**Electrochemistry**

**Basics of Electrochemistry:** Aclear-cut concept of oxidation and reduction as well as redox reactions is required to understand the chapter. So it will be better to discuss these technical terms before the main chapter.

**Oxidation and Reduction**:

**Classically oxidation** means —

1. Addition of oxygen, or

For example —

1. Addition of any electronegative element, or

For example —

1. Removal of hydrogen, and

For example —

1. Removal of any electropositive element

For example —

In **modern terminology**, **oxidation** means —

1. Increase in oxidation number (), and

For example —

1. Loss of (i.e. release of) electron(s) (from atoms, molecules, cations or anions)

For example —

**Reduction is the opposite process of oxidation**. Thus, **classically reduction** means —

1. Removal of oxygen, or

For example —

1. Removal of any electronegative element, or

For example —

1. Addition of hydrogen, and

For example —

1. Addition of any electropositive element

For example —

In **modern terminology**, **reduction** means —

1. **Decrease in oxidation** number (), and

For example —

1. **Gain of electron**(s), (to atoms, molecules, cations or anions)

For example —

**REDOX Reactions**:

Chemical reactions in which oxidation (i.e., loss of electrons or increase in oxidation number) and reduction (i.e., gain of electrons or decrease in oxidation number) take place simultaneously are termed as the **redox reactions**. Thus, in redox reactions, one substance is **oxidised** and the other substance get **reduced** and hence oxidation and reduction proceed simultaneously. Redox reactions are also termed as the **oxidation-reduction** reactions.

A **redox** reaction is composed of **two reactions** —

1. The reaction representing the oxidation is called **oxidation half-reaction**, and
2. The reaction representing the reduction is called **reduction half-reaction**.

**For example**, considering the redox reaction involving the oxidation of oxalic acid by acidic permanganate solution —

 

Thus —

**Similarly**, the molecular equation representing the oxidation of by acidic potassium dichromate solution is —

The corresponding ionic equation is —

Now —

 

Thus —

**Oxidising Agent (Oxidant) and Reducing Agent (Reductant)**:

Oxidising agent is the species which —

1. Oxidises other species and itself reduced,
2. Gives up oxygen or any other electronegative element,
3. Accepts hydrogen or any other electropositive element,
4. Gains one or more electrons, *i.e*. oxidising agent acts as electron-acceptor, and
5. The oxidation number of the effective element decreases and thus, an oxidising agent gets reduced.

Reducing agent is the species which —

1. Reduces other species and itself oxidised,
2. Accepts oxygen or any other electronegative element,
3. Gives up (lose) hydrogen or any other electropositive element,
4. Loses one or more electrons, i.e. reducing agent acts as electron-donor, and
5. The oxidation number of the effective element increases and thus, reducing agent gets oxidised.

**For example**, in the reaction —

The corresponding ionic equation is —

Now —

 

In this reaction ions oxidise ions to molecules and are reduced to ions, since the oxidation number of - atom in ions is decreased from and that of ions is increased from . Thus, **on the basis of** **oxidation number concept**, ions act as the **oxidising agent** and ions act as the **reducing agent**.

**Similarly**, when gas is passed through solution, iodine () is liberated. In this reaction, oxidises and itself reduced to . Thus, () in the reduction product of . Thus, —

The two half-reactions involved are —

**Some common Oxidising agents and their Reduction Half-Reactions**:

Commonly used oxidising agents are —

1. Hydrogen peroxide (),
2. Ferric salts, for example, ferric chloride (),
3. Halogens (),
4. Potassium dichromate (),
5. Potassium chlorate (),
6. Potassium permanganate (),
7. Nitric acid (), etc.

The reduction half-reaction for these oxidising agents along with the products obtained on reaction with a reducing agent are shown below —

**[] Hydrogen Peroxide** (): Hydrogen peroxide oxidises many substances. Depending on the medium in which the oxidation takes place, it gets reduced to different substances. For example, —

[] ***In acidic medium***, is reduced to ()

[] ***In alkaline medium***, gets reduced to ions ()

**[] Ferric Salts** (**-** ): Ferric salts are good oxidising agents. Since, - ion reacts with a reducing agent (), it gets reduced to - ion. For example, —

The ionic equation representing the reduction of ion is —

**[] Halogens** (): All the halogens are good oxidising agents, and when they oxidise a certain substance, they themselves reduced to the halides (). Thus —

 **[] Potassium Dichromate** (): In acid medium (), acts as a strong oxidising agent and reduced to . Thus —

**[] Potassium Permanganate** (): Potassium permanganate acts as a strong oxidising agent in acidic (), neutral and alkaline medium.

[] ***In acidic medium***: In acidic solution (), () is reduced to ().

[] ***In neutral or weakly alkaline solution***: In neutral or weakly alkaline solution, () is reduced directly to (reduction product).

[] ***In strongly alkaline medium***: In strongly alkaline solution, () is first reduced to potassium manganate, () and then to insoluble .

**Some common Reducing agents and their Oxidation Half-Reactions**:

Commonly used reducing agents are —

1. Nitrous acid (),
2. Oxalic acid (),
3. Acidified solution of ferrous sulphate (),
4. Sodium thiosulphate (),
5. Stannous chloride (),
6. Hydrogen sulphide (),
7. Potassium iodide (),
8. Aqueous solution of or sulphurous acid (), etc.

The oxidation half-reaction for these reducing agents along with the products obtained on reaction with a oxidising agent are shown below —

**[] Nitrous Acid** (): Nitrous acid acts as a reducing agent towards strong oxidising agents like acidified solution of , acidified solution of , etc. For example, with oxidised to and is reduced to . Thus, acts as a reducing agent and behaves as an oxidising agent.

The corresponding half-reactions are —

**Oxidation half-reaction**:

**Reduction half-reaction**:

Overall **Redox reaction** (addition):

**[] Oxalic Acid** (): Oxalic acid or ion is oxidised to —

**[] Acidified Solution of Ferrous Sulphate** (): It ion is oxidised to —

**[] Sodium Thiosulphate** (): Sodium thiosulphate or ion may be oxidised to various species as shown below —

() Thiosulphate ion, is oxidised to ion —

() Thiosulphate ion, is oxidised to dithionate ion, ion —

() Thiosulphate ion, may be oxidised to tetrathionate ion, ion

**[] Stannous Chloride** (): It is oxidised to —

**[] Hydrogen Sulphide** (): It is oxidised to sulphur —

**[] Aqueous Solution of or Sulphurous Acid** (): It is oxidised to as shown below —

() Oxidation of to —

() Oxidation of to —

**[] Potassium Iodide** (): Nature of oxidised product of depends on reaction medium:

() Acidified solution of oxidation to iodine () —

() An alkaline solution of is oxidised to potassium iodate () —

**[] Hydrogen Peroxide** (): Both in acidic and basic medium, gets oxidised to oxygen () —

**Question (1)**: Which of the following reactions is / are redox reactions? Give reason for your answer

[]

[]

[]

[]

[]

**Answer**: In equation (), the oxidation number of decreases from ; while that of iodine increases from . Thus, it is a redox reaction. Similarly —

In equation (), since the oxidation number of increases from and decreases from , it is also a redox reaction.

In the other reactions, the oxidation number of any elements does not undergo any change and hence these are not redox reactions.

**Question (3)**: Select oxidising and reducing agents in the following redox reaction and split the reaction into two half-reactions.

**Answer**: The given equation can also be represented as —

 

Thus, it is evident that in the reaction is the reducing agent at it is oxidised to . Similarly, is the oxidising agent at it is reduced to .

The corresponding half-reactions are —

**Oxidation half-reaction**:

**Reduction half-reaction**:

 //

**Electrolysis and Electrolytic conduction**:

In electrolytic conduction, charge is carried by ions of the electrolyte either in its molten stage or in its aqueous solution.

The principles of electrolytic conduction can be well explained by considering an **electrolytic** **cell** as shown in the figure given below for the electrolysis of .



**Working of an Electrolytic Cell**: The electrons are received from the end of the external battery by the electrode (**cathode**). These electrons are used up in the **reduction** reaction at the cathode. The numbers of electrons received at the electrode (terminal) are given back to the end of the external battery from the electrode (anode) of the cell where electrons are released as a result of oxidation reaction. Within the cell, current is carried by the **movements of ions**: **cations** towards the  **electrode** (cathode) and **anions** towards the  **electrode** (anode).

**Factors Affecting Electrolytic Conduction**:

The movement of ions of an electrolyte in an electrolytic cell to the oppositely charged electrodes is known as the electrolytic conduction. Electrolytic conduction depends on the mobility of ions and anything that inhibits the motion of ions causes resistance to current flow. Factors that influence the electrolytic conductivity of solutions of electrolytes include —

1. Interionic attraction,
2. Solvation of ions, and
3. Viscosity of the solvent.

All these factors depend on the attraction of solute-solute, solute-solvent and solvent-solvent during electrolysis. Further, the average **kinetic energy of the solute ions increases as the temperature is raised** and, therefore, the resistance of the electrolytic conductors generally decreases (*i.e*. conduction increases) as the temperature is raised.

Thus, the electrolysis of molten salts produces ions which are characteristic of the salt. When certain aqueous solutions are electrolysed, water is, however, involved in the electrode reactions rather than the ions derived from the solute. Hence, the current-carrying ions are not necessarily discharged at the electrodes.

The cathodic and anodic reactions involved in the electrolysis of aqueous solutions of some salts are given below —

**Quantitative Aspects of Faraday’s Law of Electrolysis**:

The **quantitative** relationships between **electricity** and the **chemical** **change** were first described by Michael Faraday. These are —

1. *The mass of a chemical substance involved (deposited) at an electrode is directly proportional to the amount of current passed through the cell.*
2. *The mass of different substances produced by a given amount of current are proportional to the equivalent masses of the substances*.

These two laws have been shown to hold very rigidly provided the passage of electricity takes place entirely by electrolytic conduction. Both the laws are applicable for —

1. Molten electrolytes as well as solutions of electrolytes, and
2. Independent of temperature, pressure or the nature of the solvent.

**Mathematically**, **Faraday’s law** may be represented as —

Here, ‘’ is the mass of the species having molar mass deposited or liberated in an electrode on passing a current ‘’ for time ‘’ and is the stoichiometric number of electrons involved in the reduction or oxidation reaction involved in the electrode.

**Faraday’s First Law of Electrolysis**:

Faraday’s first law of electrolysis states that ***the mass of the substance liberated or deposited at the electrode as a result of electrolysis is directly proportional to the quantity of the electricity passed through the electrolyte***.

If is the mass of the substance liberated or deposited at the electrode and is the quantity of electricity (in ***coulombs***) passed through the electrolyte, then —

 But,

Where: Current in amperes and, time in seconds

Where: Constant, called the **Electrochemical Equivalent ()** of the substance

If and , then

Thus, ***Electrochemical Equivalent*** of a substance is defined as the mass of the substance liberated or deposited at an electrode during electrolysis when (ampere) of current is passed through the electrolyte for second; ***or*** it is the mass of the substance liberated or deposited by the passage of of electricity.

