

LESSON

ELECTROCHEMISTRY

Introduction

Electrochemistry deals with the study of equilibrium and kinetic properties of ions in solution, the production of electrical energy from the energy released during spontaneous chemical reactions or the processes where the electrical energy is used to bring about non-spontaneous chemical reactions.

Conductance of Electrolytic Solution

Basic Quantities of electrochemistry

- **Resistance** - The resistance, 'R', of a sample of an electrolytic solution (solution that gives ions when dissolved in water) as in case of metallic conductors is defined by the expression: $R = \rho \frac{l}{A}$, where l is the length of a sample of electrolyte and A is the cross sectional area.
- **Resistivity or Specific Resistance**- The symbol ρ , is the proportionality constant. It is a property of an electrolytic solution. This property is called **resistivity or specific resistance**.
- **Conductivity or Specific conductance** κ - The reciprocal of resistivity is called **conductivity or specific conductance**, (kappa) κ where $\kappa = \frac{1}{\rho} = \frac{1}{RA}$
- **Conductance(G)**- The inverse of resistance, R, is called **conductance**, G and can be expressed as $G = \frac{1}{R}$.

S.I. units

The SI units of above quantities are:

1. Unit of Resistance(R) is ' Ω '
2. Unit of Resistivity (ρ) is 'ohm meter (Ω m)'
3. Unit of Conductivity(κ) is 'siemens per meter or ($\Omega^{-1}\text{m}^{-1}$ or Sm^{-1})'
4. Unit of Conductance(G) is 'siemens or S' or Ω^{-1}

Factors affecting the conductivity of electrolytic solutions:

The conductivity of the electrolytic solutions depends upon:

- (i) the nature of the electrolyte added
- (ii) the size of the ions produced and their hydration
- (iii) the nature of the solvent and its viscosity
- (iv) the concentration of the electrolyte
- (v) temperature (affects the kinetic energy of the ions)

Factors affecting the conductivity of metals

Electrical conductance through metals is called metallic or electronic conductance and is due to the movement of electrons. This is different from electrolytic conductance. The electronic conductance depends on:

- (i) the nature and structure of the metal
- (ii) the number of valence electrons per atom
- (iii) temperature (it decreases with increase of temperature).

As the electrons enter at one end and go out through the other end, the composition of the metallic conductor remains unchanged. The mechanism of conductance through semiconductors is more complex.

Measurement of Conductivity of Ionic Solutions

Conductivity of ionic solutions

As in case of our metallic conductors we cannot use the Wheatstone bridge for finding the resistance of ionic solution. This is because of the following reasons:

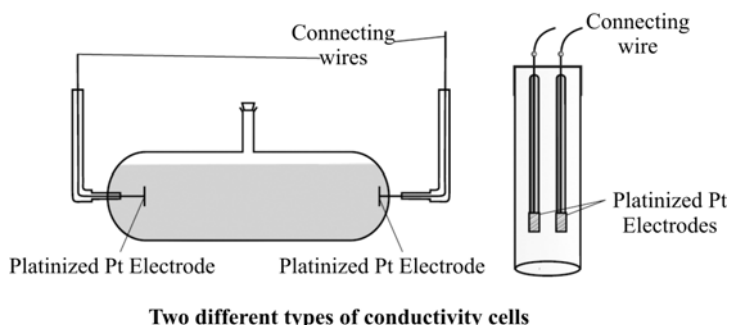
- (i) Firstly, passing direct current (DC) changes the composition of the solution.
- (ii) Secondly, a solution cannot be connected to the bridge like a metallic wire or other solid conductor.

The first difficulty is resolved by using an alternating current (AC) source of power. The second problem is solved by using a specially designed vessel called **conductivity cell**. It is available in several designs and two simple ones are shown in the figure:

Conductivity Cell

Conductivity cell is used for measuring conductivity of solutions. The solution that is to be measured for its conductivity is taken in a special cell called **conductivity cell**. The conductivity cell has two platinum electrodes coated with platinum black of surface area A and are separated by a distance l . The solution confined between these electrodes is a column of length l and area of cross section A . The resistance of such a column of solution is then given by the

equation: $R = \rho \frac{l}{A} = \frac{l}{\kappa A}$ The ratio $\frac{l}{A}$ is constant, called the **cell constant** and is denoted by G^* .

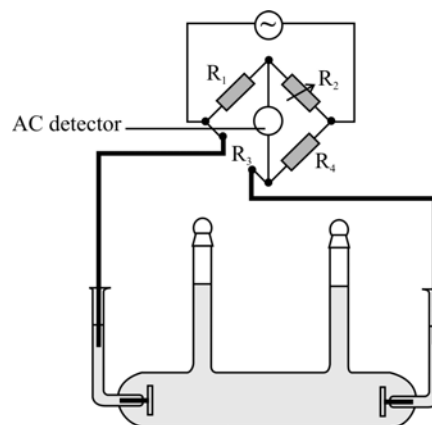


Two different types of conductivity cells

Measurement of conductivity using Conductivity Cell

Conductivity can be measured in the following way:

- The solution for which the conductivity is to be known is taken in a conductivity cell of known cell constant ($\frac{l}{A}$).
- We can know the resistance of the solution using a Wheatstone bridge (as shown in the figure) with two known resistances R_1 and R_4 , and a variable resistance R_2 , as shown in the figure. The resistance of the solution (unknown resistance R_3) is given by $R_3 = \frac{R_1 R_4}{R_2}$ when the bridge is balanced using the variable resistance R_2 .
- Conductance (conductivity) can be estimated by substituting the value of R_3 for R in the expression $\kappa = \frac{1}{\rho} = \frac{1}{RA}$.



Note: The Wheatstone Bridge is said to be balanced when there is no current flow through the A.C. detector headphone or other electronic device

Molar Conductivity

Molar conductivity is defined as the conductivity of a solution per unit concentration Thus we have:

$$\text{Molar conductivity} = \Lambda_m = \frac{\kappa}{c}$$

In the above equation, if κ is expressed in S m^{-1} and the concentration, c in mol m^{-3} then the units of Λ_m are in $\text{S m}^2 \text{mol}^{-1}$.

Unit Conversion

It may be noted that: $1 \text{ mol m}^{-3} = 1000(\text{L/m}^3) \times \text{molarity (mol/L)}$, and hence

$$\Lambda_m(\text{S m}^2 \text{mol}^{-1}) = \frac{\kappa(\text{Sm}^{-1})}{1000\text{Lm}^{-3} \times \text{molarity}(\text{mol L}^{-1})}$$

If we use S cm^{-1} as the units for κ and mol cm^{-3} , the units of concentration, then the units for Λ_m are $\text{S cm}^2 \text{mol}^{-1}$. It can be calculated by using the equation:

$$\Lambda_m(\text{S cm}^2 \text{mol}^{-1}) = \frac{\kappa(\text{Scm}^{-1}) \times 1000(\text{cm}^3 / \text{L})}{\text{molarity}(\text{mol} / \text{L})}$$

Both type of units are used in literature and are related to each other by the equations:

$$1 \text{ S m}^2 \text{mol}^{-1} = 10^4 \text{ S cm}^2 \text{mol}^{-1} \text{ or}$$

$$1 \text{ S cm}^2 \text{mol}^{-1} = 10^{-4} \text{ S m}^2 \text{mol}^{-1}.$$

Variation of Conductivity with Concentration

As we now understand the conductivity of a solution at any given concentration is the conductance of one unit volume of solution kept between two platinum electrodes with unit area of cross section and at a distance of unit length. This is clear from the equation: $G = \frac{\kappa A}{l} = \kappa$

Both conductivity and molar conductivity change with the concentration of the electrolyte.

Variation of conductivity with decrease in concentration

Conductivity always decreases with decrease in concentration both, for weak and strong electrolytes. This can be explained by the fact that the number of ions per unit volume that carry the current in a solution decreases on dilution.

Variation of Molar Conductivity with Concentration

Molar conductivity of a solution at a given concentration is the conductance of the volume V of solution containing one mole of electrolyte kept between two electrodes with area of cross section A and distance of unit length. Therefore, $\Lambda_m = \frac{\kappa A}{l} = \kappa$;

Since $l = 1$ and $A = V$ (volume containing 1 mole of electrolyte) $\Lambda_m = \kappa V$.

Variation of molar conductivity with decrease in concentration

Here we can say molar conductivity increases with decrease in concentration since the total volume, V , of solution containing one mole of electrolyte also increases. It has been found that decrease in κ on dilution of a solution is more than compensated by increase in its volume.

Note: Physically Λ_m can be seen as the conductance of the electrolytic solution kept between the electrodes of a conductivity cell at unit distance but having area of cross section large enough to accommodate sufficient volume of solution that contains one mole of the electrolyte.

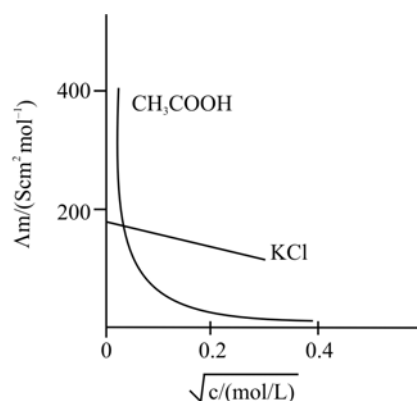
Limiting Molar Conductivity

When concentration approaches zero, the molar conductivity is known as **limiting molar conductivity** and is represented by the symbol Λ_m° . The variation in Λ_m with concentration is different for strong and weak electrolytes.

Molar conductivity for Strong Electrolytes

For strong electrolytes, Λ_m increases slowly with dilution. Kohlrausch determined the empirical relationship for molar conductivity Λ_m and the concentration of the solution c , as $\Lambda_m = \ddot{E}_m^0 - A\sqrt{c}$

where the molar conductivity at infinite dilution, \ddot{E}_m^0 , is arrived at by plotting the molar conductivity at various concentrations Λ_m v/s $\sqrt{\text{concentration}}$ and extrapolating it to zero concentration. The value of the constant A for a given solvent and temperature depends upon the type of electrolyte (e.g.- 1-1 for NaCl, 2-1 CaCl₂ or 2-2 MgSO₄, etc.), rather than its specific chemical identity.



Molar conductivity versus \sqrt{c} for acetic acid (weak electrolyte) and potassium chloride (strong electrolyte) in aqueous solutions

Kohlrausch's Law of the Independent Migration of Ions

Experimental values of A have been carefully determined for many salts as a function of concentration in very dilute solutions, and the intercept values of the resulting plots obtained. In examining such data, it was discovered that \ddot{E}_m^0 for any electrolyte can be expressed as the sum of independent contributions from the constituent cations and anions present. This is known as **Kohlrausch's Law of the Independent Migration of Ions** which states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.

Mathematically it may be expressed as:

$\ddot{E}_m^0 = \nu_+ \lambda_+^0 + \nu_- \lambda_-^0$ (where ν_+ and ν_- refer to the cations and anions respectively). Here λ_+^0 and λ_-^0 are limiting molar conductivities of the cation and anion respectively.

