

SH2 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE
NAME

SUBJECT
CLASS

REGISTRATION
NUMBER

CHEMISTRY

Paper 1 Multiple Choice

Additional Materials:

Multiple Choice Answer Sheet

Data Booklet

9647/01

Friday 16 Sept 2016

1 hour

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.

Do not use staples, paper clips, highlighters, glue or correction fluid.

Write your name, subject class and registration number on the Answer Sheet in the spaces provided unless this has been done for you.

There are **40** questions on this paper. Answer **all** questions. For each question there are four possible answers **A, B, C** and **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer. Any rough working should be done in this booklet.

This paper consists of **20** printed pages.

Instructions on how to fill in the Optical Answer Sheet

1. Enter your NAME (as in NRIC). TAN AH TECK
2. Enter the SUBJECT TITLE. CHEMISTRY
3. Enter the TEST NAME. SH2 Prelim 2016
4. Enter the CLASS. 1505648

RUB OUT ERRORS THOROUGHLY

USE PENCIL ONLY
FOR ALL ENTRIES ON THIS SHEET



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Example:

Shade the index number in a 5 digit format on the optical answer sheet: 2nd digit and the last 4 digits of the Registration Number.

Student	Example of Registration No.	Shade
Tan Ah Teck	<u>1505648</u>	55648

Section A

For each question there are four possible answers **A**, **B**, **C**, and **D**. Choose the one you consider to be correct.

- 1 3 g of hydrogen reacted with 160 g of bromine gas to give hydrogen bromide, HBr.

How many molecules are present at the end of the reaction?

A 6.02×10^{23}

C 12.0×10^{23}

B 9.03×10^{23}

D 15.1×10^{23}

- 2 In an experiment, 50 cm³ of a 0.1 mol dm⁻³ solution of a metallic salt reacts exactly with 25 cm³ of 0.1 mol dm⁻³ aqueous sodium sulfite.

The half-equation for the oxidation of sulfite ion is shown below:



If the original oxidation number of the metal ion is +3, what is the new oxidation number of the metal ion?

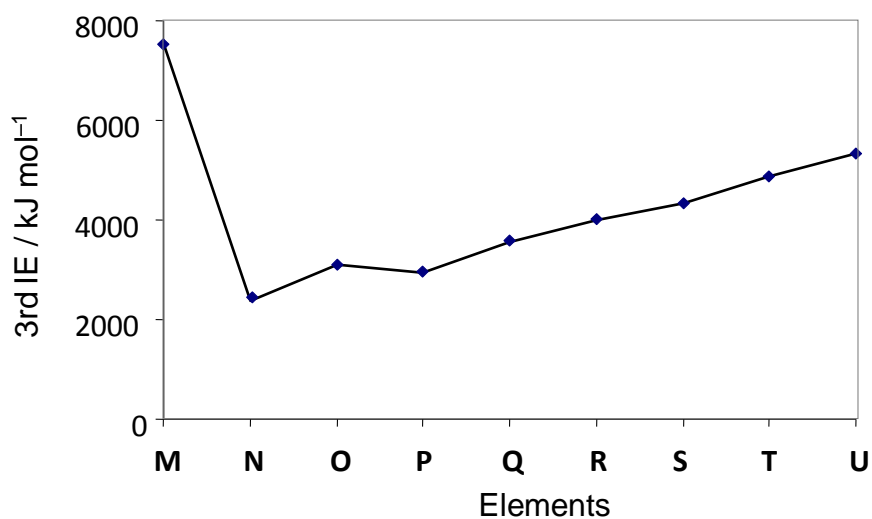
A 0

B 1

C 2

D 4

- 3 The graph below shows the variation in the **third** ionisation energies for the consecutive elements **M** to **U** in the Periodic Table, all with proton number below 20. The symbols **M** to **U** do not represent the actual elements.



What can be deduced from the above graph?

- A** **M** has a noble gas configuration.
- B** **M** reacts with **R** to form compound **MR₂**.
- C** The atomic radius of **T** is smaller than that of **S**.
- D** The decrease in 3rd I.E from **O** to **P** is due to inter-electronic repulsion.
- 4 Which set of compounds includes a giant ionic structure, a giant covalent structure and a simple covalent structure?
- A** C₆₀, C₂H₅CO₂NH₄, SiO₂
- B** Al₂O₃, PbO, SiO₂
- C** CO₂, Na₂O, SO₂
- D** AlCl₃, P₄O₆, KHF₂
- 5 Which pair of species has the same bond angle?
- A** IF₃, NF₃
- B** NO₂, SO₂
- C** XeF₄, CF₄
- D** NO₃⁻, CO₃²⁻

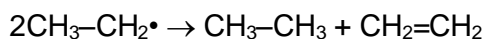
- 6 Which statement best explains why iodine is a solid while water is a liquid at room temperature?
- A Iodine has a much larger molar mass than water.
 - B Iodine has stronger and more extensive covalent bonds between its atoms in its molecular structure.
 - C The van der Waals' forces of attraction between iodine molecules are stronger than the intermolecular hydrogen bonding in water.
 - D The intermolecular hydrogen bonding in water is stronger than the intermolecular van der Waals' forces of attraction in iodine.

- 7 How does the volume of a 1.0 dm³ sample of gas change when it is heated from 20 °C to 40 °C at constant pressure?
- A It increases to about 1.1 dm³.
 - B It increases to about 2.0 dm³.
 - C It decreases to about 0.9 dm³.
 - D It decreases to about 0.5 dm³.

- 8 The data below refer to gas phase reactions at constant pressure.



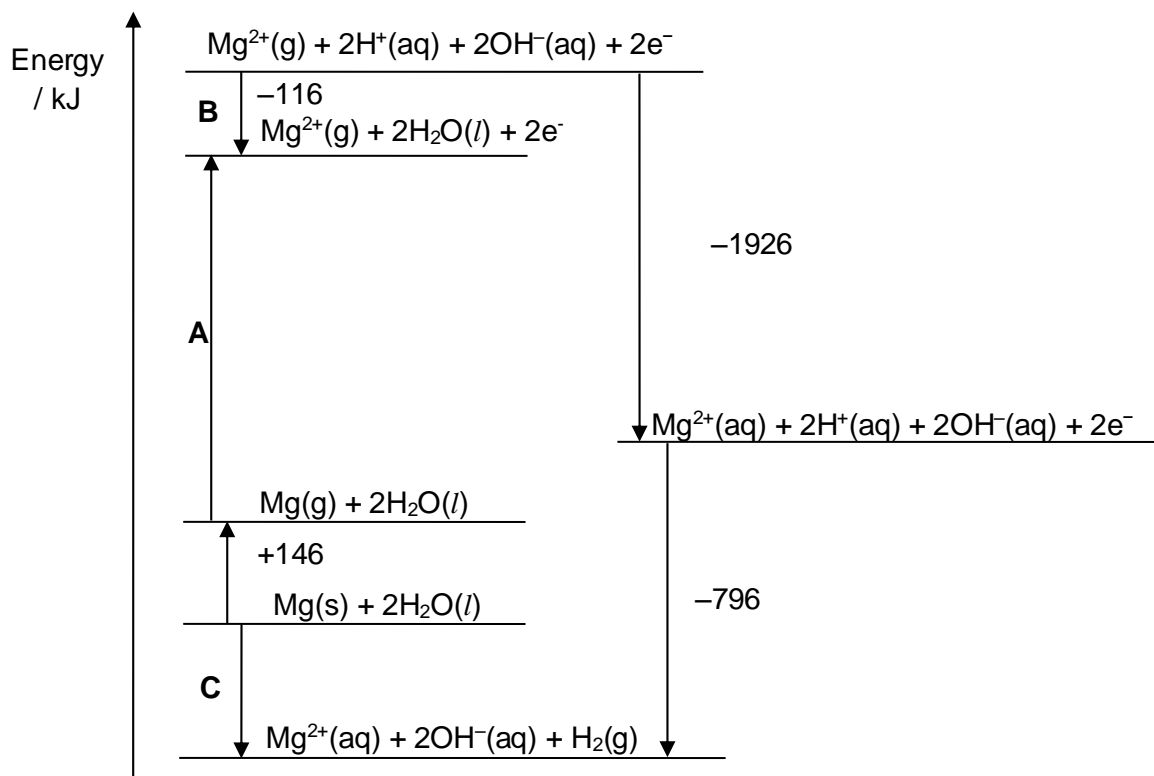
What is the enthalpy change for the following reaction?



- A +244 kJ mol⁻¹
- B -122 kJ mol⁻¹
- C -244 kJ mol⁻¹
- D -580 kJ mol⁻¹

- 9 Use of the Data Booklet is relevant to this question.

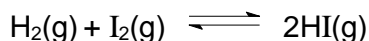
The energy level diagram shown below involves magnesium and water.



Which statement is **incorrect**?

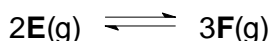
- A Step **A** represents the first and second ionisation energies of magnesium.
- B Step **B** represents $2 \times \Delta H_f(\text{H}_2\text{O})$.
- C The enthalpy change for step **C** is -274 kJ mol^{-1} .
- D The enthalpy change of hydration of magnesium ion is $-1926 \text{ kJ mol}^{-1}$.

- 10 Measured amounts of hydrogen and iodine are allowed to reach an equilibrium at 300 °C in a container of known volume.



From which experimental method can the equilibrium constant, K_c , be determined?

- A measuring the total pressure in the container
 - B slow cooling to 25 °C, breaking open the container under aqueous potassium iodide, and titrating the iodine present with aqueous sodium thiosulfate
 - C rapid cooling to 25 °C, breaking open the container under aqueous potassium iodide, and titrating the iodine present with aqueous sodium thiosulfate
 - D withdrawal of a measured sample of the equilibrium mixture, followed by complete decomposition of the hydrogen iodide present, and then titrating the total amount of iodine with aqueous sodium thiosulfate
- 11 For the reaction:

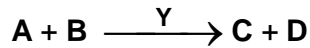


the numerical values of the equilibrium constant, K_p , are 1.50×10^7 at 500 K and 1.60×10^6 at 600 K.

Which statement about the equilibrium is true?

- A Decreasing the pressure increases the proportion of **E** in the equilibrium mixture.
 - B Adding a catalyst increases the proportion of **F** in the equilibrium mixture.
 - C The forward reaction is endothermic.
 - D The reaction is feasible at all temperatures.
- 12 The rate of removal of paracetamol, a pain-killing drug, from the body is a first order reaction with a rate constant, $k = 0.26 \text{ h}^{-1}$.
- How long will it take to remove 75% of the paracetamol that a patient consumes?
- A 0.20 h
 - B 0.26 h
 - C 2.7 h
 - D 5.3 h

- 13 Using a colorimeter, the following reaction is studied by finding the time taken for a coloured reactant, A, to decolourise. The reaction is catalysed by Y.



The following results are obtained:

Experiment	Vol of solution added / cm ³				Time taken / s
	A	B	Y	H ₂ O	
1	10	20	10	10	20
2	10	10	10	20	40
3	10	20	5	15	40
4	5	20	10	15	10

What is the rate equation for the reaction?

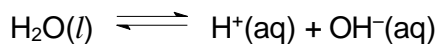
- A rate = $k[\text{A}][\text{B}]$ C rate = $k[\text{B}][\text{Y}]$
 B rate = $k[\text{A}][\text{Y}]$ D rate = $k[\text{A}][\text{B}][\text{Y}]$

- 14 Use of the Data Booklet is relevant to this question.

Which reagent can be used to convert $\text{Na}_4\text{Fe}(\text{CN})_6$ to $\text{Na}_3\text{Fe}(\text{CN})_6$?

- A $\text{Cl}^-(\text{aq})$ B $\text{Cu}^{2+}(\text{aq})$ C $\text{Fe}^{3+}(\text{aq})$ D $\text{Mn}^{2+}(\text{aq})$

- 15 Water dissociates into ions to establish following equilibrium:



Which is true about the dissociation of water?

- A Dissociation of water is an exothermic process.
 B When temperature increases, pH becomes lower than pOH.
 C Water is only neutral at room temperature.
 D For pure water, the values of its dissociation constant (K_a), ionic product (K_w) and $[\text{H}^+]$ increase in the order: $K_a < K_w < [\text{H}^+]$.

- 16 Bromocresol green indicator has a pH range of 3.8 – 5.5. It is yellow at pH < 3.8 and blue at pH > 5.5.

Which statement about bromocresol green is **incorrect**?

