

Indian National Chemistry Olympiad 2018
Theory (3 hours)

Roll No. --

I **permit/do not permit** (*strike out one*) HBCSE to make my INO academic performance and personal details public unless I communicate my consent in writing

I have read the Procedural Rules of the INOs and agree to abide by them.

Name of student: _____

Signature: _____ Exam Centre: _____ Date: January 27, 2018

Do not write anything below this line

Question No	1	2	3	4	5	Total
Marks	20	25	21	19	22	107
Marks Obtained						
Signature of Examiner						

Instructions for students

- Write your Name and Roll No. at the top of the first pages of all problems.
- This examination paper consists of **30** pages of problems including answer boxes.
- **Kindly check that the booklet has all the pages. If not, report to the invigilator immediately.**
- Adequate space has been provided in the answersheet for you to write/calculate your answers. In case you need extra space to write, you may request for additional blank sheets from the invigilator. Remember to write your roll number on the extra sheets and get them attached to your answersheet.
- **Use only a pen to write the answers in the answer boxes. Answers written in pencil will be penalized.**
- All answers must be written in the appropriate boxes. Anything written elsewhere will not be considered for assessment.
- You **must** show the main steps in the calculations.
- For objective type question, mark **X** in the correct box. Some of the objective questions may have more than one correct answer.
- A copy of the Periodic Table of the Elements is provided at the back of this page.
- Do not leave the examination room until you are directed to do so.

Fundamental Constants

Avogadro number	$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$	Mass of electron	$m_e = 9.109 \times 10^{-31} \text{ kg}$
Electronic charge	$e = 1.602 \times 10^{-19} \text{ C}$	Speed of light	$c = 2.998 \times 10^8 \text{ ms}^{-1}$
Molar gas constant	$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$	1 atomic mass unit	$(1u) = 1.660 \times 10^{-27} \text{ kg}$
Density of mercury	$= 13.6 \times 10^3 \text{ kg m}^{-3}$	Faraday constant	$F = 96485 \text{ C mol}^{-1}$

Periodic Table of the Elements

1 IA 11A H Hydrogen 1.008																	2 IIA 2A He Helium 4.003
3 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.305	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 VIII 8	9 VIII 8	10 VIII 8	11 IB 1B	12 IIB 2B	13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.88	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.933	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.732	32 Ge Germanium 72.61	33 As Arsenic 74.922	34 Se Selenium 78.09	35 Br Bromine 79.904	36 Kr Krypton 84.80
37 Rb Rubidium 84.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.94	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.71	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.29
55 Cs Cesium 132.905	56 Ba Barium 137.327	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.85	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.967	80 Hg Mercury 200.59	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium unknown	114 Fl Flerovium [289]	115 Uup Ununpentium unknown	116 Lv Livermorium [298]	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown

Lanthanide Series	57 La Lanthanum 138.906	58 Ce Cerium 140.115	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.24	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.966	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.50	67 Ho Holmium 164.930	68 Er Erbium 167.26	69 Tm Thulium 168.934	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967
Actinide Series	89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]

Problem 1

20 Marks

Lead Acid Batteries

Part A: Electrochemical processes in a lead acid cell

Conventional lead acid batteries used in cars and invertors are the most common rechargeable batteries in the market. A rechargeable lead acid cell consists of a positive electrode of $\text{Pb}_{(s)}/\text{PbO}_{2(s)}$, and a negative electrode of $\text{Pb}_{(s)}$, both immersed in aqueous H_2SO_4 electrolyte.

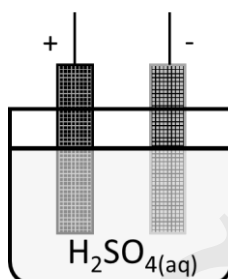


Figure 1: Schematic of a conventional lead acid cell

Standard electrode potentials for some half-cell reactions at 298 K are given below.

Half-Cell Reaction	E° (V)
$\text{PbO}_{2(s)} + \text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{PbSO}_{4(s)} + 2\text{H}_2\text{O}(\text{l})$	+1.69
$\text{PbO}_{2(s)} + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{Pb}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$	+1.46
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pb}_{(s)}$	-0.13
$\text{PbSO}_{4(s)} + 2\text{e}^- \rightarrow \text{Pb}_{(s)} + \text{SO}_4^{2-}(\text{aq})$	-0.36

- 1.1 Write the half-cell reactions that take place at cathode and at anode in above cell during discharge at 298 K. Write the overall discharge reaction and calculate the E° of this cell.

Reaction at Cathode: Reaction at Anode: Overall discharge reaction
--

Molar Enthalpies of formation (H_f°) at 298 K of some species are given below.

Species	H_f° (kJ mol ⁻¹)
$\text{PbO}_{2(s)}$	-277.4
$\text{H}_2\text{O}(\text{l})$	-285.8
$\text{Pb}^{2+}(\text{aq})$	1.6
$\text{SO}_4^{2-}(\text{aq})$	-909.3
$\text{PbSO}_{4(s)}$	-920.0

- 1.2** Calculate the standard enthalpy change (ΔH_{rxn}°) and standard Gibbs energy change (ΔG_{rxn}°) for the overall discharge reaction of the cell in **1.1**.

In a galvanic cell, the chemical energy released during the discharge reaction drives the electrical work. The Gibbs energy change of the discharge reaction represents the maximum electrical work $w_{\max(\text{el})}$ that can be extracted from the cell during discharge.

$$w_{\max(\text{el})} = -\Delta G_{rxn}^\circ$$

Maximum work is obtained when the cell is operated reversibly, i.e., at a very low current. Assume that the cell is designed to exchange heat with the surrounding to prevent overheating or overcooling.

- 1.3** For reversible operation of the cell at 298 K and all species in the cell in their standard states,
- a) determine the amount of heat absorbed by the cell from the surrounding per mole of reaction as per the cell equation in **1.1**.

- b) what fraction of $w_{\max(\text{el})}$ is obtained from the heat exchanged reversibly with the surroundings?

The concentration c of a species in a solution is related to its activity a as $a = \gamma \times c$, where γ is the activity coefficient. For highly concentrated solutions, the reaction quotient Q must be expressed in terms of activities of the species (i.e., $\gamma \neq 1$).

In commercial lead-acid batteries, highly concentrated H_2SO_4 (aq.) is used. Conventionally, the liquid and solid components in a chemical reaction are assumed to be in their 'standard states'

with activity as 1. However, due to the high concentration of sulfuric acid in the electrolyte, the activity of water also cannot be taken as 1.

- 1.4** For the discharge reaction of cell in **1.1**, write the expression for the cell EMF in terms of activities of the species involved in the reaction. Consider H_2SO_4 (aq.) to be completely dissociated and assume that only solids are in their standard states.

The lead-acid cell is considered to be discharged when the current that can be drawn from it decreases below a certain value. Discharge is also accompanied by a decrease in H_2SO_4 concentration.

Activities of water and products of activities of relevant sulphuric acid species at 298 K in a lead acid cell are listed below at two concentrations of sulphuric acid.

No.	H_2SO_4 Molality (m)	$a_{\text{H}_2\text{O}}$	$(a_{\text{H}^+})^2 \cdot (a_{\text{SO}_4^{2-}})$
1	1.00	0.9618	0.0018
2	5.00	0.7032	0.8847

- 1.5** Assuming the discharged and charged states correspond to 1.00 molal and 5.00 molal H_2SO_4 , respectively, find the drop in the cell EMF values when it is discharged at 298 K.

Following are certain facts about the cell in Fig. 1.

- (i) PbSO_4 (s) predominantly deposits on the electrodes and not in other parts of the cell.
- (ii) PbSO_4 (s) deposits on both the electrodes.
- (iii) Resistivity of PbSO_4 (s) deposits ($3 \times 10^9 \Omega \text{ cm}$) is much higher than that of PbO_2 (s) ($2 \times 10^{-4} \Omega \text{ cm}$).
- (iv) Resistivity of PbO_2 (s) ($2 \times 10^{-4} \Omega \text{ cm}$) is close to that of Pb (s) ($0.2 \times 10^{-4} \Omega \text{ cm}$).

1.6 Which of the above facts makes the cell rechargeable? (Write Statement number(s)

i - iv, as applicable)

Electrolysis of water may become a competing process during charging of the cell in Fig. 1. The relevant half-cell reactions are given below.

Half-Cell Reaction	E° (V)
$\text{O}_{2(\text{g})} + 4 \text{H}^{+}_{(\text{aq})} + 4 \text{e}^{-} \rightarrow 2 \text{H}_2\text{O}_{(\text{l})}$	+1.23
$2 \text{H}^{+}_{(\text{aq})} + 2 \text{e}^{-} \rightarrow \text{H}_{2(\text{g})}$	0.00

1.7 For the operation of the cell in Fig.1 at 298 K, indicate whether the given statement is correct or incorrect. (Mark X in the appropriate box)

- | | Correct | Incorrect |
|--|--------------------------|--------------------------|
| a. During charging of this cell, positive terminal of the DC power source is connected to the electrode that gets reduced, and negative terminal to the electrode that gets oxidised. | <input type="checkbox"/> | <input type="checkbox"/> |
| b. The EMF of the cell depends upon the amounts of the Pb species in the cell. | <input type="checkbox"/> | <input type="checkbox"/> |
| c. After a long-time of the lead-acid cell overcharging, the evolution of oxygen on one terminal and that of hydrogen on the other terminal may result in the formation of an explosive mixture of gases. | <input type="checkbox"/> | <input type="checkbox"/> |
| d. Upon completion of the charging process, oxygen starts to form on the negative electrodes. | <input type="checkbox"/> | <input type="checkbox"/> |
| e. The total energy stored in the cell is limited by the moles of $\text{Pb}_{(\text{s})}$ in the negative electrode or the moles of Pb^{4+} in the positive electrode, whichever amount is less. | <input type="checkbox"/> | <input type="checkbox"/> |

A different type of lead-based galvanic cell is given below. This cell has methane-sulphonic acid in which Pb^{2+} has high solubility. The electrolyte consists of Pb^{2+} ions dissolved in aqueous $\text{CH}_3\text{SO}_3\text{H}$ in a cell having two inert electrodes. When external power supply is connected to this cell, Pb^{2+} ions are reduced at one electrode and oxidized at the other electrode, with the products depositing on the respective electrodes.