Weak Electrolytes

Weak electrolytes have lower degree of dissociation at higher concentration. Therefore in case of weak electrolytes \ddot{E}_m^0 cannot be obtained by simple extrapolation of Λ_m on the plot of Λ_m v/s \sqrt{c} . The weak electrolytes dissociate to a greater extent with increasing dilution.

For dissociation of ethanoic acid we have we have $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$

If α is the degree of dissociation, the concentrations of the dissociated species expressed as C and that of the un-dissociated acid as $(1-\alpha)C$. The dissociation constant can be expressed as:

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{\alpha^2 C}{1-\alpha}$$

Arrhenius showed that $\alpha = \frac{\Lambda_m}{\Lambda_m^0}$; where the limiting molar conductivity is Λ_m^0 .

Thus we have

$$K_a = \frac{C\alpha^2}{(1-\alpha)} = \frac{C\Lambda_m^2}{\Lambda_m^0(\Lambda_m^0 - \Lambda_m)}$$

Application of Kohlrausch law

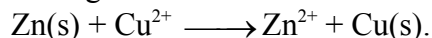
- Kohlrausch law of independent migration of ions is useful in calculating Λ_m^0 from the λ^0 of individual ions.
- In case of weak electrolytes it is possible to determine the value of its degree of dissociation α once we know the Λ_m^0 and Λ_m at a given concentration c .

- Dissociation constant $K_a = \frac{C\alpha^2}{(1-\alpha)}$ as $\alpha = \frac{\Lambda_m}{\Lambda_m^0}$

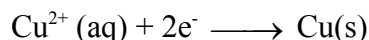
Electrochemical Cells

Any electrochemical cell uses an oxidation-reduction reaction to generate an electric current

For e.g.- Consider the cell with the following reaction



This can be seen as two half reactions,



Electrochemical cells can be classified into two types:

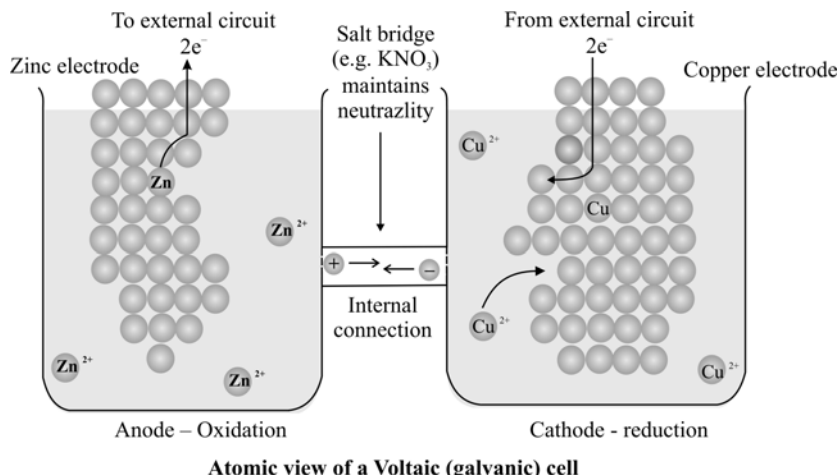
- which convert chemical energy of a spontaneous reaction to electrical energy (Galvanic or Voltaic cell).
- that make use of electric energy to carry non-spontaneous chemical changes (Electrolytic cell).

Voltaic Cells

Voltaic cell makes use of Gibbs energy of spontaneous chemical reaction into electrical work.

Half cell

Reactions in cells can be seen as **oxidation at anode** and **reduction at cathode**. These oxidation and reduction reactions individually are known as **half cell reactions**. The electrode at which oxidation takes place in an electrochemical cell is called the **anode**. The electrode at which reduction occurs is called the **cathode**. The identity of the cathode and anode can be remembered by recognizing that positive ions, or cations, flow toward the cathode, while negative ions, or anions, flow toward the anode.



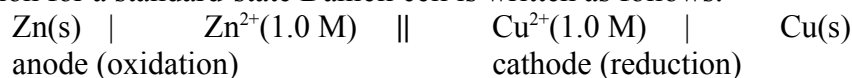
Notation for Voltaic Cells

Voltaic cells can be described by a line notation based on the following conventions:

- A single vertical line indicates a change in state or phase.
- Within a half-cell, the reactants are listed before the products.
- Concentrations of aqueous solutions are written in parentheses after the symbol for the ion or molecule.
- A double vertical line is used to indicate the junction between the half-cells.

- The line notation for the anode (oxidation) is written before the line notation for the cathode (reduction).

The line notation for a standard-state Daniell cell is written as follows.



Electrons flow from the anode to the cathode in a voltaic cell (They flow from the electrode at which they are given off to the electrode at which they are consumed). Reading from left to right, this line notation therefore corresponds to the direction in which electrons flow.

Note: The overall reaction in electrochemical cells is spontaneous and the electrical energy is the manifestation of the decrease in the Gibbs' free energy of the reaction.

The Electrode Potential

The potential of an element, which can be used as an electrode, is defined as the relative tendency of this element to undergo oxidation/reduction w.r.t another electrode that may be arbitrarily taken as a reference zero.

Standard Hydrogen Electrode (SHE) is one such electrode selected to have a zero potential at all temperatures. Potential of various elements can be measured by making SHE the anode and the potential of cathode (as measured by a voltmeter) is potential of the element. If the measurements of electrode potential for a particular element is made against the SHE, under standard conditions of temperature and concentrations, measured potential is called **Standard Potential** (E^\ominus).

Note:

- A negative E^\ominus means that the redox couple is a stronger reducing agent than the H^+/H_2 couple.
- A positive E^\ominus means that the redox couple is a weaker reducing agent than the H^+/H_2 couple.
- The arrangement of elements in their increasing reducing power is called **Electrochemical Series**.
- The difference in the potentials of two electrodes of a cell is called the **cell potential** and is given by

$$E^\ominus_{\text{cell}} = E^\ominus_{\text{cathode}} - E^\ominus_{\text{anode}}$$

The Table for Standard Electrode Potentials at 298K is given at the end of the chapter.

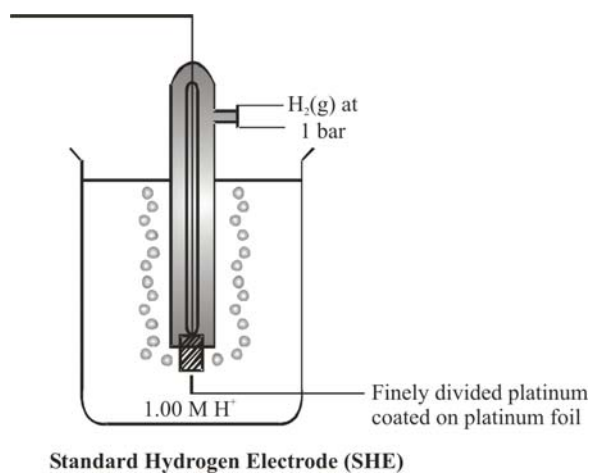
Electrolytic cell

In an electrolytic cell external source of voltage is used to bring about a chemical reaction.

Faraday's laws of electrolysis

Faraday gave two laws of electrolysis (for electrolytic cell)

- First Law – The amount of chemical decomposition produced during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte (solution or molten), where the quantity of charge Q, passed, is given by $Q = It$
Q is in coulombs when I is in ampere and t is in second.
- Second Law – The amounts (in weight) of different substances liberated by the same quantity of electricity passing through the electrolytic solution is proportional to their chemical



equivalent weights.

Modern version of Faraday's Laws – The amount of charge required for oxidation or reduction depends on the stoichiometry of the electrode reaction.

Note:

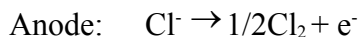
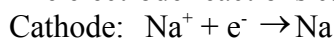
- Charge on one electron is $1.6021 \times 10^{-19} \text{ C}$.
Therefore charge on one mole of electron is –
 $N_A \times 1.6021 \times 10^{-19} \text{ C} = 6.02 \times 10^{23} \text{ mol}^{-1} \times 1.6021 \times 10^{-19} \text{ C}$
 $= 96487 \text{ C} \cong 96500 \text{ C}$
- The charge on the one mole of electrons is called the **Faraday's constant** and its approximate value can be taken as 96500C.

A study of typical electrolytic process:

The products of electrolysis depend upon the state of material being electrolyzed and the type of electrode used.

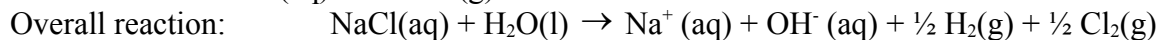
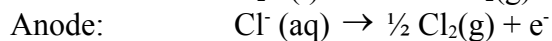
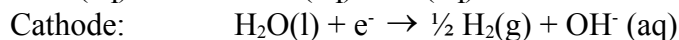
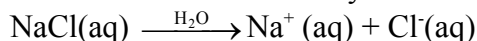
(i) Electrolysis of molten NaCl

The electrode reactions can be summarized as:



(ii) Electrolysis of aqueous NaCl

The electrode reactions may be summarized as:



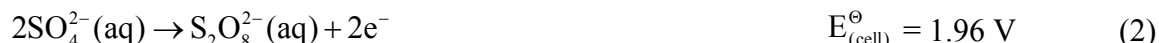
(iii) Electrolysis of H₂SO₄

During the electrolysis of sulphuric acid, the following processes are possible at the anode:

For dilute H₂SO₄



For concentrated H₂SO₄



For dilute sulphuric acid, reaction (1) is preferred but at higher concentrations of H₂SO₄ process, reaction (2) is preferred.

The Nernst Equation

Nernst showed that the potential for an electrochemical reaction is described by the following equation.

$E = E^\ominus - \frac{RT}{nF} \ln Q_c$; where E is the cell potential at some moment, E^\ominus is the cell potential when the reaction is at standard-state conditions, R is the ideal gas constant in units of joules per kelvin per mole, T is the temperature in kelvin, n is the number of moles of electrons transferred in the balanced equation for the reaction, F is the charge on a mole of electrons, and Q_c is the reaction quotient at that moment in time.

- The standard electrode potentials are replaced by electrode potentials given by Nernst equation to take into account the concentration effects.

