ELECTROCHEMISTRY

The flow of electricity through solutions of electrolytes is due to the migration of ions when potential difference is applied between the two electrodes. The cations which are positively charged move towards the negatively charged electrode known as cathode while the anions which are negatively charged move towards the positively charged electrode called the anode.

The ease with which electricity flows through a solution is called the conductance (G) of the solution. It is defined as the reciprocal of the resistance (R) of the solution.

$$G = \frac{1}{R}$$

Specific conductance:

$$K = \frac{1}{\rho} = \left(\frac{l}{a}\right)\left(\frac{1}{R}\right)$$

$$= \frac{l}{a} \times \text{conductance a}$$

where ρ = specific resistance.

Specifric conductance may be defined as the conductance of one centimetre cube of the solution of an electrolyte.

Unit: Ω^{-1} cm^{-1}

Equivalent conductance (^):

It is defined as the conducting power of all the ions produced by one gram equivalent of an electrolyte in a given solution.

Relation b/w specific conductance & equivalent conductance:

Conductance, G = Specific conductance (K)

= Equivalent conductance (^)

Molar conductance:

Molar conductance is defined as the conducting power of all the ions produced by one mole of the electrolyte in a given solution. It is denoted by $\wedge_m$

$$\wedge_m = k/c$$

Cell constant:

The specific conductance is the conductance of one cm cube of the solution. Therefore the conductance measured by using a conductivity cell (the one which is most commonly used) will be the specific conductance only if the electrodes are exactly 1 cm2 in area and km apart. This is not usually the case. The conductance obtained will therefore have to be multiplied by a certain factor in order to get the specific conductance. This factor is called the cell constant.

Since K = $\frac{\ell}{a}$ × conductance, hence, the condutance measured in a cell has to be multiplied by a factor $\frac{\ell}{a}$ in order to get the specific conductance. Evidently, the factor $\frac{\ell}{a}$ = cell constant.

$$K_{cell} = \frac{K}{G}$$

Unit of cell constant is: cm^{-1}

1. Specific conductance of a decimolar solution of potassium chloride at 18°C is 1.12 sm^{-1}. The resistance of a conductivity cell containing the solution at 18°C was found to be 550. What is the cell constant?

Solution:

$R = 55\Omega$: $G = \left(\frac{1}{55}\right)S$;

$K = 1.12$ SM^{-1}

$K_{cell} = K/G = 1.12$ $SM^{-1}/ (1/55)$ S

$= 61.6$ $m^{-1} = 0,616$ cm^{-1}

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2. The resistance of 0.01 M solution of an electrolyte was found to be 210Ω at 25°C calculate the molar conductance of the solution at 25°C. Cell constant = 0.88 cm^{-1}.

   Solution:

   $R = 210\Omega$; $G = \left(\frac{1}{210}\right)$ S;

   $K_{cell} = 0.88$ cm^{-1}

   K = cell constant × conductance

   $= 0.88$ cm$^{-1} \times \left(\frac{1}{210}\right)$ S

   $= 0.00419$ s cm^{-1}

   $= 0.419$ sm^{-1}

   Concentration of the solution,

   C = 0.01 mol dm^{-3} = 10 mol m^{-3}

   $\wedge_m$ = k/c = 0.419 sm^{-1} / 10 mol m^{-3}

   = 0.0419 sm^2 mol^{-1}

3. The resistance of 10.5 M solution of an electrolyte in a cell was found to be 450. Calculate the molar conductance of the solution if the electrodes in the cell are 2.2 cm apart and have an area of 3.8 cm^2. Solution:

   $R = 45\Omega$ ∴ G = s

   $K_{cell} = \frac{l}{a} = \frac{2.2 \text{ cm}}{3.8 \text{ cm}^2} = \qquad 0.5789$ cm^{-1}

   = 57.89 m^{-1}

   $K = 57.89$ m$^{-1} \times \left(\frac{1}{45}\right)$s = 1.286 sm^{-1}

   C = 0.5 mol dm^{-3} = 500 mol m^{-3}

   $\wedge_m$ = K/c = 1.286 sm^{-1} / 500 mol m^{-3}

   = 25.72 × 10^{-4} sm^2 mol^{-1}

Variation of Molar conductance with Dilution:

Molar conductance of an electrolyte increases with increase in dilution. This was attributed to increase in the degree of dissociation of the electrolyte.

We define degree of dissociation as the fraction of the total electrolyte in solution which exists in the form of its ions. Therefore the number of ions per unit volume actually decreases. Hence the specific conductance decreases although the molar conductance increases on progressive dilution.

Degree of dissociation (∝)

$= \frac{\wedge_m}{\wedge_m^0}$

where $\wedge_m^0$ = molar conductance at zero concentration or at infinite dilution.

