Electrochemistry

1. Introduction

Electrochemistry: is the branch of chemistry concerned with the interrelation of electrical and chemical effects. A large part of this field deals with the study of chemical changes caused by the passage of an electric current and the production of electrical energy by chemical reactions. In other words, electrochemistry is the study of production of electricity from the energy released during a spontaneous chemical reaction and the use of electrical energy to bring about non-spontaneous chemical transformations.

1.1 Why scientists make electrochemical measurements?

Scientists make electrochemical measurements on chemical systems for a variety of reasons:

1. They may be interested in obtaining thermodynamic data about a reaction.

2. They may want to generate an unstable intermediate such as a radical ion ($M^{\cdot +}$ or $M^{\cdot -}$) and study its rate of decay or its spectroscopic properties.

3. They may seek to analyze a solution for trace amounts of metal ions or organic species.

In these examples, electrochemical methods are employed as tools in the study of chemical systems.

1.2 Why it is important to study the fundamental principles of electrode reactions?

There are also investigations in which the electrochemical properties of the systems themselves are of primary interest, for example, in the design of a new power source or for the electro-synthesis of some product (The main advantage of electro-synthesis over an ordinary redox reaction is selectivity and yield which result from control of the cell potential). Many electrochemical methods have been developed. Their application requires an understanding of the fundamental principles of electrode reactions and the electrical properties of electrode-solution (electrolyte) interfaces (Figure 1). In this course, the terms and concepts employed in describing electrode reactions are introduced.

2. Electrochemical Cells

In electrochemical systems, we are concerned with the processes and factors that affect the transport of charge across the interface between chemical phases, for example, between an electronic conductor (an electrode) and an ionic conductor (an electrolyte), See Figure 1. Throughout this course, we will be concerned with the electrode/electrolyte interface and the events that occur there.

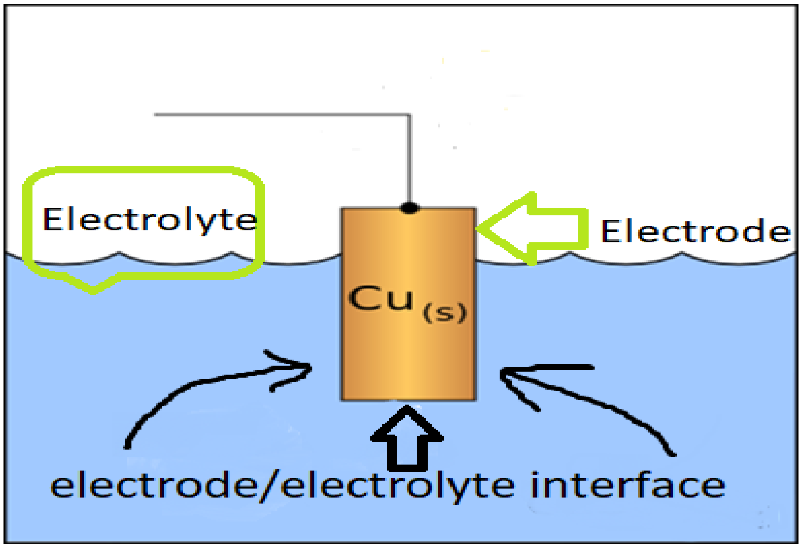

Figure 1. Copper electrode in an electrolyte

2.1 Electrode materials

Typical electrode materials include solid metals (e.g., Pt, Au), liquid metals (Hg, amalgams), carbon (graphite), and semiconductors (indium-tin oxide, Si). Electricity is the flow of free electrons in a conductor from one atom to the next atom in the same general direction. This flow of electrons is referred to as current and is designated by the symbol “I”. Electrons move through a conductor at different rates and electric current has different values. Current is determined by the number of electrons that pass through a cross-section of a conductor in one second. We must remember that atoms are very small.

Charge is transported through the electrode by the movement of electrons (and holes; the empty space of excited electrons which could be filled with recombined electrons), see Figure 2. In the electrolyte phase, charge is carried by the movement of ions. The most frequently used electrolytes are liquid solutions containing ionic species, such as, H^+, Na^+, Cl^-, in either water or a non-aqueous solvent. **To be useful in an electrochemical cell, the solvent/electrolyte system must be of sufficiently low resistance (i.e., sufficiently conductive) for the electrochemical experiment planned**.

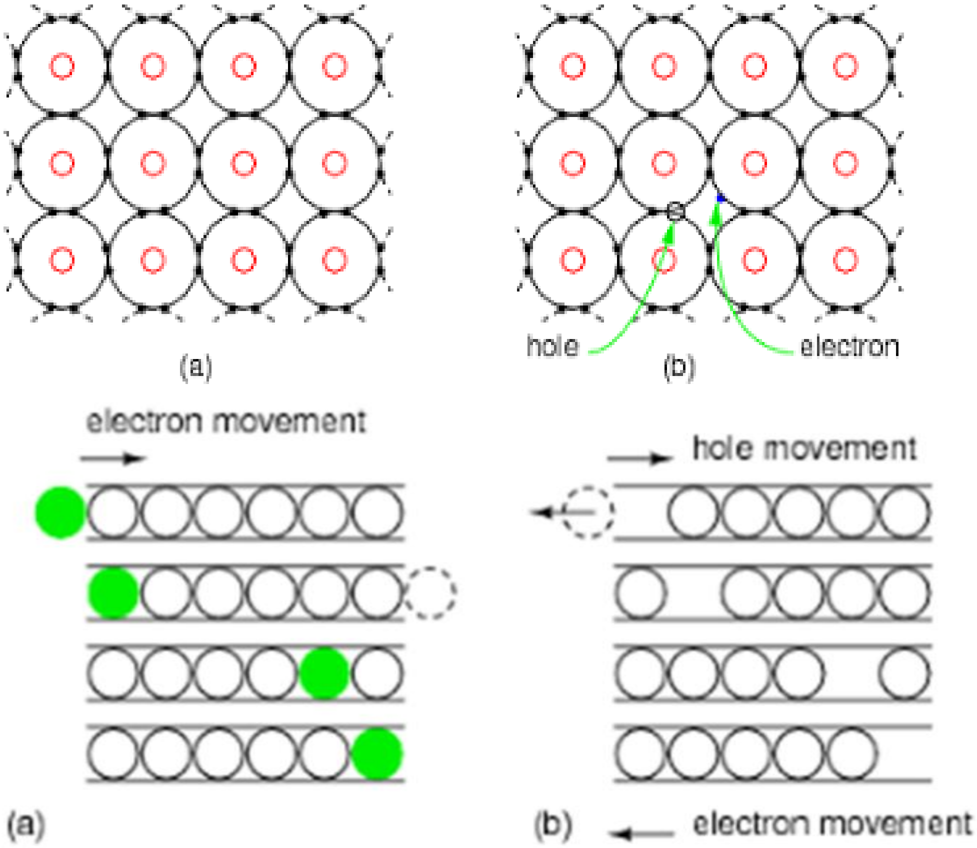

Figure 2. Electron and hole movement.

2.2. Do we experimentally need electrochemical cells?

It is natural to think about events at a single interface (ELECTRODE), but we will find that one cannot deal experimentally with such an isolated boundary. Instead, one must study the properties of collections of interfaces called **electrochemical cells**. These systems are defined most generally as two electrodes separated by at least one electrolyte phase.

3. Electro-neutrality

Nature seems to very strongly discourage any process that would lead to an excess of positive or negative charge in matter. Suppose, for example, that we immerse a piece of zinc metal in pure water. A small number of zinc atoms go into solution (DISSOLUTION) as Zn^{2+} ions, leaving their electrons behind in the metal (Figure 3):

$$\mathbf{Zn(s) \rightarrow Zn^{2+}_{(aq)} + 2e^-} \qquad \ldots\ldots\ldots\ \boldsymbol{Eq.1}$$

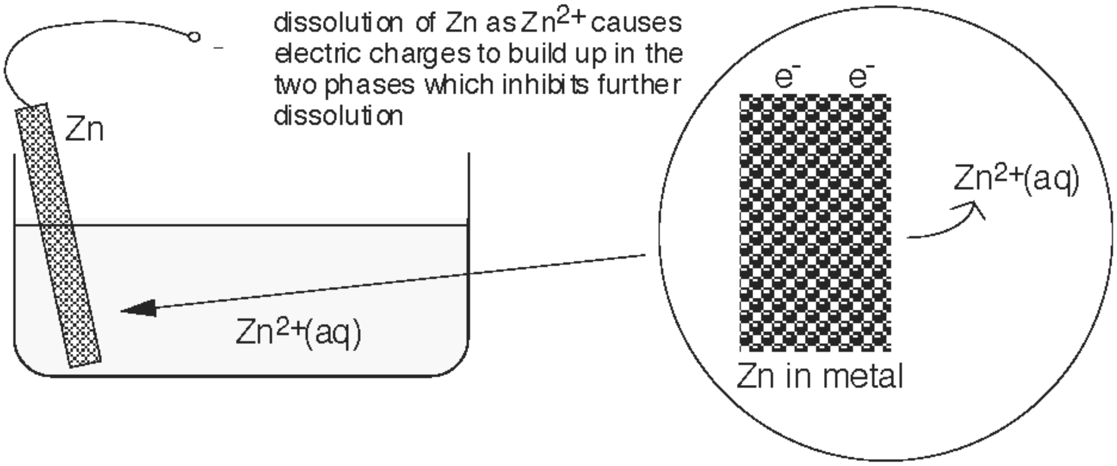

Figure 3: Oxidation of metallic zinc in contact with water.

As this process goes on, the electrons which remain in the zinc cause a negative charge to build up which makes it increasingly difficult for additional positive ions to leave the metallic phase. A similar buildup of positive charge in the liquid phase adds to this inhibition. Very soon, therefore, the process comes to a halt (STOP), resulting in a solution in which the concentration of Zn^{2+} is so low (around 10^{-10} M) that the water can still be said to be almost "pure". There would be no build-up of charge if the electrons could be removed from the metal as the positive ions go into solution.

The only way we can get the reaction in *Eq.* 1 to continue is to couple it with some other process that restores electro-neutrality to the two phases. A simple way to accomplish this would be immerse the zinc in a solution of copper sulfate instead of pure water. As you will recall if you have seen this commonly-performed experiment carried out, the zinc metal quickly becomes covered with a black coating of finely-divided metallic copper. The reaction is a simple oxidation-reduction process, a transfer of two electrons from the zinc to the copper:

$$\mathbf{Zn(s) \rightarrow Zn^{2+}_{(\boldsymbol{aq})} + 2e^{-} \qquad Cu^{2+}_{(\boldsymbol{aq})} + 2e^{-} \rightarrow Cu(s)} \ldots\ldots..\boldsymbol{Eq.}\mathbf{2}$$

The dissolution of the zinc is no longer inhibited by a buildup of negative charge in the metal, because the excess electrons are removed from the zinc by copper ions that come into contact with it. At the same time, the solution remains electrically neutral, since for each Zn^{2+}introduced to the solution, one Cu^{2+} is removed. The net reaction quickly goes to completion

$$\mathbf{Zn(s) + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(\boldsymbol{aq})} + Cu(s)} \quad \ldots\ldots\ldots\ldots\boldsymbol{Eq.}\mathbf{3}$$

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4. Types of electrochemical cells

A spontaneous chemical process is the one which can take place on its own and in such a process the Gibb's energy of the system decreases. It is this energy that gets converted to electrical energy. The reverse process is also possible in which we can make non-spontaneous processes occur by supplying external energy in the form of electrical energy. These inter conversions are carried out in equipments called Electrochemical Cells. Electrochemical cells consist of two electrodes: an anode (the electrode at which the oxidation reaction occurs) and a cathode (the electrode at which the reduction reaction occurs). There are two types of electrochemical cells: galvanic (ones that spontaneously produce electrical energy) and electrolytic (ones that consume electrical energy). Figure 4 shows a typical galvanic (Voltaic) electrochemical cells. Cell energy is extracted from a spontaneous chemical process or reaction and it is converted to electric current. For example, Daniell Cell is a Galvanic Cell in which Zinc and Copper are used for the redox reaction to take place. Zn is the reducing agent and Cu^{2+} is the oxidizing agent. The half cells are also known as **Electrodes**. The oxidation half is known as **Anode** and the reduction half is called **Cathode**. Electrons flow from anode to cathode in the external circuit. Anode is assigned **negative polarity** and cathode is assigned **positive polarity**. In Daniell Cell, Zn acts as the anode and Cu acts as the cathode. The cell potential is the difference between the reduction potential of cathode and anode.

E cell = E cathode — E anode

In the electrolytic cell the electrodes are dipped in an electrolytic solution containing cations and anions. On supplying current the ions move towards electrodes of opposite polarity and simultaneous reduction and oxidation takes place.

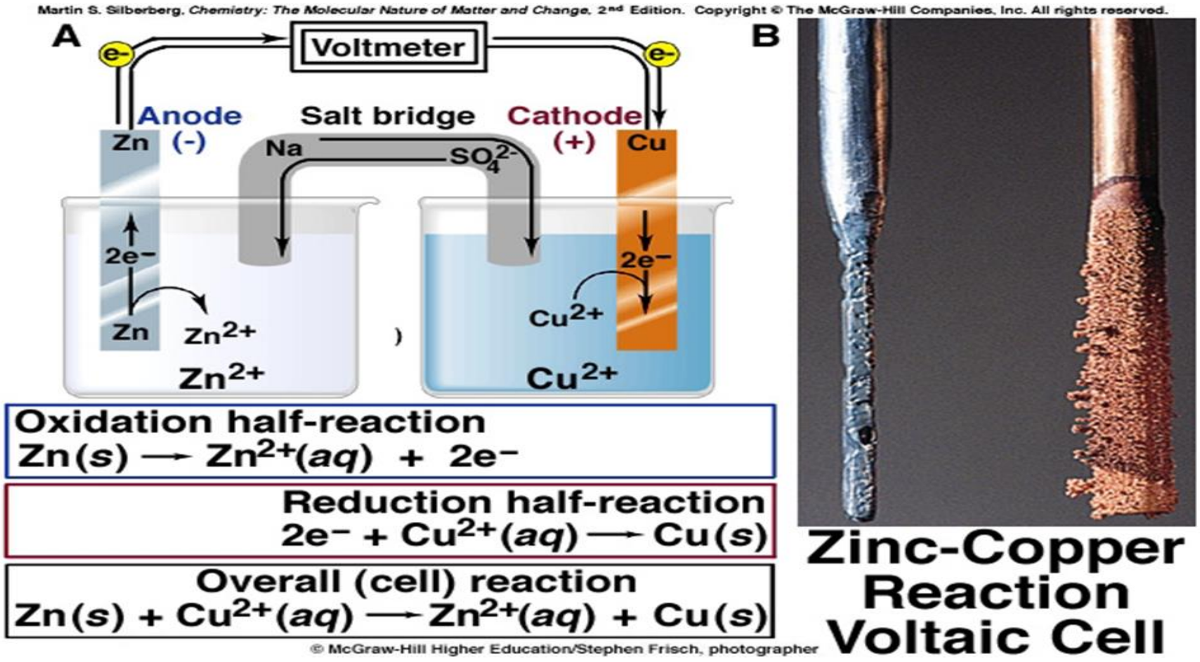


Figure 4: Typical galvanic electrochemical cells.

