

Date: 28/01/2023



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Max. Marks : 106

Answers & Solutions

Time: 3 Hrs

for

Indian National Chemistry Olympiad (INChO) (2023) (For Class XI & XII Students)

INSTRUCTIONS TO CANDIDATES

1. There are total **5** questions. Maximum marks are indicated in front of each sub-question.
2. You must show the main steps in the calculations and state the necessary assumptions wherever applicable.
3. Answers written in pencil will be penalized and all answers should be written in per only.
4. Use of non-programmable scientific calculator is allowed.
5. Do not leave the examination room until you are directed to do so.
6. The answer sheet must be returned to the invigilator. You can carry this question paper with you.

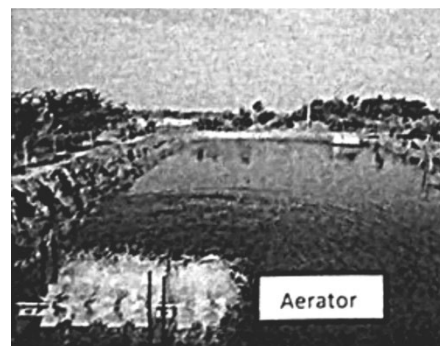
Problem-1

19 marks

Water quality in aquaculture

Aquaculture/fish farming is the controlled process of cultivating aquatic organisms for human consumption. India is the second largest fish producing country in the world. The success of fish/prawn farming in pond depends on water quality. Unutilized feed, fertilizers, and chemicals added to pond and excretions from aquatic organisms lead to degradation of water quality. Pond water is typically characterized by levels of Dissolved Oxygen (DO), alkalinity, salinity, pH, etc.

Aquatic organisms require minimum 5 ppm (parts per million; mg/L) dissolved oxygen for healthy growth. Below 2 ppm, they are not able to survive. This requires regular monitoring of DO level in aquaculture ponds and aerators are operated when DO level goes down.



1.1 In a pond, DO concentration (mark the correct option(s) with **X**)

- (i) increases with increase in temperature
- (ii) decreases with water depth
- (iii) increases during night

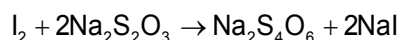
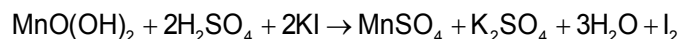
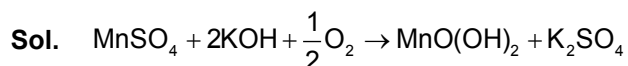
Sol. DO concentration decreases with increase in water depth. In oceans, it reaches a minimum between a few hundred meters and 1000 m deep, named as oxygen minimum layer.

DO decreases with increase in temperature due to decrease in solubility of oxygen at higher temperatures. DO decreases during night due to respiration of aquatic plants. During day time due to photosynthesis process, dissolved oxygen reaches peak in the late afternoon hours.

Hence, correct option is (ii) only.

For DO measurement in a pond, a sample bottle completely filled with the water sample (without leaving any space for air). A solution of MnSO_4 an alkaline iodide azide ($\text{KOH} + \text{KI} + \text{NaN}_3$)(AJA) are added using pipette to bottom part of the bottle. During this addition, about **4 mL** of water sample from the top **overflows, out**. Then the bottle is closed and sealed. Under alkaline conditions, the dissolved oxygen in the water oxidizes Mn^{2+} and quantitatively converts it into manganese oxy di-hydroxide (stable precipitate). Next, the whole content of sample bottle is mixed with conc. H_2SO_4 , the precipitate dissolves and I_2 is formed. The I_2 generated is titrated against standard sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$, HYPO) Solution using starch indicator.

1.2 Write the balanced equations for the chemical reactions involved in the above procedure of DO measurement.



1.3 How many moles of HYPO are equivalent to one mole of DO in this procedure?

Sol. n-factor of hypo in iodometric titration = 1

\therefore Equivalents of hypo = Equivalents of

iodine = Equivalent of $\text{MnO}(\text{OH})_2$

= Equivalent of O_2 [n.f. of I_2 is same in all the reactions]

As n. f. for dissolved oxygen is 4,

We have,

Moles of $\text{Na}_2\text{S}_2\text{O}_3 \times 1 = \text{moles of dissolved oxygen} \times 4$

$$\therefore \text{Moles of dissolved oxygen} = \frac{\text{moles of hypo}}{4}$$

So 1 mole of DO is equivalent to 4 moles of hypo.

- 1.4** A Sample bottle filled initially with 250 mL of pond water sample consumed 6 mL of 0.025 mol L^{-1} HYPO. Calculate the DO concentration in ppm in pond water.

Sol. Moles of dissolved oxygen = $\frac{\text{moles of hypo}}{4} = \frac{6 \times 0.025 \times 10^{-3}}{4}$

$$\text{Mass of DO in mg} = \frac{6 \times 0.025}{4} \times 32$$

$$\therefore \text{Concentration of DO} = \frac{48 \times 0.025}{250} \times 1000 = \frac{48}{250} \times 25 = \frac{48}{10} = 4.8 \text{ mg/L Or } 4.8 \text{ ppm}$$

The amount of MnSO_4 and AIA ($\text{KOH} + \text{KI} + \text{NaN}_3$) to be added to a sample is based on maximum possible DO concentrations in these ponds. For coastal regions having moderate climate, this value can be taken as $\sim 12.5 \text{ ppm}$. [The value corresponds to saturated DO of distilled water assuming regions having minimum (winter) temperature of 6°C . Also, waters with dissolved salts have lower DO than distilled water.]

- 1.5** Assuming that 10% extra reagents are added, calculate the moles of Mn^{2+} which must be added in the sample bottle.

Sol. DO concentration given = 12.5 mg/L

$$\text{Moles of DO} = \frac{12.5 \times 10^{-3}}{32} \text{ per L}$$

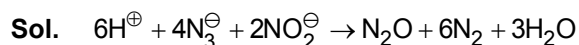
$$\text{Moles of } \text{Mn}^{+2} \text{ which must be added} = \frac{12.5 \times 10^{-3}}{32} \times 2$$

Since 10% extra Mn^{+2} is added,

$$\text{Actual moles of } \text{Mn}^{+2} \text{ required} = \frac{12.5}{32} \times 2 \times 10^{-3} \times 1.1 = 0.858 \text{ millimoles (Volume of bottle considered is 1 L)}$$

Wastes from various organisms in water generate nitrites in water and NO_2^- can react with chemical reagents used for DO estimation. Sodium azide (NaN_3) under acidic conditions reacts with nitrite producing N_2O as one of the products.

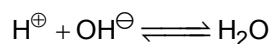
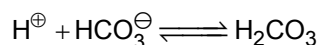
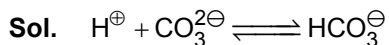
- 1.6** Write the equation for the reaction between NaN_3 and NO_2^- under acidic conditions.



The optimum pH for healthy growth of most aquatic animals is in the range 6.5 - 8.5. Waste products from organisms including gases such as CO_2 tend to make water acidic. Ability of water to neutralize acidic substances and thus, resist changes in pH is known as alkalinity (measured in terms of ppm of CaCO_3). Generally, it can be due to OH^- , CO_3^{2-} and HCO_3^- ions present in water. A certain minimum level of alkalinity is desired for proper growth of aquatic animals.

For carbonic acid (H_2CO_3): $\text{pK}_{a_1} = 6.4$ and $\text{pK}_{a_2} = 10.3$

1.7 Write the reactions of acid (represent by H^+) with these three ions responsible for alkalinity.



To determine alkalinity, water sample is titrated with standard acid first using phenolphthalein indicator. The titration is continued in **the same solution** by adding methyl orange indicator. The acid equivalents used till phenolphthalein and methyl orange end points, respectively are known as phenolphthalein (**P**) alkalinity and methyl orange (**M** or total) alkalinity (both expressed as mmol L^{-1} equivalent to standard acid consumed).

Indicator	pH of the solution	Colour	Indicator	pH of the solution	Colour
Phenolphthalein	8.3 - 10.0	Pink	Methyl orange	2.9 - 4.6	Red
	< 8.3	Colourless		> 4.6	Yellow

1.8 Depending on the ions present in water sample, the **P** and **M** alkalinity values can be related to each other. For each of the following relationship between **P** and **M**, identify the ion/s responsible.

Relationship	P = M	2P = M	M > 0; P = 0	P > M/2	P < M/2
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Sol. Methyl orange end point will be obtained when water contains only H_2CO_3 and pH is around 4.6, whereas phenolphthalein end point is obtained when water contains HCO_3^- ions predominantly as pH will be around

$$8.3 \left[\frac{1}{2} (pK_{a_1} + pK_{a_2}) \right]$$

If $P < \frac{M}{2}$, the predominant species are carbonate and bicarbonate (CO_3^{2-} and HCO_3^-).

If $P > \frac{M}{2}$, the predominant species are carbonate and hydroxide (CO_3^{2-} and OH^-).

If $2P = M$, all alkalinity is due to carbonate (CO_3^{2-})

If $P = M$, all alkalinity is due to OH^-

If $P = 0$, $M > 0$, total alkalinity is due to HCO_3^-

1.9 Calculate the pH of water containing $0.44 \text{ mg } L^{-1}$ of dissolved (hydrated) CO_2 when alkalinity is 5 ppm. (Assume that all of the alkalinity exists as bicarbonate; alkalinity of $50 \text{ ppm} \equiv 50 \text{ mg } L^{-1} \text{ CaCO}_3 \equiv 10^{-3} \text{ mol } HCO_3^- / L$)

Sol. As alkalinity is 5 ppm, we have $10^{-4} \text{ M } HCO_3^-$ ion present.

Concentration of dissolved (hydrated) $CO_2 = 0.44 \text{ mg/L}$

$$\therefore [CO_3^{2-}] = \frac{0.44 \times 10^{-3}}{44} = 10^{-5} \text{ M}$$

$$\text{pH} = \text{pK}_{a_2} + \log \frac{[\text{H}_2\text{CO}_3]}{[\text{HCO}_3^-]}$$

$$\text{pH} = 7.4 + \log \frac{10^{-5}}{10^{-4}} = 7.4 - 1$$

$$\text{pH} = 6.4$$

Dissolved calcium in pond water is required for successful embryonic development of aquatic animals. Minimum calcium hardness of 50 mg/L as CaCO_3 is desirable for freshwater aquaculture ponds. There are situations where hardness is to be increased without significantly affecting pH and alkalinity.

1.10 Of the following, the substance(s) which can be used for this purpose is/are (Mark **X** against the correct option(s))

- (i) Ca(OH)_2
- (ii) CaCO_3
- (iii) CaSO_4
- (iv) CaO

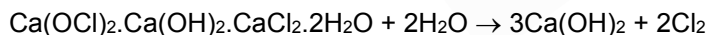
Sol. (iii) CaSO_4 can be used as it will ionise to give Ca^{2+} and SO_4^{2-} which won't affect pH and alkalinity.

