NEET | JEE
ESSENTIALS

Maximise your chance of success, and high rank in NEET, JEE (Main and Advanced) by reading this column. This specially designed column is updated year after year by a panel of highly qualified teaching experts well-tuned to the requirements of these Entrance Tests.

## Unit 4 — Equilibrium | Redox Reactions

EQUILIBRIUM

Equilibrium state of a system is the state, in which system has no tendency for a change without external stimulation and so there is no net change occurs with time. Equilibrium is attained when the rates of the two opposing processes become equal.

There are two types of equilibrium :

- **Physical equilibrium :** If the opposing processes involve only physical changes, the equilibrium is called physical equilibrium.
- **Chemical equilibrium :** If the opposing processes involve chemical changes, the equilibrium is called chemical equilibrium.

Types of Equilibrium

Physical Equilibrium

Solid-liquid equilibrium (Melting of ice)
$$H_2O_{(s)} \rightleftharpoons H_2O_{(l)}$$
ice   water
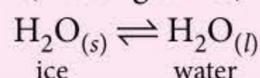
Solid-solution equilibrium (Dissolution of sugar in water)
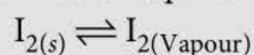$$Sugar_{(Solid)} \rightleftharpoons Sugar_{(in\ solution)}$$

Liquid-vapour equilibrium (Evaporation of water in a closed vessel)
$$H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$$

Solid-vapour equilibrium (Sublimation equilibrium)
$$I_{2(s)} \rightleftharpoons I_{2(Vapour)}$$

Gas-solution equilibrium (Dissolution of a gas in a liquid under pressure in a closed cell.)
$$CO_{2(g)} \rightleftharpoons CO_{2(in\ solution)}$$

It is governed by Henry's law which states that the mass of a gas dissolved in a given mass of a solvent at any temperature is proportional to the pressure of the gas above the solvent.

Chemical Equilibrium

A reaction in which not only the reactants react to form the products under certain conditions but also products react to form reactants under the same condition, is called a reversible reaction.

A reaction which cannot take place in the reverse direction, *i.e.*, the products formed do not react to give back the reactants under the same conditions, is called an irreversible reaction.

GENERAL CHARACTERISTICS OF EQUILIBRIA INVOLVING PHYSICAL PROCESSES

Some important characteristics of physical equilibria are as follows :

- At equilibrium, some observable property of the system becomes constant.
- Equilibria involving gases can be attained only in closed vessels. This is because if the vessel is opened, the gas will escape and there will be no equilibrium.
- Equilibrium is dynamic in nature but stable.

- At equilibrium, the concentrations of the reactants and products become constant at constant temperature.

$$e.g., CO_{2(g)} \rightleftharpoons CO_{2(aq)}; \frac{[CO_{2(aq)}]}{[CO_{2(g)}]} = K$$
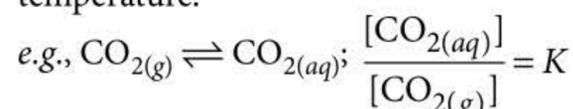
where, K is equilibrium constant.

- The magnitude of the equilibrium constant represents the extent to which the process proceeds before equilibrium is attained. For example, greater value of the K greater will be the dissolution of $CO_{2(g)}$ in water.

General Characteristics of Chemical Equilibrium

- At equilibrium, the concentration of each of the reactants and the products becomes constant. This may be represented graphically for a general reversible reaction, $A + B \rightleftharpoons C + D$, as shown in figure.
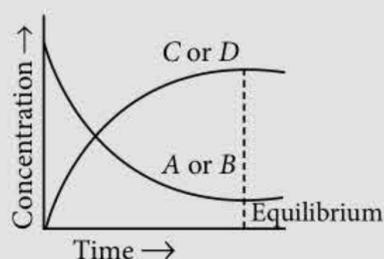
- Chemical equilibrium can be attained from either direction, *i.e.*, from the direction of the reactants as well as from the direction of the products.

- At equilibrium, the rate of forward reaction becomes equal to the rate of backward reaction and hence, the equilibrium is dynamic in nature.

- A chemical equilibrium can be established only if none of the products is allowed to escape out or separate out as a solid.

Law of Mass Action

The rate at which a substance reacts is proportional to the product of the active masses of the reactants, each raised to the power equal to its stoichiometric coefficient as represented in the balanced chemical equation.

Law of Chemical Equilibrium

Equilibrium Law

At a given temperature, the product of concentrations of the products raised to the respective stoichiometric coefficient in the balanced chemical equation divided by the product of concentrations of the reactants raised to their individual stoichiometric coefficients has a constant value which is called equilibrium constant. For a reaction, $aA + bB \rightleftharpoons cC + dD$

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Relation between K_p vs K_c

$$K_p = K_c (RT)^{\Delta n_g}$$

where, K_p = Equilibrium constant when all the reactants and products are in gaseous state.

