

NEET Revision Notes

Chemistry

Electrochemistry

Electrochemistry

Electrochemistry is the study of producing electricity from chemical reactions that occur spontaneously as well as the use of electrical energy to cause chemical reactions that don't occur spontaneously.

Electrochemical Cells

- The Gibbs energy of the system falls as the possibility of a spontaneous chemical reaction increases.
- The energy is then changed into electrical energy. External energy can also be utilised to compel the occurrence of non-spontaneous processes in the form of electrical energy.
- These interconversions are carried out using electrochemical cells.

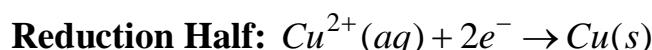
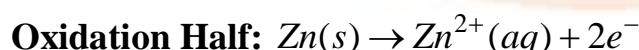
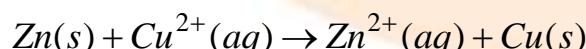
There are two types of electrochemical cells:

1. Galvanic and
2. Electrolytic cells

Galvanic cells convert chemical energy into electrical energy, whereas electrolytic cells turn electrical energy into chemical energy.

Galvanic Cells

- To extract cell energy, a spontaneous chemical process or reaction is performed, which is subsequently converted to electric current.
- A Daniel Cell, for example, is a Galvanic Cell that performs the redox process utilising Zinc and Copper.



Zn is the reducing agent, while Cu^{2+} is the oxidising agent.

- Half cells are also known as electrodes. The oxidation half is the anode, while the reduction half is the cathode.

- A form of electrode is referred to as a cathode. Electrons travel from the anode to the cathode in the external circuit.
- The anode is given negative polarity. The cathode is given positive polarity. Daniell Cell is a fictional character that Daniell Cell has developed. The anode is Zn, and the cathode is Cu.

Electrolytic Cell

- These electrodes are immersed in a solution containing both cations and anions.
- When current is applied, the ions travel to electrodes of opposite polarity, where they are reduced and oxidized simultaneously.

Preferential Discharge of Ions

- The discharge process becomes competitive when more than one cation or anion is present.
- Any ion that needs to be discharged requires energy, and if there are several ions present, the one that requires the most energy discharges first.

Electrolysis

- When an electric current is carried through an electrolyte's aqueous solution or in the fused state, the electrolyte decomposes.
- Cations gain electrons and convert into neutral atoms as they approach the cathode. Anions, meanwhile, go to the anode, where they lose electrons and become neutral atoms.
- Metal electrorefining uses impure metals as the anode and a strip of pure metal as the cathode.

Faraday's Laws of Electrolysis

Faraday proposed the following two laws to explain the relationship between the amount of substance produced and the current or equivalent weight.

1. First Law of Electrolysis

It states that "the amount (mass) of any substance deposited or liberated at any electrode is directly proportional to the amount of electricity passed through the electrolyte."

$$w \propto Q$$

$$w = ZQ$$

$$= Zit$$

Charge (Q) = current (i) \times time (t)

Z = Electrochemical equivalence

$$Z = \frac{E}{96500}$$

(where, E = Equivalent weight)

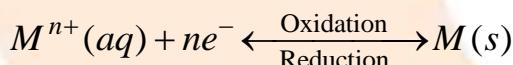
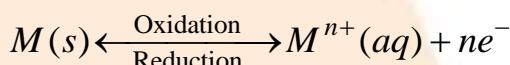
2. Second Law of Electrolysis

"When the same amount of electricity is passed through solutions of different electrolytes connected in series, the weight of substance produced at the electrodes is directly proportional to their equivalent weight," it states.

$$\text{i.e. } \frac{\text{Weight of Cu deposited } (w_1)}{\text{Weight of Ag deposited } (w_2)} = \frac{\text{Equivalent weight of Cu } (E_1)}{\text{Equivalent weight of Ag } (E_2)}$$

Electrode Potential

- When an element comes into contact with its ions, it tends to lose or gain electrons, leading it to become positively or negatively charged.
- The electrode potential is referred to as oxidation or reduction potential depending on whether oxidation or reduction has happened.



Characteristics

- The oxidation and reduction potentials have the same magnitude and sign.
- The values of E do not add up since it is not a thermodynamic property.

Standard Electrode Potential (E°)

It's defined as the electrode potential of a given electrode when compared to a standard hydrogen electrode under standard conditions. The standard conditions are as follows:

- Each ion in the solution has a concentration of 1 M.
- A temperature of 298 K.
- Each gas has a one-bar pressure.

