical change in which an element undergoes decrease in oxidation number.

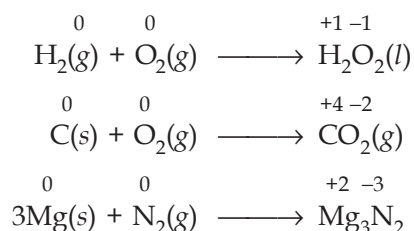
Oxidising agent. Oxidising agent is a substance in which the oxidation number of an element decreases as a result of the chemical change.

Reducing agent. Reducing agent is a substance in which the oxidation number of element increases as a result of chemical change.

● Types of Redox Reaction

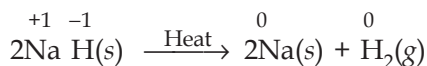
Combination Reaction. In combination reactions, compounds are formed as a result of the chemical combination of two or more elements.

For example,



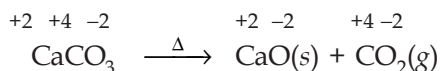
Decomposition Reaction. In these reaction compounds either of its own or upon heating decomposes to give two or more components out of which at least one is in elemental state.

For example,



All the decomposition reactions may not be redox reactions in nature.

For example,



Displacement Reaction. In displacement reactions as we know an atom/ion present in a compound gets replaced by an atom/ion of another element.

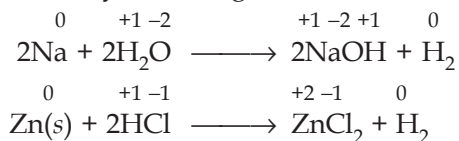


Metal Displacement Reaction. A metal in a compound can be displaced by another more reactive metal in uncombined state.

For example,



Non-metal Displacement Reaction. The non-metal displacement redox reactions include hydrogen displacement and a rarely occurring reaction involving oxygen displacement.

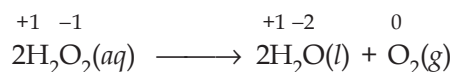


Fluorine (F₂) is so highly reactive non-metal that it displaces oxygen from water.



Disproportionation Reaction. In a disproportionation reaction an element in one oxidation state is simultaneously oxidised and reduced.

For example,

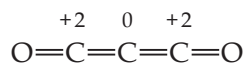


Hence, the oxygen of peroxide, which is present in -1 oxidation state is connected to zero oxidation state and in O₂ and in H₂O decreases to -2 oxidation state.

● Fractional Oxidation Numbers

Elements as such do not have any fractional oxidation numbers. When the same element are involved in different bonding in a species, their actual oxidation states are whole numbers but an average of these is fractional.

For example, In C₃O₂



The average O.N. of carbon atoms = $\frac{(2 + 2 + 0)}{3} = \frac{4}{3}$.

Fractional O.N. of a particular element can be calculated only if we know about the structure of the compound or in which it is present.

● Balancing of Redox Reactions

(i) Oxidation Number Method. Following steps are involved:

- Write the correct formula for each reactant and product.
- By assigning the oxidation change in oxidation number can be identified.
- Calculate the increase and decrease in oxidation number per atom with respect to the reactants. If more than one atom is present then multiply by suitable coefficient.
- Balance the equation with respect to all atoms. Balance hydrogen and oxygen atoms also.
- If the reaction is carried out in acidic medium, use H⁺ ions in the equation. If it is in basic medium use OH⁻ ions.
- Hydrogen atoms in the expression can be balanced by adding (H₂O) molecules to the reactants or products.

If there are the same number of oxygen atoms on the both side of equation then it represents the balanced redox reaction.

(ii) Half Reaction Method. In this method two half equation are balanced separately and then added together to give balanced equation.

Let us consider the oxidation of Fe²⁺ ions to Fe³⁺ ions by dichromate ions (Cr₂O₇²⁻) ions in acidic medium (Cr₂O₇²⁻ ions are reduced to Cr³⁺ ions).

Following steps are involved:

- Write the unbalanced equation for the reaction in ionic form.

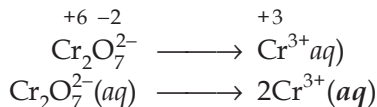


2. **Separate the equation in two half reactions:**

Oxidation half:



Reduction half:



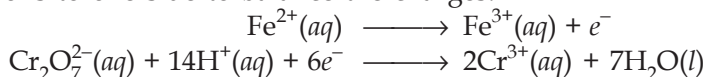
3.



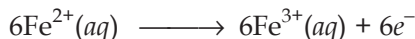
4. Add H₂O to balance O atoms and H⁺ to balance H atoms.



5. Add electrons to one side to balance the charges.



To equalise the number of electrons in both half reactions, we multiply the oxidation half reaction by 6.



6. The net ionic reaction can be written as

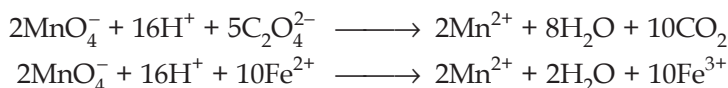


7. Verify the equation so that same type of number of atoms and the same charges on both sides of the equation.

● **Redox Reactions as the Basis for Titration**

Potassium Permanganate Titration: In these titrations potassium permanganate (pink in colour) acts as an oxidising agent in the acidic medium while oxalic acid or some ferrous salts acts as a reducing agents.

The ionic equation can be written as:



These are the examples of redox titration.

On both these titrations, potassium permanganate itself acts as indicator. It is commonly known as self indicator. The appearance of pink colour in the solution represents the end points.

Potassium Dichromate Titration: In place of potassium permanganate, potassium dichromate can also be used in the presence of dil. H₂SO₄. The ionic equation for the redox reaction with FeSO₄ (Fe²⁺ ions) is given.



The reaction is used in the estimation of ferrous ions in volumetric analysis.

Sodium Thiosulphate Titration: The redox reaction between sodium thiosulphate (S₂O₃²⁻ ions) and I₂ are also an example of redox titration.



This method based on the fact that iodine itself gives an intense blue colour with starch and has a very specific reaction with thiosulphate (S₂O₃²⁻) ions.

• Limitation of Concept of Oxidation Number

According to the concept of oxidation number, oxidation means increase in oxidation number by loss of electrons and reduction means decrease in oxidation number by the gain of electrons. However, during oxidation there is decrease in electron density while increase in electron density around the atom undergoing reduction.

• Redox Reactions and Electrode Processes—Electrochemical Cells

A device in which the redox reaction is carried indirectly and the decrease in energy appears as the electrical energy are called electrochemical cell.

Electrolytic Cell. The cell in which electrical energy is converted into chemical energy. Example, when lead storage battery is recharged, it acts as electrolytic cell.

Redox Reactions and Electrode Processes. When zinc rod is dipped in copper sulphate solution redox reaction begins hence, zinc is oxidised to Zn^{2+} ions and Cu^{2+} ions are reduced to metal.

Words that Matter

- **Redox reaction.** Reactions in which oxidation and reduction occur simultaneously are called redox reactions.
- **Oxidation.** Involves loss of one or more electrons.
- **Reduction.** Involves gain of one or more electrons.
- **Oxidising agent.** Accepting electrons.
- **Reducing agent.** Losing electrons.
- **Electrochemical cell.** It is a device in which redox reaction is carried indirectly and decrease in energy gives electrical energy.
- **Electrode potential.** It is the potential difference between the electrode and its ions in solution.
- **Standard electrode potential.** It is the potential of an electrode with respect to standard hydrogen electrode.
- **Electrochemical series.** It is activity series. It has been formed by arranging the metals in order of increasing standard reduction potential value.

NCERT TEXTBOOK QUESTIONS SOLVED

Q1. Assign oxidation number to the underlined elements in each of the following species:

- (a) $\text{NaH}_2\underline{\text{P}}\text{O}_4$ (b) $\text{NaH}\underline{\text{S}}\text{O}_4$ (c) $\text{H}_4\underline{\text{P}}_2\text{O}_7$ (d) $\text{K}_2\underline{\text{Mn}}\text{O}_4$
(e) $\text{Ca}\underline{\text{O}}_2$ (f) $\text{Na}\underline{\text{B}}\text{H}_4$ (g) $\text{H}_2\underline{\text{S}}_2\text{O}_7$ (h) $\text{KAl}(\underline{\text{S}}\text{O}_4)_2 \cdot 12\text{H}_2\text{O}$

- Sol.** (a) +1 +1 x -2
P in NaH_2PO_4
 $(+1) + 2(+1) + x + 4(-2) = 0$
 $x + 3 - 8$ or $x = +5$
- (b) S in NaHSO_4
+1 +1 x -2
NaHSO₄
 $(+1) + (+1) + x + 4(-2) = 0$
 $x - 6 = 0$
 $x = +6$

(c) P in $\text{H}_4\text{P}_2\text{O}_7$

$$\begin{array}{l} +1 \quad x \quad -2 \\ \text{H}_4\text{P}_2\text{O}_7 \\ 4(+1) + 2x + 7(-2) = 0 \\ 2x - 10 = 0 \\ x = +5 \end{array}$$

(d) Mn in K_2MnO_4

$$\begin{array}{l} +1 \quad x \quad -2 \\ \text{K}_2\text{MnO}_4 \\ 2(+1) + x + 4(-2) = 0 \\ x - 6 = 0 \\ x = +6 \text{ oxygen.} \end{array}$$

(e) Let the oxidation number of CaO_2 be x .

$$\begin{array}{l} 2 + 2x = 0 \qquad (\because \text{oxy No. of } a = +2) \\ x = -1 \end{array}$$

Thus, oxidation number of O in $\text{CaO}_2 = -1$.

(f) In NaBH_4 , H is present as hydride ion. Therefore, its oxidation number is -1 .

Thus,

$$\begin{array}{l} +1 \quad x \quad -1 \\ \text{Na B H}_4 \qquad \therefore 1(+1) + x + 4(-1) = 0 \quad \text{or } x = +3 \end{array}$$

Thus, the oxidation number of B in $\text{NaBH}_4 = +3$.

(g) $+1 \quad x \quad -2$

$$\text{H}_2\text{S}_2\text{O}_7 \qquad \therefore 2(+1) + 2(x) + 7(-2) = 0 \quad \text{or } x = +6$$

Thus, the oxidation number of S in $\text{H}_2\text{S}_2\text{O}_7 = +6$.

(h) $+1 \quad +3 \quad x \quad -2 \qquad +1 \quad -2$

$$\text{K Al (S O}_4)_2 \cdot 12(\text{H}_2\text{O}) \quad \text{or } +1 + 3 + 2x + 8(-2) + 12(2 \times 1 - 2) \quad \text{or } x = +6$$

Alternatively, since H_2O is a neutral molecule, therefore, sum of oxidation numbers of all the atoms in H_2O may be taken as zero. As such water molecules may be ignored while computing the oxidation number of S.

$$\therefore +1 + 3 + 2x - 16 = 0 \quad \text{or } x = +6$$

Thus, the oxidation number of S in $\text{KAl(SO}_4)_2 \cdot 12\text{H}_2\text{O} = +6$.

