

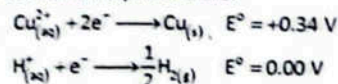
## MEASURING STANDARD ELECTRODE POTENTIALS

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

- metal/metal ion half-cell ( $\text{Cu}^{2+} / \text{Cu}^0$ )
- non-metal/non-metal ion half-cell ( $\text{Cl}^- / \text{Cl}_2$ )
- ion/ion half-cell. ( $\text{Fe}^{2+} / \text{Fe}^{3+}$ )

➤ **Measurement of Standard Electrode Potential of a  $\text{Cu}^{2+}/\text{Cu}$  half Cell:**

Figure 10.5 shows how to measure the  $E^\circ$  value for a  $\text{Cu}^{2+}/\text{Cu}$  half-cell. The  $\text{Cu}^{2+}/\text{Cu}$  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:

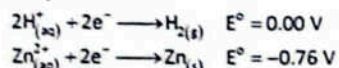


The  $E^\circ$  values show us that  $\text{Cu}^{2+}$  ions are easier to reduce than  $\text{H}^+$  ions (they have a more positive  $E^\circ$  value).  $\text{Cu}^{2+}$  ions are more likely to gain electrons than  $\text{H}^+$  ions. So  $\text{Cu}^{2+}$  ions will accept electrons from the  $\text{H}^+/\text{H}_2$  half-cell and  $\text{H}_2$  will lose electrons to the  $\text{Cu}^{2+}/\text{Cu}$  half-cell.

➤ **Measurement of Standard Electrode Potential of a  $\text{Zn}^{2+}/\text{Zn}$  Half Cell:**

Figure 10.6 shows how to measure the  $E^\circ$  value for a  $\text{Zn}^{2+}/\text{Zn}$  half cell. The voltage of the  $\text{Zn}^{2+}/\text{Zn}$  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.

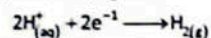
The two half-equations are:



The  $E^\circ$  values show us that  $\text{Zn}^{2+}$  ions are more difficult to reduce than  $\text{H}^+$  ions (they have a more negative  $E^\circ$  value).  $\text{Zn}^{2+}$  ions are less likely to gain electrons than  $\text{H}^+$  ions. So,  $\text{Zn}^{2+}$  will lose electrons to the  $\text{H}^+/\text{H}_2$  half-cell and  $\text{H}^+$  ions will gain electrons from the  $\text{Zn}^{2+}/\text{Zn}$  half-cell.

From these two examples, we can see that:

- Reduction takes place at the positive terminal of the cell. For example, in the  $\text{Zn}^{2+}/\text{Zn}; \text{H}^+/\text{H}_2$  cell:



- Oxidation takes place at the negative terminal of the cell. For example, in the  $\text{Zn}^{2+}/\text{Zn}; \text{H}^+/\text{H}_2$  cell:

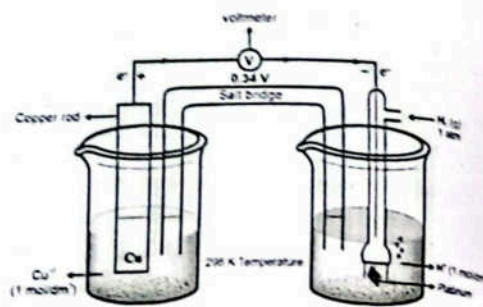
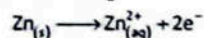


Figure: Measuring the standard electrode potential of a  $\text{Cu}^{2+}/\text{Cu}$  half-cell

**Rack Your Mind!**

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

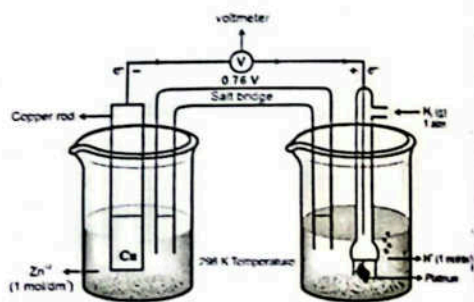


Figure: Measuring the standard electrode potential of a  $\text{Zn}^{2+}/\text{Zn}$  half-cell

## ELECTROCHEMICAL CELL (GALVANIC CELL)

Exercise 10.5

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:



A salt bridge can be substituted by a porous diaphragm.

- A galvanic cell is designed to take advantage of spontaneous transfer of electrons.

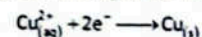
- A Galvanic Cell, is also known as a Voltaic Cell.

Examples: Daniel cell, dry cell etc.

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

If the salt bridge is removed, the emf of the cell drops to zero.

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



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

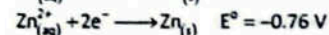
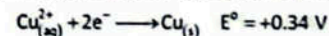
The following standard conditions are used to make the half-cell:

- The  $\text{Cu}_{(\text{aq})}^{2+}$  ions have a concentration of  $1.00 \text{ mol dm}^{-3}$
- The temperature is  $25^\circ\text{C}$  (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  $\text{Cu}^{2+}/\text{Cu}$  half-cell connected to a  $\text{Zn}^{2+}/\text{Zn}$  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:



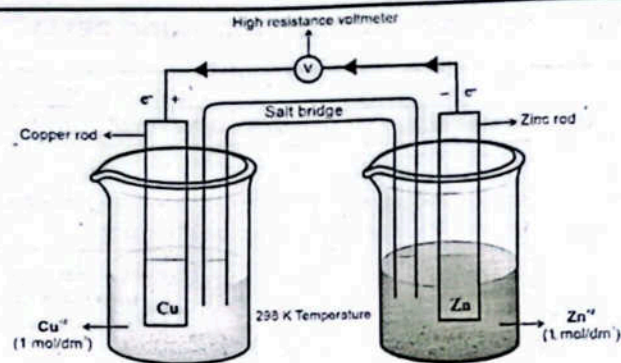
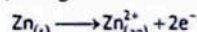


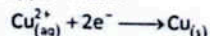
Figure: An electrochemical cell, made by connecting a  $\text{Cu}^{2+}/\text{Cu}$  half-cell to a  $\text{Zn}^{2+}/\text{Zn}$  half-cell.

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

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



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



The overall cell reaction can be represented as:



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.

$$E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ} + E_{\text{ox}}^{\circ} = +0.34 - (-0.76) = +1.10 \text{ V}$$

In a Cu-Zn galvanic cell, zinc (Zn) serves as the anode, and copper ions ( $\text{Cu}^{2+}$ ) in solution serve as the cathode.

The  $E^{\circ}$  value for the  $\text{Ag}^{+}/\text{Ag}$  half-cell is more positive than for the  $\text{Zn}^{2+}/\text{Zn}$  half-cell. So, the  $\text{Ag}^{+}/\text{Ag}$  half-cell is the positive pole and the  $\text{Zn}^{2+}/\text{Zn}$  half-cell is the negative pole of the cell.

#### Functions of Salt Bridge:

- 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.
- Keeps the electrolyte solution neutral.
- Minimizes or eliminates the liquid junction potential.



#### QUICK CHECK 10.6

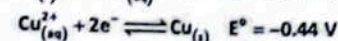
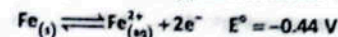
a) What is the function of salt bridge in the voltaic cell?

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

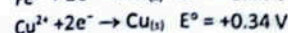
- Maintains electrical neutrality in both half-cells by allowing the flow of inert ions.
- Prevents the solutions from becoming charged (e.g., accumulation of positive or negative ions).
- Completes the electrical circuit, allowing electrons to continue flowing through the external wire.
- Minimizes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

A typical salt bridge contains a neutral electrolyte (e.g.,  $\text{KNO}_3$ ,  $\text{KCl}$ ) that doesn't react with either half-cell.

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



Given Data:

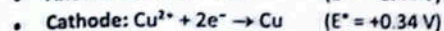


It looks like you might have written  $\text{Cu}^{2+} + 2e^{-} \rightarrow \text{Cu}_{(s)}$  also as  $-0.44 \text{ V}$  by mistake, but the standard value is  $+0.34 \text{ V}$ .

Step 1: Identify the anode and cathode

- The electrode with lower  $E^{\circ}$  is the anode (oxidation).
- The electrode with higher  $E^{\circ}$  is the cathode (reduction).

So



Step 2: Calculate Cell Potential

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

$$E_{\text{cell}}^{\circ} = (+0.34 \text{ V}) - (-0.44 \text{ V}) = +0.78 \text{ V}$$

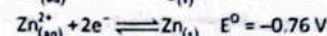
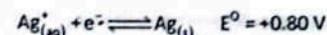
Final Answers:

- A salt bridge maintains charge balance and completes the circuit in a voltaic cell.
- The standard cell voltage for Fe-Cu voltaic cell is 0.78 V

### APPLICATIONS OF $E^{\circ}$ VALUES

#### Direction of Electron Flow

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



- The relative values of these voltages tell us that  $\text{Zn}^{2+}$  ions are more difficult to reduce than  $\text{Ag}^{+}$  ions.
- So, Zn metal will lose electrons to the  $\text{Ag}^{+}/\text{Ag}$  half-cell and  $\text{Ag}^{+}$  ions will accept electrons from the  $\text{Zn}^{2+}/\text{Zn}$  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  $\text{Zn}^{2+}/\text{Zn}$  half-cell to the  $\text{Ag}^{+}/\text{Ag}$  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.