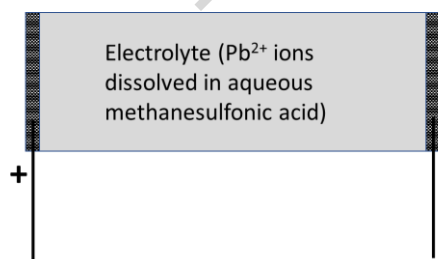


Figure 2: Simplified schematic of a lead acid cell based on methanesulphonic acid

- 1.8 Write the half-cell reactions that take place at cathode and at anode in the cell in Fig. 2 during discharge at 298 K. Write the overall discharge reaction and calculate the E° of this cell.

Cathodic:
Anodic:
Overall Discharge reaction:

- 1.9 For the cell in Fig. 2, indicate whether the given statements are true or false (Mark **X** in the appropriate box).
- | | True | False |
|---|--------------------------|--------------------------|
| a. Assuming that the volume of the electrolyte in this cell is kept constant, the pH of the electrolyte decreases during discharge of the cell. | <input type="checkbox"/> | <input type="checkbox"/> |
| b. The EMF of the cell increases with increasing Pb^{2+} ion concentration in the cell electrolyte. | <input type="checkbox"/> | <input type="checkbox"/> |
| c. The energy stored in the cell depends on the total amount of the Pb species in the cell. | <input type="checkbox"/> | <input type="checkbox"/> |

Part B: Re-using spent batteries from cars and inverters

Recently a team of scientists showed that electrolyte for the lead acid cell in Figure 2 can be obtained by recycling the electrodes of a car battery. For this, the positive and negative plates of the spent battery (Fig.1) are thoroughly washed, separately dried and crushed into powders. Addition of excess aqueous methanesulfonic acid to these powders yields the electrolyte for the new lead acid cell (Fig.2).

- 1.10 Write balanced equations for the reactions involved in this conversion.

Some small-scale recyclers recover metallic $Pb_{(s)}$ from the electrodes of spent car batteries and throw away the $PbSO_4(s)$ slurry from the cell. It has been shown that a compound **X** useful for fabricating Pb-based thin film solar cells can be obtained from the slurry without high energy inputs. For this synthesis, the $PbSO_4(s)$ slurry is stirred overnight with a near-saturated solution of salt **A**. This yields a white precipitate **B**, which is collected by filtration.

- 1.11** Upon heating in a test tube, **A** decomposes into three colourless gases: an acidic gas, a basic gas and a neutral gas. Inserting a burning stick inside the test tube extinguished it, while a rod dipped in HCl brought close to the mouth of test tube generates white fumes. Identify **A** and hence **B**.

Next, a weak monoprotic acid **C** is used to dissolve **B**. 150 mg sample of **C** is completely neutralised by 25 mL of 0.1 M NaOH solution.

- 1.12** Calculate the molar mass of **C**. Identify **C**.

- 1.13** When excess of a halide salt that is used for treatment of hyper-thyroidism is added to the solution above, the yellow salt **X** precipitates out. Identify **X**.

Problem 2

25 marks

When Rain meets the Soil

Part I: The fragrance of soil

When rain falls on soil after a dry period, a sweet earthy smell is produced known as the fragrance of first rain, which can be detected by camels even at a distance of 50 km. This scent has been captured in an increasingly famous scent “*mitti ka itir*” produced in Kannauj, India. This smell is due to the compounds geosmin (**A**) and methyl-isoborneol (**B**) produced by the actinobacteria present in soils.

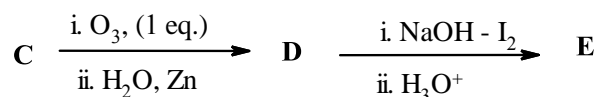
On combustion, 0.455 g of ‘A’ yields 1.318 g of CO₂.

2.1 Calculate the percentage of carbon in ‘A’. Show the calculations involved.

‘A’ undergoes **dehydration** easily under acidic condition to form an odourless **hydrocarbon** Argosmin ‘C’. 0.455g of A reacts with sodium to liberate hydrogen gas which occupies 28.01 cm³ at STP.

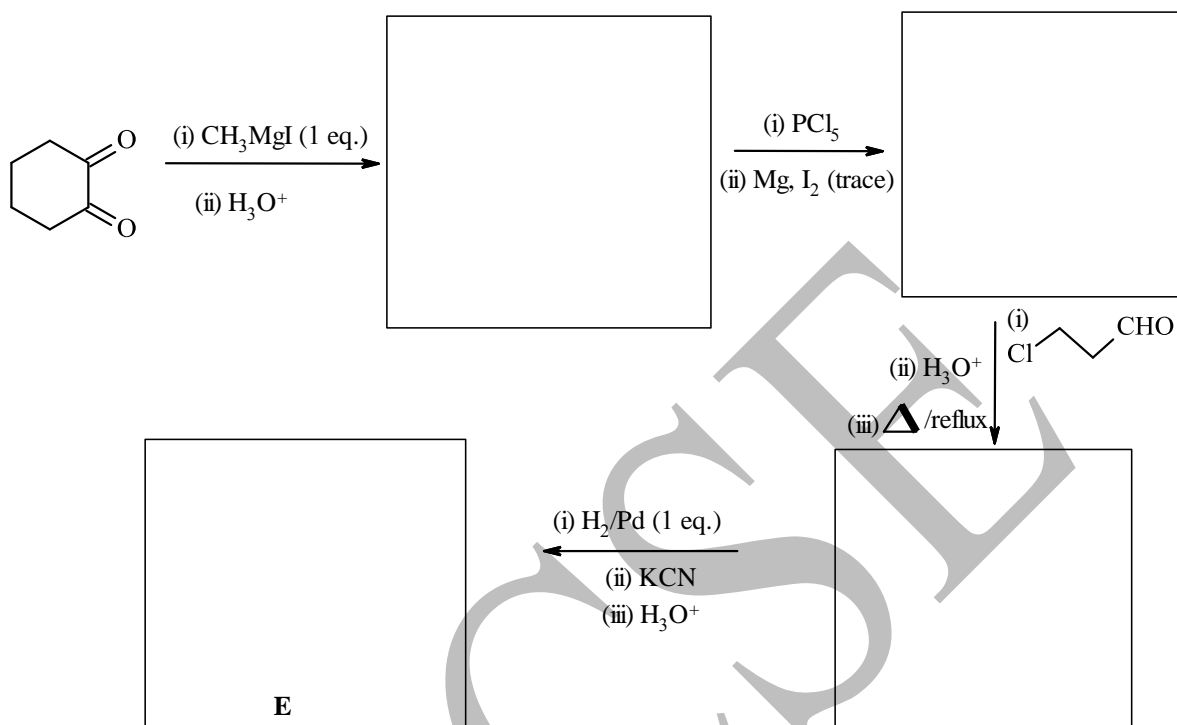
2.2 Calculate the empirical formula of A. Show the calculations involved.

C undergoes ozonolysis giving a single compound D which is further converted to E as follows.

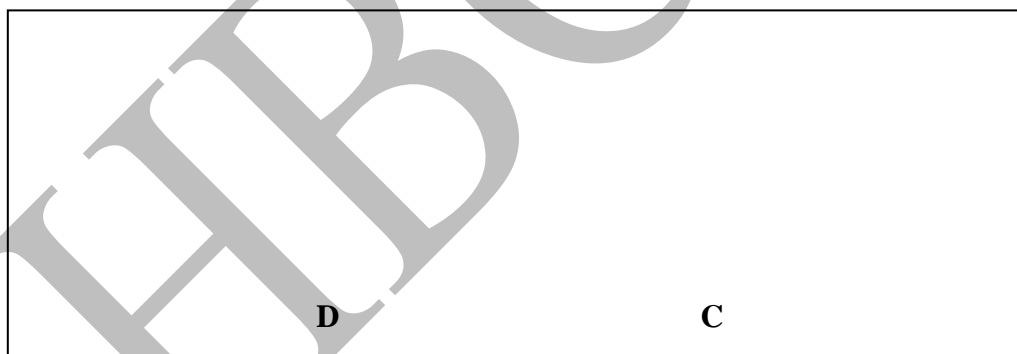


E can be synthesized by another route using cyclohexane-1,2-dione as shown below.

2.3 Draw the structures of the intermediate compounds and hence of **E** in the boxes provided.



2.4 Draw the structures of **D** and **C**.



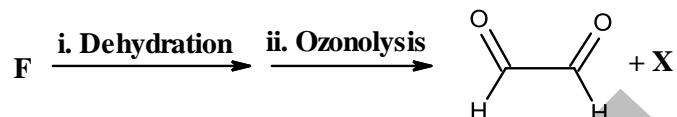
2.5 **A** has three chiral centres. Draw all possible structural isomers of **A** consistent with the above information. (no stereo isomers are required)



The Cactaceae (cactus) family of plants grows in extremely hot and dry conditions and contain the compound dehydrogeosmin 'F', which has ten times more odour than geosmin. It is believed to play a significant role in pollination in these plants.

