→ Concentration cells:→

- A cell in which electrical energy is produced by the transference of a substance from a system of high concentration to one at low concentration is known as a concentration cell.

OR

A cell in which EMF depends upon the difference of concentration is called concentration cell.

OR

Cells in which the EMF arises not due to any chemical reaction but due to transfer of matter from one half-cell to other because of a difference in the concentration of the species involved.

→ Types of concentration cells:→

Concentration cells

Electrode-concentration cells

- These are the cells in which the electrodes are of different concentrations and are dipped in the same solution of their salt, i.e. the electrolyte of only one strength.

1. Amalgum concentration cells
2. Gas concentration cells

Electrolyte-concentration cells

- These are the cells in which the two electrodes are of the same material which are dipped into two solutions of same electrolyte though of different concentrations.

1. Concentration cells without transport or transference.
2. Concentration cells with transport or transference.

→ Concentration cell without transport :→

- In this cell, the two electrolytic solutions are not in direct contant with each other and the transport of ions from one solution to other does not take place directly. These are called concentration cells without transport or transference.
- In order to understand the setting up such a cell, consider a simple electrochemical cell such as

$$\underset{1\,atm}{Pt, H_2(g)}, HCl(a_1) \,|\, AgCl(s), Ag$$

- Let activity of H^+ ions in the solution be $(a_+)_1$ and that of Cl^- be $(a_-)_1$.
- Since reduction takes place at the right hand electrode and oxidation at the left hand electrode, the two half-cell reactions will be as follows:

Reduction half-cell reaction:

$$AgCl(s) + e^- \rightleftharpoons Cl^-(a_-)_1 + Ag(s) \quad — ①$$

oxidation half-cell reaction:

$$\frac{1}{2}H_2(g) \rightleftharpoons H^+(a_+)_1 + e^- \quad — ②$$

- The net reaction taking place in the cell for one faraday of electricity is obtained by adding eq. ① and ②. Thus,

$$\frac{1}{2}H_2(g) + AgCl(s) \rightleftharpoons H^+(a_+)_1 + Cl^-(a_-)_1 + Ag(s) \quad – ③$$

- Now consider the same cell with difference that the activity of HCl solution is now a_2.

$$\underset{1\,atm}{Pt, H_2(g)}, HCl(a_2) \mid AgCl(s), Ag$$

- The net cell reaction for one faraday of electricity will now be as follows:

$$\frac{1}{2}H_2(g) + AgCl(s) \rightleftharpoons H^+{}_{(a_+)_2} + Cl^-{}_{(a_-)_2} + Ag(s) \quad — ④$$

- Finally, consider a situation when the two cells are connected to each other in such a way that they send current in opposite direction. Thus,

$$\underset{1\,atm}{Pt, H_2(g)}, HCl(a_1), AgCl(s), Ag \mid Ag, AgCl(s), HCl(a_2), \underset{1\,atm}{H_2(g), Pt}$$

- The overall reaction of the combined cell for the passage of one faraday of electricity will, evidently, be obtained by subtracting eq ④ from eq. ③ i.e.

$$H^+(a_+)_2 + Cl^-(a_-)_2 \rightleftharpoons H^+(a_+)_1 + Cl^-(a_-)_1 \quad — ⑤$$

Thus, for the flow of one faraday of electricity, the overall reaction is the transfer of one mole of each H^+ and Cl^- ions or one mole of HCl, from a solution of activity a_2 to that of activity a_1.

- Hence, EMF of such a cell would be given by

$$E_{w.o.t.} = \frac{RT}{F}\ln\frac{(a_+)_2}{(a_+)_1} + \frac{RT}{F}\ln\frac{(a_-)_2}{(a_-)_1} \quad — ⑥$$

$$= \frac{RT}{F}\ln\frac{(a_\pm)_2^2}{(a_\pm)_1^2} \quad — ⑦$$

$$\because a = (a_+)^x (a_-)^y$$
$$= (a_\pm)^{x+y}$$

Where $(a_\pm)_1$ and $(a_\pm)_2$ are the mean ionic activities of the electrolyte in the two solutions

and subscript w.o.t. stands for "without transference."

- We know that for uni-univalent eletrolyte

$$a = (a_\pm)^2 \quad — ⑧$$

so, eq. ⑦ becomes

$$E_{w.o.t.} = \frac{RT}{F} \ln\left(\frac{a_2}{a_1}\right) \quad — ⑨$$

where a_1 and a_2 are the activities of HCl in two solutions.

- It will observed that the cell reaction does not involve transfer of electrolyte from one solution to the other directly. It takes place indirectly. This cell is, therefore, a concentration cell without transference.
- If the middle electrode, viz., Ag, AgCl (s), is withdrawn, the two solutions of HCl will be in direct contact with each other. The cell will then become a concentration cell with transference.

→ Concentration cell with transport :→

- In these cells, the two solutions are in direct contact with each other. The transference of ions from one solution to the other takes place directly. Such cells are called concentration cells with transport or transference.
- Now consider a concentration cell formed by combining two hydrogen gas electrodes in contact with HCl solutions of different concentrations. The two solutions are in direct contact with each other, as shown:

$$Pt,\ \underset{1\,atm}{H_2(g)},\ HCl\,(a_1)\ |\ HCl\,(a_2),\ \underset{1\,atm}{H_2(g)},\ Pt$$

$$H^+ \longrightarrow$$
$$\longleftarrow Cl^-$$

- The reaction on the left involves oxidation and that on the right involves reduction, as usual.
- The following changes are involved for the flow of one faraday of electricity:

Left Hand electrode:

$$\frac{1}{2}H_2(g) \rightleftharpoons H^+(a_+)_1 + e^- \quad — ①$$

Right Hand electrode:

$$H^+(a_+)_2 + e^- \rightleftharpoons \frac{1}{2}H_2(g) \quad — ②$$

Thus, H^+ ions are generated at the left hand electrode and consumed at the right hand as the current follows.

- Since the solutions are in direct contact with each other, the ions are free to move from one solution to other when current flows through the cell.
- In the present case, H^+ ions moves from the solution on the left hand side to that on right hand side.
- Since anions move in direction opposite to that in which cations move, Cl^- ions migrate from right to left side.
- Let

If transport number of Cl^- ions $= t_- = 1 - t_+$
and transport number of H^+ ions $= t_+ = 1 - t_-$ $(\because t_+ + t_- = 1)$

Then, for one faraday of electricity passing through, t_- faraday will be carried by Cl^- ions and t_+ faraday by H^+ ions.

- According to Faraday's second law, t_- equivalent of Cl^- ions will be transfered from solution of activity a_2 to the solution of activity a_1. This may be represented as

$$t_- Cl^-(a_-)_2 \rightleftharpoons t_- Cl^-(a_-)_1 \quad — ③$$

- At the same time, t_+ equivalent of H^+ ions will be transformed from the solution of activity a_1 to that of activity a_2 which may be represented as

$$t_+ H^+ (a_+)_1 \rightleftharpoons t_+ H^+ (a_+)_2 \quad — ④$$

- The net result for the flow of one faraday of electricity is summed up below:

Left hand electrode :- The following operations occur at this electrode :

→ Gain of 1 gm equivalent of H^+ ions by process ①

→ Loss of t_+ gm equivalent of H^+ ions by process ④

∴ Net gain of H^+ ions = $(1-t_+)$ gram equivalent = t_- gram equivalent

At the same time

Net gain of Cl^- ions = t_- gram equivalent by process ③

Right hand electrode :- The following operations occur at this electrode:

→ Loss of 1 gm equivalent of H^+ ions by process ②

→ Gain of t_+ gram equivalent of H^+ ions by process ④

∴ Net loss of H^+ ions = $(1-t_+)$ gram equivalent = t_- gram equivalent

At the same time

Net loss of Cl^- ions = t_- gram equivalent by process ③

Thus, for every one faraday of electricity, there is a net transfer of t_- gram equivalent of H^+ ions and t_- gram of Cl^- ions from right to left, i.e., from the solution in which activity of HCl is a_2 to that in which activity of HCl is a_1.

