Chapter 10

ELECTROCHEMISTRY

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Student Learning Outcomes

After studying this chapter, students will be able to:

- Define the terms redox, oxidation, reduction, and disproportionation (in terms of electron transfer and changes in oxidation number). **(Knowledge)**
- Apply the concept of oxidation numbers in identifying oxidation and reduction reactions. **(Application)**
- Identify the oxidizing and reducing agents in a redox reaction. **(Knowledge)**
- Describe the role of oxidizing and reducing agents in the redox reaction. **(Understanding)**
- Apply the concept of changes in oxidation numbers to balance chemical equations. **(Application)**
- Explain how electrolytic cells convert electrical energy to chemical energy, with oxidation at the anode and reduction at the cathode. **(Understanding)**
- Predict the identities of substances liberated during electrolysis based on the state of the electrolyte, position in the redox series, and concentration. **(Knowledge)**
- Apply the relationship between the Faraday constant, Avogadro constant, and the charge on the electron to solve problems. **(Application)**
- Calculate the quantity of charge passed during electrolysis and the mass or volume of substance liberated during electrolysis. **(Application)**
- Deduce the Avogadro constant by an electrolytic method. **(Application)**
- Define the terms standard electrode potential and standard cell potential. **(Knowledge)**
- Describe the standard hydrogen electrode (SHE) and methods used to measure standard electrode potentials. **(Understanding)**
- Calculate the standard cell potentials by combining the potentials of two standard electrodes and then use these to predict the feasibility of a reaction and the direction of electron flow in a simple cell. **(Application)**
- Deduce the relative reactivity of elements compounds, and ions as oxidizing agents or reducing agents from their electrode potential values. **(Application)**
- Construct redox equations using relevant half-equations. **(Application)**
- Explain how voltaic (galvanic) cells convert energy from spontaneous, exothermic chemical processes to electrical energy, with oxidation at the anode and reduction at the cathode. **(Understanding)**
- Explain how voltaic cells convert chemical energy from redox reactions to electrical energy using Cu – Zn galvanic cell as an example. **(Understanding)**
- Explain how electrode potentials vary with the concentrations of aqueous ions and use the Nernst equation to predict this quantitatively. **(Understanding)**
- Explain the concept of the activity series of metals and how it relates to the ease of oxidation. **(Understanding)**
- Deduce the feasibility of redox reactions from activity series or reaction data. **(Understanding)**
- Explain the merits of photovoltaic cells as sustainable ways of meeting energy demands by making reference to the photovoltaic principle. **(Understanding)**
- Explain the use of the Winkler Method to measure biochemical oxygen demand (BOD) and its use as a measure of water pollution. **(Understanding)**

The branch of chemistry which deals with inter conversion of electrical and chemical energy i.e., electrical energy into chemical energy and chemical energy into electrical energy is called **electrochemistry**.

OXIDATION, REDUCTION, AND REDOX REACTIONS

Oxidation is a process involving loss of electron or electrons.

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

$$Zn^0 \longrightarrow Zn^{+2} + e^-$$

Here Fe^{+2} and Zn^0 have lost electrons, therefore they are oxidized.
Reduction is a process involving gain of electron or electrons.

$$C\ell^0 + e^- \longrightarrow C\ell^{-1}$$

$$Cu^{+2} + 2e^- \longrightarrow Cu^0$$

In these examples, $C\ell^0$ and Cu^{+2} have gained electrons; therefore, they are reduced.

Interesting Information!

Photosynthesis is a redox reaction which provides food for the entire planet, and another one is respiration that keeps you alive, both are redox reactions.

Rack Your Mind!

1. Calculate the oxidation number of Cr in K_2CrO_4.

Differences between Oxidation and Reduction:

Sr. No.	Oxidation	Reduction
1.	The addition of oxygen in a specie is called oxidation. e.g., $S + O_2 \longrightarrow SO_2$ $C + O_2 \longrightarrow CO_2$ $2CO + O_2 \longrightarrow 2CO_2$ In these examples, oxygen is added to S, C and CO.	The removal of oxygen or an electronegativity element from a specie is called reduction. e.g., $ZnO + C \longrightarrow Zn + CO$ $CuO + C \longrightarrow Cu + CO$ $2FeC\ell_3 + H_2 \longrightarrow 2FeC\ell_2 + 2HC\ell$
2.	The removal of hydrogen is also called oxidation. e.g., $H_2S + C\ell_2 \longrightarrow 2HC\ell + S$ $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$ So, H_2S and CH_4 are oxidized.	The addition of hydrogen to a specie is called reduction. e.g., $H_2S + Br_2 \longrightarrow 2HBr + S$ Here bromine gets reduced as it gains hydrogen to form HBr. $H_2C = CH_2 + H_2 \longrightarrow H_3C - CH_3$
3.	Loss of electron/s and hence decrease in oxidation number is called oxidation. e.g., $Zn \longrightarrow Zn^{2+} + 2e^-$ Here Zn is oxidized to form Zn^{2+} ions.	Gain of electrons and hence decrease in oxidation number is called reduction. e.g., $Zn^{2+} + 2e^- \longrightarrow Zn$ Here Zn^{2+} is reduced to form Zn.
4.	In electrochemical cells, oxidation takes place at anode.	In electrochemical cells, reduction takes place at cathode.

➢ Redox Reactions

"Those reactions in which one species (atom, ion or molecule) is **oxidized** while other is **reduced** are called redox reactions".

Oxidation Number rules can be applied to any compound, whether ionic or covalent species.

There are two ways of finding out whether or not a substance has been oxidized or reduced during a chemical reaction:

- Electron transfer
- Changes in oxidation number

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OXIDATION NUMBER AND ITS SIGNIFICANCE

Definition

"An oxidation number is a number given to each atom or ion in a compound that shows us its degree of oxidation."

Or

"It is the apparent charge on an atom (per atom) of an element in a molecule or an ion."

- The oxidation numbers are also called oxidation states.
- Oxidation numbers can be positive, negative or zero. The + or – sign must always be included.
- Higher positive oxidation numbers mean that an atom or ion is more oxidized.
- Higher negative oxidation numbers mean that an atom or ion is more reduced.

➲ Oxidation Number Rules

The oxidation number of any atom or ion can be deduced by using oxidation number rules. It is important to note that an oxidation number refers to a single atom in a compound.

Rack Your Mind!

2. In all oxidation reactions, atoms of an element in a chemical species lose electrons and increase their:
(a) Oxidation state
(b) Electrode
(c) Reductions
(d) Negative charges

i. The oxidation number of any uncombined element is zero. For example, the oxidation number of each atom in $S_8, H_2, C\ell_2$, Na, Mg and Zn is zero.

ii. In either a compound or an ion, the more electronegative element is given the negative oxidation number. In HF, fluorine has –1 oxidation number.

iii. In compounds, many atoms or ions have fixed oxidation numbers, group 1 alkali metals are always +1, group 2 alkaline earth elements are always +2, group 17 halogens in binary compounds are always –1, hydrogen is +1 (except in metal hydrides, such as NaH, where it is –1), oxygen is –2 (except in peroxides, where it is –1, and in F_2O, where it is +2).

iv. The oxidation number of an element in a mono-atomic ion is always the same as the charge on the ion, for example, $C\ell^-$ is -1, $A\ell^{3+}$ is +3.

v. The sum of the oxidation numbers in a compound is **zero**. In neutral molecules, the algebraic sum of the oxidation numbers of all the elements is zero. e.g., In $HC\ell$ (+1 – 1 = 0), $NaC\ell$ (+1 – 1 = 0).

vi. In polyatomic ions, the algebraic sum of oxidation number equals the charge on the ion. e.g., NH_4^+, CO_3^{-2} and SO_4^{-2}.

vii. For transition metals and many non-metals, Ox. No. cannot be fixed as they show variable Ox states. Therefore, there Ox. Nos. are always determined by calculations.

While applying the oxidation number rules in the following examples, 'Ox. No.' as an abbreviation for oxidation number is used.

KEEP IN MIND

- Hydrogen shows –1 oxidation state with all metals.
- Hydrogen shows +1 oxidation state with all non-metals.
- Oxygen shows negative oxidation state with all metals.
- Oxygen shows negative oxidation state with all non-metals except fluorine.
- Oxygen shows –2, –1 and –1/2 in H_2O, Na_2O_2, and KO_2 respectively.

➲ Finding Oxidation Number of an Element in a Compound or a Radical

The oxidation number or state of any atom of an element present in a compound or a radical can be determined by making use of the above-mentioned rules.

➢ Compounds of a Metal with a Non-metal

A metal always has the positive Ox. No. and nonmetals have the negative Ox. State. For example, in sodium sulfide, Na_2S:

$$2(+1) + S = 0$$
$$+2 + S = 0$$
$$S = -2$$

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➢ **Compounds of a Non-metal with a Non-metal**

In compounds containing two different non-metals, the sign of the Ox. No. depends on the electronegativity of each atom. The most electronegative element is given the negative sign.

Sample Problem 10.1

Find the oxidation No. of S in Sulfur dioxide, SO_2.

Ox. No. of each O atom = −2

For two oxygen atoms = 2 × (−2) = −4

SO_2 has no charge, so the total Ox. No. is zero. So,

$$S + 2(-2) = 0$$
$$S - 4 = 0$$
$$S = +4$$

Ox. No. of S = +4

➲ Compound Ions

Compound ions are ions with two or more different atoms. **Examples** are the sulfate ion, SO_4^{2-}, and the nitrate ion, NO_3^-.

Sample Problem 10.2

Calculate the oxidation number (Ox. No.) of Sulphur in SO_4^{2-}.

Solution:

$$[\text{Ox. No. of S}] + 4[\text{Ox. No. of 0}] = -2$$
$$S + 4(-2) = -2$$
$$S = +6$$

Thus, the oxidation number of sulphur in SO_4^{2-} is +6.

Rock Your Mind!

3. In SO_4^{2-} the oxidation number of Sulphur is:
(a) −8 (b) +8
(c) −6 (d) +6

QUICK CHECK 10.1

a) Define oxidation and reduction in terms of electron transfer with examples.

Ans. Oxidation: The loss of electrons by a substance.

Example:

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

Sodium loses one electron — **oxidation.**

Reduction: The gain of electrons by a substance.

Example:

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

Chlorine gains electrons — **reduction.**

b) Define oxidation and reduction in terms of change in oxidation number with examples.

Ans. Oxidation: Increase in oxidation number.

Example:

$$Fe_2^+ \longrightarrow Fe_3^+ + e^-$$

Oxidation number increases from +2 to +3 — **oxidation.**

Reduction: Decrease in oxidation number.

Example:

$$Cl_2 \longrightarrow 2Cl^-$$

Oxidation number decreases from 0 to −1 — reduction.

c) Determine Ox. No. of:

i) Oxygen (N) in Na_2O

Ans. Oxygen (O) in Na_2O

Let oxidation number of oxygen = x

Na = +1

$2(+1)+x = 0 \Rightarrow 2 + x = 0 \Rightarrow x = -2$ $\Rightarrow 2(+1) + x = 0 \Rightarrow 2 + x = 0 \Rightarrow x = -2$

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ii) Iodine (I) in ICl_3

Ans. Iodine (I) in ICl_3

Let Iodine = x, Chlorine = –1

$x+3(-1)=0 \quad \Rightarrow x-3=0 \quad \Rightarrow x=+3$ $x+3(-1)=0 \quad \Rightarrow x-3=0 \quad \Rightarrow x=+3$

iii) Nitrogen (N) in NO_3^{1-}

Ans. Nitrogen (N) in NO_3^-

Let N = x, O = –2

$x+3(-2)=-1 \quad \Rightarrow x-6=-1 \quad \Rightarrow x=+5$ $x+3(-2)=-1 \quad \Rightarrow x-6=-1 \quad \Rightarrow x=+5$

iv) Chromium (Cr) in $K_2Cr_2O_7$

Ans. Chromium (Cr) in $K_2Cr_2O_7$

K = +1, O = –2, Cr = x

$2(+1)+2(x)+7(-2)=0 \quad \Rightarrow 2+2x-14=0 \quad \Rightarrow 2x=12 \quad \Rightarrow x=+6$ $2(+1)+2(x)+7(-2)=0$

$\Rightarrow 2+2x-14=0 \quad \Rightarrow 2x=12 \quad \Rightarrow x=+6$

v) Manganese (Mn) in $KMnO_4$.

Solution:

(Ox. No. of K) + (Ox. No. of Mn) + 4(Ox. No. of 0) = 0

$+1 + Mn + 4(-2) = 0$

$(+1) + Mn - 8 = 0$

or $Mn = +7$

Thus, the oxidation number (Ox. No.) of Mn in $KMnO_4$ is +7.

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DISPROPORTIONATION REACTION

Disproportionation Reaction

A chemical reaction where a single substance (a species i.e. molecule, atom or ion) acts as both the oxidizing and reducing agent, resulting in two different products with different oxidation states.

This type of reaction involves the simultaneous oxidation and reduction of the same element.

Example 1:

The decomposition of hydrogen peroxide (H_2O_2) to form water (H_2O) and oxygen (O_2) is a disproportionation reaction:

$$2H_2O_2 \longrightarrow H_2O_2^{-1} + O_2^{0}$$

Rack Your Mind!

4. What are redox reactions? Give an example.

Oxidation number of oxygen in $H_2O_2 = -1$

Oxidation number of oxygen in $H_2O = -2$ (Oxygen is reduced from –1 to –2)

Oxidation number of oxygen in $O_2 = 0$ (Oxygen is oxidized from –1 to 0)

Example 2:

$$6NaOH_{(aq)} + 3Cl_{2(g)}^{0} \rightarrow 5NaCl_{(aq)}^{-1} + NaCl^{+5}O_{3(aq)} + 3H_2O$$

Oxidation number of chlorine atoms in $Cl_2 = 0$

Oxidation number of chlorine in $NaCl = -1$ (Cl is reduced from 0 to –1)

Oxidation number of chlorine in $NaClO_3 = +5$ Cl is (oxidized from 0 to +5)

Important: Disproportionation reactions can occur where ions or molecules can exist in multiple oxidation states in a reaction.

OXIDIZING AGENT (OXIDANT) AND REDUCING AGENT (REDUCTANT)

Oxidizing Agent	Reducing Agent
An oxidizing agent (atom, ion or molecule) is that substance which oxidizes some other substance, and is itself reduced to a lower oxidation state by gaining one or more electrons.	A reducing agent (atom, ion or molecule) is that substance which reduces some other substance, and is itself oxidized to a higher oxidation state by losing one or more electrons.
If an element M gains one or more electrons and is converted into M^- anion, the element M is said to be acting as an oxidizing agent, since it withdraws an electron from the other atom, in this process oxidation number of M has decreased that is: **For oxidizing agent** $X + e^- \longrightarrow X^-$ [Ox. No. = 0] [Ox. No. = −1] (Higher Oxidation State) (Lower Oxidation State) **For example,** $Cl + e^- \longrightarrow Cl^-$	If an element M loses one electron and is converted to M^+ cation, the element M is said to be acting as a reducing agent, since it is providing electrons, it gets higher oxidation state. Thus, **For reducing agent** $M \longrightarrow M^+ + e^-$ [Ox. No. = 0] [Ox. No. = −1] (Lower Oxidation State) (Higher Oxidation State) **For example,** $Na \longrightarrow Na^+ + e^-$

☑ QUICK CHECK 10.2

a) Identify the oxidized species and reduced species in the following equation. Also identify the oxidizing and reducing agents on the reactant side.

i. $Fe_2O_{3(s)} + CO_{(g)} \rightarrow Fe_{(s)} + CO_{2(g)}$

Ans.