CaO can react with H_2O to form Ca(OH)_2 , thus releasing OH^- ions and affecting alkalinity.

Ca(OH)_2 and CaCO_3 also directly release OH^- and CO_3^{2-} ions respectively.

\therefore Only (iii) is correct.

Bleaching powder is widely used in aquaculture for disinfection (chlorination) to kill pathogens and thereby prevent diseases. Bleaching powder having the composition $\text{Ca(OCl)}_2 \cdot \text{Ca(OH)}_2 \cdot \text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ generates Cl_2 on reaction with water.



The amount of bleaching powder/chlorine required to disinfect a water sample is known as its chlorine demand (CD) expressed in units of ppm (milligram of Cl_2 per L of water). CD is determined by adding a certain dosage to the water sample and determining the residual chlorine remaining after disinfection.

$$\text{Residual chlorine} = \text{Chlorine Dosage} - \text{Chlorine Demand}$$

1.11 Calculate the amount of bleaching powder required in kg to treat water in a pond of area 1 hectare and depth 1 m (10^7 L of water), if chlorine demand is 6 ppm and residual chlorine is 2 ppm.

Sol. Volume of water = 10^7 L

As residual chlorine is 2 ppm,

Chlorine dosage = Residual chlorine + Chlorine demand

$$= 8 \text{ ppm or } 8 \text{ mg/L}$$

∴ Chlorine dosage given is $8 \times 10^{-3} \times 10^7$ g for 10^7 L of water

∴ Chlorine dosage = 8×10^4 g

∴ Amount of bleaching powder required = $\frac{1}{2}$ (mole of Cl_2 dosage) \times Molar mass

$$= \frac{1}{2} \left(\frac{8 \times 10^4}{71} \right) \times 364$$

$$= 50.51 \times 10^4 \text{ g}$$

$$\approx 205.1 \text{ kg}$$

Problem-2

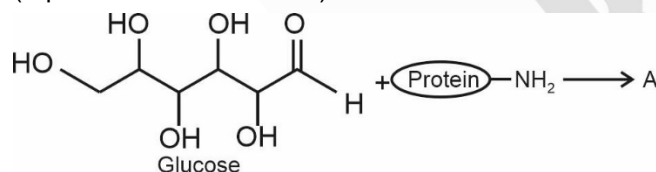
23 marks

Maillard reaction in cooking

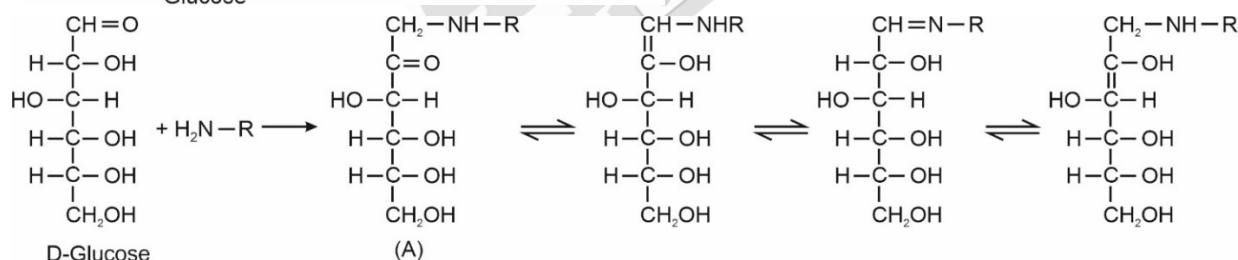
Fried and baked foods such as chips, biscuits, breads, namkeens etc, and many other cooked foods have a distinctive flavour which makes them taste and smell good. This flavour is produced due to a series of non- enzymatic reactions between amino acids and reducing sugars, which increase with temperature and proceed rapidly around 140 to 165°C. These reactions use water in the food product as a reaction medium (solvent). This set of reactions are the major cause of browning of food during cooking and is known as the Maillard reaction, reported first by Louis-Camille Maillard in 1912.

Maillard reaction between a pair of reducing sugar and amino acid molecule may proceed via multiple pathways producing a range of compounds. Two of the categories of compounds formed in this reaction are enaminsols (compounds containing alkene, amine and alcoholic functionality) and α -dicarbonyls (containing two carbonyl groups on adjacent carbons in the molecule).

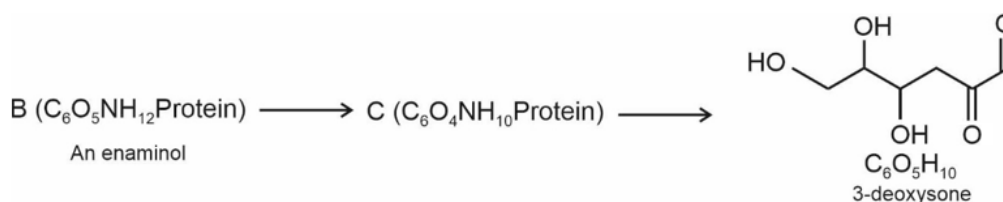
2.1 Draw the first product, A, of the Maillard reaction as glucose reacts with an amino acid from proteins in food (represent as Protein- NH_2). Draw four tautomeric structures of A (stereochemistry not required).

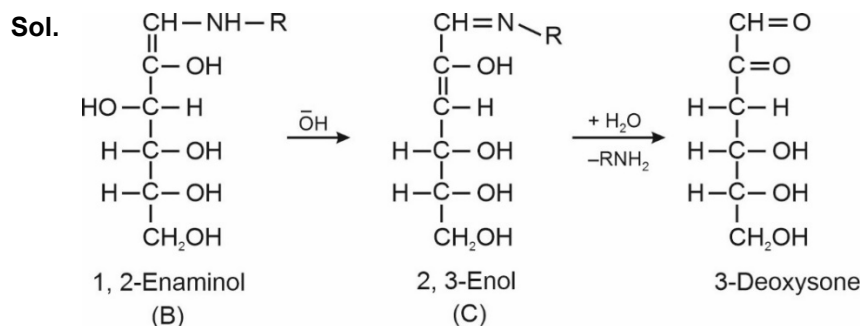


Sol.



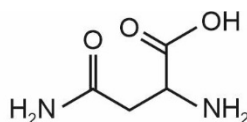
2.2 Enaminols can produce α -dicarbonyl compounds via multistep reaction. A 1, 2 enaminol **B** (obtained from glucose) transforms via intermediate **C** to produce 3-deoxysone as shown below. Draw the structures of **B** and **C**.





(Note : R = Protein)

- 2.3** Reactivity of amino acids with sugars in Maillard reactions is pH dependent. Amino acid asparagine has the following structure. Draw the structure of prominent species of asparagine at pH = 7.

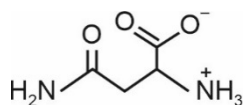


pK_a values : $-\text{COOH}$: 2.14 $\alpha\text{-NH}_2$: 8.72

Sol. Isoelectric point of asparagine (pI)

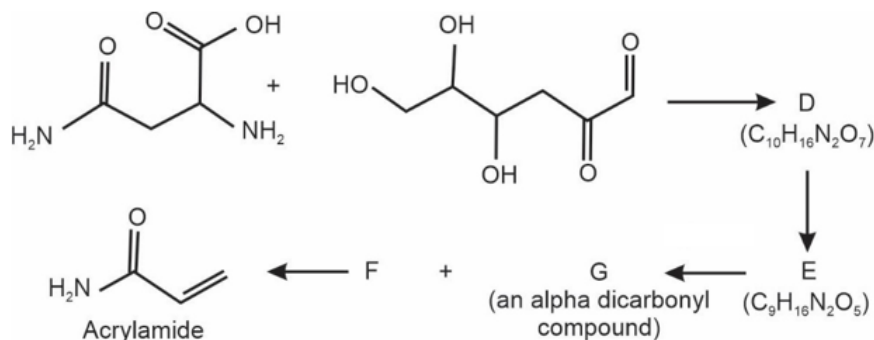
$$= \frac{\text{pK}_{a_1} + \text{pK}_{a_2}}{2} = \frac{2.14 + 8.72}{2} = 5.43$$

The structure of prominent species of asparagine at pH = 7

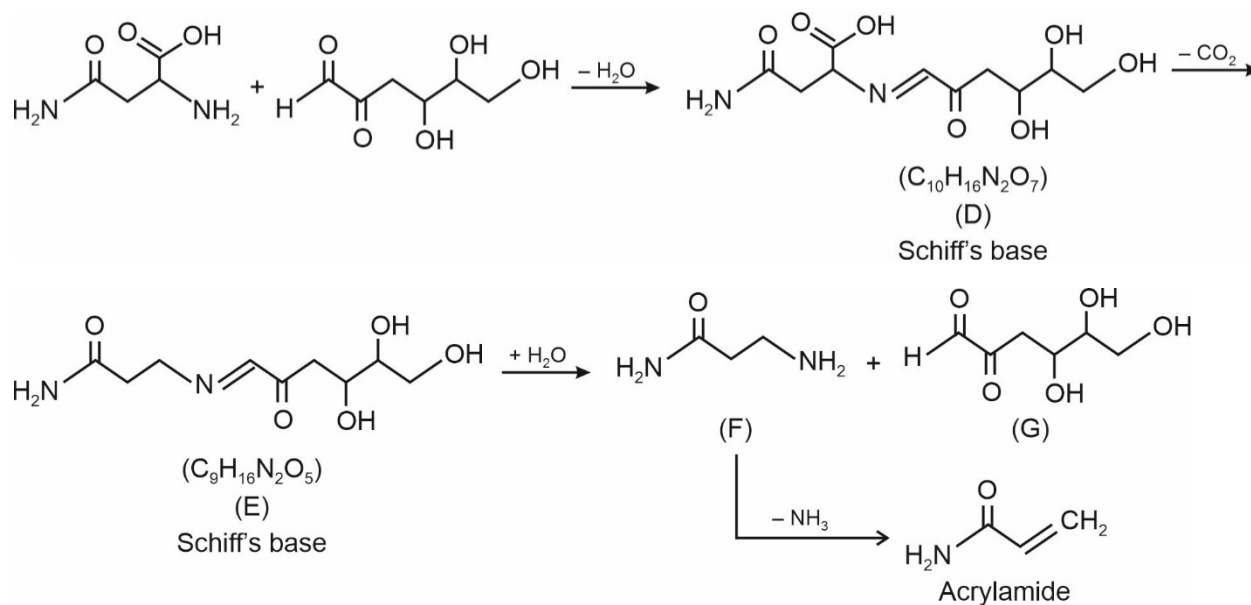


Maillard reaction products generally enhance taste, color, and flavor of food. However, longer cooking of food (to the stage of charring) can lead to production of toxic compounds having acid flavours. One such example is reaction of α -dicarbonyl compound with asparagine (available in most foods) to form acrylamide.