Q2. What are the oxidation number of the underlined elements in each of the following and how do you rationalise your results?

(a) $\text{K}\underline{\text{I}}_3$ (b) $\text{H}_2\underline{\text{S}}_4\text{O}_6$ (c) $\underline{\text{Fe}}_3\text{O}_4$ (d) $\underline{\text{C}}\text{H}_3\underline{\text{C}}\text{H}_2\text{OH}$ (e) $\underline{\text{C}}\text{H}_3\underline{\text{C}}\text{OOH}$.

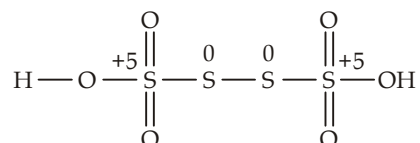
Sol. (a) In KI_3 , since the oxidation number of K is $+1$, therefore, the average oxidation number of iodine = $-1/3$. But the oxidation number cannot be fractional. Therefore, we must consider its structure, $\text{K}^+ [\text{I}-\text{I} \leftarrow \text{I}]^-$. Here, a coordinate bond is formed between I_2 molecule and I^- ion. The oxidation number of two iodine atoms forming the I_2 molecule is zero while that of iodine forming the coordinate bond is -1 . Thus, the O.N. of three I atoms, atoms in KI_3 are 0, 0 and -1 respectively.

(b) *By conventional method.* O.N. of S in $\text{H}_2\text{S}_4\text{O}_6 = \overset{+1}{\text{H}}_2 \overset{x}{\text{S}}_4 \overset{-2}{\text{O}}_6$

$$\text{or } 2(+1) + 4x + 6(-2) = 0 \quad \text{or } x = +2.5 \text{ (wrong)}$$

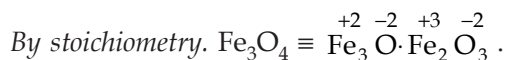
But it is wrong because all the four S atoms cannot be in the same oxidation state.

By chemical bonding method. The structure of $\text{H}_2\text{S}_4\text{O}_6$ is shown below:



The O.N. of each of the S-atoms linked with each other in the middle is zero while that of each of the remaining two S-atoms is +5.

(c) *By conventional method.* O.N. of Fe in $\text{Fe}_3\text{O}_4 = \overset{x}{\text{Fe}}_3 \overset{-2}{\text{O}}_4$ or $3x + 4(-2) = 0$ or $x = 8/3$.



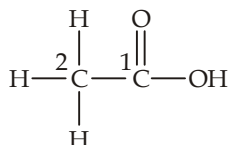
\therefore O.N. of Fe in Fe_3O_4 is +2 and +3

(d) *By conventional method.* O.N. of C in $\text{CH}_3\text{CH}_2\text{OH} = \overset{x}{\text{C}}_2 \overset{+1}{\text{H}}_6 \overset{-2}{\text{O}}$

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

(e) *By conventional method.* $\text{CH}_3\text{COOH} = \overset{x}{\text{C}}_2 \overset{+1}{\text{H}}_4 \overset{-2}{\text{O}}_2$ or $2x + 4 - 4 = 0$ or $x = 0$

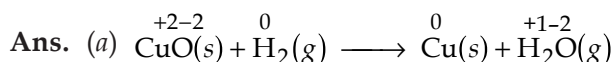
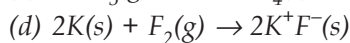
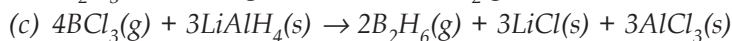
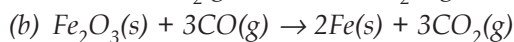
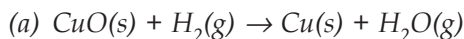
By chemical bonding method, C_2 is attached to three H-atoms (less electronegative than carbon) and one -COOH group (more electronegative than carbon).



therefore, O.N. of $\text{C}_2 = 3(+1) + x + 1(-1) = 0$ or $x = -2$

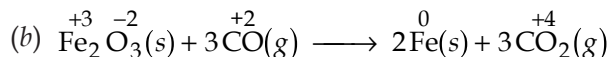
C_1 is, however, attached to one oxygen atom by a double bond, one OH (O.N. = -1) and one CH_3 (O.N. = +1) group, therefore, O.N. of $\text{C}_1 = +1 + x + 1(-2) + 1(-1) = 0$ or $x = +2$

Q3. Justify that the following reactions are redox reactions:

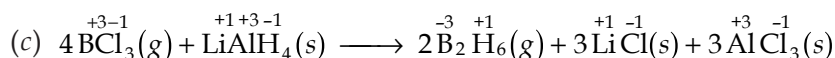


Here, O is removed from CuO, therefore, it is reduced to Cu while O is added to H_2 to form H_2O , therefore, it is oxidised. Further, O.N. of Cu decreases from

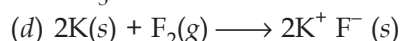
+ 2 in CuO to 0 in Cu but that of H increases from 0 in H₂ to +1 in H₂O. Therefore, CuO is reduced to Cu but H₂ is oxidised to H₂O. Thus, this is a redox reaction.



Here O.N. of Fe decreases from +3 in Fe₂O₃ to 0 in Fe while that of C increases from +2 in CO to +4 in CO₂. Further, oxygen is removed from Fe₂O₃ and added to CO, therefore, Fe₂O₃ is reduced while CO is oxidised. Thus, this is a redox reaction.

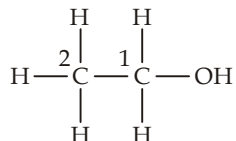


Here, O.N. of B decreases from +3 in BCl₃ to -3 in B₂H₆ while that of H increases from -1 in LiAlH₄ to +1 in B₂H₆. Therefore, BCl₃ is reduced while LiAlH₄ is oxidised. Further, H is added to BCl₃ but is removed from LiAlH₄, therefore, BCl₃ is reduced while LiAlH₄ is oxidised. Thus, it is a redox reaction.



Here, each K atom has lost one electron to form K⁺ while F₂ has gained two electrons to form two F⁻ ions. Therefore, K is oxidised while F₂ is reduced. Thus, it is a redox reaction.

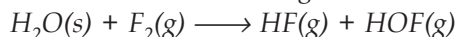
By chemical bonding, C₂ is attached to three H-atoms (less electronegative than carbon) and one CH₂OH group (more electronegative than carbon), therefore,



O.N. of C₂ = 3(+1) + x + 1(-1) = 0 or x = -2

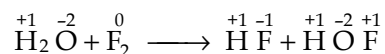
C₁ is, however, attached to one OH (O.N. = -1) and one CH₃ (O.N. = +1) group, therefore, O.N. of C₁ = +1 + 2(+1) + x + 1(-1) = 0 or x = -2

Q4. Fluorine reacts with ice and results in the change:



Justify that this reaction is a redox reaction.

Ans. Writing the O.N. of each atom above its symbol, we have,



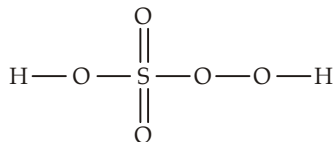
Here, the O.N. of F decreases from 0 in F₂ to -1 in HF and increases from 0 in F₂ to +1 in HOF. Therefore, F₂ is both reduced as well as oxidised. Thus, it is a redox reaction and more specifically, it is a *disproportionation reaction*.

Q5. Calculate the oxidation number of sulphur, chromium and nitrogen in H₂SO₅, Cr₂O₇²⁻ and NO₃⁻. Suggest structure of these compounds. Count for the fallacy.

Ans. O.N. of S in H₂SO₅.

By conventional method, the O.N. of S in H₂SO₅ is 2(+1) + x + 5(-2) = 0 or x = +8
This is impossible because the maximum O.N. of S cannot be more than six since it

has only six electrons in the valence shell. This fallacy is overcome if we calculate the O.N. of S by chemical bonding method. The structure of H_2SO_5 is



$$2 \times (+1) + x + 2(-1) + 3 \times (-2) = 0 \quad \text{or } x = +6$$

(for H) (for S) for (O-O) (for other O) atoms

Cr in $\text{Cr}_2\text{O}_7^{2-}$

$$2x + (-2 \times 7) = -2$$

$$2x - 14 = -2$$

$$2x = -2 + 14 \quad x = +6$$

$$x + 1(-1) + 1(-2) + 1(-2) = 0 \quad \text{or } x + 5$$

(for O^-) (for = O) for $\rightarrow \text{O}$

Thus, there is no fallacy about the O.N. of N in NO_3^- whether one calculates by conventional method or by chemical bonding method.

Q6. Write formulas for the following compounds:

(a) Mercury (II) chloride, (b) Nickel (II) sulphate, (c) Tin (IV) oxide, (d) Thallium (I) sulphate, (e) Iron (III) sulphate, (f) Chromium (III) oxide.

Ans. (a) $\text{Hg}(\text{II})\text{Cl}_2$, (b) $\text{Ni}(\text{II})\text{SO}_4$, (c) $\text{Sn}(\text{IV})\text{O}_2$, (d) $\text{Tl}_2(\text{I})\text{SO}_4$, (e) $\text{Fe}_2(\text{III})(\text{SO}_4)_3$, (f) $\text{Cr}_2(\text{III})\text{O}_3$.

Q7. Suggest a list of substances where carbon can exhibit oxidation states from -4 to $+4$ and nitrogen from -3 to $+5$.

Ans.

Compound	O.N. of Carbon	Compound	O.N. of Nitrogen
CH_4	-4	NH_3	-3
CH_3CH_3	-3	NH_2-NH_2	-2
$\text{CH}_2=\text{CH}_2$ or CH_3CH	-2	$\text{NH}=\text{NH}$	-1
$\text{CH}\equiv\text{CH}$	-1	$\text{N}\equiv\text{N}$	0
CH_2Cl_2 or $\text{C}_6\text{H}_{12}\text{O}_6$	0	N_2O	+1
C_2Cl_2 or C_6Cl_6	+1	NO	+2
CO or CHCl_3	+2	N_2O_3	+3
C_2Cl_6 or $(\text{COOH})_2$	+3	N_2O_4	+4
CO_2 or CCl_4	+4	N_2O_5	+5

Q8. While sulphur dioxide and hydrogen peroxide can act as an oxidising as well as reducing agents in their reactions, ozone and nitric acid act only as oxidants. Why?

Ans. (i) In SO_2 , O.N. of S is +4. In principle, S can have a minimum O.N. of -2 and maximum of $+6$. Therefore, S in SO_2 can either decrease or increase its O.N. and hence can act both as an oxidising as well as a reducing agent.

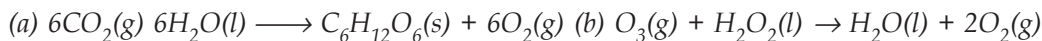
(ii) In H_2O_2 , the O.N. of O is -1 . In principle, O can have a minimum O.N. of -2 and maximum of zero ($+1$ is possible in O_2F_2 and $+2$ in OF_2). Therefore, O in H_2O_2 can either decrease its O.N. from -1 to -2 or can increase its O.N. from

-1 to zero. Therefore, H_2O_2 acts both as an oxidising as well as a reducing agent.