- A The indicator is suitable for a strong acid–weak base titration.
- B The indicator is yellow in 0.10 mol dm⁻³ of an acid with $K_a = 10^{-5}$ mol dm⁻³.
- C The indicator is green in a solution containing equimolar concentrations of CH₃CO₂H and CH₃CO₂K. (pK_b of CH₃CO₂K = 9.24)
- D When an acid in the conical flask is titrated against a base, the indicator changes from yellow to blue at the end-point.

- 17 Four compounds of some Period 3 elements are listed below.

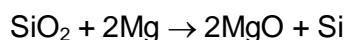


Water is added separately to each compound. Pairs of the resulting solutions are mixed together.

Which pair of solutions would give a solution of pH 7?

- A NaCl and Na₂O C NaCl and SO₂
- B Na₂O and SiCl₄ D SiCl₄ and SO₂

- 18 In the preparation of silicon, silicon dioxide is heated with magnesium.



The product mixture contains only MgO and Si only.

To separate the silicon from the product mixture, a student proposed the following methods.

- 1 Shake the mixture with aqueous hydrochloric acid and filter.
- 2 Heat the mixture gently and collect the evaporated silicon.

Which methods would work?

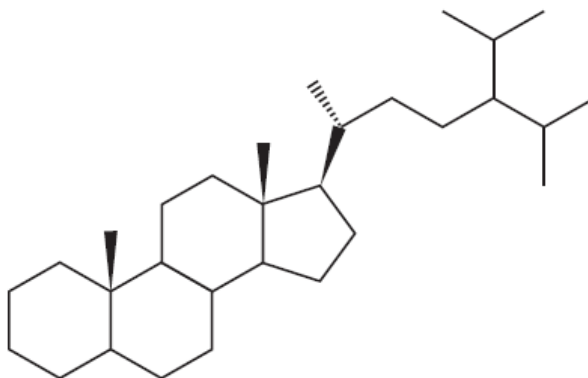
- A 1 only C 1 and 2
- B 2 only D neither 1 or 2

19 The high reactivity of fluorine is largely due to the low energy of the F–F bond.

Which statement best accounts for the weak F–F bond?

- A The F–F bond is weak because of the repulsion between the non-bonding electrons.
- B The F–F bond is weak because of the short bond length.
- C The F–F bond is weak because of the small nuclear charge of fluorine atom.
- D The F–F bond is weak because of the small size of fluorine atom.

20 The molecule 24-isopropylcholestane, which has been isolated from a class of sponge, can serve as a biomarker and has determined the first revolutionary appearances from some species.



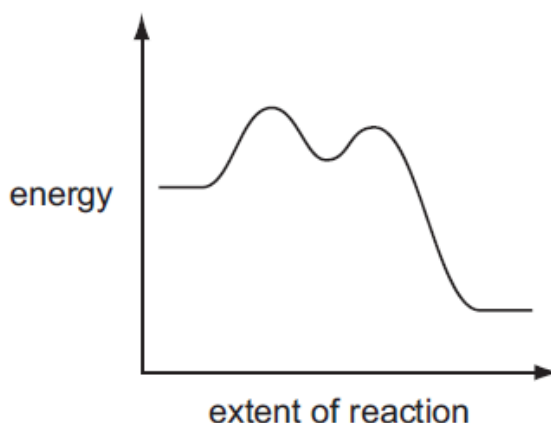
24-isopropylcholestane

Carbon atoms in a hydrocarbon molecule are classified as primary, secondary, tertiary or quaternary, depending on whether they are directly bonded to one, two, three or four other carbon atoms.

How many tertiary and chiral carbon atoms are present in a molecule of 24-isopropylcholestane?

	number of tertiary carbon atoms	number of chiral carbon atoms
A	9	4
B	9	8
C	11	4
D	11	8

21 A reaction pathway diagram is shown below.



Which reactions could have this profile?

- I $(\text{CH}_3)_3\text{CBr} + \text{NaOH} \rightarrow (\text{CH}_3)_3\text{COH} + \text{NaBr}$
- II $\text{CH}_3\text{CH}_2\text{Br} + \text{NaOH} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{NaBr}$
- III $\text{C}_6\text{H}_5\text{CH}_2\text{Cl} + \text{NH}_3 \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 + \text{HCl}$
- IV $(\text{CH}_3)_3\text{CCH}_2\text{CH}_2\text{Cl} + \text{NH}_3 \rightarrow (\text{CH}_3)_3\text{CCH}_2\text{CH}_2\text{NH}_2 + \text{HCl}$

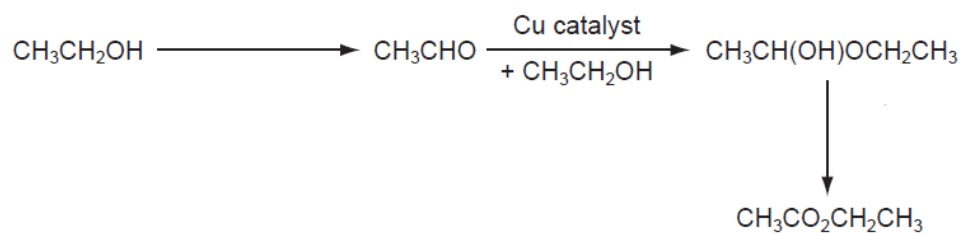
- A I and II only
- B I and III only
- C II and IV only
- D II, III and IV only

22 The alkanes used to be known as the paraffin hydrocarbons – paraffin meaning “lack of affinity” (i.e. unreactive).

Which statement is best explains the “lack of affinity” in alkanes?

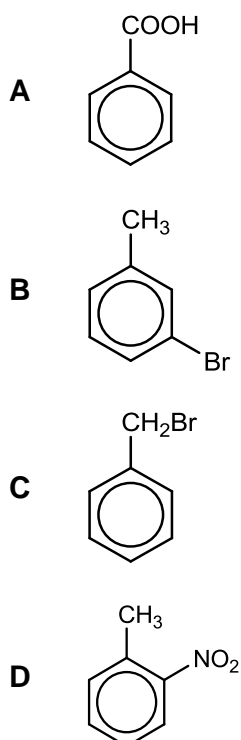
- A The atoms are arranged tetrahedrally around each carbon atom.
- B The alkanes have van der Waals forces of interaction.
- C There are no significant dipole moments in C–H and C–C bonds.
- D There is free rotation about C–C single bonds.

- 23 A new industrial preparation of ethyl ethanoate has been developed using cheap sources of ethanol.

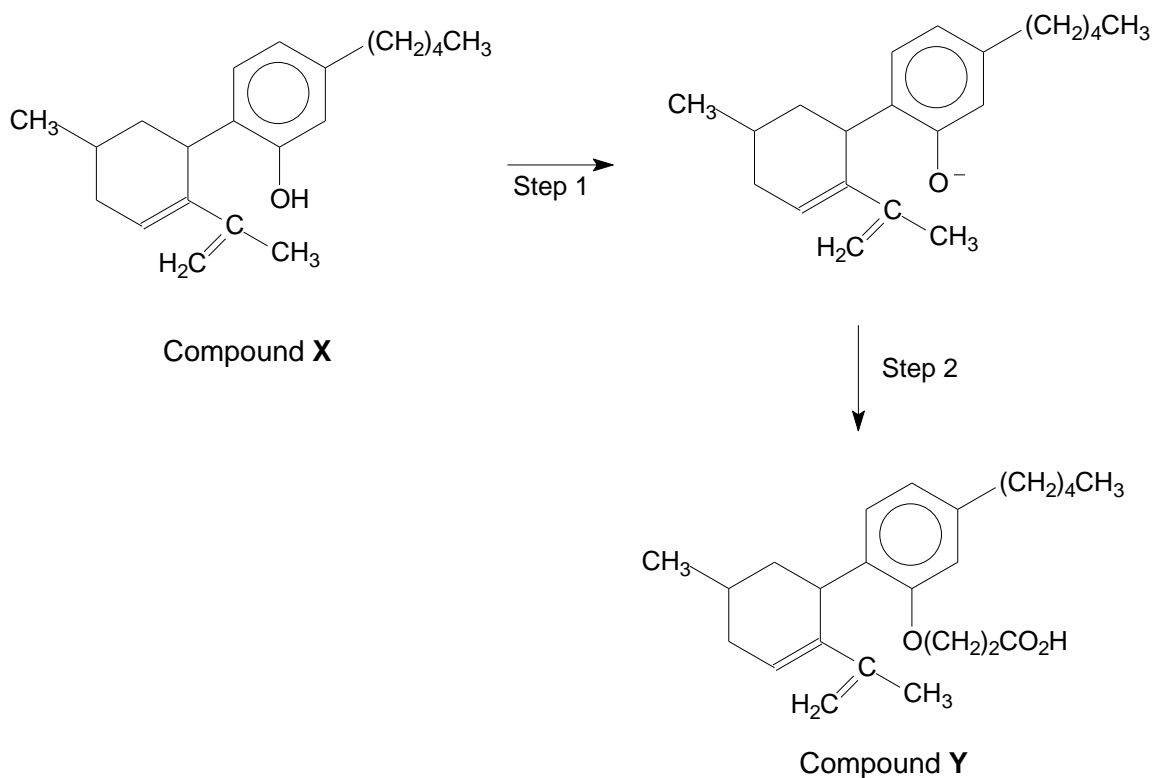


Which type of reaction is involved at some stage of this reaction sequence?

- A nucleophilic addition
 - B condensation
 - C disproportionation
 - D reduction
- 24 Which compound is least likely to be prepared directly from methylbenzene?



25 Compound Y can be prepared from compound X in the following reaction sequence.

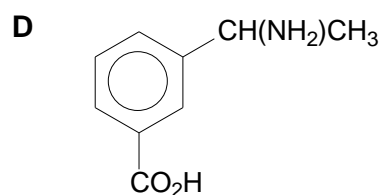
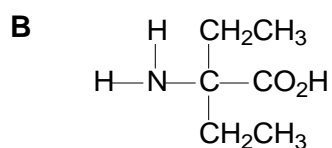
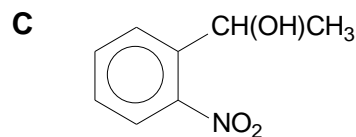
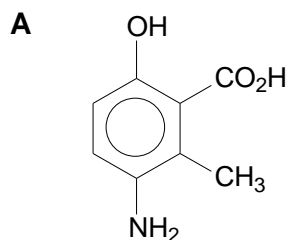


Which reagents can be used to prepare compound Y?

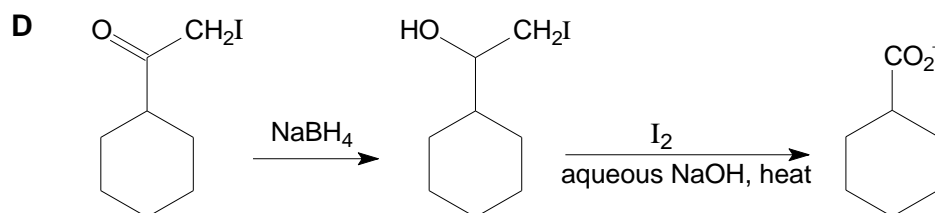
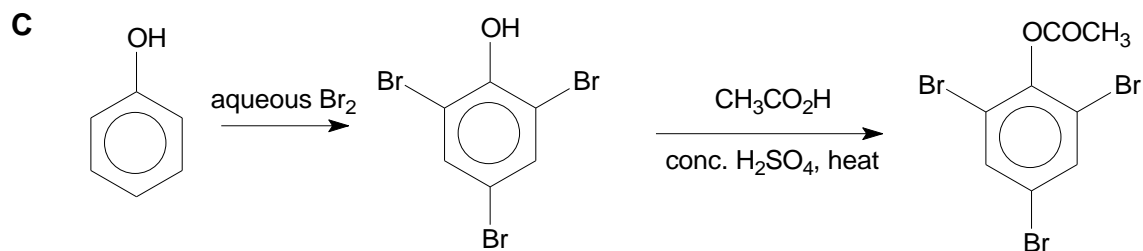
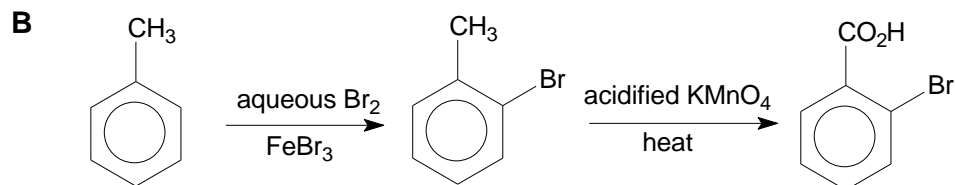
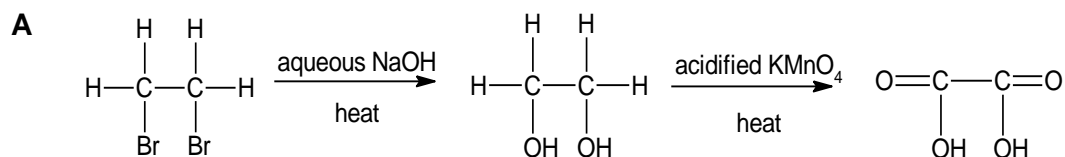
	Step I	Step II
A	Na	$\text{CH}_2(\text{OH})(\text{CH}_2)_2\text{CO}_2\text{H}$
B	NaOH	$\text{CH}_2\text{Cl}/\text{CH}_2\text{CO}_2\text{H}$
C	NaOH	$\text{CH}_2\text{Cl}/\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$
D	Na_2CO_3	$\text{CH}_2(\text{OH})\text{CH}_2\text{CO}_2\text{H}$

26 Compound **Z** is optically active and exists as zwitterions.

Which could be the structure of **Z**?