4. The specific conductance of 0.01 M solution of acetic acid was found to be 0.0163 sm^{-1} at 25°C. Calculate the degree of dissociation of the acid. Molar conductance of acetic acid at infinite dilution is 390.7 × 10^{-4} sm2 mol^{-1} at 25°C.

Solution:

K = 0.0163 sm^{-1}; C = 0.01 mol dm^{-3}

= 10 mol m^{-3}

$\wedge_m = \frac{K}{C} = \frac{0.0163 \text{ sm}^{-1}}{10 \text{ mol m}^{-3}}$

$= 16.3 \times 10^{-4}$ sm^{2}mol^{-1}

$\wedge_m^0 = 390.7 \times 10^{-4}$ sm^{2}mol^{-1} (given)

$a = \frac{\wedge_m}{\wedge_m^0} = \frac{16.3 \times 10^{-4}}{390.7 \times 10^{-4}} = 0.0472$

Ionic mobility:

It is defined as the distance travelled by an ion per second under a potential gradient of 1 volt per metre. Potential gradient is given by the potential difference applied at the electrodes divided by the distance between the electrodes.

Transport number:

From the discussion of the Hittorf's theoretical device, it is evident that the number of ions discharged at each electrode depends upon the sum of the speeds or mobilities of the two ions. According to Faraday's first law of electrolysis,

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Total quantity of electricity that passes through the solution $\Big\}$ $\propto$ Sum of the mobilities of the ions

Total quantity of electricity carried by a particular ions $\Big\}$ $\propto$ the mobility of that particular ion

The fraction of the total current carried by each ion is called its transport number.

Thus if u+ is the mobility of cation and u- that of the anion, then

Transport number of the cation, t_+.

$= \dfrac{\text{Current carried by the cation}}{\text{Total current}}$

$= \dfrac{u_+}{u_+ + u_-}$

Transport number of anion,

$t_- = \dfrac{u_-}{(u_+) + (u_-)}$

$t_- + t_- = 1$

Also

$\dfrac{\text{Mobility of cation}}{\text{Mobility of anion}} = \dfrac{\text{Fall of concentration round anode}}{\text{Fall of concentration round cathode}}$

Determination of Transport number:

1. Hittorf's method:

    This method is based on concentration changes observed in the vicinity of the electrodes.

    $t_+ = \dfrac{\begin{array}{c}\text{Number of gram equivalents lost} \\ \text{from the anodic compartment}\end{array}}{\begin{array}{c}\text{Number of gram equivalent of copper} \\ \text{deposited in the coulometer}\end{array}}$

2. **The moving Boundary method:**

    The moving boundary method rests on the direct observation of migration of ions in an electric field. The principle may be explained with reference to determination of transport number of H$^+$ ions in hydrochloric acid.

    Transport number of H$^+$ ions = ℓAC / 1000 Q

    C = Concentration of the acid.

    A = Cross sectional area of the tube

    ℓ =Distance moved

Kohlrausch's Law:

At infinite dilution, when dissociation is complete, each ion makes a definite contribution towards molar conductance of the electrolyte irrespective of the nature of the other ion with which it is associated and that the molar conductance at infinite dilution for any electrolyte is given by the sum of the contributions of the two ions. This is known as Kohlrausch's law.

Thus,

$$\wedge_m^0 = \wedge_m^0 = \lambda_+^0 + \lambda_-^0$$

where

λ_+^0 = contribution of the cation

λ_-^0 = contribution of the anion

Direct Determination of Ionic Mobility:

Ionic mobility can be measured directly by a technique based on the movement of a visible boundary between two electrlytic solutions.

The mobility of K+ ion $= \dfrac{\text{Speed of ion}}{\text{Potential gradient}}$

$= \dfrac{(x/t)\text{ms}^{-1}}{ZV\text{m}^{-1}}$

Applications of Kohlransch's Law:

1. Calculation of Molar conductance at Infinite Dilution for weak Electrolytes.
2. Determination of Transport Numbers.

    Applications of Conductance Measurement:

1. Determination of degree of dissociation of weak electrolytes.
2. Determination of ionic product of water (kw).
3. Dtermination of solubilities and solubility products of sparingly soluble salts.
4. Conductometric Titrations.
5. Precipitation Titrations.

    Ostwald's Dilution Law:

    According to Arrhenius theory of electrolytic dissociation, the molecules of an electrolyte in

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aqueous solution undergo spontaneous dissociation into positive and negative ions and that there is a dynamic equilibrium b/w ions and the unionised molecules. Ostwald, therefore applied the law of chemical equilibrium to such systems. The equilibrium constant is given by the equation.

$$K = \frac{C \propto C \, x}{C(1-\propto)} = \frac{C\propto^2}{(1-\propto)}$$

is the mathematical representation of Ostwald's dilution law.

The equilibrium constant K is called the dissociation constant of the electrolyte. It is constant at a given temperature.

