

Chapter-2

REDOX REACTIONS

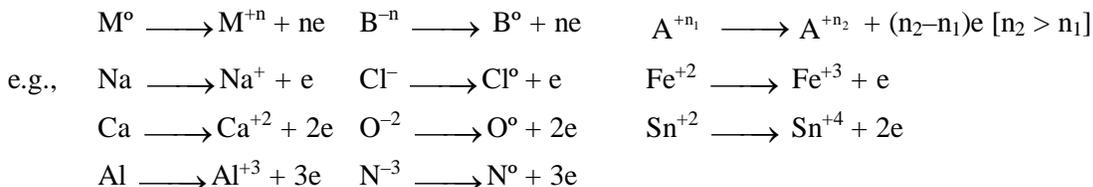
A number of chemical process like burning of LPG gas or coal, corrosion of metals like rusting of iron, digestion of food in living beings, creation of holes in ozone layer by oxidation of CFC by ozone are certain interesting examples of redox reactions

Initially oxidation was defined as addition of O_2 or loosing hydrogen by any species while reduction was defined as addition of hydrogen or loss of oxygen from any species.

Oxidation :

An oxidation is that kind of chemical process during which

- (a) De-electronation either from an atom or an ion take place.
- (b) Oxidation number of an atom increases.
- (c) Some extra energy is required in order to do work against the force of attraction acting between the valence electron and the nucleus. (i.e., it is an endothermic process).



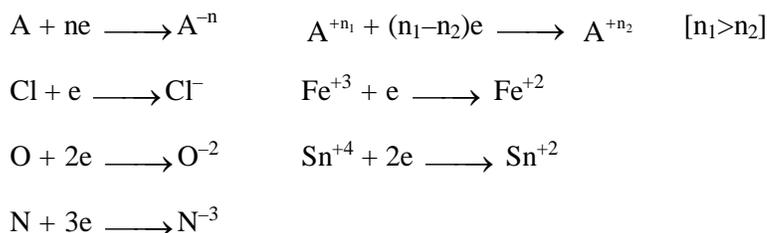
Oxidation increases down the groups from top to bottom while it decreases along the periods from left to right. The extent of oxidation depends upon the following factors :

- (a) No. of valence electrons.
- (b) Magnitude of attractive force operating between the valence electron & the nucleus.
- (c) Electronic arrangement in the valence orbitals.

Reduction

Reduction is that chemical process during

- (a) which electronation of either an atom or an ion take place.
- (b) oxidation no. of an atom decreases.
- (c) some energy is released (it is an exothermic process).



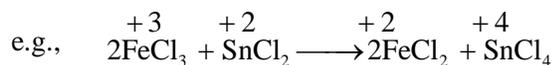
The tendency of an atom to undergo reduction decreases down the groups from top to bottom while it increases along the periods from left to right except some exceptions.

Reduction depends upon the following factors :

- No. of valence electrons.
- Magnitude of repulsive force acting between the extra electron and the valence electrons.
- Electronic arrangement in valence orbitals

Redox-Reactions :

Redox reactions are those chemical reactions during which both oxidation and reduction take place simultaneously.



Oxidising and Reducing Agent :

Oxidising agent (OA):

An oxidising agent is that

- which undergoes reduction.
- which accept electron/electrons.
- whose oxidation number decreases.
- oxidise others but itself reduced.

e.g., KMnO_4 , H_2SO_4 , HNO_3 , F_2 etc.

Identification :

- Generally the names of an oxidising agent end either in “ate” or “ic”.

e.g., $\text{H}_2\text{SO}_4 \longrightarrow$ Sulphuric acid.

$\text{HNO}_3 \longrightarrow$ Nitric acid.

$\text{KMnO}_4 \longrightarrow$ Potassium permanganate.

$\text{K}_2\text{Cr}_2\text{O}_7 \longrightarrow$ Potassium dichromate.

- The oxidation number of an atom of such molecules should be in its highest value.



- Except carbon, all the non-metals are oxidising agents. F is the strongest non-metal; being most electronegative.

Reducing Agent (R.A.):

A reducing agent is that atom or molecule :

- which undergo oxidation during reactions.
- which lose electron/electrons.

(c) whose oxidation number increases.

e.g., H_2S , FeS , Cu_2O , FeCl_2 , Na , C , Fe etc.

Identification :

(a) Generally the names of reducing agents end either in “ous” or “ide”.