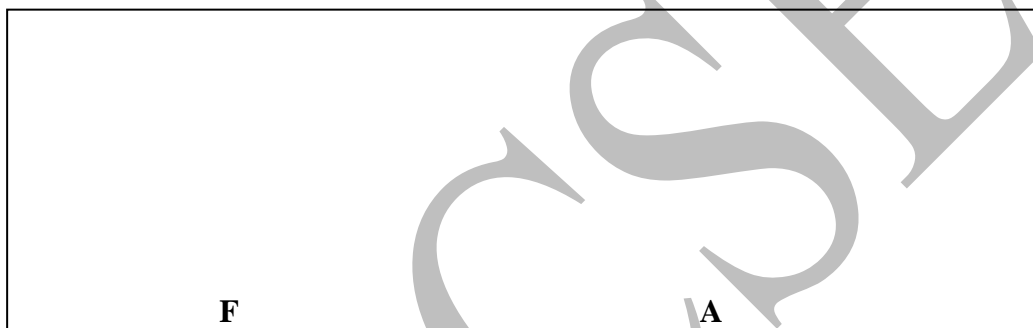
F is converted to A by addition of one mole of H_2 . The ozonolysis product of F gives a red precipitate with Fehling's solution but does not give yellow precipitate with $NaOH - I_2$.

The dehydration product of F, when subjected to ozonolysis gives the following products:



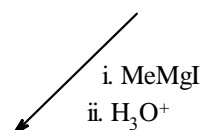
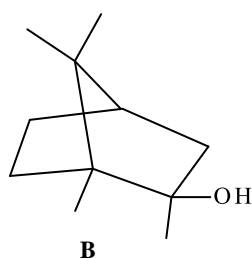
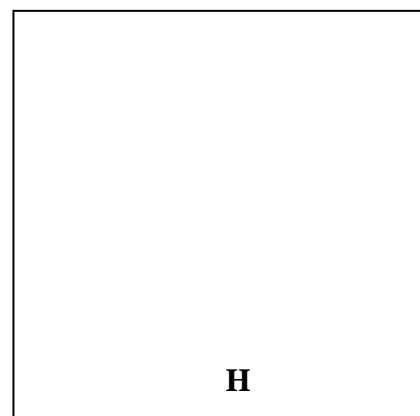
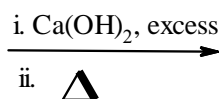
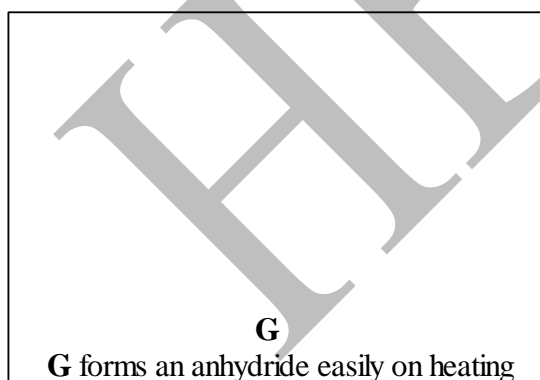
X also does not give yellow precipitate with $NaOH - I_2$.

2.6 Draw the structure of F and hence A.



The compound 'B' can be synthesized by the following route.

2.7 Draw structures for G and H in the boxes provided.

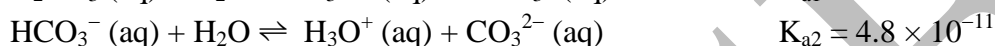
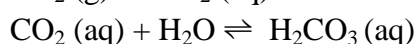
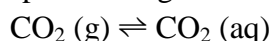


Part II: If the rain is acidic,...

As the water in clouds and rain drops equilibrates with atmosphere, it dissolves gases from the atmosphere. Usually, rain is slightly acidic because of dissolved CO_2 leading to a pH sometime as low as 5.6. The acidity of rain water in industrial areas is higher with pH as low as 3.5 to even 2 in some regions.

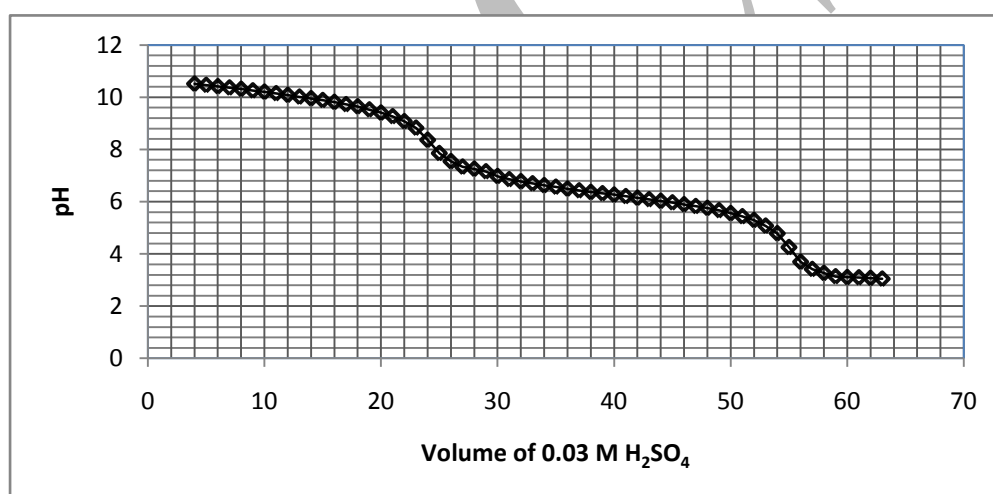
Natural water bodies often have carbonates of Na^+ , K^+ , Ca^{2+} , and Mg^{2+} , dissolved from carbonate rocks, whose buffering action neutralizes acid in the rain. This buffering mechanism is important for sustaining aquatic life.

The carbonate buffer system is composed of various species and the equilibria between these species are governed by the following reactions.



The ability of a buffer to resist change in pH depends on the total concentration of the buffering species as well as their concentration ratio. Buffer capacity of a given solution is defined as the number of moles of a strong acid or a strong base that changes the pH of 1 L of the buffer by 1 unit.

A laboratory experiment was designed to simulate the buffering action of carbonate solutions, in which 300 mL of 0.004 M Na_2CO_3 solution was titrated against sulphuric acid and the following graph was obtained.



2.8 Based on the graph, answer the following questions:

- a. For what pH range(s), we **cannot** obtain buffers based on carbonate species?

- b. What volume of 0.03 M H_2SO_4 would change the pH of 1 L 0.004 M Na_2CO_3 by 1 unit.

- c. Buffer capacity of a Na_2CO_3 solution would
- i) Increase with the concentration of $\text{Na}_2\text{CO}_3(\text{aq})$
 - ii) Remain unaffected by the concentration of $\text{Na}_2\text{CO}_3(\text{aq})$
 - iii) Decrease with the concentration of $\text{Na}_2\text{CO}_3(\text{aq})$

Next, let us do some simple calculations to understand the buffering action of a CaCO_3 solution. A saturated solution of CaCO_3 (solubility = 1.1×10^{-4} M) was prepared in distilled water. Assume that the distilled water was free of any dissolved gases and any other cations.

- 2.9** Calculate the pH of the saturated CaCO_3 solution. (Hint: amount of $\text{H}_2\text{CO}_3(\text{aq})$ formed under these conditions would be negligible.)

HBCSE

- 2.10** Determine what volume of 0.03 M H_2SO_4 would be required to lower the pH of 300 mL of saturated CaCO_3 solution by 1 unit. Assume that the volume change of the CaCO_3 solution due to acid addition is small.

--

2.11 If the saturated solution of CaCO_3 is in contact with excess solid CaCO_3 , the buffer capacity of this system would be (Mark **X** in the appropriate box)

- a. same as that of the saturated solution.
b. more than that of the saturated solution.
c. lower than that of the saturated solution.

2.12 Comparing the saturated solutions of MgCO_3 ($K_{sp} = 6.8 \times 10^{-6}$) and CaCO_3 ($K_{sp} = 2.8 \times 10^{-9}$), the correct statements is (Mark **X** in the appropriate box)

- a. Buffer capacities of both the solutions are equal
b. Buffer capacity of MgCO_3 solution will be more than that of CaCO_3
c. Buffer capacity of CaCO_3 solution will be more than that of MgCO_3

2.13 Among Na_2CO_3 , MgCO_3 , and CaCO_3 , identify the salts that fit the following descriptions and write the formula in the boxes provided.

(i) For equal volumes of saturated solutions of the three salts taken separately, solution of this salt will provide the best buffering action against acid.

(ii) After heavy rains, this salt is found only in dissolved forms in water bodies, no deposits are found in soils.

(iii) In regions receiving very high rainfall annually, deposits of this salt remain for centuries, and provide a major source of carbonate buffering against acidic rain for the longest period of time.

Acidic rain in regions lacking sufficient buffering substances lead to acidification of the water bodies, which is often detected by the loss of the sweet smell of geosmin from the region.

Problem 3

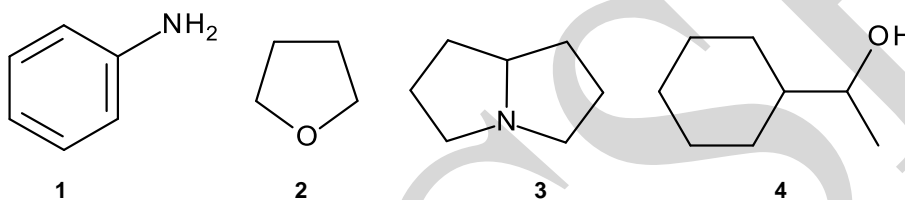
21 Marks

Hydrogen Bonding and Water of Crystallization

Part 1

Water is the most abundant molecule on the earth's surface. Water makes a major fraction of the mass of the biological as well as many non-biological entities. Water is liquid at room temperature because of extensive intermolecular hydrogen-bonding. A molecule containing H covalently bonded to an electronegative atom is known as a hydrogen bond donor, whereas a molecule with electron-rich atom which makes H-bond with an H atom is known as a hydrogen bond acceptor.