- These changes are represented as

$$t_-H^+(a_+)_2 \rightleftharpoons t_-H^+(a_+)_1$$

$$t_-Cl^-(a_-)_2 \rightleftharpoons t_-Cl^-(a_-)_1$$

- The EMF of concentration cell with transport is given by -

$$E_{w.t.} = t_- \frac{RT}{F} \ln \frac{(a_+)_2}{(a_+)_1} + t_- \frac{RT}{F} \ln \frac{(a_-)_2}{(a_-)_1} \quad — \quad ⑤$$

$$= t_- \frac{RT}{F} \ln \frac{(a_\pm)_2^2}{(a_\pm)_1^2} \quad — \quad ⑥ \qquad \because a = (a_+)^x (a_-)^y = (a_\pm)^{x+y}$$

where $(a_\pm)_1$ and $(a_\pm)_2$ are the mean ionic activities of two HCl solutions.

- We know that for uni-univalent electrolyte

$$a = (a_\pm)^2 \quad — \quad ⑦$$

So, eq. ⑥ becomes

$$E_{w.t.} = t_- \frac{RT}{F} \ln \frac{a_2}{a_1} \quad — \quad ⑧$$

where a_2 and a_1 are the activities of HCl solutions of right hand and left hand electrodes, respectively.

- Eq. ⑧ is used for calculating activity of an electrolyte at a given concentration if $E_{w.t.}$ and activity of one of the solution is known.

→ Liquid junction potential (E_l) :→

- When two salt solutions of different concentrations are placed in contact with one another, the ions from the concentrated solution will tend to diffuse into dilute one.
- The rate of diffusion of each ion is approximately proportional to the speed of the ions in the electric field.
- Suppose that positive ion moves with a greater speed than the negative ion. It means that the positive ions from the concentrated solution will diffuse ahead of the negative in the dilute solution. Thus, the dilute solution becomes positively charged with respect to the concentrated solution.
- Suppose the negative ion move faster. It means that negative ion will diffuse rapidly in dilute solution than the positive ion and the dilute solution gets a negative charge.
- In both the above mentioned cases, an electrical double layer is set up at the junction of the two solutions and thus a potential difference is set up at this junction. This potential difference developed at the junction of two solutions of different concentrations is termed as liquid junction potential (E_l).

- From the above discussion, it follows that
  (i) The liquid junction potential is due to the different migration velocities of ions.
  (ii) Magnitude of liquid junction potential depends upon relative speed of ions.
  (iii) If two ions are moving with the same speed, there will not be any liquid junction potential.
- The EMF of a concentration cell with transport includes the liquid junction is given by

$$E_{w.t.} = 2t_{-} \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1} \quad - \text{①}$$

- The EMF of concentration cell without transport does not include liquid junction potential is given by

$$E_{w.o.t.} = \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1} \quad — ②$$

Hence, liquid junction potential E_l is given by

$$E_l = E_{w.t.} - E_{w.o.t.}$$

$$= 2t_- \frac{RT}{F} \ln \frac{(a\pm)_2}{(a\pm)_1} - \frac{RT}{F} \ln \frac{(a\pm)_2}{(a\pm)_1}$$

$$= (2t_- - 1) \frac{RT}{F} \ln \frac{(a\pm)_2}{(a\pm)_1}$$

$$= (2t_- - (t_+ + t_-) \frac{RT}{F} \ln \frac{(a\pm)_2}{(a\pm)_1} \qquad (\because t_+ + t_- = 1)$$

$$= (2t_- - t_+ - t_-) \frac{RT}{F} \ln \frac{(a\pm)_2}{(a\pm)_1}$$

$$E_l = (t_- - t_+) \frac{RT}{F} \ln \frac{(a\pm)_2}{(a\pm)_1} \quad — ③$$

It is evident from Eq. ③ that the sign as well as the magnitude of L.J.P. depends on the transport numbers of the anion and cation.

If

$t_- = t_+$ then L.J.P. = 0 or negligibly small

$t_- < t_+$ then L.J.P. will be negative

$t_- > t_+$ then L.J.P. will be positive and will add to the EMF of the cell.

- Potassium chloride and ammonium nitrate are amongst the electrolytes in which the transport numbers of cations and anions are nearly the same. The solutions of these electrolytes are, therefore, frequently used as salt bridge because the liquid junction potential is then reduced to minimum.

→ Applications of concentration cells:→

1. Determination of valency of ions in doubtful cases:→

- The valency of mercurous ion was in doubt for a cosiderable time. It was finally established by determining the EMF of a concentration cell of the type given below:

Mercury, Mercurous nitrate solution (C_1) || Mercurous nitrate (C_2), Mercury

- The salt bridge represented by the two vertical lines connecting the two solutions contains saturated solution of ammonium nitrate.
- The EMF of the cell, E, assuming the activity coefficients to be equal to 1, is given by the expresson

$$E = \frac{RT}{nF} \ln \frac{C_2}{C_1}$$

Where n is the valency of mercurous ion and $C_2 > C_1$. Thus,

$$E = \frac{0.0591}{n} \log \frac{C_2}{C_1} \quad (\text{at } 25^\circ C)$$

It was found that when C_2/C_1 was 10, the EMF was 0.0295 volt. Therefore, the valency of mercurous ion is 2 and it should be represented as Hg_2^{2+}.

2. Determination of the solubility product constant :→

- The solubility product constant of a sparingly soluble salt is a kind of equilibrium constant.
- Consider the salt Mx in equilibrium with its ions in a saturated solution.

$$Mx(s) \rightleftharpoons M^+(aq) + x^-(aq)$$

- The solubility product of the salt is given by $K_{sp} = a_{M^+} + a_{X^-} = [M^+][X^-]$, assuming an ideal solution so that activities equal concentrations.
- The above reaction is the cell reaction for the following cell:

$$M,\ M^+X^-\ (\text{saturated sol.})\ |\ MX(s),\ M$$

The half cell reactions are

R.H.E.

$$MX(s) + e^- \rightleftharpoons M + X^-$$

L.H.E.

$$M \rightleftharpoons M^+(aq.) + e^-$$

Overall reaction

$$MX(s) \rightleftharpoons M^+(aq.) + X^-(aq);$$

$E^\circ = E^\circ_R - E^\circ_L$ (values of E°_R & E°_L are taken from std electrode potential at 25°c from table)

- Knowing the value of E° for cell under consideration and using the relation:

$$-\Delta G^\circ = nFE^\circ$$

$$\text{or} \quad -\Delta G^\circ = 2.303\ RT \log K_{sp}$$

$$\text{or} \quad nFE^\circ = 2.303\ RT \log K_{sp}$$

$$\log K_{sp} = \frac{nFE^\circ}{2.303\ RT}$$

i.e. $$E^\circ = \frac{2.303\,RT}{nF}\log K_{sp}$$

or $$E^\circ = \frac{0.0591}{n}\log K_{sp} \quad \text{at } 25^\circ c$$

Thus, K_{sp} can be calculated from the known value of E°.