Electrochemical Series

The half-cell potential values are standard, and they are represented as standard reduction potential values in the Electrochemical Series table at the end.

Cell Potential or EMF of a Cell

The difference between the electrode potential of two half cells is called cell potential. Electromotive force occurs when no current is drawn from the cell (EMF).

$$E_{cell} = E_{cathode} + E_{anode}$$

We use the anode's oxidation potential and the cathode's reduction potential in this equation.

Since the anode is on the left and the cathode is on the right, the following is the result:

$$= E_R + E_L$$

For a Daniel Cell, therefore:

$$E_{cell}^{\circ} = E_{Cu^{2+}/Cu}^{\circ} - E_{Zn/Zn^{2+}}^{\circ} = 0.34 + (0.76) = 1.10V$$

Cell Diagram or Representation of a Cell

The following conventions or notations are used to write the cell diagram by IUPAC regulations.

The Daniel cell is represented as follows:

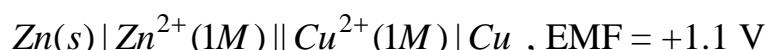


- (a) The anode half cell is written on the left, while the cathode half cell is written on the right.
- (b) The metal is separated from an aqueous solution of its own ions by a single vertical line.

Anodic Chamber: $Zn(s) | Zn^{2+}(aq)$

Cathodic Chamber: $Cu^{2+}(aq) | Cu(s)$

- (c) A double vertical line represents a salt bridge.
- (d) The molar concentration (C) is provided in brackets after the formula of the relevant ion.
- (e) The e.m.f value of a cell is inscribed on the cell's far right side. Consider the following scenario:



- (f) The working electrode may be noted adjacent to any inert electrodes that were used to construct the cell, such as platinum, when a zinc anode is connected to a hydrogen electrode, for instance.



Salt Bridge

The salt bridge keeps the balance of charges and completes the circuit by allowing ions to pass freely over it.

It has a gel inside with an inert electrolyte like Na_2SO_4 or KNO_3 as an electrolyte. Negative ions migrate to the anode and positive ions move across the salt bridge to the cathode, maintaining the equilibrium of charges in the cell.

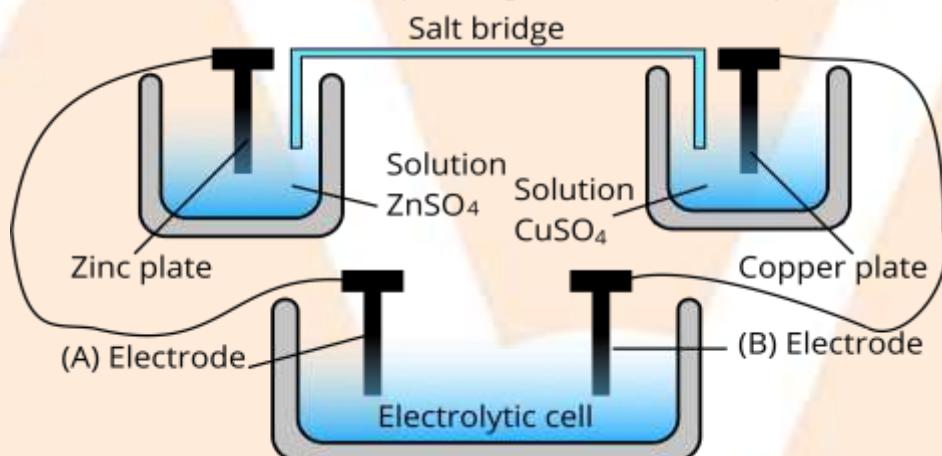


Image: Diagram of salt bridge

Spontaneity of a Reaction

$$\Delta G = -nFE_{cell}$$

ΔG must be negative and cell potential must be positive for a spontaneous cell response to occur.

The standard value of ΔG will be obtained if we utilise the standard value of cell potential in the following equation.

$$\Delta G^\circ = -nFE_{cell}^\circ$$

Types of Electrodes

Metal – Metal Ion electrodes

- Metal ions are present in an electrolyte solution that is submerged beneath a metal rod or plate.

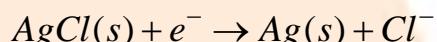
- Due to the voltage differential between these two phases, this electrode has the ability to function as both a cathode and an anode.