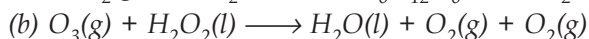
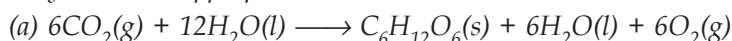
(iii) In O_3 , the O.N. of O is zero. It can only decrease its O.N. from zero to -1 or -2, but cannot increase to +2. Therefore, O_3 acts only as an oxidant.

(iv) In HNO_3 , O.N. of N is +5 which is maximum. Therefore, it can only decrease its O.N. and hence it acts as an oxidant only.

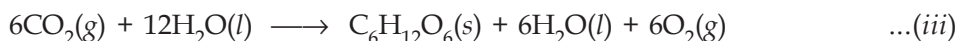
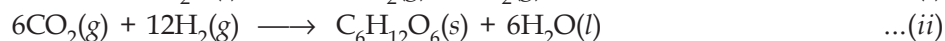
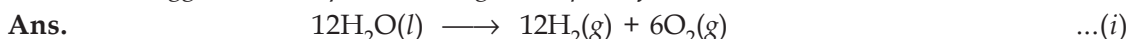
Q9. Consider the reactions:



Why it is more appropriate to write these reactions as:

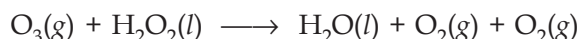
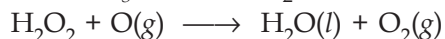


Also suggest a technique to investigate the path of above (a) and (b) redox reactions.



(a) Therefore, it is more appropriate to write the equation for photosynthesis as (iii) because it emphasises that $12\text{H}_2\text{O}$ are used per molecule of carbohydrate formed and $6\text{H}_2\text{O}$ are produced during the process.

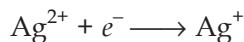
(b) The purpose of writing O_2 two times suggests that O_2 is being obtained from each of the two reactants.



The path of reactions (a) and (b) can be determined by using H_2O^{18} or D_2O in reaction (a) or by using $\text{H}_2\text{O}_2^{18}$ or O_3^{18} in reaction (b).

Q10. The compound AgF_2 is unstable. However, if formed, the compound acts as a very strong oxidising agent. Why?

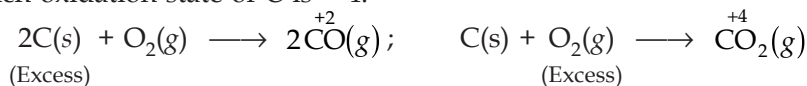
Ans. In AgF_2 , oxidation state of Ag is +2 which is very very unstable. Therefore, it quickly accepts an electron to form the more stable +1 oxidation state.



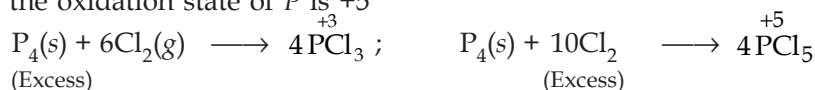
Therefore, AgF_2 , if formed, will act as a strong oxidising agent.

Q11. Whenever a reaction between an oxidising agent and a reducing agent is carried out, a compound of lower oxidation state is formed if the reducing agent is in excess and a compound of higher oxidation state is formed if oxidising agent is in excess. Justify this statement giving three illustrations.

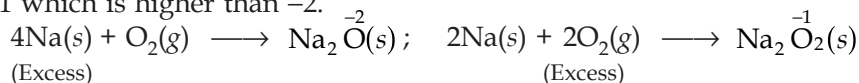
Ans. (i) C is a reducing agent while O_2 is an oxidising agent. If excess of carbon is burnt in a limited supply of O_2 , CO is formed in which the oxidation state of C is +2. If, however, excess of O_2 is used, the initially formed CO gets oxidised to CO_2 in which oxidation state of C is +4.



- (ii) P_4 is a reducing agent while Cl_2 is an oxidising agent. When excess of P_4 is used, PCl_3 is formed in which the oxidation state of P is +3. If, however, excess of Cl_2 is used, the initially formed PCl_3 reacts further to form PCl_5 in which the oxidation state of P is +5



- (iii) Na is a reducing agent while O_2 is an oxidising agent. When excess of Na is used, sodium oxide is formed in which the oxidation state of O is -2 . If, however, excess of O_2 is used, Na_2O_2 is formed in which the oxidation state of O is -1 which is higher than -2 .

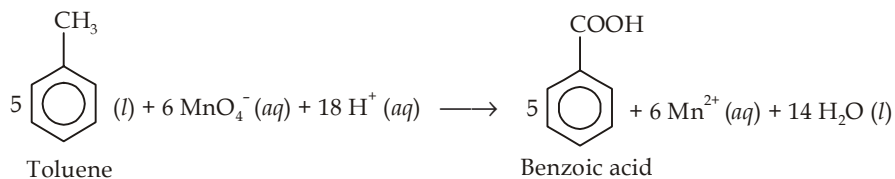
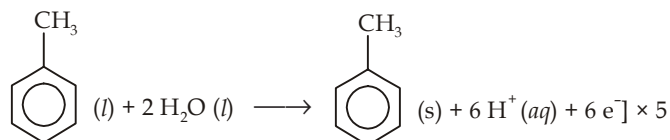


Q12. How do you account for the following observations?

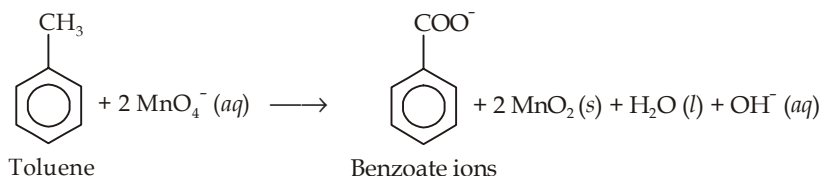
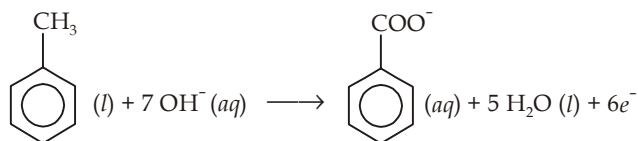
- (a) Though alkaline potassium permanganate and acidic potassium permanganate both are used as oxidants, yet in the manufacture of benzoic acid from toluene we use alcoholic potassium permanganate as an oxidant. Why? Write a balanced redox equation for the reaction.
- (b) When concentrated sulphuric acid is added to an inorganic mixture containing chloride, we get colourless pungent smelling gas HCl , but if the mixture contains bromide then we get red vapour of bromine. Why?

Ans. (a) Toluene can be oxidised to benzoic acid in acidic, basic and neutral media according to the following redox equations:

(i) **Acidic medium**

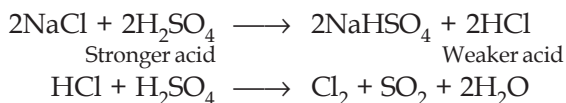


(ii) **Basic and neutral media**



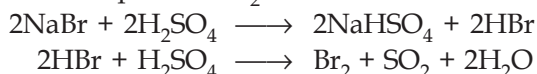
In the laboratory, benzoic acid is usually prepared by alkaline KMnO_4 oxidation of toluene. However, in industry alcoholic KMnO_4 is preferred over acidic or alkaline KMnO_4 because of the following reasons:

- The cost of adding an acid or the base is avoided because in the neutral medium, the base (OH^- ions) are produced in the reaction itself.
 - Since reactions occur faster in homogeneous medium than in heterogeneous medium, therefore, alcohol helps in mixing the two reactants, *i.e.*, KMnO_4 (due to its polar nature) and toluene (because of its being an organic compound).
- (b) When conc. H_2SO_4 is added to an inorganic mixture containing chloride, a pungent smelling gas HCl is produced because a stronger acid displaces a weaker acid from its salt.

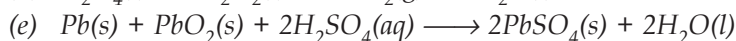
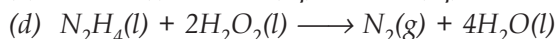
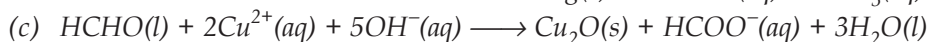
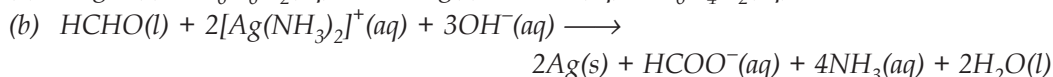
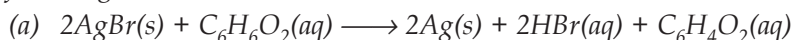


Since HCl is a very weak reducing agent, it can not reduce H_2SO_4 to SO_2 and hence HCl is not oxidised to Cl_2 .

However, when the mixture contains bromide ion, the initially produced HBr being a strong reducing agent than HCl reduces H_2SO_4 to SO_2 and is itself oxidised to produce red vapour of Br_2 .

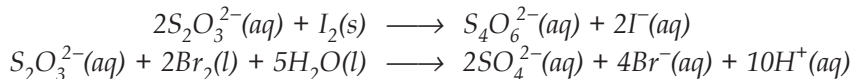


Q13. Identify the substance oxidised, reduced, oxidising agent and reducing agent for each of the following reactions.



Ans.	Substance oxidised	Substance reduced	Oxidising agent	Reducing agent
(a)	$\text{C}_6\text{H}_6\text{O}_2(aq)$	$\text{AgBr}(s)$	$\text{AgBr}(s)$	$\text{C}_6\text{H}_6\text{O}_2(aq)$
(b)	$\text{HCHO}(aq)$	$[\text{Ag}(\text{NH}_3)_2]^+$	$[\text{Ag}(\text{NH}_3)_2]^+$	$\text{HCHO}(aq)$
(c)	$\text{HCHO}(aq)$	$\text{Cu}^{2+}(aq)$	$\text{Cu}^{2+}(aq)$	$\text{HCHO}(aq)$
(d)	$\text{N}_2\text{H}_4(l)$	$\text{H}_2\text{O}_2(l)$	$\text{H}_2\text{O}_2(l)$	$\text{N}_2\text{H}_4(l)$
(e)	$\text{Pb}(s)$	$\text{PbO}_2(s)$	$\text{PbO}_2(s)$	$\text{Pb}(s)$

Q14. Consider the reactions:



Why does the same reductant, thiosulphate react differently with iodine and bromine?