Purpose of using Salt bridge (Functions of Salt Bridge)

Salt bridge is used to maintain the charge balance and to complete the circuit by facilitating the flow of Ions through it. It contains a gel in which inert electrolytes like Na_2SO_4 or KNO_3 etc are mixed. Negative ions flow to the anode and positive ions flow to the cathode through the salt bridge and charge balance is maintained and cell keeps on functioning.
In other words,

a. Salt Bridge maintains electrical neutrality in solutions.

b. It completes circuit internally

4.1 Electrode potential

Electrode potential may be defined as the tendency of an element, when it is placed in contact with its own ions to either lose or gain electrons and in turn become positively or negatively charged. The electrode potential will be named as oxidation or reduction potential depending upon whether oxidation or reduction has taken place.

$$M(s) \underset{\text{reduction}}{\overset{\text{oxidation}}{\rightleftharpoons}} M^{n+}(aq) + ne^-$$

$$M^{n+}(aq) + ne^- \underset{\text{oxidation}}{\overset{\text{reduction}}{\rightleftharpoons}} M(s)$$

4.2 Expressing the structures of cells

It is useful to set up a shorthand notation for expressing the structures of the electrochemical cells. For example, the cell pictured in Figure 4 is written compactly as:

$$\mathbf{Zn(\mathit{s}) / Zn^{2+(}aq) // Cu^{2+}(aq) / Cu(s)}$$

In this notation, a slash represents a phase boundary; a double slash represents a phase boundary whose potential is regarded as a negligible component of the overall cell potential.

2. Conductivity Theory and Measurement

2.1 Introduction to conductivity

Conductivity is one of the important chemical parameter that gives valuable information to chemists in determining solubility products, dissociation constants and others properties of electrolytic solutions and also for quality control purposes. It depends on the total number of ions present in the solution and various physical and chemical phenomena lead to variations in conductance.

2.2 What is conductivity?

Conductivity is the ability of a solution, a metal or a gas - in brief all materials - to pass an electric current. In solutions the current is carried by cations and anions whereas in metals it is carried by electrons. How well a solution conducts electricity depends on a number of factors:

- Concentration
- Mobility of ions
- Valence of ions
- Temperature

All substances possess some degree of conductivity. In aqueous solutions the level of ionic strength varies from the low conductivity of ultra-pure water to the high conductivity of concentrated chemical samples.

2.2.1 How is conductivity measured?

Conductivity may be measured by applying an alternating electrical current (I) to two electrodes immersed in a solution and measuring the resulting voltage (V). During this process, the cations migrate to the negative electrode, the anions to the positive electrode and the solution acts as an electrical conductor (Figure 1). In a traditional 2-pole cell, an alternating current is applied between the 2 poles and the resulting voltage is measured. The aim is to measure the solution resistance (Rsol) only.

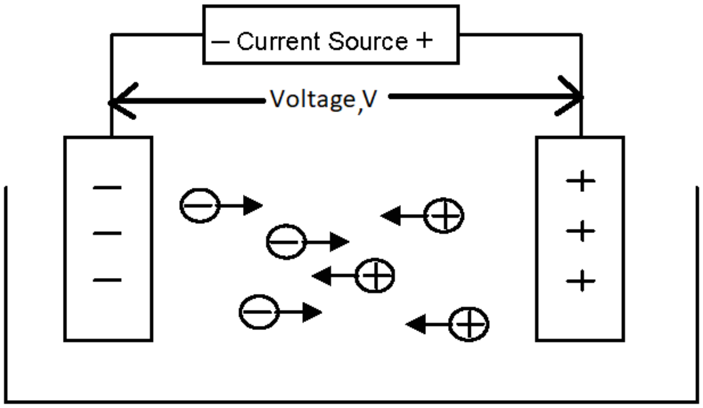


Figure 1 Migration of ions in solution.

2.3 Electrolytes

Conductivity is typically measured in aqueous solutions of electrolytes. Electrolytes are substances containing ions, i.e. solutions of ionic salts or of compounds that ionize in solution. The ions formed in solution are responsible for carrying the electric current. Electrolytes include acids, bases and salts and can be either strong or weak. Most conductive solutions measured are aqueous solutions, as water has the capability of stabilizing the ions formed by a process called solvation.

Strong electrolytes: Strong electrolytes are substances that are fully ionized in solution. As a result, the concentration of ions in solution is proportional to the concentration of the electrolyte added. They include ionic solids and strong acids, for example HCl. Solutions of strong electrolytes conduct electricity because the positive and negative ions can migrate largely independently under the influence of an electric field.

Weak electrolytes: Weak electrolytes are substances that are not fully ionized in solution. For example, acetic acid partially dissociates into acetate ions and hydrogen ions, so that an acetic acid solution contains both molecules and ions. A solution of a weak electrolyte can conduct electricity, but usually not as well as a strong electrolyte because there are fewer ions to carry the charge from one electrode to the other.

Non- electrolytes: Nonelectrolytes are compounds that do not ionize at all in solution. As a result, solutions containing nonelectrolytes will not conduct electricity. Typically, nonelectrolytes are primarily held together by covalent rather than ionic bonds. A common example of a nonelectrolyte is glucose, or $C_6H_{12}O_6$. Glucose (sugar) readily dissolves in water, but because it does not dissociate into ions in solution, it is considered a nonelectrolyte; solutions containing glucose do not, therefore, conduct electricity.

2.4 Definition of terms

1. Resistance

The resistance of the solution (R) can be calculated using Ohm's law

$V = I \times R$

$R = V/I$

Where:

V = voltage (volt)

I = current (ampere)

R = resistance of the solution (ohm)

2. Conductance (G)

Is defined as the reciprocal of the electrical resistance (R) of a solution between two electrodes.

$G = l/R$ (ohm^{-1} = mho)

The conductivity meter in fact measures the conductance, and displays the reading converted into conductivity.

3. Cell constant

This is the ratio of the distance (d) between the electrodes to the area (a) of the electrodes.

K=d/A

K = cell constant (cm^{-1})

A = effective area of the electrodes (cm^2)

d = distance between the electrodes (cm)

4. Conductivity or specific conductance (L)

It is the conductance of a material or solution between two electrodes of cross sectional area 1 cm^2 and separated by 1 cm distance. Note that this solution is occupying one cm^3 volume. It increases with increase in concentration of the electrolytic solution since the number of ions per unit area increases.

L=G x K

L= conductivity (**specific conductance)** $ohm^{-1}\ cm^{-1}$ = $moh\ cm^{-1}$

G = conductance (S), where G = 1/R

K = cell constant (cm^{-1})

5. Resistively

This is the reciprocal of the conductivity value and is measured in ohm.cm. It is generally limited to the measurement of ultra-pure water, the conductivity of which is very low.

6. Reference temperature

Conductivity readings are often referenced to a specific temperature, typically 20°C or 25°C, for comparative purposes. Automatic temperature correction Algorithms for automatic conversion of sample conductivity to a reference temperature.

7. Equivalent conductance

It is defined as the conducting power of all the ions produced by dissolving one gram equivalent of an electrolyte in solution. It is denoted by Λ.

Let us consider the V cm^3 of solution containing one equivalent of an electrolyte. Its conductance is equal to Λ.

Also we know that the conductance shown by 1 cm^3 solution containing this electrolyte is called specific conductance, L. i.e.,

the conductance of V cm^3 --------- Λ

the conductance of 1 cm^3 --------- L

Therefore: **$\Lambda = L \times V$ ………………………… (1)**

We know that the normality (N) of a solution is given by the equation:

$$N = \frac{n_e}{V(\text{in cc})} \times 1000$$

For above electrolytic solution, no. of equivalents, $n_e = 1$. Hence:

$$V(\text{in cc}) = \frac{1000}{N}$$

By substituting the above value in the equation (1), we can now write:

$$\Lambda = L \cdot \frac{1000}{N}$$

Unit of Λ:

$$= \frac{\text{Ohm}^{-1} \cdot \text{cm}^{-1}}{\text{equivalents} \cdot \text{cm}^{-3}}$$

$= \text{ohm}^{-1}\ \text{cm}^{2}\ \text{equiv}^{-1}$

8. Molar conductance: It is defined as the conducting power of all the ions produced by dissolving one gram mole of an electrolyte in the solution. It is expressed as

$$\Lambda_M = \frac{1000 \times L}{\text{Mormality}}$$

***Unit*: $\text{ohm}^{-1}\ \text{cm}^{2}\ \text{mole}^{-1}$**

2.5 Weak and Strong Electrolytes

Early studies revealed that the equivalent conductivities of electrolytes all diminish with concentration (or more accurately, with the square root of the concentration $\boldsymbol{\Lambda = \Lambda^{\infty} - b\sqrt{c}}$, see below), but they do so in several distinct ways that are distinguished by their behaviors at very small concentrations. This led to the classification of electrolytes as weak, intermediate, and strong (Figure 2).

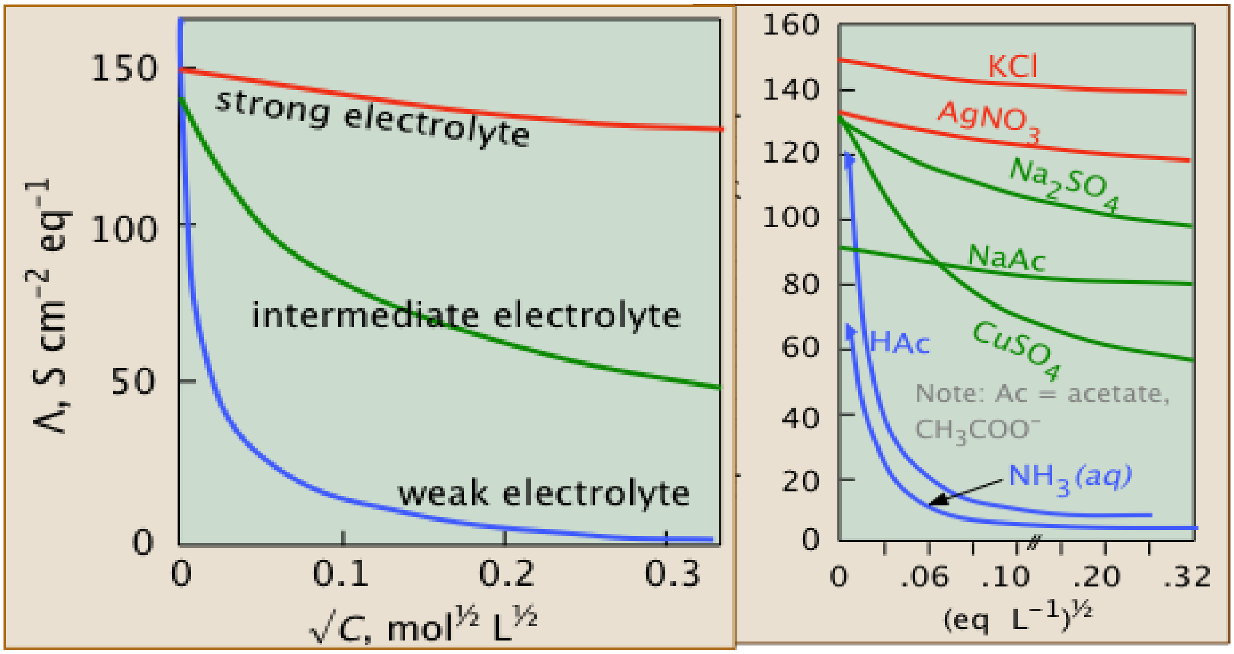


Figure 2. Plot of equivalent conductance Vs concentration for strong and weak electrolytes

You will notice that plots of conductivities vs. √*c* start at *c*=0. It is of course impossible to measure the conductance of an electrolyte at vanishingly small concentrations (not to mention zero), but for strong and intermediate electrolytes, one can extrapolate a series of observations to zero. The resulting values are known as *limiting equivalent conductance* or sometimes as "equivalent conductance at infinite dilution", titled by **Λ^{∞}.**

2.6 Effect of dilution on conductance

- The increase in dilution further increases the ionization of electrolyte.

- The specific conductance decreases with increase in ionization because the specific conductance is the conductance of the ions present in one centimeter cube of the solution. On dilution, the number of charge carrying ions present in $1cm^3$ of the solution becomes less. Hence specific conductance of an electrolyte decreases with dilution.
- Equivalent conductance/molar conductance of an electrolyte increases with dilution because both are the products of the specific conductance and volume of the solution. When volume increases by dilution, the number of ions in electrolyte solution also increases contributing to increase in conductance.

2.7 Kohlrausch’s law

At infinite dilution when the dissociation is complete, each ion makes a definite contribution towards the equivalent conductance of an electrolyte irrespective of the nature of other ion with which it is associated. *i.e* the equivalent conductance at infinite dilution for a given salt can be expressed as the sum of the contributions from the ions of the electrolyte.

$$\boldsymbol{\Lambda}^{\infty} = \boldsymbol{\lambda}^{\infty}_{cations} + \boldsymbol{\lambda}^{\infty}_{anions}$$

Where $\boldsymbol{\Lambda}^{\infty}$ is equivalent conductance of electrolyte at infinite dilution;

$\boldsymbol{\lambda}^{\infty}_{cations}$ is contribution of cations towards equivalent conductance at infinite dilution;

$\boldsymbol{\lambda}^{\infty}_{anions}$ is contribution of anions towards equivalent conductance at infinite dilution.

2.7.1 Experimental basis and theoretical explanation of Kohlrausch law

Kohlrausch observed that at infinite dilutions, the difference between the conductivities of sodium and potassium salts is constant irrespective of the associated anions, as tabulated below.

Salt pair	**Conductivity (mho cm^2 equiv)**	**Difference**
NaCl	108.90	21.20
KCl	130.10	
$NaNO_3$	105.33	21.17
KNO_3	126.50	
NaBr	111.10	21.20
KBr	132.30	

Kohlrausch argued that the constant difference in the conductivities of above pairs can be ascribed to the fact that the mobility of sodium and potassium ions at infinite dilution is not influenced by the nature of counter ions. The ions at such a low concentration migrate in the electric field as they are independent i.e., they show same ionic conductance irrespective of the nature of counter ion.

2.7.2 Applications of Kohlrausch's law

1. Calculation of equivalent conductance at infinite dilution or weak electrolytes:

It is not possible to determine the equivalent conductance at infinite dilution for weak electrolytes experimentally.

However, this can be calculated by using Kohlrausch's law.

Example: CH_3COOH: $\Lambda^\infty (CH_3COOH) = \lambda^\infty (CH_3COO^-) + \lambda^\infty (H^+)$

This equation can be obtained by the knowledge of equivalent conductance at infinite dilution for some strong electrolytes like HCl, NaCl, CH_3COONa.

CH_3COONa: $\Lambda^\infty (CH_3COONa) = \lambda^\infty (CH_3COO^-) + \lambda^\infty (Na^+)$

HCl: $\Lambda^\infty (HCl) = \lambda^\infty (H^+) + \lambda^\infty (Cl^-)$

NaCl: $\Lambda^\infty (NaCl) = \lambda^\infty (Na^+) + \lambda^\infty (Cl^-)$

It is clear that,

$$\lambda^\infty(CH_3COO^-) + \lambda^\infty(H^+) = [\lambda^\infty(CH_3COO^-) + \lambda^\infty(Na^+)] + [\lambda^\infty(H^+) + \lambda^\infty(Cl^-)] - [\lambda^\infty(Na^+) + \lambda^\infty(Cl)]$$

Example: Calculate $\wedge^{\infty}$ for NH_4OH from the following experimental results:

$\wedge^{\infty}(NaOH)= 247.8x10^{-4}$ ohm^{-1} cm^{2} $equiv^{-1}$; $\wedge^{\infty}$ (NH_4Cl)=$149.7x10^{-4}$ ohm^{-1} cm^{2} $equiv^{-1}$; $\wedge^{\infty}(NaCl)=126.45x10^{-4}$ ohm^{-1} cm^{2} $equiv^{-1}$ at $25^{0}C$.

