CHEMISTRY CHAPTER #2
ELECTRO-CHEMISTRY
E-NOTES

Electrochemistry: Branch of chemistry that deals with the study of interconversion of electrical energy to chemical energy or vice versa.

ELECTRICAL ENERGY → CHEMICAL ENERGY

OR

CHEMICAL ENERGY → ELECTRICAL ENERGY

REDOX REACTIONS: THE REACTIONS IN WHICH OXIDATION AND REDUCTION OCCUR SIMULTANEOUSLY ARE CALLED REDOX REACTIONS.

OXIDATION	***REDUCTION***
ADDITION OF OXYGEN	REMOVAL OF OXYGEN
REMOVAL OF H	ADDITION OF HYDROGEN
LOSS OF ELECTRON	GAIN OF ELECTRON
INCREASE IN BONDS WITH OXYGEN	DECREASE IN BOND WITH OXYGEN
DECREASE BONDS WITH HYDROGEN	INCREASE BONDS WITH HYDROGEN
INCREASE IN OXIDATION STATE	DECREASE IN OXIDATION STATE

EXAMPLE: $Zn + Cu^{+2} \longrightarrow Zn^{+2} + Cu$

EXAMPLE 2.2: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
ANS: $C^{-4} H_4^{(-1)4} + 2O_2 \rightarrow C^{+4}O_2^{(-2)2} + 2H_2^{+2(1)} O^{-2}$

Since CH_4 is a neutral atom, it has +4 on 4 Hydrogens and -4 on 1 Carbon. +4-4 = 0 thus charge is cancelled.

Carbon is oxidized as its oxidation state went from -4 to +4.

Oxygen is reduced as it went from 0 to -2.

Q: HOW TO FIND OXIDATION STATE OF AN UNKNOWN ATOM SUCH AS CHROMIUM?
IN THIS COMPOUND; $K_2Cr_2O_7$, we see that oxidation state of chromium is unknown thus we use x equation method,
$2(+1) + 2x + 7(-2) = 14$
$2x = 12$
$x = 6$
Thus we get the oxidation state of chromium as +6 on each of the atom.

Disproportion Reactions: In some redox reactions, the same element is reduced or oxidized simultaneously, we call these type of reactions “ Disproportion Reactions”.
EXAMPLE:
$H_2O_2 \rightarrow H_2O + ½O_2$
In the 1st part of the equation, The oxygen atom has the charge of -1 while in the second part the oxygen has the charge changed to -2
Also one oxygen atom had the charge of -1 in the first part of the equation but in the second part it's charged changed to 0

this shows that oxidation and reduction occurring at same time is disproportionation reactions.

CONCEPT 2.1:

1) $Cl_2 + 2NaOH \rightarrow NaCl + NaClO + H_2O$

In this equation a chlorine atom goes -1 charge from 0 in NaCl thus it is reduced, while another chlorine atom goes to +1 in NaClO from zero thus it is oxidized.

2) $4Fe + 3O_2 \rightarrow 2Fe_2O_3$

In this reaction oxidation and reduction occurs but with different elements which is a violation for the condition for disproportion reactions.

Verdict: It is not a disproportion reaction.

3) $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

In this reaction oxidation and reduction occurs but with different elements such as carbon and oxygen therefore it is also not a disproportion reaction.

EXAMPLE 2.3: EQUATION BALANCING USING OXIDATION STATES

$P + HNO_3 + H_2O \rightarrow H_3PO_4 + NO_2$

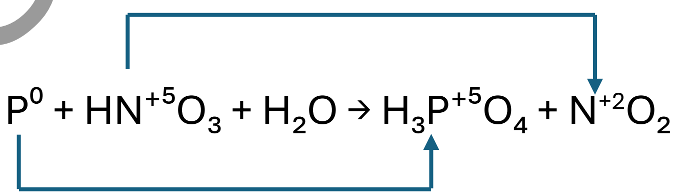
Step 1: Assign oxidation state

Step 2: Identify elements with changing oxidation states.

Nitrogen went from +5 to +2, which means it gained 3 electrons

Phosphorus went from zero to +5 means it got oxidized

Step 3: Draw the bridge:



$P^0 + HN^{+5}O_3 + H_2O \rightarrow H_3P^{+5}O_4 + N^{+2}O_2$

Step 4: multiply with such a digit that the gain and loss of electrons become equal.

5x3=15 FOR PHOSPHORUS

3x5=15 FOR NITROGEN

Now add the coefficients of these elements and balance the equation by inspecting H and O.

Final Equation:

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

CONCEPT ASSESSMENT 2.2:

$Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO + H_2O$

Step 1: Assign the oxidation state

$Cu^0 + HN^{+5}O_3 \rightarrow Cu^{+2}(NO_3)_2 + N^{+2}O + H_2O$

Step 2: Identify the change in oxidation state

Nitrogen went from a charge of +5 to a charge of +2, it got reduced while copper went from a charge of 0 to a charge of +2 thus it got oxidized.

Balance the loss and gain of electrons

2x3=6e

3x2=6e

Add coefficients and balance the rest equation by inspection method.

Balanced equation:

$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

EXAMPLE 2.4:

Construct a redox equation by this half reaction.

Reduction Half Reaction: $Cr_2O_7 \rightarrow Cr^{+3}$

Oxidation Half Reaction: $H_2SO_3 \rightarrow HSO_4$

Step 1: Balance both reactions without balancing hydrogen and oxygen.

$Cr_2O_7 \rightarrow 2Cr^{+3}$

$H_2SO_3 \rightarrow HSO_4^-$

Step 2: Balance Oxygen by adding H2O

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

$H_2SO_3 + H_2O \rightarrow HSO_4 + 3H^+$

Step 3: Charge Calculation:

On the left side of the equation the charge is +12 while on the right side the charge is +6 thus we still need to add 6e to the left side of the equation to balance the charge.

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

Now in the 2nd equation, the left side is balanced while right side has the charge of +2 thus we need to add 2e to balance.

$H_2SO_3 + H_2O \rightarrow HSO_4^- + 3H^+ + 2\bar{e}$

Step 4 : Add both equations and cancel out the charge by balancing it thus we see

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

$+\ H_2SO_3 + H_2O \rightarrow HSO_4^- + 3H^+ + 2\bar{e}$

Multiply eq 2 with 3 we get :

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

$+\ 3H_2SO_3 + 3H_2O \rightarrow 3HSO_4^- + 9H^+ + 6\bar{e}$

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

Step 5: Calculate net charge, if its equal equation is balanced

+3 → +6-3=5

3=3 BALANCEDD!!!

OXIDIZING AGENT :

Oxidizing agent is a compound or substance which gets itself reduced and oxidizes the other compound in a chemical reaction.

REDUCING AGENT:

A reducing agent is a substance which gets itself oxidized but reduces the other compound in a chemical reaction.

Example:

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

In this equation:

P goes from 0 to +5 gets oxidized (REDUCING AGENT)

While N goes from +5 to +2 gets reduced (OXIDIZING AGENT)

GALVANIC CELL / DANIEL CELL / VOLTAIC CELL:

Cell that converts chemical energy into electrical energy by the help of a spontaneous reaction is called 'Galvanic cell' or 'Daniel cell'.

CONSTRUCTION OF GALVANIC CELL:

When a zinc rod is dropped into copper sulfate solution zinc loses 2 electrons while copper gains 2 electrons to form copper metal.

REACTIONS OCCURING:

$Zn \rightarrow Zn^{2+} + 2e^-$

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

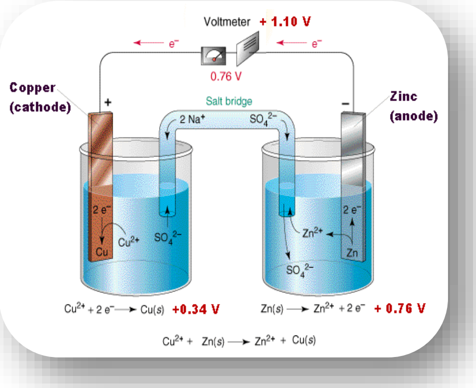
Since both are metals so both can be reduced thus we judge them from their reduction potential measured by comparing to Standard Hydrogen Electrode or SHE.

$Zn^{2+} \rightarrow Zn \quad E^o_{red} = -0.76$

$Cu^{2+} \rightarrow Cu \quad E^o_{red} = 0.34$

- Element with less reduction potential would be taken as anode to perform oxidation.
- Element with more reduction potential would be taken as cathode to perform reduction.
- Both electrodes are dipped in 1M conc solutions of their own acids like $ZnSO_4$ or $CuSO_4$.
- There a salt bridge is placed for electrical connection in between two cells.
- **SLO Question:** What would happen if salt bridge were removed? **Ans:** Electricity production would be stopped as ion concentration would be same. Salt bridge produces ion-difference to produce electricity or voltage.

