**ELECTROCHEMISTRY**

This part of chemistry deals with how electricity can be gotten from chemicals or can be converted to chemical energy. It can also be defined as the relationship between electricity and chemistry.

**TERMS USED IN ELECTROCHEMISTRY**

**1. Electrolyte**: This is a substance that will conduct electricity either in aqueous or molten state and then decompose during the process. Examples of electrolytes include aqueous or molten solutions of acids, bases or salts.

There are two types of electrolytes which are:   
i. Strong electrolytes: These are electrolytes which can **ionize completely** when in aqueous form or in molten form.

E.g. Mineral acids (HCl, HNO3, H2SO4)

Caustic alkalis (NaOH, KOH) and

Salts (NaCl, K2SO4, NH4­Cl etc.)

The conductivity of a strong electrolyte decreases slightly with an increase in concentration.

ii. Weak Electrolytes: These are electrolytes that **ionize partially** in aqueous form or molten form.

E.g. Weak (Organic) acids (HCOOH, CH3COOH)

Weak bases (NH3) and water.

The conductivity of a weak electrolyte decreases greatly with an increase in concentration.

**NB**:

i. Generally, the conductivity of an electrolyte reduces with an increase in concentration.

Where Λ= conductivity

Where c = concentration

ii. The difference between complete ionization and incomplete ionization is that

a. **Complete ionization is irreversible** while **incomplete ionization is reversible**.

**2. Electrodes**: These are materials in the form of metals, wires or plates which help in conveying electrons or current in or out of an electrolyte. There are two types of electrodes namely:

a. Anode: **In electrolysis (an electrolytic cell), this is the positive electrode** but **in an electrochemical cell, this is the negative electrode**. At the **anode**, the process of **oxidation (electron loss)** takes place (in electrolysis).

The anode carries current into the electrolyte and carries electrons out of the electrolyte

b. Cathode: **In electrolysis (an electrolytic cell), this is the negative electrode** but **in an electrochemical cell, this is the positive electrode**. At the cathode, the process of reduction (electron gain) takes place (in electrolysis)

The cathode **carries current away from the electrolyte** and **carries electrons into the electrolyte**.

**ELECTROLYSIS**

This is a part of electrochemistry.

This can be defined as the decomposition of an electrolyte due to the passage of electric current through.

The power source of an electrolytic setup is a battery or a direct current source.

Electrolysis involves three stages namely:

1. Ionisation of an electrolyte and water (if in aqueous form) or the electrolyte alone (if in molten form)

E.g. Aqueous CuSO4 (CuSO4 and water will ionise since it is in aqueous form)

CuSO4 → Cu2+ (aq) + SO42-(aq) [Complete ionisation]

H2O H+ + OH- [Incomplete ionisation]

2. Migration of ions to the electrodes. When an electric current is passed an electrolyte, the electrolyte decomposes into positively and negatively charged ions. If the electrolyte is in aqueous state, water will also decompose into hydrogen ion (H+) and hydroxide ion (OH-).

The **positively charged ions migrate towards the cathode** which is the negative electrode (**Unlike charges attract**). The **positively charged ions** in electrolysis are therefore called **Cations (Cathode ions)**.

The **negatively charged ions migrate towards the anode** which is the positive electrode. These **negatively charged ions** are called **Anions (Anode ions)**.

3. Discharge of ions at the electrode: This discharge involves reduction and oxidation. When ions get to their respective electrodes, they struggle for preferential discharge.

**THE ELECTROCHEMICAL SERIES**

**CATIONS (POSITIVE IONS)**

K+ (Potassium ion)

Na+ (Sodium ion)

Ca2+ (Calcium ion)

Mg2+ (Magnesium ion)

Al3+ (Aluminium ion)

Zn2+ (Zinc ion)

Fe2+

Sn2+

Pb2+

H+

Cu2+

Hg+

Ag+

Au3+

**ANIONS (NEGATIVE IONS)**

OH-

I-

Br-

Cl -

NO3-

SO42-

F-

**FACTORS AFFECTING PREFERENTIAL DISCHARGE**

There are three major factors which affect preferential discharge namely:

1. Position of the ion in the electrochemical series.

For **cations**, **those which are down the series are usually discharged at the cathode in preference to those that are higher the series**. This is because cations which are lower the series are less electropositive (or more electronegative) than those which are higher the series and possess a greater tendency to gain electrons (reduction) since reduction occurs at the cathode.

For **anions**, **those which are higher the series are discharged at the anode in preference to those that are lower the series**. This is because anions which are higher the series are less electronegative (or more electropositive) than those which are lower the series and possess a greater tendency to lose s at the electrons (oxidation) since oxidation occurs at the anode.

2. Concentration: Generally ions which are more concentrated are discharged at the electrodes in preference to those which are less concentrated. However for concentration to be considered as a factor of ionic discharge during electrolysis, the number of ions between the two competing ions **must not exceed three**.

For example, in the electrolysis of a brine (a concentrated form of (NaCl), Cl- is deposited at the anode in preference to OH- because Cl- is more concentrated than OH- and the number of ions in the E.C.S is two which is less than three.

At the cathode, H+ is deposited in preference to Na+ even though is more concentrated. This is because the number of ions between them is more than three in the E.C.S.

3. Nature of the electrode used in the electrolysis process: Generally, electrodes which are used during electrolysis can either be active or inactive (inert).

Inert electrodes do not take part in the electrolytic processes. In other words, they do not determine the discharge of ions during electrolysis examples include carbon and platinum electrodes.

The active electrodes are those which to a large extent determine ionic discharge i.e. they participate in electrolytic processes. An example is the mercury electrode. For example, in an electrolytic process involving an electrolyte of sodium using mercury as the cathode, sodium will always be deposited on the cathode irrespective of every other factor. This is as a result of the affinity of mercury for sodium. Sodium therefore reacts with mercury to form a complex called sodium malgam.

**NB**:

1. Any metal above hydrogen on the activity series is an active electrode.

2. Any time any metal from the activity series is used as the anode, there will be no anodic reaction because the anode will melt into the electrolyte.

3. The charge of oxygen in electrolysis only is always -4.

4. Whenever OH- is deposited on the anode, the reaction is given as

4OH- →2H2O + O2 + 4e-

**FARADAY’S LAWS OF ELECTROLYSIS**

First Law: This law states that

The mass of a substance deposited at an electrode during electrolysis is directly proportional to the quantity of charge flowing through the electrolyte.

Q is the quantity of charge measured in coulombs (C)

But

Where I = Current [measured in amperes (A)]

Where t = Time [measured in seconds (s)]

But

Where M = Molar mass of the element

Where q = the charge of the element

Where F = Faradays constant [measured in farads (F)]

The letter **‘z’** is a constant called the **electrochemical equivalent (E.C.E)**

It can be defined as the mass of a substance deposited when one coulomb of electricity is passed through the electrolyte.

**NB**: One Farad = 96500 coulombs

1F = 96500C

Second Law: This state that

If the same quantity of electricity is passed through two or more different electrolytes, the relative number of moles of the element deposited on the electrode is inversely proportional to the ionic charge of the element deposited.

The letter **‘k’** is a constant.

For two cases,

But

Where m = given mass

Where M = Molar mass

**ELECTROCHEMICAL CELLS**

These are devices used for changing chemical energy into electrical energy.

There are two types of cells namely:

1. Primary cells: These are cells whose reactions (through which electric current is generated) are **irreversible**. They cannot be recharged after they have been used. They have **high resistances** and hence **generate low currents**. They are affected by local action and polarisation.

2. Secondary cells: These are also called **accumulators**. They are the opposite of primary cells.

An electrochemical cell consists of two electrodes of which each has its own electrolyte. The two electrodes are connected by a **salt bridge** or a **porous partition**.

One electrode with its electrolyte is called **a half-cell**. The electrode is an element (mostly metals although it may me non-metals) and the electrolyte is a salt of the element. The element is said to be in contact with its own ions.

A half-cell can be represented as

E(s)/Eq+ (aq) or

An electrode has a quantitative property called the **electrode potential**.

Electrode potential is a measure in volts of the tendency of an atom of an element of the electrode to undergo oxidation and reduction.

M(s) → Mn+ + ne-: Eᶿox

Mn+ + ne- → M: Eᶿred

Eᶿox and Eᶿred of an electrode have the same value but different signs (one is negative while the other is positive).

When all the concentrations of aqueous solutions are 1moldm-3, all gases taking part in the reactions are at 1atm and the temperature is 25⁰C (Room temp), the electrode potential is called the **standard electrode potential**.

The standard hydrogen electrode was assigned a standard electrode potential of 0.000Volts

EᶿH2=0.0000V

The standard electrode potentials of other elements can be determined using the standard hydrogen electrode as a reference.

The standard electrode potential of an element is the potential difference set up between a standard hydrogen electrode and a half-cell.

It is called the electromotive force (emf) when a standard hydrogen electrode is coupled to the electrode of the element.

**NB**:

1. A/An+ is represented as

A→An+ + ne- (oxidation [you don’t need to put this])

2. An+/A is represented as

An+ +ne- → A (reduction)

3. A/An+ // Bn+/B is represented as

A→An+ + ne- EᶿA(ox)

Bn+ +ne- → B

Eᶿcell = EᶿA + EᶿB

E.g. Zn/Zn2+ is represented as

Zn→Zn2+ + 2e-

When calculating the emf of a cell,

i. Write the anodic reaction (Oxidation)

ii. Write the cathode reaction (Reduction)

iii. Make electrons gain equal to electrons lost.

iv. Add the two electrode potentials i.e.

Eᶿcell = EᶿA + EᶿB

**If the emf** of a cell (after calculation) **is positive**, then the **reaction is spontaneous** and the **Gibb’s free energy is negative**.

**If the emf is negative**, **the reaction will not take place**.

The table below shows the standard potentials of elements.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Element | Half-cell reaction (Reduction) | Half-cell reaction (Oxidation) | Standard reduction potential | Standard oxidation potential | Reducing ability | Oxidising ability |
| K |  |  | -2.93 |  | Highest reducing ability (but **can be easily oxidised**) | Lowest oxidising ability |
| Na |  |  | -2.87 |  |  |  |
| Ca |  |  | -2.71 |  |  |  |
| Mg |  |  | -2.37 |  |  |  |
| Al |  |  | -1.67 |  |  |  |
| Zn |  |  | -0.76 |  |  |  |
| Fe |  |  | -0.44 |  |  |  |
| Sn |  |  | -0.14 |  |  |  |
| Pb |  |  | -0.13 |  |  |  |
| H |  |  | 0.00 |  |  |  |
| Cu |  |  | 0.34 |  |  |  |
| Hg |  |  | 0.79  0.85 |  |  |  |
| Ag |  |  | 0.80 |  |  |  |
| Au |  |  | 1.5 |  |  |  |
| OH |  |  | Not an element |  |  |  |
| I |  |  | 0.54 |  |  |  |
| Br |  |  | 1.09 |  |  |  |
| Cl |  |  | 1.36 |  |  |  |
| NO |  |  | Not an element |  |  |  |
| SO |  |  | Not an element |  |  |  |
| F |  |  | 2.87 |  | Lowest reducing ability | Highest oxidising ability |
|  |  |  |  |  |  |  |

**DEFECTS OF PRIMARY CELLS**

1. Local action: This is caused by the presence of impurities on the zinc plate electrode. The impurities on the electrode prevent the free flow of current. Local action can be prevented by **Amalgamation**. Amalgamation is the process of coating the zinc electrode with mercury. Local action can also be prevented by using a pure zinc electrode (which can be gotten from electrolytic process).

2. Polarisation: This is defined as the process whereby hydrogen bubbles produced at the zinc electrode prevent free flow of current. The hydrogen bubbles also increase the resistance of the electrode. The bubbles produce what is known as **Hydrogen Electrode**. These bubbles also create a back emf.

Polarisation can be prevented using chemical substances called **Depolarisers**.

**DIFFERENCE BETWEEN THE ELECTROLYTIC CELL AND THE ELECTROCHEMICAL CELL**

|  |  |
| --- | --- |
| Electrolytic cell | Electrochemical cell |
| Converts electrical energy to chemical energy | Converts chemical energy to electrical energy |
| Electrons are pushed by an outside force such as a battery | Electrons are generated by oxidation at the electrode (anode) |
| Cathode is negative electrode | Cathode is the positive electrode |
| Anode is the positive electrode | Anode is the negative electrode |
| Electrodes are in the same compartment | Electrodes are in separate compartments |
| Salt bridge is not needed | Salt bridge is needed |
| Only one electrolyte is used | Two electrolytes are used |
|  |  |
|  |  |
|  |  |