1. **Assign Oxidation Numbers (O.N.):**
   - **Fe_2O_3:** O is −2. So, 2(O.N. of Fe) + 3(−2) = 0 ⇒ 2(O.N. of Fe) = +6 ⇒ O.N. of Fe = **+3**.
   - **CO:** O is −2. So, O.N. of C + (−2) = 0 ⇒ O.N. of C = **+2**.
   - **Fe:** O.N. of Fe = **0** (elemental form).
   - **CO_2:** O is −2. So, O.N. of C + 2(−2) = 0 ⇒ O.N. of C = **+4**.
2. **Identify Changes in O.N.:**
   - **Fe:** O.N. changes from +3 in Fe_2O_3 to 0 in Fe. (Decrease in O.N.)
   - **C:** O.N. changes from +2 in CO to +4 in CO_2. (Increase in O.N.)
   - **O:** O.N. remains -2 throughout.
3. **Identify Oxidized and Reduced Species:**
   - **Reduced Species:** Fe in Fe_2O_3 is reduced (its O.N. decreases from +3 to 0). So, Fe_2O_3 is the species containing the element that is reduced.
   - **Oxidized Species:** C in CO is oxidized (its O.N. increases from +2 to +4). So, **CO** is the species containing the element that is oxidized.
4. **Identify Oxidizing and Reducing Agents (on reactant side):**
   - **Oxidizing Agent:** The species that causes oxidation and gets reduced itself. Fe_2O_3 gets reduced. So, Fe_2O_3 is the oxidizing agent.
   - **Reducing Agent:** The species that causes reduction and gets oxidized itself. CO gets oxidized. So, CO is the reducing agent.

ii. $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$

Ans.

1. **Assign Oxidation Numbers (O.N.):**
   - **CH_4:** H is +1. So, O.N. of C + 4(+1) = 0 ⇒ O.N. of C = **−4**.
   - O_2: O.N. of O = **0** (elemental form).

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- **CO_2:** O is –2. So, O.N. of C + 2(–2) = 0 ⇒ O.N. of C = **+4**.
- **H_2O:** H is +1, O is –2. O.N. of O = **–2**.

2. **Identify Changes in O.N.:**
   - **C:** O.N. changes from –4 in CH_4 to +4 in CO_2. (Increase in O.N.)
   - **O:** O.N. changes from 0 in O_2 to –2 in CO_2 and H_2O. (Decrease in O.N.)
   - **H:** O.N. remains +1 throughout.
3. **Identify Oxidized and Reduced Species:**
   - **Oxidized Species:** C in CH_4 is oxidized (its O.N. increases from –4 to +4). So, CH_4 is the species containing the element that is oxidized.
   - **Reduced Species:** O in O_2 is reduced (its O.N. decreases from 0 to –2). So, O_2 is the species that is reduced.
4. **Identify Oxidizing and Reducing Agents (on reactant side):**
   - **Oxidizing Agent:** The species that causes oxidation and gets reduced itself. O_2 gets reduced. So, O_2 is the oxidizing agent.
   - **Reducing Agent:** The species that causes reduction and gets oxidized itself. CH_4 gets oxidized. So, CH_4 is the reducing agent.

b) **Identify the species in the following reaction which undergoes both oxidation and reduction.**

i. $2NaO_{2(s)} + 2H_2O_{(l)} \rightarrow 4NaOH_{(aq)} + O_{2(g)}$

Ans.

1. Identify oxidation states:
- In NaO_2 (Sodium superoxide)
- Na is always + 1
- Let the oxidation state of O be x
- So: $+1 + 2x = 0 \Rightarrow 2x = -1 \Rightarrow x = -\frac{1}{2}$

Each oxygen in O_2
- In NaOH:
  O is –2
- In O_2 (oxygen gas)
  O is 0

2. What happening to oxygen
- In NaO_2:
  Oxygen starts at –1/2

Products:
- Some oxygen atoms become –2 in NaOH → reduction
- Some become 0 in O_2 gas → oxidation

The species that undergoes both oxidation and reduction is:
The superoxide ion (O_2^-) in NaO_2
It disproportionate:
- Part of it is oxidaized to O_2 (0)
- Part of it is reduced to OH^- (via NaOH, where O is –2)

ii. $P_{4(s)} + 3OH^-_{(aq)} + 3H_2O_{(l)} \longrightarrow PH_{3(g)} + 3H_2PO^-_{2(aq)}$

Ans.

1. **Assign Oxidation Numbers (O.N.) of Phosphorus in each species:**
   - **P_4 (White phosphorus):** O.N. of P = **0** (elemental form).
   - **PH_3 (Phosphine):** H is +1. So, O.N. of P + 3(+1) = 0 ⇒ O.N. of P = **–3**.
   - **H_2PO_2 (Hypophosphite ion):** H is +1, O is –2. So, 2(+1) + O.N. of P + 2(–2) = –1 (charge of the ion)
   ⇒ +2 + O.N. of P – 4 = –1 ⇒ O.N. of P – 2 = –1 ⇒ O.N. of P = **+1**.
   - (O and H in OH^- and H_2O do not change their usual oxidation states).

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2. **Analyze the changes for Phosphorus:**
   - In the reactant P_4, P has an O.N. of 0.
   - In the product PH_3, P has an O.N. of –3 (Reduction: $0 \rightarrow -3$, decrease).
   - In the product H_2PO_2, P has an O.N. of +1 (Oxidation: $0 \rightarrow +1$, increase).
3. **Conclusion:**
   The species that undergoes both oxidation and reduction is Phosphorus in P_4. (Or you can say the species is P_4 itself).

BALANCING OF REDOX EQUATIONS BY OXIDATION NUMBER METHOD

The following steps are carried out for balancing of redox equations by oxidation number method:

i. Write down the skeleton equation of the redox reaction under consideration.
ii. Identify the elements, which undergo a change in their oxidation number during the reaction.
iii. Record the oxidation number above the symbols of the element, which have undergone a change in the oxidation number.
iv. Indicate the change in oxidation number by arrows joining the atoms on both sides of the equation. It shows number of electrons gained or lost.
v. Equate the increase or decrease in the oxidation number, i.e., electrons gained or lost by multiplying with a suitable digit.
vi. Balance the rest of the equation by inspection (hit and trial) method.

Did You Know?

Sequence of the balancing the chemical equation using inspection (hit and trial) method.

- Firstly, balance atoms of all elements except nitrogen, oxygen and hydrogen.
- Secondly, balance atoms of nitrogen (if in the equation).
- Thirdly, balance atoms of oxygen (if in the equation).
- Lastly, balance atoms of hydrogen (if in the equation).

KEEP IN MIND

a) If an element in a species undergoes only increase in oxidation number or decrease in oxidation number in a reaction. The specie containing such element is written once on the RHS of the equation.

$$Zn_{(s)} + HC\ell_{(aq)} \longrightarrow ZnC\ell_{2(aq)} + H_{2(g)}$$

b) If an element in a species undergoes both increase in oxidation number or decrease in oxidation number simultaneously in a reaction (as in case of self-redox or disproportionation reaction). The specie containing such element is written twice on the RHS of the equation. First for increase in oxidation number while second is written for decrease in oxidation number.

$$C\ell_2 + NaOH + C\ell_2 \longrightarrow NaC\ell + H_2O + NaOC\ell$$

c) If an element in a species undergoes increase or decrease in oxidation number as well as no change in oxidation number in a reaction. The specie containing such element is also written twice. First, for change in oxidation number while second is for no change in oxidation number.

$$HNO_3 + Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + H_2O + NO_2$$

$$HC\ell + K_2Cr_2O_7 + HC\ell \longrightarrow C\ell_2 + KC\ell + CrC\ell_3 + H_2O$$

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Sample Problem 10.4

Balance the following equation by oxidation number method.

$$K_2Cr_2O_7 + HC\ell \rightarrow KC\ell + CrC\ell_3 + C\ell_2 + H_2O$$

Solution:

1. Write down the skeleton of chemical equation.

$$K_2Cr_2O_7 + HC\ell \longrightarrow C\ell_2 + KC\ell + CrC\ell_3 + H_2O$$

2. Write down the oxidation number of each element.

$$K_2^{1+}Cr_2^{6+}O_7^{2-} + H^{1+}C\ell^{1-} \longrightarrow C\ell_2^0 + K^{1+}C\ell^{1-} + Cr^{3+}C\ell_3^{1-} + H_2^{1+}O^{2-}$$

3. Identify the elements that show change in oxidation number on both sides.

$$K_2^{1+}Cr_2^{6+}O_7^{2-} + H^{1+}C\ell^{1-} \rightarrow C\ell_2^0 + K^{1+}C\ell^{1-} + Cr^{3+}C\ell_3^{1-} + H_2^{1+}O^{2-}$$

(6e⁻ over Cr; 2e⁻ over Cℓ)

Here, Cr undergoes a change in oxidation state from +6 to +3 and it is reduced (acts as an oxidizing agent) while Cℓ undergoes a change in oxidation state from –1 to 0 and it is oxidized (acts as a reducing agent).

4. Write two half reactions separately i.e., reduction and oxidation reactions

$$K_2Cr_2^{6+}O_7 \longrightarrow 2Cr^{3+}C\ell_3 \quad \text{Half reduction reaction} _____ \text{(ii)}$$

$$2HC\ell^{1-} \longrightarrow C\ell_2^0 \quad \text{Half oxidation reaction} _____ \text{(iii)}$$

Decrease in Ox. No. of Cr is 6 units for one molecule of $K_2Cr_2O_7$.

Increase in Ox. No. of Cℓ is 2 units for 2 molecules of HCℓ.

Eq. (iii) is multiplied by 3 in order to equalize the loss of electrons and the gain of electrons i.e., 6 electrons in this equation.

$$3 \times 2HC\ell \longrightarrow 3C\ell_2$$

$$6HC\ell \longrightarrow 3C\ell_2 _____ \text{(iv)}$$

Now eq. (i) becomes:

$$K_2Cr_2O_7 + 6HC\ell \longrightarrow 3C\ell_2 + KC\ell + 2CrC\ell_3 + H_2O$$

5. Rest of the following equation is balanced by inspection method:

$$K_2Cr_2O_7 + 6HC\ell \longrightarrow 3C\ell_2 + 2KC\ell + 2CrC\ell_3 + H_2O$$

To balance Cℓ and K, 14 molecules of HCℓ and 2 KCℓ molecules are required, therefore, we add 8 HCℓ to left hand side

$$8HC\ell + K_2Cr_2O_7 + 6HC\ell \longrightarrow 2CrC\ell_3 + 3C\ell_2 + 2KC\ell + H_2O$$

To balance hydrogen and oxygen, $6H_2O$ are added to RHS.

Hence, the balanced equation is,

$$K_2Cr_2O_7 + 14HC\ell \longrightarrow 2KC\ell + 2CrC\ell_3 + 3C\ell_2 + 7H_2O$$

☑ QUICK CHECK 10.3

Balance the given equations by oxidation number method.

i. $Fe_2O_{3(s)} + CO_{(g)} \longrightarrow Fe_{(s)} + CO_{2(g)}$

Ans. Step 1: Oxidation numbers

- **Fe in Fe_2O_3: +3 → Fe: 0 (reduced)**
- **C in CO: +2 → C in CO_2: +4 (oxidized)**

Step 2: Determine changes

- **Fe: +3 → 0 (gain of 3 electrons per Fe, 2 Fe atoms = 6 e^- gain)**
- **C: +2 → +4 (loss of 2 electrons per C atom)**

Step 3: Equalize e^- transfer

- Multiply CO by 3 and Fe_2O_3 by 1

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Balanced equation:

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

ii. $MnO_2 + HC\ell \rightarrow MnC\ell_2 + H_2O + C\ell_2$

Ans. Step 1: Oxidation numbers

- **Mn in MnO_2:** +4 → Mn in $MnC\ell_2$: +2 (reduced)
- **$C\ell$ in $HC\ell$:** −1 → $C\ell_2$: 0 (oxidized)

Step 2: Determine changes

- **Mn:** +4 → +2 (gain of 2 electrons)
- **$C\ell$:** −1 → 0 (loss of 1 electron per $C\ell$ atom; $C\ell_2$ = 2 $C\ell$ atoms = $2e^-$ lost)

Step 3: Equalize e^- transfer

- $2C\ell^-$ oxidized = $2e^-$ loss
- 1 Mn^{4+} reduced = $2e^-$ gain → already equal

Balanced equation:

$$MnO_2 + 4HC\ell \longrightarrow MnC\ell_2 + 2H_2O + C\ell_2$$

iii. $Fe^{2+}_{(aq)} + MnO^{4}_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + Mn^{2+}_{(aq)}$

Ans. Step 1: Oxidation numbers

- $Fe^{2+} \rightarrow Fe^{3+}$ (oxidation, loss of 1 e^-)
- Mn^{7+} in $MnO_4^- \rightarrow Mn^{2+}$ (reduction, gain of 5 e^-)

Step 2: Equalize electrons

- Multiply $Fe^{2+} \rightarrow Fe^{3+}$ by 5

Step 3: Balance rest (acidic medium)

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

Balanced equation:

$$5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

iv. $K_2Cr_2O_{7(aq)} + FeSO_{4\,(aq)} + H_2SO_{4\,(aq)} \longrightarrow Cr_2(SO_4)_{3(aq)} + Fe_2(SO_4)_{3(aq)} + K_2SO_{4(aq)} + H_2O_{(\ell)}$

Ans. Step 1: Oxidation numbers

- **Cr in $Cr_2O_7^{2-}$:** +6 → Cr^{3+}: +3 (reduction, gain of $3e^-$ per Cr)
- **$Fe^{2+} \rightarrow Fe^{3+}$:** oxidation (loss of $1e^-$)

Step 2: $Cr_2O_7^{2-}$ contains 2 Cr → $6e^-$ gained

- Therefore, 6 Fe^{2+} needed (each loses $1e^-$)

Balanced half reactions:

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

Combine:

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

Include sulphates and potassium:

- $Cr_2O_7^{2-} \rightarrow Cr_2(SO_4)_3$
- $Fe^{2+} \rightarrow Fe_2(SO_4)_3$ (needs 6 $Fe^{2+} \rightarrow 3\ Fe_2(SO_4)_3$)
- K^+ and SO_4^{2-} balance with K_2SO_4

Full Balanced equation:

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + K_2SO_4 + 7H_2O$$

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ELECTROLYTIC CELL

An electrolytic cell is a device that converts electrical energy into chemical energy through a process called electrolysis.

- **Construction:**

  It consists of two electrodes, typically made of metal or another conductive material, which are immersed in an electrolyte-a substance containing free ions that carry electric current.

- **Process:**

  When a direct electric current is applied, one electrode becomes negatively charged (the cathode) and the other positively charged (the anode).

  In an electrolytic cell, positive ions in the electrolyte migrate towards the cathode, where they gain electrons (a reduction process), while negative ions move towards the anode, where they lose electrons (an oxidation process). This movement of ions and transfer of electrons results in chemical changes at the electrodes, effectively converting electrical energy into chemical energy.

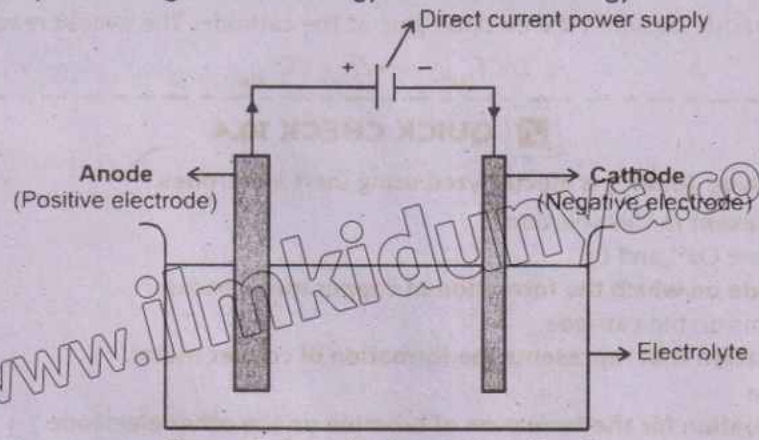


Figure: Main parts of an electrolytic cell

- **Applications of Electrolytic Cells:**

  Electrolytic cells are used in the electrolysis of sodium chloride to produce sodium metal and chlorine gas, the refining and plating of metals, and the production of chemicals like caustic soda. Electrolysis is also used to produce non-metals such as chlorine and to purify metals. Electrolysis is generally carried out in an electrolysis cell as shown in Figure.

  In the electrolysis cell:

  - **Electrolyte:** The electrolyte is the compound that is decomposed; it is either a molten ionic compound or a concentrated aqueous solution of ions
  - **Electrodes:** The electrodes are, made from either carbon (graphite) or metal, which conduct electricity to and from the electrolyte - the anode is the positive electrode - the cathode is the negative electrode
  - **DC:** The power supply must be direct current.

