

Model Question Paper-2 with effect from 2021 (CBCS Scheme)

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First Semester Engineering Degree Examination Subject Title 21CHE12/22

TIME: 03 Hours


Max. Marks: 100

Note: Answer any **FIVE** full questions, choosing at least **ONE** question from each **MODULE**.

MODULE 1			Marks
Q.1	a	Define Single Electrode Potential. Obtain the expression for single electrode potential.	7
	b	What are ions Selective Electrodes? Explain construction and working of glass electrode	7
	c	Write briefly the recycling of Li-ion battery by direct recycling method	6
OR			
Q.2	a	Explain the construction, working and applications of Li-ion batteries.	6
	b	Explain the experimental determination of P^H using glass	7
	c	Calculate the single electrode potential of Cu electrode at 27°C when the standard potential of Cu is 0.34V and $[Cu^{2+}]$ 0.1M	7
OR			
Q.3	a	Explain the following factors which affecting the rate of corrosion i) Ratio of anodic and cathodic areas ii) nature of corrosion product	7
	b	What is anodizing? Explain the process of anodizing of Al	6
	c	What is electroless plating? Distinguish between electro and electroless plating.	7
OR			
Q.4	a	What is meant by metal finishing? Mention (any five) technological importance of metal finishing.	6
	b	A thick steel sheet of area 400 cm ² is exposed to air near the ocean. After a one year period it was found to experience a weight loss 375 g due to corrosion. If the density of the brass is 7.9g/cm ² calculate the corrosion penetrating rate in mpy and mm/y (given K= 534 in mpy and 87.6 in mm/y)	7
	c	What is cathodic protection? Explain sacrificial anode and impressed voltage methods of cathodic protection	7
MODULE 3			
Q.5	a	What are polymer composites? Explain the synthesis and application of Kevlar fibre	7
	b	What are conducting polymers? Explain the various factors influencing the conduction in organic polymers.	7
	c	Briefly explain the carbon nanotubes with properties and applications.	6

OR			
Q.6	a	Explain optical and electrical properties of nanomaterials.	7
	b	What are nanomaterials? Explain the synthesis of nanomaterials by precipitation method	6
	c	What are Biodegradable polymers? Explain the properties and applications of Polylactic acid.	7
MODULE 4			
Q.7	a	Briefly explain any six basic principles of green chemistry.	6
	b	Explain the following i) Phase transfer catalyst ii) Solvent free reaction	7
	c	With a neat diagram explain the production of Hydrogen by Photocatalytic method	7
OR			
Q.8	a	Describe the hydrogen production by photo electrocatalytic method.	7
	b	Explain the synthesis of Paracetamol by conventional and green route from phenol.	7
	c	Explain the construction and working of photovoltaic cells.	6
MODULE 5			
Q.9	a	Explain the theory, instrumentation and applications of flame photometry.	7
	b	Write the principles and requirement of titrimetric analysis.	7
	c	In a COD test, 30.5 cm ³ and 15.5 cm ³ of 0.05 N FAS solutions were consumed for blank & sample titration respectively. The volume of test sample used was 25 cm ³ . Calculate the COD of the sample solution.	6
OR			
Q.10	a	Explain the determination of hardness by EDTA method.	7
	b	Define the following units of standard solution. i) Molarity ii) Normality iii) ppm	6
	c	Explain the theory and instrumentation of potentiometry.	7

Table showing the Bloom's Taxonomy Level, Course Outcome and Program Outcome				
Question		Bloom's Taxonomy Level attached	Course Outcome	Program Outcome
Q.1	(a)	L1, L2	CO.1	PO-1,2,12
	(b)	L2	CO.1	PO-1,2,12
	(c)	L2	CO.1	PO-1,2,12
Q.2	(a)	L1	CO.1	PO-1,2,12
	(b)	L2	CO.1	PO1,2,12
	(c)	L3	CO.I	PO-1
Q.3	(a)	L2	CO.2	PO-1,2,12
	(b)	L2	CO.2	PO-1,2,12
	(c)	L2	CO.2	PO-1,2,12
Q.4	(a)	L1	CO.2	PO-1,2,12
	(b)	L2	CO.2	PO1
	(c)	L2	CO.2	PO-1,2,12
Q.5	(a)	L2	CO.3	PO-1,2,12
	(b)	L2	CO.3	PO-1,2,12
	(c)	L2	CO.3	PO-1,2,12
Q.6	(a)	L2	CO.3	PO1,2,12
	(b)	L2	CO.3	PO-1,2,12
	(c)	L2	CO.3	PO-1,2,12
Q.7	(a)	L2	CO.4	PO-1,2,12
	(b)	L2	CO.4	PO-1,2,12
	(c)	L2	CO.4	PO-1,2,12
Q.8	(a)	L2	CO.4	PO-1,2,12
	(b)	L2	CO.4	PO-1,2,12
	(c)	L2	CO.4	PO-1,2,12
Q.9	(a)	L2	CO.5	PO-1,2,12
	(b)	L2	CO.5	PO-1,2,12
	(c)	L3	CO.5	PO-1
Q.10	(a)	L2	CO.5	PO-1,2,12
	(b)	L2	CO.5	PO-1,2,12
	(c)	L2	CO.5	PO-1,2,12
Lower order thinking skills				
Bloom's Taxonomy Levels	Remembering(knowledge): <i>L</i> ₁		Understanding Comprehension): <i>L</i> ₂	Applying (Application): <i>L</i> ₃
	Higher order thinking skills			
	Analyzing (Analysis): <i>L</i> ₄	Valuating (Evaluation): <i>L</i> ₅	Creating (Synthesis): <i>L</i> ₆	

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Solution and Scheme for award of marks		

AY: 2021-22

Department: Chemistry

Model Qp Set : 2

Subject with Sub. Code: Engineering Chemistry (2) CHE12/22) Semester / Division: ½ common to all

Name of Faculty: Prof. Sneha S Kulkarni

Q.No.	Solution and Scheme	Marks
	Module-1	
1a.	<p>Define single electrode potential. Obtain the expression for single electrode potential</p> <p>→ Single electrode potential It is the potential developed at the interface of substance and its solution at unit activity of ionic species, at 298 K and at 1 atmospheric gas pressure it is a gas electrode.</p> <p>→ Expression for single electrode potential is derived by Nernst in 1889. It depends on 3 quantities —</p> <ul style="list-style-type: none"> → a) System temperature → b) Electrode potential → c) Molar concentration of ionic species. <p>Let the reversible reduction electrode reaction be:</p> $M^{n+} + ne^{-} \rightleftharpoons M$ <p>If this reaction is spontaneous, there is decrease in free energy of the system and is equal to maximum energy obtainable from the system.</p>	<p>7M</p> <p>1M</p> <p>1M</p>

Q.No.	Solution and Scheme	Marks
	<p> $-\Delta G = W_{\max}$ $-\Delta G = nFE \quad \text{--- (1)}$ </p> <p> where, 'n' is number of moles of electrons transferred during reaction. 'F' is one Faraday of electricity 'E' is electrode potential ΔG is change in free energy nF is number of coulombs of charge that is transferred during the reaction. </p> <p> For the reactants and products at unit activity, ΔG°(standard) is given as </p> <p> $-\Delta G^\circ = nFE^\circ \quad \text{--- (2)}$ </p> <p> where, ΔG° = standard change in free energy. E° = standard electrode potential </p> <p> change in free energy is related to equilibrium constant of the reaction, K_{eq} by Van't Hoff reaction isotherm </p> <p> $\Delta G = -RT \ln K_{eq} + RT \ln Q \quad \text{--- (3)}$ </p> <p> where, Q is the reaction quotient, R is molar gas constant, T is the system temperature in Kelvin. </p> <p> Also, standard change in free energy </p> <p> $\Delta G^\circ = -RT \ln K_{eq}$ </p> <p> $\therefore \Delta G = \Delta G^\circ + RT \ln \frac{[M]}{[M^{n+}]} \quad \text{--- (4)}$ </p> <p> By definition, [M] = 1 Substitute ΔG and ΔG° in equation (4) gives </p> <p> $-nFE = -nFE^\circ + RT \ln \frac{1}{[M^{n+}]} \quad \text{--- (5)}$ </p>	<p>1M</p> <p>1M</p> <p>1M</p>

Divide whole equation by $-nF$ (on both sides)

$$E = E^\circ - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]} \quad \text{--- (6)}$$

$$E = E^\circ + \frac{2.303RT}{nF} \log [M^{n+}] \quad \text{--- (7)} \quad \text{--- 1M}$$

$$E = E^\circ + \frac{0.0591}{n} \log [M^{n+}] \quad \text{--- (8)}$$

$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, $T = 298 \text{ K}$, $F = 96500 \text{ Coulomb mol}^{-1}$

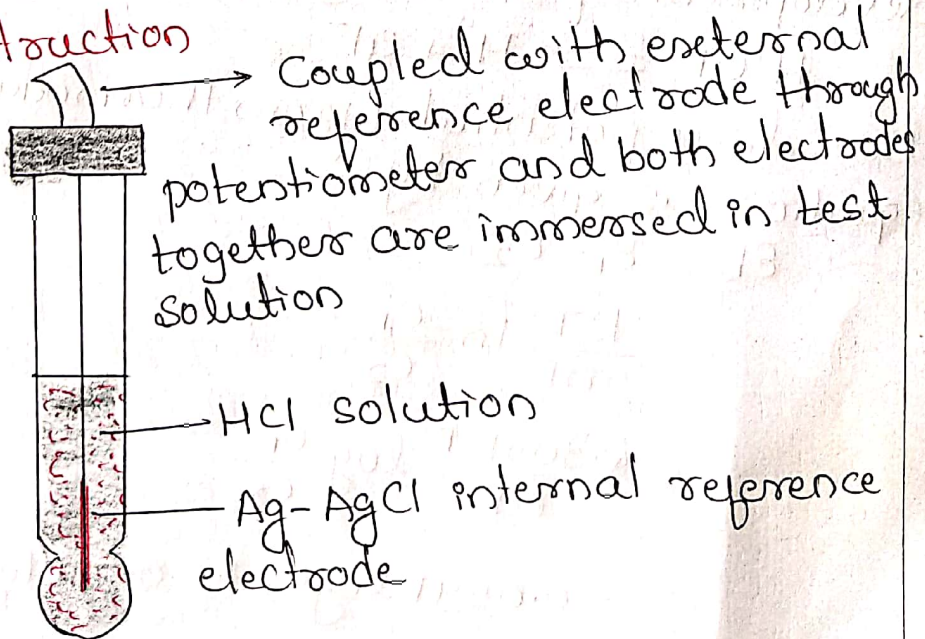
Eqⁿ 7 and 8 is the expression for single electrode potential.

1b. What are ion selective electrodes?

