

ELECTROCHEMISTRY

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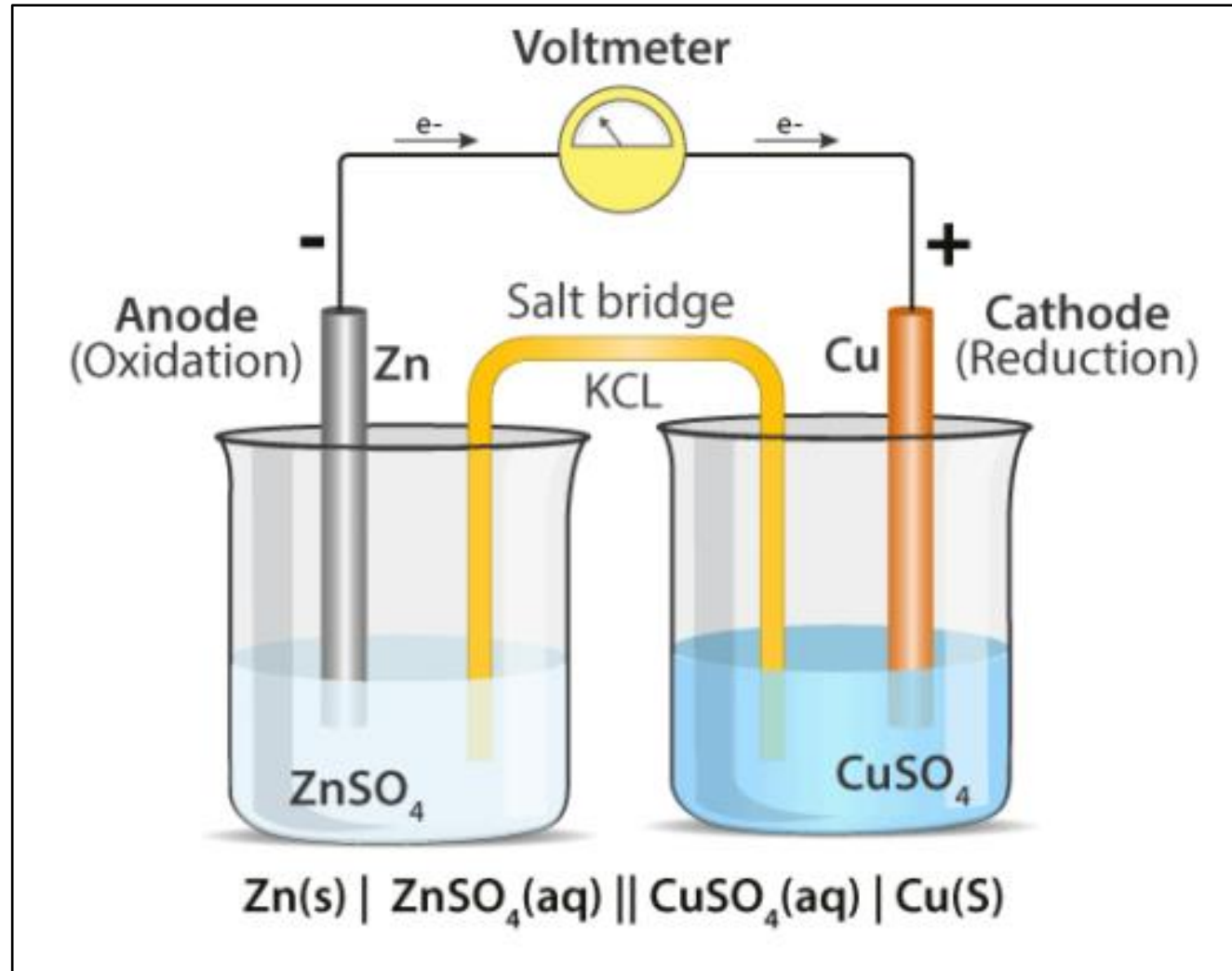
Introduction

- **The branch of chemistry that deals with the relationship between electricity (flow of electrons) and chemical reactions.**
- **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.**

Types of electrochemical cells

- An electrochemical cell is a device that can generate electrical energy from the chemical reactions occurring in it, or use the electrical energy supplied to it to facilitate chemical reactions in it. These devices are capable of converting chemical energy into electrical energy, or vice versa. A common example of an electrochemical cell is a standard 1.5-volt cell which is used to power many electrical appliances such as TV remotes and clocks.
- Such cells capable of generating an electric current from the chemical reactions occurring in them are called **Galvanic cells** or **Voltaic cells**. Alternatively, the cells which cause chemical reactions to occur in them when an electric current is passed through them are called **electrolytic cells**.