  (**Note:** The actual structure of the cell will vary according to the element extracted).

REDOX REACTIONS IN ELECTROLYSIS

During electrolysis, the positive ions (cations) move to the cathode. When they reach the cathode, they gain electrons from the cathode.

For example:

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$$

$$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$$

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Gain of electrons is reduction and it always occurs at the cathode. If metal atoms are formed, they may be deposited as a layer of metal on the cathode. Alternatively, they may form a molten layer in the cell. If hydrogen gas is formed, it bubbles off.

The negative ions **(anions)** move to the anode. When they reach the anode, they lose electrons to the anode. Loss of electrons is oxidation. Oxidation always occurs at the anode.

For example:

$$2C\ell^-_{(aq)} \longrightarrow C\ell_{2(g)} + 2e^-$$

$$4OH^-_{(aq)} \longrightarrow O_{2(g)} + 2H_2O_{(\ell)} + 4e^-$$

Electrolysis is a redox reaction. For example, when molten zinc chloride ($ZnC\ell_2$) is electrolyzed, the electrode reactions are:

- **Cathode:** $Zn^{2+}_{(\ell)} + 2e^- \longrightarrow Zn_{(s)}$ (Reduction)
- **Anode:** $2C\ell^-_{(\ell)} \longrightarrow C\ell_{2(s)} + 2e^-$ (Oxidation)

The electron loss at the anode balances the electron gain at the cathode. The overall reaction is

$$ZnC\ell_{2(\ell)} \longrightarrow Zn_{(s)} + C\ell_{2(g)}$$

☑ QUICK CHECK 10.4

Molten copper (II) bromide ($CuBr_2$) is electrolyzed using inert electrodes.

i. Which ions are present in this solution?

Ans. The ions present are Cu^{2+} and Br^-.

ii. Name the electrode on which the formation of copper metal occurs?

Ans. Copper metal forms on the cathode.

iii. Give the half-equation that represents the formation of copper metal.

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

iv. Write the half-equation for the formation of bromine on the other electrode.

Ans. $2Br^- \longrightarrow Br_2 + 2e^-$ (occurs at the anode)

MASS OF A SUBSTANCE DEPOSITED DURING ELECTROLYSIS

The mass of a substance produced at an electrode during electrolysis is proportional to the time over which a constant electric current pass and the strength of the electric current.

Combining current and time, we get the relationship:

$$Q = I \times t$$

Where
Q = Charge (in coulombs, C)
I = Current (in amperes, A)
t = Time (in seconds, s)

The mass of a substance produced at (or removed from) an electrode during electrolysis is proportional to the quantity of electricity (in coulombs) which passes through the electrolyte.

➢ **Faraday:**

The quantity of electricity is often expressed in terms of a unit called the **Faraday** (symbol F). 1 Faraday is the quantity of electric charge carried by 1 mole of electrons or 1 mole of singly charged ions. Its value is 96500 C mol^{-1}.

➢ **Electrolysis of Silver Nitrate Solution:**

During the electrolysis of silver nitrate solution, silver is deposited at the cathode.

$$Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$$

1 mol 1 mol 1 mol

1 Faraday of electricity (96500 C) is required to deposit 1 mole of silver.

➢ **Electrolysis of Copper(II) Sulphate:**

During the electrolysis of copper (II) sulphate solution, copper is deposited at the cathode.

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$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$$

1 mol 2 mol 1 mol

The equation shows that 2 moles of electrons are needed to produce 1 mole of copper from Cu^{2+} ions. So, it requires 2 Faradays of electricity (2×96500 C) to deposit 1 mole of copper.

No. of Faraday = No. of moles of electrons gained or lost

AMOUNT OF SUBSTANCE PRODUCED DURING ELECTROLYSIS

The value of F can be used to calculate the mass of substance deposited at an electrode and the volume of gas produced at an electrode.

Sample Problems 10.5

Calculate the mass of lead (Pb) deposited at the cathode during electrolysis when a current of 1.50 A flows through molten lead (II) bromide ($PbBr_2$) for 20.0 min. (relative atomic mass, Ar value: [Pb] = 207; F = 96500 C mol^{-1})

Solution:

Step 1: Write the half-equation for the reaction.

$$Pb^{2+}_{(aq)} + 2e^- \longrightarrow Pb_{(s)}$$

Step 2: Find the number of coulombs required to deposit 1 mole of product at the electrode.
2 moles of electrons are required per mole of Pb formed = 2F

$= 2 \times 96500$

$= 193000\ C\ mol^{-1}$

Step 3: Calculate the charge transferred during the electrolysis.

$Q = I \times t$

$= 1.50 \times 20 \times 60$

$= 1800\ C$

Step 4: Calculate the mass by simple proportion using the relative atomic mass.
193000 C deposits 1 mole Pb, which is 207 g Pb

so, 1800 C deposits = $\frac{207}{193000} \times 1800 = 1.93$ g Pb

AVOGADRO'S CONSTANT BY THE ELECTROLYTIC METHOD

(Exercise L.Q.4)

Q. How Avogadro's number can be derived using an electrolytic cell?

➢ **Avogadro's Constant:**

- The Avogadro's constant, L, is the number of specified particles (atoms, molecules, or ions) in 1 mole. An electrolytic method can be used to find a value for the Avogadro's constant by calculating the charge associated with 1 mole of electrons.

$$N_A = \frac{\text{Charge on 1 mole of electrons}}{\text{Charge on 1 electron}}$$

- The charge on the electron can be calculated by experiment. The results show us that the charge on the electron is approximately 1.60×10^{-19} C.

➲ **Finding the Charge on 1 Mole of Electrons**

- The charge on 1 mole of electrons can be found from a simple electrolytic experiment. The apparatus for this is shown in Figure.

Procedure:

- The procedure is to weigh the pure copper anode and pure copper cathode separately arrange the apparatus during the electrolysis of aqueous copper(II) sulfate as shown in Figure.

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- The variable resistor is used to keep the current constant pass about 0.2 amperes.
- Pass a constant electric current for a measured time interval, e.g., 40 min.
- Remove the cathode and anode and wash and dry them with distilled water and then with propanone.
- Reweigh the cathode and anode.

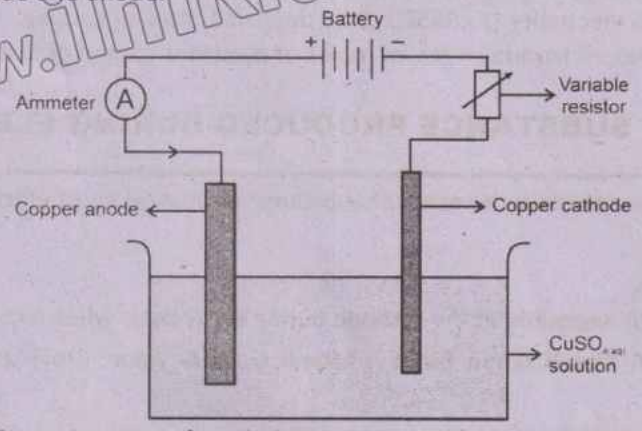


Figure: Apparatus for calculating the mass of copper deposited

- The cathode increases in mass because copper is deposited.
- The anode decreases in mass because the copper goes into solution as copper ions. The decrease in the mass of the anode is measured. This is preferred because the copper does not always stick to the cathode very well.

➲ Calculating Charge on An Electron

A sample calculation is shown below, using a current of 0.20 A for 34 min.

mass of anode at start of the experiment	= 56.53 g
mass of anode at end of experiment	= 56.40 g
mass of copper removed from anode	= 0.13 g
quantity of charge passed Q	= I × t
	= 0.20 × 34 × 60
	= 408 C

As the amount of copper removed is 0.13 g
So, 0.13 g of copper requires = 408 C

1 g of copper requires = $\frac{408}{0.13}$

63.5 g of copper requires = $\frac{408}{0.13} \times 63.5 = 99646$ C

But the equation for the electrolysis shows that 2 moles of electrons are needed to produce 1 mole of copper:

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$$

The charge on 1 mole of electrons = $\frac{190500}{2}$ = 95,250 C

If the charge on one electron is 1.60×10^{-19} C,

Charge on an electron = $\frac{95250}{6.02 \times 10^{23}} = 1.58 \times 10^{-19}$ C

☑ QUICK CHECK 10.5

a) An aqueous solution of silver nitrate is electrolysed. Calculate the mass of silver deposited at the cathode when the electrolysis is carried out for exactly 35 min using a current of 0.18 A. ($Ar[Ag] = 108; F = 96500\,C\,mol^{-1}$)

Ans. Electrolysis of Silver Nitrate ($AgNO_3$)

According to Faraday's First Law of Electrolysis:

Mass (m) = Q × Mn × F

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Where:

Q = I × t Q = I
times t = charge in coulombs
M = molar mass of Ag = 108 g/mol
N = number of electrons per ion ($Ag^+ \rightarrow Ag = 1\ e^-$)
F = Faraday's constant = 96,500 C/mol

Step 1: Calculate Q

I = 0.18 A
t = 35 min = 35 × 60 = 2100 s
Q = I × t = 0.18 × 2100 = 378 C

Step 2: Calculate Mass of Ag

$$m=\frac{Q\times M}{n\times F}=\frac{378\times 108}{1\times 96500}\approx\frac{40824}{96500}\approx 0.423g$$

b) An electric current of 1.04 A was passed through a solution of dilute sulfuric acid for 6.00 min. The volume of hydrogen produced at STP was 41.5 cm^3.

i. How many coulombs of charge were passed during the experiment?

Ans. Calculate total charge passed

I = 1.04 A
t = 6.00 min = 6 × 60 = 360 s
Q = I × t = 1.04 × 360 = 374.4 C

ii. How many coulombs of charge are required to liberate 1 mole of hydrogen gas? ($F = 96\ 500\ C\ mol^{-1}$)

Ans. Charge required to liberate 1 mole of H_2 gas

Reaction at Cathode:

$$2H^+ + 2e^- \longrightarrow H_2$$

So, 2 moles of electrons are required for 1 mole of H_2.

Charge = 2 × F = 2 × 96500 = 193000 C

ELECTRODE POTENTIALS
(Ease of oxidation and reduction)

During the redox processes, a redox equilibrium exists between two chemically related species that are in different oxidation states.

Definition:

"When a metal is put into a solution of its ions, an electric potential (voltage) is established between the metal and the metal ions in solution. This is called electrode potential".

It indicates the ease of oxidation or reduction of a substance.

Example: When a copper rod is placed in contact with an aqueous solution of its ions, the following equilibrium exists:

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

➢ **Explanation:**

There are two opposing reactions in this equilibrium.

a) Metal atoms from the rod entering the solution as metal ions. This leaves electrons behind on the surface of the electrode.

$$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^-$$

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b) Ions in solution accepting electrons from the metal rod and get deposited as metal atoms on the surface of the electrode.

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$$

The redox equilibrium is established when the rate of electron gain equals the rate of electron loss.
For unreactive metals such as copper, if this equilibrium is compared with the equilibrium set up by other metals, the equilibrium set up by copper lies further over to the right.

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$$

$Cu^{2+}_{(aq)}$ ions are therefore relatively easy to reduce. They gain electrons readily to form copper metal.

For reactive metals such as vanadium, the equilibrium lies further over to the left.

$$V^{2+}_{(aq)} + 2e^- \longrightarrow V_{(s)}$$

$V^{2+}_{(aq)}$ ions are therefore relatively difficult to reduce. They gain electrons much less readily by comparison.

The position of equilibrium differs for different combinations of metals placed in solutions of their ions.

➲ Electrical Double Layer

It is thought that the **absolute electrode potentials** cannot be measured due to the formation of an electrical double layer, when an element is placed in a solution of its ions.

Example:

A strip of Zinc in a solution containing Zn ions:

- When zinc is placed in a solution containing zinc ions, a tiny number of zinc atoms on the surface of the metal is converted to zinc ions, which go into solution. This leaves an excess of electrons on the surface of the zinc.
- The solution around the metal now has excess Zn^{2+} ions. Some of these cations near the surface of the zinc are attracted to its surface. So, an electrical double layer is formed.
- This buildup of charge causes an electric potential (voltage) between the metal and the metal ions in solution as shown in Figure 10.3.
- Due to the formation an electrical double layer, the potential cannot directly be measured.
- The difference in potential between the metal/metal ion system and another system can be measured. We call this value the **electrode potential**, E. Electrode potential is measured in volts. The system we use for comparison is the **standard hydrogen electrode (SHE).**

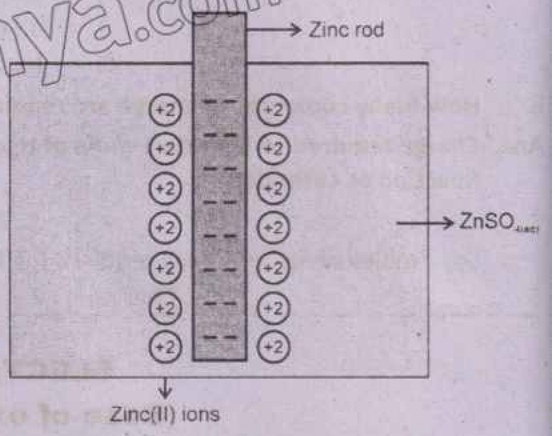


Figure: Formation of electrical double layer

STANDARD HYDROGEN ELECTRODE (SHE)

(Exercise L.Q.6)

Q. What is meant by Standard Hydrogen Electrode (SHE)? How it is used to measure the electrode potential of another electrode?

The **Standard Hydrogen Electrode (SHE)** is one of several types of half-cell that can be used as reference electrode.

➢ **Construction:**

Figure shows a standard hydrogen electrode.

SHE is a reversible electrode.

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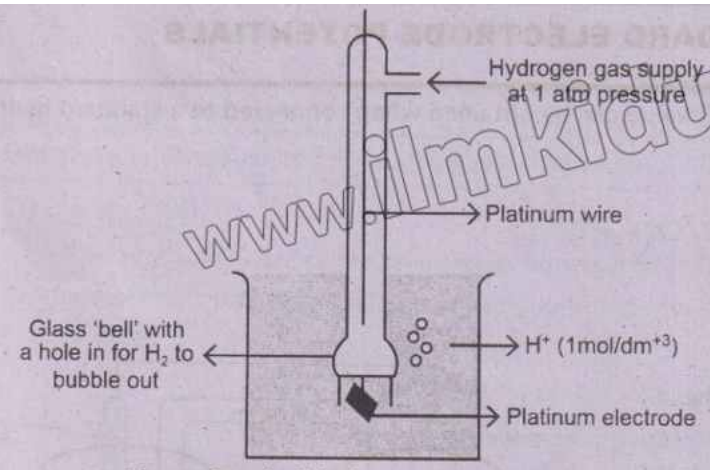


Figure: Standard hydrogen electrode (SHE)

S/Q. Why platinum black is a preferred catalyst?

Ans. Platinum black is a highly preferred catalyst due to its exceptionally high surface area, which significantly enhances its catalytic activity. This high surface area, achieved through a fine powder form, provides numerous active sites for chemical reactions to occur. It boosts reaction rates and overall efficiency.

Standard Hydrogen Electrode consists of:

- Hydrogen gas at 101 kP_a pressure, in equilibrium with H^+ ions of concentration 1.00 mol dm^{-3}
- A platinum electrode covered with platinum black in contact with the hydrogen gas and the H^+ ions.

The **platinum black** is finely divided platinum, which allows close contact of hydrogen gas and H^+ ions in solution so that equilibrium between H_2 gas and H^+ ions is established quickly. The platinum electrode is inert so it does not take part in the reaction. Standard electrode potential E° values for all half-cells are measured relative to this electrode.

When connected to another half-cell, the value read on the voltmeter gives the standard electrode potential for that half-cell. The half-equation for the hydrogen electrode can be written:

Reduction (Acts as cathode): $2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$ $\quad E^\circ = 0.00\ V$

Oxidation (Acts as anode): $H_2 \longrightarrow 2H^+ + 2e$ $\quad E^\circ = 0.00\ V$

The way that the half-equation is balanced makes no difference to the value of E°. The equation does not affect the tendency for the element to gain electrons.

Electrode Potential: Its voltage is arbitrarily fixed at 0.00 V.