**Note**: ***Coulomb is a unit of electricity***, and

 ***A Faraday* () *is a bigger unit of electricity***, and

**Relation between Chemical Equivalent () and Electrochemical Equivalent ()**:

We know that one electron is consumed to discharge unit charge

Therefore, one mole electrons () are consumed to discharge one mole charges

Now, charge on - electron

Therefore, charge of one mole electrons

Thus, of charge is consumed to discharge one mole charges

 (One Faraday) of charge is consumed to discharge or liberate of substance

Thus, the Faraday's 1st law is quite useful in determining the electrochemical equivalent of the various substances. For example, when of electricity is passed through of - is deposited,

The electrochemical equivalent of any substance can be easily calculated if we know the mass of the substance liberated or deposited when a known quantity of electricity () is passed through the electrolyte. Because —

**Problem** (): Calculate the Electrochemical equivalent of . ()

**Solution**: Electrochemical equivalent of zinc is the mass of zinc deposited when of electricity is passed through the electrolyte. Since,

 Coulombs of electricity produces

Again, atomic mass of and valency of

Thus, of electricity produces

Thus, the electrochemical equivalent of

**Problem** (): Find the mass of copper deposited from copper sulphate solution by a current of flowing for one hour (Atomic mass of )

**Solution**: Given,

Since, the atomic mass of , and valency of

We know that, of electricity can produce of the ions

Thus, the mass of - deposited //

**Problem** (): How many coulombs are required for the following reductions?

() , () , ()

**Solution**: () The electrode reaction is

 1 3

Thus, the reduction of ions to requires of electrons

 () The electrode reaction is

 1 2

Thus, the reduction of ions to requires of electrons

() The electrode reaction is

 1 5

Thus, the reduction of ions to requires of electrons

Charge on //

**Problem** (): How many electrons are required for the following oxidations?

() , ()

**Solution**: () The electrode reaction is

 2 4

Thus, the oxidation of ions to requires of electrons

Charge on

() The electrode reaction is

 1 1

Thus, the oxidation of ions to requires of electrons

Charge on //

**Problem** (): Silver is electrodeposited on a metallic vessel of total surface area by passing a current of . Calculate the thickness of - deposited. (Given density of , and the atomic mass of ).

**Solution**: Electroplating of silver over a metallic surface can be represented by the electrode reaction —

 ()

Total electrical charge used

 Total - deposited

Thus, the volume of - deposited

Let, the thickness of - layer deposited

**Problem** (): of copper was deposited by a current of . What is the electrochemical equivalent of copper?

**Solution**: Here,

 Quantity of electricity supplied

Again, amount of - deposited

 The Electrochemical equivalent of //

**Problem** (): When a current of strength is passed through a salt of a metal for , of metal was deposited. Find the valency of the metal ().

**Solution**: Here,

 Quantity of electricity supplied

Again, amount of - deposited

Thus, of electricity deposit metal

 The equivalent weight of metal

But, the atomic mass of the metal

**Problem** (): How many atoms of will be deposited from fused by a current of passed for ?

**Solution**: The electrolysis of fused is

The corresponding electrode reaction for the deposition of - is —

 2 1

Thus, the reduction of ions to requires of electrons of charge

Here,

 Quantity of electricity passed

**Problem** (): How much electricity in amperes is required to liberate gas at the rate of ?

**Solution**: The equivalent mass of

 Since,

Let, the electricity required in ampere

Thus, of gas is liberated when electricity is

 of gas is liberated when electricity is

From equation () and (), we have —

Thus, the quantity of electricity required in ampere is

**Problem** (): If a current of flows through a metallic wire for , then how many electrons flow through the wire?

**Solution**: We know that current in amperes time in seconds No. of Coulombs

Now, () means number of electrons

**Problem** (): of was electrolyzed with a current of for . What is the normality of the remaining solution?

**Solution**: Current () , time ()

Thus, we say that of is deposited or lost from the solution

**Problem** (): How much tine is required to pass of electricity through an electrolyte if the current strength is ?

**Solution**:

**Problem** (): A current of passes through the solution of for and deposits of - metal at the cathode. What is the equivalent mass of - metal?

**Solution**:

**Problem** (): How many moles of aluminium can be produced by the electrolysis of molten alumina with a current of ?

**Solution**: - moles

**Problem** (): A current of is passed through acidified water for . Calculate the volume of which will be liberated at ?

**Solution**:

**Problem** (): Calculate the charge on one electron, given the value of faraday as .

**Solution**:

**Faraday’s Second Law of Electrolysis**:

It is the extension of ***Faraday’s first law*** of electrolysis.

When the same quantity of electricity is passed through different electrolytes connected in ***series***, then the mass of the different substances deposited or liberated at the electrodes are directly proportional to their equivalent masses.

Considering three voltameters containing the solution of and acidulated water, which are connected in series and the same amount of current be passed through them for a given time.

If ‘’ is the charge passed through these electrolytes, then according to Faraday’s 2nd law of electrolysis, we have —

Taking the ratio of ), we get —

Where mass of the substance deposited or liberated

 Electro chemical equivalent of the substance, and

 Equivalent mass of the substance

According to the statement of Faraday’s second law of electrolysis —

We know that the equivalent mass of hydrogen is , that of . This means that the quantity of electricity which produces of the element is

And,

Thus, this law (Faraday’s 2nd law of electrolysis) is quite useful I the determination of equivalent masses of the element (substances).

***Another Important Relation*** —

**Problem** (): When an electric current was passed simultaneously through acidulated water and copper sulphate solution, weight of hydrogen and copper liberated are respectively. Calculate the equivalent mass of copper.

**Solution**: Given that —

Mass of hydrogen liberated , and

Mass of copper liberated

Applying the Faraday’s 2nd law of electrolysis —

**Problem** (): The same current was passed through acidulated water and solution of copper sulphate. It liberated measured at and deposited . Calculate the equivalent weight of copper, that of hydrogen being 1.

**Solution**: Given that —

Volume of hydrogen liberated at , and

Mass of copper deposited

We know that weighs

Now, equivalent mass of hydrogen; equivalent mass of copper

Applying the Faraday’s 2nd law of electrolysis —

**Problem** (): The density of . Find out the number of coulombs needed to plate an area to a thickness of , using solution as electrolyte ()

**Solution**: Density of

Volume of needed for plating

 The mass of needed for deposition

Now, we know that is deposited by

Thus, is deposited when electricity

 To deposit electricity required

**Problem** (): Calculate the volume (at NTP) of hydrogen which will be liberated when a current of is passed for through a metallic salt solution and the cathode was found to have gained in weight by . What is the equivalent weight of the metal?

**Solution**: Here,

 Quantity of electricity,

Thus, of electricity increases the mass of cathode

 Equivalent weight of metal

Again —

Since, hydrogen

**Problem** (): A current of is passed through metallic wire. What is the number of electrons passing per second through a point on a wire?

**Solution**:

[***Hints***: of electricity means electrons]

**Problem** (): An electric current is passed between - electrodes through solution of , and dilute . The solutions are being placed in series. If of hydrogen is evolved by this current in the third cell, calculate: () the mass of deposited in the 1st & 2nd cells, and () the volume of hydrogen measured in which is liberated from the 3rd cell.

**Solution**: Ans.

**Problem** (): The same current was passed successively through the solution of zinc sulphate, nickel ammonium sulphate (rendered alkaline with ammonia). The weight of deposited in a certain time were found to be respectively. Given that the equivalent weight of is , calculate that of .

**Solution**: Ans. 29.37

**Problem** (): How many grams of chlorine can be produced by the hydrolysis of molten with current flowing for (molecular weight of chlorine ).

**Solution**: Ans.

**Problem** (): A , incandescent lamp is connected in series with an electrolytic cell containing cadmium sulphate solution. What weight of cadmium will be deposited by the current flowing for ? (Atomic weight of )

**Solution**: Ans.

[***Hints***: Watt = Voltampere, ]

**Problem** (): of was deposited by a current of . What is the electro chemical equivalent of copper?

**Solution**: Ans.

**Electrochemical Cells:**

An electrochemical cell is an instrument or apparatus whereby chemical energy due to reactions converted to electrical energy and *vice-versa*. It consists of two electrodes, or metallic conductors, in contact with an electrolyte, an ionic conductor (which may be a solution, a liquid or solid). The basic apparatus of an electrochemical cell is as shown in the figure () and ().

An electrode and its electrolyte comprise an electrode compartment. The two electrodes may share the same compartment (*i.e*. same electrolyte). If the electrolytes are different, the two compartments may be joined by a salt bridge, which is a concentrated electrolyte solution in agar jelly that completes the electrical circuit and enables the cell to function.

Electrochemical Cells basically are of two types —

1. Galvanic Cells and
2. Electrolytic Cells

**Electrolytic Cells**:

Electrolytic cells are those electrochemical cells in which ***non-spontaneous chemical reactions*** are made to occur by continuous supply of electrical energy. In other words, ***electrolytic cells are the devices in which electrical energy is converted into chemical energy***.

Considering the electrolytic cell involving the electrolysis of molten using - electrodes as shown in the figure given below.



One of the electrodes is connected to the terminal of the battery and is called ***cathode***. The other electrode is connected to the terminal of the battery and is called ***anode***. The flow of electrons is from the terminal of the battery to the cathode and on the other side from anode to terminal of the battery.

Within the solution the electricity is carried out by the movement of ions. Cations are discharged at cathode and anions are discharged at the anode. Thus, it is evident that the process is non-spontaneous reaction is forced to take place by the application of electricity from an external source, like battery.

Various reactions that occur can be represented as —

**At anode**: Here, - passes into solution as, - ions, because of high electrolytic pressure

**At cathode**: Here, - ions gained the electrons and converted to metallic

So, the net chemical reaction is —

From the electrode reactions, it is evident that electrons are released at the anode and are consumed at the cathode. They travel through the external circuit from anode to cathode.

Thus, in all electrolytic cells anode is the electrode (involves oxidation) and cathode is the electrode (involves reduction).

**Galvanic Cells**:

A galvanic cell is an ***electrochemical cell*** that produces electricity as a result of ***spontaneous*** chemical reaction occurring inside it. Thus, galvanic cell is a device in which the free energy of a physical or chemical process is ***converted*** to ***electrical energy***.

Thus, a galvanic cell consisting of two electrodes dipped into an electrolyte or two electrolyte solutions, which, when electrodes are connected by some metallic conductor outside the electrolyte, produces an electric current in the external circuit. **Daniell Cell**, **Zinc-Acid Cell**, *etc*. are the examples of galvanic cells (as shown below in the figure).



**Danilel Cell**: It is a Cell, and can be represented as —

The cell consist of a copper vessel in which a concentrated solution of is taken. The - vessel itself acts as one of the electrode. A porous pot (**salt bridge**) is placed in - vessel and the porous pot contains a dilute solution of in which a - rod is dipped, which acts as another electrode.

When the two electrodes are joined with the help of a - wire (or any metallic conductor) a current begins to flow through the outer circuit. Various reactions that occur can be represented as:

**At anode**: Here, - passes into solution as - ions, because of high electrolytic pressure

**At cathode**: Here, - ions gained the electrons and converted to metallic

So, the net chemical reaction is —

Thus, in the Daniell cell oxidation occurs at - electrode (**anode**) and reduction occurs at the - electrode (**cathode**), and the overall cell reaction is represented by the redox reaction ().

**Zinc-Acid Cell**:

It is also a simple galvanic cell. It contains plates dipped in dilute . These plates’ acts as the electrodes and when these are connected with help of an external metallic conductor, the flow of current takes place in the external circuit from - plate (**anode**) to - plate (**cathode**). The reactions taking place are —

So, the net chemical reaction is —

Thus, in the ***zinc-acid*** cell oxidation occurs at - electrode (**anode**) and reduction occurs at the - electrode (**cathode**), and the overall cell reaction is represented by the redox reaction ().

**Copper-Silver Cell**:

It is also a useful simple galvanic cell. It consists - rod dipped into a solution of and - rod into a solution of . These rods acts as the electrodes and when these are connected with help of an external metallic conductor and the solutions are connected by a salt bridge containing , the flow of current takes place in the external circuit from - plate (**anode**) to - plate (**cathode**), which can be detected by using a voltmeter. The reactions taking place are —

So, the net chemical reaction is —

Thus, in the ***copper-silver*** cell oxidation occurs at - electrode (**anode**) and reduction occurs at the - electrode (**cathode**), and the overall cell reaction is represented by the redox reaction ().

