**SS 2 CHEMSTRY**

***LECTURE 5***

TOPIC: **ELECTROLYSIS**

Electrolysis is the chemical change brought about by the passage of a direct current through an electrolyte via electrodes.

**Terminologies**

1. ***Electrolytes***

An electrolyte is a substance that produces an electrically conducting solution when dissolved in a polar solvent, such as water. The dissolved electrolyte separates into cations and anions, which disperse uniformly through the solvent. Electrically, such a solution is neutral. If an electric potential is applied to such a solution, the cations of the solution are drawn to the electrode that has an abundance of electrons, while the anions are drawn to the electrode that has a deficit of electrons. The movement of anions and cations in opposite directions within the solution amounts to a current. This includes most soluble salts, acids, and bases. Some gases, such as hydrogen chloride, under conditions of high temperature or low pressure can also function as electrolytes.

1. ***Electrodes***

An electrode is a solid material in form of wire, rod or plate through which electric current enters or leaves the electrolyte.

There are two types of electrode, namely: Anodes and cathodes.

1. **Anodes**

This is the electrode through which electrons leave the electrolyte or through which conventional current enters the electrolyte. In electrolytic cell, anode is the positive electrode.

1. **Cathodes**

Cathode is the electrode through which electrons enter the electrolyte or through which the conventional current leaves the electrolyte. In electrolytic cell, the cathode is the negative electrode.

**What Is Conventional Current?**

The electrons flow is termed electron current. Electrons flow from the negative end to the positive end. Conventional current behaves as if positive charge carriers cause current to flow. Conventional current flows from the positive terminal to the negative terminal. The conventional current can be defined as charge per unit time transported in a certain direction. In conventional current, the type of charge carrier is irrelevant.

In conventional current, the flow of electrons is assumed as a flow of protons in the opposite direction. Possibly the simplest way to think about this is to pretend as if the movement of positive charge carriers constituted current flow.



**IONIC THEORY**

Ionic theory proposed that when an electrolyte is melted or dissolved in water, some if not all of the molecules of the substance dissociate into freely-moving charge ions i.e. positive ions (called cations) and negative ions (anions). The process of dissociation into ions is called ionization. When an electric current is passed through an electrolyte, the free ions lose their random movement. The positive ion becomes attracted to the negative electrode (called the cathode) while the negative ions move toward the positive electrode (called anode). It is this ionization and mobility of ions that constitute current flow.

**ELECTROCHEMICAL CELLS**

An electrochemical cell is a chemical cell through which electrical energy is converted to chemical energy or vice versa.

There are two types of electrochemical cell, namely: ***electrolytic cell*** and ***galvanic (voltaic) cell.***

**Galvanic cells**

A galvanic cell is an electrochemical cell which converts chemical potential energy to electrical potential energy through a spontaneous chemical reaction. A galvanic cell has two half-cells with each half cell containing an electrode in an electrolyte. Usually, separation is important in order to prevent direct chemical contact of the oxidation and reduction reactions, creating a potential difference. The electrons produced during oxidation reaction travel through an external circuit before being used by the reduction reaction.

**Electrolytic Cell**

An electrolytic cell is an electrochemical cell that converts electrical potential energy to chemical potential energy by using electricity to drive a non-spontaneous chemical reaction. An electrolytic cell is usually activated by applying an electrical potential across the electrode to force an internal chemical reaction between the electrodes and ions that are in the electrolyte solution. This process is referred to as electrolysis.

