# SLO 8: Electrochemistry

## 8.1 Oxidation and Reduction (Redox) Reactions

### 8.1.1 Differentiate Between Oxidation And Reduction In Terms Of

Oxidation is defined as addition of oxygen or removal of hydrogen during a chemical reaction. Reduction is defined as addition of hydrogen or removal of oxygen during a chemical reaction. Both of these processes take place simultaneously in a reaction, we can say where there is oxidation there is reduction. Examples:

1. A reaction between zinc oxide and carbon takes place by the removal of oxygen (reduction) from zinc oxide and addition of oxygen (oxidation) to carbon.
2. A reaction between hydrogen sulphide and chlorine takes place by oxidation of hydrogen sulphide and reduction of chlorine. Hydrogen is being removed from $H_2S$ and added to chlorine.
3. A reaction between sodium metal and chlorine takes place in three steps. First, sodium atom losses an electron, to form sodium ion. Simultaneously, this electron is accepted by chlorine atom (reduction process), as chlorine atom needs one electron to complete its octet. As a result, chlorine atom changes to chloride ion. Ultimately, both these ions attract each other to form sodium chloride.

## 8.2 Oxidation States and Rules for Assigning Oxidation States

### 8.2.1 Define Oxidation State

Oxidation state or oxidation number (O.N.) is the apparent charge assigned to an atom of an element in a molecule or in an ion. For example: in HCl, oxidation number of H is + 1 and that of CI is -1.

### 8.2.2 Explain The Common Rules Used For Assigning Oxidation Numbers To Free Elements, Ions, Molecules And Atoms

1. The oxidation number of all elements in the free state is zero.
2. The oxidation number of an ion consisting of a single element is the same as the charge on the ion.
3. The oxidation number of different elements in the periodic table is: in Group 1 it is +1, in Group 2 it is +2 and in Group 13 it is +3.
4. The oxidation number of hydrogen in all its compounds is +1. But in metal hydrides it is -1.
5. The oxidation number of oxygen in all its compounds is -2. But it is -1 in peroxides and +2 in OF2.
6. In any substance, the more electronegative atom has the negative oxidation number.
7. In neutral molecules, the algebraic sum of the oxidation numbers of all the elements is zero.
8. In ions, the algebraic sum of oxidation number equals the charge on the ion.

### 8.2.3 Calculate The Oxidation Number Of An Atom In A Compound And Polyatomic Ion

Practice Work. Do it yourself.

## 8.3 Oxidizing and Reducing Agents

### 8.3.1 Describe Oxidizing And Reducing Agents In A Redox Reaction

An oxidizing agent is the specie that oxidize a substance by taking electrons from it. The substance (atom or ion) which is reduced itself by gaining electrons is also called oxidizing agent. Non-metals are oxidizing agents because they accept electrons being more electronegative elements.

Reducing agent is the specie that reduces a substance by donating electron to it. The substance (atom or ion) which is oxidized by losing electrons is also called reducing agent. Almost all metals are good reducing agents because they have the tendency to lose electrons.

# 8.4 Electrochemical Cells

## 8.4.1 Define The Following Terms

1. Electrolyte: The substances, which can conduct electricity in their aqueous solutions or molten states, are called electrolytes. For example, solutions of salts, acids or bases are good electrolytes.
2. Weak electrolyte: The electrolytes which ionize to a small extent when dissolved in water and could not produce more ions are called weak electrolytes. Acetic acid ($CH_3COOH$) and $Ca(OH)_2$ when dissolved in water, ionize to a small extent and are good examples of weak electrolytes.
3. Strong electrolyte: The electrolytes which ionize almost completely in their aqueous solutions and produce more ions, are called strong electrolytes. Example of strong electrolytes are aqueous solutions of NaCl, NaOH and H SO , etc.
4. Non-electrolyte: The substances, which do not ionize in their aqueous solutions and do not allow the current to pass through their solutions, are called non-electrolytes. For example, sugar solution and benzene are non-electrolytes.
5. Electrolysis: It is defined as the chemical decomposition of a compound into its components by passing current through the solution of the compound or in the molten state of the compound. The process that takes place in an electrolytic cell is called electrolysis. Examples of these cells are Downs cell, Nelson's cell.