**Working of a Galvanic Cell**:

When - rod is dipped in a solution of , the following reaction occurs —

Thus, metallic is oxidised to , while is to metallic . It can also be represented as —

The reaction proceeds ***spontaneously*** in the forward direction, governed by the principle of chemical equilibrium. The free energy so released would normally appear as heat energy. If two half reactions, *viz*. —

are carried out in two different compartments and the electrons are allowed to flow through an external circuit — we can convert at least a part of this **free energy** into **electrical energy**.

The **direction of flow of electrons** (through external circuit) in such a cell is determined by the relative “**potential**” of one electrode with respect to the other. When the potential of the two electrodes become equal, the ***free energy difference is zero*** and there will be no passage of current.

**Difference between Galvanic Cells & Electrolytic Cells**:

Various differences between Galvanic & Electrolytic Cells are —

|  |  |
| --- | --- |
| **Electrolytic Cells** | **Galvanic Cells** |
| () It converts electrical energy into electrical energy to bring about a redox reaction.() The redox reaction taking place in it is non-spontaneous. It occurs on the supply of electricity and stops when supply of electricity is stopped.() Two electrodes are dipped into the same electrolyte.() Two electrodes are not separated by a salt bridge or porous pot.() Cathode is the electrode and anode is the electrode. | () It converts chemical energy of the reaction into electrical energy and is thus, a source of electricity.() The redox reaction taking place in it is spontaneous. () Two half-cells may have different electrolytes or the same electrolyte at different conc. (conc. cells).() Two electrodes are separated by a salt bridge or a porous pot.() Anode is the electrode and cathode is the electrode. |

**Half Reactions**:

Any redox reaction may be expressed in terms of ***two half-reactions*** — showing the loss (oxidation) and gain (reduction) of electrons. ***For example***, in ***Daniell cell***, the reduction of - ions by can be expressed as the **sum** of the following two half-reactions —

**In common practice (- system) to write all the half reactions as reduction and the overall reaction is the difference of the two** —

The reduced and oxidised substance in a half-reaction from a ***redox couple***, denoted by the notation:

***For example***, redox couple for the ***reduction half-reactions*** () and () is written as —

In general, we write a couple as , and the corresponding redox half-reaction as —

**Important**: It is useful to express the composition of an **electrode compartment** in terms of the reaction quotient, “” for the half reaction. This **quotient** is **defined** as like as the reaction quotient for the overall reaction (*i.e*. ***law of mass action***), but the **electrons** are **ignored**. ***For example***, for the half reactions involved in ***Daniell Cell***,

[Since, **activities of solids** are **unity**, ]

**Non-Redox Reactions**:

The overall reaction may not be a redox reaction though it is expressed in terms of two half reactions. ***For example***, —

[] Expansion of a gas, is **not a redox reaction** but, it can be expressed as the difference of two reduction reaction as —

The two **couples** in this case are both .

[] Another important example of an overall reaction that can be expressed as the difference of two half-reactions, but which is **not** itself a **redox reaction**, is the process of dissolving

**Problem ()**: Express the dissolution of in water as the difference of two redox half-reactions.

**Method**: First, write the overall chemical equation, then select one of the reactants and write a half-reaction, in which it is reduced to one of the products. Next, subtract that half reaction from the overall reaction to identify the 2nd half-reaction. Finally, write the 2nd half-reaction as the reduction half-reaction.

**Solution**: The chemical equation for the overall reaction is —

We select as one half-reaction, the reduction of [more precisely the reduction of the ] —

Subtraction of this equation from the overall reaction leaves —

This rearranges to —

Thus, for the dissolution of in water, the two half-redox reactions are —

And, the overall reaction is —

**Problem ()**: Express the formation of water from in **acidic solution** (a **true redox-reaction**) as the difference of two redox half-reactions.

**Solution**: Overall reaction is —

The reduction half-reactions are —

Difference of () and () results the overall reaction (). //

**Reactions at Electrodes**:

In an electrochemical cell two reduction and oxidation process responsible for the overall reaction, are separated in space: One half-reaction takes place in one electrode compartment and the other takes place in the other compartment. As the reaction proceeds, the electrons released in the half-reaction —

in one compartment travel through the external circuit and re-enter the cell through the other electrode. There, they are used to reduce the oxidized member of the couple in that compartment —

The electrode at which **oxidation occurs is called the anode**; the electrode at which **reduction occurs is called the cathode**. Thus —

 Anode reaction (Oxidation):

 Cathode reaction (Reduction): //

**Types of Electrodes (-types)**:

[] **Metal/ Metal- ion Electrodes**: It consists of a metal in contact with a solution of its salt, such as in contact with an aqueous solution of . These electrodes are denoted by —

**Half-cell reaction is**:

**For example**:

[**Note**: Electrode description runs in the order , which is opposite to the order in which the couple is written]

[] **Gas Electrodes**: Here a gas is in equilibrium with a solution of its ions in presence of an inert metal, usually ‘’ which acts as a **source** or **sink** of electrons, but takes no other part in the reaction other than acting as a catalyst. ***For example***, - electrode —

The - electrode (like any other electrode) may be **either** a **cathode** or an **anode**, **depending** on the **other electrode** in the cell and the spontaneous direction of the overall reaction. The reaction at the electrode when it is acting as a cathode is —

Here, ‘’ is the fugacity, which may be replaced by the pressure ‘’.

[] **Metal/ Insoluble- Salt Electrodes**: It consists of a metal , covered by a porous layer of insoluble salt with the whole immersed in a solution containing - ions. The electrode is denoted by

For example, electrode,

The reduction half-reaction for the electrode is typically —

For example, the half-reaction for the electrode —

**Other examples are**—

() **Lead-lead sulphate electrode of the Lead-Acid battery** —

The reduction half-reaction for this half-cell is —

() **Calomel Electrode** —

The reduction half-reaction for the calomel electrode is —

[] **Redox Electrodes or Oxidation-Reduction Electrode**: Here a species exists in solution in two oxidation states. The equation is —

A redox electrode is denoted by

Here, ‘’ is an **inert metallic conductor** that makes electrical contact with the solution. An example is —

For which the reduction half reaction is —

**Liquid Junction Potentials () or Diffusion Potentials**:

When two different electrolytes in a cell are in contact, as in Daniell cell or two salt solutions of different concentrations (for example, chemical or concentration cells with transference) are in contact in a cell, there generates an additional potential at the junction i.e. interface of two solutions, because of diffusion of ions from concentrated solution to the dilute solution, what we call **Liquid-Junction potentials**. The liquid-junction potential at the boundary is the maximum because of the unequal rate of diffusion (*i.e*. mobilities of ions) of each ion through the interface of the two electrolytes. Thus, “***The potential that is developed at the junction of two solutions because of difference in speeds of ions moving across the boundary is known as liquid-junction potential***”.

The development of , the liquid-junction potential can be well explained by the formation of an **Electrical Double Layer** at the liquid junction as —

In the case, when the mobility of ions is more as compared to ions, the ions from concentrated solution will diffuse more rapidly to the dilute solution and so the dilute solution will become charged as compared to concentrated solution. Reversely, if the speed of ions is more than the speed of ions, the dilute solution will become charged as compared to concentrated solution. Thus, in both case, **an electrical double layer** is setup at the junction of two liquids *i.e*. an additional electric field is produced. The liquid-junction potential persists till the concentration of both the solution (i.e. concentrated & dilute) become equal.

The following **generalizations** can be made from the above discussion —

1. The is because of the difference in mobility of ions of the electrolyte,
2. The magnitude of depends on the relative speed of ions, and
3. No will be developed if both the ions move with the same speed.

**Derivation of Formula for Liquid Junction Potential ()**:

Let us consider the solution of , a univalent electrolyte —

When of electricity is passed through the cell ions migrates from left to right and ions migrates from right to left (this is in accordance with usual convention that the left hand electrode is a source of electrons, *i.e*. oxidation occurs).

If we now assume that transference numbers are not dependent on concentration, then the free energy change in the above process can be calculated as —

The free energy change for ions in the left compartment is —

Similarly, the free energy change for ions in the right compartment is —

Hence, the net change in free energy is —

But,

So, for

Comparing equation () and (), we have —

Since,

Equation () is an expression for the liquid-junction potential of the cell. It can also be written as —

This equation shows that the direction of liquid-junction potential **depends** upon the **relative** **values** of the **transference numbers** of anions () and cations (). //

**Elimination of Liquid Junction Potentials**:

Since, the liquid junction potential causes interference in the measurement of exact potential difference of the cell, so it is desirable to eliminate it if possible or to minimise it. It is done either by —

1. Introducing salt bridge or
2. By the addition of indifferent electrolytes.

**Notation of Cells**:

Following notations are usually adopted for the different cells —

[] **Simple Galvanic Cells, without Liquid-Junction Potential**:

 For such cells the phase boundaries are denoted by a **vertical bar**.

 For example,

[] **Cells with Liquid-Junction Potential**:

Here, the liquid-Junction potential is denoted by “” between the interface.

For example, ***Daniell Cell***,

[] **Cells without Liquid-Junction Potential**:

Here, the liquid-Junction potential is eliminated by introducing **salt bridge**, which is represented by a **double vertical line**.

For example, ***Daniell Cell***,

**Very Important**: An **Electrolyte concentrated cell** in which the **liquid-Junction potential** is assumed to be **eliminated** is denoted as —

**The Cell Reaction**:

The cell reaction is the reaction in the cell written on the assumption that the **right hand electrode is the cathode**, and hence that the spontaneous reaction is one in which **reduction is taking place in the right hand** compartment.

To **write** the **cell reaction** corresponding to the **cell diagram**, we first write the right-hand half reaction as a **reduction** (because, we have assumed that to be **spontaneous**). Then, we **subtract** from it the **left-hand reduction half reaction**. Thus, in the cell —

The two electrodes and their reduction half-reactions are —

**Right** (**Cathode**):

**Left** (**Anode**):

**Overall** ():

**The Cell Potential/ emf of Cell**:

In a cell, in which the overall cell reaction has **not** reached chemical **equilibrium** can do **electrical work** as the reaction drives electrons through an external circuit. The work () that a given transfer of electrons can accomplish depends on the **potential difference**, between the two electrodes, and is given by ***Ohm’s law***, . This **potential difference** is called the **cell potential** and is measured in ***volts*** [].

The cell potential *i.e*. **electromotive force** (***emf***) , is **defined** as ***the potential difference between its terminals when the resistance, of the load attached to the terminals goes to infinity and hence current to zero***. The ***emf*** is thus, ***the open circuit potential difference between the terminals***.

The **maximum electrical work** that a system (the cell) can do is given by its , the ***Gibbs free energy value***, which is for spontaneous process, at constant temperature and pressure.

 Thus,

This equation relates the electrical work to , so to measure , we must ensure that the cell is () **operating reversibly** at a () specific constant **composition**. Both these conditions are achieved by measuring the **cell potential**, when it is balanced by an exactly opposing source of potential, so that the cell reaction occurs reversibly and the composition is constant. This resulting potential difference is called the **zero-current** cell potential, or the ***emf*** of the cell. **~~//~~**

**Relation between the emf of Cell () and the Gibbs free energy ()**:

**Or see below (Best)**

The relation between the reaction ***Gibbs free energy*** () and **zero-current cell potential** () is given by —

Here, number of electrons transferred, and

 The **Faraday’s** constant

Thus, the **decrease** in the **electrical energy** in a reversible cell is equal to the decrease in **Gibbs free energy** (shown by **Gibb**s in 1875 & **Helmholtz** in 1882). Hence —

Moreover, according to ***Gibbs-Helmholtz*** equation —

Comparing equation () and (), we have —

From equation (), it is quite clear that whether electrical energy () produced is equal to, less than or greater than the enthalpy change (), depends upon the sign of , *i.e*. the temperature coefficient of the ***emf***. Thus —

[] If , then —

 The electrical energy is equal to the change in enthalpy. So, there will be no heat changes when the cell works.