Note:

- The symbol \ln indicates a natural logarithm, which is the log to the base e , where e is an irrational number equal to 2.71828...
- For standard condition three terms in the equation are constants: R , T , and F . The ideal gas constant is 8.314 J/mol-K. The temperature is taken as 298K. The charge on a mole of electrons can be taken to be 96500 C.
- Substituting this information into the Nernst equation gives the following equation.

$$E = E^\ominus - \frac{0.0256}{n} \ln Q_c \quad (\text{For base 10 equation becomes } E = E^\ominus - \frac{0.059}{n} \log_{10} Q_c)$$

- Three of the remaining terms in this equation are characteristics of a particular reaction: n , E^\ominus , and Q_c .
- The standard-state potential for the Daniell cell is 1.10 V. Two moles of electrons are transferred from zinc metal to Cu^{2+} ions in the balanced equation for this reaction, so n is 2 for this cell. As we never include the concentrations of solids in either reaction quotient or equilibrium constant expressions, Q_c for this reaction is equal to the concentration of the Zn^{2+} ion divided by the concentration of the Cu^{2+} ion.

$$Q_c = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

Substituting what we know about the Daniell cell into the equation gives the following result, which represents the cell potential for the Daniell cell at 298K (25°C) at any moment in time.

$$E = E^\ominus - \frac{0.0256}{2} \ln \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

Using the Nernst Equation to Measure Equilibrium Constants

The Nernst equation can be used to measure the equilibrium constant for a reaction. To understand how this is done, we have to recognize what happens to the cell potential as an oxidation-reduction reaction comes to equilibrium. As the reaction approaches equilibrium, the driving force behind the reaction decreases, and hence the cell potential approaches zero.

$$\text{Thus at equilibrium: } 0 = E^\ominus - \frac{RT}{nF} \ln K_c$$

Rearranging this equation and substituting for E^\ominus from Nernst equation we have

$$\text{At equilibrium: } nFE^\ominus = RT \ln K_c$$

According to this equation, we can calculate the equilibrium constant for any oxidation-reduction reaction from its standard-state cell potential:

$$K_c = e^{\frac{nFE^\ominus}{RT}} \text{ or taking natural log we have}$$

$$\ln K_c = \frac{nFE^\ominus}{RT} \text{ or } 2.303 \log_{10} K_c = \frac{nFE^\ominus}{RT}$$

Electrochemical cells and Gibbs Energy of the reaction

The reversible work done by a galvanic cell is equal to decrease in its Gibbs energy and therefore, if the emf (it is the potential of the cell when no current is drawn) of the cell is E and nF is the amount of charge passed and $\Delta_r G$ is the Gibbs energy of the reaction then $\Delta_r G = -nFE$, where Electrical work done in one second is equal to electrical potential multiplied by total charge passed.

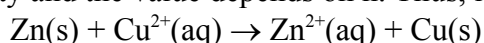
If the activity of all the reacting species is unity, then $E = E^\ominus$ and we have

$$\Delta_r G^\ominus = -nFE^\ominus$$

From the standard Gibbs energy we can calculate equilibrium constant using equation $\Delta_r G^\ominus = -RT \ln K_c$.

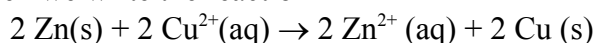
Note:

It may be remembered that $E_{(\text{cell})}$ is an intensive parameter but $\Delta_r G$ is an extensive thermodynamic property and the value depends on n . Thus, if we write the reaction



$$\Delta_r G = -2FE_{(\text{cell})}$$

but when we write the reaction



$$\Delta_r G = -4FE_{(\text{cell})}$$

Batteries

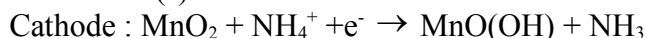
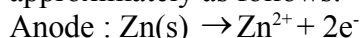
Any battery (it may have one or more than one cell connected in series) or cell that we use as a source of electrical energy is basically a galvanic cell where the chemical energy of the redox reaction is converted into electrical energy. However, for a battery to be of practical use it should be reasonably light, compact and its voltage should not vary appreciably during its use. There are mainly two types of batteries.

1. Primary Batteries

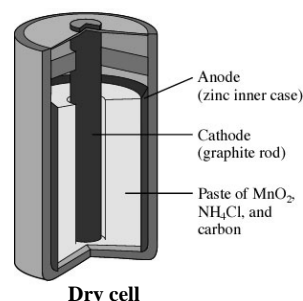
In the primary batteries, the reaction occurs only once and battery then becomes dead after use over a period of time and cannot be reused again.

(i) Dry cell

The most familiar example of this type is the dry cell (known as Leclanche cell after its discoverer) which is used commonly in our transistors and clocks. The cell consists of a zinc container that also acts as anode and the cathode is a carbon (graphite) rod surrounded by powdered manganese dioxide and carbon. The space between the electrodes is filled by a moist paste of NH_4Cl and ZnCl_2 . The electrode reactions are complex, but they can be written approximately as follows:

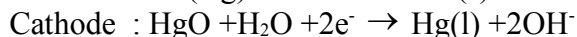


In the reaction at cathode, manganese is reduced from the +4 oxidation state to the +3 state, ammonia produced in the reactions forms complex with Zn^{2+} to give $[\text{Zn}(\text{NH}_3)_4]^{2+}$. The cell has a potential of nearly 1.5 V.

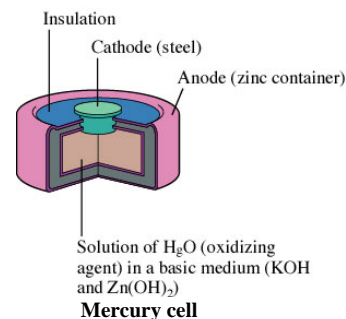


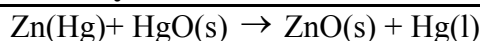
(ii) Mercury cell

Mercury cell is suitable for the low current devices like hearing aids and camera, etc. consists of zinc – mercury amalgam as anode and a paste of HgO and carbon as the cathode. The electrolyte is a paste of KOH and ZnO . The electrode reactions for the cell are given below:



The overall reaction is represented by





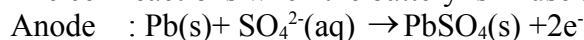
The cell potential is approximately 1.35 V and remains constant during its life as the overall reaction does not involve any ion in solution whose concentration can change during its life time.

2. Secondary Batteries

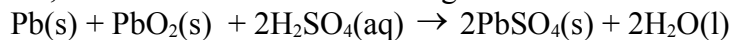
A good secondary cell can undergo a large number of discharging and charging cycles.

- (i) **Lead Storage Battery:** The most important secondary cell is the lead storage battery commonly used in automobiles and invertors. It consists of a lead anode and a grid of lead packed with lead dioxide (PbO_2) as cathode. A 38% solution of sulphuric acid is used as an electrolyte.

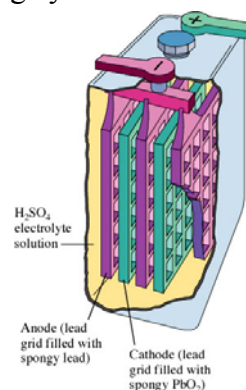
The cell reactions when the battery is in use are given below:



i.e., overall cell reaction consisting of cathode and anode reactions is:



On charging the battery the reaction is reversed and $\text{PbSO}_4(\text{s})$ on anode and cathode is converted into Pb and PbO_2 , respectively.



Lead storage battery

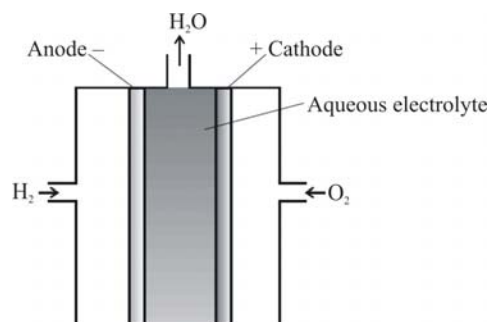
- (ii) **Nickel Cadmium Cell:** Another important secondary cell is the nickel - cadmium cell, which has longer life than the lead storage cell but more expensive to manufacture. The overall reaction during discharge is:
- $$\text{Cd(s)} + 2\text{Ni(OH)}_3(\text{s}) \rightarrow \text{CdO(s)} + 2\text{Ni(OH)}_2(\text{s}) + \text{H}_2\text{O(l)}$$



A rechargeable nickel-cadmium cell in a jelly roll arrangement and separated by a layer soaked in moist sodium or potassium hydroxide

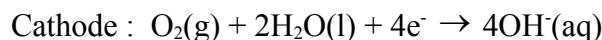
Fuel Cells

Galvanic cells that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol etc. directly into electrical energy are called **fuel cells**. One of the most successful fuel cells uses the reaction of hydrogen with oxygen to form water. In the cell, hydrogen and oxygen are bubbled through porous carbon electrodes into concentrated aqueous sodium hydroxide solution. Catalysts like finely divided platinum or palladium metal are incorporated into the electrodes for increasing the rate of electrode reactions. The electrode reactions are given below:

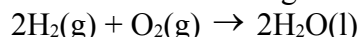


Fuel cell using H_2 and O_2 produces electricity





Overall reaction being:



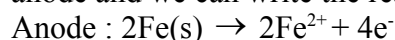
Corrosion

Corrosion slowly coats the surfaces of metallic objects with oxides or other salts of the metal. The rusting of iron, tarnishing of silver, development of green coating on copper and bronze are some of the examples of corrosion.

Rusting

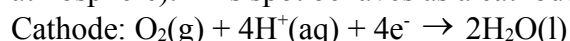
Corrosion of iron (commonly known as rusting) occurs in presence of water and air. Corrosion may be considered essentially as an electrochemical phenomenon (though the chemistry of corrosion is quite complex).

At a particular spot of an object made of iron, oxidation takes place and that spot behaves as an anode and we can write the reaction:



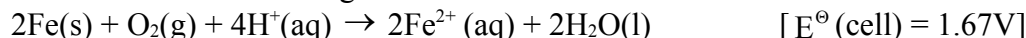
$$E^\ominus (\text{Fe}^{2+}, \text{Fe}) = -0.44\text{V}$$

Electrons released at anodic spot move through the metal and go to another spot on the metal and reduce oxygen in presence of H^+ (which is believed to be available from H_2CO_3 formed due to dissolution of carbon dioxide from air into water. Hydrogen ion in water may also be available due to dissolution of other acidic oxides from the atmosphere). This spot behaves as a cathode with the reaction:

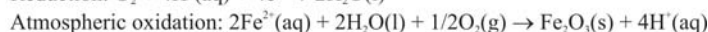
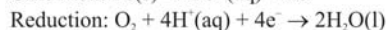
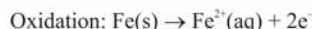
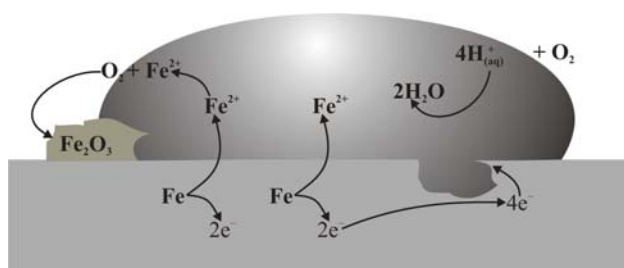
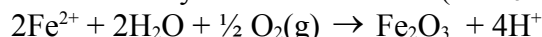


$$[E^\ominus = 1.23 \text{ V}]$$

The over all reaction being:



The ferrous ions are further oxidized by atmospheric oxygen to ferric ions which come out as rust in the form of hydrated ferric oxide ($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$) and with further production of hydrogen ions.