3.1 Identify the molecules in the figure below which would act as H-bond donors, H-bond acceptors or both (write the corresponding number/s in the box/es)



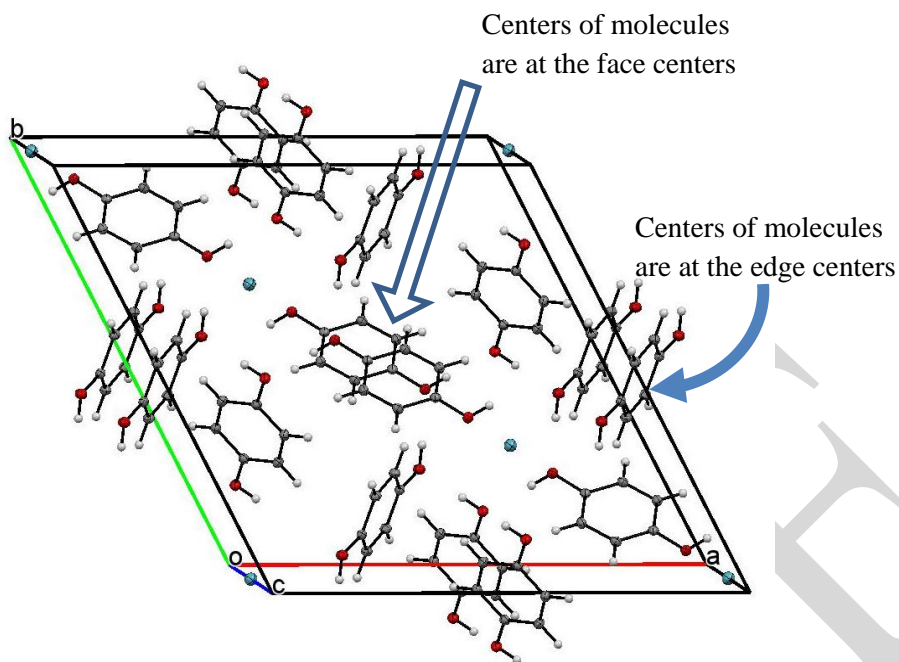
- (a) Only hydrogen bond acceptors
 (b) Only hydrogen bond donors
 (c) Both, as hydrogen bond donors and acceptors

Hydrogen bond is represented by a dotted line (----) while a covalent bond is represented by a solid line. For some compounds, intermolecular H-bonding leads to formation of porous frameworks with specific pore sizes. Such frameworks can be used to selectively trap small molecules like NH_3 , CH_4 , SO_2 , etc. in an atmosphere.

Xenon is a modern anaesthetic that has been successfully used in surgeries, which shows its ability to interact with other molecules. One challenge with this use is high cost of production, and ease of storage and transport. Interestingly, Xe can be reversibly trapped in porous three-dimensional frameworks of molecules such as water, quinol, etc, held together by H-bonds.

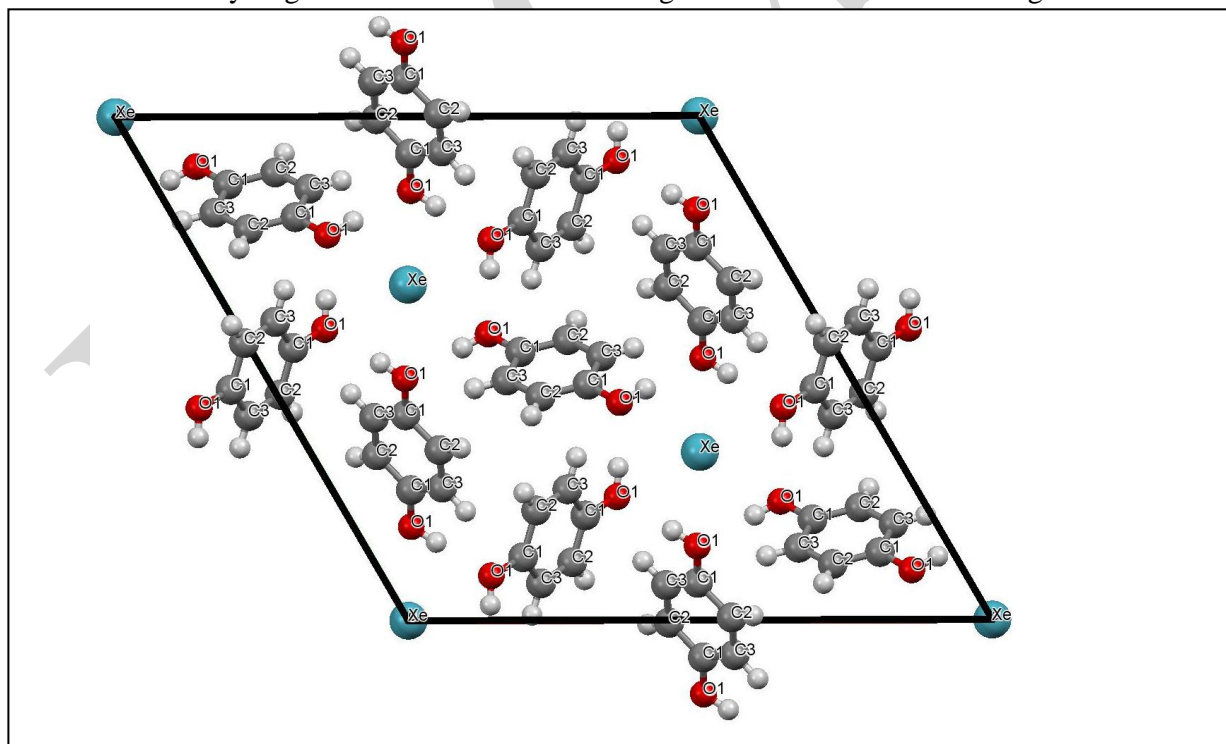
Slow evaporation of an aqueous solution of *p*-quinol saturated with Xe yields crystal of *p*-quinol framework. X-ray crystallography of these crystals indicates six *p*-quinols organized around one Xe atom. The phenyl rings in *p*-quinols are in cyclic arrangement positioned alternately above and below a plane. This arrangement generates hexagonal cavities in the structure.

The unit cell for Xe-encapsulated *p*-quinol crystal is shown below. Two molecules of *p*-quinol are centered at two opposite face centers, 8 molecules are centered at the edge centers, while the rest are inside the cell body.



A view of the above unit cell as seen along the c-axis is given in the box below, with C, O, and Xe atoms labelled (H atoms are not labelled in the structure).

3.2 Show the hydrogen bonds that define the hexagonal cavities in the structure given below.



- 3.3 By referring to the unit cell diagrams given above, calculate the number of *p*-quinol molecules and the number of Xe atoms present per unit cell. Show the steps involved in arriving at the answer.

The cell parameters for the above unit cell are: $a = 16.58 \text{ \AA}$, $b = 16.58 \text{ \AA}$, $c = 5.42 \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$.

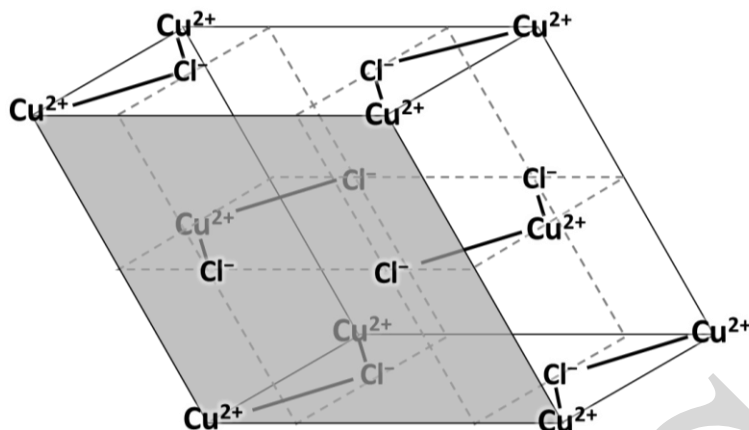
- 3.4 Determine the density of this crystal (in kg m^{-3}), assuming all the hexagonal cavities in the crystal are occupied by Xe atoms.

- 3.5 If all the hexagonal cavities in the crystal are occupied by Xe atoms, calculate the volume that Xe trapped in 1 cm^3 of *p*-quinol framework would occupy when released at 298 K and 1 atm.

Part B: Water of crystallization

Water of crystallization is the amount of water necessary for certain salts to crystallize from their solutions. Studies have shown that water of crystallization forms bonds with the ions of the salt and stabilizes the crystal structure. This water also affects the shapes and colour of their crystals.

Blue-green crystals of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ on heating lose water giving brown coloured anhydrous salt. The unit cell of anhydrous CuCl_2 is shown below where each copper is in square planar coordination and all Cu-Cl distances are equal.



