Electrochemistry

Introduction

Electrochemistry is a branch of chemistry that studies chemical reactions which take place in a solution at the interface of an electron conductor (a metal or a semiconductor) and an ionic conductor (the electrolyte), and which involve electron transfer between the electrode and the electrolyte or species in solution.

Electrochemical Cell:

An electrochemical cell is a device used for generating an electromotive force (voltage) and current from chemical reactions. The current is caused by the reactions releasing and accepting electrons at the different ends of a conductor.

An electrochemical cell consists of two half-cells. The two half-cells may use the same electrolyte, or they may use different electrolytes. Each half-cell consists of an electrode, and an electrolyte. The chemical reactions in the cell may involve the electrolyte, the electrodes or an external substance (as in fuel cells which may use hydrogen gas as a reactant).

In a full electrochemical cell, ions, atoms, or molecules from one half-cell lose electrons (oxidation) to their electrode while ions, atoms, or molecules from the other half-cell gain electrons (reduction) from their electrode.

A salt bridge is often employed to provide electrical contact between two half-cells with very different electrolytes—to prevent the solutions from mixing. This can simply be a strip of filter paper soaked in saturated potassium nitrate (V) solution. Other devices for achieving separation of solutions are porous pots and gelled solutions.

For example
The half-cell, called the anode, is the site at which the oxidation of zinc occurs as shown below.

\[ \text{Zn} \, (s) \, \rightarrow \, \text{Zn}^{2+} \, (aq) \, + \, 2e^- \]

During the oxidation of zinc, the zinc electrode will slowly dissolve to produce zinc ions (Zn\(^{2+}\)), which enter into the solution containing Zn\(^{2+}\) (aq) and SO\(_4^{2-}\) (aq) ions.

The half-cell, called the cathode, is the site at which reduction of copper occurs as shown below.

\[ \text{Cu}^{2+} \, (aq) \, + \, 2e^- \, \rightarrow \, \text{Cu} \, (s) \]

When the reduction of copper ions (Cu\(^{2+}\)) occurs, copper atoms accumulate on the surface of the solid copper electrode.

The reaction in each half-cell does not occur unless the two half cells are connected to each other.

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**Reversible & Irreversible cells:**

**Reversible electrochemical cells** are the cells whose cell reactions can be get reversed when an external emf greater than its capacity is applied. (A cell which obeys thermodynamic conditions of reversibility is known as reversible cells). For example
Daniel cell with Capacity 1.1V, when an external emf of 1.1V is applied, the cell reaction stops.

\[ \text{Zn} + \text{Cu}^{+2} \rightarrow \text{Zn}^{+2} + \text{Cu} \]

But when an increased amount of emf greater than 1.1V is applied, the cell reaction is reversed.

\[ \text{Zn}^{+2} + \text{Cu} \rightarrow \text{Zn} + \text{Cu}^{+2} \]

A cell of this type can be termed as Reversible cell.

**Irreversible electrochemical cells** are the cells whose cell reactions cannot be reversed when an external emf greater than its capacity is applied. (A cell which does not obey thermodynamic conditions of reversibility is known as irreversible cells). For example, a cell which has Zn as an anode and Ag as a cathode with sulphuric acid as an electrolyte. The cell reaction at the anode is \((\text{Zn/ H}^{+}/\text{Ag})\)

\[ \text{Zn} (s) \rightarrow \text{Zn}^{+2} (aq) + 2e^- \]

In the presence of electrolyte \((\text{H}_2\text{SO}_4)\)

\[ \text{Zn} + 2 \text{H}^+ \rightarrow \text{Zn}^{+2} + \text{H}_2 \]

The cell reaction at the cathode is

\[ 2 \text{Ag} + 2e^- \rightarrow 2 \text{Ag} \]

When an external emf applied to the cell, the chemical reactions are not reversed because one of the products of the reaction \(\text{H}_2\) gas is escaped from the reaction system. Dry cells are another familiar example for this type of cells.
**Measurement of EMF:**

**Electromotive force:** The difference of potential which causes current to flow from the higher potential electrode to the lower potential electrode is called as electromotive force of a cell. The emf of a cell can not measured directly by connecting to the electrodes of a voltmeter because some of current is drawn by the voltmeter and that can cause a change in the concentration of the electrolyte near the electrodes due to the formation of reaction products from the electrodes. If we do the measurement by this method, the value of emf is lower than the expected one.