[] If  **quantity**, then —

 The electrical energy produced is less than the enthalpy change. The additional energy in such a case is absorbed from the surroundings.

[] If  **quantity**, then —

 The electrical energy produced is less than the heat of reaction at constant pressure. The difference of energy in such a case is lost as heat to the surroundings.

[] At absolute zero (), equation (3) becomes —

 Thus, at absolute zero, the decrease in enthalpy will be equal to electrical energy obtainable from the cell.

Making the use of equation (), we can find the value of if we know the value of and using equation (), it is possible to calculate the value of , if we know the value of and thus, by knowing the values of , the value of (**entropy change**) accompanying a reaction can be calculated by using —

***OR*** **Thermodynamic Functions from Cell Potential Measurement**:

**Determination of** :

The standard cell potential is related to the standard reaction Gibbs free energy by —

Therefore, by measuring ‘’, we can obtain this important thermodynamic quantity. Its value can than can be used to calculate the of formation of ions using the convention that — if is , the process is spontaneous.

For example, for the cell —

The cell reaction is —

Therefore, with , we find —

The temperature coefficient of the cell potential gives the entropy of the cell reaction. This conclusion follows from the thermodynamic relation —

Combination of equation () and (), yields —

Hence, we have an **electrochemical technique** for obtaining **standard reaction entropies** () and through them the entropies of ions in solution.

Finally, we can evaluate the value of ‘’, the **standard reaction enthalpy** from the value of from the relation —

Thus, electrical measurement () can be used to calculate all the thermodynamic properties. //

**Problem (1)**: The standard cell potential of was measured over a range of temperatures and the data were fitted to the following polynomials —

Evaluate the standard reaction Gibbs energy, enthalpy, and entropy at .

[**Method**: The standard Gibbs free energy of reaction is obtained by using , after evaluating . The standard entropy of reaction is obtained by using equation —

This involves differentiating the polynomial with respect to ‘’ and then setting . The standard reaction enthalpy is obtained by combining the values of the standard Gibbs energy and entropy.]

**Solution**: At

Hence, from

The temperature coefficient of the cell is obtained by differentiating the polynomial —

with respect to temperature (), and thus —

At

Therefore, from the equation —

The standard reaction entropy is —

Finally, the standard enthalpy of the reaction is —

**Problem (2)**: Given that the standard potentials of the couples are respectively, evaluate .

**Solution**: The electrode reaction for —

The couple

Therefore, standard Gibbs free energy,

Similarly, for the couple

Therefore, standard Gibbs free energy,

And, for the couple

Since, , therefore, the standard Gibbs free energy for the reaction () is —

Since, for the reaction (),

**Problem (3)**: Calculate the standard potential of couple from the values of couples.

**Solution**: Exactly, same as problem () and the answer is //

**Important Conclusions Regarding Galvanic Cells**:

We know that a galvanic cell consist of **two electrodes**, one acts as the **anode** (left electrode) where **oxidation** takes place and, another acts as the **cathode** (right electrode) where **reduction** takes place. Now —

[] The value of standard reduction potential of a given electrode may be either , depending on whether the given electrode acts as terminal (**anode**) or as a terminal (**cathode**) of the galvanic cell which is obtained by coupling the given electrode with a SHE (also called NHE, normal Hydrogen Electrode). When the given electrode acts as a terminal (anode), the electrode has a value for its standard electrode potential. On the other hand, when the given electrode acts as a terminal, the electrode has a value for its standard electrode potential. **This conclusion** can also be stated in the following words — if an electrode which has  **value** of its standard reduction electrode potential is coupled with a NHE to get the galvanic cell, this electrode will act as a terminal (**anode**) of the resulted cell. On the other hand, if an electrode which has  **value** of its standard reduction electrode potential is coupled with a NHE to get the galvanic cell; this electrode will act as a terminal (**cathode**) of the resulted cell.

[] If two electrodes coupled together to get a galvanic cell, then the electrode having less value of its standard reduction electrode potential will constitute the terminal (*i.e.* anode or left hand electrode) of the resulted cell and the electrode having more value of its standard reduction electrode potential will constitute the terminal (*i.e.* cathode or right hand electrode) of the cell.

**Problem** (): Represent the cell obtained by coupling the following pairs of metal-metal electrode () () and () . The values of standard reduction potentials of these electrodes are: , , and .

**Solution**: For the pairs of electrodes — ()

Given that the standard reduction potentials of —

Therefore, electrode will constitute the cathode (right-hand electrode) and will act as anode (left-hand electrode). Thus, the cell obtained by coupling these two electrodes can be represented as —

 Anode Cathode

**Similarly**, it can be shown that the cell obtained by coupling the other two pairs can be represented as —

 Anode Cathode Anode Cathode

**Problem** (): Calculate the emf of the following cell and predict whether the given cell representation is correct or wrong. If wrong, write the correct representation and correct the cell reaction.

Given that: and

**Solution**: Obviously the value of is given by —

Since, the value of is a quantity () hence, the given **representation of the cell is wrong**.

Correct representation of the cell is obtained by interchanging the position of the electrodes, *i.e.* the correct representation is —

Oxidation reaction at anode :

Reduction reaction at cathode :

Overall Cell reaction :

This is the correct cell reaction. //

**Problem** (): Construct a galvanic cell in which the following redox reaction takes place:

**Solution**: From the given redox reaction, it is obvious that the - ions are oxidised to iodine () and - ions are reduced to - ions. Indicating that the —

Electrode constituting the oxidation terminal *i.e.* anode will be —

And, electrode constituting the reduction terminal *i.e.* cathode will be —

The galvanic cell, representing the redox reaction will be —

 - Electrode - Electrode

 (Anode) (Cathode)

The corresponding half-reactions are —

Oxidation half-reaction (at anode) :

Reduction half-reaction (at cathode) :

Overall Cell reaction :

**Very Important**: Whether the cell representation is correct or wrong can be decided by calculating its emf value ( - value). This is calculated with the help of the following expressions —

If the value of is , the cell representation is correct, but if the value of is , the cell representation is wrong. The correct representation is obtained by interchanging the position of the electrodes. In the present case —

Since, the value of is a quantity () hence, the given **representation of the cell is correct**.

**Problem** (): Construct the galvanic cell in which the following redox reaction takes place:

**Solution**: () From equation (), it is evident that is oxidised to - ions and - ions (in ) are reduced to - metals. Indicating that the —

Electrode constituting the oxidation terminal *i.e.* anode will be —

And, electrode constituting the reduction terminal *i.e.* cathode will be —

The galvanic cell, representing the redox reaction will be —

 - Electrode - Electrode

 (Anode) (Cathode)

The correctness of the answer can be verified by calculating the value of the above cell. If this value is , the representation of the cell is correct. For the given cell —

Since, the value of is a quantity () hence, the given **representation of the cell is correct**.

**Solution**: () Reaction () can also be written as—

Thus, the reaction shows that is oxidised to and is being reduced to . Thus, the galvanic cell in which the given reaction will take place will be composed of the following electrodes —

Electrode constituting the oxidation terminal *i.e.* anode will be —

And, electrode constituting the reduction terminal *i.e.* cathode will be —

The galvanic cell, representing the redox reaction will be —

 - Electrode - Electrode

 (Anode) (Cathode)

Again, for the given cell —

Since, the value of is a quantity () hence, the given **representation of the cell is correct**.

**Solution**: () Reaction () can also be written as—

Thus, the reaction shows that is reduced to and is oxidised to . Thus, the galvanic cell in which the given reaction will take place will be composed of the following electrodes —

Electrode constituting the reduction terminal *i.e.* cathode will be —

And, electrode constituting the oxidation terminal *i.e.* anode will be —

The galvanic cell, representing the redox reaction will be —

 - Electrode - Electrode

 (Anode) (Cathode)

Again, for the given cell —

Since, the value of is a quantity () hence, the given **representation of the cell is correct**.

**Solution**: () From equation () —

It is evident that is reduced to and is oxidised to . Thus, the galvanic cell in which the given reaction will take place will be composed of the following electrodes —

Electrode constituting the reduction terminal *i.e.* cathode will be —

And, electrode constituting the oxidation terminal *i.e.* anode will be —

The galvanic cell, representing the redox reaction will be —

 - Electrode - Electrode

 (Anode) (Cathode)

Again, for the given cell —

Since, the value of is a quantity () hence, the given **representation of the cell is correct**.

**Problem** (): Construct the galvanic cell by coupling the following pairs of Electrodes. Justify your answer —

Given that: , , , and

**Solution**: We know that that the half-cell, having higher value (*i.e*., more or less value) of , constitutes the cathode (right-hand electrode) and the half-cell, having lower value (*i.e*., less or more value) of , acts as the anode (left-hand electrode) of the galvanic cell. Now —

() For the couple —

Since,

Hence, Ag electrode will act as cathode and electrode will act as anode. Thus, the cell may be represented as —

 (Anode) (Cathode)

Since, the value of is a quantity () hence, the given **representation of the cell is correct**.

() For the couple —

Since,

Hence, electrode will act as cathode and electrode will act as anode. Thus, the cell may be represented as —

 (Anode) (Cathode)

Since, the value of is a quantity () hence, the given **representation of the cell is correct**.

() For the couple —

Since,

Hence, electrode will act as cathode and electrode will act as anode. Thus, the cell may be represented as —

 (Anode) (Cathode)

Since, the value of is a quantity () hence, the given **representation of the cell is correct**.

**Problem** (): What will be the spontaneous reaction, when the following half-reactions are combined together?

1. ;
2. ;

What is the ?

**Solution**: Since, value for the half-cell reaction () is smaller than that for the half-cell reaction (), hence, oxidation will take place at the half-cell reaction () and reduction will take place at the half-cell reaction (). We, therefore, write reaction () as oxidation reaction and reaction () as reduction. Now, in order to make the number of electrons equal in both the reactions, we multiply equation () by and then add it to equation (). Thus —

Thus, the overall cell reaction is —

This is the desired spontaneous cell reaction, because

Since, the value of is a quantity () hence, the given **cell reaction as written is spontaneous**. //

**Problem** (): The reaction occurs in a cell. Write the electrode reactions and compute the standard emf of the cell.

Given that: , and

**Solution**: The cell reaction show that is oxidised to *i.e.* the electrode representing the anode (left-hand electrode) is . Again, is reduced to *i.e.* the electrode representing the cathode (right-hand electrode) is . Thus, the galvanic cell is —

 (Anode) (Cathode)

Since, the value of is a quantity () hence, the given **representation of the cell as well its overall cell-reaction is correct**. Now —

**Problem** (): In the voltaic cell, answer the following —

1. Which electrode acts as anode and which electrode acts as cathode?
2. Write the half-cell reactions occurring at the two electrodes.
3. Write the overall cell reaction, and
4. Calculate the standard emf of the cell.

Given that: , and

**Solution**: () From the cell representation, it is obvious that electrode acts as anode (left-hand electrode) and electrode acts as the cathode (right-hand electrode)

 () In the cell, is oxidised to - ions at the anode and - ions are reduced to metallic at the cathode. Thus, the two half-cell reactions can be written as —

() The overall cell reaction is obtained by adding the two half-reactions occurring at the two electrodes. Thus, the overall cell reaction can be written as —

() The standard emf of the cell is calculated as —

**Measurement of Cell *emf***:

The *emf* of galvanic cell can be accurately measured using a potentiometer as shown in the figure given below. Here, the emf, of the cell, is balance by an opposing potential difference , so as to make the current through the cell zero. Measurement of ‘’ gives the value of , which is the emf of the cell.