$\wedge^{\infty}(NH_4OH) = \wedge^{\infty}(NH_4Cl) + \wedge^{\infty}(NaOH) - \wedge^{\infty}(NaCl)$………………… (**Homework**)

2. Calculation of degree of dissociation of weak electrolytes:

Equivalent conductance of a weak electrolyte depends upon its degree of dissociation. Higher the degree of dissociation, larger the equivalent conductance. With increase in dilution, the conductance increases and at infinite dilution, the electrolyte is completely dissociated so that degree of dissociation becomes one (at C→0). The degree of dissociation at any concentration is given by

$$\alpha = \frac{\textbf{Actual no of ions formed due to partial dissociation}}{\textbf{Expected no of particles formed due to complete dissociation}}$$

Since the conductance is proportional to the number of ions in the solution, the degree of ionization is equal to the conductance ratio as given below;

$$\boldsymbol{\alpha} = \frac{\wedge^{c}}{\wedge^{\infty}} = \frac{\wedge^{c}}{\boldsymbol{\lambda}^{\infty}_{cation} + \boldsymbol{\lambda}^{\infty}_{anion}}$$

Where

Λ^{c}= equivalent conductivity at given concentration.

Λ^{∞} = equivalent conductivity at infinite dilution.

$\lambda^{\infty}_{\textbf{cation}}$ = equivalent conductivity of cation at infinite dilution.

$\lambda^{\infty}_{\textbf{anion}}$ = equivalent conductivity of anion at infinite dilution.

2.8 Factors affecting the conductance of electrolyte solutions

1. Temperature: The conductance of an electrolyte solution increases with increase in the temperature due to increase in the extent of ionization.

2. Nature of electrolyte:

* The strong electrolytes undergo complete ionization and hence show higher conductivities since they furnish more number of ions.
* Whereas weak electrolytes undergo partial ionization and hence show comparatively low conductivities in their solutions.

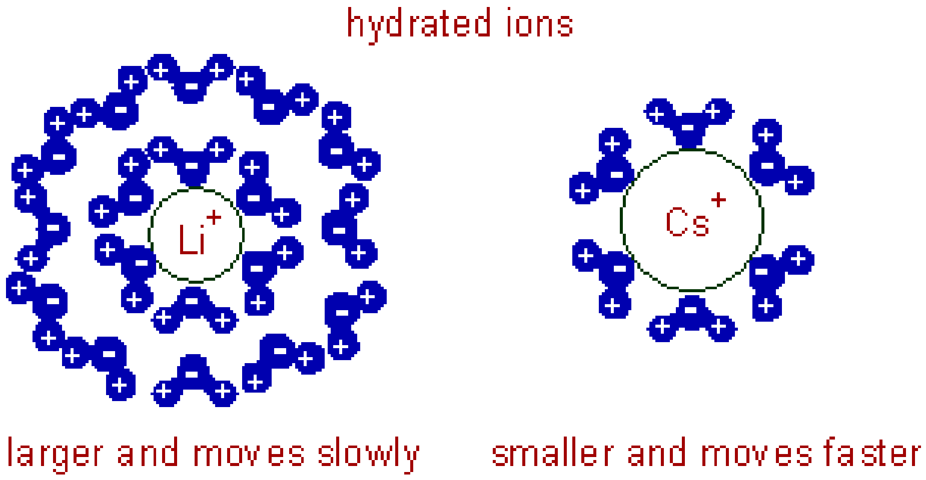
3. Ionic size & mobility:

The ionic mobility decreases with increase in its size and hence conductivity also decreases.

E.g. In molten state, the conductivities of lithium salts are greater than those of cesium salts since the size of Li^+ ion is smaller than that of Cs^+ ion.

However, in aqueous solutions the extent of hydration affects the mobility of the ion, which in turn affect the conductivity. Heavily hydrated ions show low conductance values due to larger size.

E.g. In aqueous solutions Li^+ ion with high charge density is heavily hydrated than Cs+ ion with low charge density. Hence hydrated Li+ bigger than hydrated Cs^+. As a result, lithium salts show lower conductivities compared to those of cesium salts in water.



4. **The nature of solvent and its viscosity:**

The ionic mobility is reduced in more viscous solvents. Hence the conductivity decreases.

5. Concentration:

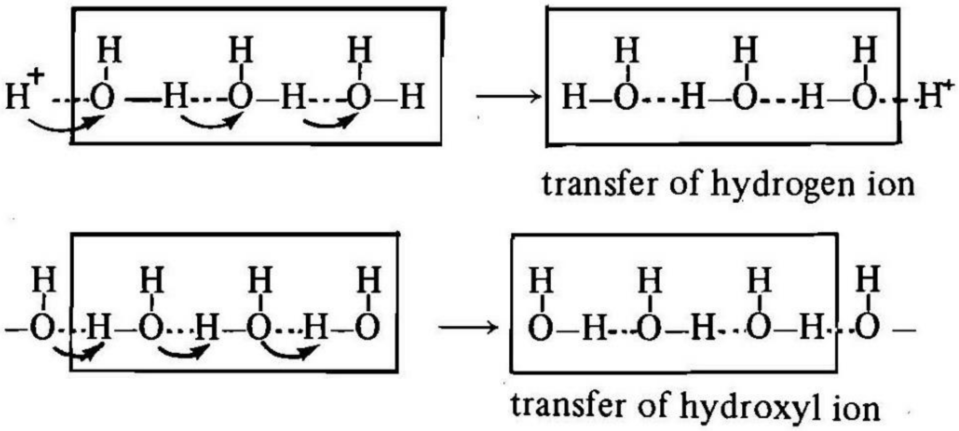
*The specific conductance (L) increases with increase in concentration of solution as the number of ions per unit volume increases.

* Whereas, both the equivalent conductivity and molar conductance increase with decrease in concentration (i.e. upon dilution) since the extent of ionization increases.

Explanation: Since the concentration decreases, one can expect decrease in equivalent conductivity due to decrease in available number of ions per unit volume. However the increase in volume (V) factor more than compensates this effect. The volume must be increased in order to get one equivalent of electrolyte since the concentration is decreased. Hence the net effect is increase in equivalent conductivity.

2.9 Conductivities of hydrogen and hydroxyl ions.

The conductivities of hydrogen and hydroxyl ions are unexpectedly high, being about 7 and 3 times that of the average value for other ions respectively. It is known that water is polymerized in chains $(H_2O)_n$, [where n = 2 – 5] and that hydrogen and hydroxyl ions are highly hydrated in aqueous solutions. Thus the very high conductivities of these two ions cannot be accounted for by the actual ease of motion of the ions themselves. It seems likely that a special mechanism takes place so that these ions do not actually have to move through the solution. It is thought that these ions are able to pass on their charge from one water molecule to another by the transfer of a hydrogen ion or a hydroxyl ion in the following way:



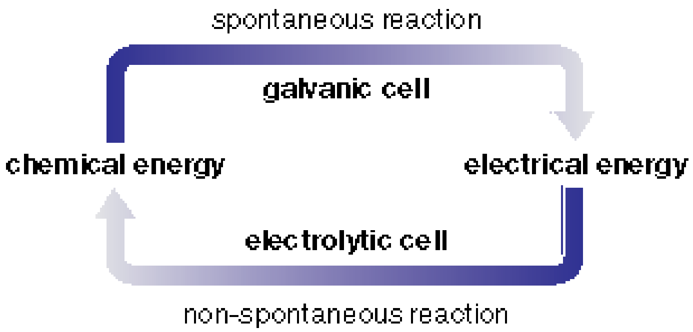
(The dotted lines indicate hydrogen bonds)

These processes can occur very rapidly and can be continued through the solution, causing the charge to transfer through the solution faster than the speed at which the ions can move, and hence resulting in abnormal conduction. This mechanism is similar to the manner of conducting electricity in metal, i.e. "one end in and the other end out."

However such mechanism involves the chain reactions of bond breaking and bond forming and hence the conductivity of hydrogen ion and hydroxyl ion respectively is still .much smaller than conduction in metals.

3. Electrolysis

We have already seen (Chapter one) how a spontaneous chemical reaction can be used to generate a flow of electrons (an electric current). In this Chapter, you will see how an electric current can be used to make a non-spontaneous redox reaction occur.



3.1 Electrolysis - the process

In an electrochemical cell or galvanic cell, a spontaneous chemical reaction produces an electric current. In an electrolytic cell, the reverse process takes place. The passage of an electric current through an electrolytic solution causes a chemical reaction. This process is known as electrolysis. In galvanic cells, chemical reactions can be used to generate a flow of electrons (an electric current). If a zinc rod is placed in copper (II) sulfate solution, a coating of copper appears on the zinc rod. This may be explained by considering the **standard electrode potentials ($E^{\bar{o}}$)** of each half-equation:

$Cu^{2+(}aq) + 2e^{-} \rightleftharpoons Cu(s) \quad E^{\bar{o}} = +0.34\ V$

$Zn^{2+}(aq) + 2e^{-} \rightleftharpoons Zn(s) \quad E^{\bar{o}} = -0.76\ V$

Since the $E^{\bar{o}}$ value for the Cu^{2+}/Cu redox pair is greater than the $E^{\bar{o}}$ value for the Zn^{2+}/Zn redox pair, Cu^{2+} ions react spontaneously with zinc metal. A galvanic cell constructed from these two half-cells would produce electrical energy. The overall equation for such a galvanic cell would be:

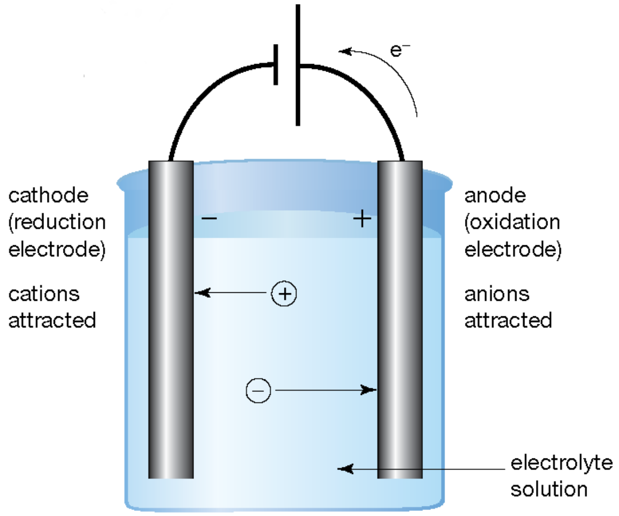
$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+(}aq) + energy$

However, if a copper rod is placed in a zinc sulfate solution, no reaction occurs. Since this reaction is the reverse of the one that produces energy, energy must be supplied for the reaction to occur:

$$\mathbf{Cu(s) + Zn^{2+}(aq) + energy \rightarrow Cu^{2+}(aq) + Zn(s)}$$

3.2 Electrolytic cells

The chemical reaction that occurs when electricity passes through a molten ionic compound or through an electrolyte solution is called electrolysis. Solutes that form solutions that can conduct electricity are called electrolytes. An electrolyte solution conducts electricity. Positive ions gain electrons at the cathode and negative ions lose electrons at the anode. This transfer of electrons has the same effect as a flow of electrons, and the solution conducts electricity. The apparatus in which electrolysis occurs is called an electrolytic cell (**Figure 3.1**).



Conducting solutions are known as electrolytes.

Electrolysis occurs in an electrolytic cell.

Figure 3.1. An electrolytic cell

3.2.1 What are the features of an electrolytic cell?

An electrolytic cell has three essential features:

1. An electrolyte solution that contains free-moving ions. These ions can donate or accept electrons, allowing electrons to flow through the external circuit.

2. Two electrodes at which the electrolysis reactions occur

3. An external source of electrons, such as a battery or power pack. This electron flow is in one direction only and is termed DC (direct current). The electrode to which electrons flow from the external power source is the negative electrode and is called the cathode, since reduction occurs there.

The electrode from which electrons are withdrawn by the power source is the positive electrode and is called the anode, since oxidation occurs there. Cations are attracted to the cathode, while anions are attracted to the anode. The cations gain electrons from the cathode and the anions give up electrons to the anode.

3.2.2 Comparing galvanic and electrolytic cells

Consider the following redox half-equations:

$\mathbf{Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \quad E^{\bar{o}} = +\,0.34\ V}$

$\mathbf{Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \quad E^{\bar{o}} = -\,0.76\ V}$

Electrical energy can be obtained from the spontaneous reaction between copper (II) ions and zinc metal in a galvanic cell:

$\mathbf{Cu^{2+}(aq) + Zn(s) \rightarrow \quad Cu(s) + Zn^{2+}(aq)}$

When standard half-cells are used, 1.1 volts **($E^{\bar{o}}$ cathode - $E^{\bar{o}}$ anode)** may be generated by the cell. If, however, an external DC power source is placed in the external circuit and connected so that the applied voltage is opposite to that generated by the galvanic cell, the reverse reaction proceeds:

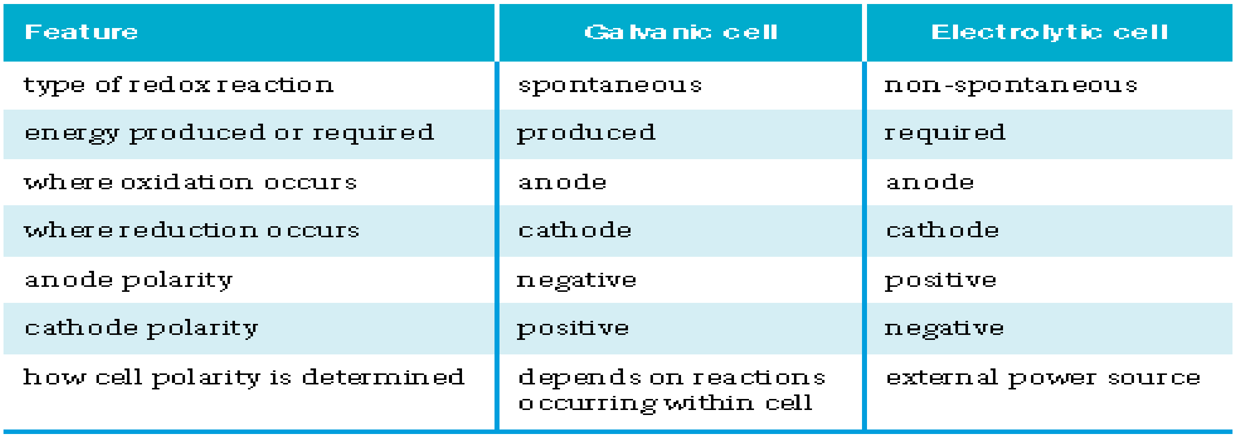
$$Cu(s) + Zn^{2+}(aq) \rightarrow Cu^{2+}(aq) + Zn(s)$$

When standard half-cells are used, more than 1.1 volts is needed to force this non-spontaneous reaction to occur.

In both galvanic and electrolytic cells, oxidation occurs at the anode and reduction occurs at the cathode. However, in an electrolytic cell, the cathode is negative since the external DC source forces electrons onto it. Zinc ions, Zn^{2+}, are therefore attracted to the cathode where they pick up electrons to form zinc atoms.

The anode in an electrolytic cell is positive since the DC source withdraws electrons from it. Electrons are supplied to the positive anode by the oxidation of the copper electrode itself. In an electrolytic cell, the polarity of the electrodes is determined by the external DC source. In contrast, the polarity of the electrodes in a galvanic cell develops due to the spontaneous redox reaction occurring within the cell itself (Figure 3.2). Table 3.1 summarizes the major similarities and differences between galvanic and electrolytic cells.

Table 3.1: Comparison of galvanic and electrolytic cells



Feature	Galvanic cell	Electrolytic cell
type of redox reaction	spontaneous	non-spontaneous
energy produced or required	produced	required
where oxidation occurs	anode	anode
where reduction occurs	cathode	cathode
anode polarity	negative	positive
cathode polarity	positive	negative
how cell polarity is determined	depends on reactions occurring within cell	external power source

An electrolytic cell consists of an electrolyte, electrodes and a power supply.