The emf of a cell can be measured with the help of Poggendroff’s method which states that the emf of a cell is determined by applying an equal and opposite external potential from an external source thereby there is no current flow in the circuit. So the applied potential is therefore equal to the magnitude of the emf of the cell.

A Potentiometer wire AB of uniform cross-section is connected to a dc source. The end ‘A’ of the wire is connected to a sliding contact through a standard cell and a galvanometer as in figure.

![Potentiometer diagram](image)

The sliding contact is moved along the length of the wire to get null deflection in the galvanometer. At this point the emf of the cell is proportional to the distance ‘AC’ of the wire. Now the unknown cell whose emf is to be measured is brought into the circuit by cutting off the standard cell. The point of null deflection is again determined. Now the
balance length of the wire is ‘AD’. Since in both occasion, electromotive forces are compensated. So it is known as compensation method.

\[
\text{EMF of the standard cell/ emf of unknown cell } = \frac{AC}{AD}
\]
\[
\text{EMF of the unknown cell} = \frac{AD}{AC} \times \text{emf of the standard cell}
\]

**Applications of emf measurement:**

Emf measurement of a cell is used to

(i) Determine the solubility of a sparingly soluble salt
(ii) Determine the pH of an aqueous solution
(iii) Determine the valency of the metal ions of the electrolyte
(iv) Determine the std. free energy change and equilibrium constant
(v) Determine the pH by using std. hydrogen electrode

**Single Electrode Potential (E):**

It is the measure of tendency of a metallic electrode to lose or gain electrons when it is contact with a solution of its own salt.

**Oxidation Potential:**

The tendency of an electrode to lose electrons is the direct measure of its tendency to oxidize and that potential is known as Oxidation Potential and the value of it in positive.

**Reduction Potential:**

The tendency of an electrode to gain electrons is the direct measure of its tendency to reduce and that potential is known as Reduction Potential and the value of it in negative.

**Helmholtz Electrical Double layer:**

An electrical double layer is formed around the surface of the electrode due to the force of attraction of positive/ negative ions present in the electrolyte and it can be
stated that “the equilibrium potential difference established between metal and its solution”.

The single electrode potential of an electrode depends on the nature of conductor, concentration of the electrolyte, temperature etc.

**Standard Electrode Potential (E°):**

The measure of tendency of a metallic electrode to lose or gain electrons when it is contact with a solution of its own salt of unit molar concentration at 25°C is known as standard electrode potential.

**Nernst Equation:**

Consider a general redox reaction,

\[ M^{n+} + ne^- \rightarrow M \]

For a general reversible chemical reaction, according to Vant-Hoff’s isotherm, loud’s free energy change \( \Delta G \) of the reaction and its equilibrium is given by,

\[ \Delta G = -RT \ln K + RT \ln \left( \frac{[\text{Product}]}{[\text{Reactant}]} \right) \]

We know that \( \Delta G° = -RT \ln K \)

Substituting the above in Van’t Hoff’s isotherm equation,

\[ \Delta G = \Delta G° + RT \ln \left( \frac{[\text{Product}]}{[\text{Reactant}]} \right) \]

Where \( \Delta G° = \) Standard free energy change.