3.6 This ionic arrangement is stabilized because (Mark **X** in the correct box(es)):

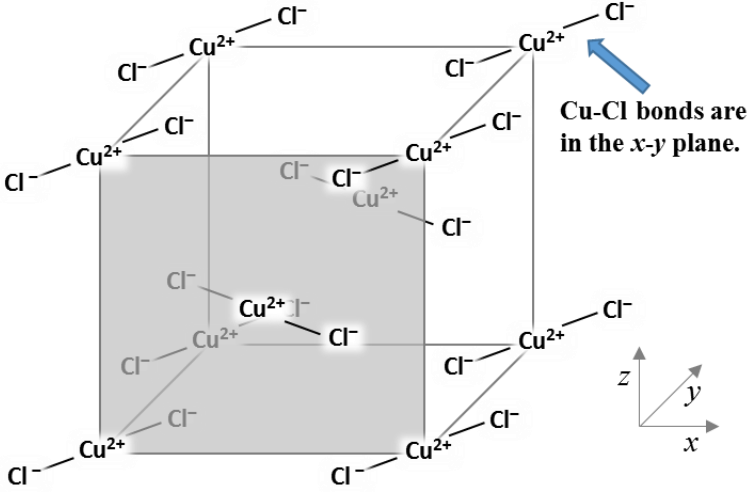
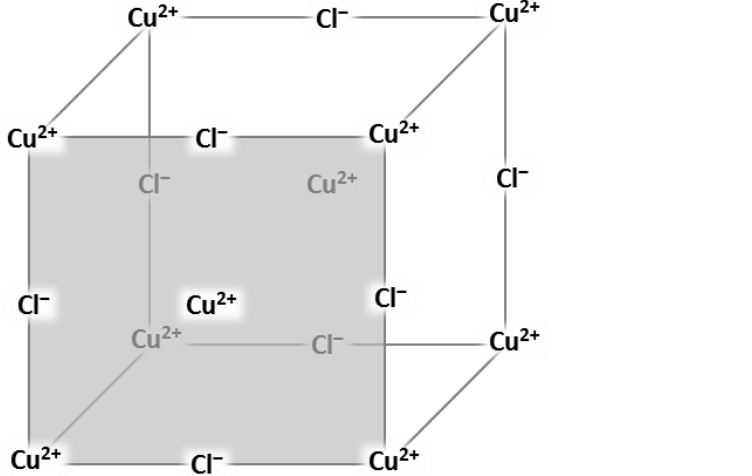
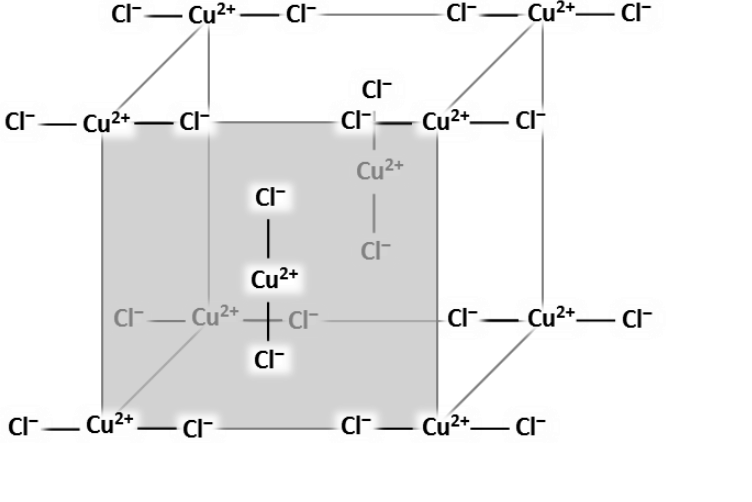
- (i) Every Cu^{2+} is stabilized by two Cl^- present perpendicular to the CuCl_4 plane.
- (ii) Every Cl^- is stabilized by two Cu^{2+} present perpendicular to the CuCl_4 plane.
- (iii) This structure has FCC arrangement of the Cu^{2+} ions.
- (iv) Layers of Cl^- ions are next to each other and are sandwiched between the layers of Cu^{2+} ions.

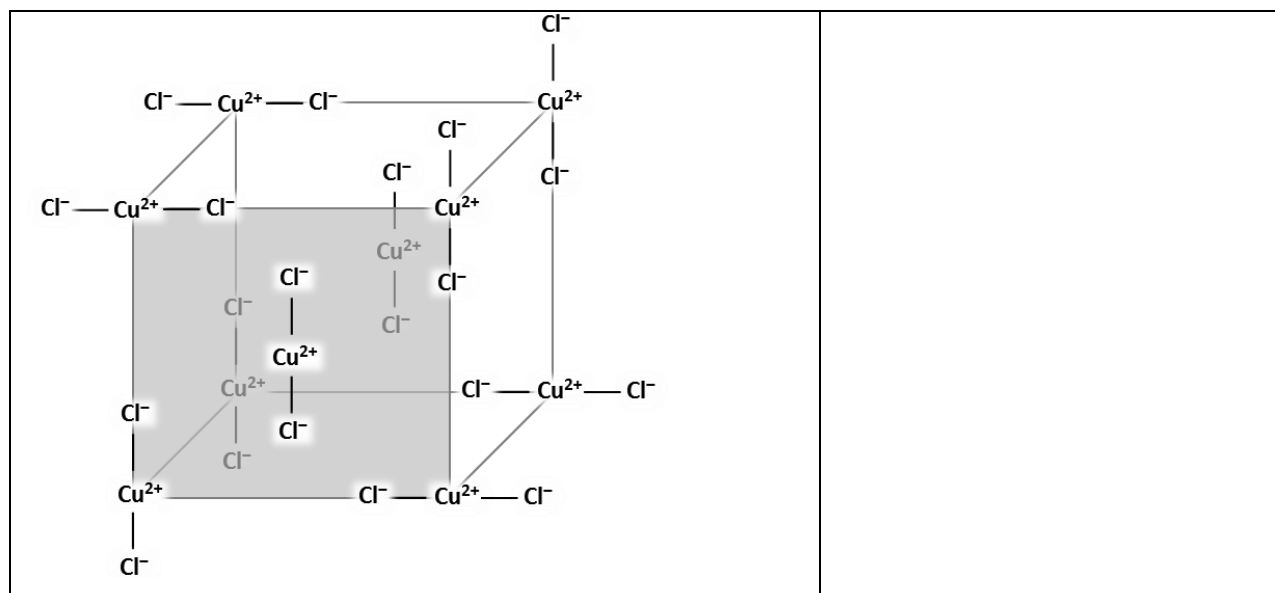
When CuCl_2 is exposed to moisture, water enters the space between the ions forming **$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$** . The water molecules induce many changes such as shift of Cu-Cl units with respect to each other and changes in Cu-Cl distances. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ crystallizes in an end-centered orthorhombic lattice stabilized by hydrogen bonds. The Cu^{2+} ions occupy all the vertices and centres of two opposite faces.

The following table shows four possible framework positions of Cl^- ions with respect to Cu^{2+} ions. Out of the four frameworks given, three are not observed because of one or more of the following reasons:

- I.** The structure would have high inter-ionic repulsions, which cannot be effectively minimized by the two molecules of water per Cu^{2+} ion.
- II.** The cell shown is not a unit cell because it cannot be repeated to generate a lattice.
- III.** The ratio of $\text{Cu}^{2+}:\text{Cl}^-$ ions is not 1:2 per unit cell.

3.7 Identify the impossible frameworks by writing the correct reasoning statement (give number **I**, **II** or **III**) against the structure. In the correct framework, show water molecules with appropriate bonds with the ions present.

Framework	Reason/s for impossible framework wherever applicable
	
	
	



Materials which can store and release thermal energy by absorbing water molecules are promising heat storage systems. Salts like $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ can be dehydrated by keeping in the sunlight, which is an endothermic process. The anhydrous salts then can be used to heat a room by exposure to water vapours. These salt-based devices can be dehydrated and hydrated again and again.

In search of a thermal energy storage material, a student checked the amount of energy released by anhydrous CuCl_2 on exposure to water. The student added 2.5 g anhydrous CuCl_2 to 50 mL water (initially at 25°C) in a covered polystyrene cup and noted 3.2°C rise in temperature.

- 3.8** Assuming that the polystyrene cup is a closed and thermally insulated system and the specific heat of water (with dissolved salts) is $4.18 \text{ J } ^\circ\text{C}^{-1}\text{g}^{-1}$, calculate the amount of heat released (enthalpy of hydration) by anhydrous CuCl_2 in kJ mol^{-1} .

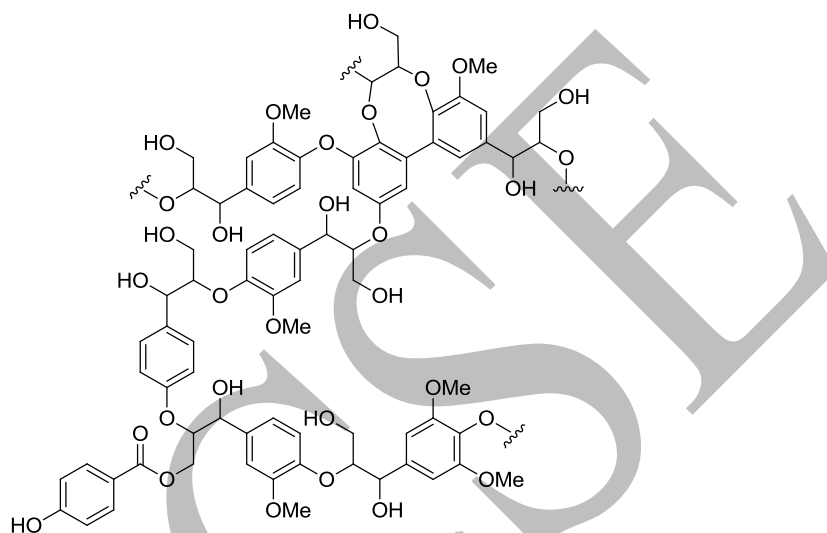
- 3.9** To heat a given room in winter for one night, 6,000 kJ of energy is used. Determine the amount of anhydrous CuCl_2 (in kg) required to be stored in the rechargeable device to achieve this amount of heating.