STANDARD ELECTRODE POTENTIAL (E°)

The voltage of an electrochemical cell will also depend on concentration, temperature, and pressure of the gas. Therefore, we should use standard conditions when comparing electrode potentials.

Conditions:

- Concentration of ions at 1.00 mol dm^{-3}
- A temperature of 25°C(298 K)
- Any gases should be at a pressure of 1 atmosphere (101 kP_a)
- The value of the electrode potential of the half-cell is measured relative to the standard hydrogen electrode.

Under these conditions, the electrode potential we measure is called the standard electrode potential. This has the symbol, E°. It is spoken of as ' **E** standard'.

"The standard electrode potential for a half-cell is the voltage measured under standard conditions with a standard hydrogen electrode (SHE) as the other half-cell".

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MEASURING STANDARD ELECTRODE POTENTIALS

There are three main types of half-cell whose E° value can be obtained when connected to a standard hydrogen electrode (SHE):

- metal/metal ion half-cell (Cu^{2+}/Cu^0)
- non-metal/non-metal ion half-cell ($C\ell^{1-}/C\ell_2$)
- ion/ion half-cell. (Fe^{2+}/Fe^{3+})

➢ Measurement of Standard Electrode Potential of a Cu^{2+}/Cu half Cell:

Figure 10.5 shows how to measure the E° value for a Cu^{2+}/Cu half-cell. The Cu^{2+}/Cu half cell is connected to the SHE and the voltage measured. The voltage is +0.34 V. The copper is the positive terminal (positive pole) of the cell and the SHE is the negative terminal. The two half-equations are:

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)} \quad E^\circ = +0.34\ V$$

$$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2}H_{2(g)} \quad E^\circ = 0.00\ V$$

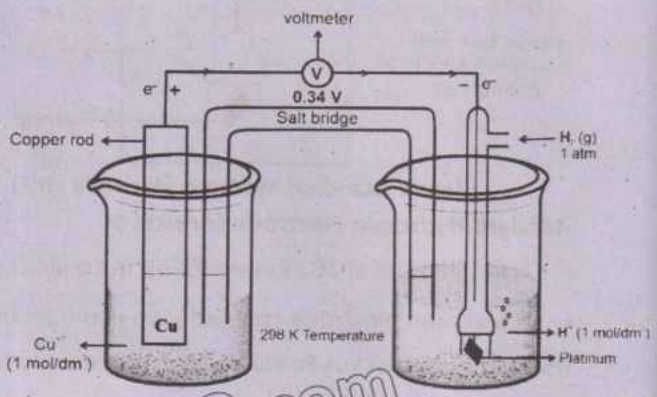


Figure: Measuring the standard electrode potential of a Cu^{2+}/Cu half-cell

The E° values show us that Cu^{2+} ions are easier to reduce than H^+ ions (they have a more positive E° value). Cu^{2+} ions are more likely to gain electrons than H^+ ions. So Cu^{2+} ions will accept electrons from the H^+/H_2 half-cell and H_2 will lose electrons to the Cu^{2+}/Cu half-cell.

➢ Measurement of Standard Electrode Potential of a Zn^{2+}/Zn Half Cell:

Figure 10.6 shows how to measure the E° value for a Zn^{2+}/Zn half cell. The voltage of the Zn^{2+}/Zn half-cell is -0.76 V. Zinc metal is the negative terminal (negative pole) of the cell and the hydrogen electrode is the positive terminal.

The two half-equations are:

$$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)} \quad E^\circ = 0.00\ V$$

$$Zn^{2+}_{(aq)} + 2e^- \longrightarrow Zn_{(s)} \quad E^\circ = -0.76\ V$$

Rack Your Mind!

5. The standard oxidation potential of Zn is 0.76 volts and reduction potential –0.76 volts. Explain.

The E° values show us that Zn^{2+} ions are more difficult to reduce than H^+ ions (they have a more negative E° value). Zn^{2+} ions are less likely to gain electrons than H^+ ions. So, Zn will lose electrons to the H^+/H_2 half-cell and H^+ ions will gain electrons from the Zn^{2+}/Zn half-cell.

From these two examples, we can see that:

- Reduction takes place at the positive terminal of the cell. For example, in the Zn^{2+}/Zn; H^+/H_2 cell:

$$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$$

- Oxidation takes place at the negative terminal of the cell. For example, in the Zn^{2+}/Zn; H^+/H_2 cell:

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$$

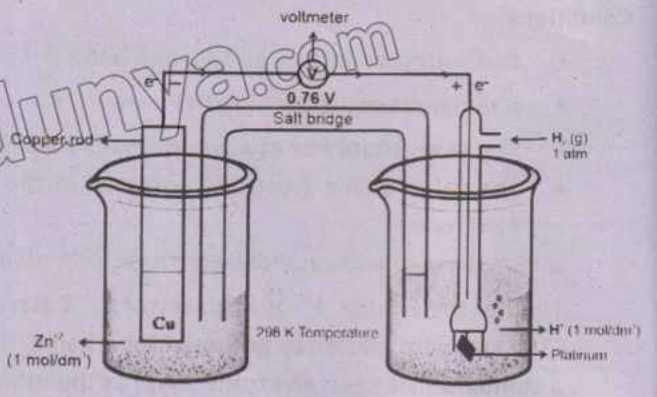


Figure: Measuring the standard electrode potential of a Zn^{2+}/Zn half-cell

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ELECTROCHEMICAL CELL (GALVANIC CELL)

(Exercise L.Q.5)

Q. Describe the construction and working principle of the Zn-Cu Galvanic cell.

➲ Galvanic Cell:

A cell in which the conversion of chemical energy into electrical energy takes place spontaneously in exothermic redox process with oxidation at anode and reduction at cathode.

For Example:

$$Cu^{2+}/Cu//Z^{2+}/Zn \text{ cell} \qquad E^{\circ} = 1.10\,V$$

- A galvanic cell is designed to take advantage of spontaneous transfer of electrons.
- A Galvanic Cell, is also known as a Voltaic Cell.

Examples: Daniel cell, dry cell etc.

For example: $Zn^{2+}_{(aq)} + 2e^{-} \longrightarrow Zn_{(s)}$ voltage = 0.76 V

In order to measure the electrode potential relating to the half-equation

$$Cu^{2+}_{(aq)} + 2e^{-} \longrightarrow Cu_{(s)}$$

A pure copper rod is placed in a solution of $Cu^{2+}_{(aq)}$ ions (for example copper(II) sulfate solution). This Cu^{2+}/Cu system is called a half-cell.

The following standard conditions are used to make the half-cell:

- The $Cu^{2+}_{(aq)}$ ions have a concentration of 1.00 mol dm^{-3}
- The temperature is 25°C (298 K)
- The copper rod must be pure.

If we connect two half-cells together, we have made an electrochemical cell. We can measure the voltage between these two half-cells. Figure 10.7 shows a Cu^{2+}/Cu half-cell connected to a Zn^{2+}/Zn half-cell to make a complete electrochemical cell.

Half-cells are connected together using:

- Wires connecting the metal rods in each half-cell to a high-resistance voltmeter; the electrons flow round this external circuit from the metal with the more negative (or less positive) electrode potential to the metal with the less negative (or more positive) electrode potential
- **Salt Bridge:** A salt bridge to complete the electrical circuit allowing the movement of ions between the two half cells so that ionic balance is maintained; a salt bridge does not allow the movement of electrons. A salt bridge can be made from a strip of filter paper (or other inert porous material) soaked in a saturated solution of potassium nitrate.
- The voltages for the half cells in Figure can be represented by the following half-equations:

$$Cu^{2+}_{(aq)} + 2e^{-} \longrightarrow Cu_{(s)} \quad E^{\circ} = +0.34\,V$$

$$Zn^{2+}_{(aq)} + 2e^{-} \longrightarrow Zn_{(s)} \quad E^{\circ} = -0.76\,V$$

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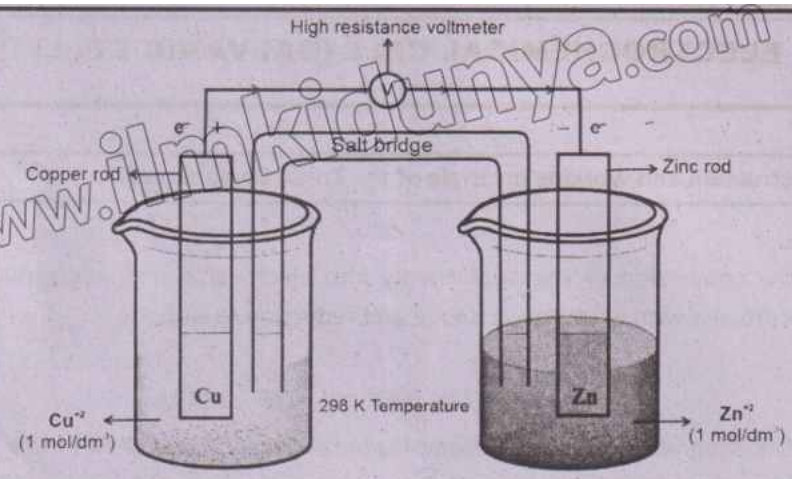


Figure: An electrochemical cell, made by connecting a Cu^{2+} / Cu half-cell to a Zn^{2+} / Zn half-cell.

An electrochemical cell is made by connecting a Cu^{2+} / Cu half-cell to a Zn^{2+} / Zn half-cell. The relative values of these voltages tell us that Zn^{2+} ions are more difficult to reduce than Cu^{2+} ions.

At the anode, zinc undergoes oxidation, losing electrons to form zinc ions:

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$$

These electrons travel through an external circuit to the cathode, where copper ions gain electrons and are reduced to form copper metal:

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$$

The overall cell reaction can be represented as:

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

This process effectively converts the chemical energy of the redox reaction into electrical energy, which can be connected to perform work.

The voltage generated by this cell is +1.10 V.

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

In a Cu-Zn galvanic cell, **zinc(Zn) serves as the anode, and copper ions (Cu^{2+}) in solution serve as the cathode.** The E° value for the Ag^+ / Ag half-cell is more positive than for the $Zn^{(2+)}$ / Zn half-cell. So, the Ag + / Ag half-cell is the positive pole and the Zn^{2+} / Zn half-cell is the negative pole of the cell.

Rack Your Mind!

6. What is emf and how we calculate the emf of a galvanic cell?

Functions of Salt Bridge:

i. The purpose of the salt bridge is to prevent any net charge accumulation in either beaker by allowing negative ions to leave the right beaker, diffuse through the bridge and enter the left beaker. If this diffusional exchange of ions does not occur, the net charge accumulating in the beakers would immediately stop the flow of electrons through the external circuit and oxidation reduction reaction would stop.

ii. Keeps the electrolyte solution neutral.

iii. Minimizes or eliminates the liquid junction potential.

QUICK CHECK 10.6

a) What is the function of salt bridge in the voltaic cell?

Ans. A salt bridge is a crucial component in a voltaic cell. Its functions are:

- **Maintains electrical neutrality** in both half-cells by allowing the flow of **inert ions**.
- Prevents the solutions from becoming charged (e.g., accumulation of positive or negative ions).
- **Completes the electrical circuit**, allowing electrons to continue flowing through the external wire.
- Minimizes **liquid junction potential**, ensuring a stable cell voltage.

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A typical salt bridge contains a **neutral electrolyte** (e.g., KNO_3, KCl) that doesn't react with either half-cell.

b) **Calculate the voltage of a cell having iron and copper electrodes.**

$$Fe_{(s)} \rightleftharpoons Fe^{2+}_{(aq)} + 2e^- \quad E^\circ = -0.44\ V$$

$$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)} \quad E^\circ = -0.44\ V$$

Given Data:

$Fe^{2+} + 2e^- \rightarrow Fe_{(s)}$ $E^\circ = -0.44$ V

$Cu^{2+} + 2e^- \rightarrow Cu_{(s)}$ $E^\circ = +0.34$ V

It looks like you might have written $Cu^{2+} + 2e^- \rightarrow Cu_{(s)}$ also as –0.44 V by mistake, but the standard value is +0.34 V.

Step 1: Identify the anode and cathode

- The electrode with lower E° is the anode (oxidation).
- The electrode with higher E° is the cathode (reduction).

So

- **Anode:** $Fe \rightarrow Fe^{2+} + 2e^-$ $(E^\circ = -0.44\ V)$
- **Cathode:** $Cu^{2+} + 2e^- \rightarrow Cu$ $(E^\circ = +0.34\ V)$

Step 2: Calculate Cell Potential

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

$$E^\circ_{cell} = (+0.34\ V) - (-0.44\ V) = +0.78\ V$$

Final Answers:

i) A salt bridge maintains charge balance and completes the circuit in a voltaic cell.

ii) The standard cell voltage for Fe–Cu voltaic cell is **0.78 V**

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APPLICATIONS OF E° VALUES

Direction of Electron Flow

- We can infer (deduce) the direction of electron flow in the wires in the external circuit by comparing the E° values for the two half-cells which make up the electrochemical cell. For example, in Figure 10.9 these voltages are:

$$Ag^+_{(aq)} + e^- \rightleftharpoons Ag_{(s)} \quad E^\circ = +0.80\ V$$

$$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)} \quad E^\circ = -0.76\ V$$

- The relative values of these voltages tell us that Zn^{2+} ions are more difficult to reduce than Ag^+ ions.
- So, Zn metal will lose electrons to the Ag^+ / Ag half-cell and Ag^+ ions will accept electrons from the Zn^{2+} / Zn half-cell.
- The electrons move through the wires in the external circuit. They do not travel through the electrolyte solution.
- So, the electron flow is from the Zn^{2+} / Zn half-cell to the Ag^+ / Ag half-cell.
- In other words, the flow is from the negative pole to the positive pole. Remember that the more positive pole attracts the negative electrons.

Feasibility of A Reaction Using E° Values

- Standard electrode potential values, E°, give us a measure of how easy or difficult it is to oxidize or reduce a species. The E° values are listed in order of increasingly negative values.
- For each half-equation, the more oxidized form is on the left and the more reduced form is on the right.
- The more positive the value of E°, the greater the tendency for the half-equation to proceed in the forward direction, and the easier it is to reduce the species on the left of the half-equation.

- The less positive the value of E°, the greater the tendency for the half-equation to proceed in the reverse direction, and the easier it is to oxidize the species on the right of the half-equation.
- To check the feasibility of reaction between Mg^{2+} and Ag

$$Mg^{2+} + Ag \longrightarrow ?$$

We need half cell equations and E° values

$$Mg^{2+} + 2e^- \rightleftharpoons Mg \qquad E^\circ = -2.32\ V$$
$$Ag^+ + 1e^- \rightleftharpoons Ag \qquad E^\circ = +0.80\ V$$

Mg^{2+} are supposed to be reduced here and Ag is supposed to get oxidized, So calculating E° cell gives us

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{red} - E^\circ_{ox} \\ &= (-2.32) - (+0.80) \\ &= -1.52\ V \end{aligned}$$

Negative value of E°_{cell} indicates the reaction is not feasible.

On the other hand reaction between Ag^+ and Mg is feasible as for this reaction E° cell will be positive a given below.

