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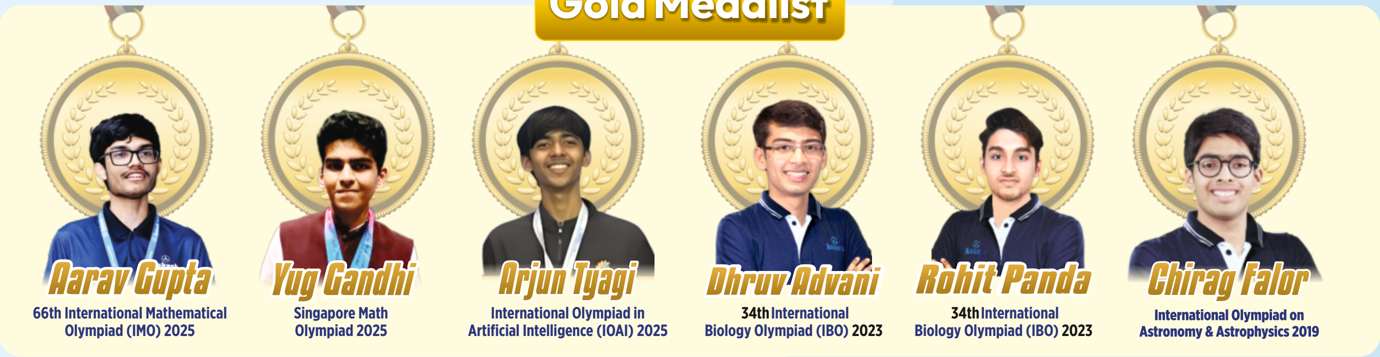
Medical | IIT-JEE | Foundations

Solutions
for
Indian National Chemistry Olympiad
INChO - 2026
Homi Bhabha Centre for Science Education (HBCSE-TIFR)

Gold Medalist



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Problem 1 — 28 marks

Fuel for Petrol Engines

Petrol is a common liquid fuel used for two and four-wheeler light passenger vehicles. It is a mixture of about 150 volatile hydrocarbons with carbon atoms between 4 to 12 per molecule. Petrol contains straight and branched-chain alkanes (paraffins), cyclic alkanes (naphthenes), unsaturated hydrocarbons with one double bond (olefins) and aromatic hydrocarbons, with an average chemical composition of $C_{8.26}H_{15.5}$. This problem will explore combustion of petrol and related fuels being used commercially in petrol engines. Some useful data:

Compound	*n*-octane (*l*)	cyclohexane (*l*)	isooctane (*l*)	ethanol (*l*)
Density (g cm^{-3})	0.70	0.77	0.69	0.79
$\Delta H^\circ_{combustion}$ (kJ mol^{-1})	–5470.3	–3918.6	–5461.0	–1366.8

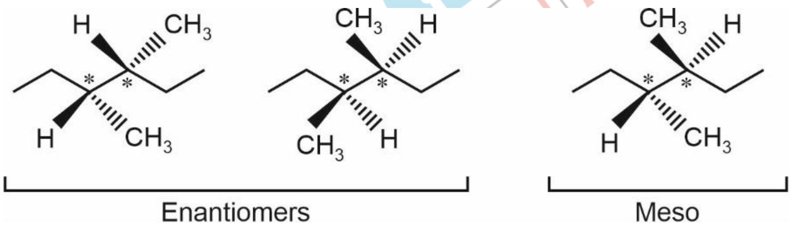
PART A: Combustion in Petrol Engines

The combustion of petrol can be understood with octane as a model fuel.

1.1 Draw structures of all possible stereoisomer(s) of octane having two chiral centers, in the wedge-dash representation.

Sol. Stereoisomer(s) of octane having two chiral centres are:

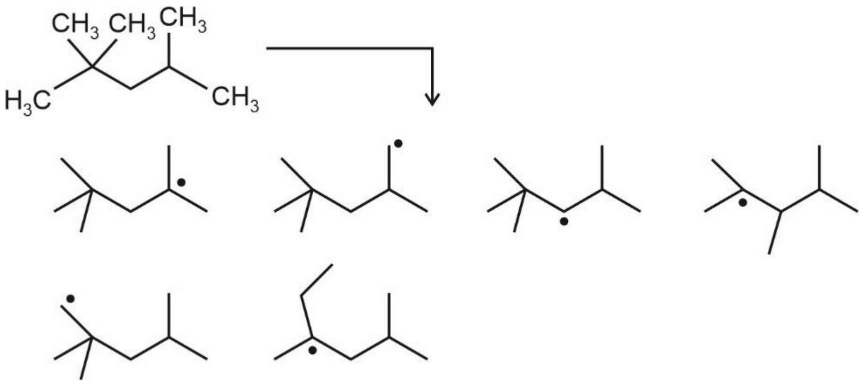
Octane : C_8H_{18}



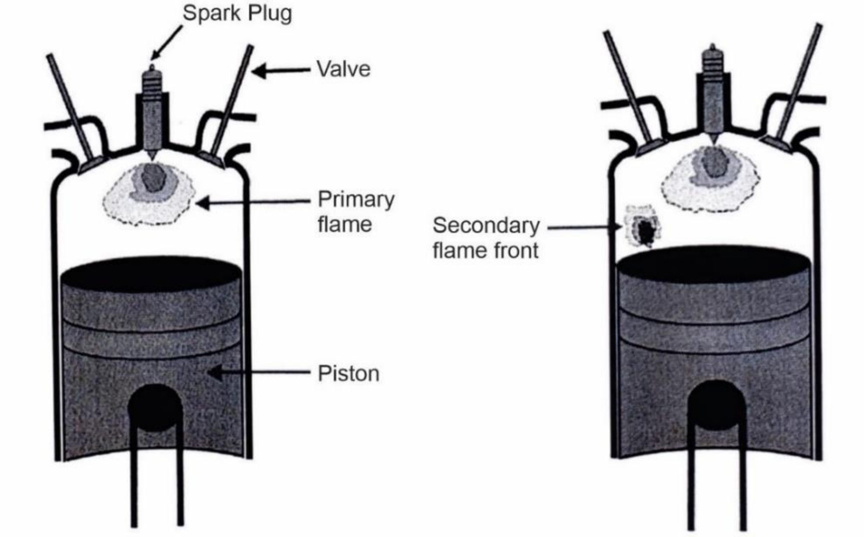
The combustion of fuel starts with a homolytic cleavage of a C–H bond in a hydrocarbon, forming alkyl radicals. These radicals can undergo rearrangement to form more stable radicals. If the radicals generated are unstable even after rearrangement, the fuel can burn at low temperatures. Among the alkyl radicals generated by the octane isomers during combustion, those formed by isooctane (2,2,4-trimethylpentane) are most stable, some of which are stabilized by rearrangement.

1.2 Draw the structure(s) of all probable alkyl radical(s) that are formed from isooctane including those after rearrangement. Identify the most stable free radical by circling its structure.

Sol. Isooctane : 2,2,4-trimethylpentane



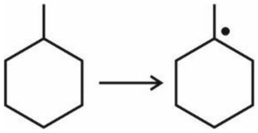
In a petrol engine under certain conditions, some components of the fuel-air mixture forming less-stable free radicals may self-ignite without ignition by the primary flame front as shown in the diagram below. Such secondary flames outside the primary flame front create secondary heat and pressure waves. Multiple pressure waves in the cylinder can create shock waves and cause jerky movements of the piston. The shock waves also create a characteristic “pinging” sound, known as knocking. Knocking tendency of a fuel (causing jerky movements in vehicle) is quantified by octane number. The fuel that causes less knocking is considered better and is assigned a higher octane number.



Smooth combustion Knocking

1.3 Arrange the following hydrocarbons in ascending order of their knocking tendency.
methylcyclohexane, isooctane, *n*-octane, toluene (methylbenzene)

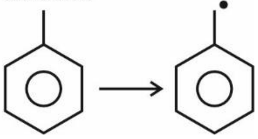
Sol. Methylcyclohexane



isooctane

n-octane

Toluene



Less stable radicals, more knocking.