Δn_g = Moles of gaseous products – moles of gaseous reactants.

IMPORTANT FEATURES OF EQUILIBRIUM CONSTANT

- Expression for equilibrium constant is applicable only when concentrations of the reactants and products have attained constant value at equilibrium state.

- The value of equilibrium constant is independent of initial concentrations of the reactants and products.

- Equilibrium constant is temperature dependent, having one unique value for a particular balanced reaction at a given temperature.

Chemical equation	Equilibrium constant
$aA + bB \rightleftharpoons cC + dD$	K_c
$cC + dD \rightleftharpoons aA + bB$	$K_c' = (1/K_c)$
$naA + nbB \rightleftharpoons ncC + ndD$	$K_c'' = (K_c^n)$

APPLICATIONS OF EQUILIBRIUM CONSTANTS

- Predicting the extent of reaction
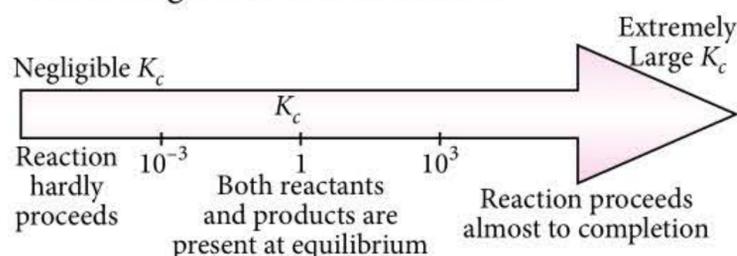
- Predicting the direction of reaction

$Q < K$	$Q = K$	$Q > K$
Reaction will shift in forward direction.	Reaction in equilibrium	Reaction will shift in backward direction.

- Relation between K_c and standard Gibbs free energy.

$$\Delta_r G° = -RT \ln K_c$$

LE CHATELIER'S PRINCIPLE

- A change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner so as to reduce or counteract the effect of the change.

Factors Affecting the Equilibrium

- Effect of change of concentration
  - With increase in concentration of any reactant at equilibrium, the equilibrium shifts to forward direction.

- Effect of change of pressure
  - Low pressure favours those reactions which are accompanied by increase in total number of moles.
  - High pressure favours those reactions which are accompanied with decrease in total number of moles.
  - Pressure has no effect on an equilibrium reaction which proceeds with no change in total number of moles.

- Effect of change of temperature
  - K_c for an exothermic reaction decreases as the temperature increases.
  - K_c for an endothermic reaction increases as the temperature increases.

- Effect of adding inert gas on equilibrium
  - At constant volume, when $(n_p = n_r)_{gaseous}$, there is no effect.
  - At constant pressure, when $(n_p \neq n_r)_{gaseous}$, effect is observed.
    When an inert gas is added, it wil increase the volume of the system. Therefore, equilibrium will shift in a direction in which there is increase in number of moles of gases.

- Effect of catalyst
  - Catalyst does not affect equilibrium constant.

Ionic Equilibrium

In weak electrolytes, equilibrium is established between ions and unionised molecules. Such an equilibrium is called ionic equilibrium,
$$AB_{(s)} + aq \rightleftharpoons A^+_{(aq)} + B^-_{(aq)}$$

The substances which dissociate almost completely into ions in aqueous solution, are called strong electrolytes. They are very good conductor of electricity, e.g., NaOH, NaCl, HCl, etc.

The substances which dissociate to a small extent in aqueous solution are called weak electrolytes. They conduct electricity to a small extent, e.g., NH_4OH, CH_3COOH, etc.

ACIDS, BASES AND SALTS

Arrhenius Concept of Acids and Bases

- Acid is a substance that dissociates in water to give hydrogen ions ($H^+_{(aq)}$).
- Base is a substance that produces hydroxyl ions ($OH^-_{(aq)}$) in water.
- Arrhenius concept explained neutralisation, salt hydrolysis, strength of acids and bases, etc.
- It also did not explain substances like NH_3, CaO are known to be basic but do not contain any hydroxyl groups and substances like CO_2, SO_2 are known to be acidic but do not contain any hydrogen. This limitation is, however overcome if water is supposed to play an important role.
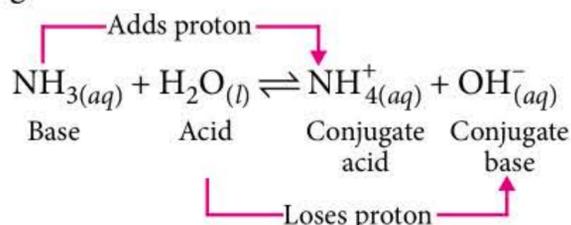
$$NH_{3(g)} + H_2O \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$
$$CO_2 + H_2O \rightleftharpoons CO^{2-}_{3(aq)} + 2H^+_{(aq)}$$
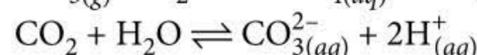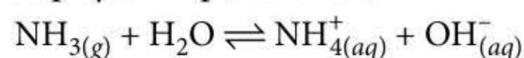
- Inability of explaining the reaction between an acid and base in absence of water.

