8. REDOX REACTIONS

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CLASSICAL CONCEPT OF OXIDATION AND REDUCTION



• Oxidation is defined as addition of oxygen or any

other electronegative component.

Or

Removal of hydrogen or any other electropositive component.

EXAMPLES







 Reduction is defined as addition of hydrogen or any other electropositive component.

Or

Removal of oxygen or any other electronegative

component.





 $H_2S + Cl_2 \rightarrow 2HCl + S$

OXIDISING AGENT

- A substance which provides oxygen or any electronegative element is called an oxidising agent.
 Or
- A substance which removes hydrogen or any other electropositive element is called an oxidising agent.
- In the above examples, O_2 and Cl_2 act as oxidising

REDUCING AGENT

• A substance which provides hydrogen or any electropositive element is called a reducing agent. or substance which Α removes oxygen or any electronegative element is called a reducing agent.



During a redox reaction:

- A reducing agent undergoes oxidation.
- An oxidising agent undergoes reduction.

ELECTRONIC CONCEPT OF OXIDATION AND REDUCTION

OXIDATION

Oxidation is the process involving loss of electrons.

REDUCTION

• Reduction is the process involving gain of electrons.

OXIDISING AGENT

• An oxidising agent is a substance whose atoms gain

electrons.

REDUCING AGENT

• A reducing agent is a substance whose atoms lose

electrons.

OXIDATION



- Here Zn atom loses electrons while Cu²⁺ ions gains electrons.
- So Zn is oxidized and Cu²⁺ is reduced.
- Cu²⁺ is the oxidising agent and Zn is the reducing agent.

OXIDATION HALF AND REDUCTION HALF REACTIONS

- Every redox reaction consist of two half cell reactions.
- They are oxidation half reaction and reduction half reaction.
- Eg:- Reaction between Na and Cl.



Na atom loses an electron to form Na⁺. $Na \rightarrow Na^+ + 1e^-$ Cl atom gains an electron to form Cl⁻. $Cl + 1e^{-} \rightarrow Cl^{-}$ Overall cell reaction (Redox reaction) is $Na + Cl \rightarrow Na^+ + Cl^-$

REDOX REACTION



EXAMPLE-1

- * A clean Zn strip is placed in a solution of CuSO₄ placed in a beaker.
- * The following changes are observed.
- * Zn metal starts to dissolve and as a result of this, its mass decreases.
- * Cu metal starts to deposit.
- The blue colour of CuSO₄ solution begins to fade.
- * The reaction proceeds with the evolution of heat.

REACTIONS



 $Zn \rightarrow Zn^{2+} + 2e^{-}$ $Cu^{2+} + 2e^- \rightarrow Cu$ $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

EXAMPLE-2

- A clean copper strip is placed in a solution of AgNO₃ kept in a beaker.
- The following changes are observed.
- Copper strip starts to dissolve and as a result its mass decreases.
- Silver starts to deposit.
- Blue colour of Cu²⁺ ions appears.
- Reaction proceeds with the evolution of heat.



REACTIONS

$$Cu \rightarrow Cu^{2+} + 2e^{-}$$

$$2Ag^+ + 2e^- \rightarrow 2Ag$$

$$Cu + 2Ag^+ \rightarrow Cu^{2+} + 2Ag$$

OXIDATION NUMBER OR OXIDATION STATE

Oxidation number is defined as the charge that an atom

would have if both the electrons in each bond were assigned

to the more electronegative element.

RULES FOR ASSIGNING OXIDATION NUMBER

- Oxidation number of an element in the free or uncombined state is zero.
- The sum of the oxidation numbers of all the atoms in a neutral molecule is zero.
- The oxidation number of mono atomic ion is equal to the charge on it.
- For polyatomic ions, sum of the oxidation numbers of all the atoms in it is equal to the charge on it.

- Oxidation number of fluorine is –1 in all its compounds.
- Oxidation number of hydrogen is +1 in all its compounds
- But in ionic hydrides the oxidation number is -1.
- Oxidation number of oxygen is –2.
- In OF₂, oxidation number of oxygen is +2

- In peroxides it is —1 and in superoxides it is -1/2.
- (i.e., KO₂)
- Oxidation number of alkalie metals is +1.
- Oxidation number of alkaline earth metals is +2.
- Oxidation number of halogens is —1.