Explain construction and working of glass electrode. --- 7M

→ Ion selective electrode
Electrode, which responds selectively to the presence of specific ions ignoring all other ions, is called ion selective electrode. 1M

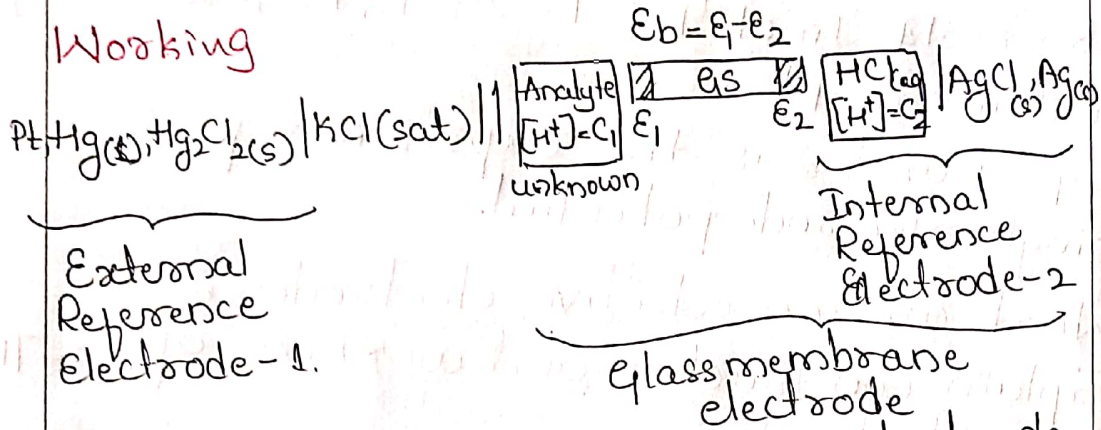
→ Construction



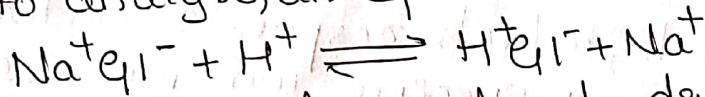
A glass membrane electrode consists of a specially made glass membrane extending out as a bulb at the end of a plane glass tube containing Ag-AgCl electrode immersed in a solution of HCl. 1M

Composition of glass membrane is 6% CaO, 22% Na₂O and 72% SiO₂.

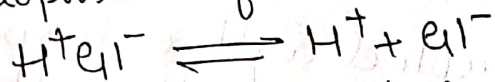
Working



Very soon after immersion of electrode into analyte, an equilibrium is reached,



$\text{H}^+ \text{Cl}^-$ further dissociates to different magnitudes on two sides & results in development of boundary potential.



Boundary potential (from thermodynamic equation) is given by —

$$E_b = E_1 - E_2$$

$$= \frac{RT}{nF} \ln \frac{C_1}{C_2}$$

$$= \frac{2.303RT}{nF} \log \frac{C_1}{C_2}$$

$$= -0.0591 \log C_2 + 0.0591 \log C_1$$

$$\begin{aligned}
 E_b &= L - 0.0591 (-\log C_1) \\
 &= L - 0.0591 (-\log [H^+]) \\
 &= L - 0.0591 \text{ pH}
 \end{aligned}$$

where, pH is referred to the pH of the test solution.

→ Glass membrane electrode potential

$$E_R = E_q = E_{\text{Ref-2}} + E_b + E_{\text{asy}}$$

where, E_{asy} is the asymmetric potential

$$E_{\text{asy}} = E_b \text{ when } C_1 = C_2$$

$$= E_{\text{Ref-2}} + (L - 0.0591 \text{ pH}) + E_{\text{asy}}$$

$$= (E_{\text{Ref-2}} + L + E_{\text{asy}}) - 0.0591 \text{ pH}$$

$$= E'_q - 0.0591 \text{ pH}$$

$$\begin{aligned}
 \text{where, } E'_q &= E_{\text{Ref-2}} - 0.0591 \log C_2 + E_{\text{asy}} \\
 &= \text{constant.}
 \end{aligned}$$

→ Cell potential is given by

$$E_{\text{cell}} = E_R - E_L$$

$$= E_q - E_{\text{Ref-1}}$$

$$= E'_q - 0.0591 \text{ pH} - E_{\text{Ref-1}}$$

$$\rightarrow \text{pH} = \frac{E'_q - E_{\text{Ref-1}} - E_{\text{cell}}}{0.0591}$$

$$= \frac{k' - E_{\text{cell}}}{0.0591} \text{ at } 298 \text{ K}$$

$$\rightarrow k' = 0.0591 \text{ pH} + E_{\text{cell}}$$

k' is glass membrane electrode assembly constant.

1M

1M

1M

Q.No.	Solution and Scheme	Marks
1c	<p>Write briefly the recycling of Li-ion battery by direct recycling method.</p> <p>→ Direct recycling method</p> <pre> graph TD A[Li-ion battery] --> B[Discharge] B --> C[Dismantling] C --> D[alkaline wash] E[NaOH] --> D D --> F[Separation] G[Spent NaOH soln to electrolyte recovery process] --> D H[Anode to separation process. Separator] --> F F --> I[Cathode] I --> J[Crushing] J --> K[alkaline wash] L[NaOH] --> K K --> M[Milling and sieving] N[Al] --> M O[Spent NaOH solution] --> M M --> P[Thermal treatment at 65°C] Q[Li2CO3(s)] --> P R[H2(g)] --> P S[A+(g)] --> P P --> T[Al] P --> U[Refreshed] U --> V[spent solution.] </pre> <p>Direct recycling method start with dismantling <u>or</u> shedding the cells. This step enables immediate recovery of the copper and aluminium foils as metals, while retaining their original compound structure.</p>	<p>6M</p> <p>2M</p> <p>2M</p>

Al and Li could be recovered by leaching. After leaching with acid, the dissolved constituents can be separated from each other and reused to manufacture new cathode material.

→ Advantages:

1. Direct recycling of Li-ion is a promising cost effective process
2. Direct recycling are low temperature & low energy processes
3. Do not require large scale and therefore could be used locally or for home scrap, avoiding the need to manufacture new cathode material

2M

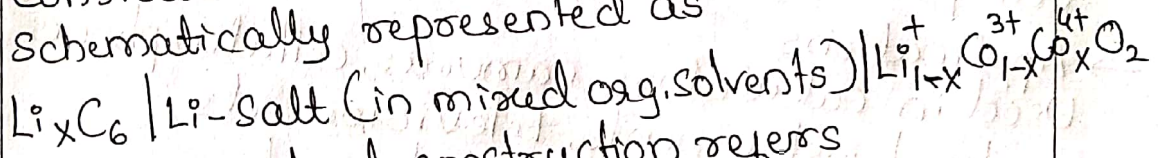
2a Explain the construction, working and applications of Li-ion batteries

6M

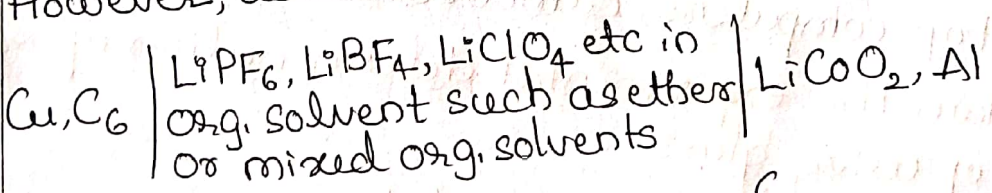
Li-ion battery

Construction

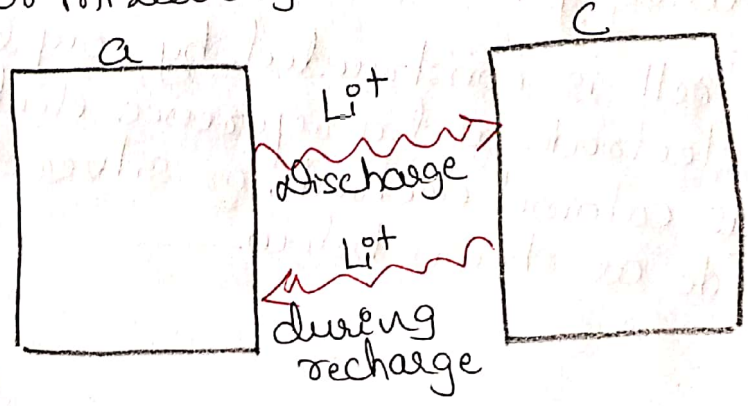
Schematically represented as



However, actual construction refers



1M



Q.No.	Solution and Scheme	Marks
	<p>→ Anode material: Highly-crystallised specialty carbon</p> <p>→ Cathodic material: LiCoO_2 - Lithium cobalt oxide</p> <p>→ Electrolyte: LiPF_6, LiBF_4, LiClO_4 mixed in org. solvents such as ether</p> <p>→ Separator: Micro-porous polypropylene This serves the purpose of an insulated separator between the electrodes and as electrolyte absorbent.</p> <p>Working: Discharge At anode: $\text{C}_6\text{Li}_x \rightleftharpoons \text{C}_6 + x\text{Li}^+ + x\text{e}^-$</p> <p>At cathode: $\text{Li}_{1-x}\text{Co}_{1-x}^{3+}\text{Co}_x^{4+}\text{O}_2 + x\text{Li}^+ + x\text{e}^- \rightleftharpoons \text{LiCoO}_2$</p> <p>Reactions in the backward direction occur during recharge.</p> <p>Cell potential: 3.7V</p>	<p>2M</p>
	<p>→ Applications Used in calculators, cameras, cellular phones medical instruments, television sets, Laptop computers, camcorders etc</p>	<p>1M</p>
<p>2b. Explain the experimental determination of pH of using glass</p>	<p>A cell is constructed by coupling glass electrode and a reference electrode such as calomel electrode or silver chloride electrode as shown below—</p>	<p>7M</p>
	<p>P.T.O</p>	

Q.No.	Solution and Scheme	Marks
	<p style="text-align: center;"> $\text{Pt(s), Hg(l), Hg}_2\text{Cl}_2 \text{KCl(aq)} \begin{array}{ c } \hline \text{A} \\ \hline \text{[H}^+\text{]} = C_1 \\ \hline \text{unknown} \\ \hline \end{array} \text{ } \begin{array}{ c } \hline \text{B} \\ \hline \text{[H}^+\text{]} = C_2 \\ \hline \text{known} \\ \hline \end{array} \text{AgCl, Ag}$ $E_b = E_1 - E_2$ </p> <p style="text-align: center;"> $E_{\text{Ref-2}}$ </p> <p style="text-align: center;"> $E_{\text{Ref-1}}$ </p> <p style="text-align: center;"> $E_{\text{cell}} = E_R - E_L$ </p> <p style="text-align: center;"> $E_R = E_{\text{eq}} \text{ (Right side electrode potential)}$ </p> <p style="text-align: center;"> $= E_{\text{eq}}^{\circ} - 0.0591 \text{ pH at } 298 \text{ K}$ <p style="text-align: center;">where E_{eq}° is constant</p> </p> <p style="text-align: center;"> $\text{Left side electrode potential } E_L = E_{\text{Ref-1}}$ </p> <p style="text-align: center;"> $E_L = E_{\text{Ref-1}} = E_{\text{SCE}}$ </p> <p style="text-align: center;"> $\text{Cell potential } E_{\text{cell}} = E_{\text{eq}}^{\circ} - 0.0591 \text{ pH} - E_{\text{SCE}}$ </p> <p style="text-align: center;"> $\text{pH} = \frac{E_{\text{eq}}^{\circ} - E_{\text{SCE}} - E_{\text{cell}}}{0.0591}$ </p> <p style="text-align: center;"> $\text{pH} = \frac{K' - E_{\text{cell}}}{0.0591} \text{ at } 298 \text{ K}$ </p> <p style="text-align: center;"> $K' \text{ is called glass electrode membrane assembly constant.}$ </p> <p style="text-align: center;"> $\text{In this way the pH of the test solution is measured.}$ </p>	<p style="text-align: center;">-1M</p> <p style="text-align: center;">2M</p> <p style="text-align: center;">2M</p> <p style="text-align: center;">2M</p>

Q.No.	Solution and Scheme	Marks
2c	Calculate the single electrode potential of Cu electrode at 27°C when the std potential of Cu is 0.34V and $[Cu^{2+}] = 0.1M$	1M
	<u>Solution:</u>	
	$T = 27 + 273 = 300K$	
	$E_{Cu}^{\circ} = 0.34V$	2M
	$Cu \rightleftharpoons Cu^{2+} + 2e^{-}$	
	$[Cu^{2+}] = 0.1M$	
	$n = 2$	
	$E_{Cu} = E_{Cu}^{\circ} + \frac{2.303RT}{nF} \log [Cu^{2+}]$	1M
	$= 0.34 + \frac{2.303 \times 8.314 \times 300}{2 \times 96500} \times \log [0.1]$	
	$= 0.34 + 0.0295 \cdot \log [0.1]$	3M
	$= 0.34 + (0.0295)(-1)$	
	$= 0.34 - 0.0295$	
	$E_{Cu} = 0.31045V$	
	Nernst equation is used.	
	$E = E^{\circ} + \frac{2.303RT}{nF} \log [M^{n+}]$	1M
	$R = 8.314$	
	$E^{\circ} = 0.34V$	
	$n = 2 (\because Cu^{2+})$	
	$[M^{n+}] = [Cu^{2+}]$	
	$F = 96500$	
	$= 0.1M$	

Module 2

3a. Explain the following factors which affecting rate of corrosion.