$\text{FeCl}_2 \longrightarrow$ Ferrous chloride.

$\text{H}_2\text{S} \longrightarrow$ Hydrogen sulphide.

(b) The O.N. of a constituent atom should be in its lowest oxidation number value. H_2S^{-2} ; HI .

(c) All the metals are reducing agents. Cs is the strongest reducing metal.

* Oxidising property increases along the periods from left to right while reducing property of the elements increases down the groups from top to bottom.

* Highest O.N. = groups no. in Mendeleev’s table (Exception Cu & Au).

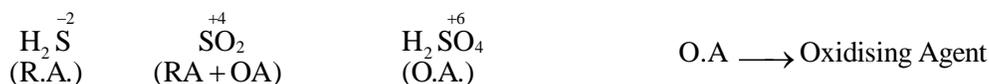
* Lowest O.N. = group no. – 8

where, G = groups no. of the element in long form of P.T.

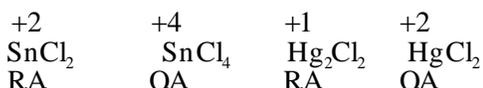
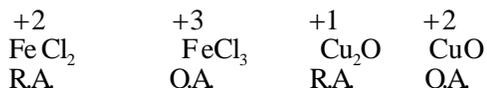
* (a) If the O.N. of an atom will be equal to its highest O.N. value then it will be an oxidising agent.

(b) If the O.N. of an atom in a molecule will be equal to its lowest O.N. value then it will be a reducing agent.

(c) If the O.N. of an atom will be in between highest & lowest O.N. then the molecule will behave like an oxidising as well as a reducing agent.



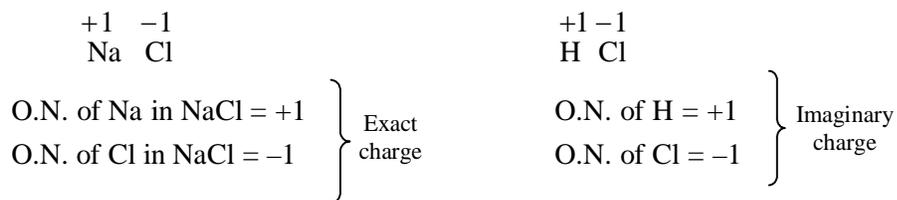
* If the same atom will form two different molecules in different O.N., then the molecule with lower O.N. atom will behave like a reducing agent while the molecule with higher O.N. value will be an oxidising agent.



Oxidation number :

Oxidation number of an atom is either real or imaginary charge which appears to be associated with an atom either in a molecule or an ion. In case of electrovalent molecules the charge will be real while in case of polar covalent molecules the charge will be imaginary. It suggests the extent of oxidation and reduction of

an atom during reactions. **It may be either a whole no., fraction or even zero.** The positive O.N. suggest the oxidation while negative O.N. suggests the reduction.



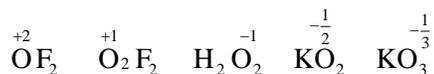
Note : the concept of oxidation number is to give a imaginary charge on every atom so that neutrality of every species is explained. Therefore to know about the exact nature and charge on the atom the structure of the species must be taken into consideration and the results derived out of the structure are more correct than what are predicted by the oxidation number.

Determination of Oxidation number

- (1) In uncombined state or free state the oxidation number of an element is zero.
 $\text{Na}^\circ, \text{P}_4^\circ, \text{F}^\circ, \text{Ca}^\circ$
- (2) In case of a molecule, the algebraic sum of the oxidation numbers of the atoms present in the molecule is equal to zero.
- (3) In case of ions or complex ion, the sum of the O.N. of the atoms present in the ion is equal to the charge present on the ion.
- (4) In combined forms :
 - (a) O.N. of Alkali metals is always +1.
Li, Na, K, Rb, Cs are alkali metals.
 - (b) O.N. of alkaline earth metals is always +2
Be, Mg, Ca, Sr, Ba are alkaline earth metals.
 - (c) O.N. of Al is always +3.
- (5) In combined forms
 - (a) O.N. of F is always -1.
 - (b) O.N. of H is usually +1, in metallic hydrides it is -1. In interstitial hydrides it is 0.
 - (c) Usually oxygen show -2 oxidation no. In peroxide its O.N. is -1. It can show positive O.N. with F.