For reversible reaction involving \( n \) electrons, the decrease in free energy \( (-\Delta G) \) will produce electrical energy \( (E) \) coulombs and is given by

\[ nFE = -\Delta G \]

\[ \Delta G = -nFE° \]
or

$$\Delta G = nF \Delta E^0$$  \hspace{1cm} (3)$$

\(\Delta G\) = Standard free energy change

\(n\) = the number of electrons

\(F\) = Faraday = 96,500 Coulombs of electricity

\(E^0\) = the standard potential.

and

Substituting Eq. (3) in Eq. (2), we get,

$$-nFE = -nFE^0 + RT \ln \left[ \frac{M}{M^{n+}} \right]$$  \hspace{1cm} (4)$$

When we apply this equation to an electrode reduction equation

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

We get,

$$-nF E_{\text{red}} = -nF E_{\text{red}}^0 + RT \ln \left[ \frac{M}{M^{n+}} \right]$$

Rearranging the above equation, we get

$$E_{\text{red}} = E_{\text{red}}^0 - \frac{RT}{nF} \ln \left[ \frac{M}{M^{n+}} \right]$$

$$E_{\text{red}} = E_{\text{red}}^0 - \frac{RT}{nF} \ln \left[ 1 \right]$$

$$\text{since } [M] = 1\text{ the activity of the solid metal}$$

The above equation may be written as,

$$E_{\text{red}} = E_{\text{red}}^0 + \frac{RT}{nF} \ln [M^{n+}]$$

where \(R = 8.314\text{ J/K/mole}\), \(T = 298^0\text{ K}\), \(F = 96500\text{ coulombs}\). Now substituting the value of \(R\), \(T\) and \(F\) we get,

$$E_{\text{red}} = E_{\text{red}}^0 + 0.0591 \log [M^{n+}] / n \hspace{1cm} (5)$$
The above equation is known as the Nernst Equation.

In general,
\[ E = E_\text{red}^0 + \frac{0.0591}{n} \log C \]  
\[ \text{Similarly for oxidation potential,} \]
\[ E = E_\text{oxi}^0 - \frac{0.0591}{n} \log [M^{n+}] \]

The Eqs (5) and (7) are known as Nernst Equation for single electrode potential.

**Applications of Nernst Equation:**
- Electrode potential of unknown metal can be determined using the Nernst equation.
- It is used to predict the corrosion tendency of metals.

Problems:
1. Calculate the reduction potential of Cu/\( \text{Cu}^{2+} \) electrode which is dipped in 0.5M of its own salt solution at 25\(^{0}\)C and the standard electrode potential or its is 0.337. Find out the emf.
   \[ E = E^0 + \frac{0.0591}{n} \log (\text{Cu}^{2+}) \text{ Volts} \quad n=2; \]
   (Ans) : Reduction Potential = 0.3230 V
2. Find out the oxidation potential of Zn/\( \text{Zn}^{2+} \) which is in contact with 0.2 M of its own salt solution at 25\(^{0}\)C and the std. electrode potential is 0.763V.
   \[ E = E^0 + \frac{0.0591}{n} \log (\text{Zn}^{2+}) \text{ V} \quad n=2; \]
   (Ans) : Oxidation potential = 0.7836 V

**REFERENCE ELECTRODES:**

The electrode of standard potential with which we can compare the potentials of another electrodes is called a reference electrode. The best reference electrode used is standard hydrogen electrode whose electrode potential at all temperature is taken as zero.
**Hydrogen electrodes:**

It consists of a small platinised platinum foil, which is sealed through the end of a glass tube. This tube is surrounded by another co-axial tube, which is sealed to the inner glass tube at the top. The outer glass tube is provided with a side-arm for passing hydrogen gas into the in-between space.

The bottom of the outer tube is flared into a bell around the platinum electrode. Openings in the bell allow escape of hydrogen gas. The platinum foil is coated with a layer finely divided platinum which adsorbs the hydrogen gas and it also speeds up the equilibrium between hydrogen gas and the hydrogen ions. This electrode when dipped in a 1N – HCl and when hydrogen at 1 atmosphere is passed through yields a normal or standard hydrogen electrode. The e.m.f of such a cell has arbitrarily been fixed at zero.