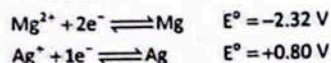
#### Feasibility of A Reaction Using $E^{\circ}$ Values

- Standard electrode potential values,  $E^{\circ}$ , give us a measure of how easy or difficult it is to oxidize or reduce a species. The  $E^{\circ}$  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  $E^{\circ}$ , 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  $E^\circ$ , 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



We need half cell equations and  $E^\circ$  values



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

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

Negative value of  $E^\circ_{\text{cell}}$  indicates the reaction is not feasible.

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

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

Therefore, the feasible reaction is

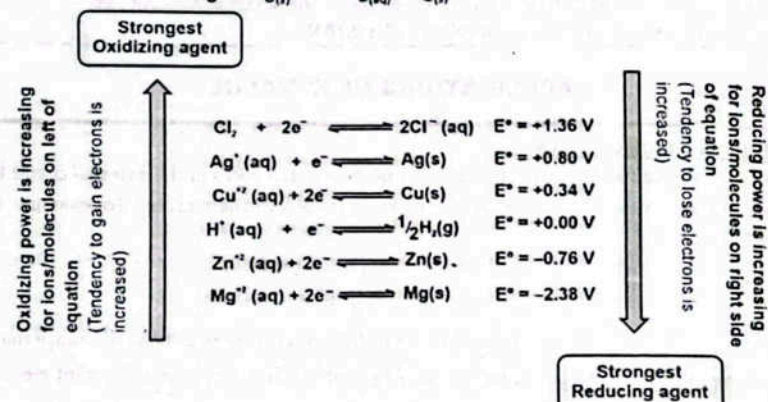


Figure: Standard electrode potentials for some oxidizing and reducing agents

### QUICK CHECK 10.7

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

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

- Ans. Explanation using standard electrode potentials:

We are given:

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

These values indicate how easily the halogens act as oxidizing agents. The higher the  $E^\circ$  value, the stronger the oxidizing agent.

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  $E^\circ$  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  $E^\circ$  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  $E^\circ = +1.07 \text{ V}$
- Chlorine ( $Cl_2$ ) has an  $E^\circ = +1.36 \text{ V}$

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  $Cl_2$ .

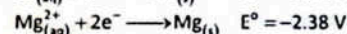
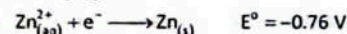
### Oxidizing and Reducing Agents Using $E^\circ$ Values

Look back at Figure. Note the following as the values of  $E^\circ$  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  $E^\circ$  value more negative than the  $E^\circ$  value for  $Zn^{2+}/Zn$ . In Figure we see that the half-equation  $Mg^{2+}/Mg$  has a more negative  $E^\circ$  value. So,  $Mg$  is a suitable reducing agent.



$Zn^{2+}$  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  $E^\circ$  values. Whereas,  $KI$  and  $FeSO_4$  are reducing agents due to their lower  $E^\circ$  values.

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



#### Rack Your Mind!

7. During a redox reaction, an oxidizing agent:
- Gains electrons
  - Is oxidized
  - Loses electrons
  - Is hydrolyzed



#### Rack Your Mind!

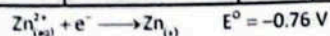
8. The reduction potential of Zn is:
- 0.76 V
  - 0.34 V
  - +0.34 V
  - +0.76 V

### VARIATION OF $E^\circ$ VALUE WITH ION CONCENTRATION

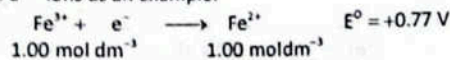
The position of an equilibrium reaction is affected by changes in concentration, temperature and pressure. If we change the concentration or temperature of half-cell X, the electrode potential also changes. Under these non-standard conditions we use the symbol  $E$  for the electrode potential. Let us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

Table: Variation of Potential with Ion Concentration

$[\text{Fe}^{3+}] (\text{mol dm}^{-3})$	$[\text{Fe}^{2+}] (\text{mol dm}^{-3})$	$E^\circ (\text{V})$	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



- If  $[\text{Zn}^{2+}]$  is greater than  $1.00 \text{ mol dm}^{-3}$ , the value of  $E$  becomes less negative / more positive (say  $-0.61 \text{ V}$ ).
  - If  $[\text{Zn}^{2+}]$  is less than  $1.00 \text{ mol dm}^{-3}$ , the value of  $E$  becomes more negative / less positive (say  $-0.80 \text{ V}$ ).
- 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  $E^\circ$  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  $\text{Fe}^{3+}$  ions and  $\text{Fe}^{2+}$  ions as an example.

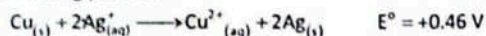


### NERNST EQUATION

(Exercise 10.2)

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:



When  $E_{\text{cell}}^\circ$  is plotted against concentration, we obtain a graph as shown in Figure.

Note that we have plotted the value of  $E_{\text{cell}}$  (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  $E_{\text{cell}}$  more positive.

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

$$E = E^\circ + \frac{RT}{zF} \ln \left[ \frac{\text{[oxidized form]}}{\text{[reduced form]}} \right]$$

where,

$E$  is the electrode potential under non-standard conditions



#### 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).

$E^\circ$  is the standard electrode potential  
 $R$  is the gas constant,  $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$   
 $T$  is the kelvin temperature  
 $z$  is the number of electrons transferred in the reaction  
 $F$  is the value of the Faraday constant in  $\text{C mol}^{-1}$

$\ln$  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.

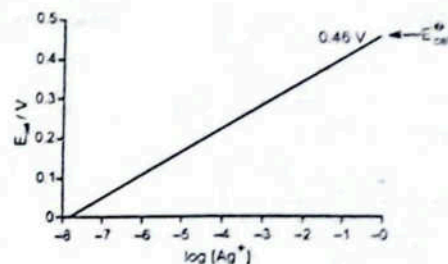


Figure: Increasing the concentration of silver ions in the cell reaction

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  $\ln x = 2.303 \log_{10} x$ .
- At standard temperature the values of  $R$ ,  $T$  and  $F$  are constant. The equation then becomes

$$E = E^\circ + \frac{0.059}{z} \log \left[ \frac{\text{[oxidized form]}}{\text{[reduced form]}} \right]$$

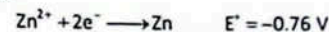
Or

$$E = E^\circ - \frac{0.059}{z} \log_{10} \left[ \frac{\text{[Reduced form]}}{\text{[Oxidized form]}} \right]$$

#### Sample Problem

What is the electrode potential of a Zn electrode dipped in a solution containing  $\text{Zn}^{2+}$  ions (0.1 M). The  $E^\circ$  value of  $\text{Zn}^{2+} / \text{Zn}$  is  $-0.76 \text{ V}$ .

Solution: Using Half equation and  $E^\circ$ ,



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

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

As Concentration of  $\text{Zn}^{2+}$  is decreased to shift equilibrium backward and electrode potential decreases to  $-0.78 \text{ V}$ .

### ACTIVITY SERIES OF METALS

- The activity series of metals is a ranking of metals based on their reactivity, specifically their tendency to lose electrons and undergo oxidation.
- Metals higher in the activity series have more negative standard reduction potentials.
- It means they are more likely to lose electrons and undergo oxidation. Thus 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. They react vigorously with substances like water to form ions and release hydrogen gas.
- The metals which are placed 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.
- The position of a metal in the activity series directly correlates with its ease of oxidation and overall reactivity. In other words, these have a greater tendency to gain electrons and undergo reduction and 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. Metals with more positive potentials are less reactive and oxidize less readily (as given in Table).