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{red} - E^\circ_{ox} \\ &= (-0.80) - (-2.32) \\ &= +1.52\ V \end{aligned}$$

Therefore, the feasible reaction is

$$2Ag^+ + Mg_{(s)} \longrightarrow Mg^{2+}_{(aq)} + Ag_{(s)}$$

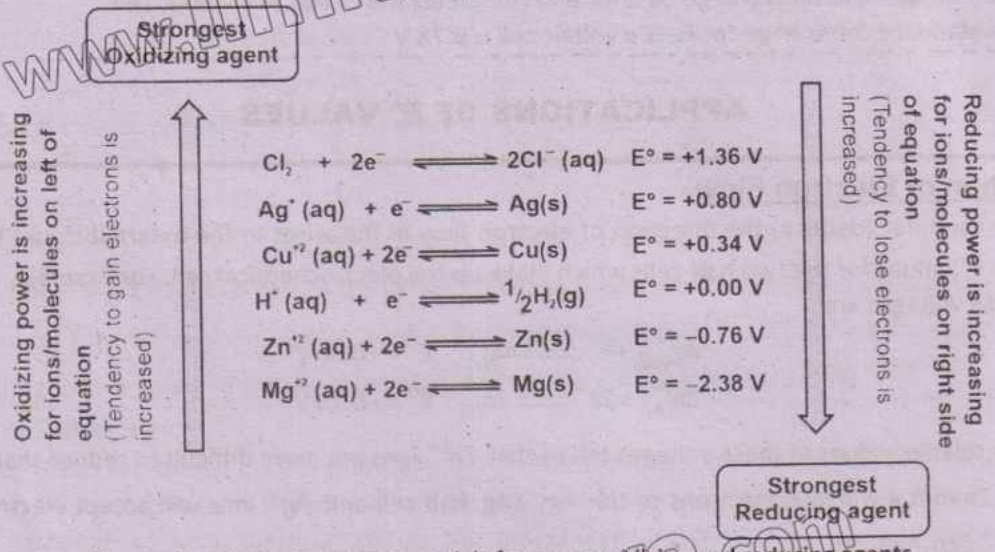


Figure: Standard electrode potentials for some oxidizing and reducing agents

QUICK CHECK 10.7

a) Explain the following keeping in view the standard electrode potential values

$$E^\circ_{Cl_2/2Cl^-} = +1.36\ V,\ E^\circ_{Br_2/2Br^-} = +1.07\ V,\ E^\circ_{I_2/2I^-} = +0.54\ V$$

Ans. Explanation using standard electrode potentials:

We are given:

- $E^\circ_{Cl_2/2Cl^-} = +1.36\ V$
- $E^\circ_{Br_2/2Br^-} = +1.07\ V$
- $E^\circ_{I_2/2I^-} = +0.54\ V$

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These values indicate how easily the halogens act as oxidizing agents. The higher the E° value, the stronger the oxidizing agent.

i. The aqueous solution of iodine can be oxidized with bromide or iodide ions.

Ans. This statement is **incorrect** as written. It likely means:

"The aqueous solution of iodine can be oxidized by chlorine or bromine ions."

But using the actual meaning with the given standard potentials:

- Iodine (I_2) has a **lower** E° value than both bromine and chlorine.
- Hence, **iodine is a weaker oxidizing agent** than both chlorine and bromine.
- So, **iodide ions (I^-)** can be oxidized to iodine by both Cl_2 and Br_2 (which have higher E° values).
- But **iodine cannot oxidize Br^- or Cl^-** because it is not strong enough as an oxidizing agent.

Corrected Explanation:

Aqueous iodine **cannot** oxidize bromide or chloride ions because its standard electrode potential (+0.54 V) is **lower** than that of bromine (+1.07 V) and chlorine (+1.36 V). Therefore, I_2 is **not strong enough** to pull electrons from Br^- or Cl^- ions.

ii. Why bromine does not react with chloride ions?

Ans.

- Bromine (Br_2) has an E° = +1.07 V
- Chlorine (Cl_2) has an E° = +1.36 V

Since Cl_2 is a stronger oxidizing agent than Br_2, Br_2 cannot oxidize Cl^- ions to Cl_2.

Explanation:

Bromine does not react with chloride ions because the standard electrode potential of chlorine is higher than that of bromine. Therefore, Br_2 is not strong enough to oxidize Cl^- to Cl_2.

Oxidizing and Reducing Agents Using E° Values

Look back at Figure. Note the following as the values of E° for each of these reduction reactions gets more negative.

The species on the left of the equation become weaker oxidizing agents. They accept electrons less readily.

The species on the right of the equation become stronger reducing agents. They release electrons more readily.

Cu will not reduce Zn^{2+} ions to Zn. So how can we reduce Zn^{2+} ions? The answer is to react the Zn^{2+} ions with a stronger reducing agent, which should have an E° value more negative than the E° value for Zn^{2+}/Zn. In Figure we see that the half-equation Mg^{2+}/Mg has a more negative E° value. So, Mg is a suitable reducing agent.

$$Zn^{2+}_{(aq)} + e^- \longrightarrow Zn_{(s)} \qquad E^\circ = -0.76\ V$$

$$Mg^{2+}_{(aq)} + 2e^- \longrightarrow Mg_{(s)} \qquad E^\circ = -2.38\ V$$

Zn^{2+} is the better oxidizing agent. It is more likely to accept electrons than Mg^{2+} ions. Mg is the better reducing agent. It is more likely to release electrons than Zn.

Compounds can also act as oxidizing and reducing agents. **For example** $KMnO_4$ (+0.54 V) $K_2Cr_2O_7$ (+1.33 V) are oxidizing agent because of their higher E° values. Whereas, KI and $FeSO_4$ are reducing gents due to their lower E° values.

Few compounds, such as H_2O_2 can act both as oxidizing as well as reducing agents.

Rock Your Mind!

7. During a redox reaction, an oxidizing agent:
(A) Gains electrons
(B) Is oxidized
(C) Loses electrons
(D) Is hydrolyzed

Rock Your Mind!

8. The reduction potential of Zn is:
(A) −0.76 Va (B) −0.34 V
(C) +0.34 V (D) +0.76 V

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VARIATION OF E° VALUE WITH ION CONCENTRATION

The position of an equilibrium reaction is affected by changes in concentration, temperature and pressure. If we change the concentration or temperature of half-cell X, the electrode potential also changes. Under these non-standard conditions we use the symbol E for the electrode potential. Let us take an example of a metal/metal ion equilibrium:

Table: Variation of Potential with Ion Concentration

$[Fe^{3+}]$(mol dm^{-3})	$[Fe^{2+}]$(mol dm^{-3})	E^{O}(V)	Effect
> 1.00	1.00	+ 0.85	More positive
< 1.00	1.00	+ 0.70	Less positive
1.00	> 1.00	+0.70	Less positive
1.00	< 1.00	+0.85	More positive

$$Zn^{2+}_{(aq)} + e^- \longrightarrow Zn_{(s)} \qquad E^{\circ} = -0.76\ V$$

- If $[Zn^{2+}]$ is greater than 1.00 mol dm^{-3}, the value of E becomes less negative / more positive (say –0.61 V).
- If $[Zn^{2+}]$ is less than 1.00 mol dm^{-3}, the value of E becomes more negative / less positive (say –0.80 V).

Le-Chatelier's principle can be applied to redox equilibria. If we increase the concentration of the species on the left of the equation, the position of equilibrium will shift to the right. So, the value of E becomes more positive / less negative change in contraction of ions and its effect on E° is shown in Table 10.1. If two different ions are present in the half-cell, we have to consider both ions. Let us take the equilibrium between Fe^{3+} ions and Fe^{2+} ions as an example.

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

1.00 mol dm^{-3} 1.00 mol dm^{-3}

NERNST EQUATION

(Exercise L.Q.3)

Q. How electrode potential varies with concentration of an aqueous solution? Use the Nernst equation to explain this variation.

If we consider a cell made up from a silver/silver ion electrode and a copper/copper(II) ion electrode, the reaction taking place is:

$$Cu_{(s)} + 2Ag^{+}_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)} \qquad E^{\circ} = +0.46\ V$$

When E°_{cell} is plotted against concentration, we obtain a graph as shown in Figure.

Note that we have plotted the value of E_{cell} (non-standard conditions for the cell as a whole) against the logarithm of the silver ion concentration. The above redox cell reaction makes the value of E_{cell} more positive.

Interesting Information!

Nernst Equation:
The Nernst equation is an equation relating the capacity of an atom/ion to take up one or more electrons (reduction potential) measured at any conditions to that measured at standard conditions (standard reduction potential of 298 K and one molar or one atmospheric pressure).

The effect of concentration and temperature on the value of E_{cell} can be deduced using the Nernst equation. For a given electrode, e.g., a $Cu_{(s)} / Cu^{2+}_{(aq)}$ electrode, the relationship is:

$$E = E^{\circ} + \frac{RT}{zF} \ell n \frac{[\text{oxidized form}]}{[\text{reduced form}]}$$

where,

E is the electrode potential under non-standard conditions

E° is the standard electrode potential

R is the gas constant, 8.314 J K^{-1} mol^{-1}

T is the kelvin temperature

Z is the number of electrons transferred in the reaction

F is the value of the Faraday constant in C mol^{-1}

ln is the natural logarithm

[oxidized] refers to the concentration of the oxidized form in the half-equation

[reduced] refers to the concentration of the reduced form in the half-equation.

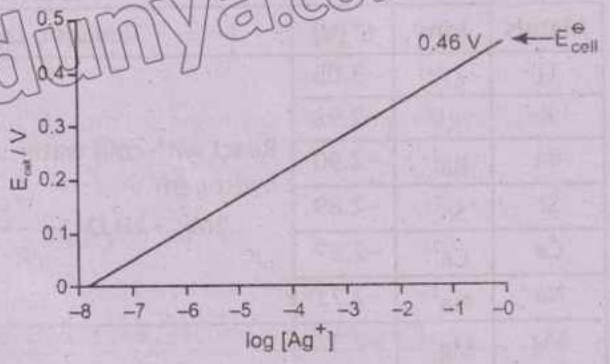


Figure: Increasing the concentration of silver ions in the cell reaction

Fortunately, for a metal/metal ion electrode, we can simplify this equation in three ways:

- The natural logarithm, ℓn, is related to log to the base 10 by the relationship $\ell n x = 2.303 \log_{10} x$
- At standard temperature the values of R, T and F are constant, The equation then becomes

$$E = E^\circ + \frac{0.059}{z} \ell og \frac{[\text{oxidized form}]}{[\text{reduced form}]}$$

Sample Problem

What is the electrode potential of a Zn electrode dipped in a solution containing Zn^{2+} ions (0.1 M), The e° value of Zn^{2+} / ZnO is –0.76 V.

Using Half equation and E°,

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

$$E = (-0.76) + \frac{8.31 \times 298}{2 \times 96500} \ell n(0.1)$$

$$E = -0.76 + (-0.029) = -0.78 \text{ V}$$

Since, Concentration of Zn^{2+} is decreased to shift equilibrium backward and electrode potential decreases to –0.78 V.

ACTIVITY SERIES OF METALS

- The activity series of metals is a ranking of metals based on their reactivity, particularly their tendency to lose electrons and undergo oxidation.
- Metals higher in the activity series have more negative standard reduction potentials, meaning they are more likely to lose electrons and undergo oxidation. Hence such metals act as reducing agents.
- Metals at the top of the series are the most reactive with water, oxygen and acid. For example, alkali metals like cesium and sodium are highly reactive and oxidize readily, reacting vigorously with substances like water to form ions and release hydrogen gas.
- In contrast, metals lower in the activity series, such as noble metals like gold and silver, do not oxidize easily. They are less reactive and do not readily lose electrons, that is why they do not react with water.

  Metals at the bottom of the series are the least reactive with water, oxygen and acid. Thus, the position of a metal in the activity series directly correlates with its ease of oxidation and overall reactivity. Conversely, metals lower in the activity series have more positive standard reduction potentials, indicating a greater tendency to gain electrons and undergo reduction. Hence such metals act as oxidizing agents.
- **Activity series of metals is actually reactivity series.**

  Thus, the activity series can be understood in terms of standard reduction potentials: metals with more negative potentials are more reactive and oxidize more readily, while those with more positive potentials are less reactive and oxidize less readily as given in Table.

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Table: Activity Series of Metals

Metals	Ions	E° (V)	Reaction Occurring	Trend	For Entry Test
Li	Li^{1+}	−3.05	React with cold water, replacing hydrogen $2M_{(s)} + 2H_2O_{(\ell)} \longrightarrow 2MOH_{(aq)} + H_{2(g)}$	Decreasing ease of oxidation, reactivity and acting reducing agent	Increasing strength as an oxidizing agents Increasing reduction potential
K	K^{1+}	−2.93			
Ba	Ba^{2+}	−2.90			
Sr	Sr^{2+}	−2.89			
Ca	Ca^{2+}	−2.87			
Na	Na^{1+}	−2.71			
Mg	Mg^{2+}	−2.37	Reacts with steam (but not with cold water) replacing hydrogen. $M_{(s)} + H_2O_{(\ell)} \longrightarrow MO_{(aq)} + H_{2(s)}$		
Aℓ	$A\ell^{3+}$	−1.66			
Zn	Zn^{2+}	−0.76			
Cr	Cr^{3+}	−0.74			
Fe	Fe^{2+}	−0.44			
Cd	Cd^{2+}	−0.40			
Co	Co^{2+}	−0.28	Do not react with water. React with acids, replacing hydrogen. $M_{(s)} + HC\ell_{(aq)} \longrightarrow MC\ell_{(aq)} + H_{2(g)}$		
Ni	Ni^{2+}	−0.25			
Sn	Sn^{2+}	−0.14			
Pb	Pb^{2+}	−0.13			
H_2	H^+	0.00	Included as reference		
Cu	Cu^{2+}	+0.34	Unreactive with water or acids.		
Hg	Hg^{2+}	+0.92			
Ag	Ag^{1+}	+0.80			
Pt	Pt^{2+}	+1.18			
Au	Au^{3+}	+1.50			

FEASIBILITY OF REDOX REACTIONS FROM ACTIVITY SERIES OR REACTION DATA

- The activity series is actually a reactivity series of metals, in order of reactivity from highest to lowest.
- It is used to determine the products of single displacement reactions; whereby metal M_1 will replace another metal M_2 in a solution if M_1 is higher in the series.

Rack Your Mind!

9. Na and K can displace hydrogen from acids but Pt, Cu cannot. Explain.

➲ Feasibility of a Reaction

From the activity series of metals, we can determine whether the reaction is feasible or not. We sum up the potentials of half reactions, if potential of the cell is positive it means the reaction is possible, however, if emf is negative, the reaction is not feasible. Let us see the reactions:

$$Fe^{2+}_{(aq)} + 2e^- \rightleftharpoons Fe_{(s)} \qquad E^\circ_{(ox)} = -0.44\ V$$

$$Ag^{+}_{(aq)} + 1e^- \rightleftharpoons Ag_{(s)} \qquad E^\circ_{(ox)} = +0.080\ V$$

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The overall reaction is

$$Fe_{(s)} + 2Ag^{+}_{(aq)} \longrightarrow Fe^{2+}_{(aq)} + 2Ag_{(s)} \quad E^{\circ}_{(cell)} = 0.080 - (-0.44) = +1.24\ V$$

The cell potential is positive; hence the reaction is feasible.

$Fe_{(s)} + 2Ag^{+}_{(aq)} \longrightarrow Fe^{2+}_{(aq)} + 2Ag_{(s)}$ $E^{\circ}_{(cell)} = 0.080 - (-0.44) = +1.24$ V From the activity series of metals, we have

$$Al^{3+}_{(aq)} + 3e^{-} \rightleftharpoons Al_{(s)} \qquad E^{\circ}_{(red)} = -1.66\ V$$

$$Ag^{+}_{(aq)} + 1e^{-} \rightleftharpoons Ag_{(s)} \qquad E^{\circ}_{(ox)} = +0.080\ V$$

$$Al^{3+}_{(aq)} + Ag_{(s)} \rightleftharpoons Al_{(s)} + Ag^{+}_{(aq)} \qquad E^{\circ}_{(red)} = -1.66 + 0.080 = -0.86\ V$$

The sum of E° values of the two half-cell reactions is negative. Hence the reaction is not feasible.

☑ QUICK CHECK 10.8

a) State the Nernst equation, why is it significant in electrochemistry.

Ans. State the Nernst Equation and Its Significance

Nernst Equation:

For a half-cell reaction at 25°C (298 K), the Nernst equation is:

$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{[Red]}{[Ox]}$$

or, more commonly written for oxidation-reduction reactions:

$$E = E^{\circ} - \frac{0.0591}{n} \log Q$$

Where:

- E = electrode potential at non-standard conditions
- E° = standard electrode potential
- n = number of electrons transferred
- Q = reaction quotient (ratio of product to reactant concentrations)

Significance in Electrochemistry:

- It allows the calculation of cell/electrode potentials under non-standard conditions.
- Explains how electrode potential changes with concentration, pressure, or temperature.
- Crucial for predicting direction of redox reactions, and in designing electrochemical cells.

b) What is the effect of variation in ion concentration on the standard electrode potential of a half reaction?