In super oxides it is $-\frac{1}{2}$ (eg. Pot. superoxide KO_2).

In ozonides it is $-\frac{1}{3}$ (e.g., Pot. Ozonide KO_3).

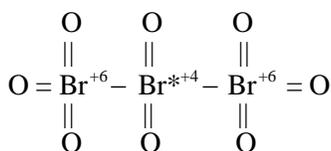
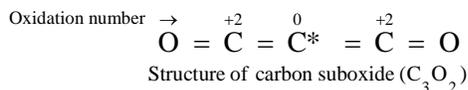


- (d) O.N. of halogens are usually -1. But in interhalogen compounds it show +ve O.N. value

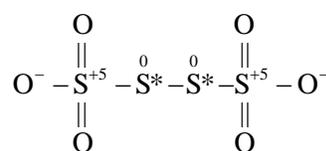


F always show -ve O.N. value.

- (6) Higher O.N. of an atom of an element in a molecule or an ion can't exceed its group no. in Mendeleev's periodic table except Cu & Au (cupric and auric as +2 and +3 respectively while they belong to first B group in Mendeleev's table).
- (7) Alkyl groups like $-\text{CH}_3$ or $-\text{C}_2\text{H}_5$ or $-\text{alkyl}$ are taken as +1 in oxidation number.
- (8) If same types of atoms are bounded together, then number of bonds which are formed in between identical atoms are awarded zero oxidation number for each such bond e.g., carbon suboxide, tribromo octaoxide, tetrathionate ion etc and the various species have been given the respective oxidation number as shown in the diagram below :



Structure of tribromooctaoxide (Br_3O_8)



Structure of tetrathionate ion ($\text{S}_4\text{O}_6^{2-}$)

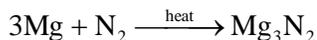
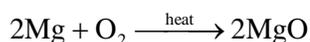
Types of Redox Reactions

There are different types of redox reactions as discussed below :

- (1) Combination reactions or addition reactions :



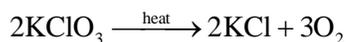
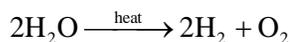
The examples are :



- (2) Decomposition reactions :



The examples are



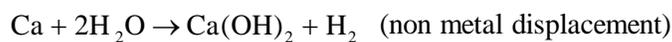
In such reactions often oxygen is liberated.

However, decomposition of magnesium carbonate is not a redox reaction.

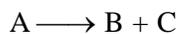
- (3) Displacement reactions :



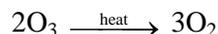
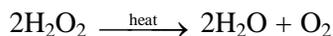
Examples are



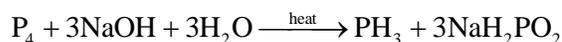
(4) Disproportionation reactions : The reactions may be written as



The examples are



Some disproportionation reactions require medium also. e.g.,



Balancing of Equations

- (1) Ion-electron method.
- (2) Oxidation number method.

Ion electron method

- (1) First of all the O.N. of all those atoms are calculated, which are undergoing change during the reaction.
- (2) Oxidising and reducing agents are identified.
- (3) Two separate half reactions are made with the help of oxidising & reducing agents to represent reduction & oxidation.
- (4) No. of lost and no. of gained electrons are calculated.
- (5) No. of atoms except H and O are balanced on both sides of the half reactions.
- (6) In acidic medium, one H_2O is added on oxygen deficient side for each deficiency of oxygen and 2H^+ ion on the other side.
- (7) In alkaline medium,
 - (a) For each excess of oxygen, one H_2O is added on the same side and 2OH^- ion on the other side.
 - (b) If H remains unbalanced then for each excess of H, one OH^- is added on the same side and one H_2O on the other side.
- (8) Now, both half reactions are coupled together in order to eliminate the common electron and ions.
- (9) Finally, total no. of atoms and charge on both side of the reaction must be conserved.

Oxidation number method

- (1) First of all the O.N. of all those atoms are calculated, which are changing during the reaction.
- (2) Oxidising and reducing agents are identified.
- (3) Now, cross-multiplication is done. O.A. is multiplied by no. of lost electrons while R.A. by no. of gained electrons.
- (4) Finally, no. of atoms are counted on both sides and they remain conserved.
- (5) In alkaline medium the balancing should be done from right hand side.
- (6) If the same atom will be present in different molecules then balancing will be done from that side, containing maximum no. of such molecules.