Table: Activity Series of Metals

Metals	Ions	$E^\circ$ (V)	Reaction Occurring	Trend	For Entry Test
Li	$\text{Li}^+$	-3.05	React with cold water, replacing hydrogen $2\text{M}_{(s)} + 2\text{H}_2\text{O}_{(l)} \rightarrow 2\text{MOH}_{(aq)} + \text{H}_{2(g)}$	Decreasing ease of oxidation, reactivity and acting reducing agent	Increasing strength as an oxidizing agent Increasing reduction potential
K	$\text{K}^+$	-2.93			
Ba	$\text{Ba}^{2+}$	-2.90			
Sr	$\text{Sr}^{2+}$	-2.89			
Ca	$\text{Ca}^{2+}$	-2.87			
Na	$\text{Na}^+$	-2.71	Reacts with steam (but not with cold water) replacing hydrogen. $\text{M}_{(s)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{MO}_{(aq)} + \text{H}_{2(g)}$		
Mg	$\text{Mg}^{2+}$	-2.37			
Al	$\text{Al}^{3+}$	-1.66			
Zn	$\text{Zn}^{2+}$	-0.76			
Cr	$\text{Cr}^{3+}$	-0.74			
Fe	$\text{Fe}^{2+}$	-0.44	Do not react with water. React with acids, replacing hydrogen. $\text{M}_{(s)} + \text{HCl}_{(aq)} \rightarrow \text{MCl}_{(aq)} + \text{H}_{2(g)}$		
Cd	$\text{Cd}^{2+}$	-0.40			
Co	$\text{Co}^{2+}$	-0.28			
Ni	$\text{Ni}^{2+}$	-0.25			
Sn	$\text{Sn}^{2+}$	-0.14			
Pb	$\text{Pb}^{2+}$	-0.13	Included as reference		
$\text{H}_2$	$\text{H}^+$	0.00			
Cu	$\text{Cu}^{2+}$	+0.34			
Hg	$\text{Hg}^{2+}$	+0.92			
Ag	$\text{Ag}^+$	+0.80			
Pt	$\text{Pt}^{2+}$	+1.18	Unreactive with water or acids.		
Au	$\text{Au}^{3+}$	+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  $\text{M}_1$  will replace another metal  $\text{M}_2$  in a solution if  $\text{M}_1$  is higher in the series.

#### 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:



#### Rack Your Mind!

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

The overall reaction is



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

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



The sum of  $E^\circ$  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:

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

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
- $E^\circ$  = 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 ( $E^\circ$ ) 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  $\rightarrow$  increases  $E$ .
- Decrease in ion concentration: shifts equilibrium  $\rightarrow$  decreases  $E$ .

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

- c) Give answers using  $E^\circ$  values ( $E_{\text{Ag}^+/\text{Ag}}^\circ = +0.80 \text{ V}$ ,  $E_{\text{Cr}^{3+}/\text{Cr}}^\circ = -0.91 \text{ V}$ ,  $E_{\text{Fe}^{2+}/\text{Fe}}^\circ = -0.44 \text{ V}$ ).

1. Which of  $\text{Ag}^+$ ,  $\text{Cr}^{3+}$  and  $\text{Fe}^{2+}$ , is the strongest oxidizing agent? Which is the least oxidizing? Explain with reason.

Ans.  $E_{\text{Ag}^+/\text{Ag}}^\circ = +0.80 \text{ V}$

$$E_{\text{Fe}^{2+}/\text{Fe}}^\circ = -0.44 \text{ V}$$

$$E_{\text{Cr}^{3+}/\text{Cr}}^\circ = -0.91 \text{ V}$$

Strongest and Weakest Oxidizing Agent:

- Oxidizing agents = species that gain electrons (i.e., get reduced).
- Higher  $E^\circ \rightarrow$  more easily reduced  $\rightarrow$  stronger oxidizing agent.

So:

- Strongest oxidizing agent:  $\text{Ag}^+$  ( $E^\circ = +0.80 \text{ V}$ )
- Weakest oxidizing agent:  $\text{Cr}^{3+}$  ( $E^\circ = -0.91 \text{ V}$ )

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  $E^\circ$  of their conjugate ion  $\rightarrow$  better reducing agent.

Order (increasing reducing power):

d) What is the electrode potential of a Cu electrode dipped in a solution containing  $\text{Cu}^{2+}$  ions (0.01 M). The  $E^\circ$  value of  $\text{Cu}^{2+}/\text{Cu}^0$  is +0.34 V?Ans. Electrode potential of Cu electrode in 0.01 M  $\text{Cu}^{2+}$  Solution:

Given Data:

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

Using the Nernst Equation:

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

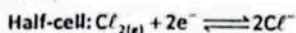
$$E = 0.34 - \frac{0.0591}{2} \log \left( \frac{1}{0.01} \right)$$

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

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

e) What is the electrode potential of  $\text{Cl}_2/\text{Cl}^-$  half cell at 25 °C, if concentration of  $\text{Cl}^-$  is 0.05 mol  $\text{dm}^{-3}$ .To Find: The electrode potential of the  $\text{Cl}_2/\text{Cl}^-$  half-cell at 25°C, we use the Nernst equation:

Given:

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

$$[\text{Cl}^-] = 0.05 \text{ mol dm}^{-3}$$

$$T = 25^\circ\text{C} = 298 \text{ K}$$

Assume:

$$P_{\text{Cl}_2} = 1 \text{ atm}$$

Nernst Equation (at 25°C):

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

$$n = 2 \text{ (number of electrons transferred)}$$

$$[\text{Cl}^-] = 0.05$$

Calculations:

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

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

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

$$\log(400) \approx 2.60$$

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

$$E = 1.36 - 0.0768 = 1.28 \text{ V}$$

In short, the electrode potential of the  $\text{Cl}_2/\text{Cl}^-$  half-cell decreases from the standard 1.36 V to 1.28 V when the  $\text{Cl}^-$  concentration is lower (0.05 M), as calculated using the Nernst equation.

## 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

- The photovoltaic effect continues as long as light is present, making it a sustainable method for generating electricity.
- A photovoltaic system is a renewable energy source that converts sunlight into electrical energy.
- 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.

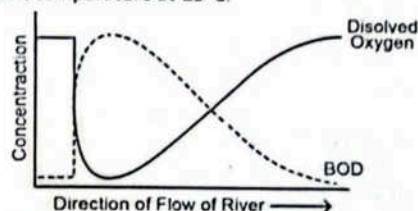


Figure 10.12: Inverse relationship between BOD and DO

## Rack Your Mind!

10. The capacity of organic matter in natural water to consume oxygen within five days is called:
- DO
  - BOD
  - COD
  - 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 8 mg /  $\text{dm}^3$ . The minimum level of DO should be 5 mg /  $\text{dm}^3$ .
- Below 5 mg /  $\text{dm}^3$ , 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.

### 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.

#### Principle:

- Potassium oxide is oxidized to  $I_2$  with the dissolved oxygen (DO) present in the water sample after adding  $MnSO_4$ ,  $NaOH$  and  $KI$ .
- The basic Manganic oxide formed from  $NaOH$  and  $MnSO_4$  acts as an oxygen carrier to enable the dissolved oxygen in the molecular form to take part in the reaction.
- The DO present in the sample oxidises the  $Mn^{2+}$  to its higher valency which precipitates as a brown hydrated oxide after the addition of  $NaOH$  and  $KI$ . On acidification, manganese reverts back to the divalent state and an equivalent amount of iodine is liberated from the  $KI$  present. This liberated iodine is titrated against standard sodium thiosulphate (hypo) solution, using starch indicator.

#### Reaction:

- $MnSO_4 + 2KOH \rightarrow Mn(OH)_2 + K_2SO_4$
- $2Mn(OH)_2 + O_2 \rightarrow 2MnO(OH)_2$  (Basic Manganic Oxide)
- $MnO(OH)_2 + H_2SO_4 \rightarrow MnSO_4 + 2H_2O + O$
- $2KI + H_2SO_4 + O \rightarrow K_2SO_4 + H_2O + I_2$
- $I_2 + Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$

### Solution File Rack Your Brain!

Sr. #	Option	Explanation
1.	S.Q	<p>Given Data:  <math>K_2CrO_4</math>: Oxidation Number of O = -2            Oxidation Number of K = +1</p> <p>Required:            Oxidation Number of Cr = x = ?</p> <p>Solution:  <math>2(O.S \text{ of } K) + (O.S \text{ of } Cr) + 4(O.S \text{ of } O) = 0</math>  <math>2(+1) + (x) + 4(-2) = 0</math>  <math>+2 + x - 8 = 0</math>  <math>x = +8 - 2 = +6</math></p> 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	$NaOCl$ $0 \text{ No. of } Na + 0 \text{ No. of } O + 0 \text{ No. of } Cl = 0$ $(+1) + (-2) + 0 \text{ No. of } Cl = 0$ $+1 - 2 + 0 \text{ No. of } Cl = 0$ $0 \text{ No. of } Cl = -1$
4.	S.Q	<b>Redox Reactions:</b> "Those reactions in which one species (atom, ion or molecule) is oxidized while other is reduced are called redox reactions".