Problem 4

19 Marks

Lignin

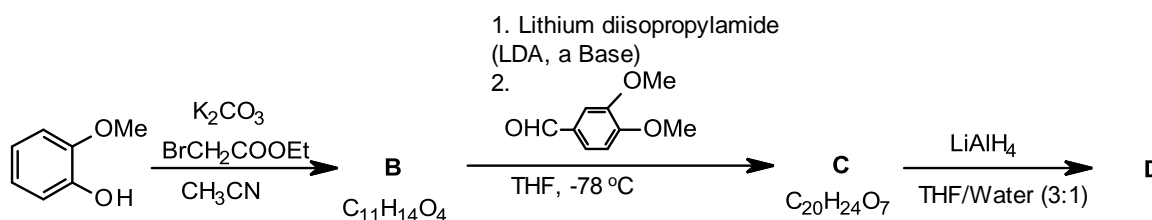
Lignin is a biopolymer that constitutes 15 - 40% of the dry weight of plants. Its major function is to provide structural support to the plant. Lignin has the potential of yielding several industrially important chemicals, a concept known as Bio refinery (similar to petroleum refinery). A major challenge in this conversion is the depolymerization of lignin. A representative structure of lignin is:



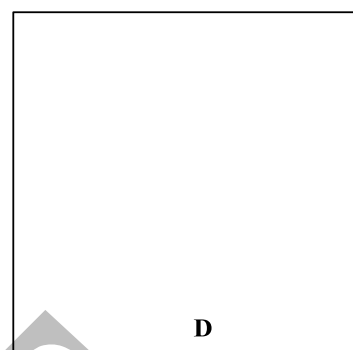
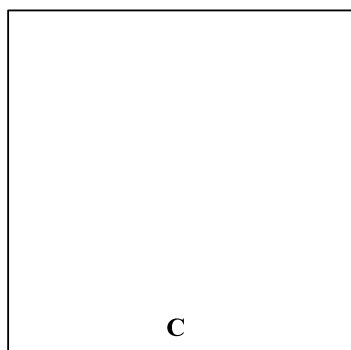
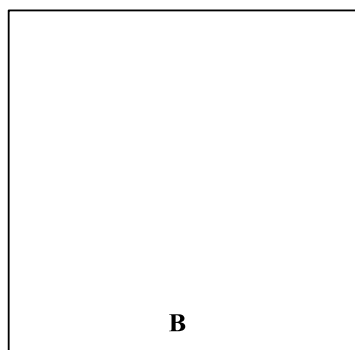
4.1 In the above structure of lignin, identify the functional groups present. (Mark **X** against the correct option/s)

- | | | | | | |
|-----------------|--------------------------|---------------------|--------------------------|---------------|--------------------------|
| a) Diaryl ether | <input type="checkbox"/> | b) Aryl alkyl ether | <input type="checkbox"/> | c) Ester | <input type="checkbox"/> |
| d) 1° Amino | <input type="checkbox"/> | e) Lactone | <input type="checkbox"/> | f) 2° Alcohol | <input type="checkbox"/> |

Direct chemical depolymerization of lignin is a difficult process. Oxidized forms of lignin can be depolymerized, but it is expensive and involves hazardous reagents. In 2014, a group led by an American scientist Shannon S. Stahl showed that formic acid in the presence of sodium formate can be used efficiently to depolymerize the oxidized forms of lignin. To understand the mechanism of this process, model compounds **D** and **E** that represent structural units of lignin and oxidized lignin, respectively, were prepared. Following scheme illustrates the synthesis of **D**.

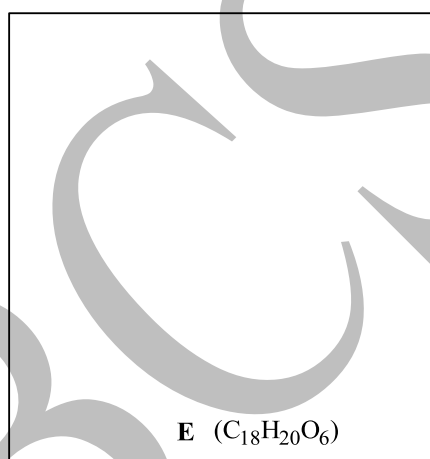
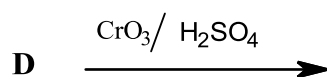


4.2 Identify structures of **B**, **C** and **D**.



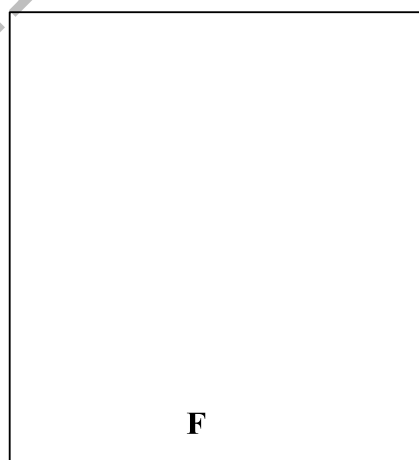
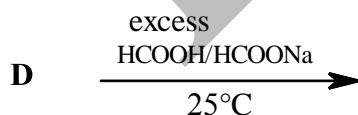
D on oxidation using $\text{CrO}_3/\text{H}_2\text{SO}_4$ gave an unexpected product **E** and two minor products. **E** gives no reaction with Tollen's reagent or with saturated NaHCO_3 .

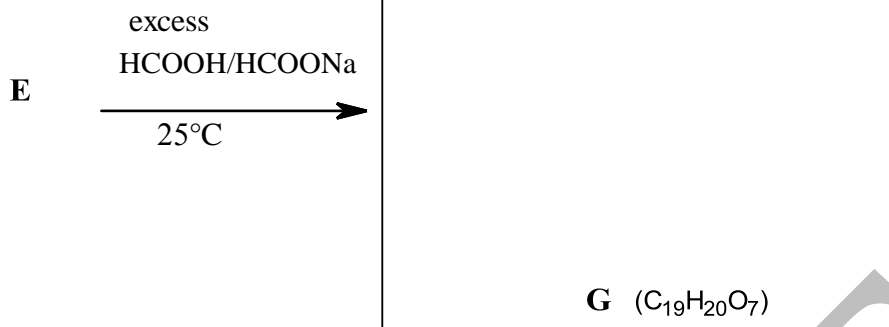
4.3 Identify structure of **E**.



Both model compounds **D** and **E** were treated with excess formic acid in the presence of aqueous sodium formate at room temperature to give products **F** and **G**, respectively.

4.4 Identify structures of **F** and **G**.

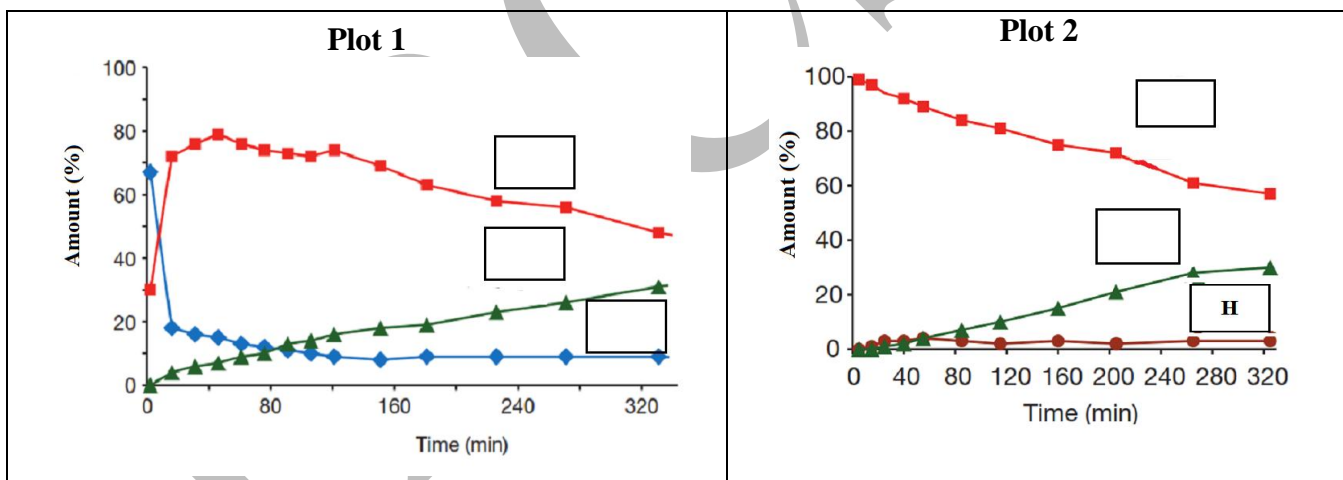




On heating with excess formic acid in aqueous sodium formate at 110 °C, **D** gave only **F**, whereas, **E** gave a mixture of **G**, **H**, **I**, and **J**. For this reaction of **E** at 110°C, variation in the amounts of **E**, **G**, and **J** over time is presented in **Plot 1**.

When **G** was heated with formic acid in aqueous sodium formate to 110°C, **H**, **I** and **J** were obtained. For this reaction, variation in the amounts of **G**, **H** and **J** with time are given in **Plot 2**. The rates of formation of **I** and **J** were same.

4.5 Identify the curves corresponding to **E**, **G** and **J** in **Plots 1**, and for **J** in **Plot 2**. (Write the appropriate letter in the corresponding boxes in the plots)



4.6 From the curve for **H** in **plot 2**, we can infer that (Mark **X** in the correct box/es)

- i) **H** is formed at a very low rate.
- ii) **H** is formed by the reaction of **G** and **J**.
- iii) **H** is in equilibrium with **G**.
- iv) **H** is formed as well as consumed during the reaction.

C-H bond and its Deuterium analogue, C-D bond, differ in their bond energies. This difference in bond energies also affects the rate of reactions where these bonds are involved. A new sample of compound **E** was prepared by substituting a Deuterium in place of Hydrogen at the chiral carbon in **E**. This substitution decreased the rate of reaction of **E** with formic acid/sodium formate at 110 °C.

4.7 Choose the correct inference of the reaction of **E** with formic acid/sodium formate at 110 °C. (Mark **X** against the correct option/s)

- a) The rate decreased because the bond energy of C-H bond is more than of C-D bond
- b) A change in rate due to Deuterium substitution suggests breaking of a C-H bond during the reaction and it is the rate determining step
- c) The change in rate suggests that the rate determining step involves a base.
- d) The change in rate suggests a protonation/deuteration step by formic acid and it is the rate determining step.

Among **H**, **I** & **J**, compound **H** decolorized acidic KMnO_4 solution and compound **J** gave a positive test with aqueous ferric chloride. **I** gives the iodoform test.