Salt Bridge:



- It's U shaped.
- Filled with electrolyte/salt in gel form.
- **Its functions are:**
  (1) Electrical connection between 2 electrolytes.
  (2) Makes electricity with producing a difference in ions.
- When salt bridge is connected, anode starts losing e^- and becomes positive electrode. The e^- move from voltmeter to cathode and cathode gains $2e^-$.

- ***Reactions at Anode and Cathode:***

Anode:

$Zn(s) \rightarrow Zn^{+2} + 2e^-$

Cathode:

$2e^- + Cu^{+2}(aq) \rightarrow Cu(s)$

Overall Reaction:

$Zn(s) + Cu^{+2}(aq) \rightarrow Zn^{+2}(aq) + Cu(s)$

- ***Voltage Produced / EMF / Cell Potential*:**

$E°$ cell = $E°$ cathode − $E°$ anode
$E°$ cell = 0.34 − (−0.76)
$E°$ cell = **1V / 1.1V**

CELL POTENTIAL: The force with the electrons are pushed to flow through the wire from anode to cathode is called ‘Cell Potential’ or EMF. It’s measured in Volts (V).
EMF produced by cell is also cell potential.
$\mathcal{E}^o$ depends upon difference in the electrode potential between two connected half-cells at standard conditions.
(1atm,1M conc and 25C or 298K temperature) .

$$\mathcal{E}^o_{cell} = \mathcal{E}^o_{cathode} - \mathcal{E}^o_{anode}$$

- The cell potential has positive value for any spontaneous redox reaction.
- The half-cell reaction at 1 atm pressure, 1M concentration of electrolyte and 298K temperature is called “Standard Electrode Potential”.
- Since electrode potential cant be found by a voltmeter thus we need a standard electrode to compare the values of the electrode used, for this purpose we use Standard Hydrogen Electrode or SHE.

- In short Half cell potential = Electrode potential

STANDARD HYDROGEN ELECTRODE: Potential of a single electrode can't be just found with a voltmeter therefore we need a standard hydrogen electrode to find and compare the values. SHE has electrode potential of zero and it indicates about anode or cathode by measuring oxidizing or reducing potential.

- SHE is made up of platinum as it's inert or a noble metal and doesn't react easily.
- When SHE is reacted with an element whose reduction potential is greater (less oxidizing potential) then SHE is reduced.
- When SHE is reacted with an element whose oxidizing potential is greater (less reduction potential) then SHE is oxidized.

Q: Why H_2 gas is added in SHE?
A: To maintain the H^+ ion concentration in the solute where SHE is dipped in.

- ***Method to measure electrode potential:***
  SHE is the primary reference electrode used to measure the half cell potential of elements as it itself has a 0V potential initially.
- ***Consider Zn and Cu that are elements:***

- ***DETERMINING THE STANDARD ELECTRODE POTENTIAL OF Zn AND Cu:***
- The half cell of Zn is set up by Zn electrode dipped in an acidic electrolyte of Zn itself such as $ZnSO_4$ (1M).
- It's connected to SHE and a voltmeter is attached. SHE is made up of platinum rod dipped in HCl.
- Form a connection between electrolytes by a salt bridge.

- When they're connected, voltmeter shows deflection which indicates the current flow from Zn to H electrode.
- Zn loses 2ē to Hydrogen electrode.

Q: How we know Zn lost 2ē why no gained?
A: The voltmeter shows a positive reading and its being oxidized. The reading at the voltmeter shows a reading of +0.76V. We got oxidation potential of Zn.
By formula : $\mathcal{E}^{o}_{cell} = \mathcal{E}^{o}_{anode} + \mathcal{E}^{o}_{cathode}$
(this formula is only valid for electrode potentials)
$\mathcal{E}^{o}_{cathode} + \mathcal{E}^{o}_{anode}\ \mathcal{E}^{o}_{cell} =$
Since : $\mathcal{E}^{o}_{cathode} = 0$ and $\mathcal{E}^{o}_{cell} = +0.76V$ THEN:
$+0.76V = 0 + \mathcal{E}^{o}_{anode}$

$\mathcal{E}^{o}_{anode} = +0.76V$

How Cathode potential was 0?
SHE was the cathode gaining electrons and it has electrode potential of 0.

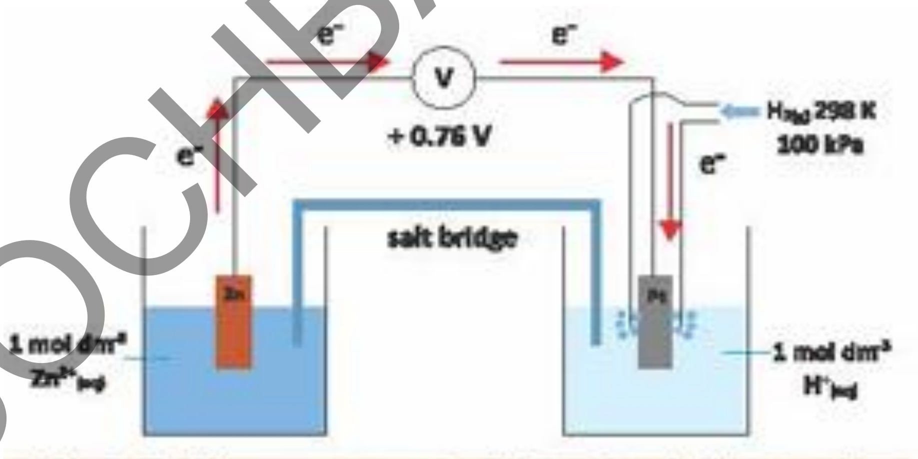


Fig 2.3: Measurement of Standard Electrode Potential of Zn/Zn²⁺ Electrode

Here we can see the whole process!!

DETERMINATION OF STANDARD ELECTRODE POTENTIAL OF Cu BY STANDARD HYDROGEN ELECTRODE:

We use the same setup, connect electrolytes through a salt bridge and attach a voltmeter, electrolyte is changed due to change in element, its $CuSO_4$. We see that Cu gains 2e from Hydrogen thus it acts as cathode while hydrogen acted as anode. Reading of voltmeter is +0.34V.
By formula: $\mathcal{E}^o_{cell} = \mathcal{E}^o_{anode} + \mathcal{E}^o_{cathode}$
By putting values we get:
$0.34V = 0 + \mathcal{E}^o_{cathode}$
$\mathcal{E}^o_{cathode} = 0.34V$

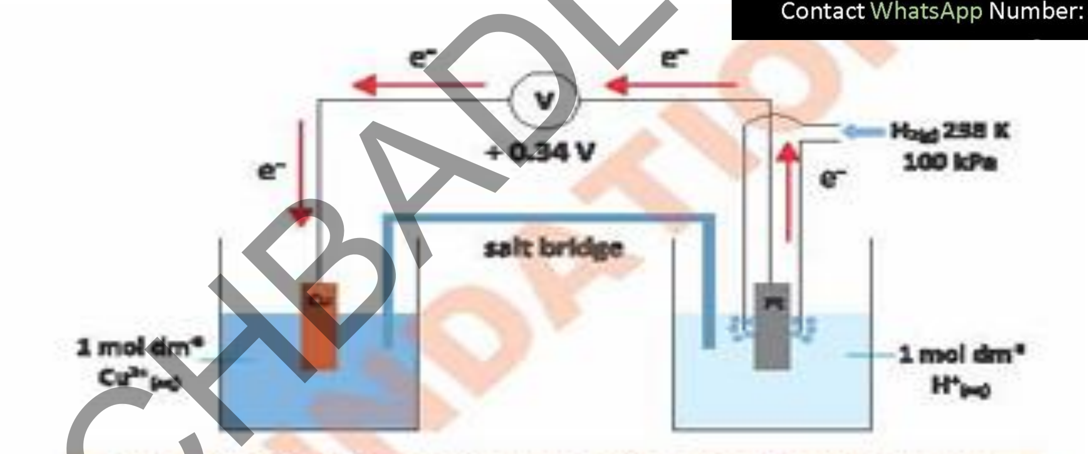


Fig 2.4: Measurement of Standard Electrode Potential of Cu^{2+}/Cu Electrode

FEASIBILITY OF A REACTION: A reaction is feasible or spontaneous if it can occur on its own without the help of any external support of energy such as current. In electrochemistry, we check feasibility of a reaction through cell potentials;