Limitations: (1) The hydrogen electrode is readily affected by compounds of Hg, As, S and oxidizing agents like Fe$^{3+}$, MnO$^{4-}$, Cr$_2$O$_7^{2-}$ etc., and consequently, this electrode cannot be used in solutions containing these ions. (2) It cannot be used in the presence of ions of many metals. (3) It cannot be used in solutions containing redox systems. (4) It is quite cumbersome to set up a hydrogen electrode.
Calomel electrode:

Calomel electrode is the mercury-mercurous chloride electrode. The potential of the calomel electrode, on the hydrogen scale has been found to vary with the concentration of the potassium chloride solution used. The reduction potentials for the various KCl concentrations at 25°C are:

<table>
<thead>
<tr>
<th>KCl concentration</th>
<th>Electrode potential (in volt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1N</td>
<td>0.3335</td>
</tr>
<tr>
<td>1.0N</td>
<td>0.2810</td>
</tr>
<tr>
<td>Saturated</td>
<td>0.2422</td>
</tr>
</tbody>
</table>

When the KCl solution is 0.1N, 1.0N and saturated it is called respectively as decinormal, normal and saturated calomel electrode. The electrode reaction taking place in this half-cell is:

\[ \text{HgCl}_2(s) + 2e^- \rightarrow \text{Hg}^{(l)} + 2\text{Cl}^{-(aq)} \]

The potential of this electrode is equal to the e.m.f of the cell:

\[ \text{Pt, H}_2(1 \text{ atm}) | \text{H}^{+} =? | | \text{KCl}(0.1N \text{ or } N \text{ or Satd.}) | \text{HgCl}_2 | \text{Hg}^{+} \]

Since potential of hydrogen electrode is zero.

Construction:

It consists of a tube in the bottom of which is a layer of mercury, over which is placed a paste of Hg + HgCl₂. The remaining portion of cell is filled with a solution of normal or decinormal or saturated solution of KCl. A platinum wire dipping into the mercury layer, is used for making electrical contact. The side tube is used for making electrical contact with a salt bridge. The saturated calomel electrode is formulated as:
**Ion-selective electrode:**

Ion-selective electrode possesses the ability to respond only to certain specific ions thereby developing a potential wrt that species only in a mixture and ignoring the other ions totally. In other words the potential developed by an ion-selective electrode depends only on the concentration of species/ions of interest. For example glass membrane is only H+ ions selective. The material employed for some ion-selective membranes are mentioned below:

**Solid state membranes:** (i) For fluoride ions - lanthanum tri fluoride crystal doped with europium di fluoride; (ii) For chloride ions - pressed pallet of Ag$_2$S + AgCl. The electrode has a Teflon body and the pellet is held in position by using epoxy resin.

**Liquid state membranes:** (i) For certain alkali and alkaline - earth cations - netural monocyclic crown ethers and phosphate diester; (ii) For anions - iron phenanthrolic complexes. Liquid state membrane is usually obtained by absorbing the active molecules on an inert porous support such as porous polymer.
Limitations: (i) Usually ion-selective membranes can be used in solution of pH value upto 10, since higher pH values affect these. (ii) Although ion-selective membranes are very thin, yet their resistances are extremely high, so it is necessary to use electronic potentiometers to measure the potential difference.

Applications: In the determination of: (i) concentration of cations, e.g., H\(^+\), Li\(^+\), Na\(^+\), K\(^+\), NH\(_4\)\(^+\), Ag\(^+\), Pb\(^{2+}\), Cd\(^{2+}\), hardness and anions, e.g., halide ions(X\(^-\)), NO\(_3\)\(^-\), CN\(^-\), S\(_2\)\(^-\) etc.