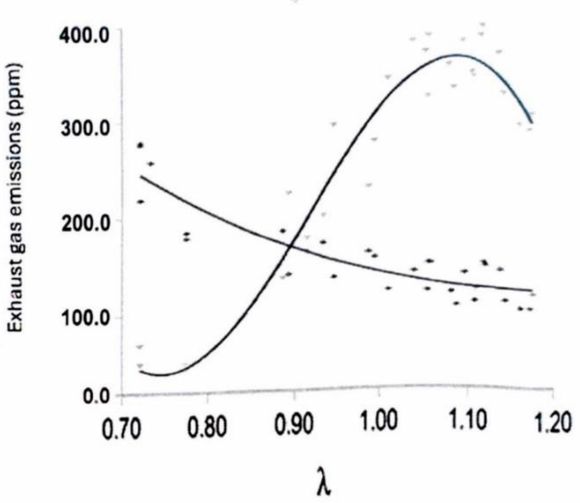
Knocking tendency :

	Toulene	<	isooctane	<	methylcycloalkane	<	n-octane
O.N :	121		100		75		–10 to – 20

1.4 Estimate the stoichiometric amount of air (in g) required for the complete combustion of 100 cm^3 of a liquid fuel mixture containing *n*-octane and cyclohexane [70:30, v/v assuming volumes are additive]. Write balanced equations for the combustion of each component. Assume composition of air (v/v) at NTP as: Argon (0.95%), Nitrogen (78.08%) & Oxygen (20.95%).

Air-fuel ratio (λ) is the relative stoichiometric ratio between the mass of air and the mass of fuel that are injected in the engine. When $\lambda = 1$, the combustion mixture in the engine contains a stoichiometric amount of air and fuel; values of $\lambda < 1$ signify fuel-rich mixtures, while $\lambda > 1$ correspond to air-rich mixtures. This ratio affects the composition of emitted gases from the engine.

Concentration values of two gases in a petrol engine exhaust as a function of λ are presented as two curves in the graph here.



Sol. $V_{\text{fuel mix}} = 100\ \text{cm}^3$

$$\downarrow$$

n-octane + cyclohexane
$(70\ \text{cm}^3)$ $(30\ \text{cm}^3)$

For n-octane :

$2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$

For cyclohexane :

$C_6H_{12} + 9O_2 \rightarrow 6CO_2 + 6H_2O$

Taking the standard value of densities :

$\rho_{\text{octane}} = 0.70\ \text{g/cm}^3$ $\rho_{\text{cyclohexane}} = 0.77\ \text{g/cm}^3$

$$\text{Moles of octane } = \frac{d \times V}{Mw} = \frac{0.70 \times 70}{114} = 0.43 \text{ moles}$$

$$\text{Moles of cyclohexane } = \frac{0.77 \times 30}{84} = 0.275 \text{ moles}$$

Total moles of O_2 required = 12.5 × 0.43 + 9 × 0.275 = 7.85 moles

$$\text{Total moles of air required } = \frac{7.85}{0.2095} = 37.47 \text{ moles}$$

$$\text{Molar mass of air } = \frac{0.95 M_{Ar}}{100} + \frac{78.08}{100} \times M_{N_2} + \frac{20.95}{100} \times M_{O_2}$$

$$= \frac{0.95 \times 40}{100} + \frac{78.08}{100} \times 28 + \frac{20.95}{100} \times 32 = 28.95 \text{ g/mol}$$

Total mass of air = 28.95 × 37.47 = 1084.76 g

1.5 If 20% excess air (λ = 1.2) is injected in a petrol engine for combustion of a fuel mixture containing octane (85% v/v), cyclohexane (5% v/v), 2-butene (5% v/v) and toluene (5% v/v), identify the gases emitted in the exhaust in significant concentrations (above 200 ppm). Mark X for the correct option(s).

(a) CO_2 (b) CO (c) Ar

(d) NOx (e) N_2 (f) O_2

(g) unburnt hydrocarbons (HC)

Sol. As the all the components of the fuel mix are hydrocarbons the final combustion (complete) products will be CO_2 and H_2O. Which will be more than 200 ppm.

As $\gamma = 1.2$ means air is 20% in excess. So unburnt O_2, N_2 and Ar will be there in exhaust.

20% of initial 20.95% $O_2 \simeq 4\% \simeq 40000$ ppm

which is more than 200 ppm.

As per graph : Curve 1 should represent unburnt fuel and partial combustion products like CO, as its more for $\lambda < 1$. Hence CO is less than 200 ppm at $\lambda \simeq 1.2$.

Curve 2 should represents remaining pollutants such as NOx which is more than 200 ppm for $\lambda = 1.2$.

So, it will be significant

So, significant gases in exhaust will be :

CO_2, Ar, N_2, O_2 and NOx i.e. a, c, d, e and f

PART B: Mixing Ethanol with Isooctane

Most governments have been imposing vehicle emissions regulations that are continually being tightened further. BS VI emission standards notified by the Government of India limit values of exhaust gases for two wheelers fitted with spark ignition engines as follows: CO (500 mg km^{-3}), HC (100 mg km^{-3}), NOx (90 mg km^{-3}).

[Reference: *The Emission Standards for Bharat Stage VI (BS-VI), Ministry of Road Transport and Highways, May 2020*].

Changing fuel compositions can address some of the emission concerns. Ethanol is one of the alternative transportation fuels which is available as a byproduct from agricultural sources.

1.6 Consider the liquid fuel for an engine is changed from isooctane (F_0) to a mixture containing 80% isooctane and 20% ethanol (v/v, assuming volumes are additive), known as F_{20}.

(i) Estimate the difference in calorific values of these two fuels, $C(F_{20}) - C(F_0)$, heat released per g.

(ii) By what percent CO_2 emission is reduced on changing the fuel from F_0 to F_{20} for the same distance covered by the vehicle? Assume 100% efficient combustion and the efficiency of engines in the two cases to be identical.

Sol. (i) 100 mL fuel has 80 mL isooctane and 20 mL ethanol.

mass of isooctane = 0.69 × 80 = 55.2 g

mass of ethanol = 0.79 × 20 = 15.8 g

moles of isooctane = $\frac{55.2}{114} = 0.4842$

moles of ethanol = $\frac{15.8}{46} = 0.3435$

Calorific value of F_{20} $= \frac{5461 \times 0.4842 + 1366.8 \times 0.3435}{55.2 + 15.8}$

= 43.855 kJ

$\Delta C = C(F_{20}) - C(F_0)$

$= 43.855 - 47.9$

$= -4.045$ kJ

From $C_8H_{18} \rightarrow 8CO_2$

So, CO_2 per g of isooctane $= \frac{1}{114} \times 8 \times 44 = 3.09$ g

From $C_2H_5OH \rightarrow 2CO_2$

CO_2 per g of ethanol $= \frac{1}{46} \times 2 \times 44 = 1.91$ g

So, CO_2 from F_{20} mixture = 0.8 × 3.09 + 0.2 × 1.91 = 2.85 g

% CO_2 reduction $= \frac{3.09 - 2.85}{3.09} \times 100 = 7.8\%$

PART C: Ethanol Blended Petrol

Ethanol blended petrol in different proportions is being used in different parts of the world including India. E_{85} is blend of 85% ethanol and 15% petrol, E_{20} is 20% ethanol blended with 80% petrol and so on. The ignition temperature of fuel is the temperature at which it spontaneously ignites in atmospheric air without an external source of ignition. Certain facts associated with ethanol blended fuels are:

F1. Ethanol forms an azeotrope with water.

F2. Addition of double bonds to alkyl chain of a fuel mixture stabilizes some of its alkyl radicals.

F3. Ethanol molecules are inherently rich in oxygen.

F4. The ignition temperature of ethanol is 365 °C and that of petrol is 247 - 280 °C.

F5. Ethanol-blended petrol absorbs water from atmosphere.

F6. Oxygen containing fuels inhibit formation of soot.

F7. Latent heat of evaporation of ethanol is much higher than that of octanes.

1.7 State which of the following statements are correct/incorrect for petrol engines and write the fact/s (**F1 - F7**) which justify your answer.

S1. The E_{20} blended fuel will exhibit lower knocking than E_0.

S2. Temperature of air fuel mixture in an engine at the start of combustion would be lower for E_{85} than for E_{20}.

S3. E_{85} fuel can be more damaging to the engine parts having metallic surfaces than E_{20}.

S4. E_{85} fuel will result in more emissions of unburnt HC than E_{20} fuel, at $\lambda = 1$.

S5. Emission of particulate matter is significantly increased with E_{85}.

Sol. S1 : Correct

F3 and F7 justifies the answer as E_{20} will have higher octane rating.

S2 : Correct

F7 justifies it as higher latent heat means more cooling during vaporisation, hence lower intake change temperature.

S3 : Correct

F1 and F5 supports.

Water and ethanol creates corrosive environment as ethanol absorbs moisture from air.

S4 : Incorrect

F3 and F6 supports.

Ethanol has oxygen hence less O_2 required in combustion. Oxygenated fuels reduce hydrocarbon emissions.

S5 : Incorrect

F6 supports it.