4.8 Identify compounds **H**, **I** and **J**.

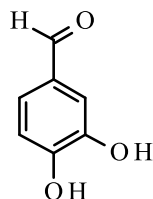
H $\text{C}_{18}\text{H}_{18}\text{O}_5$	I $\text{C}_{11}\text{H}_{12}\text{O}_4$	J
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4.9 The major conclusion/s of the above studies with model compounds **D** and **E** is/are: (Mark **X** in the correct box/es)

- a) Depolymerisation of oxidized lignin is via cleavage of C-C bonds in $\begin{array}{c} \text{OH} \quad \text{O} \\ | \quad || \\ -\text{C}-\text{C}- \end{array}$ units.
- b) Oxidized lignin undergoes depolymerisation by formic acid/sodium formate by cleavage of ether linkages.
- c) Selective oxidation of 2° alcohol groups on lignin is essential for an efficient depolymerisation reaction by formic acid/sodium formate.
- d) Every C-O bond cleavage consumes one molecule of formic acid

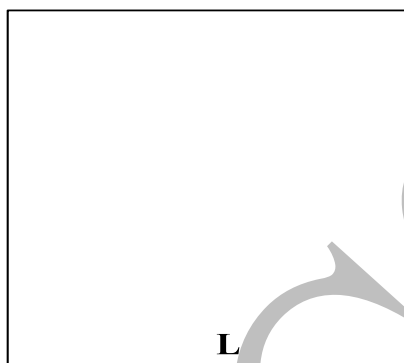
A naturally occurring popular flavor compound **K** used initially by Aztecs in Central America was introduced to the Europeans in 1520. In later periods, 90% of the supply of this compound was sourced from a plant cultivated in Madagascar. It was also produced from small molecules obtained from waste lignin from the paper industry. Currently, >99% of **K** is produced using petrochemicals.

Protocatechualdehyde with dimethyl sulphate in the presence of NaOH gives **K** along with **L** and **M**. In this reaction, the product ratios can be controlled by the reaction conditions. With excess of NaOH and excess of dimethyl sulfate, product **L** was formed exclusively.



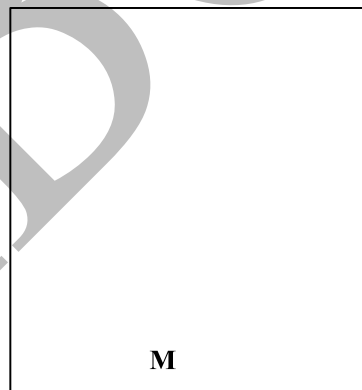
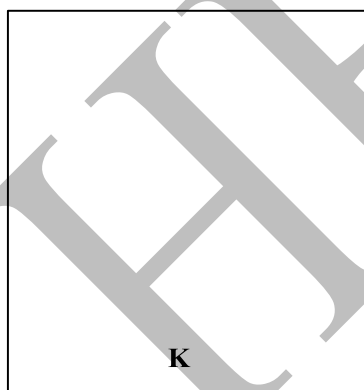
Protocatechualdehyde

4.10 Identify **L**.



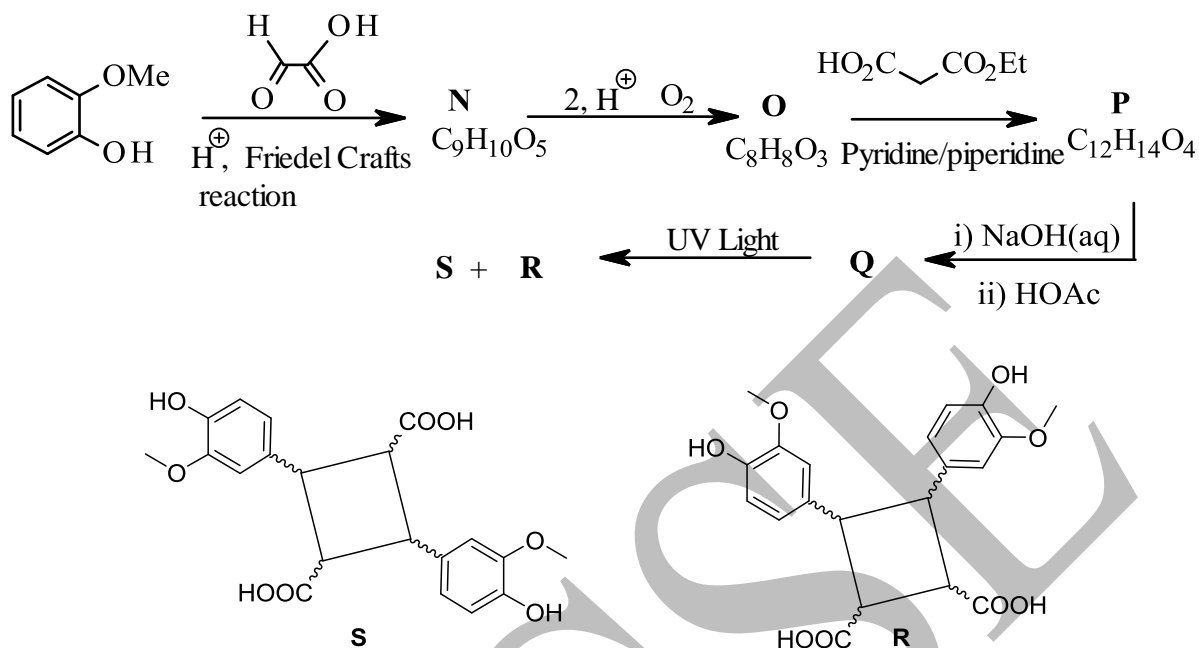
When one equivalent of NaOH and one equivalent of dimethyl sulphate were used, **K** was formed in 87% yield. The same reaction when carried out with excess of NaOH and only one equivalent of dimethyl sulfate, **M** was formed in 95% yield.

4.11 Identify **K** and **M**.



Plants use phenylalanine to make several small aromatic organic molecules which are later used in the formation of the lignin framework. Some of these small molecules get attached to the carbohydrates in the cell wall. Compounds **R** and **S** shown below are formed as a result of sunlight induced photochemical reaction of **P**.

R and **S** were chemically synthesized by the following scheme. Air oxidation of **N** in presence of an acid gave **O**.

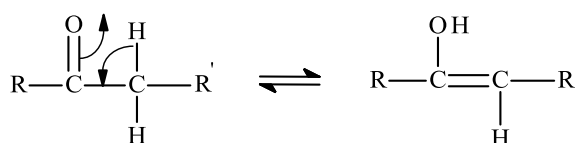


4.12 Identify **N**, **O**, **P** and **Q**

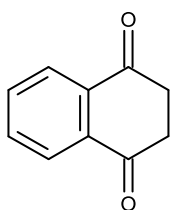
N	O	P	Q
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Problem 5**22 marks****Keto-Enol Tautomerism: Kinetics and Thermodynamics**

Two compounds having the same molecular formula but different structural arrangement of atoms in molecules are known as structural isomers, e.g., C_2H_6O represents both ethyl alcohol and dimethyl ether. One form of structural isomerism is tautomerism, in which the same molecule dynamically interconverts between two or more structural forms. Carbonyl compounds exhibit keto-enol tautomerism, represented as follows:



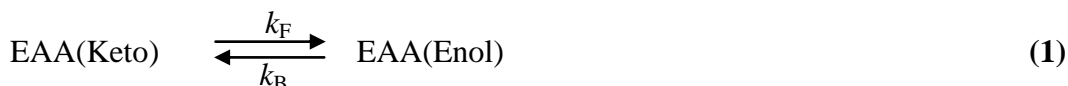
5.1 For the following compound, write the possible tautomers.



Many carbonyl compounds with acidic alpha hydrogen are important for industrial synthesis of many chemicals. Ethyl acetoacetate (EAA), i.e., ethyl-3-oxo butanoate is one such widely used compound. In solution, EAA is an equilibrium mixture of the keto and an enol form.

5.2 Draw the structures of possible enol forms for EAA and identify the most stable enol form.

The most stable enol form is observed experimentally. To study the kinetics of the following reaction, a detailed experiment was conducted.



Four flasks (**A - D**) were taken, each containing 25 mL solution **S** of EAA (15 g L^{-1}) in anhydrous methanol. The flasks were maintained at 20°C throughout this study. Excess of freshly prepared bromine solution in methanol (25 mL) at 20°C was added rapidly to each flask at $t = 0 \text{ s}$. The enol form reacts extremely rapidly with bromine while the keto form does not. This reaction results in an acidic solution. Bromination of enol is a very fast reaction compared to the enolization of EAA. The mono-brominated ester formed is stable and doesn't react further under these reaction conditions.

5.3 Write the balanced chemical equation for the reaction that would take place on addition of bromine to solution **S**.

Excess of 2,4,4-trimethyl-1-pentene was added rapidly to flasks **A**, **B**, **C** and **D** at $t = 10, 40, 75,$ and 100 s , respectively.