$$NH_{3(g)} + HCl_{(g)} \longrightarrow NH_4Cl_{(s)}$$
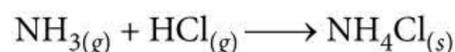
Bronsted-Lowry Concept of Acids and Bases

- Acid is a substance that is capable of donating a hydrogen ion.
- Base is a substance that is capable of accepting a hydrogen ion.

$$\underset{\text{Base}}{NH_{3(aq)}} + \underset{\text{Acid}}{H_2O_{(l)}} \rightleftharpoons \underset{\substack{\text{Conjugate} \\ \text{acid}}}{NH^+_{4(aq)}} + \underset{\substack{\text{Conjugate} \\ \text{base}}}{OH^-_{(aq)}}$$

(Adds proton / Loses proton)

- The acid-base pair that differs only by one proton is called a conjugate acid-base pair.
- A strong Bronsted acid has a weak conjugate base and vice-versa.
- It cannot explain the reactions between acidic oxides like CO_2, SO_2 etc. and the basic oxides like CaO, BaO, etc. which take place even in the absence of the solvent.

$$CaO + SO_3 \longrightarrow CaSO_4$$

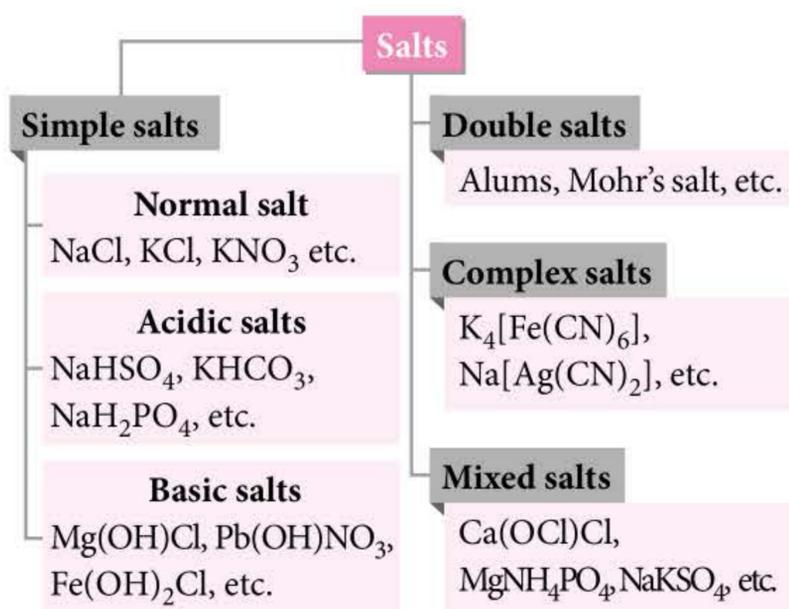- Substances like BF_3, $AlCl_3$, etc. do not have any hydrogen but are known to behave as acids.

Lewis Concept of Acids and Bases

- An acid is a species which accepts an electron pair.
- A base is a species which donates an electron pair.

e.g., $BF_3 + :NH_3 \longrightarrow BF_3 : NH_3$

- Electron deficient species like $AlCl_3$, BF_3, etc. can act as Lewis acids while species like H_2O, NH_3, OH^-, etc. which can donate a pair of electrons, can act as Lewis bases.
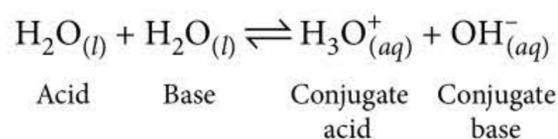
Formation of Salts

When acids and bases are mixed in right proportion, they react with each other to form salts.

Salts

Simple salts

Normal salt
NaCl, KCl, KNO_3 etc.

Acidic salts
$NaHSO_4$, $KHCO_3$, NaH_2PO_4, etc.

Basic salts
$Mg(OH)Cl$, $Pb(OH)NO_3$, $Fe(OH)_2Cl$, etc.

Double salts
Alums, Mohr's salt, etc.

Complex salts
$K_4[Fe(CN)_6]$, $Na[Ag(CN)_2]$, etc.

