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Class 12
Chemistry

Chapter 2
Electrochemistry
Handwritten Notes

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ELECTROCHEMISTRY

Electrochemistry

Electrochemistry is concerned with conversion of electrical energy into chemical energy in electrolytic cell as well as the conversion of chemical energy into electrical energy in galvanic or voltaic cells. It involves redox reactions in which transfer of electrons between two or more substances takes place. It deals with energy sources that are highly efficient, such as batteries and fuel cells. It involves transfer of electrons.

Electro → electricity / electrons
Chemistry → Redox Reactions
So, electrical energy ⇌ chemical energy.

Oxidation – Reduction Concepts

- Oxidation: A reaction in which a substance loses an electron.
- Reduction: A reaction in which a substance gains an electron.

Together, they form redox reaction. Redox reactions involve change in oxidation state/numbers.

- Oxidation State or Number: The apparent charge on an atom of an element in a molecule or ion. It maybe zero, positive or negative. Oxidation = Increase in oxidation no. (electron loss). Reduction = Drecrease in oxidation no. (electron gain).

If Oxygen gain and Hydrogen is lost then its oxidation.
If Oxygen is lost and Hydrogen is gained then its reduction

Example: $2Na^{0}_{(s)} + Cl2^{0}_{(g)} \longrightarrow 2Na^{+1}Cl^{-1}_{(s)}$

$Na_{(s)}: 0 \rightarrow +1$ (oxidation)

$Cl_{2(g)}: 0 \rightarrow -1$ (reduction)

Oxidation reaction: $2Na^{0} \longrightarrow 2Na^{+1} + 2e^{-}$

Reduction reaction: $Cl_2^{0} + 2e^{-} \longrightarrow 2Cl^{-1}$

Disproportionation Reaction: A disproportionation reaction is a type of redox reaction where the same element is both oxidized and reduced simultaneously. Also called self-oxidation-reduction. In $2H_2O_2^{-1} \longrightarrow 2H_2O^{-2} + O_2^{0}$, Oxygen in H_2O_2 is partially oxidized to O_2 (state = 0) and partially reduced to H_2O (oxidation state = −2).

Rules for assigning oxidation state

- Element in its free state has an oxidation state of 0 (O_2, H_2, Fe)
- Ions, the oxidation state is equal to the ionic charge. ($Fe^{2+} = +2$)
- Hydrogen usually has an oxidation state +1. But in metal hydrides, hydrogen has state of −1.
- Oxygen generally has state of −2. Superoxide has −1/2 (O_2^{-}) Peroxide has −1 (O_2^{-2})
- The more electronegative element gets the negative oxidation state.
- Sum of oxidation state of neutral molecule is 0.
- Sum of oxidation state of all atoms in ion equals to overall charge of the ion.

Balancing Equations

- Redox Method (Oxidation Number Method): Based on the principle that total electrons lost = total electrons gained in the redox reaction. Used to balance redox reactions by comparing changes in oxidation numbers.

Steps: 1) Assign oxidation state to each element.
2) Identify the element changing oxidation state.
3) Draw bridge between elements and show electron loss or gain.
4) Multiply electron loss or gain by a number to get a common number.
5) Inspection Method, Hydrogen and Oxygen.

+ sign comes when electrons are lost (oxidation)
− sign comes when electrons are gained (reduction).

Example: $P + HNO_3 + H_2O \longrightarrow H_3PO_4 + NO$

1) Assigning oxidation number to each element.

$P^{0} + H^{+1}N^{+5}O_3^{(-2)3} + H_2^{(+1)2}O^{-2} \longrightarrow H_3^{3(+1)}P^{+5}O_4^{(-2)4} + N^{+2}O^{-2}$

2) Identify element with changing oxidation state.

$P^{0} + HN^{+5}O_3 + H_2O \longrightarrow H_3P^{+5}O_4 + N^{+2}O$

$P^{0} \rightarrow P^{+5}$ (5e⁻ loss) (oxidation)

$N^{+5} \rightarrow N^{+2}$ (3e⁻ gain) (reduction)

3) Draw bridge between atom whoose oxidation state changed by the number of electron gained or lost.

$P^{0} + HN^{+5}O_3 + H_2O \longrightarrow H_3P^{+5}O_4 + N^{+2}O$ (3e⁻ gain; 5e⁻ lose)

4) Equalize number of electron loss and gain by multiply.

$$3P^{\circ} + 5HN^{+5}O_3 + H_2O \longrightarrow 3H_3P^{+5}O_4 + 5N^{+2}O$$

(3×5 = 15 e⁻ gain; 5×3 = 15 e⁻ loss)

Coeffecient 3 with P and H_3PO_4 and coefficient 5 with HNO_3 and NO.

5) Balance rest of equation by inspection method.

As in the left side we have 15 + x oxygen, and right side has 12+5 = 17 oxygen

So, to balance we need,

$15 + x = 17$, $x = 2$

$$3P + 5HNO_3 + 2H_2O \longrightarrow 3H_3PO_4 + 5NO$$

- Construction of Redox Equations (Ion Electron Method): Any redox reaction consists of two half-reactions. (Oxidation half reaction and Reduction half reaction). Each half reaction is balanced separately.

Steps: 1) Balance atoms (except H and O).
2) Balance oxygen atoms using H_2O (for acidic/neutral materia)
3) Balance hydrogen atoms using H^+
4) Balance charge using electrons (e^-)
5) Equalise the number of electrons lost and gained in both half-reactions.
6) Add the half-reactions to get the overall balanced redox equation.
7) Balance the remaining parts by inspection method if needed.

For basic material oxygen is balanced using OH^-

Example: $Cr_2O_7^{-2} + H_2SO_3 \longrightarrow Cr^{+3} + HSO_4^-$

Reduction Half = $Cr_2O_7^{-2} \longrightarrow Cr^{+3}$

Oxidation Half = $H_2SO_3 \longrightarrow HSO_4^-$

1) Balance each half-reaction. First, consider reduction half-reaction. Two Cr atoms on the left requires 2 Cr^{+3} on right.

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$$

There are seven O atoms on the left and none on the right. We will add $7H_2O$ on right.