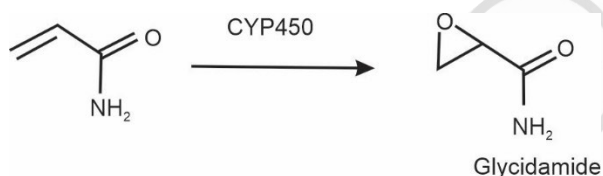
- 2.4** Draw the intermediates (**D**, **E**, **F**, **G**) formed during reaction of asparagine and α -dicarbonyl product (shown below) under cooking conditions to form acrylamide.



Sol.

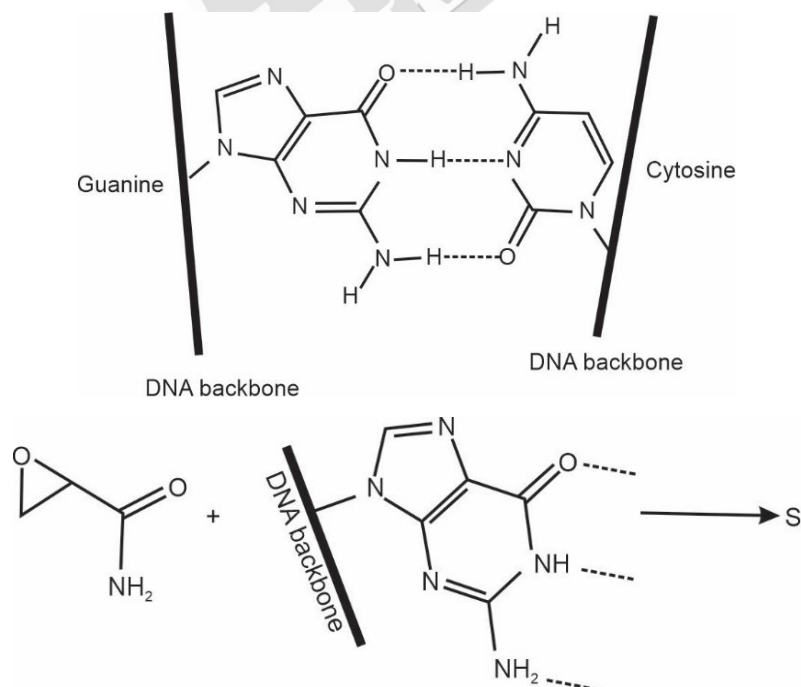


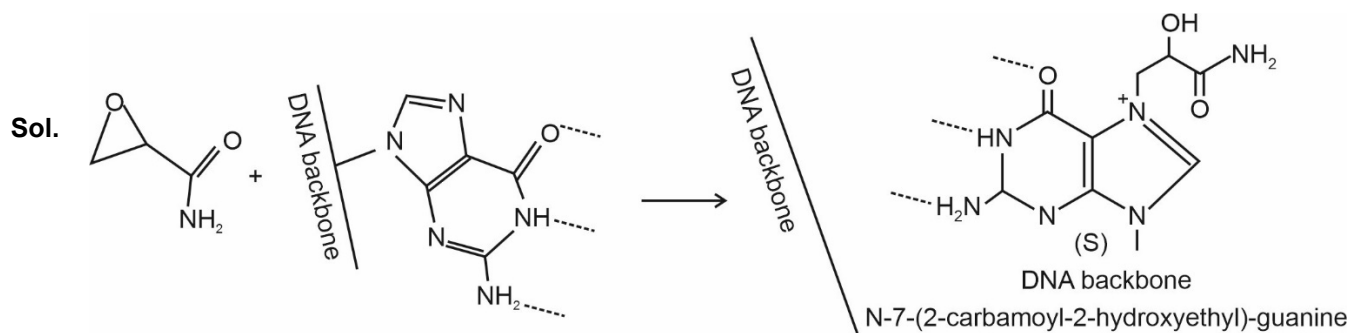
Acrylamide is a known carcinogen. As it is absorbed by our body, it is converted to glycidamide by the enzyme cytochrome P450 (CYP450).



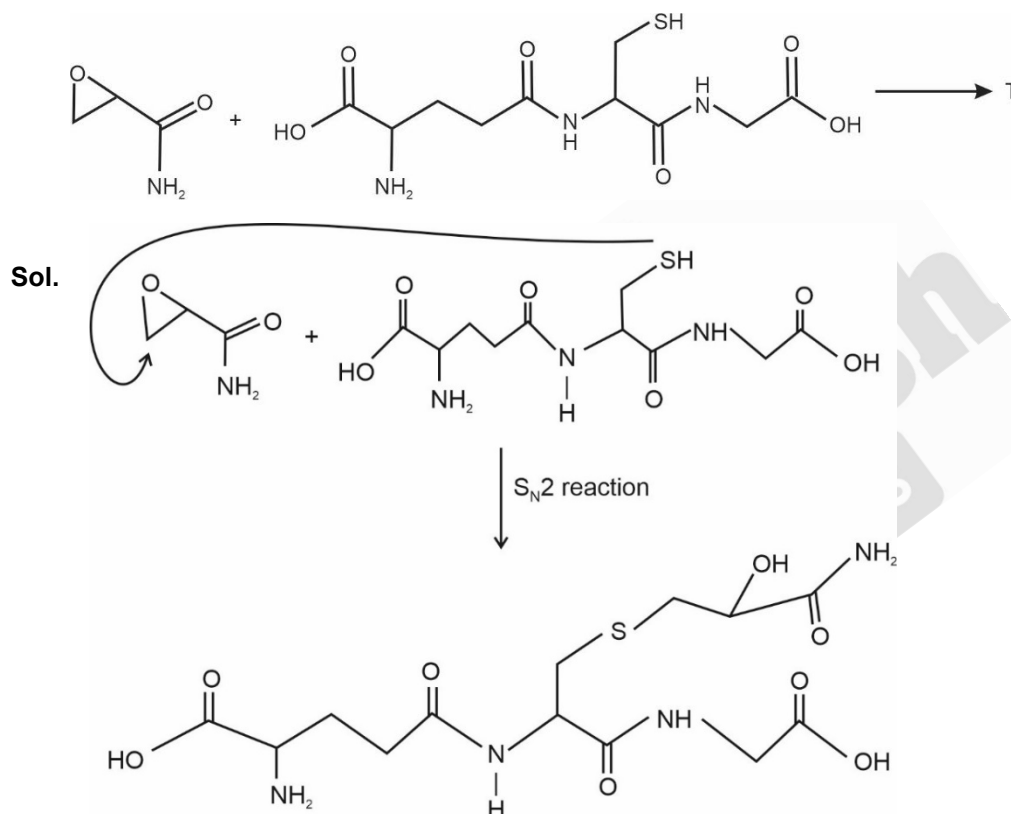
Glycidamide can react with DNA bases by covalently modifying them, thus showing carcinogenic properties.

2.5 Draw the modified guanine site S within a DNA chain due to reaction with glycidamide. In a DNA chain, guanine is H-bonded with cytosine.





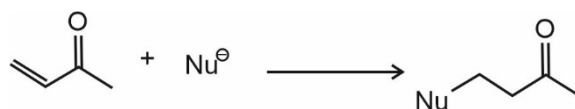
- 2.6** A tripeptide glutathione (common in many foods, and also synthesized by our body) acts as a natural inhibitor to glycidamide and acrylamide. Both acrylamide and glycidamide get attached covalently to glutathione, and get excreted in the urine. Draw the major product T as glycidamide reacts with glutathione.



Sulphur is more nucleophilic as compared to nitrogen therefore attack of sulphur atom takes place.

- 2.7** Some commercial food products are modified with additives such as flavonoids, vitamins, etc which trap the Malliard intermediates or trap acrylamide during overcooking.

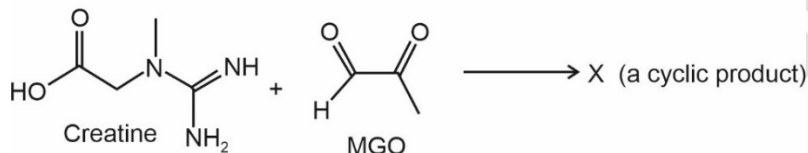
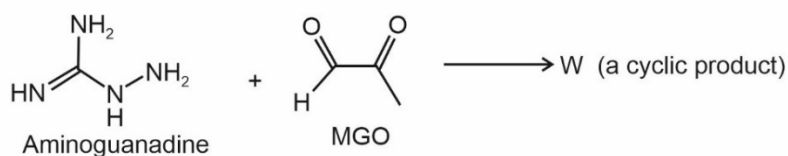
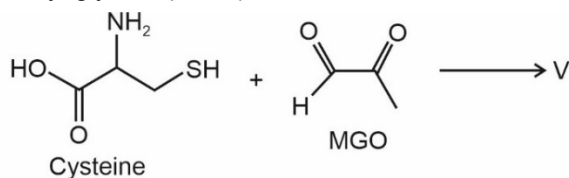
- (i) Trapping acrylamide: Niacin (vitamin B₃) can react with acrylamide making it unavailable for further absorption in the body. This reaction happens via an addition mechanism, in which a nucleophile approaches an α, β -unsaturated carbonyl compound at the β position. Given below is a generalized form of this mechanism.



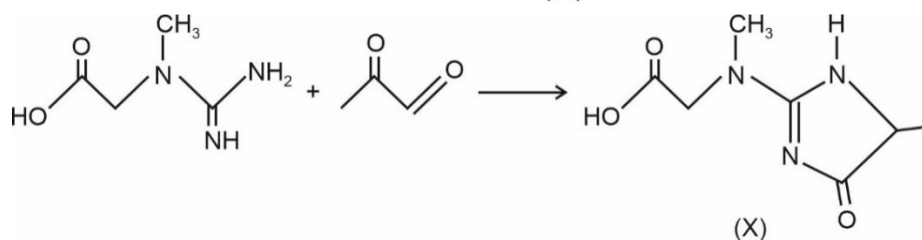
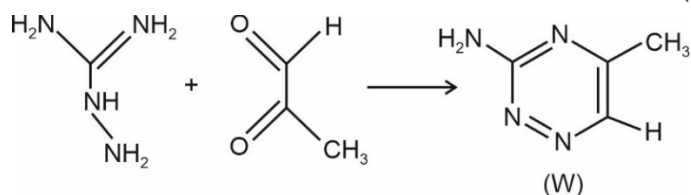
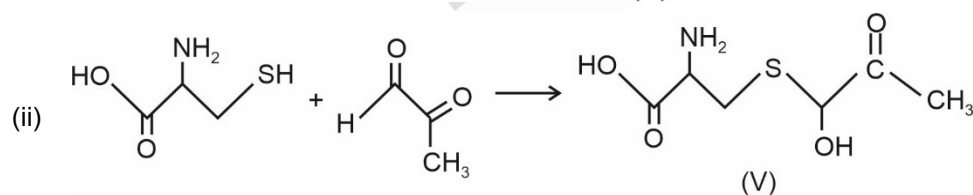
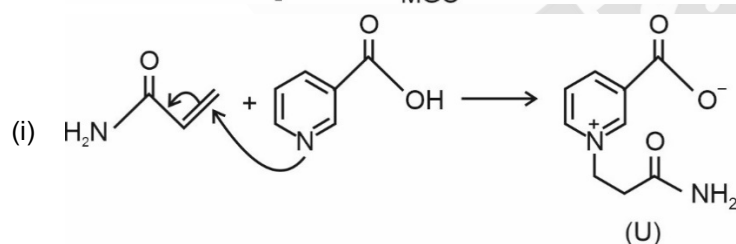
Draw the structure of U in the reaction of acrylamide with niacin.