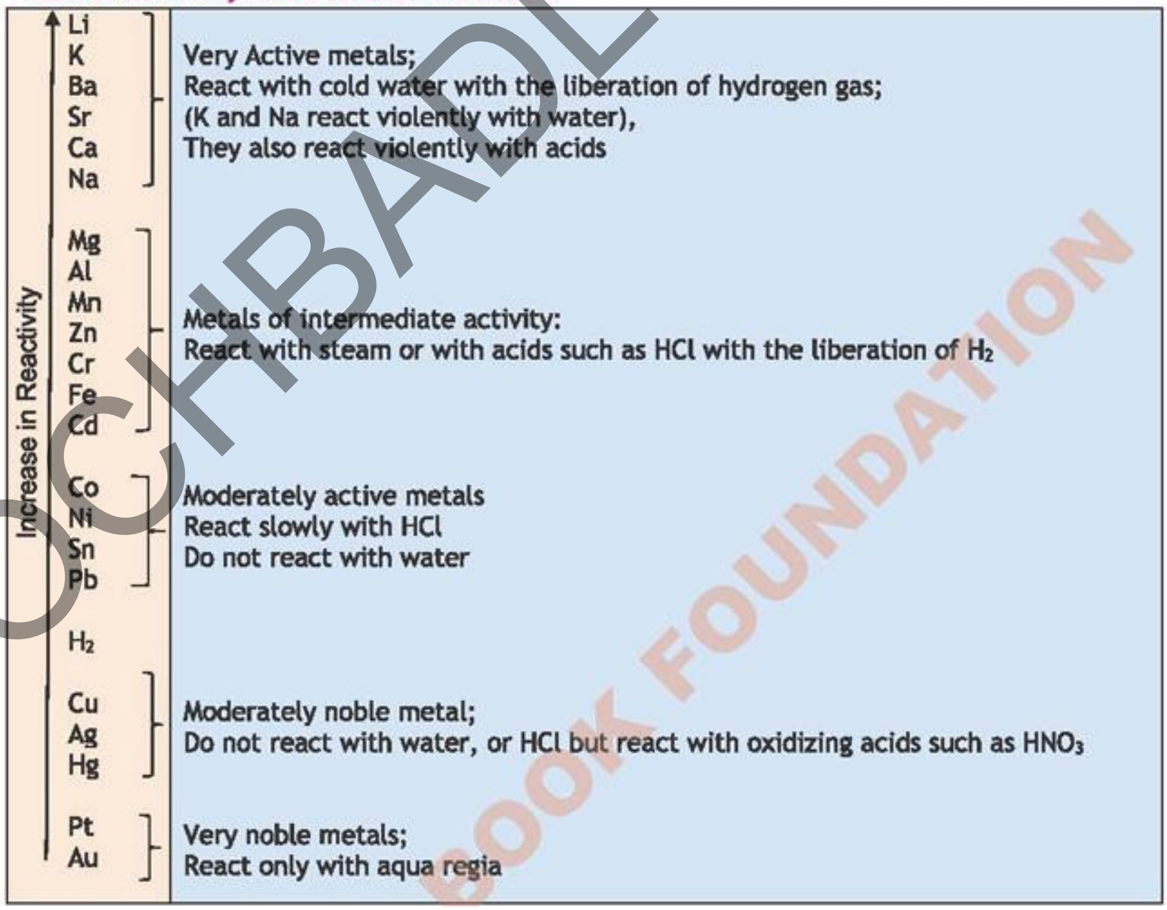
If a reaction is spontaneous then cell potential must be greater than zero or +ve.
If a reaction has cell potential in negative or less than zero then its non-spontaneous.

2.5 NERST EQUATION IS FORMATIVE

ELECTROCHEMICAL SERIES: Its a table formed upon the activity or reactivity of a metal. Metals having more activity can displace others having low reactivity.
EXAMPLE : $0Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$

THIS REACTION IS FEASIBLE AS Zn HAS MORE ACTIVITY THAN Cu.
Table:

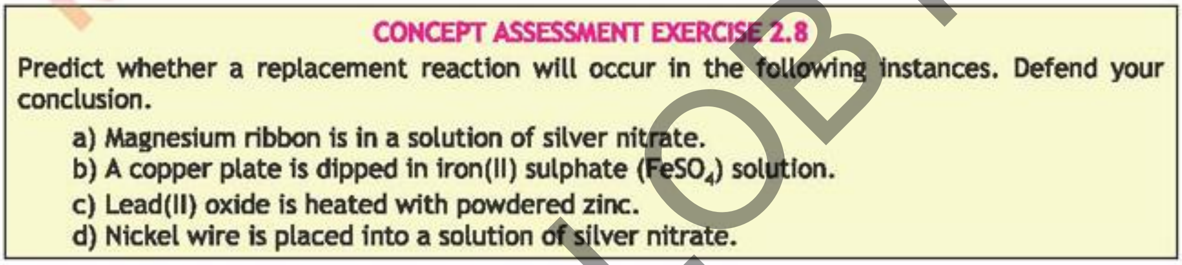
Table 2.2 Activity series of common metals



Increase in Reactivity		
↑	Li K Ba Sr Ca Na	Very Active metals; React with cold water with the liberation of hydrogen gas; (K and Na react violently with water), They also react violently with acids
	Mg Al Mn Zn Cr Fe Cd	Metals of intermediate activity: React with steam or with acids such as HCl with the liberation of H_2
	Co Ni Sn Pb	Moderately active metals React slowly with HCl Do not react with water
	H_2	
	Cu Ag Hg	Moderately noble metal; Do not react with water, or HCl but react with oxidizing acids such as HNO_3
	Pt Au	Very noble metals; React only with aqua regia

- Applications:
- We use it to predict feasibility of a reaction and reducing potential. $\mathcal{E}^{o}_{REDUCTION} \propto 1/$ ACTIVITY

- Calculation of cell voltage
- Determination of metal being anode or cathode
  MORE ACTIVITY = LESS REDUCTION = ANODE
  LESS ACTIVITY = MORE REDUCTION = CATHODE



CONCEPT ASSESSMENT EXERCISE 2.8

Predict whether a replacement reaction will occur in the following instances. Defend your conclusion.

a) Magnesium ribbon is in a solution of silver nitrate.
b) A copper plate is dipped in iron(II) sulphate ($FeSO_4$) solution.
c) Lead(II) oxide is heated with powdered zinc.
d) Nickel wire is placed into a solution of silver nitrate.

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1. Magnesium Ribbon dipped in Silver Nitrate ($AgNO_3$)

Prediction: ✓ Reaction will take place
Balanced Equation:
$Mg(s) + 2AgNO_3(aq) \rightarrow Mg(NO_3)_2(aq) + 2Ag(s)$

Magnesium is more reactive than silver in the reactivity series. It displaces silver from its nitrate solution in a single displacement reaction. Silver is deposited as a solid, and magnesium nitrate is formed in solution.

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2. Copper Plate dipped in Iron(II) Sulphate ($FeSO_4$) Solution

Prediction: ✕ No reaction will take place
Reason:
Copper is **less reactive** than iron, so it **cannot displace** iron from its sulphate solution. Displacement only happens when a more reactive metal replaces a less reactive one from its compound.

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3. Lead Dioxide (PbO_2) heated with Powdered Zinc

Prediction: ✓ Reaction will take place
Balanced Equation:
$PbO_2 + 2Zn \rightarrow Pb + 2ZnO$

Zinc is a powerful reducing agent and is more reactive than lead. When heated, zinc reduces lead dioxide to metallic lead, itself getting oxidized to zinc oxide. This is a redox reaction (reduction-oxidation).

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4. Nickel Wire placed in Silver Nitrate ($AgNO_3$) Solution

Prediction: ✓ Reaction will take place
Balanced Equation:
$Ni(s) + 2AgNO_3(aq) \rightarrow Ni(NO_3)_2(aq) + 2Ag(s)$

Nickel is more reactive than silver and can displace silver from its nitrate solution. This forms nickel nitrate in solution and silver gets deposited as a grey metal.