3. Determination of activity coefficients of electrolytes:→

- For determination of activity coefficient of HCl, consider a cell without liquid junction containing HCl.
- The two electrodes are so chosen that one is reversible with respect to the cation of electrolyte and other is reversible with respect to the anion.
- The first electrode is hydrogen electrode and the other can be the silver-silver chloride electrode. Accordingly, the cell arrangement is as follows:

$$Pt\,;\ H_2(g)(1\,atm)\ |\ HCl\ (m)\ |\ AgCl(s),\ Ag(s)$$

where m is the molality of HCl solution.

The cell reaction is

$$\frac{1}{2}H_2(g) + AgCl(s) \rightleftharpoons Ag(s) + H^+(m) + Cl^-(m)$$

EMF of the cell is given by

$$E = E^\circ - 0.0591\log\frac{a_{H^+}\,a_{Cl^-}}{(a_{H_2})^{1/2}}$$

$$\text{or} \quad E = E^\circ - 0.0591 \log a_{H^+} a_{Cl^-}$$

Because activity of each Ag(s), AgCl(s) and $H_2(g)$ at 1 atm pressure is taken as unity. For uni-univalent electrolyte, activity is given by

$$a_{H^+} a_{Cl^-} = (a_\pm)^2 = (\gamma_\pm m)^2 = \gamma_\pm^2 m^2$$

where $\gamma_\pm$ = mean ionic activity coefficient

m = molality of HCl

hence

$$E = E^\circ - 0.0591 \log \gamma_\pm^2 m^2$$

$$= E^\circ - 0.0591 \log \gamma_\pm^2 - 0.0591 \log m^2$$

$$= E^\circ - 2 \times 0.0591 \log \gamma_\pm - 2 \times 0.0591 m$$

$$E = E^\circ - 0.1182 \log \gamma_\pm - 0.1182 \log m$$

Rearranging

$$E + 0.1182 \log m = E^\circ - 0.1182 \log \gamma_\pm$$

The two unknowns E° and $\gamma_\pm$ in above equation can be determined by measuring the EMFs of the cell over various concentrations of HCl, including dilute concentrations. At infinite dilution, $m = 0$ and $\gamma_\pm = 1$ so that $\log \gamma_\pm = 0$. Thus, a plot of $E + 0.1182 \log m$ v/s m, extrapolated to $m = 0$ gives E° as the y intercept.

Knowing the value of E°, $\gamma_\pm$ of HCl at any concentration can be determined from EMF data of the cell at that concentration.

→ Potentiometric titrations:→

- The potential of an electrode depends upon the concentration of the ion to which it is reversible in accordance with Nernst equation.
- In a titration, there is change in ionic concentration which can be followed by measuring the potential of a suitable electrode.
- The potentiometric titrations are, thus, those titrations which involve the measurement of electrode potential with addition of the titrant.
- The end point is determined by plotting a curve of potential versus the volume of titrant and recording the inflection point.

→ Advantage of potentiometric titrations:→

- The necessary apparatus required is generally inexpensive, reliable and readily available in most laboratories.
- It is easy to interpret titration curves with a minimum of methamatical effort.
- The method can be used for coloured solutions and in solutions where precipitation occurs during the reaction.
- The method is applicable for analysis of dilute solutions with high degree of accuracy.
- In potentiometric titrations, several components may be titrated in the same solution without the possibility of indicators interferring with each other, for instance, iodide and bromide may be titrated together.
- The method may be made automatic by bringing relay in operation which will stop the liquid from running from the burette when EMF reaches a certain value.

→ Indicator electrodes:→

- Glass electrode
- Membrane electrode
- Quinhydrone electrode
- Tungsten and molybdenum electrode
- Hydrogen electrode
- Antimony- Antimony oxide electrode

→ Types of potentiometric titrations:→

1. Acid-Base titrations
2. Complexometric titrations
3. Oxidation-reduction titrations
4. Precipitation titrations

→ Potentiometric titrations :→

→ Acid - base titrations :→

- The neutrilisation of acids and bases are always accompanied by change in the concentration of H^+ or OH^- ion (i.e. pH of the solution), it is evident that hydrogen electrode may be used in these titrations.
- The reference electrode used in this case is N - calomal electrode.
- The apparatus used for acid base titrations is shown in figure 1. A known volume of the acid to be titrated is kept in a beaker having an automatic stirrer. It also has a standard hydrogen electrode. It is connected to a N-calomel electrode through a salt bridge. The hydrogen and calomel electrodes are connected to a potentiometer, and the EMF of the solution is recorded. After the each addition of base from burette into the beaker, the EMF is measured. This procedure is continued. Then the values of EMF are plotted against the ml of base added and a curve is obtained as shown in fig. 2.

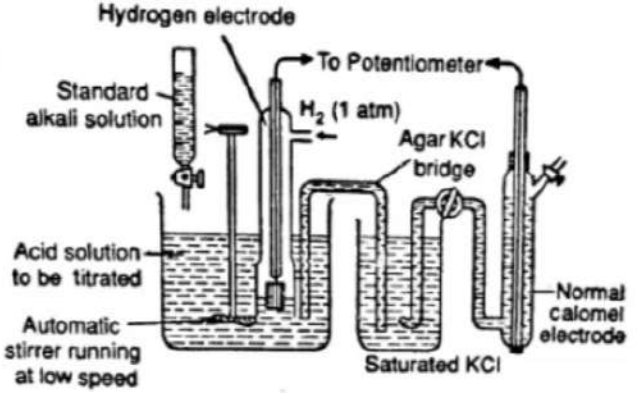


Figure. 1

- The potential of any hydrogen electrode is given by

$$E = E^0 - 0.0591 \log H^+ \quad \text{at } 25^\circ C$$

$$E = E^\circ + 0.0591\, pH \quad (\because pH = -\log H^+)$$

- Thus, the change in EMF of a cell is proportion to the change in pH during reaction. The point where the EMF increases at one gives the end point. This method is not very accurate.
- For more satisfactory method of detecting the end point $\Delta E/\Delta V$ is plotted against V.

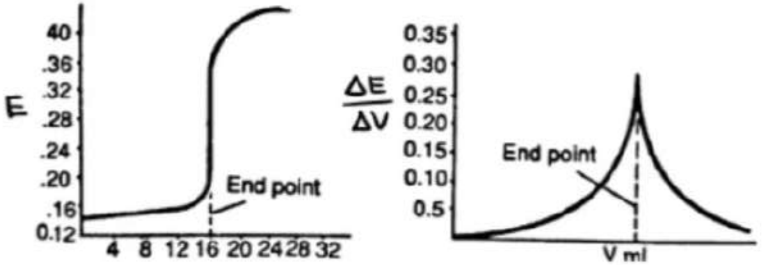


Figure 2.

→ Potentiometric titrations :→

→ Complexometric titrations :→

- Complexometric titration can be followed with an electrode of metal whose ion is involved in complex formation.
- For example, a silver electrode may be used to follow the titration of cyanide ion with a standard silver solution.
- The potential of the silver electrode is given by following equation

$$E = E^{0} + 0.0591 \log [Ag^{+}] \quad (25^{\circ}c) \quad — ①$$

- The silver ion concentration will be determined by the equilibrium constant for the complex formation.

$$Ag^{+} + 2CN^{-} \rightleftharpoons Ag(CN)_2^{-} \quad - ②$$

$$K_a = \frac{[Ag(CN)_2^{-}]}{[Ag^{+}][CN^{-}]^{2}} \quad — ③$$

- In this case, solid silver cyanide begins to be precipited soon after the equivalence point. A small addition of silver does niether change the concentration of the complex nor of the silver ion to any extent, so that the titration curve has an almost horizontal portion shortly after the equivalence point.
- Potentiometric end-point detection has been sucessfully applied to EDTA titrations particularly by Reilley (1956).