		<b>Example:</b> $2Fe + 3Cl_2 \rightarrow 2FeCl_3$ In this reaction, Iron (Fe) is oxidized while chlorine ( $Cl_2$ ) 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. $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^- \quad E^{\circ}_{oxi} = 0.76 \text{ volts}$ For the reverse reaction, which is reduction of $Zn^{2+}$ ion by gain of two electrons the $E^{\circ}_{red}$ is with a reverse sign i.e., $Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)} \quad E^{\circ}_{red} = -0.76 \text{ volts}$ As both the reactions are opposite to each other, therefore their values of $E^{\circ}_{oxi}$ and $E^{\circ}_{red}$ are same but with an opposite sign. $Zn_{(s)} \rightleftharpoons Zn^{2+}_{(aq)} + 2e^-$
6.	S.Q	<b>Electromotive force (emf):</b> 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). It measures the tendency of the cell reaction to take place. <b>Calculation of emf of a Cell:</b> Let us find the emf or cell potential of Daniel cell. The half-cell reactions are: $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^- \quad (\text{Oxidation half})$ $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)} \quad (\text{Reduction half})$ 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 $E^{\circ}_{cell} = E^{\circ}_{oxi} + E^{\circ}_{red}$ $= 0.76V + 0.34V$ $= 1.10V$
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. $M \rightarrow M^+ + 1e^- \quad (\text{Oxidation})$ $2H^+ + 2e^- \rightarrow H_2 \quad (\text{Reduction})$ 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. $Na \rightarrow Na^+ + 1e^- \quad E^{\circ}_{oxi} = 2.714 \text{ volt}$ $K \rightarrow K^+ + 1e^- \quad E^{\circ}_{oxi} = 2.925 \text{ volt}$ 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. $Cu \rightarrow Cu^{2+} + 2e^- \quad E^{\circ}_{oxi} = -0.34 \text{ volt}$ 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
- V.** Which of the following half-reactions represents a reduction process?  
 a)  $Zn_{(s)} \rightarrow Zn_{(aq)}^{2+} + 2e^-$       b)  $Fe_{(aq)}^{2+} \rightarrow Fe_{(aq)}^{3+} + e^-$       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)  $Cu_{(aq)}^+ + 2e^- \rightarrow Cu_{(s)}$       b)  $Cu_{(aq)}^+ + e^- \rightarrow Cu_{(s)}$       c)  $Cu_{(aq)}^+ \rightarrow Cu_{(aq)}^{2+} + e^-$       d)  $2Cu_{(aq)}^+ \rightarrow Cu_{(aq)}^{2+} + Cu_{(s)}$
- 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 ( $E^\circ$ ) 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).
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 $E^\circ$ 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 ( $E_{cell}^\circ$ ). A positive  $E_{cell}^\circ$  indicates a spontaneous reaction, while a negative  $E_{cell}^\circ$  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<sup>+</sup> ions. Therefore, water is reduced to hydrogen gas instead of Na<sup>+</sup> being reduced to Na metal.

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

(i) CrCl<sub>3</sub>                      (ii) Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>                      (iii) Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>

Ans. Oxidation Number of Chromium (Cr)

(i) CrCl<sub>3</sub>:

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<sub>3</sub>.

(ii) Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>:

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<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.

(iii) Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>:

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<sub>2</sub>O<sub>7</sub><sup>2-</sup>.

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:



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<sup>+</sup> ions (reducing them to H<sub>2</sub> 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<sup>+</sup> ions, so they do not displace hydrogen from acids.

In short, electrochemical reactivity (position in the series) determines whether a metal can reduce H<sup>+</sup> to H<sub>2</sub>.

i. Calculate the number of Faradays required to deposit 108 g of Ag<sup>+</sup>, 63.5 g of Cu<sup>2+</sup> and 27 g of Al<sup>3+</sup>.

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<sup>+</sup> (Silver)

Molar mass (Ag) = 108 g/mol

Valency (n) = 1

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

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

2. For 63.5 g of Cu<sup>2+</sup> (Copper)

Molar mass (Cu) = 63.5 g/mol

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 Al<sup>3+</sup> (Aluminum)

Molar mass (Al) = 27 g/mol

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<sup>+</sup> (108 g): 1 Faraday

• Cu<sup>2+</sup> (63.5 g): 2 Faradays

• Al<sup>3+</sup> (27 g): 3 Faradays

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

j. In an electrolysis experiment, a current of 0.500 A was passed through a solution of AgNO<sub>3</sub> 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<sup>-1</sup> and the charge on a silver ion is +1. Calculate the value of Avogadro's number (N<sub>A</sub>) from this data.

Ans. Given Data:

Current (I) = 0.500 A

Time (t) = 30.0 minutes = 1800 seconds

Mass of Ag deposited (m) = 0.503 g

Molar mass of Ag (M) = 107.87 g mol<sup>-1</sup>

Charge on Ag<sup>+</sup> 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<sup>+</sup> + e<sup>-</sup> → Ag, 1 mole of Ag requires 1 mole of electrons (1 Faraday = 96,485 C).

Total charge required for  $4.663 \times 10^{-3}$  mol Ag:

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

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

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

Step 4: Calculate Avogadro's number ( $N_A$ )

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

$$N_A = \frac{F}{e} = \frac{1.930 \times 10^5}{1.602 \times 10^{-19}} = 1.20 \times 10^{24}$$

Final Answer:  $N_A = 1.20 \times 10^{24} \text{ mol}^{-1}$

(Note: Due to error in statement of Question the answer comes  $1.20 \times 10^{24}$  molecules, however it should be  $6.02 \times 10^{23}$ ).

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

- Identify which metal will be the anode and which will be the cathode. Justify your answer.
- Write the balanced overall cell reaction.
- Calculate the standard cell potential ( $E^\circ_{\text{cell}}$ ).

Solution:

i) Identifying Anode and Cathode

• Standard Reduction Potentials ( $E^\circ$ ):



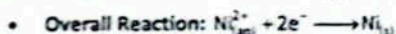
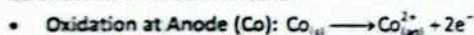
• Comparison:

- Nickel has a less negative (higher) reduction potential than cobalt.
- Cathode (Reduction): The electrode with the higher reduction potential ( $\text{Ni}^{2+}/\text{Ni}$ ).
- Anode (Oxidation): The electrode with the lower reduction potential ( $\text{Co}^{2+}/\text{Co}$ ), where oxidation occurs.

Reason:

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

ii) Balanced Overall Cell Reaction



iii) Standard Cell Potential ( $E^\circ_{\text{cell}}$ )

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

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

- The positive  $E^\circ_{\text{cell}}$  confirms the reaction is spontaneous.
- Cobalt (anode) dissolves, while nickel (cathode) deposits.

Final Answers:

- Anode:  $\text{Co}_{(\text{s})}$  (oxidation)      ii)  $\text{Ni}_{(\text{aq})}^{2+} + \text{Co}_{(\text{s})} \rightarrow \text{Ni}_{(\text{s})} + \text{Co}_{(\text{aq})}^{2+}$       iii)  $E^\circ_{\text{cell}} = +0.03 \text{ V}$   
Cathode:  $\text{Ni}_{(\text{aq})}^{2+}$  (reduction)

## 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  $0.010 \text{ mol dm}^{-3}$  solution of zinc sulfate ( $\text{ZnSO}_4$ ) at 298 K. The standard electrode potential ( $E^\circ$ ) for  $\text{Zn}_{(\text{aq})}^{2+} + 2e^- \rightleftharpoons \text{Zn}_{(\text{s})}$  is  $-0.76 \text{ V}$ . (Gas constant,  $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ , Faraday constant,  $F = 96500 \text{ C mol}^{-1}$ )

Given Data:

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

Nernst Equation:

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

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

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

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

Substitute Values

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

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

$$E = -0.76 + 0.0591$$

$$E = -0.7009 \text{ V}$$

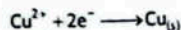
Final Answer:

$$E = -0.70 \text{ V}$$

**Q.8** A constant current of 2.00 A is passed through a solution of copper(II) sulfate ( $\text{CuSO}_4$ ) for 30.0 minutes. Calculate the mass of copper deposited at the cathode. (Molar mass of  $\text{Cu} = 63.5 \text{ g mol}^{-1}$ , Faraday constant,  $F = 96500 \text{ C mol}^{-1}$ )

Given Data:

Current ( $I$ ) = 2.00 A  
 Time ( $t$ ) = 30.0 minutes = 1800 seconds  
 Molar mass of  $\text{Cu} = 63.5 \text{ g mol}^{-1}$   
 Faraday constant ( $F$ ) = 96500  $\text{C mol}^{-1}$   
 Reaction at Cathode:



Step 1: Calculate Total Charge Passed ( $Q$ )

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

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

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

Final Answer: 1.18 g

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

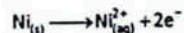
- Write the balanced overall cell reaction.
- Determine the standard electrode potential ( $E^\circ$ ) of the  $\text{Ni}^{2+}/\text{Ni}_{(s)}$  half-cell.
- Identify which electrode is the anode and which is the cathode.

Ans.

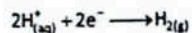
a) **Balanced Overall Cell Reaction**

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

Oxidation (Anode):



Reduction (Cathode):



Overall Reaction:



b) **Standard Electrode Potential ( $E^\circ$ ) of  $\text{Ni}^{2+}/\text{Ni}$**

Given Data:

$$\text{Measured } E_{\text{cell}} = 0.25 \text{ V}$$

SHE reference potential:

$$E_{\text{H}^+/\text{H}_2}^\circ = 0 \text{ V}$$

Using

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

$$0.25 = 0 - E_{\text{Ni}^{2+}/\text{Ni}}^\circ$$

$$E_{\text{Ni}^{2+}/\text{Ni}}^\circ = -0.25 \text{ V}$$

d) **Anode and Cathode Identification**

- Anode (Negative terminal):  $\text{Ni}_{(s)}$  (oxidation).
- Cathode (Positive terminal): SHE (reduction).