Electrons are supplied to the cathode and withdrawn from the anode by the power supply.

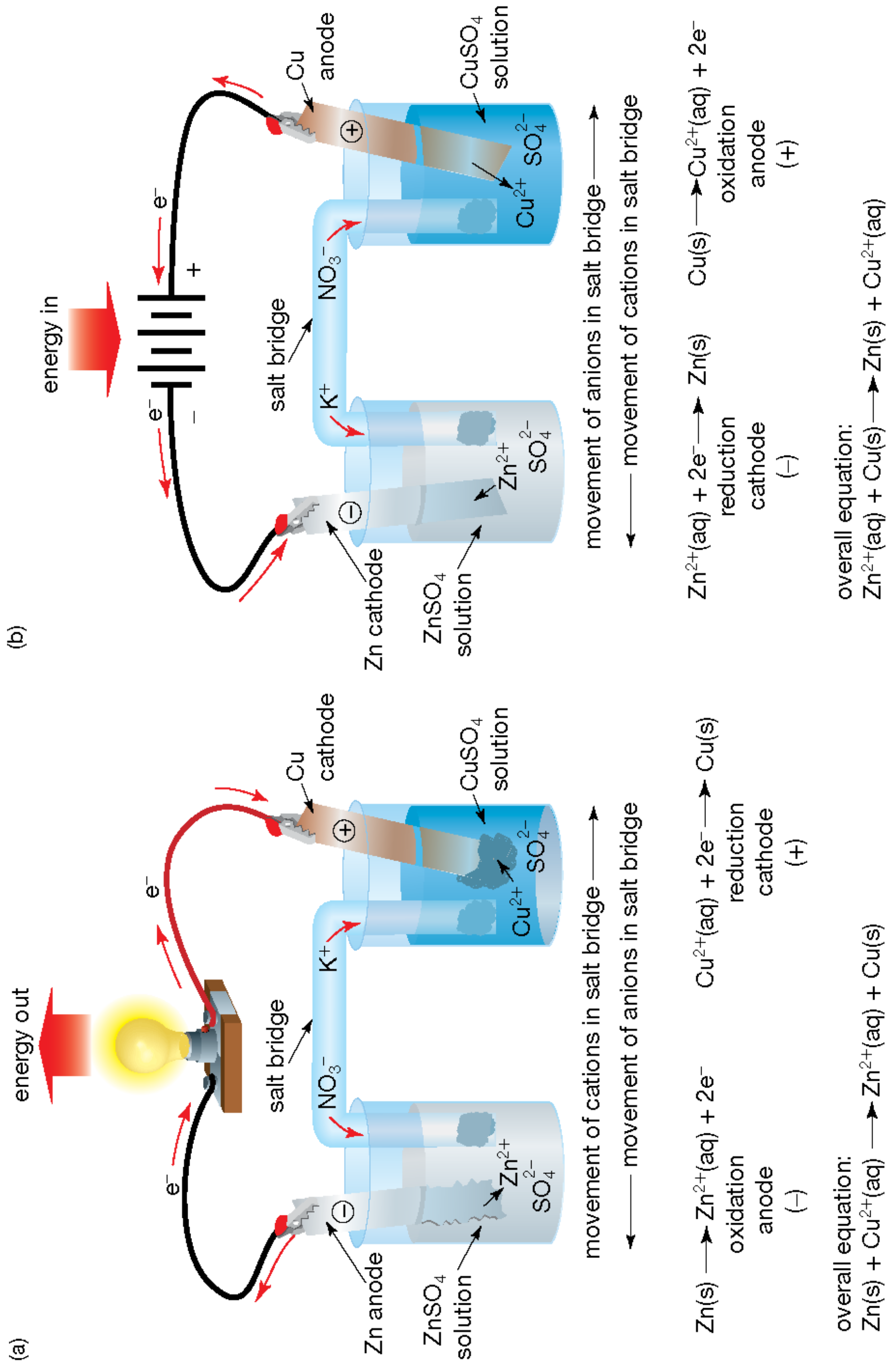


Figure 3.2. Comparison of zinc–copper half-cells in electrochemical and electrolytic reactions (a) Daniell cell showing fully labelled components, half-equations and overall equation (b) Electrolytic cell showing fully labelled components, half-equations and overall equation.

3.3 Electrolysis of molten ionic compounds

The simplest cases of electrolysis involve the electrolysis of molten ionic substances that are pure, using inert electrodes. As an example, let us consider the electrolysis of molten sodium chloride. Solid sodium chloride does not conduct electricity. However, when an electric current is passed through molten sodium chloride, a chemical reaction may be clearly observed. A shiny bead of sodium is produced at the cathode and chlorine gas is evolved at the anode (**Figure 3.3)**.

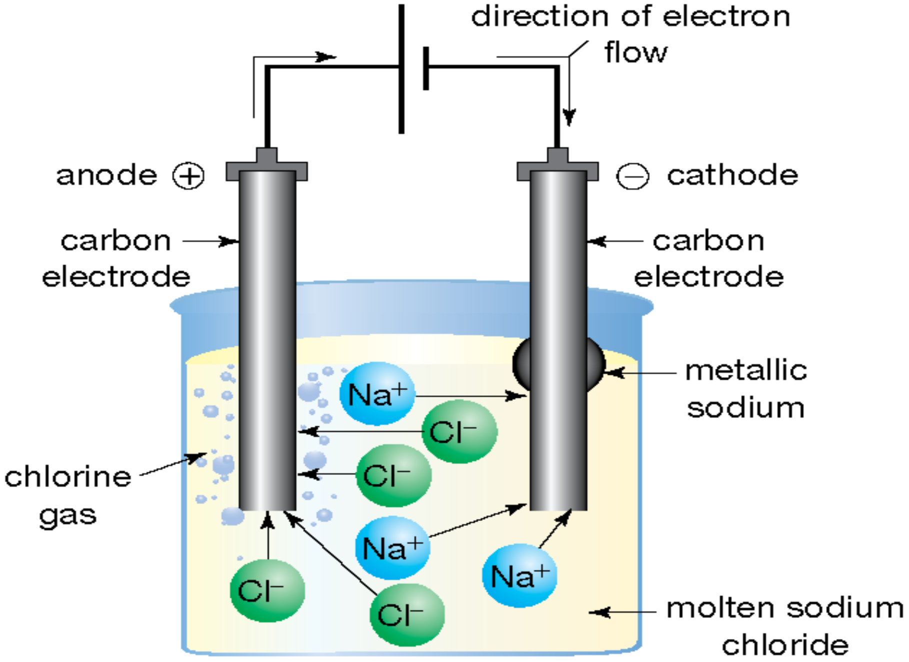


Figure 3.3. Electrolysis of molten sodium chloride.

In solid sodium chloride, the oppositely charged sodium ions, Na^+, and chloride ions, Cl^-, are held tightly together. Heating the solid causes the ions in the crystal to separate so they are then free to move. The molten liquid is called a melt. In an electrolytic cell, the sodium ions are attracted to the negative cathode where they are reduced:

$$Na^+(l) + e^- \rightarrow Na(l)$$

The chloride ions are attracted to the positive anode where they undergo (suffer) oxidation:

$$2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$$

Since, in a redox reaction, the same number of electrons are consumed as are produced, the overall equation is:

$$2Na^+(l) + 2Cl^-(l) \rightarrow 2Na(l) + Cl_2(g)$$

3.4 Electrolysis of water

When a current is applied via two electrodes in pure water, nothing happens. There is no current flow and no electrolysis. If, however, an electrolyte such as H_2SO_4 or KNO_3 is added in ***low*** concentration, the resulting solution conducts electricity and electrolysis occurs. The products of the electrolysis of water, in this case, are hydrogen and oxygen (Figure 3.4).

At the cathode, water is reduced to form hydrogen:

$$2H_2O\ (l) + 2e^- \rightarrow H_2\ (g) + 2OH^-\ (aq)$$

At the anode, water is oxidized to form oxygen:

$$2H_2O\ (l) \rightarrow O_2\ (g) + 4H^+\ (aq) + 4e^-$$

The region around the cathode becomes basic owing to an increase in OH^- ions, whereas the region around the anode becomes acidic, owing to an increase in H^+ ions. The overall cell reaction may be obtained by adding the half-equations:

$$6H_2O\ (l) \rightarrow 2H_2\ (g) + O_2\ (g) + 4H^+\ (aq) + 4OH^-\ (aq)$$

However, some of the ions produced re-form into reactants:

$$4H^+\ (aq) + 4OH^{-(}aq) \rightarrow 4H_2O(l)$$

and so do not need to be included in the final overall equation:

$$2H_2O\ (l) \rightarrow 2H_2(g) + O_2(g)$$

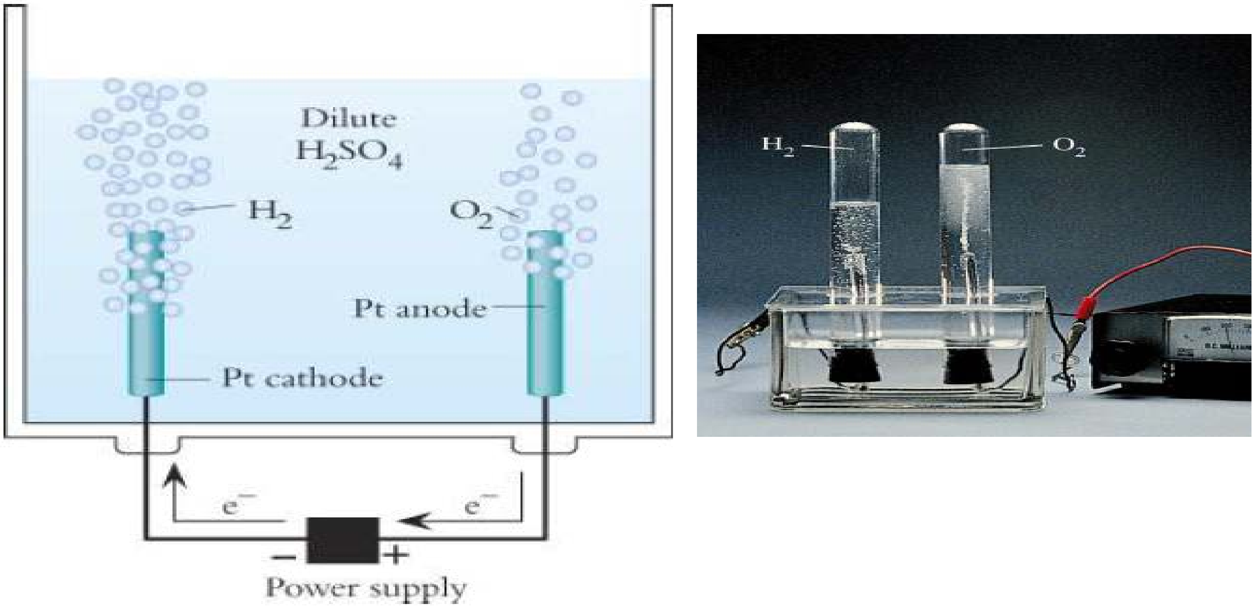


Figure 3.4 Electrolysis of water

3.5 Electrolysis of aqueous solutions of ionic compounds

When a molten salt is electrolysed, the products are predictable. However, as seen previously, when an aqueous solution of an ionic compound is electrolysed, water may react at one or both of the electrodes in preference to the ions from the salt. Hydrogen sometimes appears at the cathode, rather than a metal, and oxygen sometimes appears at the anode, rather than a metal cation or a halogen. For this reason, we need to be able to predict the products of electrolysis when there is more than one possible reaction around an electrode.

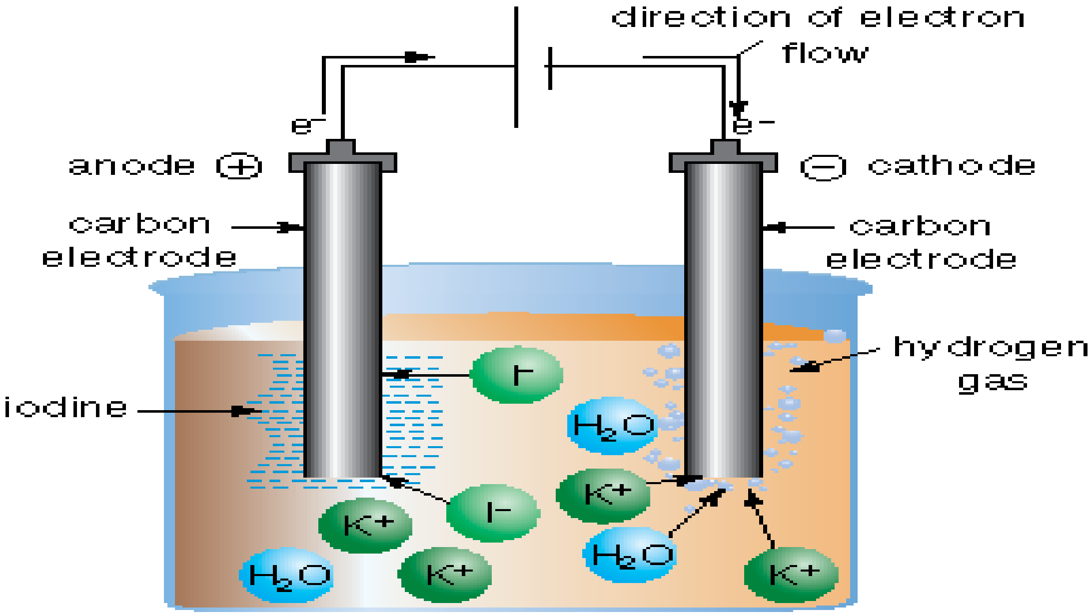


Figure 3.5. Electrolysis of dilute potassium iodide

How to predict reactions during electrolysis of aqueous solutions of ionic compounds?

In aqueous solutions, there is a mixture of at least two oxidizing agents and two reducing agents. If non-inert electrodes are used, then even more possibilities may exist. Which oxidizing agent and which reducing agent react? Although electrolytic products depend on a number of factors, the following procedure is useful.

1. List the species present, including all metals that are used as electrodes. (Given)

2. Write half-equations involving these species in descending order of E^{o}. (Given)

3. Circle the species present in the electrolytic cell that could participate.

4. Select the oxidising agent with the highest E^{o} (the strongest oxidizing agent). This will be reduced at the cathode, since it requires less energy for reduction than an oxidizing agent with a lower E^{o}.

5. Select the reducing agent with the lowest E^{o} (the strongest reducing agent). This will be oxidized at the anode, since it requires less energy for oxidation than a reducing agent with a higher E^{o}.

6. Write the overall equation.

7. Determine the minimum voltage required to achieve the reaction by using the formula: **Minimum voltage required = $E^{\bar{o}}$ oxidizing agent – $E^{\bar{o}}$ reducing agent**

The electrolysis of dilute potassium iodide is shown above. With potassium ions, iodide ions and water present in the cell, the possible half-cell reactions are:

$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l) \quad E^{\bar{o}} = +1.23\ V$

$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq) \quad E^{\bar{o}} = +0.54\ V$

$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq) \quad E^{\bar{o}} = -0.83\ V$

$K^+(aq) + e^- \rightleftharpoons K(s) \quad E^{\bar{o}} = -2.93\ V$

Reduction occurs at the cathode, so there are two possible reactions in this cell. The species that requires the least energy for reduction (the oxidizing agent with the highest $E^{\bar{o}}$ value - the strongest oxidizing agent) reacts at the cathode. So, water reacts in preference to potassium ions at the cathode:

$2H_2O\ (l) + 2e^- \rightarrow H_2\ (g) + 2OH^-\ (aq) \quad E^{\bar{o}} = -0.83\ V$

Hydrogen gas is evolved at this electrode and the solution around the cathode becomes alkaline, owing to an increase in hydroxide ion concentration.