Oxygenated fuels inhibit soot formation. Ethanol reduces PM emissions.

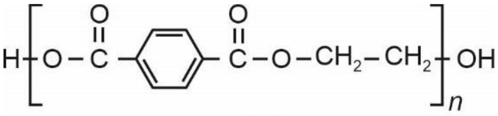
Problem-2 21 marks

Polymer Recycling

Polymer recycling aims at recovering and reusing polymers to reduce waste as well as to obtain new raw materials. This is achieved through mechanical or chemical recycling. In mechanical recycling, polymers are melted and reshaped. In chemical recycling, polymers are broken down into molecular building blocks (monomers) for creating new materials or getting back the same material. Both approaches aim to create a circular economy or give value added products. Here we look at two polymers.

Part A. Polyethylene terephthalate

Polyethylene terephthalate (PET) is chemically recycled by cleaving its ester bonds, converting it into its monomers one of which is terephthalic acid (TPA, benzene-1,4-dicarboxylic acid).



PET

The ester bonds can be cleaved using various methods, two of which are:

1. **Neutral hydrolysis:** PET is broken down at high temperatures and high pressures in the presence of water or steam.
2. **Acid or alkaline hydrolysis:** PET is broken down at relatively lower temperature and moderate pressures in presence of acids (like H_2SO_4) or bases (like NaOH) as catalysts.

Consider a sample of 1 kg PET pieces heated with aqueous NaOH (molar equivalents > 2n in PET).

2.1 (i) Write the structures of the products obtained when the reaction with NaOH is complete.

(ii) From this reaction mixture, one can separate out two monomers which can be reacted together to produce fresh PET. One of these compounds is a solid at room temperature, and other is a water-miscible liquid (B.P.196°C).

From the following list of possible processes (I - IX), identify the sequence required to obtain the two monomers from the above reaction mixture.

(I) filtration

(II) distillation at 100°C and pressure < 1 atm

(III) solvent extraction with toluene

(IV) treatment with $NaHCO_3$ (aq)

(V) addition of water

(VI) treatment with $I_2(s)$

(VII) treatment with $H_2SO_4(aq)$

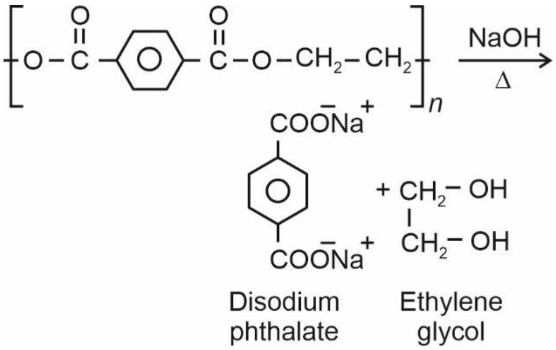
(VIII) distillation at 100°C and 1 atm

(IX) heating in inert gas atmosphere

Write the process numbers in correct sequence in the second column in the given table (assuming that each separation step is 100% efficient). For each step, write the constituents of mixture on which the process is to be carried out in third column. In the fourth column, write the compound(s) which is/are separated out in that process.

S. No.	Process No. (I - IX)	Constituents of Mixture on which the process is carried out	Compound(s) separated out after the process (if applicable)
1.			
2.			
3.			
4.			
5.			
6.			

Sol. (i) PET on reaction with NaOH along with heating

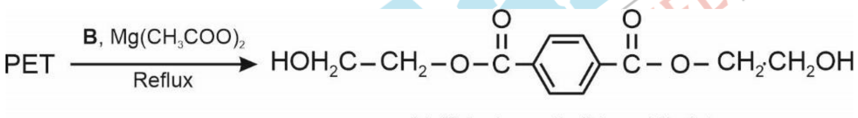


(ii) Ethylene glycol is soluble in water (B.pt 196°C)

Terephthalic acid is solid at room temperature

S. No.	Process No.	Constituents of Mixture on which the process is carried out	Compound(s) separated out after the process (if applicable)
1.	(VII) treatment with H_2SO_4(aq)	Reaction mixture (Na_2TPA + ethylene glycol + NaOH)	Terephthalic acid precipitates
2.	(I) Filtration	Mixture containing solid terephthalic acid	Terephthalic acid
3.	VIII Distillation at 100°C & 1 atm	Filtrate (aq. ethyleneglycol Na_2SO_4)	Water
4.	(II) Distillation at 100°C and <1 atm	Residue (liq Ethylene glycol & solid Na_2SO_4)	Ethylene glycol

In a third method, PET is boiled (refluxed) with a liquid B (3*n* equivalent) in presence of $Mg(CH_3COO)_2$ as per the following scheme.



bis(2-hydroxyethyl) terephthalate

2.2 (i) Draw the structure of **B**.

(ii) Identify the role of magnesium acetate in the above reaction, [Mark X against the correct option(s)]

(a) Lewis acid actalyst **(b)** Dehydrating agent

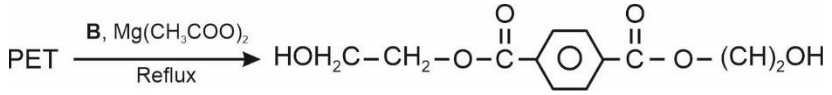
(c) Acetylating reagent **(d)** Brønsted base catalyst

(iii) This process is an example of: [Mark X against the correct option(s)]

(a) elimination reaction. **(b)** addition reaction.

(c) nucleophilic substitution reaction. **(d)** electrophilic substitution reaction.

Sol. (i)



B is ethylene glycol

CH_2-OH
|
CH_2OH

(ii) Role of $Mg(CH_3COO)_2$ is (a) Lewis acid catalyst

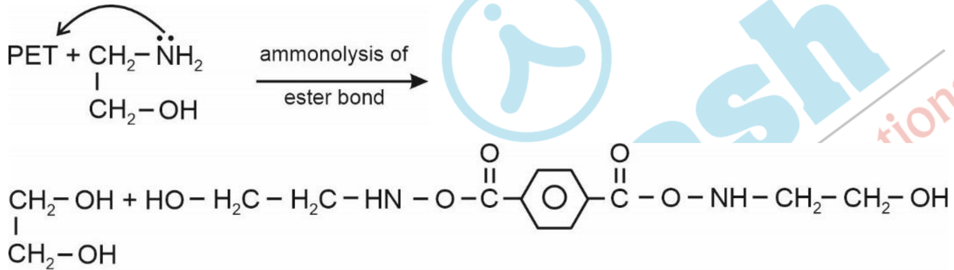
(iii) The process is an example (c) Nucleophilic substitution reaction

Ester + alcohol → Transesterification involves nucleophilic substitution at acyl carbon

In a fourth process, PET pieces are heated with excess liquid ethanolamine (2-aminoethanol, 4*n* equivalents) in presence of $Zn(CH_3COO)_2$.

2.3 Write the structure(s) of the product(s) obtained after completion of the reaction.

Sol.



N, N-bis(2-hydroxyethyl) terephthalamide and Ethylene glycol

The four methods described above can be used (with appropriate subsequent separation and reaction steps) to obtain fresh PET.

2.4 Among the four depolymerization pathways, it is possible to obtain the PET polymer back with least amount of chemical waste/by products as well as with least energy input by:

[Mark X against the correct option]

(a) hydrolysis with H_2O

(b) hydrolysis with NaOH(aq)

(c) treatment with **B** in presence of $Mg(CH_3COO)_2$

(d) treatment with ethanolamine in presence of $Zn(CH_3COO)_2$

Sol. (c) Treatment with ethylene glycol in presence of $Mg(CH_3COO)_2$.

This produces N, N-bis(2-hydroxyethyl) which can be directly depolymerized.

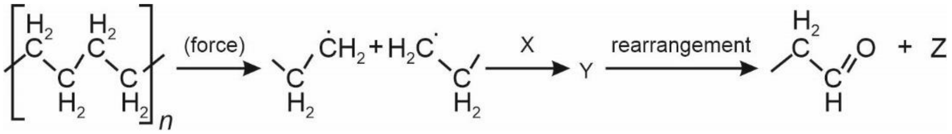
Part B: Polythene

Polythene is usually recycled mechanically. The quality of recycled products depends a lot on the purity of polythene. While polythene is inert to many substances (gases, water, acids, bases, oils, etc), mechanical tension/compressions or abrasion can cause chemical changes in it. When the molecules of polythene are pulled apart, the force may break some bonds. When a polythene sample abrased in presence of air was studied using spectroscopy, it showed presence of -CHO functional groups. Aldehydes can also undergo slow oxidation in air via free-radical pathways. Samples of original and abrased (damaged) polythene sheets are given below.

