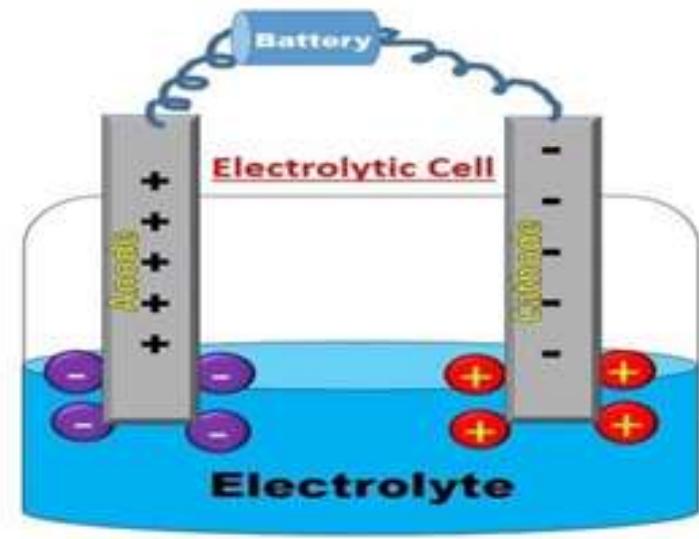




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Chemistry Department



Electrochemistry



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Electrochemistry

Introduction

The term ***electrochemistry*** is reserved for the study of the processes that convert chemical energy to electrical energy and vice versa. Electrochemistry is the study of chemical processes that cause electrons to move. This movement of electrons is called electricity, which can be generated by movements of electrons from one element to another in a reaction known as an oxidation-reduction ("redox") reaction. A redox reaction is a reaction that involves a change in oxidation state of one or more elements. When a substance loses an electron, its oxidation state increases; thus, it is oxidized. When a substance gains an electron, its oxidation state decreases, thus being reduced.

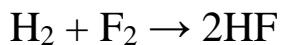
For electrochemical reactions, a redox reaction can be separated in two, oxidation, which occurs at the anode and reduction that occurs at the cathode.

➤ Oxidation-reduction (redox) reaction

We generally think of a "chemical reaction" as a process in which the atoms in one or more reactants undergo some kind of a rearrangement into new substances, the products of the reaction. There are, however, many reactions in which it is convenient to regard electrons as participants in the transformation of reactants into products. Reactions of this kind are known generally as electron-

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transfer reactions, or more commonly as oxidation-reduction (redox) reactions. For example, for the redox reaction



can be rewritten as follows:

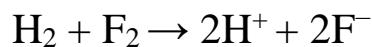
- Oxidation reaction



- Reduction reaction:



- Overall Reaction

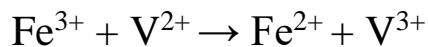


Oxidation is the loss of electrons, whereas ***reduction*** refers to the acquisition of electrons, as illustrated in the respective reactions above. The species being oxidized is also known as the reducing agent or reductant, and the species being reduced is called the oxidizing agent or oxidant. In this case, H₂ is being oxidized (and is the reducing agent), while F₂ is being reduced (and is the oxidizing agent).

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Example

Given the redox reaction

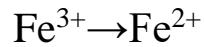


Which species is oxidized? Which is reduced? Identify the reducing agent and the oxidizing agent.

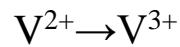
Solution

Fe^{3+} is reduced into Fe^{2+} and V^{2+} is oxidized into V^{3+} . This is because the oxidized species loses electrons, and the reduced species gains electrons.

Iron gains an electron



and vanadium loses an electron



Thus, Fe^{3+} is the oxidizing agent and V^{2+} is the reducing agent.

Rules for redox reactions

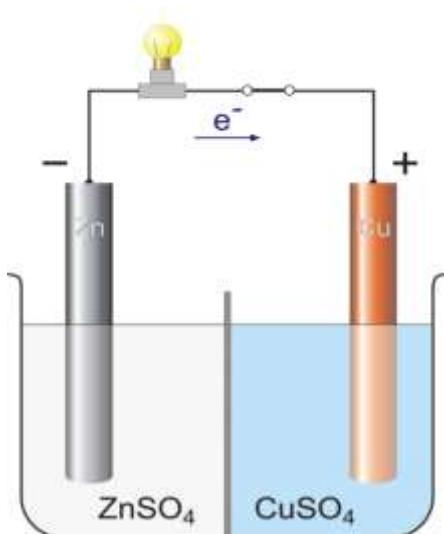
- 1) Free elements have an oxidation state of zero. (e.g., He, N₂, O₂)
- 2) The sum of the oxidation state has to equal the total net charge for a compound. (e.g., MnO⁻⁴ has a net charge of -1 with Mn (+7) O₄ (-8) = -1)
- 3) The number of electrons lost = electrons gained
- 4) The atoms on either side of the reaction must balance

Electrochemistry

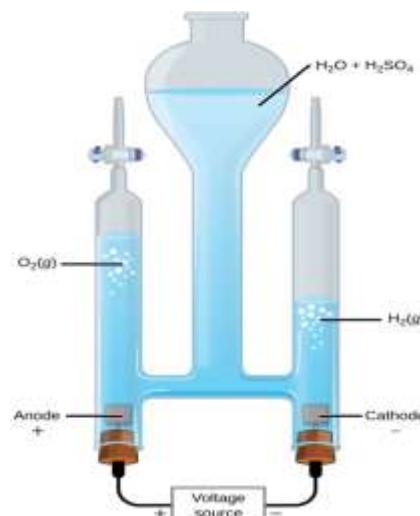
➤ Types of electrochemical cells

Voltaic Cells or Galvanic Cells, derived from the names Luigi Galvani (1737-1798) and Alessandro Volta (1745-1827), are the cells that use spontaneous redox reactions to produce electric current, electrons flow from one terminal (anode) to another (cathode) when connected by an external circuit and a salt bridge (converting chemical energy into electrical energy). Example cases of spontaneous electrochemical processes include batteries, fuel cells and corrosion.

Electrolytic Cells are the cells at which electric current removes electrons from one reactant and gives electrons to another (converting electrical energy into chemical energy). Example cases include electrolysis, used to decompose stable compounds such as H_2O or Fe_2O_3 into its elements, and electroplating.



Galvanic (Voltaic / Electrogenetic) cell

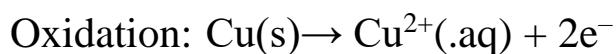
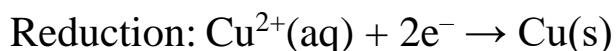


Electrolytic cell

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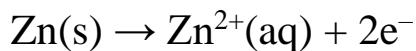
➤ Electrode potential

Electrochemistry is the study of reactions in which charged particles (ions or electrons) cross the interface between two phases of matter, typically a metallic phase (the electrode) and a conductive solution, or electrolyte. A process of this kind can always be represented as an electrode reaction in which one or more electrons appear explicitly in the reaction equation, either as reactants ("oxidation") or as products ("reduction"):



When a metal such as iron, copper, or zinc is immersed in an electrolyte, a small quantity of metal cations will be released into the solution.

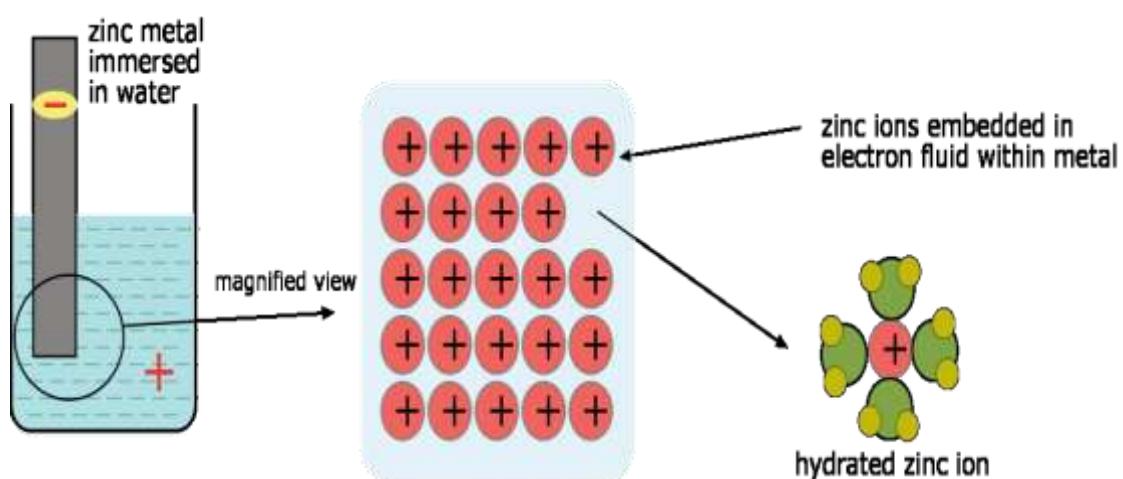
For example, if the metal is zinc and the solution contains ZnNO_3 , the process can be described by



A metal can be thought of as an assembly of positive ions immersed in a fluid-like sea of electrons, whose mobility is responsible for the typical metallic properties such as electrical and heat conductivity. As Zn^{2+} ions leave the metal and attach themselves to water

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molecules (the solvent), the electron left behind cause the metal to assume a negative charge. As this negative charge builds up, it makes it energetically more difficult for the metal to release cations into the solution. Similarly, the Zn^{2+} ions released into the solution create a positive charge that soon begins to inhibit their further dissolution. As a result, the reaction quickly grinds to a halt before any chemically significant concentration of Zn^{2+} ions appears in the solution.