Ans. Effect of Ion Concentration on Standard Electrode Potential

- Standard electrode potential (E°) is fixed, measured at standard conditions (1 M, 1 atm, 25°C).
- However, the actual electrode potential (E) varies with ion concentration, as shown by the Nernst equation.
- **Increase in ion concentration (oxidant):** shifts equilibrium → increases E.
- **Decrease in ion concentration:** shifts equilibrium → decreases E.

So, electrode potential becomes more positive or more negative depending on concentration changes.

c) Give answers using E° values ($E^{\circ}_{Ag^{+}/Ag} = +0.80\ V$, $E^{\circ}_{Cr^{2+}/Cr} = -0.91\ V$, $E^{\circ}_{Fe^{2+}/Fe} = -0.44\ V$).

i. Which of Ag^{+}, Cr^{2+} and Fe^{2+}, is the strongest oxidizing agent? Which is the least oxidizing? Explain with reason.

Ans. $E^{\circ}_{Ag^{+}/Ag} = +0.80\ V$

$E^{\circ}_{Fe^{2+}/Fe} = -0.44\ V$

$E^{\circ}_{Cr^{2+}/Cr} = -0.91\ V$

Strongest and Weakest Oxidizing Agent:

- Oxidizing agents = species that gain electrons (i.e., get reduced).
- Higher E° → more easily reduced → stronger oxidizing agent.

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So:

- Strongest oxidizing agent: Ag^+ ($E^\circ = +0.80$ V)
- Weakest oxidizing agent: Cr^{2+} ($E^\circ = -0.91$ V)

ii. Arrange Ag, Cr and Fe in increasing order of their reducing powers.

Ans. Increasing order of reducing power (Ag, Cr, Fe):

Reducing agents = metals (Ag, Fe, Cr) that lose electrons (get oxidized).

Lower E° of their conjugate ion → better reducing agent.

Order (increasing reducing power):

$$Ag < Fe < Cr$$

d) What is the electrode potential of a Cu electrode dipped in a solution containing Cu^{2+} ions (0.01 M), The E° value of Cu^{2+}/Cu^0 is +0.34 V?

Ans. Electrode potential of Cu electrode in 0.01 M Cu^{2+} Solution:

Given Data:

- $E^\circ_{Cu^{2+}/Cu} = +0.34\,V$
- $[Cu^{2+}] = 0.01M$
- $n = 2$

Using the Nernst Equation:

$$E = E^\circ - \frac{0.0591}{n}\log\frac{1}{[Cu^{2+}]}$$

$$E = 0.34 - \frac{0.0591}{2}\log\left(\frac{1}{0.01}\right)$$

$$E = 0.34 - 0.02955 \times \log(100)$$

$$E = 0.34 - 0.02955 \times 2 = 0.34 - 0.0591 = 0.2809\ V$$

e) What is the electrode potential of $C\ell^-/C\ell_2$ half cell at 25 °C, if concentration of $C\ell^-$ is 0.05 mol dm^{-3}.

$$C\ell_2 + 2e^- \rightleftharpoons 2C\ell^- \qquad E^\circ = 1.36\ V$$

To Find: The electrode potential of the $C\ell_2/C\ell^-$ half-cell at 25°C, we use the Nernst equation:

Given:

Half-cell: $C\ell_{2(g)} + 2e^- \rightleftharpoons 2C\ell^-$

Standard Electrode Potential: $E^\circ = 1.36$ V

$[C\ell^-] = 0.05$ mol dm^{-3}

$T = 25°C = 298$ K

Assume: $PC\ell_2 = 1$ atm

Nernst Equation (at 25°C):

$$E = E^\circ - \frac{0.0591}{n}\log\left(\frac{1}{[C\ell^-]^2}\right)$$

$n = 2$ (number of electrons transferred)

$[C\ell^-] = 0.05$

Calculations:

$$E = 1.36 - \frac{0.0591}{2}\log\left(\frac{1}{(0.05)^2}\right)$$

$$E = 1.36 - 0.02955\log\left(\frac{1}{0.0025}\right)$$

$$E = 1.36 - 0.02955\log(400)$$

$$\text{Log}\,(400) \approx 2.60$$

$$E = 1.36 - 0.02955 \times 2.60$$

$$E = 1.36 - 0.0768 = 1.28\ V$$

In short, the electrode potential of the $C\ell_2/C\ell^-$ half-cell **decreases** from the standard 1.36 V to **1.28 V** when the $C\ell^-$ concentration is lower (0.05 M), as calculated using the **Nernst equation**.

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PHOTOVOLTAIC CELLS

The word 'photovoltaic' is composed of photo (light) and volt (electrical potential). The cell which converts light energy into electrical energy is called photovoltaic cell.

➲ Principle of Photovoltaic Cells

- The central principle behind the operation of PV cells is the photovoltaic effect, which involves the generation of voltage and electric current in a material upon exposure to light.
- The photovoltaic effect involves the excitation of electrons from the valence band to the conduction band in semiconductors, facilitated by the energy from photons.
- This process is improved by the presence of a PN junction, which separates the electrons and holes, creating a voltage that drives an electric current.

➲ Merits of Photovoltaic Cell as Sustainable Source of Energy

i. The photovoltaic effect continues as long as light is present, making it a sustainable method for generating electricity.
ii. A photovoltaic system is a renewable energy source that converts sunlight into electrical energy.
iii. The photovoltaic systems use the sun's energy, making them a sustainable energy source that is independent of fossil fuels.

WINKLER METHOD, BOD AND DO

➲ Biochemical Oxygen Demand (BOD)

"Biochemical oxygen demand (BOD) is the capacity of organic matter in natural water to consume oxygen within a period of five days."

- The value of BOD is the amount of oxygen consumed as a result of biological oxidation of dissolved organic matter in the sample.
- The oxidation reaction is catalyzed by microorganisms which are already present in the natural water.
- It is measured experimentally through **Winkler method** by calculating the concentration of oxygen at the beginning and at the end of five days period, in which a sealed water sample is maintained in the dark at constant temperature at 25°C.

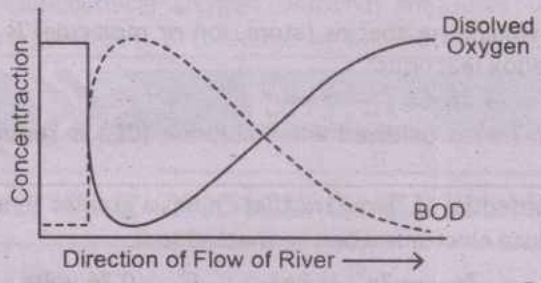


Figure 10.12: Inverse relationship between BOD and DO

Rack Your Mind!

10. The capacity of organic matter in natural water to consume oxygen within five days is called:

A) DO B) BOD
C) COD D) PAN

➲ Dissolved Oxygen (DO)

"Dissolved oxygen (DO) is defined as the amount of oxygen dissolved in water. It is dissolved either from the atmosphere or released by plants during photosynthesis in water."

- Its concentration is between 5 to 8mg / dm^3. The minimum level of DO should be 5mg / dm^3.
- Below 5mg / dm^3, the water supposed to be polluted.
- Dissolved Oxygen (DO) and Biochemical Oxygen Demand (BOD) have an inverse relationship as shown in Figure.
- As bacteria consume oxygen in the water while decomposing organic matter, BOD increases, leading to lower dissolved oxygen (DO) level.

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➲ Winkler Method

- Winkler method is a technique used to measure the amount of dissolved oxygen (DO) in water samples.
- It is based on the idea that dissolved oxygen (DO) in the sample solution, has oxidizing properties and reacts with KI.
- The amount of iodine formed is measured by titrating with sodium thiosulfate using starch as an indicator which turns the solution dark blue, indicating the endpoint.
- The amount of iodine formed is proportional to the amount of dissolved oxygen in the solution.



Sr. #	Option	Explanation
1.	S.Q	**Given Data:** K_2CrO_4: Oxidation Number of O = –2 Oxidation Number of K = +1 **Required:** Oxidation Number of Cr = x = ? **Solution:** 2(O.S of K) + (O.S of Cr) + 4(O.S of O) = 0 2(+1) + (x) + 4(–2) = 0 +2 + x – 8 = 0 x = +8 – 2 = +6 Oxidation Number of Cr is +6 in K_2CrO_4.
2.	A	In all oxidation reactions, atoms of an element in a chemical species lose electrons and increase their oxidation state.
3.	D	SO_4^{-2} (0.No of S) + 4 (0.No. of O) = –2 = 0.No of S + 4(–2) = –2 = 0.No of S – 8 = 0.No of S = –2 + 8 = +6
4.	S.Q	**Redox Reactions:** "Those reactions in which one species (atom, ion or molecule) is **oxidized** while other is **reduced** are called redox reactions". **Example:** $2Fe + 3C\ell_2 \longrightarrow 2FeC\ell_3$ In this reaction, Iron (Fe) is **oxidized** while chlorine ($C\ell_2$) is **reduced**. So, this is a redox reaction.
5.	S.Q	Standard oxidation potential of Zn means that Zn has a greater tendency of 0.76 volts than SHE to oxidize or to lose electrons when connected to it. $Zn_{(s)} \rightarrow Zn^{+2}_{(aq)} + 2e^-$ $\quad E^\circ_{oxi} = 0.76$ volts For the reverse reaction, which is reduction of Zn^{+2} ion by gain of two electrons the E°_{red} is with a reverse sign i.e., $Zn^{+2}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$ $\quad E^\circ_{red} = -0.76$ volts As both the reactions are opposite to each other, therefore their values of E°_{oxi} and E°_{red} are same but with an opposite sign. $Zn_{(s)} \rightleftharpoons Zn^{+2}_{(aq)} + 2e^-$
6.	S.Q	**Electromotive force (emf):** The force with which electrons moves from anode towards the cathode through an external circuit in a galvanic cell is called the electromotive force (emf).

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		It measures the tendency of the cell reaction to takes place. **Calculation of emf of a Cell:** Let us find the emf or cell potential of Daniel cell. The half-cell reactions are. $Zn_{(s)} \rightarrow Zn^{+2}_{(aq)} + 2e^-$ (Oxidation half) $Cu^{+2}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ (Reduction half) The overall cell reaction is $Zn_{(s)} + Cu^{+2}_{(aq)} \rightarrow Cu_{(s)} + Zn^{+2}_{(aq)}$ The cell voltage or emf of the cell is given by $E^\circ_{cell} = E^\circ_{oxd} + E^\circ_{red}$ $= 0.76\,V + 0.34\,V$ $= 1.10\,V$
7.	A	During a redox reaction, an oxidizing agent Gains electrons.
8.	A	The reduction potential of Zn is –0.76 V
9.	S.Q	Displacement of hydrogen from acids involve oxidation of metal and reduction of H^+ to H_2 gas from acid. $M \rightarrow M^+ + 1e^-$ (Oxidation) $2H^+ + 2e^- \rightarrow H_2$ (Reduction) In electrochemical series, those metals which are listed above H_2 have lesser values of reduction potential than H_2 electrode so they possess high values of oxidation potentials. Na and K possess high values of oxidation potential so they liberate H_2 when react with acids as they are present above H_2 in electrochemical series. $Na \rightarrow Na^+ + 1e$ $E^\circ_{oxi} = 2.714$ volt $K \rightarrow K^+ + 1e^-$ $E^\circ_{oxi} = 2.925$ volt On the other hand Pt, Cu, Au, Ag etc. are listed below H_2 indicating greater reduction potential so they have negative potential to undergo oxidation. e.g. $Cu \rightarrow Cu^{+2} + 2e^-$ $E^\circ_{oxi} = -0.34$ volt Therefore these metals are not able to liberate H_2 gas when treated with acids.
10.	B	BOD (Biochemical Oxygen Demand) measures the amount of oxygen consumed by microorganisms to decompose organic matter in water over five days.

Exercise

MULTIPLE CHOICE QUESTIONS (MCQs)

Q.1 Four choices are given for each question. Select the correct choice.

I. The activity series of metals arranges metals in order of their:

a) Atomic mass b) Density c) Ease of oxidation d) Ease of reduction

II. According to the activity series, which of the following metals would most readily displace hydrogen gas from dilute acids?

a) Copper (Cu) b) Silver (Ag) c) Magnesium (Mg) d) Platinum (Pt)

III. The salt bridge allows transfer of _____ in Zn – Cu voltaic cell.

(a) Zn^{2+} ions b) SO_4^{2-} ions (c) Both d) None of these

IV. If Zn–Cu galvanic cell works ideally after complete discharge, both compartments will have:

a) $CuSO_4$ solution b) $ZnSO_4$ solution c) Cu^{+2} ions d) Zn solid

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V. **Which of the following half-reactions represents a reduction process?**

a) $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$ b) $Fe^{2+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + e^-$ c) $Cl_{2(g)} + 2e^- \rightarrow 2Cl^-_{(aq)}$ d) $2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$

VI. **Which of the following half-reactions represents the oxidation process occurring in the disproportionation of Cu^+?**

a) $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ b) $Cu^+_{(aq)} + e^- \rightarrow Cu_{(s)}$ c) $Cu^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + e^-$ d) $2Cu^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + Cu_{(s)}$

VII. **If salt bridge is not used between two half cells in a Galvanic cell, then the voltage**

a) Decrease slowly b) Decrease rapidly c) Does not change d) Drop to zero

VIII. **In an electrolysis experiment, if a charge of 96,500 Coulombs is passed through a solution, the amount of substance liberated or deposited at the electrode is directly related to:**

a) Mass number of the ion
b) One mole of electrons being transferred
c) Avogadro's number of ions being discharged
d) Standard electrode potential of the metal ion

IX. **The experimental determination of Avogadro's number through electrolysis typically involves measuring:**

a) The current and voltage applied.
b) The mass of the substance deposited or liberated by a known charge.
c) The conductivity of the electrolytic solution.
d) The temperature changes during electrolysis.

X. **The principle of measuring DO by Winkler's Method is based on**

a) Iodimetry b) Iodometry c) Acid-Base titration d) Complexometry

XI. **A positive value for the standard electrode potential (E°) of a metal ion/metal half-cell (e.g., Cu^2 / Cu) indicates that:**

a) The metal is a strong reducing agent.
b) The metal ion is readily oxidized.
c) The metal ion is readily reduced.
d) The metal will readily displace hydrogen from dilute acids.

XII. **Which of the following changes would typically lead to an increase in the rate of electrolysis?**

a) Decreasing the concentration of the electrolyte
b) Increasing the distance between the electrodes
c) Decreasing the surface area of the electrodes
d) Increasing the current passed through the electrolytic cell

Answer Key with Explanations

Sr.No.	Option	Answer	Explanation
I	c)	Ease of oxidation	Metals are arranged based on how easily they lose electrons. More reactive metals oxidize easily and appear higher in the series.
II	c)	Magnesium (Mg)	Magnesium is more reactive than hydrogen in the series. It donates electrons to H^+ ions, releasing hydrogen gas quickly.
III	b)	SO_4^{2-} ions	The salt bridge carries SO_4^{2-} ions to maintain charge balance. It completes the circuit by allowing ion flow without mixing solutions.
IV	b)	$ZnSO_4$ solution	Zn oxidizes and Cu^{2+} reduces to Cu, consuming Cu^{2+} ions. The leftover electrolyte in both half-cells becomes $ZnSO_4$.
V	c)	$Cl_2 + 2e^- \rightarrow 2Cl^-$	In reduction, a species gains electrons. Cl_2 gains electrons to form Cl^-, so it's a reduction.
VI	d)	Drop to zero	Without a salt bridge, charge builds up in the half-cells. This stops electron flow, and the cell immediately loses voltage.
VII	d)	$2Cu^+ \rightarrow Cu^{2+} + Cu$	In disproportionation, the same element is oxidized and reduced. One Cu^+ loses an electron (oxidized), and the other gains (reduced).

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VIII	b)	One mole of electrons	96,500 C is 1 Faraday, the charge of 1 mole of electrons. The amount of substance deposited depends on electrons transferred.
IX	b)	Mass deposited by known charge	Mass of metal deposited for a known charge gives moles of atoms. This helps calculate the number of atoms (Avogadro's number).
X	b)	Iodometry	Winkler's method involves titration of iodine formed by DO. It is a redox reaction measured using iodometric titration.
XI	c)	Ion is reduced	A positive E° means the ion gains electrons easily. It is more likely to be reduced than hydrogen.
XII	d)	Increase current	More current increases the number of electrons flowing per second. This speeds up ion discharge and increases the rate of electrolysis.