Original Sample	Abrased Sample

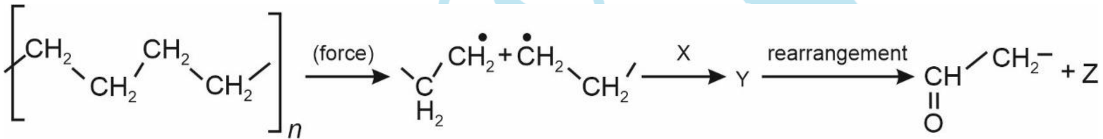
Original Sample Abrased Sample

The formation of aldehydes during mechanical abrasion can take place through the following pathway



2.5 Draw the structures of the species X, Y, Z

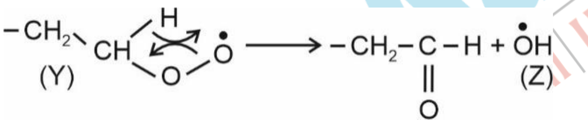
Sol.



X must be O_2

$Y \rightarrow -CH_2-CH_2-O-\dot{O}$

Rearrangement is as follows



2.6 The abrased plastic looks less transparent than the fresh polymer. This is because (Mark X against the correct option(s)):

(a) the carbonyl groups change the refractive index of plastic in some regions.

(b) the carbonyl groups enhance light absorption by polymer across the whole visible spectrum.

(c) the carbonyl groups attract more dust particles to the plastic as these are positively charged.

(d) during abrasion, the molecular arrangements/packing change, increasing scattering of light through the sample.

Sol. (a) The carbonyl group changes the refractive index of plastic due to change in structures

(d) During abrasion, molecular arrangement/packing change, increasing scattering of light through sample

Polythene is recycled by melting the polymer (in ambient air) and recasting it into required shape(s) on cooling.

2.7 Assuming that there is no external substance added during melting, the alkyl chains having –CHO groups can affect recycling of abrased polythene by (Mark X against the correct option(s))

(a) decreasing the melting point of polythene.

(b) causing free-radical driven cleavage in polymer chains.

(c) increasing the viscosity of molten polymer.

(d) decreasing the branching in polymer.

Sol. (b) Free radical driven cleavage in polymer chain.

(c) Increasing viscosity of molten polymer due to increased polarity and intermolecular forces.

2.8 Which of the following limitations of polymer recycling apply to mechanical and chemical recycling. Mark X in the appropriate cells.

		Mechanical Recycling	Chemical recycling
(a)	Lower quality plastic products		
(b)	By-products generated as waste during recycling		
(c)	Limited number of recycling cycles due to change in composition after every cycle		

Sol.

		Mechanical Recycling	Chemical recycling
(a)	Lower quality plastic products	×	
(b)	By-products generated as waste during recycling		×
(c)	Limited number of recycling cycles due to change in composition after every cycle	×	

Problem-3 **21 marks**

CaO Production

Calcium carbonate ($CaCO_3$) is found in rocks as minerals *viz*, calcite and aragonite, limestone, eggshells, etc. It has medical use as calcium supplement and as an antacid. It is used on large scale in construction industry as a building material and as an ingredient of cement.

3.1 $CaCO_3$ can be prepared by mixing calcium oxide and water followed by passing $CO_2(g)$. Write the balanced equations for the two reactions.

When $CaCO_3$ is heated in a closed vessel, the following heterogenous equilibrium is attained

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g) \qquad \text{...reaction 1}$$

Sol. $CaO + H_2O \longrightarrow Ca(OH)_2.$

$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O.$

3.2 Consider K_c is the equilibrium constant where c indicates the concentrations of reacting species in moles per litre. Calculate K_c for the equilibrium at 835°C and a CO_2 partial pressure of 0.236 atm, assuming ideal gas behaviour.

Sol. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$$K_p = (p_{CO_2})_e = 0.236 \text{ atm}$$

$$K_p = K_c(RT)' \Rightarrow K_c = \frac{K_p}{RT}$$

$$K_c = \frac{0.236}{0.08205 \times 1108.15} = 2.6 \times 10^{-3}\text{ M}$$

3.3 Using the values given in the table below, calculate

(i) The standard free energy change of reaction 1 at 25°C and 850°C. (Assume that the enthalpy and entropy values are temperature independent)

(ii) The temperature below which $CaCO_3(s)$ will not convert to $CaO(s)$ in presence of CO_2 at a partial pressure of 1 atm.

Thermodynamic Data at 1 atm and 25°C		
Substance	ΔH°_f (kJ mol^{-1})	S°(J K^{-1} mol^{-1})
CO_2 (g)	–393.5	213.6
CO_3^{2-} (aq)	–676.3	–53.1
Ca^{2+}(aq)	–542.9	–55.2
$CaCO_3$(s)	–1206.9	92.9
CaO(s)	–635.6	39.8
CO_2(g)	–412.9	121.3

Sol. (i) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$.

$$(\Delta H_f^\circ)_{reaction} = (\Delta H_f^\circ)_P - (\Delta H_f^\circ)_R.$$

$$= [-635.6 - 393.5] - [-1206.9]$$

$$= 177.8 \times 10^3 \text{ J mol}^{-1}$$

$$(\Delta S^\circ)_{reaction} = [39.8 + 213.6] - [92.9]$$

$$= 160.5 \text{ J mol}^{-1} \text{ K}^{-1}$$

$\Delta G_{reaction} = ?$

At 25°C,

$$\Delta G_{25^\circ C} = 177.8 \times 10^3 - 298.15 \times 160.5$$

$$= 177.8 \times 10^3 - 47829.$$

$$= 129.97 \text{ kJ/mol.}$$

At 850°C,

$$\Delta G_{850^\circ C} = 177.8 \times 10^3 - 1123.15 \times 160.5$$

$$= 177.8 \times 10^3 - 180265.575$$

$$= -2.465 \text{ kJ/mol.}$$

(ii) $K_p = p_{CO_2} = 1\,\text{atm}.$

$$\Delta G^\circ = -RT\ln K_p = 0.$$

$$\Delta H - T\Delta S = 0 \Rightarrow \frac{\Delta H}{\Delta S} = T = \frac{177.8\times 10^3}{160.5} = 1107.79\,\text{K}.$$

Below 1107.79 K, $CaCO_3$(s) will not convert to CaO

3.4 Consider a 10 kg block of $CaCO_3$ taken in a 20 L closed container and the system is allowed to reach equilibrium at 600°C. In the table below, certain modifications are listed. For each of the modification in Column I, write the relative change/s (from the list A-E) observed in the modified system at equilibrium with respect to the original 20 L system.

A. The amount of CaO (s) increases.

B. The amount of CO_2 (g) increases.

C. No change in the system.

D. The amount of CaO (s) decreases.

E. The amount of CO_2 (g) decreases.

Modification	Observed relative change/s (A–E)
1. Temperature of the 20 L container is increased.	
2. The same amount of $CaCO_3$ is taken in a 40 L container at 600 °C.	
3. Half of $CaCO_3$ is removed from the (original) 20 L container at 600 °C.	
4. Finely powdered 10 kg $CaCO_3$ solid is taken in another 20 L container at 600 °C.	

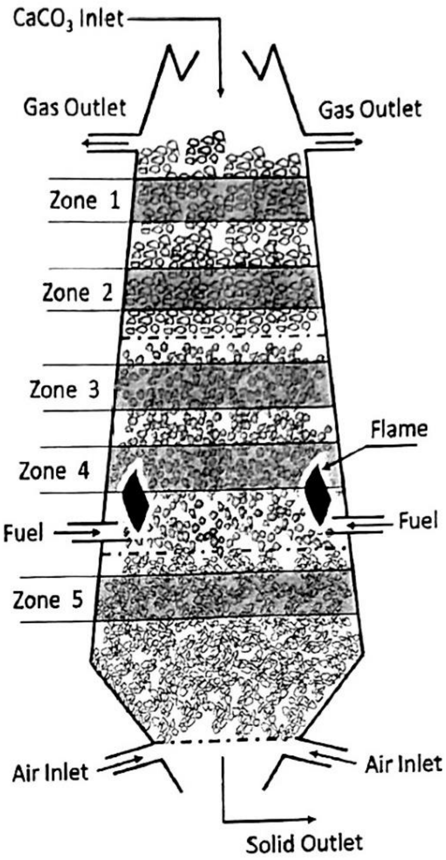
A schematic diagram of a furnace for conversion of limestone to lime is given here.

Sol.