**The Difference Between Electrolytic And Galvanic Cells**

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| S/N | **Electrolytic cell** | **Galvanic cell** |
| 1. | An electrolytic cell converts electrical energy into chemical energy | A galvanic cell converts chemical energy into electrical energy |
| 2.  | The anode is positive and cathode is the negative electrode. The reaction at the anode is oxidation and at the cathode is reduction. | The anode is negative and the cathode is positive electrode. The reaction at the anode is oxidation while the reaction at the cathode is reduction. |
| 3. | The external battery supplies the electrons. The electrons enter through the cathode and come out through the anode. | The electrons are supplied by species getting oxidized. They move from anode to the cathode in the external circuit. |
| 4. | Both electrodes are immersed in the same container in solution of or molten electrolyte. The electrolyte may be melt or aqueous solution of some salt, acid or alkali. | The two half cells are arranged in different containers, being connected through the salt bridge or semi-permeable membrane. |
| 5. | Have different uses such as electroplating, extracting pure metals from their ores, production of oxygen and hydrogen for commercial and industrial use. | Commonly referred to as accumulators or batteries and are usually used as a source of electric current. |

***ELECTROLYTIC REACTION***

To explain what happens in an electrolytic cell let us examine the decomposition of molten sodium chloride into sodium metal and chlorine gas. The reaction is written below.

2NaCl (l) ⇌ 2Na (s) + Cl2(g)

If molten NaCl(l) is placed into the container and inert electrodes of C(s) are inserted, attached to the positive and negative terminals of a battery, an electrolytic reaction will occur.

Electrons from the negative terminal travel to the cathode and are used to reduce sodium ions into sodium atoms. The sodium will plate onto the cathode as it forms. The sodium ions are migrating towards the cathode.

Na+ + e− ⇌ Na(s)

The negative Chlorine ions migrate towards the anode and release electrons as they oxidize to form chlorine atoms. The chlorine atoms will combine together to form chlorine gas which will bubble away.

2Cl- ⇌ Cl2(g) + 2e-

Note that the site of oxidation is still the anode and the site of reduction is still the cathode, but the charges on these two electrodes are reversed. Anode is now positive charged and the cathode has a negative charged.

The conditions under which the electrolyte cell operates are very important. The substance that is the strongest reducing agent (the substance with the highest standard cell potential value in the table) will undergo oxidation. The substance that is the strongest oxidizing agent will be reduced. If an aqueous solution of sodium chloride were used in the above system, hydrogen would undergo reduction instead of sodium, because it is a stronger oxidizing agent that sodium.





During the discharge or deposition of ions at the electrode, there are factors that determine which of the ions that move to which electrode (anode or cathode). Before that, let’s look at electrochemical series of ions.

**ELECTROCHEMICAL SERIES**

Electrochemical series is the series of elements in their order of ***standard electrode potential.*** Standard electrode potential of an element is the potential difference between the element and one molar solution of its ion. It is measured in ***volt*** and it is denoted by ***E0***. It is the tendency of an ion to undergo reduction; hence it is also called ***standard reduction potential.*** Let us not forget, that reduction is gain of electrons.

Electrochemical series is also known as ***activity series.***

**Electrochemical series of cations and their standard electrode potential**



**Electrochemical series of anions**



This is a list of elements in order of their ability to be reduced.

For cations, the higher the element in the series, the less likely it is that this will gain electrons (that is be reduced).

For anions, the higher it is on the series, the less likely will it lose electrons (that is be oxidized)

The ions higher replace the ions lower in the series from their salts. For example:

Zinc replaces copper from its salts

Zn2+(aq) + CuSO4(aq) ZnSO4(aq) + Cu2+

And so on.

**PREFERENTIAL DISCHARGE OF IONS**

Preference simply means selection of an item instead of others.

Most electrolytes contain more than one cation and or more than on anion. This preferential discharge talks about the factors that govern which of the cations migrate to the cathode and which of the anode migrate to the anode.

1. ***The position of ions in the series***

The ion whose position is lower in the electrochemical series shows higher tendency to discharge at the electrodes than the ion higher in the series.

For the cations, those that are lower in the series have higher reduction potentials (reducing ability or ability to gain electrons) than those that are higher in the series.

For the anions, those are lower in the series have oxidizing ability (ability to lose electrons) than those that are higher in the series.

Example, the electrolysis of dilute sodium chloride, NaCl(aq) which contains Na+, H+, Cl- and OH-.