(ii) pH of a solution by using H\(^+\) ion-selective glass electrode; (iii) concentration of a gas by using gas-sensing electrode. For example glass electrode is employed for measuring the CO\(_2\)(g) level in blood. The glass electrode is kept in contact with a very thin-walled CO\(_2\)(g) permeable silicone rubber membrane soaked in dilute NaHCO\(_3\) solution. Then the electrode is dipped in the blood sample under-test. Since the membrane is permeable to CO\(_2\)(g). So CO\(_2\)(g) permeates into the membrane thereby causing reaction between NaHCO\(_3\) and CO\(_2\)(g). Eventually the pH value is altered, which is sensed by the glass electrode. In other words observed potential of such a glass electrode can be employed to measure the concentration of CO\(_2\)(g) in the blood sample.
**GLASS ELECTRODE:**

When two solutions of different pH values are separated by a thin glass membrane, there develops a difference of potential between the two surface of the membrane. The potential difference developed is proportional to the difference in pH value. The glass membrane functions as an ion-exchange resin, and an equilibrium is set up between the Na+ ions of glass and H+ ions in solution. For a particular type of glass the potential difference varies with the H+ ion concentration, and is given by the expression:

\[ E_G = E_G^0 + 0.0592 \text{ V pH} \]

Over a range of pH of the test solutions from 0 to 10.

**Construction:**

A glass electrode consists of thin-walled glass bulb containing AgCl coated Ag electrode or simply a Pt electrode in 0.1M - HCl. The glass electrode may be shown schematically as:

\[ \text{Ag} | \text{AgCl} (s), \text{HCl}(0.1M) | \text{Glass or Pt, 0.1M HCl} | \text{Glass}^+ \]

HCl in the bulb furnishes a constant H+ ion concentration. Thus it is a silver-silver chloride electrode, reversible with respect of chloride ions.

Glass electrode is used as the “internal reference electrode”. For the determination of pH of solution, especially colored solution containing oxidizing or reducing agents. Usually calomel electrode is used as the second electrode. In order to determine the pH of a solution, the glass electrode is placed is the solution under – test and this half-cell is coupled with saturated calomel electrode. The e.m.f. of the cell is measured. Due to the higher resistance, special electron-tube voltmeters are used to measure the e.m.f of the above cell. The e.m.f. of the complete cell is given by

\[ E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} \]

\[ = 0.2422 \text{ V} - [ E_G^0 + 0.0592 \text{ V pH} ] \]

\[ \text{pH} = \frac{0.2422 \text{ V} - E_{\text{cell}} - E_G^0}{0.0592 \text{ V}} \]

The \( E_G^0 \) value of a glass electrode can be determined by using a solution of known pH.
Advantages of glass electrode:

(1) It is simple and can easily be used. (2) Equilibrium is rapidly achieved. (3) The results are accurate. (4) It is easily poisoned.

Limitations:

(1) The glass electrode can be used in solutions with pH range of 0 to 10. Electrodes composed of special glasses can be used for measurements up to a pH of 12. However, above 12 pH cations of solution affect the glass interface and render the electrode useless.

(2) Although glass membrane of electrode is very thin yet its resistance is extremely high, which cannot be measured by ordinary potentiometers. It is therefore necessary to use special electronic potentiometers.

Electrochemical Series:

Using a hydrogen electrode as reference, if the metals are arranged in a series of increasing order of their standard electrode reduction potential it is known as emf series.

Importance of Electrochemical Series:

The activity series correlates many chemical properties of the elements. Some of the more important ones are given below:
1. Metals with large negative reduction potentials at the top of the series are good reducing agents in the Free State. They are the metals most easily oxidized to their ions by the removal of electrons.

2. The elements with large positive reduction potentials at the bottom of the series are good oxidizing agents when in the oxidized form, i.e. when the metals are in the form of ions and the non-metals are in the elemental state.

3. The reduced form of any element will reduce the oxidized form of any element below it, for example, metallic zinc will reduce copper(II) ions according to the equation

$$\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Cu} + \text{Zn}^{2+}$$

Most metals will reduce the halogens that are found at the bottom of the series and iodide ion will reduce elemental bromine forming iodine and bromide ion.