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

There are 14H atoms on the right and none on the left, so we add $14H^+$ on left.

$$Cr_2O_7^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$$

Now balance charges. The left side has one di-negative and 14 mono-positive charges, $-2 + 14 = +12$. The right side has two tri-positive charges corresponding to $+3 \times 2 = +6$. Thus left side needs $6e^-$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O \quad \text{——— (i)}$$

In other half reaction (oxidation half-reactio), S atoms are already balanced.

$$H_2SO_3 \longrightarrow HSO_4^-$$

Balance O atoms. As there are there O atoms on the left and four on the right, we will add one H_2O to the left.

$$H_2SO_3 + H_2O \longrightarrow HSO_4^-$$

There are four H atoms on the left and one on the right. We will add $3H^+$ to right.

$$H_2SO_3 + H_2O \longrightarrow HSO_4^- + 3H^+$$

For charge, the left side is neutral but the right side has a net charge of $(-1) + (+3) = +2$. Thus, we will add $2e^-$ to the right.

$$H_2SO_3 + H_2O \longrightarrow HSO_4^- + 3H^+ + 2e^- \quad \text{——— (ii)}$$

Step2) Equalize the number of electrons transferred in the two half-reactions and add half-reactions. And multiplying equation (ii) by three to balance electrons in both equations

$$3H_2SO_3 + 3H_2O \longrightarrow 3HSO_4^- + 9H^+ + 6e^-$$

Now,

$$Cr_2O_7^{-2} + \cancel{14}^{5}H^+ + \cancel{6e^-} \longrightarrow 2Cr^{+3} + \cancel{7}^{4}H_2O$$

$$3H_2SO_3 + \cancel{3H_2O} \longrightarrow 3HSO_4^- + \cancel{9H^+} + \cancel{6e^-}$$

$$Cr_2O_7^{-2} + 3H_2SO_3 + 5H^+ \longrightarrow 2Cr^{+3} + 3HSO_4^- + 4H_2O$$

Since charges are equal on both sides, therefore equation is balance.

Oil Rig
- Oxidizing is loss
- Reduction is gain

Oxidizing and Reducing Agents

- Oxidizing Agent: A substance which oxidizes other substance. It accepts electrons. The substance itself reduces. Oxidation state decreases.
- Reducing Agent: A substance which reduces other substance. It realeses electrons. The substance itself is oxidized. Oxidation state increases.

Example: $3P^{0} + 5H^{+1}N^{+5}O_3^{(-2)3} + 2H_2^{(+1)2}O^{-2} \longrightarrow 3H_3^{3(+1)}P^{+5}O_4^{(-2)4} + 5N^{+2}O^{-2}$

P is undergoing oxidation, so its reducing agent. Whereas N present in HNO_3 is undergoing reduction HNO_3 is an oxidizing agent.

$Mn^{+4}O_2 + 4HCl^{-1} \longrightarrow Mn^{+2}Cl_2 + 2H_2O + Cl_2^{0}$

Mn present in MnO_2 is undergoing reduction, therefore MnO_2 is oxidizing agent. Cl of HCl is oxidised, so HCl is a reducing agent.

Electrode, Electrode Potential and Electrochemical Series

- Galvanic Cell (Daniel Cell): A galvanic cell is an electrochemical cell in which natural (spontaneous) redox reaction produces electric current. It uses chemicals to make electricit
  - Zinc rod
  - Copper rod
  - Zinc Sulphate ($ZnSO_4$) solution
  - Copper(II) sulphate ($CuSO_4$) solution
  - Copper wire (to connect both metals)
  - Salt bridge filled with electrolyte like KCl, KNO_3 or Na_2SO_4.
  - Two separate containers
  - Voltmeter

Procedure: Put the zinc rod into zinc sulphate solution in one container. Put the copper rod into copper sulphate solution in the other container. Connect the zinc and copper rods with a wire. Connect the two solutions using a salt bridge. Now, the chemical reaction starts, and electric current flows through the external wire. Without a salt bridge, no current flows because charges would build up and stop the reaction.

Role of Salt Bridge: Allows ions to move between the two solutions without mixing them. Keeps both sides electrically neutral. Prevents charge buildup. Allows the reaction (and electricity flow) to continue.

Oxidation Half cell: Also called anode half-cell. Half cell in which oxidation occurs. The reaction taking place in oxidation half-cell is called the oxidation half reaction. Happens at electrode called anode. Reaction: $Zn_{(s)} \longrightarrow Zn^{+2}_{(aq)} + 2e^{-}$

Reduction Half cell: Also called cathode half-cell. Half cell in which reduction occurs. The reaction taking place in the reduction half-cell is called the reduction half reaction. Happens at electrode called cathode. Reaction: $Cu^{2+}_{(aq)} + 2e^{-} \longrightarrow Cu_{(s)}$

Flow of electrons: Zince losses electrons more easily than copper. So the flow is zince electrode → through wire → Copper electrode.

Overall reaction: $Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

- **Cell Potential:** The potential of the cell to do work on its surroundings by driving an electric current through a wire. The voltage produced by a galvanic cell under standard conditions. Also called electromotive force (emf), the force with which electrons are pushed to flow through the wire from anode to cathode. Measured in volts using voltmeter. Depends on the difference between standard electrode potentials of two half-cells. $E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$

Uder Standard Conditions: Temperature 25°C (298K). Solution concentration: $1 mol/dm^3$. Gas pressure 1 atm. The electrode with a more negative E° value acts as anode (oxidation). The electrode with a more positive E° value acts as cathode. (reduction). A positive E°_{cell} indicates a spontaneous redox reaction. Standard Hydrogen Electrode (SHE) is used as refrence electrode. Its potential is 0.00V.