Mixed salts
$Ca(OCl)Cl$, $MgNH_4PO_4$, $NaKSO_4$ etc.

Relative Strength of Acids & Bases

- $$\frac{\text{Strength of acid } (HA)_1}{\text{Strength of acid } (HA)_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

- $$\frac{\text{Strength of base } (BOH)_1}{\text{Strength of base } (BOH)_2} = \sqrt{\frac{K_{b_1}}{K_{b_2}}}$$

- $K_a = K_{a_1} \times K_{a_2} \times K_{a_3}$ (For tribasic acid)

  $K_{a_1} > K_{a_2} > K_{a_3}$

- Strong acids have very weak conjugate bases.

IONISATION CONSTANT OF WATER AND ITS IONIC PRODUCT

$$\underset{\text{Acid}}{H_2O_{(l)}} + \underset{\text{Base}}{H_2O_{(l)}} \rightleftharpoons \underset{\substack{\text{Conjugate} \\ \text{acid}}}{H_3O^+_{(aq)}} + \underset{\substack{\text{Conjugate} \\ \text{base}}}{OH^-_{(aq)}}$$

The dissociation constant is given as :

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]}$$

Ionic product of water (K_w)

$$K_w = [H^+][OH^-]$$

At 298 K, $[OH^-] = [H^+] = 1.0 \times 10^{-7}$ M

$$\therefore \quad K_w = (1 \times 10^{-7} \text{ M})^2 = 1 \times 10^{-14} \text{ M}^2$$

$$K_a \times K_b = K_w$$

THE pH SCALE

- pH may be defined as negative logarithm of hydronium ion concentration.

$$pH = -\log [H_3O^+]$$

- $pK_w = pH + pOH = 14$

  $pK_w = pK_a + pK_b = 14$

- pH of a solution can be determined with pH paper or more accurately by pH meter.

SALT HYDROLYSIS

The reaction of the cation or anion of the salt with water to produce acidic or basic solution, is called salt hydrolysis.

Degree of hydrolysis : The degree of hydrolysis of a salt is defined as the fraction of the total salt which is hydrolysed.

- Salts of weak acid and strong base

$$K_h = \frac{K_w}{K_a} \; ; h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w}{K_a \cdot C}}$$

$$pH = -\frac{1}{2}(\log K_w + \log K_a - \log C)$$

- Salts of strong acid and weak base

$$K_h = \frac{K_w}{K_b} \; ; h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w}{K_b \cdot C}}$$

$$pH = -\frac{1}{2}(\log K_w - \log K_b + \log C)$$

- Salts of weak acid and weak base

$$K_h = \frac{K_w}{K_a K_b} \; ; h = \sqrt{K_h} = \sqrt{\frac{K_w}{K_a K_b}}$$

$$pH = \frac{1}{2}(pK_w + pK_a - pK_b)$$

BUFFER SOLUTIONS

- A buffer solution is defined as a solution which any change in its pH value even when small amounts of acid or base are added to it.

- Acidic buffer : It is the solution of a mixture of a weak acid and its salt with a strong base, e.g., $CH_3COOH + CH_3COONa$.

- Basic buffer : It is the solution of a mixture of a weak base and its salt with a strong acid, e.g., $NH_4OH + NH_4Cl$.

pH of acidic buffer (Henderson Hasselbalch equation)

$$pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$= pK_a + \log \frac{[\text{Conjugate base}]}{[\text{Acid}]}$$

**pH of Buffer Mixture**

pH of basic buffer (Henderson Hasselbalch equation)

$$pOH = pK_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$pH = pK_a + \log \frac{[\text{Base}]}{[\text{Conjugate acid}]}$$

SOLUBILITY EQUILIBRIA AND SOLUBILITY PRODUCT OF SPARINGLY SOLUBLE SALTS

Solubility product of an electrolyte at a specified temperature may be defined as the product of the molar concentration of its ions in a saturated solution, each concentration raised to the power equal to the number of ions produced on dissociation of one molecule of the electrolyte.

$$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$$

$$K_{sp} = [A^{y+}]^x[B^{x-}]^y$$
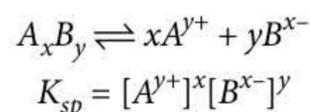
COMMON ION EFFECT

If to an ionic equilibrium, $AB \rightleftharpoons A^+ + B^-$, a salt containing a common ion (AC or BD) is added, the equilibrium shifts in the backward direction. This is called common ion effect.

Applications of Solubility Product and Common Ion Effect

- In the precipitation of salts, a salt precipitates if K_{sp} < ionic product.

- In the removal of hardness of water.

- In qualitative analysis.

- In fractional precipitation.