The only way we can get the oxidation of the metal to continue is to couple it with some other process that restores electroneutrality to both the metal and the liquid. A simple way to accomplish this would be to 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

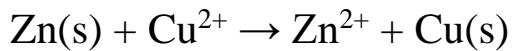
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simple oxidation-reduction process, a transfer of two electrons from the zinc to the copper:



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+} ion introduced to the solution, one Cu^{2+} ion is removed.

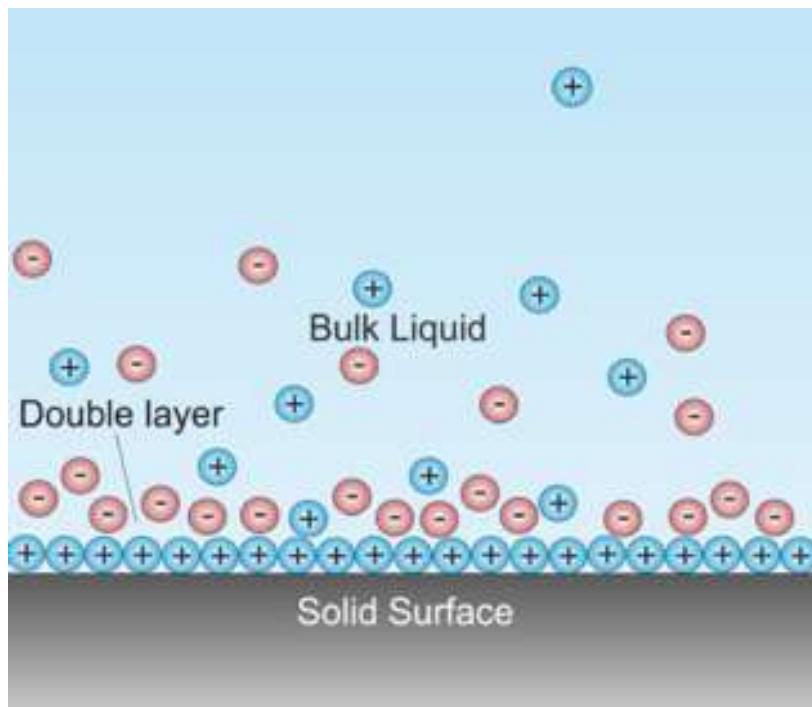
The net reaction



The transition region between a metallic electrode and the solution consists of a region known as the *electric double layer*. As its name implies, this consists of an inner adsorbed monomolecular layer of cations (those released by the metal), and an outer region containing an excess of anions (such as NO_3^-) that compensates for any charge unbalance. As a result, a potential called electrode potential is generated.

At equilibrium $I_a = I_c$ and $I_{\text{net}} = 0$

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➤ Galvanic cells

Galvanic or Voltaic cells are devices for converting chemical energy into electrical energy.

When a net reaction proceeds in an electrochemical cell, oxidation occurs at one electrode (the anode) and reduction takes place at the other electrode (the cathode). A galvanic cell consists of two compartments called half-cells. The half-cell where oxidation occurs is called the anode. The other half-cell, where reduction occurs, is called the cathode. The electrons in voltaic cells flow from the negative electrode to the positive electrode (from anode to cathode). Daniell cell is an example of the galvanic cells. A typical Daniell cell consists of two pieces of metal, one zinc and the other copper, each immersed in a solution containing a dissolved salt of the

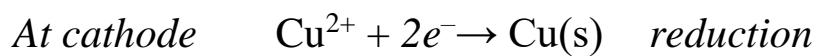
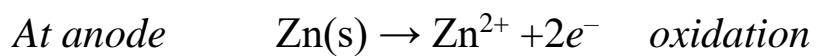
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corresponding metal. The two solutions are separated by a salt bridge or a porous diaphragm.

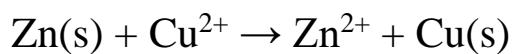
Note: In galvanic cell: anode is the negative electrode and cathode is the positive electrode.

If we connect the zinc and copper by means of a metallic conductor, the excess electrons that remain when Zn^{2+} ions emerge from the zinc in the left cell would be able to flow through the external circuit and into the right electrode, where they could be delivered to the Cu^{2+} ions which become "discharged", that is, converted into Cu atoms at the surface of the copper electrode. The net reaction is the oxidation of zinc by copper (II) ions.

The figure below shows that $Zn(s)$ is continuously oxidized, producing aqueous Zn^{2+} . Conversely, in the cathode, Cu^{2+} is reduced and continuously deposits onto the copper bar:

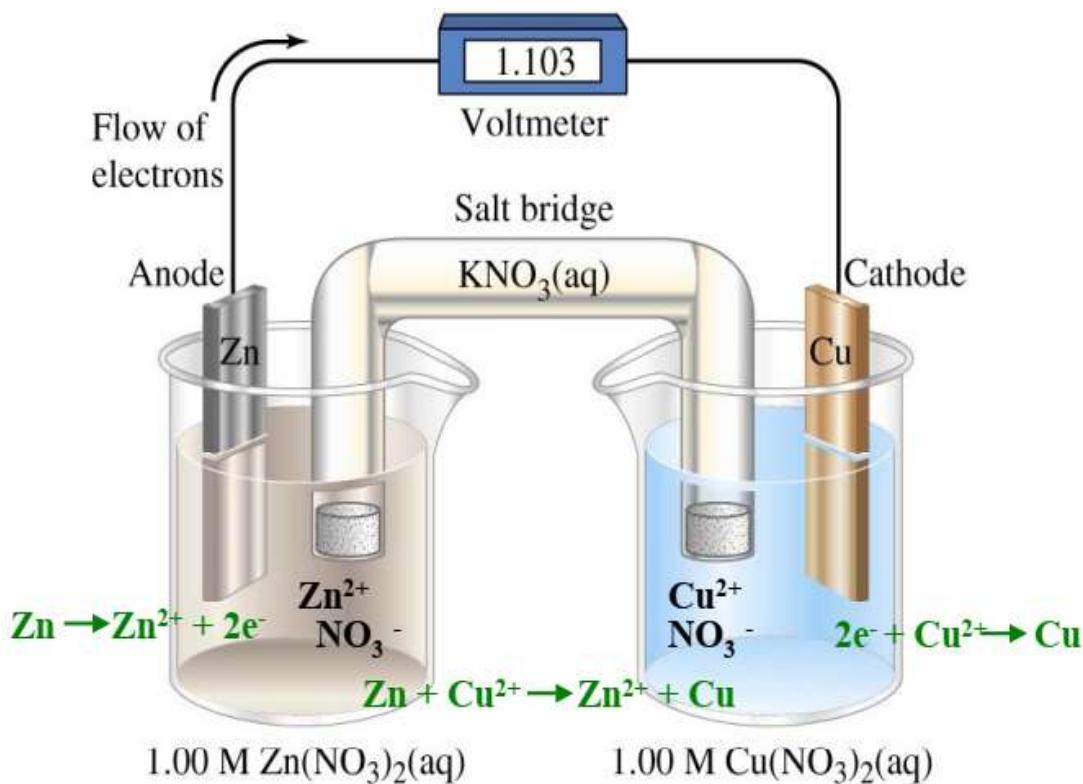


The overall reaction:



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As a result, the solution containing Zn(s) becomes more positively charged as the solution containing Cu(s) becomes more negatively charged.



The salt bridge or the porous diaphragm

For the galvanic cell to work, the solutions in the two half-cells must remain electrically neutral. Therefore, a salt bridge containing an ionic salt (KCl, KNO₃ or Na₂SO₄) is added to keep the solutions neutral by adding the anions (Cl⁻, NO₃⁻ or SO₄²⁻) into the anode solution and the cations (K⁺ or Na⁺) into the cathode solution. As oxidation and reduction proceed, ions from the salt bridge migrate to prevent charge buildup in the cell compartments. A semipermeable porous membrane often replaces the salt bridge that allows ions to

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diffuse through it. The salt bridge or the porous diaphragm serve three functions: 1) make electrical contact completing the circuit, 2) maintain electrical neutrality, and 3) prevent the spontaneous mixing of the half-cells.