At anode: $M \rightarrow M^{n+} + ne^-$

At cathode: $M^{n+} + ne^- \rightarrow M$

Gas Electrodes

- In conjunction with their respective ions, electrode gases like H_2 and Cl_2 are utilized. For instance, a diluted solution of HCl (H^+) ions is used in conjunction with H_2 gas.
- The metal must be inert to avoid interacting with the acid.
- The potentials of other electrodes are also measured using the hydrogen electrode as a reference. Its potential is set to 0V for reference.
- The electrode is referred to as the "Standard Hydrogen Electrode (SHE)" and the concentration of the HCl used as a reference is 1 M.
-
- Metal – Insoluble Salt Electrode
- We employ a variety of salts that are only very little soluble in the metal itself as electrodes.
- For instance, when using AgCl with Ag, there may be a gap between these two phases, as demonstrated by the following reaction:



A silver rod is submerged in a solution comprising $AgCl(s)$ and Cl^- ions to create this electrode.

Calomel Electrode

Calomel paste (Hg_2Cl_2) and an electrolyte that contains Cl^- ions are mixed with mercury.

At cathode: $Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2Cl^-(aq)$

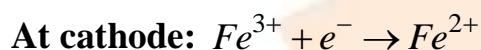
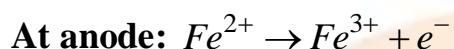
At anode: $2Hg(l) + 2Cl^-(aq) \rightarrow Hg_2Cl_2(s) + 2e^-$

This electrode is also used to establish other potentials as a reference point. In its standard form, it is also known as Standard Calomel Electrode (SCE).

Redox Electrode

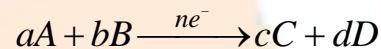
In these electrodes, the same metal is employed in two different oxidation states in the same half cell. For instance, when Fe^{2+} and Fe^{3+} are dissolved in the same container and an inert platinum electrode is used to transfer electrons.

Possible reactions include the following:



Nernst Equation

The relationship between electrode voltage and ion concentration is established. As a result, the reduction potential increases together with the increase in ion concentration. for a common electrochemical reaction type.



The Nernst equation can be written as:

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{2303}{nF} RT \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Here, substitute the values of R and F as follows:

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Applications of Nernst Equation

Equilibrium Constant from Nernst Equation

For a Daniel Cell, at equilibrium

$$E_{\text{cell}} = 0 = E_{\text{cell}}^0 - \frac{2.303RT}{2F} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$E_{\text{cell}}^{\circ} = \frac{2.303RT}{2F} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

But at equilibrium:

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

$$E_{cell}^a = \frac{2.303RT}{2F} \log K_c$$

$$E_{cell}^o = \frac{2.303 \times 8.314 \times 298}{2 \times 96500} \log K_c$$

$$= \frac{0.0591}{2} \log K_c$$

In general:

$$E_{cell}^\circ = \frac{0.0591}{n} \log K_c$$

$$\log K_c = \frac{n E_{cell}^\circ}{0.0591}$$

Concentration Cells

When two electrodes of the same metal are individually dipped into two solutions of the same electrolyte with variable concentrations, and the solutions are connected by a salt bridge, concentration cells are created. For illustration:



These are of two types:

1. Electrode Concentration Cells

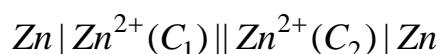


$$E_{cell} = 0 - \frac{0.059}{n} \log \frac{P_2}{P_1}$$

Where, $P_2 < P_1$ for spontaneous reaction.

2. Electrolyte Concentration Cell

At 298 K, the EMF of concentration cell can be written as



$$E_{cell} = \frac{0.0591}{n_1} \log \frac{c_2}{c_1}$$

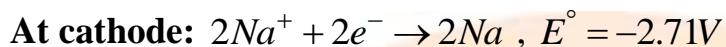
Where, $C_2 > C_1$ for spontaneous reaction

Cases of Electrolysis

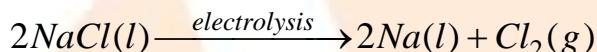
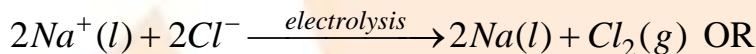
- **Electrolysis of Molten Sodium Chloride**



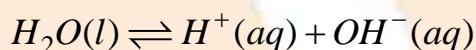
The reactions is taking place at the two electrodes may be shown as follows:



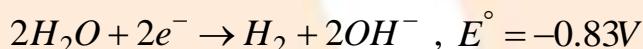
Overall reaction:



Electrolysis of an aqueous solution of Sodium Chloride

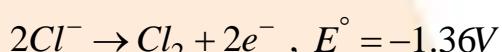
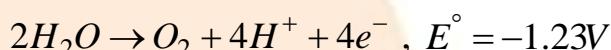


At cathode:



Thus H_2 gas is generated at cathode value Na^+ ions remain in solution.