'Chemical equilibrium based model' for describing the strength of sludge !

A new model, based on chemical equilibrium theory, was established to evaluate the strength of sludges in biological wastewater treatment systems. The effectiveness of this model was demonstrated by the experimental results with an anaerobic hydrogen producing sludge. The Gibbs free energy of adhesion ($\Delta G°$) under shear could also be calculated using this model. The equilibrium constant $K°$ and $\Delta G°/RT$ at a shear intensity of 800 per second were estimated to be 6.54 ± 0.12 and 1.88 ± 0.02, respectively. The two parameters could be used to evaluate the strength of the hydrogen producing sludge.

REDOX REACTIONS

Chemical reactions involve transfer of electrons from one chemical substance to another. These electron-transfer reactions are termed as oxidation-reduction or redox reactions.

OXIDATION AND REDUCTION

Oxidation

Oxidation is a process which involves addition of oxygen, removal of hydrogen, addition of non-metal, removal of metal, increase in +ve charge, loss of electrons and increase in oxidation number, *e.g.,*
(i) Addition of oxygen : $2Mg + O_2 \rightarrow 2MgO$
(ii) Removal of hydrogen : $H_2S + Cl_2 \rightarrow 2HCl + S$
(iii) Addition of non-metal : $Fe + S \rightarrow FeS$
(iv) Removal of metal : $2KI + H_2O_2 \rightarrow 2KOH + I_2$
(v) Increase in +ve charge : $Fe^{2+} \rightarrow Fe^{3+} + e^-$
(vi) Loss of electrons (also known as de-electronation)
$H_2^0 \rightarrow 2H^+ + 2e^-$

Reduction

Reduction is just reverse of oxidation. Reduction is a process which involves removal of oxygen, addition of hydrogen, removal of non-metal, addition of metal, decrease in +ve charge, gain of electrons and decrease in oxidation number, *e.g.,*
(i) Removal of oxygen : $CuO + C \rightarrow Cu + CO$
(ii) Addition of hydrogen : $Cl_2 + H_2 \rightarrow 2HCl$
(iii) Removal of non-metal :
$2HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2 + SnCl_4$
(iv) Addition of metal : $HgCl_2 + Hg \rightarrow Hg_2Cl_2$
(v) Decrease in +ve charge : $Fe^{3+} \rightarrow Fe^{2+}$
(vi) Gain of electrons (also known as electronation)
$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$

Oxidising and Reducing Agents

An oxidising agent is a substance in which the oxidation number of its element decreases while a reducing agent is a substance in which the oxidation number of its element increases.

- **Oxidation number :** Charge on an atom produced by donating or accepting electrons is called oxidation number or oxidation state, *e.g.,*
  - ➢ For homonuclear species like N_2, Cl_2, H_2, P_4, S_8, etc., oxidation state is zero.
  - ➢ Oxidation state of H is +1 but –1 when combined with non-metals.
  - ➢ Oxidation state of oxygen is –2, but in peroxide it is –1. In OF_2, it is +2 as oxidation state of fluorine is always –1.

Types of Redox Reactions

- **Combination reaction :** The reaction in which two atoms or molecules combine together to form a third molecule, *e.g.,*
$$\overset{0}{C} + \overset{0}{O_2} \longrightarrow \overset{+4\,-2}{C\,O_2};$$

- **Decomposition reaction or intramolecular redox reaction :** The reaction in which a molecule breaks down to form two or more components out of which one must be in the elemental state, *e.g.,*
$$2\overset{+1\,-2}{H_2\,O} \overset{\Delta}{\longrightarrow} 2\overset{0}{H_2} + \overset{0}{O_2}$$
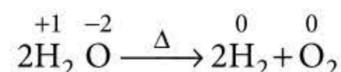
- **Displacement reaction or intermolecular redox reaction :** The reaction in which an atom or ion in a compound is replaced by an atom or ion of some other element, *e.g.,*
$$X + YZ \longrightarrow XZ + Y$$

(a) **Metal displacement reaction :** The reaction in which a metal in the compound is displaced by some other metal in the elemental state, e.g.,

$$\overset{+2}{Cu}SO_4 + \overset{0}{Zn} \longrightarrow \overset{0}{Cu} + \overset{+2}{Zn}SO_4$$
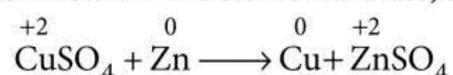
(b) **Non-metal displacement reaction :** The reaction in which a metal or a non-metal displaces another non-metal from its compound, e.g.,

$$2\overset{0}{Na} + 2\overset{+1}{H_2O} \longrightarrow 2Na\overset{+1}{O}H + \overset{0}{H_2}$$
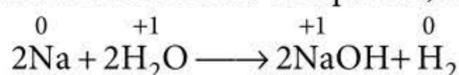
- **Disproportionation reaction or auto-redox reaction :** The reaction in which the same species is simultaneously oxidised as well as reduced, e.g.,

$$2\overset{-1}{H_2O_2} \longrightarrow 2\overset{-2}{H_2O} + \overset{0}{O_2}$$
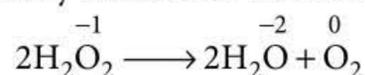
Applications of Redox Reactions

- In extraction of metals, e.g.,
$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$
- In electrochemical cells.
- In photosynthesis.
- In quantitative analysis.