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. How and why electrical double layer is formed?

Ans. An electrical double layer forms at the interface between a solid electrode and an electrolyte solution. It consists of two layers: a layer of charge on the electrode surface and a layer of opposite charge in the solution. This structure arises due to electrostatic interactions between the electrode and the ions in the solution.

b. Why electrode potential of Cu is called reduction potential?

Ans. The electrode potential of Cu is called a reduction potential because it represents the tendency of Cu^{2+} ions to gain electrons (reduction) and form solid copper. A positive value indicates a strong tendency to gain electrons.

c. What are the advantages of salt bridge in a galvanic cell?

Ans. A salt bridge:

- Maintains electrical neutrality by allowing ion flow between half-cells.
- Prevents the solutions from mixing while completing the circuit.
- Enables continuous electron flow, allowing the cell to produce electricity.

d. How can we predict the feasibility of a chemical reaction using the cell voltage?

Ans. The feasibility of a reaction can be predicted by calculating the standard cell potential (E°_{cell}). A positive E°_{cell} indicates a spontaneous reaction, while a negative E°_{cell} suggests a non-spontaneous reaction.

e. During electrolysis of aqueous NaCℓ, why Na is not liberated at the cathode?

Ans. Sodium (Na) is not liberated at the cathode during the electrolysis of aqueous NaCℓ because water has a lower reduction potential than Na^+ ions. Therefore, water is reduced to hydrogen gas instead of Na^+ being reduced to Na metal.

f. Calculate the Ox. No. of chromium (Cr) in the following compounds:

(i) $CrCℓ_3$ **(ii)** $Cr_2(SO_4)_3$ **(iii)** $Cr_2O_7^{2-}$

Ans. Oxidation Number of Chromium (Cr)

(i) $CrCℓ_3$**:**

Given Data: Oxidation Number of Cℓ = −1

Required: Oxidation Number of Cr = x = ?

Solution:

Oxidation No. of Cr + 3(Oxidation No. of Cℓ) = 0

$$x + 3(-1) = 0$$

$$x - 3 = 0$$

$$x = +3$$

Oxidation Number of Cr is **+3** in $CrCℓ_3$.

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(ii) $Cr_2(SO_4)_3$:

Given Data: Oxidation Number of O = –2

Oxidation Number of S = +6

Required: Oxidation Number of Cr = x = ?

Solution:

2(Oxidation No. of Cr) + 3(Oxidation No. of S) + 12(Oxidation No. of O) = 0

$$2x + 3(+6) + 12(-2) = 0$$
$$2x + 18 - 24 = 0$$
$$2x = 24 - 18 = +6$$
$$x = +3$$

Oxidation Number of Cr is **+3** in $Cr_2(SO_4)_3$.

(iii) $Cr_2O_7^{2-}$:

Given Data: Oxidation Number of O = –2

Required: Oxidation Number of Cr = x = ?

Solution:

2(Oxidation No. of Cr) + 7(Oxidation No. of O) = –2

$$2x + 7(-2) = -2$$
$$2x - 14 = -2$$
$$2x = +14 - 2 = +12$$
$$x = +6$$

Oxidation Number of Cr is **+6** in $Cr_2O_7^{-2}$.

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g. The order of decreasing reactivity of metals based on their position is K > Mg > Zn > Fe > Cu. Write balanced chemical equations for the reactions that would occur (if any) when:

i) Copper is added to a solution of magnesium sulphate.

ii) Iron is added to a dilute solution of hydrochloric acid.

Ans. i) Copper is added to a solution of magnesium sulphate:

No reaction occurs because copper is less reactive than magnesium.

ii) Iron is added to a dilute solution of hydrochloric acid:

$$Fe_{(s)} + 2HC\ell_{(aq)} \longrightarrow FeC\ell_{2(aq)} + H_{2(g)}$$

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h. Explain why some metals higher in the activity series can displace hydrogen from acids, while others lower in the series cannot.

Ans. Metals higher in the activity series (e.g., Zn, Mg) are more reactive and have a greater tendency to lose electrons (oxidize) compared to hydrogen. When reacted with acids, these metals displace H^+ ions (reducing them to H_2 gas) because their reduction potential is lower than hydrogen's.

Metals lower in the series (e.g., Cu, Ag) are less reactive than hydrogen. Their reduction potential is higher, meaning they cannot supply electrons to reduce H^+ ions, so they do not displace hydrogen from acids.

In short, electrochemical reactivity (position in the series) determines whether a metal can reduce H^+ to H_2.

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i. Calculate the number of Faradays required to deposit 108 g of Ag^{1+}, 63.5 g of Cu^{2+} and 27 g of $A\ell^{3+}$.

Ans. Number of Faradays=Mass of substance (g)/Equivalent mass of substance

The **equivalent mass (E)** is calculated as:

$$E = \frac{\text{Molar mass (M)}}{\text{Valency (n)}}$$

1. For 108 g of Ag^+ (Silver)

Molar mass (Ag) = 108 g/mol

Valency (n) = 1

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$$\text{Equivalent mass (E)} = \frac{108}{1} = 108 \text{ g/equivalent}$$

$$\text{Number of Faradays} = \frac{108\text{g}}{108\text{g/equivalent}} = 1\text{F}$$

2. For 63.5 g of Cu^{2+} (Copper)

$$\text{Molar mass (Cu)} = 63.5 \text{ g/mol}$$
$$\text{Valency (n)} = 2$$

$$\text{Equivalent mass (E)} = \frac{63.5}{2} = 31.75 \text{ g/equivalent}$$

$$\text{Number of Faradays} = \frac{63.5\text{g}}{31.75\text{g/equivalent}} = 2\text{F}$$

3. For 27 g of $A\ell^{3+}$ (Aluminum)

$$\text{Molar mass (A}\ell\text{)} = 27 \text{ g/mol}$$
$$\text{Valency (n)} = 3$$

$$\text{Equivalent mass (E)} = \frac{27}{3} = 9 \text{ g/equivalent}$$

$$\text{Number of Faradays} = \frac{27\text{g}}{9\text{g/equivalent}} = 3\text{F}$$

Final Answer:

- **Ag^+ (108 g):** 1 Faraday
- **Cu^{2+} (63.5 g):** 2 Faradays
- **$A\ell^{3+}$ (27 g):** 3 Faradays

(Each Faraday = 96,485 C/mol, but here we only calculate the number of Faradays.)

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j. In an electrolysis experiment, a current of 0.500 A was passed through a solution of $AgNO_3$ for 30.0 minutes. The mass of silver deposited on the cathode was found to be 0.503 g. Given that the molar mass of silver is 107.87 g mol^{-1} and the charge on a silver ion is +1. Calculate the value of Avogadro's number (N_A) from this data.

Ans. Given Data:

$$\text{Current (I)} = 0.500 \text{ A}$$
$$\text{Time (t)} = 30.0 \text{ minutes} = 1800 \text{ seconds}$$
$$\text{Mass of Ag deposited (m)} = 0.503 \text{ g}$$
$$\text{Molar mass of Ag (M)} = 107.87 \text{ g mol}^{-1}$$
$$\text{Charge on } Ag^+ \text{ ion (n)} = 1$$

Step 1: Calculate the total charge passed (Q)

$$Q = I \times t = 0.500 \text{ A} \times 1800 \text{ s} = 900 \text{ C}$$

Step 2: Determine moles of Ag deposited

$$\text{Moles of Ag} = \frac{m}{M} = \frac{0.503\text{g}}{107.87\text{g mol}^{-1}} = 4.663 \times 10^{-3} \text{ mol}$$

Step 3: Relate charge to moles of electrons (Faraday's Law)

Since $Ag^+ + e^- \rightarrow Ag$, **1 mole of Ag requires 1 mole of electrons (1 Faraday = 96,485 C).**

Total charge required for 4.663×10^{-3} mol Ag:

$$Q_{theory} = \text{Moles of Ag} \times F = 4.663 \times 10^{-3} \times 96{,}485 \text{ C}$$

But the **actual charge used (Q) = 900 C**, so:

$$F = \frac{Q}{\text{Moles of Ag}} = \frac{900}{4.663 \times 10^{-3}} = 1.930 \times 10^5 \text{ C mol}^{-1}$$

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Step 4: Calculate Avogadro's number (N_A)

Since $F = N_A \times e$ (where $e = 1.602 \times 10^{-19}$ C),

$$N_A = \frac{F}{e} = \frac{1.930 \times 10^{5}}{1.602 \times 10^{-19}} = 6.02 \times 10^{23}\ mol^{-1}$$

Final Answer: $N_A = 6.02 \times 10^{23}\ mol^{-1}$

---

k. A cell is set up with a standard nickel electrode ($Ni^{2+}_{(aq)} + 2e^- \rightleftharpoons Ni_{(s)}$ $E^\circ = -0.25$ V) and a standard cobalt electrode ($Co^{2+}_{(aq)} + 2e^- \rightleftharpoons Co_{(s)}$ $E^\circ = -0.28$ V).

i) Identify which metal will be the anode and which will be the cathode. Justify your answer.

ii) Write the balanced overall cell reaction.

iii) Calculate the standard cell potential (E°_{cell}).

Solution:

i) Identifying Anode and Cathode

- **Standard Reduction Potentials (E°):**
  - $Ni^{2+} + 2e^- \rightleftharpoons Ni_{(s)}$ $E^\circ = -0.25$ V
  - $Co^{2+} + 2e^- \rightleftharpoons Co_{(s)}$ $E^\circ = -0.28$ V
- **Comparison:**
  - Nickel has a less negative (higher) reduction potential than cobalt.
  - **Cathode (Reduction):** The electrode with the higher reduction potential (Ni^{2+}/Ni).
  - **Anode (Oxidation):** The electrode with the lower reduction potential (Co^{2+}/Co), where oxidation occurs.

Justification:

Since, $E^\circ_{(Ni^{2+}/Ni)} > E^\circ_{(Co^{2+}/Co)}$, Ni^{2+} gains electrons (reduction) at the cathode, while Co loses electrons (oxidation) at the anode.

ii) Balanced Overall Cell Reaction

- **Oxidation at Anode (Co):** $Co_{(s)} \longrightarrow Co^{2+}_{(aq)} + 2e^-$
- **Reduction at Cathode (Ni):** $Ni^{2+}_{(aq)} + 2e^- \longrightarrow Ni_{(s)}$
- **Overall Reaction:** $Ni^{2+}_{(aq)} + 2e^- \longrightarrow Ni_{(s)}$

iii) Standard Cell Potential (E°cell)

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

$$E^\circ_{cell} = (-0.25\ V) - (-0.28\ V) = +0.03\ V$$

- The positive E°_{cell} confirms the reaction is spontaneous.
- Cobalt (anode) dissolves, while nickel (cathode) deposits.

Final Answers:

i) **Anode:** $Co_{(s)}$ (oxidation)
Cathode: $Ni^{2+}_{(aq)}$ (reduction)

ii) $Ni^{2+}_{(aq)} + Co_{(s)} \rightarrow Ni_{(s)} + Co^{2+}_{(aq)}$

iii) $E^\circ_{cell} = +0.03\ V$

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DESCRIPTIVE QUESTIONS

Q.3 How electrode potential varies with concentration of an aqueous solution? Use the NERNST equation to explain this variation.

Ans. **See Page No. (356)**

Q.4 How Avogadro's number can be derived using an electrolytic cell?

Ans. **See Page No. (345)**

Q.5 Describe the construction and working principle of the Zn – Cu Galvanic cell.

Ans. **See Page No. (351)**

Q.6 What is meant by Standard Hydrogen Electrode (SHE)? How it is used to measure the electrode potential of another electrode?

Ans. **See Page No. (348)**

NUMERICAL PROBLEMS

Q.7 Calculate the electrode potential for a zinc electrode immersed in a 0.010 mol dm^{-3} solution of zinc sulfate ($ZnSO_4$) at 298 K. The standard electrode potential (E°) for $Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$ is –0.76 V. (Gas constant, R = 8.31 J K^{-1} mol^{-1}, Faraday constant, F = 96500 C mol^{-1})

Given Data:

- Standard electrode potential (E°) = –0.76 V (for $Zn^{2+} + 2e^- \rightleftharpoons Zn_{(s)}$)
- Concentration of Zn^{2+} ($[Zn^{2+}]$) = 0.010 mol dm^{-3}
- Temperature (T) = 298 K
- Gas constant (R) = 8.31 JK^{-1} mol^{-1}
- Faraday constant (F) = 96500 C mol^{-1}
- n (number of electrons transferred) = 2

Nernst Equation:

$$E = E^\circ - \frac{RT}{nF} \ln\left(\frac{1}{[Zn^{2+}]}\right)$$

Since the activity of solid Zn(s) is **1**, the equation simplifies to:

$$E = E^\circ - \frac{0.0591}{n} \log_{10}[Zn^{2+}]$$

(At 298 K, $\frac{RT\ln(10)}{F} \approx 0.0591$ V)

Substitute Values

$$E = -0.76 - \frac{0.0591}{2} \log_{10}(0.010)$$

$$E = -0.76 - \frac{0.0591}{2} \times (-2) \qquad (\because \log_{10}(0.010) = -2)$$

$$E = -0.76 + 0.0591$$

$$E = -0.7009 V$$

Final Answer: $E \approx -0.70$ V

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Q.8 A constant current of 2.00 A is passed through a solution of copper(II) sulfate ($CuSO_4$) for 30.0 minutes. Calculate the mass of copper deposited at the cathode. (Molar mass of Cu = 63.5 g mol^{-1}, Faraday constant, F = 96500 C mol^{-1})

Given Data:

Current (I) = 2.00 A

Time (t) = 30.0 minutes = 1800 seconds

Molar mass of Cu = 63.5 g mol^{-1}

Faraday constant (F) = 96500 C mol^{-1}

Reaction at Cathode:

$$Cu^{2+} + 2e^- \longrightarrow Cu_{(s)}$$

Step 1: Calculate Total Charge Passed (Q)

$$Q = I \times t$$
$$= 2.00\ A \times 1800\ s = 3600\ C$$

Step 2: Determine Moles of Electrons Transferred

$$\text{Moles of } e^- = \frac{Q}{F} = \frac{3600}{96500} = 0.0373 \text{ mol}$$

Step 3: Relate Moles of Electrons to Moles of Cu Deposited

Since 2 moles of e– deposit 1 mole of Cu:

$$\text{Moles of Cu} = \frac{\text{Moles of } e^-}{2} = \frac{0.0373}{2} = 0.01865 \text{ mol}$$

Step 4: Calculate Mass of Copper Deposited

$$\text{Mass of Cu} = \text{Moles of Cu} \times \text{Molar mass}$$
$$= 0.01865 \times 63.5 = 1.184\ g$$

Final Answer: 1.18 g

Q.9 A galvanic cell consists of a standard hydrogen electrode (SHE) and a $Ni^{2+}_{(aq)}/Ni_{(s)}$ half-cell. The measured cell potential at 298 K is 0.25 V, and the nickel electrode is the negative terminal.

a) Write the balanced overall cell reaction.

b) Determine the standard electrode potential (E°) of the $Ni^{2+}_{(aq)}/Ni_{(s)}$ half-cell.

c) Identify which electrode is the anode and which is the cathode.

Ans.

a) Balanced Overall Cell Reaction

Since the **nickel electrode is negative**, it acts as the **anode** (oxidation), and SHE is the **cathode** (reduction).

Oxidation (Anode):

$$Ni_{(s)} \longrightarrow Ni^{2+}_{(aq)} + 2e^-$$

Reduction (Cathode):

$$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$$

Overall Reaction:

$$Ni_{(s)} + 2H^+_{(aq)} \longrightarrow Ni^{2+}_{(aq)} + H_{2(g)}$$

b) Standard Electrode Potential (E°) of Ni^{2+}/Ni

Given Data:

Measured E_{cell} = 0.25 V

SHE reference potential:

$$E^\circ_{H^+/H_2} = 0\ V$$

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

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$$0.25 = 0 - E^{\circ}_{Ni^{2+}/Ni}$$

$$E^{\circ}_{Ni^{2+}/Ni} = -0.25V$$

c) **Anode and Cathode Identification**

- **Anode (Negative terminal):** $Ni_{(s)}$ (oxidation).
- **Cathode (Positive terminal):** SHE (reduction).