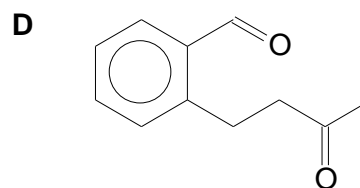
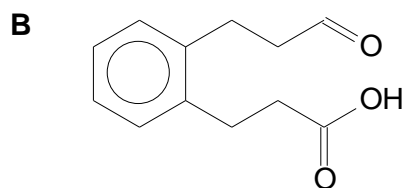
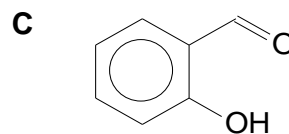
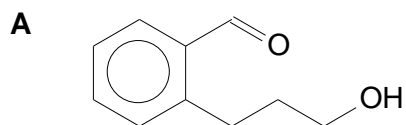


27 Which is the most feasible synthetic route?



- 28 Compound Y gives a positive result when treated with $[\text{Ag}(\text{NH}_3)_2]^+$ and PCl_5 but a negative result when treated with alkaline $\text{Cu}(\text{II})$ tartrate.

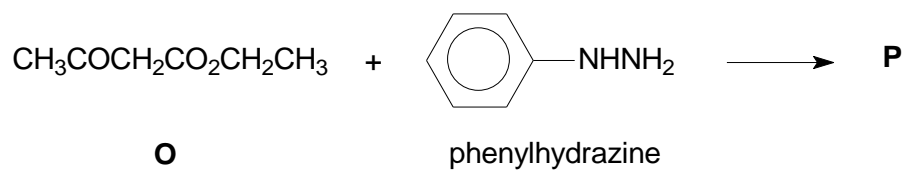
What could Y be?



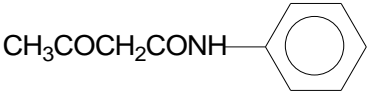
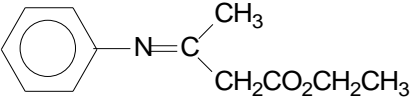
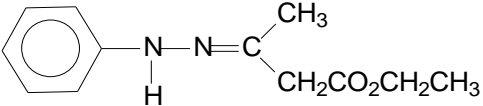
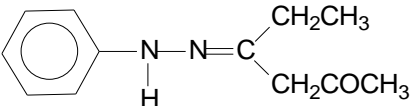
- 29 What is the order of increasing $\text{p}K_a$ of the organic compounds?

- A $\text{CCl}_3\text{CH}_2\text{OH}$, $\text{CHCl}_2\text{CH}_2\text{OH}$, $\text{CH}_3\text{CO}_2\text{H}$
- B $\text{CH}_3\text{CHClCO}_2\text{H}$, $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$, $\text{C}_6\text{H}_5\text{OH}$
- C $\text{C}_6\text{H}_5\text{OH}$, $\text{CH}_3\text{CHClCO}_2\text{H}$, $\text{CH}_3\text{CHF}_2\text{CO}_2\text{H}$
- D $\text{CH}_2\text{ClCH}_2\text{CO}_2\text{H}$, $\text{CH}_3\text{CHClCO}_2\text{H}$, $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$

- 30 The first stage in the synthesis of compound **P**, a drug used in reducing fever, is the reaction between compound **O** and phenylhydrazine.



What is **P**?

- A** 
- B** 
- C** 
- D** 

Section B

For each of the questions in this section, one or more of the three numbered statements **1** to **3** may be correct. Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct.)

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2, and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

31 For which pair does the first species contain more unpaired electrons than the second species?

- 1** N^- , C^+
- 2** Mn^{2+} , Co^{2+}
- 3** Mn^{4+} , Co

32 Which reactions represent standard enthalpy changes?

- 1** $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s})$
- 2** $6\text{C}(\text{s}) + 6\text{H}(\text{g}) \rightarrow \text{C}_6\text{H}_6(\text{l})$
- 3** $\text{CH}_3\text{OH}(\text{l}) + \frac{3}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$

33 At 298 K, the numerical values for the dissociation constant of the aliphatic carboxylic acids, RCO_2H and $\text{R}_1\text{CO}_2\text{H}$ in aqueous solution are 2.1×10^{-8} and 2.2×10^{-4} respectively.

Which statements can be inferred from the given information?

- 1** The pH of 1 mol dm^{-3} RCO_2H is greater than 1 mol dm^{-3} $\text{R}_1\text{CO}_2\text{H}$.
- 2** The K_b of RCO_2^- is greater than that of R_1CO_2^- .
- 3** The acid strength of RCO_2H is greater than that of $\text{R}_1\text{CO}_2\text{H}$.

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2, and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

34 Which statements correctly describe the role of ammonia in the reactions below?

	<i>reaction</i>	<i>role of ammonia</i>
1	$\text{CuO} + 6\text{NH}_3 \rightarrow [\text{Cu}(\text{NH}_3)_4]^{2+} + 2\text{NH}_2^- + \text{H}_2\text{O}$	Brønsted acid
2	$2\text{Na} + 2\text{NH}_3 \rightarrow 2\text{NaNH}_2 + \text{H}_2$	oxidising agent
3	$\text{CH}_3\text{Cl} + \text{NH}_3 \rightarrow \text{CH}_3\text{NH}_2 + \text{HCl}$	Brønsted base

35 Barium sulfate is opaque to X-rays and barium ions are toxic to humans. In hospitals, before an X-ray examination is carried out, patients with digestive tract problems are sometimes given a 'barium meal', consisting of a suspension of barium sulfate in water.

[Given: K_{sp} of $\text{BaSO}_4 = 1.3 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$; K_{sp} of $\text{BaCO}_3 = 5.5 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$]

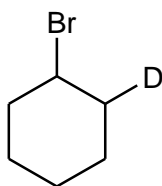
Which statements regarding the 'barium meal' are true?

- Barium sulfate is used because it is insoluble in water and hence is not poisonous when ingested by mouth.
- Barium carbonate can be used since it is also insoluble in water.
- Barium hydroxide can also be used since it is thermally stable in the human body.

36 Deuterium, D, is the ${}^2_1\text{H}$ isotope of hydrogen. DBr has the same chemical properties as HBr.

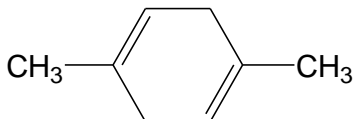
Which compounds could be made by the reaction of DBr with another compound in a single reaction?

1

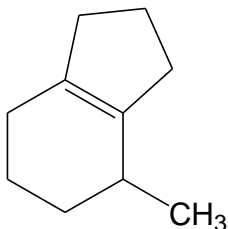
2 $\text{CHBr}_2\text{CHDBr}$ 3 $\text{CH}_3\text{CHBr(OD)}$

37 Which compounds form a single organic product when each is heated separately with acidified potassium manganate(VII) solution?

1



2

3 $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH=CH}_2$

38 Ethyl propanoate, $\text{CH}_3\text{CH}_2\text{OCOCCH}_2\text{CH}_3$ undergoes acidic hydrolysis in the presence of H_2^{18}O .

Which products are formed?

1 $\text{CH}_3\text{CH}_2^{18}\text{OH}$ 2 $\text{CH}_3\text{CH}_2\text{CO}^{18}\text{OH}$ 3 $\text{CH}_3\text{CH}_2\text{OH}$

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2, and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

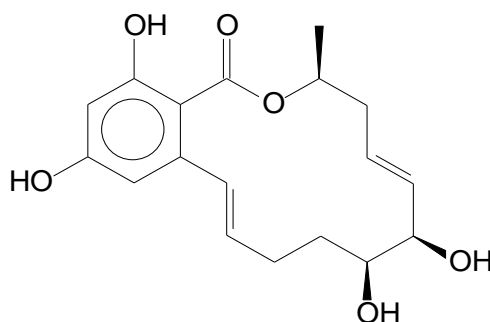
No other combination of statements is used as a correct response.

- 39** The structure of benzene, C_6H_6 , is a regular hexagon in which the π electrons are described as delocalised.

Which statements support this structure?

- 1 Benzene does not undergo addition reactions.
- 2 The length of the C-C bonds in benzene are intermediate between C–C bond in an alkane and C=C bond in an alkene.
- 3 The hydrogenation of benzene is less exothermic than that predicted for cyclohexa-1,3,5-triene.

- 40** *Aigialomycin D*, a fungal metabolite, has the structure shown below.



Aigialomycin D

Which observations are correct?

- 1 It reacts with hot, acidified $K_2Cr_2O_7$ to give a diketone.
- 2 One mole of *Aigialomycin D* reacts with Na metal to produce 2 moles of hydrogen.
- 3 It reacts with cold, dilute acidified $KMnO_4$ to give a product that has 7 chiral centres in each molecule.

– End of Paper –

SH2 H2 Preliminary Exam Paper 1 Worked Solutions

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

Section A



Amt of $\text{H}_2 = 3/2$ mol

Amt of $\text{Br}_2 = 160/159.8 = 1$ mol (limiting agent)

Hence, amt of HBr formed = 2 mol

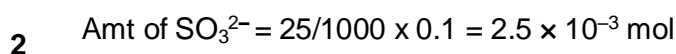
No of molecules present at the end of reaction

$$= (2+1/2) \times 6.0 \times 10^{23}$$

$$= 1.5 \times 10^{22}$$

$$= 15.1 \times 10^{23}$$

Ans: **D**



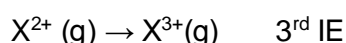
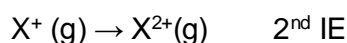
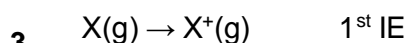
$$\text{Amt of } e^- = 2 \times 2.5 \times 10^{-3} = 5.0 \times 10^{-3} \text{ mol}$$

$$\text{Amt of metallic salt} = 50/1000 \times 0.1 = 5.0 \times 10^{-3} \text{ mol}$$

Hence mole ratio of metallic salt : e^- is 1:1

Since original oxidation number of the metal in the salt is +3, after gaining 1 e^- , the new oxidation number will be +2.

Ans: **C**



3rd ionization energy peaks at Grp II elements, where the removal of the electron involves an electron in the inner quantum shell, hence requiring a lot more energy.