BALANCING OF REDOX REACTIONS

By Oxidation Number Method

- Identify the element whose oxidation number have changed.
- Calculate the increase or decrease in oxidation number per atom and thereby identify oxidising and reducing agents. If more than one atom of the same element is involved, find total increase or decrease in oxidation number by multiplying with the number of atoms involved.
- Multiply the formula of oxidising and reducing agents by suitable integers so that
  total increase = total decrease.
- Balance all atoms other than H and O.
- Finally balance H and O atoms by adding H_2O molecules.
  - For acidic medium, first balance O– atoms by adding H_2O molecules to the side deficient in O and H^+ ions to the side deficient in hydrogen.
  - For basic medium, first balance O– atoms by adding H_2O molecules to the side deficient in O. Then, to balance H add H_2O molecules to the side deficient in H add equal number of OH^- ions to the other side.

By Ion-electron/Half-reaction Method

- Find the atoms whose oxidation numbers undergo a change.
- Split the reaction in two half equations, oxidation half-reaction and reduction half- reaction.
- Balance each half-reaction by balancing all other elements except H and O.
- Balance the oxidation numbers of the half- reactions by adding electrons to the side necessary.
- Balance the charge on the two sides of the half-reaction by adding H^+ ions (if medium is acidic) or adding OH^- ions (if medium is basic).
- Balance H and O by adding H_2O molecules to the side deficient.
- Multiply the two half-reaction by suitable integers so that, on adding, electrons gained in one are cancelled by the electrons lost in the other.

Equivalent Weights of Oxidising and Reducing Agents

Eq. wt. of oxidising agent

$$= \frac{\text{Molecular weight}}{\text{No. of electrons gained by one molecule}}$$
or
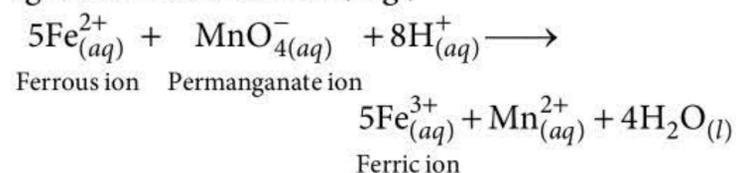Change in O.No. per mole

Eq. wt. of reducing agent

$$= \frac{\text{Molecular weight}}{\text{No. of electrons lost by one molecule}}$$
or
Change in O.No. per mole

## REDOX REACTIONS AS THE BASIS FOR TITRATIONS

Redox titrations can be used to determine the exact amount of an oxidising agent (or a reducing agent) in a given solution by titrating it against the standard solution (whose normality or molarity is known) of a suitable reducing agent (or the oxidising agent) in presence of an indicator.
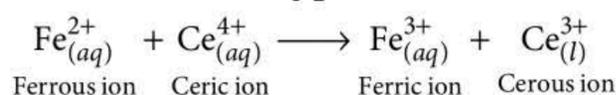
Types of Redox Titrations

- **Potassium permanganate titration :** In this titration, reducing agents like $FeSO_4$, Mohr's salt [$(NH_4)_2SO_4.FeSO_4.6H_2O$], H_2O_2, oxalic acid $(COOH)_2$, sodium oxalate $(COONa)_2$, etc. are directly titrated against $KMnO_4$ as the oxidising agent in acidic medium, e.g.,

$$5\underset{\text{Ferrous ion}}{Fe^{2+}_{(aq)}} + \underset{\text{Permanganate ion}}{MnO^-_{4(aq)}} + 8H^+_{(aq)} \longrightarrow$$
$$5\underset{\text{Ferric ion}}{Fe^{3+}_{(aq)}} + Mn^{2+}_{(aq)} + 4H_2O_{(l)}$$