- **Standard Hydrogen Electrode:** SHE is the refrence electrode used to measure electrode potential of other half-cells. It's structure is:
  - Platinum electrode coated with platinum black
  - Hydrogen gas at 1atm bubbled into 1M HCl
  - Operated at 298K

Oxidizing agents:
$2H \rightarrow H_2SO_4, HNO_3$
$2K \rightarrow KMnO_4, K_2Cr_2O_7$
$FSC \rightarrow FeCl_3, SO_3, CO_2$
Halogens → F_2, Cl_2, Br_2, I_2
$H_2O_2, MnO_2, CrO_3, CaO$
High electronegativity = good oxidizing agent.
Small size = good agent

Reducing agents:
Metals → group 1 and 2
Electropositivity should be more = good agent (electronegativity low)
Size big = good agent
Hydrides → LiH, NaH
H + Halogen → HI, HBr...
Pure C, P, H, S
$H_2S, Cu_2O, SnCl_2, FeCl_2$

Electrode:
- Solid conductor (usually metal placed in contact with an electrolyte solution.
- Allows transfer of electron

Electrode Potential:
- Measure of tendency of an electrode to gain or loss electrons when it is in contact with its ions in solution.
- Measured in volts.

Standard Electrode Potential:
- The Standdard electrode potential (E°) is the potential of a half-cell under standard conditions (1M conc., 1 atm pressure, 25°C)

Its electrode potential is arbitarily chosen as zero at all temperatures. Assigned a standard potential of 0.00 V. Can act as:

Cathode (Reduction): $2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$ $E^\circ_{H^+_{(aq)}/H_{2(g)}} = 0.00V$

Anode (Oxidation): $H_{2(g)} \longrightarrow 2H^+_{(aq)} + 2e^-$ $E^\circ_{H_{2(g)}/H^+_{(aq)}} = 0.00V$

Can act as both anode and cathode depending up the nature of the electrode with which it is connected.

If above H then its oxidized (anode) and below H then its reduction (cathode).

- **Method to measure the electrode potentials:** SHE is the primary refrence electrode used to measure the standard electrode potentials of other half-cells, such as copper and zinc.

Determination of Standard Electrode Potential of Zn^{2+}/Zn Electrode:

Zinc rod in 1M $ZnSO_4$. Connected to SHE via salt bridge. Electrotons flow from zinc to hydrogen electrode. Zinc is anode, SHE is cathode. Cell potential (E°_{cell}) = 0.76V

$E^\circ_{cell} = E^\circ_{anode} + E^\circ_{cathode}$

$0.76 = E^\circ_{anode} + 0$

$E^\circ_{anode} = +0.76$ (oxidation)

So, $E^\circ(Zn^{2+}/Zn) = -0.76V$ (reduction)

Determination of Standard Electrode Potential of Cu^{2+}/Cu Electrode: Copper rode in 1M $CuSO_4$. Connected to SHE via salt bridge. Electrons flow from hydrogen to copper electrode. SHE is anode, Cu is cathode. Cell potential (E°_{cell}) = 0.34 V.

$E^\circ_{cell} = E^\circ_{anode} + E^\circ_{cathode}$

$0.34 = 0 + E^\circ_{cathode}$

$E^\circ_{cathode} = +0.34V$

So, $E^\circ(Cu^{2+}/Cu) = +0.34V$ (reduction)

and $-0.34V$ is oxidation.

- **Determination of Cell Potential:** Each redox reaction consists of two-half-reactions. The more positive reduction potential is used as cathode (reduction). The less positive (or more negative) reduction potential is reversed and used as anode (oxidation). Overall cell reaction is the sum of the two half-reactions. $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$.
- **Feasibility of a Reaction:** The sign of the sum of E° values of the two half-cells reactions. If this value is positive, a reaction occurs spontaneously or will be feasible. The negative value indicates that the reaction is not feasible.
  - If $E^\circ_{cell} > 0$, its spontaneous
  - If $E^\circ_{cell} < 0$, its non-spontaneous

Example: $Sn + Fe^{2+} \longrightarrow Sn^{2+} + Fe$

The standard reduction potential values are:

$E^\circ_{Fe} = -0.14V$, (cathode, reduction)

$E^\circ_{Sn} = -0.44V$ (anode, oxidation)

$Sn^\circ + Fe^{+2} \longrightarrow Sn^{+2} + Fe^\circ$ (oxidation; reduction)

$Sn \longrightarrow Sn^{2+} + 2e^-$ (oxidation half-reaction)

$Fe^{2+} + 2e^- \longrightarrow Fe$ (reduction half-reaction)

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

$E^\circ_{cell} = -0.44 - (-0.14)$

$E^\circ_{cell} = -0.30V$

As, its negative, therefore the given reaction is not feasible. Howere reverse reaction can be feasible.

Nernst Equation

The electrode potential ~~between~~ ~~concen~~ is influenced by the concentration of the ions involved in the redox reaction. Nernst equation shows relationship between standard electrode potential (E°) to the actual electrode potential (E) under non-standard conditions.

Mathematically: $E = E^\circ + RT/nF \ln [\text{oxidized species}]/[\text{reduced species}]$

- n = no. of electrons transferred from reduced species to oxidized species.
- R = the univeral gas constant ($8.314 J mol^{-1}$)
- T = Kelvin temperature 298 K / 25C°
- F = Charge of a mol of electron and charge of 1mol of electron is $9.648 \times 10^4 C mol^{-1}$
- [oxidized species] = Conc. of speacies with higher oxidation state.

- [reduced species] = Conc. of species with lower oxidation state.
- ln = 2.303 log

$$E = E^\circ + \frac{2.303RT}{nF} \log \frac{[\text{oxidized species}]}{[\text{reduced species}]}$$

$$\frac{2.303RT}{F} = \frac{2.303 \times 8.314 \times 298}{9.648 \times 10^4} = 0.059 JC^{-1} = 0.059V$$

$$E = E^\circ + 0.059/n \log [\text{oxidized species}]/[\text{reduced species}]$$

Another equation:

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{molar conc. product}]}{[\text{molar conc. reactants}]}$$

$1JC^{-1} = 1V$

- Electrode potentials and concentration: The electrode potential depends on the concentration of ions in the solution. For example, the standard electrode potential of copper is +0.34V when Cu^{2+} concentration is 1M. If the Cu^{2+} concentration is decreased (for example, by adding water), the equilibrium shifts to produce more Cu^{2+} ions, making reduction harder because fewer ions are available to accept electrons. This lowers electrode potential, so it is no longer standard value. Increasing, ion concentration makes reduction easier because more ions are avalaible to gain and increases the electrode potential. The Nernst equation can be used to calculate how changes in ion concentration affects the electrode potential.