TYPES OF ELECTRO-CHEMICAL CELLS:

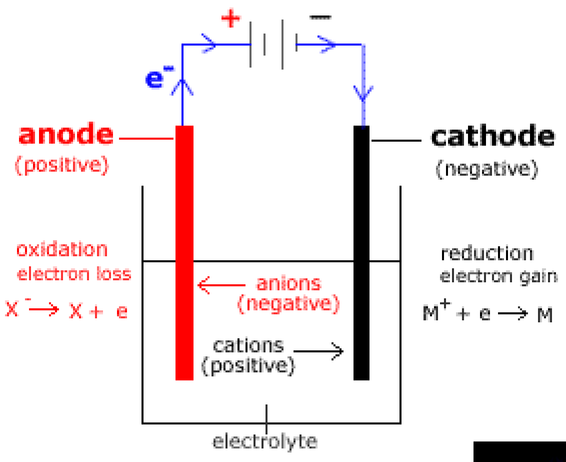
ELECTRO-CHEMICAL CELLS: Cells that convert electrical energy to chemical energy or vice versa are called Electro-Chemical cells. It has 2 types ; ELECTROLYTIC AND GALVANIC.

ELECTRICAL ENERGY → CHEMICAL ENERGY

OR

CHEMICAL ENERGY → ELECTRICAL ENERGY

- ***ELECTROLYTIC CELL:*** Device that converts electrical energy to chemical energy by electrolysis is called an electrolytic cell.
- Electrodes with less reduction potential would be taken as cathode here and the high reducing potentials would be taken as anode. Thus, the movement of electrons would be from Cathode to Anode. Also, this involves the inclusion of a non spontaneous reaction.
- An electrolyte is also present which ensures redox reaction occurs.



DIFFERENCE IN ELECTROLYTIC AND GALVANIC CELL:

Feature	**Galvanic Cell**	**Electrolytic Cell**
Purpose	Converts chemical energy into electrical energy	Converts electrical energy into chemical energy
Spontaneity	Spontaneous redox reaction	Non-spontaneous redox reaction
Energy Source	No external power source required	Requires an external power source (like a battery)
Electron Flow	From anode to cathode through the external circuit	From anode to cathode through the external circuit
Anode Charge	Negative	Positive
Cathode Charge	Positive	Negative
Reaction Direction	Oxidation at anode, reduction at cathode	Oxidation at anode, reduction at cathode
Salt Bridge	Used To maintain electrical neutrality	Not required (usually)

Feature	**Galvanic Cell**	**Electrolytic Cell**
Example	Daniell Cell	Electrolysis of water or molten NaCl

ELECTROLYSIS: Electrolysis is a process in which a chemical reaction occurs by means of electrical current in an aqueous state or in a molten state.

Apparatus: Apparatus is the components of the electrolytic cell which are as follows:

1) ***ELECTROLYTE IN MOLTEN OR AQUEOUS STATE***
2) ***ELECTRIC SUPPLY SUCH AS A BATTERY***
3) ***2 METALLIC ELECTRODES***
4) ***WIRES TO ESTABLISH THE CONNECTION BETWEEN THE ELECTRODES***

PROCESS OF ELECTROLYSIS:

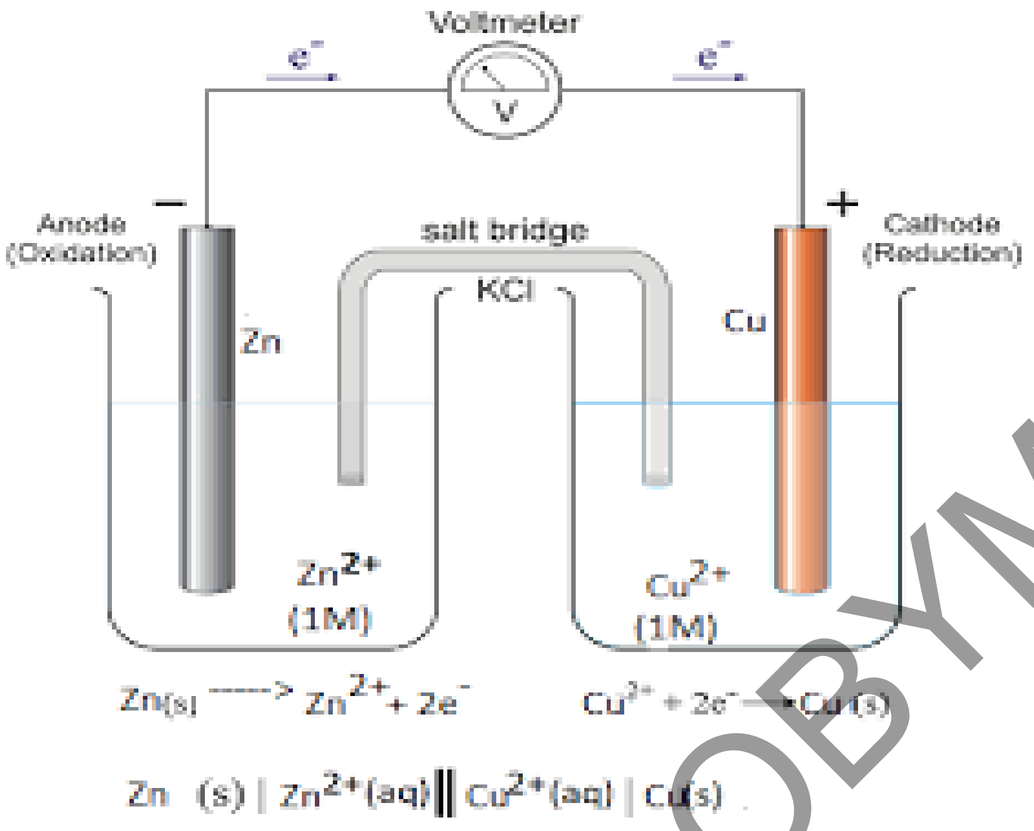
- Electrodes are connected with the battery in the following manner: Positive terminal is connected with the anode (+) and cathode is connected with the negative (-) terminal of the battery.

- Electrodes must be connected to each other
- A chemical reaction takes place at each electrode, one loses the electrons and one gains them.
- Direction of the flow of electrons is from anode to cathode.

***UNIT:* SI UNIT FOR THE CHARGE IS COULOUMB.**

ANOTHER UNIT FOR THE ELECTRIC CHARGE WHICH IS MORE CONVINIENT IS CALLED FARADAY (F). IT IS ACTUALLY THE CHATGE ON 1 MOL OF ELECTRONS WHICH IS: $1.602\times10^{-19} \times 6.022\times10^{23} = 96487$ COULOUMB.

SI unit for current is Ampere (A). Ampere is the amount of charge flowing through an area per second which is Coulomb per second.



FACTORS AFFECTING THE PRODUCTS OF ELECTROLYSIS: Obviously the reaction depends on some factors which affect the rate and products of the redox reaction taking place, they are;

1: State of Electrolyte:

Now according to the function of the electrolytic cells, molten or fused state of electrolyte is used. In that case the electrolytes will be deposited at the electrodes. Such that if we use NaCl then Na^+ and Cl^- ions would deposit at electrodes.

Case 2: If we use Aqueous NaCl or Brine as the electrolyte then other than Na, H_2 gas would be at the cathode.

This is because the H_2 is lower in the activity series and Na is at the top of the activity series.

2: Position in Electrochemical Series: Generally, in reactions the element's position in the series can determine its reduction or oxidation in the reaction. The element which are at the top have high reducing potential thus when a lower positioned element is present in the electrolyte, the one at the top will stop from being oxidized and the other element would be oxidized as it is a weak reducing agent.

3: Concentration of substance: The concentration also affects the oxidation/reduction of a substance, higher concentrated are usually reacted while lower ones remain unreacted. Ions with lower concentrations aren't discharged instead water molecules are discharged.

Examples:

1. 1-Fused NaCl:

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

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

Net reaction: $2Na^+ + 2Cl^+ \rightarrow 2Na + Cl_2$

2. Electrolysis of concentrated aqueous NaCl (brine)

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

Electrolysis of Aqueous NaCl (Brine)

At the Cathode (Reduction):

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

At the Anode (Oxidation):

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

Net Ionic Equation:

$2H_2O + 2Cl^- \rightarrow H_2 + Cl_2 + 2OH^-$

3: Electrolysis of Dilute NaCl solution:

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

Cathode (Reduction):

$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$

Anode (Oxidation):

$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$

Net Ionic Equation:

$2H_2O \rightarrow 2H_2 + O_2$

RELATION BETWEEN FARADAY AND AVOGADRO CONSTANT AND CHARGE ON ELECTRON:

The amount of a substance produced at an electrode during electrolysis depends on the period of time for which a constant current is passed and the quantity of charge in coulombs that passes through the electrolyte. The relation between current and time is:

$$Q = I \times t$$

Where, Q = Quantity of charge in coulombs (C)

I= Current amount passed

t= Time in seconds

The quantity of electricity can be expressed by Faraday constant (F). One faraday is the amount of electric charge carried by one mole of electrons.