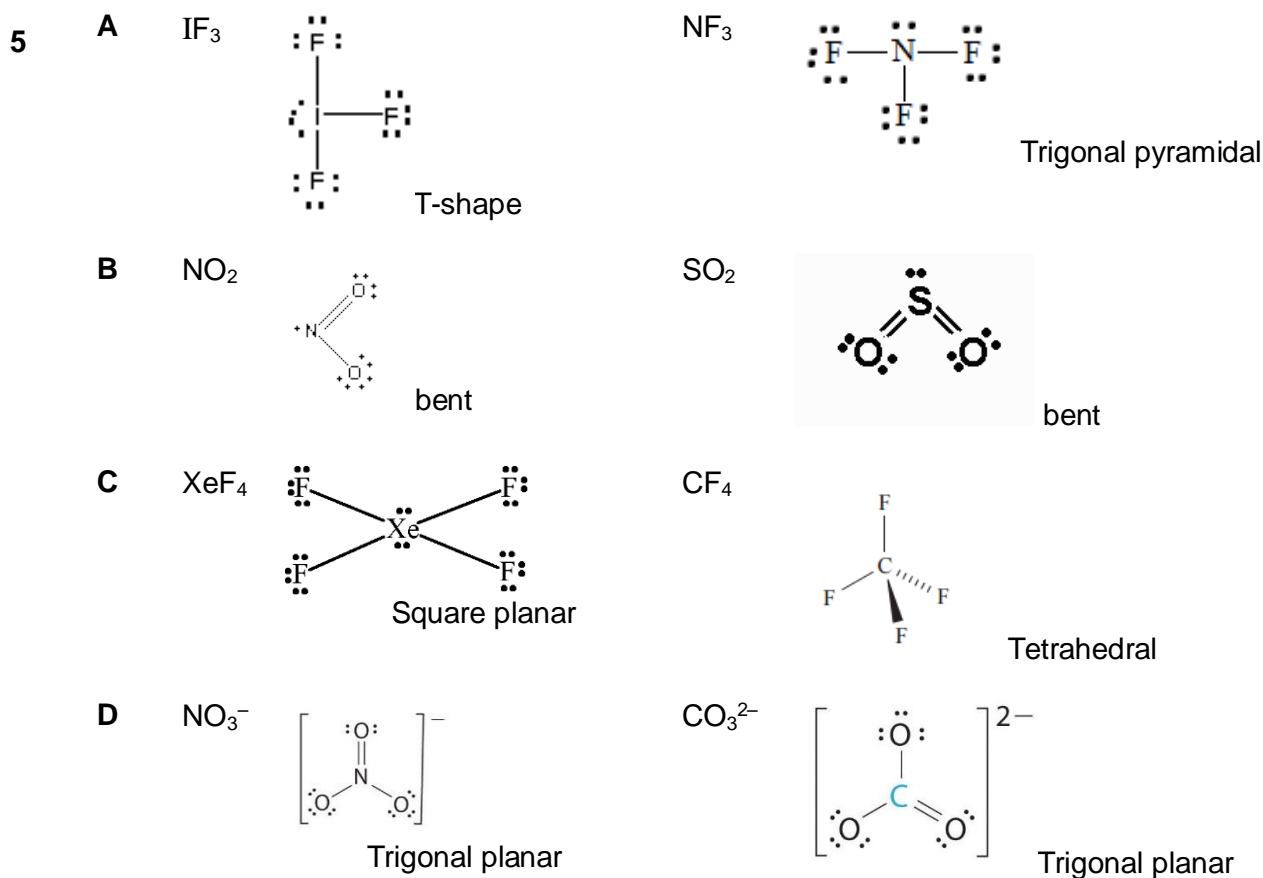
Hence element **M** is in Grp II. Element **R** is in Grp VII. So the compound **MR₂** is formed between elements **M** and **R**.

Element **O** is in Grp IV and element **P** is in Grp V. The 3rd IE of **O** involves removing the 2s electron whereas for **P**, it involves removing the 2p electron. Since electron in 2p subshell has less nuclear attraction than electron in 2s subshell, less energy is required to remove it.

Ans: **B**

4	A	C ₆₀ C ₂ H ₅ COONH ₄ SiO ₂	simple covalent structure giant ionic structure giant covalent structure
	B	CO ₂ Na ₂ O SO ₂	simple covalent structure giant ionic structure simple covalent structure
	C	Al ₂ O ₃ PbO SiO ₂	giant ionic structure giant ionic structure giant covalent structure
	D	AlCl ₃ P ₄ O ₆ KHF ₂	simple covalent structure simple covalent structure giant ionic structure

Ans: **A**



Note: Though NO₂ and SO₂ have the same shape, they have different bond angles due to different repulsion between lone pair-bond pair and lone electron-bond pair.

Ans: **D**

6

The dominant intermolecular forces of attraction between iodine is temporary dipole induced dipole interactions, while that between water is hydrogen bonding. Since iodine exists as solid while water exists as liquid at rtp, it implies that the temporary dipole induced dipole interactions between iodine are stronger than the H-bonds between water, requiring more energy to break, and energy at r.t.p is insufficient to break them, hence they exist as solid.

Ans: **C**

7 At constant pressure,

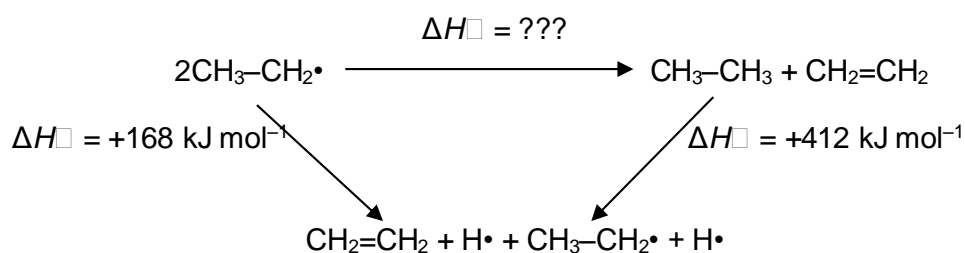
$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\frac{1.0}{293} = \frac{V_2}{313}$$

$$V_2 = 1.07 \text{ dm}^3 \text{ (approximately } 1.1 \text{ dm}^3\text{)}$$

Ans: A

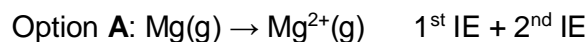
8



By Hess's law, $\Delta H = +168 - 412 = -244 \text{ kJ mol}^{-1}$

Ans: C

9



Option B: **Standard enthalpy change of formation of water** refers to the energy released or absorbed when 1 mole of water is formed from its constituent elements in their standard states under standard conditions.

Standard enthalpy change of neutralisation is the energy released when one mole of water is formed from H^+ and OH^- under standard conditions.

Therefore, step B represents $2 \times \Delta H_{\text{neutralisation}}$

Option C: By Hess's law, ΔH for step C = $+146 + 736 + 1450 + 166 - 1926 - 796$
 $= -274 \text{ kJ mol}^{-1}$

Option D: **Standard enthalpy change of hydration** is the energy released when one mole of gaseous ions is hydrated into aqueous ions under standard conditions.

Ans: B

- 10 Equilibrium constant, K_c , is temperature dependent, i.e. it changes only if temperature changes.

Option **A** is **not** true as the total pressure of the reaction mixture remains constant since the total number of gaseous particles remained unchanged.

Option **B** is **not** true as the position of the equilibrium has time to change due to slow cooling of reaction mixture. The eqm constant determined is likely one at well below 300 °C.

Option **C** is true as the position of the equilibrium has no or little time to change due to rapid cooling of reaction mixture. The eqm constant determined is likely to be one at 300 °C.

Option **D** is **not** true as the method gives only the initial amount of iodine used.

Ans: **C**

- 11 Option **A** is **not** true as decreasing the pressure favours forward reaction to produce more **F**; less **E** would remain.

Option **B** is **not** true as adding a catalyst would not affect the position of the equilibrium, but allows the equilibrium to be established faster.

Option **C** is **not** true as the equilibrium constant decreases with increasing temperature, which implies backward reaction is favoured as temperature increases. Thus backward reaction must be endothermic.

Option **D** is true as it can be deduced that $\Delta H < 0$ and $\Delta S > 0$ (due to an increase in no of gaseous particles in the reaction); thus $\Delta G = \Delta H - T\Delta S < 0$ at all temperatures; reaction should be feasible at all temperatures.

Ans: **D**

12
$$t_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2}{0.26} = 2.66 \text{ h}$$

When 75% of the paracetamol consumed is removed, it means 25% (= $\frac{1}{4}$) of the paracetamol consumed remains and 2 $t_{1/2}$ must have lapsed.

$$\therefore t = 2t_{1/2} = 5.3 \text{ h}$$

Ans: **D**

- 13 Since total vol of reaction was kept constant in all 4 expts, concentration of each reactant \propto its volume used

Comparing data from expt 1 & 2, when vol of **B** is halved (while keeping vol of **A** and **Y** constant), rate is also halved \Rightarrow order of reaction wrt **B** is 1

Comparing data from expt 1 & 3, when vol of **Y** is halved (while keeping vol of **A** and **B** constant), rate is also halved \Rightarrow order of reaction wrt **Y** is 1

Comparing data from expt 1 & 4, when vol of **A** is halved (while keeping vol of **B** and **Y** constant), rate remains unchanged \Rightarrow order of reaction wrt **A** is 0

Ans: **C**

- 14 Using E^\ominus values from *Data Booklet*, only $\text{Fe}^{3+}(\text{aq})$ can oxidise $\text{Na}_4\text{Fe}(\text{CN})_6$ to $\text{Na}_3\text{Fe}(\text{CN})_6$ as $E^\ominus_{\text{cell}} = +0.77 - (+0.36) = +0.41 \text{ V} > 0$ and reaction is feasible.

Option **A** is **not** true as $\text{Cl}^-(\text{aq})$ is a reducing agent.

Option **B** is **not** true as $E^\ominus_{\text{cell}} = +0.15 - (+0.36) < 0$ if $\text{Cu}^{2+} \rightarrow \text{Cu}^+$ or $E^\ominus_{\text{cell}} = +0.34 - (+0.36) < 0$ if $\text{Cu}^{2+} \rightarrow \text{Cu}$

Option **D** is **not** true as $E^\ominus_{\text{cell}} = -2.38 - (+0.36) < 0$

Ans: **C**

- 15 Option **A** is **not** true as dissociation of water involves breaking of O–H bonds and must be endothermic.

Option **B** is **not** true as dissociation of water always results in the same amount of $\text{H}^+(\text{aq})$ and $\text{OH}^-(\text{aq})$ formed; $\text{pH} = \text{pOH}$

Option **C** is **not** true as $[\text{H}^+(\text{aq})] = [\text{OH}^-(\text{aq})]$ is always true, i.e. water is neutral, at all temperatures.

Option **D** is true as values of $K_a = \frac{K_w}{55.5} = 1.8 \times 10^{-16}$, $K_w = 10^{-14}$ and $[\text{H}^+] = 10^{-7}$

Ans: **D**

- 16 Option **A** is true and hence is **not** the answer. At the equivalence point of a strong acid – weak base titration, the solution usually has $\text{pH} < 7$.

Option **B** is true and hence is **not** the answer. pH of 0.10 mol dm^{-3} acid with $K_a = 10^{-5} \text{ mol dm}^{-3}$ is 3 and the indicator is yellow in colour.

Option **C** is true and hence is **not** the answer. pH of a solution with $[\text{CH}_3\text{CO}_2\text{H}] = [\text{CH}_3\text{CO}_2\text{K}] = 4.76$ ($\text{p}K_a$) (between 3.8 - 5.5); solution has $[\text{In}] \approx [\text{HIn}^+]$ and indicator will be green in the solution.

Option **D** is **not** true and hence is the answer. The end-point of an acid-base titration occurs when $[\text{In}] \approx [\text{HIn}^+]$ and colour of the solution should be green (due to about equal amount of both yellow and blue species). Colour change at end-point should be from yellow to **green**, not blue.

Ans: **D**

- 17 NaCl dissolves in water to form a neutral solution of $\text{pH} = 7$.

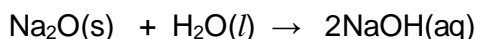


Na^+ does not hydrolyse in water because of low charge density. Cl^- is a weak conjugate base of the strong acid HCl ; hence does not hydrolyse in water.

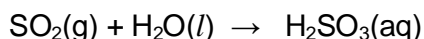
SiCl_4 hydrolyses in water to give an acidic solution of $\text{pH} = 2$



Na_2O dissolves in water to form a strongly alkaline solution of NaOH ($\text{pH} = 13$ or 14).



SO_2 dissolves in water to form an acidic solution of $\text{H}_2\text{SO}_3(\text{aq})$



Hence mixing of

- | | | | |
|----------|---|----------|---|
| A | NaCl and $\text{Na}_2\text{O} \rightarrow \text{pH} > 7$ | C | NaCl and $\text{SO}_2 \rightarrow \text{pH} < 7$ |
| B | Na_2O and $\text{SiCl}_4 \rightarrow \text{pH} = 7$ | D | SiCl_4 and $\text{SO}_2 \rightarrow \text{pH} < 7$ |

Ans: **B**

- 18 Si is insoluble in HCl , while MgO reacts with HCl to give MgCl_2 and water (acid-base reaction). Hence Si remains as residue while the filtrate contains $\text{MgCl}_2(\text{aq})$.

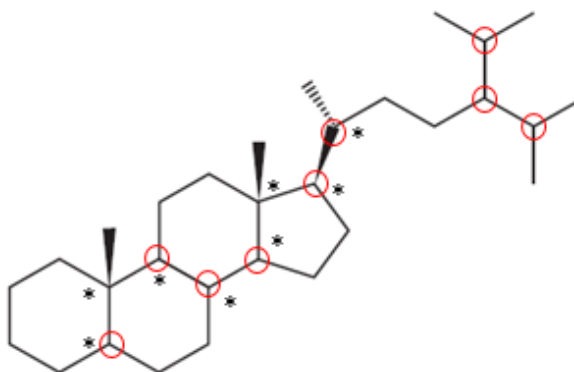
MgO and Si do not evaporate on heating due to high melting/boiling point.