- (ii) Trapping intermediate species such as α -dicarbonyls: The following pharmaceuticals and food ingredients trap α -dicarbonyls (during cooking conditions). Draw the major product of their reactions with methyl glyoxal (MGO).



Sol.



Some general observations about reactions in food are:

Fact I: The first step of Maillard reaction generates water as a bi-product, and excess water may favour-backward reaction.

Fact II: NaCl enhances the hydrolysis rate of sucrose (a non-reducing sugar) to glucose and fructose in aqueous solution.

Fact III: The first step of Maillard reaction may proceed slowly, and the forward reaction may be facilitated by either H^+ or high temperatures.

Fact IV: The amines are less likely to be found as $-Na_3^+$ with increase in pH.

Fact V: Metal ions in food such as Na^+ , Ca^{2+} , etc, can increase the rate of Maillard reaction (by stabilizing negative charges in intermediates).

2.8 Given below are a few statements about the Maillard reaction in different foods. Indicate if they are true (T) or false (F). For each statement, identify which of the above fact(s) explain or correlate with your answer. Write "Fact I", "Fact II", "Fact III", "Fact IV", "Fact V" or "None" in the box provided.

- (a) The rate of the initial step of the Maillard reaction is decreased at pH values lower than the pK_a value of the amino group.
- (b) Very low pH decreases the reactivity of carbonyl group of the carbohydrate.
- (c) In recipes of stir frying, onions brown faster with lemon/tamarind juice than when stir fried alone.
- (d) Higher salt concentration promotes the Maillard reaction in food dishes containing sucrose.
- (e) During cooking, potatoes kept earlier in salt water tend to brown faster than potatoes kept earlier in water.
- (f) In soups, vegetables such as carrots, cauliflowers, etc, get less browned during boiling in a pressure cooker than during open vessel boiling.

- Sol.**
- (a) True
 - (b) False
 - (c) False
 - (d) True
 - (e) True
 - (f) False

Problem-3

20 marks

Historical alum production and dyeing

Ancient civilizations including Egyptian, Chinese and Indians, had found aluminium sulphate useful in dyeing of clothes and tanning of leather. Pure crystalline aluminium sulphate was not abundant in nature. Aluminium is abundant in earth's crust as alumina or exists as sulphates with other metal sulphates, which all were called alums. Only two of these: potassium aluminium sulphate $[KAl(SO_4)_2 \cdot 12H_2O]$ and ammonium aluminium sulphate $[NH_4Al(SO_4)_2 \cdot 12H_2O]$ could be easily obtained as colourless crystals of high purity. These two alums became of great economic importance, due to their better dyeing properties.

3.1 A 1 M solution of ammonical alum would have pH in the range.

- (i) 0 – 1.0
- (ii) 1.0 – 6.0
- (iii) 6.0 – 8.0
- (iv) 8.0 – 13.0
- (v) 13.0 – 14.0

Sol. Cations of ammonical alum i.e. NH_4^+ and Al^{3+} undergo hydrolysis giving NH_4OH and $\text{Al}(\text{OH})_3$ along with H^+ ions. The resulting solution becomes acidic whose pH ranges between 1.0 to 6.0.

Hence answer is (ii).

	Molar mass (g mole ⁻¹)	Solubility at 20 °C (g per 100 g water)	Solubility at 60 °C (g per 100 g water)
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	278.02	25.6	101
$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	666.43	36.4	59.2
$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	474.40	6.0	33.3
$\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	453.33	6.6	21.1

The first large scale industry to produce synthetic alum was set up in the 17th century in Whitby, England, in the regions having shale rocks with some fossils in it. The rocks had aluminosilicates ($\text{Al}_2\text{O}_3 \cdot x\text{SiO}_2$), pyrites (FeS_2) and carbon, which were essential ingredients to prepare alum. Alum obtained had to be free from iron salts for using as mordant.

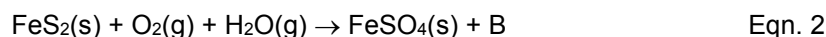
The steps involved in this process of producing alum were:

- I. Mineral rocks were piled on wooden logs which were burned for months. Carbon (fossils) in rocks also supported the fire.
- II. The burned rocks were soaked in rainwater to dissolve the sulphates generated by oxidation. The soluble salts were dissolved from the charred rock. The silicates were left behind as slag.



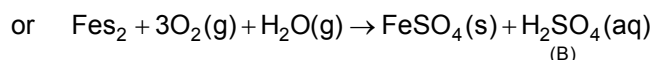
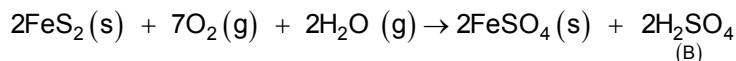
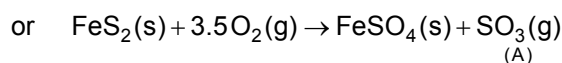
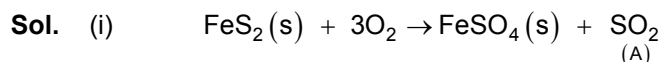
- III. The supernatant liquor was separately collected, and concentrated by evaporation at low heat.
- IV. The concentrated fluid was then treated with stocked human urine (containing urea which decomposes to give ammonia) or roasted sea weed (containing potassium oxide) as an alkali source to produce ammonium alum or potash alum, respectively.

3.2 Two of the reactions in Step-I are:

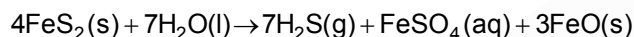


- (i) Identify A and B, and balance the equations.
- (ii) During rainy season, rotten egg smell is observed in shale rocks (both burnt and unburnt). Write a balanced equation for the reaction giving rise to rotten egg smell.
- (iii) In Step III, a fresh egg was added to the heated solution at frequent intervals. If the egg sank, the heating was continued. If the egg floated, heating was stopped, and the next step (Step IV) was carried out. This technique of using egg helped to: (Mark X against the correct option(s))
 - (a) stop the reaction that was producing rotten egg smell.
 - (b) ensure homogenization of solution during evaporation.
 - (c) prevent precipitation of iron sulphate during cooling.

- (d) nucleate/seed more number of alum crystals under hot conditions.
 (e) prevent loss of sulphate as SO_2 gas.
 (f) consistently obtain saturation point of $\text{Al}_2(\text{SO}_4)_3$ in solution.
- (iv) For Step IV, write the balanced chemical reactions which led to production of potash alum and ammonical alum, respectively.

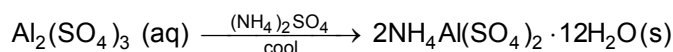
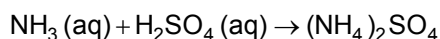
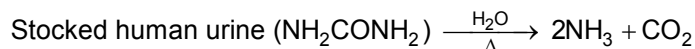
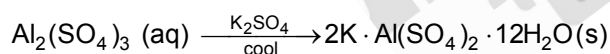
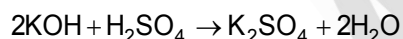


- (ii) Rotten egg smell is observed due to the formation of H_2S .



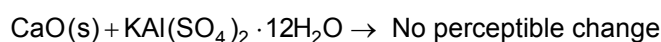
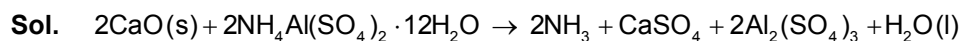
- (iii) (a) Stop the reaction that was producing rotten egg smell. (F)
 (b) Ensure homogenisation of solution during evaporation. (F)
 (c) Prevent precipitation of iron sulphate during cooling. (T)
 (d) Nucleate/seed more number of alum crystals under hot conditions. (F)
 (e) Prevent loss of sulphate as $\text{SO}_2(\text{g})$. (F)
 (f) Consistently obtain saturation point of $\text{Al}_2(\text{SO}_4)_3$ in solution. (F)

- (iv) $\text{K}_2\text{O}(\text{roasted seaweed}) + \text{H}_2\text{O} \rightarrow 2\text{KOH}$



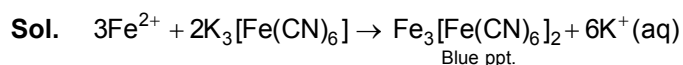
Potash alum and ammonia alum crystals are isomorphous and look alike. So by physical appearance, are hard to distinguish. Quicklime (CaO) is used to distinguish the two.

3.3 Write balanced chemical equation(s) for reaction(s) of quicklime which can differentiate potash and ammonia alum.



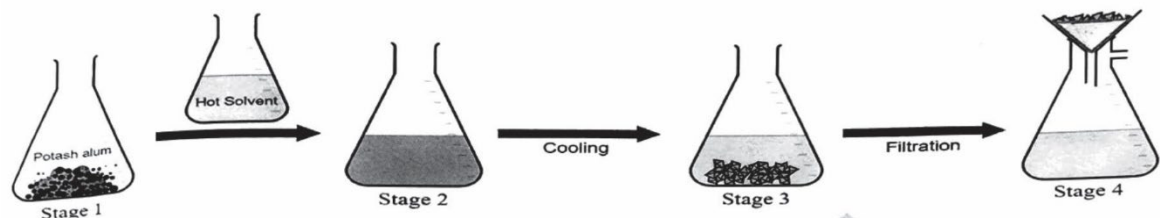
3.4 In the alum crystals obtained, a very small amount of Fe^{2+} may remain which may not be detectable with eyes. One way to determine its presence in alum is by the addition of a reagent which will develop a dark colour with it. Among the following substances available in past, identify the reagent useful to detect Fe^{2+} and write the corresponding balanced equation for the reaction.

- (i) CaCO_3
- (ii) $\text{K}_3[\text{Fe}(\text{CN})_6]$
- (iii) $\text{Ca}(\text{OH})_2$
- (iv) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$



Answer is (ii).