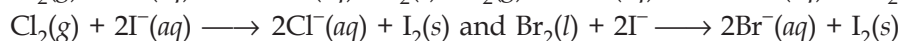
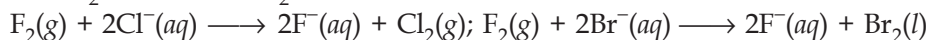
Ans. The average O.N. of S in $\text{S}_2\text{O}_3^{2-}$ is +2 while in $\text{S}_4\text{O}_6^{2-}$ it is +2.5. The O.N. of S in SO_4^{2-} is +6. Since Br_2 is a stronger oxidising agent than I_2 , it oxidises S of $\text{S}_2\text{O}_3^{2-}$ to a higher oxidation state of +6 and hence forms SO_4^{2-} ion. I_2 , however, being weaker oxidising

agent oxidises S of $S_2O_3^{2-}$ ion to a lower oxidation of +2.5 in $S_4O_6^{2-}$ ion. It is because of this reason that thiosulphate reacts differently with Br_2 and I_2 .

Q15. Justify giving reactions that among halogens, fluorine is the best oxidant and among hydrohalic compounds, hydroiodic acid is the best reductant.

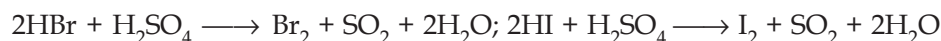
Ans. Halogens have a strong tendency to accept electrons. Therefore, they are strong oxidising agents. Their relative oxidising power is, however, measured in terms of their electrode potentials. Since the electrode potentials of halogens decrease in the order: $F_2 (+2.87V) > Cl_2 (+1.36V) > Br_2 (+1.09V) > I_2 (+0.54V)$, therefore, their oxidising power decreases in the same order.

This is evident from the observation that F_2 oxidises Cl^- to Cl_2 , Br^- to Br_2 , I^- to I_2 ; Cl_2 oxidises Br^- to Br_2 and I^- to I_2 but not F^- to F_2 . Br_2 , however, oxidises I^- to I_2 but not F^- to F_2 , and Cl^- to Cl_2 .

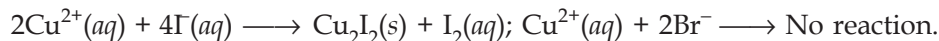


Thus, F_2 is the best oxidant.

Conversely, halide ions have a tendency to lose electrons and hence can act as reducing agents. Since the electrode potentials of halide ions decreases in the order: $I^- (-0.54 V) > Br^- (-1.09 V) > Cl^- (-1.36 V) > F^- (-2.87 V)$, therefore, the reducing power of the halide ions or their corresponding hydrohalic acids decreases in the same order: $HI > HBr > HCl > HF$. Thus, hydroiodic acid is the best reductant. This is supported by the following reactions. For example, HI and HBr reduce H_2SO_4 to SO_2 while HCl and HF do not.

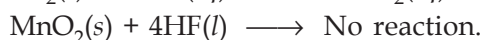
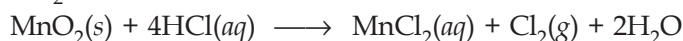


Further I^- reduces Cu^{2+} to Cu^+ but Br^- does not.



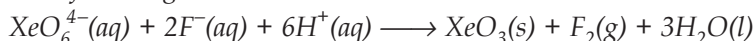
Thus, HI is a stronger reductant than HBr.

Further among HCl and HF, HCl is a stronger reducing agent than HF because HCl reduces MnO_2 to Mn^{2+} but HF does not.



Thus, the reducing character of hydrohalic acids decreases in the order: $HI > HBr > HCl > HF$.

Q16. Why does the following reaction occur?

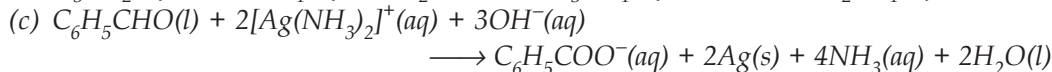
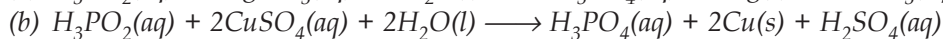
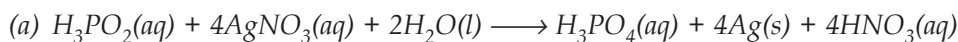


What conclusion about the compound Na_4XeO_6 (of which XeO_6^{4-} is a part) can be drawn from the reaction?

Ans. $\overset{+8}{Xe}O_6^{4-}(aq) + 2\overset{-1}{F}^-(aq) + 6\overset{+1}{H}^+(aq) \longrightarrow \overset{+6}{Xe}O_3(s) + \overset{0}{F}_2(g) + 3H_2O(l)$

Here, O.N. of Xe decreases from +8 in XeO_6^{4-} to +6 in XeO_3 while that of F increases from -1 in F^- to 0 in F_2 . Therefore, XeO_6^{4-} is reduced while F^- is oxidised. This reaction occurs because $Na_2XeO_6^{4-}$ (or XeO_6^{4-}) is a stronger oxidising agent than F_2 .

Q17. Consider the reactions:

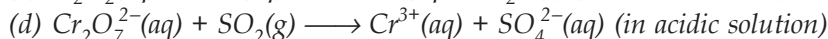
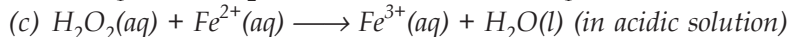
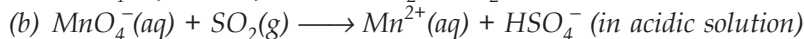


What inference do you draw about the behaviour of Ag^+ and Cu^{2+} from these reactions?

Ans. Reactions (a) and (b) indicate that H_3PO_2 (hypophosphorous acid) is a reducing agent and thus reduces both AgNO_3 and CuSO_4 to Ag and Cu respectively. Conversely, both AgNO_3 and CuSO_4 act as oxidising agent and thus oxidise H_3PO_2 to H_3PO_4 (orthophosphoric acid)

Reaction (c) suggests that $[\text{Ag}(\text{NH}_3)_2]^+$ oxidises $\text{C}_6\text{H}_5\text{CHO}$ (benzaldehyde) to $\text{C}_6\text{H}_5\text{COO}^-$ (benzoate ion) but reaction (d) indicates that Cu^{2+} ions cannot oxidise $\text{C}_6\text{H}_5\text{CHO}$ to $\text{C}_6\text{H}_5\text{COO}^-$. Therefore, from the above reactions, we conclude that Ag^+ ion is a strong deoxidising agent than Cu^{2+} ion.

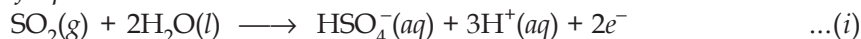
Q18. Balance the following redox reactions by ion-electron method.



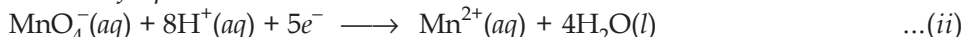
Ans. (a) Do it yourself.

(b) The balanced half reaction equations are:

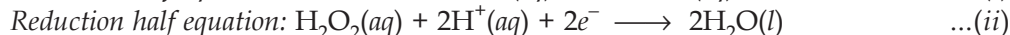
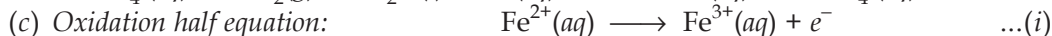
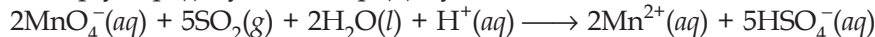
Oxidation half equation:



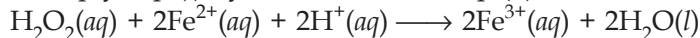
Reduction half equation:



Multiply Eq. (i) by 5 and Eq. (ii) by 2 and add, we have,

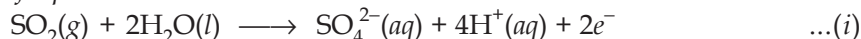


Multiply Eq. (i) by 2 and add it to Eq. (ii), we have,

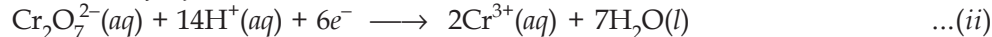


(d) Following the procedure detailed on page 8/23, the balanced half reaction equations are:

Oxidation half equation:



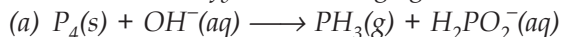
Reduction half equation:

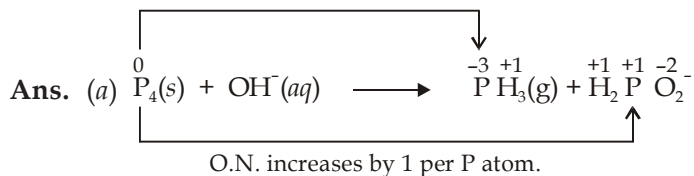
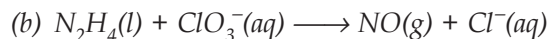


Multiply Eq. (i) by 3 and add it to Eq. (ii), we have,



Q19. Balance the following equation in basic medium by ion electron method and oxidation number method and identify the oxidising agent and the reducing agent.





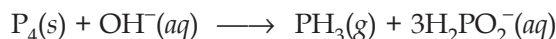
P_4 acts both as an oxidising as well as a reducing agent.

Oxidation number method:

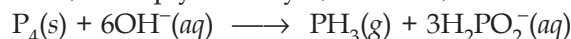
Total decrease in O.N. of P_4 in $PH_3 = 3 \times 4 = 12$

Total increase in O.N. of P_4 in $H_2PO_2^- = 1 \times 4 = 4$

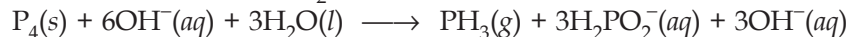
Therefore, to balance increases decreases in O.N. multiply PH_3 by 1 and $H_2PO_2^-$ by 3, we have,



To balance O atoms, multiply OH^- by 6, we have,



To balance H atoms, add $3H_2O$ to L.H.S. and $3OH^-$ to the R.H.S., we have,



or $P_4(s) + 3OH^-(aq) + 3H_2O(l) \longrightarrow PH_3(g) + 3H_2PO_2^-(aq)$... (i)

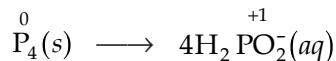
Thus, Eq. (i) represents the correct balanced equation.

Ion electron method. The two half reactions are:

Oxidation half reaction:



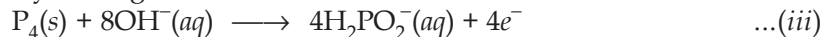
Balancing P atoms, we have,



Balance O.N. by adding electrons,



Balance charge by adding 8 OH^- ions,

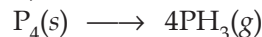


O and H get automatically balanced. Thus, Eq. (iii) represents the balanced oxidation half reaction.

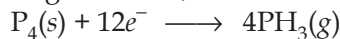
Reduction half reaction:



Balancing P atoms, we have,



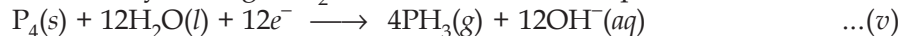
Balance O.N. by adding electrons,



Balance charge by adding $12OH^-$ ions,



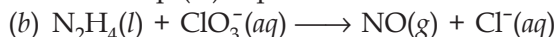
Balance O atoms, by adding $12H_2O$ to L.H.S. of above equation.