OXIDATION AND REDUCTION IN TERMS OF OXIDATION NUMBER

OXIDATION

• A chemical change in which there is an increase in

oxidation number.

REDUCTION

• A chemical change in which there is a decrease in oxidation number.

$$\begin{array}{ccccc} 0 & +2 & +2 & 0 \\ Zn + Cu^{2+} \rightarrow & Zn^{2+} + Cu \end{array}$$

- Oxidation number of Zn increases from 0 to +2 and it is oxidized.
- The oxidation number of Cu decreases from +2 to 0 and it is reduced.

OXIDISING AGENT

 A substance which undergoes a decrease in oxidation number.

REDUCING AGENT

- A substance which undergoes an increase in oxidation number.
- Eg:- In the above example, Cu²⁺ is the oxidising agent and
 - Zn is the reducing agent.

OXIDATION NUMBER AND NOMENCLATURE

- In the naming of compounds of metals which exhibit variable valency, Roman numerals are used to indicate the oxidation number of the metal atoms.
- This system of naming is known as the 'Stock System'.
 According to the Stock System, the oxidation numbers are indicated by Roman Numerals in brackets after the name of

the metal.



Cu₂O : Copper (I) Oxide CuO : Copper (II) Oxide SnO₂ : Tin (IV) Oxide SnO : Tin (II) Oxide

FeSO₄ : Iron (II) Sulphate

FeO : Iron (II) Oxide

Fe₂O₃ : Iron (III) Oxide

MnO: Manganese (II) Oxide

MnO₂ : Manganese (IV) Oxide

CALCULATION OF OXIDATION NUMBER

Calculate the oxidation Number of Mn in KMnO₄?

Let the oxidation number of Manganese = x Let the oxidation number of Oxygen = $-2 \times 4 = -8$ Let the oxidation number of Potassium = +1Therefore, oxidation number of Manganese = +1 + x - 8 = 0x = -1 + 8

Calculate the oxidation Number of Cr in K, Cr, O,?

Let the oxidation number of Chromium = 2xLet the oxidation number of Oxygen $= -2 \times 7 = -14$ Let the oxidation number of Potassium $= +1 \times 2 = +2$ Therefore, oxidation number of Chromium = +2 + 2x - 14 = 02x = -2 + 142x = +12

x = +6

Calculate the oxidation Number of C in CO²⁻?

Let the oxidation number of Carbon = x Let the oxidation number of Oxygen = $-2 \times 3 = -6$ Therefore, oxidation number of Carbon = x - 6 = -2x = -2 + 6x = +4 Calculate the oxidation Numbers of the elments in the following compounds.


REDOX REACTIONS AND ELECTRODE PROCESSES

ELECTROCHEMICAL CELL OR GALVANIC CELL

An electrochemical cell is a device used for the conversion of chemical energy into electrical energy.

Eg:- Daniel Cell

CONSTRUCTION AND WORKING OF DANIEL CELL



- The Daniel cell consists of a Zn rod dipped in ZnSO₄ solution.
- A copper rod dipped in copper sulphate solution.
- The two solutions are connected by salt bridge
- The two electrodes are connected externally by a metallic wire
 - through a voltmeter.
- A potential difference is developed.
- It is indicated by the stream of electrons flowing from Zn to Cu.

- The cell is represented as, Zn | Zn²⁺ || Cu²⁺ | Cu.
- Here oxidation takes place at the zinc electrode
- Reduction takes place at the copper electrode.
- The 'Zn' electrode at which oxidation takes place is the anode
- The 'Cu' electrode at which reduction takes place is the

cathode.

CELL REACTIONS

Anode reaction : $Zn \rightarrow Zn^{2+} + 2e^{-}$

Cathode reaction : $Cu^{2+} + 2e^- \rightarrow Cu$

Overall reaction : $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

The flow of electrons from Zn to Cu produces a current in the circuit.



- Salt bridge is a 'U' shaped tube.
- It contains a concentrated solution of an electrolyte like
 - KCl, KNO_3 , NH_4NO_3 etc mixed with gelatin or agar-agar.

FUNCTIONS OF SALT BRIDGE

 It allows the movement of ions from one solution to other without mixing of the two solutions.
 It maintains the electrical neutrality of the solution.

ELECTRODE POTENTIAL

The tendency of an electrode to lose or gain electrons

when it is in contact with its own ions in the solution

is called its electrode potential.

The electrode potential may be of two types.