Modification	Observed relative change(s)
1. Temperature of the 20 L container is increased.	A, B
2. The same amount of $CaCO_3$ is taken in a 40 L container at 600 °C.	A, B
3. Half of $CaCO_3$ is removed from the (original) 20 L container at 600 °C.	C
4. Finely powdered 10 kg $CaCO_3$ solid is taken in another 20 L container at 600 °C.	C

1. When temperature of 20 L container is increased, since it is an endothermic reaction, the reaction will move in forward direction.
2. Volume of vessel is doubled from 20 L to 40 L $\Rightarrow p_{CO_2}$ decreases; driving the reaction in forward direction.
3. Half of the $CaCO_3$ is removed - but it does not alter the equilibrium - no shift at all.
4. Taking powdered $CaCO_3$ only increases rate of reaction, but there is no shift in forward or backward direction.

3.5



Write correct symbol (>, =, or <) comparing average temperatures (*T*) of Zone 3 and 4 in the space below and mark X against options (a) – (d) supporting your answer.

T(Zone 3) _____ *T*(Zone 4), due to:

(a) Downward movement of $CaCO_3$ (S)

(b) Positive ΔH of reaction 1

(c) Low specific heat of $CaCO_3$ (s)

(d) Upward flow of air

Sol. T(Zone 3) < T(Zone 4).

a, b, d.

3.6 Identify the zones in the diagram where

A. CO_2 pressure is the lowest.

B. $CaCO_3$ is the hottest.

C. Maximum percent conversion of $CaCO_3$ takes place.

D. Solid has maximum percentage of CaO.

E. The gaseous mixture has highest pressure.

Portland cement is made up of four main components designated as C_2S (Ca_2SiO_3), C_3S, (Ca_3SiO_5), C_3A and C_4AF where C stands for calcium oxide, S for Silica, A for Alumina and *F* for iron(**III**) oxide.

Sol. A. Zone 5 – p_{CO_2} is least as it is moving upward.

B. Zone 3 – $CaCO_3$ is the hottest.

C. Zone 4 – Flame causes maximum % conversion of $CaCO_3$.

D. Zone 5 – CaO is collected.

E. Zone 1 – CO_2 has an upward movement.

3.7 Write balanced equation for the formation of C_4AF starting from CaO and appropriate oxides.

Cement production is the largest single industrial emitter of CO_2 (~8% of global CO_2) as 1 kg of cement produced releases 1 kg of CO_2 in atmosphere. Reduction of CO_2 emissions from cement manufacturing will require reducing or utilising the CO_2 from decomposition of $CaCO_3$ and from combustion of fuels in the CaO furnace.

Some of these emissions can be reduced by using $Ca(OH)_2$ partly in place of CaO as input in cement production, which produces hydrated phases of the cement components.

Sol. $C_4AF = 4CaO.\ Al_2O_3.Fe_2O_3$.

$4CaO + Al_2O_3 + Fe_2O_3 \rightarrow Ca_4Al_2Fe_2O_{10}$.

$C \rightarrow CaO$

$A \rightarrow Al_2O_3$

$F \rightarrow Fe_2O_3$

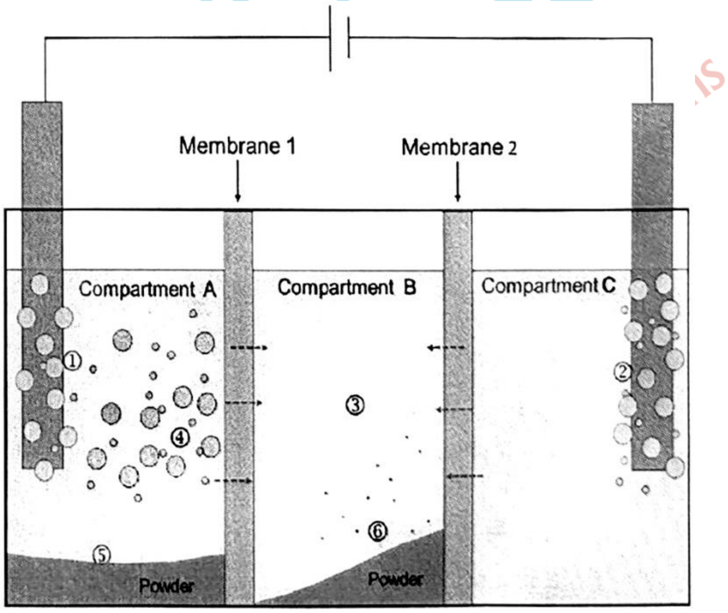
3.8 Write balanced equation for the formation of hydrated phase of C_3A starting from calcium hydroxide and appropriate oxides.

Sol. $C_3A = 3CaO{\cdot}Al_2O_3$.

$3Ca(OH)_2 \rightarrow 3CaO + 3H_2O$

$3Ca(OH)_2 + Al_2O_3 + 3H_2O \rightarrow Ca_3Al_2O_6{\cdot}6H_2O$.

3.9 An electrochemical set up uses $CaCO_3$ and produces $Ca(OH)_2$ along with gases that can be separately collected and utilized. This setup shown in diagram here consists of three compartments separated by two ion-selective membranes. $CaCO_3(s)$ is added to one of the compartments and all compartments are filled with water.



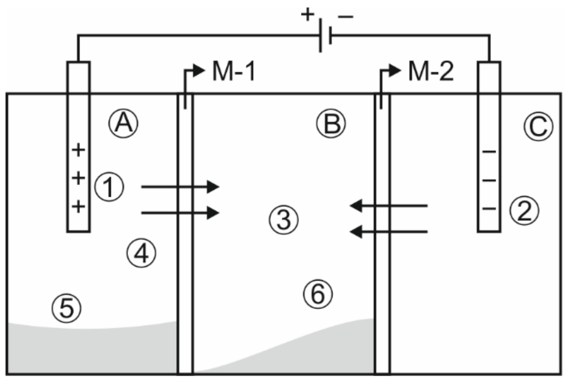
Different reactions take place in different regions in the three compartments. For example, in region labelled by 3, the predominant reaction is:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

(i) Write the balanced chemical equations for predominant reaction in regions 1, 2, 4, 5 and 6.

(ii) Write the overall reaction for the process taking place in the electrochemical setup.

Sol.



M-1, M-2
are two membranes

Reactions in different regions:

1. $H_2O \longrightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-]$ Oxidation takes place.

2. $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-]$ Reduction takes place.

4. $Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$

5. $CaCO_3 + 2H^+ \longrightarrow Ca^{2+} + CO_2\uparrow + H_2O$.

6. $Ca^{2+} + 2OH^- \longrightarrow Ca(OH)_2$.

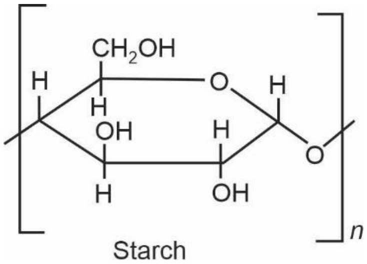
Overall reaction :

$$2CaCO_3(s) + 4H_2O(l) \longrightarrow 2Ca(OH)_2(s) + 2H_2(g) + O_2(g) + 2CO_2(g)$$

Problem-4 17 marks

Urinary Amylase

Amylase is an enzyme that hydrolyses starch into smaller carbohydrates such as glucose, maltose, maltotriose (containing 3 glucose units), and oligosaccharides (containing a few units of glucose). Over time, amylase may also break oligosaccharides, maltotriose, etc into glucose units. It is present in plant and animal bodies supporting starch metabolism. Very small concentrations of amylase or other enzymes may be found in human and animal urines.



Starch

4.1 Draw the structure of the cyclic form of maltose with proper stereochemistry. Note: Do not use Fischer projection.

In humans and animals, amylase is significantly produced in the pancreas and used in the intestinal tract to digest food. However, if the pancreas is diseased or injured, amylase may get into blood and later in urine. Thus, an increased level of amylase in urine is an indicator of pancreatic dysfunction.

In a biochemical training course, students were trying different analytical methods for urine analysis. Urine samples were obtained from two persons, one of whom was having pancreatic dysfunction. These urine samples were diluted 10 times and the diluted samples U1 and U2 were given to three students, who used different approaches to analyze the samples.

Student-1 : To 10 mL each of U1 and U2 in two test tubes, he added 2 mL of 1% starch solution. After keeping these mixtures for 10 minutes, he added 2 mL of Tollen's reagent and placed the test tubes in a hot water bath. In 30 minutes, both test tubes developed a silver mirror.

