

Electrochemistry

It is a branch of chemistry that deals with the relationship between chemical energy and electrical energy and their inter conversions.

ELECTROCHEMICAL CELLS

These are devices that convert chemical energy of some redox reactions to electrical energy. They are also called Galvanic cells or Voltaic cells. An example for Galvanic cell is Daniel cell.

Electrode Potential

When a metal rod is dipped in its own salt solution, there is a tendency of metal ions from the solution to deposit on the metal electrode. At the same time, metal atoms of the electrode have a tendency to go into the solution as ions. This tendency of a metal to lose or gain electron when it is in contact with its own solution is called electrode potential. When the concentrations of all the species involved in a half-cell is unity then the electrode potential is known as standard electrode potential. According to IUPAC convention, standard reduction potential is taken as the standard electrode potential. In a galvanic cell, the half-cell in which oxidation takes place is called anode and it has a negative potential. The other half-cell in which reduction takes place is called cathode and it has a positive potential. In a cell, the electrons flow from negative electrode to positive electrode and the current flows in opposite direction.

The potential difference between the two electrodes of a galvanic cell is called the cell potential and is measured in volts. The **cell potential** is the difference between the electrode potentials (reduction potentials) of the cathode and anode. The cell **electromotive force (emf)** of the cell is the potential difference between the two electrodes, when no current is flow through the cell. By convention, while representing a galvanic cell, the anode is written on the left side and the cathode on the right side. Metal and electrolyte solution are separated by putting a vertical line and a salt bridge is denoted by putting a double vertical line. For Daniel cell, the cell representation is $\text{Zn(s)}/\text{Zn}^{2+}(\text{aq})//\text{Cu}^{2+}(\text{aq})/\text{Cu(s)}$ Under this convention the emf of the cell is positive and is given by the potential of the half-cell on the right hand side minus the potential of the half-cell on the left hand side

Measurement of Electrode Potential

The potential of individual half-cell cannot be measured. We can measure only the difference between the two half-cell potentials that gives the emf of the cell. For this purpose a half-cell called **standard hydrogen electrode (SHE)** is used. It consists of a platinum electrode coated

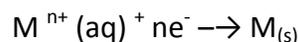
with platinum black. The electrode is dipped in an acidic solution of one molar concentration and pure hydrogen gas at 1 bar pressure and 298K is bubbled through it. It is represented as $\text{Pt(s)}/\text{H}_2(\text{g})/\text{H}^+(\text{aq})$. By convention, the electrode potential of SHE is taken as zero.

To determine the electrode potential of an electrode, it is connected in series with the standard hydrogen electrode and the emf of the resulting cell is determined by the equation, $E_{\text{cell}} = E_{\text{R}} - E_{\text{L}}$. Since the electrode potential of SHE is zero, the value of E_{cell} is equal to the electrode potential of the given electrode. If the standard electrode potential of an electrode is greater than zero (i.e. +ve), then its reduced form is more stable compared to hydrogen gas. Similarly, if the standard electrode potential is negative then hydrogen gas is more stable than the reduced form of the species.

Electrochemical series: It is a series in which various electrodes are arranged in the decreasing order of their reduction potential. In this table, fluorine is at the top indicating that fluorine gas (F_2) has the maximum tendency to get reduced to fluoride ions (F^-). Therefore fluorine gas is the strongest oxidising agent and fluoride ion is the weakest reducing agent. Lithium has the lowest electrode potential indicating that lithium ion is the weakest oxidising agent while lithium metal is the most powerful reducing agent in an aqueous solution.

Nernst Equation

Nernst proposed an equation to relate the electrode potential of an electrode (or, emf of a cell) with the electrolytic concentration. He showed that for the electrode reaction:



the electrode potential can be given by:

1) Variation of conductivity and Molar conductivity with concentration

Both conductivity and molar conductivity change with the concentration of the electrolyte. For both strong and weak electrolytes, conductivity always decreases with dilution. This is because conductivity is the conductance of unit volume of electrolytic solution. As dilution increases, the number of ions per unit volume decreases and hence the conductivity decreases. For both strong and weak electrolyte, the molar conductivity increases with dilution (or decreases with increase in concentration), but due to different reasons.