### ADDITIONAL SLOs BASED MCQs

- By electrolysis of brine solution which of the following is deposited at anode?  
 A.  $\text{H}_2$  B.  $\text{Cl}_2$  C.  $\text{O}_2$  D. Na
- Which of the following is reducing agent?  
 A.  $\text{KMnO}_4$  B. HI C.  $\text{K}_2\text{Cr}_2\text{O}_7$  D.  $\text{H}_2\text{SO}_4$
- The oxidation number of Mn in potassium manganate is:  
 A. +7 B. +6 C. +5 D. +2
- 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
- In the extraction of Al by electrolysis. Why it is necessary to dissolve  $\text{Al}_2\text{O}_3$  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  $\text{Al}_2\text{O}_3$  to form ions D. Molten  $\text{Al}_2\text{O}_3$  would not conduct electricity
- 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
- 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 lightens in colour
- Which is not a galvanic cell?  
 A. Daniel cell B. NICAD C. Fuel cell D. Dry Cell
- Voltage of silver oxide battery is:  
 A. 1.5V B. 1.8V C. 2V D. 2.2
- 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
- The following standard half cells are connected  

$$\text{Cd}_{(aq)}^{2+} + 2e^- \rightleftharpoons \text{Cd}_{(s)} E_{\text{red}}^\circ = -0.40 \text{ V}$$

$$\text{Ag}_{(aq)}^+ + e^- \rightleftharpoons \text{Ag}_{(s)} E_{\text{red}}^\circ = +0.80 \text{ V}$$
 What is cell potential of the Cd electrode relative to the Ag electrode?  
 A. -2.0V B. -0.04V C. +1.2V D. +0.40V
- 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
- The cell reaction  $\text{Zn} + \text{Cu}^{2+}_{(aq)} \rightarrow \text{Zn}^{2+}_{(aq)} + \text{Cu}$ , is best represented by:  
 A.  $\text{Cu}|\text{Cu}^{2+}||\text{Zn}^{2+}|\text{Zn}$  B.  $\text{Pt}|\text{Zn}^{2+}||\text{Cu}^{2+}|\text{Cu}$  C.  $\text{Zn}|\text{Zn}^{2+}||\text{Cu}^{2+}|\text{Cu}$  D.  $\text{Zn}|\text{Cu}^{2+}||\text{Zn}^{2+}|\text{Cu}$
- 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
- 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 <sup>-</sup> and OH <sup>-</sup> are present at anode according to E.C series OH <sup>-</sup> should oxidize to give O <sub>2</sub> but to high conc. Cl <sup>-</sup> is oxidized to give Cl <sub>2</sub> at anode.
2.	B	Among the following the reducing agent is HI.
3.	B	The oxidation number of Mn in K <sub>2</sub> MnO <sub>4</sub> 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 <sub>2</sub> O <sub>3</sub> 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 lightens 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 +0.80 + 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 <sup>2+</sup>    Cu <sup>2+</sup>  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 e <sup>-</sup> 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 dissolved 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<sup>3</sup>. The minimum level of DO should be 5 mg/dm<sup>3</sup>. Below 5 mg/dm<sup>3</sup>, 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.

Q.3 What is the principle of photovoltaic cell?

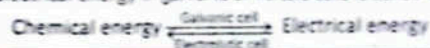
Ans. Principle of Photovoltaic Cells

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 semiconductor, 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."



Q.5 Differences between oxidizing agent and reducing Agent.

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 <sub>4</sub> /H <sub>2</sub> SO <sub>4</sub> , K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> /H <sub>2</sub> SO <sub>4</sub> , HNO <sub>3</sub> , Cl <sub>2</sub> , Br <sub>2</sub> etc.	(iii) The reducing agent lose electrons and its oxidation number is increased. e.g., FeSO <sub>4</sub> , HI, SO <sub>2</sub> , 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<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. (ii) Oxidation of P is +5 in Na<sub>3</sub>PO<sub>4</sub>.

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

Oxidation	Reduction
"Addition of oxygen or removal of hydrogen is called oxidation"	"Addition of hydrogen or removal of oxygen is called reduction"
<ul style="list-style-type: none"> <li>Loss of electron and hence increase in oxidation number is called oxidation. e.g., Zn → Zn<sup>2+</sup> + 2e<sup>-</sup></li> <li>In electrochemical cells oxidation takes place at anode.</li> </ul>	<ul style="list-style-type: none"> <li>Gain of electron and hence decrease in oxidation number is called reduction. e.g., Cu<sup>2+</sup> + 2e<sup>-</sup> → Cu</li> <li>In electrochemical cells reduction takes place at cathode.</li> </ul>

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<sub>2</sub><sup>(-1)</sup>O<sup>(-1)</sup>.

In superoxide it has -1/2 oxidation state e.g. K<sup>(+1)</sup>O<sup>(-1/2)</sup>.

Q.9 Calculate the oxidation number of underlined elements: HNO<sub>3</sub>; CrO<sub>3</sub>

Ans. HNO<sub>3</sub>

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  $\text{HNO}_3$ .

$\text{Cr}_2\text{O}_3$

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  $\text{Cr}_2\text{O}_3$ .

**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  $E^\circ$ .

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  $\text{Zn}^{+2}$  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



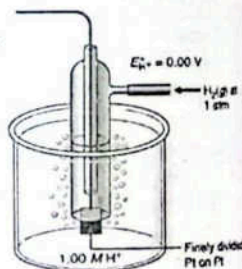
**Q.13 What is Standard Hydrogen Electrode (SHE)? Explain with the help of diagram.**

**Ans. Standard Hydrogen Electrode (SHE):**

A standard hydrogen electrode consists of a piece of platinum foil, coated with a layer of finely divided platinum black (to give it a large surface area) and is connected with a platinum wire. It is immersed in 1 M HCl solution. Pure  $\text{H}_2$  gas at one atmospheric pressure is continuously bubbled into 1 M HCl 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.

$$E^\circ = 0.00 \text{ V}$$



**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.



**SELF-ASSESSMENT Chapter # 10**Total Mark: 30  
(1 × 6 = 6)**Q.1** Encircle the correct option.

- (i) Which of the following half-reactions represents a reduction process?  
A.  $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$  B.  $Fe^{3+}_{(aq)} \rightarrow Fe^{2+}_{(aq)} + e^-$  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 Winkler'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  $Ag^+$ , 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  $0.010 \text{ mol dm}^{-3}$  solution of zinc sulfate ( $ZnSO_4$ ) at 298 K. The standard electrode potential ( $E^\circ$ ) for  $Zn^{2+} + 2e^- \rightleftharpoons Zn$  is  $-0.76 \text{ V}$ . (Gas constant,  $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ , Faraday constant,  $F = 96500 \text{ C mol}^{-1}$ )

**HYDROCARBONS****Student Learning Outcomes**

After studying this chapter, students will be able to:

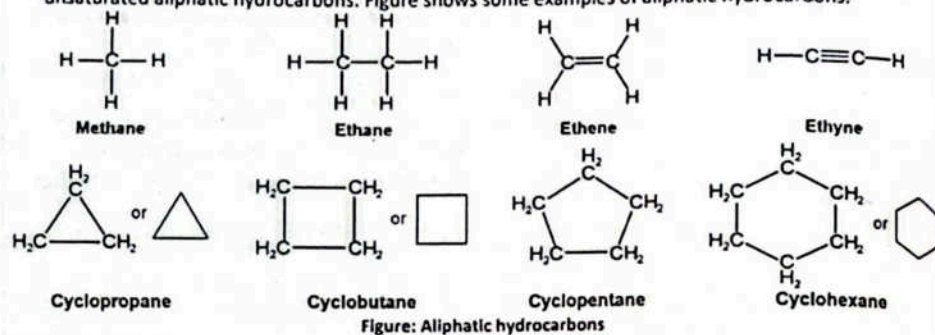
- Classify hydrocarbons as aliphatic and aromatic. (Understanding)
- Describe the nomenclature of alkanes and cycloalkanes. (Understanding)
- Explain the shapes of alkanes and cycloalkanes exemplified by ethane and cyclopropane. (Understanding)
- Explain the unreactive nature of alkanes towards polar reagents. (Understanding)
- Define homolytic and heterolytic fission, free radical initiation, propagation and termination. (Understanding)
- Describe the mechanism of free radical substitution in alkanes exemplified by methane and ethane. (Understanding)
- Identify organic redox reactions. (Understanding)
- Explain the nomenclature of alkenes. (Understanding)
- Explain the shape of the ethene molecule in terms of s and p C–C bonds. (Understanding)
- Describe the structure and reactivity of alkenes as exemplified by ethene. (Understanding)
- Explain with suitable examples the terms isomerism, stereoisomerism, and structural isomerism. (Understanding)
- Explain the dehydration of alcohols and dehydrohalogenation of RX for the preparation of ethene. (Understanding)
- Describe the chemistry of alkenes by the following reactions of ethene: hydrogenation, hydrohalogenation, hydration, halogenation, halo hydration, epoxidation, ozonolysis, and polymerization. (Understanding)
- Explain the concept of conjugation in alkenes having alternate double bonds. (Understanding)
- Describe the mechanism of electrophilic addition in alkenes, using bromine/ ethene and hydrogen bromide propene as examples. (Understanding)
- Use the IUPAC naming system for alkenes. (Understanding)
- Explain the inductive effects of alkyl groups on the stability of primary, secondary and tertiary cations formed during electrophilic addition (this should be used to explain Markovnikov addition). (Understanding)