Oxidation occurs at the anode, so there are two possible reactions. The species that requires the least energy for oxidation (the reducing agent with the lowest $E^{\bar{o}}$ value) reacts at the anode. Thus, iodide ions react in preference to water molecules at the anode:

$2I^-\ (aq) \rightarrow I_2(s) + 2e^- \quad E^{\bar{o}} = +0.54\ V$

The solution around the anode appears yellow-brown, owing to the formation of iodine.

The overall electrolytic cell reaction would be:

$2H_2O\ (l) + 2I^-\ (aq) \rightarrow H_2\ (g) + 2OH^-\ (aq) + I_2(s)$

To achieve this reaction, a potential difference greater than the spontaneous reverse reaction would need to be applied. So more than +0.54 − (−0.83) = 1.37 volts should be delivered to this electrolytic cell.

Sample Problem: What products form during electrolysis of aqueous solution of KBr? Write the overall equation. How many volts should be delivered to this electrolytic cell?

Knowing that:

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4\bar{e}$ $E^{\bar{o}} = 1.23$ V (reduction potential)

$2Br^-(aq) \rightarrow Br_2(g) + 2\bar{e}$ $E^{\bar{o}} = 1.07$V (reduction potential)

$2H_2O(l) + 2\bar{e} \rightarrow H_2(g) + 2OH^-(aq)$ $E^{\bar{o}} = -0.83$V

$K^+(aq) + \bar{e} \rightarrow K(s)$ $E^{\bar{o}} = -2.93$V

Plan: The reduction half-reaction with the less negative potential, and the oxidation half-reaction with the less positive potential will occur at their corresponding electrodes.

Solution:

$K^+(aq) + \bar{e} \rightarrow K(s)$ $E^{\bar{o}} = -2.93$V

$2H_2O(l) + 2\bar{e} \rightarrow H_2(g) + 2OH^-(aq)$ $E^{\bar{o}} = -0.83$V

The water reduction at -0.83, but the reduction of K^+ is at a higher negative potential so $H_2(g)$ is produced at the cathode

$2Br^-(aq) \rightarrow Br_2(g) + 2\bar{e}$ $E^{\bar{o}} = 1.07$V (reduction potential)

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4\bar{e}$ $E^{\bar{o}} = 1.23$ V (reduction potential)

The water half-cell has more potential than the Br^-, so the Br^- will be oxidized. Thus, $Br_2(g)$ forms at the anode.

The overall electrolytic cell reaction would be:

$2H_2O(l) + 2Br^-(aq) \rightarrow H_2(g) + 2OH^-(aq) + Br_2(s)$

To achieve this reaction:

Minimum voltage required = $E^{\bar{o}}$ oxidizing agent – $E^{\bar{o}}$ reducing agent

So more than +1.07 − (−0.83) = 1.9 volts should be delivered to this electrolytic cell.

3.7 Commercial applications of electrolysis

1. **Producing aluminium**: Compared with today's methods, this process was on a small scale and very expensive. In fact, aluminium metal was considered more expensive than gold! The breakthrough came in 1886 with the development of what we now call the **Hall–Héroult** cell.

2. **Industrial electrolysis of brine:** Chlorine gas, hydrogen gas and sodium hydroxide are three important industrial chemicals. They may be produced simultaneously by electrolysis of a concentrated aqueous sodium chloride solution (brine). Recently, a new type of electrolytic cell, the **membrane cell**, was developed for this reaction.

3. **Electroplating:** Electroplating is the coating of an object with a thin film of metal deposited by an electrolytic solution during electrolysis. Electroplating is often used to produce an attractive and durable finish on articles such as knives and forks (silver plate). It is also used to protect corrosion-prone metals. 'Gold' rings, which cause fingers to turn green, are actually copper rings that have been electroplated with gold.

4. Calculations in electrolysis -Faraday's laws

4.1 Faraday's first law of electrolysis

Faraday's first law of electrolysis may be stated as follows:

The amount of any substance deposited, evolved or dissolved at an electrode during electrolysis is directly proportional to the quantity of electric charge passed through the cell.

The quantity of electric charge transferred by an electric current depends on the magnitude of the current used and the time for which it flows. The electric charge can be calculated using the formula:

$Q = It$

where Q is the electrical charge in coulombs (C)

I is the current in amperes (A)

t is the time in seconds (s).

In an experimental circuit, there is no meter that measures the charge in coulombs. However, an ammeter could be used to measure the rate at which charge flows in a circuit. If, for example, a current of 3.00 amperes flows for 10.0 minutes, the quantity of electricity is $(3.00 \times 10.0 \times 60) = 1.80 \times 10^3$ coulombs. The charge flowing through an electrolytic cell can be increased by either increasing the magnitude of the current or by increasing the time.

4.2 Faraday's second law of electrolysis

Faraday's second law of electrolysis may be stated as follows: *In order to produce 1 mole of a substance by electrolysis, 1, 2, 3 or another whole number of moles of electrons (faradays) must be consumed, according to the relevant half-cell equation.*

In the half-cell equation:

$Ag^+(aq) \quad + \quad e^- \rightarrow \quad Ag(s)$

1 mole of silver ions	**1 mole of electron**	**1 mole of silver atoms**

1 mole of electrons is needed to discharge 1 mole of Ag^+ (aq) ions. This liberates 1 mole of silver atoms. Thus, 1 faraday, or 96500 coulombs, is needed to discharge 1 mole of silver atoms. The number of faradays (moles of electrons) needed to liberate 1 mole of an element during electrolysis is found from the equation for the electrode reaction. Some examples are given below. The number of moles of electrons required in a reaction is proportional to the charge, Q, in coulombs.

n(electrons) = Q / F

Michael Faraday discovered in 1833 that there is always a simple relationship between the amount of substance produced or consumed at an electrode during electrolysis and the quantity of electrical charge **Q** which passes through the cell. For example, the half-equation

$$\mathbf{Ag^+ + e^- \rightarrow Ag \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{ Eq. 1}}$$

tells us that when 1 mol Ag^+ is plated out as 1 mol Ag, 1 mol e^- must be supplied from the cathode. Since the negative charge on a single electron is known to be 1.6022×10^{-19} C, we can multiply by the Avogadro constant to obtain the charge per mole of electrons. This quantity is called the Faraday Constant, symbol F:

$F = 1.6022 \times 10^{-19}\ \text{C} \times 6.0221 \times 10^{23}\ \text{mol}^{-1} = 9.649 \times 10^{4}\ \text{C mol}^{-1} \approx 96500$ coulombs.

Thus in the case of Eq. (1), 96500 C would have to pass through the cathode in order to deposit 1 mol Ag. For any electrolysis the electrical charge **Q** passing through an electrode is related to the amount of electrons $\mathbf{n_{e-}}$ by

$$F = \frac{Q}{n_{e-}}$$

Thus F serves as a conversion factor between $\mathbf{n_{e-}}$ and **Q.**

Often the electrical current rather than the quantity of electrical charge is measured in an electrolysis experiment. Since a **coulomb** is defined as the quantity of charge which passes a fixed point in an electrical circuit when a current of one ampere flows for one second, the charge in coulombs can be calculated by multiplying the measured current (in amperes) by the time (in seconds) during which it flows:

$Q = It$

In this equation *I* represents current and *t* represents time. If you remember that

Coulomb = 1 ampere × 1 second

1 C = 1 A s

You can adjust the time units to obtain the correct result. Now that we can predict the electrode half-reactions and overall reactions in electrolysis, it is also important to be able to calculate the quantities of reactants consumed and the products produced. For these calculations we will be using the Faraday constant:

1 mol of electron = 96500 C

Charge (Q) = current (C/s) x time (s)

(C/s) = 1 coulomb of charge per second = 1 ampere (A)

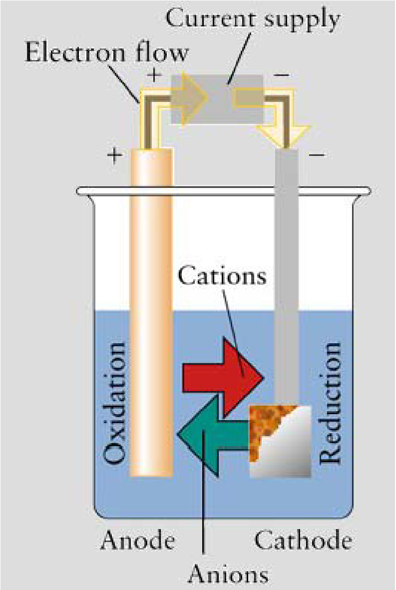
Simple conversion for any type of problem:

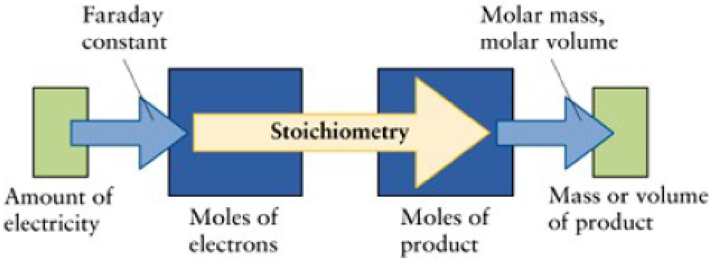
1. Convert any given time to seconds

2. Use the stoichiometry conversion of 1 mol of electron = 96500 **C (Faraday's Constant)**

Quantitative electrolysis.

1





We will focus a lot on metal plating or metal electrodeposition reactions.

$M^{n+} + ne^- \rightarrow M$

Required equations. $n\ mol\ e^- = 1\ mol\ M$

Charge = current flowing x time taken

Coulombs C   Amperes A   Seconds s

Charge passed by 1 mole electrons = 1F = 96, 500 C.

How much Ca will be produced in an electrolytic cell of molten $CaCl_2$ if a current of 0.452 A is passed through the cell for 1.5 hours?

Anode: $2Cl^- (l) \longrightarrow Cl_2 (g) + 2e^-$

Cathode: $Ca^{2+} (l) + \boxed{2e^-} \longrightarrow Ca (s)$

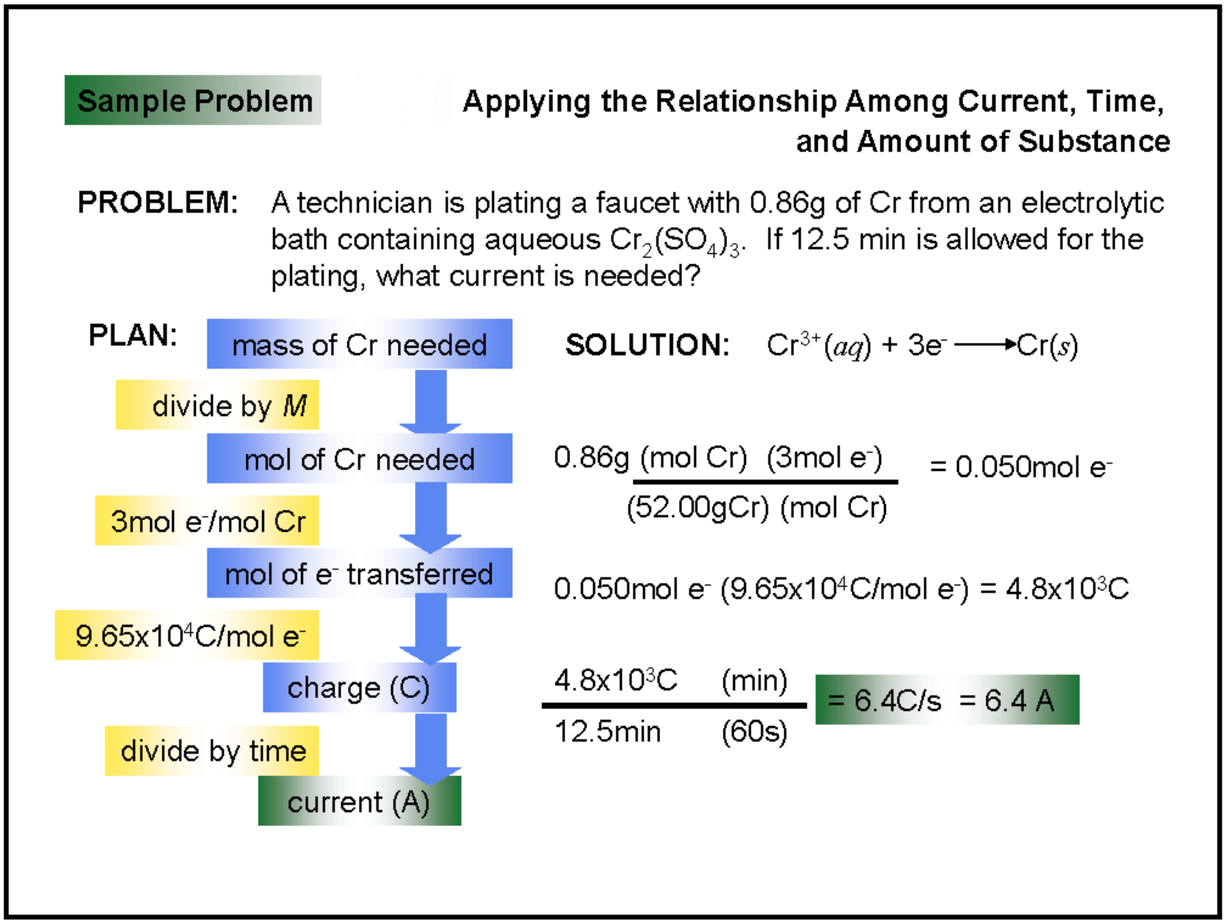
$$Ca^{2+} (l) + 2Cl^- (l) \longrightarrow Ca (s) + Cl_2 (g)$$

2 mole e^- = 1 mole Ca

$$\text{mol Ca} = 0.452 \frac{\cancel{C}}{\cancel{s}} \times 1.5\ \cancel{hr} \times 3600 \frac{\cancel{s}}{\cancel{hr}} \times \frac{1\ \cancel{mol\ e^-}}{96,500\ \cancel{C}} \times \frac{1\ mol\ Ca}{2\ \cancel{mol\ e^-}}$$

= 0.0126 mol Ca

= 0.50 g Ca



Sample Problem **Applying the Relationship Among Current, Time, and Amount of Substance**

PROBLEM: A technician is plating a faucet with 0.86g of Cr from an electrolytic bath containing aqueous $Cr_2(SO_4)_3$. If 12.5 min is allowed for the plating, what current is needed?

PLAN:

mass of Cr needed

divide by *M*

mol of Cr needed

$3 mol e^-/mol Cr$

mol of e^- transferred

$9.65x10^4 C/mol e^-$

charge (C)

divide by time

current (A)

SOLUTION: $Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$

$$\frac{0.86g\ (mol\ Cr)\ (3mol\ e^-)}{(52.00gCr)\ (mol\ Cr)} = 0.050mol\ e^-$$

$$0.050mol\ e^-\ (9.65x10^4C/mol\ e^-) = 4.8x10^3C$$

$$\frac{4.8x10^3C\quad (min)}{12.5min\quad (60s)} = 6.4C/s\ = 6.4\ A$$

Sample Problems

Example 1: The electrolysis of dissolved Bromine sample can be used to determine the amount of Bromine content in sample. At the cathode, the reduction half reaction is

$Br^{2+}(aq) + 2\ \bar{e} \rightarrow 2\ Br^-$

What mass of Bromine can be deposited in 3.00 hours by a current of 1.18 A?