Charge on one electron= 1.60217662 x10^{-19} C

Charge on one mole of electrons =

1.60217662 x 10^{-19} c x 6.022 x 10^{23} per mol

= 96485.332 C/ mol

It is therefore concluded that 96485.332 C is the charge on one mole of electrons. This quantity of charge is referred to as one Faraday, Thus, the quantity of the change in electrolysis can be determined from the number of Faraday's of charge, which passes. For most calculations, the value of the Faraday will be taken as 96500 C.

The relationship between the Faraday constant (F), Avogadro constant (N_A), and the charge on the electron (e^-) can be expressed by the equation:

$$F= N_A \times e^-$$

DETERMINATION OF AVOGADRO'S NO BY EXPERIMENTAL ELECTROLYSIS:

Electrolysis provides a concrete way to measure the Avogadro Constant experimentally. In this experiment, a known electrolyte is electrolysed. The mass of metal deposited at the cathode is determined by passing known amperes of current for a known time. Suppose you electrolysed AgN03 using Ag electrodes. The experimental data shows that when 0.1 amperes is passed for exactly 30 minutes through the aqueous solution of silver nitrate solution, the amount of Ag deposited on the cathode is 0.201g. From this data:

0.201g of Ag = Required 180C

107.86g of Ag = Requires x

Upon resolving=

x x 0.201g = 107.86 x 180

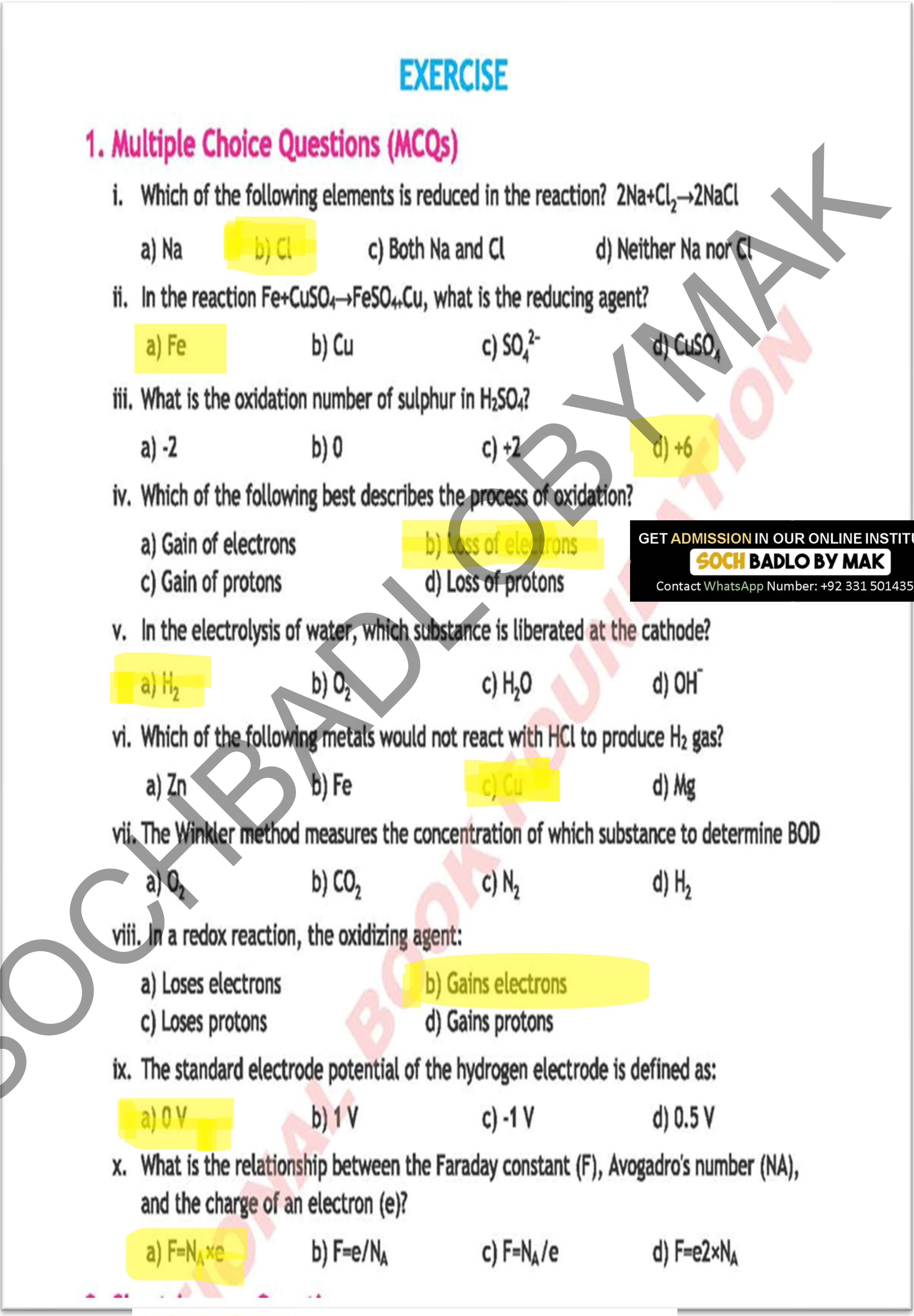
x = 107.868 x 180C / 0.201g

$x = 96600\text{C}$

This is the charge on 1 mol of e^- and charge on 1e is $1.602\text{x}10^{-19}$ thus to find electrons in 1 mole we divide

$96600\text{C} / 1.602\text{x}10^{-19} = 6.0298\text{x}10^{23}$

This is very close to N_A.



EXERCISE

1. Multiple Choice Questions (MCQs)

i. Which of the following elements is reduced in the reaction? $2Na+Cl_2 \rightarrow 2NaCl$

a) Na b) Cl c) Both Na and Cl d) Neither Na nor Cl

ii. In the reaction $Fe+CuSO_4 \rightarrow FeSO_4+Cu$, what is the reducing agent?

a) Fe b) Cu c) SO_4^{2-} d) $CuSO_4$

iii. What is the oxidation number of sulphur in H_2SO_4?

a) -2 b) 0 c) +2 d) +6

iv. Which of the following best describes the process of oxidation?

a) Gain of electrons b) Loss of electrons
c) Gain of protons d) Loss of protons

v. In the electrolysis of water, which substance is liberated at the cathode?

a) H_2 b) O_2 c) H_2O d) OH^-

vi. Which of the following metals would not react with HCl to produce H_2 gas?

a) Zn b) Fe c) Cu d) Mg

vii. The Winkler method measures the concentration of which substance to determine BOD

a) O_2 b) CO_2 c) N_2 d) H_2

viii. In a redox reaction, the oxidizing agent:

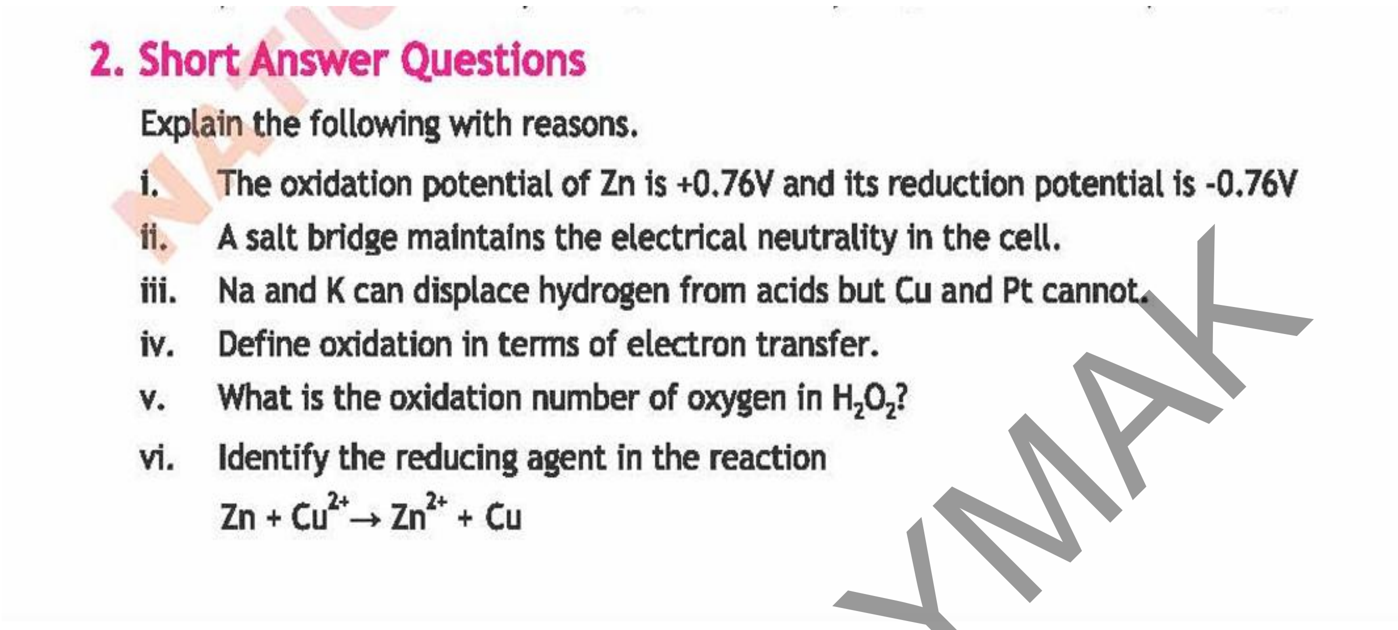
a) Loses electrons b) Gains electrons
c) Loses protons d) Gains protons

ix. The standard electrode potential of the hydrogen electrode is defined as:

a) 0 V b) 1 V c) -1 V d) 0.5 V

x. What is the relationship between the Faraday constant (F), Avogadro's number (NA), and the charge of an electron (e)?