At anode:



As a result, the over-voltage principle is used at the anode to evolve Cl_2 gas while leaving OH^- ions in the solution.

Batteries

When Galvanic cells are joined in series to produce a larger voltage, the arrangement is referred to as a "battery."

Primary Batteries

As long as active components are available, primary cells can be used indefinitely. The cell stops functioning and cannot be utilised once they are gone. A Dry Cell, a Leclanche Cell, a Mercury Cell, for instance.

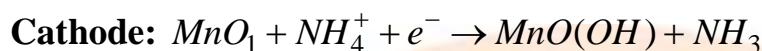
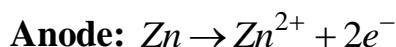
Dry Cell

Anode: Zinc container

Cathode: Carbon (graphite) rod surrounded by powdered MnO_2 and carbon

Electrolyte: NH_4Cl and $ZnCl_2$

Reaction:



This cell's typical potential is 1.5 V, and it cannot be replaced once it has been used. This potential diminishes when the battery is continuously depleted.

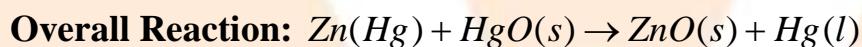
Mercury Cells

These are utilised in hearing aids and other small pieces of equipment.

Anode: $Zn - Hg$ Amalgam

Cathode: Paste of HgO and carbon

Electrolyte: Paste of KOH and ZnO



The cell potential is roughly 1.35 V and remains constant throughout the life of the cell.

Secondary Batteries

There are numerous applications for secondary batteries that allow for multiple recharges. For instance, lead storage batteries and $Ni - Cd$ batteries.

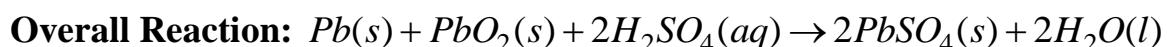
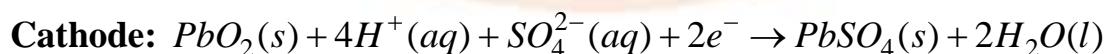
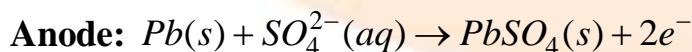
Lead Storage Battery

Anode: Lead (Pb)

Cathode: Grid of lead packed with lead oxide (PbO_2)

Electrolyte: 38% solution of H_2SO_4

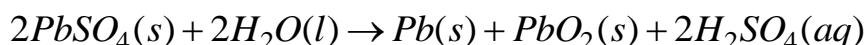
Discharging Reaction



The cell is connected to a cell with a greater potential, which functions as an electrolytic cell and reverses the processes, to recharge it. $Pb(s)$ and $PbO_2(s)$

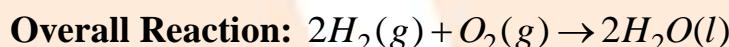
are regenerated at the pertinent electrodes. The voltage generated by these cells is almost constant.

Recharging Reaction:



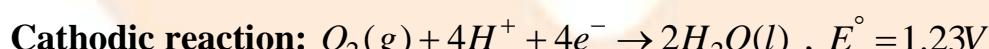
Fuel Cells

- The reactants in a fuel cell are supplied externally from a reservoir as opposed to being stored inside the cell, which is how it differs from a conventional battery.
- Fuel cells are used in space vehicles, and the two gases are supplied from outside storage. This cell's electrolyte is KOH, and the electrodes are carbon rods.



Corrosion

- It involves a redox process and the growth of an electrochemical cell on the surface of iron or any other metal.
- At one location, oxygen is reduced to produce water, whereas at another, iron is oxidised (anode) (cathode) Rust, which is symbolised as $Fe_2O_3 \cdot xH_2O$, is created by first oxidising iron to form Fe^{2+} , which is then transformed into Fe^{3+} in the presence of oxygen which reacts with water.