Example: The standard electrode potential of Cu^{2+}/Cu system is +0.34V. What is the electrode potential of a solution containing 0.5M Cu^{2+} ions.

$E = E^\circ + 0.059/n \log [\text{oxidized species}]/[\text{reduced species}]$

$E_{Cu^{2+}/Cu} = E^\circ_{Cu^{2+}/Cu} + 0.059/n \log [\text{oxidized species}]/[\text{reduced species}]$

$E_{Cu^{2+}/Cu} = 0.34 + 0.059/2 \log 0.5/1$ $\quad \because Cu^{+2} = 0.5$ and $Cu = 1$

$E_{Cu^{2+}/Cu} = 0.34 + 0.0295 \times (-0.301)$

$E_{Cu^{2+}/Cu} = 0.331V$

Electrochemical Series

The electrochemical series is a list of elements (particularly metals) arranged in the order of their electrode standard potentials, measured under standard conditions. (1M ion conc, 25°C, 1 atm) with refrence to the standard hydrogen electrode (SHE). The International Union of Pure and Applied Chemistry (IUPAC) recommends expressing half-cell reactions as reduction reactions, so their E° values are known as standard reduction potential. To obtain oxidation potential of an electrode, simply reverse the sign of reduction potential. Any change in standard conditions will alter the electrode potential values.

- Activity Series of Metals: A displacement/replacement reaction occurs when a more reactive element displaces a less reactive element from its compound. $A + XY \longrightarrow X + AY$

Example: When Zn metal is added to $CuSO_4$ solution. Zn is oxidized to Zn^{2+} and Cu^{2+} is reduced to Cu metal. $Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$.

When Cu metal is placed in $ZnSO_4$ solution, no reaction occurs because Cu is less reactive than Zn. Cu^{2+} has a higher reduction potential then Zn^{2+}.

Metals like Mg and Al can also displace Cu^{2+}, but Ag can not. Reactive Metals like Na and K can displace H_2 from water. Less reactive metals like Cu and Ag cannot.

Activity Series: Ranks metals (and hydrogen) based on their ease of oxidation. Metals are arranged in decreasing order of activity. A metal higher in the series can donate electrons to ions of metal lower in the series.

Key observations: Metals higher in the activity series can displace metals lower in the series from their compounds. The greater the gap between two elements in the series, the more vigours the displacement reaction.

Example: $Ba_{(s)} + PbO_{(s)} \longrightarrow BaO_{(s)} + Pb_{(s)}$

Ba is more reactive, so it gets oxidized and displaces Pb.

$Fe + MgCl_2 \longrightarrow$ No Reaction

Fe is less reactive than Mg, so it can not displace Mg^{2+}

Cu, Ag, Hg
Moderately noble metals, no reaction with water or HCl. React with oxidizing acids (HNO_3)
Pt, Au very noble metals. React only with aqua regia

Li, K, Ba, Sr, Ca, Na very active. React with cold water. (K and Na react violently). Also react voilently with acids
Mg, Al, Mn, Zn, Cr, Fe, Cd Intermediate activity. React ~~slowly~~ with HCl, do not react with water, but steam
Co, Ni, Sn, Pb moderate, react slow with HCl and not with water
H_2

The Relative Reactivity of Species as Oxidizing or Reducing Agents

Electrode potential values (also called reduction potentials) help compare the reactivity of elements, compounds, and ions as oxidizing or reducing agents.

- Higher reduction potential: Indicates a stronger oxidizing agent. The species has a greater tendency to gain electrons. (be reduced).
- Lower reduction potential: Indicates a stronger reducing agent. The species has a greater tendency to lose electrons. (be oxidized).

Example: Comparison of Cu^{2+} and Zn^{2+}

$Cu^{2+} + 2e^- \longrightarrow Cu \quad E^\circ = +0.34V$

$Zn^{2+} + 2e^- \longrightarrow Zn \quad E^\circ = -0.76V$

Cu^{2+} has a higher reduction potential than Zn^{2+}. Therefore, Cu^{2+} is a stronger oxidizing agent then Zn^{2+}.

Reaction between $KMnO_4$ and $FeSO_4$ in Acidic Solution.

$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \quad E^\circ = +1.52V$

$Fe^{2+} \longrightarrow Fe^{3+} + e^- \quad E^\circ = +0.77V$

MnO_4^- has a higher reduction potential then Fe^{2+}. Therefore MnO_4^- acts as a strong oxidizing agent. Fe^{2+} acts as a strong reducing agent.

Types of Electro-chemical cells

Devices that convert electrical energy into chemical energy and vice versa are electrochemical cells. There are two types: Electrolytic cells and Galvanic (Voltaic) Cells.

- Electrolytic Cells: Cell which uses electricity to continue the chemical reaction. Non-spontaneous in nature. Example, Dawn Cell, Nelson's Cell. The process is called electrolysis. Electrolysis is a process in which a chemical reaction occurs by means of an electric current in a molten state or in an ageuous state.

Working of Electrolytic Cells: Oxidation occurs at the anode (positive electrode) where electrons are lost. Reduction occurs at the cathode (negative electrode) where electrons are gained. The battery pushes electrons to start the reaction, making the reaction non-spontaneous

Apparatus: An electrolytic cell containing an electrolyte (molten or ageous). Two electrodes dipped into the solution. A battery connected to the electrodes. Electrons move through wires by metallic conduction, and through the solution by ions (cations and anions) The electrodes are the point where conduction changes from metal → electrolyte and back. At one electrode, ions gain electrons, at the other lose electrons. Then electrons then return to the battery through the wire. Hence, a redox reaction happens at the electrodes.

Units used in Electrolysis: The SI unit of charge is the coulomb (C), which equals the charge on 6.25×10^{18} electrons. A more convienient unit in chemistry is the Fraday (F), which is the charge carried by 1 mole of electrons, equal to 96487 C. The unit of current is ampere (A), which is equal to 1 coulomb per second.