**The series of a few metals are given in the table:**

<table>
<thead>
<tr>
<th>Standard reduction potentials</th>
<th>Electrode reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Elements</strong></td>
<td><strong>Oxidised form</strong></td>
</tr>
<tr>
<td>Magnesium</td>
<td>Mg^{2+} + 2e^-</td>
</tr>
<tr>
<td>Aluminium</td>
<td>Al^{3+} + 3e^-</td>
</tr>
<tr>
<td>Zinc</td>
<td>Zn^{2+} + 2e^-</td>
</tr>
<tr>
<td>Chromium</td>
<td>Cr^{3+} + 3e^-</td>
</tr>
<tr>
<td>Iron</td>
<td>Fe^{2+} + 2e^-</td>
</tr>
<tr>
<td>Lead</td>
<td>Pb^{2+} + 2e^-</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>2H^+ + 2e^-</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu^{2+} + 2e^-</td>
</tr>
<tr>
<td>Mercury</td>
<td>Hg^{2+} + 2e^-</td>
</tr>
<tr>
<td>Silver</td>
<td>Ag^+ + e^-</td>
</tr>
<tr>
<td>Platinum</td>
<td>Pt^{2+} + 2e^-</td>
</tr>
<tr>
<td>Gold</td>
<td>Au^+ + e^-</td>
</tr>
</tbody>
</table>
Applications of Electrochemical Series:

1. Prediction of Relative Oxidizing and Reducing Powers: If the electrode potential is positive, they are strong oxidizing agents. If the potential is negative, they are strong reducing agents.

2. Reactivity of a metal with Acid – Liberating \( \text{H}_2 \) Gas: Metals with higher position above \( \text{H}_2 \) have a great tendency for oxidation and they displace \( \text{H}_2 \) from acids.

3. Prediction of Spontaneity of Redox Reactions: For spontaneous reactions \( E_{\text{cell}} \) always have positive sign and for non-spontaneous reaction the \( E_{\text{cell}} \) is negative.

4. To Predict Displacement Ability of metals: If a metal has a lower value of reduction potential it means it has a greater tendency to get oxidized and displace the other metal with have a greater reduction potential from the solution of the latter.

5. To Calculate Equilibrium Constants. Equilibrium constants of the reversible reactions can be calculated.

Potentiometric Titrations:

Potentiometric titration is very important application of emf measurement. In this method a cell is constructed in which at least one of the electrodes is reversible with respect to one of the ions taking part in the titration reaction.

Theory:

We know that the potential of an electrode dipping in a solution of an electrolyte depends upon the concentration of active ions.

\[
E = E^0 + \frac{RT}{nF} \log C
\]

A small change in the active ion concentration in the solution changes the electrode potential correspondingly. During the course of titration the concentration of the active ion decreases, thereby electrode potential of the indicator electrode decreases. Thus measurement of indicator electrode potential can serve as a good indication of end-point or equivalence point of the titration reaction. The potential of the indicator
electrode is usually measured potentiometrically by connecting it with a reference electrode like saturated calomel electrode.

**Detection of end-point:**

We know that the emf of a cell changes by the addition of small lots of titrant, so the concentration of reversible ion in contact with indicator electrode changes. We thus record the change in emf with every small addition. The change of potential will be slow at first, but at equivalence the point change will be sharp or quite sudden. The values are then plotted against corresponding volume changes. A curve like the one shown in Fig. is obtained. The end-point corresponds to the point of inflexion, i.e., point where the slope of the curve is maximum as shown. Alternatively change in emf with every small addition of titrant is plotted against volume V. The maximum of the curve gives the end-point.

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**Oxidation - reduction titrations:**

Titrations involving oxidizing agents and reducing agents can be followed potentiometrically by using platinum indicator electrode. The apparatus for titration of a ferrous salt with acidified K₂Cr₂O₇ in Fig.
On adding \(K_2Cr_2O_7\) from the burette, emf of the cell will increase first slowly, but at the equivalence point, there will be sudden jump in potential, since change in the ratio of \(Fe^{2+}\) / \(Fe^{3+}\) ions concentration, is quite rapid at the equivalence point.

\[
E = E^0 + \frac{RT}{F} \ln \left( \frac{Fe^{2+}}{Fe^{3+}} \right)
\]

**Precipitation titration:**

Titration involving precipitation can also be followed potentiometrically by the use of active metal electrode. We may illustrate the method by the titration of \(AgNO_3\) with the standard KCl solution run from the burette. Ag electrode dipping in \(AgNO_3\) solution is used as indicator electrode. The potential of \(Ag^+ / Ag\) half-cell is measured by connecting it with saturated calomel electrode through a salt bridge of \(NH_4NO_3\).