- **Potassium dichromate titration :** In this titration, reducing agents given in potassium permanganate titration are directly titrated against $K_2Cr_2O_7$ as the oxidising agent in acidic medium. *e.g.*,
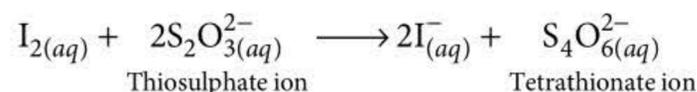
$$6Fe^{2+}_{(aq)} + Cr_2O^{2-}_{7(aq)} + 14H^+_{(aq)} \longrightarrow 2Cr^{3+}_{(aq)} + 6Fe^{3+}_{(aq)} + 7H_2O_{(l)}$$
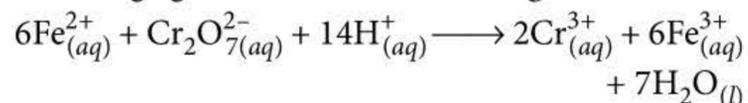
- **Ceric sulphate titration :** In this titration, the reducing agents such as Fe^{2+} salts, Cu^+ salts, nitrites, arsenites, oxalates, etc. are directly titrated against ceric sulphate, $Ce(SO_4)_2$ as the oxidising agent.

$$\underset{\text{Ferrous ion}}{Fe^{2+}_{(aq)}} + \underset{\text{Ceric ion}}{Ce^{4+}_{(aq)}} \longrightarrow \underset{\text{Ferric ion}}{Fe^{3+}_{(aq)}} + \underset{\text{Cerous ion}}{Ce^{3+}_{(l)}}$$

- **Iodimetric titration :** This titrations involve the direct use of iodine as the oxidising agent (in neutral or slightly acidic medium) using starch as an indicator. The various reducing agents used in these titrations are thiosulphates, sulphites, arsenites and antimonites.

$$I_{2(aq)} + \underset{\text{Thiosulphate ion}}{2S_2O^{2-}_{3(aq)}} \longrightarrow 2I^-_{(aq)} + \underset{\text{Tetrathionate ion}}{S_4O^{2-}_{6(aq)}}$$

- **Iodometric titration :** This titration is carried out in two steps. In the first step, oxidising agents such as $KMnO_4$, $K_2Cr_2O_7$, $CuSO_4$, peroxides, etc. are treated with an excess of KI when I_2 is liberated quickly and quantitatively.

$$2MnO^-_{4(aq)} + 16H^+_{(aq)} + 10I^-_{(aq)} \longrightarrow 2Mn^{2+}_{(aq)} + 5I_{2(s)} + 8H_2O_{(l)}$$
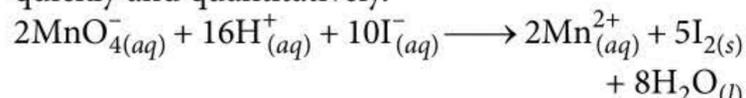
In the second step, the liberated iodine is titrated against a standard solution of sodium thiosulphate using starch as an indicator.

Electrochemical Cell

- It is a device which converts chemical energy produced in an indirect redox reaction into electrical energy.
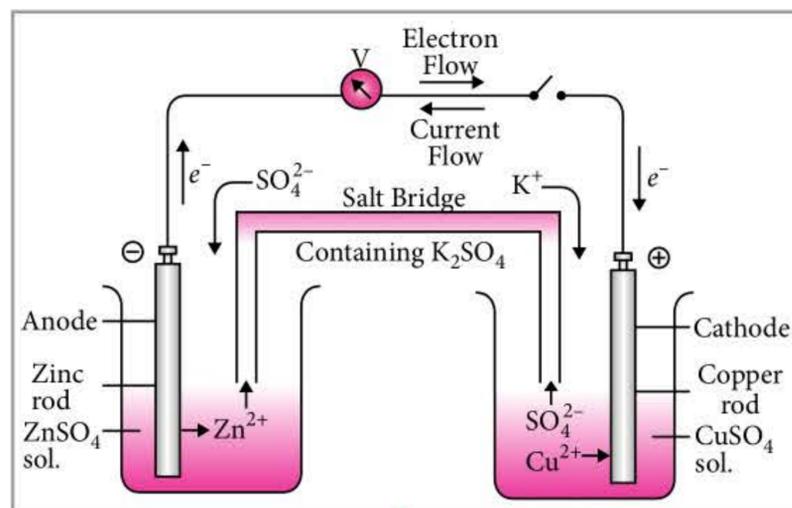
- Representation of an electrochemical cell $Zn \mid Zn^{2+} (C_1) \parallel Cu^{2+} (C_2) \mid Cu$

- Redox couple is defined as a combination of the oxidised and reduced forms of the same substance taking part in an oxidation or reduction half reaction.

- At anode : $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$
- At cathode : $Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$

Important generalisation :
- Oxidation occurs at the anode while reduction occurs at the cathode.
- Anode acts as the negative pole while cathode acts as the positive pole.
- Electrons flow from anode to cathode in the external circuit while current flows from cathode to anode.
- Chemical energy of the redox reaction occurring in the galvanic cell is converted into electrical energy.