→ Potentiometric titrations:→

→ Oxidation-Reduction or Redox titrations:→

- Like acid-base titrations, the redox titrations are also carried out potentiometrically.
- In this case, the electrode reversible with respect to H^+ ion is replaced by an inert metal, such as platinum wire, immersed in a solution containing both the oxidised and reduced forms of same species. The electrode acts as an oxidation-reduction electrode.
- Let us consider the redox reaction involving oxidation of Fe^{+2} ions by Ce^{+4} ions.

$$Fe^{+2}(aq.) + Ce^{+4}(aq) \rightleftharpoons Fe^{+3}(aq.) + Ce^{+3}(aq.) \quad -①$$

- With the presence of both the Fe^{+2} and Fe^{+3} ions, the electrode behaves as an oxidation-reduction electrode whose potential, according to the Nernst equation is given by.

$$E = E^\circ_{el} + \frac{RT}{F} \ln \frac{[Fe^{+3}]}{[Fe^{+2}]} \quad — ②$$

$$= E^\circ_{el} + 0.0591 \log \frac{[Fe^{+3}]}{[Fe^{+2}]} \quad \text{at } 25^\circ c \quad -③$$

∴ For Ce^{+4}/Ce^{+3}

$$E = E^\circ_{el} + 0.0591 \log \frac{[Ce^{+4}]}{[Ce^{+3}]} \quad - ④$$

- At the equivalence point, $[Fe^{+2}] = [Ce^{+4}]$ and $[Fe^{+3}] = [Ce^{+3}]$ so that the electrode potential at equivalence point

$$E_{eq} \quad E^\circ_1 + 0.0591 \log \frac{[Fe^{+3}]}{[Fe^{+2}]} = E^\circ_2 + 0.0591 \frac{[Ce^{+4}]}{[Ce^{+3}]} \quad — ⑤$$

The above equations may be written as

$$E_{eq} = E_1^\circ + 0.0591 \log \frac{[Fe^{+3}]}{[Fe^{+2}]} \quad — ⑥$$

and $$E_{eq} = E_2^\circ + 0.0591 \log \frac{[Ce^{+4}]}{[Ce^{+3}]} \quad — ⑦$$

— Adding and simplifying, keeping in mind that at equivalence point

$$[Fe^{+2}] = [Ce^{+4}] \text{ and } [Fe^{+3}] = [Ce^{+3}]$$

$$2E_{eq} = E_1^\circ + 0.0591 \log \frac{[Fe^{+3}]}{[Fe^{+2}]} + E_2^\circ + 0.0591 \log \frac{[Fe^{+2}]}{[Fe^{+3}]}$$

or $$2E_{eq} = E_1^\circ + E_2^\circ$$

or $$E_{eq} = \frac{E_1^\circ + E_2^\circ}{2} \quad — ⑧$$

- For potentiometric measurments, the oxidation-reduction electrode (viz, $Pt; Fe^{+3}, Fe^{+2}$) is combined with a reference electrode, e.g. Calomal electrode, to form a galvanic cell which is represented as

$$Hg, Hg_2Cl_2(s), KCl \text{ (sat. sol.)} \parallel Fe^{+2}, Fe^{+3}; Pt$$

— Before the equivalence point, the EMF of cell would be given by

$$E = E_L - E_R = E_{el}^\circ + 0.0591 \log \frac{[Fe^{+3}]}{[Fe^{+2}]} - E_{calomal}$$

$$= 0.77 + 0.0591 \log \frac{[Fe^{+3}]}{[Fe^{+2}]} - 0.24 \quad — ⑨$$

and after the equivalence point, EMF of cell is given by

$$E = 1.61 + 0.0591 \log \frac{[Ce^{+4}]}{[Ce^{+3}]} - 0.24 \quad - ⑩$$

At the equivalence point, as already discussed, the EMF of cell is given by

$$E = \frac{0.77 + 1.61}{2} - 0.24 \quad - ⑪$$

- The EMF of the cell is measured potentiometrically at each stage of titration and the EMF data thus obtained are processed for the equivalence point.
- The redox titration curve is exactly similar to the acid-base titration curve.

→ Potentiometric titrations:→

→ Precipitation titrations:→

- Suppose solution of silver nitrate is standardise by titrating against a standard solution of potassium chloride.
- The silver electrode is used as the indicator electrode in this case.
- The potential of the half cell, Ag^+, Ag, is measured by connecting it with calomel electrode.
- The solution is titrated against a standard solution of potassium chloride the strength of which is about 10 times higher.
- As the reaction proceeds, the Ag^+ ions get gradually precipitated as silver chloride.

$$Ag^+ + NO_3^- + (K^+ + Cl^-) \rightleftharpoons AgCl\downarrow + K^+ + NO_3^-$$

- The concentration of Ag^+ ions goes on decreasing and hence the potential of the silver electrode goes on decreasing continuously on progressive addition of KCl solution.
- The potential of silver electrode according to Nernst equation is given by

$$E_{el} = E^\circ_{el} + 0.0591 \log [Ag^+] \quad (\text{at } 25^\circ c)$$

- The electrode potential will change slowly at first but more and more rapidly as the end point approaches.
- At the end point, the concentration of Ag^+ ions is very small due to slight solubility of AgCl. Hence, the change in electrode potential is maximum at the end point.
- If the addition of KCl is continued further, the concentration of Ag^+ ions remains almost unaffected except for very small decrease on account of the common ion effect.
- The addition of KCl beyond the end point, there, cause only a small change in potential.
- The titration curve is same as in the case of acid-base titration.

→ Definition of pH and pKa :→

→ Ionic product of water or Dissociation of water :→

- Pure water is essentially a covalent compound. However, it ionises very slightly and the following equilibrium is established :

$$H_2O \rightleftharpoons H^+ + OH^- \quad — ①$$

where H^+ = A hydrogen ion

OH^- = A hydroxyl ion

- The removal of one orbital electron from hydrogen atom gives the positive hydrogen ion or hydrogen cation, which is in fact a bare proton.
- The bare proton has no separate existance in solution and owes its solubility of solvation by a water molecule to give the hydronium ion, H_3O^+.
- The ionisation equilibrium of water is thus represented more accurately as:

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \quad — ②$$

- However, as many qualitative and quantitative considerations remain essentially same for the unsolvated and solvated proton, it is usual for convenience to refer to the unsolvated proton, H^+.
- On applying the law of mass action to eq ①, we get

$$K = \frac{[H^+][OH]}{[H_2O]} \quad — ③$$

K = Ionisation constant = Defined as the product of concentration of H^+ and OH^- ions expressed in gram ions per litre.

- As water is ionised to very slight extent (about 1 in 10^7 water molecules), the concentration of water molecules is very large as compared with H^+ and OH^- ions so that it can be regarded as practically constant.

Therefore eq. ③ may be written as

$$K_W = K[H_2O] = [H^+][OH^-] \quad — \quad ④$$

where K_W = Ionic product of water

- Conductivity measurements show that in pure water,

$$[H^+] = 10^{-7} \text{ mole/litre at } 25°c$$

- Furthermore in pure water

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

Therefore eq. ④ may written as

$$K_W = [10^{-7}][10^{-7}]$$

$$\text{or} \quad K_W = 10^{-14} \text{ mole/litre at } 25°c \quad — ⑤$$

- For all aqueous solutions, the product of $[H+]$ and $[OH-]$ is constant at constant temperature.
- If extra H^+ ions are introduced, the ionisation of H_2O is supressed to the point at which $[H^+][OH^-] = 10^{-14}$. Similarly, if extra OH^- ions are introduced, the ionisation of water is again supressed to maintain the constancy of $[H^+][OH^-]$.