The crude alum crystals obtained in step IV were recrystallized using water as solvent to separate any residual Fe^{2+} from the alum. The steps are shown below

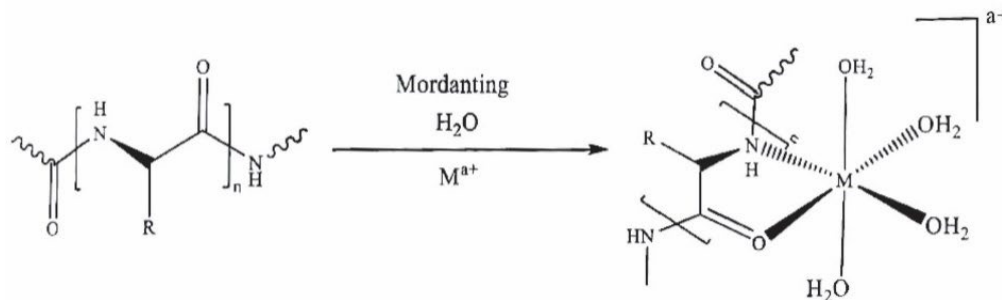


3.5 The statement(s) correct for the above process of recrystallization is/are (Mark **X** against the correct option(s))

- (i) Hot solvent melted the solid.
- (ii) More Fe^{2+} was present in hot solvent than in cold solvent.
- (iii) The impurities settled faster than the pure crystals on cooling.
- (iv) Stage 3 contained saturated solution of alum.

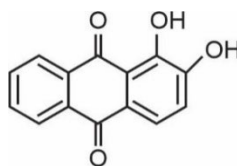
- Sol.**
- (i) Hot solvent melted the solid (F)
 - (ii) More Fe^{2+} was present in hot solvent than in cold solvent (F)
 - (iii) The impurities settled faster than the pure crystal on cooling (F)
 - (iv) Stage 3 contained saturated solution of alum (T)

In fabric dyeing, mordants impact dye brightness, wash-fastness, and colour by aiding dye-fiber bonding. For example, animal fibres (silk, wool) have amino and carboxyl groups. Mordants bind hydrated metal ions to fibre amino and carboxyl groups as shown below:

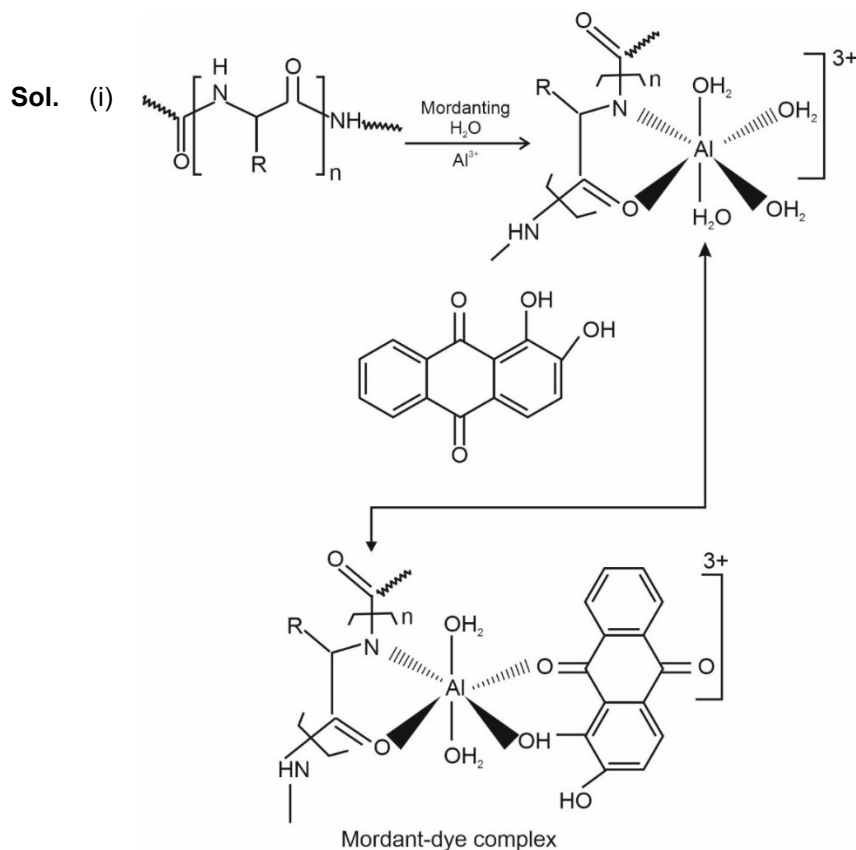


[Note that the protein chains are non-planar.]

Alizarin dye, whose molecular structure is illustrated below, is a bidentate ligand that binds with the mordanted fibre. Usually one alizarin molecule binds to one metal ion.



- 3.6** (i) Show the full structure of the species formed around Al^{3+} ion as mordant-dye-fiber bonding and show the overall charge of the complex species.
- (ii) Write the number of optically active isomers for the species.



- (ii) Total eight optically active isomers are possible for the above mordant-dye complex.

3.7 The metal ions left in the effluents from dyeing industry are of environmental concern. Aluminum sulphate has replaced potash alum as the standard mordant since it produces identical results in terms of fabric colour at similar mass usage. The suggested quantity of both mordants required is 15% of the mass of the dry cotton cloth. A study shows that after use as mordant, 92% of aluminium is present in effluent water.

- (i) What will be the mass of hydrated aluminium sulfate or potash alum required if a dyer mordantes 2 kg fabric?
- (ii) Compare the mass of aluminium left in effluent water, using hydrated aluminium sulfate vs potash alum.

Sol. (i) Mass of hydrated aluminium sulphate or potash alum required = $2 \times \frac{15}{100} = 0.3 \text{ kg} = 300 \text{ g}$

(ii) Mass of Al left in effluent water using hydrated aluminium sulphate = $\frac{0.3 \times 54 \times 1000}{666.43} \times \frac{92}{100} = 22.364 \text{ g}$

Mass of Al left in effluent water using potash alum = $\frac{0.3 \times 27 \times 1000}{474.40} \times \frac{92}{100} = 15.70 \text{ g}$

Hence mass of aluminium left in effluent water using hydrated aluminium sulphate is more than when potash alum is used.

Problem-4

23 marks

The Odyssey of Match sticks

While use of fire has been synonymous with human civilization, easy and safe generation of fire had always been a challenge. An ideal fire generation device should produce a flame instantaneously from a very fast reaction/process, which requires:

- (i) a (easily combustible) fuel
- (ii) an oxidizer
- (iii) a mechanism to initiate burning of fuel

In this process, additionally fumes, hot gases, sparkles, and ashes are likely to be produced depending on the substances used. Today, we have safety matchboxes, where risks from fumes, sparkles, falling ash and spontaneous combustion of match sticks have been minimized. A binder is used to keep the various chemical components of a match stick together as a solid mass on a wooden stick or stiff paper.

The current state is achieved through an interesting historical journey as described below.

A. The start of a long journey

The discovery of phosphorous in 1669 created new possibilities to generate fire. In 1781, a *phosphoric taper* was introduced in France as a fire-making device based on a 4-inch glass vial (Figure 1). A piece of white phosphorous was placed at the bottom of the vial along with a thin wax candle (taper/wick) under air-tight conditions. When this vial was dipped in warm water ($> 40^\circ\text{C}$) followed by breaking of the seal, the taper lighted up in flame.

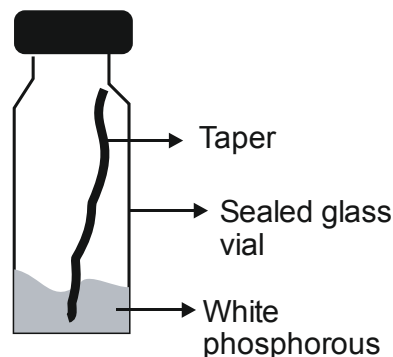
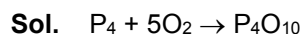


Figure 1. Phosphoric Taper

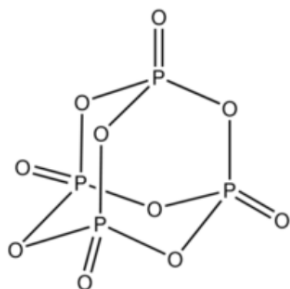
4.1 Identify the initiator fuel and oxidizer in this set up.

Sol. White phosphorus is the initiator fuel and oxidiser is the aerial oxygen in the set up.

- 4.2** Write a balanced chemical equation for the reaction initiating fire. Draw the chemical structure of the final phosphorous compound formed in this reaction.



And the structure of P_4O_{10} is



- 4.3** Dipping of the vial in warm water before breaking the seal resulted in a better and reliable burning of the taper, as this process (mark **X** against the correct option(s))

- (i) initiates phosphorous burning with bright white light
- (ii) triggers white phosphorous to red phosphorous isomerism
- (iii) melts the phosphorous and adheres it to the taper
- (iv) reduces the inactive phosphorus oxide surface layer to phosphorus
- (v) minimizes sparking during phosphorous burning

Sol. Dipping of the vial in warm water before breaking the seal resulted in a better and reliable burning of the taper, in this process, melts the phosphorus and adheres it to taper.

∴ Correct options are (iii).

B. Instantaneous light box

In 1805, instantaneous match boxes were invented in France that soon became popular in Europe. These match boxes had two parts: (i) a stoppered bottle of concentrated sulfuric acid, and (ii) wooden sticks with a mixture of potassium chlorate, sugar, and binder (gum) on the tips. The stick tip when dipped into the acid solution and withdrawn, caused it to catch fire.

- 4.4** Identify the initiator fuel and oxidizer in this set up.

Sol. The initiator fuel in the instantaneous light box is sucrose (sugar) and potassium chlorate ($\text{KClO}_3/\text{HClO}_3$) acts as an oxidiser in this set up.

- 4.5** A lot of char formed on the stick at the end to the reaction Name the possible source(s) of the char.

Sol. A lot of char is formed on the stick at the end of the reaction. The possible source of char is sucrose (sugar).

- 4.6** After multiple usage of the match box and/or further storage for a long period of time, the match sticks did not burn, nor did it form any char in acid. The most likely reason for this inactivity is (mark **X** against the correct option)

- (i) KClO_3 reacts with sugar over time
- (ii) H_2SO_4 absorbs atmospheric water and gets diluted
- (iii) KClO_3 absorbs atmospheric water and converts to HClO_3
- (v) The sugar absorbs atmospheric water and hydrolyzes

Sol. After multiple usage of the match box and on storage for a long time period, the match box did not burn because H_2SO_4 absorbs atmospheric water and gets diluted.

Hence, correct answer is option (ii).

C. Friction light

In 1820s, friction stick light, also known as Lucifer, was developed in England. Here, the match stick head contained KClO_3 and antimony (III) sulfide. The match stick head was kept between folds of sandpaper and pulled to create fire. KClO_3 present in the match stick decomposed easily due to heat produced by friction. Here, the ignition was typically followed by splattering of sparks and burning particles in all direction.

4.7 Identify the initiator fuel and oxidizer in this set up.

Sol. The initiator fuels are antimony sulphide and potassium chlorate works as an oxidizer in this set up.