The **resistor** between is a uniform solid-wire of total resistance . The contact point is adjusted until the galvanometer, shows no deflection when the tap key is closed, indicating **zero current** passing through the cell . The fact that **no current flows** through the cell when key is closed shows that the terminal of the cell is at the same potential as the point and terminal of the cell is at the same potential as point . Hence, when balance is achieved, the potential drop across the resistor equals the **zero-current potential drop** across the cell’s terminals, which is the *emf* .

***Ohms law*** gives —

Where ‘’ is the current in the upper part of the circuit and is the resistance of the wire between ; we have —

Measurement of , thus, allows to be found.

In practice, one balances the circuit twice, once with cell and once with a standard cell of accurately known *emf*, in place of . Let be the resistances needed to balance . Then —

Hence, we have —

From which can be calculated.

Instead of using a potentiometer, one can measure cell ***emfs*** with an electric digital voltmeter that draws a negligible current. //

**The Nernst Equation**:

The electrode ***potential*** and ***emf*** of a cell depends on the nature of the () **electrode**, () **temp** and the () **activities** of the ions in solution. The variation of the electrode potential and cell potential *i.e*. emf with the activities of ions in solution can be obtained from thermodynamic point of view. ***For example***, for a general reaction, such as —

occurring in a cell, the ***Gibbs free energy*** is given by —

Where, the reaction quotient, and,

 The free energy change for the reaction in the standard state *i.e*. when the activities of all the reactants and products are all unity

 Since,

 And,

Equation () is known as the ***Nernst equation*** for the standard ***emf*** of the cell, *i.e*. ***zero-current*** cell () potential at any cell composition.

If both the **reactant** and **products** are in the ***standard state***, then all ***activities*** are (unity), and so that , and hence . Therefore —

At temperature, equation () reduces to —

Again,

Hence, from equation (), we have —

**Standard Potentials ()**:

The standard electrode potential of electrode “” is defined using a cell with “” on the **right side** of the **cell diagram**, and by ***IUPAC*** **cell-diagram convention**, **reduction** occurs at the right electrode. Therefore, the standard electrode potential for the electrode “” corresponds to a chemical reaction in which **reduction occurs** at electrode “”. Actually, ***all electrode potentials are reduction potentials***.

A **galvanic cell** is a combination of **two electrodes**, each one of which can be considered as making a characteristic contribution to the **overall cell potential**. Although it is not possible to measure the contribution of a single electrode, we can define the potential of one of the electrodes as having a zero potential and then assign values to others as that basis. The specially selected electrode is the ***Standard Hydrogen Electrode* ()** —

The standard potential, of other couple is then assigned by considering a cell in which it is the right – hand electrode and the **SHE is the** **left-hand electrode**. ***For example*** —

The standard potential () of couple is the , of the following cell —

Likewise, the standard electrode potential of the couple is the standard potential of the following cell —

Although the standard potential is often written as though it refers to a half-reaction, such as —

It should be understood that these equations are only shorthand for writing—

And that the standard potential is determined by properties of the - electrode as well as the species to which the potential refers. //

**Cell Diagram and *IUPAC* conventions**:

A galvanic cell is represented by a diagram in which the following **conventions** are used —

1. A vertical line indicate a **phase boundary**, however the phase boundary between the **miscible liquids** is indicated by a dashed or **dotted vertical line**.
2. Two species present in the same phase are separated by a comma.

***For example*, Daniell Cell,** —

The following ***IUPAC* conventions** define the ***Cell emf*** and ***Cell reaction*** for a given cell diagram —

() The cell emf ‘’ is defined as —

 Reduction potential of right hand electrode, and

 Reduction potential of left hand electrode

() The cell reaction is defined to involve oxidation in the left side and reduction on the right side.

() Always reduction potentials are used

***For example*, Daniell Cell,** —

() **A**  The Spontaneous Cell reaction or Cell diagram

**The Standard Potential () of a Cell in terms of Reduction Potentials**:

The standard potential of a cell formed from any two electrodes can be calculated by taking the difference of their standard potentials. This rule follows from the fact that a cell such as —

is equivalent to two cells joined back to back as: —



The overall potential of this composite cell, and therefore of the cell of interest, is —

**Some Standard Reduction Potentials are given below**:

 **Couple**

These reduction values can be used in the same way, and the standard cell potentials is the difference right-left of the corresponding standard potentials, because —

It then follows that, if the result gives —

 Then the corresponding cell reaction is **spontaneous** in the direction as written (in the sense that ).

**Problem (1)**: Can displaces from solution (*i.e*. reduction of - ions to metallic ) when the ions are at unit activity.

Given:

**Solution**: The complete reaction is —

The two reduction half-reactions are —

So, the difference of () and (), yields the complete reaction —

Since,

Therefore, the reaction is **spontaneous**, hence, displaces from solution (*i.e*. reduction of - ions to metallic ) //

**Problem (2)**: The corrosion of iron in acidic environment is given by —

Does the equilibrium constant favours the formation of ?

Given:

**Solution**: The reaction is —

Hence, the two reduction half-reactions are —

So, the difference of () and (), yields the complete reaction —

Since,

Therefore, the reaction is **spontaneous**, *i.e*. proceeds in the forward direction, which implies the reaction has , favouring products. //

**Problem (3)**: Calculate the equilibrium constant for the disproportionation —

Given:

**Solution**: The electrode reactions are —

**Reduction**:

**Oxidation**:

So, the cell diagram is —

And, the cell reaction is —

Therefore, the standard emf of the cell is —

Now, —

Since, , so the equilibrium strongly towards the **right of the reaction** as written, so - ion disproportionates almost **totally** in the solution. //

**Problem (4)**: For the cell —

Calculate the value of equilibrium constant (), assuming that the displacement of goes virtually to completion.

**Solution**: We have —

Therefore, the equilibrium constant —

Since, , so the equilibrium strongly towards the **right of the reaction** as written. //

**Problem (5)**: Calculate the equilibrium constant for the reaction —

Given:

**Solution**: The electrode reactions are —

**Reduction**:

**Oxidation**:

So, the cell diagram is —

And, the overall cell reaction is —

Therefore, the standard emf of the cell is —

Now, —

Since, , so the equilibrium strongly towards the **right of the reaction** as written. //

**The Composition Dependence of Individual Potentials**

**(. Single Electrode Potentials)**

We know that the overall cell potential depends on the composition in accord with the ***Nernst equation***, *viz*. —

Similar equations may also be written for the individual reduction potentials. ***For example***, the potential of a electrode at any arbitrary - ion activity is given by the expression —

Where: is the reaction quotient for the half reaction —

**Proof of Equation () . to Prove** —

**Proof**: Let us consider a cell in which the **left hand side electrode** is a **standard hydrogen electrode** (). ***For example***, the reaction in the cell —

The ***Nernst equation*** is —

When the - electrode has its standard composition, , but the electrode has an arbitrary composition. Under these conditions —

And the cell potential can be regarded as arising solely from the electrode. We can then write —

**Problem (1)**: Calculate the change that takes place in the potential difference of a electrode when an excess of is added at . The activity of ion is in the saturated solution at this same temperature.

**Solution**: The Cell reaction is —

And, the Nernst equation is therefore —

The change in potential, when the activity of ions changes from is therefore —

The activity of is —

**Problem (2)**: Calculate is added to a ***calomel electrode*** compartment at , for which initially .

**Solution**: Same as above, Answer

**The Electrochemical Series**:

We know that for the two redox couples , *i.e*. the cell is —

And the corresponding cell reaction is —

The cell reaction will be spontaneous as written only if . Because in the cell reaction, is reducing and we can conclude that, has a ***thermodynamic*** tendency to reduce if is lower than . ***More briefly***: ***Low Reduces High***, ***for example***, —

And, thus ‘’ has a **thermodynamic tendency** to reduce ‘’ from the solution to metallic ‘’. Hence, the spontaneous cell reaction is —

Further, if the **reaction** is ***spontaneous***, we can expect equilibrium constant, and in fact for this reaction, experimentally it has been found that .

Thus, if we arrange the redox couples *i.e*. in the order of their reducing power, we will have a series, called ***Electrochemical Series* or *Reactivity Series***. A part of the series is shown below. The reduced member of a couple with a lower standard potential can reduce the oxidised member of couples with higher standard potentials. ***For example***, —

To determine **whether - can displace - from its aqueous solution** at — from the table we see that the couples lie above . Therefore, **- cannot displace - from its aqueous solution** *i.e*. cannot reduce - ions to . //

**Important Conclusions Derived from Electrochemical Series**:

[] Since, the half-cell reactions are reduction reactions, the standard electrode potential value given in the electrochemical series are the standard reduction electrode potentials. The value of standard reduction electrode potentials () and standard oxidation potentials () of an electrode are equal to each other but they have opposite sign, *i.e.* if one has sign, the other has sign and vice versa. Thus, —

For example, —

[] Some standard reduction electrode potentials are , while others are . Negative value of standard reduction electrode potential () of a given electrode, implies that this electrode will constitute **negative terminal** (**anode**) of the galvanic cell which is obtained by coupling the given electrode with a normal (or standard) hydrogen electrode. On the other hand, the value of standard reduction electrode potential () of a given electrode implies that this electrode will constitute **positive terminal** (**cathode**) of the galvanic cell which is obtained by coupling the given electrode with a normal (or standard) hydrogen electrode.

[] As we proceed from top to bottom in the series (down the series), the values of standard reduction electrode potentials go on increasing and hence more and more positive (). On proceeding from bottom to top, values become more and more negative ().

[] The electrodes, having values for their standard reduction electrode potentials, have been placed **above - electrode**, while the electrodes, having values for their standard reduction electrode potentials, have been put **below - electrode**.

**Applications of Electrochemical Series**: **OR**

**Applications of Standard Reduction Electrode Potentials**:

[] **To predict which half-cell will constitute the Cathode and which half-cell will form the Anode**: If we are given two half-cells (**electrodes**) and their standard reduction electrode potentials, we can predict which half-cell will constitute the cathode and which half-cell will act as anode of thee galvanic cell, which is obtained by coupling these two half-cells. The half-cell having higher value (*i.e.* more or less value) of its standard reduction electrode potential will form the cathode, while the half-cell having lower value (*i.e.* less or more value) for its standard reduction electrode potential, will act as anode of the galvanic cell.

[] **To predict whether a given cell representation is correct or wrong**: Whether a given cell representation is correct or wrong, can be decided with the help of values of two electrodes which constitute the galvanic cell. If the difference

The cell representation is correct. On the other hand if is a quantity, the cell representation is wrong.

[] **To calculate the value of Reduction Electrode Potential of a given Electrode at non-standard conditions: To calculate the value of by using Nernst Equation**: With the help of the value of standard reduction electrode potential of a given electrode, we can also calculate the value of the value of reduction electrode potential of the same electrode when the species appearing in the reduction reaction taking place at the electrode are not in their standard conditions (Non-standard conditions). This value is calculated with the help of Nernst equation which is written as —

Further, in the equation number of electrons involved and is the Faraday constant.

[] **To calculate the value of Potential (emf) of a given Cell at standard conditions: To calculate the value of** : With the help of value we can calculate the value of standard potential (standard emf) of a given galvanic cell (- value). The value of is given by:

This equation is applied when the reactants and the products appearing in the cell reaction are in their standard conditions.

[] **To calculate the value of Potential (emf) of a given Cell at non-standard conditions: To calculate the value of by using Nernst Equation**: If the reactants and the products appearing in the cell reaction are not in their standard states (non-standard conditions), the emf of the cell (- value) is determined with the help of Nernst equation —

 EMF of the cell in non-standard state

 EMF of the cell in the standard state of reactants & products

Further, in the equation number of electrons involved and is the Faraday constant.

If the cell reaction (REDOX REACTION) is

Then, the Nernst equation for this reaction is —

[] **Reducing and oxidising property of substances in Aqueous Solution**:

Oxidising agents undergo reduction in aqueous medium by accepting electrons. On the other hand, reducing agents loses electrons in aqueous medium *i.e.* undergo oxidation.