Electrochemical cell



- The two primary types of electrochemical cells are

1. Galvanic cells (also known as Voltaic cells)

2. Electrolytic cells

Galvanic Cell / Voltaic Cell	Electrolytic Cell
Chemical energy is transformed into electrical energy in these electrochemical cells.	Electrical energy is transformed into chemical energy in these cells.
The redox reactions that take place in these cells are spontaneous in nature.	An input of energy is required for the redox reactions to proceed in these cells, i.e. the reactions are non-spontaneous.
In these electrochemical cells, the anode is negatively charged and the cathode is positively charged.	These cells feature a positively charged anode and a negatively charged cathode.
The electrons originate from the species that undergoes oxidation.	Electrons originate from an external source (such as a battery).

Concept of Electrode Potential

When a metal is placed in a solution of its ions, the metal acquires either a positive or negative charge with respect to the solution. On account of this, a definite potential difference is developed between the metal and the solution. This potential difference is called electrode potential.

- The potential difference is established due to the formation of electrical double layer at the metal – solution interface.

- Following two changes occur when a metal rod is dipped in its salt solution,

(a) Oxidation: Metal ions pass from the electrode into solution leaving an excess of electrons and thus a negative charge on the electrode.



(b) Reduction: Metal ions in solution gain electrons from the electrode leaving a positive charge on the electrode. Metal ions start depositing on the metal surface leading to a positive charge on the metal.



- The magnitude of the electrode potential of a metal is a measure of its relative tendency to lose or gain electrons, i.e., it is a measure of the relative tendency to undergo oxidation (loss of electrons) or reduction (gain of electrons).

Concept of Electrode Potential (contd...)

- Depending on the nature of the metal electrode to lose or gain electrons, the electrode potential may be of two types:

1. Oxidation potential: When electrode is negatively charged with respect to solution, i.e., it acts as anode. Oxidation occurs.



2. Reduction potential: When electrode is positively charged with respect to solution, i.e., it acts as cathode. Reduction occurs.



- It is not possible to measure the absolute value of the single electrode potential directly. Only the difference in potential between two electrodes can be measured experimentally. It is, therefore, necessary to couple the electrode with another electrode whose potential is known. This electrode is termed as reference electrode. The EMF of the resulting cell is measured experimentally.
- The **EMF of the cell** is equal to the sum of potentials on the two electrodes.
Emf of the cell = $E_{\text{Anode}} + E_{\text{Cathode}}$ = Oxidation potential of anode + Reduction potential of cathode
- Knowing the value of reference electrode, the value of other electrode can be determined.