## 8.4.2 Describe An Electrochemical Cell And Its Two Types

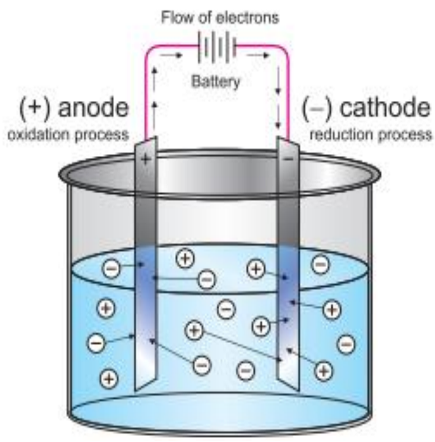
Electrochemical cell is a system in which two electrodes are dipped in the solution of an electrolyte which are connected to the battery. Electrochemical cell is an energy storage device in which either a chemical reaction takes place by using electric current (electrolysis) or chemical reaction produces electric current (electric conductance). Electrochemical cells are of two types.

**Electrolytic cells**

The type of electrochemical cell in which a non-spontaneous chemical reaction takes place when electric current is passed through the solution, is called an electrolytic cell.

### *Construction of Electrolytic Cell:*

It consists of solution of an electrolyte, two electrodes that are dipped in the electrolytic solution and connected to the battery. Electrode connected to positive terminal is anode and electrode connected to the negative terminal is called cathode.

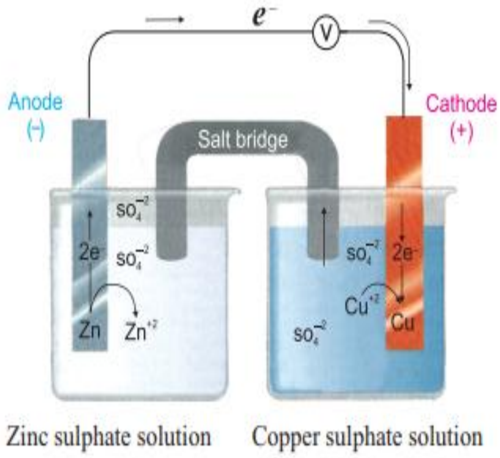



### *Working of an Electrolytic Cell*

When electric current is applied from battery, the ions in the electrolyte migrate to their respective electrodes. The anions, which are negatively charged, move towards the anode and discharge there by losing their electrons. Thus, oxidation takes place at anode. While cations, which are positively charged ions, move towards cathode. Cations gain electrons from the electrode and as a result reduction takes place at cathode.

**Galvanic Cell**

The electrochemical cell in which a spontaneous chemical reaction takes place and generates electric current is called galvanic or voltaic cell. Example of this type of cell is a Daniel cell.




## *Construction of a Daniel Cell*

A galvanic cell consists of two cells, each called as half-cell, connected electrically by a salt bridge. In each of the half-cell, an electrode is dipped in 1M solution of its own salt and connected through a wire to an external circuit.

The left half-cell consists of an electrode of zinc metal dipped in 1M solution of zinc sulphate. The right half-cell is a copper electrode dipped in 1M solution of copper sulphate. Salt bridge is a U-shaped glass tube. It consists of saturated solution of strong electrolyte supported in a jelly type material. The ends of the U tube are sealed with a porous material like glass wool. The function of the salt bridge is to keep the solutions of two half cells neutral by providing a pathway for migration of ions.

## *Working of Daniel Cell*

The Zn metal has tendency to lose electrons more readily than copper. As a result, oxidation takes place at Zn-electrode. The electrons flow from Zn-electrode through the external wire in a circuit to copper electrode. These electrons are gained by the copper ions of the solution and copper atoms deposit at the electrode. The respective oxidation and reduction processes going on at two electrodes. As a result of redox reaction, electric current is produced. The batteries which are used for starting automobiles, running calculators and toys and to lit the bulbs work on the same principle.