Student-2 : She followed the following steps:

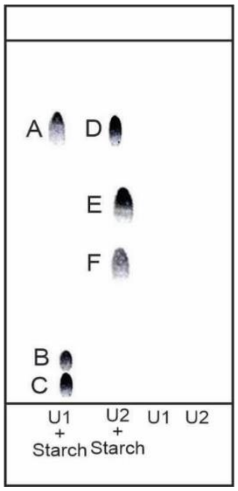
(i) Took 5 mL of U1 and U2 each in two test tubes and added 1 mL of 1% starch solution each.

(ii) After 10 minutes, she took these two mixtures (U1 + starch; U2 + starch) and spotted these at the baseline on a TLC plate coated with silica gel. She also spotted U1 and U2 on the TLC plate.

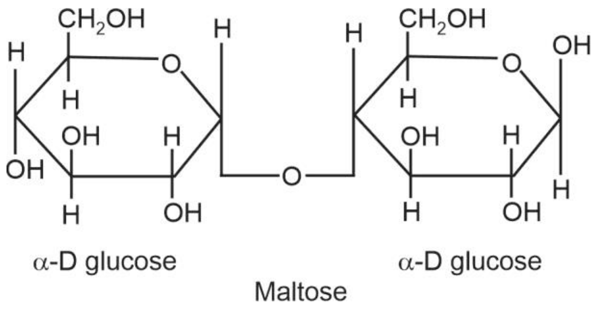
(iii) She ran the chromatogram using butanol-water mixture as eluent, with small amount of acetic acid added (to enhance miscibility of butanol in water).

(iv) She dried the plate and then dipped it in 0.1% $AgNO_3$ solution, followed by a dip in 2 M NaOH solution. The plate turned completely brownish black.

(v) She dipped this brownish-black plate in a 1M$Na_2S_2O_3$ solution. Most of the colour on the plate disappeared except for few spots which are shown here.



Sol.



4.2. (a) For the positive Tollen's test observed by Student 1 (in test tube), write a balanced chemical equation for reaction of one of the components of urine-starch mixture with the Tollen's reagent. Draw the structures of the components and products with correct stereochemistry.

(b) Write balanced chemical equation(s) for the reaction(s) which took place during Step iv of the procedure done by Student 2 causing grey-black colouration all over the TLC plate.

(c) Write balanced chemical reaction which led to the disappearance of the black color from most regions of the TLC plate in Step v.

(d) Spots B and E correspond to oligosaccharides and maltose, respectively. Write balanced chemical equation for the reaction(s) responsible for the formation of the coloured spot for maltose in the TLC plate.

(e) Identify the compounds in the reaction mixture responsible for the spots *A, D, F* in the TLC plates.

(f) In the TLC plate, the sequence and positions of spots are consistent with (mark *X* against the correct option/s):

(A) compounds with more –OH groups having higher mobility in the eluent (mobile phase) than compounds with fewer –OH groups.

(B) compounds with more –OH groups having lower affinity with silica gel (stationary phase) than compounds with fewer –OH groups.

(C) increased mobility of compounds with increased number of –OH groups per unit molar mass.

(D) lower mobility of larger carbohydrate molecules than smaller ones.

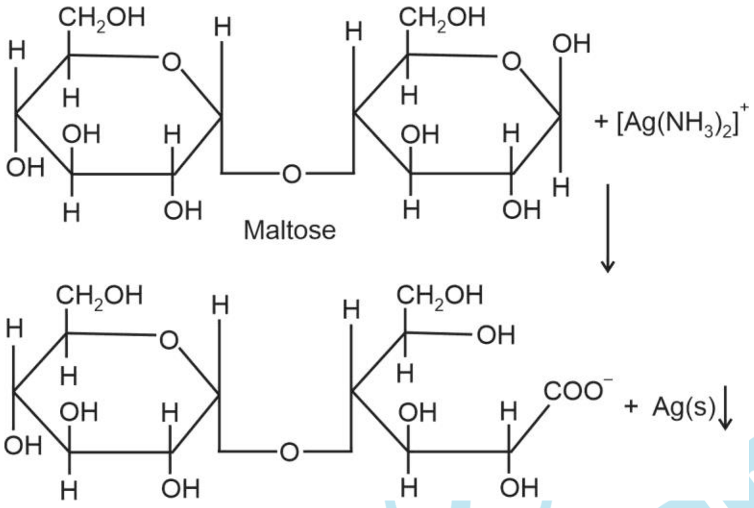
Sol. (a) Student-1 observed a silver mirror. This is because the amylase in the urine (from the patient with pancreatic dysfunction) hydrolysed the starch into maltose (a reducing sugar). Maltose reacts with Tollen's reagent to form carboxylate and metallic silver.

$\text{R–CHO} + 2[\text{Ag(NH}_3)_2]^+ + 3\text{OH}^- \rightarrow$

$\text{RCOO}^- + 2\text{Ag(s)} + 4\text{NH}_3 + 2\text{H}_2\text{O}$

* Component can be Maltose, glucose or Maltotriose

Starch $\xrightarrow{\text{Amylase}}$ Glucose + Maltose + Maltotriose



Or

$$\underset{\text{Glucose}}{\text{CHO–(CHOH)}_4\text{–CH}_2\text{OH}} + 2[\text{Ag(NH}_3)_2]^+ + \text{OH}^- \longrightarrow$$

$$^-\text{OOC–(CHOH)}_4\text{–CH}_2\text{OH} + 2\text{Ag}\downarrow + 4\text{NH}_3 + 2\text{H}_2\text{O}$$

(b) $2AgNO_3 + 2NaOH \rightarrow Ag_2O(s) + 2NaNO_3 + H_2O$

Ag_2O is then reduced to metallic silver by the reducing sugars which causes grey-black colouration over the TLC plate.

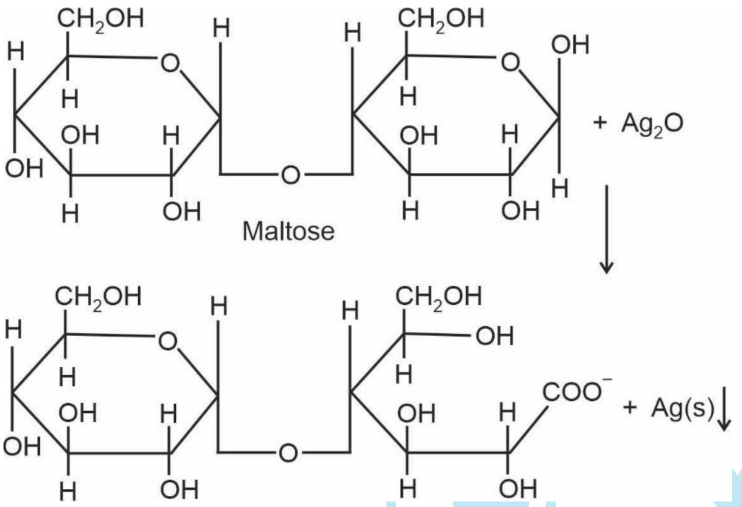
$$R\text{–}CHO + Ag_2O \xrightarrow{OH^-} R\text{–}COO^- + 2Ag(s) + H_2O$$

(c) The background clears because $Na_2S_2O_3$ dissolves unreacted silver compound by forming a soluble complex but it doesn't dissolve the metallic silver spots.

$$\underset{\text{(unreacted)}}{Ag_2O} + 4Na_2S_2O_3 + H_2O \rightarrow 2Na_3[Ag(S_2O_3)_2] + 2NaOH$$

(d) Spot E represents maltose

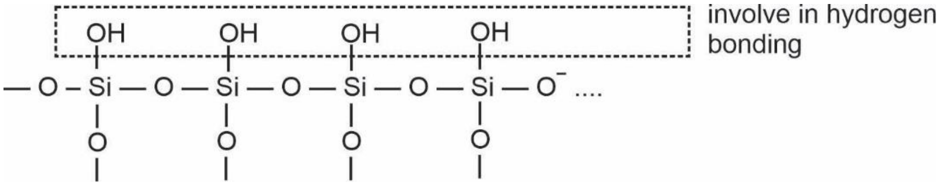
The reaction responsible for its colour is the redox reaction wherein the hemiacetal group of maltose reduces Ag^+ to Ag.



(e) Identification of spots are based on the chromatographic principles.

Smaller, less polar molecules generally travel further in a polar stationary phase (silica) with a moderately polar eluent.

Spot A ⇒	Glucose (the monosaccharide, high mobility)
Spot D ⇒	Glucose (the monosaccharide, high mobility)
Spot F ⇒	Maltotriose



⇒ Starch > Maltotriose > Maltose > glucose (extent of H-bonding)

Polysaccharide > Oligosaccharide > Disaccharide > Monosaccharide (extent of H-bonding)

∴ Higher is the extent of H-bonding, lower is the mobility.

(f) [A] ⇒ False

More –OH groups increases affinity for silica, lowering mobility.

[B] ⇒ False

More –OH groups increase affinity for the stationary phase

[C] ⇒ False

[D] ⇒ True

Larger carbohydrates (polysaccharides) have lower mobility due to size and high hydrogen bonding with silica.

Student-3 : She followed Steps i-iii as student 2 but after running the TLC, dipped the TLC plate in a mixture of conc. sulphuric acid with phenol. She also got the same spots but their colour intensities were different from the TLC obtained by student 2. She could recall that (i) colour intensity of a spot would approximately depend on the amount of coloured substance(s) present in it and (ii) volume of each solution placed initially on the TLC plate may vary.

4.3 (a) The colour of the maltose spot after treatment of the TLC plate with the phenol-acid mixture was due to a compound Z (molecular formula: $C_{18}H_{14}O_4$). Before formation of Z, an intermediate Y($C_6H_6O_3$) was formed at the spot region. Write the structures of Y and Z.

(b) Consider $I(S_i)$ represents the light absorption intensity of spot S_i. The ratio $I(D) : I(E)$ in TLC of *student-3* was lower than in TLC of *student-2*. Write the balanced equation for the reaction that took place on TLC of *student-3* which caused decrease in the intensity ratio $I(D) : I(E)$.

(c) Intensity ratio of spots $I(F) : I(B)$ in TLC of *student-3* : (Mark X against the correct statement(s)).

(A) would be always higher than ratio of spots in TLC of *student-2* because of the same reaction mentioned in 4.3(b).

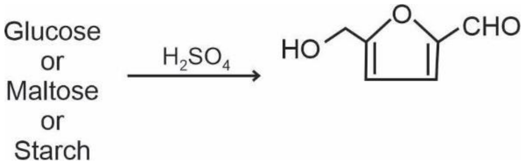
(B) would be always lower than ratio of spots in TLC of *student-2* because of a chemical process different from that mentioned in 4.3(b).

(C) cannot be compared with ratio of spots in TLC of *student-2* as all these spots may be obtained by spotting different volumes of sample mixtures.

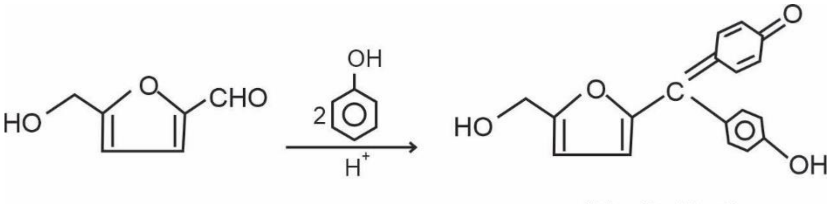
Sol. (a) Intermediate Y($C_6H_6O_3$) :

Conc. H_2SO_4 dehydrates hexoses (like glucose)

The dehydration of a hexose yields 5-hydroxymethyl furfural. (HMF)



Compound Z($C_{18}H_{14}O_4$) : This is the coloured condensation product formed when Y reacts with 2 molecules of phenol.



(Z) $C_{18}H_{14}O_4$

(b) The decrease in the intensity ratio I(D) : I(E) suggest that a chemical reaction occurred on TLC plate before phenol-acid treatment.

⇒ Since conc. H_2SO_4 was used, it leads to hydrolysis of maltose (spot-D) into glucose (spot E).

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{(glucose)}}{2C_6H_{12}O_6}$$

(c) The correct statement is (C)

The intensity of spot depends on both the concentration of the substance and volume of the sample spotted.

4.4 Which of the two urine samples came from the patient with pancreatic dysfunction.

(A) U1 (B) U2

Sol. ⇒ The correct answer is B(U2)

In the TLC, spots B and C represents larger polysaccharides/carbohydrate

⇒ Spot D, E and F represent smaller hydrolysis products like Maltose & glucose.

(U2 + starch) showed intense spot at the (D, E & F) compared to (U1 + starch).

⇒ This indicates U2 has high amylase activity & U1 has poor starch breakdown.

⇒ High amylase activity in urine is clinical indicator of pancreatic dysfunction.

4.5 In this experiment, urine samples (without starch) were spotted on the TLC plates to (Mark X against the correct box(es)):

(A) ensure that the urine samples do not have identical compositions.

(B) identify any substances in urine which can lead to wrong interpretations from the analysis of urine starch mixture.

(C) identify reference spots for the urinary amylase in the TLC.

(D) check if any amount of glucose or starch is already present in the urine.

Sol. The correct boxes are (B) and (D).

In this experiment, urine samples (w/o starch) were spotted on the TLC plates to

⇒ identify any substance in urine which can lead to wrong interpretations from the analysis of urine starch mixture.

⇒ Check if any amount of glucose/starch is already present in the urine.

Problem-5 **19 marks**

A purple haze

Iodine is a purple-black crystalline solid at room temperature that has a unique ability to sublime into a violet-purple vapour.

Iodine was accidentally discovered by French chemist Bernard Courtois while preparing potassium nitrate for gunpowder. He took seaweed ash and mixed it with sulfuric acid. The mixture gave off purple vapour, which then formed shiny purplish-black crystals on the sides of the vessel. Courtois had discovered solid iodine!

5.1 The ground-state electronic configuration of iodine atom is represented by (Mark X against the correct answer).

(a) $[Ar]3d^{10}4s^{2}4p^{5}$ **(b)** $[Xe]5d^{10}6s^{2}6p^{5}$

(c) $[Kr]4d^{10}5s^{2}5p^{5}$ **(d)** $[Ar]4d^{10}5s^{2}5p^{5}$

Sol. Answer (c)

${}_{53}I \Rightarrow [Kr]4d^{10}\,5s^{2}\,5p^{5}$

Part A: Extraction of Iodine

Iodine discovery had a profound impact on medical practice. Many commercial uses evolved, including as a disinfectant, in pharmaceuticals, as a catalyst, pigments for ink, etc. Radioactive isotopes of iodine are today used to treat thyroid cancer.

Elemental iodine is not naturally found in its free state. It is found in seaweeds as iodide (I^-), and in caliche (saltpetre deposits) and associated groundwaters as iodate (IO_3^-).

5.2 Write the balanced chemical equation(s) of the reaction(s) which produced iodine in the accidental discovery by Bernard Courtois.

Sol. After seaweed is burned and leached, the iodine exists in the solution primarily as iodide ions (I^-)

⇒ H_2SO_4 is added to decompose SO_3^{2-} to S^{2-} present in the ash

$Na_2SO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + SO_2\uparrow$

$Na_2S + H_2SO_4 \rightarrow Na_2SO_4 + H_2S\uparrow$

⇒ MnO_2 is then added as an oxidising agent in the presence of H_2SO_4 to liberate I_2.

$2NaI + MnO_2 + 3H_2SO_4 \rightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + I_2\uparrow$

To meet the growing market demand, extraction of iodine from natural resources has grown, with Chile and Japan as the leading producers. The commercial recovery of iodine depends on the source. Two of the methods are given below –

Method 1 (From iodates): To heaps of Chilean saltpetre containing trace amounts of iodates, water is poured to dissolve the saltpetre and the iodate. After crystalizing out nitrate salts, the mother liquor is collected, concentrated and divided into two parts.

(i) One part of the concentrate is first reduced with slight excess of sodium bisulphite to give iodide.

(ii) The solution obtained in step i is then mixed with the remaining concentrate to yield iodine.

5.3 Write balanced ionic equations for the two steps in the production of iodine from iodate.

Sol. **Production from chile saltpeter**

Iodine is present as $Ca(IO_3)_3$

Step-I : $2IO_3^- + 6HSO_3^- \rightarrow 2I^- + 6SO_4^{2-} + 6H^+$

Step-II : $5I^- + IO_3^- + 6H^+ \rightarrow 3I_2 + 3H_2O$

5.4 Write the oxidation number of all iodine species in the above reaction mixture.

Sol. Step-I : $2\overset{+5}{I}O_3^- + 6HSO_3^- \rightarrow 2\overset{-1}{I^-} + 6SO_4^{2-} + 6H^+$

Step-II : $5\overset{-1}{I^-} + \overset{+5}{I}O_3^- + 6H^+ \rightarrow 3\overset{0}{I_2} + 3H_2O$

5.5 The nature of solution in step ii after iodine formation is: (Mark X against the correct answer)

(a) acidic **(b)** basic **(c)** neutral

Sol. Even though H⁺ ions are consumed during this process, the reaction specifically requires an acidic environment to proceed.