2) Faraday's second law

It states that when same quantity of electricity is passed through solutions of different substances, the amount of substance deposited or liberated is directly proportional to their chemical equivalence. For e.g. when same quantity of electricity is passed through solutions of

two substances A and B, then $\frac{\text{Mass of A deposited}}{\text{Equivalent mass of A}} = \frac{\text{Mass of B deposited}}{\text{Equivalent mass of B}}$

Batteries

A battery is basically a galvanic cell in which the chemical energy of a redox reaction is converted to electrical energy. They are of mainly 2 types – primary batteries and secondary batteries. 1) Primary batteries: Here the reaction occurs only once and after use over a period of time, they become dead and cannot be reused. E.g. Dry cell, mercury button cell etc. (Primary cells cannot be recharged and reused).

1. Dry Cell

It is a compact form of Leclanche cell. It consists of a zinc container as anode and a carbon (graphite) rod surrounded by powdered manganese dioxide (MnO_2) and carbon as cathode. The space between the electrodes is filled by a moist paste of ammonium chloride (NH_4Cl) and zinc chloride (ZnCl_2).

The electrode reactions are:

Anode: $\text{Zn(s)} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$ Cathode: $\text{MnO}_2 + \text{NH}_4^+ + \text{e}^- \rightarrow \text{MnO(OH)} + \text{NH}_3$ Ammonia produced in this reaction forms a complex with Zn^{2+} and thus corrodes the cell. The cell has a potential of nearly 1.5 V.

2. Mercury cell

Here the anode is zinc – mercury amalgam and cathode is a paste of HgO and carbon. The electrolyte is a paste of KOH and ZnO . The electrode reactions are: Anode reaction: $\text{Zn(Hg)} + 2\text{OH}^- \rightarrow \text{ZnO(s)} + \text{H}_2\text{O} + 2\text{e}^-$ Cathode reaction: $\text{HgO} + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Hg(l)} + 2\text{OH}^-$ The overall reaction is : $\text{Zn(Hg)} + \text{HgO(s)} \rightarrow \text{ZnO(s)} + \text{Hg(l)}$

The cell has a constant potential of 1.35 V since the overall reaction does not involve any ion in solution.

3. Fuel cells

These are galvanic cells which convert the energy of combustion of fuels like hydrogen, methane, methanol, etc. directly into electrical energy. One example for fuel cell is **Hydrogen – Oxygen fuel cell**, which is used in the Apollo space programme. Here hydrogen and oxygen are bubbled through porous carbon electrodes into concentrated aqueous sodium hydroxide solution. To increase the rate of electrode reactions, catalysts like finely divided platinum or palladium metal are filled into the electrodes.

Advantages of Fuel cells

1. The cell works continuously as long as the reactants are supplied.
2. It has higher efficiency as compared to other conventional cells.
3. It is eco-friendly (i.e. pollution free) since water is the only product formed.
4. Water obtained from $H_2 - O_2$ fuel cell can be used for drinking.

Corrosion

It is the process of formation of oxide or other compounds of a metal on its surface by the action of air, water-vapour, CO_2 etc. Some common examples are: The rusting of iron, tarnishing of silver, formation of green coating on copper and bronze (verdigris) etc. Most familiar example for corrosion is rusting of iron. It occurs in presence of water and air. It is a redox reaction. At a particular spot of the metal, oxidation takes place and that spot behaves as anode. Here Fe is oxidized to Fe^{2+} . $2 Fe (s) \rightarrow 2 Fe^{2+} + 4 e^-$ Electrons released at anodic spot move through the metal and go to another spot on the metal and reduce oxygen in presence of H^+ . This spot behaves as cathode. The reaction taking place at this spot is: $O_2(g) + 4 H^+(aq) + 4 e^- \rightarrow 2 H_2O(l)$ The overall reaction is: $2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2 H_2O(l)$ The ferrous ions (Fe^{2+}) are further oxidised to ferric ions (Fe^{3+}) and finally to hydrated ferric oxide ($Fe_2O_3 \cdot x H_2O$), which is called rust.

Methods to prevent corrosion

1. By coating the metal surface with paint, varnish etc.
2. By coating the metal surface with another electropositive metal like zinc, magnesium etc. The coating of metal with zinc is called galvanisation and the resulting iron is called galvanized iron.
3. By coating with anti-rust solution.
4. An electrochemical method is to provide a sacrificial electrode of another metal (like Mg, Zn, etc.) which corrodes itself but saves the object (sacrificial protection)

Electrolytic Cells and Electrolysis

In an electrolytic cell, the electrical energy is converted to chemical energy. The dissociation of an electrolyte by the passage of electricity is called electrolysis. For e.g. when $CuSO_4$ solution is electrolysed by Cu electrodes, Cu is deposited at the cathode and Cu^{2+} ions are liberated from the anode.