Corrosion of iron in atmosphere

Prevention of Corrosion

One of the simplest methods of preventing corrosion is to prevent the surface of the metallic object to come in contact with atmosphere. This can be done by:

1. Covering the surface by paint or by some chemicals (e.g. bisphenol).
2. Other simple method is to cover the surface by other metals (Sn, Zn etc.) that are either inert or react to save the object.
3. An electrochemical method is to provide a sacrificial electrode of another metal (like Mg, Zn etc.) which corrodes itself but saves the object.

Table : Standard Electrode Potentials at 298 K

Reaction (Oxidised form + ne^- \rightarrow Reduced form)	E^\ominus / V
$Fe(g) + 2e^- \rightarrow 2F^-$	2.87
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.81
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51
$Au^{3+} + e^- \rightarrow Au(s)$	1.40
$Cl_2(g) + 2e^- \rightarrow 2Cl^-$	1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33
$O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23
$MnO_2(s) + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.23
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09
$NO_3^- + 4H^+ + 3e^- \rightarrow NO(g) + 2H_2O$	0.97
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.92
$Ag^+ + e^- \rightarrow Ag(s)$	0.80
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77
$O_2(g) + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68
$I_2 + 2e^- \rightarrow 2I^-$	0.54
$Cu^+ + 2e^- \rightarrow Cu(s)$	0.52
$Cu^{2+} + 2e^- \rightarrow Cu(s)$	0.34
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-$	0.22
$AgBr(s) + e^- \rightarrow Ag(s) + Br^-$	0.10
$2H^+ + 2e^- \rightarrow H_2(g)$	0.00
$Pb^{2+} + 2e^- \rightarrow Pb(s)$	-0.13
$Sn^{2+} + 2e^- \rightarrow Sn(s)$	-0.14
$Ni^{2+} + 2e^- \rightarrow Ni(s)$	-0.25
$Fe^{2+} + 2e^- \rightarrow Fe(s)$	-0.44
$Cr^{3+} + 3e^- \rightarrow Cr(s)$	-0.74
$Zn^{2+} + 2e^- \rightarrow Zn(s)$	-0.76
$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	-0.83
$Al^{3+} + 3e^- \rightarrow Al(s)$	-1.66
$Mg^{2+} + 2e^- \rightarrow Mg(s)$	-2.36
$Na^+ + e^- \rightarrow Na(s)$	-2.71
$Ca^{2+} + 2e^- \rightarrow Ca(s)$	-2.87
$K^+ + e^- \rightarrow K(s)$	-2.93
$Li^+ + e^- \rightarrow Li(s)$	-3.05

Increasing strength of oxidising agent

Increasing strength of reducing agent

SOLVED PROBLEMS

***Example 1:** Resistance of a conductivity cell filled with 0.1M KCl solution is 100 Ω . If the resistance of the same cell when filled with 0.02 M KCl solution is 520 Ω , calculate the conductivity and molar conductivity of 0.02 M KCl solution. The conductivity of 0.1 M KCl solution is 1.29 S/m.

Solution: The cell constant is given by the equation:

$$\text{Cell constant} = G^* = \text{conductivity} \times \text{resistance} = 1.29 \text{ S/m} \times 100 \Omega = 129 \text{ m}^{-1} = 1.29 \text{ cm}^{-1}$$

$$\text{Conductivity of 0.02 M KCl solution} = \text{cell constant} / \text{resistance}$$

$$= G^* / R = 129 \text{ m}^{-1} / 520 \Omega = 0.248 \text{ S m}^{-1}$$

$$\text{Concentration} = 0.02 \text{ mol / L}$$

$$= 1000 \times 0.02 \text{ mol / m}^3$$

$$= 20 \text{ mol / m}^3$$

$$\text{Molar conductivity} = \Lambda_m = \kappa / c$$

$$= 248 \times 10^{-3} \text{ S m}^{-1} / 20 \text{ mol m}^{-3}$$

$$= 124 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$$

$$\text{Alternatively, } \kappa = 1.29 \text{ cm}^{-1} / 520\Omega$$

$$= 0.248 \times 10^{-2} \text{ S cm}^{-1}$$

$$\text{and } \Lambda_m = \kappa \times 1000 \text{ cm}^3 \text{ L}^{-1} / \text{molarity}$$

$$= (0.248 \times 10^{-2} \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}) / 0.02 \text{ mol L}^{-1}$$

$$= 124 \text{ S cm}^2 \text{ mol}^{-1}$$

***Example 2:** The electrical resistance of a column of 0.05 M NaOH solution of diameter 1 cm and length 50 cm is 5.55×10^3 ohm. Calculate its resistivity, conductivity and molar conductivity.

Solution: $A = \pi r^2 = 3.14 \times 0.5^2 \text{ cm}^2 = 0.785 \text{ cm}^2$ or

$$0.785 \times 10^{-4} \text{ m}^2 \text{ and } l = 50 \text{ cm or } 0.5 \text{ m}$$

$$R = \rho l / A \text{ or}$$

$$\rho = RA / l = 5.55 \times 10^3 \Omega \times 0.785 \text{ cm}^2 / 50 \text{ cm}$$

$$= 87.135 \Omega \text{ cm}$$

$$\text{Conductivity} = \kappa = 1 / \rho = (1 / 87.135) \text{ S cm}^{-1}$$

$$= 0.01148 \text{ S cm}^{-1}$$

$$\text{Molar conductivity, } \Lambda_m = \kappa \times 1000 \text{ cm}^3 \text{ L}^{-1} / \text{molarity}$$

$$= 0.01148 \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1} / 0.05 \text{ mol L}^{-1}$$

$$= 229.6 \text{ S cm}^2 \text{ mol}^{-1}$$

If we want to calculate the values of different quantities in terms of 'm' instead of 'cm',

$$\rho = RA / l$$

$$= 5.55 \times 10^3 \Omega \times 0.785 \times 10^{-4} \text{ m}^2 / 0.5 \text{ m}$$

$$= 87.135 \times 10^{-2} \Omega \text{ m}$$

$$\kappa = 1 / \rho = 100 / 87.135 \Omega \text{ m} = 1.148 \text{ S m}^{-1}$$

$$\text{and } \Lambda = \kappa / c = (1.148 \text{ S m}^{-1}) / 50 \text{ mol m}^{-3}$$

$$= 229.6 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}.$$

***Example 3:** Calculate Λ_m^0 for CaCl_2 and MgSO_4 . (Λ_m^0 for various cations are $\text{Ca}^{2+} = 119.0$, $\text{Mg}^{2+} = 106.0$, $\text{Cl}^- = 76.3$, $\text{SO}_4^{2-} = 160.0$)

Solution: We know from Kohlrausch law that $\Lambda_m^0(\text{CaCl}_2) = \lambda^0(\text{Ca}^{2+}) + 2\lambda^0(\text{Cl}^-)$
 $= 119.0 \text{ S cm}^2 \text{ mol}^{-1} + 2(76.3) \text{ S cm}^2 \text{ mol}^{-1}$
 $= (119.0 + 152.6) \text{ S cm}^2 \text{ mol}^{-1}$
 $= 271.6 \text{ S cm}^2 \text{ mol}^{-1}$

$\Lambda_m^0(\text{MgSO}_4) = \lambda^0(\text{Mg}^{2+}) + \lambda^0(\text{SO}_4^{2-})$
 $= 106.0 \text{ S cm}^2 \text{ mol}^{-1} + 160.0 \text{ S cm}^2 \text{ mol}^{-1}$
 $= 266 \text{ S cm}^2 \text{ mol}^{-1}$.

***Example 4:** Λ_m^0 for NaCl, HCl and NaAc are 126.4, 425.9 and 91.0 $\text{S cm}^2 \text{ mol}^{-1}$ respectively.

Calculate Λ_m^0 for HAc.

Solution: $\Lambda_m^0(\text{HAc}) = \lambda^0(\text{H}^+) + \lambda^0(\text{Ac}^-)$
 $= \lambda^0(\text{H}^+) + \lambda^0(\text{Cl}^-) + \lambda^0(\text{Ac}^-) + \lambda^0(\text{Na}^+) - \lambda^0(\text{Cl}^-) - \lambda^0(\text{Na}^+)$
 $= \Lambda^0(\text{HCl}) + \Lambda^0(\text{NaAc}) - \Lambda^0(\text{NaCl})$
 $= (425.9 + 91.0 - 126.4) \text{ S cm}^2 \text{ mol}^{-1}$
 $= 390.5 \text{ S cm}^2 \text{ mol}^{-1}$.

***Example 5:** The molar conductivity of KCl solution at different concentrations at 298 K are given below:

$c/\text{mol L}^{-1}$	$\Lambda_m / \text{S cm}^2 \text{ mol}^{-1}$
0.000198	148.61
0.000309	148.29
0.000521	147.81
0.000989	147.09

Show that a plot between Λ_m and $c^{1/2}$ is a straight line. Determine the values of Λ_m^0 and A for KCl.

Solution: Taking the square root of concentration we obtain:

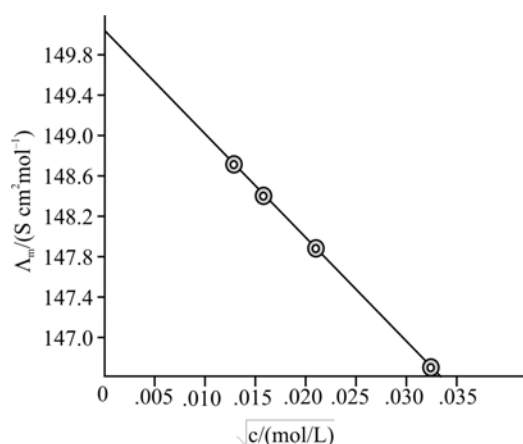
$\sqrt{c^{1/2}} / (\text{mol L}^{-1})^{1/2}$	$\Lambda_m / \text{S cm}^2 \text{ mol}^{-1}$
0.01407	148.61
0.01758	148.29
0.02283	147.81
0.03145	147.09

A plot of Λ_m (y-axis) and $\sqrt{c^{1/2}}$ (x-axis) is shown in Fig.

It can be seen that it is nearly a straight line. From the intercept ($\sqrt{c^{1/2}} = 0$), we find that

$$\Lambda_m^0 = 150.0 \text{ S cm}^2 \text{ mol}^{-1} \text{ and}$$

$$A = -\text{slope} = 87.46 \text{ S cm}^2 \text{ mol}^{-1} / (\text{mol/L}^{-1})^{1/2}$$



***Example 5:** The conductivity of 0.001028 M acetic acid is $4.95 \times 10^{-5} \text{ S cm}^{-1}$. Calculate its dissociation constant if Λ_m^0 for acetic acid is $390.5 \text{ S cm}^2 \text{ mol}^{-1}$.