- i) Ratio of anodic and cathodic areas
ii) Nature of corrosion product

→ Ratio of anodic and cathodic area

→ Small anode and large cathode, the rate of corrosion increases $a \ll c$

Ex: steel tap and Brass tank

Steel tap acts as anode which is small compared to brass tank as it acts as cathode.

Here the corrosion is more aggressive and localised.

→ Large anode and small cathode, the rate of corrosion decreases.

Ex: steel tank and brass tap

In the above example steel tank acts as large anode and brass tap acts as small cathode. It leads to decreased corrosion. $a > c$

In this case, the corrosion is less aggressive and it is uniform.

→ Nature of corrosion product.

Some metals and alloys exhibit an inherent property of forming a protective coating of their compounds when exposed to different media.

7M

1M

1M

1M

 $\frac{1}{2}$ M

1M

Q.No.	Solution and Scheme	Marks
	<p>When the corrosion product film over the object metal surface —</p> <ol style="list-style-type: none"> i) inert to the metal surface & medium ii) Continuous (non porous) iii) Adherent to the metal surface, it starts acting as barrier between the metal and medium. Further corrosion of the metal is prevented. This is known as passivation of metal. <p>Ex:</p> <p>Mild steel - H_2SO_4</p> <p>aluminium - fuming HNO_3</p> <p>lead - dil. H_2SO_4.</p>	<p>2M</p> <p>$\frac{1}{2}M$</p>
<p>3b</p>	<p>what is anodizing? Explain the process of anodizing of Al.</p> <p>→ Anodizing</p> <p>It is a type of chemical conversion coating method of surface conversion coating method where surface metal atoms of the object are chemically converted into a protective, barrier material.</p> <p>→ Process</p> <p>Aluminium article is made an anode in an electrolytic bath containing oxidizing agent such as chromic acid, sulphuric acid, phosphoric acid, boric acid, oxalic acid etc.</p>	<p>6M</p> <p>1</p>

Q.No.	Solution and Scheme	Marks
	<ul style="list-style-type: none"> → Cathode is made of lead <u>or</u> stainless steel. <u>or</u> copper. → Moderate temperature and current densities are maintained to have better barrier material between the metal and medium. → There is formation of aluminium oxide coating over aluminium, which grows in thickness with time. 	2
	$2Al + 3[O] \longrightarrow Al_2O_3 \downarrow$ <ul style="list-style-type: none"> → Outer, porous oxide film is made non-porous through "sealing process" by immersion into boiling water <u>or</u> metal salt solution. There is hydration of Al_2O_3 into $Al_2O_3 \cdot H_2O$, which will have expanded size and thus, seal the pores. 	2
	<ul style="list-style-type: none"> → It is only applicable for nonferrous metals. <p>Applications</p> <ul style="list-style-type: none"> → Used for many design <u>or</u> architectural purposes → Used for making of window frames, soapboxes etc. 	
3c	<p>What is electroplating? Distinguish between electro and electroless plating.</p> <p>The process of electrolytic deposition of a layer of metal onto conducting object surface. <u>or</u></p> <p>The process of deposition of a thin and uniform layer of a metal <u>or</u> metal alloy onto the electrically conducting object surface by electrolysis is known as electroplating.</p>	7M 1M

Q.No.	Solution and Scheme		Marks
Property	Electroplating	Electroless plating	
1. Driving force	power supply	Autocatalytic redox reaction	
2. Site of oxidation reaction	Separate anode	Object surface to be coated	
3. Site of reduction reaction	Object surface to be plated	surface activated object	
4. Oxidation Reaction	<p>When anode is active</p> $M \rightarrow M^{n+} + ne^{-}$ <p>When anode is inert</p> $\frac{1}{2}H_2O \rightarrow nH^{+} + \frac{n}{2}O_2 + ne^{-}$	$R \rightarrow O + ne^{-}$ <p>where</p> <p>R = Reducing Agent</p> <p>O = Oxidized species</p>	6M
5. Reduction Reaction	$M^{n+} + ne^{-} \rightarrow M$	$M^{n+} + ne^{-} \rightarrow M$	
6. Time taken for deposition	Short	Long	
7. Throwing power	Low	High	
8. Plating cost	Low	High	
9. Nature of deposit	Pure metal <u>or</u> definite alloy, hard deposit	Usually metal contaminated with R <u>or</u> O derived species harder deposit.	
10. Features of deposit	May be porous & less corrosion resistant	Non porous, relatively hard & more corrosion resistant.	

Q.No.	Solution and Scheme	Marks
4a	<p>What is meant by metal finishing? Mention (any five) technological importance of metal finishing.</p> <p>→ Metal finishing Process of surface modification by way of deposition of another metal or alloy or polymer or ceramic or oxide layer to bring about intended surface characteristics is known as metal finishing.</p> <p>→ Technological importance</p> <ol style="list-style-type: none"> i Better corrosion resistance ii Better optical reflectance iii Better hardness, strength, wear or abrasion resistance, impact resistance iv Better electrical conductance or insulation v Electroforming or reforming of articles vi Electrotyping vii Electrochemical machining, electropolishing and electrochemical etching viii Manufacturing printed circuit boards, capacitors, contacts etc. 	6M 6M (5+1)
4b	<p>A thick steel sheet of area 400 cm^2 is exposed to air near the ocean. After a one year period it was found to experience a weight loss 375 g due to corrosion. If the density of the brass is 7.9 g/cm^3. Calculate the corrosion penetrating rate in mpy and mm/y (given $K = 534 \text{ in mpy}$ and 87.6 in mm/y)</p>	7M

To calculate CPR in mpy

	Given	CPR in mpy
K		534
W (wt loss)	375g	375 x 1000 mg
P	7.9 g/cm ³	7.9 g/cm ³
A	400 cm ²	400 x 0.155 in ²
T	1 year	365 x 24 hrs
CPR	-	?

$$CPR = \frac{K \times W}{(D) P \times A \times T}$$

$$= \frac{534 \times 375 \times 1000}{7.9 \times 400 \times 0.155 \times 365 \times 24}$$

$$= \frac{200250000}{4290648}$$

$$= 46.6712 \text{ mpy}$$

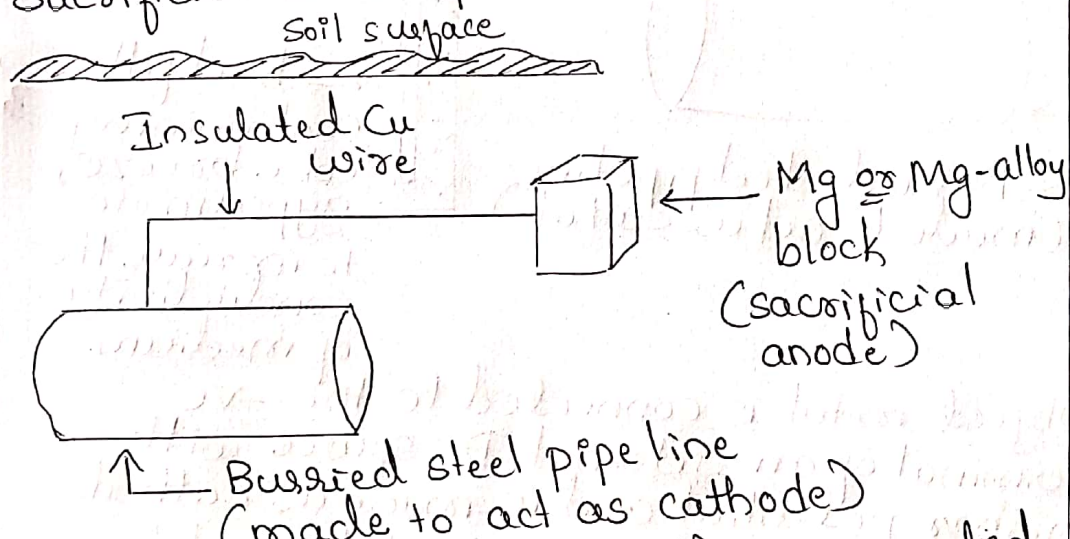
To calculate CPR in mm/y

	Given	CPR in mm/y
K		87.6
W (wt loss)	375g	375 x 1000 mg
P	7.9 g/cm ³	7.9 g/cm ³
A	400 cm ²	400 cm ²
T	1 year	365 x 24 hrs
CPR	-	?

$$CPR = \frac{K W}{D(P) \times A \times T}$$

$$= \frac{87.6 \times 375 \times 1000}{7.9 \times 400 \times 365 \times 24}$$

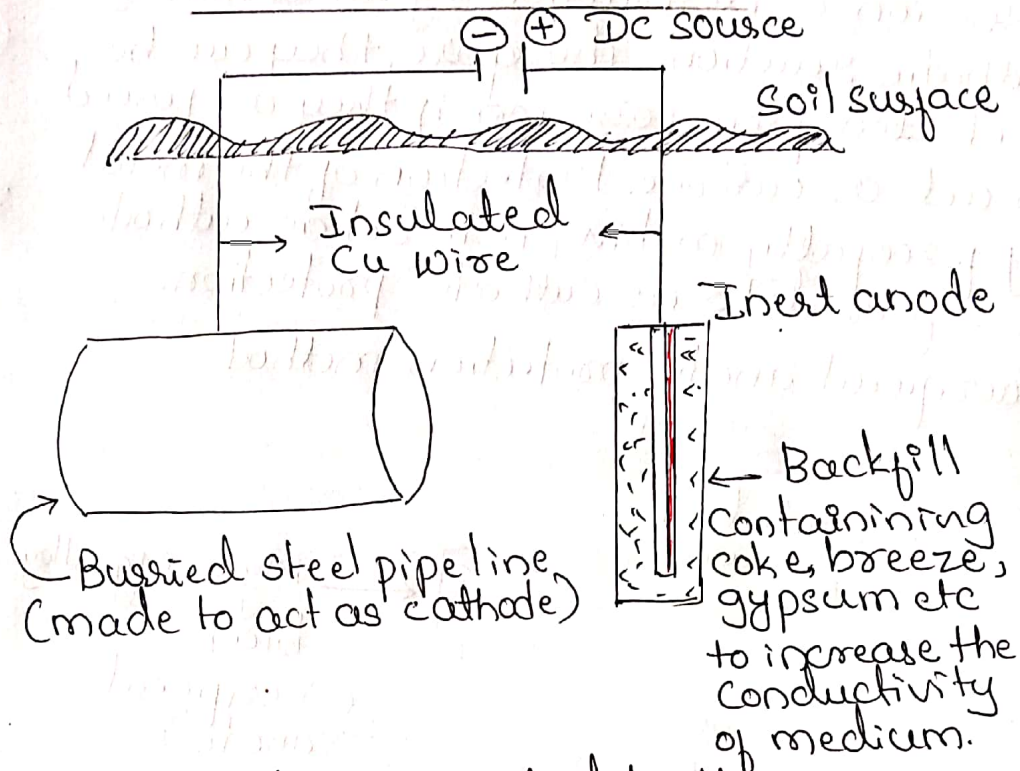
$$= 1.186 \text{ mm/y} \approx \text{mm/y}$$