The law was found to hold good in the case of weak electrolytes, such as acetic acid and ammonium hydroxide, as the value of K was found to be fairly constant in these cases.

Strong electrolytes:

X-ray analysis of crystals of ionic solids, such as NaF, NaCl, KCl, Na_2SO_4 and NaOH, which are strong electrolytes, has revealed that the crystal lattice in these substances consists exclusively of ions. There are no molecules. Hence, in such cases the question of equilibrium between unionised molecules and their ions, as assumed in Arrhenius theory, does not arise at all.

According to Coulomb's law, the electrostatic forces vary inversely as the dielectric constant of the medium. Therefore, when crystals are dissolved in water, the dielectric constant of which is about 80 times greater than that of air, the electrostatic forces of attraction between the ions are considerably weakened. As a result of this, the ions begin to move more freely and conduct electricity more strongly.

The Debye-Huckel Theory of strong Electrolytes:

The Debye-Huckel theory of strong electrolytes suggests that the increase in molar conductance with dilution in the case of strong electrolytes is due to the increase in the mobilities of the ions due to weaker interionic attraction rather than to increase in the degree of ionization which remains unity over moderate concentrations. Thus, interionic attraction, rather than partial dissociation, is the cause of the decrease in conductance with increase in concentration. Three concepts dominate the Debye-Huckel theory, i.e. asymmetry effect, electrophoretic effect and viscous effect. Each ion of the electrolyte is surrounded by ions of opposite charge, giving rise to an ionic atmosphere. The force of attraction exerted by the ionic atmosphere on the central-ion before electricity is passed, is uniform in all directions and thus cancels out. However, on passing the electricity this force becomes greater behind the ion than infront so that the ion experiences a retarding force which tends to drag it backwards; the drag on the central ion is called the asymmetry effect. The electrophoretic effect also tries to slow down the motion of the ions at higher concentrations because of the tendency of the ionic atmosphere associated with molecules of the water of hydration to move in a direction opposite to that in

which the central ion is moving. The third factor, the viscous effect, arises from the drag of the solvent on the movement of the ion. For an ion of a given charge, size and shape, the greater the viscosity of the solvent, the greater is the

viscous drag and hence the smaller is the ionic mobility and the conductance.

The three effects have been combined in the Debye-Huckel - Onsages equations,
$$\Lambda_m - \Lambda_m^0 - (A + B\Lambda_m^0)C^{1/2}$$
where A and B are the Debye-Huckel coefficients.

The plot of Λ_m versus $C^{1/2}$ for a strong electrolyte gives a straightline, in agreement with the experimental results.
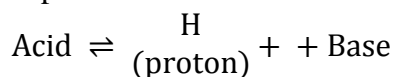
ACIDS AND BASES:

According to Arrhenius concept, an acid is a substance that dissociates to give hydrogen ions when dissolved in water. Thus hydrogen chloride gas is an acid because when dissolved in water, it gives hydrogen ions.

Base is a substance which dissociates into hydroxyl ions when dissolved in water.

Proton Transfer Theory: Concept of Lowry and Bronsted:

In 1923, Lowry and Bronsted suggested a more general definition of acids and bases. According to their concept, an acid is defined as a substance which has a tendency to donate a proton to any other substance and a base as a substance which has a tendency to accept a proton from any other substance. In other words, an acid is a proton-donor and a base is a proton acceptor.

$$Acid \rightleftharpoons \underset{(proton)}{H} + + Base$$

Conjugate Acids and Bases:

$$CH_3COOH + H_2O \rightleftharpoons \underset{Acid}{H_3O^+} + \underset{Base}{CH_3COO^-}$$
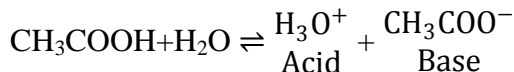
Acetic acid donates a proton to water and thus acts as an acid. Water accepts a proton and, therefore acts as a base. In the reverse reaction, hydronium ion (H_3O^+) donates a proton to the acetate ion and, therefore, a .is as an acid. The acetate ion accepts a proton and therefore, behaves as a base. Such pairs of substances which can be formed from one another by the gain or loss of a proton are known as conjugate acid - base pairs.

Thus, acetic acid is the conjugate acid of acetic ion and acetate ion is the conjugate base of acetic acid.

Relative strength of Acid-Base pairs:

According to the concept of Lowry and Bronsted, the strength of an acid depends upon its tendency to lose protons and the strength of a base depends upon its tendency to gain protons. If an acid, such as hydrochloric acid, is a strong acid, it will have a strong tendency to donate protons Thus, the equilibrium.

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$
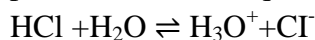
lies very much to the right and the reverse reaction, representing the gain of proton by the chloride ions leading to the reformation of HC1, will take place to a very small extent. Thus chloride ion is a weak base.