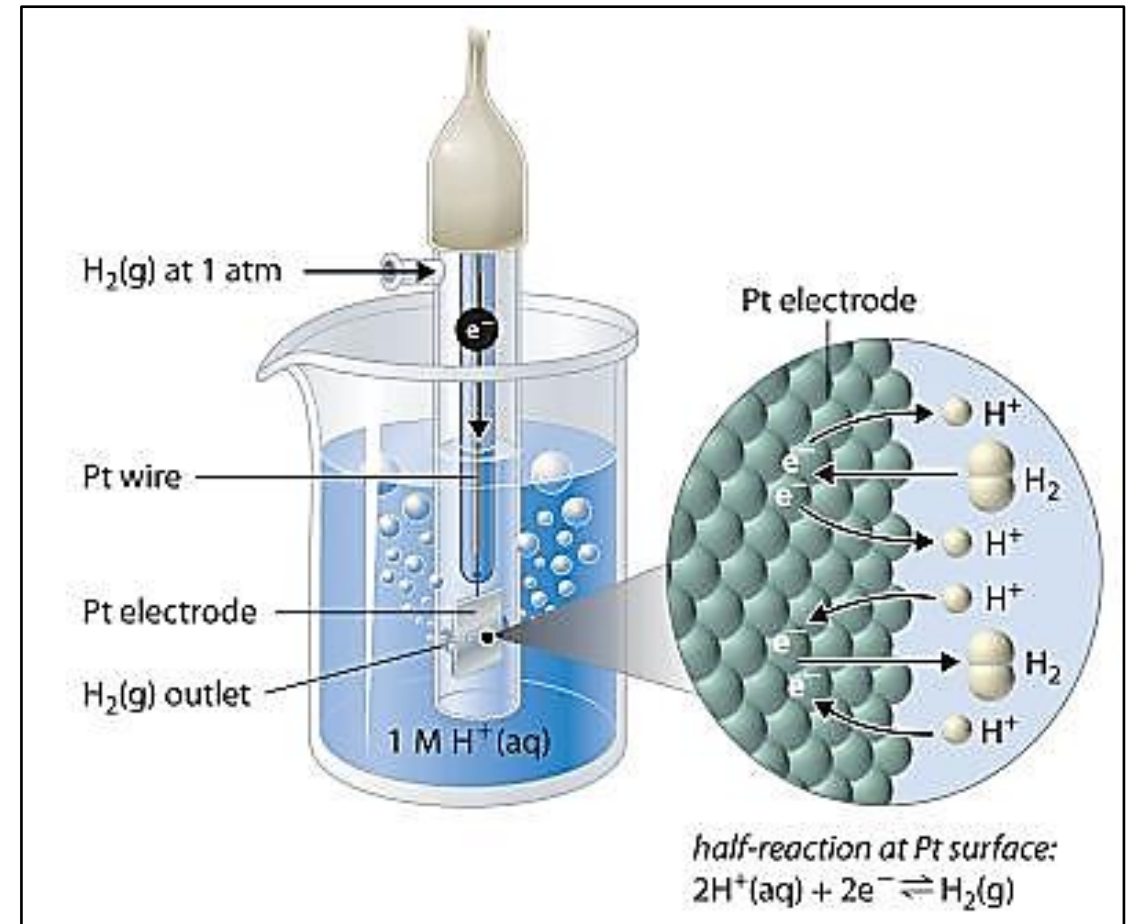
Standard Electrode Potential

- In order to compare the electrode potentials of various electrodes, it is necessary to specify the concentration of the ions present in solution in which the electrode is dipped and the temperature of the half-cell.
 - The potential difference developed between metal electrode and the solution of its ions of unit molarity (1M) at 25°C (298 K) is called standard electrode potential (E^0).
 - According to the IUPAC convention, the reduction potential alone be called as the electrode potential (E^0), i.e., the given value of electrode potential be regarded as reduction potential unless it is specifically mentioned that it is oxidation potential.
 - Standard reduction potential of an electrode means that reduction reaction is taking place at the electrode. If the reaction is reversed and written as oxidation reaction, the numerical value of electrode potential will remain same but the sign of standard potential will have to be reversed. Thus
 - **Standard reduction potential = - (Standard oxidation potential)**
- or*
- **Standard oxidation potential = - (Standard reduction potential)**

Standard Hydrogen Electrode (SHE)

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 is zero, which forms the basis one needs to calculate cell potentials using different electrodes or different concentrations. It is important to have this common reference electrode just as it is important for the International Bureau of Weights and Measures to keep a sealed piece of metal that is used to reference the S.I. Kilogram.

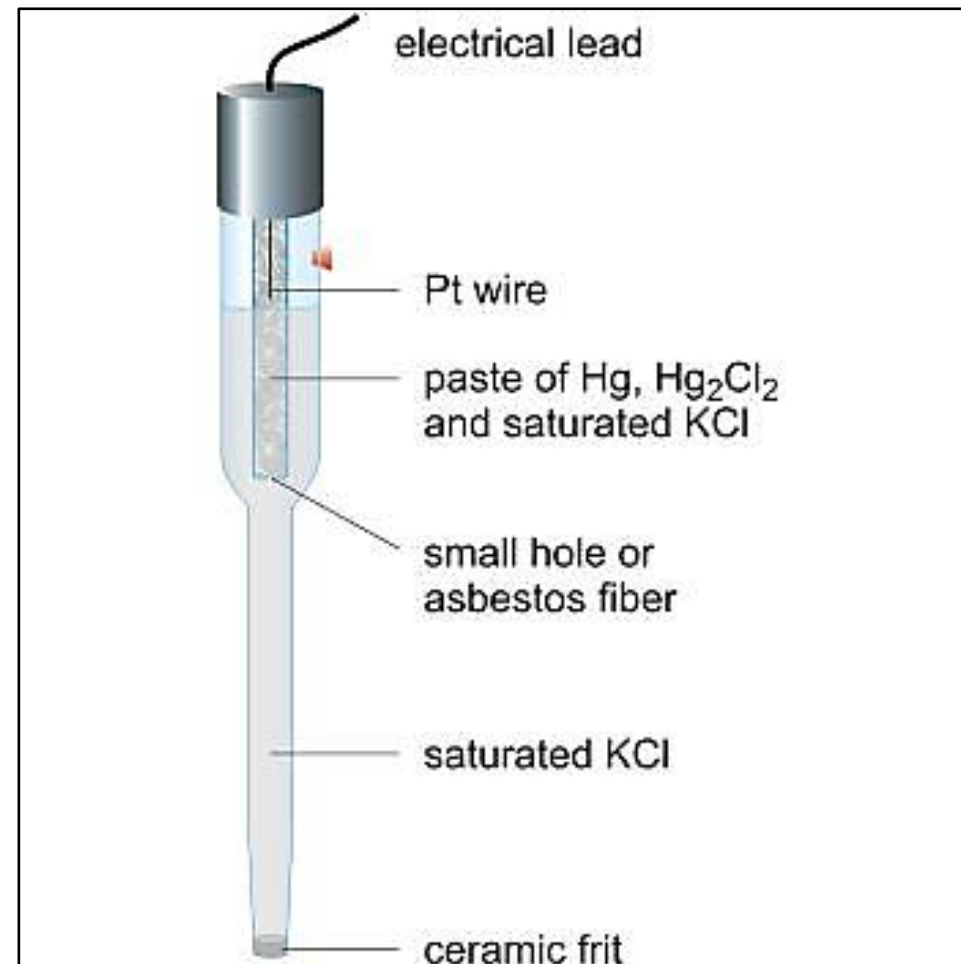
SHE is composed of a 1.0 M $\text{H}^+(\text{aq})$ solution containing a square piece of platinized platinum (connected to a platinum wire where electrons can be exchanged) inside a tube. During the reaction, hydrogen gas is then passed through the tube and into the solution causing the reaction:



Standard Calomel Electrode

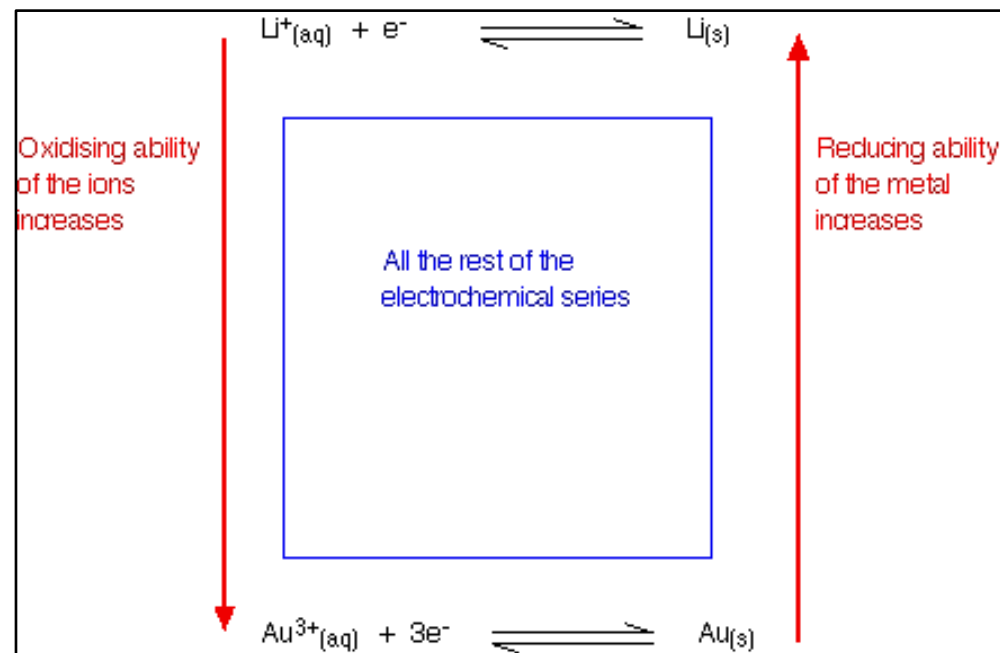
It consists of mercury at the bottom over which a paste of mercury-mercurous chloride is placed. A solution of potassium chloride is then placed over the paste. A platinum wire sealed in a glass tube helps in making the electrical contact. The electrode is connected with the help of the side tube through a salt bridge

The potential of the calomel electrode depends upon the concentration of the potassium chloride solution. If potassium chloride solution is saturated, the electrode is known as saturated calomel electrode (SCE) and if the potassium chloride solution is 1 N, the electrode is known as normal calomel electrode (NCE) while for 0.1 N potassium chloride solution, the electrode is referred to as decinormal calomel electrode (DNCE). The electrode reaction when the electrode acts as cathode is:





Electrochemical Series

- The electrochemical series is built up by arranging various redox equilibria in order of their standard electrode potentials (redox potentials). The most negative E° values are placed at the top of the electrochemical series, and the most positive at the bottom.
- Metals at the top of the series are good at giving away electrons. They are good reducing agents. The reducing ability of the metal increases as you go up the series.
- Metal ions at the bottom of the series are good at picking up electrons. They are good oxidizing agents. The oxidizing ability of the metal ions increases as you go down the series.