As the titration proceeds the concentration of \(Ag^+\) ions decreases, due to the precipitation of \(Ag^+\) ions as \(AgCl\).

\[
Ag^{+}NO_3^{-} + K^{+}Cl^{-} \rightarrow AgCl + K^{+}NO_3^{-}
\]
And the reduction potential of indicator electrode goes on decreasing progressively on the addition of KCl. At the end – point the Ag+ concentration becomes very small on account of slight solubility of AgCl. If addition of KCl is continued the Ag+ ion concentration is not affected, except a very small decrease due to decrease in solubility of AgCl on account of common ion effect. Therefore addition of KCl beyond end – point causes only a very small decrease in electrode potential or emf of the cell. On plotting $\Delta E / \Delta V$ versus $V$, the point of maxima gives

CONDUCTOMETRIC TITRATION:

Conductometric titration is a method of volumetric analysis based on the change in conductance of the solution, at the equivalence point during titration. This method is based on the fact that conductance of an aqueous solution, containing an electrolyte, depends upon: (i) the number of free ions in the solution; (ii) the charge on the free ions; (iii) mobility of the ions.

During the course of titration, the number of free ions in the solution changes not only have that evened the identity of the ions also changes. As a result of this,
conductance of the solution also undergoes a change. Let us take a few specific cases to illustrate.

1. **Acid-base titrations**: (i) Titration of a strong acid with a strong base: Before base is added, the conductivity of acid solution is high. This is represented by point A on the curve. The acid is taken in the conductivity bottle and the alkali in the burette. On gradual addition of NaOH from the burette, highly mobile H⁺ ions are removed by the added OH⁻ ions to form nearly non-conducting water molecules.

\[
\begin{align*}
H^+Cl^- + Na^+OH^- & \rightarrow Na^+Cl^- + H_2O \\
\text{Acid} & \quad \text{Base} & \quad \text{Salt} & \quad \text{Water} \\
\text{ (Non-Conducting) } & 
\end{align*}
\]

Hence the conductivity of the solution decreases progressively till the equivalence point B is reached. On further addition of NaOH, the conductivity of the solution will rise along the curve BC. Thus the descending branch of the curve gives the conductance of a mixture of acid and salt and the ascending branch gives the conductance of mixture of salt and excess base. At the minimum point B, there is no excess of either acid or base and hence it corresponds to the equivalence point.

**References:**

2. Sivakumar & Sivakumar, Engineering chemistry
Model Questions:

1. Electrochemical cells capable of producing emf by using
   a) Thermal energy  b) electrical energy  c) chemical energy  d) photo energy
2. Electrolytic cells capable of converting electrical energy into
   a) Thermal energy  b) chemical energy  c) photo energy  d) mechanical energy
3. In electrochemical cells electronation takes place at
   a) Electrolyte b) cathode  c) anode d) electrode
4. In electrochemical cells de-electronation takes place at
   a) Electrolyte b) cathode  c) anode d) electrode
5. Anode is capable of loosing
   a) Protons b) neutrons  c) electrons d) None
6. Two half cells are connected by means of
   a) Salt bridge b) acid bridge  c) base bridge d) paper bridge
7. The sign of reduction potential is always
   a) Positive  b) negative  c) neutral  d) Both b & c
8. Effectiveness of SHE is affected by the presence of
   a) Fe  b) Fe^{2+}  c) Fe^{3+}  d) F^{-}
9. Concentration of KCl in normal calomel electrode
   a) .1N  b) 1N  c) 1M  d) .1M
10. Concentration of KCl in decinormal calomel electrode
    a) .1N  b) 1N  c) 1M  d) .1M
11. A device which is capable of producing small amount of electricity is known as (a)
    Anode (b) Cathode (c) Cell (d) Half cell
12. If a cell does not obey the thermodynamic condition of reversibility then the type of cell is (a) Primary (b) Secondary (c) Cell (d) Half cell
13. If a cell obeys the thermodynamic condition of reversibility then the type of cell is (a) Primary (b) Secondary (c) Cell (d) Half cell
14. Nature of the reaction takes place at the anode is (a) Reduction  (b) Redox  (c) Oxidation  (d) Hydration