Exercise

Q. Suggest the O.N. of the underlined atoms in the following molecules and ions :

- (i) KMMnO_4 (ii) $\text{K}_2\text{CCr (iii) $\text{H}_2\text{SO (iv) HNO_3
(v) Ca(OCl)Cl (vi) CCrO_5 (vii) $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}^+]\text{SO}_4$ (viii) $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$
(ix) $[\text{CO(\text{NH}_3)_6]\text{Cl}_3$ (x) $\text{K}_4[\text{Fe}(\text{CN})_6]$ (xi) $\text{K}_3[\text{Fe}(\text{CN})_6]$
(xii) $\text{K}_2[\text{HgI}_4]$ (xiii) $\text{NO (xiv) $\text{C}_2\text{O}_4^{-2}$
(xv) BrO_3^- (xvi) $\text{SO (xvii) $\text{ClO}_4^-$$$$$

A. (i) Let the charge on Mn be x.

Since K is an alkali metal, oxidation number of K is +1 and O has oxidation number of -2. But KMnO_4 is a molecule. Therefore, sum of all oxidation numbers on atoms will be zero. Hence equation would be : $+1 + x - 8 = 0$



(ii) $\text{K}_2\text{CCr$

$\text{K} = +1$, $\text{Cr} = x$, $\text{O} = -2$ and total charge on molecule will be zero.

$$+1 \times 2 + 2x - 2 \times 7 = 0$$



(iii) +6, (iv) +5,

(v) Ca(OCl)Cl

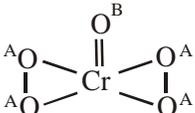
In this specie one Cl is bonded to Ca while other Cl atom is bonded to O. Cl is less electronegative than O but Cl is more electronegative than metal Ca.

$$\text{Ca} = +2 \quad \text{O} = -2 \quad \text{Cl} = x \quad \text{Cl} = -1$$

$$\text{Thus equation is } +2 - 2 + x - 1 = 0$$



(vi) CCrO_5

Structure of this compound is  popularly known as butterfly structure.

Each peroxy oxygen atom (^AO) = -1, Cr = x, $\text{O}^B = -2$ therefore charge equation is

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

$$\text{or } x = +6$$

(vii) +1, (viii) +3, (ix) +3, (x) +2, (xi) +3, (xii) +2, (xiii) +5, (iv) +3, oxalate ion, (xv) +5, (xvi) +6, (xvii) +7

Q. Calculate oxidation number of methyl ethyl or alkyl group.

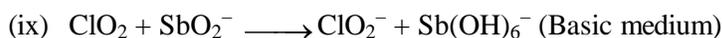
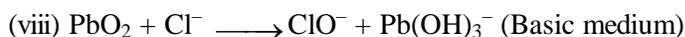
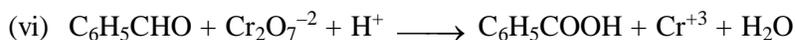
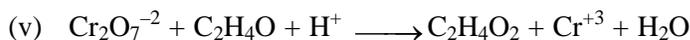
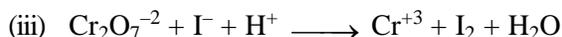
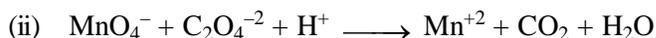
A. Let the compounds be $\underline{\text{C}}\text{H}_3\text{Br}$, $\underline{\text{C}}_2\underline{\text{H}}_5\text{Br}$ and $\underline{\text{R}}\text{Br}$

Calculation for methyl bromide $\underline{x} - 1 = 0$, $\underline{x} = +1$

Calculation for ethyl bromide $\underline{x} - 1 = 0$, $\underline{x} = +1$

Calculation for alkyl group $\underline{x} - 1 = 0$, $\underline{x} = +1$

Q. Balance the given ionic equations in the suggested medium according to ion-electron method.



A. (i) $\text{MnO}_4^- + \text{Fe}^{+2} \longrightarrow \text{Mn}^{+2} + \text{Fe}^{+3}$ in acidic medium.

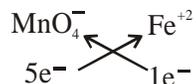
In the given equation oxidising agent is MnO_4^- as $x - 8 = -1$; or $x = +7$. Mn belongs to 7th group and shows highest oxidation number as +7. It acts as a oxidising agent.

Mn is getting reduced from +7 to +2 oxidation number hence it is an oxidising agent while Fe^{+2} is a reducing agent.