- Iron can be protected from rusting by painting it or covering it with another metal, such as zinc. The latter process is known as galvanization.
- Iron is shielded while Zn is oxidised first because Zn has a higher propensity for oxidation than iron. This method of separating one metal from the other is known as cathodic protection.

Conductance (G)

It is the inverse of resistance and is described as the ease with which electric current flows through a wire.

$$G = \frac{1}{R}$$

SI unit is Siemen (S).

$$1S = 1\text{ohm}^{-1}(\text{mho})$$

Conductivity

It is the reciprocal of resistivity (ρ) .

$$\kappa = \frac{1}{\rho} = \frac{1}{R} \times \frac{\ell}{A} = G \times \frac{\ell}{A}$$

Now if $\ell = 1\text{cm}$ and $A = 1\text{cm}^2$, then $\kappa = G$

As a result, the conductance of a solution with a cross-sectional area of 1cm^2 and a length of 1cm can be used to describe an electrolytic solution's conductivity.

Factors Affecting Electrolyte Conductance

Electrolyte

An electrolyte is a substance that conducts electricity when it dissociates into ions in solution when it is dissolved or molten.

Examples of strong electrolytes include HCl, NaOH, KCl, while weak electrolytes include $\text{CH}_3\text{COOH}, \text{NH}_4\text{OH}$.

The conductance of electricity by ions present in solutions is referred to as electrolytic or ionic conductance. The electricity that passes through an electrolyte solution is controlled by the following variables.

- (i) **Electrolyte nature or interionic attractions:** The flexibility of ion mobility is greater and conductance is higher the less solute-solute interactions there are.
- (ii) **Ion Solvation:** As the number of interactions between the solute and the solvent rises, so does the degree of solvation, and the electrical conductance falls.
- (iii) **The nature of the solvent and its viscosity:** The solvent's resistance to ion flow, and the electrical conductance all increase as the solvent-solvent interactions increase.
- (iv) **Temperature:** Reduced interactions between solute and solute, solute and solvent, and solvent and solvent when the temperature of an

electrolytic solution rises lead to an increase in electrolytic conductance.

Measurement of Conductance

$$\text{It is known that, } \kappa = \frac{1}{R} \times \frac{l}{A}$$

We can determine the value of κ by measuring l , A , and R . The resistance of the solution R between two parallel electrodes is computed using the "Wheatstone's" bridge method.

It consists of a conductivity cell with an unknown resistance R_2 , a conductivity cell with two fixed resistances R_3 and R_4 , and a variable resistance R_1 . The bridge is balanced when there is no current flowing through the detector. Then, under these conditions:

$$\frac{R_1}{R_2} = \frac{R_3}{R_4} \quad \text{or} \quad R_2 = \frac{R_1 R_4}{R_3}$$

Molar Conductivity

It is the combined conductivity of all the ions produced when one mole of an electrolyte is dissolved between two large electrodes spaced one centimetre apart.

Mathematically, it can be expressed as,

$$\Lambda_m = \kappa \times V, \quad \Lambda_m = \frac{\kappa \times 1000}{C}$$

where, V is the volume of solution in cm^3 containing 1 mole of electrolyte and C is the molar concentration.

$$\begin{aligned} \text{Units: } \Lambda_m &= \frac{\kappa \times 1000}{C} = \frac{\text{Scm}^{-1}}{\text{molcm}^{-3}} \\ &= \text{ohm}^{-1}\text{cm}^2\text{mol}^{-1} \text{ or } \text{Scm}^2\text{mol}^{-1} \end{aligned}$$

Equivalent Conductivity

It measures the electrical conductivity of a comparable electrolyte sandwiched between two substantial electrodes spaced a centimetre apart.

Mathematically, it can be written as,

$$\Lambda_{eq} = \kappa \times V =$$

$$\Lambda_{eq} = \frac{\kappa \times 1000}{N}$$

Where, v is the volume of solution in cm^3 containing 1 equivalent of electrolyte and N is normality.

$$= \frac{\text{Scm}^{-1}}{\text{equivalent cm}^{-3}} = \frac{\text{Ohm}^{-1}\text{cm}^2\text{equivalent}^{-1}}{\text{Scm}^2\text{equivalent}^{-1}}$$

Variation of Conductivity and Molar Conductivity with Dilution

Conductivity decreases when concentration decreases because there are fewer ions per unit volume carrying the current in the solution. Molar conductivity increases as concentration drops. One mole of electrolyte solution's total volume V has increased as a result, which is why. Increases in a solution's volume more than make up for the loss in κ caused by dilution.