→ pH value :→

- From eq. ④ and ⑤, we have

$$[H^+][OH^-] = 10^{-14} \quad — \quad ⑥$$

In case of pure water, $[H^+] = [OH^-]$

Therefore, equation ⑥ becomes as

$$[H^+][H^+] = 10^{-14}$$

$$[H^+] = 10^{-7}$$

- It means if the concentration of H^+ ions in solution is 1×10^{-7} gm ions per litre, it is neutral and if more, it is acidic and if less it is alkaline. Thus the acidity or alkalinity of the solution can be expressed in the terms of its H^+ ion concentration.
- It is not very convenient to express acidity and basicity in terms of H^+ ions as its values are usually very small, especially in case of weakly ionised substances.
- In order to overcome this difficulty, S.P. Sörenson, Danish biochemist in 1909 introduced a new notation to express the H^+ ion concentrations. According to Him, the pH of solution is, " numerically equal to the negative power to which 10 must be raised in order to express the H^+ ion concentration."

$$[H^+] = 10^{-pH}$$

or $\quad \log[H^+] = -pH \log 10$

or $\quad \log[H^+] = -pH \qquad (\because \log 10 = 1)$

$$pH = -\log[H^+] \quad - \quad ⑦$$

Hence pH is the negative logarithm of hydrogen ion concentration.

- For pure water or neutral solution in which

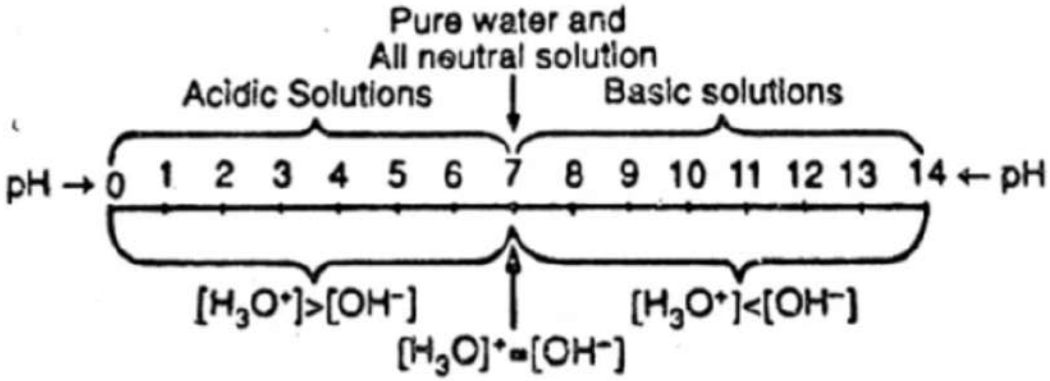
$$[H^+] = 1 \times 10^{-7}$$

or $$pH = -\log[10^{-7}]$$

$$pH = 7$$

The pH of neutral solution is 7.

- In acidic solution $[H^+] > 10^{-7}$ therefor $pH < 7$
- In alkaline solution $[OH^-] > [H^+]$ and therefore $[OH^-] > 10^{-7}$ and $[H^+] < 10^{-7}$ therefore $pH > 7$.
- Thus, if pH value of a solution is 7, it is neutral. If pH value is less than 7, the solution is acidic, and if it is more than 7, the solution is alkaline.
- A pH scale ranges from 0 to 14. This is shown in following figure.



→ Some other logarithmic expressions :→

- Just as pH is used to indicate hydrogen ion concentration, pOH is used to indicate the hydroxyl ion concentration. Thus,

$$pOH = -\log[OH^-] \quad - ⑧$$

- Ionic product of water, K_w, is expressed in a similar manner as

$$pK_w = -\log K_w$$

- We know that

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

taking logs and reversing sign, we have

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

$$pK_w = pH + pOH \quad - ⑨$$

This relationship holds good for water as well as for any aqueous solution.

- Since K_w at 25°c is about 10^{-14}, pK_w is 14.0. Hence,

$$pH + pOH = 14$$

- We may also represent dissociation constants of acids and bases (K_a and K_b) in the following expressions.

$$pK_a = -\log K_a \quad - ⑩$$

and $$pK_b = -\log K_b \quad - ⑪$$

→ Determination of pH using hydrogen electrode :→

→ The hydrogen electrode in contact with a solution of H^+ ions involves following reaction

$$H^+ + e^- \rightleftharpoons \frac{1}{2} H_2 \,(1\ \text{atm})$$

→ The potential of hydrogen electrode is given by Nernst equation

$$E_{el} = E^\circ_{el} + 2.303 \frac{RT}{F} \log [H^+]$$

By convention, $= E^\circ_{el}$, i.e., the standard electrode potential of hydrogen electrode, is zero.

$$E_{el} = \frac{2.303\,RT}{F} \log [H^+]$$

$$\text{or} \quad E_{el} = 0.0591 \log [H^+]$$

$$\text{or} \quad E_{el} = -0.0591\, pH \qquad (\because pH = -\log[H^+])$$

- Thus, the potential of a hydrogen electrode depends upon the pH of the solution with which it is in contact.
- The potential of hydrogen electrode can be determined by combining the hydrogen electrode with a reference electrode, say, calomel electrode.
- The complete cell is represented as

$$Pt, H_2(1\ \text{atm}), H^+\ (c = \text{unknown}) \,||\, KCl\ (\text{sat. sol.}), Hg_2Cl_2(s), Hg$$

- The EMF of the cell is determined potentiometrically. This is given by

$$E = E_R - E_L$$

$$E = 0.2422 - (-0.0591\,pH)$$

or $$0.0591\,pH = E - 0.2422$$

or $$pH = \frac{E - 0.2422}{0.0591}$$

→ Determination of pH using quinhydrone electrode :→

– The quinone- hydroquinone system involves the following equilibrium:

$$\underset{\text{Quinone (Q)}}{C_6H_4O_2} + 2H^+ + 2e^- \rightleftharpoons \underset{\text{Hydroquinone }(QH_2)}{C_6H_6O_2}$$

– For the reduction reaction given above, the potential developed on a platinum electrode immersed in this system is given by the Nernst equation as

$$E_{el} = E^\circ_{el} - \frac{2.303RT}{2F} \log \frac{[QH_2]}{[Q][H^+]^2} \quad — ①$$

$$= E^\circ_{el} + \frac{2.303RT}{2F} \log \frac{[Q][H^+]^2}{[QH_2]} \quad — ②$$

$$= E^\circ_{el} + \frac{2.303RT}{2F} \log \frac{[Q]}{[QH_2]} + \frac{2.303RT}{2F} \log [H^+]^2$$

$$= E^\circ_{el} + \frac{2.303RT}{2F} \log \frac{[Q]}{[QH_2]} + \frac{2.303RT}{2F} 2 \log [H^+]$$

$$= E^\circ_{el} + \frac{2.303RT}{2F} \log \frac{[Q]}{[QH_2]} + \frac{2.303RT}{F} \log [H^+] \quad — ③$$