➤ **The electromotive force (emf)**

The electromotive force (emf) is the maximum potential difference between two electrodes of a galvanic or voltaic cell. This quantity is related to the tendency for an element, a compound or an ion to acquire (i.e. gain) or release (lose) electrons. emf of Daniell cell is about 1.1 V, which depends on nature of the electrode, concentration of ions (pressure of gases), and temperature.

➤ **Cell notation**

In order to make it easier to describe a given electrochemical cell, a special symbolic notation has been adopted. The cell notation is symbols or expressions to express the composition of the electrochemical cell.

In this notation the cell we described above would be



- A double vertical line (\parallel) is used to separate the anode half reaction from the cathode half reaction. This represents the salt bridge.

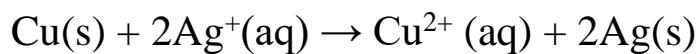
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- The anode (where oxidation occurs) is placed on the left side.
- The cathode (where reduction occurs) is placed on the right side.
- A single vertical line (|) is used to separate different states of matter on the same side, and a comma (,) is used to separate like states of matter on the same side. For example:



Example 1

Write the cell notation for this reaction:



Solution

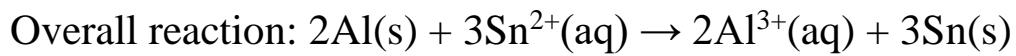
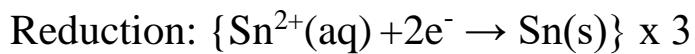
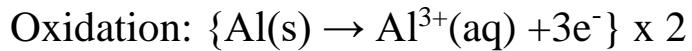


Example 2

Write cell reactions for this cell notation:



Solution

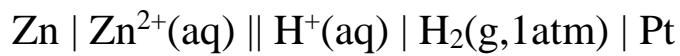
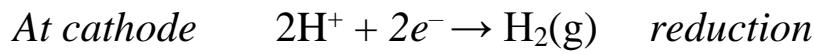
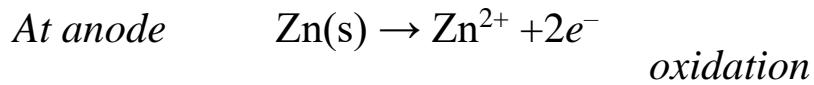


➤ Relative electrode potential

It is physically impossible to measure the *absolute* potential difference between a piece of metal and the solution in which it is immersed. However, we can measure the *relative* electrode potential. It is the difference between the potentials of two electrodes that dip into the same solution, or more usefully, are in two different solutions.

Instead, the voltage of a special cell, composed of the specific electrode being studied and a selected *reference* electrode whose potential is known, is normally measured; the voltage is referred to as the relative electrode potential, E . An arbitrary zero standard electrode potential has been chosen by scientists to be the Standard Hydrogen Electrode (SHE). In which the half-cell has 1M H⁺, 1 atm H₂ (g) and an inert Pt electrode. SHE may act as an anode or a cathode according to the other electrode in the cell.

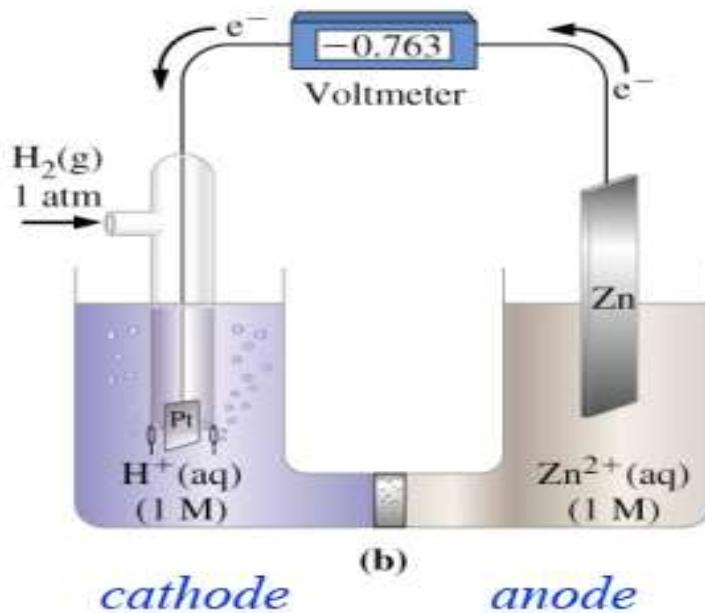
When the electrode Zn | Zn²⁺ is coupled with the SHE, the zinc electrode is the anode,



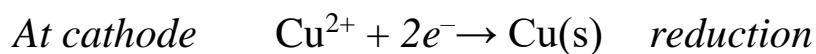
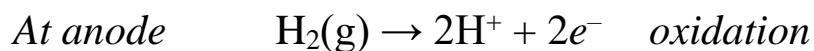
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The potential has been measured to be 0.76 V. However, in this cell, Zn is oxidized, and its electrode is the anode.

$$E^\circ = 0.76 \text{ V} \text{ (standard zinc potential)}$$

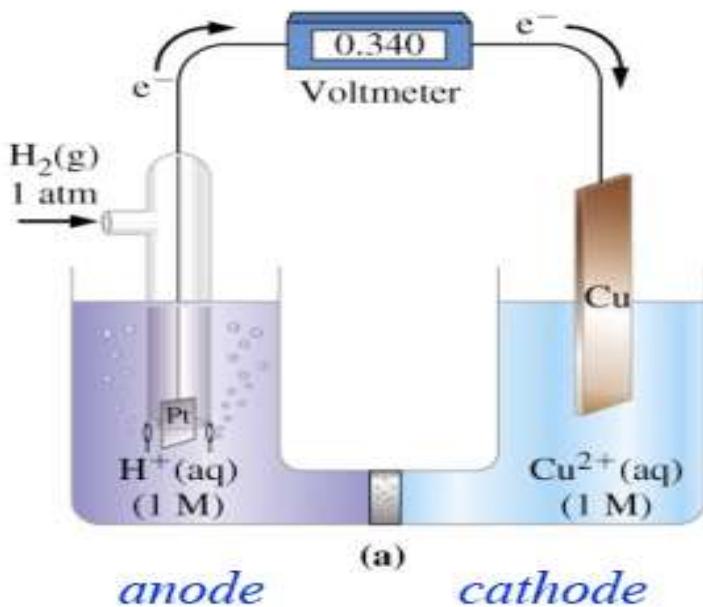


When a half cell $\text{Cu}^{2+} \mid \text{Cu}$ is coupled with the SHE,



The copper electrode is the cathode, where reduction takes place. The potential across the cell has been measured to be 0.339 V.

$$E^\circ = 0.339 \text{ V} \text{ (standard copper potential)}$$



➤ Electrochemical series

Using the above mentioned method, E° values for hundreds of electrodes have been determined and are usually tabulated in order of increasing tendency to accept electrons (increasing oxidizing power), which called the electrochemical series.

- The electrochemical series is defined as the arrangement of the elements in order of their chemical activity. The electrochemical series has been established by measuring the electrode potentials compared to standard hydrogen electrode.
- These electrode potentials are *reducing*, *standard*, and *relative* potentials.
- Elements at the top of the series (negative potential, before hydrogen) are good reducing agents. Li metal is the strongest reducing agent.

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- Element ions at the bottom of the series (positive potential) are good oxidizing agents. Au^{3+} ion is the strongest oxidizing agent.
- Active metals can displace less active metals from a solution of their salts.

| Equilibrium (Oxidants \leftrightarrow Reductants) | E° (volts) |
|--|-------------------|
| Lithium: $\text{Li}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Li}(\text{s})$ | -3.03 |
| Potassium: $\text{K}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{K}(\text{s})$ | -2.92 |
| Calcium: $\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Ca}(\text{s})$ | -2.87 |
| Sodium: $\text{Na}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Na}(\text{s})$ | -2.71 |
| Magnesium: $\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Mg}(\text{s})$ | -2.37 |
| Aluminum: $\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \leftrightarrow \text{Al}(\text{s})$ | -1.66 |
| Zinc: $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Zn}(\text{s})$ | -0.76 |
| Iron: $\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Fe}(\text{s})$ | -0.44 |
| Lead: $\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Pb}(\text{s})$ | -0.13 |
| Hydrogen: $2\text{H}^+(\text{aq}) + 2\text{e}^- \leftrightarrow \text{H}_2(\text{g})$ | 0.00 |
| Copper: $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Cu}(\text{s})$ | +0.34 |
| Silver: $\text{Ag}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Ag}(\text{s})$ | +0.80 |
| Gold: $\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \leftrightarrow \text{Au}(\text{s})$ | +1.50 |

Metal Reducing Activity Increasing ↑ ↓ **Metal Oxidizing Activity Increasing**

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➤ Standard cell potential

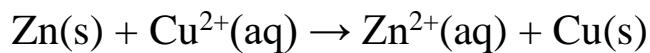
For standard cell potential, temperature of the reaction is assumed to be 25 °C, the concentration of the reactants and products is 1 M, and reaction occurs at 1 atm pressure. The standard cell potential is denoted E°_{cell} , and can be written as

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

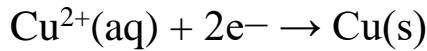
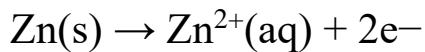
Note: To use this equation, the cell potentials must be in reduction form.