1. OXIDATION POTENTIAL

The tendency of an electrode to lose electrons.

 $M \rightleftharpoons M^{n+} + ne^{-}$ $Zn \rightleftharpoons Zn^{2+} + 2e^{-}$

2. REDUCTION POTENTIAL

The tendency of an electrode to gain electrons.

$$M^{n+} + ne^- \rightleftharpoons M$$

 $Cu^{2+} + 2e^- \rightleftharpoons Cu$

STANDARD ELECTRODE POTENTIAL (E°)

The potential of an electrode under standard conditions i.e., 298K temperature, 1 atm pressure and 1M concentration is called standard electrode potential (E °).



1. COMBINATION REACTIONS

A combination reaction may be represented as

 $A + B \rightarrow C$

Either A or B or both A and B must be in the elemental form.

 $C + O_2 \rightarrow CO_2$ $3Mg + N_2 \rightarrow Mg_3N_2$ $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ **2. DECOMPOSITION REACTIONS**

A decomposition reaction leads to the breakdown of a compound into two or more components at least one of which must be in the elemental state. $2H_2O \xrightarrow{\Delta} 2H_2 + O_2$ $2\text{NaH} \longrightarrow 2\text{Na} + \text{H}_2$ $2KClO_3 \xrightarrow{\Delta} 2KCl + 3O_2$

All decomposition reactions are not redox reactions

$CaCO_3 \rightarrow CaO + CO_2$

3. DISPLACEMENT REACTIONS

In a displacement reaction, an ion or an atom in a compound is replaced by an ion or atom of another element.

It may be denoted as $X + YZ \rightarrow XZ + Y$

A. METAL DISPLACEMENT

A metal in a compound can be displaced by another metal in the uncombined state.

 $CuSO_4 + Zn \rightarrow Cu + ZnSO_4$ $Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr$

B. NON METAL DISPLACEMENT

The non metal displacement2NredoxreactionsincluderedoxreactionsincludehydrogendisplacementandhydrogendisplacementMgrarelyoccurringreactioninvolving oxygendisplacement.2H

 $2Na + 2H_2O \rightarrow 2NaOH + H_2$

 $Zn + 2HCl \rightarrow ZnCl_2 + H_2$

 $Mg + 2HCl \rightarrow MgCl_2 + H_2$

 $2H_2O + 2F_2 \rightarrow 4HF + O_2$

4. DISPROPORTIONATION REACTION

In this reaction, an element in one oxidation state is simultaneously oxidized and reduced. One of the reacting substances always contains an element that can exist in at least three oxidation states.

Eg:- $2H_2O_2 \rightarrow 2H_2O + O_2$

BALANCING OF REDOX REACTIONS

1. OXIDATION NUMBER METHOD

- The various steps involved in this method are:
- Write the skeletal equation representing the chemical

change.

- Indicate the oxidation numbers of all atoms involved in the reaction.
- Identify the elements which undergo change in oxidation number.

- Calculate the change in oxidation number per atom.
- Multiply this number of change in oxidation number

with the number of atoms which are undergoing the

change.

- Equate the increase in oxidation number of the reducing agent with the decrease in oxidation number of the oxidising agent.
- For this, the oxidising agent is multiplied by the change in oxidation number of reducing agent and the reducing agent is multiplied by the change in oxidation number of oxidising agent.

- Balance all other atoms except hydrogen and oxygen.
- Finally balance hydrogen and oxygen atoms.
- For this, add H₂O to the side deficient in oxygen.
- In acid solution, add H⁺ to the side deficient in hydrogen atoms.
- In basic solution, add H₂O to side deficient in hydrogen atoms

and add equal number of OH⁻ ions on the other side.

Example. 13.3. Balance the equation, $SnCl_2 + FeCl_3 \longrightarrow SnCl_4 + FeCl_2$ had write the bulanced half equations and then the half equations are composed In constinue the tollowing store are involved in the fault reaction: notation Skeleton equation is, $SnCl_2 + FeCl_3 \longrightarrow SnCl_4 + FeCl_2$ 1. Denote the oxidation numbers. 2. +2 -1 +3 -1 +4 -1 +2 -1 of odd yd viol stag enddronad $SnCl_2 + FeCl_3 \longrightarrow SnCl_4 + FeCl_2$ 3. Identify the element which undergo change in oxidation numbers +2 $SnCl_2 + FeCl_3 \longrightarrow SnCl_4 + FeCl_2$

Oxidation number of Sn in $SnCl_2$ changes from +2 to +4 while that of Fe in FeCl₃ changes from +3 to +2. Thus, $SnCl_2$ is the reducing agent and FeCl₃ is the oxidising agent.