Factors affecting the Products of Electrolysis

Electrolysis drives a non-spontaneous redox reaction. The products released depend on:

- State of the Electrolyte: For molten electrolyte, its own ions are discharged. And for ageous electrolyte, contains water ions too, so water may produce H_2 at the cathode.
- Position in the Electrochemical Series: Ions higher in the series are more easily reduced, lower ones are oxidized. In ageous sidutions, Cations less reactive than hydrogen (eg. Cu^{2+}) are discharged at the cathode. More reactive cations (Na^+, Mg^{2+}) are not discharged, instead water is reduced to hydrogen gas.
- Concentration of Electrolyte: High ion concentration makes it easier for those ions to be discharged. If an ion is in low concentration, water may discharge instead.

Example: Electrolysis of fused NaCl

At anode: $2Cl^- \rightarrow Cl_2 + 2e^-$

At cathode: $2Na^+ + 2e^- \rightarrow 2Na$

Net reaction: $2Na^+ + 2Cl^- \longrightarrow 2Na + Cl_2$

Electrolysis of concentrated ageous NaCl (brine)

Since the solution contains a higher concentration of Cl^- ions. So, they are discharged at the anode instead of OH^- ions. Na^+ ions being more reactive than hydrogen remain in solution and are not discharged, instead water molecules are discharged at cathode.

At anode: $2Cl^- \rightarrow Cl_2 + 2e^-$

At cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

New reaction: $2H_2O + 2Cl^- \longrightarrow H_2 + Cl_2 + 2OH^-$

Electrolysis of dilute aqeous NaCl

In dilute aqeous NaCl solution, Cl^- ions have lower concentration. So, chloride ions are not discharged at the anode. Instead, OH^- ions are discharged at anode. Na^+ ions being more reactive than hydrogen remain in the solution and water molecules are discharged at cathode.

At anode: $4OH^- \longrightarrow O_2 + 4e^- + 2H_2O$

At cathode: $4H_2O + 4e^- \longrightarrow 2H_2 + 4OH^-$

Net reaction: $4H_2O \longrightarrow 2H_2 + O_2$

Relation between the Faraday Constant, Avogadro Constant, the Charge on Electron

The amount of substance produced at an electrode during electrolysis depends on the period of time for which a constant current is passed and the quantity of charge in coulombs that passes through the electrolyte. The relation between current and time is: $Q = I \times t$, where Q is quantity of charge in coulombs, I is current in ampere and t is time in seconds. The quantity of electricity can be expressed by Faraday constant (F). One faraday is the amount of electric charge carried by one mole of electrons.

Charge on one electron = $1.60217662 \times 10^{-19} C$

Charge on one mole of electrons = $1.60217662 \times 10^{-19} C \times 6.022 \times 10^{23}$ per mol

Charge on one mole of electrons = $96485.332\ C mol^{-1}$

This quantity of charge is referred to as one Faraday. Thus, the quantity of change in electrolysis can be determined from the number of Faraday's of charge, which passes. For most calculations, the value of the Faraday will be taken as 96500C. The relationship between the Faraday constant, avagadro constant and charge on electron can be expressed by: $F = N_A \cdot e$

Example: $Na^+ + e^- \longrightarrow Na$

To deposit one mole of Na, the amount of electricity needed is 1F (96500 C)

$Cu^{2+} + 2e^- \longrightarrow Cu$

But to deposit one mole of Cu, 2 mole of electrons are required. So, the amount of electricity needed is 2F.

SHORT QUESTIONS

The oxidation potential of Zn is +0.76V and its reduction potential is -0.76V.
The standard oxidation potential of zinc is +0.76V because zinc is a highly reactive metal and has a strong tendency to lose electrons to form Zn^{2+} ions. Therefore the oxidation reaction: $Zn(s) \rightarrow Zn^{2+} + 2e^-$ is spontaneous, giving a positive oxidation potential. The reduction potential of zinc is -0.76V because Zn^{2+} ions do not readily gain electrons to form zinc metal. Since reduction is the reverse process, it is non-spontaneous, therefore the reduction potential is negative.
A salt bridge maintain the electrical neutrality in the cell.
A salt bridge maintains electrical neutrallity in a galvanic cell by allowing the migration of ions between the two half-cells. During the cell reaction, positive ions accumulate in the cathode compartment, while negative ions accumulate in the anode compartment, which would stop the flow of electrons if not balanced. The salt bridge contains an inert electrolyte such as KCl or KNO_3, whose ions move to neutrallize charges. Anions migrate toward the anode and cations towards cathode, preventing charge build up. This maintains electrical neutrallity and allows cell to continue functioning, ensuring a continuous current.
Na and K can displace hydrogen from acids but Cu and Pt cannot.
Sodium (Na) and Potassium (K) can displace hydrogen from acids because they are highly reactive metals, placed above hydrogen in the electrochemical (activity) series. They have a strong tendency to lose electrons, forming positive ions and therefore readily replace hydrogen from acids to produce hydrogen gas. On the other hand, Copper (Cu), and Platinum (Pt) cannot displace hydrogen from acids because they are less reactive metals and lie below hydrogen in the activity series. They do not lose electrons easily and thus cannot reduce hydrogen ions of the acids to hydrogen gas.
Define oxidation in terms of ~~oxidation~~ electron transfer.
Oxidation is a chemical process in which an atom, ion, or molecule loses electrons. In terms of electrons transfers, oxidation involves the removal of one or more electrons, resulting in an increase in oxidation state. For example: $Zn \rightarrow Zn^{2+} + 2e^-$. Here zinc is oxidized because it loses electrons.
What is the oxidation number of oxygen in H_2O_2?
In hydrogen peroxide (H_2O_2), the oxidation number of oxygen is -1. This is because oxygen is bonded to another oxygen atom, and in peroxides, oxygen does not exhibit its usual oxidation state of -2. The O–O single bond reduces its ability to attract electrons completely, so each oxygen in H_2O_2 has an oxidation number of -1 instead of -2. Therefore, H_2O_2 is classified as a peroxide because the oxidation state of oxygen is -1.
Identify the reducing agent in the reaction $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$
The reducing agent in this reaction is Zn. This is because zinc loses electrons and gets oxidized to Zn^{2+}. By losing electrons, zinc provides electrons to Cu^{2+}, causing copper ions to gain electrons and get reduced to metallic copper. Therefore, the substance that loses electrons and causes reduction of the other is the reducing agent, which in this reaction is zinc.
Explain what happens at the anode during the electrolysis of aqeous sodium chloride.
During the electrolysis of aqeous sodium chloride (brine), chloride ions (Cl^-) are oxidized at the anode because the anode is the positive electrode where oxidation takes place. Chloride ions lose electrons to form chlorine gas. $2Cl^- \rightarrow Cl_2 + 2e^-$. Although OH^- ions are present, Cl^- ions are discharged in prefrence due to their lower discharge potential. As a result, chlorine gas is released at the anode, confirming that oxidation of chloride ions occurs during this process.
What does a positive standard electrode potential indicate about a substance's tendency to gain electrons?
A positive standard electrode potential indicates that a substance has a strong tendency to gain electrons and undergo reduction. The more positive the electrode potential, the more readily the substance accepts electrons. A positive value means the reduction process