In the context of industrial iodine production from chile saltpeter. The solution is maintained in acidic state to prevent the iodine from becoming unstable, as iodine is unstable in strongly alkaline or neutral medium.

Method 2 (From iodide): Iodide solution from natural sources is first treated with aqueous copper sulphate and ferrous sulphate. The white solid that precipitates out is filtered, washed with water, dried, and finely ground. This purified white solid is then heated with potassium carbonate solution to give potassium iodide solution and a red-brown precipitate. The precipitate is filtered off and the solution is oxidized with sodium dichromate and sulfuric acid to liberate iodine.

5.6 Write balanced chemical equations for the three steps described in Method 2.

Sol. Step-I : $2CuSO_4 + 2NaI + 2FeSO_4 \rightarrow \underset{\text{(white solid)}}{Cu_2I_2\downarrow} + Fe_2(SO_4)_3 + Na_2SO_4$

Step-II : $Cu_2I_2 + K_2CO_3 \rightarrow 2KI + \underset{\text{(red brown ppt)}}{Cu_2O\downarrow} + CO_2\uparrow$

Step-III : $6KI + Na_2Cr_2O_7 + 7H_2SO_4 \rightarrow 3I_2 + Cr_2(SO_4)_3 + Na_2SO_4 + 3K_2SO_4 + 7H_2O$

Common table salt is “iodised” by the addition of potassium iodide or iodate. In an experiment, 50 g of iodised salt (containing iodate) was dissolved in 250 mL water. To 50 mL of this salt solution taken in a 250 mL conical flask, 2 mL of 2 M sulphuric acid and 5 mL of 0.6 M potassium iodide solution were added. The yellow-brown solution obtained was titrated against 0.002 M sodium thiosulfate until solution colour in the flask became very pale. Then 1 mL of starch indicator was added, and the titration was continued till the dark blue-black colour completely disappeared. The burette reading was 12.4 mL.

5.7 Write balanced chemical equations for the reactions involved in titration and calculate the iodine content (in mg) per kg of salt.

Sol. Reaction 1 : $IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$

Reaction 2 : $I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$

Moles of $Na_2S_2O_3$ = M × V

= 0.002 × 0.0124

= 2.48 × 10^{-5} mole

Moles of I_2 = 1.24 × 10^{-5} moles

Moles of IO_3^- in sample (50 mL)

$= \frac{1}{3} \times \text{moles of } I_2$

$= \frac{1}{3} \times 1.24 \times 10^{-5}$ moles

= 4.133 × 10^{-6} moles

Moles of iodine in 50 mL sample

= 4.133 × 10^{-6} moles

Mass of iodine in 50 mL sample

= 4.133 × 10^{-6} × 127 g

= 0.525 mg

Total iodine in 250 mL sample

= 0.525 × 5 mg

= 2.625 mg

Sine 50 g of salt contain 2.625 mg iodine content = 2.625 mg

In 1000 g of salt iodine content

$= \frac{2.625}{50} \times 1000$

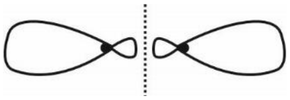
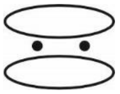
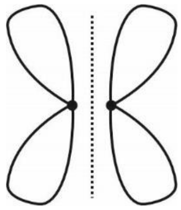
= 52.5 mg/kg

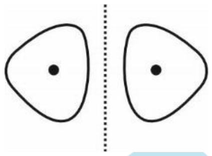
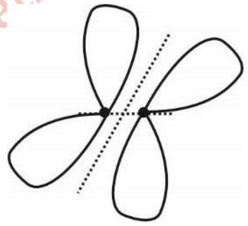
Part-II: Bonding and Colour of Iodine

Iodine exists as a highly coloured diatomic molecule and the colour arises from an electronic transition between the molecular orbitals (MOs) of iodine.

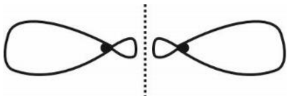
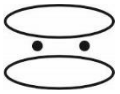
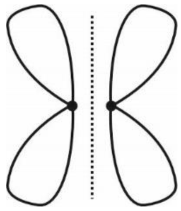
5.8 Assign labels to appropriate MO shape of I_2 molecules arising from the valence shell atomic orbitals (AOs) of two iodine atoms. Take *z*-axis as the internuclear axis. Four of the eight labels are given:

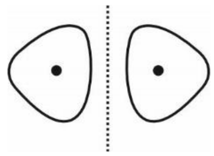
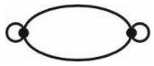
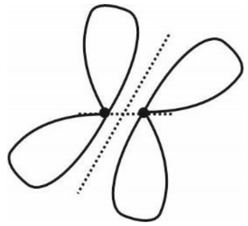
$\sigma 5s$, $\sigma^* 5s$, $\pi 5px$, $\pi 5py$

Orbital Shape				
Label				

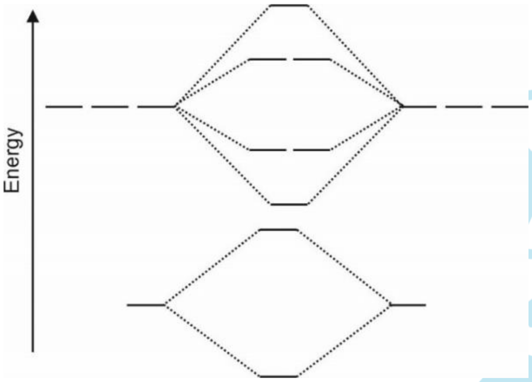
Orbital Shape				
Label				

Sol.

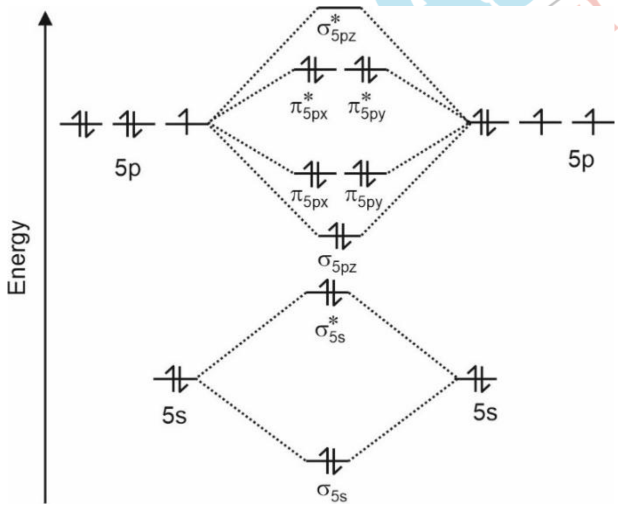
Orbital Shape				
Label	σ^*_{5pz}	π_{5px} / π_{5py}	π_{5py} / π_{5px}	π^*_{5px} / π^*_{5py}

Orbital Shape				
Label	π^*_{5px} / π^*_{5py}	σ_{5pz}	σ_{5s}	π^*_{5py} / π^*_{5px}

5.9 The diagram given below shows relative energies of some of the valence shell AOs of iodine combining to form MOs of I_2. Label the MOs of I_2 and fill in the electrons in MOs.

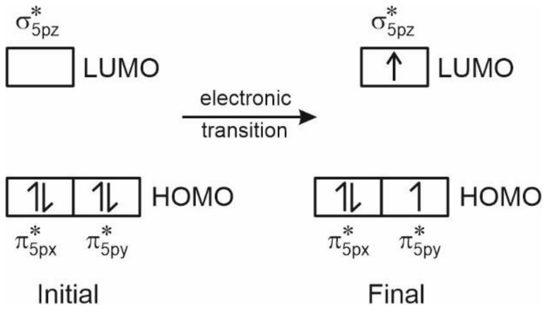


Sol.



5.10 The violet colour of iodine vapour is a result of the excitation of electron(s) between molecular orbitals. Identify the MOs involved in this electronic transition in initial and final state.

Sol.



5.11 Iodine has poor solubility in water, but solubility increases in KI solution due to formation of the triiodide ion I_3^-. Identify the AO of I^- and MO of I_2 which combine to form the HOMO in triiodide ion.

Sol. $KI + I_2 \rightarrow KI_3$

$I^- \rightarrow 5s^2 5p^6$

Assuming *z*-axis as internuclear axis, 5pz of I^- donates the lone pair to LUMO (σ^*_{5pz}) of I_2 to from I_3^-

AO of $I^- \Rightarrow$ 5pz

MO of I_2 = σ^*_{5pz} (LUMO)

❑ ❑ ❑