Q.No.	Solution and Scheme	Marks
4c.	<p>What is cathodic protection? Explain sacrificial anode and impressed voltage methods of cathodic protection</p>	7M
→	<p>Cathodic protection Metals undergo corrosion by oxidation <u>or</u> anodic reaction. They do not undergo corrosion <u>or</u> destruction by reduction <u>or</u> cathodic reaction. Therefore, they can be protected from corrosion if they are forced to act as cathode. Protection of the metal by forcefully making it to act as cathode is referred to as cathodic protection.</p>	7M
→	<p>Sacrificial anodic protection method</p>  <p>Soil surface</p> <p>Insulated Cu wire</p> <p>Mg <u>or</u> Mg-alloy block (sacrificial anode)</p> <p>Busried steel pipe line (made to act as cathode)</p>	3½
→	<p>Object metal (such as steel) is connected to a block of an anodic metal such as Zn, Al Mg, <u>or</u> their alloys.</p>	
→	<p>Whenever there is demand of electrons by the corrosives in the medium, anodic metal will sacrificially undergo oxidation & release the electrons. Thus the object metal is protected.</p>	
→	<p>As long as anodic metal block is existent, protection is achieved. When it disappears fresh block is replaced.</p>	

Applications

→ Employed for buried pipelines used for water or oil, water tanks, ocean going ships, piers etc.

b) Impressed voltage (current) cathodic protection of metals.



→ Object metal is connected to the -ve terminal of an external DC source with higher potential and is made as cathode.

→ An inert anode such as graphite or platinum immersed in a backfill containing coke breeze gypsum etc. is connected to the positive terminal. Backfill is used to increase the conductivity.

→ Electrons are demanded by corrosive medium at the object surface, are supplied from the external battery and object metal is protected. As and when battery potential decreases, it is recharged.

→ Application: Employed for buried pipe lines used for water or oil, ships etc.

3/2

Module - 3

5a. What are polymer composites? Explain the synthesis and applications of Kevlar fibre.

1M

→ Polymer composites

Harmonious combination of two or more materials, at least one of them being a polymer and another being reinforcing material is referred to as polymer composite.

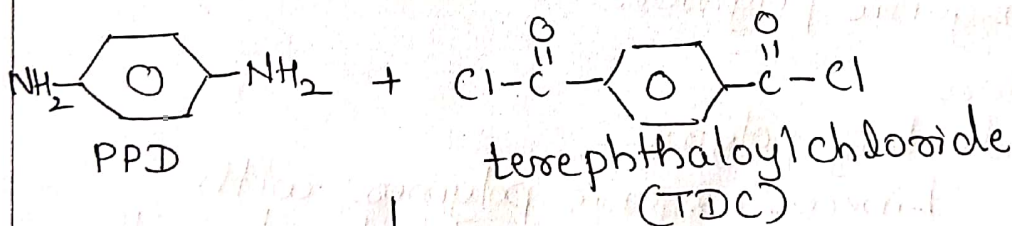
1M

→ Synthesis of Kevlar fibre.

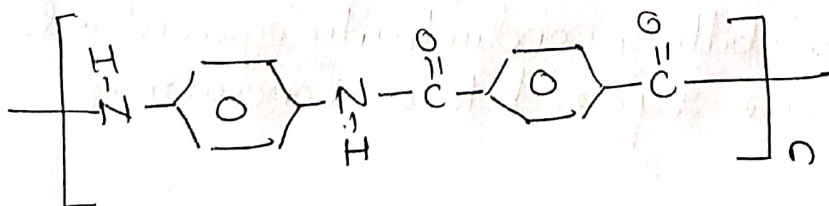
Kevlar is polyamide, in which all the amide groups are separated by para-phenylene groups. The chemical composition of Kevlar is polypara-phenylene terephthalamide.

3M

→ It is synthesized by reacting para-phenylene diamine with terephthaloyl chloride with elimination HCl. It is condensation polymerization reaction.



$-\text{HCl}$ Condensation polymerization



1M

Q.No.	Solution and Scheme	Marks
	<p>properties of Kevlar</p> <ul style="list-style-type: none"> → High tensile strength at low weight → Low elongation to break → High modulus → Low electrical conductivity → High cut resistance → Flame resistant, high toughness <p>Applications</p> <ul style="list-style-type: none"> → Body armour: Bullet proof vests & helmets → Ropes & cables → Belts and hoses for industrial applications → Composites for aircraft body parts, boats and sporting goods. → Fibre-optic cables for communication, data transmission & ignition → Sailing motor cycle outer wear → Adhesives and sealants. 	2M
	<p>5b. What are conducting polymers? Explain the various factors influencing the conduction in organic polymers.</p> <ul style="list-style-type: none"> → Factors → Conducting polymers <p>Linear, organic polymers with conjugate single and double bonds with suitable doping by oxidation or reduction or proton etc. with delocalised π electron system, exhibiting conductivity equivalent to metals are referred to as conducting polymers.</p>	7M
	<p>1 Effect of dopant</p>	1M

Q.No.	Solution and Scheme	Marks
	<p>It has been observed that conductivity increases by doping. The conductivity of doped poly acetylene is comparable to that of copper on an equal weight basis. Doping is the oxidation or reduction of polymer molecules to yield poly cations or polyanions.</p> <p>The kind of oxidative or reductive dopant, proton dopant, their proportion, solvent used in synthesis will all be influencing the conductivity of the polymers to different levels.</p> <p>Some common oxidizing agents are HClO_4, FeCl_3, AsF_5, I_2, NH_4BF_4, SO_3CF_3, HCl, HNO_3 and some reductants are Li, K, Na etc.</p> <p>2. Effect of Temperature</p> <p>The conductivity of semiconducting materials increases with rise in temperature because higher thermal excitation releases more of the electrons from inter atomic bonds. Under the applied electric field these higher number of electrons in the polymeric substance give rise to increased electronic conduction with rise in temperature.</p> <p>3. Effect of Band gap</p> <p>The conductivity of conducting polymers increases with decrease in band gap. The band gap represents the amount of energy required to excite and promote an electron from the highest occupied energy level or valence band to the next empty band</p>	<p>3 1/2</p> <p>3 1/2</p>

Q.No.	Solution and Scheme	Marks
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immediately above it. Metals have zero band gaps. Polymers have large band-gaps and are insulators. Conducting polymers have lower band gaps. A band gap of $\sim 1\text{ eV}$ is reported for conducting polymers

5c Briefly explain the carbon nanotubes with properties and applications

6M

Carbon nanotubes are allotropes of carbon with a cylindrical shape. They are nanoscale tube like structures, which are like nanowires, in terms of aspect of ratio but unlike wires, tubes are hollow. Nanotubes may be single walled or multiwalled. Carbon nanotubes, composed of interlocking carbon atoms, are 1000 times thinner than human hair and can be 100 times stronger than steel.

1M

→ Properties

CNT's have very high surface areas, aspect ratios and mechanical strength. The tensile strength of CNTs is nearly 100 times greater than when compared to steel. The electrical conductivity reaches that of copper and thermal conductivity reaches that of diamond.

2M

Structures 1D

C-C bond length: 1.42 \AA

Density: $1.2 - 2.0\text{ g/cm}^3$

Electrical conductivity

CNT with arm chair structure give good conductivity, zig-zag or chiral structure gives semi conductivity.

Thermal conductivity : Higher than diamond
 Strengths : Many fold stronger than steel
 Hardness : Harder than diamond
 Exhibit hydrophobic property and oil absorption property.

Applications

- CNT's are used for reinforcing different structures where lightness and strength of materials required.
- CNT's are used as hydrogen storage material for fuel cells and some secondary batteries
- They catalyse many organic reactions.
- Used for filtering air and water for purification purposes.
- Functionalized CNT's are used as sensors and used for diagnosis and therapeutic applications.

3M

6a. Explain optical and electrical properties of nanomaterials.

7M

→ Optical properties

Nanomaterials have unique optical properties as a result of the way light interacts with their nanostructure. Due to interference, scattering, surface plasmons and quantum fluorescence.

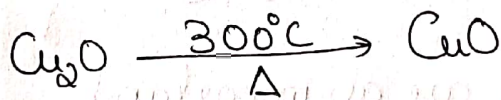
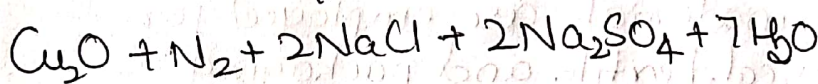
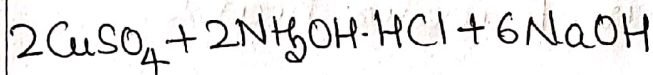
Nanoparticles will have quantized energy states. Excitation or deexcitation of electrons from/to these discrete energy

Q.No.	Solution and Scheme	Marks
	<p>States happens by certain definite wave length. Quantum confinement causes the energy gap to increase; therefore, more energy is needed. Higher energy means shorter wavelength (blue shift) or lower energy means longer wavelength (red shift). This is how one can control the size and shape of nanoparticles and control the color.</p> <p>Nanoparticles of metals exhibit surface plasmon resonance (SPR). When light strikes the nanoparticle, electrons on the surface start oscillating about their position in a small space and depending on the frequency of oscillation, resonating electrons absorb/scatter radiation of different wavelength.</p> <p>→ Electrical properties</p> <p>Substances can be classified as good conductors, semiconductors and insulators depending upon their electrical conductivity or resistivity.</p> <p>The energy gap between the valence band and conduction band and the presence and number of electrons in the conduction band decides the conductivity of the material. In a good conductor like a metal, there is overlapping of VB and CB i.e. valence band and conducting band.</p> <p>Larger the numbers of atoms in a bulk metal and overlapping of their orbitals results in overlapping of VB with CB and</p>	<p>3/2</p>