- Hydrocarbons is a class of organic compounds that consists of only carbon and hydrogen. Hydrocarbons are abundantly found in petroleum and natural gas.
- Uses of Hydrocarbons:** They are frequently used as domestic and industrial fuels. Generally, hydrocarbons have many synthetic applications.
- Unsaturated hydrocarbons**, especially alkenes, are used as the starting materials for a number of industrial products. Most of the products in the form of medicines, plastics, perfumes, polymers have their origins in hydrocarbons.
- Classification:** Hydrocarbons are broadly divided into two classes:
  - Aliphatic hydrocarbons
  - Aromatic hydrocarbons

### ALIPHATIC AND AROMATIC HYDROCARBONS

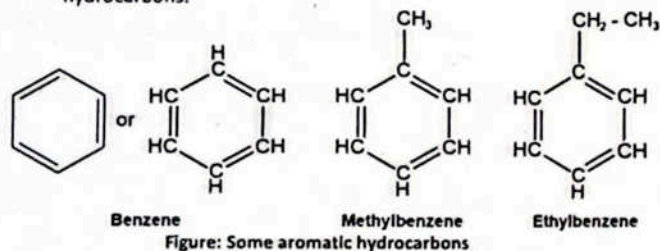
#### Aliphatic Hydrocarbons

The compounds that are not aromatic are called aliphatic hydrocarbons. Aliphatic compounds may be open chain and cyclic, also they may be saturated or unsaturated. If there are only carbon and hydrogen atoms in an aliphatic compound, it is called aliphatic hydrocarbon. Alkanes are acyclic aliphatic hydrocarbons, whereas cycloalkanes are cyclic aliphatic hydrocarbons. Alkenes and alkynes are acyclic and unsaturated aliphatic hydrocarbons. Figure shows some examples of aliphatic hydrocarbons.



#### Aromatic Hydrocarbons

Aromatic hydrocarbons is a special class of cyclic hydrocarbons that have high carbon to hydrogen ratio and are based on benzene ( $C_6H_6$ ) or resembling compounds. Benzene is the basic aromatic compound and other compounds such as toluene and phenol are its derivatives. Figure presents the structures of some aromatic hydrocarbons.



#### Rack Your Mind!

1. Methyl benzene is also called:  
 A) Xylene B) Toluene  
 C) Cyclohexane D) n-heptane

#### Interesting Information

The term aromatic was derived from the Greek word 'aroma' meaning 'fragrant' and is used in organic chemistry for a special class of compounds (aromatic compounds) having characteristic odour.

### NOMENCLATURE

#### Alkanes or Paraffins (Latin Parum-Little, affins = affinity)

Alkanes are saturated hydrocarbons with the general formula  $C_nH_{2n+2}$ . Methane ( $CH_4$ ) is the simplest member of this family. The homologous series of alkanes with condensed structural formulae and molecular formulae are shown in Table.

Table: Condensed structural formulae and molecular formulae of alkanes

IUPAC Name	Molecular formula	Condensed structure
Methane	$CH_4$	$CH_4$
Ethane	$C_2H_6$	$CH_3CH_3$
Propane	$C_3H_8$	$CH_3CH_2CH_3$
Butane	$C_4H_{10}$	$CH_3CH_2CH_2CH_3$
Pentane	$C_5H_{12}$	$CH_3CH_2CH_2CH_2CH_3$
Hexane	$C_6H_{14}$	$CH_3CH_2CH_2CH_2CH_2CH_3$
Heptane	$C_7H_{16}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$
Octane	$C_8H_{18}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
Nonane	$C_9H_{20}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
Decane	$C_{10}H_{22}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

#### Did You Know?

Butane is a fuel used in lighters. Isobutane is used as a propellant in products such as shaving gel.

#### Alkyl Group:

The group obtained after the removal of one hydrogen atom from an alkane is called an alkyl group. The resulting alkyl groups are named by replacing -ane of the alkanes with -yl. Few examples are shown in Table 2 & Table 3.

Table: alkyl groups, their names and abbreviations

Alkane	Alkyl group	Abbreviation
$CH_4$ Methane	$CH_3$ - Methyl	Me-
$CH_3 - CH_3$ Ethane	$CH_3 - CH_2$ - Ethyl	Et-

For alkanes with more than two carbon atoms, more than one alkyl groups can be derived.

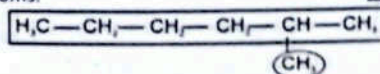
Table: Alkyl groups, straight chain and branched and their names

Alkane	Possible Alkyl Groups			
$CH_3CH_2CH_3$ Propane	$CH_3CH_2CH_2-$ n-Propyl group (Propyl)		$CH_3CHCH_3$ isoPropyl group (1-Methylethyl)	
$H_3CH_2CH_2CH_3$	$CH_3CH_2CH_2CH_2-$ n-Butyl group (Butyl)	$CH_3CH_2CHCH_3$ sec-Butyl group (1-Methylpropyl)	$CH_3CHCH_2-$   $CH_3$ IsoButyl group (2-Methylpropyl)	$H_3C-C-CH_3$   $CH_3$ tert-Butyl group (1,1-Dimethylpropyl)

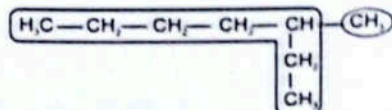
### Nomenclature of Alkanes

Branched chain alkanes are named according to the following rules.

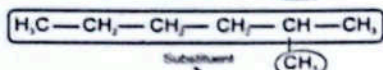
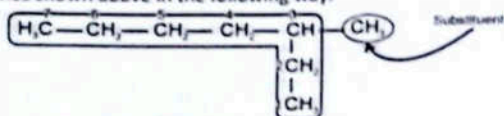
1. Locate the longest continuous chain of carbon atoms; this chain determines the parent name for the alkane. We designate the following compound as a hexane because the longest continuous chain contains six carbon atoms.



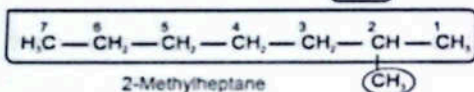
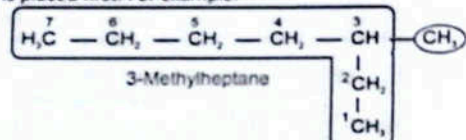
The longest continuous chain may not always be obvious from the way the formula is written. Notice, for example, that the following alkane is designated as a heptane because the longest chain contains seven carbon atoms.



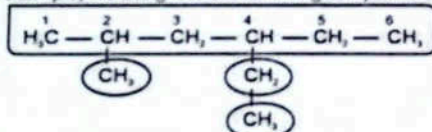
2. Number the longest chain beginning from the end nearest to the substituent. Applying this rule, we number the two alkanes shown above in the following way.



3. Use the numbers obtained by the application of rule 2 to designate the location of the substituent group. The parent name is placed last, and the substituent group, preceded by the number designating its location on the chain, is placed first. For example:



4. When two or more substituents are present, give each substituent a number corresponding to its location on the longest chain. For example, we designate the following compound as 4-Ethyl-2-methylhexane.



4-Ethyl-2-methylhexane

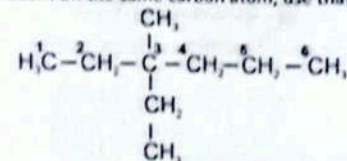
The substituent groups should be listed alphabetically (i.e. ethyl before methyl). While deciding on alphabetical order ignored multiplying prefixes such as "di" and "tri".

### Rack Your Mind!

2. Write down names of the following compounds according to IUPAC system.

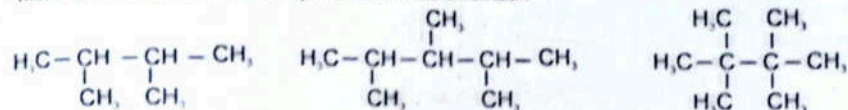
- (a)  $(\text{CH}_3\text{CH}_2)_3\text{CH}$  (b)  $(\text{C}_6\text{H}_5)_3\text{CH}$

5. When two substituents are present on the same carbon atom, use that number twice.



3-Ethyl-3-methylhexane

6. When two or more substituents are identical, indicate this by the prefixes di, tri, tetra, and so on. Then make certain that each and every substituent has a number.