## 8.4.3 Distinguish Between Galvanic (Voltaic) Cell And Electrolytic Cell Based On Their Parts, Working And Examples

| Electrolytic Cell | Galvanic Cell |
|---|---|
| It consists of one complete cell connected to a battery. | It consists of two half-cells connected through a salt bridge. |
| Anode has positive charge while cathode has negative charge. | Anode has negative charge while cathode has positive charge. |
| Electrical energy is converted into chemical energy. | Chemical energy is converted into electrical energy. |
| Current is used for non-spontaneous chemical reaction to take place. | Redox reaction takes place spontaneously and produces electrical current. |

## 8.4.4 Deduce The Direction Of Movement Of Cations And Anions Towards Respective Electrodes In An Electrolytic Cell

In an electrolytic cell, the movement of ions is driven by the electric field created by an external power source. The direction of movement is as follows:

- Cations (Positively charged ions): Move toward the cathode, which is the negative electrode. Upon reaching the cathode, they gain electrons and undergo reduction to become neutral atoms.
- Anions (Negatively charged ions): Move toward the anode, which is the positive electrode. Upon reaching the anode, they lose electrons and undergo oxidation to become neutral atoms or molecules

## 8.4.5 Infer The Electrical Conductivity Of Solutions Based On The Dissociation Of Substances Into Ions

1. Strong Electrolytes: These substances dissociate almost completely into ions. Because they provide a high concentration of mobile charge carriers, their solutions exhibit high electrical conductivity.
2. Weak Electrolytes: These substances dissociate only partially. Due to the low concentration of free ions compared to the total amount of solute, these solutions have low or moderate conductivity.
3. Non-Electrolytes: Substances like sugar or ethanol do not dissociate into ions at all. Without mobile ions to carry a charge, their solutions are non-conductive or poor conductors.
4. Solvent Polarity: Solvents with high dielectric constants, like water, better facilitate the separation of ions, leading to higher conductivity than non-polar solvents.
5. Ion Mobility: Smaller ions or those with higher charges generally move faster through the solution, contributing to higher conductivity.

## 8.4.6 Identify The Reactivity Of Elements Using The Reactivity Series

- Most Reactive: Potassium (K) > Sodium (Na) > Calcium (Ca) > Magnesium (Mg) > Aluminum (Al).
- Moderately Reactive: Zinc (Zn) > Iron (Fe) > Tin (Sn) > Lead (Pb).
- Non-Metals: Carbon (C) and Hydrogen (H) are often included to help predict extraction methods and reactions with acids.
- Least Reactive: Copper (Cu) > Mercury (Hg) > Silver (Ag) > Gold (Au) > Platinum (Pt).

## 8.4.7 Illustrate Metal Displacement Reactions In An Aqueous Medium

A metal displacement reaction in an aqueous medium occurs when a more reactive metal (the displacing metal) is added to a solution of a less reactive metal's salt (the displaced metal).

- Oxidation: The more reactive metal loses electrons to form cations, which enter the solution.
- Reduction: The ions of the less reactive metal in the solution gain those electrons to form neutral metal atoms, which deposit as a solid.

**Visible Changes:**

- Color Change of Solution: If the initial salt solution is colored (e.g., blue copper sulfate), it may fade or change as new ions form.
- Solid Deposition: A new solid (the displaced metal) typically coats the surface of the original metal or settles at the bottom.
- Metal Dissolution: The original piece of more reactive metal may slowly shrink or appear to "dissolve".

**Example: Zinc and Copper Sulfate**

When a strip of Zinc is placed in a blue Copper Sulfate ($CuSO_4$) solution:

$$Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$$

The blue color of the solution fades as colorless Zinc Sulfate forms, and a reddish-brown layer of copper metal deposits on the Zinc strip.