Q.No.	Solution and Scheme	Marks
	<p>energy levels are continuous and the metals are very good conductors. Some metals which are good conductors become semiconductors <u>or</u> insulators as their size is reduced to nanoscale. When the number of atoms decreases like in a nanomaterial, very few orbitals overlap and the energy levels separate <u>or</u> become discontinuous. This is sometimes known as quantum confinement. Electrons do not find space to move around; instead they are confined to very small space <u>or</u> nanospace. Thus, with the increased discontinuity, nanomaterials tend to become semiconductors <u>or</u> insulators.</p> <p>Nanomaterials also show very interesting tunnelling effect. An electron is seen on the other side of the barrier without enough kinetic energy because of the wave property of the particles. Though, the intensity gets lowered. Also some of the nanostructures exhibit exceptional electrical conductivity like carbon nanotubes <u>or</u> graphene because of their unique structure.</p>	<p>3/2</p>
6b	<p>What are nanomaterials? Explain the synthesis of nanomaterials by precipitation method.</p> <p>→ Nanomaterials.</p> <p>Nanomaterials are the materials having nanoscale dimension in at least one direction. Materials containing particles, in an unbound state <u>or</u> as an aggregate <u>or</u> as an agglomerate</p>	<p>6M</p> <p>4M</p>

Q.No.	Solution and Scheme	Marks
	<p>where, for 50% <u>or</u> more of the particles in the number size distribution, one <u>or</u> more external dimensions is in size range 1nm to 100nm.</p> <p>→ Precipitation method</p> <p>This method relies on precipitation of nanosized particles within a continuous fluid solvent. An inorganic metal salt, such as chloride, nitrate and so on is dissolved in water. Metal cations exist in the form of metal hydroxide species.</p> <p>Ex: $Al(H_2O)_3^{3+}$ The ppt is washed, dried & calcined.</p> <p>The typical example of synthesis of CuO nanomaterials is explained as follows.</p> <p>→ Synthesis of CuO nanoparticles</p> <p>CuO nanoparticles were synthesized by aqueous precipitation method. using 55g of $CuSO_4$ penta hydrate mixed with 25g of hydroxyl ammonium chloride in 125ml distilled water.</p> <p>The mixture was allowed to cool in a cold water bath with swirling well and solution of 40g of $NaOH$ in 750ml distilled water was added.</p> <p>The ppt was allowed to settle down and supernatant liquid was poured off. The oxide is transferred to 250ml flask and the volume is made up. The content is washed by repeated decantation until the</p>	<p>1M</p> <p>4M</p>

washing is chloride free. The suction filtration is applied and residue is washed with 95% alcohol and ether. The residue is dried at 200-250°C in air oxidized conditions to obtain Cu_2O and then further the temp is increased to 300°C which leads to the formation of CuO . For the formation of Cu_2O nanoparticles from Cu_2O precipitant, the following reaction mechanism can be formulated and represented as —



Advantages:

- It is very simple and rapid method of precipitation of nanoparticles.
- Particle size and crystallinity can be controlled by optimizing conditions.

6c What are biodegradable polymers? Explain the properties & applications of polylactic acid

→ Biodegradable polymers.

The polymers which breakdown after their intended use by microbial decomposition into biocompatible CO_2 , nitrogen, methane, water, biomass and inorganic

7M

1M

Q.No.	Solution and Scheme	Marks
	<p>Compounds are called as biodegradable polymers.</p> <p>Properties of Polylactic acid</p> <ul style="list-style-type: none"> → Is an amorphous or crystalline thermoplastic polymer. → Glass transition temperature, $T_g = 60-65^\circ\text{C}$ → Melting point, $MP = 130-180^\circ\text{C}$ → Soluble in ethyl acetate, propylene carbonate, pyridine, hot benzene, dioxane etc. → Has high surface energy. → Degrades on exposure to water, heat & light. <p>Applications</p> <ul style="list-style-type: none"> → PLA-based materials are employed for the biomedical, textile and packaging purposes → Micro and nanoparticles are an important category of delivery systems used in medicine controlled drug delivery and fracture fixation devices like screws, resorbable sutures, plates, pins, rods, wires etc. and various molded articles. → Porous PLA scaffolds have been found to be potential reconstruction matrices for damaged tissues & organs. → Fibres for textile industry or sutures films and nonwoven textile for clothes. → High surface-molded cups, spoons & forks, trays, paper coatings etc. 	<p>3M</p> <p>3M</p>

Module - 4

7a Briefly explain any six basic principles of green Chemistry. 6M

1. Better to prevent than Cure

Design chemical synthesis to prevent waste. Leave no waste, or treat or cleanup.

Waste prevention is necessary because of the following reasons.

→ If a process produces waste, it invokes the need for its treatment/disposal which in turn amounts to additional expenditure.

→ Secondly if the waste is toxic or hazardous the release of waste into the environment leads to its pollution, which further invokes the need for treatment causing additional expenses.

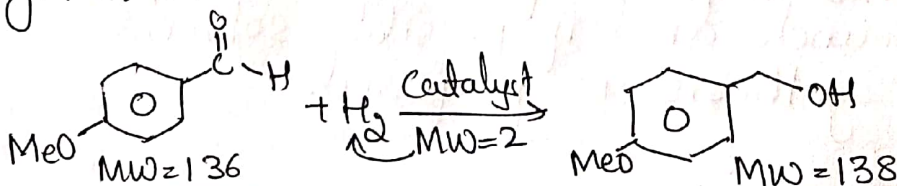
Ex: The bottom of ash of thermal power station can be used as a raw material for cement and brick industry.

Effluent coming out from cleaning of machinery parts may be used as coolant water in thermal power stations.

2. Atom economy

Design, synthesize so that the final product contains the maximum proportion of starting materials.

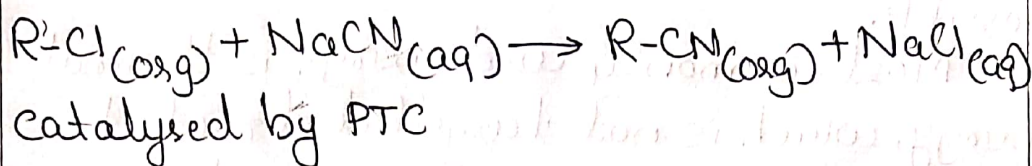
Ex: The % Atom economy of the reaction given below is _____



Q.No.	Solution and Scheme	Marks
11	$\% \text{ Atom Economy} = \frac{\text{Relative MW of desired product}}{\text{Relative MW of all reactants}} \times 100$ $= \frac{138}{(136+2)} \times 100$ $= 100\%$	
3.	<p>Less hazardous chemical synthesis Design, synthesize to use and generate substances with little <u>or</u> no toxicity to either humans <u>or</u> the environment. An important example of concerning the use of safe chemicals is the manufacture of polystyrene foam sheet packaging material where in chemist have replaced the use of hazardous CFC by CO_2 as the blowing agent.</p>	1
4.	<p>Designing safer chemicals. Design chemical products that are fully effective & have little <u>or</u> no toxicity. Ex: Benzene is the starting material for the synthesis of adipic acid. Benzene is carcinogenic & being VOC it pollutes the air.</p>	1
5.	<p>Use safer solvents and reaction conditions. Avoid using solvents, separation agents <u>or</u> other supporting chemicals. If you must use these chemicals; use safer ones. This principle aims to use green solvents in place of volatile halogenated compounds and if possible solvent free synthesis is preferred.</p>	1

Q.No.	Solution and Scheme	Marks
6.	<p>Design for energy efficiency Run chemical reactions at room temperature and pressure whenever possible.</p> <p>Most commonly used energy is thermal energy, which is not targeted direct at a bond <u>or</u> ongoing reaction instead most of the energy is wasted in heating up reactors, solvents & surrounding environment. This problem is avoided by using alternative sources such as photochemical, microwave <u>or</u> ultrasound energy.</p>	1
7b	<p>Explain the following i) Phase transfer catalyst ii) solvent free reactions</p> <p>→ Phase transfer catalytic Reactions</p> <p>A phase transfer catalyst <u>or</u> PTC is a catalyst that facilitates the migration of a reactant from one phase into another phase. where reaction occurs.</p> <p>→ Ionic reactants are often soluble in an aqueous phase but insoluble in an organic phase in the absence of phase transfer catalyst.</p> <p>→ Types of PTC</p> <p>i) Quaternary ammonium salts Ex: benzyltrimethyl ammonium chloride methylcaprylammonium chloride</p> <p>2) Organic phosphonium salts Ex: Hexadecyl tributyl phosphonium bromide</p>	<p>1M</p> <p>1M</p> <p>2M</p>

Phase transfer catalysis refers to the acceleration of the reaction upon the addition of the phase transfer catalyst.



Example:

Cyanation of alkyl chloride - a major way to produce nitriles.

The alkyl chlorides are poorly soluble in aqueous cyanide solution & the sodium cyanide does not dissolve well in organic solvent. In the presence of suitable PTC a rapid reaction ensures the production of alkyl nitrile.

→ Advantages

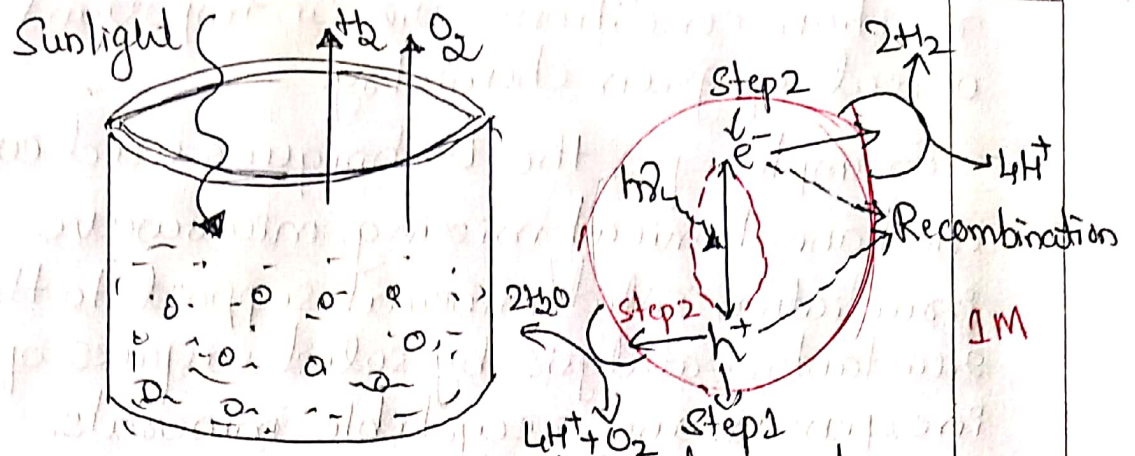
1. Elimination of organic solvents
2. High yields and purity of products
3. Simplicity of procedure
4. Low investment cost.
5. Minimization of industrial waste.
6. High reactivity & selectivity of the active species.

b) Solvent free Reactions

Avoiding organic solvents during the reactions in organic synthesis leads to clean, efficient and economical technology.

Use of organic solvents is objectionable from the standpoint of environmental hazard. This is why solvent free.