4. Calculate the change in oxidation number per formula unit of both oxidising and reducing agents,

O.N. increases by 2 -----

under perhod and (d) fam electrics or half real

- 5. Multiply $SnCl_2$ by 1 and $FeCl_3$ by 2. $SnCl_2 + 2FeCl_3 \longrightarrow SnCl_4 + 2FeCl_2$
- 6. Balance all other atoms except H and O
 - $SnCl_2 + 2FeCl_3 \longrightarrow SnCl_4 + 2FeCl_2$
- 7. Balance H and O atoms. This step is not required in this case since H and O are not involved.
- : Balanced equation is $SnCl_2 + 2FeCl_3 \longrightarrow SnCl_4 + 2FeCl_2$

2. ION ELECTRON METHOD OR HALF REACTION METHOD

- The various steps involved in this method are
- Write the skeletal equation represents the chemical change.
- Indicate the oxidation numbers of all atoms involved in the reaction.

Find the elements whose oxidation numbers are changed.

- Separate the redox reaction into half reactions.
- i.e., oxidation half and reduction half reactions.
- Balance each half reaction separately by the following steps.
- Balance all atoms other than hydrogen and oxygen.
- Calculate the oxidation number on the left and on the right.

- Add electrons to whichever side is necessary, to make up for the difference.
- Balance half reaction so that both sides will have the same charge.
- Add water molecules to complete the balancing of the equation.
- Add the two balanced half equations.

Balance the redox reaction

 $Cr_{2}O_{7}^{--} + Fe^{++} + H^{+} \rightarrow Cr^{+++} + Fe^{+++} + H_{2}O$ Solution : Step (1) Find the elements whose oxidation numbers are changed. $^{+6-2}_{Cr_{2}O_{7}^{--}} + Fe^{++} + H^{+} \rightarrow Cr^{+++} + Fe^{+++} + H_{2}O$

In this, the oxidation number of chromium decreases from +6 to +3 i.e., Cr undergoes reduction and the oxidation number of Fe^{++} increases from +2 to +3 i.e., Fe^{++} is oxidised to Fe^{+++}

Step (2) Separate the redox reaction into two half reactions

The half reactions are:

 $Fe^{++} \rightarrow Fe^{++++}$ (oxiadation half)

 $Cr_2O_7^{--} \rightarrow Cr^{+++}$ (reduction half)

Step (3) Balance each half reaction separately

(a) Oxidation half reaction : $Fe^{++} \rightarrow Fe^{+++}$

i. Balance all atoms other than O and H. In this, other atoms are already balanced.

ii. Calculate the oxidation number on both sides and add electrons to account for the difference.

In this, Ox:No on left is +2 and that on right is +3. To account for the difference add one electron to the right. Thus we get,

$$Fe^{++} \rightarrow Fe^{+++} + le^{-}$$

iii. Balance the charge on either side

In this, charge is already balanced.

iv. Add Water: In view of oxygen and hydrogen being absent, this step is not necessary.

(b) Reduction half reaction, $\operatorname{Cr}_2\operatorname{O}_7^{--} \to \operatorname{Cr}^{+++}$

Balance all atoms other than O and H
 There are two Cr atoms on the left, but only one on right.

Therefore, $Cr_2O_7^{--} \rightarrow 2Cr^{+++}$

ii. Calculate oxidation number on both sides and add electrons to account for the difference. The ox: no: of Cr on the left is +6 and on the right is +3. Each Cr atom must gain three electrons. Since there are two Cr atoms, add six electrons on the left. Thus,

is considered in the electronic used in $cr_2O_7^{--} + 6e^- \rightarrow 2Cr^{+++}$ in both electronic produced in an indication of the helf or $cr_2O_7^{--}$ and $cr_2O_7^{--}$.

iii. Balance the charge on either side

Since the reaction is occurring in acid medium, H^+ ions will be added to account for the extra positive charge on one side or the other. The total charge on the left is -8; on the right is +6. Therefore, 14H⁺ will be added to the left. Thus,

$$Cr_2O_7^{--} + 14H^+ + 6e^- \rightarrow 2Cr^{+++}$$
 or $t = 0$ and $t = 1$ and $t = 0$

iv. Add water to complete the balancing. Since there are 14H atoms and 7 O atoms on the left side, add $7H_2O$ on the right. Thus,