## 8.4.8 Determine The Half-Cell In Which Oxidation Occurs And The Half-Cell In Which Reduction Occurs In A Voltaic Cell

In a voltaic (galvanic) cell, we can determine which half-cell is the site of oxidation or reduction by applying these fundamental electrochemical rules:

1. Oxidation always occurs at the Anode. In a voltaic cell, the anode is the negative (-) electrode because it is the source of electrons.
2. Reduction always occurs at the Cathode. The cathode is the positive (+) electrode where electrons are consumed.
3. Chemical Changes: The electrode that loses mass over time is typically the anode, as the solid metal is oxidized into aqueous ions. The electrode that gains mass (often forming a coating) is typically the cathode, as aqueous ions are reduced into solid metal.

### 8.4.9 Deduce The Direction Of The Flow Of Electrons In A Voltaic Cell

Electrons always flow from the anode to the cathode through the external circuit. If we know the direction of electron flow, the starting point is the oxidation half-cell and the destination is the reduction half-cell.

### 8.4.10 Explain The Production Of Electrical Energy In A Dry Cell

In a dry cell, electrical energy is produced through a spontaneous redox reaction that converts chemical energy into electrical energy.

- Anode (Negative Electrode): The outer zinc (Zn) container serves as the anode.
- Cathode (Positive Electrode): A central carbon (graphite) rod acts as the cathode. It is surrounded by a mixture of manganese oxide $MnO_2$ and carbon powder.
- Electrolyte: A moist paste containing ammonium chloride ($NH_4Cl$) and zinc chloride ($ZnCl_2$) enables the movement of ions to maintain charge balance.

**Process of Energy Production**

When cell is connected to an external circuit, chemical reactions occur simultaneously at both electrodes:

1. Oxidation at Anode: Zinc atoms from the container lose electrons and enter the electrolyte as zinc ions.
$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$
2. Electron Flow: The released electrons travel through the external circuit from the negative zinc terminal to the positive carbon rod, creating an electric current that powers the connected device.
3. Reduction at the Cathode: Electrons arrive at the cathode and are accepted by the manganese dioxide in the presence of ammonium ions.
$$2MnO_2(s) + 2NH_4^+(aq) + 2e^- \rightarrow Mn_2O_3(s) + 2NH_3(g) + H_2O(l)$$
4. Waste Management: The byproduct ammonia is neutralized by zinc ions to form a complex ion, $[Zn(NH_3)_2]^{2+}$ which prevents gas buildup within the cell.

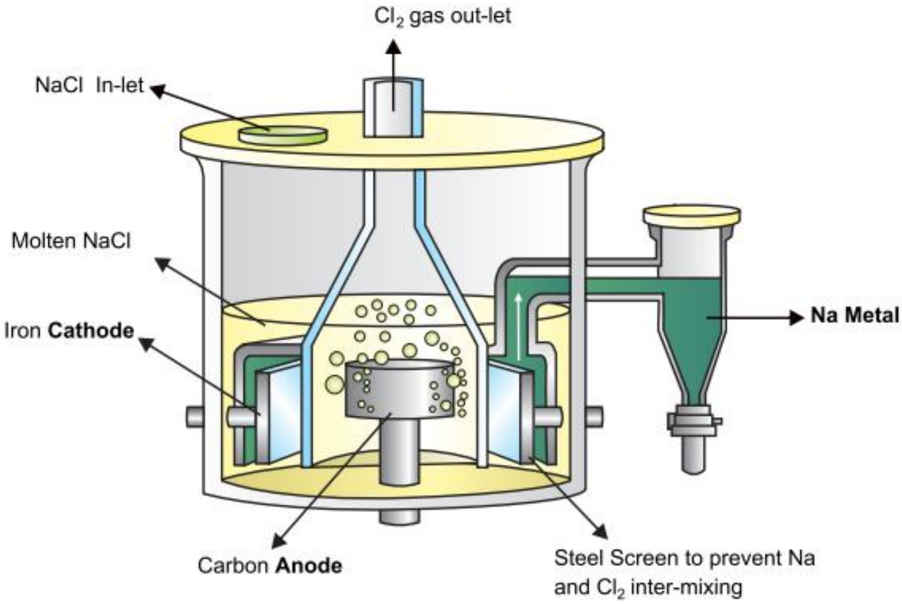
As these reactions proceed, the chemical reactants are eventually consumed, leading to a decline in voltage until the cell becomes "dead".