4.8 (i) Write the balanced equation for the decomposition reaction of potassium chlorate.

Assuming that the friction caused the temperature to rise to 450 K, determine

(ii) The enthalpy change per mole and

(iii) The free energy change per mole for the decomposition reaction at this temperature.

Sol. (i) $2\text{KClO}_3(\text{s}) \xrightarrow{\text{Heat}} 2\text{KCl}(\text{s}) + 3\text{O}_2(\text{g})$

(ii) $2\Delta H_{\text{rxn}}^\circ = 2(\Delta H_{\text{KCl}}^\circ) + 3(\Delta H_{\text{O}_2}^\circ) - 2(\Delta H_{\text{KClO}_3}^\circ)$

$$\Delta H_{\text{Reaction}}^\circ = -38.8 \text{ kJ/mole}$$

(iii) $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$

$$\Delta H^\circ = -436.5 + 397.7 = -38.8$$

$$\Delta S^\circ = \left(\frac{3}{2} \times 205.2 + 82.6 \right) - 143.1 = 247.3$$

$$\therefore \Delta G^\circ = -38.8 \text{ kJ} - 450 \times 247.3 \text{ J}$$

$$= -150.085 \text{ kJ/mole}$$

The standard enthalpy of formation (ΔH_f°) and standard entropy (S°) of the substances (both quantities can be assumed to be independent of temperature) are given below:

Substance	ΔH_f° (kJ mol ⁻¹)	S° (J K ⁻¹ mol ⁻¹)
$\text{O}_2(\text{g})$	0	205.2
$\text{KCl}(\text{s})$	-436.5	82.6
$\text{KClO}_3(\text{s})$	-397.7	143.1

4.9 The decomposition reaction of KClO_3 happens easily on slight heat (generated by friction), but not at room temperature. This is because the reaction has (mark the correct option with **X**)

- (i) positive ΔS
- (ii) low ΔH
- (iii) negative ΔH
- (iv) high activation energy

Sol. $2\text{KClO}_3(\text{s}) \rightarrow 2\text{KCl}(\text{s}) + 3\text{O}_2(\text{g})$

$$\begin{aligned}\Delta H_{\text{R}}^{\circ} &= 2(\Delta H_{\text{KCl}}^{\circ}) + 3(\Delta H_{\text{O}_2}^{\circ}) - 2(\Delta H_{\text{KClO}_3}^{\circ}) \\ &= 2(-436.5) + 2(397.7) \\ &= -77.6 \text{ kJ mol}^{-1} \\ \Delta S^{\circ} &= 3(205.2) + 2(82.6) - 2(143.1) \\ &= 494.6 \text{ J K}^{-1}\text{mol}^{-1}\end{aligned}$$

So, ΔG° is always negative for such a reaction and it should always be spontaneous.

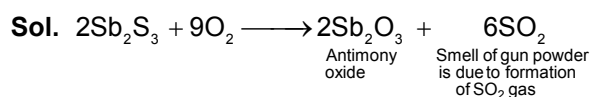
The decomposition reaction of KClO_3 happens easily on slight heat, but not a room temperature. This is because the reaction has high activation energy.

\therefore Answer will be (iv)

D. The current model: Safety Matches

Current safety match boxes have two parts: i. a match stick, and ii. a striking surface on the side of the container box. The match stick head contains a mixture of potassium chlorate, antimony sulfide, paraffin wax, ammonium phosphate, and glue. The striking surface contains a mixture of red phosphorous and an abrasive such as powdered glass. When the match stick head is struck on the abrasive surface, the red phosphorus is converted to white phosphorous and transferred to the match stick head. The white phosphorus reacts in air and initiates the conversions of KClO_3 and antimony (III) sulfide, which finally produce heat for the ignition of the match stick.

4.10 Burning of the match stick produces antimony (III) oxide and a species that smells of gunpowder. Write the balanced chemical equation for this reaction.



4.11 The presence of wax in match stick head (mark the correct option with **X**)

- (i) ensures steady burning of the match stick over a few seconds
- (ii) prevents fume formation via condensation of the hot gases produced
- (iii) absorbs toxic gases and prevents health hazards
- (iv) prevents spontaneous decomposition of KClO_3

Sol. The presence of wax in match stick head

- (i) Ensures steady burning of match stick over a few seconds

Wax helps the flame travel down the match stick

Consider the match stick head as a sphere with a diameter of 0.4 cm (**Figure 2**) in which 50% volume is occupied by the chemical mixture containing potassium chlorate and antimony sulfide with mass percentages 40% and 18% respectively.

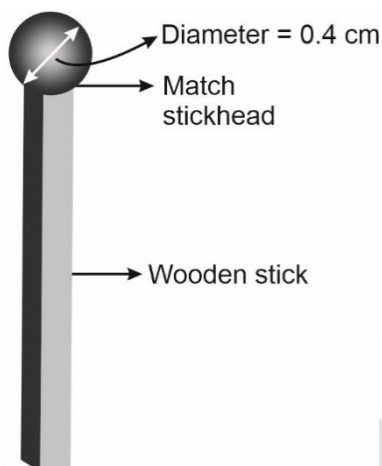


Figure 2

Given estimated values-

Match stick head mixture, Density = 4.0 g cm^{-3} ; Specific heat = $2.1 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$

Specific heat of the wood = $1.76 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$

ΔH° of white phosphorous oxidation = $-2984 \text{ kJ mol}^{-1}$

ΔH° of potassium chlorate decomposition in air = -78 kJ mol^{-1}

ΔH° of antimony sulfide decomposition in air = -700 kJ mol^{-1}

4.12 If $5.0 \text{ } \mu\text{g}$ of white phosphorous is transferred to the match stick head, how much energy it can generate from its reaction in air? If all this energy heats up $1 \text{ mm} \times 0.5 \text{ mm} \times 0.1 \text{ mm}$ region of match stick head, estimate the spot temperature at this specific region. Assume room temperature to be 300 K .

Sol. Moles of white phosphorus = $\frac{5 \times 10^{-6}}{31 \times 4}$

Heat released due to reaction of P_4 in air

$$= 2984 \times \frac{5 \times 10^{-6}}{31 \times 4} \text{ kJ}$$

$$= \boxed{0.1203 \text{ joule}}$$

$$\Delta H = mC_p \Delta t$$

$$\text{Mass} = \text{density} \times \text{volume}$$

$$\text{Volume} = (.1 \text{ cm}) (.05 \text{ cm}) (.01 \text{ cm})$$

$$= 5 \times 10^{-5} \text{ cm}^3$$

$$\text{Mass} = 4 \times 5 \times 10^{-5} \text{ gm}$$

$$= 20 \times 10^{-5} \text{ gm}$$

$$= 2 \times 10^{-4} \text{ gm}$$

$$\Delta H = mC_p \Delta t$$

$$0.1203 = (2 \times 10^{-4}) (2.1) (T - 300)$$

$$\Rightarrow 286.4 = T - 300$$

$$\boxed{T = 586.4 \text{ K}} \text{ Spot temperature.}$$

- 4.13** Determine the temperature rise of wood in contact with match stick head after completion of reactions in the chemical mixture on stick head. Assume that the heat released from combustion is available to $1/10^{\text{th}}$ of the length of the stick and 50% heat escapes as hot gases and flame. Mass of wooden stick = 0.1 g.

Sol. Volume of match stick head

$$\frac{4\pi}{3} r^3 = .0334933 \text{ cm}^3$$

$$\text{Volume of chemicals} = .0167466 \text{ cm}^3$$

$$\text{Total mass of chemicals} = .066986 \text{ gm}$$

$$\text{Mass of KClO}_3 = .02679$$

$$\text{Moles of KClO}_3 = \frac{.02679}{122.55} = 2.186 \times 10^{-4} \text{ mole}$$

$$\text{Mass of Sb}_2\text{S}_3 = .0120576 \text{ gm}$$

$$\text{Moles of Sb}_2\text{S}_3 = \frac{.0120576}{340} = 3.546 \times 10^{-5} \text{ mole}$$

Heat released (Assuming only due to KClO_3 and Sb_2S_3)

$$= 78 \times 10^3 \times \left(2.186 \times 10^{-4} \right) + 700 \times 10^3 \left(3.546 \times 10^{-5} \right)$$

due to KClO_3 due to Sb_2S_3

$$= (17.0508 + 24.822) \text{ joule}$$

$$= 41.8728 \text{ joule}$$

Heat released = 50%

$$\Rightarrow \left(\frac{41.8728}{2} \right) = \left(\frac{.1}{10} \right) (1.76) (\Delta T)$$

$$\Delta T = 1189.57 \text{ K} \text{ Temperature rise}$$

Problem-5

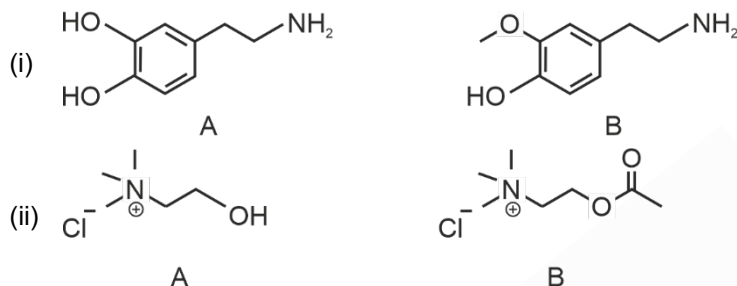
21 marks

Chemistry and Brain

Our brain communicates with and exerts control over other organs of the body through the central nervous system (CNS), consisting of neurons. Neurons send a message through neurotransmitters, chemicals which cross the synapses at boundary of two cells.

A cell membrane is made of bilayers of lipids and has an oil like environment within the membrane bilayer, and the cytoplasm is mainly aqueous. Small molecules are able to enter into these bilayers depending on their structural features.

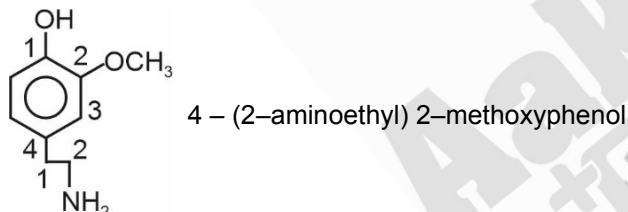
5.1 For each of the following pairs of molecules of biological origin, choose molecule (A or B) that has more affinity to cell membranes than cytoplasm.



Sol. (i) "Molecule B" has more affinity to cell membranes (made of lipids and has oil like environment) as molecule B contains ($-\text{O}-\text{CH}_3$) group, rest part of both molecules is same.
 (ii) "Molecule B" has more affinity to cell membranes as OH group is more polar.