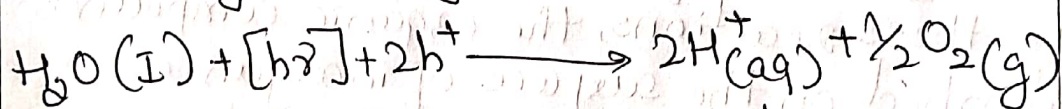
Q.No.	Solution and Scheme	Marks
	<p>reaction conditions are an important object of green chemistry.</p> <p>Examples for the techniques used are mechanochemical mixing, microwave irradiation solid/mineral support to the reactants, catalysis by solid surfaces of inexpensive and recyclable minerals. (eg: alumina, silica, clay, doped clay surface)</p> <p>→ Advantages</p> <ol style="list-style-type: none"> 1. A wide variety of industrially important compounds and intermediates such as enones, imines, enamines and nitroalkenes have been prepared by this environmentally friendly solvent free approach. 2. In these reactions, the organic compounds adsorbed on the surface of inorganic oxides such as ammonia, silica, clay or doped supports absorb microwaves whereas the solid support does not absorb or restrict their transmission. 3. The bulk temperature is relatively low in such solvent free reactions. <p>7C With a neat diagram explain the production of hydrogen by photocatalytic method TM</p> <p>→ Hydrogen production by photocatalytic Reaction.</p> <p>Input: Photocatalytic particles, sunlight & water</p> <p>Output: Oxygen & hydrogen</p>	



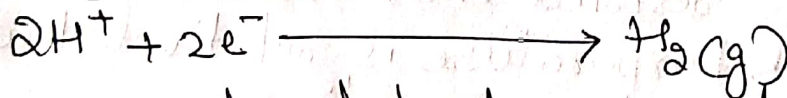
→ Splitting of water to get hydrogen by using a photocatalyst & using solar energy is called photocatalytic water splitting.

→ The light energy excites an electron (e^-) in the catalyst.

Thus produced hole (h^+) will react with neighbouring water molecule.



→ The H^+ ions combine to produce hydrogen at the surface of the co-catalyst.



The produced hydrogen can be used as the fuel in the hydrogen fuel cell.

→ Here holes are oxidizing the water & electrons reduce hydrogen ions to hydrogen gas.

8a. Describe the hydrogen production by photoelectrocatalytic method

→ H_2 production by photoelectro catalytic water splitting

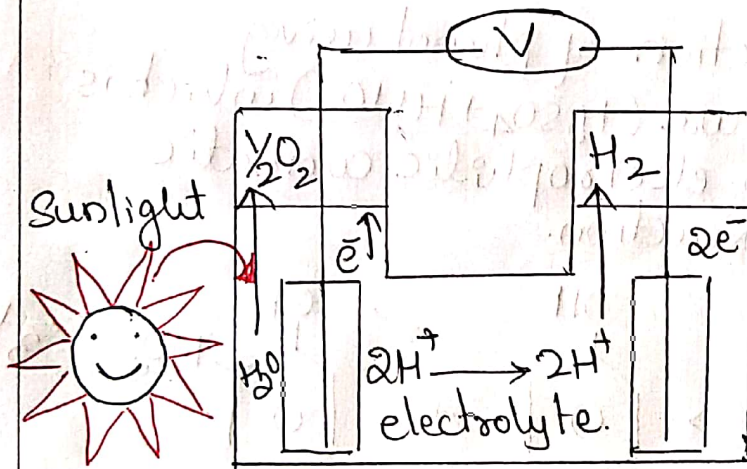
Photoelectro (PEC) catalytic water splitting is artificial photosynthesis approaches for hydrogen fuel production.

It involves photogenerated carriers on the surface and reactants adsorbed on the surface or in electrolyte.

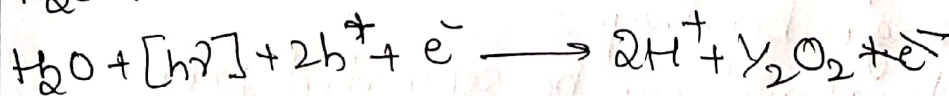
The reaction takes place at the electrode electrolyte interface.

Input: Semiconductor photocatalyst (anode), sunlight, water

Output: Hydrogen and Oxygen

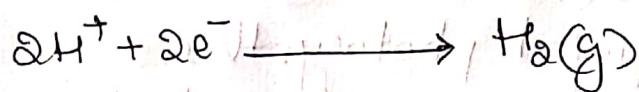


The light energy excites an electron (e^-) in the semi conducting material (electrode). Thus produced hole (h^+) will react with the neighbouring H_2O molecule.



P.T.O

The H^+ ions formed will then bond with other proton and combine with two electrons to form H_2 gas



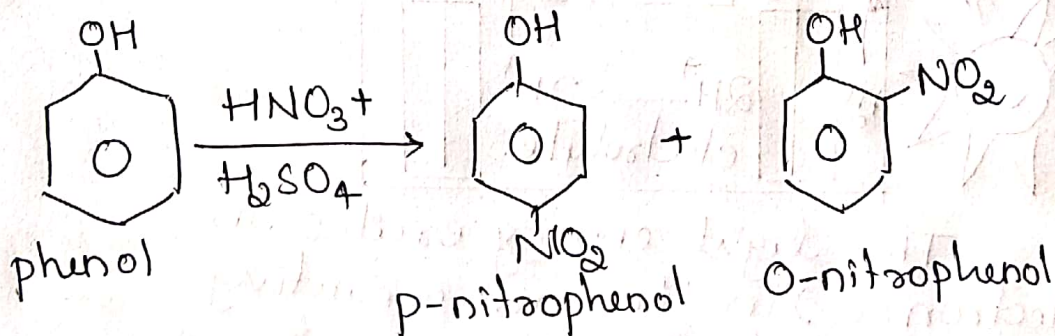
The produced H_2 gas can be used as the fuel in hydrogen fuel cell.

8b Explain synthesis of paracetamol by conventional and green route from phenol

→ Synthesis of paracetamol by conventional route using phenol

Step 1:

Nitration reaction of phenol using nitrating mixture ($H_2SO_4 + HNO_3$) which is an example of electrophilic aromatic substitution Reaction.



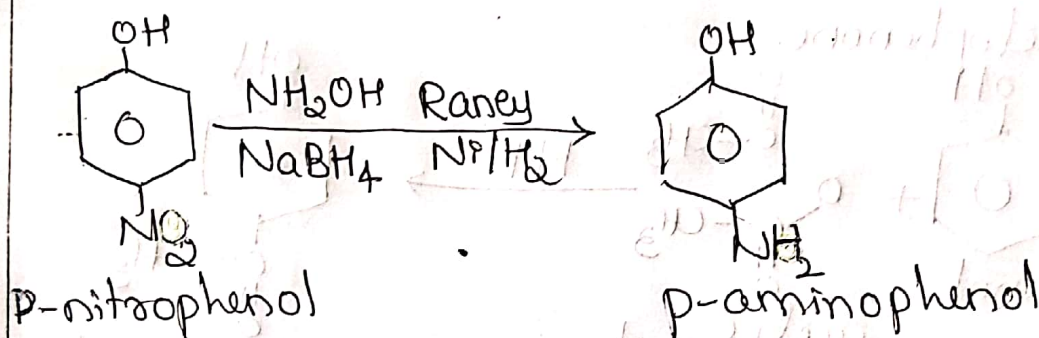
p-nitrophenol is more stable than o-nitrophenol because of intermolecular hydrogen bonding.

p-nitrophenol can be separated from o-nitrophenol by HPLC or column chromatography

Only p-nitrophenol is further used for synthesis of paracetamol.

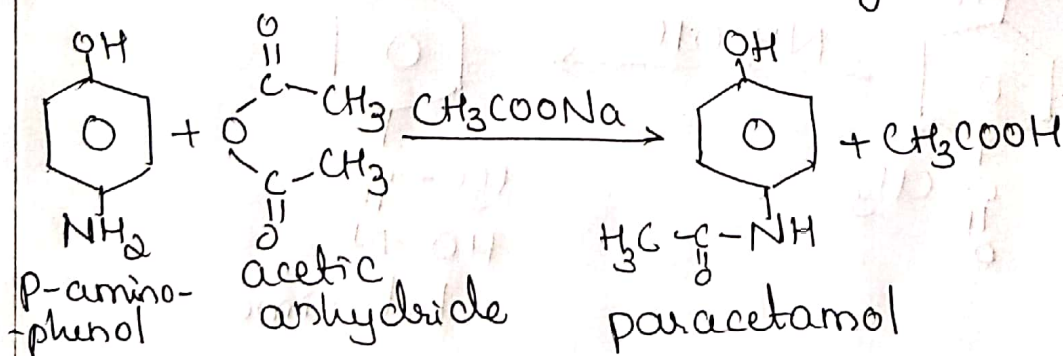
Step II:

Reduction of nitro group ($-\text{NO}_2$) to amine group ($-\text{NH}_2$) using reducing agents such as sodium borohydride (NaBH_4), hydroxylamine (NH_2OH), metals in acidic medium (Sn/HCl) or using Raney Ni in presence of $\text{H}_2(\text{g})$



Step III:

Nucleophilic addition reaction of p-aminophenol with acetic anhydride in presence of sodium acetate. The N atom (of NH_2) is more nucleophilic than the O atom of (OH) & hence the reaction occurs with NH_2 group

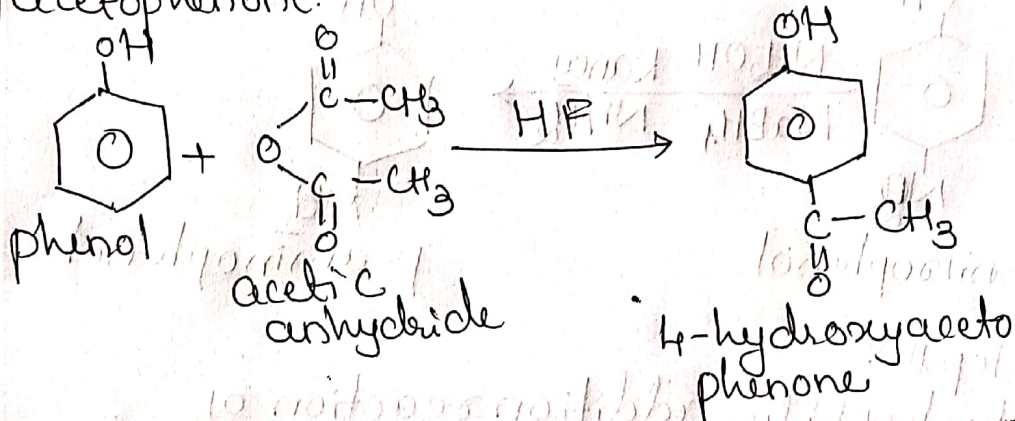


The drawback of this method is the % atom economy calculated for this synthesis is 36%.

→ Synthesis of paracetamol by Green Route

Step I:

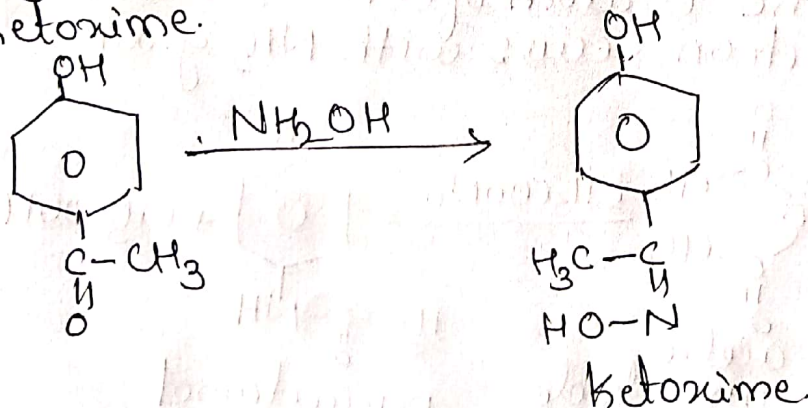
Phenol reacts with acetic anhydride in the presence of strong acid HF to undergo acylation reaction which is an electrophilic substitution, to produce 4-hydroxyacetophenone.