- The stronger an acid, the weaker must be its conjugate base and vice versa.
- Water is a very weak base because is conjugate acid H_3O^+ is a very strong acid.

Influence of solvent on Acid strength:

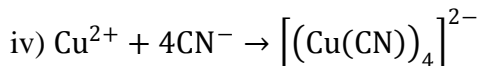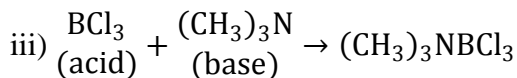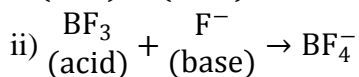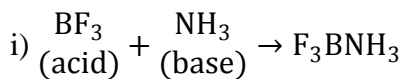Acid strength is a relative one. It depends also on the substance which acts as a base.

The capacity of the acid to dissociate also depends upon the basic strength of the solvent which acts as a base.

Influence of solvent on Base strength:

The nature of the solvent plays an equally important role in the dissociation and relative strengths of bases as well. If the solvent is a weak acid, such as water, it will be possible to compare the strengths of different bases as they will dissociate to different extends. But it the solvent is even a slightly stronger acid, e.g. acetic acid it will not be possible to distinguish between the strengths of different bases.

The Lewis concept:

According to Lewis, an acid is a species that is capable of accepting a pair of electrons to form a covalent bond and a base is a species that is capable of donating a pair of electrons to form a covalent bond.

i) $\underset{\text{(acid)}}{BF_3} + \underset{\text{(base)}}{NH_3} \rightarrow F_3BNH_3$

ii) $\underset{\text{(acid)}}{BF_3} + \underset{\text{(base)}}{F^-} \rightarrow BF_4^-$

iii) $\underset{\text{(acid)}}{BCl_3} + \underset{\text{(base)}}{(CH_3)_3N} \rightarrow (CH_3)_3NBCl_3$

iv) $Cu^{2+} + 4CN^- \rightarrow \left[(Cu(CN))_4\right]^{2-}$

We see that the Lewis definition does not attribute acidity to any particular element but rather to unique electronic arrangement.

From eqn. (i) we can say that NH_3 acts as a base by virtue of its tendency to donate the lone pair

of electrons on the N atom to BF_3 which acts as an acid.

Dissociation of weak Acids & Bases:

Consider the dissociation of a weak monobasic acid HA in water, represented by the equation.

$HA + H_2O \rightleftharpoons H_2O^+ + A^-$
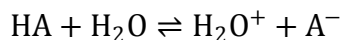
Equilibrium constant,

$K_c = \frac{[H_2O^+][A^-]}{[HA][H_2O]}$

$K_a = [H^+][A^-]/HA$

where $Ka = K_c \times K$

The constant K_a is characteristic of the acid concerned and is known as the dissociation constant of the acid. This varies only with temperature, like other equilibrium constants.

Relative strengths of weak acids:

$\frac{\text{Strength of one acid ,}HA_1}{\text{Strength of another acid ,}HA_2} = \sqrt{\frac{K_{a1}}{K_{a2}}}$

1. The dissociation constants of formic and acetic acids are 1.77×10^{-4} and 1.75×10^{-5} respectively. Calculate the relative strengths of the two acids.
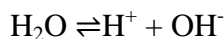
Solution:

$\frac{\text{Strength of formic acid}}{\text{Strength of acetic acid}} = \frac{K_a \text{formic acid}}{K_a \text{formic acid}}$

$= \sqrt{\frac{1.77 \times 10^{-4}}{1.77 \times 10^{-5}}} = 3.18$

Therefore, formic acid is 3.18 times stronger than acetic acid.

Ionic product of water, K_w:

For the water dissociation equilibrium

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

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

Where K_w is the ionic product of water.

For a weak acid, HA, the dissociation equilibrium is HA $\rightleftharpoons$ H$^+$ + A$^-$ and the dissociation constant of the acid is given by

$K_a = [H^-][A^-]/HA$

Similarly for a weak base, BOH, the dissociation equilibrium is BOH $\rightleftharpoons$ B$^+$ + OH$^-$ and the dissociation constant of the base is given by $K_b = [B^+][OH^-]/[BOH]$.

The pH scale:

Every aqueous solution, whether acidic, alkaline or neutral, contains both H+ and OH$^-$ ions. The product of their concentrations is always constant, equal to 1×10^{-14} at 25°C. Whether the solution is acidic or alkaline depends upon which of the two ions is present in greater concentration then the other. But, since knowing the concentration of one of these ions, that of the other can be calculated, it is convenient to express acidity or alkalinity of a solution by referring to the concentration of hydrogen ions only.

Now H$^+$ ion concentration can vary within wide limits, usually from about 1 mole per litre to about 10^{-14} mole per litre.

Sorensen, therefore introduced a more convenient scale for indicating H$^+$ ion concentration which he called the pH scale.