- Instead of taking quinone and hydroquinone, a small amount of quinhydrone is taken which is an equimolar compound of quinone (Q) and hydroquinone (QH_2).
- Since hydroquinone (QH_2) is a weak acid, its ionisation is very small particularly if the pH of the solution is less than 7. Therefore, the concentration of hydroquinone (QH_2) is same as that of quinone (Q), i.e. the quantity $[Q]/[QH_2]$ is unity. The middle term of eq. 3, therefore, reduces to zero. Hence,

$$E_{el} = E^\circ_{el} + \frac{2.303RT}{F} \log [H^+]$$

$$= E^\circ_{el} + 0.0591 \log [H^+] \quad \text{at } 25^\circ c$$

$$E_{el} = E^\circ_{el} - 0.0591 pH \text{ —— } ④ \qquad \because pH = -\log [H^+]$$

- The standard electrode potential of quinhydrone electrode, $E^\circ_{el} = +0.06996$ V

$$\therefore \quad E_{el} = +0.06996 - 0.0591 \, pH \quad — ⑤$$

- Thus, the potential of the quinhydrone electrode, like hydrogen electrode, depends upon the pH of the solution with which it is in contact, i.e., the quinhydrone electrode behave as a reversible hydrogen electrode. Consequently, this electrode can be used for measuring pH values of solutions.
- This electrode is preferred to the hydrogen electrode as it can be setup easily by merely adding a pinch of quinhydrone to the solution under examination and inserting a clean platinum electrode for making electrical connection. This electrode gives accurate results even in the presence of oxidising ions which usually interfere with working of hydrogen electrode.

- The quinhydrone electrode is combined with a saturated calomel electrode to form a cell. The combination may be represented as

$$Hg,\ Hg_2Cl_2(s),\ KCl(\text{Sat. Sol.}) \parallel H^+(\text{unknown conc.})\ Q,\ QH_2;\ Pt$$

The EMF of above cell is given by

$$E = E_R - E_L$$

$$E = (0.6996 - 0.0591\,pH) - 0.2422 \quad \text{at } 25^\circ C$$

or $$0.0591\,pH = 0.6996 - 0.2422 - E$$

or $$pH = \frac{0.6996 - 0.2422 - E}{0.0591} \quad — ⑥$$

→ Limitations of quinhydrone electrode :→

- The quinhydrone electrode cannot be used for solution of pH more than 8. In more alkaline solution, hydroquinone ionises appreciably as an acid and also gets oxidised partly by atomspheric oxygen. This alters the normal equilibrium between quinone and hydroquinone which forms the basis of the above equation.

→ Determination of pH using glass electrode :→

- When a glass surface is kept in contact with a solution containing hydrogen ions, a potential is developed between the glass and the solution.
- The magnitude of this potential difference for a given variety of glass varies with the concentration of the hydrogen ions and, at 25°c, is given by the equation.

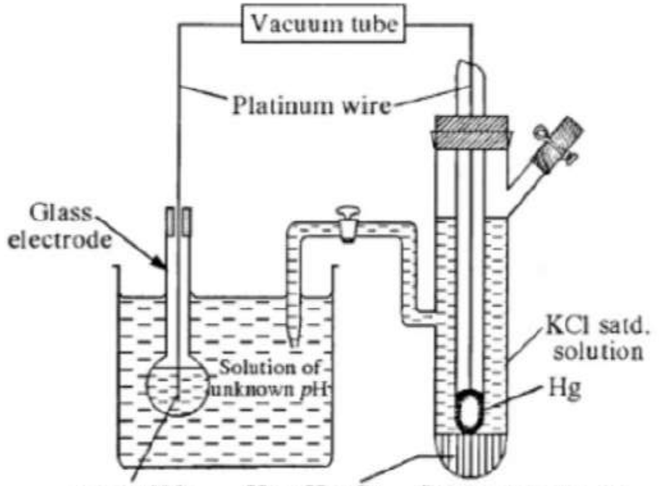
$$E_G = E^o_G + 0.0591 \log [H^+] \quad — ①$$

$$E_G = E^o_G - 0.0591 pH \quad — ② \quad (\because pH = -\log[H^+])$$

Where E^o_G is a constant for the given glass electrode.

- The electrode reaction is assumed to involve the reduction of H^+ ions. The glass electrode, thus, functions in the same manner as a reversible hydrogen electrode.
- The glass electrode is made of a special glass of relatively low melting point and high electrical conductivity. It is blown in the form of a bulb which is then sealed to the bottom of a glass tube.
- A solution of 0.1 molar HCl, which furnishes a constant H^+ ion concentration, is placed inside the bulb and a Ag, AgCl electrode or a simply a platinum wire is inserted to make electrical contact.
- The reference electrode employed is usually the calomel electrode. The cell is represented as

$Pt, 0.1M\ HCl\ |\ glass\ |\ Experimental\ sol.\ |\ KCl\ (sat.sol.)\ Hg_2Cl_2(s), Hg$



Determination of pH using glass electrode

- The EMF of such a cell can be determined conveniently by means of a potentiometer. Since the potential of the calomel electrode is known, that of the glass electrode can be easily calculated and the pH of the experimental solution is evaluated.
- The value of E_G° is first obtained by working with solutions of known pH.
- The pH of the solution is given by

$$pH = \frac{E_G^\circ - 0.2422 - E}{0.0591} \quad \text{at } 25^\circ C$$

- The glass electrode has a number of advantages over other electrodes. It can be used even in strong oxidising solutions which interefere even with quinhydrone electrode.
- It can also be used in the presence of metallic ions, poisons etc.
- It is simple to operate and is, therefore, extensively used in chemical, industrial, agricultural and biological laboratories.

→ Buffer solutions:→

- A buffer solution is one which can resist change in its pH on the addition of an acid or a base.

OR

Such solutions which oppose the change in their pH on addition of small amount of an acid or a base are called buffer solutions.

- Consider a solution of sodium chloride in water. Its pH is 7. The addition of even 1ml of 1M HCl to one litre of sodium chloride solution lowers the pH of the solution from 7 to about 3. Similarly, the addition of 1 ml of 1M NaOH solution to one litre of sodium chloride solution raises the pH of the solution from 7 to about 11. Sodium chloride solution, therefore, is not a buffer.
- The pH of an aqueous solution of ammonium acetate is also 7. But the addition of the same amount of acid or alkali, as the one added in the case of sodium chloride solution, does not cause any appreciable alteration in the pH of ammonium acetate solution. Thus, ammonium acetate solution is a buffer as it can resist alterations in its pH on the addition of an acid or a base.
- Why a solution of ammonium acetate is a buffer why that of sodium chloride is not?
- Ammonium acetate, exists almost entirely in the form of its ions, viz., NH_4^+ and CH_3COO^- ions.
- If an acid is added to this solution, the H^+ ions furnished by the acid combine with acetate ions to form weakly dissociated molecules of acetic acid:

$$CH_3COO^- + H^+ \longrightarrow \underset{\text{Weakly dissociated}}{CH_3COOH}$$

Since most of H^+ ions added are taken up by acetate ions to form acetic acid which itself is only slightly dissociated, the H^+ ion concentration (pH) of ammonium acetate solution changes only slightly.

- Now, suppose a base is added to ammonium acetate solution. The OH^- ions furnished by the base will be taken up by NH_4^+ ions to form weekly dissociated NH_4OH.

$$NH_4^+ + OH^- \longrightarrow \underset{\text{Weakly dissociated}}{NH_4OH}$$

Since most of the OH^- ions added are taken up by NH_4^+ ions to form weakly dissociated NH_4OH, there is very little change in the pH of ammonium acetate solution.

- Buffer solutions are considered to possess reverse acidity as well as reverse alkalinity. Thus, ammonium acetate has reverse acidity due to presence of NH_4^+ ions and reverse alkalinity due to the presence of CH_3COO^- ions.
- Sodium chloride solution is not buffer. In aqueous solution it is almost entirely dissociated into Na^+ and Cl^- ions. If H^+ ions added to this solution, the hydrogen ion concentration increases, i.e., the pH falls immediately. Because HCl, likely to be formed, is itself almost completely dissociated. If OH^- ions are added to the solution, the pH rises. Because NaOH, likely to be formed, is itself almost completely dissociated.