Ans: **A**

- 19 Inter-electronic repulsion between the lone pairs on F atoms in a F_2 molecule causes the F-F bond to be longer and weaker than expected.

Ans: **A**

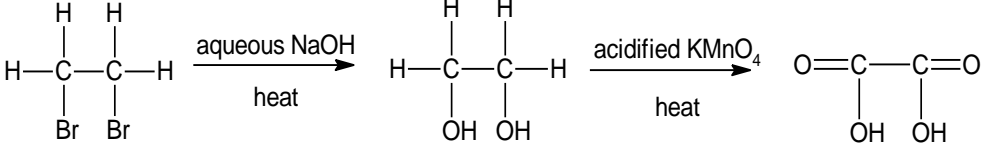
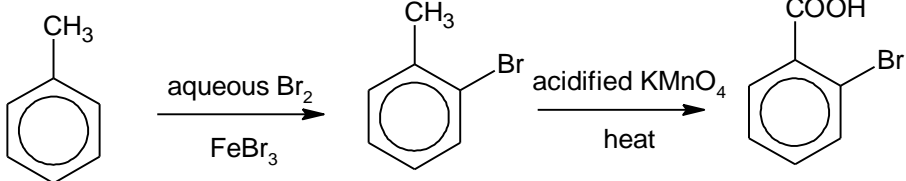
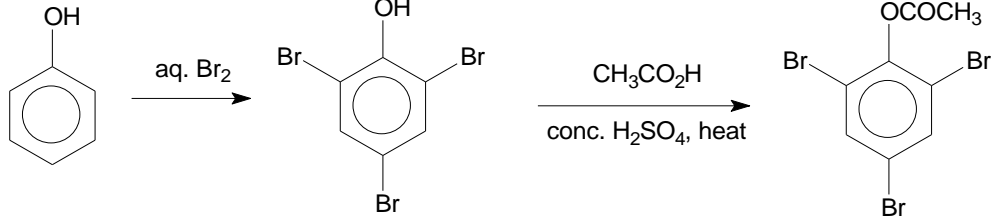
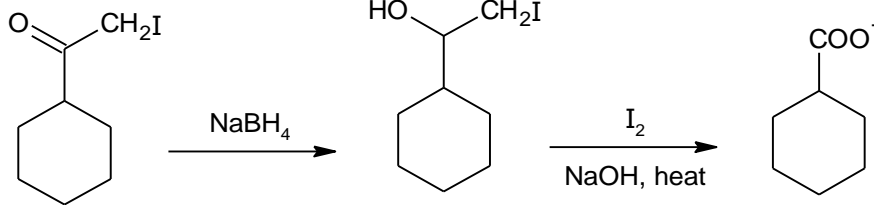
- 20 Tertiary carbons circled in red.
Chiral carbons with *



Ans: **B**

- 21 Reaction pathway diagram shows S_N1 mechanism, i.e. 2-step reaction.
- S_N1 is favoured when the reactant can form a stable carbocation intermediate, hence usually involves tertiary halogenoalkanes (i.e. option **I**) and not primary halogenoalkanes (options **II** and **IV**). Electron donating alkyl groups can help to ease the positive charge on the carbocation.
- For option **III**, $C_6H_5CH_2Cl$ can form a stable carbocation $C_6H_5CH_2^+$, the carbocation is stabilised by resonance as the electron deficient carbon is adjacent to a benzene ring.
- Ans: **B**
- 22 Due to the lack of dipole moments in alkane molecules, there is a lack of electron-rich and electron deficient centres to attract nucleophiles and electrophiles for reaction.
- Ans: **C**
- 23 Step 1: oxidation of primary alcohol to aldehyde
Step 2: nucleophilic addition of aldehyde
Step 3: oxidation (loss of hydrogen)
- Ans: **A**
- 24 Option **A**: oxidation of methyl side-chain on $C_6H_5CH_3$ gives C_6H_5COOH
Option **B**: electrophilic substitution of $C_6H_5CH_3$ gives 2-bromomethylbenzene or 4-bromomethylbenzene as the main products, 3-bromomethylbenzene is a minor product. Alkyl chain on benzene is 2,4-directing.
Option **C**: Free radical substitution of methyl side-chain on $C_6H_5CH_3$ gives $C_6H_5CH_2Br$.
Option **D**: electrophilic substitution of $C_6H_5CH_3$ gives in 2-nitromethylbenzene or 4-nitromethylbenzene as the main products.
- Ans: **B**
- 25 In Step **I**, phenol can only be deprotonated by either (i) Na or (ii) NaOH but not Na_2CO_3 .
Step **II** is a nucleophilic attack on an electron deficient carbon (C bonded to Cl instead of C bonded to OH since the C-Cl bond is weaker). Check that the number of carbon atoms are correct.
- Ans: **B**
- 26 A zwitterion is a dipolar species with no net charges (where $-CO_2H$ can be deprotonated by the $-NH_2$ group). So options **A**, **B** and **D** have possibility of forming zwitterions. **X** must also contain a chiral centre (carbon bonded to four different groups) since it is optically active.
- Ans: **D**

27

<p>A</p>	 <p>(COOH)₂ will get oxidised to CO₂ and H₂O when KMnO₄ is used as oxidising agent.</p>
<p>B</p>	 <p>The 1st step should be carried out under anhydrous conditions as water will destroy the halogen carrier, FeBr₃.</p>
<p>C</p>	 <p>The 2nd step can only be carried out with acid chloride (in the presence of aq NaOH) as phenols are too unreactive to react with carboxylic acid in a condensation reaction.</p>
<p>D</p>	 <p>The 1st step is a reduction of ketone to a secondary alcohol. The 2nd step is an iodoform (oxidation) reaction due to presence of -CH(OH)CH₂I.</p> <p>Note: -CH₃ can be replaced by -CH₂I or -CHI₂ in the structure. Both steps are feasible.</p>

Ans: D

28

Positive test with [Ag(NH₃)₂]⁺ (Tollen's reagent) => Aldehyde is present.Positive test with PCl₅ => RCO₂H or ROH is present (not phenol)

Negative test with alkaline Cu(II) tartrate (Fehling's solution) => aliphatic aldehyde is absent.

Ans: A

29	A	CCl ₃ CH ₂ OH, CHCl ₂ CH ₂ OH, CH ₃ COOH CH ₃ COOH is the most acidic as it is a carboxylic acid, the first two molecules are alcohols.
	B	CH ₃ CHClCOOH, CH ₃ CH ₂ COOH, C ₆ H ₅ OH CH ₃ CHClCOOH and CH ₃ CH ₂ COOH are more acidic than C ₆ H ₅ OH as they are carboxylic acids while C ₆ H ₅ OH is phenol. CH ₃ CHClCOOH is most acidic as the electron withdrawing Cl disperses the negative charge on the conjugate base and hence stabilises it.
	C	C ₆ H ₅ OH, CH ₃ CHClCOOH, CH ₃ CHF ₂ COOH Phenol is less acidic than carboxylic acids.
	D	CH ₂ ClCH ₂ COOH, CH ₃ CHClCOOH, CH ₃ CH ₂ COOH CH ₃ CHClCOOH is more acidic than CH ₂ ClCH ₂ COOH due to the closer proximity of the electron withdrawing Cl to the -COOH, which can better help to disperse the charge on the conjugate base.

Ans: **B**

- 30 2, 4-dinitrophenylhydrazine reacts with carbonyl compounds via condensation, forming a new C=N bond. Phenylhydrazine reacts in similar way with the ketone in compound **O**. The ester functional group does not react with phenylhydrazine.

Ans: **C**

Section B

31	1	N ⁻	1s ² 2s ² 2p ⁴	2 unpaired e ⁻
		C ⁺	1s ² 2s ² 2p ¹	1 unpaired e ⁻
	2	Mn ²⁺	[Ar] 3d ⁵	5 unpaired e ⁻
	Co ²⁺	[Ar] 3d ⁷	3 unpaired e ⁻	
3	Mn ⁴⁺	[Ar] 3d ³	3 unpaired e ⁻	
	Co	[Ar] 3d ⁷ 4s ²	3 unpaired e ⁻	

Ans: **B**

- 32 Option 2: Hydrogen should exist as molecular H₂(g) instead of H(g) under standard conditions.
Option 3: H₂O should exist as liquid instead of gas under standard conditions.

Ans: **D**

- 33 Option 1 is true as RCO₂H has a smaller K_a means it is a weaker acid and dissociates in aq solution to give a lower [H⁺(aq)] and thus has a higher pH.

Option 2 is true as K_a x K_b = K_w = 10⁻¹⁴ mol² dm⁻⁶. An acid with a larger K_a would give a conjugate base with a lower K_b value and vice versa.

Option 3 is **not** true as R₁CO₂H has a larger K_a means it is the stronger acid.

Ans: **B**

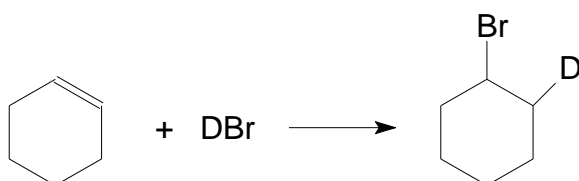
- 34 Option 1 is true as each NH_3 donates H^+ (act as Bronsted acid) to form NH_2^- .
 Option 2 is true as Na is oxidised to Na^+ in NaNH_2 .
 Option 3 is **not** true as NH_3 acts a nucleophile in the reaction.

Ans: B

- 35 Option 1 is true as BaSO_4 will remain insoluble and not dissociate to give poisonous Ba^{2+} ions.
 Option 2 is **not** true as BaCO_3 will react with $\text{HCl}(\text{aq})$ in the stomach to release poisonous Ba^{2+} ions.
 Option 3 is **not** true as $\text{Ba}(\text{OH})_2$ will react with $\text{HCl}(\text{aq})$ in the stomach to release poisonous Ba^{2+} ions.

Ans: D

36



- 1
 2 $\text{CHBr}=\text{CHBr} + \text{DBr} \rightarrow \text{CHBr}_2\text{CHDBr}$
 3 cannot be formed in a single step

Ans: B

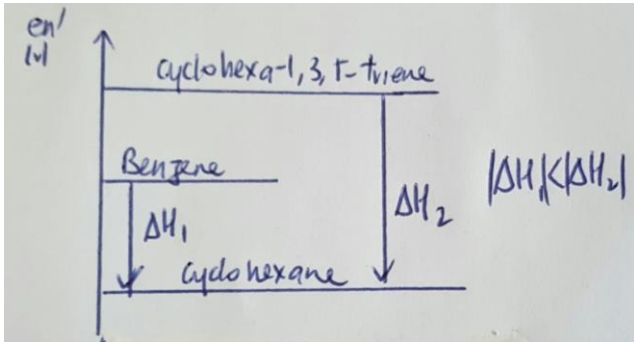
37

1	<p>$2\text{CH}_3\text{COCH}_2\text{CO}_2\text{H}$</p>
2	
3	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + \text{CO}_2 + \text{H}_2\text{O}$

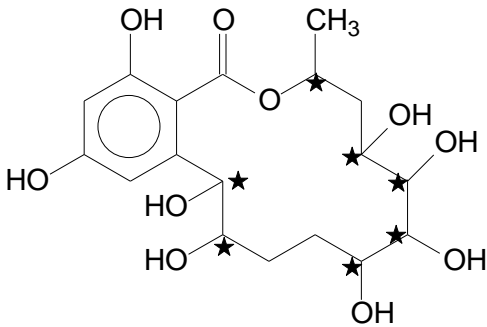
Ans: A

- 38 $\text{CH}_3\text{CH}_2\text{OCOCH}_2\text{CH}_3 + \text{H}_2^{18}\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{CH}_2\text{CO}^{18}\text{OH}$ as the H of H_2^{18}O adds to the alcohol and the ^{18}OH of H_2^{18}O adds to the carboxylic acid in hydrolysis (H-OH bond in water breaks).

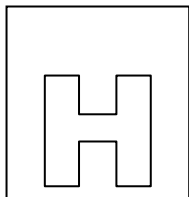
Ans: C

39	1	Benzene does not undergo addition reactions. True. Addition will result in a loss of aromatic stability of benzene (loss of "alternate single and double bond")
	2	The length of the C-C bonds in benzene are intermediate between C-C bond in an alkane and C=C bond in an alkene. True. The bond order of all C-C bonds in benzene are 1.5 due to resonance which arises from the continuous overlap of unhybridised p-orbitals.
	3	The hydrogenation of benzene is less exothermic than that predicted for cyclohexa-1,3,5-triene. True. Benzene is more stable than cyclohexa-1,3,5-triene due to resonance. Thus, it exists at a lower energy level (see below). Hydrogenation of benzene gives cyclohexane. 