Limiting Molar Conductivity (Λ_m)

Molar conductivity at infinite dilution, also known as limiting molar conductivity, is the value of molar conductivity as the concentration approaches zero. Extrapolation of the Λ_m versus \sqrt{c} curve can be used to determine the molar conductivity at infinite dilution in the case of a strong electrolyte. However, because the curve becomes nearly parallel to the y-axis as concentration approaches zero, extrapolation of the curve cannot be used to derive the value of molar conductivity of a weak electrolyte at infinite dilution.

Debye, Huckel, and Onsagar found the mathematical link between Λ_m and Λ_m° for a strong electrolyte. In its simplest form, the equation is as follows:

$$\Lambda_m = \Lambda_m^\circ - bc^{1/2}$$

Kohlrausch's Law

It claims that an electrolyte limiting molar conductivity can be represented as the sum of the anion and cation's individual contributions. The limiting molar conductivity of an electrolyte that produces v_+ cations and v_- anions upon dissociation is given by:

$$\Lambda_m^\circ = v_+ \lambda_+^\circ + v_- \lambda_-^\circ$$

Applications of Kohlrausch's Law

- (i) Calculation of molar conductivities of weak electrolyte at infinite dilution

The molar conductivity of acetic acid at infinite dilution, for instance, can be calculated using the molar conductivities of strong electrolytes like HCl, CH_3COONa , and NaCl at infinite dilution, as shown below.

$$\Lambda_m^{\circ}(CH_3-COOH) = \Lambda_m^{\circ}(CH_3-cooNa) + \Lambda_m^{\circ}(HCl) - \Lambda_m^{\circ}(NaCl)$$

(ii) Determination of degree of dissociation of weak electrolytes

$$\text{Degree of dissociation } \alpha = \frac{\Lambda_m^c}{\Lambda_m^{\circ}}$$

(iii) Determination of dissociation constant of weak electrolytes:

$$K = \frac{c\alpha^2}{1-\alpha}$$

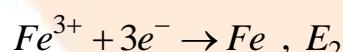
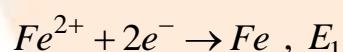
$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^{\circ}}$$

$$K = \frac{c(\Lambda_m^c / \Lambda_m^{\circ})^2}{1 - \Lambda_m^c / \Lambda_m^{\circ}} = \frac{C(\Lambda_m^c)^2}{\Lambda_m^{\circ}(\Lambda_m^* - \Lambda_m^c)}$$

Use of ΔG in Relating EMF values of Half Cell Reactions

- The EMFs of the two reactions cannot directly mingle when two half-cell reactions come together to generate another half-cell reaction.
- Nevertheless, in any situation, thermodynamic functions like ΔG can be added and used to link EMF values.

Consider the following three half-cell responses:



Subtracting the first reaction from the second reaction results in the third reaction. On the other hand, EMF readings do not adhere to the same pattern.

That is: $E_3 \neq E_2 - E_1$. But the ΔG values can be related according to the reactions:

$$\Delta G_3 = \Delta G_2 - \Delta G_1$$

$$-n_3FE_3 = -n_2FE_2 + n_1FE_1$$

$$-E_3 = -3E_2 + 2E_1$$

$$\Rightarrow E_3 = 3E_2 - 2E_1$$

Examples:

1. Using the data given below find out the strongest reducing agent.

$$E^\circ_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} = 1.33\text{V}$$

$$E^\circ_{\text{Cl}_2/\text{Cl}^-} = 1.36\text{V}$$

$$E^\circ_{\text{MnO}_4^-/\text{Mn}^{2+}} = 1.51\text{V}$$

$$E^\circ_{\text{Cr}^{3+}/\text{Cr}} = -0.74\text{V}$$

- (A) Cl^-
- (B) Cr
- (C) Cr^{3+}
- (D) Mn^{2+}

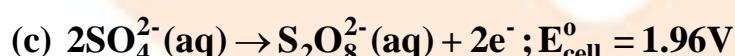
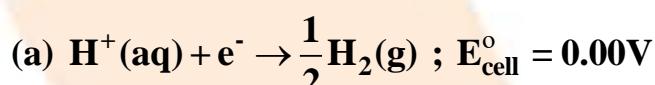
Correct Answer: Option (B)

Explanation:

According to the electrochemical series and standard reduction potential of metal, the stronger the reducing agent is, the larger the negative value of the standard reduction potential.