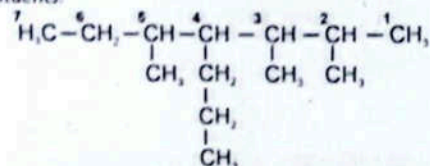
2,3-Dimethylbutane

2,3,4-Trimethylpentane

2,2,3,3-Tetramethylbutane

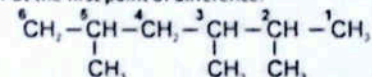
Application of these six rules allows us to name most of the alkanes that we shall encounter. Two other rules, however, may be required occasionally.

7. When two chains of equal length compete for selection as the parent chain, choose the chain with the greater number of substituents.



2,3,5-Trimethyl-4-n-propylheptane

8. When branching first occurs at an equal distance from either end of the longest chain, choose the name that gives the lower number at the first point of difference.



2,3,5-Trimethylhexane (not 2,4,5-Trimethylhexane)

### Nomenclature of Cycloalkanes

Cycloalkanes are named by attaching the prefix 'cyclo' to the names of the alkanes possessing the same number of carbon atoms. Figure 11.3

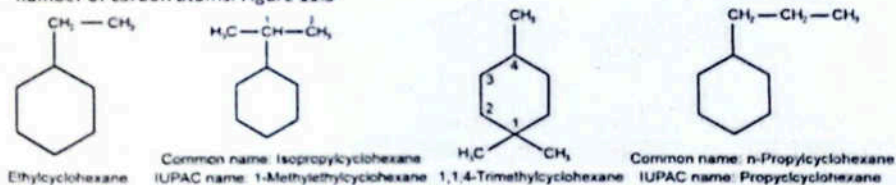
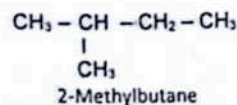


Figure: Naming cycloalkanes

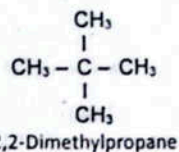
 QUICK CHECK 11.1

a) Write down the structural formulas for 2-methylbutane and 2,2-dimethylpropane.

Ans. 2-Methylbutane (Isopentane)

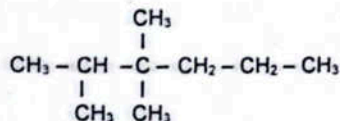


2,2-Dimethylpropane (Neopentane)

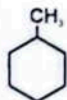


b) Write down displayed formula of 2,3,3-trimethylhexane and methylcyclohexane.

Ans. 2,3,3-trimethylhexane



Methylcyclohexane



c) Give two differences between molecules of cyclopentane and pentane?

Ans.

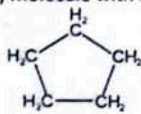
1. Chemical Formulas

Cyclopentane:  $\text{C}_5\text{H}_{10}$ , Pentane:  $\text{C}_5\text{H}_{12}$

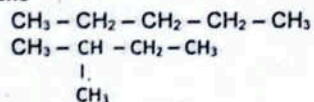
Pentane has two hydrogen atom more than cyclopentane.

2. Structure

Cyclopentane: It is a cyclic (ring-shaped) molecule with five carbon atoms forming a closed ring.



3. Pentane



A pentane is a straight chain or branched molecule.

d) Eicosane is a straight chain alkane whose molecules contain 20 carbon atoms. What is the molecular formula of eicosane?

Ans. The molecular formula of eicosane (a straight-chain alkane with 20 carbon atoms) is:



Explanation:

General formula for alkanes:  $\text{C}_n\text{H}_{2n+2}$

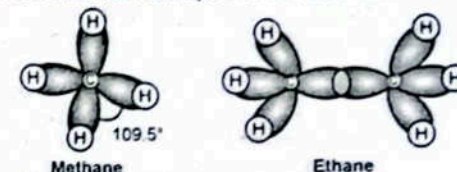
For  $n = 20$ :

$$\text{H} = (2 \times 20) + 2 = 42$$

## Shapes of Alkanes and Cycloalkanes

The carbon atom in an alkane has four  $sp^3$  hybridized orbitals and forms four single bonds that are equidistant from each other. Alkane molecules have a tetrahedral shape around carbon atoms. Carbon atoms in alkane molecules form sigma bonds with surrounding carbon and hydrogen atoms.

As a result, carbon atoms in alkanes are surrounded by 4 pairs of bonding electrons which equally repel each other to form  $109.5^\circ$  bond angles and a C-C bond length of  $1.54 \text{ \AA}$ . The shapes of organic molecules are generally represented using ball and stick formula. The shapes of some straight chain alkanes

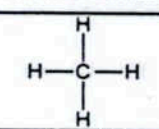
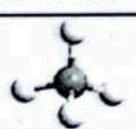
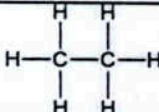
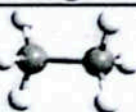
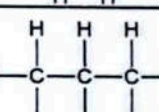
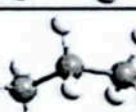
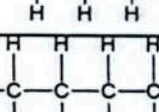



Methane  
 $sp^3$  hybrid tetrahedral

Ethane

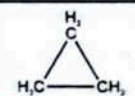

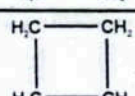
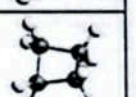
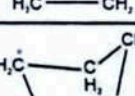
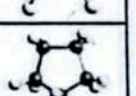
Figure:  $sp^3$  hybridised methane and ethane are shown (Table).

Table: Shapes of some straight chain alkanes

IUPAC name & Molecular Formula	Structural Formula	3D Structure
Methane $\text{CH}_4$		
Ethane $\text{C}_2\text{H}_6$		
Propane $\text{C}_3\text{H}_8$		
Butane $\text{C}_4\text{H}_{10}$		

Cycloalkanes are cyclic, meaning that the carbon atoms of the molecule are arranged in the form of a ring. Cycloalkanes are also saturated, meaning that all of the carbon atoms that make up the ring are singly bonded to other atoms. The structural shapes of cyclopropane, cyclobutane and cyclopentane are shown below (Table)

Table: Shapes of few cycloalkanes

IUPAC name & Molecular formula	Structural formula	3D Structure
Cyclopropane $\text{C}_3\text{H}_6$		
Cyclobutane $\text{C}_4\text{H}_8$		
Cyclopentane $\text{C}_5\text{H}_{10}$		

### Physical Properties of Alkanes

#### 1. Physical State:

Alkanes containing upto four carbon atoms are colourless, odourless, gases while pentane to heptadecane ( $C_5$  to  $C_{17}$ ) are colourless, odourless liquids. The higher members from  $C_{18}$  onwards are waxy solids which are also colourless and odourless.

#### 2. Non-Polarity and Solubility:

Alkanes are non-polar or very weakly polar and are insoluble in polar solvents like water, but soluble in non-polar solvents, such as hexane, benzene, ether, etc.

#### 3. Effect of Increase in Number of C-atoms on Physical Constants:

Their physical constants, e.g. boiling points, melting points, density, etc. increase with the increase in number of carbon atoms, whereas solubility decreases with the increase in molecular mass. The boiling points of alkanes having branched chain structures are lower than their isomeric normal chain alkanes.  
normal > iso > neo

e.g., straight chain butane has a higher boiling point  $-0.50^\circ\text{C}$  than 2-Methylpropane (isobutane,  $-11.7^\circ\text{C}$ )

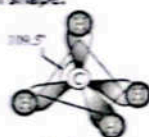
#### QUICK CHECK 11.2

a) Why do branched alkanes have lower boiling points than the straight-chain alkanes?

Ans. The straight chain alkanes have greater polarizability and greater inter molecular forces than the branched chain alkanes. e.g., Boiling points of

n-pentane	isopentane	neopentane
309K	301K	283K

b) Explain why alkanes have a tetrahedral shape.



Methane

- Tetrahedral symmetry ensures maximum separation of bonds, minimizing electron repulsion.
- Free rotation around C-C single bonds allows flexible conformations.

c) Draw the shapes of cyclopropane and cyclopentane.

Ans. Cyclopropane,



Cyclopentane



### REACTION MECHANISM AND MODES OF BOND BREAKING

Reaction mechanism is the series of steps that take place in the course of the overall reaction. Like all chemical reactions, organic reactions involve the breaking of chemical bonds. There are two ways in which covalent bonds can break.

#### (a) Homolytic Fission (Homolysis)

Homolytic fission occurs when the covalent bond breaks evenly to produce free radicals. Free Radical is a species that contains an unpaired electron and is very reactive. Free radicals are extremely reactive because of the tendency of unpaired electrons to become paired.

#### Homolytic Cleavage

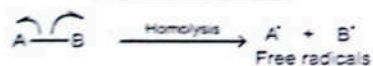


Figure: Homolytic fission and free radical formation

#### (b) Heterolytic Fission (Heterolysis)

Heterolytic fission occurs when the covalent bond breaks in such a way that the originally shared pair of electrons is gained by one atom only and oppositely charged ions are produced. This bond fission is shown by full curly arrows in mechanisms.