## 8.5 Electrochemical Industries

### 8.5.1 Explain The Manufacturing Of Sodium Metal From Fused NaCl In Down Cell

On the industrial scale, molten sodium metal is obtained by the electrolysis of fused NaCl in the Downs cell. This electrolytic cell is a circular furnace. In the center, there is a large block of graphite, which acts as an anode while cathode around it is made of iron.

The fused NaCl produces $Na^+$ and $Cl^-$ ions, which migrate to their respective electrodes on the passage of electric current. The electrodes are separated by steel gauze to prevent the contact between the products. The $Cl^-$ ions are oxidized to give $Cl_2$ gas at the anode. It is collected over the anode within an inverted coneshaped structure. While $Na^+$ is reduced at cathode and molten Na metal floats on the denser molten salt mixture from where it is collected in a side tube. Following reactions take place during the electrolysis of the molten sodium chloride:




Molten NaCl ionizes as: $2NaCl \rightleftharpoons 2Na^+ + 2Cl^-$

Half-cell reaction at anode (oxidation): $2Cl^- \longrightarrow Cl_2 + 2e^-$

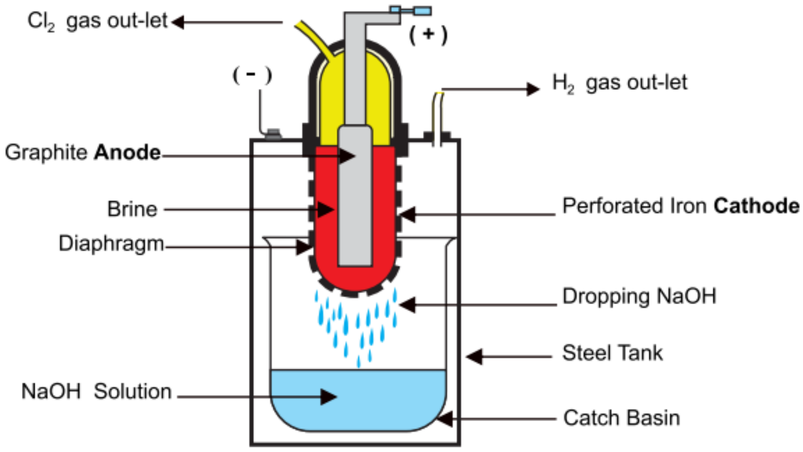
Half-cell reaction at cathode (reduction): $2Na^+ + 2e^- \longrightarrow 2Na$

Overall galvanic reaction is the sum of these two half-cell reactions:

$$2NaCl \rightleftharpoons Cl_2 + 2Na$$

## 8.5.2 Explain The Manufacturing Of Sodium Hydroxide From Aqueous Solution Of NaCl In Nelson Cell

On industrial scale caustic soda (sodium hydroxide) NaOH, is produced in Nelson's cell by the electrolysis of aqueous solution of NaCl called brine. It consists of a steel tank in which graphite anode is suspended in the center of a U-shaped perforated iron cathode. This iron cathode is internally lined with asbestos diaphragm. Electrolyte brine is present inside the iron cathode.



Aqueous solution of sodium chloride consists of $Na^+$, $Cl^-$, $H^+$ and $OH^-$ ions. These ions move towards their respective electrodes and redox reactions take place at these electrodes. When electrolysis takes place $Cl^-$ ions are discharged at anode and $Cl_2$ gas rises into the dome at the top of the cell. $H^+$ ions are discharged at cathode and $H_2$ gas escapes through a pipe. Sodium hydroxide solution slowly percolates into a catch basin.