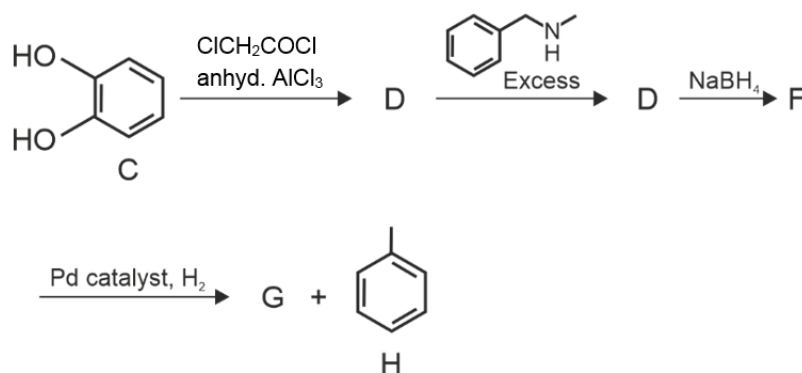
5.2 Give the IUPAC name of compound B in 5.1 (i).

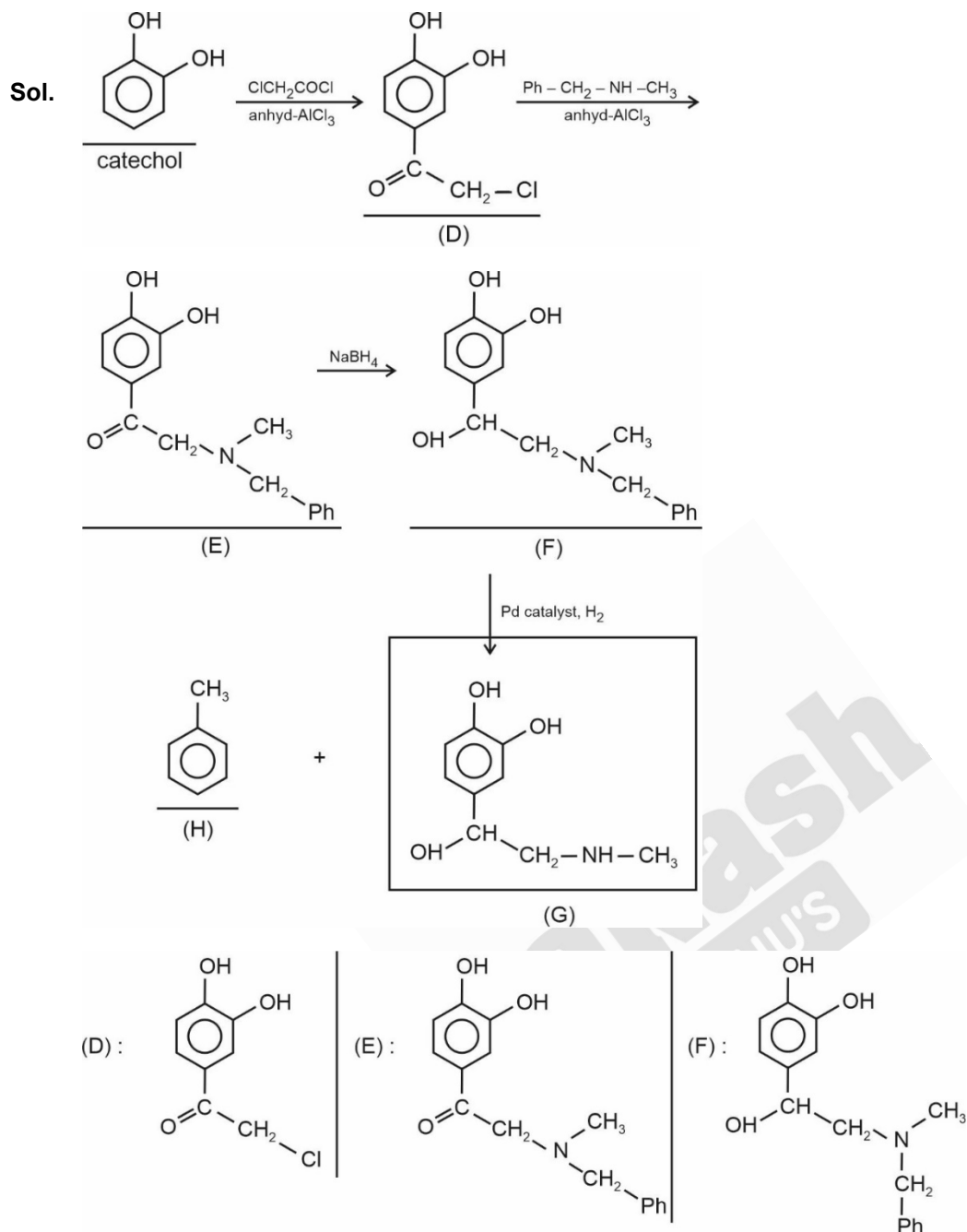
Sol. IUPAC name of Compound B in sol (i)



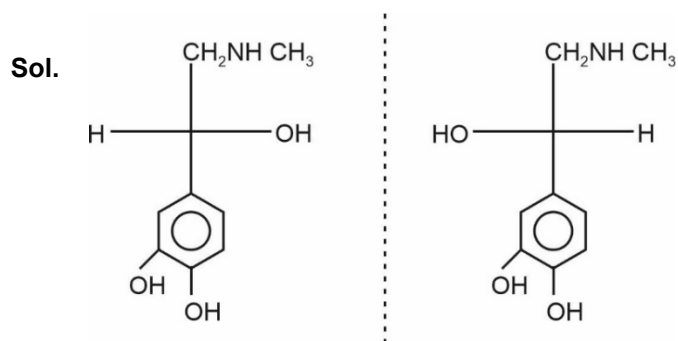
Catecholamines are a group of neurotransmitters that are either secreted by neurons or the adrenal gland. One such example is dopamine, which controls pleasure or euphoria in our brain. The amount of dopamine in the cells are regulated by way of several biosynthetic mechanisms and finally converted to homovanillic acid and excreted through urine. Other examples are epinephrine (**G**) and norepinephrine that are derived from the amino acid phenylalanine.

5.3 The following is a chemical synthesis route to epinephrine (**G**) starting from catechol. Identify the intermediates **D**, **E**, **F** and propose a structure of **G**. **G** was stable to acid/alkaline hydrolysis conditions.



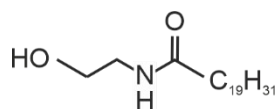


5.4 Draw the structures of the stereoisomers of **G** in Fischer projection.



Fisher projection of stereoisomers of **G** (ephedrine).

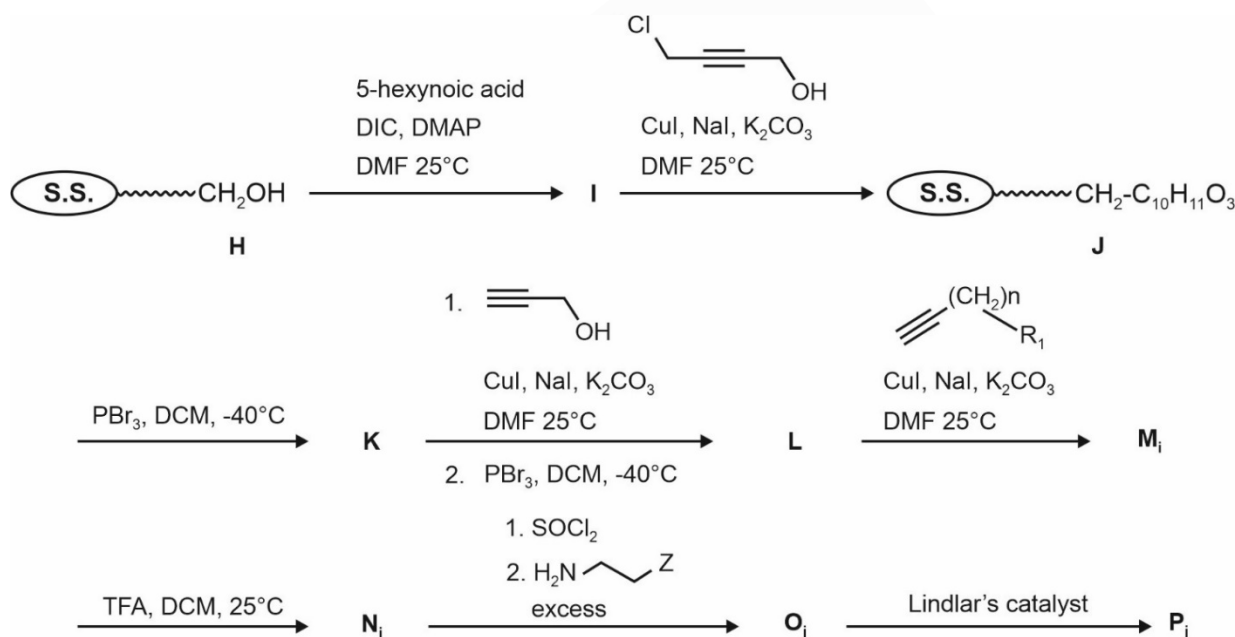
Another group of neurotransmitters are derived from lipids. Anandamide is a lipid, first isolated and identified by William A Devane in 1992. It is present in the brain cells, and binds with the receptor proteins of brain cells. It is responsible for calmness, dream states and the mood "Ananda" as in Sanskrit. Hence, the name anandamide.



Anandamide

Anandamide has short duration neurological effect and has attracted scientists to use its structural variants as therapeutic agents. A series of anandamide analogues were synthesized by solid phase synthesis technique, in which the starting material is attached to a solid support. After a sequence of reactions building larger molecules, the product can be easily separated from the reaction mixture by simple filtration. Then the support is removed by an appropriate reagent.

In a scheme of synthesis shown below, several analogues $P_1 - P_4$ of anandamide (represented as P_j) were produced. These were obtained by varying number of methylene units (n) and functional groups R_1 in reagent in the conversions $L \rightarrow M_i$ and by varying Z in the reagent in the conversions $N_i \rightarrow O_j$ in the scheme given below. Solid support is represented as **S.S.**

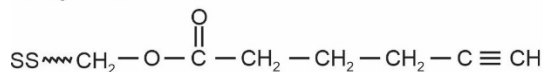


Reagent	Function	Reagent	Function
DIC (N,N'-Diisopropylcarbodiimide)	a dehydrating agent	TFA (Trifluoroacetic acid)	a strong acid
DMF (N,N'-Dimethylformamide)	a solvent	DCM (Dichloromethane)	a solvent
DMAP (4-dimethylaminopyridine)	a base	CuI + NaI	a catalyst

- 5.5** Draw the structure of **I**, **K**, **L**, **M_i**, **N_i** and **O_i** formed using reagents having $n = 5$, $R_1 = H$ and $Z = OH$ during the conversions **L** \rightarrow **M_i** and **N_i** \rightarrow **O_j**.

Sol.