15. Nature of the reaction takes place at the cathode is (a) Reduction  (b) Redox  (c) Oxidation  (d) Hydration

16. The tendency of an electrode to lose electrons is defined as its ---- potential
   a) Oxidation* b) Reduction c) Redox d) None

17. The tendency of an electrode to lose electrons is defined as its ---- potential
   a) Oxidation b) Reduction c) Redox d) None

18. The tendency of an electrode to lose or gain electrons when it is in contact with its own salt solution of one molar concentration at 25°C is defined as its ---- potential
   a) Oxidation b) Reduction c) Redox d) Standard Electrode

19. $E_{cell}$ of spontaneous reaction is always
   a) Positive* b) negative c) neutral d) No sign

20. In calomel electrode _______ are used as electrodes.
   a) Hg + Hg$_2$Cl$_2$ b) Hg + HgCl c) Hg + KCl d) Hg + NaCl

21. ______ electrode can be used as an internal reference electrode.
   a) Glass* b) Calomel c) hydrogen  d) Platinum

22. $E_{cell}$ of non-spontaneous reaction is always
   b) Positive  b) negative c) neutral d) No sign

23. A measure of tendency of losing an electron in the presence of its ionic solution is termed as------------- potential  a) Single electrode potential b) Std.electrode potential c) reduction electrode  d) Oxidation electrode

Answers:

1.c  7.b  13.b  19.a
2.b  8.c  14.c  20.a
3.b  9.b  15.a  21.a
4.b  10.a 16.a  22.b
5.c  11.c 17.b  23.c
Part A

1. Define electrochemical cells.
2. Define single electrode potential.
3. Define electromotive force.
4. Define standard electrode potential.
5. Distinguish between galvanic cell and electrolytic cell.
6. Distinguish between reversible and irreversible cell giving one example for each.
7. Represent a galvanic cell according to IUPAC convention.
8. Why is a salt bridge used in the construction of a cell?
9. Describe hydrogen electrode.
10. Define a reference electrode.
11. Voltmeter cannot be used in the precise measurement of EMF of the galvanic cell. Give reason.
12. What is electromotive series? What is its significance?
13. Write down the expression to calculate emf of Daniel cell. Daniel cell is Zn | ZnSO₄ || CuSO₄ | Cu
14. Write Nernst equation for \( \text{M} \rightleftharpoons \text{M}^{n+} + n\text{e}^- \)
15. Write the construction of saturated calomel electrode.
16. Mention the application of Nernst equation.

Part B

1. Briefly discuss about reversible & irreversible cells with suitable example.
2. Explain about the measurement of emf.
3. Define Nernst equation and the terms involved in it.
4. Explain in detail about SHE.
5. Give a brief note on calomel electrode.
6. Explain about electrochemical series and its significance.
7. Write about the potentiometric titration of Fe$^{2+}$ Vs K$_2$Cr$_2$O$_7$.
8. Write about the potentiometric titration of Ag$^+$ Vs Cl$^-$.
9. Give a detail note on Conductometric titration of HCl Vs NaOH.
10. Discuss about the construction and functions of Glass electrode.
11. Write in detail about the measurement of pH by using glass electrode.

Assignment Questions:
1. Nernst Equation and its applications
2. Problems based on Nernst Equation
3. Glass Electrode and measurement of pH
4. Potentiometric titration of Fe$^{3+}$ Vs K$_2$Cr$_2$O$_7$
5. Potentiometric titration of Ag$^+$ Vs Cl$^-$
6. Conductometric titration of Acid Vs Bases.