ADDITIONAL SLOs BASED MCQs

1. **By electrolysis of brine solution which of the following is deposited at anode?**
   A. H_2 B. Cl_2 C. O_2 D. Na
2. **Which of the following is reducing agent?**
   A. $KMnO_4$ B. HI C. $K_2Cr_2O_7$ D. H_2SO_4
3. **The oxidation number of Mn in potassium manganate is:**
   A. +7 B. +6 C. +5 D. +2
4. **All of the following statements about (oxidation) state is / are correct EXCEPT:**
   A. It is apparent charge on an atom in a compound B. Its value is either zero, positive or negative
   C. It can be variable D. Maximum oxidation state can be +7
5. **In the extraction of Al by electrolysis. Why it is necessary to dissolve Al_2O_3 in molten cryolite?**
   A. Cryolite provides the ions needed to carry current B. To decrease high melting point of the electrolyte
   C. Cryolite reacts with Al_2O_3 to form ions D. Molten Al_2O_3 would not conduct electricity
6. **All of the following is / are characteristic of electrolytic cell except:**
   A. Electrical energy into chemical energy B. Anode has negative charge and cathode positive charge
   C. Reverse of addition reaction D. Endothermic process
7. **A solution of copper (II) sulphate is electrolyzed using copper electrode, which of the following would be happen?**
   A. The anode loses weight B. The cathode loses weight
   C. The solution darkens in colour D. The solution lighters in colour
8. **Which is not a galvanic cell?**
   A. Daniel cell B. NICAD C. Fuel cell D. Dry Cell
9. **Voltage of silver oxide battery is:**
   A. 1.5V B. 1.8V C. 2V D. 2.2
10. **Coinage metal Cu, Ag, Au, are the least reactive because they have:**
    A. Negative reduction potential B. Positive reduction potential
    C. Negative oxide potential D. Positive oxide potential
11. **The following standard half cells are connected**

$$Cd^{+2}_{(aq)} + 2e^{-} \rightleftharpoons Cd_{(s)} E^{\circ}red = -0.40v$$

$$Ag^{+2}_{(aq)} + e^{-} \rightleftharpoons Ag_{(s)} E^{\circ}red = +0.80v$$

What is cell potential of the Cd electrode relative to the Ag electr
    A. -2 .0v B. - 0.04v C. +1.2v D. +0.40v
12. **Zinc displaced copper from copper sulphate solution because:**
    A. Atomic no. of zinc is higher than that of copper
    B. Zinc has more negative electrode potential than copper
    C. Zinc has positive electrode potential than copper
    D. Zinc sulphate is more soluble in water than copper sulphate
13. **The cell reaction $Zn + Cu^{2+}_{(aq)} \rightarrow Zn^{+2}_{(aq)} + Cu$, is best represented by:**
    A. $Cu|Cu^{2+}||Zn^{2+}|Zn$ B. $Pt|Zn^{2+}||Cu^{2+}|Cu$ C. $Zn|Zn^{2+}||Cu^{2+}|Cu$ D. $Zn|Cu^{2+}||Zn^{2+}|Cu$
14. **Which of the following is type of electrolytic cell?**
    A. Ni – Cd cell B. Down's Cell C. Silver oxide cell D. Dry alkaline cell

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15. **If the salt bridge is not used between two half cells, then the voltage:**
A. Decrease rapidly B. Decrease slowly C. Does not change D. Drops to zero

Answer Key with Explanations

Sr.No.	Option	Explanations
1.	B	In Electrolysis of brine soln. Cl^- and OH^- are present at anode according to E.C series OH^- should oxidize to give O_2 but to high cone. Cl^- is oxidized to give Cl_2 at anode.
2.	B	Among the following the reducing agent is HI.
3.	B	The oxidation number of Mn in K_2MnO_4 is+6.
4.	D	The correct statement among the following is maximum oxidation state can be +7.
5.	B	In the extraction of Al by electrolysis. It is necessary to dissolve Al_2O_3 in molten cryolite to decrease high melting point of the electrolyte.
6.	B	The incorrect statement about electrolytic cell is anode has negative charge and cathode positive charge.
7.	D	A solution of copper (II) sulphate is electrolyzed using copper electrode then solution lighters in colour.
8.	C	Fuel is not a galvanic cell.
9.	A	Voltage of silver oxide battery is 1.5V.
10.	B	Coinage metal Cu, Ag, Au, are the least reactive because they have positive reduction potential.
11.	C	Element with low R.P will be oxidized oxidation pot of Cd will be=+0.40 Ag with high R.P will be reduced red pot of Ag is = 0.40 +0.80 by adding both weight = +1.20V
12.	B	Zinc displaced copper from copper sulphate solution because Zinc has more negative electrode potential than copper.
13.	C	$Zn\|Zn^{2+}\|\|Cu^{2+}\|Cu$
14.	B	Electrolytic cell like Down's cell uses electricity to carry out non-spontaneous chemical reaction.
15.	D	Due to charge accumulation, flow of $\bar{e}$ is stopped and voltage drop to zero.

ADDITIONAL SHORT ANSWER QUESTIONS

Q.1 What is Winkler method?

Ans. Winkler method is a technique used to measure the amount of dissolved oxygen (DO) in water samples. It is based on the idea that dissolved oxygen (DO) in the sample solution, has oxidizing properties and reacts with KI. The amount of iodine formed is measured by titrating with sodium thiosulfate using starch as an indicator which turns the solution dark blue, indicating the endpoint. The amount of iodine formed is proportional to the amount of dissolved oxygen in the solution.

Q.2 Differentiate between dissolve and biological oxygen demand.

Ans. Dissolved oxygen (DO) is defined as the amount of oxygen dissolved in water. It is dissolved either from the atmosphere or released by plants during photosynthesis in water. Its concentration is between 5 to 8 mg/dm^3. The minimum level of DO should be 5 mg/ dm^3. Below 5 mg/dm^3, the water supposed to be polluted.

The capacity of organic matter in natural water to consume oxygen within a period of five days. The value of BOD is the amount of oxygen consumed as a result of biological oxidation of dissolved organic matter in the sample is called biological oxygen demand.

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Q.3 What is the principle of photovoltaic cell?

Ans. Principle of Photovoltaic Cells

The central principle behind the operation of PV cells is the photovoltaic effect, which involves the generation of voltage and electric current in a material upon exposure to light. The photovoltaic effect involves the excitation of electrons from the valence band to the conduction band in semiconductors, facilitated by the energy from photons. This process is improved by the presence of a PN junction, which separates the electrons and holes, creating a voltage that drives an electric current.

Q.4 Define electrochemistry.

Ans. Electrochemistry:

"The branch of chemistry concerned with the conversion of electrical energy into chemical energy in electrolytic cells and chemical energy into electrical energy in galvanic or voltaic cells is called electrochemistry."

$$\text{Chemical energy} \underset{\text{Electrolytic cell}}{\overset{\text{Galvanic cell}}{\rightleftharpoons}} \text{Electrical energy}$$

Q.5 Differences between oxidizing agent and reducing Agent.

Ans.

Oxidizing Agent	Reducing Agent
(i) A specie which oxidize a substance in a redox reaction is called an oxidizing agent or oxidant.	(i) A specie which reduces a substance in a redox reaction is called as a reducing agent or reductant.
(ii) In the process, the oxidizing agent is reduced itself.	(ii) In the process, the reducing agent is oxidized itself.
(iii) An oxidizing agent gain electrons and its oxidation number decreases in the reaction. **e.g.,** $KMnO_4/H_2SO_4$, $K_2Cr_2O_7/H_2SO_4$, HNO_3, Cl_2, Br_2 etc.	(iii) The reducing agent lose electrons and its oxidation number is increased. **e.g.,** $FeSO_4$, HI, SO_2, Na, K etc.

Q.6 Define Oxidation and Oxidation number. Give two examples.

Ans. Oxidation: There are three definitions

(i) Loss of electron **(ii)** Loss of hydrogen **(iii)** Gain of oxygen

Oxidation Number/Oxidation State:

"The apparent charge on an atom of an element in a molecule or in an ion is called oxidation number or oxidation state."

Examples:

(i) Oxidation number of Cr is +6 in $K_2Cr_2O_7$. **(ii)** Oxidation of P is + 5 in Na_3PO_4.

Q.7 What is difference between oxidation and reduction process, give one example of each?

Ans.

Oxidation	Reduction
"Addition of **oxygen** or removal of **hydrogen** is called oxidation"	"Addition of **hydrogen** or removal of **oxygen** is called oxidation"
• Loss of **electron** and hence increase in **oxidation number** is called oxidation. **e.g.,** $Zn \longrightarrow Zn^{+2} + 2e^-$	• Gain of **electron** and hence **decrease** in **oxidation number** is called **reduction**. **e.g.,** $Cu^{+2} + 2e^- \longrightarrow Cu$
• In electrochemical cells oxidation takes place at **anode**.	• In electrochemical cells **reduction takes place** at **cathode**.

Q.8 Write down the oxidation states of oxygen in peroxide and super oxides.

Ans. Oxidation States of Oxygen in Peroxides and Super Oxides:

In peroxides, oxygen has – 1 oxidation state **e.g.** $H_2^{2(+1)}O^{2(-1)}$.

In superoxide it has –1/2 oxidation state **e.g.** $K^{+1}O^{(-1/2)}$.

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Q.9 Calculate the oxidation number of underlined elements: $H\underline{N}O_3$: $\underline{Cr}O_3$

Ans. $H\underline{N}O_3$

Given Data: Oxidation Number of O = −2

Oxidation Number of H = +1

Required: Oxidation Number of N = x = ?

Solution:

(Oxidation No. of H) + (Oxidation No. of N) + 3(Oxidation No. of O) = 0

$$(+1) + x + 3(-2) = 0$$
$$+1 + x - 6 = 0$$
$$x = +6 - 1 = +5$$

Oxidation Number of N is **+5** in HNO_3.

$\underline{Cr}O_3$

Given Data: Oxidation Number of O = −2

Required: Oxidation Number of Cr = x = ?

Solution:

(Oxidation No. of Cr) + 3(Oxidation No. of O) = 0

$$x + 3(-2) = 0$$
$$x - 6 = 0$$
$$x = +6$$

Oxidation Number of Cr is **+6** in CrO_3.

Q.10 Define anode and cathode.

Ans. Anode:

An anode is an electrode of a polarized electrical device through which conventional current enters the device.

Cathode:

An electrode of the device through which conventional current leaves the device.

Q.11 Define electrolytic cell. Give example.

Ans. Electrolytic Cell:

In this cell, electrical energy is converted into chemical energy. Non-spontaneous redox reaction takes place. Electrical energy is used to carry out reaction. Electrolysis takes place. Anode is positive and cathode is negative. **e.g.,** Down's cell (to prepare pure Na-metal), Nelson's cell (to prepare caustic soda commercially) etc.

Q.12 Define electrode potential and standard electrode potential.

Ans. Electrode Potential:

The tendency of a metal to form its ions or get deposited on the metal when it is dipped into solution of its own ions is called electrode potential.

Standard Electrode Potential:

"The potential set up when an electrode is in contact with one molar solution of its own ions at 298 K is known as standard electrode potential or standard reduction potential of the element."

It is represented as E°.

For example, a rod of Zn will have an accumulation of negative charge owing to the net ionization of some **of its atoms. This layer of negative** charge will attract Zn^{+2} ions around the rod. In this way, an electrical **double layer is formed around the Zn rod** as shown in figure. The equilibrium state is represented as

$$Zn_{(s)} \rightleftharpoons Zn^{+2}_{(aq)} + 2e^-$$

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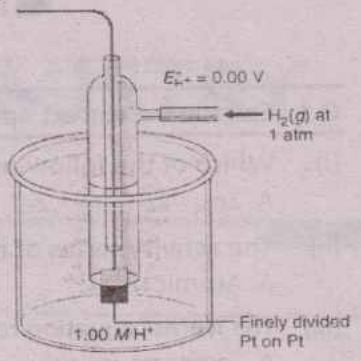
Q.13 What is Standard Hydrogen Electrode (SHE)? Explain with the help of diagram.

Ans. Standard Hydrogen Electrode (SHE):

A standard hydrogen electrode consists of a piece of platinum foil, coated with a layer of finally divided platinum black (to give it a large surface area) and is connected with a platinum wire. It is immersed in 1 M $HC\ell$ solution. Pure H_2 gas at one atmospheric pressure is continuously bubbled into 1 M $HC\ell$ solution.

The platinum acts as an electrical conductor and also facilitates the attainment of equilibrium between the gas and its ions in solution. The electrode potential (oxidation or reduction) of this standard hydrogen electrode is arbitrarily taken as zero at all temperatures.

$E^\circ = 0.00$ V



Q.14 Write down the importance of standard Hydrogen Electrode (SHE).

Ans. Importance of Standard Hydrogen Electrode (SHE):

- SHE is used as a standard electrode.
- Standard Hydrogen Electrode is used as a reference electrode and has a potential of 0.0 volts.
- SHE is used to find the reduction potential of different electrodes.
- SHE serves as a medium for cell potential calculations.

Q.15 Differentiate between Galvanic cell and Electrolytic cell.

Ans. Differences between Galvanic Cell and Electrolytic Cell:

Electrolytic Cell	Voltaic/Galvanic Cell
• In this cell, electrical energy is converted into chemical energy.	• In this cell, the chemical energy is converted into electrical energy.
• Non-spontaneous redox reaction takes place.	• Spontaneous redox reaction takes place.
• Electrical energy is used to carry out reaction.	• Electrical energy is generated by a chemical reaction.
• Electrolysis takes place.	• No electrolysis takes place.
• Anode is positive and cathode is negative.	• Anode is negative and cathode is positive.
• **Example:** Down's cell (to prepare pure Na-metal), Nelson's cell (to prepare caustic soda commercially) etc.	• **Example:** Zn-Cu cell (Daniel cell), lead storage battery, silver oxide cell etc.

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SELF-ASSESSMENT Chapter # 10

Total Mark: 30

Q.1 Encircle the correct option. (1 × 6 = 6)

(i) Which of the following half-reactions represents a reduction process?

A. $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$ B. $Fe^{2+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + e^-$ C. $Cl_{2(g)} + 2e \rightarrow 2Cl^-_{(aq)}$ D. $2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$

(ii) The activity series of metals arranges metals in order of their:

A. Atomic mass B. Density C. Ease of oxidation D. Ease of reduction

(iii) The Nernst equation relates electrode potential to:

A. Temperature only B. Ion concentration and temperature

C. Pressure only D. Volume only

(iv) In the Cu-Zn galvanic cell, metal which oxidized is:

A. Copper B. Zinc C. Both D. Neither

(v) The principle of measuring DO by Wrinkler's Method is based on

A. Iodimetry B. odometry C. Acid-Base titration D. Complexometry

(vi) Which of the following changes would typically lead to an increase in the rate of electrolysis?

A. Decreasing the concentration of the electrolyte

B. Increasing the distance between the electrodes

C. Decreasing the surface area of the electrodes

D. Increasing the current passed through the electrolytic cell

Q.2 Write short answers of the following questions. (2 × 8 = 16)

(i) Determine Oxidation No. of Oxygen (O) in Na_2O

(ii) What is the function of salt bridge in the voltaic cell?

(iii) Why bromine does not react with chloride ions?

(iv) Calculate Number of Faradays required to deposit 108 g of Ag^{1+}, 63.5 g of Cu^{2+} and 27 g of Al^{3+}.

(v) How and why electrical double layer is formed?

(vi) Write the principle of the Winkler Method for measuring BOD.

(vii) What is meant by the term standard electrode potential?

(viii) The photovoltaic cells generate electricity. How?

Q.3 Extensive Questions. (2 × 4 = 8)

(a) How electrode potential varies with concentration of an aqueous solution? Use the NERST equation to explain this variation.

(b) Calculate the electrode potential for a zinc electrode immersed in a 0.010 mol dm^{-3} solution of zinc sulfate ($ZnSO_4$) at 298 K. The standard electrode potential (E°) for $Zn^{2+} + 2e^- \rightleftharpoons Zn$ is –0.76 V. (Gas constant, R = 8.31 J K^{-1} mol^{-1}, Faraday constant, F = 96500 C mol^{-1})

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