3 1/2

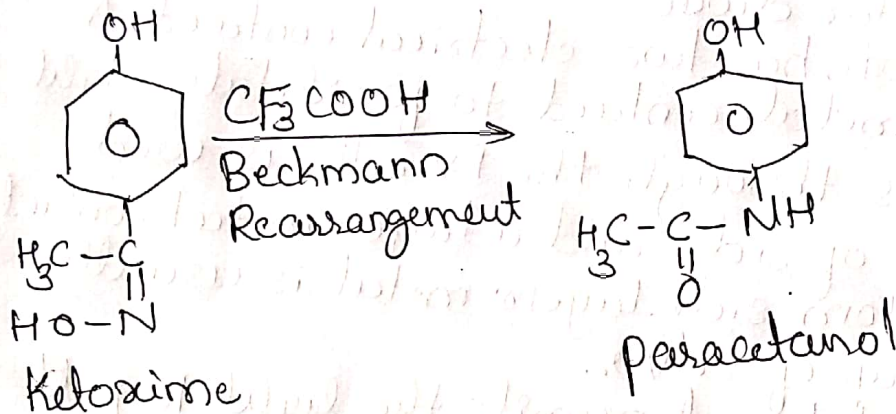
Step II:

4-hydroxyacetophenone reacts with hydroxylamine to give corresponding ketoxime.



Step III:

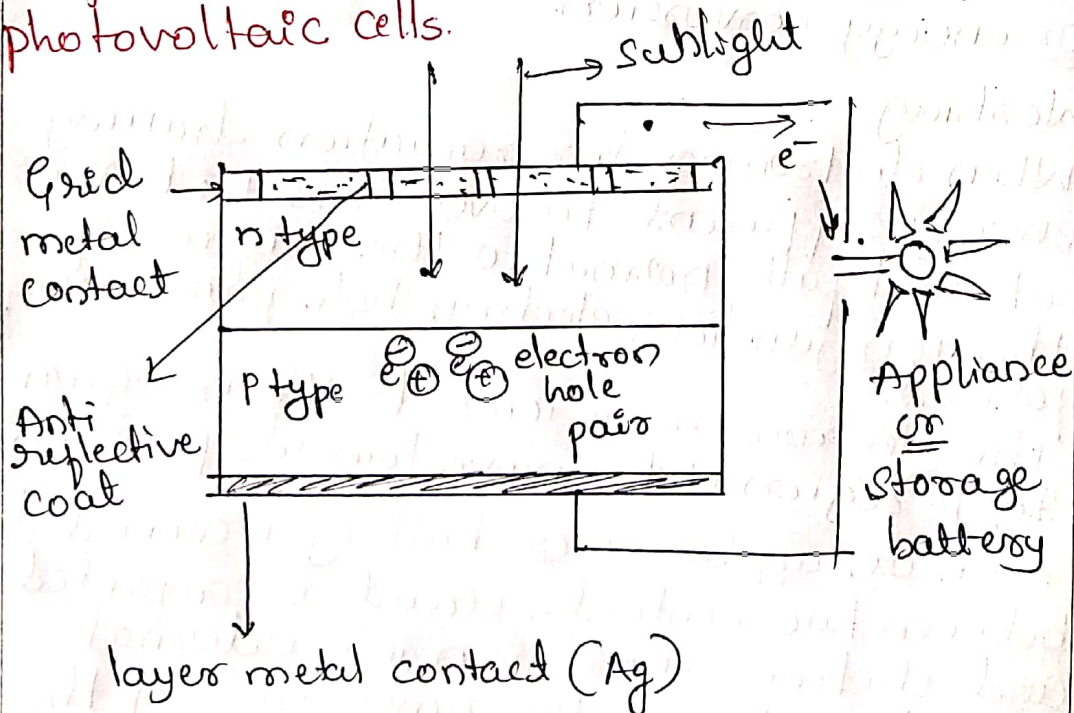
Oximes in acidic medium (trifluoroacetic acid) undergoes "Beckmann - rearrangement" to produce substitute amides. Beckmann rearrangement of the above ketoxime gives paracetamol.



% Atom economy calculated for this green synthesis $\approx 58\%$.

8c. Explain construction and working of photovoltaic cells.

6M



Q.No.	Solution and Scheme	Marks
	<p>Photovoltaic cells are the devices that convert solar energy directly into electrical energy from semiconductor diode.</p> <p><u>Construction</u></p> <ul style="list-style-type: none"> → Photovoltaic cells are made of semiconductor diode → The diode has two electrical contact. A grid metal contact to facilitate light to pass through the PV cells is used on top of side and a layer metal contact on bottom side. layer metal is usually made up of silver. → The metal grid permits the light to fall on the diode between the grid lines. → An anti-reflective coat (Si_3N_4 & TiO_2) is used between the grid lines to increase the efficiency of light absorption or energy conversion. <p><u>Working</u></p> <ul style="list-style-type: none"> → When electromagnetic radiation having energy sufficient to overcome the barrier potential falls normal to the surface of the p-n junction, electron-hole pairs are formed. → The electrons move towards the n-region → Holes move towards p-region → When an appliance or battery is connected between two contacts, circuit is completed and electrons are driven into external circuit enabling the functioning of the appliances or charging of the battery. 	<p>3M</p> <p>3M</p>

Q.No.

Solution and Scheme

Marks

Charged battery is used for application such as lighting and telecommunication.

→ Depending on the energy requirement PV cells are connected either in series or parallel and designed to make modules or panels or arrays.

Module 5

9a Explain the theory, instrumentation and application of flame photometry

7M

→ Theory

An analysis by way of measurement of emission intensities of characteristic light by the element when a solution of element is sprayed into the flame is flame photometry. The wavelength of light emitted is function of nature of the substance and the amount of light emitted is a function of concentration.

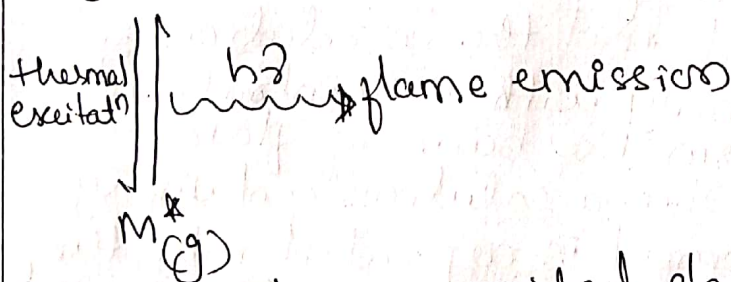
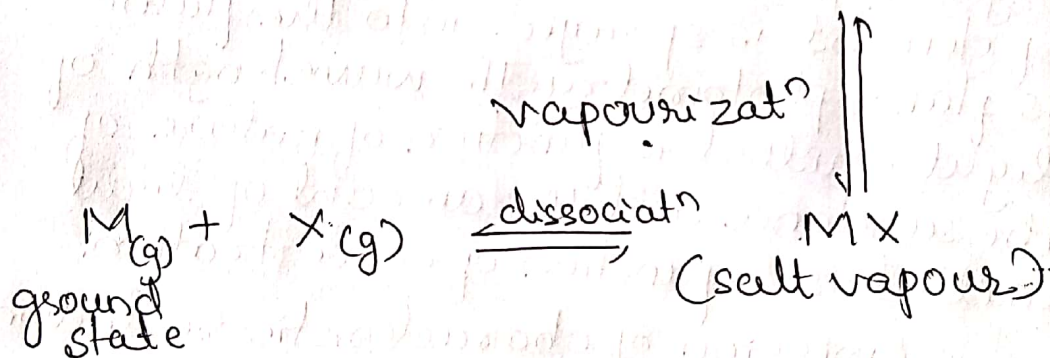
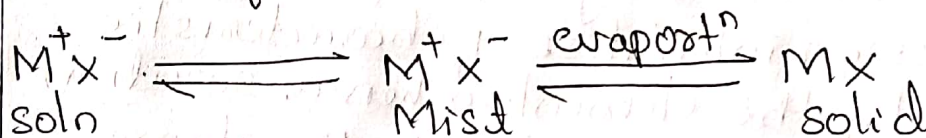
3M

Emission of characteristic radiation by an element and the co-relation of emission intensity with concentration of element, form the basis of flame photometry. When a solution containing the sample element is aspirated into the flame; solvent evaporated. Further, solid salt is also evaporated into flame, dissociated into ions ~~at~~ its constituent atoms. A fraction of metal atom is excited. Being unstable in the excited state, excited atoms revert back to their ground state by emitting light radiation.

of specific element.

The intensity of emitted light is proportional to the number of atoms in the excited state, which in turn is proportional to the concentration of element in the solution fed into the flame. Thus, by measuring the emission intensity of the analyte, concentration of sample element determined.

Sequential changes that take place when a metal salt solution is aspirated into the flame are summarized below.



(Gaseous atom in excited state)

The intensity of the emitted radiation, measured as detector response is related to the analyte concentration by an expression:

$$E = k \alpha c$$

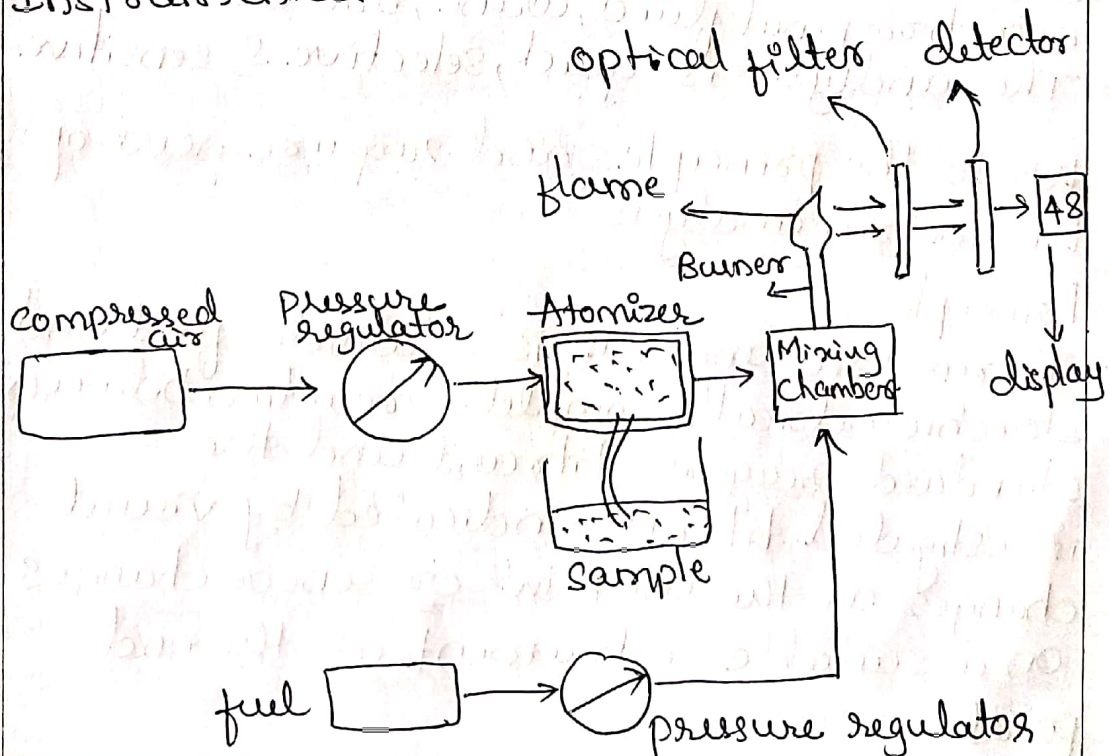
1/2

where E is the detector response, K is a constant, α is the efficiency of atomic excitation and 'c' is the concentration of metal salt solution.