a) $F=N_A \times e$ b) $F=e/N_A$ c) $F=N_A/e$ d) $F=e2 \times N_A$



2. Short Answer Questions

Explain the following with reasons.

i. The oxidation potential of Zn is +0.76V and its reduction potential is -0.76V

ii. A salt bridge maintains the electrical neutrality in the cell.

iii. Na and K can displace hydrogen from acids but Cu and Pt cannot.

iv. Define oxidation in terms of electron transfer.

v. What is the oxidation number of oxygen in H_2O_2?

vi. Identify the reducing agent in the reaction

$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

i. The oxidation potential of Zn is +0.76 V and its reduction potential is –0.76 V.

Explanation: Oxidation potential and reduction potential are equal in magnitude but opposite in sign.

- A positive oxidation potential (+0.76 V) shows zinc **readily loses electrons**, it's easily oxidized.
- A negative reduction potential (–0.76 V) means zinc **does not easily gain electrons**, confirming its tendency to undergo oxidation.

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ii. A salt bridge maintains the electrical neutrality in the cell.

Explanation: During redox reactions in an electrochemical cell, positive and negative ions move toward opposite electrodes. A **salt bridge allows the flow of ions** to balance charges in both half-cells, preventing charge build-up, which would otherwise stop the reaction.

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iii. Na and K can displace hydrogen from acids but Cu and Pt cannot.

Explanation: Sodium (Na) and potassium (K) are **more reactive than hydrogen**, so they displace hydrogen gas when reacting with acids. Copper (Cu) and platinum (Pt) are **less reactive than hydrogen** in the reactivity series, so they **cannot** displace hydrogen from acids.

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iv. Define oxidation in terms of electron transfer.

Answer: Oxidation is the loss of electrons by an atom, ion, or molecule.

- Example: $Zn \rightarrow Zn^{2+} + 2e^-$ (zinc loses electrons; it's oxidized).

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v. What is the oxidation number of oxygen in H_2O_2?

Solution: Let the oxidation state of oxygen in H_2O_2 (hydrogen peroxide) be x.
Each hydrogen (H) has +1 oxidation number.
Total for 2 H: +2

Total for 2 O: 2x

The molecule is neutral, so sum must be zero:

$2(+1) + 2x = 0$

$2 + 2x = 0$

$x = -1$

Answer: Oxidation number of O in H_2O_2 is –1.

---

vi. Identify the reducing agent in the reaction:

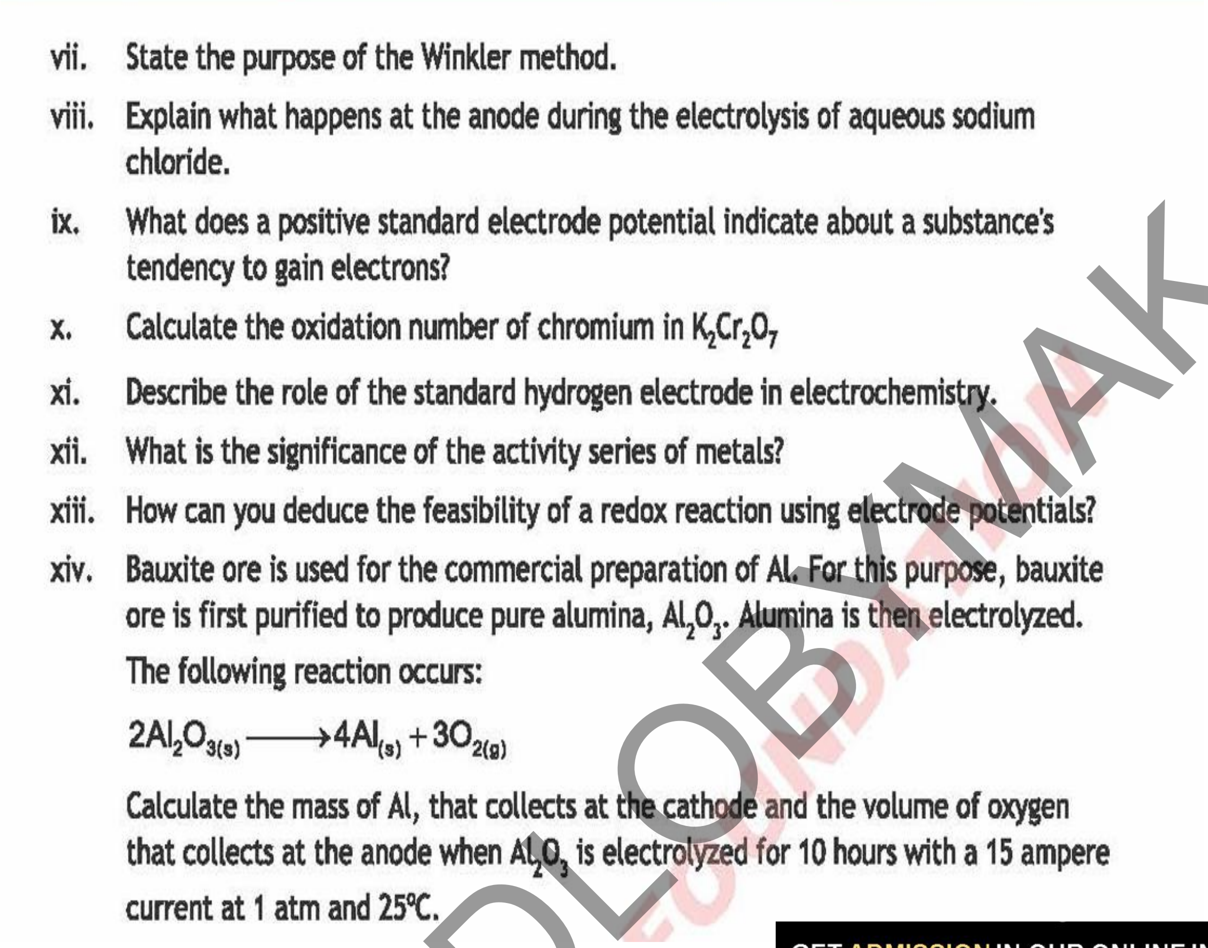
Oxidation: $Zn \rightarrow Zn^{2+} + 2e^-$

Reduction: $Cu^{2+} + 2e^- \rightarrow Cu$

Explanation:

- **Zn** loses electrons ($Zn \rightarrow Zn^{2+} + 2e^-$) → Zn is **oxidized** → so it is the **reducing agent**.
- Cu^{2+} gains electrons ($Cu^{2+} + 2e^- \rightarrow Cu$) → it is reduced.

Answer: The reducing agent is Zn.



vii. State the purpose of the Winkler method.

viii. Explain what happens at the anode during the electrolysis of aqueous sodium chloride.

ix. What does a positive standard electrode potential indicate about a substance's tendency to gain electrons?

x. Calculate the oxidation number of chromium in $K_2Cr_2O_7$

xi. Describe the role of the standard hydrogen electrode in electrochemistry.

xii. What is the significance of the activity series of metals?

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

xiv. Bauxite ore is used for the commercial preparation of Al. For this purpose, bauxite ore is first purified to produce pure alumina, Al_2O_3. Alumina is then electrolyzed. The following reaction occurs:

$$2Al_2O_{3(s)} \longrightarrow 4Al_{(s)} + 3O_{2(g)}$$

Calculate the mass of Al, that collects at the cathode and the volume of oxygen that collects at the anode when Al_2O_3 is electrolyzed for 10 hours with a 15 ampere current at 1 atm and 25°C.

vii: Formative

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viii. Explain what happens at the anode during the electrolysis of aqueous sodium chloride.