Example

What is the standard cell potential for the following reaction?



Solution



- Cu(s) is the *cathode*
- Zn(s) is the *anode*.

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

- Oxidation half reaction (anode): $E^\circ = -0.76 \text{ V}$
- Reduction half reaction (cathode): $E^\circ = +0.34 \text{ V}$

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Therefore:

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

$$E^\circ_{\text{cell}} = 0.34 - (-0.76) = +1.10 \text{ V}$$

For a spontaneous reaction, E°_{cell} is positive and ΔG° is negative (ΔG° is the standard Gibbs free energy, used to determine if a reaction occurs spontaneously). Thus, when ΔG° is negative the reaction is spontaneous. Merging electrochemistry with thermodynamics gives this formula:

$$\Delta G^\circ = -nE^\circ F$$

where n is the number of electrons transferred and F is the Faraday constant (96500 C)

Remember that standard free energy (ΔG°) is related to the equilibrium constant K:

$$\Delta G^\circ = -RT \ln K$$

so,

$$-nE^\circ F = -RT \ln K$$

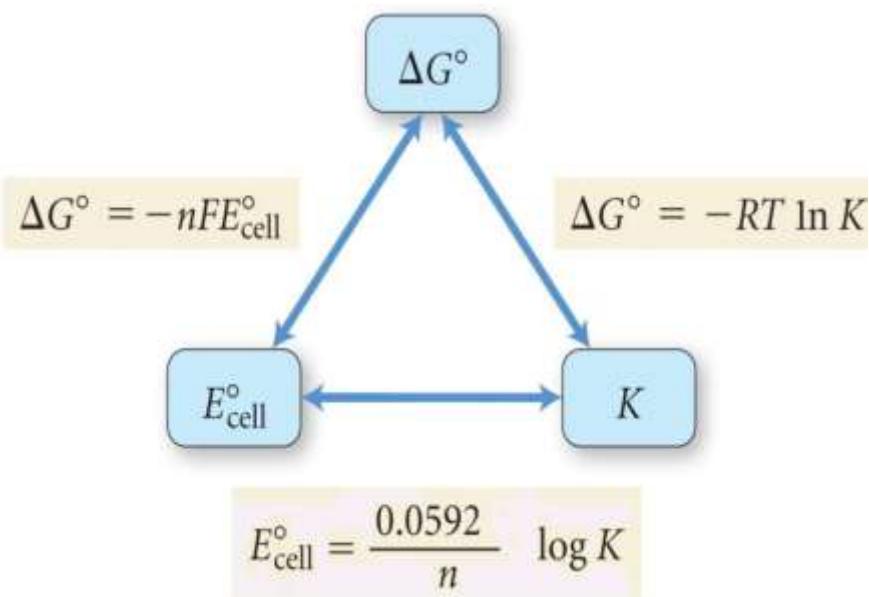
$$\therefore E^\circ = \frac{RT}{nF} \ln K$$

An older form of this equation used logs under standard temperature conditions (298 K)

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$$E^\circ = \frac{2.303 \times 8.314 \times 298}{n \times 96500} \log K$$

$$\therefore E^\circ = \frac{0.059}{n} \log K$$

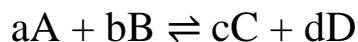


| Reaction under standard conditions | E^\bullet_cell | K | ΔG° |
|------------------------------------|-------------------------|-----|------------------|
| Spontaneous | + | > 1 | - |
| Equilibrium | 0 | = 1 | 0 |
| Non-spontaneous | - | < 1 | + |

➤ Nernst equation and cell potential under non-standard conditions

Nernst found that there is a quantitative relationship between the concentration of the ions that take part in the cell reaction and the cell potential.

The general Nernst equation correlates the Gibb's Free Energy ΔG and the cell potential of the galvanic cell. For the reaction



The non-standard Gibbs free energy is,

$$\Delta G = \Delta G^\circ + RT \ln Q$$

where Q is the reaction quotient,

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$\therefore \Delta G = \Delta G^\circ + RT \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

and

$$\Delta G = -nEF \quad , \quad \Delta G^\circ = -nE^\circ F$$

therefore,

$$\therefore -nEF = -nE^\circ F + RT \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$\therefore E = E^\circ - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$\therefore E = E^\circ - \frac{0.059}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

This is known as the **Nernst equation**. The equation allows us to calculate the cell potential of any galvanic cell for any concentrations.

➤ Reference electrode

In most electrochemical experiments, our interest is concentrated on only one of the electrode reactions. Since all measurements must be on a complete cell involving two electrode systems, it is common practice to employ a *reference electrode* as the other half of the cell. The reference electrode is that one whose potential is known, constant, and independent of the concentration of the solution under study.

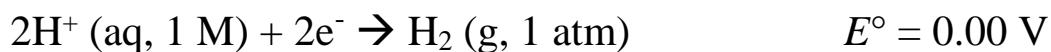
The ideal reference electrode must have some characteristic properties such as:

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- (i) The electrode reaction must be reversible and obey Nernst equation.
- (ii) The electrode potential must be constant with time.
- (iii) The electrode potential should be returned to its original value after being subjected to small currents.
- (iv) The electrode potential should exhibit little effect with temperature.

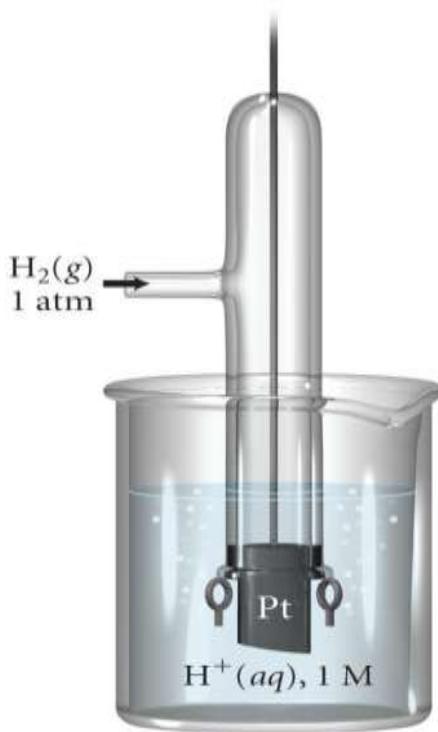
1) Hydrogen electrode

It is a primary standard electrode. The standard hydrogen electrode, or SHE, is composed of an inert solid like black platinum (Pt sheet coated with spongy Pt) on which hydrogen gas is adsorbed, immersed in a solution containing hydrogen ions (1 M concentration) and hydrogen gas (1 atm pressure). Its potential arbitrarily assigned a value of zero. The half-cell reaction for the SHE is given by

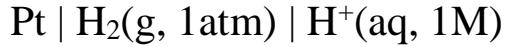


$$E = E^\circ - \frac{0.059}{2} \log \frac{P(\text{H}_2)}{[\text{H}^+]^2}$$

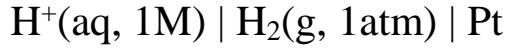
Electrochemistry



When acting as anode



When acting as cathode

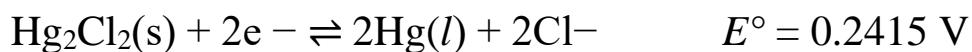


Practical application of the SHE is limited by the difficulty in preparing and maintaining the electrode, primarily due to the requirement for $\text{H}_2(\text{g})$ and pure Pt in the half-cell. Most potentiometric methods employ one of two other common reference half-cells – the *saturated calomel electrode* (SCE) or the *silver-silver chloride electrode* (Ag/AgCl).

Electrochemistry

2) Saturated calomel electrode (SCE)

It is a secondary standard electrode. The SCE is a half-cell composed of mercurous chloride (Hg_2Cl_2 , calomel) in contact with a mercury pool (Hg). These components are layered under a saturated solution of potassium chloride (KCl). A platinum wire is generally used to allow contact to the external circuit. The half reaction is described by



$$E = E^\circ - \frac{0.059}{2} \log[\text{Cl}^-]^2$$

When acting as anode



When acting as cathode



The role of Hg in SCE is to compensate the decrease in Hg when the electrode acts as anode.