Quantitative analysis can be carried out by preparing a series of standard solutions of metals to be analyzed, aspirating into the flame and measuring the emission intensity of each solution in a flame photometer. A calibration curve is obtained by plotting emission intensity against the concentration of metal in the standard solutions. The test solution also is aspirated into the flame & emission intensity is measured. Emission intensity is compared on calibration curve and concentration of metal in the test solution is determined.

3M

Instrumentation



1/2

Q.No.	Solution and Scheme	Marks
	<p>The flame photometer consists of an atomizer, mixing chamber, burner, filter, detector and read out device. Air at certain pressure is passed into an atomizer and the solution suction. This produces, draws a solution of sample to atomizer. Here it joins the air stream as a fine mist and passes into the mixing chamber where, it mixes with the fuel gas and gets dissociated in the burner flame. Radiation from the resulting flame passes through a lens, and through an optical filter which permits only the radiation characteristic of element under investigation to pass through the photo cell. The output from the photo cell is measured on a suitable digital read out system.</p> <p>Applications</p> <ul style="list-style-type: none"> → The flame photometer may be used for determination of Ca in blood serum, cerebrospinal fluid, urine, bile etc. → The analysis is quick, selective & sensitive. 	
9b	<p>Write the principles and requirements of titrimetric analysis</p> <p>Principle</p> <ul style="list-style-type: none"> → Titrimetric analysis is relatively fast and stoichiometrically complete reaction between standard reagent - titrant and the investigated titrand; indicated by visual changes at the endpoint or sensor changes on a suitable instrument. at the end point. 	7M 2

Q.No.	Solution and Scheme	Marks
	<p>Requirements for titrimetric analysis.</p> <p>→ The reaction between titrant and titrand should be possible to be written as a stoichiometric equation and it should go to completion in stoichiometric proportions.</p> <p>→ The reaction between two should be relatively fast. Many ionic reactions between titrant and titrand are relatively fast.</p> <p>→ End of the reaction between titrant and titrand should be indicated by a color change or formation of a precipitate or a change in chemical property indicating the stoichiometric equivalence point.</p> <p>→ An indicator should be available and it should sharply indicate the endpoint of reaction or titration by changes stated above. Especially when the detection of equivalence point is required to be known without color or visual changes it is achieved by following course of the reaction or titration by —</p> <ul style="list-style-type: none"> i) potentiometry ii) conductometry or iii) amperometry iv) spectrometry etc. 	5
90	<p>In a COD test 30.5cm^3 and 15.5cm^3 of 0.05N FAS solutions were consumed for blank & sample titration respectively. The volume of test sample used was 25cm^3. Calculate COD of sample.</p> <p>Solution:</p> <p>Sample water taken for analysis (Z) = 25ml</p>	6M

Q.No.	Solution and Scheme	Marks
	<p>Main titre value (P) = 15.5 cm^3 Blank titre value (Q) = 30.5 cm^3 $(Q - P) = (30.5 - 15.5)$ $= 15.0 \text{ cm}^3$</p> <p>Concentration of FAS (Y) = 0.05 N COB = ?</p> <p>1000 ml of 1N FAS = 8 g oxygen 1 ml of 1N FAS = $\frac{8}{1000}$ g of O_2 $(Q - P)$ ml of YN FAS = $\frac{8}{1000} \times (Q - P) \times Y$</p> <p>Expression in terms of ppm the above equation becomes</p> $\text{COB} = \frac{8}{1000} \times (Q - P) \times Y \times \frac{10^6}{25} \text{ ppm}$ $= \frac{8}{1000} \times (30.5 - 15.5) \times 0.05 \times \frac{10^6}{25}$ $= \frac{8}{1000} \times 15.0 \times 0.05 \times \frac{10^6}{25}$ $= \frac{8 \times 15.0 \times 10^3 \times 0.05}{25}$ $= 0.24 \times 10^3$ $= 240 \text{ ppm or mg/L}$	<p>1M</p> <p>2M</p> <p>3M</p>

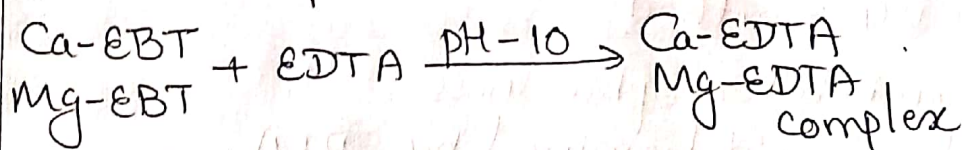
Q.No.	Solution and Scheme	Marks
10a	<p data-bbox="311 129 1252 264">Explain the determination of hardness by EDTA method</p> <p data-bbox="311 273 933 340">Determination of hardness</p> <p data-bbox="215 340 1364 1534"> → Hardness is determined by EDTA - complexometric method. The method involves the titration of known volume of hard water against std. EDTA solution using EBT as metal ion indicator, at pH = 10. The complexation reaction is complete at this pH and color change happens to be sharp at the end point. The indicator forms relatively less stable wine red colored Ca-EBT & Mg-EBT complexes. When EDTA solution is added initially, it will react with freely available Mg^{2+} & Ca^{2+} ions & towards the endpoint, it snatches Ca^{2+} & Mg^{2+} ions from the less stable Ca-EBT & Mg-EBT complexes to form more stable colorless Ca-EDTA & Mg-EDTA complexes. Free EBT is liberated which is blue color in pH-10 medium. This marks the end of the titration. </p> <p data-bbox="295 1534 821 1601">On adding indicator</p> $ \begin{array}{l} Ca^{2+} \\ Mg^{2+} \end{array} + EBT \longrightarrow \begin{array}{l} Ca-EBT \\ Mg-EBT \\ \text{complex} \\ \text{(wine red)} \end{array} $ <p data-bbox="295 1803 702 1870">During titration</p> $ \begin{array}{l} Ca^{2+} \\ Mg^{2+} \end{array} + EDTA \xrightarrow{pH-10} \begin{array}{l} Ca-EDTA \\ Mg-EDTA \\ \text{colorless} \end{array} $	<p data-bbox="1364 145 1444 212">7M</p> <p data-bbox="1364 795 1396 862">4</p> <p data-bbox="1364 1702 1396 1758">2</p>

Q.No.

Solution and Scheme

Marks

At the endpoint



+ EBT
blue

Knowing the molarity and the volume of EDTA consumed, hardness of water is calculated.

Calculations:

Sample water volume taken for analysis = Z mL

volume of EDTA consumed = P mL

Strength of EDTA soln (std) = Y M

Molecular weight of CaCO_3 = 100 g

1M

It is known that _____

1000 mL of 1M EDTA = 100 g CaCO_3

1 mL of 1M EDTA = $\frac{100}{1000}$ g CaCO_3

P mL of Y M EDTA = $\frac{100}{1000} \times P \times Y$ g

By expt

Z mL of hard water = P mL of Y M EDTA

= $\frac{100}{1000} \times P \times Y$ g CaCO_3

10^6 mL of hard water _____

= $\frac{100}{1000} \times P \times Y \times \frac{10^6}{Z}$ g CaCO_3

Total hardness = $\frac{100}{1000} \times P \times Y \times \frac{10^6}{Z}$ ppm

10b Define the following units of standard solution
 i) molarity
 ii) Normality iii) ppm.

5M

→ Molarity

Number of gram moles of substance in one litre of solution

$$1M = \frac{\text{Number of gram moles of substance}}{1000 \text{ mL of solvent}}$$

5M

→ Normality

Number of gram equivalent of substance in one litre of solution.

$$N = \frac{\text{No. of equivalents of solute}}{\text{Vol. of solution in litre}}$$

→ Ppm

A part per million is one part of solute per million parts of the solution.

$$\text{ppm} = \frac{\text{No. of parts of components (solute)}}{\text{Total numbers of parts of all components of the solution}} \times 10^6$$

10c Explain the theory and instrumentation of potentiometry 7M

Theory

Change in the electrode potential with changing ionic species or their molar concentration and corresponding quantitative change in cell potential is the principle behind the potentiometric analysis.

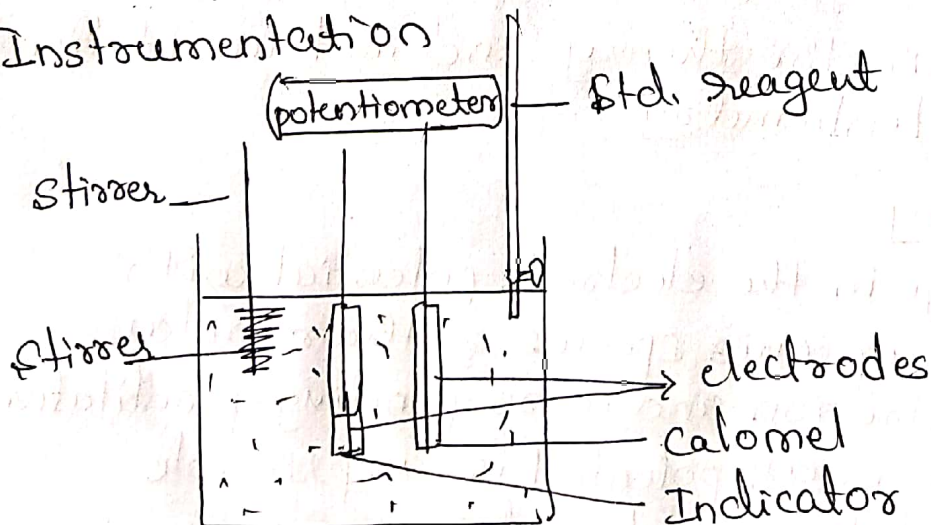
When a metal M is immersed in a solution containing its own ions M^{n+} , the electrode potential is given by Nernst equation

$$E = E^{\circ} + \frac{0.0591}{n} \log [M^{n+}] \text{ at } 298 \text{ K}$$

A suitable indicator electrode and a reference electrode are coupled & dipped in the analyte to construct a galvanic cell.

- Cell potential measured is a function of the concentration of the ions in the analyte 3
- Cell potential changes abruptly at equivalence point as the nature of ions changes abruptly.
- From the equivalents points, the concentration of ions in the analyte.
- Cell potentiometry is used to determine the equivalence points in
 - i) Redox reaction
 - ii) Acid-base titration
 - iii) Precipitation titration

Instrumentation



Potentiometer consists of one indicator electrode, a reference electrode & a potentiometer to measure the cell potential

→ The cell responds to the changes in concentration of analyte or titrant or the reaction products.

→ A simple arrangement of potentiometric titration is shown in the figure. The solution to be titrated is taken in the beakers.

→ Indicator electrode which helps in identifying the concentration of analyte in test solution or indicating the endpoint of reaction

→ Reference electrode will have known potential which will not change with time or will regain its potential after drawing or passing small current. Usually Ag-AgCl electrode or Calomel is used as reference electrode

3

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