To cancel out electrons, multiply Eq. (iii) by 3 and add it to Eq. (v), we have,

$$4\text{P}_4(\text{s}) + 24\text{OH}^-(\text{aq}) + 12\text{H}_2\text{O}(\text{l}) \longrightarrow 4\text{PH}_3(\text{aq}) + 12\text{H}_2\text{PO}_2^-(\text{aq}) + 12\text{H}_2\text{O}(\text{l}) + 12\text{OH}^-(\text{aq})$$

or $\text{P}_4(\text{g}) + 3\text{OH}^-(\text{aq}) + 3\text{H}_2\text{O}(\text{l}) \longrightarrow \text{PH}_3(\text{aq}) + 3\text{H}_2\text{PO}_2^-(\text{aq}) \dots(\text{vi})$
 Thus, Eq. (vi) represents the correct balanced equation.

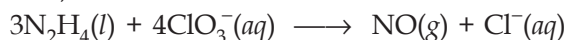


Oxidation number method

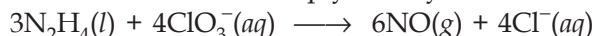
Total increase in O.N. of N = $2 \times 4 = 8$

Total decreases in O.N. of Cl = $1 \times 6 = 6$

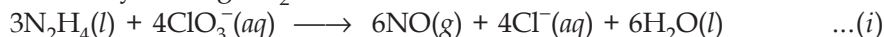
Therefore, to balance increase/decrease in O.N. multiply N_2H_4 by 3 and ClO_3^- by 4, we have,



To balance N and Cl atoms, multiply NO by 6 and Cl^- by 4, we have,

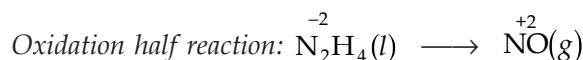


Balance O atoms by adding $6\text{H}_2\text{O}$,

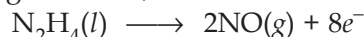


H atoms get automatically balanced and thus Eq. (i) represents the correct balanced equation.

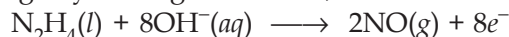
Ion electron method.



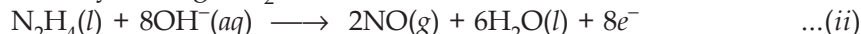
Balance O.N. by adding electrons,



Balance charge by adding 8OH^- ions,



Balance O atoms by adding $6\text{H}_2\text{O}$,

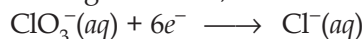


Thus, Eq. (ii) represents the correct balanced oxidation half equation.

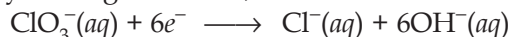
Reduction half reaction



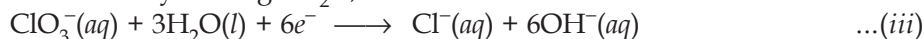
Balance O.N. by adding electrons,



Balance charge by adding OH^- ions,

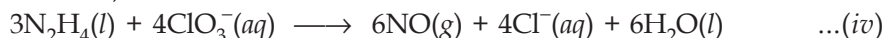


Balance O atoms by adding $3\text{H}_2\text{O}$,

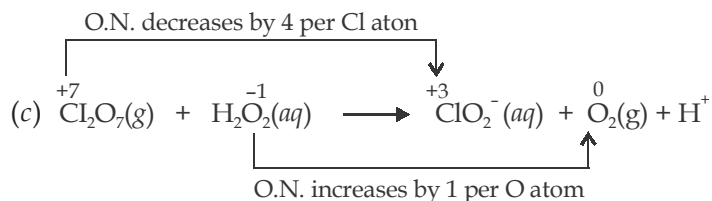


Thus, Eq. (iii) represents the correct balanced reduction half equation.

To cancel out electrons gained and lost, multiply Eq. (ii) by 3 and Eq. (iii) by 4 and add, we have,



Thus, Eq. (iv) represents the correct balanced equation



Thus, $\text{Cl}_2\text{O}_7(\text{g})$ acts an oxidising agent while $\text{H}_2\text{O}_2(\text{aq})$ as the reducing agent.

Oxidation number method

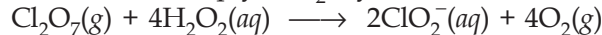
Total decrease in O.N. of $\text{Cl}_2\text{O}_7 = 4 \times 2 = 8$

Total increase in O.N. of $\text{H}_2\text{O}_2 = 2 \times 1 = 2$

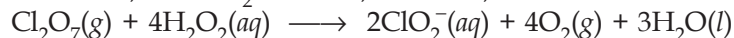
\therefore To balance increase/decrease in O.N. multiply H_2O_2 and O_2 by 4, we have,



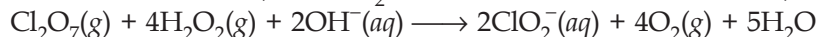
To balance Cl atoms, multiply ClO_2^- by 2, we have,



To balance O atoms, add $3\text{H}_2\text{O}$ R.H.S., we have,



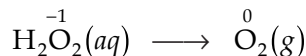
To balance H atoms, add $2\text{H}_2\text{O}$ to R.H.S. and 2OH^- to L.H.S., we have,



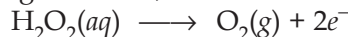
This represents the balanced redox equation.

Ion electron method

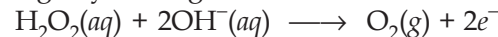
Oxidation half reaction:



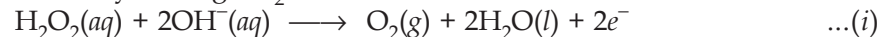
Balance O.N. by adding electrons,



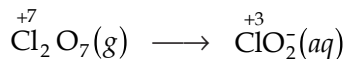
Balance charge by adding 2OH^- ions,



Balance O atoms by adding $2\text{H}_2\text{O}$,

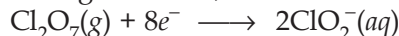


Reduction half reaction:

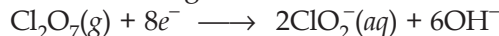


Balance Cl atoms; $\text{Cl}_2\text{O}_7(\text{g}) \longrightarrow 2\text{ClO}_2^-(\text{aq})$

Balance O.N. by adding electrons,



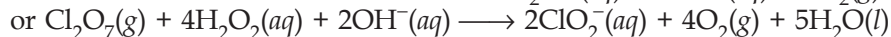
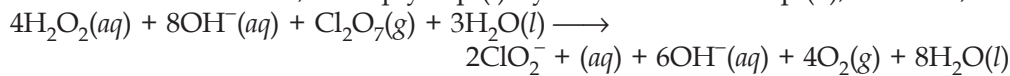
Add 6OH^- ions to balance charge:



Balance O atoms by adding $3\text{H}_2\text{O}$ to L.H.S., we have,



To cancel out electrons, multiply Eq. (i) by 4 and add it to Eq. (ii), we have,



Q20. Write four informations about the reaction:



Ans. Let x be the O.N. of C.

\therefore O.N. of C in cyanogen, $(\text{CN})_2 = 2(x - 3) = 0$ or $x = +3$

O.N. of C in cyanide ion, $\text{CN}^- = x - 3 = -1$ or $x = +2$

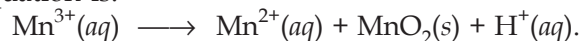
O.N. of C in cyanate ion, $\text{CNO}^- = x - 3 - 2 = -1$ or $x = +4$

The four information about the reaction are:

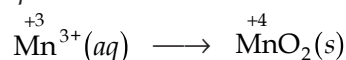
- The reaction involves decomposition of cyanogen, $(\text{CN})_2$ in the alkaline medium to cyanide ion, CN^- and cyanate ion, CNO^- .
- The O.N. of C decreases from +3 in $(\text{CN})_2$ to +2 in CN^- ion and increases from +3 in $(\text{CN})_2$ to +4 in CNO^- ion. Thus, cyanogen is simultaneously reduced to cyanide ion and oxidised to cyanate ion.
- It is an example of a redox reaction in general and a disproportionation reaction in particular.
- Cyanogen is a pseudohalogen (behaves like halogens) while cyanide ion is a pseudohalide ion (behaves like halide ion).

Q21. The Mn^{3+} ion is unstable in solution and undergoes disproportionation to give Mn^{2+} , MnO_2 and H^+ ion. Write a balanced ionic equation for the reaction.

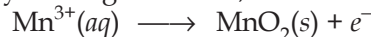
Ans. The skeletal equation is:



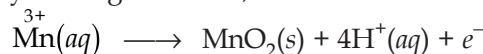
Oxidation half equation:



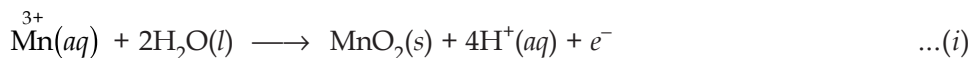
Balance O.N. by adding electrons,



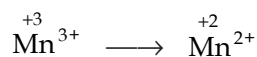
Balance charge by adding 4H^+ ions,



Balance O atoms by adding $2\text{H}_2\text{O}$:



Reduction half equation:



Balance O.N. by adding electrons:



Adding Eq. (i) and Eq. (ii), the balanced equation for the disproportionation reaction is



Q22. Consider the elements: Cs, Ne, I, F

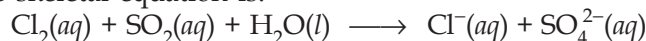
- Identify the element that exhibits $-ve$ oxidation state.
- Identify the element that exhibits $+ve$ oxidation state.
- Identify the element that exhibits both $+ve$ and $-ve$ oxidation states.
- Identify the element which neither exhibits $-ve$ nor $+ve$ oxidation state.

Ans. (a) F. Fluorine being the most electronegative element shows only a $-ve$ oxidation state of -1 .

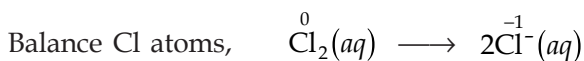
- (b) Cs. Alkali metals because of the presence of a single electron in the valence shell, exhibit an oxidation state of +1.
- (c) I. Because of the presence of seven electrons in the valence shell, I shows an oxidation state of -1 (in compounds of I with more electropositive elements such as H, Na, K, Ca, etc.) or an oxidation state of +1 (in compounds of I with more electronegative elements, i.e., O, F, etc.) and because of the presence of d-orbitals it also exhibits +ve oxidation states of +3, +5 and +7.
- (d) Ne. It is an inert gas (with high ionization enthalpy and high positive electron gain enthalpy) and hence it neither exhibits -ve nor +ve oxidation states.

Q23. Chlorine is used to purify drinking water. Excess of chlorine is harmful. The excess chlorine is removed by treating with sulphur dioxide. Present a balanced equation for the reaction for this redox change taking place in water.

