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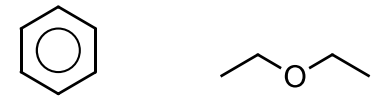
TJC Paper 2 Answers

1 Planning (P)

(i) Which of the following two organic solvents would be a good choice to dissolve crude γ-butyrolactone to perform a liquid-liquid extraction? Explain your answer.



benzene diethyl ether

• **Diethyl ether**

γ-butyrolactone is •polar with the presence of electronegative O atom and is able to form permanent dipole-permanent dipole interactions (pd-pd) with polar diethyl ether

(ii) One common mistake when performing a liquid-liquid extraction is to mix-up the layers and hence the organic product would be lost in the discarded layer.

Using the following data in the table,

Solvent	Density (g cm^{-3})
Benzene	0.877
Diethyl ether	0.713
Water	1.000

Identify if the organic solvent identified in (i) would be the upper or lower layer? Explain your answer.

• **Upper layer.**

Diethyl ether is less dense (ρ = 0.713 g cm^{-3}) than water (ρ = 1.000 g cm^{-3}). Therefore, diethyl ether will be the upper layer and water will be the bottom layer.

(iii) The experimental procedures of the purification of crude γ-butyrolactone via liquid-liquid extraction is described below:

1. Dissolve the crude γ-butyrolactone in 30 cm^3 of the organic solvent.
2. Cool the flask in an ice bath and then add 20 cm^3 of 6 mol dm^{-3} hydrochloric acid dropwise, while stirring, to quench the reaction.
3. Place the reaction mixture in a separating funnel and separate the aqueous layer from the organic layer. Reject the aqueous layer.
4. Add about half its volume of **chemical reagent A.** Shake the reaction mixture in the separating funnel cautiously, releasing the pressure at intervals.
5. Transfer the organic layer into a conical flask and add some **chemical reagent B**. Filter off **chemical reagent B** and evaporate the solvent at room temperature.

State the identities of chemical reagents **A** and **B**, explaining the role each plays in

the experimental procedures 4 and 5.

[5]

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Chemical reagent **A**:

- **Chemical reagent A – aqueous sodium carbonate**

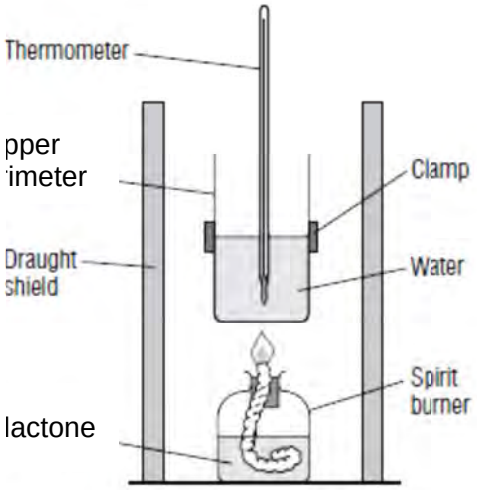
It is to react with excess aqueous hydrochloric acid present to quench the reaction. Carbon dioxide will be released and it is essential to release the pressure to prevent building up of the internal pressure in the separating funnel.

Chemical reagent **B**:

- **Chemical reagent B – anhydrous $MgSO_4$/ $NaSO_4$/ $CaCl_2$/ $CaSO_4$.**

It is to dry the organic layer containing γ-butyrolactone by removing traces of water.

(b) The following experimental set-up can be used to design an experiment to determine the enthalpy change of combustion of γ-butyrolactone.



You are to plan a step-by-step method to determine the enthalpy change of combustion, ΔH_c, under laboratory conditions, of γ -butyrolactone. You should use the apparatus in the diagram above and any apparatus required that is normally found in a school laboratory.

Your method should cover the following points:

1. appropriate quantities to be used in the experimental procedures
2. how the raw data is to be recorded
3. how this data is to be processed to determine the enthalpy change of combustion of γ -butyrolactone

Given:

1) Specific heat capacity of copper calorimeter = 0.385 J g^{-1} K^{-1}
2) 4.2 J of heat is needed to raise the temperature of 1 cm^3 (1 g) of water by 1 ^oC.

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Experimental Procedures:

Experimental procedures:

1. **Weigh the empty copper calorimeter using an electronic balance.**
2. **Using a burette, add 50.00 cm^3 of distilled water into the calorimeter. Cover it with a lid and place a thermometer in it. Clamp the flask at a suitable height so that the spirit burner can be placed below easily.**
3. **Record the initial temperature of the distilled water.**
4. **Fill the spirit burner with γ-butyrolactone**
5. **Weigh the spirit burner (and lid) containing γ-butyrolactone and record the mass.**
6. **Place the spirit burner about 1 cm under the copper calorimeter, and light the wick. After observing that the temperature has risen for 10 °C [fixed temperature rise], record the final temperature and extinguish the flame.**
7. **Cool the experimental set-up and reweigh the spirit burner and cap.**
8. **Calculate the mass of γ-butyrolactone used.**

Recording of raw data:

Processing of raw data:

Mass of calorimeter / g	**m_1**
Mass of spirit burner before combustion / g	**m_2**
Mass of spirit burner after combustion / g	**m_3**
Mass of γ-butyrolactone used for combustion / g	**(m_2 - m_3)**

Initial temperature of water / °C	**T_1**
Final temperature of water / °C	**T_2**

Analysis of raw data:

M_r of γ-butyrolactone = 4(12) + 6 + 2(16) = 86

Quantity of heat produced in combustion = heat absorbed by the water + heat absorbed by the copper calorimeter

Q = [50 x 4.2 x (T_2 - T_1)] + [m_1 x 0.385 x (T_2 – T_1)] J

$$\Delta H_c = - \frac{[50 \times 4.2 \times (T_2 - T_1)] + [m_1 \times 0.385 \times (T_2 - T_1)]}{\frac{m_2 - m_3}{86}}$$ **J mol^{-1}**

- **logical, coherent steps/measurements that would lead to fruitful results**
- **appropriate choice of apparatus**
- **tables with clear headings and units**
- **calculation of quantity of heat produced during combustion**

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• calculation of ΔH_c

(c) Upon analysis of his raw data, the research student obtained a value less than the literature value of –2010 kJ mol^{-1}.

(i) Other than heat loss to the surrounding, suggest another reason to explain his observation, explaining your answer clearly.

[2]

• Combustion of the crude γ-butyrolactone could be incomplete.

•Reason: The draught shield used for minimising heat loss to the surrounding could have blocked the constant air supply, resulting in incomplete combustion and lesser amount of heat evolved from the incomplete combustion.

OR

•Some of the γ-butyrolactone may have vaporised.

•Reason: This would result in a smaller final total mass of spirit burner and γ-butyrolactone measured. Thus the mass of γ-butyrolactone combusted determined (m_2 – m_3 calculated) is larger than actual values, and a less exothermic ΔH_c would be calculated.

[Total: 12]

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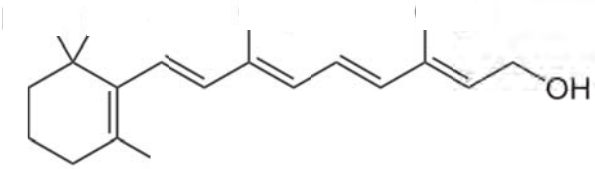
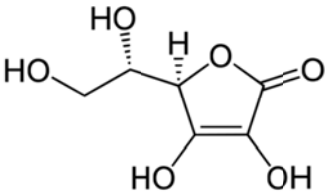
2 This question is about the applications of solubility in nutrition and pharmaceutics.

(a) Vitamins are an important part of daily nutrition. Vitamins soluble in lipids are able to be stored within the body, but water-soluble vitamins are not stored and need replacement every day. The structures of two vitamins are shown below.



Vitamin A



Vitamin C

In terms of structure and bonding, discuss whether vitamins A and C can be stored in the body or need daily replacement. You may assume lipids to be non-polar solvents.

●Vitamin C needs daily replacement while vitamin A can be stored in the body.

●●Both vitamins are simple covalent/discrete molecules. Vitamin A has hydrogen bonding but mainly van der Waals' forces between its molecules due to a large alkyl group bonded to the –OH, while Vitamin C has mainly hydrogen bonding between its molecules due to many –OH groups in the molecule.

●Vitamin C is water-soluble as it is capable of forming multiple hydrogen bonds with water, and the energy released from the hydrogen bonds formed between vitamin C and water is enough to overcome the hydrogen bonds between vitamin C molecules and between water molecules.

●Vitamin A is soluble in lipids as it is capable of forming strong van der Waals' forces of attraction with lipids (non-polar), and the energy released from the van der Waals' forces formed between vitamin A and fat is enough to overcome the van der Waals' forces between vitamin A molecules and between lipid molecules.

[5]

(b) Proteins are necessary in the human diet, as they are an important source of amino acids via digestion. Amino acids are generally soluble in water and crucial to many biological processes in the body. At varying pH, the net charge of a protein molecule is the arithmetic average of all charges, and each protein has an isoelectric point. This isoelectric point is dependent on the exact amino acid sequence and the number of acidic and basic R-groups present in it.

(i) In terms of structure and bonding, explain why amino acids are generally soluble in water.

●Amino acids exist as zwitterions, and are held in a crystalline lattice through ionic bonds.

●The energy released when ion-dipole interactions are formed between zwitterions and water is enough to overcome the ionic bonds between zwitterions and the hydrogen bonds between water molecules.

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(ii) With reference to an amino acid, explain what is meant by the term *isoelectric point*.

●It is the pH at which an amino acid exists as electrically neutral zwitterions.

(iii) Proteins tend to coagulate near to or at their respective isoelectric points. For instance, in milk, casein (a type of protein) clumps together and precipitates as it reaches its isoelectric point of 4.6 and forms curd. However, proteins generally do not coagulate at extreme pH, remaining soluble and discrete. Explain this phenomenon with reference to the casein in milk at a pH of 4.6 and 1.

●At pH of 4.6, there is no net charge on casein because there is an equal number of positively charged and negatively charged R-groups.

●Many ionic bonds will be formed between oppositely charged R-groups belonging to different casein strands, and coagulation occurs.

●However, at a pH of 1, it is extremely acidic, and all / most of the R-groups will be protonated. The net charge on casein will become very positive. There is electrostatic repulsion between casein strands, and they do not coagulate.

[6]

(c) Calcium is best known for its role in bone health. It is common to increase calcium intake by consuming calcium supplements, which usually contain calcium carbonate extracted from oyster shells. However, calcium citrate is an increasingly common replacement for calcium carbonate, because calcium citrate does not have any reaction with stomach acid that would cause discomfort, unlike calcium carbonate.

(i) Suggest a reason why consumption of calcium carbonate causes discomfort in the stomach.

●The reaction of acid on calcium carbonate would produce carbon dioxide gas, causing bloating.

OR The heat released from the reaction of acid on calcium carbonate may cause pain.

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(ii) Calcium is absorbed only in the intestines and when it is a free aqueous Ca^{2+} ion. The upper part of the small intestines has a pH of about 4 to 5 due to the presence of some stomach acid, and the pH increases throughout until about 8 to 9 at the end of the small intestines.

Deduce how the absorption of calcium will likely vary with pH.

●The absorption of calcium is likely highest at the start when the pH is low, and absorption decreases with increasing pH.

●When the pH increases, there is an increase in the concentration of the hydroxide ion. Precipitation of calcium hydroxide increases and absorption decreases as there are less free aqueous Ca^{2+} ions.

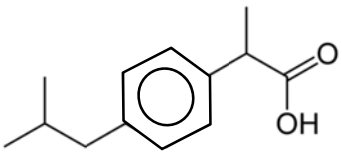
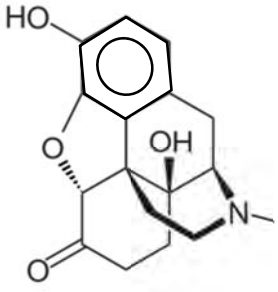
[3]

(d) In pharmaceutics, an important aspect of a drug is how it is absorbed into the human body, which is related to its lipophilicity, i.e. its ability to dissolve in non-polar solvents such as lipids. Lipophilicity of a compound can be measured by its log*P* value, which is defined as:

$$\log P = \log_{10}\left(\frac{[\text{solute}]_{\text{octanol}}}{[\text{solute}]_{\text{water}}}\right)$$

Octanol is considered non-polar and is immiscible with water. Usually, in order to calculate log*P*, a compound (solute) is dissolved in an octanol-water mixture and shaken vigorously, after which its concentration in each layer is determined.

Ibuprofen and oxymorphone are both analgesics, i.e. painkillers. The following table contains data about these two drugs.

	ibuprofen	oxymorphone
Structure		
Relative molecular mass	206	301
Solubility in water	1 mg cm^{-3}	250 mg cm^{-3}
log*P*	?	0.98

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(i) In an experiment where a mixture comprising 100 cm^3 of octanol and 100 cm^3 of water was shaken with ibuprofen, it was found that a total of 30.3 g of ibuprofen dissolved in the mixture.

Using this information and the data given above, determine the log*P* value for ibuprofen.

Mass of ibuprofen dissolved in 100 cm^3 water = 0.001 x 100 = 0.100 g

Mass of ibuprofen dissolved in 100 cm^3 octanol = 30.3 – 0.100 = ●30.2 g

$$\log P = \log_{10}\left(\frac{[\text{ibuprofen}]_{\text{octanol}}}{[\text{ibuprofen}]_{\text{water}}}\right) = \log_{10}\left(\frac{\frac{30.2}{206 (0.100)}}{\frac{0.1}{206 (0.100)}}\right)$$

$$= ●2.48$$

log*P* value of ibuprofen: .....

(ii) Drugs meant for topical use, i.e. applied onto the skin, need to have high skin permeability. One pathway of delivery of the drug requires it to penetrate the lipid matrix beneath the skin, for which a higher degree of lipophilicity is necessary.

Using the log*P* value calculated in **(d)(i)** and the data given above, state and explain whether ibuprofen or oxymorphone is more suitable for topical use.

Answers for this part question will be marked based on candidate's answer for (d)(i). (ECF was given, as long as the higher log*P* value was selected.)

●Ibuprofen is more suitable.

●A higher degree of lipophilicity means that it is more soluble in non-polar solvents (lipids) compared to water. Hence the drug with the higher log*P* is more suitable.

(iii) Deduce how a high pH may affect the log*P* of ibuprofen.

●A high pH will deprotonate ibuprofen and cause it to become an anion.

●This increases its solubility in water and cause $[ibuprofen]_{water}$ to increase and $[ibuprofen]_{octanol}$ to decrease. Hence log*P* value will decrease.

[6]

[Total: 20]

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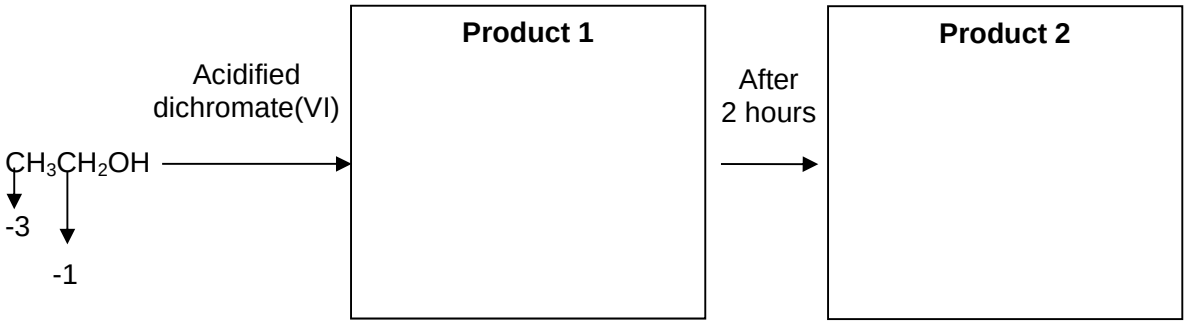
3 (a) Use of *Data Booklet* is relevant to this question.

Ethanol undergoes oxidation with acidified dichromate(VI) under different conditions to produce different products. The oxidation state of the carbon atoms in ethanol are indicated below.



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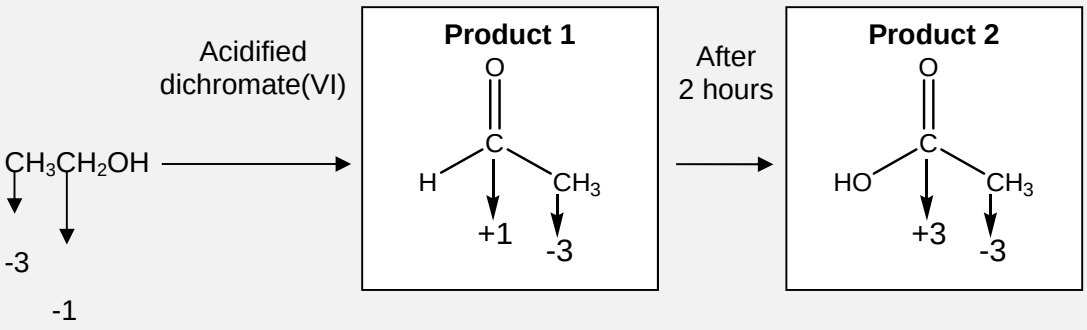

- **1 mark for both structures**
- **1 mark for all 4 O.S. states of C that are clearly labeled**

(i) Draw the structures of the possible products formed. Label the oxidation states of all the carbon atoms in your structures.

(ii) In an experiment, it was found that 0.2 mol of acidified dichromate(VI) reacted with 0.3 mol of ethanol. Using your answer in **(a)(i)**, deduce the product formed from the reaction.

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$2Cr_2O_7^{2-} \equiv 3CH_3CH_2OH$

3 mol of CH_3CH_2OH lose 12 mol of electrons

1 mol of CH_3CH_2OH lose 4 mol of electrons

O.S. of C of product = +3

- **Hence the product formed is CH_3COOH**

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(iii) Hence, construct a balanced ionic equation for the reaction in **(a)(ii)**.

$CH_3CH_2OH + H_2O \rightarrow CH_3COOH + 4H^+ + 4e^-$ x 3

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ x 2

$2Cr_2O_7^{2-} + 28H^+ + 3CH_3CH_2OH + 3H_2O \rightarrow 3CH_3COOH + 12H^+ + 4Cr^{3+} + 14H_2O$

● $2Cr_2O_7^{2-} + 16H^+ + 3CH_3CH_2OH \rightarrow 3CH_3COOH + 4Cr^{3+} + 11H_2O$

[4]

(b) Isotopes are first founded by J. J Thompson in 1913. Variation of isotopes of carbon, nitrogen and oxygen has a wide range of application. One use is the use of isotope tracers to determine structures.

(i) Oxygen-18, ^{18}O, which is an isotope of the naturally occurring oxygen-16, ^{16}O, is one such isotope used as a tracer for organic compounds.

The table below shows the relative abundance of the oxygen isotopes.

Relative Isotopic Mass	Abundance
16	99.757
17	0.038
18	0.205

Calculate the relative atomic mass of oxygen. Leave your answers to 3 decimal places.

● relative atomic mass of oxygen $= \frac{(16 \times 99.757) + (17 \times 0.038) + (18 \times 0.205)}{100}$

$= 16.004$

(ii) Would you expect the atomic radius of ^{16}O and ^{18}O to differ? ....**No**.....

Explain.

● Isotopes have same number of electrons and protons and different number of neutrons. Since both are isoelectronic and the nuclear charge (no. of protons) is the same, the atomic radius of both atoms should be the same.

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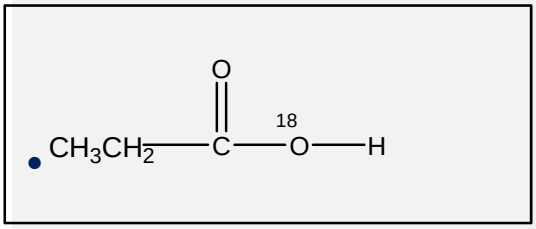
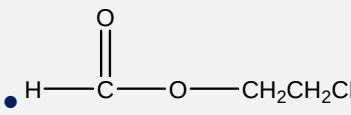
(iii) In order to study the mechanism of organic reactions, tracer studies using isotopes can be used. ^{18}O in water can be used to understand the hydrolysis of esters.

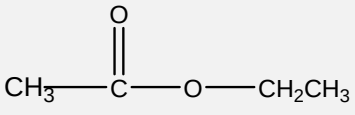
Draw the structures of the two products formed when methylpropanoate is hydrolysed with $H_2{}^{18}O$ in an acidic medium. Label the ^{18}O isotope clearly.

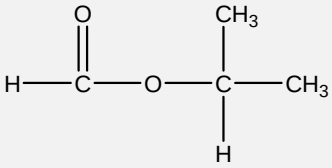


CH_3OH

(iv) Draw all the possible structural isomers of esters with the same molecular formula as methylpropanoate.

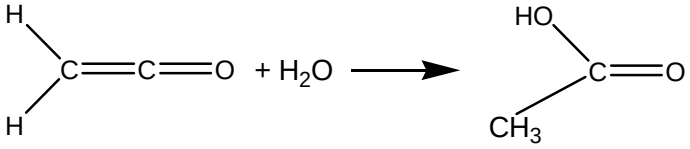






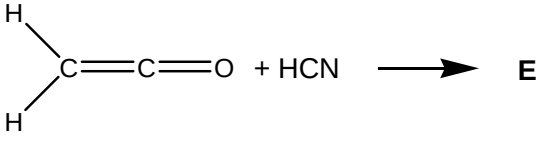
[4]

(c) Ketene is a reactive compound that undergoes addition reaction as shown below

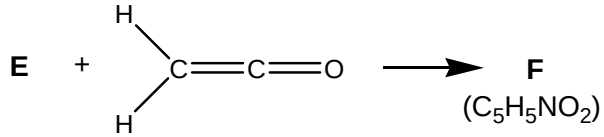


Compound **F** is an ester formed via a two-step process.

Step 1:



Step 2:



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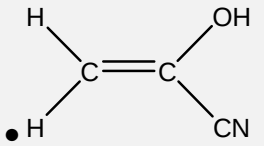
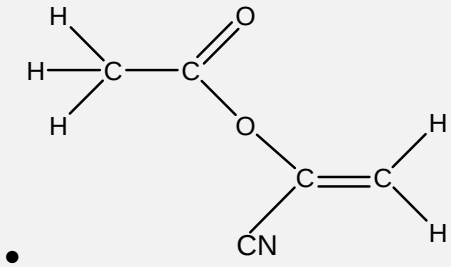
The first step involves an addition reaction to form the cyanohydrin intermediate.

Suggest the structure of compound **E** and **F**.

Compound **E**



Compound **F**



[2]

[Total: 10]

For Examiner's Use

4 (a) When heated in chlorine, aluminium and phosphorous form chlorides.

Describe the reactions, if any, of the chlorides with water, suggesting the pH of the resulting solution and writing equations where appropriate.

[5]

•$AlCl_3$ undergoes hydration in water and dissolves to give an aqueous solution.

$AlCl_3 + 6H_2O \longrightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$

•Hydrolysis also occurs due to the high charge density of Al^{3+} ions. It polarizes the water molecule and weakens the O-H bond of water making it easier for a H^+ ion to leave the water molecule. An acidic solution of pH = 3 is obtained.

$[Al(H_2O)_6]^{3+} \rightleftharpoons [Al(H_2O)_5OH]^{2+} + H^+$

•PCl_5 undergoes hydrolysis due to energetically accessible vacant 3d orbitals for dative bonding with water. It forms strongly acidic solution, pH = 1

$PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$

• Both pH values correct (1m)

(b) There is said to be a diagonal relationship between elements of the second and third periods of the Periodic Table exemplified by beryllium and aluminium where they exhibit similar chemical properties.

Using the diagonal relationship between beryllium and aluminium, describe, with the aid of an equation, what would be observed when a few drops of water is added to solid $BeCl_2$.

[2]

•Vigorous reaction with white fumes of HCl observed.

•$BeCl_2 + 2H_2O \longrightarrow Be(OH)_2 + 2HCl$

(c) Boron and silicon also show a diagonal relationship. For example, both BCl_3 and $SiCl_4$ are readily hydrolysed by water.

(i) By analogy with the reaction of $SiCl_4$, suggest a balanced equation for the hydrolysis of BCl_3.

•$BCl_3 + 3H_2O \longrightarrow B(OH)_3 + 3HCl$

(ii) Explain why BCl_3 can undergo hydrolysis like $SiCl_4$. [2]

•The B atom in BCl_3 has vacant 2p orbital to accept the lone pair of electrons from oxygen of water to form a dative bond. Thus BCl_3 can undergo hydrolysis.

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(d) Another pair of elements that show diagonal relationship is nitrogen and sulfur. One of the most readily prepared sulfur nitrides is S_4N_4, which can be made by passing dry $NH_3(g)$ into a solution of SCl_2 in an organic solvent.

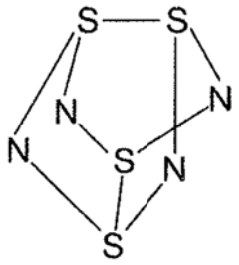
The reactants react in a ratio of 8 : 3, and sulfur and ammonium chloride are produced.

(i) Construct a balanced equation for this reaction.

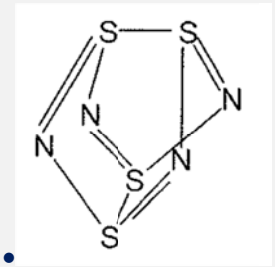
•$6SCl_2 + 16NH_3 \longrightarrow 2S + 12NH_4Cl + S_4N_4$

The shape of the molecule of S_4N_4 is described as follows.

* The four N atoms are in a plane.
* All the N atoms have an octet configuration.
* There are two S atoms above the plane, and two S atoms below the plane.
* All the S atoms are in equivalent environment to each other.
* The single lines represent the atoms that are bonded to each other. These do not necessarily represent single bonds between those atoms.



(ii) Using the information given about the structure of S_4N_4, draw the pi bonds in the diagram above.



(iii) State the oxidation state of S in S_4N_4.

oxidation state of S in S_4N_4: .....

•Oxidation state : +3

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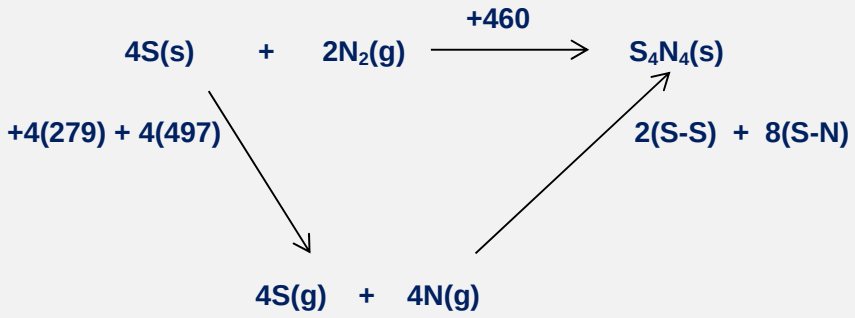
(iv) Construct a suitable energy cycle to calculate the average S-N bond energy in S_4N_4, using the following data.

$\Delta H_f^{\theta}(S_4N_4)$ = +460 kJ mol^{-1}
ΔH_{at}^{θ}(sulfur) = +279 kJ mol^{-1}
ΔH_{at}^{θ}(nitrogen) = +497 kJ mol^{-1}
(S-S) bond energy in S_4N_4 = +204 kJ mol^{-1}

[6]



•Using Hess' Law,

460 = 4(279) + 4(497) + 2(S-S) + 8(S-N)
460 = 4(279) + 4(497) + 2(–204) – 8(S-N)

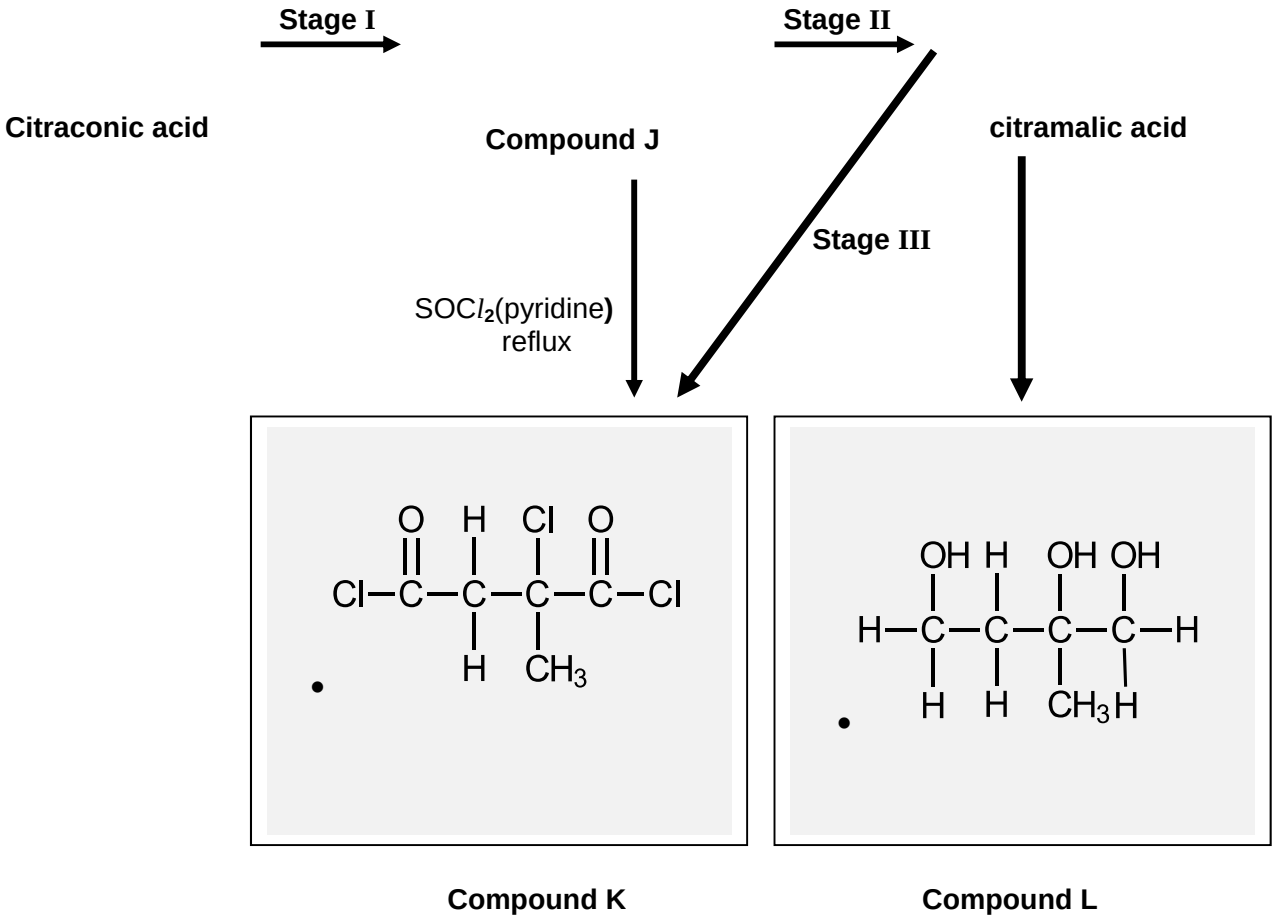
•Average S-N bond energy = 280 kJ mol^{-1}
• cycle

[Total: 15]

For Examiner's Use

5 Citraconic acid is one of several isomeric carboxylic acids obtained from citric acid. Studies showed that citraconic acid was involved in vitamin B12 synthesis.

(a) Citraaconic acid can be converted into citramalic acid by the following scheme:



(i) State the functional groups present in citramalic acid.

•**Carboxylic acid and** •**tertiary alcohol**

(ii) State the reagents and conditions needed for Stages **I**, **II** and **III**.

	Reagents and Conditions
Stage **I**	•**HCl(g), room temperature**
Stage **II**	•**NaOH(aq), reflux, followed by H_2SO_4(aq)**

Stage **III**	•**PCl_5(s), cold**

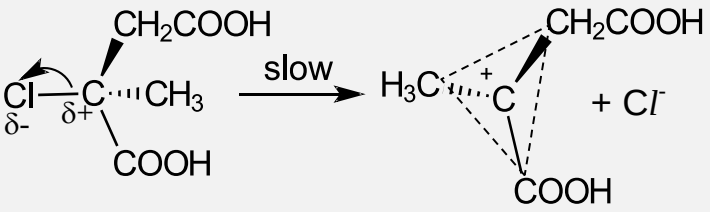
For Examiner's Use

(iii) Draw the structures of the organic compounds **K** and **L** in the boxes in the scheme.

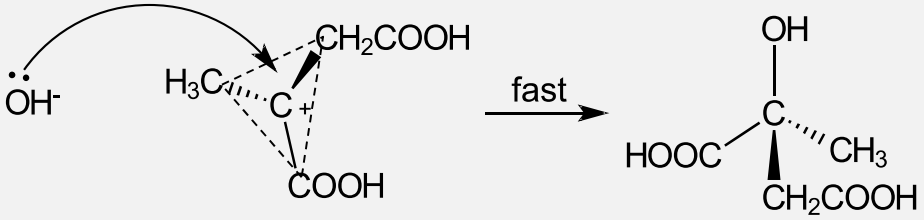
(iv) Name and describe the mechanism involved in Stage **II**.

•**Name of mechanism: Nucleophilic substitution (S_N1)**

•**Step 1:**



•**Step 2:**



(v) In view of the mechanism describe in **(iv)**, explain if the citramalic acid formed in Stage **II** is optically active.

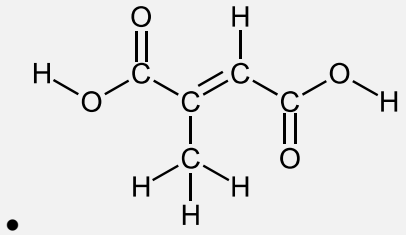
[12]

- ✓ **Citramalic acid formed from Stage II is a racemic mixture, hence it is optically inactive.**
- ✓ **The positively-charged carbon atom has a trigonal planar shape, thus, the nucleophile, OH^- ion, can attack from either the top or bottom of the plane with equal probabilities, resulting in the formation of equal amount of each enantiomer.**
  Since equal amount of each enantiomers are formed, a racemic mixture which is optically inactive is formed.

For Examiner's Use

(b) Mesaconic acid is a stereoisomer of citraconic acid.

(i) Draw the displayed structure of mesaconic acid.



(ii) Suggest a simple test to differentiate between citraconic acid and mesaconic acid. Explain the basis of your test.

[3]

- **Melting point test**
- **Due to the presence of intra-molecular hydrogen bonding, the cis-isomer will have a lower melting point.**

[Total: 15]

End of Paper

2013 H2 Chemistry Prelims MCQ Solutions

1	2	3	4	5	6	7	8	9	10
B	**D**	**C**	**C**	**D**	**D**	**D**	**C**	**A**	**A**
11	12	13	14	15	16	17	18	19	20
D	**B**	**A**	**B**	**C**	**B**	**A**	**B**	**C**	**C**
21	22	23	24	25	26	27	28	29	30
C	**C**	**C**	**D**	**A**	**D**	**A**	**D**	**D**	**B**
31	32	33	34	35	36	37	38	39	40
C	**A**	**A**	**B**	**A**	**B**	**A**	**D**	**B**	**D**