5.4 The 2,4,4-trimethyl-1-pentene added will (Mark **X** in the appropriate box(es))

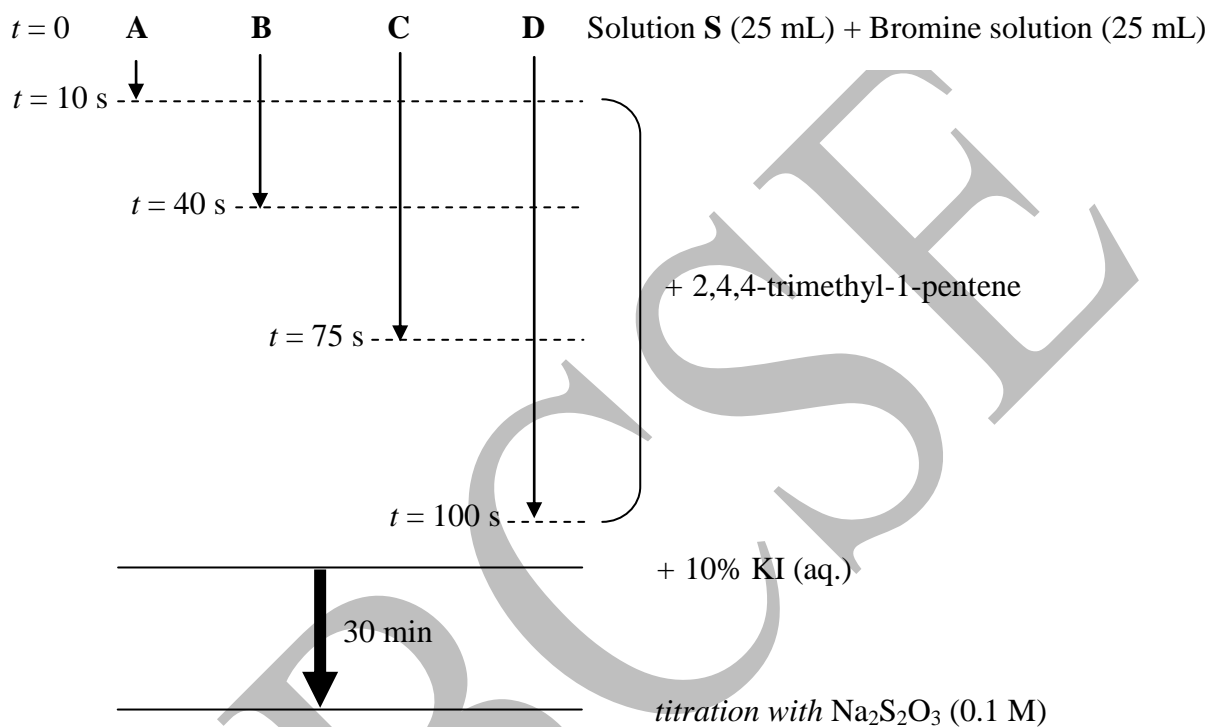
- | | |
|---|--------------------------|
| (i) increase the rate of keto to enol conversion. | <input type="checkbox"/> |
| (ii) consume unreacted bromine. | <input type="checkbox"/> |
| (iii) react with monobrominated ester and hence ensure complete bromination of EAA. | <input type="checkbox"/> |
| (iv) stop the enolization reaction. | <input type="checkbox"/> |

After addition of 2,4,4-trimethyl-1-pentene, about 10 mL of 10% aqueous KI solution was added to each of the flasks **A - D** and allowed to stand for 30 minutes. The reaction mixture was still acidic. During this time, brominated ester is converted back to EAA. Then, the liberated iodine is titrated with 0.1 M sodium thiosulphate solution using starch indicator. Assume that there is no reaction between iodine and any form of EAA.

5.5 Write the balanced equation of the reaction for the liberation of iodine.

5.6 Write the balanced equation for reaction of iodine with sodium thiosulphate.

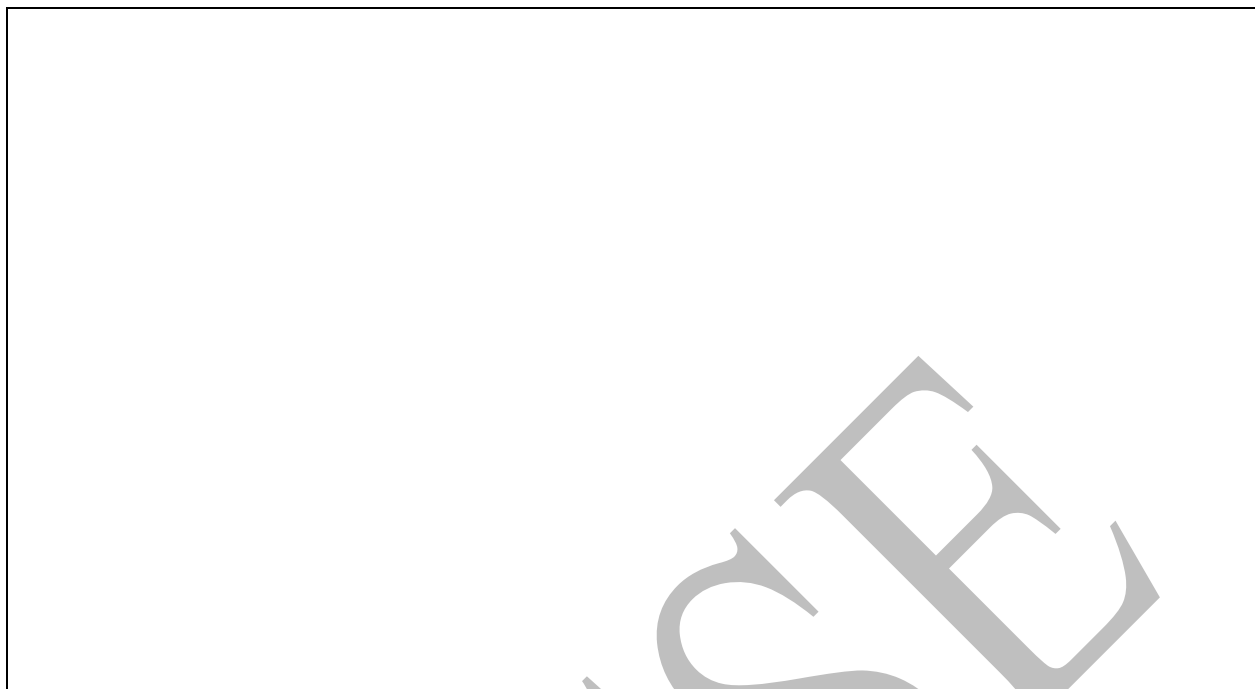
The experiment can be summarized as follows:



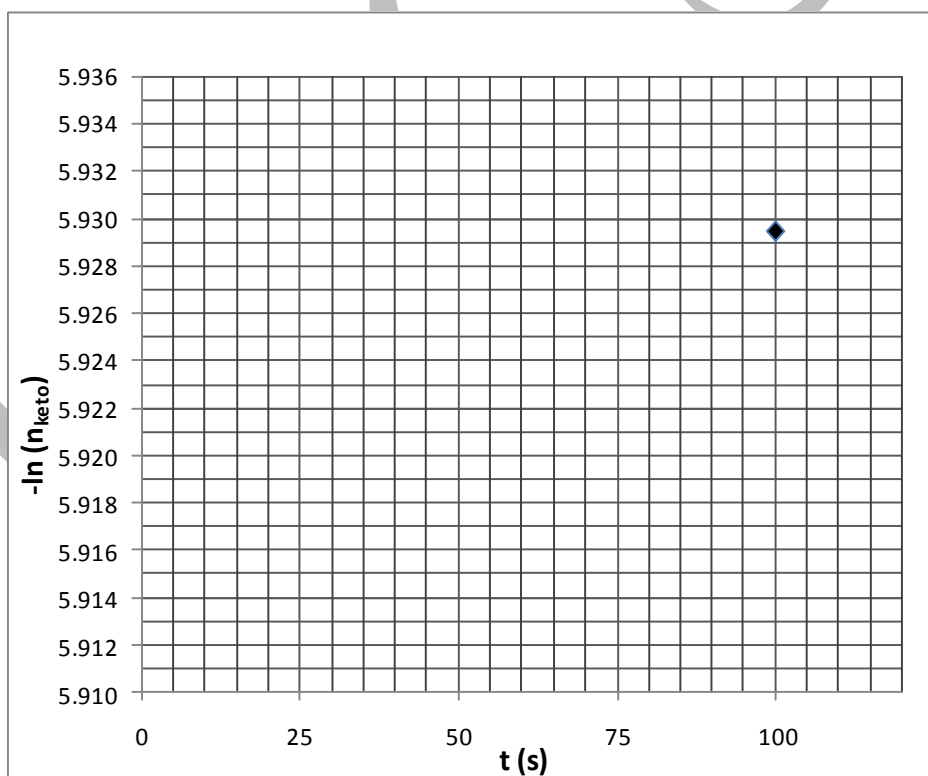
Following volumes of sodium thiosulphate solution were consumed in titration with the solutions in the flasks **A**, **B** and **C** at 20°C .

Flask	Volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution used (mL)
A	3.78
B	4.02
C	4.30

5.7 From this data, find n_{keto} , the number of moles of keto form of EAA at the time of addition of 2,4,4-trimethyl-1-pentene, for the flasks **A**, **B** and **C**. Show detailed calculations for flask **A**. You may assume volumes to be additive during mixing of solutions in this experiment.



The following graph indicates the plot of $-\ln(n_{\text{keto}})$ versus time (t). Point corresponding to flask **D** is indicated on the graph.



- 5.8** Plot the values corresponding to flasks **A**, **B** and **C** in the graph above. Using the graph, find the following for conversion of EAA (keto) to EAA (enol) in reaction (1).
- The order of the reaction.
 - Rate constant k_F for the reaction.

c. Equilibrium constant K_{eq} for the reaction. Report the answer upto 5 significant figures.

When the above experiment was carried out at 40°C , the values of K_F and K_{eq} were found to be $5.25 \times 10^{-4} \text{ s}^{-1}$ and 0.06272, respectively.

5.9 Using the above information, find the values of ΔH° (in kJ mol^{-1}) and ΔS° (in $\text{kJ mol}^{-1} \text{ K}^{-1}$) for the enolization reaction (1). Assume ΔH° and ΔS° to be independent of temperature. Show necessary calculations.

Reaction kinetics is very important for the industrial use of a reaction, as the reaction rates affect the time in which a certain amount of product can be synthesised. This time of production in turn affects the cost of the final product.

An industrialist has 8.5 kg of EAA and hopes to produce compound **Y** (Molar mass = 174 g), which is obtained in equimolar amount from the Enol form of EAA.



5.10 For what value of k' , the industrialist would obtain a certain amount of **Y** in minimum amount of time? (Mark **X** in the appropriate box(es))

(i) $k' \approx 0$

(ii) $k' \rightarrow \text{infinity}$

5.11 The industrialist did not know the value of k' , but wanted to know the minimum time that would be required to produce 10 kg of **Y** using the available EAA in methanol as solvent at 40°C. Estimate this time assuming that (i) the kinetics of the enolization reaction of EAA in this large scale reaction is same as determined in the laboratory experiment described above and (ii) other effects such as changes in temperature and solution volume during the progress of reaction are negligible.

Rough Page

HBCSE

Rough Page

HBCSE