

ELECTROCHEMISTRY

Electrochemistry is the study of chemical processes that cause electrons to move. This movement of electrons is called electricity. In other words, it is the study of relationship between chemical energy and electric energy or the interconversion of the two. The movements of electrons from one element to another occur as a result of a reaction known as an oxidation-reduction ("redox") reaction.

Electrode: A metal (M) in contact with its salt solution (M^{n+}) is defined as an electrode. The metal either undergoes oxidation (loss of electrons) or reduction (gain of electrons).

During oxidation process, $M \longrightarrow M^{n+} + ne^{-}$

the metal acquires a net negative charge while the M^{n+} ions go into the solution. The negative charge developed on the metal attracts the positive M^{n+} ; thereby a layer of positive charge is developed around the metal. Thus an electrical double layer is formed (Helmoltz double layer).

Similarly, during reduction, $M^{n+} + ne^{-} \longrightarrow M$

The metal acquires a net positive charge due to the accumulation of M^{n+} from the solution. The positive charge developed on the metal attracts the negative electrons from the solution; thereby a layer of negative charge is developed around the metal. Thus an electrical double layer is formed (Helmoltz double layer).

Irrespective of the nature of reaction taking place on the electrode, because of the exchange of ions between the metal and its solution, a potential difference is developed. This potential difference becomes constant at equilibrium and is then known as the electrode potential.

Electrode potential: It is the measure of the tendency of the metal to lose electrons (oxidation potential) or gain electrons (reduction potential) when it is in contact with its salt solution. It is denoted by E and its unit is Volt.

Standard electrode potential: It is the measure of the tendency of the metal to lose electrons (oxidation potential) or gain electrons (reduction potential), when it is in contact with its salt solution (having a concentration of 1M) maintained at a temperature of 25°C. It is denoted by E° and its unit is Volt.

Factors on which Electrode potential depends:

- Nature of the electrode
- Concentration of electrolyte
- Temperature

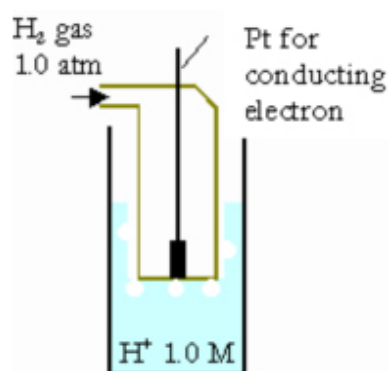
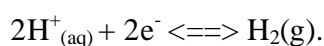
Nerst equation is used to derive the relation between electrode potential and the electrolyte concentration as well as the temperature

Standard Hydrogen Electrode

A Standard Hydrogen Electrode (SHE) is an electrode that scientists use for reference on all half-cell potential reactions. The value of the standard electrode potential of SHE is zero, which forms the basis one needs to calculate cell potentials using different electrodes or different concentrations.

What is a SHE made of?

SHE is composed of an inverted containing 1.0 M $\text{H}^+(\text{aq})$ solution in which a Pt wire coated with Pt black is dipped. The setup is maintained at 25°C. During the reaction, hydrogen gas maintained at 1 atmosphere is then passed through the tube and into the solution causing the reaction:



Standard Hydrogen Electrode (SHE)

The SHE is represented as: $\text{Pt}, \text{H}_2(\text{g}) (1\text{atm})/\text{H}^+ (1\text{M})$.

The SHE can act as the anode or the cathode depending on the nature of the other electrode to which it is attached. Since the E° of SHE is zero, the electrode potential of the other electrode will be equal to E°_{cell} .

It is a common practice to express the electrode potential as reduction potential.


Standard reduction potential of an electrode is defined as the reduction potential of an electrode as determined with respect to a standard hydrogen electrode.


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Electrochemical Series (importance of Reduction Electrode Potential)

A series in which the standard reduction potentials of various electrodes have been arranged in the increasing order (downwards) is called electrochemical series.

The standard reduction potential of hydrogen electrode is zero. The electrodes above hydrogen have negative reduction potential while those placed below it have positive reduction potential.

Table 1: Electrochemical Series		
	Equilibrium (Oxidants \leftrightarrow Reductants)	E° (volts)
 Metal Reducing Activity Increasing	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 Oxidizing Activity Increasing

Application of Electrochemical Series:

1. To predict the oxidizing and reducing powers:

In an electrochemical series, the species placed above hydrogen are more difficult to be reduced and their standard reduction potential is negative. Li is the strongest reducing agent.