The pH of a solution is the negative algorithm (to the base 10) of the concentration (in moles per litre) of hydrogen ions which it contains.

Thus, pH = -log [H$^+$]

For a pure water or a neutral solution in which

$[H^+] = 1 \times 10^{-7}$ mol dm^{-3}

pH = -log[H$^+$] = -log(1×10^{-7}) = 7 at 25°C

2. Calculate the pH of (a) 0.0001M HCl solution (b) 0.04M HNO$_3$ solution, assuming complete dissociation In each case.

Solution:

a) Concentration of HCl = 0.0001M

Since HCl is completely dissociated, hence

$[H^+] = 0.0001$ mol dm^{-3}

pH = -log[H$^+$) = -log [0.0001] = 4

b) Concentration of HNO$_3$ = 0.04M

Since HNO$_3$ is completely dissociated, hence,

$[H^+] = 0.04$ mol dm^{-3}

pH = -log [H$^+$] = -log [0.04] = 1.398

3. Calculate the hydrogen ion concentration in moles per litre of a solution whose pH is 5.4.

Solution:

pH of the solution = 5.4

pH = -log [H$^+$]

log [H$^+$] = -5.4 = $\overline{6}.600$

[H+] = 3.98×10^{-6} mol dm^{-3}

pH = - log [H$^+$] = -log [0.0001] = 4

pOH:

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

pOH = -log [OH$^-$]

Ionic product of water, kw, is also frequently expressed in a similar manner as,

$pK_w = -\log K_w$

Remembering that $[H^+][OH^-] = K_w$ and taking logs and reversing signs, we have

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

or

$pH + pOH = pK_w$

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

Notes

If pH of a solution is 7, it is neutral.

If pH < 7, acidic

pH > 7, alkaline

4. Calculate the pH and pOH of 0.03M solution of HCI at 25°C

Solution:

HCI being a strong electrolyte, is completely dissociated in aqueous solution. Hence, the hydrogen ion concentration, [H$^+$] is equal to the given concentration of HCI in solution.

[H$^+$] = 0.03 M = 3×10^{-2} mol dm^{-3}

pH = -log [H$^+$] = -log(3×10^{-2})

= 1.52

Since,

pH+pOH = 14 at 25°C

pOH = 14 - 1.52 = 12.48

Buffer solutions:

For many purposes in chemistry, industry and biology it is necessary to have solutions whose pH does not change much even on the addition of appreciable amounts of strong acids or strong alkalies. Such solutions are called buffer solutions.

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

Consider a solution of sodium chloride in water. It's pH is 7. The addition of even 1 ml of 1M HCI solution 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.

Buffer capacity and Buffer Index:

Van slyke introduced a quantity called buffer index, p, as a quantitative measure of the buffer capacity. It is defined as

β = dB/d (pH) where dB is the increment of a strong base added to a buffer solution and d(pH) is the resulting increment in pH.

The capacity of a solution to resist alteration in its pH, is known as its buffer capacity.

Calculation of pH of Buffer Mixtures:
Buffer Mixture of a weak acid and its salt:

pH = pK$_a$+log[[sald]/[Acid]]

The above equation is known as Henderson - Hasselbalch equation, enables the calculation of pH of a buffer solution made by mixing known quantities of a weak acid and its salt.

Buffer Mixture of a weak base and its salt:

pOH = pK$_b$ +log ([salt]/(Base])

Hydrolysis of salts:

Salts are strong electrolytes. When dissolved in water, they dissociate almost completely into positively charged ions (cations) and negatively charged ions (anions). In some of the salts, the anions of the salt react with H+ ions furnished by water thereby lowering the concentration of H$^+$ ions in solution. Since the product of [H$^+$] and OH$^-$ ions is constant {[H$^+$][OH$^-$] = K$_w$},

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therefore, the concentration of OH⁻ions in the solution increases. The solution, therefore, becomes alkaline.

In the case of some other salts the cations of the salt react with OH' ions furnished by water thereby lowering the concentration of OH' ions in solution. Since Kw is constant, the concentration of H⁺ ions in the solution increases. The solution, therefore becomes acidic.

The phenomenon of the interaction of anions and cations of the salt with the H⁺ and OH⁻ ions furnished by water yielding acidic or alkaline (or sometimes even neutral) solutions is known as salt hydrolysis.

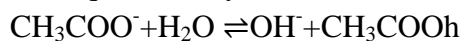For study of Hydrolysis, it is convenient to divide the salts into four categories:

1. Salts of strong acids and strong bases such as potassium chloride and sodium nitrate.
2. Salts of weak acids and strong bases, such as potassium cyanide and sodium acetate.
3. Salts of strong acids and weak bases, such as ammonium chloride and aniline hydrochloride.
4. Saits of weak acids and weak bases, such as ammonium acetate.

- Saits of strong acids and strong bases do not hydrolyse to give alkaline solutions.