Solution:

3.00 hours **x** 60 min/hour **x** 60 sec/1 min **x** 1.18 **C (A)** / 1 sec **x** 1 mol e^-/96500 **C**

= 0.132 mol e^-

Example 2: Calculate the quantity of electrical charge needed to plate 1.386 mol Cr from an acidic solution of $K_2Cr_2O_7$ according to half-equation

$K_2Cr_2O_7\ (aq) + 12H^+(aq) + 12e^- \rightarrow 2Cr(s) + 7\ H_2O(l)$

Solution: 12 mol e^- is required to plate 2 mol Cr, giving us a stoichiometric ratio $S(e^-/\text{Cr})$. Then the Faraday constant can be used to find the quantity of charge

$$n\text{Cr} \xrightarrow{S(e^-/\text{Cr})} ne^- \xrightarrow{F} Q$$

$$Q = 1.386 \text{ mol Cr } \frac{12 \text{ mol } e^-}{2 \text{ mol Cr}} \times \frac{9.649 \times 10^4 \text{ C}}{1 \text{ mol } e^-} \times$$

= 8.024 × 105 C

Example 3 (Homework): How long (in hours) must a current of 5.0 amperes be maintained to electroplate 60 g of calcium from molten $CaCl_2$?

A. 27 hours **B. 8.3 hours** **C. 11 hours** **D. 16 hours** **E. 5.9 hours**

4.3 Faradaic and Nonfaradaic Processes

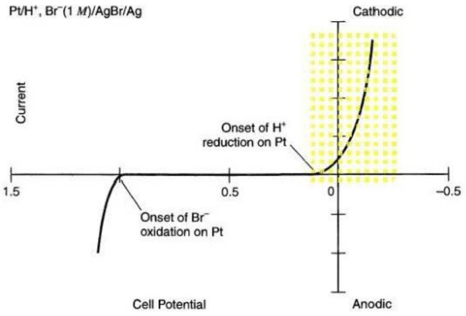
- Two types of electrochemical processes

1) Faradaic process

: charges (e.g., electrons) are transferred across the metal-solution interface.

➔ Electron transfer causes oxidation or reduction to occur.

➔ Since this reactions are governed by Faraday's law (i.e., the amount of chemical reaction caused by the flow of current is proportional to the amount of electricity passed), they are called faradaic processes.



2) Nonfaradaic process

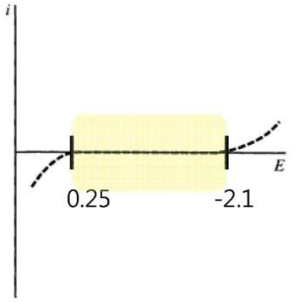
In a specific range of potentials

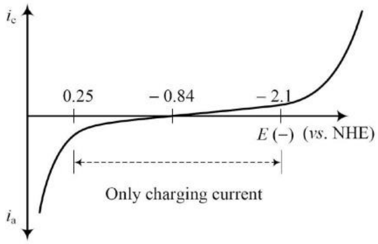
: charge-transfer reactions are thermodynamically or kinetically unfavorable

➔ no charge-transfer reactions occur

➔ However, processes such as adsorption and desorption can occur on the surface of electrodes

➔ Although charge does not cross the interface, external currents can flow (at least transiently) when the potential or solution composition changes.





➔ Nonfaradaic current: dependent on the surface area of electrodes and concentration of electrolytes

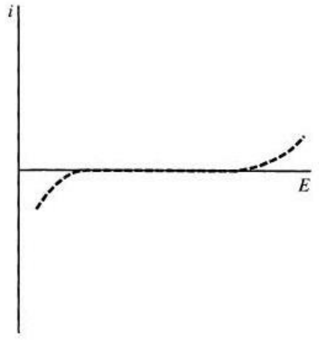
➔ Both faradaic and nonfaradaic processes can simultaneously occur when electrode reactions take place

4.4 Ideal Polarized Electrode

- Ideal polarized (or ideal polarizable) electrode (IPE)

  ➔ defined as an electrode at which no charge transfer can occur across the metal-solution interface, regardless of the potential imposed by an outside source of voltage

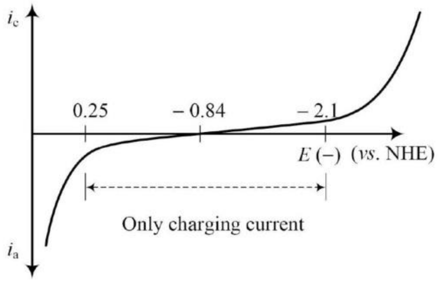
- While no real electrode can behave as an IPE over the whole potential range available in a solution, some electrode-solution systems can approach ideal polarizability over limited potential ranges



(*a*) Ideal polarizable electrode

- For example, a mercury electrode in contact with a deaerated potassium chloride solution approaches the behavior of an IPE over a potential range about 2 V wide.

  ➔ At sufficiently positive potentials, the mercury can oxidize in a charge-transfer reaction:



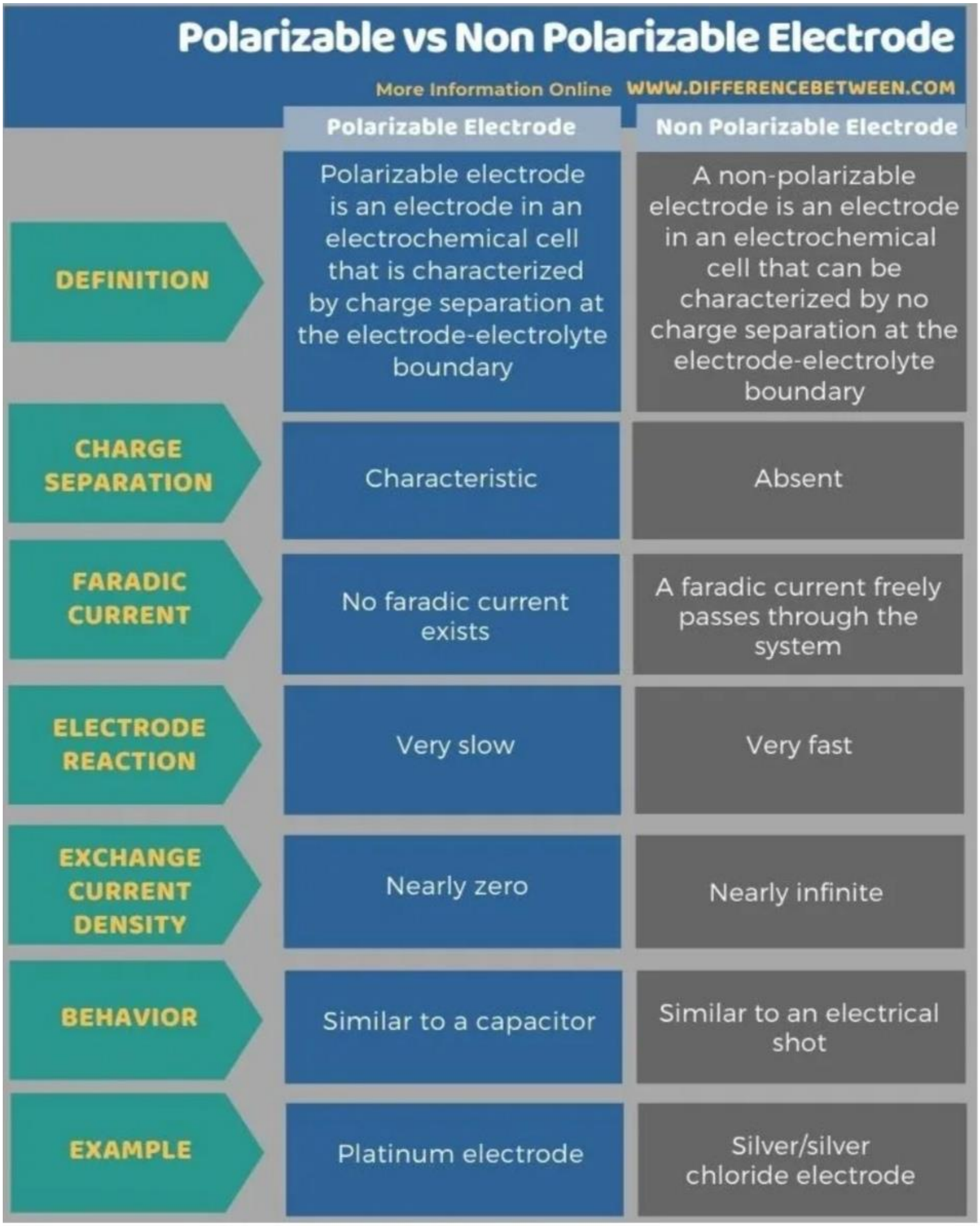
$$Hg + Cl^- \rightarrow \tfrac{1}{2}Hg_2Cl_2 + e \qquad (\text{at} \sim +0.25 \text{ V } vs. \text{ NHE})$$

➔ at very negative potentials K^+ can be reduced:

$$K^+ + e \xrightarrow{Hg} K(Hg) \qquad (\text{at} \sim -2.1 \text{ V } vs. \text{ NHE})$$

➔ In the potential range between these processes, the reduction of water is thermodynamically possible (-0.828 V vs. NHE), but occurs at a very low rate at a mercury surface unless quite negative potentials are reached.

$$H_2O + e \rightarrow \tfrac{1}{2}H_2 + OH^-$$



Polarizable vs Non Polarizable Electrode

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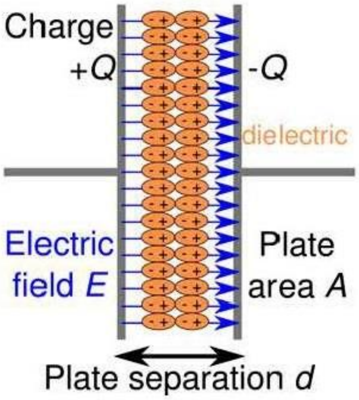
	Polarizable Electrode	Non Polarizable Electrode
DEFINITION	Polarizable electrode is an electrode in an electrochemical cell that is characterized by charge separation at the electrode-electrolyte boundary	A non-polarizable electrode is an electrode in an electrochemical cell that can be characterized by no charge separation at the electrode-electrolyte boundary
CHARGE SEPARATION	Characteristic	Absent
FARADIC CURRENT	No faradic current exists	A faradic current freely passes through the system
ELECTRODE REACTION	Very slow	Very fast
EXCHANGE CURRENT DENSITY	Nearly zero	Nearly infinite
BEHAVIOR	Similar to a capacitor	Similar to an electrical shot
EXAMPLE	Platinum electrode	Silver/silver chloride electrode

4.5 Capacitance and Charge of an Electrode

- The behavior of the electrode-solution interface of IPE
  : analogous to that of a capacitor
  → Since charge cannot cross the IPE interface when the potential across it is changed



- A capacitor is an electrical circuit element composed of two metal sheets separated by a dielectric material.

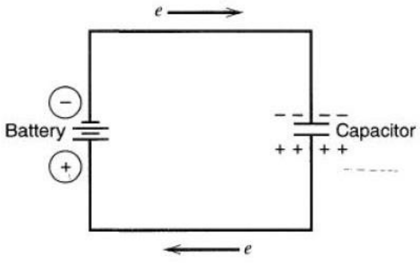
- The behavior of IPE is governed by the equation of capacitor

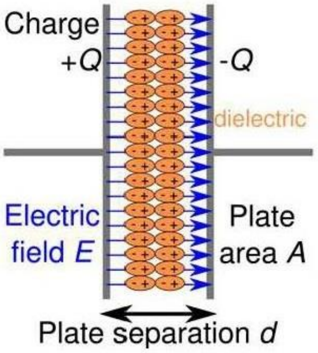
$$\frac{q}{E} = C$$

: where q is the charge stored on the capacitor (in coulombs, C), E is the potential across the capacitor (in volts, V), and C is the capacitance (in farads, F).

Principle of a capacitor

- When a potential is applied across a capacitor, charge will accumulate on its metal plates until q satisfies the equation of q = CE
- During this charging process, a current (called the charging current) will flow.
- The charge on the capacitor consists of an excess of electrons on one plate, a deficiency of electrons on the other, and a polarized dielectric

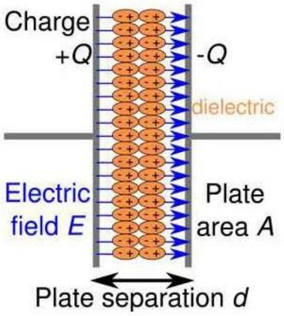




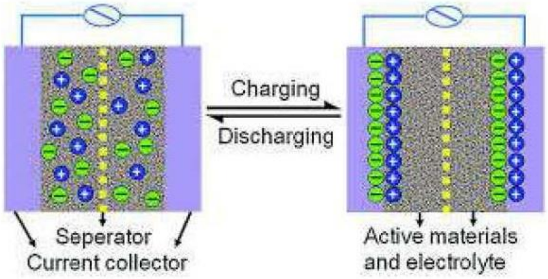
Capacitance and Charge of an Electrode

Principle of nonfaradaic processes

- The electrode-solution interface of nonfaradic processes behaves like a capacitor
  ➔ suggest a model of the nonfaradic processes resembling a capacitor
- Electrolytes in nonfaradic processes
  : regarded as dielectric materials in capacitors

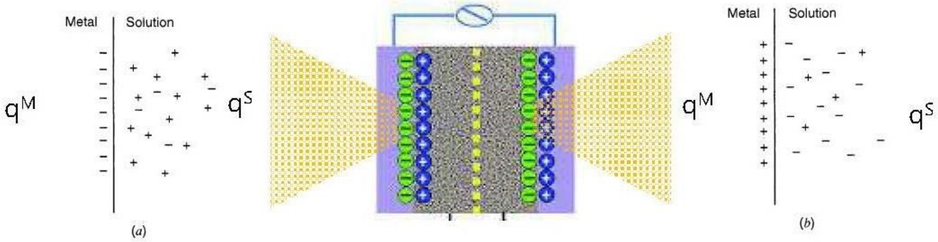


Polarization of dielectric



Ion (charge) separation

- At a given potential, there exist a charge (electron or hole) on the metal electrode, q^M, and a charge (ion) in the solution, q^S
- Whether the charge on the metal is negative or positive with respect to the solution depends on the potential across the interface and the composition of the solution.
- At all times, $q^M = -q^S$.
- The charge on the metal, q^M, represents an excess or deficiency of electrons and resides in a very thin layer (<0.1 Å) on the metal surface.
- The charge in solution, q^S, is made up of an excess of either cations or anions in the vicinity of the electrode surface.