→ Buffer capacity and Buffer index :→

- The capacity of a solution to resist alteration in its pH, is known as its buffer capacity.
- Van slyke introduced a quantity called buffer index, β, as a quantitative measure of the buffer capacity. It is defined as

$$\beta = \frac{dB}{d(pH)}$$

where dB = The increment of a strong base added to a buffer solution.
d(pH) = The resulting increment in pH.

✯ The quantity dB is given in moles per 1000 gm of the solvent.

- β is always a positive quantity.
- Addition of a strong acid is equivalent to −dB, i.e. a negative increment of base and to −dpH (since pH decreases on the addition of the acid). Hence, β remains positive.

$$\beta = \frac{-dB}{-d(pH)}$$

- The value of β depends not only on the nature of the buffer, but also on the pH, which is determined by the relative concentrations of the acid and its conjugate base.
e.g. For $CH_3COOH - CH_3COONa$ system, buffer functions best around its pKa value of 4.76

→ Mechanism of buffer action:→

- A buffer solution consist of a weak acid and its salt solution (acidic buffer) or a weak base and its salt solution (basic buffer).

→ Action of acidic buffer:→

- Consider a mixture of sodium acetate and acetic acid in water.

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \text{ (weakly ionised)}$$

$$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+ \text{ (completely ionised)}$$

- Suppose a strong acid is added to the above mixture. The H^+ ions added will be taken up immeadiately by CH_3COO^- ions to form very slightly dissociated CH_3COOH:

$$H^+ + CH_3COO^- \rightarrow CH_3COOH \text{ (weakly ionised)}$$

Thus, the H^+ ions added are neutrilised by the acetate ions present in the mixture. There is very little change in the pH of the mixture.

- If, on the other hand, a strong base is added, the OH^- ions added are neutrilised by the acetic acid present in the mixture:

$$OH^- + CH_3COOH \rightarrow CH_3COO^- + H_2O$$

Thus, again, there is very little change in the pH of the mixture.

- For the above buffer mixture, reverse acidity is due to CH_3COOH and reverse basicity is due to CH_3COO^- ions.

→ Action of basic buffer:→

- Consider a mixture of ammonium hydroxide and ammonium chloride.

$$NH_4OH \rightleftharpoons NH_4^+ + OH^- \text{ (weakly ionised)}$$

$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^- \text{ (completely ionised)}$$

- If a strong acid is added, the H^+ ions added are neutrilised by the base NH_4OH.

$$H^+ + NH_4OH \longrightarrow NH_4^+ + H_2O$$

- If a strong base is added, the OH^- ions added are neutrilised by NH_4^+ ions.

$$OH^- + NH_4^+ \longrightarrow NH_4OH \text{ (weakly ionised)}$$

- In this case, reverse acidity is due to NH_4^+ ions and reverse basicity is due to NH_4OH.

→ Calculation of pH of Buffer Mixtures:→

A. Buffer mixture of a weak acid and its salt. Henderson-Hasselbalch equation.

- Consider a buffer solution containing a weak acid HA and its highly dissociated salt BA.
- The ionisation of weak acid is represented as:

$$HA = H^+ + A^-$$

or $$K_a = \frac{[H^+][A^-]}{[HA]}$$

or $$[H^+] = K_a \frac{[HA]}{[A^-]} \quad — ①$$

Where K_a = Dissociation constant of the weak acid.

- The salt BA is almost completely ionised. Thus, high concentration of the A^- ions provided by almost complete ionisation of the salt BA supresses the ionisation of the weak acid, so that it may be assumed that the free A^- ions are entirely due to the salt. Thus

$$[A^-] = [Salt]$$

and $$[HA] = [Acid]$$

Substituting these values in eq. ①

$$[H^+] = K_a \frac{[Acid]}{[Salt]}$$

Taking logarithm of both sides, we get

$$\log [H^+] = \log K_a + \log \frac{[Acid]}{[Salt]}$$

or $-\log[H^+] = -\log K_a - \log\frac{[Acid]}{[Salt]}$

or $pH = K_a - \log\frac{[Acid]}{[Salt]}$ $(\because pH = -\log[H^+],\ pK_a = -\log K_a)$

or $pH = K_a + \log\frac{[Salt]}{[Acid]}$ — ②

Eq. ② is called Henderson - Hasselbalch equation.

B. Buffer mixture of a weak base and its salt :-

$$[OH^-] = K_b\frac{[Base]}{[Salt]}$$

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

→ Hydrolysis of salt :→

- Pure water is weakly ionised into H^+ and OH^- ions as:

$$H_2O \rightleftharpoons H^+ + OH^-$$

- The concentration of H^+ and OH^- ions is same. Pure water, therefore, is neutral.

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

- When a salt is dissolved in water, it ionises into ions.
  e.g. The salt AB will ionise as

$$AB \rightarrow A^+ + B^-$$

- The ions of the salt may react with the ions of water to give.

$$A^+ + OH^- \rightarrow AOH$$
$$B^- + H^+ \rightarrow HB$$

- Now the solution will be acidic or alkaline depending upon the relative strengths of the acid HB and the base AOH.
- If the acid is strong and the base is weak, then the solution will be acidic in nature.
- If the base is strong and the acid is weak, then the solution will be basic in nature.
- The phenomenon in which a salt interacts with water to produce either an acidic or basic solution is termed as hydrolysis.
- Actually, hydrolysis involves the interaction of the ions of a salt with water to produce H^+ or OH^- ions in solution. Thus it may be defined as:

  "The interaction between the ions of salt and the ions of water to given free H^+ or OH^- ions in solution."

- Hydrolysis may be considered as the reverse of neutrilisation. Neutrilisation involves the combination H^+ and OH^- ions giving water. Hydrolysis, on the other hand, leads to the formation of H^+ or OH^- ions.
- Salts may be divided into four categories:-

1. Salts of strong acids and strong bases:→

- Salts of strong acids and strong bases do not hydrolyse. Because possible products of such interactions are themselves almost completely dissociated. Consequently, there is no change in the concentrations of H^+ and OH^- ions and the solution remains neutral.

$$NaCl \rightarrow Na^+ + Cl^-$$
$$H_2O \rightarrow H^+ + OH^-$$
$$Na^+ + OH^- \rightarrow NaOH \text{ (highly ionised)}$$
$$H^+ + Cl^- \rightarrow HCl \text{ (highly ionised)}$$

Examples:- $NaCl$, KCl, Na_2SO_4, K_2SO_4 etc.

2. Salts of weak acids and strong bases:→

- These salts give alkaline solution when dissolved in water.

$$CH_3COONa \rightarrow CH_3COO^- + Na^+$$
$$H_2O \rightarrow H^+ + OH^-$$
$$CH_3COO^- + H^+ \rightarrow CH_3COOH \text{ (weakly ionised)}$$
$$Na^+ + OH^- \rightarrow NaOH \text{ (highly ionised)}$$

- Thus, the solution has more of OH^- ions than the H^+ ions. Hence, it is alkaline in nature.
- Examples:- Na_2CO_3, KCN etc.

3. Salts of strong acids and weak bases:→

- These salts produce acidic solutions when dissolved in water.