Hydrolysis constant:

The hydrolytic reaction of sodium acetate may be written as

$CH_3COO^- + Na^+ + H_2O \rightleftharpoons CH_3COOH + Na^+ + OH^-$
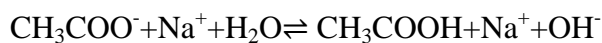
The equation may be rewritten as,

$CH_3COO^- + H_2O \rightleftharpoons OH^- + CH_3COOh$

Applying the law of chemical equilibrium and taking the concentration of water as constant)

We have,

$$K_h = \frac{[OH^-][CH_3COOH]}{[CH_3COO^-]}$$

K_h is known as hydrolysis constant Relation between K_b, K_a, and K_w:

$K_b = \frac{K_w}{K_a}$

Degree of hydrolysis $\mathcal{X}$:

Degree of hydrolysis Z is defined as the fraction of the total salt that has undergone hydrolysis on the attainment of equilibrium.

$\mathcal{X} = \sqrt{K_w/(K_a X C)}$

5. Calculate the degree of hydrolysis of 0.10M solution of sodium acetate at 25°C. $K_a = 1.75 \times 10^{-5}$ & $K_w = 1.008 \times 10^{-14}$.

Solution:

$$K_h = \frac{K_w}{K_a} = \frac{1.008 \times 10^{-14}}{1.75 \times 10^{-5}}$$

$= 5.76 \times 10^{-10}$

Assuming that the degree of hydrolysis ($\mathcal{X}$)is small

$\mathcal{X} = \sqrt{K_a/c} = \sqrt{\frac{5.75 \times 10^{-10}}{0.10}}$

$= 7.589 \times 10^{-5}$

Thus, the degree of hydrolysis $= 7.589 \times 10^{-5}$

pH of the Hydrolysed salt solution :

pH = 14 $- \frac{1}{2} pK_w + \frac{1}{2} \log c + \frac{1}{2} pK_a$

Hydrogen Ion Indicators or Acid - Base Indicators

A hydrogen ion (or acid-base) indicator is a substance which changes its colour within limits with variation in pH of the solution to which it is added. This gives an

easy method of determining pH of a solution by simply adding a suitable indicator and noting

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the colour easy method of determining pH of a solution by simply adding a suitable indicator and noting the colour.

The pH range, over which the colour change occurs varies considerably from one indicator to another.

For example, methyl orange gives full acid colour (red) when added to a solution the pH of which is 3 or below and full basic colour (yellow) in a solution whose pH is 4.4 or above. In solutions having pH between 3 and 4.4, methyl orange gives a colour, intermediate between red and yellow.
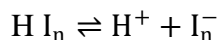
$$H\,I_n \rightleftharpoons H^+ + I_n^-$$

colour A   colour B

Indicator constant,

$$K_{in} = \frac{[H^+][In^-]}{[HIn]}$$

Acid - Base Titrations and use of indicators:

The process of acid - base titrations is accompanied by a change in pH. A plot between pH of the solution during titration and the amount of acid (or alkali) added from a burettle is called a titration curve.

The solubility product:

In a saturated solution of a salt, there exists a dynamic equilibrium between the excess of the solute and the ions furnished by that part of the solute which has gone in solution.

For example, the case when a sparingly soluble salt, like silver chloride, is added to water. A very small amount dissolves and the rest of it remains in the solid state. Here the solid silver chloride is in equilibrium with silver and chloride ions furnished by the dissolved silver chloride. The may be represented as

$$AgCI\ (S_1\ said.soln) \rightleftharpoons Ag^+\ (aq) + Cl\ (aq)$$
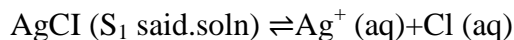
Applying the law of chemical equilibrium, the equilibrium constant would be given by

$$K = \frac{a_{Ag^+} \times a_{Cl^-}}{a_{AgCl}}$$

Since activity of a solid is taken as unity by convention, the above expression may be put as

$$K_{sp} = a_{Ag^+} \times a_{Cl^-}$$

K_{sp} is known as the solubility product of Silver Chloride.

It is constant at a given temperature.

The solubility product of a sparingly soluble salt forming a saturated solution in water is given by the product of the concentrations of the ions raised to a power equal to the number of times the ions occur in the equation representing the dissociation of the electrolyte.

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

Applications of solubility product principle:

1. Determination of solubilities of sparingly soluble salts.
2. Predicting precipitation Reactions.
3. Precipitation of soluble salts.
4. Inorganic analysis.
5. Other precipitation Reactions.
6. Dissolution of precipitates of phosphates, carbonates, sulphides, etc. in Acid solutions.

Galvanic cells:

A galvanic cell is a device in which the free energy of a physical or chemical process is converted into electrical energy. Such a cell consists of two electrodes immersed in one or more suitable electrolytes. When the electrodes are connected externally, a chemical reaction occurs in the ceil involving oxidation at one

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electrode and reduction at the other electrode. The electrode at which oxidation occurs is called the anode while the electrode at which reduction occurs is called the cathode.