ELECTRODE POTENTIAL

- **Electrode potential :** The tendency of an electrode to lose or gain electrons.

- If the concentration of electrolytes is taken as unity (1 mol L^{-1}) or if any gas appears in the electrode reaction, it is taken at 1 atm pressure and temperature is taken as 298 K, then the electrode potentials is called standard electrode potential ($E°$).

➢ By convention, the standard electrode potential ($E°$) of hydrogen electrode is 0.00 volt.
➢ A negative $E°$ means that the redox couple is a stronger reducing agent than the H^+/H_2 couple.
➢ A positive $E°$ means that the redox couple is a weaker reducing agent than the H^+/H_2 couple.
- The electrode potential is termed as oxidation potential if the electrode loses electrons and is called the reduction potential if the electrode gains electrons.

Electromotive series

A list of oxidising agents, arranged in decreasing order of their strength is called the activity or electromotive or electrochemical series.
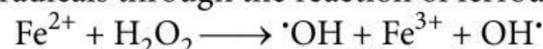
Applications :

- To compare the relative strength of oxidising and reducing agents.
- Comparison of reactivity of metals.
- To predict whether a metal will liberate hydrogen from the aqueous solution of acids or not.
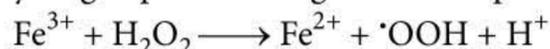
SPEED PRACTICE

1. Calculate the pH of a solution formed by mixing of 0.2 M NH_4Cl and 0.1 M NH_3. The pK_b of ammonia is 4.75.
   (a) 8   (b) 7.67   (c) 8.95   (d) 10.55

2. For a gaseous phase reaction, $A + 2B \rightleftharpoons AB_2$, $K_c = 0.3475$ at 200 °C. When 2 moles of B are mixed with one mole of A, the total pressure required to convert 60% of A to AB_2 is
   (a) 190.5 atm   (b) 181.5 atm
   (c) 101.0 atm   (d) 281.5 atm.

3. The change in the oxidation number of S in H_2S and SO_2 in the following industrial reaction :
   $2H_2S_{(g)} + SO_{2(g)} \longrightarrow 3S_{(s)} + H_2O_{(g)}$, will be
   (a) −2 to 0, +4 to 0   (b) −2 to 0, +4 to −1
   (c) −2 to −1, +4 to 0   (d) −2 to −1, +4 to −2

4. For a sparingly soluble salt A_pB_q, the relationship of its solubility product (K_{sp}) with its solubility (S) is
   (a) $K_{sp} = S^{p+q} \cdot p^p \cdot q^q$ (b) $K_{sp} = S^{p+q} \cdot p^q \cdot q^q$
   (c) $K_{sp} = S^{pq} \cdot p^q \cdot q^q$ (d) $K_{sp} = S^{pq} \cdot (pq)^{p+q}$

5. A 20 litre container at 400 K contains $CO_{2(g)}$ at pressure 0.4 atm and an excess of SrO (neglect the volume of solid SrO). The volume of the container is now decreased by moving the movable piston fitted in the container. The maximum volume of the container, when pressure of CO_2 attains its maximum value, will be
   (Given that : $SrCO_{3(s)} \rightleftharpoons SrO_{(s)} + CO_{2(g)}$, $K_p = 1.6$ atm)
   (a) 10 litre   (b) 4 litre
   (c) 2 litre   (d) 5 litre. **(NEET 2017)**

6. Which of the following is a set of reducing agents?
   (a) HNO_3, Fe^{2+}, F_2 (b) F^-, Cl^-, MnO_4^-
   (c) I^-, Na, Fe^{2+} (d) $Cr_2O_7^{2-}$, CrO_4^{2-}, Na

7. The ionisation constant of benzoic acid is 6.46×10^{-5} and K_{sp} for silver benzoate is 2.5×10^{-13}. How many times is silver benzoate more soluble in a buffer of pH 3.19 as compared to its solubility in pure water?
   (a) 2   (b) 3.32   (c) 4   (d) 4.32

8. Which set represents an odd nature with respect to oxidation number per atom of underlined atoms?
   (a) $H_2\underline{S}O_5$, $H_2\underline{S}_2O_8$, $K_2\underline{Cr}_2O_7$
   (b) $\underline{Cr}O_5$, $\underline{Cr}O_4^{2-}$, $\underline{S}O_4^{2-}$
   (c) $H\underline{N}O_2$, $\underline{N}_2O_3$, $\underline{N}F_3$
   (d) $\underline{N}H_4^+$, $\underline{N}_3H$, $\underline{N}H_3$