Electrochemical series (contd...)

- E° value shows whether the position of the equilibrium lies to the left or right of the hydrogen equilibrium.
- That difference in the positions of equilibrium causes the number of electrons which build up on the metal electrode and the platinum of the hydrogen electrode to be different. That produces a potential difference which is measured as a voltage.
- Obviously if you connect one standard hydrogen electrode to another one, there will be no difference whatsoever between the positions of the two equilibria. The number of electrons built up on each electrode will be identical and so there will be a potential difference of zero between them.

Metal Reducing Activity Increasing 	Equilibrium (Oxidants \leftrightarrow Reductants)	E° (volts)	 Metal Oxidizing 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	

Applications of Electrochemical series

1. Oxidizing and Reducing Strengths

Electrochemical series helps us to identify a good Oxidising agent and Reducing agent

2. Calculation of Standard emf (E_0) of Electrochemical Cell

The standard emf of the cell is the sum of the standard reduction potential of the two half cell: reduction half cell and oxidation half cell

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red}} + E^{\circ}_{\text{ox}}$$

3. Predicting the Feasibility of Redox Reaction

4. Predicting the Product of Electrolysis

Difference between Electrochemical series and Galvanic Series

Electrochemical series	Galvanic Series
<ul style="list-style-type: none">• Based on increasing order of standard electrode potentials of metals and non-metals• Position of metal is fixed• Comprises of metals and non metals• Position of alloy is not mentioned• Predicts relative displacement tendencies.	<ul style="list-style-type: none">• Based on corrosion tendencies of metals and alloys• Position of metal is not fixed• Comprises of metals and alloys• Position of pure metal and same metal in alloy is different• Predicts the relative corrosion tendencies

Nernst Equation

- The Nernst Equation enables the determination of cell potential under non-standard conditions.
- It takes into account the values of standard electrode potentials, temperature, activity and the reaction quotient for the calculation of cell potential.
- It relates the measured cell potential to the **reaction quotient** and allows the accurate determination of equilibrium constants (including solubility constants)

Nernst Equation (Derivation)

For any cell reaction, Gibbs free energy can be related to standard electrode potential as:

$$\Delta G = -nFE$$

Where, ΔG = Gibbs free energy, n = number of electrons transferred in the reaction, F = Faradays constant (96,500 C/mol) and E = cell potential. Under standard conditions, the above equation can be given as,

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

According to the theory of thermodynamics, Gibbs free energy under general conditions can be related to Gibbs free energy under the standard condition and the reaction quotient as:

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

Where, Q = reaction quotient, R = universal gas constant and T = temperature in Kelvin. Incorporating the value of ΔG and ΔG° , from the first two equations, we get:

$$-nFE = -nFE^\circ + RT \ln Q$$

$$E = E^\circ - (RT/nF) \ln Q$$

Converting natural log to \log_{10} , the above equation is known as the Nernst equation. Here, it relates the reaction quotient and the cell potential. Special cases of Nernst equation:

$$E = E^\circ - (2.303RT/nF) \log_{10} Q$$

At standard temperature, $T = 298\text{K}$:

$$E = E^\circ - (0.0592\text{V}/n) \log_{10} Q$$

At standard temperature $T = 298\text{ K}$, the $2.303RT/F$, term equals 0.0592 V .

Nernst Equation (contd...)

Consider a cell reaction



The Nernst Equation can be written as,

$$E = E^{\circ} - (2.303RT/nF) \log_{10} Q$$

ie
$$E = E^{\circ} - (2.303RT/nF) \log_{10} [M]/[M^{n+}]$$

At equilibrium, $Q = K_{eq}$

As the redox reaction in the cell proceeds, the concentration of reactants decreases while the concentration of products increases. This goes on until equilibrium is achieved.

At equilibrium, $\Delta G = 0$. Hence, cell potential, $E = 0$.

Thus, The Nernst equation can be modified to:

$$E^{\circ} - (2.303RT/nF) \log_{10} K_{eq} = 0$$

$$E^{\circ} = (2.303RT/nF) \log_{10} K_{eq}$$

Where, K_{eq} = equilibrium constant and F = faradays constant. Thus, the above equation gives us a relation between standard electrode potential of the cell in which the reaction is taking place and the equilibrium constant.