No. of electrons lost by oxidising agent = $7 - 2 = 5$ electrons.

No. of electrons gained by reducing agent = $3 - 2 = 1$ electron.

To balance the system, cross multiplication is followed. Now equation of L.H.S. can be written as:

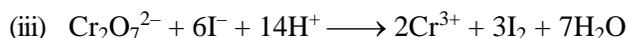
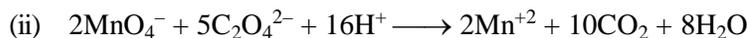


Now adding 8H^+ to neutralise 4O^{2-} , equation will be

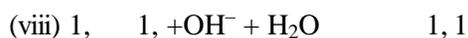


Note : Follow all the steps of balancing the equation as shown in ion-electron method.

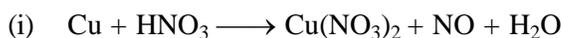
The answers from (ii) to (v) are as under :



The answers for (vi) to (x) are written as coefficients for reactant and products respectively.



Ex. Balance the equation



[Ans. 3, 8, / 3, 2, 4] coefficients for reactants and products.



[Ans. 2, 10, 8, / 2, 6, 8, 5] coefficients for reactants and products.



[Ans. 5, 2, 4, / 2, 2, 5, 4] coefficients for reactants and products.

Ex. Write balanced equation for Fe^{+2} and MnO_4^- in acidic medium.



Ex. Write balanced equation for oxidation of oxalic acid by KMnO_4 in acidic medium.

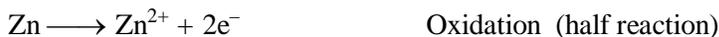


REDOX REACTIONS, ELECTRODE PROCESS & ELECTROCHEMICAL SERIES

To observe a competitive electron transfer, many experiments have been carried out and the important initial ones are as under :

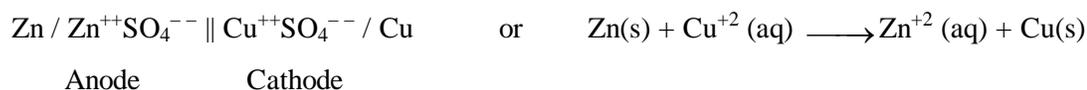
- (i) Whenever zinc rod is placed in copper nitrate solution then blue colour of Cu^{+2} ion gradually diminishes and concentration of Cu^{+2} decreases continuously. Copper is deposited on zinc rod.
- (ii) When copper rod is dipped in silver nitrate solution, the solution gradually becomes blue. A final observation is the deposition of silver on the rod of copper.
- (iii) If copper rod is dipped in copper sulphate solution and zinc rod is dipped in zinc sulphate solution in separate beakers and if both are connected through a salt bridge and also connected externally by

conducting wire then the observation is that zinc rod gradually loses its volume (Zn^{++} ions go to solution). While copper deposits on cathode and thus cathode made up of copper increases in volume and weight. The entire setup is known as Daniell cell. The two half reactions in the zinc and copper cells can be written as



The entire cell which consists of both the electrodes, salt bridge and external connection is known as an electrochemical cell (in this case a Daniell cell which gives a theoretical electrode potential of 1.1 volt).

The entire cell is represented as under :

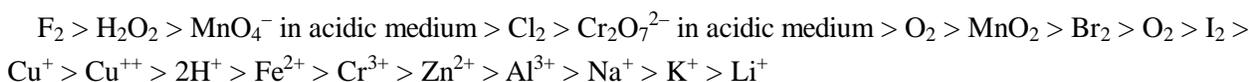


Oxidation takes place on anode while reduction takes place on cathode.

Electrochemical Series

The systematic arrangement of elements in the order of their increasing reducing power is called as “Electrochemical series”. In the modern table of electrochemical series the std. reduction potential forms the basis of comparison of the activities of elements. In this series Li with $E^0 = -3.04$ volts is at the top while F with $E^0 = +2.87$ volts is at the bottom.

On the basis of standard electrode potential series at 298 K, it can be inferred that the decreasing oxidising character can be given the following order for selected species :



Feasibility of Reaction

The values of std. electrode potentials tell us the ease with which an element will be reduced or oxidised for example, the tendency of an element to undergo reduction and to act as oxidising agent increases from top to bottom that is, fluorine has greatest tendency to undergo reduction and is most powerful oxidising agent. Whereas Li is most powerful reducing agent. In other words, the electrochemical series provides us a clue that an element appearing first in the series will display all others below it from their aqueous salt solutions. Thus, from the relative positions of elements in electrochemical series we can predict the direction of a redox reaction.