Ans: A

40	1	It reacts with hot, acidified $K_2Cr_2O_7$ to give a diketone. False. Hot acid will hydrolyse the ester to give a secondary alcohol which will then be oxidised to give a ketone. The other two secondary alcohols will also be oxidised to give 2 ketones. So the product will be a triketone.
	2	One mole of Aigialomycin reacts with Na metal to produce 2 moles of hydrogen gas. True. One mol of hydroxyl group react with Na to produce 0.5 mole of gas. Since there is 4 hydroxy groups per mol of Aigialomycin, 2 moles of hydrogen gas are produced.
	3	It reacts with cold, dilute acidified $KMnO_4$ to give a product that has 7 chiral centres. True. Alkene undergo mild oxidation to give diol. Product is shown below. 

Ans: C



**SH2 PRELIMINARY
EXAMINATIONS**

Higher 2

CANDIDATE
NAME

SUBJECT
CLASS

REGISTRATION
NUMBER

CHEMISTRY

Paper 2 Structured

Answer on the Question Paper.

Additional Materials: Data Booklet

9647/02

Wednesday 24 Aug 2016

1½ hours

READ THE INSTRUCTIONS FIRST	For Examiner's Use	
Write your name, subject class and registration number on all the work you hand in.	1	/7
Write in dark blue or black ink in the spaces provided.	2	/8
You may use a soft pencil for any diagrams, graphs or rough working.	3	/4
Do not use paper clips, highlighters, glue or correction fluid.	4	/12
Answers all questions.	5	/17
The number of marks is given in brackets [] at the end of each question or part question.	6	/ 12
	Total	/ 60

- 1 "Lethal Dose", LD, is a means of measuring toxicity. LD₅₀ is the amount of a material which causes the death of 50% of a group of test animals. Its value is expressed as the mass of a chemical administered per kg body mass of a test animal.

"Lethal Concentration", LC, is another means of measuring toxicity. The value of LC₅₀ is the concentration of a chemical in air that kills 50% of the test animals during the observation period.

The table below shows the values for the LD₅₀ and LC₅₀ along with the toxicity ratings.

Toxicity rating	Commonly used term	LD ₅₀ : Oral (mg kg ⁻¹)	LC ₅₀ : Inhalation (ppm)
1	Extremely Toxic	1 or less	10 or less
2	Highly Toxic	1 – 50	10 – 100
3	Moderately Toxic	50 – 500	100 – 1000
4	Slightly Toxic	500 – 5000	1000 – 10 000
5	Practically Non-toxic	5000 – 15 000	10 000 – 100 000
6	Relatively Harmless	15 000 or more	100 000 or more

- (a) 9.90×10^{-4} mol of a toxic compound, C₄H₅NO, was found to cause death in 50% of the test animals weighing 1 kg.

Calculate the LD₅₀ of C₄H₅NO and state its toxicity rating.

[2]

- (b) Phosphine, PH_3 , is a gas widely used in the semiconductor industries as a dopant and a precursor for the deposition of compound semiconductors.

For safety considerations, the permissible limits of phosphine must not exceed $\frac{1}{10}$ of the LC_{50} value.

When expressing the concentration of a small quantity of gas, parts per million (ppm) can be used. Ppm is usually used for volume of gases and is expressed as shown in the equation below:

$$\text{Concentration of gas (in ppm)} = \frac{\text{volume of gas}}{\text{volume of air}} \times 10^6$$

- (i) Given that the LC_{50} for phosphine is 55 mg m^{-3} at room temperature, convert the LC_{50} to ppm and determine its toxicity rating.

[3]

- (ii) A semiconductor factory releases 36 g of phosphine in a day. Using your answer in (b)(i), determine the minimum volume of the factory that will ensure the volume of phosphine is within the permissible limits at room temperature.

[2]

[Total:7]

- 2 (a) Liquefaction of air is done industrially by surrounding pre-cooled high-pressure air in a coil surrounded by cold water. The air cools down by a large amount when it expands into a region of low pressure. This behaviour is **not** exhibited by ideal gases.

(i) State **two** assumptions of the kinetic theory of gases.

.....
.....
..... [2]

(ii) Suggest why air cools when it expands.

.....
..... [1]

(iii) Conversely, gases can be liquefied at room temperature by compressing them under high pressures. Explain why a gas liquefies when compressed.

.....
..... [1]

- (b) Critical temperature is the maximum temperature at which a gas can be converted into a liquid by an increase in pressure. When the temperature is above the critical temperature, the vapour cannot be liquefied no matter how much pressure is applied.

(i) Draw the dot-and-cross diagram for N_2O , where N is the central atom.

[1]

(ii) Arrange the gases, N_2O , F_2 and H_2O , in an increasing order of their critical temperatures. Explain your answer.

..... < <

.....

.....

.....

.....

.....

..... [3]

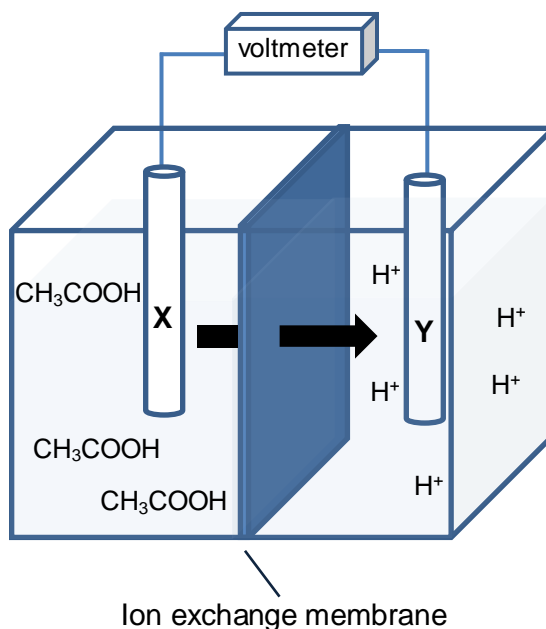
[Total: 8]

- 3 Hydrogen is a better source of fuel compared to fossil fuels as it is clean and renewable. The conventional method of obtaining pure hydrogen is to electrolyse water. However, many industries still prefer fossil fuel or coal as the main source of energy. One reason is the high cost of electrolysis.

(a) State another reason why the use of hydrogen as a fuel is not popular.

..... [1]

- (b) The diagram below shows an alternative method of producing hydrogen from organic material where ethanoic acid is converted by bacteria to carbon dioxide.



- (i) Complete the table below.

Electrode	Type of reaction	Polarity
X		
Y		

[1]

- (ii) Construct an equation for the reaction at each electrode.

Electrode X:

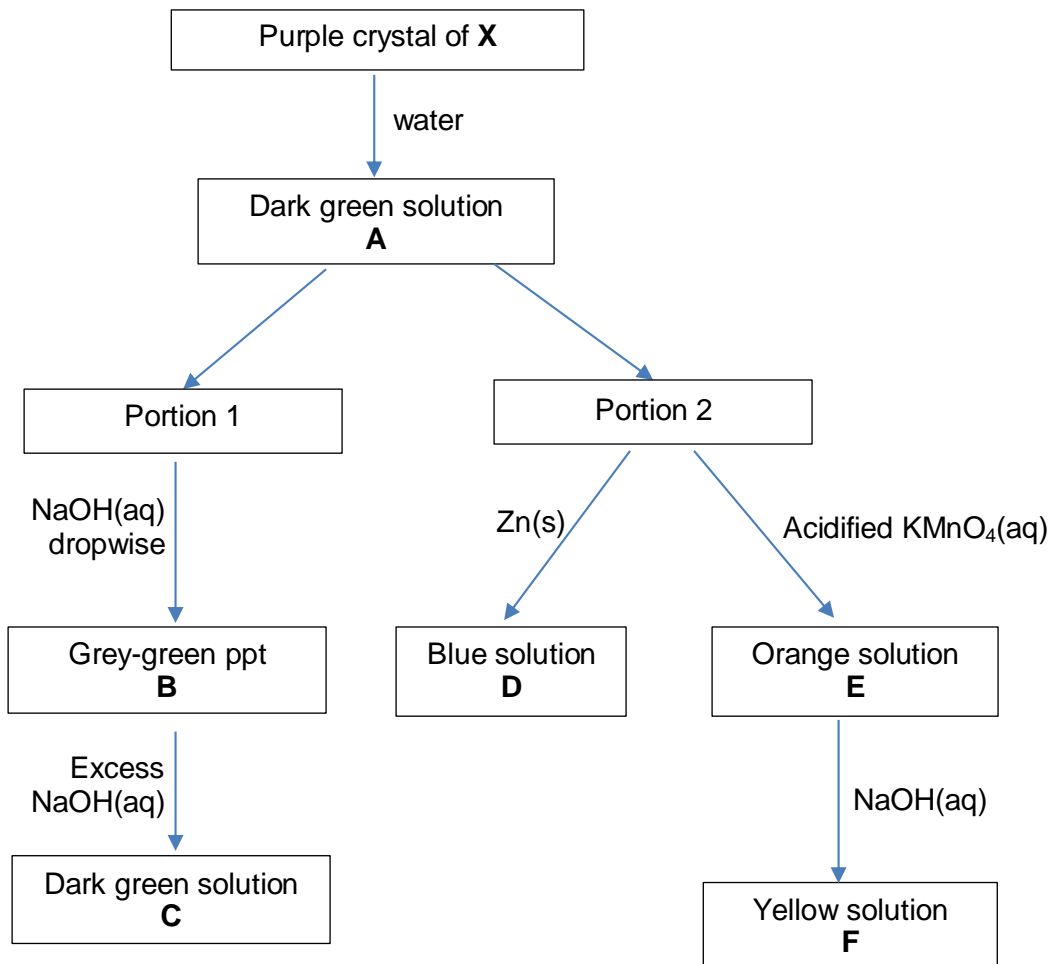
Electrode Y:

[2]

[Total: 4]

- 4 Chromium is a transition element which exhibits more than one oxidation state in its compounds, many of which are coloured.

The flow chart below shows the reaction of a purple chromium(III) compound, **X**, which has a crystalline structure.



- (a) (i) Write the electronic configuration of the chromium ion in **A**.

[1]

- (ii) Suggest an explanation for **A** being coloured.

.....

 [3]

- (b) (i) Explain why **B** dissolves in excess NaOH(aq) to form **C**. You should use the ideas behind the Le Chaterlier's principle and solubility product, K_{sp} , in your answer.

.....

 [2]

- (ii) Identify the chromium-containing species in **D**.

[1]

- (iv) State the type of reaction and write an equation for the conversion of **E** to **F**.

.....
 [2]

- (c) Consider the two chromium complexes, $[\text{CrCl}(\text{NH}_3)_5]\text{SO}_4$ and $[\text{CrF}(\text{NH}_3)_5]\text{Cl}_2$.

- (i) Describe a chemical test, which does **not** involve silver nitrate, that could distinguish between aqueous solutions of $[\text{CrCl}(\text{NH}_3)_5]\text{SO}_4$ and $[\text{CrF}(\text{NH}_3)_5]\text{Cl}_2$.

.....

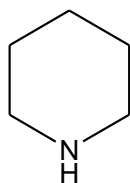
 [2]

- (ii) Explain why the ionic radius of Cr^{2+} is much smaller than that of Ca^{2+} .

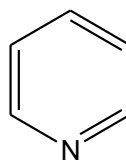
.....
 [1]

[Total: 12]

- 5 Piperidines are cyclic amines while pyridines are heterocyclic organic compounds structurally related to benzene.

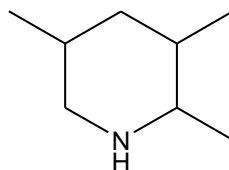


piperidine

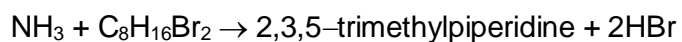


pyridine

- (a) The structure of 2,3,5-trimethylpiperidine is shown below.



It can be synthesised by reacting ammonia with a dibromo compound **G**.



G

- (i) Suggest the structure of compound **G**.

[1]

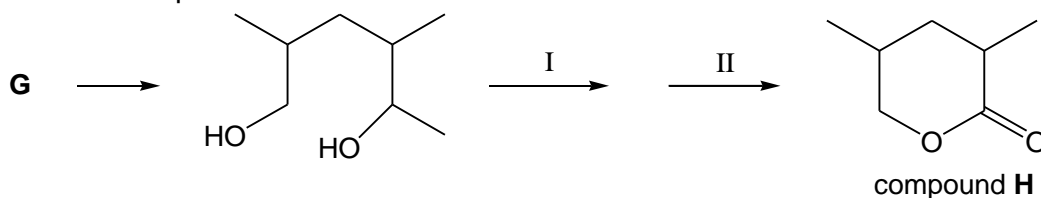
- (ii) When compound **G** is reacted with NaOH in ethanol, a mixture of isomeric alkenes with molecular formula C_8H_{14} is formed.