For thermodynamic treatment of galvanic cells, it is essential that these cells operate in a thermodynamically reversible manner. This implies that the cell generate infinitesimally small current so that the cell reaction always remains virtually in a state of equilibrium.

A reversible galvanic cell consists of two reversible electrodes one of which acts as the cathode and the other as the anode. Each electrode along with the electrolyte is called the half-cell and the reaction that occurs in the half cell is called the half-cell reaction.

Some common types of reversible electrodes are:

1. Metal-metal ion electrode in which a metal rod is dipping in a solution of its ions is represented as $M(S)$, $M^{z+}(aq)$. The half-cell reaction is represented as

$M^{z+}(aq) + Ze^- \rightleftharpoons M(s)$
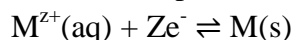
2. Hydrogen electrode in which hydrogen gas is bubbled in a solution of an acid and a platinum wire is used for making the electrical contact. The electrode is represented as Pt: H_2g, H^+. The half-cell reaction in this case is

$H^+ (aq) + e^- \rightleftharpoons \frac{1}{2} H_2(g)$
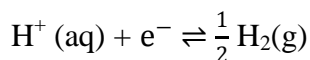
3. Calomel electrode which consists of mercury, solid mercurous chloride and a saturated solution of potassium chloride. The electrode is represented as H_g, $Hg_2 Cl_2(s)$, KCI (saturated solution). The halt-cell reaction in this case is

$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l)+2Cl^-(aq)$
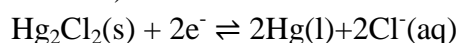
4. Quinhydrone electrode (an oxidation - reduction electrode) consists of a platinum wire placed in a solution containing hydroquinone (QH_2) and quinone (Q) in equtmolar amounts The electrode is represented as

Pt; Q, QH_2; H + (aq). The Half-cell reaction in this case is
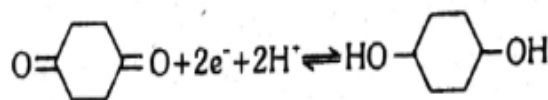
Electrode Potential:

The tendency of an electrode to lose or gain electrons when it is in contact with its own ions in solution, is called electrode potential. The tendency to gain electrons, i.e. to get reduced, is called reduction potential. The tendency to lose electrons i.e. to get oxidised is called oxidation potential.

The potential of a reversible hydrogen electrode in which the gas at one atmospheric pressure is bubbled through a solution of H^+ ions of unit activity (or, to be approximately 1M concentration) has been fixed as zero. This electrode is known as standard hydrogen electrode and is represented as

Pt; $H_2(g)$ (1 atm); H^+ (aq) (c = 1M)
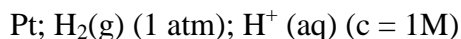
According to the latest convention adopted by IUPAC, the electrode potential is given a positive sign if the electrode reaction involves reduction when connected to the standard hydrogen electrode and a negative sign if the electrode reaction involves oxidation when connected to the standard hydrogen electrode whose potential is arbitarily taken as zero.

The potential of a single electrode cannot be determined experimentally. The electrode is combined with a standard hydrogen electrode to give a complete cell whose EMF can be easily

measured Since the potential of SHE is taken as zero, the EMF of I he cell gives the potential of the electrode.

Nernst Equation:

The potential of an electrode (say Mn^+ ,M) depends upon the concentration of M+ ions also. The effect of concentration on electrode potential is given by Nernst equation.

The potential of electrode reaction:

M^{n+} (aq) + ne⁻ $\rightleftharpoons$ M(s) is given by the relation

$Eel = E_{el}^0 + \frac{0.0591}{n} \log[M^{n+}]$ at 25°C

where E_{el}^0 is the standard electrode potential.

Electrochemical series:

The standard electrode potentials of a number of electrodes have been tabulated. The values arranged in a decreasing order constitute what is called the electrochemical series.

Electrical Energy in a Galvanic cell:

The electrical energy in a galvanic cell is given by nFE. This energy, according to Gibbs and Helmholtz, orginates from the free energy decrease (-ΔG) of the reaction occurring in the cell. Thus,

-ΔG = nFE

The electrical energy is related to the enthalpy of the cell reaction by the equation.

$nFE = -\Delta h + TnF \left(\frac{\partial E}{\partial T}\right)_P$

The standard EMF of a galvanic cell is related to the equilibrium constant as

$\log K = \frac{nFE°}{2.303 \ RT}$

EMFs of Galvanic cells and cell Reaction:

A galvanic cell is formed by the combination of any two suitable electrodes. The EMF of the cell and the cell reaction are determ.ned by the latest convention according to which both the half-cell reactions are written as reduction reactions along with their standard electrode potential in the form of chemical equations and after balancing the number of electrons, if necessary, the half-cell reaction with a lower electrode potential is subtracted from the one with a higher electrode potential. The resultant gives the EMF of the cell as well as the cell reaction. The two electrodes are combined in such a way that oxidation occurs at the left hand electrode and reduction at the right electrode.