The standard reduction potential of chromium has the highest value among the available alternatives, making it the most potent reducing agent. As a result, choice B is the right one.

2. E°_{cell} for some half-cell reactions are given below. On the basis of these mark the correct answer



(A) In dilute sulphuric acid solution, hydrogen will be reduced at the cathode.

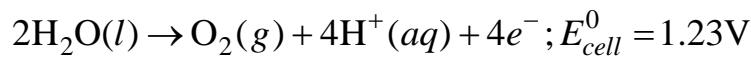
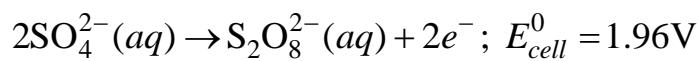
(B) In concentrated sulphuric acid solution, water will be oxidized at the anode.

(C) In dilute sulphuric acid solution, water will be oxidized at the anode.

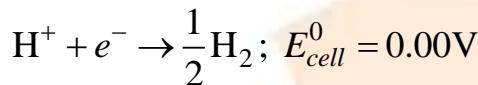
(D) In dilute sulphuric acid solution, SO_4^{2-} ion will be oxidized to tetrathionate ion at the anode

Correct Answer: Option (i, iii)

Explanation: In the electrolysis of sulphuric acid, the following reactions occur



The reaction will lower the value of E_{cell}^0 is preferred at anode so the second reaction is feasible.



At the cathode, reduction of water occurs. Therefore, in dilute sulphuric acid solution, hydrogen will be reduced at the cathode.

3. $\Lambda_{m(\text{H}_2\text{O})}^0$ is equal to _____

(A) $\Lambda_{m(\text{HCl})}^0 + \Lambda_{m(\text{NaOH})}^0 - \Lambda_{m(\text{NaCl})}^0$

(B) $\Lambda_{m(\text{HNO}_3)}^0 + \Lambda_{m(\text{NaNO}_3)}^0 - \Lambda_{m(\text{NaOH})}^0$

(C) $\Lambda_{m(\text{HNO}_3)}^0 + \Lambda_{m(\text{NaOH})}^0 - \Lambda_{m(\text{NaNO}_3)}^0$

(D) $\Lambda_{m(\text{NH}_4\text{OH})}^0 + \Lambda_{m(\text{HCl})}^0 - \Lambda_{m(\text{NH}_4\text{Cl})}^0$

Correct Answer: Option (i, iii)

Explanation:

Kohlrausch law states that limiting molar conductivity of any salt species is equal to the sum of the limiting molar conductivity of cations and anions of the electrolyte

$$\Lambda_{m(\text{H}_2\text{O})}^0 = \Lambda_{m(\text{HCl})}^0 + \Lambda_{m(\text{NaOH})}^0 - \Lambda_{m(\text{NaCl})}^0$$

$$\Lambda_{m(\text{H}^+)}^0 + \Lambda_{m(\text{OH}^-)}^0 = \Lambda_{m(\text{H}^+)}^0 + \Lambda_{m(\text{Cl}^-)}^0 + \Lambda_{m(\text{Na}^+)}^0 + \Lambda_{m(\text{OH}^-)}^0 - \Lambda_{m(\text{Na}^+)}^0 - \Lambda_{m(\text{Cl}^-)}^0$$

$$\Lambda_{m(\text{H}_2\text{O})}^0 = \Lambda_{m(\text{HNO}_3)}^0 + \Lambda_{m(\text{NaOH})}^0 - \Lambda_{m(\text{NaNO}_3)}^0$$

$$\Lambda_{m(\text{H}^+)}^0 + \Lambda_{m(\text{OH}^-)}^0 = \Lambda_{m(\text{H}^+)}^0 + \Lambda_{m(\text{NO}_3^-)}^0 + \Lambda_{m(\text{Na}^+)}^0 + \Lambda_{m(\text{OH}^-)}^0 - \Lambda_{m(\text{Na}^+)}^0 - \Lambda_{m(\text{NO}_3^-)}^0$$

Therefore (i, iii) options are correct.