is spontaneous, and the substance acts as a good oxidizing agent, as it easily gains electrons during a chemical reaction.

Calculate the oxidation number of chromium in $K_2Cr_2O_7$

In potassium dichromate ($K_2Cr_2O_7$), let the oxidation number of chromium be x. We know, Oxidation number of K = +1 and O = -2. The compound is neutral so the sum of oxidation numbers = 0:

$2(+1) + 2(x) + 7(-2) = 0 \implies x = +6$

Therefore, the oxidation number of chromium in $K_2Cr_2O_7$ is +6.

Describe the role of the standard hydrogen electrode in electrochemistry.

The Standard Hydrogen Electrode (SHE) serve as the reference electrode in electrochemistry. It is assigned a fixed potential of 0.00V and is used to measure and compare the electrode potentials of other electrodes. It consists of platinum metal dipped in 1M H^+ solution with hydrogen gas bubbling over it at 1 atm pressure. By connecting SHE, with another half-cell, the standard electrode potential of that cell can be determined. Therefore, SHE provides a universal standard for comparing oxidation and reduction tendencies of different substances.

What is the significance of activity series of metals?

The activity series of metals is a list of metals arranged in order of their reactivity, from most reactive to least reactive. It is significant because it helps predict chemical reactions, such as which metal can displace another metal from its salt solution and which metals can displace hydrogen from acids. It also indicates the ease of oxidation, as metals higher in the series lose electrons more readily, while those lower resist oxidation. Therefore, the activity series is important for understanding displacement reactions, extraction of metals, corrosion and electrochemical processes.

How can you deduce the feasibility of a redox reaction using electrode potentials?

The feasibility of a redox reaction can be determined by calculating the cell potential ($E°_{cell}$) using standard electrode potentials. The reduction potential of the cathode is subtracted from the oxidation potential of the anode: $E°_{cell} = E°_{cathode} - E°_{anode}$. If $E°_{cell}$ is positive, the redox reaction is feasible and spontaneous. If $E°_{cell}$ is negative, the reaction is not spontaneous and therefore not feasible under standard conditions.

Bauxite ore is used for the commericial preparation of Al. For this purpose, bauxite ore is first purified to produce pure alumina, Al_2O_3. Alumina is the electrolyzed. The following reaction occurs: $2Al_2O_{3(s)} \longrightarrow 4Al_{(s)} + 3O_{2(g)}$. Calculate the mass of Al, that collects at cathode and the volume of oxygen that collects at anode when Al_2O_3 is electrolyzed for 10 hours with a 15 ampere current at 1 atm and 25°C.

Current (I) = 15A, $t = 10h = 36000s$.

Total charge $Q = It = 15 \times 36000 = 540000C$.

Number of moles of electrons: $n(e^-) = Q/F = 540000/96485 = 5.597$ mol

For the half-reaction, 3 mol e^- produce 1 mol Al ($Al^{3+} + 3e^- \longrightarrow Al$)

$n(Al) = n(e^-)/3 = 5.597/3 = 1.8656$ mole

Mass of aluminum: $n(Al) \times M_{Al} = 1.8656 \times 26.98 = 50.3g$

From the overall reaction $2Al_2O_3 \longrightarrow 4Al + 3O_2$, 12 e^- produce 3 mol O_2, so 1 mol e^- produces 1/4 mol O_2.

$n(O_2) = 1/4\, n(e^-) = 0.25 \times 5.597 = 1.3992$ mol

Using $PV = nRT$

$V = nRT = 1.3992 \times 0.08206 \times 298.15 = 34.2\ dm^3$

Which of the following compounds will give more mass of metal, when 15 ampere current is passed through a molten mass of these salts for 1hr.

a) NaCl b) $CaCl_2$

To determine which compound gives more mass of metal, we compare the number of electrons needed to deposit one mole of each metal. For NaCl, $Na^+ + e^- \rightarrow Na$. Sodium requires 1 electron to deposit 1 mole of Na. For $CaCl_2$, $Ca^{2+} + 2e^- \rightarrow Ca$ Calcium requires 2 electrons to deposit 1 mole of Ca. With the same current and same time, the same number of electrons is supplied, so the metal requiring fewer electrons (Na) will deposit more moles of metals. Therefore, sodium (from NaCl) will give more mass of metal than calcium from CaCl, because Na^+ needs only one electron, while Ca^{2+} requires two electrons to form metal.