Applications of Nernst Equation

The Nernst equation can be used to calculate:

- 1. Single electrode reduction or oxidation potential at any conditions**
- 2. Standard electrode potentials**
- 3. Comparing the relative ability as a reductive or oxidative agent**
- 4. Finding the feasibility of the combination of such single electrodes to produce electric potential.**
- 5. Emf of an electrochemical cell**
- 6. Unknown ionic concentrations**
- 7. The pH of solutions and solubility of sparingly soluble salts can be measured with the help of the Nernst equation.**

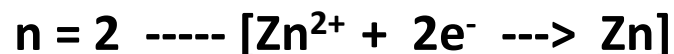
Numerical 1

The standard electrode potential of zinc ions is 0.76V. What will be the potential of a 2M solution at 300K?

Solution:

Given -

$$E^{\circ} = 0.76\text{V}$$



$$F = 96500 \text{ C/mole}$$

$$[\text{Mn}^{+}] = 2 \text{ M}$$

$$R = 8.314 \text{ J/K mole}$$

$$T = 300 \text{ K}$$

The Nernst equation for the given conditions can be written as follows;

$$E_{\text{M}^{n+}/\text{M}} = E^{\circ} - [(2.303RT)/n F] \times \log 1/[\text{M}^{n+}]$$

Substituting the given values in Nernst equation we get,

$$\begin{aligned} E_{\text{Zn}^{2+}/\text{Zn}} &= 0.76 - [(2.303 \times 8.314 \times 300)/(2 \times 96500)] \times \log \frac{1}{2} \\ &= 0.76 - [0.0298 \times (-0.301)] \\ &= 0.76 + 0.009 = 0.769\text{V} \end{aligned}$$

Therefore, the potential of a 2M Zn solution at 300K is 0.769V.

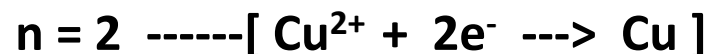
Numerical 2

Calculate the electrode potential of copper, if the concentration of CuSO₄ is 0.206 M at 23.1°C. Given that $E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = 0.34\text{V}$

Solution:

Given -

$$E^{\circ} = 0.34\text{V}$$



$$F = 96500 \text{ C/mole}$$

$$[\text{CuSO}_4] = 0.206 \text{ M}$$

$$R = 8.314 \text{ J/K mole}$$

$$T = 296.1 \text{ K}$$

The Nernst equation for the given conditions can be written as follows;

$$E_{\text{M}^{n+}/\text{M}} = E^{\circ} - [(2.303RT)/n F] \times \log 1/[\text{M}^{n+}]$$

Substituting the given values in Nernst equation we get,

$$\begin{aligned} E_{\text{Cu}^{2+}/\text{Cu}} &= 0.34 - [(2.303 \times 8.314 \times 296.1)/(2 \times 96500)] \times \log 1/0.206 \\ &= 0.34 - [0.0294 \times (0.6861)] \\ &= 0.34 - 0.0202 = 0.3198 \text{ V} \end{aligned}$$

Therefore, the electrode potential of a copper at 296.1K is 0.3198 V.

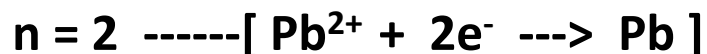
Numerical 3

Calculate the standard electrode potential of lead electrode, if the concentration of Pb^{2+} is 0.0096 M at 301⁰K and electrode potential is - 0.18025V

Solution:

Given -

$$E = - 0.18025\text{V}$$



$$F = 96500 \text{ C/mole}$$

$$[\text{Pb}^{2+}] = 0.0096 \text{ M}$$

$$R = 8.314 \text{ J/K mole}$$

$$T = 301 \text{ K}$$

The Nernst equation for the given conditions can be written as follows;

$$E_{\text{M}^{n+}/\text{M}} = E^{\circ} - [(2.303RT)/n F] \times \log 1/[\text{M}^{n+}]$$

Substituting the given values in Nernst equation we get,

$$\begin{aligned} E^{\circ} &= - 0.18025 + [(2.303 \times 8.314 \times 301)/(2 \times 96500)] \times \log 1/0.0096 \\ &= - 0.18025 + [0.0299 \times (2.018)] \\ &= - 0.1200 \text{ V} \end{aligned}$$

Therefore, the standard electrode potential of a lead electrode is - 0.1200V.