The substance having a value of has a tendency to gain electrons to undergo reduction and thus acts as oxidising agents in aqueous medium. On the other hand, substance having a value of has a tendency to lose electrons to undergo oxidation and thus, acts as the reducing agents in aqueous medium.

***Variation of Oxidising power of oxidising agent and Reducing power of reducing agent in Electrochemical Series***:

Higher the value of , higher is the tendency of the substance to accept electrons to undergo reduction in aqueous solution and hence higher is the oxidising power of the substance. Since, values **increases down the electrochemical series** (), the oxidising power of the oxidising agents also **increases** in the same direction. For example, - ion is the weakest oxidising agent and - is the strongest oxidising agent. The increasing order of oxidising power (or strength) of oxidising agents down the series shows that strong oxidising agents have large values of .

Lower the value of , lower is the tendency of the substance to lose electrons to undergo oxidation in aqueous solution and hence lower is the reducing power of the substance. Since, values **increases down the electrochemical series,** the reducing power of the reducing agents **decreases** in the series. For example, - is the strongest reducing agent and - ion is the weakest reducing agent. The decreasing order of reducing power (or strength) of reducing agents down the series shows that strong reducing agents have large values of .

Since, couple has the lowest value of (most negative); lithium is the strongest reducing agent.

**Question**: Explain: **Why - metal is the strongest reducing agent in the aqueous solution**?

**Solution**: When an alkali metal, (like lithium) acts as a reducing agent in aqueous solution, it loses its electron and is oxidised to the hydrated cation, —

This equation represents the reducing property of alkali metals. This oxidation reaction actually takes place through the following steps — [Born-Haber Cycle]

Evidently, the oxidation of ion, (i.e. reducing property of an alkali metal) will be high, if ‘’ has a large value. Now, since sublimation energy () of all the alkali metals is almost same, so the value of depends on the difference of .

For - metal, hydration energy () is greater than that of its ionization energy () while for other metals hydration energy is less than their respective ionization energy. Thus, it is only for - metal that a is value and for other alkali metals it is . Thus, - metal is the strongest reducing agent in aqueous solution.

**Question**: Explain: **The relative order of Oxidising Power of Halogen molecules () and Reducing Power of Halide ions () in aqueous solution**:

**Solution**: In aqueous solution, halogen molecule acts as an oxidising agent as —

Because of the large value of , - molecules are capable of accepting an electron and hence act as an oxidising agents. On the other hand, - ions are capable of losing an electron and hence act as reducing agent. Since, decreases from , the oxidising power of - molecules decreases from .

**Problem (1)**: The values of standard reduction electrode potentials (- values) of some half-cell reactions are given below: ( = Oxidising agent & = Reducing agent) —

Select the strongest reducing agent and strongest oxidising agent.

**Solution**: In the given reduction reactions, the species written on LHS accept electrons and are reduced to the species written on the RHS. Thus, the species given on RHS act as reducing agents.

We know that the species which has the lowest value acts as the strongest reducing agent while the species having the highest value acts as the strongest oxidising agent . Thus, since the value of is the lowest, hence - ion acts as the strongest reducing agent. Similarly, since the value of is the highest, implies that - ion is the strongest oxidising agent.

**Problem (2)**: On the basis of the following - values, predict whether ferricyanide ion is stronger or weaker oxidising agent than ferric ion:

**Solution**: The given reactions are oxidation reactions. On writing them as reduction reactions we get —,

Now, since the value of standard reduction electrode potential for couple is greater than the value of standard reduction electrode potential for couple, is stronger oxidising agent than .

**Problem (3)**: The standard reduction potential values of some electrodes are given as:

Which of these species is the most powerful reducing agent?

**Solution**: Let us write the reduction reactions so that the oxidising agents are written on the LHS and reducing agents are shown on the RHS. Thus —

 Oxidising Agent Reducing Agent

Since, electrode has the lowest value of (most negative value), - metal is the most powerful reducing agent.

**Problem (4)**: Will be oxidised to ions by reacting with ? Given that —

**Solution**: The oxidation of to ions by can be represented by the following redox reactions —

The reaction will occur spontaneously if and only if is lower than . Now, since , therefore, should be a quantity. Actually, it is a quantity as shown below —

Thus, will be oxidised to ions spontaneously, when it is allowed to react with .

***A Very Important Conclusion***: The essential condition to make a redox reaction to occur spontaneously is that the value of standard reduction potential of the species which is being oxidised (*i.e.* the species which loses electrons or acts as a reducing agent) should be lower than that of the species which is being reduced (*i.e.* the species which gains electrons or acts as a oxidising agent).

**Problem (5)**: Predict whether the reaction: will occur or not. Given that —

**Solution**: In the given redox reaction, - ion is being reduced to by and - ion is being oxidised to by . Thus, acts as oxidising agent and acts as the reducing agent. We know that the given redox reaction is possible only when the value of standard reduction potential of oxidising agent () is higher than that of the reducing agent (). But, in this case —

Thus the reaction **will not occur** spontaneously as written. //

**Problem (6)**: Predict whether the reaction: will occur or not. Given that —

**Solution**: In the given redox reaction, - ion is being reduced to by and - ion is being oxidised to by . Thus, acts as oxidising agent and acts as the reducing agent. We know that the given redox reaction is possible only when the value of standard reduction potential of oxidising agent () is higher than that of the reducing agent (). But, in this case —

Thus the reaction **will not occur** spontaneously as written. //

**Problem (7)**: Will metallic tin reduce ?

Given that —

**Solution**: If metallic tin () reduce to , metallic tin itself oxidised to . Thus —

 RA OA

Now, we see that since —

Thus the given redox reaction **is possible** i.e. metallic tin will reduce to . //

**Problem (8)**: Write the Nernst equation and calculate cell potential for the cell —

Given that —

**Solution**: The representation of the cell as given in the question shows that —

Since, - electrons are involved in the cell reaction (), the Nernst equation for this cell reaction can be written as —

**Problem (9)**: A galvanic cell consists of metallic - plate immersed in solution and metallic - plate immersed in solution. Calculate the of the cell. Write the chemical equations for the electrode reactions and represent the cell.

Given that —

**Solution**: Obviously, the two electrodes of which the cell is composed are —

Again, since —

Therefore, constitutes the cathode (reduction will occur) of the cell and forms the anode (oxidation will occur) of the cell.

Thus, the cell diagram (representation of the cell) will be —

The reactions taking place at the electrodes are —

Since, - electrons are involved in the cell reaction (), the Nernst equation for this cell reaction at can be written as —

———×××———

**Calculating the Pressure Dependence of a Potential**:

To find an explicit relation to determine the dependence of pressure on the potential value, let us try to solve the following relevant problem —

**Problem**: - gas is bubbled over a - electrode dipping into aqueous . Calculate the change in potential of the electrode when the - pressure is increased from to a pressure of .

**[Method**: Write the ***half reaction*** and the ***reaction quotient*** of the reaction and then setup the ***Nernst equation*** for the electrode potential. Express the **difference** in potential arising from a change in pressure in terms of the ***Nernst equation***, and then substitute the data. For simplicity, assume that the gas behaves **perfectly** at the pressure specified and so **replace** ***fugacity*** by ***pressure***.]

**Solution**: The electrode half reaction is —

Therefore, —

When the pressure (fugacity) of changes from , the change in potential is —

Now, putting —

**Problem ()**: Vapour pressure measurements gives the stoichiometric activity coefficients of in a . Find at for the cell —

Given:

**Solution**: By convention, the left-hand side electrode of the cell involves oxidation, so the two half-reactions and the overall cell reactions are —

Therefore, the Standard emf of the cell,

Again, from the ***Nernst equation*** of the overall cell reaction —

Since, the activities of the solids are pressure

Now, —

**Problem ()**: Find the value of , for the cell —

Given:

**Solution**: Same as above

**Problem ()**: Find for a cell whose overall cell reaction is —

Given:

**Solution**: From the overall cell reaction —

Oxidation half-reaction:

Reduction half-reaction:

Hence, the cell diagram is —

Since,

Again,

[This very high value of implies at equilibrium, virtually no remains in solution]

**Problem ()**: Find for a cell whose overall cell reaction is —

Given:

Calculate the same quantities for the reverse reaction also.

**Solution**: Same as above;

For the reverse reaction;

**Classification of Galvanic Cells (Concentration Cells)**:

Galvanic Cells are basically of two types —

1. Chemical Cells, and
2. Concentration Cells

To form a galvanic cell, we bring two half-cells together. If the electrochemical reactions in the half-cells differ, the overall cell reaction is a chemical reaction and the cell is a **chemical cell**. ***For example*** —

If the electrochemical reactions in the two half-cells are the same but one species say is at a **different concentration** in each half-cell, the cell will have a **non-zero *emf*** and its overall cell reaction will be a physical reaction that amounts to the transfer of from one concentration to the other. This is a **concentration cell**. ***An example***, is a cell composed of two chlorine electrodes with different pressures of —

Here, are the pressures at the left and right electrodes respectively.

Adding the two half-reactions, *viz*. —

We obtain the following overall cell reaction —

Thus, for any concentration cell,  **is zero**, since, are equal. The ***Nernst equation*** with fugacity approximated by pressure gives for () —

A cell with a ***liquid junction*** involves transport of ions across the liquid junction and is therefore, said to be a **cell with transference**. The ***Daniell cell***, viz. —

is a **chemical cell with transference**. But the cell, —

is a chemical cell without transference.

**Concentration Cells are of - Types**:

[] **Electrode Concentration Cells or Amalgam Cells**:

These are the cells in which two **electrodes** are of **different concentrations** are dipped in the **same solution** of their **salt**, *i.e*. the electrolyte of only one strength.

***For example***, - Amalgam Cell:

[] **Electrolytic Concentration Cells**: **Important**

These are the cells in which the **two electrodes** are of the **same materials** which are dipped into **two solutions** of **same electrolyte** but of **different concentrations**.

**Electrolytic Concentration Cells are of two types**—

() **Concentration Cells without Transference or Transport:**

In these type cells, there is no direct transfer of electrolyte from one solution to another. The transfer occurs due to the result of chemical reactions. In general, a concentration cell without transference can be designated if two simple cells with **electrodes reversible** with respect to each of the ions constituting the electrolyte are oppositely combined. ***For example***, —

() **Concentration Cells with Transference:** In these types cells, the ***liquid junction potential*** between the junction of two solutions is **taken into account**. ***For example***, —

***EMF* of a Concentration Cell without Transference or Transport**:

Considering a cell having the electrodes reversible with respect to as —

Therefore, the ***Left-hand electrode reaction*** —

And, the ***Right-hand electrode reaction*** —

So, the net cell reaction is —

Hence, the ***emf*** of the cell with net cell reaction (), will be —

**Now, let us consider, the cell with different activities** of , *i.e*. —

The corresponding overall reaction of which is —

And, the ***emf*** of the cell will be —

Now, on connecting the two cells containing of activities with emf in opposition, we will get the resulting cell —

The corresponding overall reaction of which is —

And, ***emf*** of this cell will be —

Since , there occurs a **transfer** of **electrolyte** from concentrated to dilute solution, which follows from equation (), as shown above.

Since,

Therefore, from equation (), we have —

Again, *i.e*. activity in terms of fugacity,

Finally, for dilute solution,

Thus, the emf of a concentrated cell without transference depends upon the concentration of the solution in the both sides. //

***EMF* of a Concentration Cell with Transference or Transport**:

In these types of cells, the liquid junction potential between the junctions of two solutions is taken into account. Consider the cell of the type —

In the above cell, the two solutions of are in contract with each other and thus, there is a direct transfer of from the more conc. solution () to the less conc. solution ().