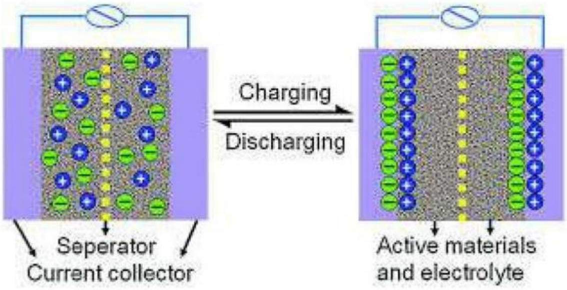


Capacitance and Charge of an Electrode

- Electrical double layer

  : the whole array of charged species and oriented dipoles existing at the metal-solution interface
- The double-layer capacitance, C_d, of the electrode-solution interface

  : typically in the range of 10 to 40 μF/cm^2 (F=C/V)
- However, unlike real capacitors, whose capacitances are independent of the voltage across them, Q is often a function of potential



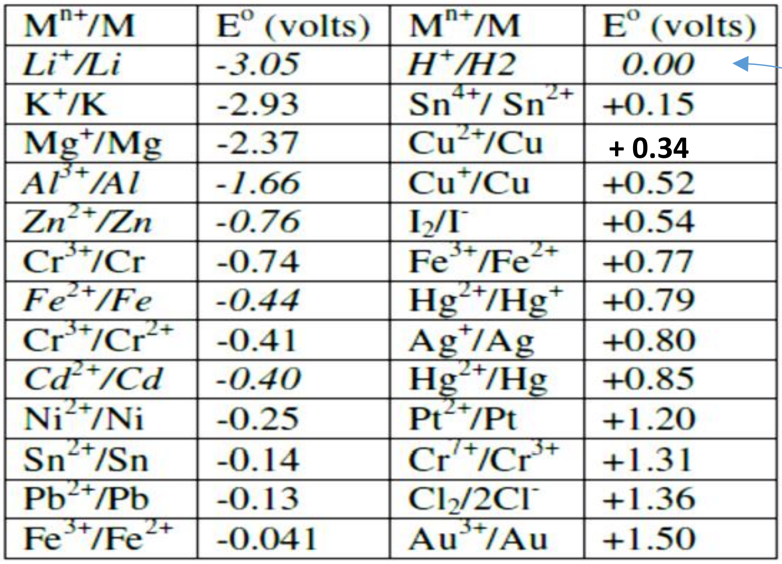
6. TYPES OF ELECTRODES

6.1 Standard reduction potential (E^o):

It is defined as potential developed at the interface between the metal and the solution, when a metal is dipped in a solution containing its own ions of unit concentration at 298K. [If the electrodes involve gases then it is one atmospheric pressure] It is denoted as E^0.

6.2 Electrochemical series:

The arrangement of elements in the order of their standard reduction potential is referred to as **electrochemical series**. Such an arrangement of few elements given in the table below:



M^{n+}/M	E^o (volts)	M^{n+}/M	E^o (volts)
Li^+/Li	-3.05	$H^+/H2$	0.00
K^+/K	-2.93	Sn^{4+}/Sn^{2+}	+0.15
Mg^+/Mg	-2.37	Cu^{2+}/Cu	**+ 0.34**
Al^{3+}/Al	-1.66	Cu^+/Cu	+0.52
Zn^{2+}/Zn	-0.76	I_2/I^-	+0.54
Cr^{3+}/Cr	-0.74	Fe^{3+}/Fe^{2+}	+0.77
Fe^{2+}/Fe	-0.44	Hg^{2+}/Hg^+	+0.79
Cr^{3+}/Cr^{2+}	-0.41	Ag^+/Ag	+0.80
Cd^{2+}/Cd	-0.40	Hg^{2+}/Hg	+0.85
Ni^{2+}/Ni	-0.25	Pt^{2+}/Pt	+1.20
Sn^{2+}/Sn	-0.14	Cr^{7+}/Cr^{3+}	+1.31
Pb^{2+}/Pb	-0.13	$Cl_2/2Cl^-$	+1.36
Fe^{3+}/Fe^{2+}	-0.041	Au^{3+}/Au	+1.50

i) A **negative** value indicates **oxidation** tendency and a **positive** value indicates **reduction** tendency with respect to hydrogen (standard hydrogen electrode). **ii)** The metal with **lower** electrode potential is more reactive and as the electrode potential **increases**, the reactivity **decreases**, and metals with higher electrode potentials are nobler. **iii)** Metals with **lower** electrode potentials have the tendency to replace metals with **higher** electrode potential from their solutions for example, Zn displaces Cu, and Cu displaces Ag. When a metal in elemental form is placed in a solution of another metal salt it may be more energetically feasible for this "elemental metal" to exist as an ion and the "ionic metal" to exist as the element. Therefore the elemental metal will "displace" the ionic metal and the two swap places. Only a metal **higher** in the reactivity series will displace another.

A metal can displace metal ions listed below it in the activity series, but not above. For example, zinc is more active than copper and is able to displace copper ions from solution

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

iv) Metals with **negative** electrode potentials can liberate hydrogen from **acidic** solutions.

6.3 What is a spontaneous electrochemical reaction?

Let's look again at the Daniell cell described before. The standard half-cell potentials are:

$$\text{(Anode)}\ Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^{-} \quad (oxidation)\ E^{o}_{Zn/Zn^{2+}} = 0.76V$$
$$\text{(Cathode)}\ Cu^{2+} + 2e^{-} \rightarrow Cu_{(s)}\ (reduction)\ E_{Cu^{2+}/Cu} = 0.34V$$

Therefore,

$$\begin{aligned} E^{o}_{cell} &= E^{o}_{(ox)} + E^{o}_{(red)} \\ E^{o}_{cell} &= 0.76 + 0.34V \\ E^{o}_{cell} &= 1.10V \end{aligned} \tag{1}$$

The complete notation scheme (cell diagram) for a galvanic cell is written with the anode on the left and a double vertical line denoting the presence of a porous plate or salt bridge. For the Daniell cell:

$$Zn/\ Zn^{2+}\ //\ Cu^{2+}/\ Cu.$$

The voltmeter measures the voltage generated by the redox reaction. The voltage reading will be positive when the electrodes are connected properly for spontaneous reaction. A spontaneous redox reaction occurs when the species with higher reduction potential is connected as the cathode. Otherwise, the voltage reading will be negative.

The sign of ΔE^{o}_{cell} is positive for a spontaneous reaction and negative for non-spontaneous reaction.

6.4 Nernst Equation:

It relates electrode potential with the concentration of ions. For measurements taken under standard conditions (1atm, 1 M solutions), ΔE^{o}_{cell} measures the electric potential difference between the half- cells. For measurements taken under non-standard conditions (the usual laboratory situation), the Nernst equation is used to calculate ΔE_{cell}. The Nernst equation gives us the relationship between the overall cell potential difference for a redox reaction ΔE_{cell} and the concentrations of the metal-ion solutions. The Nernst equation is;

$$\Delta E_{cell} = \Delta E^{o}_{cell} - \frac{RT}{nF}\ln Q \qquad (2)$$

where F is Faraday constant. R the universal gas constant, n the number of electrons transferred, and Q is the reaction quotient. When natural (ln) is converted to base ten (log) and (RT/nF) are evaluated using R=8.315 $JK^{-1}mol^{-1}$, T=298.15 K, and F=96500 $Cmol^{-1}$ the equation becomes;

$$\Delta E_{cell} = \Delta E^{o}_{cell} - \frac{0.0592V}{n}\log Q \qquad (3)$$

In this form, galvanic cells are used to determine the concentration of the metal ions present under conditions other than standard conditions. If we apply the Nernst equation to Daniell cell we will get

$$\Delta E_{cell} = \Delta E^{o}_{cell} - \frac{0.0592V}{n}\log\frac{[Zn^{2+}]}{[Cu^{2+}]} \qquad (4)$$

6.4.1. Thermodynamics and Equilibrium:

For a general reaction or process of A and B giving products C and D :

$$aA + bB \rightarrow cC + dD$$

the reaction quotient, Q, is:

$$Q = \frac{[c]^{c}[D]^{d}}{[A]^{a}[B]^{b}} \qquad (6)$$

The ΔG of a process at any concentration of A, B, C, and D, is given by:

$$\Delta G = \Delta G^o + RT \ln Q \qquad (7)$$

Where ΔG^O is the free energy of the reaction under the defined standard conditions of 1 atm and 1 M concentrations of reactants. ΔG is the observed change in free energy at conditions other than standard. At equilibrium $Q = K_{eq}$. The reaction favors neither products nor reactants at equilibrium, and ΔG = 0. Under these conditions equation (6) becomes:

$$\Delta G^o = -RT \ln K_{eq} \qquad (8)$$

The cell potential of a redox process is related to the free-energy change as follows:

$$\Delta G^o = -nFE^o \qquad (9)$$

In this equation, F is Faraday's constant, the electrical charge on 1 mol of electron 1F = 96500 C/mol e^- = 96500 J/V-mol e^- and n represents the number of moles of electrons transferred in the reaction. For the case when both reactants and products are in their standard states, equation (8) takes the following form:

$$\Delta G^o = -nFE^o$$

6.5 Single Electrodes or Half Cells: Types

A single electrode or a half cell is composed of an electronic conductor, in contact with an electrolytic conductor. An electronic conductor may be a metal, a gas adsorbed on metal or a metal coated with sparingly soluble salt and an electrolytic conductor may be electrolytic solution, or fused salts. At the junction of the metallic and electrolytic conductor, a potential difference is established due to transfer of electrons or ions. Such a potential difference set up between these two types of conductors is known as electrode potential, or half-cell potential. Various types of single electrodes or half cells are:

6.5.1 Metal-Metal Ion electrodes

A metal rod/plate is dipped in an electrolyte solution containing metal ions. There is a potential difference between these two phases and this electrode can act as a cathode or anode both.

Anode: $M \longrightarrow M^{n+} + ne^{-}$

Cathode: $M^{n+} + ne^{-} \longrightarrow M$

This type of an electrode consists of a metal rod dipped in a solution of its own ions. E.g., zinc rod dipped in zinc sulfate solution or a copper rod dipped in copper sulfate solution. The electrode reaction may be represented as

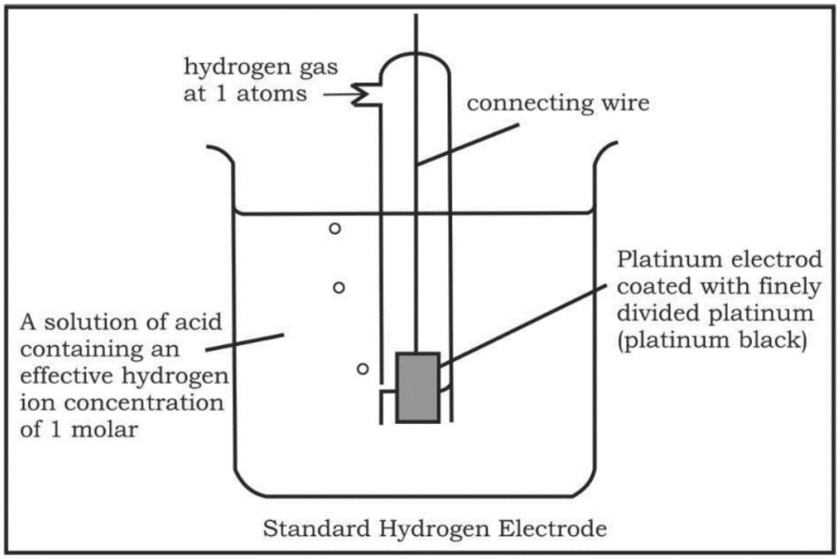
$$M^{n+}_{(aq)} + ne^{-} \rightleftarrows M(s)$$

If the metal behaves as a positive electrode (electrode involves reduction), then equilibrium will shift towards right. The concentration of M^{n+} ions in solution will, therefore, decrease.

If the metal rod behaves as a negative electrode (electrode involves oxidation) the above equilibrium will shift towards left. The concentration of M^{n+} ions in solution will, therefore, increase. Thus the electrode is reversible with respect to M^{n+} ions and is represented as M(S), M^{n+} (aq).

6.5.2 Gas Electrodes

Electrode gases like H_2, Cl_2 etc. are used with their respective ions. For example, H_2 gas is used with a dilute solution of HCl (H^+ ions). The metal should be inert so that it does not react with the acid.



Standard Hydrogen Electrode

Anode: $H_2 \longrightarrow 2H^+ + 2e^-$

Cathode: $2H^+ + 2e^- \longrightarrow H_2$

The hydrogen electrode is also used as the standard to measure other electrode potentials. Its own potential is set to 0 V as a reference. **When it is used as a reference electrode the concentration of diluted HCl is taken as 1 M and the electrode is called "Standard Hydrogen Electrode (SHE)".**

Examples of this type of electrode are; Hydrogen electrode, Oxygen electrode, Chlorine electrode.

These electrodes consist of a gases continuously bubbling through solutions of their ions at a steady value of gas pressure. In this type of electrodes, a gaseous nonmetal is in contact with the solution of its own ions. Since the gases are nonconductors of electricity, an inert metal such as platinum, gold or graphite is dipped in the solution containing the ions of the gas and the gas is bubbled over it. The metal absorbs the gaseous nonmetal and the equilibrium rapidly gets established between the gaseous nonmetal and its ions.

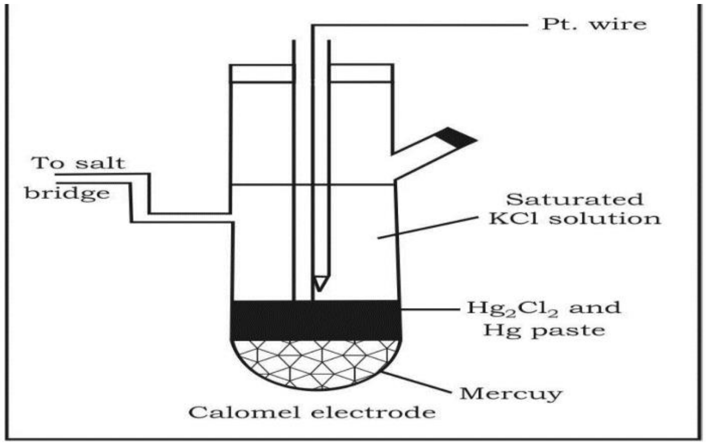
6.5.3 Metal-Insoluble salt electrode

We use salts of some metals which are sparingly soluble with the metal itself as electrodes. For example, if we use AgCl with Ag there is a potential gap between these two phases which can be identified in the following reaction:

$$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-$$

This electrode is made by dipping a silver rod in a solution containing AgCl(s) and Cl^- ions. These electrodes consist of a metal and a sparingly soluble salt of the same metal dipping in a solution of a soluble salt having the same anion. An important electrode of this type is the **calomel electrode**. Another example of this type **is Silver-Silver Chloride-Hydrochloric Acid electrode.** The most frequently used electrode of this type is the calomel electrode, which consists of mercury in contact with mercurous chloride (calomel) as a paste, over which is placed a solution containing chloride ions, usually KCl. Mercury is used with two other phases, one is a calomel paste (Hg_2Cl_2) and electrolyte containing Cl^- ions.

The electrode may be represented as: **Hg | Hg_2Cl_2 | *sat* KCl**



This electrode is also used as another standard to measure other potentials. Its standard form is also called Standard Calomel Electrode (SCE).

Cathode :

$$Hg_2Cl_2(s) + 2e^- \longrightarrow 2Hg(l) + 2Cl^-(aq)$$

Anode:

$$2Hg(l) + 2Cl^-(aq) \longrightarrow Hg_2Cl_2(s) + 2e^-$$

6.5.4 Redox Electrode (Inert metal Oxidation Reduction electrodes)

In these electrodes two different oxidation states of the same metal are used in the same half-cell. For example, Fe^{2+} and Fe^{3+} are dissolved in the same container and an inert electrode of platinum is used for the electron transfer. Following reactions can take place:

Anode: $Fe^{2+} \longrightarrow Fe^{3+} + e^-$

Cathode: $Fe^{3+} + e^- \longrightarrow Fe^{2+}$

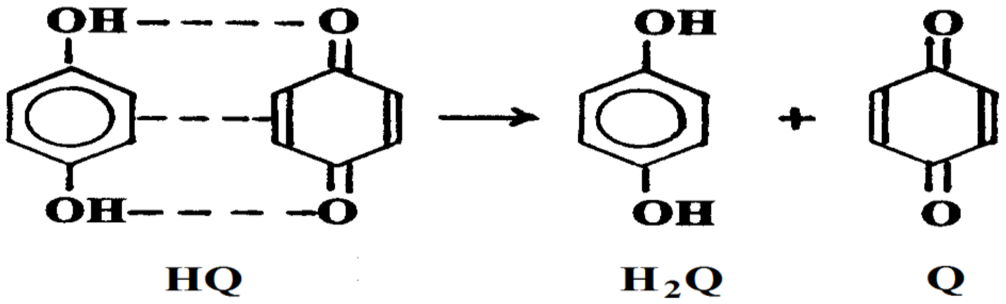
The term oxidation reduction electrode is used for those electrodes **in which potential is developed** due to the presence of ions of the **same substance in two different oxidation states.** This type of electrode consists of an inter electrode (Pt/Au) immersed in a mixed solution containing the substance in both the oxidized and reduced forms, e.g, when a Pt wire is inserted into the solution containing Fe^{2+} and Fe^{3+} ions, it is found that wire acquires a potential. This potential at the electrode arise from the **tendency of the ions in one**

oxidation state to change into the other more stable oxidation state. The electrode reaction may be represented as

$$Fe^{3+}\ (aq) + e^- \rightleftarrows Fe^{2+}\ (aq)$$

The function of the inert metal is to pick up electrons and to provide the electrical contact to the electrode.