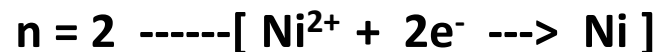
Numerical 4

Calculate the concentration of NiCl_2 in the Nickel electrode having a potential of -0.16942 V at 24.9°C . Given that $E^\circ_{\text{Ni}^{2+}/\text{Ni}} = -0.14 \text{ V}$

Given –

$$E^\circ = -0.14 \text{ V}$$

$$E = -0.16942 \text{ V}$$



$$F = 96500 \text{ C/mole}$$

$$R = 8.314 \text{ J/K mole}$$

$$T = 297.9 \text{ K}$$

The Nernst equation for the given conditions can be written as follows;

$$E_{\text{M}^{n+}/\text{M}} = E^\circ - [(2.303RT)/n F] \times \log 1/[\text{M}^{n+}]$$

Substituting the given values in Nernst equation we get,

$$\begin{aligned} E_{\text{Ni}^{2+}/\text{Ni}} &= -0.14 - [(2.303 \times 8.314 \times 297.9)/(2 \times 96500)] \times \log 1/[\text{Ni}^{2+}] \\ -0.16942 &= -0.14 + [0.0296 \times (\log \text{Ni}^{2+})] \end{aligned}$$

$$\log [\text{Ni}^{2+}] = (-0.16942 + 0.14) / 0.0296 \quad \text{Therefore, } [\text{Ni}^{2+}] = \text{Antilog} (-0.9939) = 0.1014$$

Therefore, the concentration of NiCl_2 is 0.1014 M .

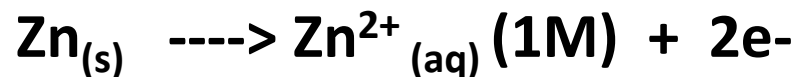
Numerical 5

Calculate the standard emf of the following cell and also write the cell reactions

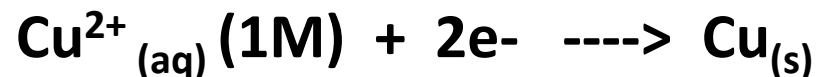


Solution:

The cell reactions can be written as follows:



----- (Oxidation at anode)



----- (Reduction at cathode)



----- (Overall cell reaction)

$$\begin{aligned} \text{Now, } E^0(\text{cell}) &= E^0\text{Cathode} - E^0\text{Anode} \\ &= E^0\text{Cu} - E^0\text{Zn} \\ &= 0.337 - (-0.763) \\ &= 1.10 \text{ V} \end{aligned}$$

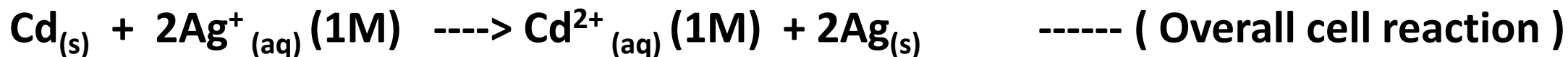
Numerical 6

Calculate the standard emf of the following cell and also write the cell reactions



Solution:

The cell reactions can be written as follows:



$$\begin{aligned} \text{Now, } E^{\circ}(\text{cell}) &= E^{\circ}\text{Cathode} - E^{\circ}\text{Anode} \\ &= E^{\circ}\text{Ag} - E^{\circ}\text{Cd} \\ &= 0.799 - (- 0.403) \\ &= 1.202 \text{ V} \end{aligned}$$

Numerical 7

The standard emf of the following cell is 0.462 V. If standard potential of Cu electrode is 0.337 V What is the standard potential of Ag electrode?



Solution:

$$\text{Now, } E^0(\text{cell}) = E^0\text{Cathode} - E^0\text{Anode}$$

$$= E^0\text{Ag} - E^0\text{Cu}$$

$$0.462 = E^0\text{Ag} - 0.337$$

$$E^0\text{Ag} = 0.462 + 0.337$$

$$= 0.799 \text{ V}$$

Numerical 8

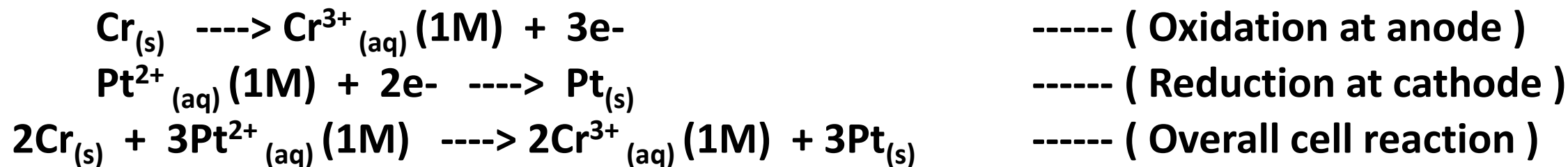
The standard emf of the following cell is 1.94 V. If standard potential of Cr electrode is -0.740 V what is the standard potential of Pt electrode? Also write cell reactions.