3) Silver-silver chloride electrode (Ag/AgCl)

It is a secondary standard electrode. The silver/silver chloride reference electrode is composed of a silver wire (Ag), coated with a layer of solid silver chloride (AgCl), immersed in a solution that is saturated with potassium chloride (KCl). The pertinent half reaction is

Electrochemistry



$$E = E^\circ - \frac{0.059}{1} \log[\text{Cl}^-]$$

When acting as anode

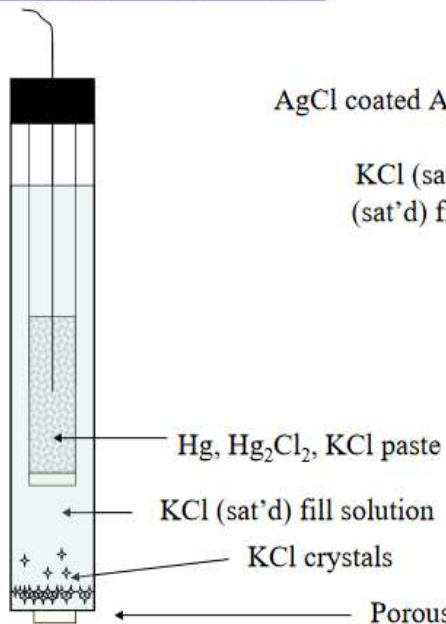


When acting as cathode

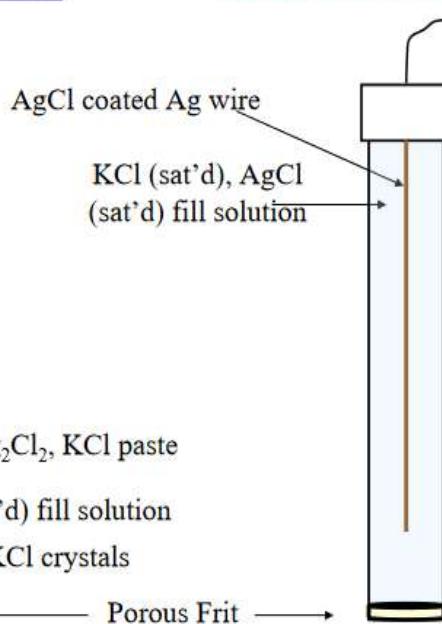


The role of Ag in Ag/AgCl electrode is to compensate the decrease in Ag when the electrode acts as anode.

Saturated Calomel Electrode



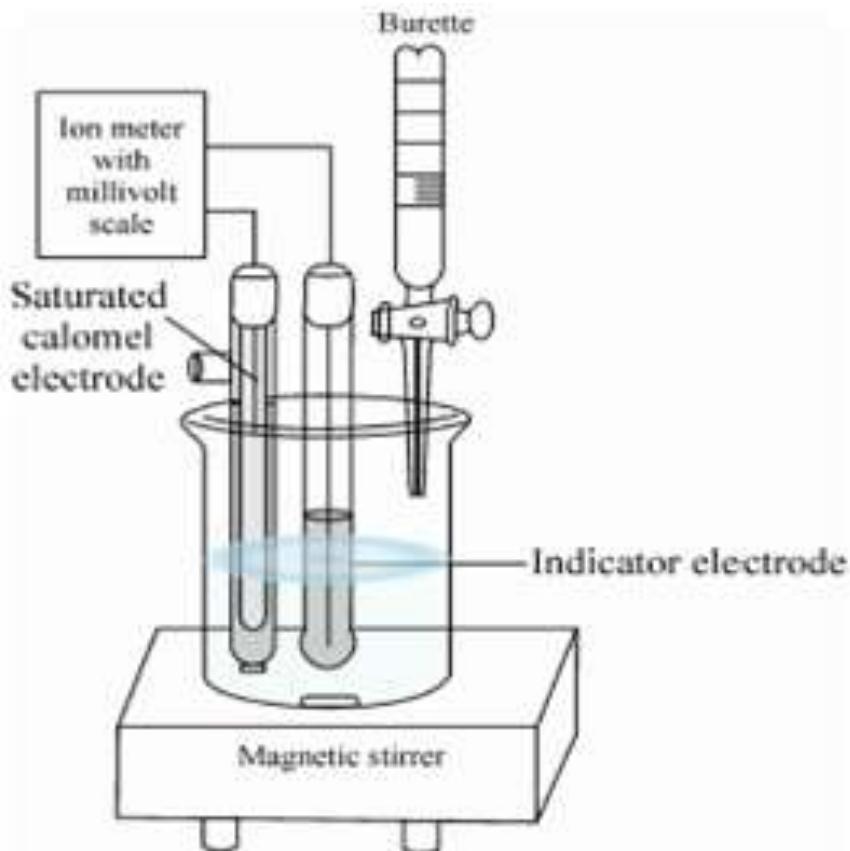
Ag/AgCl Electrode



➤ Potentiometric titration

It should be clear by now that at least two electrodes are necessary to make a potential measurement. In potentiometry, those two electrodes are generally called the *indicator* electrode and the *reference* electrode. The indicator electrode possesses some characteristic that allows it to selectively respond to changes in the activity of the analyte being measured. For the measured potential to have meaning in this context, the reference electrode must be constructed so that its composition is fixed and its response is stable over time, with observed changes in measured potential due solely to changes in analyte concentration.

Potentiometric titration belongs to chemical methods of analysis in which the endpoint of the titration is monitored with an indicator electrode that records the change of the potential as a function of the volume of the added titrant of exactly known concentration in order to find out the concentration of the studied solution. Potentiometric titrations are especially versatile because indicator electrodes suitable for the study of almost every chemical reaction used in titrimetric are now available.



Advantages of potentiometric titrations

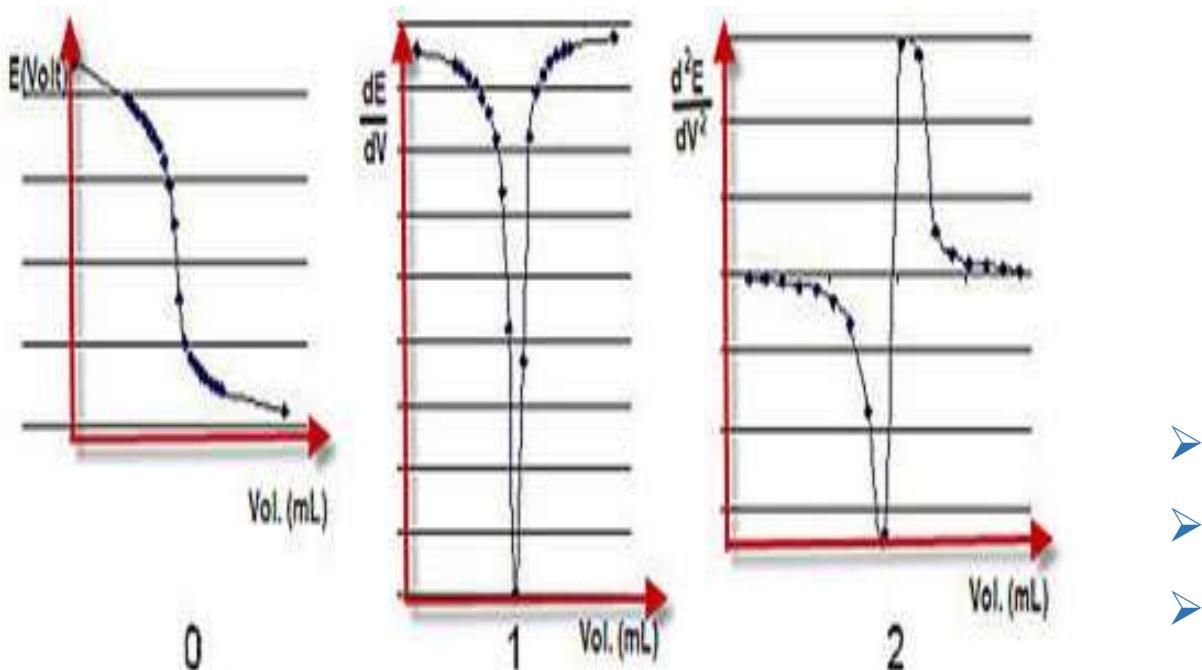
- 1) Used when the suitable indicators in normal titration are not available.
- 2) Suitable for diluted, colored, and turbid solutions.
- 3) Suitable for the determination of two or more components in a single operation.

Electrochemistry

Types for indicator electrodes

- 1) For neutralization reactions: hydrogen electrode, glass electrode, and quinhydrone electrode.
- 2) For redox reactions: Pt electrode.
- 3) For metal ions determination: metallic electrodes

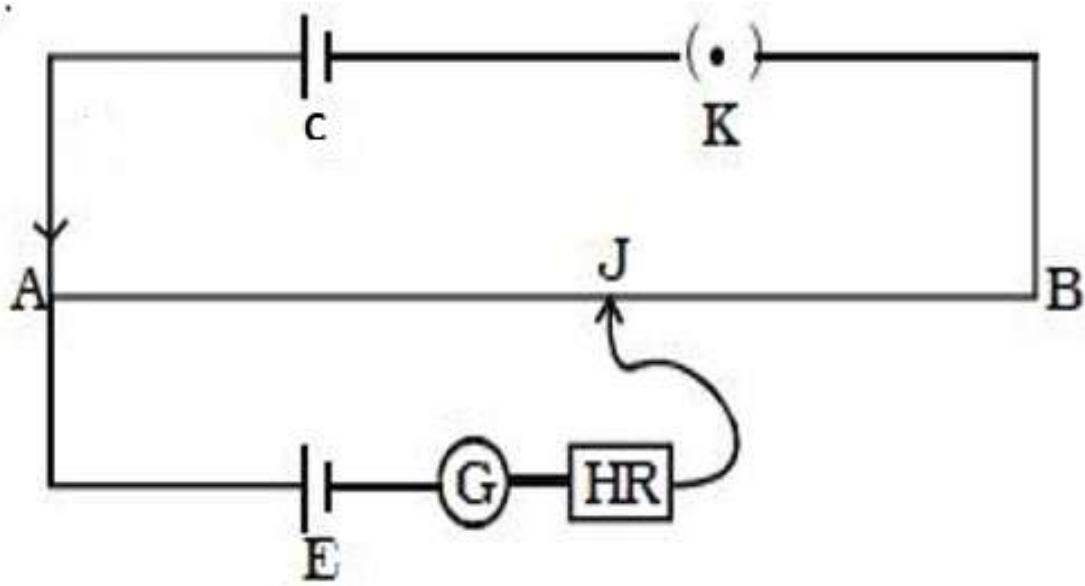
The end point in the potentiometric titrations determined graphically by means of one of the following curves.



➤ Measurement of emf of a galvanic cell

When current is applied on a cell, its emf gradually changes due to either the internal resistance or the polarization. In order to obtain correct emf of the cell, the measurements should be carried out in such a way that no current is applied on the cell. Since this is not possible in practice, the measurement is carried out under conditions in which the current applied on the cell is so small as to be negligible. The principle of the method was first described by Poggendorff and the method is known as the *Poggendorff's compensation method*.

In this method, the unknown emf of a cell is opposed by a cell of known emf and hence the name compensation method.



Electrochemistry

The basic potentiometer circuit is shown in the figure. When a metal is in contact with its own ion solution it develops a potential with respect to the electrolyte. AB is a wire of uniform resistance. The ends A and B of the wire are connected to the two electrodes of a lead storage battery C, through a variable resistance R. Along the wire AB there is a gradual fall of potential which is proportional to the length of the wire. One electrode of the cell, E, whose emf is to be measured, is connected through a galvanometer, G to A. The other electrode is connected through a key, K, to AB by a sliding contact D. The potential difference between the anode and cathode is called the emf of the cell.

After pressing the key K, the contact J is moved along the wire until there is no deflection of the galvanometer, indicating that no current is flowing. At this position the fall of potential along the wire AB from A to J is equal to the potential of the cell E. If now the cell E is replaced by a standard cell S, the potential of which is very accurately known, a new position of the contact, J', is found when no current flows through the galvanometer. At this position:

$$\frac{\text{Balancing length of the galvanic cell}}{\text{Balancing length of the standard cell}} = \frac{\text{Potential of cell } E}{\text{Potential of cell } S}$$

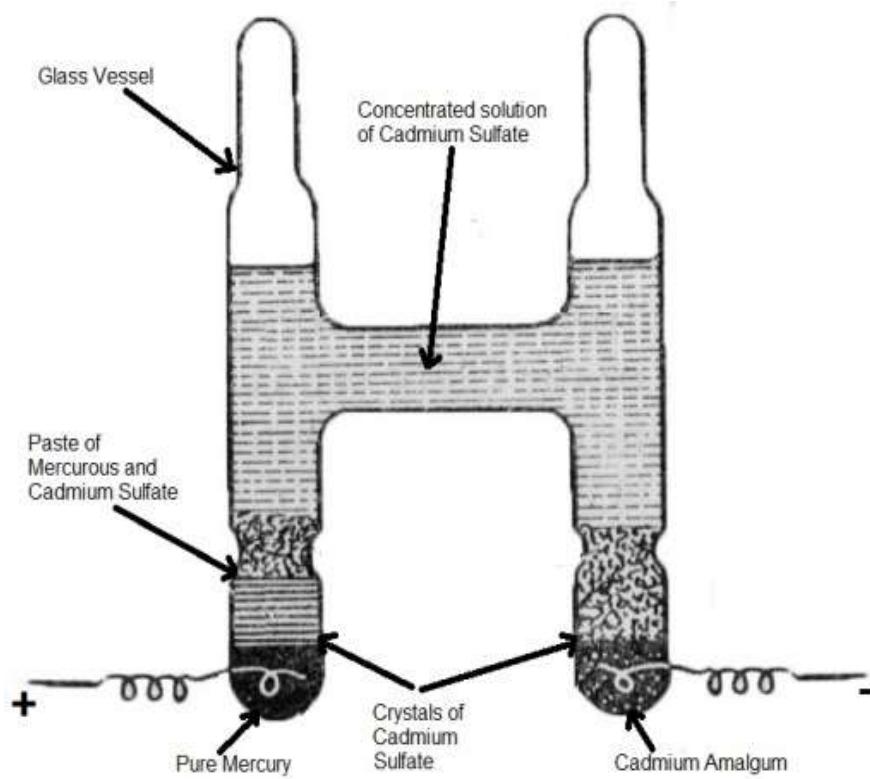
From the known value of the potential of the standard cell, S, and the experimentally determined value of the lengths of wire, the potential of the cell, E, may be obtained.

Electrochemistry

➤ Weston standard cell (Cadmium cell)

The standard cell is that cell whose emf is known and remains constant during measurements. e.g. Weston cell

The Weston cell is a reversible cell whose emf remains constant for a longer period provided no appreciable current is applied on the cell, therefore, such cells are never used as a source of energy but are used as a secondary standard of voltage for electrical measurements. Its emf when constructed in accordance with the standard specifications is 1.0183 V at 25 °C. The Weston cell has small temperature coefficient, i.e. its potential is affected by 4×10^{-5} mV per degree.



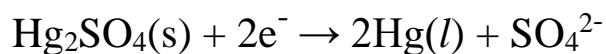
Electrochemistry

Weston standard cell as shown consists of H shaped glass vessel, each leg containing concentrated solution of cadmium sulfate ($3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$) in the upper part, then crystals of cadmium sulfate, paste of mercurous sulfate (Hg_2SO_4) and cadmium sulfate ($3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$). Mercury (Hg) is at the bottom of one leg and crystals of cadmium sulfate, and cadmium amalgam (Cd(Hg) 12.5 %) at the bottom of the second leg. The two limbs of the vessel are hermetically sealed. Cadmium sulfate solution acts as an electrolyte, mercury acts as a + ve electrode, cadmium amalgam acts as a – ve electrode. The crystals of $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ are put in the cell in order to keep the electrolyte saturated. The connections of the cell into the external circuit are made by platinum wires sealed into the glass.

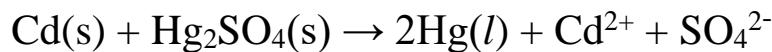
At anode:



At cathode:



Overall reaction



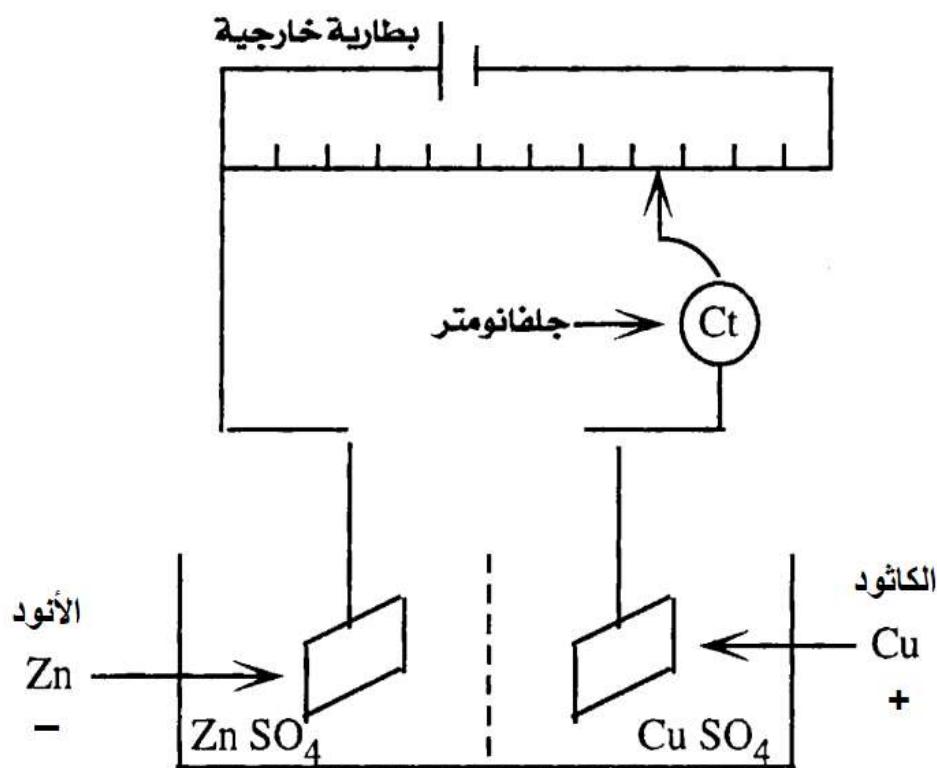
Cell notation

12.5 % Cd(Hg) | $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ (saturated solution) | $\text{Hg}_2\text{SO}_4(\text{s})$ | Hg

➤ Reversible and irreversible cells

Galvanic cells may be either reversible or irreversible in the thermodynamic sense. A reversible cell is one whose electrode reactions can be reversed (recharged). Daniel cell is an example of the reversible cell. In irreversible cell, the electrode reactions cannot be reversed (cannot be recharged) e.g. Dry cell.

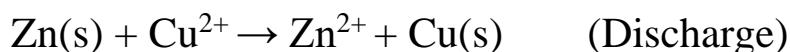
In reversible cells, if the emf of an external source is infinitesimally higher than that of the cell, the current will go in the opposite direction, i.e., the cell reaction will be reversed; on the other hand, if the value is slightly lower, the current will flow from the cell as usual.



Electrochemistry

1) emf (Daniell) > emf (external)

The current will flow from Daniell cell to the external source (usual way).



2) emf (Daniell) = emf (external)

The cell reactions will stop and there is no flow of current in the cell.

3) emf (external) > emf (Daniell)

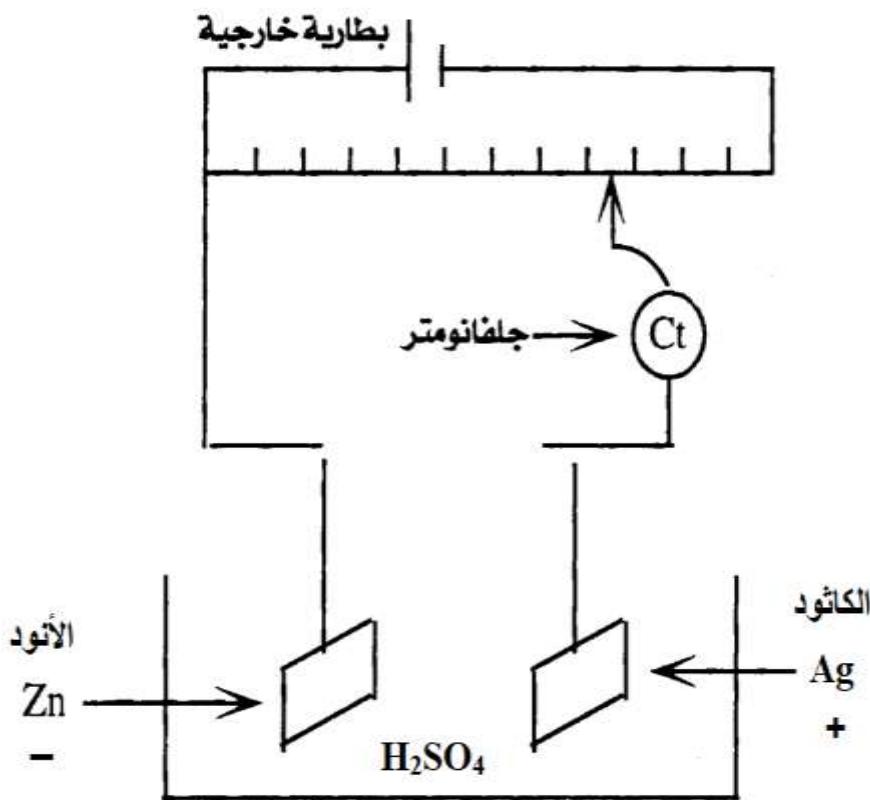
The current will flow from the external source to Daniell cell and the cell operates in the reverse way.



When the cell cannot be brought back to its original condition by reversing the current, the cell is irreversible. As an example of an irreversible cell consider zinc and silver electrodes which dip into a solution of sulfuric acid.

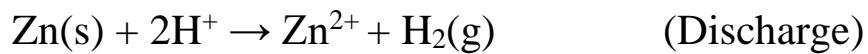
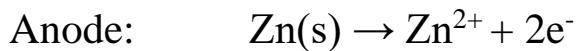


Electrochemistry



1) emf (galvanic) > emf (external)

The current will flow from the cell to the external source (usual way).



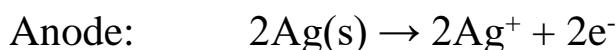
2) emf (galvanic) = emf (external)

The cell reactions will stop and there is no flow of current in the cell.

Electrochemistry

3) emf (external) > emf (galvanic)

The current will flow from the external source to galvanic cell **but** the cell reactions are not the same.



➤ Concentration cells

A concentration cell is a galvanic cell that is comprised of two half-cells with the same electrodes, but differing in concentrations and the voltage of the cell reaches equilibrium by transferring the ions from the half-cell with the higher concentration to the half-cell with the lower concentration.

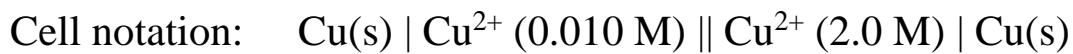
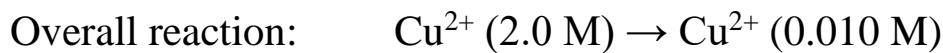
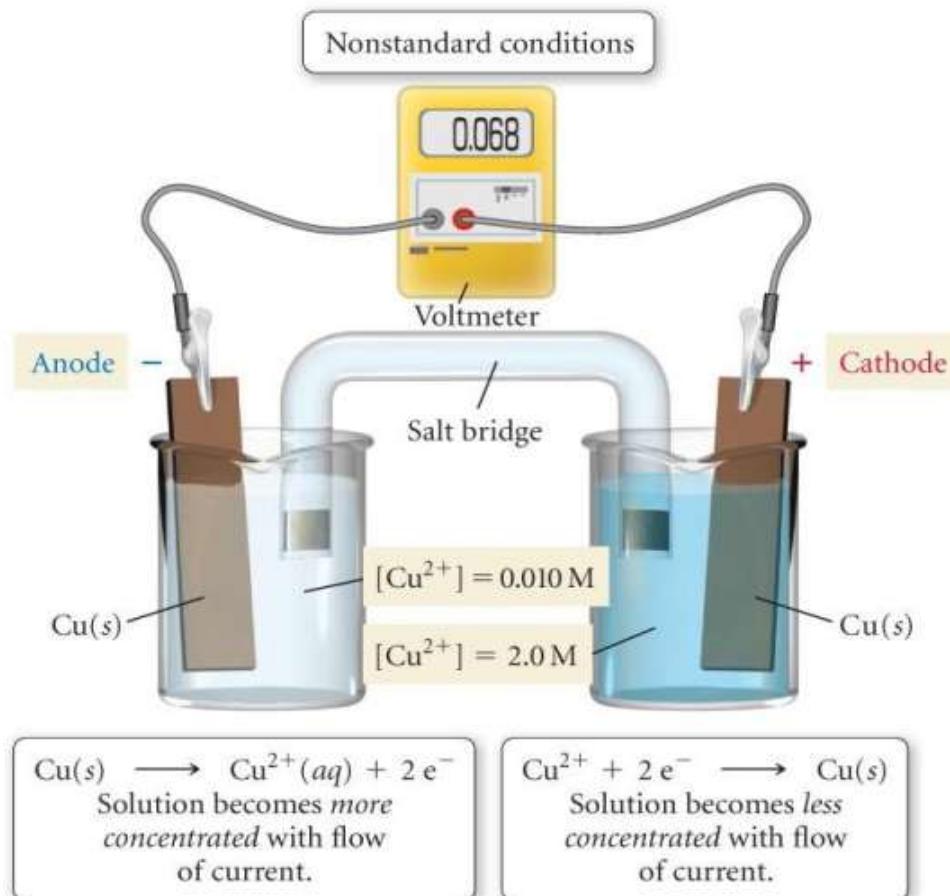
The standard cell potential, commonly written as E°_{cell} , of a concentration cell is equal to zero because the electrodes are identical. However, because the ion concentrations are different, there is a potential difference between the two half-cells. One can find this potential difference via the Nernst Equation,

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{n} \log \frac{C_1}{C_2}$$

The equilibrium is reached when the concentration of the two half-cells becomes the same ($C_1 = C_2$). This occurs by oxidation the

Electrochemistry

electrode in lower concentration, and reduction the electrode in higher concentration. The anode has the lowest concentration of ions and the cathode has the highest concentration of ions



Electrochemistry

➤ **Electrolysis**

Water-soluble substances are distinguished as *Electrolytes or Nonelectrolytes*.