Suggest the structures of all the isomers.

You may use skeletal representations in your answers.

[2]

- (iii) Compound **G** can be converted to compound **H** by first converting it to a diol, followed by two more steps as shown.

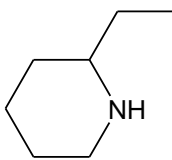
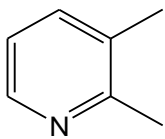


Complete the table below.

Step	Reagents and Conditions	Type of reaction
I		
II		

[4]

- (b) The table below shows the pK_b values of three monoprotic bases, ammonia, 2-ethylpiperidine and 2,3-dimethylpyridine.

	NH_3 ammonia	 2-ethylpiperidine	 2,3-dimethylpyridine
pK_b	4.74	3.55	7.43

- (i) Give an equation which represents the reaction of 2-ethylpiperidine with water.

[1]

- (ii) Explain why 2-ethylpiperidine has a lower pK_b value than ammonia.

.....

..... [1]

A 10.0 cm³ sample of **J**, a solution containing 2-ethylpiperidine and 2,3-dimethylpyridine, was titrated against 0.50 mol dm⁻³ HCl(aq) in the presence of two indicators, bromothymol blue and methyl orange.

It was found that 12.20 cm³ of HCl(aq) were needed to change the colour of the first indicator and a **further 7.80 cm³** were needed to change the colour of the second indicator.

(iii) Use the data to calculate the concentration of each of the two bases in **J**.

[3]

(iv) Calculate the initial pH of **J**.

[2]

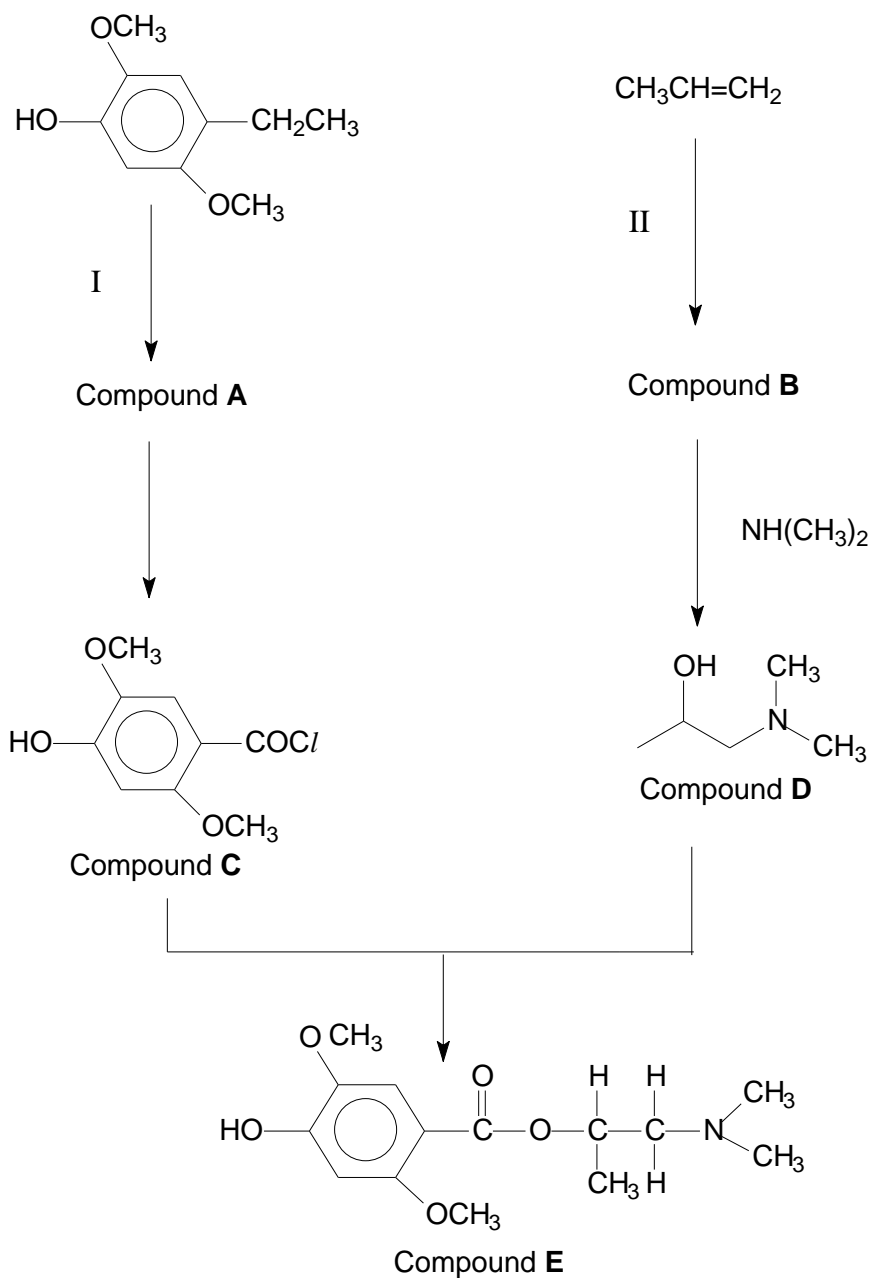
- (v) Hence, sketch the shape of the pH curve during this titration, showing the pH values and volumes of $\text{HCl}(\text{aq})$ at significant points.

[3]

[Total: 17]

- 6 The reaction scheme below shows the synthesis of compound **E** starting from an alkene and a phenol derivative.

[The CH_3O - group can be considered to be inert.]



- (a) (i) State reagents and conditions for steps I and II.

Step I:

Step II:

[2]

(ii) Suggest the identities of compounds **A** and **B**.

Compound A	Compound B

[2]

(iii) Describe a mechanism for the reaction taking place in step II. In your answers, include all necessary curly arrows, lone pairs and relevant dipoles.

[3]

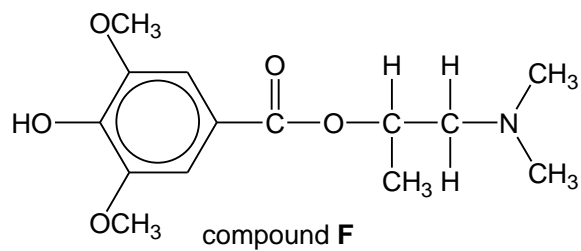
(iv) State the type of stereoisomerism exhibited by **D**. Draw appropriate structures to illustrate your answer.

[2]

(v) Draw the organic product formed when compound **A** reacts with compound **D**.

[1]

(b) Compound **F** is an isomer of **E**.



Describe a simple chemical test to distinguish between compounds **E** and **F**.

.....

 [2]

[Total: 12]

Suggested Answers for 2016 SH2 Chemistry Paper 2

(P) (a) **Preliminary Calculation**

For titration, 25cm³ of sea water is used,

$$\text{Amt of } Cl^- \text{ in } 25.0 \text{ cm}^3 = 25/1000 \times 2.0 \times 10^{-3}$$

$$= 5.0 \times 10^{-5} \text{ mol}$$

$$= \text{Amt of } Ag^+$$

Assuming titre volume to be 25.00 cm³,

$$\text{Required } [AgNO_3] = (5.0 \times 10^{-5})/25 \times 1000$$

$$= 2.0 \times 10^{-3} \text{ mol dm}^{-3}$$

Hence, the 0.1 mol dm⁻³ silver nitrate solution provided is unsuitable for use in the titration (i.e. too concentrated)

∴ Need to dilute the given 0.1 mol dm⁻³ silver nitrate solution to 2.0 x 10⁻³ mol dm⁻³

∴ Need to dilute it 50 times.

Preparation of a standard silver nitrate solution of 2.0 x 10⁻³ mol dm⁻³

1. Using a burette, transfer 5.00 cm³ of the given silver nitrate solution into a 250 cm³ volumetric flask. Top up to the mark using deionised water.
2. Cap the flask, invert it and shake to obtain a homogeneous solution.

Precipitation Titration

1. Fill a burette with the newly-prepared 2.0 x 10⁻³ mol dm⁻³ silver nitrate solution.
2. Pipette 25.0 cm³ of sea water into a 250 cm³ conical flask.
3. Add 1 cm³ of potassium chromate(VI) solution into the conical flask.
4. Titrate until brick-red precipitate first appears.
5. Repeat titration till results within ±0.10cm³ are obtained.

Sample calculation of concentration of chloride ions in sea water

Let concentration of standard silver nitrate solution be **M** mol dm⁻³, titre volume be **y** cm³, volume of sea water used for titration be 25.0 cm³

$$\text{Amt of } Ag^+ = y/1000 \times M$$

$$= yM/1000 \text{ mol}$$

$$= \text{Amt of } Cl^-$$

$$[Cl^-] = yM/1000 \div 25/1000$$

$$= yM/25 \text{ mol dm}^{-3}$$

- (b) The student obtained a titre volume of 20.60 cm³ from her experiment.

Determine the concentration of chloride ions remaining in the solution at the end point.

You may assume the following:

- 25.0 cm³ of sea water was used in the titration
- 1 cm³ of 1.00 mol dm⁻³ potassium chromate(VI) solution, K₂CrO₄ was used as the indicator
- K_{sp} value of Ag₂CrO₄ is 1.1 × 10⁻¹²



$$\text{Amt of CrO}_4^{2-} = 1/1000 \times 1.00$$

$$= 1.0 \times 10^{-3} \text{ mol}$$

$$\text{At endpoint, } [\text{CrO}_4^{2-}] = (1.0 \times 10^{-3}) / [(25.0+1+20.60)/1000]$$

$$= 0.02146 \text{ mol dm}^{-3}$$

$$\text{IP of Ag}_2\text{CrO}_4 = K_{\text{sp}}$$

$$[\text{Ag}^+]^2 [\text{CrO}_4^{2-}] = 1.1 \times 10^{-12}$$

$$[\text{Ag}^+]^2 [0.02146] = 1.1 \times 10^{-12}$$

$$[\text{Ag}^+] = 7.16 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\text{IP of AgCl} = K_{\text{sp}}$$

$$[\text{Ag}^+] [\text{Cl}^-] = 1.8 \times 10^{-10}$$

$$[7.16 \times 10^{-6}] [\text{Cl}^-] = 1.8 \times 10^{-10}$$

$$[\text{Cl}^-] = 2.51 \times 10^{-5} \text{ mol dm}^{-3}$$

- (c) Subsequently, the student investigates the solubility of silver chloride in aqueous hydrochloric acid.

By considering the ions present in a solution of silver chloride in aqueous hydrochloric acid, predict and explain how the solubility of silver chloride will be affected by the concentration of the acid.

Prediction: Solubility of AgCl decreases when concentration of HCl increases.



In the presence of HCl, there is common ion effect. [Cl⁻] increases, position of equilibrium shifts right, solubility decreases.

- (d) Identify the following variables in the investigation of solubility of silver chloride in hydrochloric acid.

Independent variable: concentration of HCl / amount of HCl / concentration of Cl⁻

Dependent variable: mass of AgCl that dissolved / solubility of AgCl / amount of AgCl that dissolved

- (e) Calculate the solubility of silver chloride in a 2 mol dm⁻³ hydrochloric acid solution.

$$[\text{Ag}^+] [\text{Cl}^-] = 1.8 \times 10^{-10}$$

$$[x] [x+2.0] = 1.8 \times 10^{-10}$$

Assume $x \ll 2.0$,

$$[x] [2.0] = 1.8 \times 10^{-10}$$

$$x = 9.00 \times 10^{-11} \text{ mol dm}^{-3}$$

[1]

[Total:12]

- 1 One means of measuring toxicity is using LD, which stands for "Lethal Dose". LD₅₀ is the amount of a material which causes the death of 50% of a group of test animals. LD₅₀ value is expressed as the weight of a chemical administered per kg body mass of a test animal.

Another means of measuring toxicity is using LC, which stands for "Lethal Concentration". The concentrations of the chemical in air that kills 50% of the test animals during the observation period is the LC₅₀ value.

The table below shows the values for the LD₅₀ and LC₅₀ along with the toxicity ratings.