Solution: $\Lambda_m = \frac{\kappa}{c} = \frac{4.95 \times 10^{-5} \text{ S cm}^{-1}}{0.001028 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{\text{L}}$
 $= 48.15 \text{ S cm}^2 \text{ mol}^{-1}$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0} = \frac{48.15 \text{ S cm}^2 \text{ mol}^{-1}}{390.5 \text{ S cm}^2 \text{ mol}^{-1}} = 0.1233$$

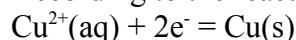
$$K_a = \frac{c\alpha^2}{(1-\alpha)} = \frac{0.001028 \times (0.1233)^2}{1-0.1233} = 1.78 \times 10^{-5}$$

***Example 6:** A solution of CuSO_4 is electrolysed for 10 minutes with a current of 1.5 amperes. What is the mass of copper deposited at the cathode?

Solution: $t = 600 \text{ s}$

$$\begin{aligned} \text{Charge} &= \text{current} \times \text{time} \\ &= 1.5 \text{ A} \times 600 \text{ s} = 900 \text{ C} \end{aligned}$$

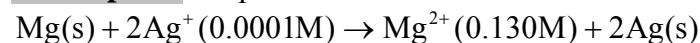
According to the reaction:



We require $2F$ or $2 \times 96487 \text{ C}$ to deposit 1 mol or 63 g of Cu.

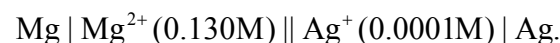
$$\begin{aligned} \text{For } 900 \text{ C, the mass of Cu deposited} \\ &= (63 \text{ g mol}^{-1} \times 900 \text{ C}) / (2 \times 96487 \text{ C mol}^{-1}) \\ &= 0.2938 \text{ g.} \end{aligned}$$

***Example 7:** Represent the cell in which the following reaction takes place



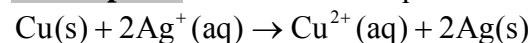
Calculate its E if $E^\ominus = 3.17 \text{ V}$.

Solution: The cell can be written as



$$\begin{aligned} E &= E^\ominus(\text{cell}) + \frac{RT}{2F} \ln \frac{[\text{Ag}^+]^2}{[\text{Mg}^{2+}]} \\ &= 3.17 \text{ V} + \frac{0.059 \text{ V}}{2} \log \frac{(0.0001)^2}{0.130} = 3.17 \text{ V} - 0.21 \text{ V} \\ &= 2.96 \text{ V.} \end{aligned}$$

***Example 8:** Calculate the equilibrium constant of the reaction:



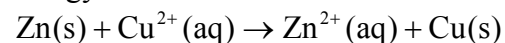
$$E^\ominus = 0.46 \text{ V}$$

$$\text{Solution: } E^\ominus(\text{cell}) = \frac{0.059 \text{ V}}{2} \log K_c \text{ or}$$

$$\log K_c = \frac{0.46 \text{ V} \times 2}{0.059 \text{ V}} = 15.6$$

$$K_c = 3.92 \times 10^{15}.$$

***Example 9:** The standard electrode potential for Daniell cell is 1.1V. Calculate the standard Gibbs energy for the reaction:



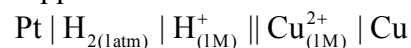
$$\text{Solution: } \Delta_r G^\ominus = -nFE^\ominus$$

$$\Delta_r G^\ominus = -2 \times 1.1 \text{ V} \times 96497 \text{ C mol}^{-1}$$

$$= -21229 \text{ J mol}^{-1}$$

$$= -21.229 \text{ kJ mol}^{-1}.$$

Example 10: The potential of the following cell is 0.34 volt. Calculate the standard potential of the copper half-cell.



Solution:

Here the copper electrode is cathode.

$$E_{\text{cell}}^{\ominus} = E_{\text{oxi}(\text{anode})}^{\ominus} - E_{\text{oxi}(\text{cathode})}^{\ominus}$$

$$\therefore E_{\text{cell}}^{\ominus} = E_{\frac{1}{2}\text{H}_2|\text{H}^+}^{\ominus} - E_{\text{Cu}^2+/\text{Cu}}^{\ominus}$$

$$\therefore 0.34 \text{ volt} = 0.00 \text{ volt} - E_{\text{Cu}|\text{Cu}^{2+}}^{\ominus}$$

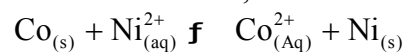
$$E_{\text{Cu}|\text{Cu}^{2+}}^{\ominus} = -0.34 \text{ volt}$$

The standard reduction potential $E_{\text{Cu}^{2+}|\text{Cu}}^{\ominus} = +0.34 \text{ volt}$.

Example 11: The standard oxidation potentials of the half cells $\text{Co}|\text{Co}^{2+}$ and $\text{Ni}|\text{Ni}^{2+}$ are +0.28 volt and +0.23 volt respectively. Calculate the equilibrium constant of the reaction occurring by combining these two half cells at 25°C

Solution:

The oxidation potential of half-cell $\text{Co}|\text{Co}^{2+}$ is higher it will function as anode and Ni will function as cathode. Hence, the total reaction occurring in the cell will be



$$E_{\text{cell}}^{\ominus} = E_{\text{Co}|\text{Co}^{2+}}^{\ominus} - E_{\text{Ni}|\text{Ni}^{2+}}^{\ominus} = 0.28 - 0.23 = 0.05 \text{ volt}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{0.0592}{n} \log \frac{[\text{Co}^{2+}]}{[\text{Ni}^{2+}]}$$

When the cell reaction attains the equilibrium state the value of E_{cell} becomes equal 0.00 and under these circumstances, $[\text{Co}^{2+}]/[\text{Ni}^{2+}] = K_c$

$$\therefore 0.00 = 0.05 - \frac{0.0592}{2} \log K_c \therefore -0.05 = -0.0296 \log K_c$$

$$\therefore \log K_c = \frac{0.05}{0.0296} = 1.69$$

$$\therefore K_c = \text{Anti log}(1.69) = 48.98$$

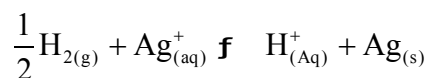
Example 12: The potential of the following cell is 1.04 volt at 25°C. Calculate the pH of the HCl solution. ($E_{\text{Ag}^+/\text{Ag}}^{\ominus} = -0.80 \text{ volt}$)



Solution:

$$E_{\text{cell}}^{\ominus} = E_{\frac{1}{2}\text{H}_2|\text{H}^+}^{\ominus} - E_{\text{Ag}|\text{Ag}^+}^{\ominus} = 0.00 - (-0.80) = 0.80 \text{ volt}$$

Cell reaction:



Here $n = 1$

$$E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{0.0592}{n} \log \frac{[\text{H}^+]}{[\text{Ag}^+]}; 1.04 = 0.80 - \frac{0.0592}{1} \log \frac{[\text{H}^+]}{[0.01]}$$

$$\therefore 1.04 - 0.80 = 0.0592(\log \text{H}^+ - \log 0.01)$$

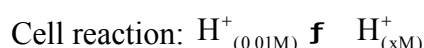
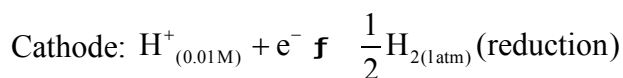
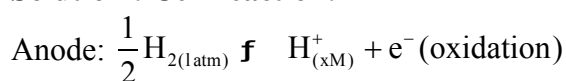
$$\therefore \frac{0.24}{0.0592} = -\log[\text{H}^+] + (-2.0000) \quad \therefore 4.50 + 2.00 = -\log[\text{H}^+]$$

$$\therefore -\log[\text{H}^+] = \text{pH} = 6.50$$

Example 13: The potential of the following given cell is 0.59 volt. Calculate ionic product of water (K_w).



Solution : Cell reaction:



The H^+ ion concentration change only in the cell $\therefore E_{\text{cell}}^{\ominus}$ in the cell will be 0.00 volt

The concentration of OH^- in solution of KOH is equal to 0.01 M. In aqueous solution, the existence of H^+ and OH^- ions is always there and their concentration product becomes equal to K_w . Hence, for KOH solution,

$$[\text{H}^+][\text{OH}^-] = K_w, \text{ but } [\text{OH}^-] = 0.01\text{M}$$

$$\therefore [\text{H}^+] \text{ In solution KOH} = \frac{K_w}{0.01}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{0.0592}{1} \log \frac{\text{concentration of } \text{H}^+ \text{ in KOH solution}}{\text{concentration of } \text{H}^+ \text{ in HCl solution}}$$

$$\therefore 0.59 = 0.00 - \frac{0.0592}{1} \log \frac{K_w / 0.01}{0.01}$$

$$\therefore \frac{0.59}{0.0592} = -\log \frac{K_w}{(0.01)^2} = -\log K_w + \log(0.01)^2$$

$$\therefore 9.968 = -\log K_w - 4.00$$

$$\therefore \log K_w = -9.968 - 4.00 = -13.968$$

$$\therefore K_w = \text{Anti log } \overline{14.032} = 1.076 \times 10^{-14}$$

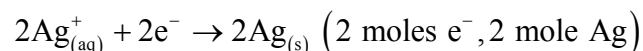
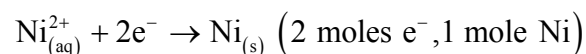
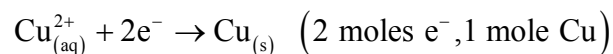
Example 14: Two cells containing NiSO_4 and CuSO_4 are combined in the series and electricity is passed. How much nickel metal will be deposited if 1.00 gram, copper is deposited on copper electrode? If cell-containing NiSO_4 is replaced by cell containing AgNO_3 , how many grams of silver

will be obtained? (At. wt.: Cu = 63.5, Ni = 58.7, Ag = 108)

Solution: Moles of 1 gram of copper = $\frac{\text{Weight of copper (in gram)}}{\text{At.wt.of Cu (gram/mole)}} = \frac{1.0}{63.5} = 0.01575 \text{ mole}$

The same quantity of electricity is passed through each cell.

The chemical reactions at cathode in each cell:



Observing the above reactions, 1 mole Cu, 1 mole Ni and 2 moles Ag are deposited by 2 moles of e^- . According to the second law of Faraday, proportion of moles of metals.

$$\text{Cu: Ni: Ag} = 1: 1: 2$$

In experiment 0.01575 mole from 1g. of Cu are obtained. As a result, the proportion of the moles of the metals produced are

$$\text{Cu: Ni: Ag} = 0.01575: 0.01575: (2 \times 0.01575).$$

$$\begin{aligned} \text{Weight of nickel metal} &= \text{moles of Ni} \times \text{at. wt. (gram/mole) of Ni} \\ &= 0.01575 \times 58.7 = 0.9245 \text{ gram nickel will be obtained.} \end{aligned}$$

$$\begin{aligned} \text{Weight of Ag metal} &= \text{moles of Ag} \times \text{at. wt. (gram/mole) of Ag.} \\ &= (2 \times 0.01575) \times 108 = 3.402 \text{ gram Ag will be obtained.} \end{aligned}$$

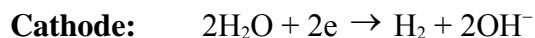
Example 15: An acidic solution of Cu^{+2} salt containing 0.4 g of Cu^{+2} is electrolysed until all the Cu is deposited. The electrolysis is continued for seven more minute with the volume of solution kept at 100 mL and the current at 1.2 ampere. Calculate volume of gases evolved at N.T.P. during entire electrolysis. At. Wt. of Cu = 63.6.