Note that H+ and OH- are from water.

H+ will discharge at the cathode in preference to Na+ because H+ is lower than Na+ in the electrochemical series. On the other hand, OH- will discharge in preference to Cl- because OH- is lower than Cl- in the series.

1. ***Concentration of ions in the electrolyte***

This factor is useful in concentrated electrolytes. If the electrolyte is concentrated, it means the ions produced by the electrolyte are more than the ions produced by water. This factor applicable for ***ANIONS*** and not for cations, because the cations involved mostly are very far from each other so that the difference of their reduction potential is large and cannot be overrode by the concentration of the higher cation. But for anions, the distance between anions involved is often close and so concentration can override the difference in the potential for oxidation.

For example: in the electrolysis of brine (concentrated sodium chloride), H+ still discharge at the cathode because the distance between Na+ and H+ is very far, while at the anode, Cl- will discharge in preference of OH- because they are very close to each other and concentration of Cl- can cancel the potential of OH-.

1. ***Nature of electrode***

The electrode used can also influence the ions that are discharged at the respective electrodes.

*Inert electrodes are the electrodes that do not take part in electrolysis. E.g. Pt, Cu and C (graphite).*

However, care is taken when using Pt and C. Chlorine gas attacks Pt and oxygen attacks graphite. Therefore, during electrolysis of electrolyte that will liberate Cl2(g) at the anode, Pt is not used as the anode. Also, graphite is not used as the anode if oxygen is will liberate at anode.

In the electrolysis of aqueous sodium chloride using platinum electrode, H+ is preferentially discharged. If mercury cathode is used, however, the mercury will tend to associate with the Na+ to form ***sodium amalgam, Na/Hg,*** so that the discharge of Na+ requires less energy than that of H+ and so occur as preference.

Na+(aq) + Hg(l) + e- Na/Hg(l)

Other electrodes may also influence the ionic discharge, because they possess characteristics similar to those of the ion in the electrolyte. Example, if a copper anode is used in the electrolysis of a solution of CuSO4, SO42- nor OH- will discharge. Instead, the copper atoms from the anode will go into solution as Cu2+ because those atoms will give up their electrons more readily than SO42- or OH-. This principle is used to purify copper metal.

**COMMON EXAMPLES OF ELECTROLYSIS**

1. ***Electrolysis of acidified water***

Acidified water is a dilute H2SO4. It is made by adding few drops of H2SO4 in H2O. In solution, the following dissociations take place:

H2SO4(aq) 2H+(aq) + SO4-(aq)

H2O(l)  H+ + OH-

Using platinum electrode, H+ will discharge at the cathode to form hydrogen gas (H+). That means, hydrogen is liberated at the cathode.

2H+ + 2e- H2(g)

OH- is less electronegative, hence discharges at the anode to form water and oxygen. That means, oxygen is liberated at the anode.

4OH-(aq) 2H2O(l) + O2(g) + 4e-

1. ***Electrolysis of brine (conc. NaCl)***

In brine, there is low concentration of H+ and OH- but high concentration of Na+ and Cl-. So, Cl- will preferentially discharge at the anode.

Because of the distance between Na+ and H+, Na+ ions which is far higher than H+ in the series still remains more electropositive. Hence, H+ would preferentially discharge at the cathode.

At the cathode:

2H+(aq) + 2e- H2(g)

At the anode:

2Cl-(aq) Cl2(g) + 2e-

**ELECTROLYSIS OF COPPER (II) TETRAOXOSULPHATE (VI) SOLUTION USING COPPER ELECTRODE**

This is used for purification of copper. The impure Cu electrode is used as the anode and the pure Cu electrode as the cathode.

In this case electrolyte remains the same while the anode (impure Cu) dissolves and dissociate into the solution.

Cu(s) Cu2+(aq) + 2e-

At the cathode, the Cu2+ is being attracted and deposited on the surface.

At the end of the experiment all the Cu in the anode are found to have transferred to the cathode leaving the impurities at the anode.