#### Heterolytic cleavage

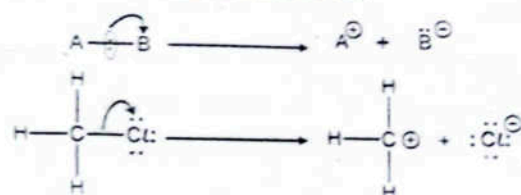


Figure: Heterolytic fission and formation of radical ions

### UNREACTIVE NATURE OF ALKANES TOWARDS POLAR REAGENTS

The alkanes or paraffins (Latin: parum = little, affinis = affinity) are inert towards acids, alkalis, oxidizing and reducing agents under ordinary condition.

#### (i) Non-Polar Nature

The lack of reactivity of alkanes under normal conditions may be explained on the basis of the non-polarity of the bonds forming them. The electronegativity values of carbon (2.5) and hydrogen (2.1) do not differ appreciably and the bonding electrons between C-H and C-C are equally shared making them almost non-polar and generally unreactive.

#### (ii) Inertness of a Sigma Bond

The unreactive nature of alkanes can also be explained on the basis of inertness of a sigma bond. In a sigma bond the electrons are very tightly held between the nuclei which makes it a very stable bond. A lot of energy is required to break it. e.g., C-H bond energy is about 412 kJ/mol.

#### Did You Know?

Hydrocarbon combustion produces  $\text{CO}_2$ , a greenhouse gas contributing to climate change. Incomplete combustion can release carbon monoxide (CO) and particulate matter, which have serious health and environmental consequences.

### REACTIONS OF ALKANES

Under high temperature or suitable conditions, alkanes undergo two types of reactions.

- Thermal and Catalytic Reactions. e.g., Combustion and cracking
- Free radical substitution reactions are the reactions that involve replacement of one atom, or group of atoms by another through the free radical mechanism.

(Exercise 11.3)

Q. Describe the free radical halogenation of methane using  $\text{Cl}_2$  as an example.

#### Free radical Substitution Reactions

Substitution reactions of alkanes take place in the presence of light energy through the formation of highly reactive free radicals.

The extent of halogenation of alkanes depends upon the concentration of  $\text{X}_2$  used.

#### Example:

##### Halogenation:

- The substitution of a halogen atom with a hydrogen of an alkane, called halogenation.
- With Chlorine and Bromine: Alkanes react with chlorine and bromine in the presence of sunlight or UV light resulting in the successive replacement of hydrogen atoms with halogens.

- **With Fluorine:** Reaction of alkanes with fluorine is highly violent and results in a mixture of carbon, fluorinated alkanes and hydrofluoric acid.
- **With Iodine:** Iodine does not substitute directly because the reaction is too slow and reversible.
- The extent of halogenation depends upon the amount of halogen used.
- **Order of Reactivity:** The order of reactivity of halogens is:  
 $F_2 > Cl_2 > Br_2 > I_2$

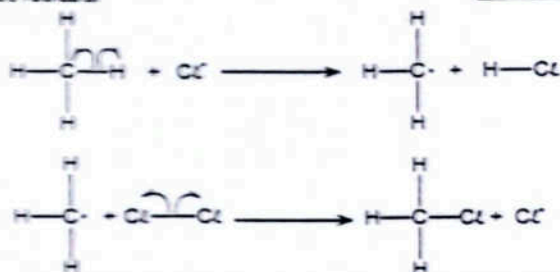
#### Free Radical Substitution Mechanism of Alkanes:

Halogenation involves the following three steps.

- (i) **Initiation step** is the first step in the mechanism of free radical substitution of alkanes by halogens. It involves the breaking of the halogen-halogen bond using energy from the UV light. It is homolytic fission.



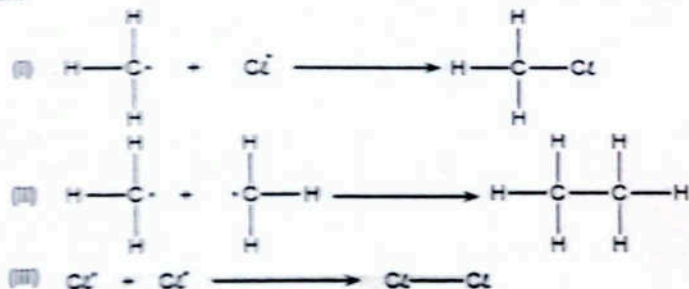
- (ii) **Propagation step** is the second step in the free radical substitution in which the initially formed radicals attack the alkane molecule generating more free radicals.



- (iii) **Termination step** is the final step in a free radical substitution in which two free radicals react together to form a product.

The termination step may take place in different ways. The chloride and alkyl radicals may combine to form a chloroalkane or two chloride radicals may also react to make the chlorine molecule.

Another termination mode is the formation of alkane with double number of carbon atoms which takes place when two alkyl radicals merge together. This type of termination is rare and the alkanes with double carbon atoms are formed in traces. However, its presence is evident of free radical substitution mechanism.



By repetition of step (ii), propagation step, a mixture of halogen substituted products (chloroalkanes) is obtained. The more the chlorine gas in reaction mixture to start with, the greater the proportions of chlorine atoms in the chloroalkane molecules formed.

#### MCQ

The slowest and rate determining step in halogenation of alkane is:

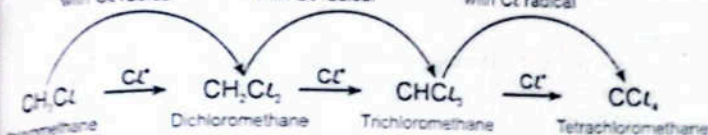
- (a) Initiation  
 (b) Propagation  
 (c) Termination  
 (d) Cannot be predicted

#### Smart Thinking

The final product obtained by heating  $\text{H}_3\text{C}-\text{CH}_3$  with excess of chlorine in the presence of sunlight is:

- (a) Monochloro ethane  
 (b) Dichloro ethane  
 (c) Tetrachloro ethane  
 (d) Hexachloro ethane

**Note:** Trichloromethane is also known as chloroform. Tetrachloromethane is also known as carbon tetrachloride and it is used as a non-polar inert solvent.



#### Interesting Information

Haloalkanes are anaesthetic in nature. The anesthetic power of a haloalkane increases with the number of halogen atoms. Use of these as organic solvents in lab is strictly monitored due to their toxic nature.

#### QUICK CHECK 11.3

- a) Explain why alkanes have high stability?  
 Ans. Stability of Alkanes is due to:
1. **Strong C-C and C-H Bonds:**  
High bond dissociation energies (e.g., C-C: 348 kJ/mol, C-H: 413 kJ/mol).
  2. **Nonpolar Bonds:**  
Electronegativity difference between C and H is negligible ( $\Delta EN = 0.4$ ), making them resistant to electrophilic/nucleophilic attacks.
  3. **Saturated Hydrocarbons:**  
Only single bonds ( $\sigma$ -bonds) with no reactive  $\pi$ -electrons (unlike alkenes/alkynes).
  4. **Tetrahedral Symmetry:**  
 $sp^3$  hybridization minimizes steric strain and electron repulsion.
  5. **Inertness to Common Reagents:**  
Unreactive toward acids, bases, and oxidizing agents at room temperature.
  6. **Combustion Requires High Energy:**  
Need strong ignition sources (e.g., heat/sparks) to break stable  $\sigma$ -bonds.
- Conclusion:** Stability arises from strong, nonpolar, single bonds and lack of functional groups.
- b) What are major types of reactions that alkanes undergo?  
 Ans.
1. **Combustion:**  
Burns in oxygen to form  $\text{CO}_2 + \text{H}_2\text{O} + \text{energy}$  (e.g., methane:  $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ ).
  2. **Halogenation (Free Radical Substitution):**  
Reacts with halogens ( $\text{Cl}_2/\text{Br}_2$ ) under UV light to form alkyl halides (e.g.,  $\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl}$ ).
  3. **Cracking (Thermal Decomposition):**  
Breaks into smaller alkanes/alkenes at high temperatures (e.g.,  $\text{C}_{10}\text{H}_{22} \rightarrow \text{C}_8\text{H}_{18} + \text{C}_2\text{H}_4$ ).
  4. **Isomerization:**  
Converts straight-chain alkanes to branched isomers (catalyzed by acids/metal catalysts).
  5. **Reforming:**  
Converts alkanes to cycloalkanes/aromatics (e.g., hexane  $\rightarrow$  benzene).
- Conclusion:** Alkanes are unreactive except under extreme conditions (heat/light).
- c) How the termination step occurs in the halogenation of alkenes?  
 Ans. See Free Radical Substitution Mechanism of Alkanes: (iii. Termination Step)
- d) State the conditions under which a mixture of halogenoalkanes is obtained from the halogenation of alkanes.  
 Ans. A mixture of halogenoalkanes is obtained during the halogenation of alkanes under the following conditions:
1. **Excess Alkane (Low Halogen Concentration)**  
Prevents complete substitution, yielding mono-, di-, tri-, etc., halogenated products.
  2. **Non-Selective Free Radical Mechanism**
    - Initiation:



