

Indian National Chemistry Olympiad 2020
Theory (3 hours)

Roll No. - -

Exam Centre: _____ Date: February 1, 2020

Do not write anything below this line

Question No	1	2	3	4	5	6	Total
Marks	16	22	24	13	29	15	119
Marks Obtained							
Signature of Examiner							

Instructions for students

- Write last four digits of your Roll No. at the top of all pages.
- This examination booklet consists of **29** pages of problems including answer boxes.
- **Kindly check that the booklet has all the pages. If not, report to the invigilator immediately.**
- All answers must be written in the appropriate boxes. Anything written elsewhere will not be considered for assessment.
- 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 (**Please draw a box and write the Q. No. in the box on this sheet for evaluation**). 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 (except for graph) will be penalized.**
- 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 end.
- 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	$c = 2.998 \times 10^8 \text{ m s}^{-1}$
Molar gas constant	$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ $= 0.08205 \text{ L atm K}^{-1} \text{ mol}^{-1}$	1 atomic mass unit	$(1 \text{ amu}) = 1.660 \times 10^{-27} \text{ kg}$
1 atm = 101325 Pa		$\text{pH} = -\log [\text{H}^+]$	$\text{pK}_a = -\log K_a$

IUPAC Periodic Table of the Elements

1													13						14		15		16		17		18																														
1 H hydrogen 1.008 [1.0078, 1.0082]													5 B boron 10.81 [10.806, 10.821]	6 C carbon 12.011 [12.009, 12.012]	7 N nitrogen 14.007 [14.006, 14.008]	8 O oxygen 15.999 [15.999, 16.000]	9 F fluorine 18.998	10 Ne neon 20.180													13 Al aluminium 26.982	14 Si silicon 28.085 [28.084, 28.086]	15 P phosphorus 30.974	16 S sulfur 32.06 [32.059, 32.076]	17 Cl chlorine 35.45 [35.446, 35.457]	18 Ar argon 39.95 [39.792, 39.963]																					
3 Li lithium 6.94 [6.938, 6.997]	4 Be beryllium 9.0122	Key: atomic number Symbol name conventional atomic weight standard atomic weight																								11 Na sodium 22.990	12 Mg magnesium 24.305 [24.304, 24.307]													19 K potassium 39.098	20 Ca calcium 40.078(4)	21 Sc scandium 44.956	22 Ti titanium 47.867	23 V vanadium 50.942	24 Cr chromium 51.996	25 Mn manganese 54.938	26 Fe iron 55.845(2)	27 Co cobalt 58.933	28 Ni nickel 58.693	29 Cu copper 63.546(3)	30 Zn zinc 65.38(2)	31 Ga gallium 69.723	32 Ge germanium 72.630(8)	33 As arsenic 74.922	34 Se selenium 78.971(8)	35 Br bromine 79.904 [79.901, 79.907]	36 Kr krypton 83.798(2)
19 K potassium 39.098	20 Ca calcium 40.078(4)	21 Sc scandium 44.956	22 Ti titanium 47.867	23 V vanadium 50.942	24 Cr chromium 51.996	25 Mn manganese 54.938	26 Fe iron 55.845(2)	27 Co cobalt 58.933	28 Ni nickel 58.693	29 Cu copper 63.546(3)	30 Zn zinc 65.38(2)	31 Ga gallium 69.723	32 Ge germanium 72.630(8)	33 As arsenic 74.922	34 Se selenium 78.971(8)	35 Br bromine 79.904 [79.901, 79.907]	36 Kr krypton 83.798(2)	37 Rb rubidium 85.468	38 Sr strontium 87.62	39 Y yttrium 88.906	40 Zr zirconium 91.224(2)	41 Nb niobium 92.906	42 Mo molybdenum 95.95	43 Tc technetium [101.07(2)]	44 Ru ruthenium 101.07(2)	45 Rh rhodium 102.91	46 Pd palladium 106.42	47 Ag silver 107.87	48 Cd cadmium 112.41	49 In indium 114.82	50 Sn tin 118.71	51 Sb antimony 121.76	52 Te tellurium 127.60(3)	53 I iodine 126.90	54 Xe xenon 131.29																						
55 Cs caesium 132.91	56 Ba barium 137.33	57-71 lanthanoids	72 Hf hafnium 178.49(2)	73 Ta tantalum 180.95	74 W tungsten 183.84	75 Re rhenium 186.21	76 Os osmium 190.23(3)	77 Ir iridium 192.22	78 Pt platinum 195.08	79 Au gold 196.97	80 Hg mercury 200.59	81 Tl thallium 204.38 [204.38, 204.39]	82 Pb lead 207.2	83 Bi bismuth 208.98	84 Po polonium	85 At astatine	86 Rn radon	87 Fr francium	88 Ra radium	89-103 actinoids	104 Rf rutherfordium	105 Db dubnium	106 Sg seaborgium	107 Bh bohrium	108 Hs hassium	109 Mt meitnerium	110 Ds darmstadtium	111 Rg roentgenium	112 Cn copernicium	113 Nh nihonium	114 Fl flerovium	115 Mc moscovium	116 Lv livermorium	117 Ts tennessine	118 Og oganesson																						



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57 La lanthanum 138.91	58 Ce cerium 140.12	59 Pr praseodymium 140.91	60 Nd neodymium 144.24	61 Pm promethium	62 Sm samarium 150.36(2)	63 Eu europium 151.96	64 Gd gadolinium 157.25(3)	65 Tb terbium 158.93	66 Dy dysprosium 162.50	67 Ho holmium 164.93	68 Er erbium 167.26	69 Tm thulium 168.93	70 Yb ytterbium 173.05	71 Lu lutetium 174.97
89 Ac actinium	90 Th thorium 232.04	91 Pa protactinium 231.04	92 U uranium 238.03	93 Np neptunium	94 Pu plutonium	95 Am americium	96 Cm curium	97 Bk berkelium	98 Cf californium	99 Es einsteinium	100 Fm fermium	101 Md mendelevium	102 No nobelium	103 Lr lawrencium

For notes and updates to this table, see www.iupac.org. This version is dated 1 December 2018.
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United Nations
Educational, Scientific and
Cultural Organization



International Year
of the Periodic Table
of Chemical Elements

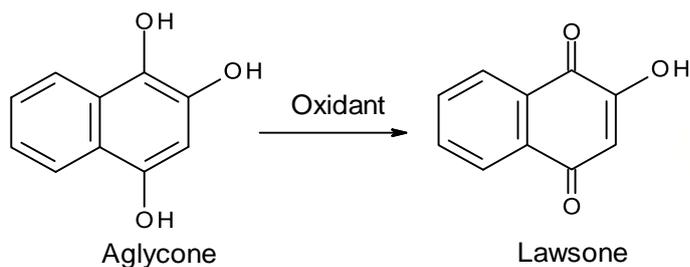


Problem 1

16 marks

Chemistry of the artificial hair dyes

Dyeing of hair is an ancient art. Earlier, dyes were obtained from plants such as indigo, henna, turmeric and amla. In dyeing with natural henna, an aglycone molecule (structure shown below), gets converted to orange colored Lawsone in the presence of an oxidant (such as air).



Hydroquinone (1,4-dihydroxybenzene) and analogous 1,4-diimine derivatives also undergo similar transformations under the influence of an oxidant.

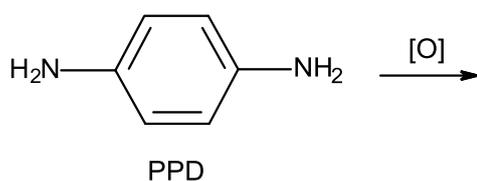
A chemistry teacher at a hair salon once observed the barber preparing a low-cost hair colorant for a customer by mixing a spoonful of brownish-white crystalline solid with H_2O_2 and shaving cream. A little investigation indicated that the white solid was a chemical called PPD (*p*-phenylenediamine).

On further reading, the teacher realized that PPD was one of the first synthetic chemical launched for hair dyeing market in the year 1907. Later he found that most of the hair colorants being sold in the market, including the so-called "natural/herbal" hair colours had PPD in them. Hair proteins have iso-ionic points (when the number of +ve and -ve charged species in protein are equal) around $\text{pH} = 4.8\text{--}6.8$. Therefore, some of the hair dyes are also +vely charged species, which hair proteins absorb from neutral-alkaline solutions.

In this problem, we will explore how colourless PPD leads to the intense black and numerous other hair colours.

Under oxidizing condition, PPD gets converted to corresponding diimine A ($\text{C}_6\text{H}_6\text{N}_2$).

1.1 Draw the structure of A.



Key Ingredients : Henna Powder, Sodium Perborate, P-Phenylene Diamine, Tartaric Acid, Indigofera Tinctoria, Hibiscus.

INGREDIENTS :
 Henna, Paraphenylene Diamine, Sodium Perborate, Magnesium Sulphate, Sodium CMC, Tartaric Acid, SLS Powder, Herbal Powder and Perfume.

This Mehndi Powder Contents :
 Mehndi Leaves, Paraphenylene Diamine, Citric Acid, Magnesium, Sodium Sulphide, Dry Hea Powder & Chandan Powder Paro... after dilution

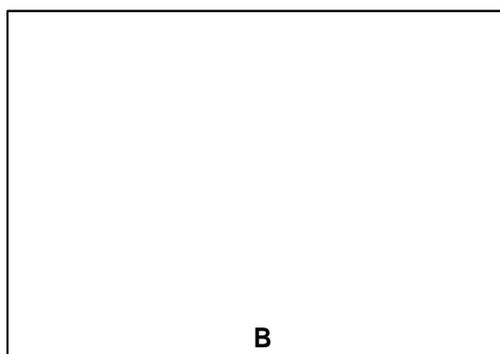
Contains : Powder Hair Dye
 Mehandi Powder, Amla Powder, Shikakai Powder, Reetha Powder, Neem Leaves Powder, Barium Peroxide, 2-N-Paraphenylenediamine & Citric Acid

POISON. For external use only.
INGREDIENTS : Natural Henna, Amla, Shikakai, Barium Peroxide, Citric Acid, Phenylenediamine.

POISON
 INGREDIENTS
 ONLY FOR EXTERNAL USE ONLY.
 HENNA POWDER, PARA-PHENYLENEDIAMINE
 BARIUM PEROXIDE, CITRIC ACID.

In aqueous solutions in the pH range 7-10, a small fraction of **A** molecules exists in monoprotonated form **B**.

1.2 Draw the structure of **B**.

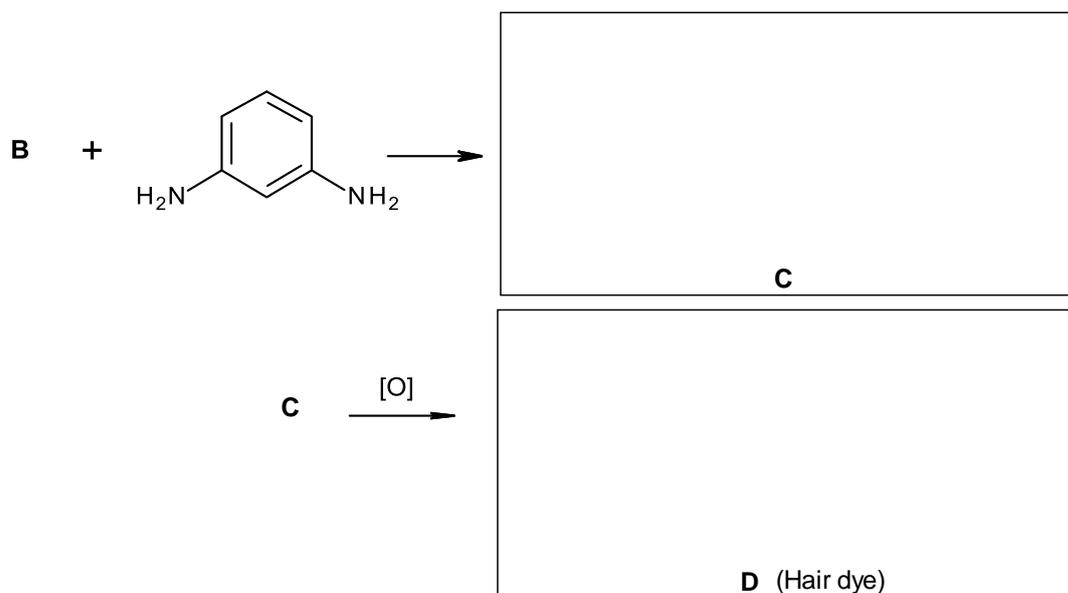


Usually colour in organic molecules originates due to extended conjugation. Black colour is generated from PPD by two pathways **I** and **II**.

Pathway I: In many commercial hair colorants, the white powder contains a mixture of several compounds (called couplers) along with PPD. Under oxidizing conditions, PPD reacts with different couplers producing different hair colors, which in specific combination give black colour.

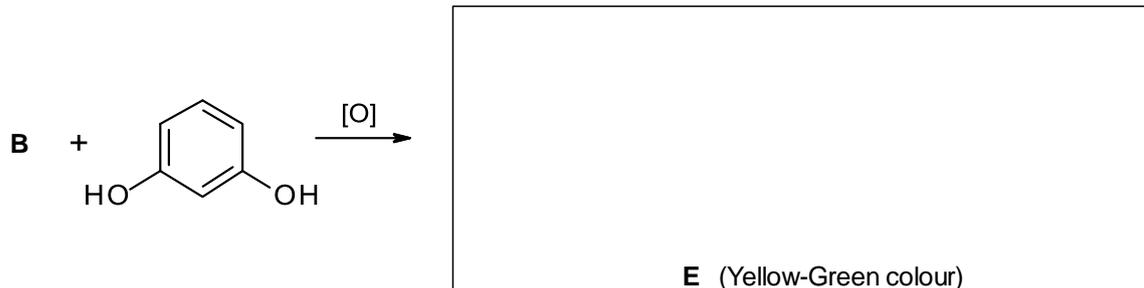
For example, oxidized form of PPD (**B**) reacts with the coupler *m*-phenylenediamine in aqueous phase to form the thermodynamically stable product **C**, which on further oxidation produces a blue hair dye **D** (a cationic species having two rings).

1.3 Write the structure of **C** and dye **D**.



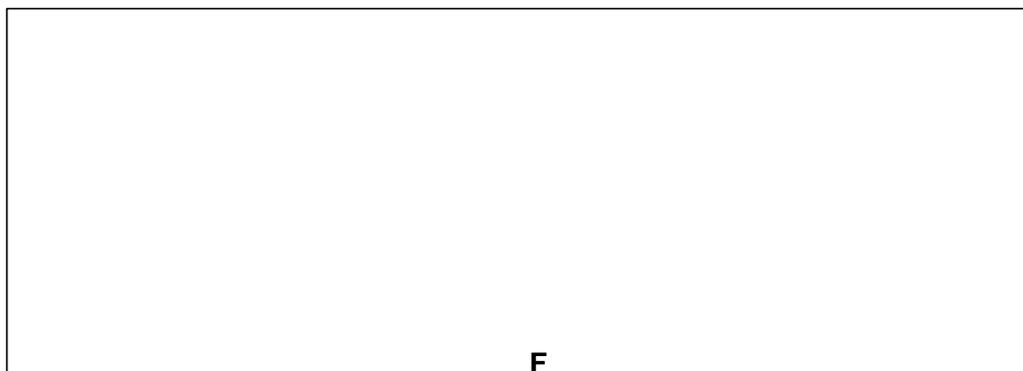
When resorcinol is used as a coupler, a yellow-green dye **E** is produced which reacts with diazomethane to form a compound having molecular formula $C_{20}H_{18}N_4O_2$.

1.4 Write the structure of **E**.



Pathway II: When PPD is alone subjected to oxidation, the oxidized form **A** slowly gets polymerized to give an intermediate **F**, which on further oxidation gives an intense black hair colour.

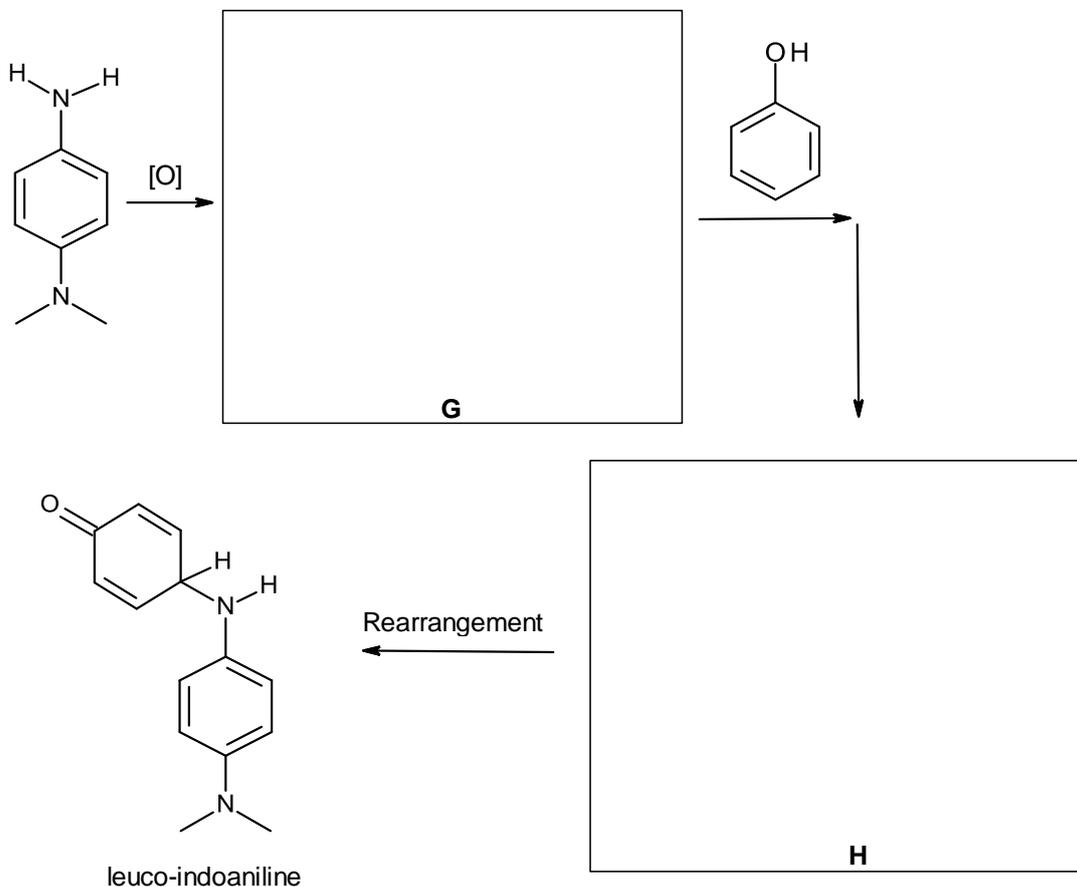
1.5 Write the part-structure of the polymer (**F**).



The oxidative coupling of 4-dimethylamino aniline with phenol can take a different pathway. A $2 e^-$ oxidation of 4-dimethylamino aniline generates a cationic intermediate species **G**. Reaction of phenol with **G**, produces a colourless species leuco-indoaniline, which gets easily oxidized to give a dye, indoaniline.

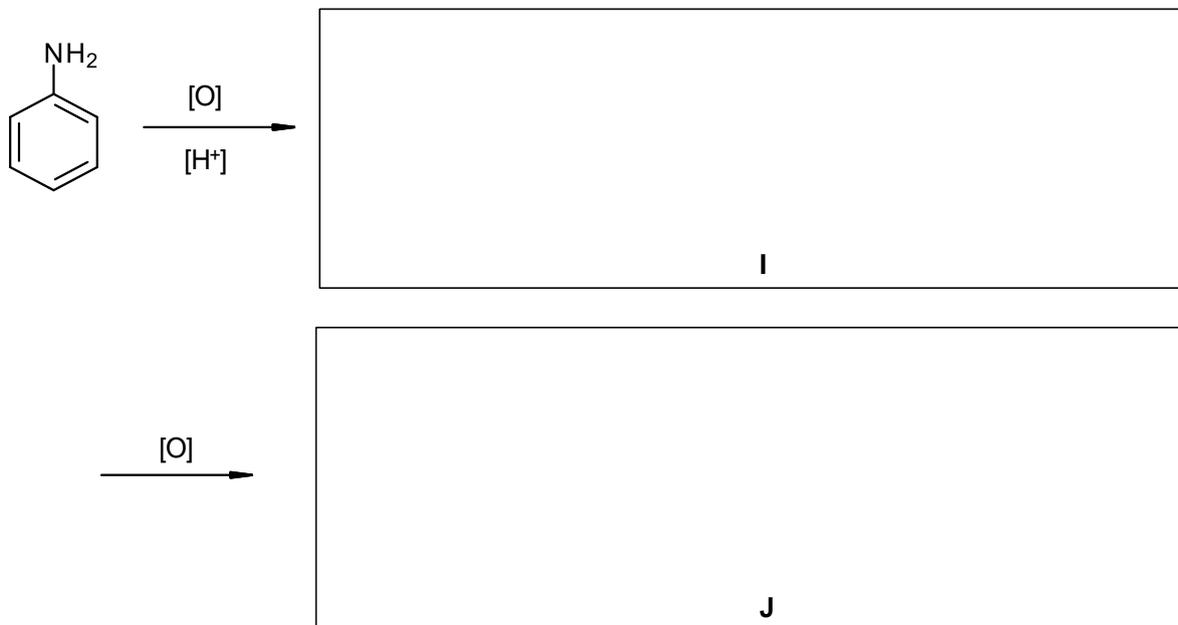
Quantum mechanical calculations indicate that conversion from **G** to leuco-indoaniline can go through a very low energy pathway involving formation of another intermediate species **H**. Due to π - π stacking interactions *between two rings*, **H** can easily rearrange to produce leuco-indoaniline.

1.6 Draw the most stable resonance form of **G** and possible structure of **H**.



Around the period of discovery of poly-PPD, scientists were able to polymerize aniline also. Some poly-anilines were found to be good electrical conductors, leading to Nobel Prize award in 2000 to Alan G. MacDiarmid, Alan J. Heeger and Hideki Shirakawa. In acidic medium and presence of an oxidant, aniline first forms a polymer **I** having empirical formula $C_{12}H_{10}N_2$, which on subsequent partial oxidation (with 50% of the polymer chain getting oxidized) produces **J**. Protonated form of **J** exhibits high electrical conductivity.

1.7 Write the part structures of polymers **I** and **J**.

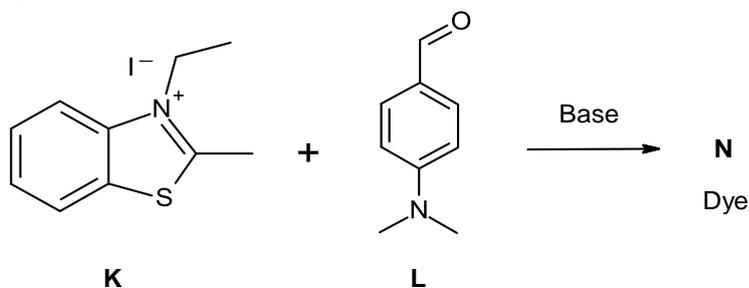


A particular brand of hair colour (labelled “herbal black henna”) contains the following ingredients: barium peroxide, citric acid, magnesium carbonate, and PPD, along with some herbs (*Amla*, *Neem* leaves, *Shikakai*, Coffee seeds, *Tulsi*, etc.) which don’t participate in the colour forming reactions. Application of its paste with water makes the hair black. A paste of natural henna leaves is also applied to hair for giving orange colour.

1.8 When a paste of henna leaves was mixed (in 1:1 ratio) with the “herbal black henna”, black colour was not produced in significant intensity. Write the chemical reaction that took place and **prevented** formation of black colour.

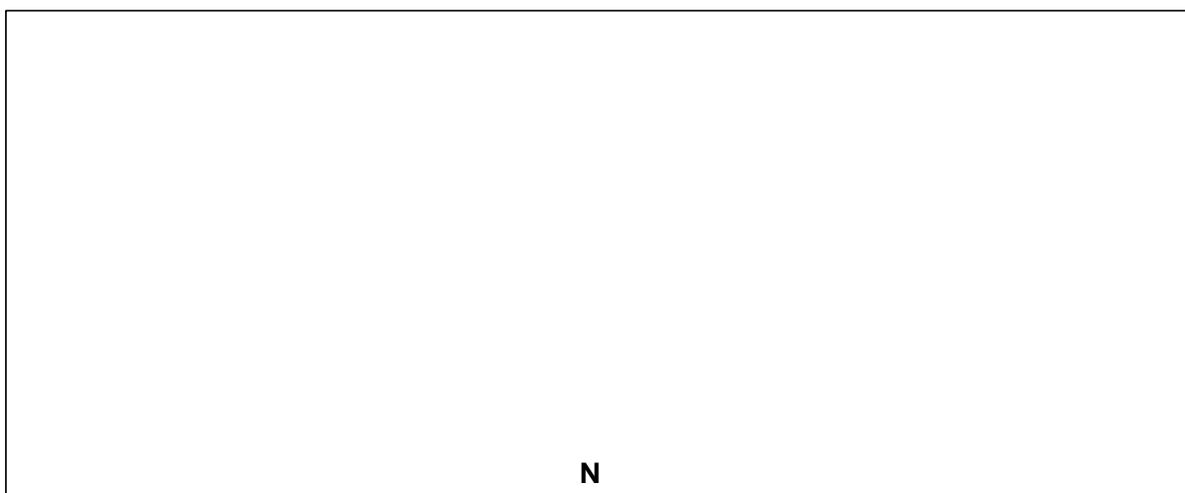
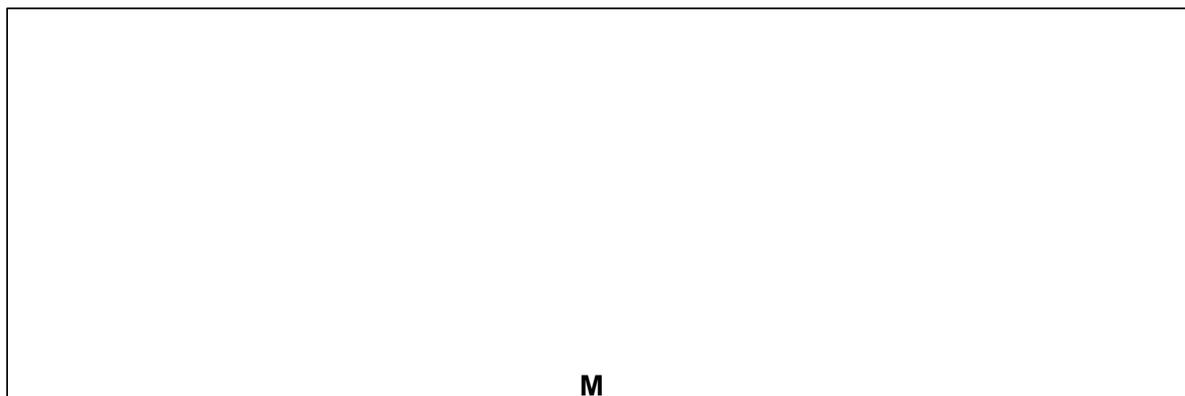
PPD based hair dyes can lead to skin allergies and related diseases. Hence, researchers are trying for new hair dyes. Efforts have been made to prepare hair colours using 4-(N,N-dimethylamino) benzaldehyde.

The reaction of 3-ethyl-2-methylbenzothiazolium iodide (**K**) with 4-(N,N-dimethylamino) benzaldehyde (**L**) in presence of a base gives an intensely coloured dye **N**, which has the longest possible conjugation of π -bonds.



The reaction proceeds through the formation of intermediate **M** (obtained from reaction of **K** with base).

1.9 Draw the possible structure(s) of the intermediate **M** and the dye(s) **N**.



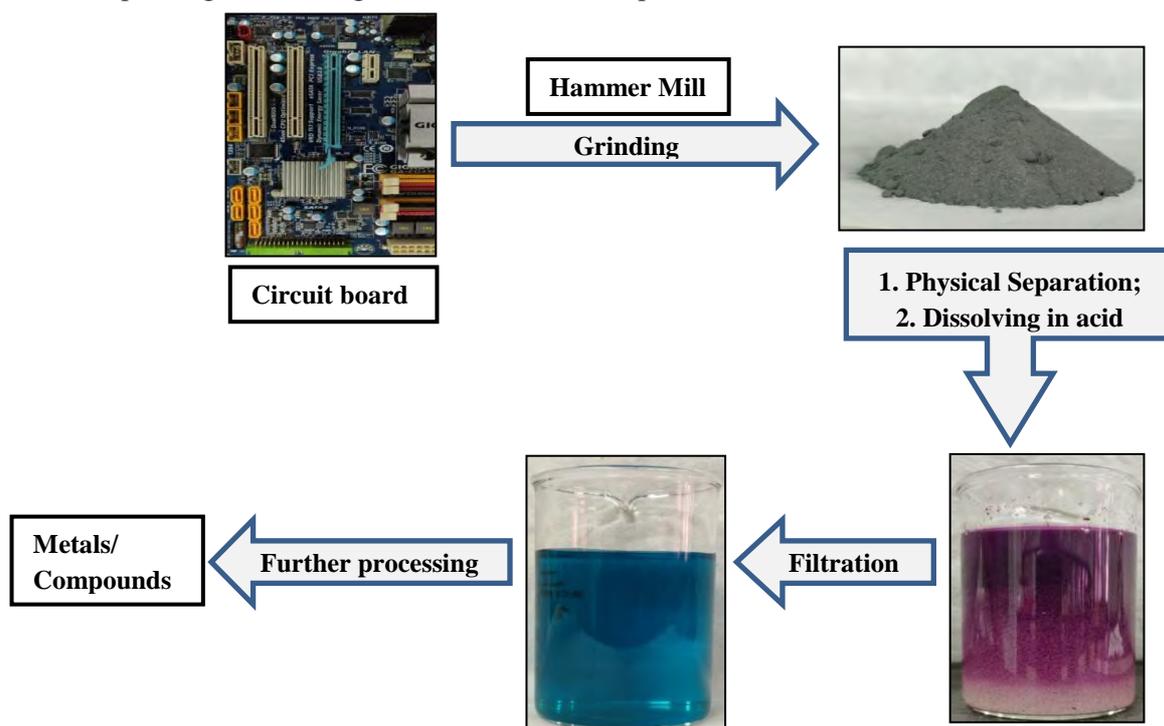
Problem 2

22 marks

Towards a new Metallurgy from e-waste

The global market for electrical and electronic equipment continues to expand, while the lifespan of products is becoming shorter. A large amount of metals mined from earth crust are now being piled up in heaps of electronic waste (e-waste). With many of the natural metal ores being exhausted, there is a need to develop chemistry to extract metals and their compounds from e-waste.

One of the most complex components in e-waste are Printed Circuit boards (PCBs). The average metallic composition of a typical PCB from a computer is 20.1% Cu, 7.2% Fe, 3.6% Al, 2.8% Zn, 2.1% Pb, 3.3% Sn, and 0.7% Ni. Apart from these, Ag or some other metals are also present in some e-waste depending on the design of the electronic components.



Consider a sample of PCB waste that contains all the above mentioned 8 metals including Ag. To extract metals, e-waste is first grinded to a powder form and then subjected to separation processes. Pieces of metallic Fe and Al, present in component casing, etc, are separated by magnetic separation and Eddy current technique, respectively. Note that these physical methods may only separate the elemental forms and not compounds or alloys of Fe and Al.

Chemical processing of the ground powder starts by dissolving in concentrated nitric acid. The reaction of metals with nitric acid varies greatly depending on the metal, its form and the concentration of the acid.

2.1 A common reaction product is NO gas. List the **other** possible N-containing molecules/ions that can result from reactions of nitric acid with metals.

2.2 An important task for the recycler is to know the amount of HNO_3 solution required for complete dissolution of the metals present in an e-waste powder. Which of the following information would be **necessary** to know the minimum required amount of nitric acid? (Mark **X** in the box (es))

- a) Stoichiometric ratio of metals and their compounds and nitric acid in their reactions
- b) Mass percentages of various metals and their compounds present in the ground e-waste
- c) Density of pure metals and their compounds present in e-waste
- d) Atomic masses of various metals present
- e) Concentration of nitric acid
- f) ΔH of the reactions representing formation of metal nitrates

<input type="checkbox"/>

2.3 If metallic copper reacts with 1 M HNO_3 , NO gas is produced.

- a) Write the individual oxidation and reduction reactions indicating the electron transfer and the balanced equation for the overall reaction.
- b) Calculate the minimum volume of 1 M HNO_3 required to completely dissolve 100 g of Cu.

In the following part, we are presenting a model procedure for separation of the components from ground PCB.

2.4 Treatment of ground PCB powder with concentrated HNO_3 produces a white precipitate \mathbf{P}_1 . A major fraction of \mathbf{P}_1 is due to a metal \mathbf{Y} , which is one of the major components of solder, reacting with the acid and forming the hydrated form of its oxide liberating a brown gas. Identify \mathbf{Y} and write the balanced chemical equation of this reaction.

The filtrate \mathbf{F}_1 obtained after removing \mathbf{P}_1 from the mixture is then mixed with dil. HCl and filtered to obtain a precipitate \mathbf{P}_2 and a filtrate \mathbf{F}_2 . \mathbf{P}_2 is boiled with water for few minutes and filtered while hot to obtain filtrate \mathbf{F}_3 . To a small portion of \mathbf{F}_3 , addition of K_2CrO_4 yields a yellow precipitate, \mathbf{P}_3 .

2.5 Identify the composition of \mathbf{P}_2 and \mathbf{P}_3 .

\mathbf{P}_2 -	\mathbf{P}_3 -
------------------	------------------

From the filtrate F_2 , metals M_1 (which was present in P_2 but has not completely precipitated in the previous step) and M_2 are precipitated out by passing H_2S gas through the solution, which on filtration, gives a precipitate P_4 and filtrate F_4 .

Apart from M_1 and M_2 , there are two more metals M_3 and M_4 in F_2 that can be precipitated with H_2S . However, the precipitation of these is governed by the pH of the solution. K_{sp} values of the sulphides of these metals are: $M_1: 1 \times 10^{-28}$; $M_2: 1 \times 10^{-37}$; $M_3: 1 \times 10^{-22}$; $M_4: 1 \times 10^{-23}$

2.6 Determine the minimum $[H^+]$ required to separate M_1 and M_2 from M_3 and M_4 by passing H_2S through the solution. (Assume that the precipitation is complete when the concentration of precipitated metal ion reduces to 10^{-6} M and the saturated concentration of H_2S in water as well as in acidic solutions is 3.8 g L^{-1} . M_1, M_2, M_3 and M_4 are divalent in nature). Show all steps of calculations. For H_2S , $K_{a1} = 1.0 \times 10^{-7}$, $K_{a2} = 1.0 \times 10^{-19}$.

The precipitate P_4 is re-dissolved in 6 M HNO_3 and mixed with concentrated H_2SO_4 and boiled. M_1 precipitates then as P_5 and a filtrate F_5 is obtained. On passing H_2S gas through filtrate F_5 , a black precipitate P_6 is obtained.

2.7 Identify the composition of P_5 and P_6 .

P_5 -	P_6 -
---------	---------

The filtrate F_4 is boiled well in air to expel a gas and then NH_4Cl is added followed by excess of NH_4OH . During this process M_5 and M_6 gets precipitated as P_7 , which after filtration leaves filtrate, F_6 . The precipitate P_7 after washing with water is relatively safe for disposing in soil (as its components are found in many natural soils).

2.8 Identify which gas was *necessary* to be expelled by boiling and the composition of precipitate P_7 .

Gas -	P_7 -
-------	---------

2.9 If excess NH_4OH is added before adding NH_4Cl , then two other metals M_3 and M_4 also get precipitated. Write the chemical reactions for precipitations for these metals.

2.10 Determine the pH of a solution prepared by adding 50 g of NH_4Cl to 100 mL water followed by addition of 100 mL solution of 1 M NH_4OH . ($K_b(\text{NH}_4\text{OH}) = 1.8 \times 10^{-5}$)

The filtrate F_6 is saturated with H_2S to obtain M_3 and M_4 as precipitate P_8 . The precipitate P_8 on treating with dilute HCl leads to dissolution of precipitate M_4 only that is separated as filtrate F_7 . The filtrate is neutralized using aqueous NaOH solution and on passing H_2S again through the filtrate dirty white precipitate P_9 is obtained.

2.11 Identify precipitates of M_3 and M_4 in P_8 .

M_3 - M_4 -

2.12 Which of the following reagents used above is **not** essential for the separation of metals from e-waste in the method presented above: HNO_3 , HCl , NH_4Cl , NH_4OH , H_2S , K_2CrO_4 , NaOH .

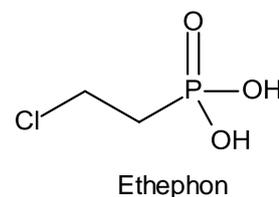
Problem 3

24 Marks

Growth Hormones for Apples

The red colour of the peel is a key quality marker for many varieties of apples, which affects consumer preferences for the fruit in market. Several chemicals are used at different stages of apple growth to modify anthocyanin content of the fruit and hence its colour.

Ethephon (structure given) is a major agrochemical used in India which promotes fruit maturity, increases the red skin color and allows early harvest of apples. One of the routes to prepare Ethephon is by using phosphorus trichloride and 1,2-epoxyethane to give a phosphite **A** ($C_6H_{12}Cl_3O_3P$). **A** undergoes rearrangement to a phosphonate **B** which hydrolyses to yield Ethephon.



3.1 Give the structures of **A** and **B**.

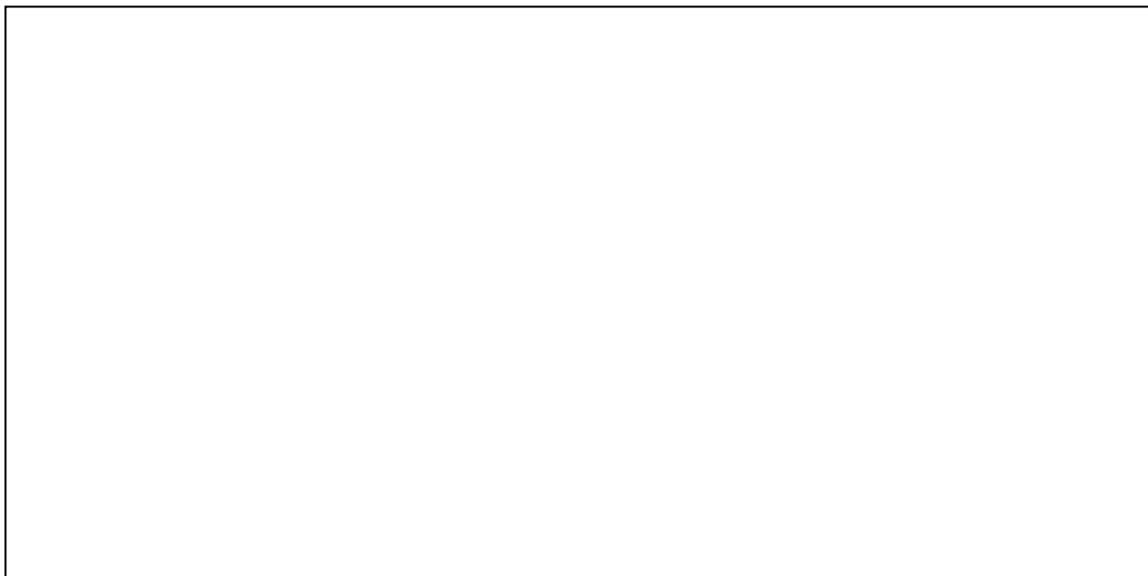
A	B
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3.2 Using the data of bond energies given below and by showing appropriate calculations, determine if the rearrangement $A \rightarrow B$ will lead to heating or cooling of the reaction mixture.

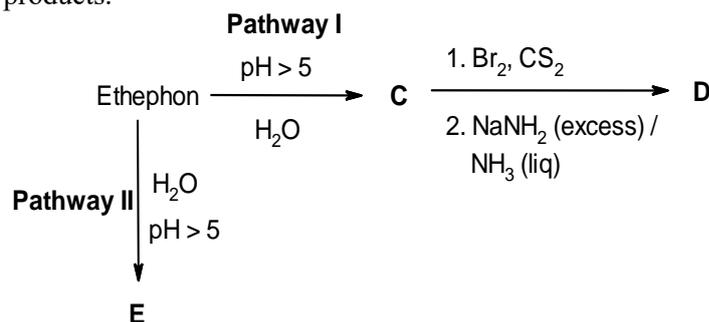
Bonds	Bond dissociation energy (kJ mol ⁻¹)	Bonds	Bond dissociation energy (kJ mol ⁻¹)
P–O	335	C–O	358
P=O	544	C–P	264
C–C	348	C–Cl	338

Commercially, Ethepon is sold in about 360 g L^{-1} aqueous solutions.

3.3 Determine the pH of the above Ethepon solution. For Ethepon, $\text{pK}_{\text{a}1} = 2.82$, $\text{pK}_{\text{a}2} = 7.21$.



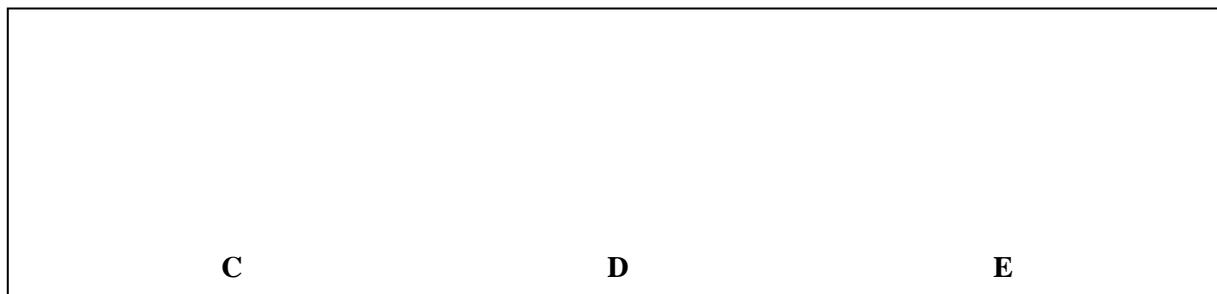
In aqueous solutions with $\text{pH} > 5$, Ethepon undergoes slow decomposition via two different pathways to give different products.



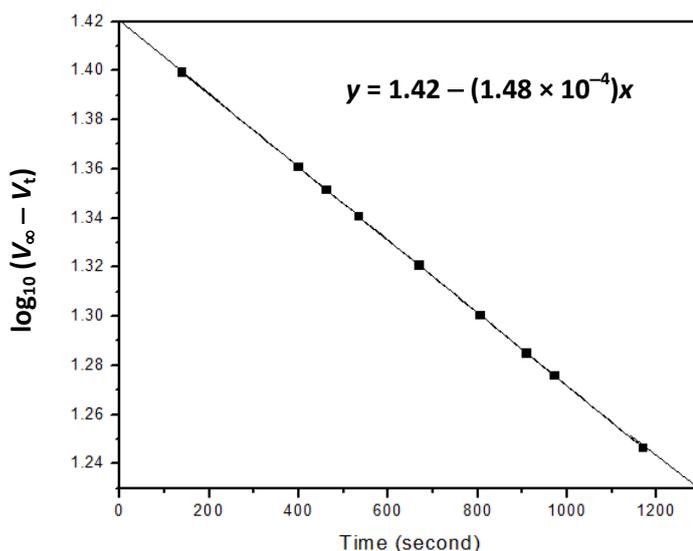
In **pathway I**, one of the decomposition products **C** is a natural plant hormone. **C** is a colourless gas at room temperature which if treated with bromine followed by treatment with NaNH_2 in liquid ammonia gives a colourless gas **D**.

In **Pathway II**, one of the decomposition products is a carbon containing compound **E**, which is toxic for liver in animals. Pure **E** is a viscous oily liquid at room temperature.

3.4 Draw the structures of **C**, **D**, and **E**.



A 0.04 M solution of Ethepon was prepared in aqueous NaOH . The solution had a $\text{pH} = 7.5$ at time $t = 0 \text{ s}$. The volume of gas **C** evolved (V_t) from this solution was monitored as a function of time t at 30°C . The data obtained is presented in the graph below.



3.5 Using the data in the above graph, calculate the rate constant of the decomposition pathway I.

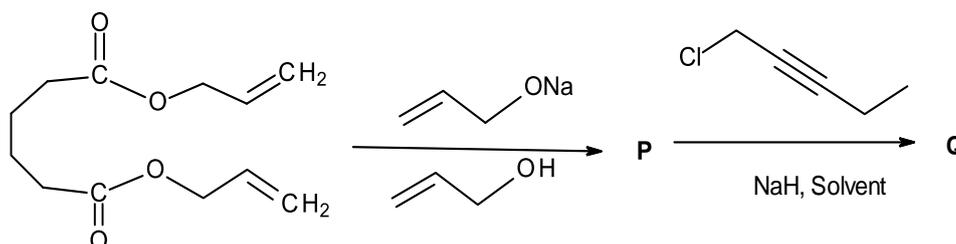
Ethephon solutions for farm applications are prepared usually in carrier water (dilute solutions of sodium or calcium carbonate), which generates solutions with pH of about 7-8.

3.6 A farmer took a 200 mL bottle of 360 g L^{-1} Ethephon and diluted the content in carrier water at 30°C to obtain 200 L solution at 12:30 pm. After that he went for lunch and started spraying this solution on plants at 2:30 pm. If decomposition by pathway I was predominant during this time, by what fraction did the concentration of Ethephon drop in the spray solution due to lunch break by the farmer?



Due to toxic effects of Ethephon by-products, there has been constant search for other plant growth regulators. Another such hormone being used is methyl jasmonate extracted from jasmine flower. It also promotes ripening, enhances the red color, and decreases the chlorophyll content in the apples. One of the routes to synthesize methyl jasmonate is detailed below.

The first step involves a reaction of the following diester with a base to yield a cyclic product **P**. **P** on isolation and subsequent reaction with the given alkyl halide gives the compound **Q**, following the reaction sequence given below:



3.7 Draw the structures of **P** and **Q**.



3.8 The formation of **P** will be favoured if the solution of starting material is (Mark **X** in the correct box)

i) concentrated

ii) dilute

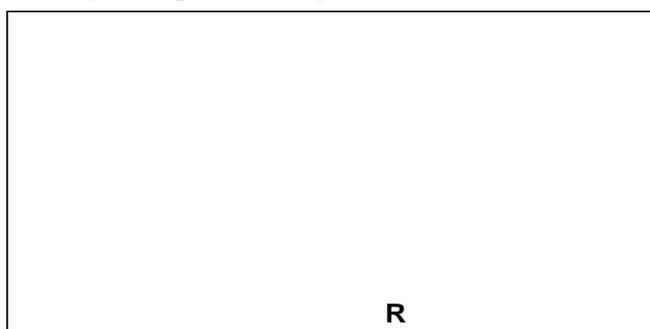
3.9 The most suitable solvent for conversion of **P** to **Q** is (Mark **X** in the correct box)

(i) N,N-dimethyl formamide

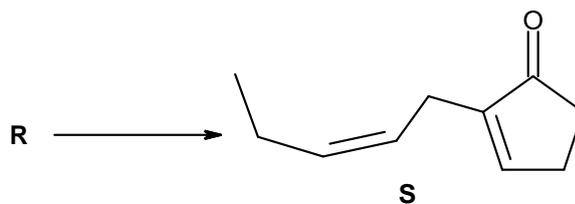
(ii) ethanol

(iii) n-hexane

3.10 **Q** on treatment with palladium acetate and triphenyl phosphine yields a compound **R** and, among other products, a gas which turns lime water milky. Draw the structure of **R**.



R is then converted to S.



3.11 The best reagent for converting R to S is (Mark X in the appropriate box)

a) $H_2 / 5\% Pd - CaCO_3$

b) $Na/C_2H_5OH + NH_3$

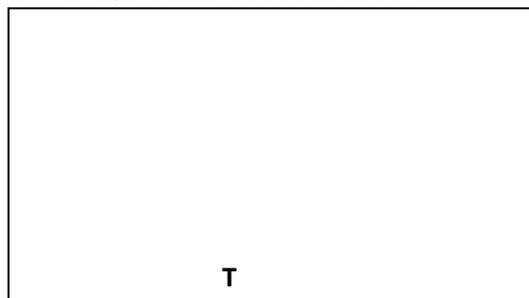
c) $LiAlH_4 / AlCl_3$

d) conc H_2SO_4

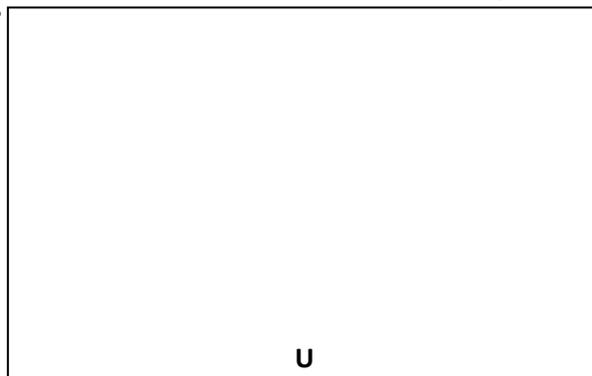
e) $NaOH/H_2O/ Heat$

f) Pyridinium Chlorochromate/ $Al_2O_3/Hexane$

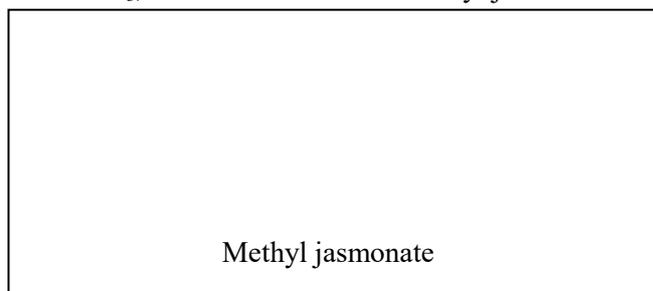
3.12 T is the other stereoisomer of S. Draw the structure of T.



3.13 S on treatment with the dimethyl malonate in sodium methoxide and methanol gives the addition product U. Draw the structure of U?



3.14 U is then mixed with 1 equivalent of adipic acid and heated at $190^\circ C$ for 6 hours. At the end, excess aqueous $NaHCO_3$ is added to the flask and shaken well. Then the aqueous portion is removed leaving behind a liquid in the flask from which the methyl jasmonate is obtained by distillation. The aqueous solution on evaporation gives sodium monomethyl adipate and $NaHCO_3$. Draw the structure of methyl jasmonate.



3.15 Write the number of the optical stereoisomers of methyl jasmonate (such that the configuration at the unsaturated bond is same as that in S).

Problem 4**13 marks****Water and Heat**

In this problem, we will try to estimate the impact of evaporation on temperature changes in a kitchen. Usually an important parameter related to air temperature is its relative humidity, which can be defined as

$$\text{Relative humidity} = \frac{\text{Amount of water vapour per unit volume of air}}{\text{Saturation vapour content per unit volume of air at that temperature}}$$

Saturation vapour content of air m_{sat} (in g per m³ of air) is a function of air temperature and is given by:

$$m_{\text{sat}} = 22 + 0.72 (T - 298)$$

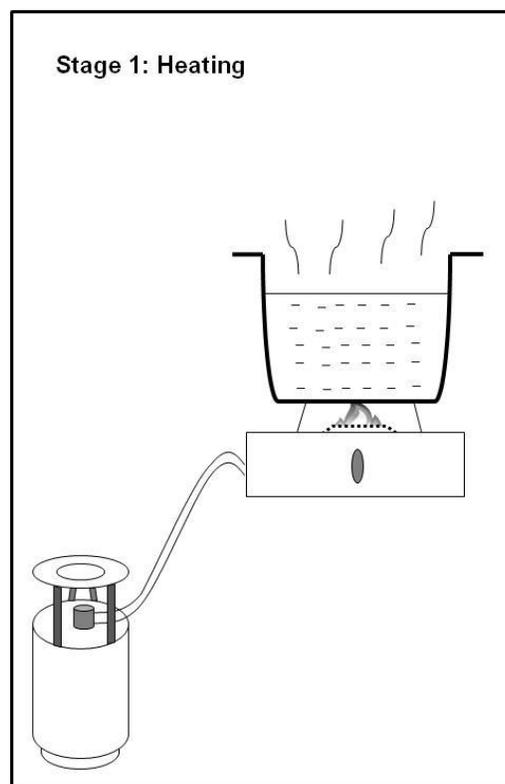
where T is the air temperature in K.

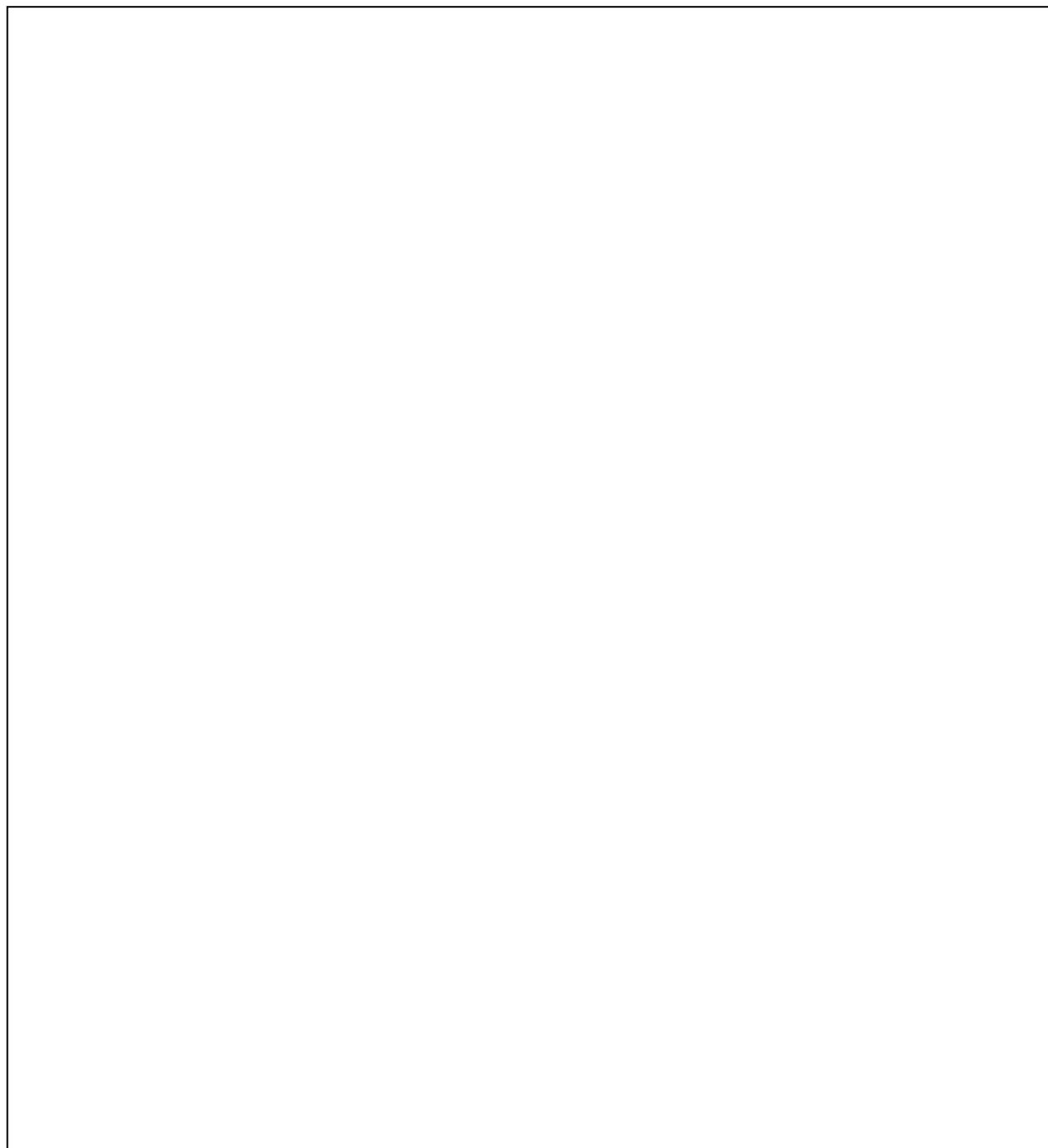
A kitchen has an air volume of 12.1 m³ and a LPG (predominantly butane) cylinder based stove. Consider the kitchen a closed system and assume kitchen walls, door and window as adiabatic. On a day, the kitchen air had a relative humidity of 13.0%, temperature of 25 °C and a pressure of 1 atm. In a steel vessel (heat capacity: 110 J K⁻¹), 1.800 kg of water was kept on flame for heating. When the water just started boiling, the gas flame was turned off. During this process, the mass of gas cylinder decreased by 15.2 g. When the temperature of water is changing (during heating or cooling), the amount of water that evaporates at any given temperature is variable. For simplicity, in this situation assume that whatever water evaporates in a process, it evaporates at the middle temperature of the starting and the final temperatures of that process.

Assume the following quantities to be constant over the temperature range involved in this problem.

- 1) Calorific value of butane = 49.1 kJ g⁻¹
- 2) Specific Heat of Water = 4.18 J g⁻¹K⁻¹
- 3) Latent Heat of Evaporation of water = 42.20 kJ mol⁻¹
- 4) For air (assuming to be ideal diatomic gas), $C_p = 5R/2$;
 $C_v = 7R/2$, where R is the universal gas constant

- 4.1** Consider Stage 1 to be the period of heating of water till the flame was just turned off. Assume that during this stage, there was negligible change in temperature and pressure of the kitchen air. Determine the increase in relative humidity of the air at the end of this stage, if all the heat released from flame was absorbed by the water-vessel system.

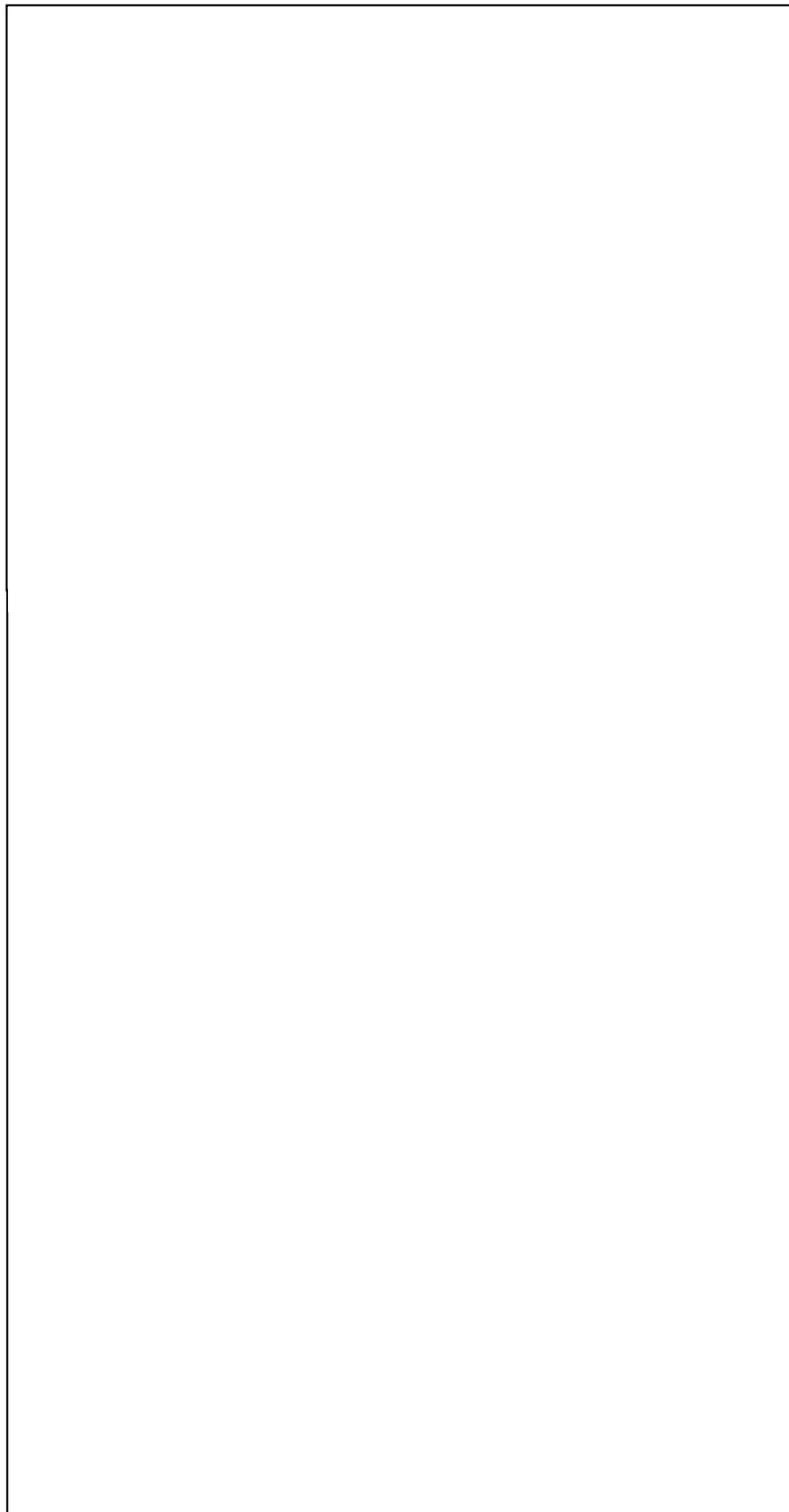




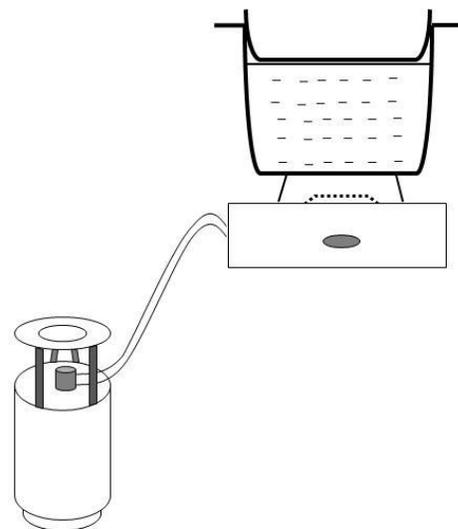
If you could not determine the increase in relative humidity in above question, take this value to be 50% for further questions in this problem.

- 4.2** Consider Stage 2 to be the period after the flame was just turned off. During this stage, the water starts cooling, which leads to heating of air. Determine the kitchen air temperature in K when the system reaches thermal equilibrium under the following two possibilities. Note: Starting point of both these possibilities is the end of Stage 1 (defined in **4.1**).

Possibility a) After switching off the flame, the water surface in the vessel was covered with a thin lid of negligible heat capacity and there was negligible air space in the container (thus assume no water evaporated during this phase).



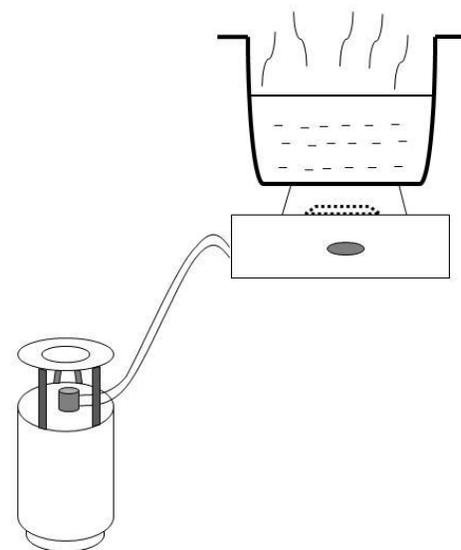
Stage 2 (possibility a):
Cooling without evaporation



Possibility b) If the vessel was kept open during cooling stage (hence, the water could evaporate).



Stage 2 (possibility b):
Cooling with evaporation



This problem shows that how important evaporation from hot foods is in controlling heating of surrounding air particularly in absence of air circulation.

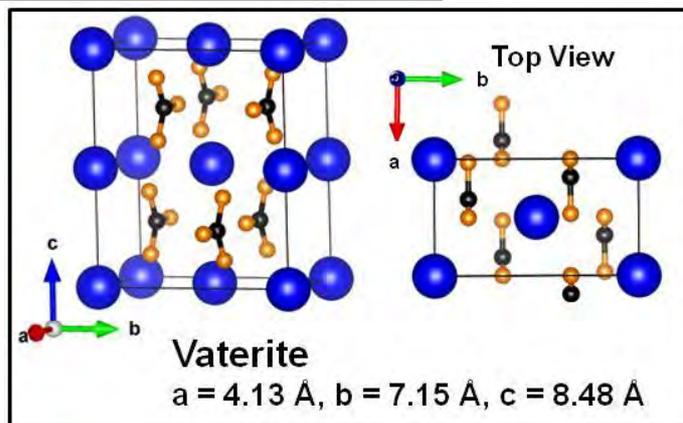
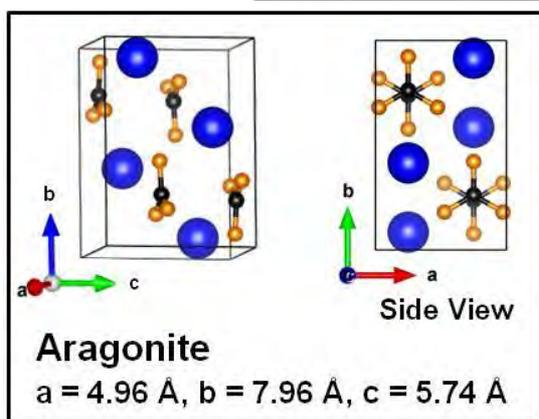
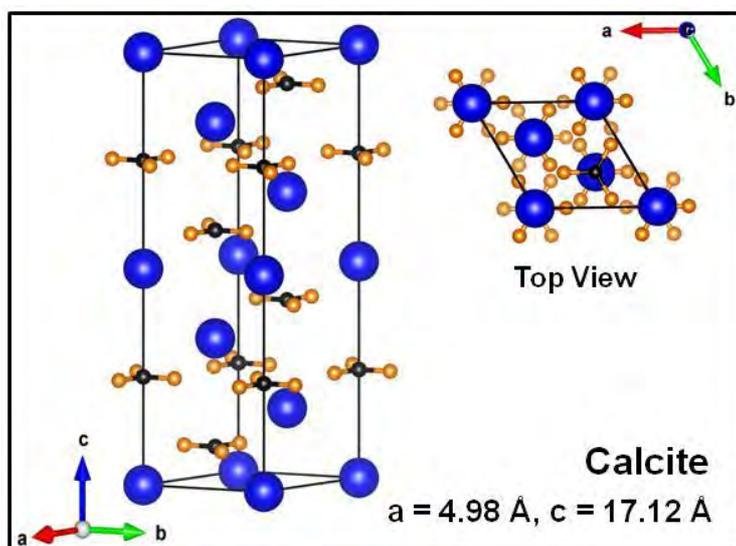
Problem 5

29 marks

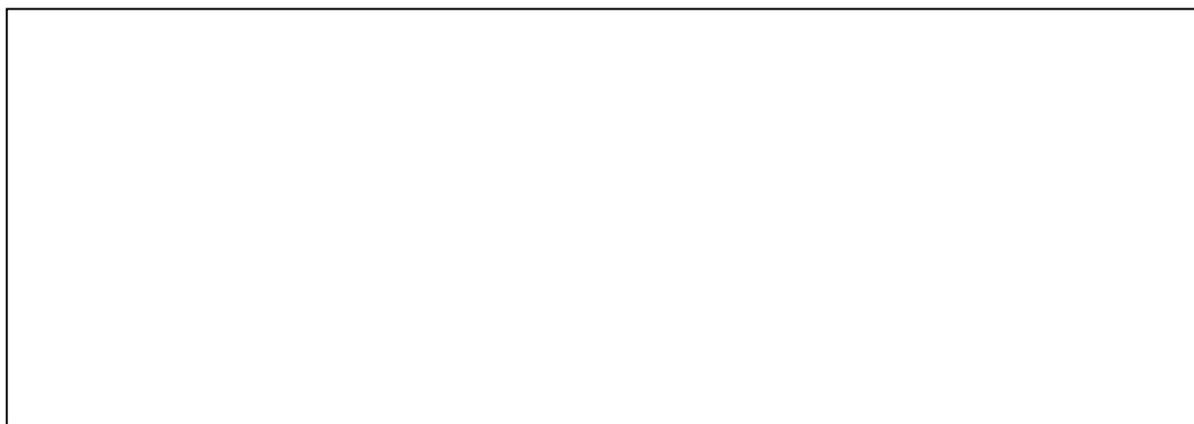
The different forms of Solid CaCO_3

CaCO_3 is one of the most common minerals in living & non-living natural world. In industries, it deposits in many systems due to presence of Ca^{2+} in waters and CO_2 in air. In all these systems, CaCO_3 is found in 6 different forms: one amorphous form, two hydrated crystalline forms and three anhydrous crystalline forms (Calcite, Aragonite and Vaterite) with different physico-chemical properties. Formation and dissolution conditions of these forms are very important to understand while dealing with these systems.

At STP, calcite is thermodynamically the most stable form. Calcite crystallizes in hexagonal structure. Aragonite and vaterite crystallize in orthorhombic structure. Following figures shows the unit cells of the three anhydrous crystalline forms: (Big balls indicate Ca^{2+} ions, small black and gray balls indicate C and O atoms, respectively.)



5.1 Density of aragonite = 2.93 g cm^{-3} . Calculate the densities (in g cm^{-3}) of calcite and vaterite.



5.2 Determine the % change in volume in a crystalline CaCO_3 sample as it undergoes the following transitions .

i) from calcite to aragonite

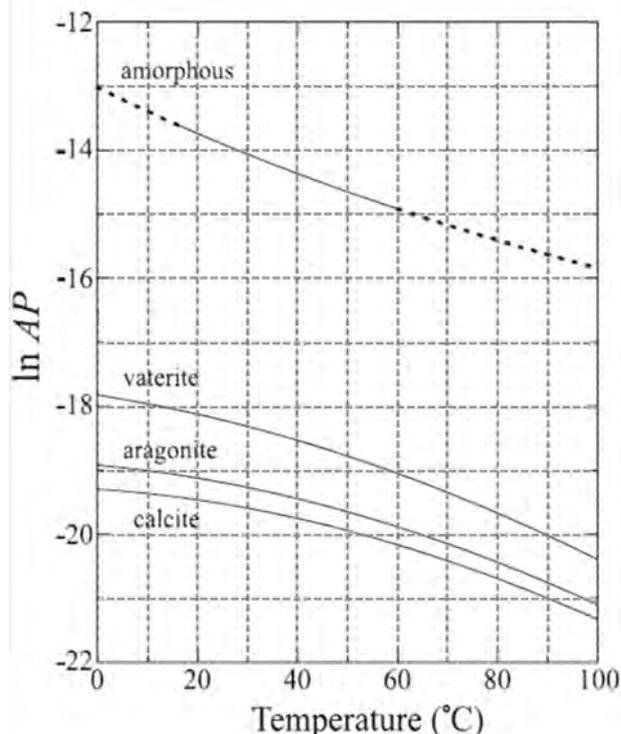
ii) from aragonite to vaterite

5.3 Based on above calculations, which anhydrous crystalline form can become more stable than calcite at higher pressures?

The three anhydrous crystalline forms have lower solubility in water than amorphous CaCO_3 . A plot of $\ln AP$ in solutions ($AP =$ product of activities of $\text{Ca}^{2+}(\text{aq})$ and $\text{CO}_3^{2-}(\text{aq})$ in solution) that are in equilibrium with the different solid forms of CaCO_3 at different temperatures is given here.

A sample of water was kept with calcite till equilibrium was reached. Then the supernatant was taken out in another container and was subjected to fast evaporation along with stirring at 25°C using suitable apparatus. Slow evaporation can lead to the formation of the crystalline phases before formation of amorphous phase.

5.4 After what percent reduction in water volume of the above supernatant (from calcite) at 25°C , would amorphous CaCO_3 start precipitating?



Adapted from J. Phys.: Condens. Matter **21** (2009) 425102 (6pp)



The crystalline forms under suitable temperature and pressure conditions can also directly interconvert into each other.

- 5.5** Calculate the change in the molar entropy of CaCO_3 during the transformation of aragonite to calcite at 25°C , given that the enthalpies of formation for calcite and aragonite are -1206.9 and $-1207.0 \text{ kJ mol}^{-1}$, respectively (determined by calorimetry).

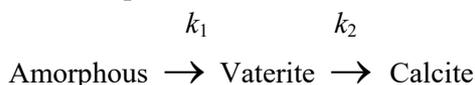


Though calcite is thermodynamically the most stable form of CaCO_3 , many natural materials (e.g. conch shells and mollusk's shells) have predominantly aragonite form. It has been observed that the presence of cations in solution whose ionic size is larger than that of Ca^{2+} favour formation of aragonite phase.

- 5.6** Based on the above hypothesis, identify which of the following ions would facilitate the formation of aragonite phase: Mg^{2+} , Sr^{2+} , Pb^{2+} , Mn^{2+} , Fe^{3+}



At a range of environmentally relevant temperatures ($7.5 - 25^\circ\text{C}$), particles of amorphous CaCO_3 rapidly dehydrate and crystallize to form particles of vaterite, which slowly transforms to calcite.



The second stage of the transformation is approximately 10 times slower than the first. The rate constant for vaterite to calcite transformation (k_2) at 10° C is $8.6 \times 10^{-5} \text{ s}^{-1}$. Assume no change in the solution that is in contact with the solid CaCO_3 during this time scale.

- 5.7 Assuming amorphous to calcite transformation as a sequence of consecutive unimolecular processes, calculate the mass percentages of amorphous and vaterite forms of the total CaCO_3 mass present after 30 min at 10 °C. Amount of vaterite $m_V(t)$ at a particular time t is given by,

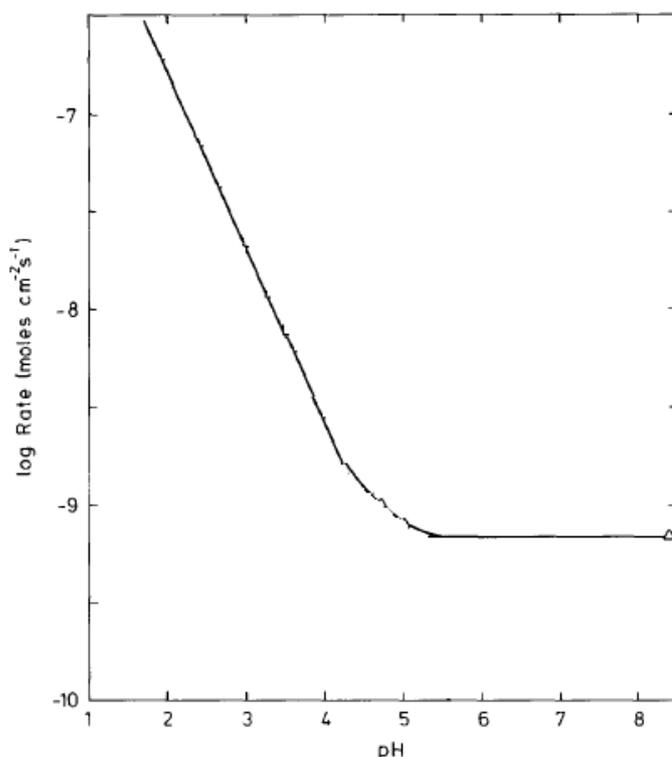
$$m_V(t) = \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) m_A(0)$$

where, k_1 is the rate constant for the formation of vaterite from amorphous form and $m_A(t)$ is the amount of amorphous form at time t .

- 5.8 If 1 kg of amorphous CaCO_3 had precipitated at $t = 0$, calculate (i) the time in which the maximum amount of vaterite would be observed, and (ii) the mass of this maximum amount of vaterite.

Dissolution of calcium carbonate

Scales of CaCO_3 are found in heated water boilers and pipelines. The hardest ones are due to calcite and aragonite forms. These can be removed by mechanically scrapping or chemically dissolving using acids and chelating agents such as EDTA (represented here as H_mY^{x-} , $m = 0-4$, $x = 4-0$). The pH dependence of the initial rate of calcite dissolution in solutions of different pH (prepared using HCl, water and NaOH) in inert atmosphere and under stirring conditions is shown below.

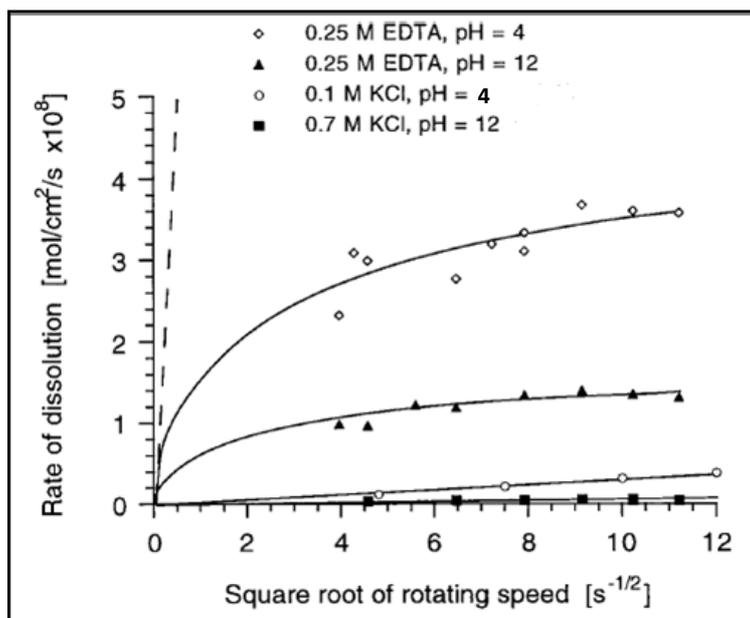


Adapted from Chemical Geology, 42 (1984) 119–136

5.9 Identify whether each of the following statements can be inferred / cannot be inferred about dissolution of calcite from the above graph (Mark **X** in the appropriate box).

		Yes	No
(i)	There is no dissolution of calcite in solutions with $\text{pH} > 5.3$.		
(ii)	Dissolution of calcite follows an overall zero order kinetics at $\text{pH} > 5.3$.		
(iii)	Dissolution of calcite follows an overall first order kinetics below $\text{pH} = 4.0$.		
(iv)	Dissolution of calcite follows a second order kinetics with respect to $[\text{H}^+]$ in the pH range $4.0 - 5.0$.		
(v)	Dissolution of calcite becomes faster with increasing solution pH .		
(vi)	H_2O also has a dissolution pathway for calcite independent of H^+ .		

The following graph shows the effect of EDTA and pH on initial rates of calcite dissolution with respect to the stirring rate (rotating speed) in inert atmosphere. The pH of the EDTA and KCl solutions were adjusted using HCl (aq.) and NaOH (aq.).



Adapted from Journal of Colloid and Interface Science 204(1998), 187–197.

Consider r_z , the initial rate of dissolution per unit surface area of calcite due to dissolving species Z with initial concentration $[Z]$ in the solution, to be given by $r_z = k_z [Z]$ where k_z is the rate constant of the dissolution reaction due to species Z . The pK_a values of EDTA are 2.0, 2.7, 6.2 and 10.3, respectively. Assume that

- the predominant species dissolving calcite in the given solutions are $H^+(aq)$ and $H_m Y^{x-}(aq)$ ($m = 0 - 4$, $x = 4 - 0$).
- the rates of dissolution due to multiple species in a given system are additive.
- at the given pH values, the predominant species of EDTA is present as almost 100% of the total EDTA concentration.

5.10 Determine the ratios of rate constants of dissolution due to $H_2Y^{2-}(aq)$, $Y^{4-}(aq)$ and $H^+(aq)$ by considering the appropriate rates of dissolution at the rotating speed of 100 s^{-1} .

5.11 The following table has some statements related to the different forms and dissolution kinetics of CaCO_3 . Choose the correct option for each pair of statements (from i - iv given below and mark **X** in the box):

- i. Statement **A** is correct and Statement **B** is wrong
- ii. Statement **A** is wrong and Statement **B** is correct
- iii. Both Statements **A** and **B** are correct and **B** is the reason for **A**
- iv. Both Statements **A** and **B** are correct and **B** is not the reason for **A**

		i	ii	iii	iv
a.	Statement A : The transformation of aragonite to calcite is a thermodynamically feasible process. Statement B : The transformation of aragonite to calcite is an enthalpy driven process.				
b.	Statement A : Dissolved CaCO_3 precipitates on the hotter regions of hot water pipes resulting in formation of scales. Statement B : The solubility of CaCO_3 decreases with increase in temperature.				
c.	Statement A : The rate of dissolution of per mole of calcite will be more if its particle size is small. Statement B : The rate of dissolution of calcite in acidic EDTA solution also depends on the ionic mobilities of $\text{H}^+(\text{aq})/\text{EDTA}(\text{aq})$ species.				

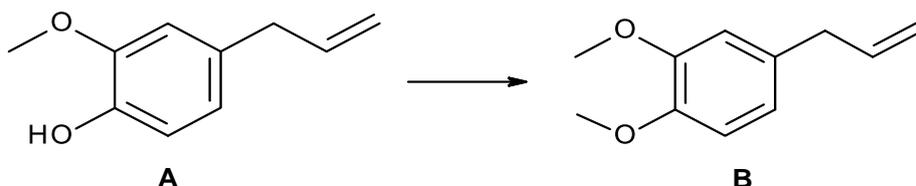
Problem 6

15 Marks

Derivatizing Eugenol

Eugenol (**A**) is a compound present in cloves, tulsi, and many other plants. It is used to darken the colour of natural henna on skin. It is used in foods, cosmetics and pharmaceuticals as antimicrobial, analgesic and antioxidant.

Eugenol can be easily converted to 1-allyl-3,4-dimethoxybenzene (**B**).

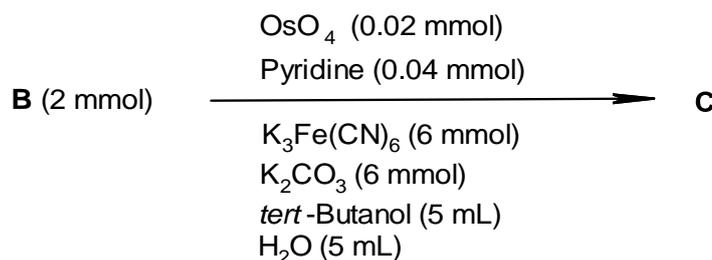


6.1 From the following sets of reagents, identify which can be used for this conversion of **A** to **B**. (Mark **X** in the correct box/es)

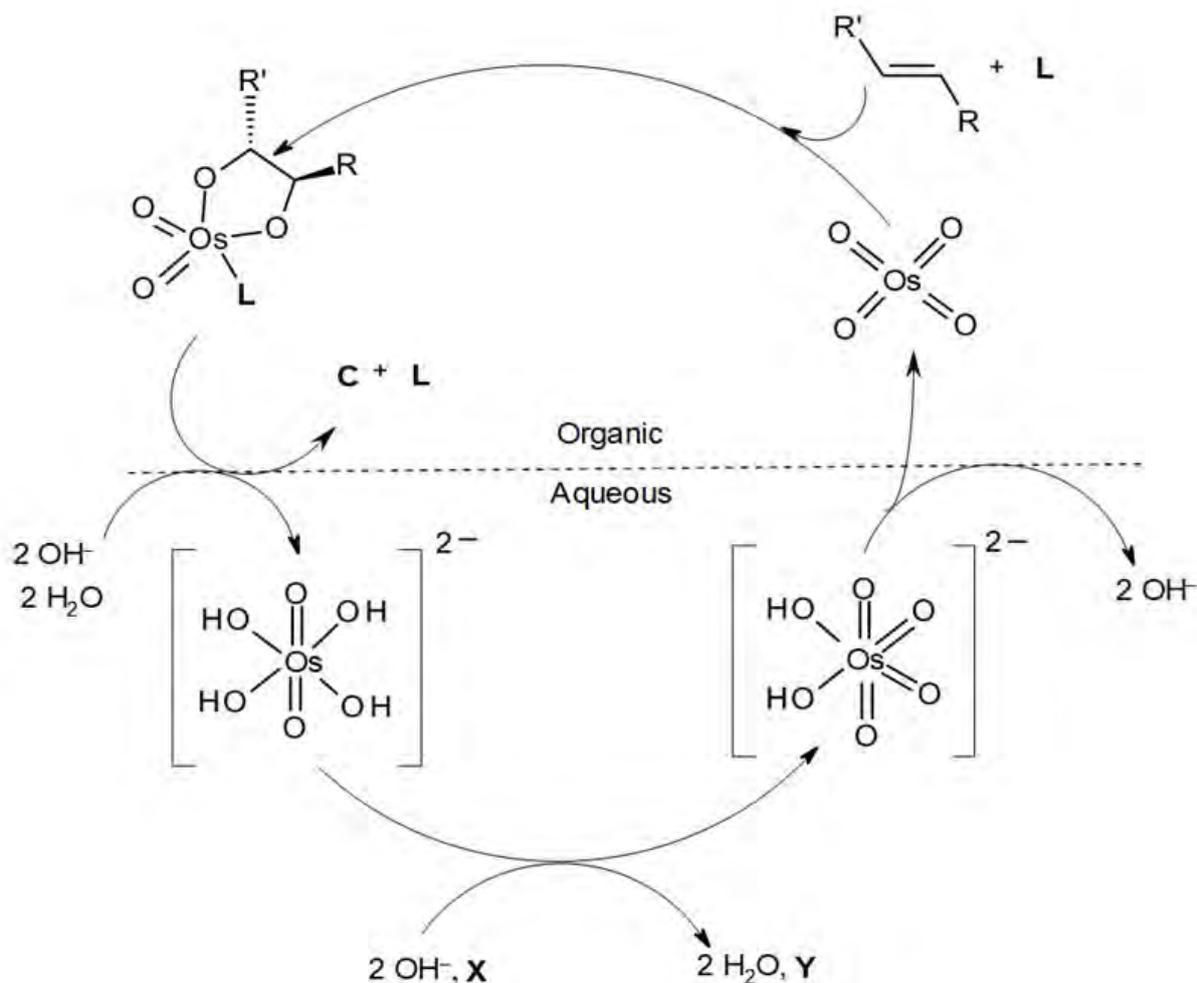
- | | | | | | |
|---|--------------------------|---|--------------------------|---|--------------------------|
| (a) $\text{CH}_3\text{I}/\text{K}_2\text{CO}_3$ | <input type="checkbox"/> | (b) $(\text{CH}_3)_2\text{SO}_4/\text{KOH}$ | <input type="checkbox"/> | (c) $\text{CH}_3\text{I}/\text{H}_2\text{SO}_4$ | <input type="checkbox"/> |
| (d) $\text{Me}_2\text{SO}/\text{KOH}$ | <input type="checkbox"/> | (e) $\text{Me}_2\text{S}/\text{H}_2\text{SO}_4$ | <input type="checkbox"/> | | |

Several derivatives of Eugenol have been studied and have been found to have useful pharmaceutical properties. Here we will look at methods of obtaining two such derivatives.

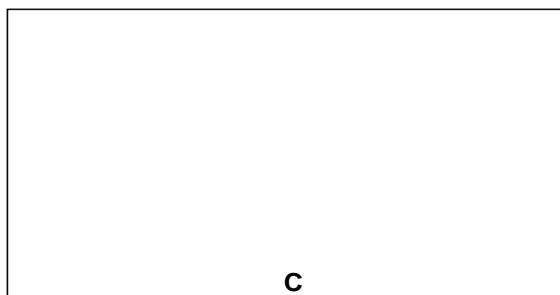
Compound **B** can be oxidized with molar equivalent amounts of OsO_4 in aqueous medium to yield **C**. However, toxicity and high cost of OsO_4 prevents its wider use despite high yield and selectivity. An different pathway was developed by an American chemist Barry Sharpless for the same transformation. This method uses fractional molar equivalents of OsO_4 (relative to the olefin) along with a few other reagents, listed on the arrow below.



The mixture is slightly turbid due to presence of small amount of non-aqueous phase in the system. A generic mechanism of this reaction is given below. **L** is a species which coordinates with the Os center facilitating the reaction, and **X** and **Y** are two other species in the reaction mixture.



6.2 i) Draw the structure of product C.



ii) The overall reaction $B \rightarrow C$ can be classified as (Mark **X** in the appropriate box(es)):

a) redox reaction

b) addition reaction

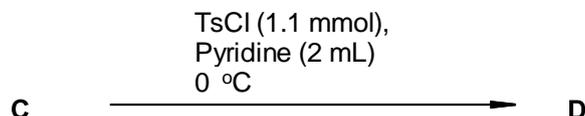
c) hydrolysis reaction

d) acid base reaction

iii) List the species (both ionic and non-ionic) that will exist in the reaction flask at the end of reaction, other than the following: H_2O , H^+ , OH^- , product C

When the product **C** is treated with *p*-toluene sulfonyl chloride using the following procedure, a monoester **D** is produced as the single main product.

Step I: To a solution of compound **C** (1 mmol) in pyridine (2 mL), *p*-toluenesulfonyl chloride (TsCl, 1.1 mmol) was added at 0°C. The reaction mixture was stirred at 0°C (for about 20-30 min) till the compound **C** was no more detected (using chromatography).

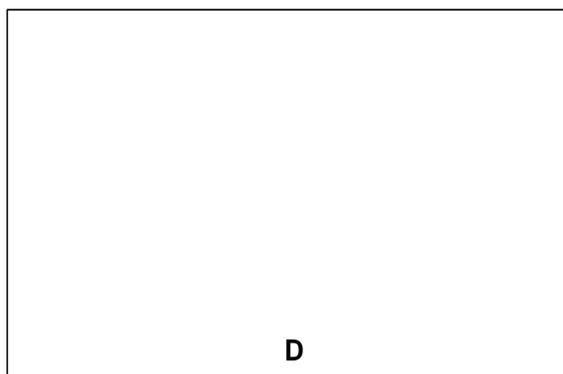


Step II: Water (10 mL) was added to the reaction mixture followed by diethyl ether (5 mL), which led to formation of two layers in the reaction flask.

Step III: The ether layer was separated using a separating funnel. This ether solution was treated multiple times with 5% aq HCl (10 mL), followed by removal of the acidic layer.

Step IV: Finally, the ether layer was washed with 10% NaHCO₃ (aq) and then treated with anhydrous sodium sulphate (to remove water from the solution). The solvent was evaporated to produce **D** as the single product.

6.3 Write the structure of **D**.



6.4 Which compound(s) were removed from the organic layer by using (i) water and (ii) HCl solution?

(i)

(ii)

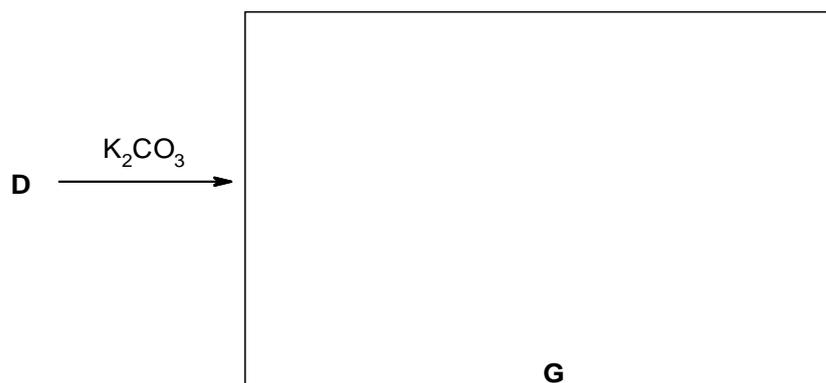
However, while carrying out the above procedure, a chemist forgot to treat the mixture with water in **Step II** and proceeded by adding diethyl ether, and then followed by **Steps III** and **IV**. The chemist identified two compounds **E** & **F** in the ether medium.

6.5 Identify **E** & **F**



When compound **D** is treated with solid K_2CO_3 , compound **G** is formed.

6.6 Draw the structure of compound **G**.



Rough Page

Rough Page

Rough Page