At the anode (+), chloride ions (Cl^-) lose electrons (are oxidized) to form chlorine gas:

$2Cl^- \rightarrow Cl_2(g) + 2e^-$

Meanwhile, water oxidation is less favourable because the standard electrode potential for Cl^- oxidation is lower (more favourable) than that of water, so chlorine is produced at the anode.

---

ix. What does a positive standard electrode potential indicate about a substance's tendency to gain electrons?

A positive standard electrode potential means the substance has a strong tendency to gain electrons (i.e., it is a good oxidizing agent) and get reduced. The more positive the potential, the greater the substance's ability to accept electrons.

---

x. Calculate the oxidation number of chromium in $K_2Cr_2O_7$.

Let the oxidation state of Cr be x.

- Potassium (K) has +1, and there are 2 K^+: total +2.
- Oxygen has -2, and there are 7 O: total -14.
- The compound is neutral, so sum of oxidation numbers = 0.

So:
$2(+1) + 2(x) + 7(-2) = 0$
$2 + 2x - 14 = 0$
$2x - 12 = 0$
$2x = 12$
$x = +6$

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

---

xi. Describe the role of the standard hydrogen electrode in electrochemistry.

The standard hydrogen electrode (SHE) serves as the universal reference electrode with a defined potential of 0.00 V. It allows the measurement of standard electrode potentials (E°) of other half-cells by connecting them to the SHE in an electrochemical cell.

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xii. What is the significance of the activity series of metals?

The activity series ranks metals according to their reactivity. It helps predict:

- Whether a metal can displace another from a compound.
- The feasibility of redox reactions.
- Which metals will corrode more easily.
- Metals higher in the series are more reactive and lose electrons readily.

---

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

To determine feasibility:

- Calculate the standard cell potential (E°cell) by subtracting E° of the anode from E° of the cathode:

E° cell = E°(cathode) - E°(anode)

- If E° cell > 0, the redox reaction is feasible (spontaneous).
- If E° cell < 0, the reaction is not feasible (non-spontaneous).

---

xiv. Calculation of mass of Al and volume of O_2 produced

First, calculate total charge passed during 10 hours at 15 A:

$Q = I \times t$
$Q = 15\ A \times (10\ h \times 3600\ s/h)$
$Q = 15 \times 36{,}000 = 540{,}000\ C$

Each mole of electrons = 96,500 C (Faraday's constant).

From the reaction:
$2Al_2O_3 \rightarrow 4Al + 3O_2$

For Al:

- 4Al need 12 moles of electrons (because $Al^{3+} \rightarrow Al$ requires $3e^-$ each → $4 \times 3 = 12$ moles e^-).

For O_2:

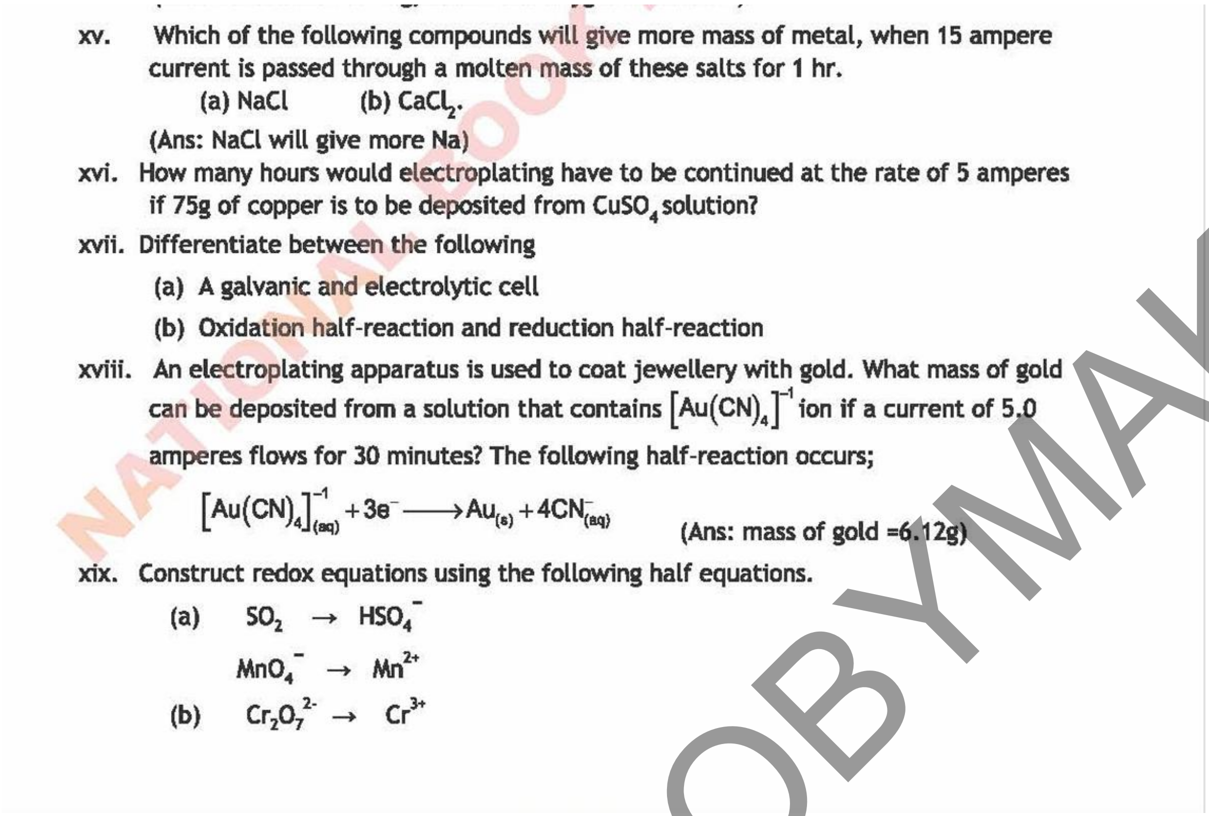
- $3O_2$ need 12 moles of electrons (since $O^{2-} \rightarrow O_2$ requires $4e^-$ per O_2 molecule → 3×4=12 moles e^-).

Total moles of electrons passed:
$n(e^-) = Q / F = 540{,}000\ C / 96{,}500\ C/mol = 5.6\ mol\ e^-$

So for Al:
4 mol Al ↔ 12 mol e^-
So,
mol Al produced = (4/12) × 5.6 = 1.87 mol Al
Mass Al = mol × molar mass (Al) = 1.87 × 27.0 = 50.5 g

For O_2:
3 mol O_2 ↔ 12 mol e^-
mol O_2 produced = (3/12) × 5.6 = 1.4 mol O_2
Volume O_2 at 1 atm, 25°C using molar volume (24.45 L/mol):
Volume = 1.4 mol × 24.45 L/mol = 34.2 L

Answer:
Mass of Al collected at cathode = 50.5 g
Volume of O_2 collected at anode = 34.2 L



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

(a) NaCl (b) $CaCl_2$.

(Ans: NaCl will give more Na)

xvi. How many hours would electroplating have to be continued at the rate of 5 amperes if 75g of copper is to be deposited from $CuSO_4$ solution?

xvii. Differentiate between the following

(a) A galvanic and electrolytic cell

(b) Oxidation half-reaction and reduction half-reaction

xviii. An electroplating apparatus is used to coat jewellery with gold. What mass of gold can be deposited from a solution that contains $[Au(CN)_4]^{-1}$ ion if a current of 5.0 amperes flows for 30 minutes? The following half-reaction occurs;

$$[Au(CN)_4]^{-1}_{(aq)} + 3e^- \longrightarrow Au_{(s)} + 4CN^-_{(aq)}$$

(Ans: mass of gold =6.12g)

xix. Construct redox equations using the following half equations.

(a) $SO_2 \rightarrow HSO_4^-$

$MnO_4^- \rightarrow Mn^{2+}$

(b) $Cr_2O_7^{2-} \rightarrow Cr^{3+}$

---

xv. Which of the following compounds will give more mass of metal when 15 A current is passed through molten mass of these salts for 1 hour?

(a) NaCl → gives Na

(b) $CaCl_2$ → gives Ca

Number of equivalents deposited = (It)/(96500) × (Molar mass/valency)

For Na: valency = 1
For Ca: valency = 2
Since mass deposited ∝ (Molar mass / valency),

Na: 23/1=23
Ca: 40/2=20

So Na will give more mass.

Answer: NaCl will give more Na.

---

xvi. How many hours would electroplating have to be continued at 5 A if 75 g of copper is to be deposited from $CuSO_4$ solution?

Moles of Cu to deposit = mass / molar mass = 75 g / 63.5 g/mol ≈ 1.18 mol
Electrons needed (since $Cu^{2+} + 2e^- \rightarrow Cu$): 1.18 mol × 2 = 2.36 mol e^-
Total charge needed Q = 2.36 mol × 96500 C/mol ≈ 227,740 C
Time = Q/I = 227,740 C / 5 A = 45,548 s
Convert to hours: 45,548 s / 3600 ≈ 12.65 hours

Answer: ~12.65 hours

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xvii. Differentiate the following

(a) **Galvanic vs Electrolytic Cell:**

Galvanic Cell	**Electrolytic Cell**
Converts chemical → electrical energy	Converts electrical → chemical energy

Galvanic Cell	**Electrolytic Cell**
Spontaneous redox reaction	Non-spontaneous redox reaction
Positive cell potential	External voltage required

(b) **Oxidation vs Reduction Half-Reaction:**

- **Oxidation Half-Reaction:** loss of electrons, increases oxidation state, occurs at anode.
- **Reduction Half-Reaction:** gain of electrons, decreases oxidation state, occurs at cathode.

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xviii. Gold electroplating calculation

Total time = 30 minutes = 1800 s
Total charge Q = I × t = 5 A × 1800 s = 9000 C
Moles of electrons = Q/F = 9000/96500 ≈ 0.0933 mol e^-
From equation:
$[Au(CN)4]^- + 3e^- \rightarrow Au + 4CN^-$

So mol Au deposited = 0.0933 mol e^- / 3 ≈ 0.0311 mol Au
Mass of Au = 0.0311 mol × 197 g/mol ≈ 6.12 g

Answer: Mass of gold deposited ≈ 6.12 g

---

xix. Construct redox equations

(a) Combine the oxidation of SO_2 and reduction of MnO_4^- in acidic solution:

Oxidation half:

$SO_2 + 2H_2O \rightarrow HSO_4^- + 3H^+ + 2e^-$

Reduction half:

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

To balance electrons: multiply oxidation half by 5, reduction half by 2:

$5(SO_2 + 2H_2O \rightarrow HSO_4^- + 3H^+ + 2e^-)$

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

Final balanced redox equation:

$5SO_2 + 2MnO_4^- + 2H_2O + 2\times 8H^+ \rightarrow 5HSO_4^- + 2Mn^{2+} + (5\times 3+2\times 4)H_2O$

Simplified:

$5SO_2 + 2MnO_4^- + 2H_2O + 16H^+ \rightarrow 5HSO_4^- + 2Mn^{2+} + 18H_2O$

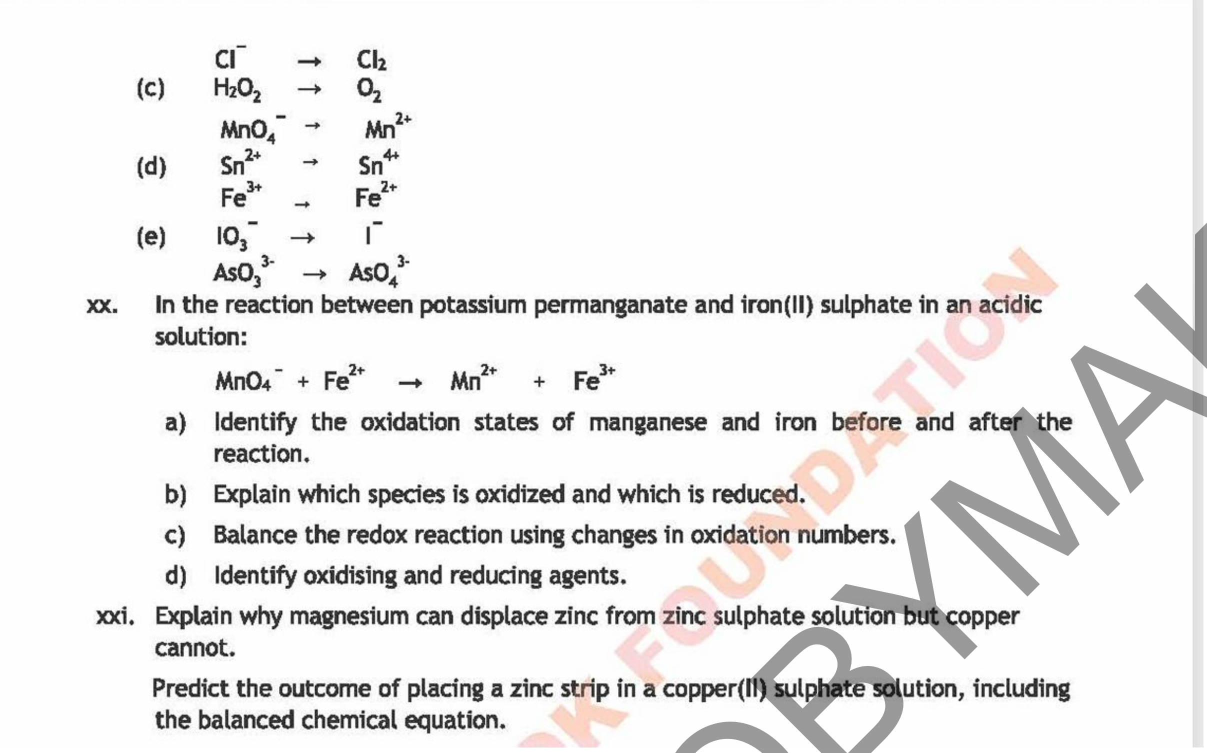
(b) Dichromate reduction in acid:

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

Oxidation half from your problem wasn't given, so pair with a generic reducing agent producing $6e^-$ to balance:

Redox equation example:

$3SO_2 + Cr_2O_7^{2-} + 2H^+ \rightarrow 3SO_4^{2-} + 2Cr^{3+} + H_2O$



Cl^- → Cl_2

(c) H_2O_2 → O_2

MnO_4^- → Mn^{2+}

(d) Sn^{2+} → Sn^{4+}

Fe^{3+} → Fe^{2+}

(e) IO_3^- → I^-

AsO_3^{3-} → AsO_4^{3-}

xx. In the reaction between potassium permanganate and iron(II) sulphate in an acidic solution:

$$MnO_4^- + Fe^{2+} \rightarrow Mn^{2+} + Fe^{3+}$$

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

b) Explain which species is oxidized and which is reduced.

c) Balance the redox reaction using changes in oxidation numbers.

d) Identify oxidising and reducing agents.

xxi. Explain why magnesium can displace zinc from zinc sulphate solution but copper cannot.

Predict the outcome of placing a zinc strip in a copper(II) sulphate solution, including the balanced chemical equation.

Half-Reactions (Redox)

(a)

$Cl^- \rightarrow Cl_2$

Oxidation half-reaction:

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

(b)

$H_2O_2 \rightarrow O_2$

Oxidation half-reaction:

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

(c)

$MnO_4^- \rightarrow Mn^{2+}$

Reduction half-reaction:

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

(d)

$Sn^{2+} \rightarrow Sn^{4+}$

Oxidation half-reaction:

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

$Fe^{3+} \rightarrow Fe^{2+}$

Reduction half-reaction:

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

(e)

$IO_3^- \rightarrow I^-$

Reduction half-reaction:

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

$AsO_3^{3-} \rightarrow AsO_4^{3-}$

Oxidation half-reaction:

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

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xx. Reaction:

$MnO_4^- + Fe^{2+} \rightarrow Mn^{2+} + Fe^{3+}$

a) Oxidation States:

- Mn: +7 (in MnO_4^-) → +2 (in Mn^{2+}) → **reduced**
- Fe: +2 → +3 → **oxidized**

b) Redox Identification:

- **Oxidized:** $Fe^{2+} \rightarrow Fe^{3+}$

- **Reduced:** $MnO_4^- \rightarrow Mn^{2+}$

c) Balanced Redox Reaction:

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

d) Agents:

- **Oxidizing agent:** MnO_4^-
- **Reducing agent:** Fe^{2+}

xxi. Displacement Explanation

Magnesium vs. Zinc vs. Copper:

- Magnesium is **more reactive** than zinc, so it can displace zinc from zinc sulfate.
- Copper is **less reactive** than zinc, so it cannot displace zinc from the solution.

Zinc in Copper(II) Sulfate Solution

Reaction:

$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$

Outcome:
Zinc displaces copper. Solid copper forms as a red deposit, and the solution becomes zinc sulphate.