Solution:

$$\begin{aligned}\text{Now, } E^0(\text{cell}) &= E^0\text{Cathode} - E^0\text{Anode} \\ &= E^0\text{Pt} - E^0\text{Cr} \\ -0.740 &= E^0\text{Pt} - 1.94 \\ E^0\text{Pt} &= -0.740 + 1.94 \\ &= 1.2\text{ V}\end{aligned}$$

The cell reactions can be written as follows:



Numerical 9

Construct a cell from Ni^{2+}/Ni and Cu^{2+}/Cu half cells. Write the cell reactions and calculate the standard potential of the cell.

[Given : $E^0\text{Ni} = -0.257 \text{ V}$ and $E^0\text{Cu} = 0.337 \text{ V}$]

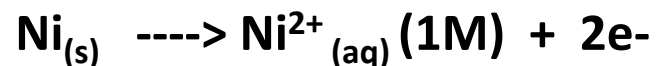
Solution:

As the Cu electrode has higher reduction potential than Ni electrode it will be a cathode and Ni electrode will be an anode

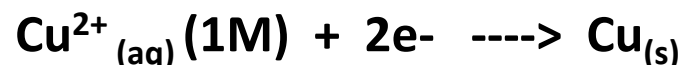
Therefore a cell can be written as,



The cell reactions can be written as follows:



----- (Oxidation at anode)



----- (Reduction at cathode)



----- (Overall cell reaction)

$$\begin{aligned}\text{Now, } E^0(\text{cell}) &= E^0\text{Cathode} - E^0\text{Anode} \\ &= E^0\text{Cu} - E^0\text{Ni} \\ &= 0.337 - (-0.257) \\ &= 0.594 \text{ V}\end{aligned}$$

Numerical 10

Write the half cell reactions of the following cell at 25°C

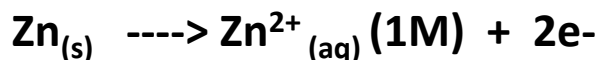


Calculate the emf of above cell

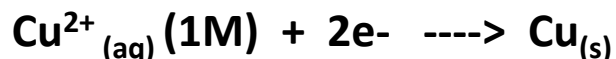
[Given : $E^0\text{Zn} = -0.76\text{ V}$ and $E^0\text{Cu} = 0.34\text{ V}$]

Solution:

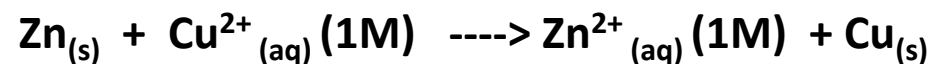
The cell reactions can be written as follows:



----- (Oxidation at anode)



----- (Reduction at cathode)



----- (Overall cell reaction)

$$\begin{aligned}\text{Now, } E^0(\text{cell}) &= E^0\text{Cathode} - E^0\text{Anode} \\ &= E^0\text{Cu} - E^0\text{Zn} \\ &= 0.34 - (-0.76) \\ &= 1.10\text{ V}\end{aligned}$$

$$\begin{aligned}\text{And } E(\text{cell}) &= E^0(\text{cell}) - 0.0591/2 (\log [\text{Zn}^{2+}]/[\text{Cu}^{2+}]) \\ &= 1.1 - 0.0591/2 (\log 1/1) \\ &= 1.1 - 0 \\ &= 1.1\text{ V}\end{aligned}$$

Numerical 11

- Calculate the e.m.f. of Daniel cell at 25°C when the concentration of ZnSO₄ and CuSO₄ is 0.001M and 0.01M respectively. The standard potential of the cell is 1.1 volt.

Solution:

$$\begin{aligned} E(\text{cell}) &= E^0(\text{cell}) - 0.0591/2 (\log [\text{Zn}^{2+}]/[\text{Cu}^{2+}]) \\ &= 1.1 - 0.0591/2 (\log 0.001/0.01) \\ &= 1.1 + 0.0591/2 (\log 0.01/0.001) \\ &= 1.1 + 0.02955 \\ &= 1.12955 \text{ V} \end{aligned}$$