When is greater than , it means that the left-hand electrode will become , whereas right-hand electrode will get charge. If of electricity is passed through the cell, then of the dissolves at , *i.e*. left electrode —

And, reduction will take place at right electrode, *i.e*. .

Thus, the overall cell reaction is —

This implies that electrons will flow from left to right. As the electric current is constituted by ions, it means that ions are moving from left to right while ions are moving from right to left.

Suppose are the transport numbers of ions respectively.

For the passage of of electricity through the cell, the is carried by - ion of hydrogen from left to right, *i.e*. from the solution of activity . Thus, we can write —

Since,

Similarly, of electricity will be carried by - ion of chlorine from right to left, *i.e*. from the solution of activity . Thus, we can write —

The net transfer of materials from the two solutions will be obtained by adding equations (), () and () —

From equation (), it is evident that equivalent of is transferred from the solution of activity to the solution of activity by the passage of **one Faraday of electricity**. The *emf* of the complete cell will be given by —

Since,

**Problem (1)**: Show that the emf of the cell —

**Problem (2)**: Find the cell reaction and calculate the potential of the following cell with transference at .

The transport number of . Is the cell reaction spontaneous as written? What would be the cell potential if the above cell is converted into one without liquid-junction potential?

 **Ref: KL Kapoor Vol 3, page 535**

**Application of EMF Measurements OR Applications of Concentration Cells**:

The EMF measurements has a number of useful applications, some of these are —

1. Determination of Activity and Activity coefficients of electrolytes,
2. Determination of transport numbers of ions,
3. Determination of valency of ions in doubtful cases,
4. Determination of solubility product, and
5. Determination of of a solution.

[] **Determination of Activity and Activity Coefficients of Electrolytes**:

Suppose we want to determine the activity coefficient of hydrochloric acid. For this, considering a cell without liquid junction potential containing . The two electrodes are so chosen that one is reversible with respect to the cation of the electrolyte (in this case, the - ion) and the other is reversible with respect to the anion of the electrolyte (in this case, the - ion). Evidently, the first electrode is the hydrogen electrode (standard) and the other electrode can be the silver- silver chloride () electrode. Thus, the cell diagram will be —

The corresponding cell reaction is —

According to Nernst equation, the EMF of the cell at is given by —

Because, activity of the solid species and at is taken as unity

Now, we know that —

Where: mean ionic activity, and

 Molality of

Thus, from equation (), we have —

The two unknowns, in the above equation can be determined by measuring EMF, of the cell over various molalities of , including very low concentrations. At infinite dilution, and so that . Thus, a plot of ***versus*** , which on extrapolated to gives as the - intercept. Knowing the value of , the mean ionic activity coefficient at any other concentration can be determined from the EMF data of the cell at that concentration.

**Problem (1)**: Calculate the mean ionic activity coefficient of in the cell

The EMF of the cell is . The standard electrode potential of
 is .

**Solution**: For the given cell —

Since , hence from —

We have —

**Problem (2)**: Calculate the mean ionic activity coefficient of in the cell

The EMF of the cell is. The standard electrode potential of
 is .

**Solution**: For the given cell —

[] **Determination of Transport Numbers of the Ions of the Electrolyte**:

We know that the EMF of a concentration cell with transference (), in which the end electrodes are reversible with respect to cation, is given by —

The EMF of the same cell with the same solution but without transference (), is —

Dividing equation () by (), we have —

Thus, the ratio of the EMF’s of the two concentration cells, one with transference and the other without transference, gives the transference number of the anion, if the end electrodes are reversible with respect to the cation.

If the end electrodes are reversible with respect to the anion, then the ratio of the two EMF’s will give the transference number of the cation of the electrolyte. //

[] **Determination of Valency of the Ions in Doubtful cases**:

The valency of the mercurous ion was in doubt for a long time, and was finally established by determining the EMF of a concentration cell of the type given below —

The salt bridge, which is the saturated solution of ammonium nitrate, connects the two solutions.

The EMF of the cell (), assuming the activity coefficients to be equal to unity, is given by the following expression —

Where: is the valency of the mercurous ion and

Thus, we can write —

It was found that when was , the EMF was . Therefore, the valency of mercurous ion is and, it should be represented as . //

 [] **Determination of the Solubility Product of the Electrolyte**:

The solubility product of a sparingly soluble salt is a kind of equilibrium constant. Consider the salt in equilibrium with its ions in a saturated solution.

The solubility product of the salt is given by —

Assuming ideal behaviour of the solution, we can consider that the activities equals to their molar concentration.

Now, a galvanic cell is so selected that one of the electrode is reversible with respect to the cation () and the other electrode is reversible with respect to the anion (), example of such salts can be . For the above general reaction, the following cell is proposed where is a sparingly soluble salt and its solubility is so small, that the saturated solution can be safely taken as very dilute solution.

 Left hand Electrode Right hand Electrode

 Oxidation occurs Reduction occurs

The half-cell reactions are —

Right hand Electrode (Reduction electrode):

Left hand Electrode (Oxidation electrode):

And, the overall cell reaction is —

By knowing the value of , for the cell under consideration and using the relations —

Thus, can be calculated from the known value of .

**Problem (3)**: Calculate the solubility product of in water at from the cell:

The standard potentials are and

**Solution**: The half-cell reactions (*i.e*. electrode reactions) are —

 (Reduction electrode):

 (Oxidation electrode):

Thus, the overall cell reaction is —

The standard EMF of the cell, is therefore —

Again, we know that —

Here,

**Problem (3)**: The EMF of the cell:

Calculate — () the solubility product and () solubility of in and in . Given that is dissociated and is dissociated.

**Solution**: Since, at is dissociated, hence the ion concentration () on side

 If ‘’ be the concentration of ions on the side due to solubility of . Then, assuming that activity coefficients are each equal to unity, the EMF of the cell is given by —

Substituting the values of we get —

Since, at is dissociated, hence the ion concentration is given by

[] **Determination of of the Electrolyte**:

The of a solution is defined as the logarithm of the - ion concentration in of the solution. Thus, —

Thus, any potentiometric method available for measuring - ion concentration in a solution can be used for the determination of its ‘’ value. This can be done by using electrode reversible to - ions as described below —

[] **Determination of by using - Electrode**:

The potential of a hydrogen electrode in contact with a solution of ions involving the reaction —

Given by the Nernst equation —

By convention, , i.e. the electrode potential of standard hydrogen electrode, is zero.

But, we know that —

Thus, the potential of a hydrogen electrode depends upon the of the solution with which it is in contact. This can be determined by combining the hydrogen electrode with a reference electrode, say, a standard calomel electrode. With calomel electrode the complete cell is represented as —

The EMF of the cell is determined potentiometrically, and this is given by —

 [] **Determination of of the Electrolyte - Electrode**:

The quinone-hydroquinone system involves the following equilibrium —

 Quinone () Hydroquinone ()

For the reduction reaction given above, the potential developed on a - electrode immersed in this system is given by the Nernst equation as —

Instead of taking quinone and hydroquinone, a small amount of quinhydrone, which is an equimolar compound of quinone [] and hydroquinone [] is taken. Since, hydroquinone [] is a weak acid, its ionization is very small particularly if the of the solution is less than . Therefore, the concentration of hydroquinone [] is the same as that of quinone [], i.e., the quantity is unity. Thus, the above equation reduces to —

Since, the standard electrode potential () of a quinhydrone electrode is

Thus, the potential of the quinhydrone electrode, just as that of the hydrogen electrode, depends upon the of the solution with which it is in contact, i.e., the quinhydrone electrode behaves as a reversible hydrogen electrode. Consequently, this electrode can be used for measuring values of solutions. //

**Advantage of Quinhydrone Electrode**:

This electrode is preferred to the hydrogen electrode as it can be set up easily by merely adding a pinch of quinhydrone to the solution under examination and inserting a clean - electrode for making electrical connection. The electrode gives accurate results even in the presence of oxidising ions which usually interfere with the working of the hydrogen electrode.

The quinhydrone electrode is combined with a saturated calomel electrode to form the cell. The cell diagram may be represented as —

The EMF of the cell is given by —

The EMF of the above cell (), can be determined potentiometrically and of the concerned solution thus, can be estimated.

**Limitation of Quinhydrone Electrode**:

The quinhydrone electrode cannot be used for solutions of . In more alkaline solutions, quinhydrone ionizes appreciably as an acid and also gets oxidised partly by atmospheric oxygen. This alters the normal equilibrium between quinone and hydroquinone which forms the basis of the equation —

**Problem (4)**: While determining the of a solution, the quinhydrone electrode was in conjugation with a saturated calomel electrode, as represented below:

The EMF of the cell was found to be . Calculate the o the solution at this temperature, .

**Solution**: For the cell, EMF is given by —

Here:

 [] **Determination of of the Electrolyte by using - Electrode**:

It is found that when a thin glass bulb containing a solution of some is dipped in another solution say contained in a beaker having different , then across the glass bulb a potential () is developed. This is characteristic of the difference in the values of the solutions across the glass membrane. The bulb is made into an electrode which contains a solution of definite and outside in the beaker is taken the solution of which is to be known, at the follows the equation —

Here, is a constant for the given glass electrode. It depends upon the of the solution inside the bulb, the kind of glass used and the assembly within the bulb.

The electrode reaction is assumed to involve the reduction of ions. The glass electrode, thus, functions in the same manner as a reversible hydrogen electrode.

**Construction of Glass Electrode**: The glass electrode is made of a special glass of relatively low melting point and high electrical conductivity. A solution of which furnishes a constant ion concentration, is placed inside the bulb and a electrode or simply a - wire is inserted to make electrical contact. The reference electrode employed is usually the calomel electrode. The cell diagram is —

The EMF of such a cell can be determined conveniently by means of a potentiometer. Since the potential of the calomel electrode is known, that of the glass electrode can be easily calculated and the of the experimental solution is evaluated. The value of is first obtained by working with solution of known .

The of the solution is given by —

**Advantages of Glass Electrode**:

The glass electrode has a number of advantages over other electrodes, some of these are —

1. It can be used even in strong oxidising solutions which interfere with quinhydrone electrode,
2. In can be used in the presence of metallic ions, poisons, etc., and
3. It is simple to operate and is, therefore, extensively used in chemical, industrial, agricultural and biological laboratories.

**Limitations of Glass Electrode**:

Following are the limitations of using glass electrode —

1. It can be used up to a , but being sensitive to ions above a of , the linear relationship between glass electrode altered. So an alkaline error is introduced beyond a of , which should be taken into consideration, and
2. It does not function properly in some organic solvents like pure alcohol.

[] **Determination of using - Electrode**:

The antimony () - antimony oxide () electrode works as an electrode reversible to hydrogen ions. It consists of a rod of antimony placed in a solution having hydrogen ion.

**Electrode reaction**:

The corresponding Nernst equation will be —

**Advantages of - Electrode**:

1. Easy to use, cheap and durable,
2. It can be used in viscous solutions, and
3. It has low resistance.

**Advantages of - Electrode**:

1. It can only be used within range , at lower , dissolves and at higher , dissolves, and
2. It cannot be used in presence of oxidising agents, reducing agents, complexing agents and noble metals

**Problem (5)**: Determining the of a solution at from the following data for the Cell:

Given that the EMF of the cell is and electrode potential of calomel electrode at is

**Solution**: For the cell, EMF is given by —

**Problem (6)**: The given cell consists of glass electrode coupled with calomel electrode as follows:

Given that , determine the of the solution

**Solution**: In these types of cell, calomel electrode acts as the cathode and

The cell EMF is given by —

Substituting the values, we get —

**Potentiometric Titrations**:

**Principle**: The principle underlying the potentiometric titrations is that the potential of a electrode depends upon the concentration of the ion with which it is reversible, which may be calculated from the Nernst equation. In a titration, there is continuous change in ionic concentration of the electrolyte solution (analyte) in the cell after each addition of small volume of the titrant, which can be followed by measuring the potential of the cell formed by the electrolyte sampled with a suitable electrode. The **potentiometric titrations** are thus, ***those titrations which involves the measurement of electrode potentials with addition of titrants***. Therefore, ***equivalence*** point can be found by plotting a graph between measured potentials of solution versus volume of titrants added.