Ans. The skeletal equation is:



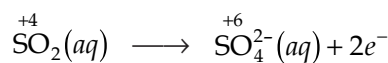
Reduction half equation:



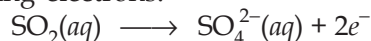
Balance O.N. by adding electrons:



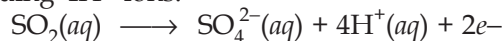
Oxidation half equation:



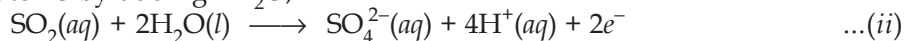
Balance O.N. by adding electrons:



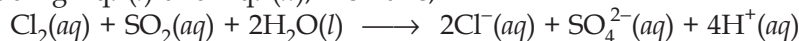
Balance charge by adding 4H^+ ions:



Balance O atoms by adding $2\text{H}_2\text{O}$,



Adding Eq. (i) and Eq. (ii), we have,



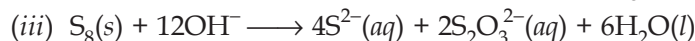
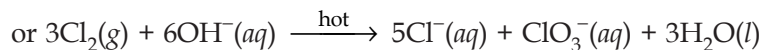
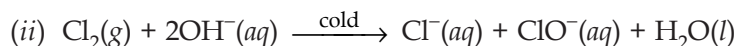
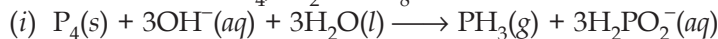
This represents the balanced redox reaction.

Q24. Refer to the periodic table given in your book and now answer the following questions.

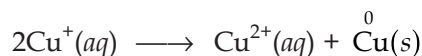
(a) Select the possible non-metals that can show disproportionation reaction.

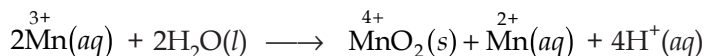
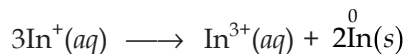
(b) Select three metals that show disproportionation reaction.

Ans. (a) The non-metals are: P_4 , Cl_2 and S_8 .



(b) The metals are: Cu^+ , Ga^+ , In^+ , Mn^{3+} , etc.





Q25. In Ostwald's process for the manufacture of nitric acid, the first step involves the oxidation of ammonia gas by oxygen gas to give nitric oxide gas and steam. What is the maximum weight of nitric oxide that can be obtained starting only with 10.0 g of ammonia and 20.0 g of oxygen?

Ans. The balanced equation for the reaction is:



Here, 68 g of NH_3 will react with $\text{O}_2 = 160 \text{ g}$

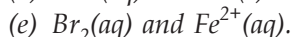
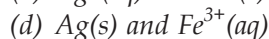
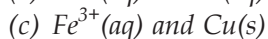
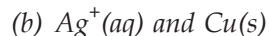
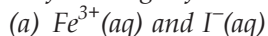
$$\therefore 10 \text{ g of } \text{NH}_3 \text{ will react with } \text{O}_2 = \frac{160 \text{ g}}{68 \text{ g}} \times 10 \text{ g} = 23.6 \text{ g}$$

But the amount of O_2 which is actually available is 20.0 g which is less than the amount which is needed. Therefore, O_2 is the **limiting reagent** and hence calculations must be based upon the amount of O_2 taken and not on the amount of NH_3 taken. From the equation,

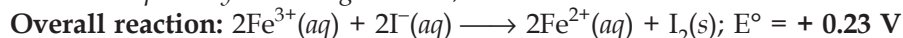
$$160 \text{ g of } \text{O}_2 \text{ produce NO} = 120 \text{ g}$$

$$\therefore 20 \text{ g of } \text{O}_2 \text{ will produce NO} = \frac{120}{160} \times 20 = \mathbf{15 \text{ g}}$$

Q26. Using the standard electrode potentials given in the Table 8.1, predict if the reaction between the following is feasible:

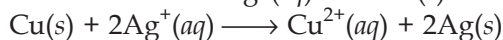


Ans. (a) It may be noted that for oxidation reactions, i.e., Eq. (i), the sign of the electrode potential as given in Table 8.1 is reversed. To get the equation for the overall reaction, the number of electrons lost in Eq. (i) and gained in Eq. (ii) must be cancelled. To do so, Eq. (ii) is multiplied by 2 and added to Eq. (i). Further, it may be noted that whenever any half reaction equation is multiplied by any integer, its electrode potential is not multiplied by that integer. Thus,

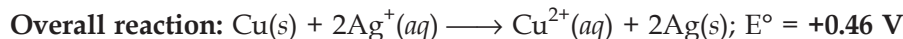
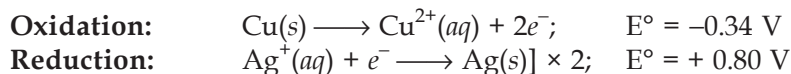


Since the EMF for the above reaction is **positive**, therefore, the above reaction is feasible.

(b) The possible reaction between $\text{Ag}^+(aq)$ and $\text{Cu}(s)$ is

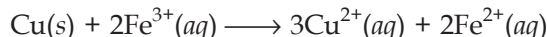


The above redox reaction can be split into the following two half reactions. Writing electrode potential for each half reaction from Table 8.1, we have,

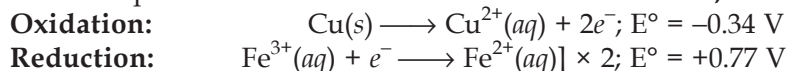


Since the EMF of the above reaction comes out to be **positive**, therefore, *the above reaction is feasible*.

- (c) Suppose the reaction between $\text{Fe}^{3+}(\text{aq})$ and Cu(s) occurs according to the following equation.



The above reaction can be split into the following two half reactions. Writing electrode potential for each half reaction from Table 8.1, we have,



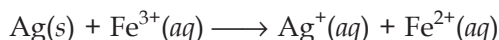
Since the EMF of the reaction is positive, therefore, *the above reaction is feasible*.

Alternatively, if the reaction between $\text{Fe}^{3+}(\text{aq})$ and Cu(s) occurs according to the following equation.

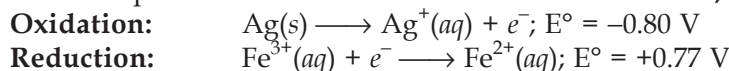


The EMF of the reaction comes out to be *-ve*, i.e., -0.376 V ($-0.34 \text{ V} - 0.036 \text{ V}$) and hence this reaction is not feasible.

- (d) Suppose the reaction between Ag(s) and $\text{Fe}^{3+}(\text{aq})$ occurs according to the following equation:



The above reaction can be split into the following two half reactions. Writing electrode potential for each half reaction from Table 8.1, we have,



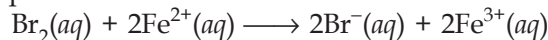
Since the EMF of the reaction is **negative**, therefore, the above reaction is *not feasible*.

Alternatively, the reaction between Ag(s) and $\text{Fe}^{3+}(\text{aq})$ may occur according to the following equation

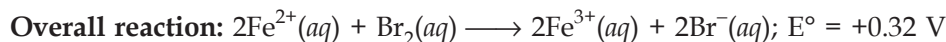
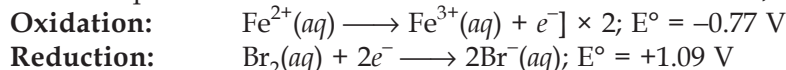


On similar lines, we can calculate the e.m.f. of this reaction comes to be even more **negative**, i.e., -0.836 V , and hence this redox reaction is also not *feasible*.

- (e) Suppose the reaction between $\text{Br}_2(\text{aq})$ and $\text{Fe}^{2+}(\text{aq})$ occurs according to the following equation:



The above reaction can be split into the following two half reactions. Writing electrode potential for each half reaction from the Table 8.1, we have

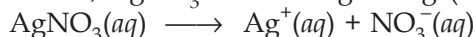


Since the EMF for the above reaction is **positive**, therefore, *this reaction is feasible*.

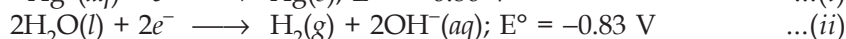
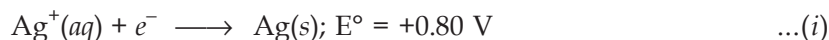
Q27. Predict the products of electrolysis in each of the following:

- (i) An aqueous solution of AgNO_3 with silver electrodes.
- (ii) An aqueous solution of silver nitrate with platinum electrodes.
- (iii) A dilute solution of H_2SO_4 with platinum electrodes.
- (iv) An aqueous solution of CuCl_2 with platinum electrodes.

Ans. (i) In aqueous solution, AgNO_3 ionises to give $\text{Ag}^+(\text{aq})$ and $\text{NO}_3^-(\text{aq})$ ions.

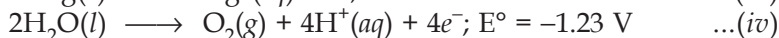
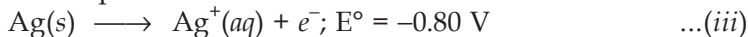


Thus, when electricity is passed, $\text{Ag}^+(\text{aq})$ ions move towards the cathode while NO_3^- ions move towards the anode. In other words, at the cathode, either $\text{Ag}^+(\text{aq})$ ions or H_2O molecules may be reduced. Which of these will actually get discharged would depend upon their electrode potentials which are given below:



Since the electrode potential (*i.e.*, reduction potential) of $\text{Ag}^+(\text{aq})$ ions is higher than that of H_2O molecules, therefore, **at the cathode**, it is the $\text{Ag}^+(\text{aq})$ ions (rather than H_2O molecules) which are reduced.

Similarly, at the anode, either Ag metal of the anode or H_2O molecules may be oxidised. Their electrode potentials are:



Since the oxidation potential of Ag is much higher than that of H_2O , therefore, **at the anode**, it is the Ag of the silver anode which gets oxidised and not the H_2O molecules. It may, however, be mentioned here that the oxidation potential of NO_3^- ions is even lower than that of H_2O since more bonds are to be broken during reduction of NO_3^- ions than those in H_2O .

Thus, when an aqueous solution of AgNO_3 is electrolysed, Ag from Ag anode dissolves while $\text{Ag}^+(\text{aq})$ ions present in the solution get reduced and get deposited on the cathode.

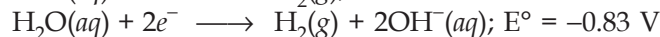
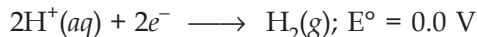
- (ii) If, however, electrolysis of AgNO_3 solution is carried out using platinum electrodes, instead of silver electrodes, oxidation of water occurs at the anode since Pt being a noble metal does not undergo oxidation easily. As a result, O_2 is liberated at the anode according to equation (iv).

Thus, when an aqueous solution of AgNO_3 is electrolysed using platinum electrodes, Ag^+ ions from the solution get deposited on the cathode while O_2 is liberated at the anode.

- (iii) In aqueous solution, H_2SO_4 ionises to give $\text{H}^+(\text{aq})$ and $\text{SO}_4^{2-}(\text{aq})$ ions.