How many hours would electroplating have to be continued at the rate of 5 ampere if 75g of copper is to be deposited from $CuSO_4$ solution?
Current $I = 5A$
Mass of copper to deposit $m = 75g$
Molar mass of $Cu = 63.5 g/mol$
Copper ion: $Cu^{2+} + 2e^- \rightarrow Cu$
First calculate moles of Cu: $n = m/M = 75/63.5 = 1.18$ mol
Since 2 moles of electrons deposit 1 mole Cu: $n(e^-) = 2 \times 1.18 = 2.36$ mol
Charge required: $Q = n(e^-) \times F = 2.36 \times 96485 = 227720 C$
Now, using $Q = It$: $t = Q/I = 227720/5 = 45544s$
Convert into hours: $45544/3600 = 12.65$ hours
Electroplating must be continued for approximately 12 hours and 40 minutes.
Differentiate between the following:
a) galvanic and electrolytic cell

Galvanic Cell	Electrolytic Cell
Converts chemical energy into electrical energy.	Converts electrical energy into chemical energy.
Spontaneous reaction ($E°_{cell}$ is positive)	Non-spontaneous ($E°_{cell}$ is negative)
Anode is negative and Cathode is positive	Anode is positive and cathode is negative
Used to produce electricity	Used for electroplating, electrolysis and metal extraction

b) oxidation half-reaction and reduction half-reaction

Oxidation Half-reaction	Reduction Half-reaction
It involves loss of electrons	It involves gain of electrons
Oxidation number of element increases	Oxidation number of the element decreases
Occurs at anode	Occurs at cathode
Example: $Zn \rightarrow Zn^{2+} + 2e^-$	Example: $Cu^{2+} + 2e^- \rightarrow Cu$

An electroplating apparature is used to coat jewellary with gold. What mass of gold can be deposited from a solution that contains $[Au(CN)_4]^{-1}$ ion if a current of 5.0 amperes flows for 30 minutes? The following half-reaction occurs: $[Au(CN)_4]^{-1}_{(aq)} + 3e^- \rightarrow Au_{(s)} + 4CN^-_{(aq)}$
Current $I = 5.0A$
Time $t = 30 min = 30 \times 60 = 1800s$
Half reaction: $[Au(CN)_4]^- + 3e^- \rightarrow Au + 4CN^-$
This shows 3 electrons deposit 1 mole of gold
Calculate charge passed: $Q = It = 5 \times 1800 = 9000 C$
Calculate moles of electrons: $n(e^-) = Q/F = 9000/96485 = 0.0933$ mol
Moles of Gold deposited: Since 3 mol electrons deposit 1 mol gold $n(Au) = 0.0933/3 = 0.0311$
Mass of Gold deposited: Atomic mass of gold 197 g/mol, $n \times M = 0.0311 \times 197 = 6.13g$
Approximately 6.1 grams of gold are deposited when a 5 ampere current flows for 30 minutes.
Construct redox equations using the following half reactions
a) $SO_2 \rightarrow HSO_4^-$ $MnO_4^- \rightarrow Mn^{2+}$
Balance the oxidation half-reaction:
The sulfur is oxide from +4 in SO_2 to +6 in HSO_4^-. The half reaction is balanced by adding water to balance oxygen, hydrogen ions to balance hydrogen, and electrons to balance the charge
$SO_2 + 2H_2O \rightarrow HSO_4^- + 3H^+ + 2e^-$
Balance the reduction half-reaction:

The magnese is reduced from +7 in MnO_4^- to +2 in Mn^{2+}. The half-reaction is balanced by adding water to balance oxygen, hydrogen ions to balance hydrogen, and electrons to balance the charge:

$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

Combine half-reactions:

To equalize the electron transfer, multiply the oxidation half reaction by 5 and the reduction half-reaction by 2. Then, combine and cancel common species.

$5SO_2 + 10H_2O \longrightarrow 5HSO_4^- + 15H^+ + 10e^-$

$2MnO_4^- + 16H^+ + 10e^- \longrightarrow 2Mn^{2+} + 8H_2O$

$10e^- + 16H^+ + 2MnO_4^- + 5SO_2 + 10H_2O \longrightarrow 2Mn^{2+} + 8H_2O + 5HSO_4^- + 15H^+ + 10e^-$

Final balanced equation:

$5SO_2 + 2MnO_4^- + H^+ + 2H_2O \rightarrow 5HSO_4^- + 2Mn^{2+}$

b) $Cr_2O_7^{2-} \rightarrow Cr^{3+}$ $\quad Cl^- \rightarrow Cl_2$

Balance the half reactions:

The chromium half-reaction is balanced for mass and charge in acidic solution.

$6e^- + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$

The chloride half-reaction is balanced for mass and charge.

$2Cl^- \rightarrow Cl_2 + 2e^-$

Equalize:

Multiply the oxidation half by 3

$6Cl^- \rightarrow 3Cl_2 + 6e^-$

Add halves and cancel electrons:

$Cr_2O_7^{2-} + 14H^+ + 6Cl^- \longrightarrow 2Cr^{3+} + 7H_2O + 3Cl_2$

c) $H_2O_2 \longrightarrow O_2$ $\quad MnO_4 \longrightarrow Mn^{2+}$

Balance the reduction half reaction:

$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

Balance the oxidation half reaction:

$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$

Combine Half Reactions and Simplify:

To balance the electrons transferred, the reduction half-reaction is multiplied by 2, and the oxidation half-reaction by 5

$2MnO_4^- + 16H^+ + 10e^- + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2 + 10H^+ + 10e^-$

Final equation:

$2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$

d) $Sn^{2+} \rightarrow Sn^{4+}$ $\quad Fe^{3+} \rightarrow Fe^{2+}$

Balance oxidation half:

$Sn^{2+} \longrightarrow Sn^{4+} + 2e^-$

Balance reduction half:

$Fe^{3+} + 1e^- \longrightarrow Fe^{2+}$

Equalize:

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

Combine and simplify:

$Sn^{2+} + 2Fe^{3+} \longrightarrow Sn^{4+} + 2Fe^{2+}$

e) $IO_3^- \longrightarrow I^-$ $\quad AsO_3^{3-} \longrightarrow AsO_4^{3-}$

Balance reduction half:

$IO_3^- + 6H^+ + 6e^- \longrightarrow I^- + 3H_2O$

Balance oxidation half:

$AsO_3^{3-} + H_2O \longrightarrow AsO_4^{3-} + 2H^+ + 2e^-$

Final equation:

$IO_3^- + 3AsO_3^{3-} \longrightarrow I^- + 3AsO_4^{3-}$

In the reaction between potassium premaganate and iron (II) sulphate in an acidic solution $MnO_4^- + Fe^{2+} \longrightarrow Mn^{2+} + Fe^{3+}$

a) Identify the oxidation states of magnese and iron before and after the reaction

Magnese in $MnO_4^- \rightarrow +7$ and in $Mn^{2+} \rightarrow +2$

Iron in $Fe^{2+} \rightarrow +2$ and in $Fe^{3+} \rightarrow +3$

b) Explain which species is oxidized and which is reduced

$Fe^{2+} \rightarrow Fe^{3+}$ is oxidized (loss of $1e^-$).