Potentiometric titrations are of - types —

1. Acid-Base Titrations,
2. Oxidation-Reduction (Redox) Titrations, and
3. Precipitation Titrations.

**Acid-Base Titrations**:

Suppose we want to titrate a solution of against . Any electrode whose potential depends upon - ion *conc*. (- electrode, quinhydrone electrode, glass electrode) is placed in the solution. It is connected to a reference electrode ( calomel electrode or electrode) to form a galvanic cell. If hydrogen electrode is used as the indicating electrode and a saturated calomel electrode is used as the reference electrode, then the galvanic cell will be —

The ***EMF*** of the cell is measured potentiometrically, and it is given by —

Suppose is to be titrated against . The concentration of the titrant is usually times higher than that of the solution to be titrated so that the volume change is as small as possible.

As the titration proceeds, the - ion *conc*. goes on decreasing, i.e. of the solution goes on increasing, hence, according to the above equation, the EMF of the cell goes on increasing. It is evident that the EMF of the cell would increase by for every - fold decrease in the - ion *conc*. or - unit increase in the of the solution.

 During titration, addition of to , the EMF of the cell changes slowly at first but more and more rapidly as the end point approaches.

After the end point, further addition of produces very little change in the- ion *conc*. and hence there is very little change in the EMF of the cell.

Figure (), given below shown a plot of against the volume of added during the course. From the figure, it can be seen that the EMF of the cell initially rises gradually and thereafter more rapidly neat the equivalence point. Beyond the equivalence point, the EMF of the cell again increases slightly on adding more of .

To determine the equivalence point, a plot of the slope of the titration curve is drawn, which is a plot of the change of EMF with the change in volume () is plotted against the volume of added. The resulting curve rises to a maximum at the equivalence point. The volume at the equivalent point is determined by drawing a vertical line from the peak of the volume axis.



**Oxidation-Reduction (Redox) Titrations**:

Like acid-base titrations, the redox titrations are also carried out potentiometrically. In this case, the electrode reversible with respect to - ions is replaced by an inert metal, such as - wire, immersed in a solution containing both the oxidised and reduced forms of the same species. The electrode acts as an oxidation-reduction electrode.

As an example, considering the following redox reaction —

The reaction involves the oxidation of ions by ions being carried out potentiometrically. Prior to the addition of ions, the solution contains only the ions. On adding small amount of ions to the solution, a small amount of ions is oxidised to ions. With the presence of both the ions, the electrode behaves as an oxidation-reduction electrode whose potential, according to Nernst equation, is given by —

Evidently, the electrode potential is controlled by the ratio . For example, if the ratio is , the electrode potential would be —

With further addition of ions, the ratio changes, thereby changing the value of . For every ten-fold change in the ratio , the potential of the electrode would change by , evidently.

At the equivalence point, so that the electrode potential at the equivalence point, is given by —

The above equations may be written as —

Adding and simplifying followed by putting

The numerical values of , respectively, according to the equation

Beyond the equivalence point, as a result of which the electrode potential thereafter is controlled only by the ratio.

For potentiometric measurements, the oxidation-reduction electrode () is combined with a reference electrode, , a saturated calomel electrode, to form the galvanic cell, which can be represented as — (using electrochemical series)

***Before the equivalence point***, the EMF of the cell would be given by —

***And, after the equivalence point***, the EMF of the cell would be given by —

***At the equivalence point***, the EMF of the cell would be given by —

The EMF of the cell is measured potentiometrically at each stage of titration and the EMF data thus obtained are proposed for the equivalence point. The redox titration curve is exactly similar to the acid-base titration curve.

**Precipitation Titrations**:

Suppose we want to standardise a solution of by titrating it against a saturated solution of . The - electrode is used as the indicator electrode in this case.

The potential of the half-cell, , is measured by connecting it with the calomel electrode, as usual. The solution is titrated against a saturated solution of , the strength of which is about times higher. As the reaction proceeds, the ions get gradually precipitated as .

The concentration of ions goes on decreasing and hence the potential of the electrode given by the Nernst equation —

The potential goes on decreasing continuously on the progressive addition of solution. The electrode potential will change slowly at first but more and more rapidly as the end point approaches. At the end point, the concentration of ions is very small as this is now on account of slight solubility of . Hence, the change in electrode potential is the maximum at the end point. If the addition of is continued further, the concentration of ions remains almost unaffected except for very small decrease on account of the common ion effect. The addition of beyond the end point, therefore, causes only a small change in the electrode potential.

The potentiometric titration curve obtained in this case is exactly similar to the one obtained in the case of acid-base titrations.

**Advantages of the Potentiometric Titrations**:

There are number of advantages of potentiometric titrations over the ordinary titrations involving the use of indicators. Some of these are —

1. Potentiometric titrations can be carried out in coloured solutions, while indicators cannot be used in such cases.
2. In ordinary acid-base titrations, one must have prior information about the relative strength of acids and bases before a proper indicator is selected. However, no such information is required in the case of potentiometric titrations.
3. The titrations can be used for the titration of mixtures of two acids (having different degrees of ionization) with the same base (). In such a case, two different equivalence points are obtained. Such titrations otherwise cannot be easily conducted.
4. A high degree of accuracy is obtained in results with this process, even in the case of very dilute solutions.

**Applications of Electrolysis in Metallurgy & Industry**:

**Electrolysis in Metallurgy**: Important applications of electrolysis in metallurgy are

1. Electrolytic extraction of metals, *i.e*. Electrometallurgy, and
2. Electro-refining

() **Electrolytic extraction of metals (Electrometallurgy)**:

Electrometallurgy is the process of extraction of metal from ore by electrolysis. Metals like sodium, potassium, magnesium, calcium, aluminium, etc. are obtained by the electrolysis of fused electrolytes. For example, considering the extraction of - metal by the electrolysis of fused .

() **Electro-refining**:

The metals obtained from their ores usually contain impurities. Therefore, metals like copper, iron, lead, nickel, etc. are usually purified by electrolysis.

For example, considering the purification of raw copper extracted from its ore. For this, a cell is so constructed that the anode is the impure metal and any impurities are removed during the process of electrolysis when the metal travels from anode to cathode. During the electro-refining of metals, the cathode has a decomposition of pure metals from a solution containing metal ion. In the case of purification of copper (up to ) by electrolysis, cathode is a pure piece of copper, while the anode is an impure piece of copper as shown in the figure given below.



The electrolyte is an aqueous solution of copper sulphate with dilute sulphuric acid. On passing electric current, the from the anode moves through a sulphuric acid – copper (II) sulphate solution into the cathode where it becomes solid copper. While this is occurring, the impurities are left at the bottom of the tank. This leftover residue is called anode mud.

**Electrolysis in Industry**: Important applications of electrolysis in industry are —

1. Electroplating,
2. Electro-synthesis,
3. Electro-typing, and
4. Electro-forming

() **Electroplating**: Electroplating is the process of converting the articles made up of cheap metals by a thin covering of precious metals such as iron with nickel, chromium, silver or gold with one or more of the following aim of view —

1. Protection of metal against corrosion,
2. Giving shining appearance to articles,
3. Replacing work-out materials, and
4. Giving reflecting properties to reflectors

**Process of electroplating**: The positive electrode should be the metal that we want to coat the object with. The negative electrode will be the object that we want to coat by the metal. The electrolyte should be a solution of the coating metal, usually as metal nitrate or sulphate, for example solution as electrolyte for - coating or plating. The experimental setup for - plating is as shown below in the figure.



In the figure, the object to be plated (*e.g*. a spoon) is made from the cathode of an electrolytic cell, the anode is a bar of - metal and the electrolyte is a solution of in water. When a direct current is passed through the cell, - ions from the migrate to the anode (the spoon), where they are neutralized by electrons and stick to the spoon as - metal. Meanwhile, the - anode bar give up electrons to become - ions in the solution. Thus, the anode bar gradually dissolves to replenish the - ions in the solution. The net result is that - metal has been transferred from the anode to the cathode, here spoon. The process continues until the desired coating thickness is built upon the spoon.

In electroplating with silver, silver cyanide is used as the electrolyte rather than other compounds of silver such as silver nitrate (), because the cyanide ion () reacts with - ion to form the complex ion, . This limits the supply of free - ions in the solution, so they can deposit themselves only very gradually onto the cathode. This produces a shiner and more adherent silver plating.

**Electro-Synthesis**: Electro-synthesis is a method which uses electrolysis reactions to produce certain products. For example, needs to undergo electrolysis in order to be used for alkaline batteries. The solution for the electro-synthesis of is . The anode is graphite, where is oxidized. While at the cathode hydrogen is reduced from . Overall reaction is —

**Electro-Typing**: Electro-typing is the process which is used for the reproduction of the work of art like wood craving. A large number of printing plates are obtained from the original type. The impression of the type is taken on the block of wax. The impression on wax is then coated with black lead to give it metallic surface and then it is subjected to the process of electro deposition. Thus, a film of copper is formed on the prepared surface.

**Electro-Forming**: The electro forming is an important application of electro deposition. Reproduction of objects by electro-deposition on some sort of mould or form is known as electro-forming.

In the reproduction of coins, molls, engraving, etc., a mould are first made by impressing the object, say in wax. The surface of the wax, which bears exact impression of the object, is coated by powdered graphite in order to make it conducting the mould is then dipped in an electro-forming cell as a cathode. After obtaining coating of desired thickness, the article and the wax core, is melted out of the metal shell. //

**Commercial Cells**:

These are the **electrochemical cells**, employed commercially as the source of electrical energy. Broadly speaking, commercial cells are of **two types** —

1. **Primary Cells**: ***For example***, Leclanche or Dry Cell
2. The **Secondary Cells**: ***For example***, Lead Storage Cell (Battery)

**Primary Cells**:

The Cells that can be used only so long the active materials are present are called primary cells. Once these are consumed, the cell cannot be recharged by passage of current through it, and hence it has to be discarded. One of the examples is the **Leclanche** or **dry cell** represented as —

The reactions involved are —

 Anode:

 Cathode:

 Overall:

The generated in the above electrochemical reaction causes the following secondary reactions —

Since, these reactions are not involved directly in the electrode reactions; they do not contribute anything towards the cell ***emf*** **of** . Since, the cathode electrode is a function of , the cell potential falls rapidly on continuous discharge.

Another example of the ***primary cell***, which provides more constant voltage, is the **Ruben – Mallory Cell**. Here, the use of a large excess of hydroxyl ions makes the cell less sensitive to change. The cell is represented as —

The reactions involved are —

 Anode:

 Cathode:

 Overall:

**Secondary Cells or Batteries**:

The term battery means either a single galvanic cell or several galvanic cells connected in series, in which case the ***emf* are additive**. These are **reversible** cells and can be used again and again by recharging the cell, hence the name **secondary cells**. One of the important **examples** is the **Lead Storage Cell** (**Battery**), where lead acts as anode and lead impregnated with lead dioxide acts as cathode. The electrolyte is a solution of at room temperature. The cell diagram is —

The reactions involved are —

 Anode:

 Cathode:

 Overall:

The ***emf*** of **lead-storage cell** depends on the ***activity*** of solution. At , some of the values are .

To **recharge** the cell, it is connected with a cell of potential higher than that of the cell in such a way that the lead-storage cell now acts as the electrolytic cell, where lead is deposited on the cathode, is formed at the anode and is regenerated. The specific gravity of the solution rises due to the increase in concentration. The recharging is carried out only up to a certain specific gravity value.

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