Brine ionizes to produce ions: $2NaCl \longrightarrow 2Na^+ + 2Cl^-$

Reaction at anode (oxidation): $2Cl^- \longrightarrow Cl_2 + 2e^-$

Reaction at cathode (reduction): $4OH^- \longrightarrow 2H_2O + O_2 + 4e^-$

$2Na^+ + 2OH^- \longrightarrow 2NaOH$

Overall cell reaction of this process: $2NaCl + 2H_2O \longrightarrow H_2 + Cl_2 + 2NaOH$

# 8.6 Corrosion and its Prevention

## 8.6.1 Define The Term 'Corrosion'

Corrosion is slow and continuous eating away of a metal by the surrounding medium. It is a redox chemical reaction that takes place by the action of air and moisture with the metals. The most common example of corrosion is rusting of iron.

## 8.6.2 Describe The Rusting Of Iron As An Example Of Corrosion

Corrosion of iron is called rusting. The important condition for rusting is moist air (air having water vapors in it). There will be no rusting in water vapors free of air or air free of water. Stains and dents on the surface of iron provide the sites for this process to occur. This region is called anodic region and following oxidation reaction takes place here:

$$2Fe \longrightarrow 2Fe^{+2} + 4e^-$$

This loss of electrons damages the object. The free electrons move through iron sheet until they reach to a region of relatively high $O_2$ concentration near the surface surrounded by water layer. This region acts as cathode and electrons reduce the oxygen molecule in the presence of $H^+$ ions:

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$$

The $H^+$ ions are provided by the carbonic acid, which is formed because of presence of $CO_2$ in water. That is why acidic medium accelerates the process of rusting. The overall redox process is completed without the formation of rust.

$$2Fe + O_2 + 4H^+ \longrightarrow 2Fe^{+2} + 2H_2O$$

The $Fe^{+2}$ formed spreads throughout the surrounding water and react with $O_2$ to form the salt $Fe_2O.nH_2O$ which is called rust. It is also a redox reaction.

$$2Fe^{+2} + \frac{1}{2}O_2 + (2+n)H_2O \longrightarrow Fe_2O_3 + nH_2O + 4H^+$$

The rust layer of iron is porous and does not prevent further corrosion. Thus, rusting continues until the whole piece of iron is eaten away.

## 8.6.3 Explain The Following Methods Used To Prevent Corrosion

**Barrier Coatings (Using Paint And Galvanizing)**

Greasing or painting of the surface can prevent the rusting of iron. With development of technologies, modern paints contain a combination of chemicals called stabilizers that provide protection against the corrosion in addition to prevention against the weathering and other atmospheric effects.

The process of coating a thin layer of zinc on iron is called galvanizing. This process is carried out by dipping a clean iron sheet in a zinc chloride bath and then heating it. After this iron sheet is removed, rolled into molten zinc metal bath and finally air-cooled. Advantage of galvanizing is that zinc protects the iron against corrosion even after the coating surface is broken.

**Electroplating (Using Tin And Chromium)**

Tin is electroplated on steel by placing steel into a container containing tin salt solution. Steel is connected to an electrical circuit, acting as cathode. While the other electrode made of tin metal acts as anode. When an electrical current passes through the circuit, tin metal ions present in the solution deposit on steel.

Electroplating of chromium is carried out by the object to be electroplated is dipped in aqueous solution of chromium sulphate containing a little sulphuric acid, that acts as an electrolyte. The object to be electroplated acts as cathode while anode is made of antimonial lead. The electrolyte ionizes and provides $Cr^{+3}$ ions, which reduce and deposit at cathode.

**Sacrificial Protection (Using Magnesium Blocks)**

Sacrificial protection is a method of corrosion prevention where a more reactive metal is used to protect a less reactive one. Magnesium is higher in the reactivity series than iron. Because it is more reactive, the magnesium acts as the anode and undergoes oxidation, losing electrons and corroding preferentially. The released electrons flow through the electrical connection into the steel structure, making the steel the cathode. This excess of electrons prevents the iron atoms in the steel from losing their own electrons, effectively stopping the oxidation (rusting) process.