$Mn^{7+} \rightarrow Mn^{2+}$ is reduced (gain of 5e-)
c) Balance the redox reaction using changes in oxidation number.
Change in oxidation number: Mn +7 → +2 (gain 5e-). Fe +2 → +3 (loss 1 e-). To cancel electrons, multiply Fe change by 5
$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$
d) Identify oxidizing and reducing agents.
Oxidizing agent is MnO_4^- (it is reduced, so it oxidizes Fe^{2+})
Reducing agent is Fe^{2+} (it is oxidized, so it reduces MnO_4^-)
Explain why magnessium can displace zinc from zince sulphate solution but copper can not. Predict the outcome of placing a zinc strip in a copper (II) sulphate solution, including the balanced chemical equation.
Magnesium is more ~~th~~ reactive than zinc and is placed above zinc in the activity series of metals. Therefore, magnesium has a greater tendency to lose electrons from Mg^{2+} ions. Due to this higher reactivity, magnesium can displace zinc from zinc sulphate solution. However, copper is less reactive than zinc, so it cannot displace zinc from its compound.
When a zinc strip is placed in copper (II) sulfate solution, zinc being more reactive displaces copper from the solution. Zinc becomes Zn^{2+} by losing electrons, while Cu^{2+} gains electrons and forms copper metal. $Zn_{(s)} + CuSO_{4(aq)} \rightarrow ZnSO_{4(aq)} + Cu_{(s)}$. This shows that zinc is oxidized and copper ions are reduced, resulting in deposition of copper on the zinc strip.
Predict the outcome of mixing ageous solutions of $FeSO_4$ and $AgNO_3$ with Cu based on their standard electrode potentials. Explain your reasoning.
Compare standard reduction potentials (E°):
$Ag^+ + e^- \longrightarrow Ag$ ($E^\circ = +0.80\,V$)
$Cu^{2+} + 2e^- \longrightarrow Cu$ ($E^\circ = +0.34V$)
$Fe^{2+} + 2e^- \longrightarrow Fe$ ($E^\circ = -0.44\,V$)
A species with higher (more positive) reduction potential has a greater tendency to gain electrons (be reduced). A metal will be oxidized if its corresponding reduction potential is lower than that of the ion it is placed with.
Copper placed in $AgNO_3$ (Ag^+) solution:
Ag^+ has a higher reduction potential (+0.80 V) than Cu^{2+} (+0.34 V), so Ag^+ will be reduced and Cu will be oxidized. The cell potential is positive:
$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 0.80 - 0.34 = +0.46V$
So the reaction is spontaneous: $Cu_{(s)} + 2Ag^+_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$
Silver metal plates out on the copper strip. Oxidizing Agent Ag^+. Reducing agent Cu
Copper placed in $FeSO_4$ (Fe^{2+}) solution:
Fe^{2+} has a much lower reduction potential (-0.44V) than Cu^{2+} (+0.34V). That means Fe^{2+} is less likely to be reduced than Cu^{2+}, copper metal is less reactive than iron metal in this sense, so copper will not be oxidized by Fe^{2+}. The cell potential would be negative:
$E^\circ_{cell} = E^\circ_{Fe^{2+}/Fe} - E^\circ_{Cu^{2+}/Cu} = -0.44 - 0.34 = -0.78$
So the reaction is non-spontaneous and no displacement occurs.
No reaction, the copper strip remains unchanged and iron stays as Fe^{2+} in solution
Using the Nernst equation, calculate the cell potential of a galvanic cell with the following half-reactions of $Zn^{2+} + 2e^- \longrightarrow Zn$ ($E^\circ = -0.76V$) and $Cu^{2+} + 2e^- \longrightarrow Cu$ ($E^\circ = +0.34V$) if the concentration of Zn^{2+} ~~+ 2e-~~ is 0.1 M and Cu^{2+} is 1.0M.
$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$
Cathode = Cu^{2+}/Cu (because of higher E°)
Anode = Zn^{2+}/Zn
$E^\circ_{cell} = 0.34 - (-0.76) = 1.10V$
Now, for a reaction involving 2 electrons (n = 2)
$E = E^\circ - 0.0592/n \log$ product/reactant $\quad \therefore Q = Zn^{2+}/Cu^{2+} = 0.1/1.0 = 0.10$
$E = 1.10 - 0.0592/2 \log(0.10)$
$E = 1.10 - 0.592/2\,(-1)$
$E = 1.13V$ (approximately)
A voltaic cell is constructed using a copper electrode in a 1M solution of copper (II) sulphate and a zinc electrode in a 1M zinc sulphate solution.
a) Calculate the cell potential under standard conditions using the given

Standard reduction potentials: $E^\circ(Cu^{2+}/Cu) = +0.34V$ and $E^\circ(Zn^{2+}/Zn) = -0.76$
Cathode: Cu^{2+}/Cu
Anode: Zn^{2+}/Zn
$E_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 0.34 - (-0.76) = 1.10V$
b) Discuss how the Nernst equation can be used to predict the effect of changing the concentration of Cu^{2+} ions on the cell potential.
$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$
The Nernst equation (at 25°C, n=2) is:
$E = E^\circ - 0.0592/n \log Q = 1.10 - 0.0592/2 \log([Zn^{2+}]/[Cu^{2+}])$
So, when $[Cu^{2+}]$ increases, the reaction quotient $Q = [Zn^{2+}]/[Cu^{2+}]$ decreases (smaller $Q \Rightarrow \log Q$ more negative), making the subtraction term negative and increasing E.
Conversely, decreasing $[Cu^{2+}]$ increases Q, lowers E.
Short numeric illustration with $Zn^{2+} = 1.0M$:
If $[Cu^{2+}] = 1.0M$ $E = 1.10V$
If $[Cu^{2+}] = 0.1M$, using nernst equation, $Q = 10$, $E = 1.0704V$ (decreases)
If $[Cu^{2+}] = 2.0M$, using nernst equation, $Q = 0.5$, $E = 1.109$ (increases)