Electrolytes are electrovalent (ionic) substances that form ions in solution which conduct an electric current. NaCl, CuSO₄ and KNO₃ are examples of electrolytes.



Nonelectrolytes are covalent substances which furnish neutral molecules in solution. Their water-solutions do not conduct an electric current. Sugar, alcohol and glycerol are typical nonelectrolytes.



A phenomenon of decomposition of an electrolyte to its original components/elements by passing an electric current through its solution is termed electrolysis.

For example, when water is electrolyzed by passing an electric current through it, we can separate it into hydrogen and oxygen.



Electrochemistry

➤ Mechanism of Electrolysis

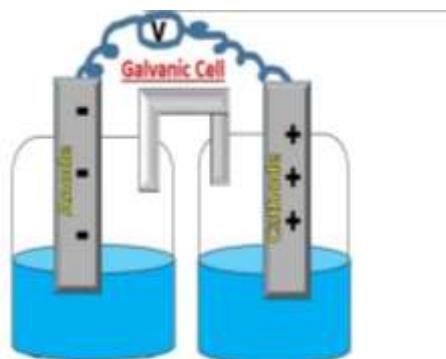
- The cations migrate to the cathode and form neutral atoms by accepting electrons from it (Reduction).
- The anions migrate to the anode and yield neutral particles by transfer of electrons to it (Oxidation).

As a result of the loss of electrons by anions and gain of electrons by cations at their respective electrodes, chemical reaction takes place.

Such as:

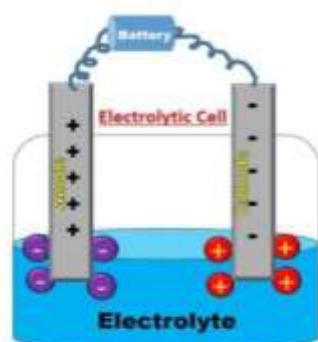
Electrolytic cells

The cell at which electrolysis process is happened is called *electrolytic cell*. It is a device for converting electrical energy into chemical energy. Here, anode is the positive electrode and cathode is the negative electrode.



Changes chemical energy into Electrical energy .

1. Anode is -ve
2. Cathode is +ve
3. Spontaneous reaction occurs.
4. Does not require external voltage source.



Changes electrical energy into Chemical reaction.

1. Anode is +ve
2. Cathode is -ve
3. Non-Spontaneous reaction occurs.
4. Require external voltage source.

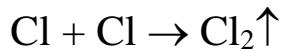
Electrochemistry

Examples

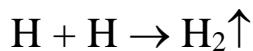
Electrolysis of hydrochloric acid solution

In solution, HCl is ionized, $\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$

At anode: $\text{Cl}^- \rightarrow \text{Cl} + \text{e}^-$ (oxidation)



At cathode: $\text{H}^+ + \text{e}^- \rightarrow \text{H}$ (reduction)



The overall reaction is $2\text{HCl} \rightarrow \text{H}_2 \uparrow + \text{Cl}_2 \uparrow$ (decomposition)

Electrolysis of CuCl₂ solution

In solution, CuCl₂ is ionized, $\text{CuCl}_2 \rightarrow \text{Cu}^{2+} + 2\text{Cl}^-$

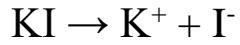
At anode (+ve): $2\text{Cl}^- \rightarrow \text{Cl}_2 \uparrow + 2\text{e}^-$

At cathode (-ve): $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu} \downarrow$



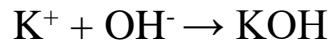
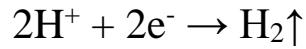
The overall reaction is $\text{CuCl}_2 \rightarrow \text{Cu} \downarrow + \text{Cl}_2 \uparrow$ (decomposition)

Electrolysis of KI solution



At anode (+ve): $2\text{I}^- \rightarrow \text{I}_2 \uparrow + 2\text{e}^-$

At cathode (-ve): $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$



Electrochemistry

Electrolysis of CuSO₄ solution



➤ Faraday's laws of electrolysis

(1) Faraday's first law

The amount of liberated/deposited substances at an electrode during electrolysis is directly proportional to the quantity of electricity that passes through the solution.

If m is mass of substance (in grams) deposited on electrode by passing Q coulombs of electricity", then

$$m \propto Q$$

$$Q(\text{coloumb}) = I(\text{ampere}) \times t(\text{second})$$

Where I is the strength of current in Amperes and t is the time in seconds.

$$m \propto I t$$

$$m = Z \cdot I \cdot t$$

Electrochemistry

Where Z is the electrochemical equivalent

$$Z = \frac{m}{It}$$

Thus, the electrochemical equivalent is the amount of a substance that deposited by 1 Ampere current passing for 1 second (i.e. by one coulomb). Z value differs from one ion to another.

➤ **With the help of the first law of electrolysis, we are able to calculate:**

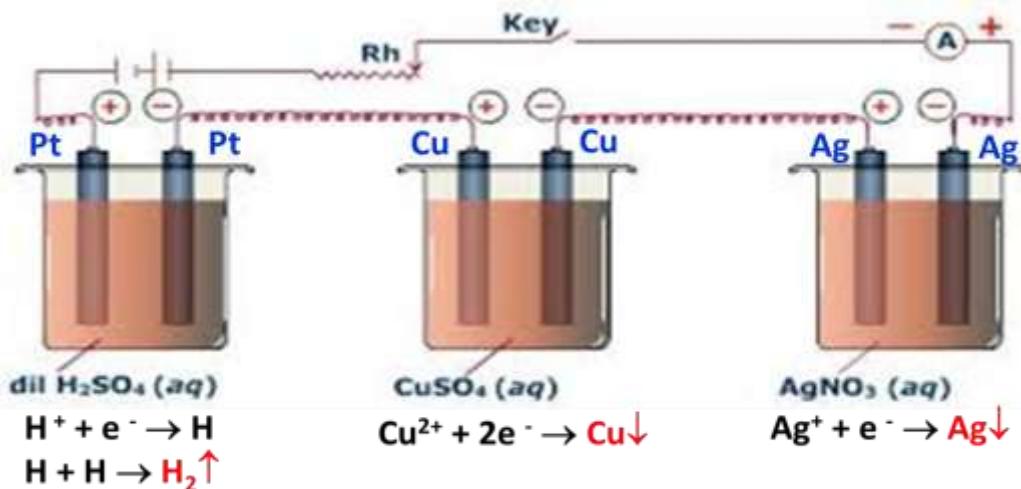
- 1) The value of electrochemical equivalent of different substances.
- 2) The masses of different substances produced by passing a known quantity of electricity through their solutions.
- 3) The quantity of electricity that passes through the electrolytic solution.

(2) Faraday's second law

When the same quantity of electricity passes through different electrolytic solutions, the amounts of liberated/deposited substances at an electrode are directly proportional to their equivalent weights.

$$m \propto eq. wt$$

Electrochemistry



After passing 1 Ampere current for 1 Hour:

Mass of hydrogen : Mass of copper : Mass of silver

0.0379 grams 1.2 grams 4.1 grams

1 31.66 108

$$\frac{\text{Mass of liberated hydrogen}}{\text{Mass of deposited copper}} = \frac{\text{Equivalent weight of hydrogen}}{\text{Equivalent weight of copper}} = \frac{1}{31.66}$$

$\therefore m \propto e$ (equivalent weight)

The second law of electrolysis helps to calculate:

- (1) The equivalent weights of metals.
- (2) Mass of deposited substance.
- (3) The Avogadro's number.

Electrochemistry

➤ **Combination of first law and second law**

Faraday's first law: $m \propto It$

Faraday's second law: $m \propto eq. wt$

$$\therefore m \propto It eq. wt$$

$$m = \frac{It eq. wt}{F}$$

Where F is Faraday's constant (96500 C)

$$F = \frac{It eq. wt}{m}$$

Where F is the **Faradays constant**, which is the quantity of electricity required to liberate/deposit the gram equivalent weight of any substance. This quantity is constant (96500 coulombs) and independent of the nature of substance.

$$\therefore m = Z It$$

$$\therefore m = \frac{It eq. wt}{F}$$

$$Z = \frac{eq. wt}{F}$$

Electrochemistry

➤ Metallic and Electrolytic Conductors

Electrolytes and metals are good conductors of electricity.

Electrolytes are the second type of conductors while the first type of conductors is the metallic conductors.

| Face of Comparison | Metallic Conductors | Electrolytic Conductors |
|-------------------------------------|--|---|
| Nature | Solids | Solutions |
| Conduction | Via the movement of free electrons. | Via the movement of ions. |
| Effect of Temperature | The conductance decreases with temperature due to the repulsion forces between electrons. | The conductance increases with temperature due to an increase in the kinetic energy of ions. |
| Effect of Electrical Current | It has no effect. | It leads to the decomposition of electrolyte (Electrolysis). |