Thus, when electricity is passed, $\text{H}^+(\text{aq})$ ions move towards cathode while $\text{SO}_4^{2-}(\text{aq})$ ions move towards anode. In other words, at cathode either $\text{H}^+(\text{aq})$ ions or H_2O molecules are reduced. Their electrode potentials are:



Since the electron potential (*i.e.*, reduction potential) of $\text{H}^+(\text{aq})$ ions is higher than that of H_2O , therefore, **at the cathode**, it is $\text{H}^+(\text{aq})$ ions (rather than H_2O molecules) which are reduced to evolve H_2 gas.

Similarly at the anode, either $\text{SO}_4^{2-}(\text{aq})$ ions or H_2O molecules are oxidised. Since the oxidation potential of SO_4^{2-} is expected to be much lower (since it

involved cleavage of many bonds as compared to those in H_2O) than that of H_2O molecules, therefore, **at the anode**, it is H_2O molecules (rather than SO_4^{2-} ions) which are oxidised to evolve O_2 gas.

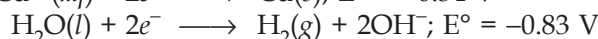
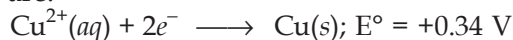
From the above discussion, it follows that during electrolysis of an aqueous solution of H_2SO_4 , only the electrolysis of H_2O occurs liberating H_2 at the cathode and O_2 at the anode.

(iv) In aqueous solution, CuCl_2 ionises as follows:



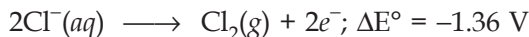
On passing electricity, $\text{Cu}^{2+}(aq)$ ions move towards cathode and $\text{Cl}^-(aq)$ ions move towards anode.

Thus, at cathode, either $\text{Cu}^{2+}(aq)$ or H_2O molecules are reduced. Their electrode potentials are:



Since the electrode potential of $\text{Cu}^{2+}(aq)$ ions is much higher than that of H_2O , therefore, **at the cathode**, it is $\text{Cu}^{2+}(aq)$ ions which are reduced and not H_2O molecules.

Similarly, at the anode, either $\text{Cl}^-(aq)$ ions or H_2O molecules are oxidised. Their oxidation potentials are:



Although oxidation potential of H_2O molecules is higher than that of Cl^- ions, nevertheless, oxidation of $\text{Cl}^-(aq)$ ions occurs in preference to H_2O since due to **overvoltage*** much lower potential than -1.36 V is needed for the oxidation of H_2O molecules.

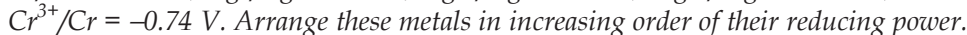
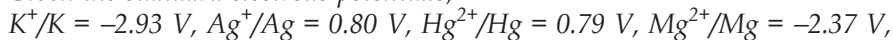
Thus, when an aqueous solution of CuCl_2 is electrolysed, Cu metal is liberated at the cathode while Cl_2 gas is evolved at the anode.

Q28. Arrange the following metals in the order in which they displace each other from the solution of their salts.

Al, Cu, Fe, Mg and Zn.

Ans. It is based upon the relative positions of these metals in the activity series. The correct order is Mg, Al, Zn, Fe, Cu

Q29. Given the standard electrode potentials,



Ans. Lower the electrode potential, better is the reducing agent. Since the electrode potentials increase in the order; K^+/K (-2.93 V), Mg^{2+}/Mg (-2.37 V), Cr^{3+}/Cr (-0.74 V), Hg^{2+}/Hg (0.79 V), Ag^+/Ag (0.80 V), therefore, reducing power of metals decreases in the same order, i.e., K, Mg, Cr, Hg, Ag.

Q30. Depict the galvanic cell in which the reaction, $\text{Zn}(s) + 2\text{Ag}^+(aq) \longrightarrow \text{Zn}^{2+}(aq) + 2\text{Ag}(s)$ takes place. Further show:

(i) which of the electrode is negatively charged.

(ii) the carriers of current in the cell and

(iii) individual reaction at each electrode.

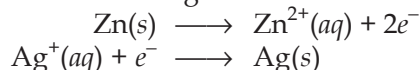
Ans. The given redox reaction is $\text{Zn}(s) + 2\text{Ag}^+(aq) \longrightarrow \text{Zn}^{2+}(aq) + 2\text{Ag}(s)$

Since Zn gets oxidised to Zn^{2+} ions, and Ag^+ gets reduced to Ag metal, therefore,

oxidation occurs at the zinc electrode and reduction occurs at the silver electrode. Thus, galvanic cell corresponding to the above redox reaction may be depicted as:



- (i) Since oxidation occurs at the zinc electrode, therefore, electrons accumulate on the zinc electrode and hence, *zinc electrode is negatively charged*.
- (ii) The ions carry current. The electrons flow from Zn to Ag electrode while the current flows from Ag to Zn electrode.
- (iii) The reactions occurring at the two electrodes are:



MORE QUESTIONS SOLVED

I. VERY SHORT ANSWER TYPE QUESTIONS

Q1. Define electrochemical cell.

Ans. Electrochemical cell is a device in which the redox reaction is carried indirectly and the decrease in free energy appears as electrical energy.

Q2. What is a redox couple?

Ans. A redox couple consists of oxidised and reduced form of the same substance taking part in the oxidation or reduction half reaction.

Q3. Define oxidation in terms of electronic concept.

Ans. Oxidation involves loss of one or more electrons by a species during a reaction.

Q4. What is the source of electrical energy in a galvanic cell?

Ans. In a galvanic cell due to redox reaction released energy gets converted into the electrical energy.

Q5. What is the oxidation state of Ni in $\text{Ni}(\text{CO})_4$?

Ans. Zero.

Q6. What is the oxidation number of P in H_3PO_4 ?

Ans. $\overset{+1}{\text{H}}_3 \overset{x}{\text{P}} \overset{-2}{\text{O}}_4$ let the oxidation no. of P in H_3PO_4 be x.

Calculate the sum of the oxidation numbers of all the atoms

$$\begin{aligned} 3(+1) + x + 4(-2) &= 0 \\ = 3 + x - 8 &= x - 5 = 0 \\ x &= +5 \end{aligned}$$

Q7. What is salt bridge?

Ans. It is a U-shaped tube filled with agar-agar containing inert electrolyte like KCl or KNO_3 which does not react with solutions.

Q8. What is meant by reducing agent? Name the best reducing agent.

Ans. A species which loses electrons as a result of oxidation is a reducing agent. Li (Lithium).

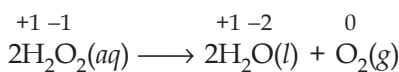
Q9. Why is standard hydrogen electrode called reversible electrode?

Ans. A standard hydrogen electrode is called reversible electrode because it can react both as anode as well as cathode in an electrochemical cell.

Q10. What is a disproportionation reaction? Give one example.

Ans. In a disproportionation reaction an element in one oxidation state is simultaneously oxidised and reduced.

For example,



Here the oxygen of peroxide, which is present in -1 state is converted to zero oxidation state in O_2 and decreases to -2 oxidation state in H_2O .

Q11. What is a standard hydrogen electrode?

Ans. Standard hydrogen electrode is known as reference electrode. Its electrode potential is taken as 0.000 volt.

Q12. What is meant by cell potential?

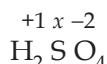
Ans. It is the difference in Standard Reduction Potential (SRP) of cathode and SRP of anode.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode (SRP)}} - E^\circ_{\text{anode (SRP)}}$$

Q13. Calculate the oxidation number of sulphur in H_2SO_4 and Na_2SO_4 .

Ans. Let the oxidation number of S in H_2SO_4 be x .

Write the oxidation number of each atom above its symbol.



Calculate the sum of the oxidation numbers of all the atoms.

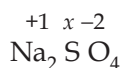
$$2(+1) + x + 4(-2) = 0$$

$$x - 6 = 0$$

$$x = +6$$

In Na_2SO_4

Write the oxidation number of each atom its symbol.



Calculate the sum of the oxidation numbers of all the atoms.

$$2(+1) + x + 4(-2) = 0$$

$$2 + x - 8 = 0$$

$$x = +6$$

Q14. Define Oxidation and Reduction in terms of oxidation number.

Ans. Oxidation involves increase in O.N while reduction involves decrease in O.N.

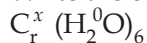
Q15. Define EMF of cell.

Ans. EMF of a cell is the difference in the electrode potentials of the two electrodes in a cell when no current flows through the cell.

Q16. Calculate the oxidation number of Cr in $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ion.

Ans. As H_2O is a neutral molecule O.N of $\text{H}_2\text{O} = 0$

Write the oxidation number of Cr above its symbol and that of H_2O above its formula,



$$x + 6(0) = x$$

Since $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ is an ion, the sum of the oxidation numbers must be $x = +3$.

Q17. How can CuSO_4 solution not be stored in an iron vessel?

Ans. It is because $E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \text{ V}$ which is lower than that of Cu.

$$\begin{aligned} E^\circ_{\text{Cell}} &= E^\circ_{\text{Cu}^{2+}/\text{Cu}} - E^\circ_{\text{Fe}^{2+}/\text{Fe}} \\ &= +0.34 \text{ V} - (-0.44 \text{ V}) \\ &= 0.78 \text{ V} \end{aligned}$$

Since, $E^\circ_{\text{Cell}} = +\text{ve}$, $\Delta G = -\text{ve}$

i.e., reaction will take place, we cannot store CuSO_4 in an iron container.

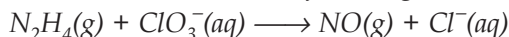
Q18. How will you identify cathode and anode in electrochemical cell?

Ans. At cathode there is gain of electrons.

At anode there is loss of electrons.

In electrochemical cell anode is written on L.H.S while cathode is written on R.H.S.

Q19. Identify the oxidant and the reductant in the following reaction.

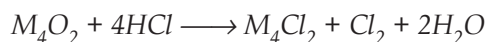


Ans. N_2H_4 is reducing agent i.e., reductant whereas ClO_3^- is oxidising agent i.e., oxidant.

Q20. What is oxidation number of Fe in $[\text{Fe}(\text{CO})_5]$?

Ans. $x + 5(0) = 0$
 $x = 0$

Q21. In the reaction



which species is oxidised.

Ans. HCl gets oxidised.

II. SHORT ANSWER TYPE QUESTIONS

Q1. What is meant by electrochemical series? What are characteristics of electrochemical series?

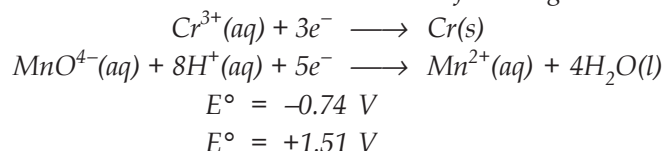
Ans. Electrochemical series is the series of elements in which elements are arranged in decreasing order of their reduction potential.

Reducing power goes on increasing whereas oxidising power goes on decreasing down the series.

Q2. What is standard hydrogen electrode? For what purpose it is used? What are signs of oxidation potential and reduction potential decided by using SHE (Standard hydrogen electrode)?