Solution. For I part of electrolysis



$$\begin{aligned} \therefore \text{Eq. of O}_2 \text{ formed} &= \text{Eq. of Cu} \\ &= \frac{0.4 \times 2}{63.6} = 12.58 \times 10^{-3} \end{aligned}$$

For II part of electrolysis: Since Cu^+ ions are discharged completely and thus further passage of current through solution will lead the following changes.

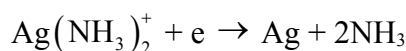


$$\text{Eq. of H}_2 = \text{Eq. of O}_2 = \frac{\text{It}}{96500} = \frac{1.2 \times 7 \times 60}{96500} = 5.22 \times 10^{-3}$$

$$\begin{aligned} \therefore \text{Total Eq. of O}_2 & & \text{Eq. of H}_2 &= 5.22 \times 10^{-3} \\ = 5.22 \times 10^{-3} + 12.58 \times 10^{-3} & & \therefore 2 \text{ Eq. of H}_2 \text{ at NTP} & \\ = 17.8 \times 10^{-3} & & = 22.4 \text{ litre} & \end{aligned}$$

$$\begin{aligned} \therefore 4 \text{ Eq. O}_2 \text{ at NTP} &= 22.4 \text{ litre} & \therefore 5.22 \times 10^{-3} \text{ Eq. at NTP} \\ \therefore 17.8 \times 10^{-3} \text{ Eq. O}_2 \text{ at NTP} & & = \frac{22.4 \times 5.22 \times 10^{-3}}{2} \text{ litre} \\ & & = 58.46 \text{ mL} \\ & = \frac{22.4 \times 17.8 \times 10^{-3}}{4} \text{ litre} \\ & = 99.68 \text{ mL} \\ \therefore \text{Total volume of O}_2 + \text{H}_2 &= 99.68 + 58.46 = 158.14 \text{ mL} \end{aligned}$$

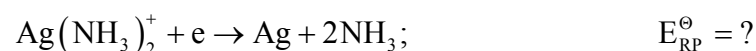
Example 16: Dissociation constant for $\text{Ag}(\text{NH}_3)_2^+$ into Ag^+ and NH_3 is 6×10^{-14} . Calculate E^\ominus for the half reaction.



Given, $\text{Ag}^+ + e \rightarrow \text{Ag}$ has $E^\ominus = 0.799 \text{ V}$.

Solution: Use

$$\text{Ag} \rightarrow \text{Ag}^+ + e; \quad E_{\text{OP}}^\ominus = 0.799 \text{ V}$$



$$\text{and } E_{\text{cell}}^\ominus = E_{\text{cell}}^\ominus + \frac{0.059}{1} \log_{10} \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2}$$

$$\text{Also } E_{\text{cell}}^\ominus = 0 \text{ and } E_{\text{cell}}^\ominus = E_{\text{OP}}^\ominus_{\text{Ag}/\text{Ag}^+} + E_{\text{RP}}^\ominus_{\text{Ag}(\text{NH}_3)_2^+/\text{Ag}}$$

$$\therefore E_{\text{cell}}^\ominus = \frac{0.059}{1} \log_{10} K_C = \frac{0.059}{1} \log_{10} 6 \times 10^{-14} = -0.780 \text{ V}$$

$$\begin{aligned} \therefore E_{\text{Ag}(\text{NH}_3)_2^+/\text{Ag}}^\ominus &= -0.780 + 0.799 \\ &= +0.019 \text{ V} \end{aligned}$$

Example 17: Calculate the equilibrium constant for the reaction, $\text{Fe} + \text{CuSO}_4 \rightleftharpoons \text{FeSO}_4 + \text{Cu}$ at 25°C .

Given $E_{\text{OP}_{\text{Fe}}}^\ominus = 0.44 \text{ V}$; $E_{\text{OP}_{\text{Cu}}}^\ominus = -0.337 \text{ V}$

Solution. In the change Fe is oxidized and Cu^{2+} is reduced

$$\begin{aligned} \therefore E_{\text{cell}} &= E_{\text{OP}}_{\text{Fe}/\text{Fe}^{2+}} + E_{\text{RP}}_{\text{Cu}^{2+}/\text{Cu}} \\ &= E_{\text{OP}}_{\text{Fe}/\text{Fe}^{2+}} - \frac{0.059}{2} \log_{10} [\text{Fe}^{2+}] + E_{\text{RP}}_{\text{Cu}^{2+}/\text{Cu}} + \frac{0.059}{2} \log_{10} [\text{Cu}^{2+}] \\ E_{\text{cell}} &= E_{\text{OP}}_{\text{Fe}/\text{Fe}^{2+}} + E_{\text{RP}}_{\text{Cu}^{2+}/\text{Cu}} + \frac{0.059}{2} \log_{10} \frac{[\text{Cu}^{2+}]}{[\text{Fe}^{2+}]} \quad (1) \end{aligned}$$

For $\text{Fe} + \text{CuSO}_4 \rightleftharpoons \text{FeSO}_4 + \text{Cu}$

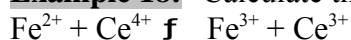
$$K_c = \frac{[\text{Fe}^{2+}]}{[\text{Cu}^{2+}]} \text{ and at equilibrium } E_{\text{cell}} = 0$$

\therefore By Equation (1)

$$0 = 0.44 + 0.337 + \frac{0.059}{2} \log_{10} \frac{1}{K_c}$$

$$\therefore K_c = 2.18 \times 10^{26}$$

Example 18: Calculate the equilibrium constant for the reaction:



Given $E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^{\ominus} = 1.44 \text{ V}$ and $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\ominus} = 0.68 \text{ V}$

Solution.
$$E_{\text{cell}}^{\ominus} = \frac{0.059}{1} \log_{10} K_c$$

$$E_{\text{cell}}^{\ominus} = E_{\text{OP}_{\text{Fe}^{2+}/\text{Fe}^{3+}}}^{\ominus} + E_{\text{RP}_{\text{Ce}^{4+}/\text{Ce}^{3+}}}^{\ominus} = -0.68 + 1.44$$

$$= 0.76 \text{ V}$$

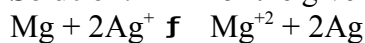
$$\therefore \log_{10} K_c = \frac{0.76}{0.059} = 12.8814$$

$$\therefore K_c = 7.6 \times 10^{12}$$

Example 19: For the cell $\text{Mg}_{(\text{s})} | \text{Mg}_{(\text{aq})}^{+2} || \text{Ag}_{(\text{aq})}^{+} | \text{Ag}_{(\text{s})}$, calculate the equilibrium constant at 25°C and the maximum work that can be obtained during operation of cell. Given

$$E_{\text{Mg}/\text{Mg}^{+2}}^{\ominus} = +2.37 \text{ V} \quad \text{and} \quad E_{\text{Ag}^{+}/\text{Ag}}^{\ominus} = +0.80 \text{ V}, \quad R = 8.314 \text{ J}$$

Solution. For the given cell, at equilibrium, the reaction is



$$E_{\text{cell}} = 0 = E_{\text{OP}_{\text{Mg}/\text{Mg}^{+2}}}^{\ominus} + E_{\text{RP}_{\text{Ag}^{+}/\text{Ag}}}^{\ominus}$$

$$0 = E_{\text{OP}_{\text{Mg}/\text{Mg}^{+2}}}^{\ominus} - \frac{0.059}{2} \log_{10} [\text{Mg}^{+2}] + E_{\text{RP}_{\text{Ag}^{+}/\text{Ag}}}^{\ominus} + \frac{0.059}{2} \log_{10} [\text{Ag}^{+}]^2$$

$$0 = E_{\text{OP}_{\text{Mg}/\text{Mg}^{+2}}}^{\ominus} + E_{\text{RP}_{\text{Ag}^{+}/\text{Ag}}}^{\ominus} + \frac{0.059}{2} \log_{10} \frac{[\text{Ag}^{+}]^2}{[\text{Mg}^{+2}]}$$

$$0 = 2.37 + 0.80 + \frac{0.059}{2} \log_{10} \frac{1}{K_c}$$

$$\therefore \log_{10} \frac{1}{K_c} = -107.457$$

$$\text{or } \log_{10} K_c = 107.457 \quad \text{and} \quad E_{\text{cell}}^{\ominus} = 2.37 + 0.80 = 3.17 \text{ V}$$

Now maximum work that can be obtained by cell is given by

$$-\Delta G^{\ominus} = W_{\text{max}}$$

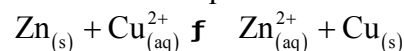
$$\therefore W_{\text{max}} = -\Delta G^{\ominus}$$

$$= n E^{\ominus} F = 2 \times 96500 \times 3.17$$

$$= 6.118 \times 10^5 \text{ joule}$$

$$= 6.118 \times 10^2 \text{ kJ}$$

Example 20: The potential of a standard electrochemical cell is 1.10 volt at 25°C temperature. Calculate the equilibrium constant and free energy change of the following given reaction:



Solution: For this reaction $n = 2$

$$\Delta G^\ominus = -nFE_{\text{cell}}^\ominus = -RT \ln K$$
$$= -2.303 RT \log K$$

$$\therefore \log K = \frac{nFE_{\text{cell}}^\ominus}{2.303RT} \quad (R = 8.314 \text{ JK}^{-1}\text{mol}^{-1})$$

$$= \frac{2 \times 96500 \times 1.1}{2.303 \times 8.314 \times 298} = 37.2074$$

$$\therefore K = 1.61 \times 10^{37}$$

$$\Delta G^\ominus = -nFE_{\text{cell}}^\ominus = -2 \times 96500 \times 1.1 \text{ coulomb-volt or joule}$$
$$= -212300.0 \text{ joule}$$

$$4.184 \text{ joule} = 1 \text{ calorie}$$

$$\therefore -\frac{212300}{4.184} = -50740.9 \text{ calorie} = -50.7409 \text{ kcal}$$

PROBLEMS**Exercise I****Theoretical Questions**

- Q.1** Arrange the following metals in the order in which they displace each other from the solution of their salts.
Al, Cu, Fe, Mg and Zn.
- Q.2** Given the standard electrode potentials,
 $K^+/K = -2.93V$, $Ag^+/Ag = 0.80V$,
 $Hg^{2+}/Hg = 0.79V$
 $Mg^{2+}/Mg = -2.37 V$, $Cr^{3+}/Cr = -0.74V$
Arrange these metals in their increasing order of reducing power.
- Q.3** Depict the galvanic cell in which the reaction $Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$ takes place. Further show:
(i) Which of the electrode is negatively charged?
(ii) The carriers of the current in the cell.
(iii) Individual reaction at each electrode.
- Q.4** Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration.
- Q.5** Predict the products of electrolysis in each of the following:
(i) An aqueous solution of $AgNO_3$ with silver electrodes.
(ii) An aqueous solution of $AgNO_3$ with platinum electrodes.
(iii) A dilute solution of H_2SO_4 with platinum electrodes.
(iv) An aqueous solution of $CuCl_2$ with platinum electrodes.