The most frequently used electrode of this type is the quinhydrone electrode which consists from a platinum dipped into a solution saturated with quinhydrone. Quinhydrone (**HQ**) is a slightly soluble compound formed by the combination of one mole of quinone (**Q**) and one mole of hydroquinone (**H_2Q**) – see below scheme. The electrode reaction is:



$C_6H_4O_2 + 2H^+ + 2e^- \leftrightarrow C_6H_4(OH)_2$

Quinone (Q) **Hydroquinone (H_2Q)**

6.5.5 Ion selective electrode (ISE):

"Ion selective electrode is one which selectively responds to a specific ion in a mixture and the potential developed at the electrode is a function of the concentration of that ion in the solution" **The glass electrode is one of the ion-selective electrodes**, they are sophisticated electrode systems based on the existence of the membrane potential between the solution and a suitable membrane. The membrane potential is due to the selective ion-exchange, that is adsorption and desorption of a certain kind of ions on the membrane surface. Due to the selective ion-exchange the membrane exhibits potential response in the presence of certain ion and the membrane potential can also be expressed by the **Nernst equation**.

7. Conductometric Titration

The determination of the end point of a titration by means of conductance measurements is known as conductometric titration. In these titrations measurement of actual specific conductance of the solution is not required, and any quantity proportional to it is sufficient. The titrant is added by a burette and change of conductance as a function of added titrant is used to determine the equivalence point.

Some typical examples of conductometric titration and interpretation of their curves are given in following paragraphs. In all cases, the equivalence points are located at the intersection of lines of differing slope. One of the requirements of these titrations is that the titrant should be at least ten times as concentrated as the solution being titrated, in order to keep the volume change small.

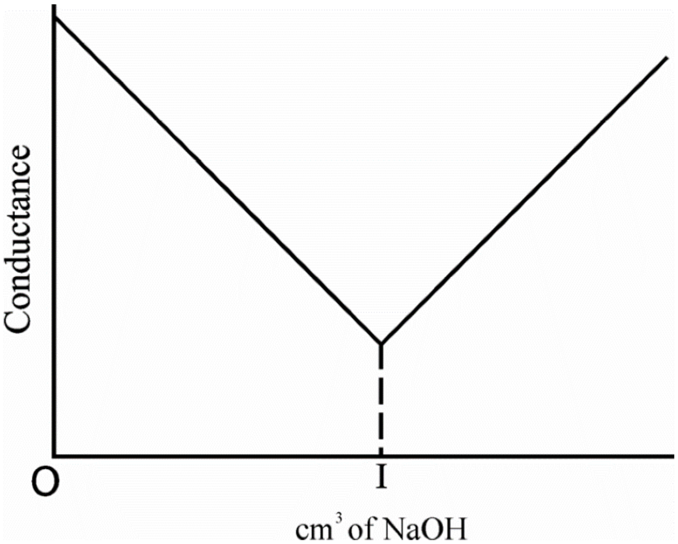
Acid-Base Titration

(i) Strong Acid with a Strong Base

When a strong alkali, e.g., sodium hydroxide is added to a solution of a strong acid, e.g., hydrochloric acid, the following reaction occurs:

$$(H^+ + Cl^-) + (Na^+ + OH^-) = Na^+ + Cl^- + H_2O$$

In this type of reaction, the conductance first falls, due to the replacement of the H^+ (Λ_m^∞ = 350)by the added cation Na^+ (Λ_m^∞ = 40-80) and after the equivalence point has been reached, Λ_m^∞ the conductance rapidly rises with further addition of strong alkali due to large Λ_m^∞ value of the hydroxyl ion (= 198). The two branches of the curve are straight lines **(See the Figure below)** provided the volume increase is negligible and their intersection gives the endpoint. At the neutral point the conductance of the system will have a minimum value, from which the equivalence point of the reaction can be determined.



Conductometric titration of a strong acid (HCl) vs. a strong base (NaOH)

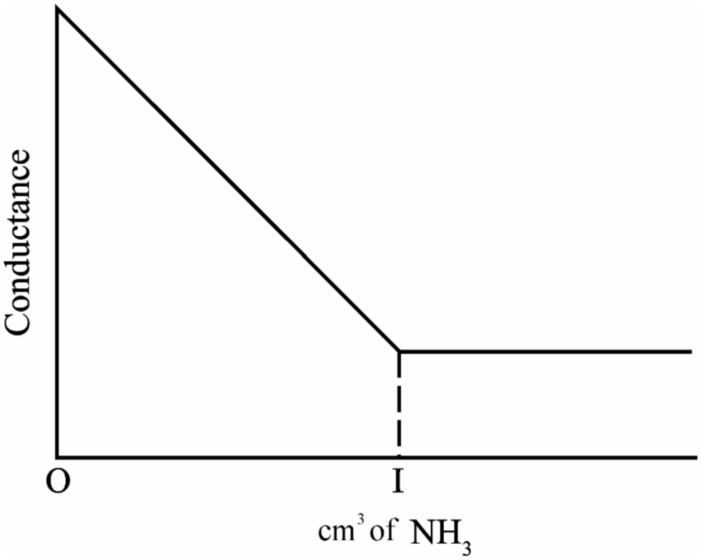
In actual practice the lines may be slightly curved due to variation in temperature, heat of neutralization, interionic effect and slight increase in the volume of the solution because of the addition of titrant. In spite of this, the inflection is sharp enough to get the end point.

(ii) Strong Acid with a Weak Base

The titration of a strong acid with a weak base may be illustrated by the neutralization of dilute HCl by dilute NH_4OH.

$$H^+Cl^- + NH_4OH \longrightarrow NH_4^+ + Cl^- + H_2O$$

The first branch of the graph **(See the Figure below)** represents the neutralization of the acid i.e, replacement of fast moving H^+ ions by slow moving NH_4^+ ions). After the neutralization (end point) is completed, the graph becomes almost horizontal, since the excess aqueous NH_4OH is not noticeably ionized in the presence of NH_4Cl. As NH_4OH is a weakly ionized electrolyte it has a very small conductivity compared with that of the acid or its salt.



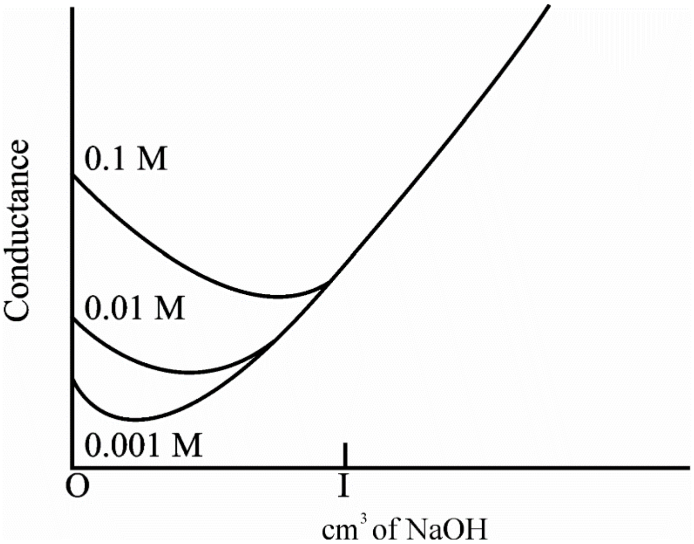
Conductometric titration of a strong acid (HCl) vs. a weak base (NH_4OH)

(iii) Weak Acid with a Strong Base

Consider the titration of the weak acid like CH_3COOH with strong base NaOH.

$$(CH_3COO^- + H^+) + (Na^+ + OH^-) \longrightarrow (CH_3COO^- + Na^+) + H_2O$$

Initially the conductance is low due to the weak ionization of acetic acid. On the addition of base, there is decrease in conductance not only due to the replacement of H^+ by Na^+ but also suppresses the dissociation of acetic acid due to common ion acetate. But very soon, the conductance increases on adding NaOH as NaOH neutralizes the un-dissociated CH_3COOH to CH_3COONa which is the strong electrolyte. This increase in conductance stays raise up to the equivalence point **(See the Figure below)**. The graph near the equivalence point is curved due the hydrolysis of salt CH_3COONa. Beyond the equivalence point, conductance increases more rapidly with the addition of NaOH due to the highly conducting OH^- ions. Finding an accurate end point is difficult in this type of titration and generally titration of weak acid and moderately strong acids with a strong base are not recommended for conductometric titration.



Conductometric titration of a weak acid (acetic acid) vs. a strong base (NaOH)

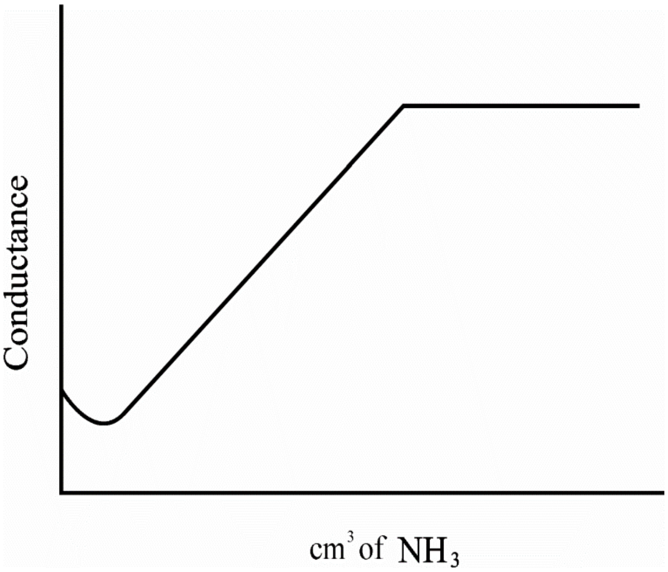
(iv) Weak Acid with Weak Base

When a weak acid is titrated with a weak base the initial portion of the conductance titration curve is similar to that for a strong base, since the salt is a strong electrolyte in spite of the fact that the acid and base are weak.

Consider the titration curve of CH_3COOH and NH_3

$$CH_3COOH + NH_3 \longrightarrow CH_3COONH_4$$

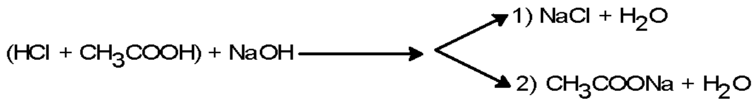
Conductivity decreases as the anion formed suppresses the ionization, passes through a minimum and then increases up-to the end point. This is because of the conversion of non-conducting weak acid into its conducting salt. It is observed that such titrations curves are generally curved **(See the Figure below)** because the incompleteness of reaction permits extra hydroxide ions (or hydrogen ions if a weak base is being titrated) to be present. This causes an increase in conductivity. It is observed that with more incompleteness of the reaction, the more curvature is observed in the graph.



Conductometric titration of a weak acid (acetic acid) vs. a weak base (NH_4OH)

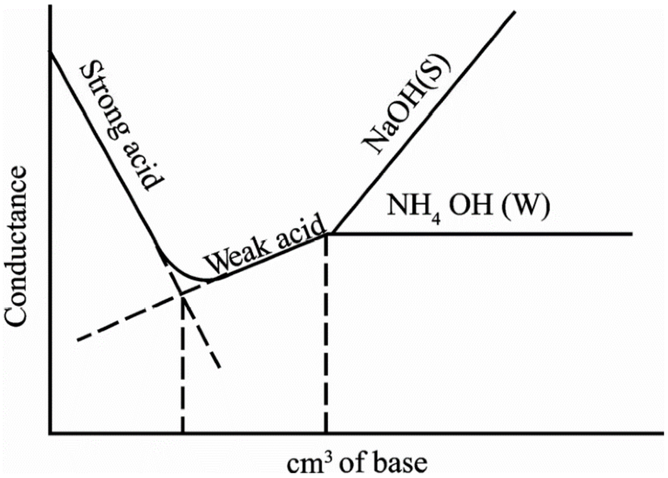
(v) Mixture of a Strong Acid and a Weak Acid vs. a Strong Base or a Weak Base:

Consider the titration of the:



$$(HCl + CH_3COOH) + NaOH \longrightarrow \begin{cases} 1)\ NaCl + H_2O \\ 2)\ CH_3COONa + H_2O \end{cases}$$

In this curve there are two break points. The first break point corresponds to the neutralization of strong acid. When the strong acid has been completely neutralized only then the weak acid starts neutralizing. The second break point corresponds to the neutralization of weak acid and after that the conductance increases due to the excess of OH^- ions in case of a strong base as the titrant. However, when the titrant is a weak base, it remains almost constant after the end point similar to **the Figure below:**



Conductometric titration of a mixture of a strong acid (HCl) and a weak acid (CH_3COOH) vs. a strong base (NaOH) or a weak base (NH_4OH)

7.4 Transport number and Ionic conductance

The transport number (t) is defined as the fraction of total current carried by the particular ionic species in the solution. Or Transport number can be defined as fraction of current transported by a particular type of ion in a solution of electrolyte.

So, transport number for cation

$$t_+ = \frac{I_+}{I}$$

And transport number for anion

$$t_- = \frac{I_-}{I};$$

where I_+ is the amount of current carried by cation and I- is the amount of current carried by anion. Current carried by any type of ion depends upon speed of ions (u), charge of the ions (c) and valency of ion (z). Thus

$$I_+ \propto u_+ c_+ z_+$$

And

$$I_- \propto u_- c_- z_-$$

Hence,

$$t_+ = \frac{u_+ c_+ z_+}{(u_+ c_+ z_+) + (u_- c_- z_-)}$$

And

$$t_- = \frac{u_- c_- z_-}{(u_+ c_+ z_+) + (u_- c_- z_-)}$$

Thus,

$$t_+ = \frac{u_+}{(u_+) + (u_-)}$$

And

$$t_- = \frac{u_-}{(u_+) + (u_-)}$$

Let us consider at infinite dilution the ionic conductance of cation is λc and ionic conductance of anion is λa. Now as ionic conductance varies directly proportional to speed of that particular type of ion $u_+ \propto \lambda_c$ and $u_- \propto \lambda_a$

Thus,

$$t_+ = \frac{\lambda_c}{(\lambda_c + \lambda_a)} \text{ and } t_- = \frac{\lambda_a}{(\lambda_c + \lambda_a)}$$

$$\text{or, } t_+ = \frac{\lambda_c}{\Lambda_0} \text{ and } t_- = \frac{\lambda_a}{\Lambda_0}$$

$$\text{and } t_+ + t_- = 1$$

So, transport number of a particular type of ion can be expressed as fraction of conductance at infinite dilution offered by that particular type of ion.

7.3Determination of Transport Number

Three method have been generally employed:

1. **Hittorf**, involves measurement of **changes of concentration** in the vicinity of the electrodes.
2. In the second, known as the **"moving boundary"** method, the rate of motion of the boundary between two solutions under the influence of current is studied.
3. The third method, is based on **electromotive force measurements** of suitable cells.