Concentration cells:

In concentration cells, the cell potential arises due to transfer of matter from, one half-cell to the other because of a difference of concentrations of the species involved. The concentration cells are of two types

i) Electrode concentration cells

ii) Electrolyte - concentration cells

In electrode - concentration cells, two like electrodes at difference of concentrations are dipping in the same solution whereas in electrolyte concentration cells, two elecrodes of the same metal are dipping in solutions of metal ions of different concentrations.

Electrolyte - concentration cells are further classified into

i) Concentration cells without transference and

ii) Concentration cells with transference

The cell potential (or EMF) of the cell without transference is given by $E_{w.o.t} = \frac{RT}{F} \ln \left(\frac{a_2}{a_1}\right)$

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

The cell potential (or EMF) of the cell with transference is given by $E_{w.t} = \left(\frac{RT}{F}\right) \ln \left(\frac{a_2}{a_1}\right)$

where t - is the transference number of the anion.

The liquid junction potential of a concentration cell is given by

$$E_t = E_{w.t} - E_{w.o.t}$$
$$= (t_- - t_+)(RT/F)\ln[(a\pm)_2/(a\pm)_1]$$

i.e., it depends on the difference of the transference numbers of the anion and the cation. If, as in the case of an electrolyte such as KCl, the transference numbers of the cation and the anion are equal, $E_l=0$.

Activity and Activity coefficient:
The activity, a_1 of a uni-univalent electrolyte such as HCl, is given by $a = a_+ a_-$ and the mean ionic activity, $a_\pm$, of this electrolyte is given by $a_\pm = (a_+ a_-)^{1/2}$, where a_+ and a_1 are the activities of the cation and the anion, respectively. "
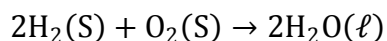Thus, $a = (a_\pm)^2$
The activity coefficient of a uni-univalent electrolyte is given by
γ = a/m where m is the molarity of the electrolyte.
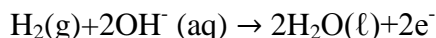
Fuel Cells:
Fuel cells are galvanic cells in which chemical energy is directly converted into electrical energy.
The hydrogen - oxygen fuel - cell is based on the combustion of H2 to form water.
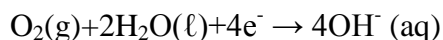$2H_2(S) + O_2(S) \rightarrow 2H_2O(\ell)$
It consists of two electrodes of porous graphite impregnated with platinum catalyst, placed in an aqueous NaOH or KOH solution. The net oxidation half-cell reaction is
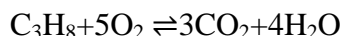$H_2(g)+2OH^- (aq) \rightarrow 2H_2O(\ell)+2e^-$
The net reduction half-cell reaction is
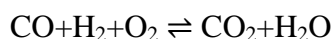$O_2(g)+2H_2O(\ell)+4e^- \rightarrow 4OH^- (aq)$
Thus, the overall fuel cell reaction is $2H_2(g) +O_2(g) \rightarrow 2H_2O(\ell)$
Fuel cells based on the combustion of hydrocarbons such as CH_4, C_2H_6, C_3H_8 etc. in the presence of catalysts have also been operated. The overall fuel cell reaction involving the combustion of C_3H_8 is represented as
$C_3H_8+5O_2 \rightleftharpoons 3CO_2+4H_2O$
In coal - fired fuel cells, coal is gassified at about 650°C to five a mixture of H_2 and CO which serve as the fuel for the cell. Molten Na_2CO_3 is used as the electrolyte. An alloy of pt with Cr, V, T; etc. acts as the catalyst. The overall fuel reaction is
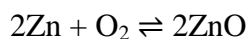$CO+H_2+O_2 \rightleftharpoons CO_2+H_2O$
Recently, a zinc-airfirelcell (ZAFC), in which Zincm etal is used in place of hydrogen gas as a source of power in autom obiles.
In this cell, the OH^- ions produced by the catalytic reduction of oxygen of the air ($O_2(g) + 2H_2O+4e^- \rightleftharpoons 4OH^-$) travel through the liquid electrolyte and reach the zinc anode where they react to form zinc oxide,
$Z_n+4OH^- \rightleftharpoons ZnO + 2H_2O+4e^-$
the overall fuel cell reaction being
$2Zn + O_2 \rightleftharpoons 2ZnO$
H_2 - O_2 fuel edits for manned space flights have also been designed. In these cells. Solid ion - exchange materials are used in place of solutions of KOH or NaOH.

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