Ans. Standard hydrogen electrode is used as reference electrode. Its electrode potential is taken as 0.000 volt. Hydrogen electrode can be made. If we use a piece of platinum coated with finely divided black containing hydrogen gas absorbed in it. Platinum black catalyses the reaction and equilibrium is attained faster. When the given electrode acts as anode SHE, we give -ve sign to its reduction potential and +ve sign to its oxidation potential.

Q3. Consider a voltaic cell constructed with the following substances:



(a) Which substances are oxidised and reduced in this cell?

(b) Which are the negative and positive electrode?

Ans. (a) Cr is getting oxidised and MnO_4^- is getting reduced.

(b) Cr is negative electrode, Pt in MnO_4^- acts as positive electrode.

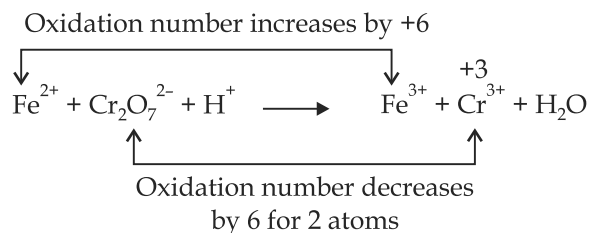
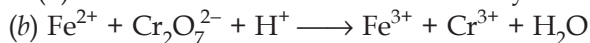
Q4. (a) Give two important functions of salt bridge.

(b) Balance the following equation by oxidation number method:



Ans. (a) (i) It completes the internal circuit.

(ii) It maintains the electrical neutrality.



Q5. Write the O.N of all the atoms for the following well known oxidants?

(i) KMnO_4 (ii) $\text{K}_2\text{Cr}_2\text{O}_7$ (iii) KClO_4

Ans. (i) KMnO_4 ; K(+1); Mn(+7), O(-2)

(ii) $\text{K}_2\text{Cr}_2\text{O}_7$; K(+1); Cr(+6); O(-2)

(iii) KClO_4 ; K(+1); Cl(+7); O(-2)

Q6. (a) Arrange the following in order of increasing O.N of iodine:

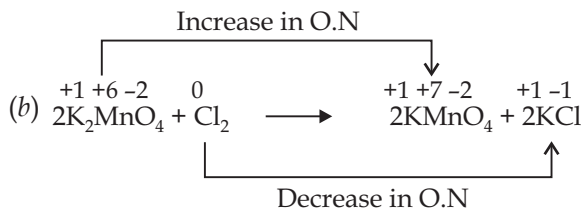
I_2 , HI , HIO_2 , KIO_3 , ICl .

(b) Identify the oxidant and reductant in the following redox reaction:



Ans. (a) The increasing order is

$\text{HI} < \text{I}_2 < \text{ICl} < \text{HIO}_2 < \text{KIO}_3$



chlorine is an oxidant and K_2MnO_4 is reductant.

Q7. Write the cell reactions:



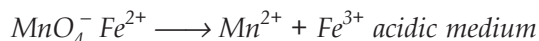
$$E^\circ \text{Zn}^{2+}/\text{Zn} = -0.76 \text{ V}, E^\circ \text{Cd}^{2+}/\text{Cd} = 0.40 \text{ V}$$

Ans. At anode: $\text{Zn}(s) \longrightarrow \text{Zn}^{2+}(aq) + 2e^-$

At cathode: $\text{Cd}^{2+}(aq) + 2e^- \longrightarrow \text{Cd}(s)$



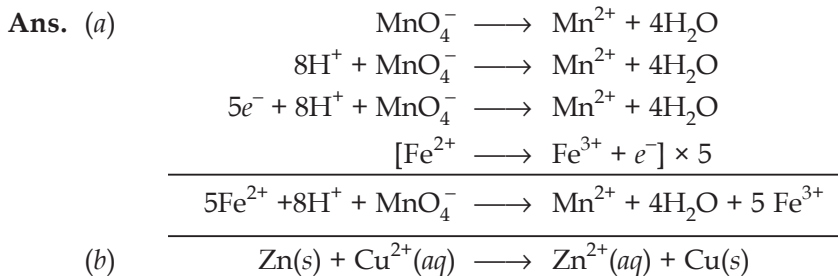
Q8. (a) Balance the following equation by oxidation number method or by ion electron (half reaction) method.



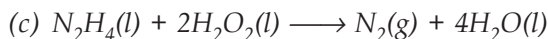
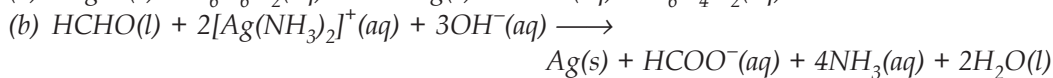
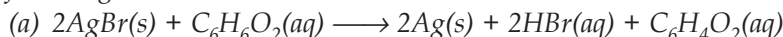
(b) Consider the cell,



The standard electrode potentials are $E^\circ \text{Zn}^{2+}/\text{Zn} = -0.76 \text{ V}$; $E^\circ \text{Cu}^{2+}/\text{Cu} = +0.34 \text{ V}$ write down the cell reaction.



Q9. Identify the substance oxidised, reduced, oxidising agent and reducing agent for each of the following reactions.



Ans. (a) Ag^+ is reduced, $\text{C}_6\text{H}_6\text{O}_2$ is oxidised.

Ag^+ is oxidising agent whereas $\text{C}_6\text{H}_6\text{O}_2$ is reducing agent.

(b) HCHO is oxidised, Ag^+ is reduced.

Ag^+ is oxidising agent whereas HCHO is reducing agent.

(c) N_2H_4 is getting oxidised it is reducing agent.

H_2O_2 is getting reduced it acts as an oxidising agent.

Q10. (a) Calculate the oxidation number of

(i) C in CH_3COOH (ii) S in $\text{S}_2\text{O}_8^{2-}$

(b) Give one example of disproportionation reaction.

Ans. (a) (i)

$$4 \times 1 - 2 \times 2 + 2(x) = 0$$

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

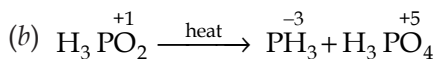
$$2x = 0$$

$$x = 0$$

(ii) $2x - 12 - 2 = -2$

$$2x = 12$$

$$x = +6$$



Since P undergoes decrease as well as increase in oxidation state thus it is an example of disproportionation reaction.

III. MULTIPLE CHOICE QUESTIONS

1. Among the following molecules, in which does bromine show the maximum oxidation number?

(a) $\text{Hg}_2(\text{BrO}_3)_2$ (b) Br - Cl (c) KBrO_4 (d) Br_2

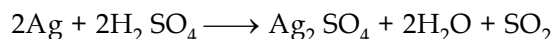
2. Which of the following halogens do not exhibit a positive oxidation number in their compounds?

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

3. Which of the following is most powerful oxidizing agent in the following.

(a) O_3 (b) KMnO_4 (c) H_2O_2 (d) $\text{K}_2\text{Cr}_2\text{O}_7$

4. On the reaction



sulphuric acid acts as

- (a) an oxidizing agent (b) a reducing agent
(c) a catalyst (d) an acid as well as an oxidant
5. The oxidation number of the carboxylic carbon atom in CH_3COOH is
(a) +2 (b) +4 (c) +1 (d) +3
6. When methane is burnt in oxygen to produce CO_2 and H_2O the oxidation number of carbon changes by
(a) -8 (b) zero (c) +8 (d) +4
7. The oxidation number of carbon is zero in
(a) HCHO (b) CH_2Cl_2 (c) $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ (d) $\text{C}_6\text{H}_{12}\text{O}_6$
(e) all of the above
8. Which of the following are not redox reactions?
(a) $\text{Mg} + \text{N}_2 \longrightarrow \text{Mg}_3\text{N}_2$
(b) $\text{K}_4[\text{Fe}(\text{CN})_6] + \text{H}_2\text{SO}_4 + \text{H}_2\text{O} \longrightarrow \text{K}_2\text{SO}_4 + \text{CO} + \text{FeSO}_4 + (\text{NH}_4)_2\text{SO}_4$
(c) $\text{I}_2 + 3\text{Cl}_2 \longrightarrow \text{ICl}_3$
(d) $\text{CuSO}_4 + \text{NH}_3 \longrightarrow [\text{Cu}(\text{NH}_3)_4]\text{SO}_4$
9. Which one among the following is not example of autoredox reaction?
(a) $\text{P}_4 + \text{OH}^- \longrightarrow \text{H}_2\text{PO}_4^- + \text{PH}_3$ (b) $\text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + \text{O}_2$
(c) $\text{S}_2\text{O}_3^{2-} \longrightarrow \text{SO}_4^{2-} + \text{S}$ (d) $\text{AgCl} + \text{NH}_3 \longrightarrow [\text{Ag}(\text{NH}_3)_2]\text{Cl}$
10. In the ethylene molecule the two carbon atoms have the oxidation numbers.
(a) -1, -1 (b) -2, -2 (c) -1, -2 (d) +2, -2

- Ans. 1. (c) 2. (a) 3. (a) 4. (d) 5. (d)
6. (d) 7. (e) 8. (b) and (d) 9. (d) 10. (b)

IV. HOTS QUESTIONS

Q1. (a) Formulate possible compounds of 'Cl' in its O.S. is: 0, -1, +1, +3, +5, +7.

(b) List three measures used to prevent rusting of iron.

Ans. (a) Cl_2 , HCl , HOCl , HOCIO , HOCIO_2 , HOCIO_3 respectively.

(b) (i) galvanization (coating iron by a more reactive metal)

(ii) greasing/oiling

(iii) painting

Q2. Account for the following:

(a) While H_2O_2 can act as oxidising as well as reducing agent in their reactions, O_3 and HNO_3 acts as oxidants only.

(b) When conc. H_2SO_4 is added to an inorganic mixture containing chloride, HCl is produced but if a mixture contains bromide, then we get red vapours of bromine.

Ans. (a) In H_2O_2 oxidation number of O = -1 and can vary from 0 to -2 (+2 is possible in OF_2). The oxidation number can decrease or increase, because of this H_2O_2 can act both oxidising and reducing agent.

(b) HCl is a weak reducing agent and can reduce H_2SO_4 to SO_2 and hence HCl is not oxidised to Cl_2 . When NaBr is heated HBr is produced, which is a strong reducing agent and itself oxidised to red vapour of Br_2 .

Q3. Account for the following:

- (a) HNO_3 acts only as an oxidising agent while HNO_2 can act both as reducing and oxidising agent.
- (b) ClO_4^- does not show disproportionation reaction.
- (c) Ozone acts as an oxidising agent.

[Hint: (a) The oxidation number of nitrogen in HNO_3 is +5 thus increase in oxidation number +5 does not occur hence HNO_3 cannot act as reducing agent but acts as an oxidising agent. In HNO_2 oxidation number of nitrogen is +3, it can decrease or increase with range of -3 to +5, hence it can act as both oxidising and reducing agent.

(b) Chlorine is in maximum oxidation state +7 in ClO_4^- so it does not show the disproportionation reaction.

(c) Because it decomposes to give nascent oxygen.