Numerical Problems

- Q.6** Calculate the standard cell potentials of galvanic cell in which the following reactions take place:
(i) $2Cr(s) + 3Cd^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 3Cd$
(ii) $Fe^{2+}(aq) + Ag^+(aq) \rightarrow Fe^{3+}(aq) + Ag(s)$
Calculate the $\Delta_r G^\ominus$ and equilibrium constant of the reactions.
- Q.7** Write the Nernst equation and emf of the following cells at 298 K:
(i) $Mg(s)|Mg^{2+}(0.001M)||Cu^{2+}(0.0001 M)|Cu(s)$
(ii) $Fe(s)|Fe^{2+}(0.001M)||H^+(1M)|H_2(g)(1bar)|Pt(s)$
(iii) $Sn(s)|Sn^{2+}(0.050 M)||H^+(0.020 M)|H_2(g) (1 bar)|Pt(s)$
(iv) $Pt(s)|Br_2(l)|Br^-(0.010 M)||H^+(0.030 M)|H_2(g) (1 bar)|Pt(s)$.
- Q.8** In the button cells widely used in watches and other devices the following reaction takes place:
 $Zn(s) + Ag_2O(s) + H_2O(l) \rightarrow Zn^{2+}(aq) + 2Ag(s) + 2OH^-(aq)$
Determine $\Delta_r G^\ominus$ and E^\ominus for the reaction.

- Q.9** The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 S cm^{-1} . Calculate its molar conductivity.
- Q.10** The resistance of a conductivity cell containing 0.001M KCl solution at 298 K is 1500Ω . What is the cell constant if conductivity of 0.001M KCl solution at 298 K is $0.146 \times 10^{-3} \text{ S cm}^{-1}$.
- Q.11** The conductivity of sodium chloride at 298 K has been determined at different concentrations and the results are given below:
- | | | | | | |
|--------------------------------------|-------|-------|-------|-------|--------|
| Concentration/M | 0.001 | 0.010 | 0.020 | 0.050 | 0.100 |
| $10^2 \times \kappa/\text{S m}^{-1}$ | 1.237 | 11.85 | 23.15 | 55.53 | 106.74 |
- Calculate Λ_m for all concentrations and draw a plot between Λ_m and $c^{1/2}$. Find the value of Λ_m^0 .
- Q.12** Conductivity of 0.00241 M acetic acid is $7.896 \times 10^{-5} \text{ S cm}^{-1}$. Calculate its molar conductivity. If Λ_m^0 for acetic acid is $390.5 \text{ S cm}^2 \text{ mol}^{-1}$, what is its dissociation constant?
- Q.13** How much charge is required for the following reductions:
 (i) 1 mol of Al^{3+} to Al.
 (ii) 1 mol of Cu^{2+} to Cu.
 (iii) 1 mol of MnO_4^- to Mn^{2+} .
- Q.14** How much electricity in terms of Faraday is required to produce
 (i) 20.0 g of Ca from molten CaCl_2 .
 (ii) 40.0 g of Al from molten Al_2O_3 .
- Q.15** How much electricity is required in coulomb for the oxidation of
 (i) 1 mol of H_2O to O_2 . (ii) 1 mol of FeO to Fe_2O_3 .
- Q.16** A solution of $\text{Ni}(\text{NO}_3)_2$ is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode?
- Q.17** Three electrolytic cells A,B,C containing solutions of ZnSO_4 , AgNO_3 and CuSO_4 , respectively are connected in series. A steady current of 1.5 amperes was passed through them until 1.45 g of silver deposited at the cathode of cell B. How long did the current flow? What mass of copper and zinc were deposited?
- Q.18** Using the standard electrode potentials, predict if the reaction between the following is feasible:
 (i) $\text{Fe}^{3+}(\text{aq})$ and $\text{I}^-(\text{aq})$
 (ii) $\text{Ag}^+(\text{aq})$ and $\text{Cu}(\text{s})$
 (iii) $\text{Fe}^{3+}(\text{aq})$ and $\text{Br}^-(\text{aq})$
 (iv) $\text{Ag}(\text{s})$ and $\text{Fe}^{3+}(\text{aq})$
 (v) $\text{Br}_2(\text{aq})$ and $\text{Fe}^{2+}(\text{aq})$.

Exercise II

Theoretical Questions

- Q.1** What is meant by Faraday constant?

- Q.2** Explain with examples the terms weak and strong electrolytes. How can these be distinguished?
- Q.3** Why do we get different products at cathode during the electrolysis of molten NaCl and aqueous sodium chloride?
- Q.4** (i) State Kohlrausch's law of independent migration of ions.
(ii) How can the law be applied for calculating degree of dissociation of weak electrolytes?
- Q.5** Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration. What is the effect of temperature on the molar conductivity?
- Q.6** What are the factors effecting the conductivity of electrolytic solutions?
- Q.7** Why is it not possible to determine Λ° for a weak electrolyte? Explain.
- Q.8** What is corrosion?
- Q.9** What are primary cells? How does a dry cell function?
- Q.10** Giving suitable examples explain the difference between galvanic cell and electrolytic cell.
- Q.11** Write down the expression for molar conductance. State the meaning of symbols used. What are its units?
- Q.12** Can we store copper sulphate in iron vessel? Why?
 $E^\ominus : \text{Cu}^{2+} | \text{Cu} = 0.34 \text{ V}$, $E^\ominus : \text{Fe}^{2+} | \text{Fe} = - 0.44 \text{ V}$.
- Q.13** How is electrical energy obtained in fuel cells?
- Q.14** How does the molar conductance of the electrolyte vary upon dilution?

Numerical Problems

- Q.15** How much charge is required for the following reductions:
(i) 1 mol of Cu^{2+} to Cu.
(ii) 1 mol of MnO_4^- to Mn^{2+}
- Q.16** How many faradays of charge would be required to reduce 21.0 g of $\text{Na}_2[\text{CdCl}_4]$ to metallic cadmium? If current strength is 7.5 ampere, how much time will be needed?(At. Wt. of Cd = 112.4)
- Q.17** In an electrolytic cell, how many moles of copper will be deposited from a solution of CuSO_4 by 24125C of electricity?
- Q.18** In a simple electrochemical cell, the half cell reaction with their standard electrode potentials are:
 $\text{Pb(s)} - 2\text{e}^- \rightarrow \text{Pb}^{2+}(\text{aq})$; $E^\ominus = - 0.13 \text{ V}$ $\text{Ag(s)} - \text{e}^- \rightarrow \text{Ag}^+(\text{aq})$; $E^\ominus = + 0.80 \text{ V}$
Which of the following reactions take place? Also calculate the e.m.f. of cell:

- (i) $\text{Pb}^{2+}(\text{aq}) + 2\text{Ag}(\text{s}) \rightarrow 2\text{Ag}^+(\text{aq}) + \text{Pb}(\text{s})$
 (ii) $\text{Pb}^{2+}(\text{aq}) + \text{Ag}(\text{s}) \rightarrow \text{Ag}^+(\text{aq}) + \text{Pb}(\text{s})$
 (iii) $\text{Ag}^+(\text{aq}) + \text{Pb}(\text{s}) \rightarrow \text{Ag}(\text{s}) + \text{Pb}^{2+}(\text{aq})$
 (iv) $2\text{Ag}^+(\text{aq}) + \text{Pb}(\text{s}) \rightarrow 2\text{Ag}(\text{s}) + \text{Pb}^{2+}(\text{aq})$

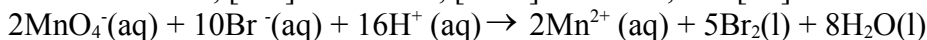
Q.19 Write the Nernst equation and e.m.f. of the following cells at 298 K:

- (i) $\text{Mg}(\text{s}) | \text{Mg}^{2+} (0.001\text{M}) || \text{Cu}^{2+} (0.0001 \text{M}) | \text{Cu}(\text{s})$
 (ii) $\text{Fe}(\text{s}) | \text{Fe}^{2+} (0.001 \text{M}) || \text{H}^+(1\text{M}) | \text{H}_2(\text{g}) (1 \text{bar}) | \text{Pt} (\text{s})$
 (iii) $\text{Sn}(\text{s}) | \text{Sn}^{2+} (0.050 \text{M}) || \text{H}^+(0.020 \text{M}) | \text{H}_2(\text{g}) (1 \text{bar}) | \text{Pt}(\text{s})$.

Given data-



Q.20 Calculate the emf of a cell operating with the following reaction at 25°C, in which $[\text{MnO}_4^-] = 0.010 \text{M}$, $[\text{Br}^-] = 0.010 \text{M}$, $[\text{Mn}^{2+}] = 0.15 \text{M}$, and $[\text{H}^+] = 1.0 \text{M}$.



Given data-



Q.21 In the commercial preparation of aluminum, aluminum oxide, Al_2O_3 , is electrolyzed at 1000°C. (The mineral cryolite is added as a solvent.) Assume that the cathode reaction is $\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$

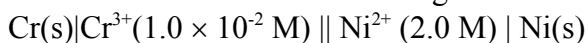
How many coulombs of electricity are required to give 5.12 kg of aluminum?

Q.22 Consider the given standard potential (in volts) in 1 M solution:



- (i) Comment on the relative stabilities of + 2 and + 3 oxidation states of iron and manganese.
 (ii) Which of the two metals may be more easily oxidized to + 2 state?

Q.23 Calculate the emf of the following cell at 25°C.



Given data –



Flashback

CBSE 2002

Q.1 How does a fuel cell operate?

(1 out of 70)

Q.2 The measured resistance of a conductance cell containing $7.5 \times 10^{-3} \text{M}$ solution of KCl at 25°C was 1005 ohms. Calculate (i) specific conductance (ii) molar conductance of the solution. Cell constant = 1.25cm^{-1} .

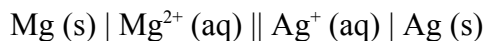
(3 out of 70)

CBSE 2003

Q.1 Why does the molar conductance increase on diluting the solution of a weak electrolyte? Electrolytic conductivity of 0.30 M solution of KCl at 298 K is $3.72 \times 10^{-2} \text{ S cm}^{-1}$. Calculate its molar conductivity.