The species placed below hydrogen are easily reduced and their E° values are positive. Gold is a very strong oxidizing agent.

In general oxidizing agents have $+E^\circ$ values. Higher the positive value, stronger is the oxidizing agent. Similarly, reducing agents have $-E^\circ$ values. Higher the negative value, stronger is the reducing agent.

2. To predict whether a metal will react with acid to give hydrogen gas.

Metals placed above hydrogen in the series have great tendency for oxidation so they will displace hydrogen from acids.

3. To predict the spontaneity of any redox reaction.

For any spontaneous reaction, free energy change (ΔG) should be negative

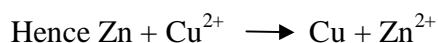
$$\text{Since } \Delta G = -nF E_{\text{cell}}$$

Hence E_{cell} should be positive for spontaneous reaction.

4. To predict the replacement tendency:

If a metal has lower values of reduction potential, it shows a great tendency to assume the oxidized form and it will displace another metal (with higher reduction potential) from the solution of the latter.

$$\text{For example: } E^\circ (\text{Zn}^{2+}/\text{Zn}) < E^\circ (\text{Cu}^{2+}/\text{Cu})$$



Zinc will displace Cu^{2+} from the solution of Cu^{2+} spontaneously

5. To predict correct metallurgical methods:

E° values of Cu, H_2O and Al are +0.34, -0.83 and -1.66V. It means Cu gets easily reduced than water and water gets easily reduced than Al. Hence Cu can be produced by electrolysis of aqueous CuSO_4 but not Al. This is due to the fact that when $\text{Al}^{3+}_{(\text{aq})}$ is electrolyzed, water will be electrolyzed but not $\text{Al}^{3+}_{(\text{aq})}$

6. for calculation of equilibrium constants (K_{eq})

$$\Delta G = -RT \ln K_{\text{eq}}$$

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

$$E^\circ = \frac{RT}{nF} \ln K_{\text{eq}}$$

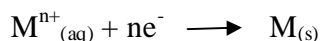
$$\ln K_{\text{eq}} = \frac{nFE^\circ}{RT}$$

Nernst Equation

The *Nernst Equation* helps to determine the electrode potential under non-standard conditions. It also tells us the effect of electrolyte concentration and temperature on the electrode potential.

Derivation of Nernst Equation of an electrode:

Consider the following electrode reaction:



Let the free energy change of the above reaction be (ΔG) and free energy under standard condition be (ΔG°), activity of product (M) be $a_{product}$ and activity of reactant (M^{n+}) be $a_{reactant}$

From thermodynamics, the Gibbs energy change under non-standard conditions can be related to the Gibbs energy change under standard Equations via

$$\Delta G = \Delta G^{\circ} + RT \ln \frac{a_{product}}{a_{reactant}} \quad (\text{eq 1})$$

Where R is the Gas Constant and T is the temperature in K

ΔG is also related to electrode potential (E) and under standard conditions ΔG° is related to E° via

$$\Delta G = -nFE \quad \text{and} \quad \Delta G^{\circ} = -nFE^{\circ}$$

where

- n is the number of electrons transferred in the reaction (from balanced reaction),
- F is the Faraday constant (96,500 Coulombs/mol), and

Hence, putting the value of ΔG and ΔG° in eq 1, we get:

$$nFE = nFE^{\circ} + RT \ln \frac{a_{product}}{a_{reactant}}$$

Thus, $E = E^{\circ} - \frac{RT}{nF} \ln \frac{a_{product}}{a_{reactant}} = E^{\circ} - \frac{2.303RT}{nF} \log \frac{a_{product}}{a_{reactant}} \quad (\text{eq 2})$

Eq 2 is the Nernst equation under non standard conditions

Under standard conditions (T=298K) and putting the value of $R = 8.314 \text{ J/K/mol}$ and $F = 96500 \text{ C}$, we get:

$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{a_{product}}{a_{reactant}} \quad (\text{eq 3})$$

Under dilute concentrations, activity of reactant and product can be replaced by molar concentration terms:

$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{[M]_{(s)}}{[M^{n+}]_{(aq)}} \quad (\text{eq 4})$$

For pure solid $[M]_s = 1$; eq 4 reduces to:

$$E = E^\circ - \frac{0.0591}{n} \log \frac{1}{[M^{n+}](aq)} \quad (\text{eq 5})$$

Eq 5 represents the Nernst equation of the electrode M at 298 K (under standard condition)

Under non-standard conditions, at temp T,

$$\text{Nernst equation of the electrode is: } E = E^\circ - \frac{2.303 RT}{nF} \log \frac{1}{[M^{n+}](aq)} \quad (\text{eq 6})$$

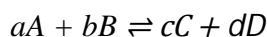
From eq 6, it can be concluded that

- E increases as $[M^{n+}]$ is increased
- E decreases with increase in temperature)

Nernst equation of a cell

An anode and a cathode connected by an electrical circuit is known as the cell.

Consider a redox reaction occurring in a cell:



$$E = E_{cell}^\circ - \frac{2.303 RT}{nF} \log \left(\frac{C^c D^d}{A^a B^b} \right)$$

$$E_{cell}^\circ = E_{cathode}^\circ - E_{anode}^\circ$$

Application of Nernst equation

1. Nernst equation can be used to study the effect of electrolyte concentration on electrode potential

Numerical

Calculate the electrode potential of a copper wire dipped in 0.1M CuSO_4 solution at 25°C . The standard electrode potential of copper is 0.34V.

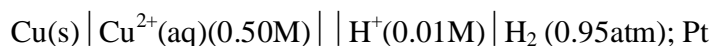
Solution: $\text{Cu}^{2+}_{(aq)} + 2e^- \rightleftharpoons \text{Cu}(s)$

$$E = E^\circ - \frac{2.303 RT}{nF} \log \left(\frac{1}{\text{Cu}^{2+}} \right) = 0.34 - \frac{2.303 \times 8.314 \times 298}{2 \times 96500} \log \left(\frac{1}{0.1} \right) = -0.31 \text{ V}$$

2. Nernst equation is used for the calculation of potential of a cell under non-standard condition

Numerical

Calculate the potential of the following electrochemical cell at 25°C :



Given: $E_{cathode}^\circ = 0.00\text{V}$ and $E_{anode}^\circ = 0.34\text{V}$

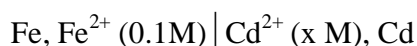
$$\text{Solution: } E_{cell}^\circ = E_{cathode}^\circ - E_{anode}^\circ = 0.00 - 0.34\text{V} = -0.34\text{V}$$

$$\text{Potential of cell} = E_{\text{cell}} = E^{\circ}_{\text{cell}} - 0.059/2 \log \frac{[Cu^{2+}]P_{H_2}}{[H^+]^2} = -0.34 - 0.059/2 \log \frac{0.50 \times 0.95}{0.01^2} = -0.449 \text{ V}$$

3. Determination of unknown concentration of one of the ionic species in a cell is possible with the help of Nernst equation provided E°_{cell} and concentration of other ionic species is known

Numerical

Determine the concentration of Cd^{2+} in the following electrochemical cell:



Given: emf of cell $E = -0.02 \text{ V}$ and $E^{\circ} = 0.04 \text{ V}$ at 25°C

Solution: overall cell reaction: $Fe(s) + Cd^{2+} \rightleftharpoons Fe^{2+} + Cd(s)$

$$E = E^{\circ} - 0.059/2 \log \frac{[Fe^{2+}]}{[Cd^{2+}]} = -0.02 - 0.059/2 \log \frac{0.1}{x}$$

$$x = 0.00093 = 0.001 \text{ M}$$

Electrochemical Cell

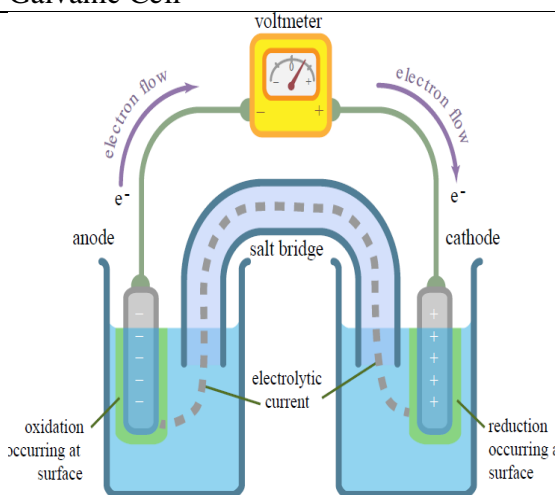
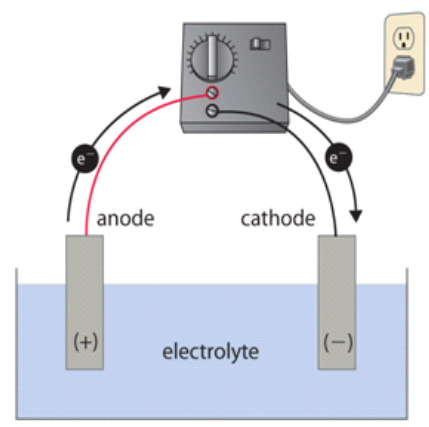
An electrochemical cell is a device for the conversion of electrical energy into chemical energy or vice versa

There are two types of electrochemical cell: Galvanic/Voltaic Cell and electrolytic cell.

Electrolytic cells are very similar to voltaic (galvanic) cells in the sense that both have a cathode and anode side, and both have a consistent flow of electrons from the anode to the cathode. However, there are also striking differences between the two cells. The main differences are outlined below:

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Difference between Galvanic cell and Electrolytic Cell

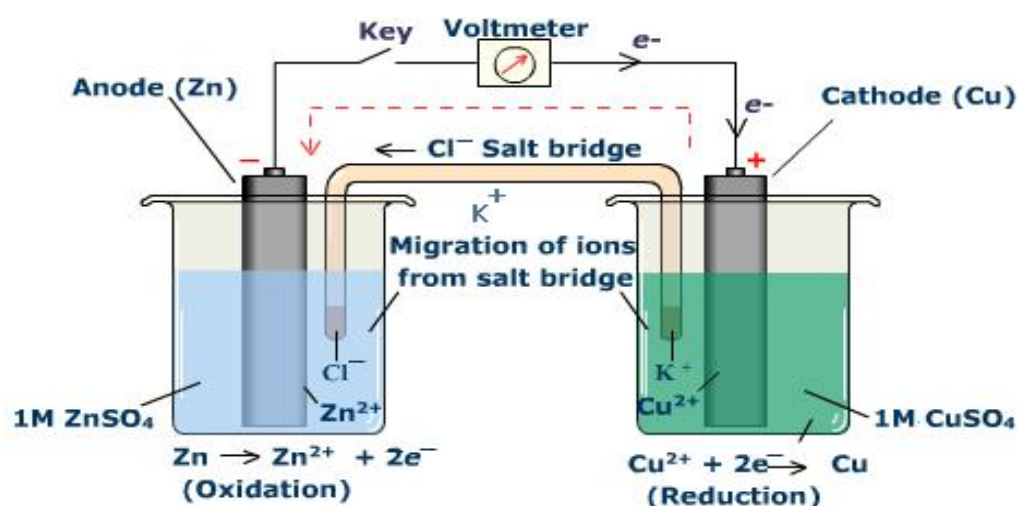
S.No	Galvanic Cell	Electrolytic Cell
1		 <p style="text-align: center;">ELECTROLYTIC CELL</p>
2	<p>Anode and cathode are placed in separate containers. Both containers are connected via an external circuit for the flow of electrons from anode to cathode. A second connection (salt bridge) brings about a flow of ions between the two electrolytic solutions so as to maintain electrical neutrality.</p>	<p>Anode and cathode are placed in same container having the same electrolytic solution i.e both electrodes are dipped in the same salt solution. Salt bridge is absent.</p>
3	<p>Anode is the negative electrode where oxidation takes place. Anodic reaction: $X \longrightarrow X^+ + e^-$ Cathode is the positive electrode where reduction takes place Cathodic reaction: $Y^+ + e^- \longrightarrow Y$ Overall redox reaction: $X + Y^+ \longrightarrow X^+ + Y$ Redox reaction is spontaneous ($\Delta G < 0$)</p>	<p>Anode is the positive electrode where oxidation takes place Anodic reaction: $X \longrightarrow X^+ + e^-$ Cathode is the negative electrode where reduction takes place Cathodic reaction $Y^+ + e^- \longrightarrow Y$ Overall redox reaction: $X + Y^+ \longrightarrow X^+ + Y$ Redox reaction is non-spontaneous ($\Delta G > 0$)</p>
4	<p>The potential difference generated is due to redox reaction taking place between cathode and anode and causes the electrons to flow from anode to cathode and hence causes current to flow when circuit is completed</p>	<p>The potential difference generated is due to the electric energy from an external source and causes the electrons to flow from anode to cathode and hence causes the redox reaction to take place.</p>
5	<p>Energy from redox reaction is converted to electrical energy</p>	<p>Electrical energy from external source is converted to chemical energy to drive the redox reaction.</p>
6	<p>Example: dry cell or Daniel Cell</p>	<p>Example: electrolytic purification of metals</p>

Galvanic Cell

It is a device which converts chemical energy from a spontaneous redox reaction to electrical energy.

Example of galvanic cell is Daniel Cell. It consists of a separate anodic compartment (Zn electrode dipped in ZnSO_4 solution) and a separate cathodic compartment (Cu electrode dipped in CuSO_4 solution). Both compartments are connected externally by a wire and a salt bridge. The wire allows for the flow of electrons from the anode to the cathode; while the salt bridge is required for maintaining electrical neutrality between the two electrolytic solutions.

Schematic diagram of a Daniel cell is:



The **cell diagram** is a shorthand notation to represent the redox reactions of a galvanic cell. For the Daniel cell described, the cell diagram is as follows: $\text{Zn(s)}|\text{Zn}^{2+}(\text{aq})||\text{Cu}^{2+}(\text{aq})|\text{Cu(s)}$

- A double vertical line (||) is used to separate the anode half reaction from the cathode half reaction. This represents the salt bridge.
- The anode (where oxidation occurs) is placed on the left side of the ||.
- The cathode (where reduction occurs) is placed on the right side of the ||.
- 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.

EMF of a Galvanic Cell

EMF is the maximum potential difference between two electrodes of a cell. It is the EMF that causes current to flow from the electrode of higher potential to the one of lower potential.

$$\text{EMF of a cell} = E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

For a cell to operate spontaneously, ΔG is < 0 (negative) and since $\Delta G = -nFE_{\text{cell}}$, E_{cell} is positive.

If the cell operates under standard conditions, $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$

For a Daniel Cell,

- Oxidation half reaction: $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{e}^{-}$ $E^{\circ} = -0.763\text{V}$
 - Reduction half reaction: $\text{Cu}^{2+}(\text{aq}) + \text{e}^{-} \rightarrow \text{Cu(s)}$ $E^{\circ} = +0.342\text{V}$
- Net reaction: $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$

$$\text{Therefore: } E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = 0.340\text{V} - (-0.763\text{V}) = +1.103\text{V}$$

Role of the salt bridge:

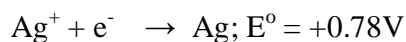
Salt bridge is an inverted U-tube containing an aqueous solution of electrolyte (KCl, KNO_3 , K_2SO_4). The electrolyte should not react chemically with the redox reaction. Agar-agar or gelatin is added to the aqueous solution of the electrolyte to convert it into a semi-solid paste.

Salt bridge helps to

1. Maintain electrical neutrality of the two electrolytic solutions in the two half cells (anode and cathode)
2. It helps to provide cations and anions to replace the ions that are lost or produced in the two half cells
3. It helps to allow the flow of current by completing the electrical circuit
4. It helps to prevent the intermixing of the two electrolytic solution in the two half cells

Numericals:

Q1. Given:



Give the cell diagram and find the emf of the cell

Solution:



$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = +0.78\text{V} - (-0.40\text{V}) = 1.18\text{V}$$

Q2. For the cell: $\text{Zn}|\text{Zn}^{2+}(1\text{M})||\text{Fe}^{2+}(1\text{M})|\text{Fe}^{3+}(1\text{M})$

$E^\circ(\text{Fe}^{3+}|\text{Fe}^{2+}) = +0.77\text{V}$ and $E^\circ(\text{Zn}|\text{Zn}^{2+}) = +0.76\text{V}$

Write the cell reaction and calculate the value of E_{cell}° for the above cell

Solution:

Anodic cell reaction: $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$; $E^\circ = -0.76\text{V}$. (eq1)

Cathodic cell reaction: $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$; $E^\circ = +0.77\text{V}$

Cathodic cell reaction has to be multiplied by 2;

Cathodic cell reaction: $2\text{Fe}^{3+} + 2\text{e}^- \rightarrow 2\text{Fe}^{2+}$; $E^\circ = +0.77\text{V}$. (eq2)

Adding eq 1 and eq2

$\text{Zn} + 2\text{Fe}^{3+} \rightarrow 2\text{Fe}^{2+} + \text{Zn}^{2+}$

$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = +0.77\text{V} - (-0.76\text{V}) = +1.53\text{V}$

Concentration Cells

In concentration cells, the emf arises due to the changes in the concentration of either the electrolytes or the electrodes. This is in contrast to galvanic cells in which the emf arises due to decrease in free energy of the chemical reaction taking place in the cell.

Concentration cells are of two types.

a. **Electrode concentration cell:** concentration of electrode is different. Example: gas electrode concentration cell. This cell consists of two hydrogen electrodes maintained at different partial pressures of the hydrogen gas (p_1 and p_2) and are dipped in the same electrolyte HCl solution.

Cell representation: $\text{Pt}, \text{H}_2(\text{g})(p_{\text{H}_2} = p_1) | \text{H}^+ | \text{H}_2(\text{g})(p_{\text{H}_2} = p_2)$

Anodic cell reaction: $\text{H}_2(p_1) \rightarrow 2\text{H}^+ + 2\text{e}^-$

Cathodic cell reaction: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(p_2)$

Overall cell reaction: $\text{H}_2(p_1) \rightarrow \text{H}_2(p_2)$

$$E_{\text{cell}} = \frac{2.303RT}{2F} \log_{10} \frac{p_1}{p_2}$$

b. **Electrolyte concentration cell:** these cells consist of two identical electrodes dipped in two solutions of the same electrolyte at different concentrations.

Cell representation: $\text{M} | \text{M}^{n+}(\text{C}_1) || \text{M}^{n+}(\text{C}_2) | \text{M}$

Where C_1 and C_2 are concentration of the M^{n+} ions and $\text{C}_2 > \text{C}_1$

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = (E^\circ - \frac{2.303RT}{nF} \log 1/\text{C}_2) - (E^\circ - \frac{2.303RT}{nF} \log 1/\text{C}_1) = \frac{2.303RT}{nF} \log_{10} \frac{\text{C}_2}{\text{C}_1}$$

Corrosion: It is the process of chemical or electrochemical interaction of metal with its environment. As a result of corrosion, useful properties of metal such as ductility, malleability and electrical conductivity is lost.

Example is the rusting of iron or tarnishing of silver

Cause of Corrosion: Metals exist in nature in the form of ores i.e the oxides, sulphides, sulphates or carbonates. The existence of metals in ore state is thermodynamically stable and has less energy as compared to the metals. Thus, it is the natural tendency of metals to interact chemically or electrochemically with their environment to form ore and thus undergo corrosion.

Effect of corrosion:

- i. Loss of useful properties of metal and hence loss in its efficiency
- ii. Increase in maintenance and production cost
- iii. Contamination of product
- iv. Unpredictable failure of machinery
- v. Contamination of water due to corroded pipes
- vi. Leakage of toxic liquid or gas from corroded pipes and tubes

Electrochemical theory or Wet theory of Corrosion

When corrosion occurs under wet conditions (in the presence of moisture in the atmosphere), transfer of electrons takes place from anodic parts of metal surface to the cathodic parts through the conducting aqueous medium. The phenomenon is similar to a galvanic cell. Such phenomenon is known as electrochemical corrosion and is more common than dry corrosion.

Mechanism of wet corrosion:

Electrochemical corrosion involves:

- a) Formation of separate anodic and cathodic areas with current flowing through the conducting aqueous medium
- b) Oxidation occurs at the anode with the generation of metallic ions (corrosion occurs at the anode)
- c) while reduction occurs at the cathode with the formation of non-metallic ions like OH^- or O^{2-}
- d) The metallic and non-metallic ions diffuse towards each other through the conducting aqueous medium and corrosion products are formed in between the anode and cathode areas.

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Rusting of iron in aqueous medium in the presence of oxygen or in acidic environment is an example of electrochemical corrosion.

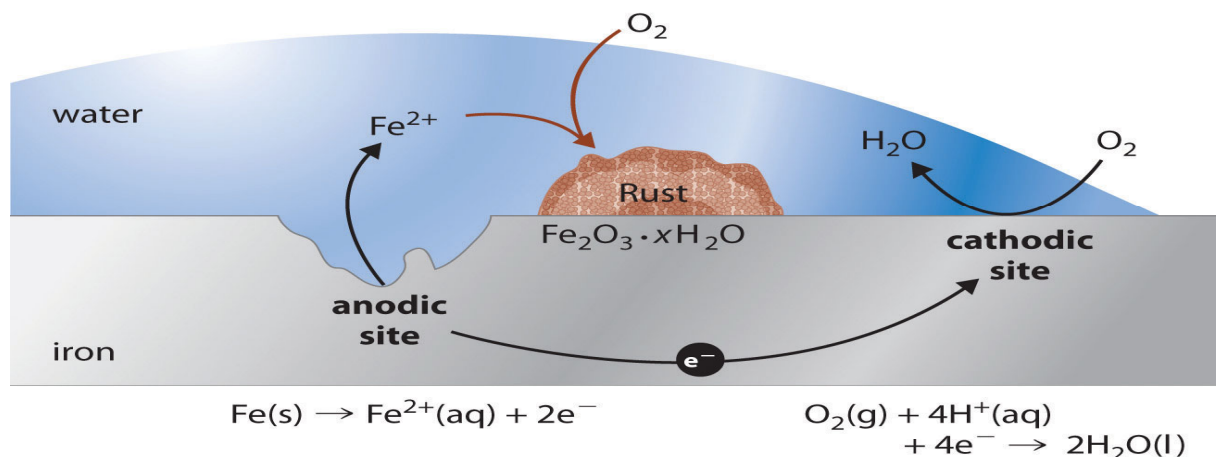
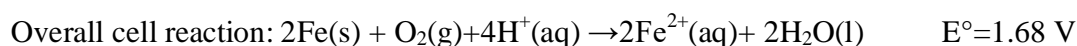
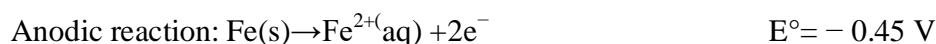
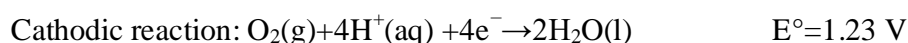


Illustration of the mechanism of electrochemical corrosion of iron

Iron is oxidized to $\text{Fe}^{2+}(\text{aq})$ at an anodic site on the surface of the iron, which is often an impurity or a lattice defect. Oxygen is reduced to water at a different site on the surface of the iron, which acts as the cathode. Electrons are transferred from the anode to the cathode through the electrically conductive metal. Water is a solvent for the Fe^{2+} that is produced initially and acts as a salt bridge. Rust ($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$) is formed by the subsequent oxidation of Fe^{2+} by atmospheric oxygen.



The sign and magnitude of E° for the corrosion process indicate that there is a strong driving force for the oxidation of iron by O_2 under standard conditions (1 M H^{+})

The Fe^{2+} ions produced in the initial reaction are then oxidized by atmospheric oxygen to produce the insoluble hydrated oxide containing Fe^{3+} as represented in the following equation:



Factors affecting rusting of iron:

- a) Presence of water
- b) Presence of oxygen

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Difference between dry corrosion (chemical corrosion) and wet corrosion (electrochemical corrosion):

S. No	Dry corrosion	Wet Corrosion
1	It occurs in dry conditions	It occurs in wet condition in the presence of electrolyte or moisture
2	It involves direct chemical attack of metal with its environment	It involves the formation of innumerable number of galvanic cells and corrosion occurs by electrochemical mechanism
3	It occurs on both homogenous as well as heterogenous surfaces	It occurs only on heterogenous metal surface.
4	Corrosion is uniform	Corrosion is not uniform
5	It is a slow process	It is a fast process
6	Corrosion products accumulate at the same place where corrosion occurs	Corrosion occurs at the anode but products accumulate in between the anode and cathode