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$
$$H_2O \rightarrow H^+ + OH^-$$
$$NH_4^+ + OH^- \rightarrow NH_4OH \text{ (weakly ionised)}$$
$$H^+ + Cl^- \rightarrow HCl \text{ (highly ionised)}$$

Thus, solution has a largre concentration of H^+ ions than the OH^- ions. Hence the solution is acidic in nature. Example:- $CuSO_4$ etc.

4. Salts of weak acids and weak bases:→

- Such salts give acidic or basic or even neutral solutions, depending upon the nature of the acid and the base produced, when dissolved in water.

$$CH_3COONH_4 \rightarrow CH_3COO^- + NH_4^+$$
$$H_2O \rightarrow H^+ + OH^-$$
$$CH_3COO^- + H^+ \rightarrow CH_3COOH \text{ (weakly ionised)}$$
$$NH_4^+ + OH^- \rightarrow NH_4OH \text{ (weakly ionised)}$$

Both products are weakly ionised. therefore, concentrations of H^+ and OH^- are same. Hence, the solution is neutral.

- In case of $(NH_4)_2CO_3$, the solution is slightly basic because NH_4OH is relatively a stronger base than the H_2CO_3 acid.

→ Corrosion:→

- When metals are exposed to atmospheric condition they react with air and water in the environment to form undesirable compounds, usually oxides. This process is called corrosion.
- Almost all metals except the less reactive metals such as gold, platinum and palladium, undergo corrosion.
- For example- Silver tarnishes, copper develops a green coating, lead or stainless steel lose their lusture to corrosion.
- The corrosion is defined as "the chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the material and its properties."

→ Types of corrosion:→

1. General or uniform corrosion:→

- In this corrosion, there is a uniform decrease in the volume of metal and soluble corrosion products are formed.
- Example:- oxidation and tarnishing of metals.

2. Pitting corrosion:→

- In this corrosion, pits are formed on the surface.
- Pitting is usually the result of the breakdown or cracking of the protective film.

3. Crevice corrosion:→

- It is a local corrosion and is created by dirt deposits, corrosion products, crack in paint coating etc.

4. Filiform corrosion:→

- It is characterised by the formation of thread like filaments of corrosion products on the surface of the metal coated with paint film when exposed to humid atmosphere.

5. Intergranular corrosion :→

- It is found in alloy metals.
- This type of corrosion takes place because of loss of coherence between the grains.

6. Exfoliation and selective leaching:→

- This type of corrosion involves the selective removal of one metal (electro-chemical active) from certain alloys under certain environmental conditions.

7. Waterline corrosion:→

- When water is stored in a steel tank, it is generally found that the maximum corrosion takes place along a line just beneath of level of water meniscus.

8. Stress corrosion:→

- It is defined as a crack formation due to simultaneous effects of static tensile strength and corrosion.

9. Soil corrosion:→

- This corrosion depends on acidity of soil, degree of aeration, electrical conductivity, salt contents, presence of bacteria and micro-organism and soil texture.

10. Microbial corrosion:→

- This corrosion occures when organism produce an electron flow, resulting in modification of the local environment to corrosive one.

→ Theories of corrosion:→

1. The electrochemical or wet or immersed theory:→

- This theory is based on Nernst theory, according to which all metals have tendency to pass into solution.
- The tendency of metal to pass into solution when immersed into solution of its salt is measured in terms of electrode potential.
- If a metal having higher electrode potential comes into contact with another metal having a lower electrode potential, a galvanic cell is setup and the metal having higher electrode potential become anodic and goes into solution to a measurable extent.
- The extent of galvanic corrosion depends upon the difference in the electrode potential of the two electrodes and their respective areas.
- The greater is the difference in the potentials of the cathode and anode, the greater will be corrosion.
- For example:- Iron corrosion in acidic solution consists of two half cells reactions.

$$Fe \longrightarrow Fe^{2+} + 2e^- \quad (\text{Anode reaction})$$

$$2H^+ + 2e^- \longrightarrow H_2 \quad (\text{Cathode reaction})$$

- The corrosion of iron occurs by oxygen in the presence of aqueous solution involves following reactions.

$$Fe \longrightarrow Fe^{2+} + 2e^- \quad (\text{Anode reaction})$$

$$2e^- + \tfrac{1}{2}O_2 + H_2O \longrightarrow 2OH^- \quad (\text{Cathode reaction})$$

2. chemical corrosion or Dry corrosion or direct chemical attack theory:→

- Direct chemical attack includes all kinds of corrosion in which there is no appreciable flow of current through the metal for perceptible distance.
- This type of corrosion occurs mainly through the action of atomspheric gases such as oxygen, halogens, sulphur dioxide, hydrogen sulphide, nitrogen etc. on the metal surfaces.
- In this type of corrosion generally a solid film of the corrosion product is formed on the surface of the metal which resist further corrosion.
- However, if a liquid or soluble corrosion product is formed, then metal is exposed to further attack.
- Example:- Chlorine and iodine attack silver, generating a protecting film of silver halide.
- Dry or chemical corrosion is of three main types:-

a. oxidation corrosion:-

- This type of corrosion is due to direct chemical action of oxygen at low or high temperatures on metals, generally in the presence of moisture.
- Example:- oxidation corrosion of alkali and alkaline metals.

b. Corrosion by other gases:→

- Gases like CO_2, SO_2, Cl_2, H_2S, F_2 etc. also cause corrosion of metals.
- Example:- AgCl layer formed when chlorine attacks on silver metal.

c. Liquid metal corrosion:→

- This type of corrosion is due to the chemical action of flowing liquid metal at high temperature on solid metal or alloy. It occurs in devices used for nuclear power.

→ Methods of combating corrosion:- (Prevention of metals from corrosion):→

- Corrosion control methods may be classified into four categories:-

1. Material selection and design:→

- Choice of the right type of material is the main factor for corrosion control.
- The selection of metal should be based on its chemical properties besides its cost and structure.
- Noble metals are most immune to corrosion but they cannot be used for economical reasons.
- The metal used should be as pure as possible. Presence of even minute amounts of some impurities may lead to severe corrosion. For example, minute quantities of iron in magnesium or lead in zinc in die-casting allows are harmful.
- The component should be designed in such a way that stationary pool of liquid should not be collected.
- Moisture should be excluded wherever practiable, no corrosion occurs without the presence of moisture

2. Protective Coatings:→

- Protective coatings are used to isolate the anode and cathode regions.
- These protective coatings may be metallic, inorganic, non-metallic or of organic substances.
- For applying any type of coating, metal surface is prepared in following manner:-

(i) Grease and other surface contamination is removed.
(ii) Oxide scales, rust and corrosion products are removed.
(iii) Etching treatment to aid in proper adhesion or buffing or polishing is given.

- Protective coatings are of following types

A. Metallic coatings:- Hot dipping, Electroplating, Metal cladding.
B. Non-metallic coatings:- Oxide coating, organic coating, Paints and lacqures, Plastic coating, Vitreous enamel.

3. Cathodic and Anodic protection:→

- When it is impossible to alter the nature of corrosion medium, corrosion control may be achieved by cathodic or anodic protection.

A. Cathodic Protection:-

- The principle involved in cathodic protection is to force the metal behave like a cathode. since there will be no anode on the metal, corrosion will not occur.

B. Anodic Protection:-

- In this method the metal is passivated by applying current in a direction that renders it more anodic.

4. Corrosion inhibitors:→

- Inhibitors are the substances which when added to the electrolyte solution reduces the rate of corrosion.
- Inorganic inhibitors- silicates, chromates, borates etc.
- Organic inhibitors- organic colloids, amines, pyridines, quinolines, dicyclohexylammonium nitrite, cyclohexylamine carbonate etc.