(2 out of 70)

Q.2 (i) State the factors that influence the value of cell potential of the following cell :



(ii) Write Nernst equation to calculate the cell potential of the above cell.

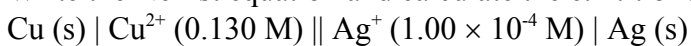
(2 out of 70)

CBSE 2004

Q.1 How does molar conductivity vary with concentration for (i) weak electrolyte and for (ii) strong electrolyte? Give reasons for these variations.

(2 out of 70)

Q.2 Write the Nernst equation and calculate the e.m.f. of the following cell at 298 K:



Given: $E^{\ominus}_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$ and $E^{\ominus}_{\text{Ag}^{+}/\text{Ag}} = +0.80 \text{ V}$.

(3 out of 70)

CBSE 2005

Q.1 Predict the products of electrolysis obtained at the electrodes in each case when the electrodes used are of platinum:

(i) An aqueous solution of AgNO_3

(ii) An aqueous solution of H_2SO_4 .

(2 out of 70)

Q.2 The E^{\ominus} values at 298 K corresponding to the following two reduction electrode processes are:

(i) $\text{Cu}^{+}/\text{Cu} = +0.52 \text{ V}$

(ii) $\text{Cu}^{2+}/\text{Cu}^{+} = +0.16 \text{ V}$

Formulate the galvanic cell for their combination. What will be the cell potential? Calculate the $\Delta_r G^{\ominus}$ for the cell reaction. ($F = 96500 \text{ C mol}^{-1}$)

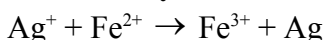
(3 out of 70)

Q.3 The half-reactions are

(i) $\text{Fe}^{3+} + e^{-} \rightarrow \text{Fe}^{2+}$, $E^{\ominus} = 0.76 \text{ V}$

(ii) $\text{Ag}^{+} + e^{-} \rightarrow \text{Ag}$, $E^{\ominus} = 0.80 \text{ V}$

Calculate K_c for the following reaction at 25° C :



($F = 96500 \text{ C mol}^{-1}$)

(5 out of 70)

CBSE 2006

Q.1 (a) State two advantages of $\text{H}_2 - \text{O}_2$ fuel cell over ordinary cell.

(2 out of 70)

(b) Silver is electrodeposited on a metallic vessel of total surface area 900 cm^2 by passing a current of 0.5 amp for two hours. Calculate the thickness of silver deposited.

[Given: Density of silver = 10.5 g cm^{-3} , Atomic mass of silver = 108 amu, $F = 96,500 \text{ C mol}^{-1}$]

(3 out of 70)

CBSE 2007

- Q.1** On the basis of the standard electrode potential values stated for acid solution, predict whether Ti^{4+} species may be used to oxidized Fe^{II} to Fe^{III} .

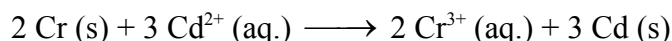
Reaction	E° / V
$\text{Ti}^{\text{IV}} + e^- \rightarrow \text{Ti}^{3+}$: + 0.01
$\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$: + 0.77

(2 out of 70)

- Q.2** Define conductivity and molar conductivity for the solution of an electrolyte.

(2 out of 70)

- Q.3** Calculate the standard cell potential of the galvanic cell in which the following reaction takes place:



Also calculate the $\Delta_r G^\circ$ value of the reaction.

(Given: $E^\circ_{\text{Cr}^{3+}/\text{Cr}} = -0.74 \text{ V}$; $E^\circ_{\text{Cd}^{2+}/\text{Cd}} = -0.40 \text{ V}$ and $F = 96500 \text{ C mol}^{-1}$)

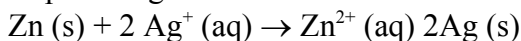
(3 out of 70)

CBSE 2008

- Q.1** Express the relation between the conductivity and the molar conductivity of a solution.

(1 out of 70)

- Q.2** Depict the galvanic cell in which the reaction



takes place, Further indicate what are the carriers of the current inside and outside the cell. State the reaction at each electrode.

(2 out of 70)

- Q.3** The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500Ω . What is the cell constant if the conductivity of 0.001 M KCl solution at 298 K is $0.146 \times 10^{-3} \text{ S cm}^{-1}$?

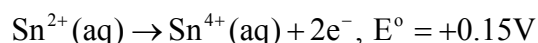
(2 out of 70)

CBSE 2009

- Q.1** What type of cell is a lead storage battery ? Write the anode and the cathode reactions and the overall cell reaction occurring in the use of a lead storage battery.

OR

Two half cell reactions of an electrochemical cell are given below :



Construct the redox equation from the two half cell reactions and predict if this reaction favours formation of reactants or product shown in the equation.

(2 out of 70)

- Q.2** A copper-silver cell is set up. The copper ion concentration in it is 0.10 M. The concentration of silver ion is not known. The cell potential measured 0.422 V. Determine the concentration of silver ion in the cell.

Given : $E^\circ_{\text{Ag}^+/\text{Ag}} = +0.80 \text{ V}$, $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$

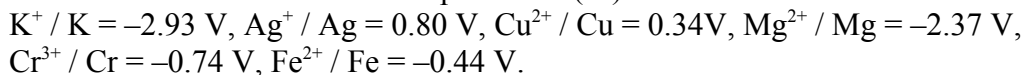
(3 out of 70)

CBSE 2010

Q.1 Express the relation among the cell constant, the resistance of the solution in the cell and the conductivity of the solution. How is the conductivity of a solution related to its molar conductivity ?

(2 out of 70)

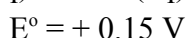
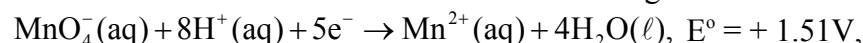
Q.2 Given that the standard electrode potentials (E°) of metals are :



Arrange these metals in an increasing order of their reducing power.

OR

Two half-reactions of an electrochemical cell are given below :



Construct the redox reaction equation from the two half-reactions and calculate the cell potential from the standard potentials and predict if the reaction is reactant or product favoured.

(2 out of 70)

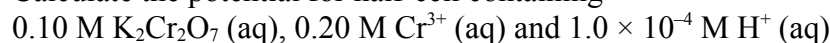
Q.3 Express the relation among the cell constant, the resistance of the solution in the cell and the conductivity of the solution. How is the conductivity of a solution related to its molar conductivity?

(2 out of 70)

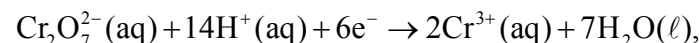
CBSE 2011

Q.1 (a) What type of a battery is lead storage battery? Write the anode and cathode reactions and the overall cell reaction occurring in the operation of a lead storage battery.

(b) Calculate the potential for half-cell containing



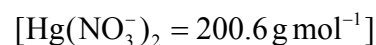
The half-cell reaction is



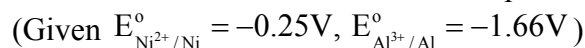
and the standard electrode potential is given as $E^\circ = 1.33 \text{ V}$.

OR

(a) How many moles of mercury will be produced by electrolysis of 1.0 M $Hg(NO_3)_2$ solution with a current of 2.00 A for 3 hours?



(b) A voltaic cell is set up at 25°C with the following half-cells Al^{3+} (0.001 M) and Ni^{2+} (0.50 M). Write an equation for the reaction that occurs when the cell generates an electric current and determine the cell potential.



(5 out of 70)

ANSWERS

Exercise I**Numerical Problems**

- Q.6** (i) $E^\ominus = 0.34\text{V}$, $\Delta_r G^\ominus = -196.86\text{ kJ mol}^{-1}$, $K = 3.16 \times 10^{34}$,
(ii) $E^\ominus = 0.03\text{V}$, $\Delta_r G^\ominus = -2.895\text{ kJ mol}^{-1}$, $K = 3.2$
- Q.7** (i) 2.68 V (ii) 0.53 V (iii) 0.08 V (iv) -1.315 V
- Q.8** 1.105 V **Q.9** 124.0 S cm² mol⁻¹ **Q.10** 0.210 cm⁻¹
- Q.12** 1.85×10^{-5} **Q.13** 3F, 2F, 5F **Q.14** 1F, 4.44 F
- Q.15** 2F, 1F **Q.16** 1.803 g
- Q.17** 14.40 min, Copper 0.427g, Zinc 0.437 g

Exercise II**Theoretical Questions**

- Q.1** It represents 96500 C of charge
- Q.11** $\Lambda = \frac{\kappa}{c}$ where c, the concentration of the electrolyte is expressed in mol m⁻³. The units of κ thus take the form Sm²mol⁻¹.

Numerical Problems

- Q.15** (i) 2F, (ii) 5F **Q.16** 0.140 F, 29.98 min **Q.17** $\frac{1}{8}$ mol
- Q.18** +0.93V **Q.19** (i) 2.68V (ii) 0.53 V (iii) 0.08V (iv) -1.315V
- Q.20** 0.29V **Q.21** 5.49×10^7
- Q.22** (i) Mn²⁺ is more stable than Fe²⁺ but Fe³⁺ is more stable than Mn³⁺
(ii) Mn will be oxidized to Mn²⁺ more readily as compared to Fe to Fe²⁺
- Q.23** 0.56V

Flashback**CBSE 2002**

- Q.2** (i) 0.001243 ohm⁻¹ cm⁻¹ (ii) 165.73 ohm⁻¹ cm² mol⁻¹

CBSE 2003

- Q.1** 124 S cm² mol⁻¹
- Q.2** (ii) $E_{\text{cell}}^\ominus - \frac{2.303RT}{2F} \log \frac{[\text{Mg}^{2+}(\text{aq})]}{[\text{Ag}^+(\text{aq})]^2}$

CBSE 2004

- Q.2** $E_{\text{cell}} = E_{\text{Ag}^+/\text{Ag}}^\ominus - E_{\text{Cu}^+/\text{Cu}}^\ominus - \frac{0.059}{2} \log \frac{[\text{Cu}^{2+}(\text{aq})]}{[\text{Ag}^+(\text{aq})]^2}$, 0.251V

CBSE 2005

- Q.2** $E_{\text{cell}}^\ominus = 0.36\text{V}$, $\Delta_r G^\ominus = -34740\text{ J mol}^{-1}$ **Q.3** $K_c = 4.746$

CBSE 2006

- Q.1** (b) $4.2 \times 10^{-4}\text{cm}$

CBSE 2007

- Q.1** Ti⁴⁺ would not oxidize Fe⁺² **Q.3** 196.86 KJmol⁻¹

CBSE 2008**Q.3** 0.219 cm^{-1} **CBSE 2009****Q.2** 0.069M **CBSE 2010****Q.2** $E^\circ = 1.46\text{V}$ **CBSE 2011****Q.1** (b) $E_{\text{cell}} = 0.78\text{V}$ **OR** (a) 0.112 moles of Hg (b) $E_{\text{cell}} = 1.46\text{V}$