Characteristics:

- (1) The values of standard electrode potential tell us the ease with which the given element will be reduced when compared with hydrogen.
- (2) The tendency of an element to undergo reduction increases from top to bottom, that is, the power to act as reducing agent decreases.

-
- (a) The reduction of Lithium ion into Li-atom ($\text{Li}^+ + e \longrightarrow \text{Li}$) is not feasible but its oxidation $\text{Li} \longrightarrow \text{Li}^+ + e$ is feasible. That is, Li is the most powerful reducing agent.
 - (b) Fluorine has the greatest tendency to undergo reduction and thus it is the most powerful oxidising agent.
 - (3) The elements appearing prior to hydrogen in the series have a greater tendency to get oxidised and so act as better reducing agent than hydrogen.
 - (4) An element appearing first in the electrochemical series will displace all others below it from their aqueous salt solutions.

Therefore in chemical series,

- (a) The tendency for reduction to occur, tendency to gain electrons and power to act as oxidising agent increases from top to bottom.
- (b) The tendency for oxidation to occur, tendency to lose electrons and power to act as reducing agent decreases from top to bottom.

Importance:

- (1) The electrochemical series provides a ready reference to select a reducing agent for the metallurgical processes of elements.
- (2) The series is used to arrange the metals in the decreasing or increasing order of their activities.
- (3) The series helps us to select a metal to be electroplated on an object made of some other metal. Thus, a displacement reaction is feasible or not, it can be predicted by using the standard electrode potential series. e.g.,
$$\text{Zn} + \text{CuSO}_4 \longrightarrow \text{ZnSO}_4 + \text{Cu}$$
 (reaction is feasible because zinc is more reactive than copper).
$$\text{Cu} + \text{ZnSO}_4 \longrightarrow \text{No reaction}$$
 (reaction is not feasible because copper is less reactive than zinc)
- (4) The choice of oxidising agent can be made by a quick survey of the series. e.g., F_2 is the strongest oxidising agent while Li is the strongest reducing agent in aqueous medium.
- (5) The series can be used to select suitable electrodes for the construction of desired electrochemical cell. e.g., Daniell cell ($\text{Zn} / \text{Zn}^{++} \parallel \text{Cu}^{++}/\text{Cu}$).
- (6) The series can be used to select a suitable source of electrical energy.
- (7) The series is used to predict the product of electrolysis.

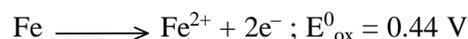
Corrosion

Any process of deterioration (destruction) and consequent loss of a solid metallic material through an unwanted chemical or electrochemical attack by its environment starting at its surface is called corrosion.

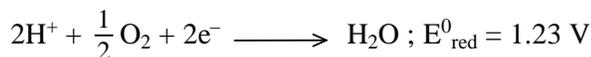
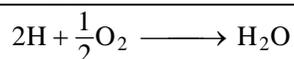
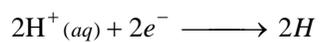
Corrosion always occurs at anodic areas. More active metals are corroded more easily. Corrosion is enhanced by the presence of (a) impurities, (b) air and moisture, (c) electrolytes and (d) stains in metal like dents, scratches, welding parts, etc. Corrosion of iron is called rusting. In the process of rusting, Fe metal is converted to dark brown coloured rust with formula $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ and therefore it is in oxidation process for iron metal and oxidising agent is oxygen in presence of weak acid (H_2CO_3). **Hence rusting of iron is a redox process.**

Electrode reactions in rusting of iron

Oxidation at anode



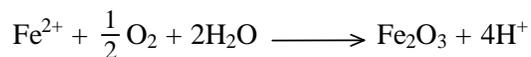
Reduction at cathode



Net reaction of corrosion cell



The Fe^{2+} ions so formed move through water and reach at the surface of iron where they are oxidised to Fe^{3+} ions by atmospheric oxygen and constitute the rust which is hydrated ferric oxide.



Rust

Prevention of corrosion

- (1) By coating with a suitable material (barrier protection)
- (2) By alloying with suitable metals e.g. Fe, Cr, V, Ni, W, etc.
- (3) By cathodic protection
- (4) By using artificial anode (Sacrificial protection).