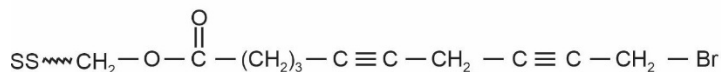
Compound I



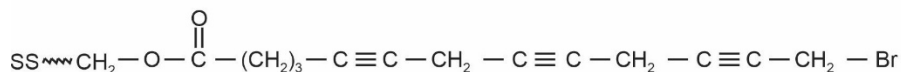
Compound J



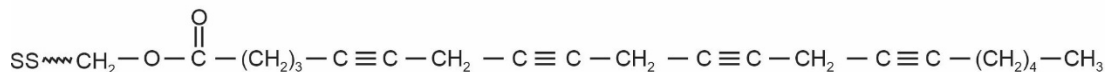
Compound K



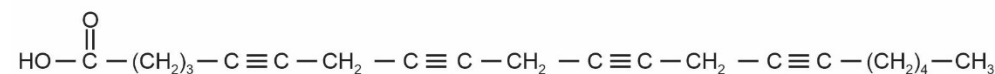
Compound L



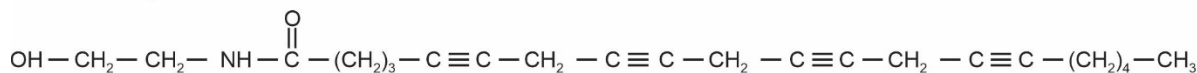
Compound M_i



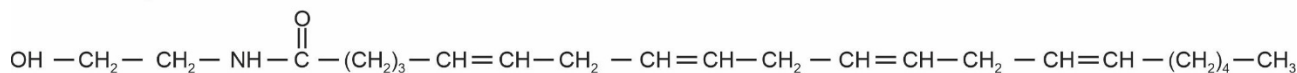
Compound N_i



Compound O_j



Compound P_j



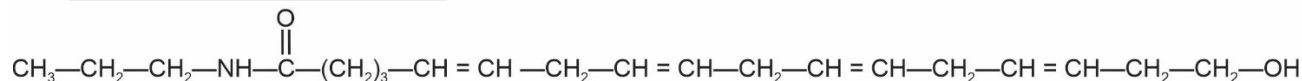
(All alkenes at cis position)

- 5.6** Draw the structures with correct stereochemistry of **P_j** obtained from sets of reagents having the given n , R_1 and Z .

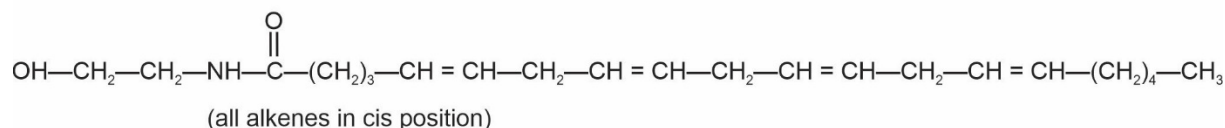
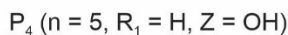
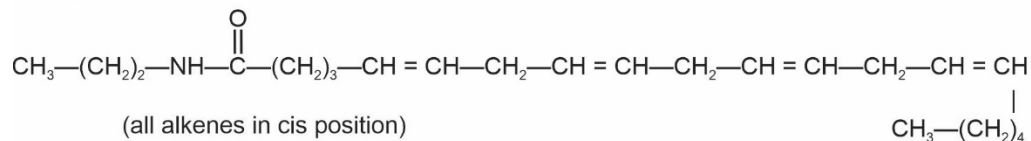
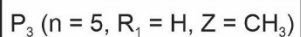
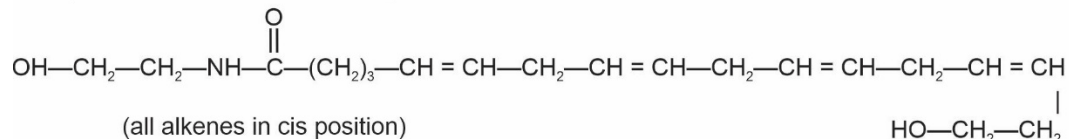
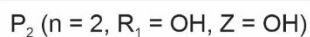
P₁ $n = 2$, $R_1 = \text{OH}$ and $Z = \text{CH}_3$	P₃ $n = 5$, $R_1 = \text{H}$ and $Z = \text{CH}_3$
P₂ $n = 2$, $R_1 = \text{OH}$ and $Z = \text{OH}$	P₄ $n = 5$, $R_1 = \text{H}$ and $Z = \text{OH}$

Sol.

P₁ ($n = 2$, $R_1 = \text{OH}$ and $Z = \text{CH}_3$)



(all alkenes in cis position)

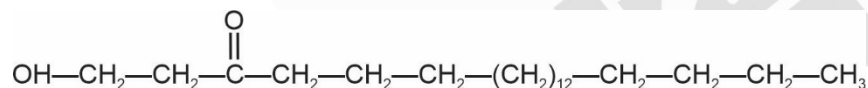


5.7 Draw the structure of **P_j** obtained from set of reagents having $n = 5$, $R_1 = H$ and $Z = OH$, when Pt in the presence of excess H_2 was used as the reducing agent for **O_i** in place of Lindlar's catalyst.

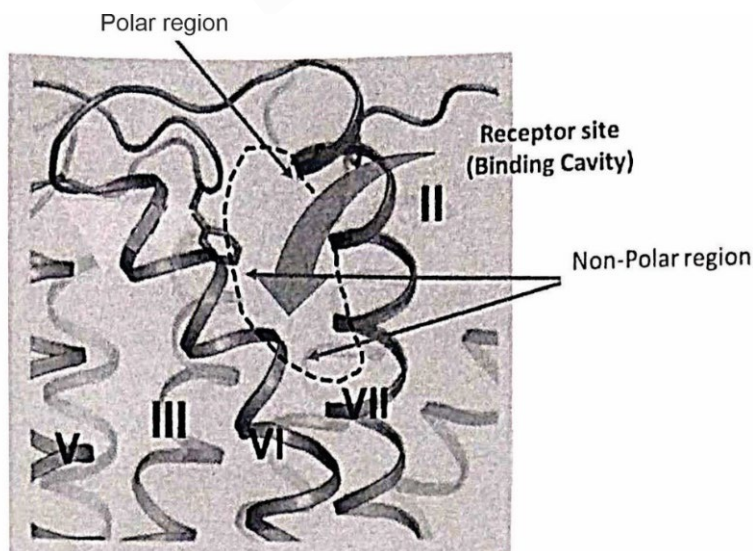
Sol. Structure of P_j when H₂/Pt is used instead of Lindlar's catalyst

∴ Triple bonds will directly get converted into single bonds instead of double bonds

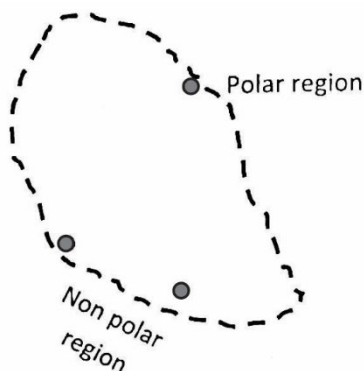
Structure of P_j



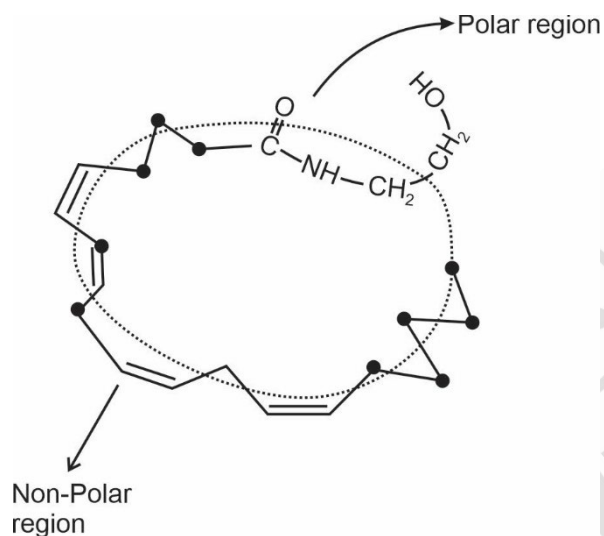
One of the receptor proteins of anandamide in neurons has a pocket-like binding site (dashed line shows its cross-section) formed by seven protein helices (indicated with roman numerals, helices I and IV are not shown in the view). The binding site has a polar region and a hydrophobic non-polar region. Unique structure of anandamide provides the correct geometry for it to bind in this pocket.



- 5.8** Draw the structure of anandamide showing the correct stereochemistry and appropriate geometry suitable for binding with the above protein receptor. Dashed line shows the boundary of the binding pocket.



Sol.



- 5.9** Among the following, molecule(s) more lipophilic than anandamide is/are (mark **X** against the appropriate option(s))

P₁ ☐

P₂ ☐

P₃ ☒

P₄ ☐

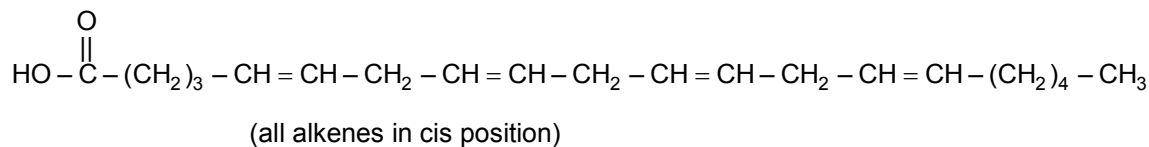
Sol. Compound P₃ is more lipophilic (More affinity towards lipids) as it is having CH₃ group instead of OH.

The protein receptors in brain cells are also the main targets of aromatic polycyclic phenols called cannabinoids – narcotic molecules present in Hashish and Marijuana. These molecules do not break down during metabolic functions of the brain cells and stay longer in the binding pocket. This causes longer mood effects, addiction to the narcotic and permanently damages the functions of brain cells.

Anandamide gets degraded fast leaving a very short duration mood effect. One of the degradation pathway of anandamide is enzymatic hydrolysis to a fatty acid Q.

- 5.10** Draw the structure of **Q**.

Sol. Fatty acid **Q** (Structure)



Fatty acid **Q** is a precursor in the biosynthesis of molecules critical to metabolism. Also, **Q** is a biosynthetic product of linoleic acid. In mammals, **Q** becomes an essential fatty acid if there are problems in its biosynthesis.

5.11. Among the following, the false statement/s is/are (mark **X** against the appropriate option(s))

- (i) Saturated fatty acids are essential to maintain a good level of **Q**.
- (ii) Linoleic acid is an essential fatty acid.
- (iii) Dietary supplementation of **Q** is good for health and for good mood.
- (iv) Cannabinols are good replacements of fatty acids for good health.

Sol. False statement are (i) and (iv).

Cannabinols are good replacements of fatty acids for good health.

Saturated fatty acids are essential to maintain a good level of **Q**.