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

Step (4) Add the two half reactions together. Before doing this, multiply the oxidation half reaction by 6 so that electrons are balanced.

$$6(Fe^{2+} \rightarrow Fe^{+++} + 1e^{-})$$
 (oxidation half reaction)

$$Cr_{2}O_{7}^{--} + 6e^{-} + 14H^{+} \rightarrow 2Cr^{+++} + 7H_{2}O$$
 (reduction half reaction).

$$6Fe^{++} + Cr_{2}O_{7}^{--} + 14H^{+} + 6e^{-} \rightarrow 6Fe^{+++} + 2Cr^{+++} + 7H_{2}O + 6e^{-}$$

i.e., $6Fe^{++} + Cr_{2}O_{7}^{--} + 14H^{+} \rightarrow 6Fe^{+++} + 2Cr^{+++} + 7H_{2}O$.
This is the balanced equation.

Example 13.5 Balance the following redox reaction occurring in basic medium.

 $Zn + NO_3^- \rightarrow Zn^{++} + NH_4^{++}$ holds be used as

Solution: ${}^{0} +5 -2 +2 -3 +1$ Step (1): $Zn + NO_{3}^{-} \rightarrow Zn^{++} + NH_{4}^{+}$

In this, Zn undergoes oxidation and NO3 undergoes reduction.

Step (2) : Oxidation : $Zn \rightarrow Zn^{++}$ Reduction : $NO_3^- \rightarrow NH_4^+$ Step (3) : Balance each half reaction separately as, (a) oxidation half reaction:

 $Zn \rightarrow Zn^{++}$

i. Balance all atoms other than H and O: already done

ii. Add electrons to make up for the difference in oxidation number,

 $Zn \rightarrow Zn^{++} + 2e^{-}$

iii. Balance the charges : already done

iii. Balance the charges : already done iv. No need to add water Therefore, the balanced oxidation half reaction is,

$$Zn \rightarrow Zn^{++} + 2e$$

(b) Reduction half reaction in bits it worplished Ministration of bost of permissions and the

Example 13.6 If 10 moles of example
$$Md_3^- \rightarrow Md_4^+$$
 solution (0.01 M KMnO₄ solution

Balance atoms other than H and O: already done the stole to the local sector of the

Add electrons to make up for the difference in oxidation number. As the oxidation number of nitrogen changes from +5 to -3, there is a difference of 8 electrons.

 $\mathbb{O}_{1}^{\mathbb{O}_{1}} \to \mathbb{O}_{2}^{\mathbb{O}_{2}} + \mathbb{O}_{2}^{\mathbb{O}_{2}} \to \mathbb{O}_{1}^{\mathbb{O}_{2}} \to \mathbb{O}_{1}^{\mathbb{O}_{2}} \to \mathbb{O}_{2}^{\mathbb{O}_{2}} \to \mathbb{O}_{1}^{\mathbb{O}_{2}} \to \mathbb{O}_{2}^{\mathbb{O}_{2}} \to \mathbb{O}_{1}^{\mathbb{O}_{2}} \to \mathbb{O}_{2}^{\mathbb{O}_{2}} \to \mathbb{O}_{2}^{\mathbb{O}_{2}}$

iii. Balance the charges: There are 9 negative charges on the left, on the right it is +1. As the reaction is in basic medium add 10 OH⁻ on the right.

 $NO_3^- + 8e^- \rightarrow NH_4^+ + 10 \text{ OH}^-$

iv. Add water to complete balancing.

$$NO_3^- + 7H_2O + 8e^- \rightarrow NH_4^+ + 10 OH^-$$

This is the balanced reduction half reaction.

Step (4) Add the two half reactions. Before doing this, the oxidation half reaction is multiplied by 4 so that electrons are balanced.

 $4 (Zn \rightarrow Zn^{++} + 2e^{-})$

 $NO_3^- + 7H_2O + 8e^- \rightarrow NH_4^+ + 10 \text{ OH}^-$

 $4Zn + NO_3^- + 7H_2O \rightarrow Zn^{++} + NH_4^+ + 10 \text{ OH}^-$

This is the final balanced equation.