Toxicity Rating	Commonly used term	LD ₅₀ : Oral (mg kg ⁻¹)	LC ₅₀ : Inhalation (ppm)
1	Extremely Toxic	1 or less	10 or less
2	Highly Toxic	1 – 50	10 – 100
3	Moderately Toxic	50 – 500	100 – 1000
4	Slightly Toxic	500 – 5000	1000 – 10,000
5	Practically Non-toxic	5000 – 15,000	10,000 – 100,000
6	Relatively Harmless	15,000 or more	100,000 >

- (a) 9.90×10^{-4} mol of a toxic compound, C₄H₅NO, was found to cause death in 50% of test animals weighing 1 kg.

Calculate the LD₅₀ of the compound and state its toxicity rating.

[2]

$$\text{Mass of compound} = 9.90 \times 10^{-4} \times (48 + 5 + 14 + 16)$$

$$= 0.08217 \text{ g}$$

$$\text{Hence, LD}_{50} = \frac{0.08217 \text{ g}}{1 \text{ kg}} = 82.17 \text{ mg/kg}$$

$$\approx \underline{\underline{82.2 \text{ mg/kg}}}$$

[1]

The compound is moderately toxic/3

[1]

- (b) Phosphine is a gas that is widely used in the semi-conductor industry as a dopant and as a precursor for the deposition of compound semiconductors.

For safety of operations, the permissible limits of phosphine must not exceed $\frac{1}{10}$ of its LC_{50} value.

When expressing a small quantity of gas, parts per million (ppm) can be used to indicate it. Ppm is usually used for volume of gases and is expressed in the equation below:

$$\text{Concentration in ppm} = \frac{\text{volume of gas}}{\text{volume of air}} \times 10^6$$

- (i) Given that the LC_{50} for phosphine is 55 mg m^{-3} at room temperature, convert the LC_{50} to ppm and determine its toxicity rating. [3]

$$\begin{aligned} \text{Volume of PH}_3 &= \frac{55 \times 10^{-3}}{34.0} \times 24 \text{ dm}^3 \\ &= 1.6176 \times 10^{-3} \times 24 \text{ dm}^3 \\ &= \mathbf{0.03882 \text{ dm}^3} \end{aligned} \quad [1]$$

$$\begin{aligned} LC_{50} &= \frac{0.03882 \times 10^{-3}}{1} \times 10^6 \\ &= 38.82 \\ &\approx \mathbf{38.8 \text{ ppm}} \end{aligned} \quad [1]$$

The toxicity rating is highly toxic/2 [1]

- (ii) A semiconductor factory releases 36 g of phosphine in a day.

Using your value in (i), determine the minimum volume of the factory that will allow the volume of phosphine to be within permissible limits at room temperature. [2]

$$\begin{aligned} \text{Allowed amount of PH}_3 \text{ in ppm} &= 38.82 \div 10 \\ &= \mathbf{3.882 \text{ ppm}} \end{aligned} \quad [1]$$

Given amount of PH_3 produced a day is 36g

$$3.882 = \frac{\text{vol of PH}_3}{\text{vol of factory}} \times 10^6$$

$$3.882 = \frac{36}{34 \times 24} \times 10^6$$

$$\text{Minimum volume of factory} = \mathbf{6.546 \times 10^6 \text{ dm}^3} \quad [1]$$

[Total:7]

- 2 (a) Liquefaction of air is done industrially by surrounding pre-cooled high-pressure air in a coil surrounded by cold water. The air cools down by a large amount when it expands into a region of low pressure.

This behaviour is not exhibited by ideal gases.

- (i) State two assumptions of the kinetic theory of gases.

A gas is composed of tiny particles that have **negligible volumes** compared to the volume in which they move or the volume of the gas container.

There are **no attractive or repulsive forces between the gas particles**. [2]

- (ii) Suggest why air cools when it expands.

For expansion of air, energy is needed to **overcome the intermolecular forces of attraction** between the air molecules, which is absorbed from the surroundings. [1]

- (iii) Conversely, gases can be liquefied at room temperature by compressing them under high pressure. Explain why a gas liquefy when compressed.

When compressed, the gas particles are **close enough for the intermolecular forces of attraction to be significant** and liquification occurs. [1]

- (b) Critical temperature is the maximum temperature at which a gas can be converted into a liquid by an increase in pressure. When the temperature is above the critical temperature, the vapour cannot be liquefied no matter how much pressure is applied.

- (i) Draw the dot - and - cross diagram for the N_2O , where N is the central atom.



- (iii) Arrange the gases N_2O , F_2 and H_2O , in increasing order of their critical temperatures and explain your answer.



The hydrogen bonds between water molecules is the strongest, followed by the weaker permanent dipole-dipole interactions between N_2O molecules and the temporary dipole-induced dipole between the F_2 molecules being the weakest.

Hence, H_2O can remain as a liquid even at high temperature due to strongest intermolecular forces and hence it has the highest critical temperature or the stronger the intermolecular forces, a higher temperature is needed to convert the liquid to gas and hence the higher the temperature.

[3]

[Total:8]

3 Hydrogen is a better source of fuel compared to fossil fuels as it is clean and renewable. The conventional method of obtaining pure hydrogen is to electrolyse water. However, many industries still prefer fossil fuel or coal as the main source of energy. One reason is the high cost of electrolysis.

(a) State another reason why the use of hydrogen as a fuel is not popular.

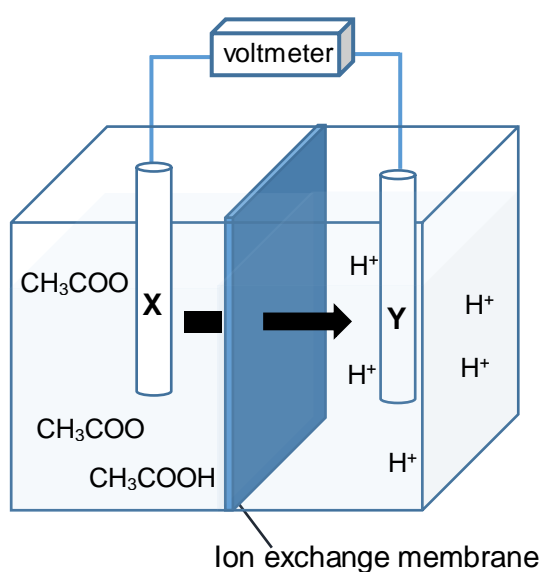
Hydrogen exists as a **gas** and it is **difficult/high cost to store or transport**.

Or

Hydrogen is dangerous as it is **explosive**.

[1]

(b) The diagram below shows an alternative method of producing hydrogen from organic material where ethanoic acid is converted by bacteria to carbon dioxide.

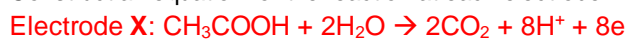


(i) Complete the table below.

Electrode	Type of reaction	Polarity
X	Oxidation	Negative
Y	Reduction	Positive

[1]

(ii) Construct an equation for the reaction at each electrode.

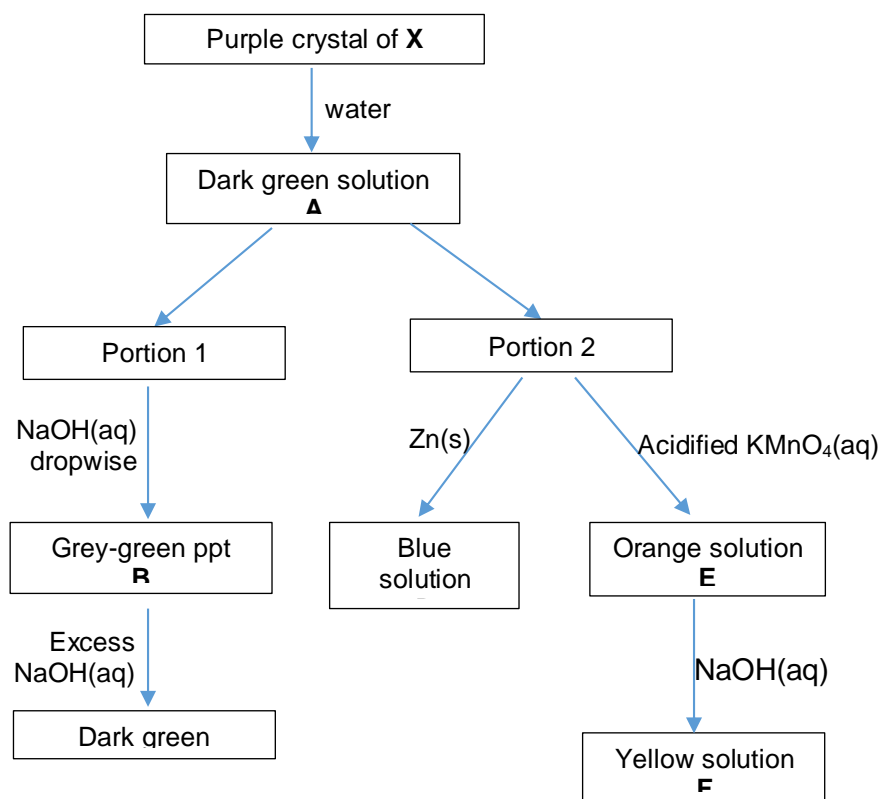


[2]

[Total: 4]

- 4 Chromium is a transition element which exhibits more than one oxidation state in its compounds, many of which are coloured.

The flow chart below shows the reaction of a purple chromium(III) compound, X, which has a crystalline structure.



- (a) (i) Write the electronic configuration of the chromium ion in A.



[1]

- (ii) Suggest an explanation for A being coloured.

When ligand approach Cr^{3+} , the 3d orbitals of Cr^{3+} splits into 2 different energy levels (d-d splitting).

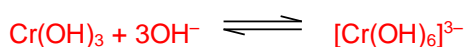
When an electron in the lower energy d orbital is excited to the higher energy d orbital, a photon with wavelength in the visible region is absorbed (d-d transition).

The colour of A observed is the complementary colour.

[3]

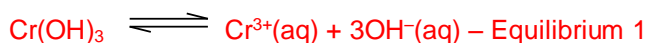
- (b) (i) Explain why B dissolves in excess NaOH(aq) to form C. You should use the ideas behind the Le Chatelier's principle and solubility product, K_{sp} , in your answer.

B is $\text{Cr}(\text{OH})_3$ and C is $[\text{Cr}(\text{OH})_6]^{3-}$.



When excess OH^- is added, equilibrium shifts to the right to form $[\text{Cr}(\text{OH})_6]^{3-}$. This decreases the concentration of Cr^{3+} and hence causing the ionic product of $\text{Cr}(\text{OH})_3$ to fall below its K_{sp} . Therefore, $\text{Cr}(\text{OH})_3$ dissolves.

Or



When excess OH^{-} is added, position of equilibrium 2 shifts right to form $[\text{Cr(OH)}_6]^{3-}$. The concentration of Cr^{3+} decreases and the ionic product of Cr(OH)_3 falls below its K_{sp} .

- (ii) Identify the chromium-containing species in D.



- (iv) State the type of reaction and write an equation for the conversion of E to F.

Acid base reaction or Neutralisation reaction



- (c) Consider the two chromium complexes, $[\text{CrCl}(\text{NH}_3)_5]\text{SO}_4$ and $[\text{CrF}(\text{NH}_3)_5]\text{Cl}_2$.

- (i) Describe a chemical test, which does **not** involve silver nitrate, that could distinguish between aqueous solutions of $[\text{CrCl}(\text{NH}_3)_5]\text{SO}_4$ and $[\text{CrF}(\text{NH}_3)_5]\text{Cl}_2$.

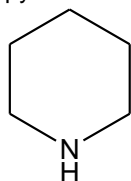
Add $\text{Ba}(\text{NO}_3)_2(\text{aq})$ or $\text{BaCl}_2(\text{aq})$ or $\text{Ba}(\text{OH})_2(\text{aq})$ or $\text{Ca}(\text{NO}_3)_2(\text{aq})$. $[\text{CrCl}(\text{NH}_3)_5]\text{SO}_4$ will form a white precipitate and $[\text{CrF}(\text{NH}_3)_5]\text{Cl}_2$ will not form any white precipitate or the solution will remain colourless. [2]

- (ii) Explain why the ionic radius of Cr^{2+} is much smaller than that of Ca^{2+} .

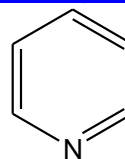
Cr^{2+} has higher nuclear charge (more protons) than Ca^{2+} and the electrons in the d orbitals are poorly shielding. Therefore, the nuclear attraction on valence electron is higher in Cr^{2+} and electrons are attracted closer to the nucleus in Cr^{2+} . [1]

[Total: 12]

- 5 Piperidines are cyclic amines while pyridines are [heterocyclic organic compounds](#) structurally related to [benzene](#).

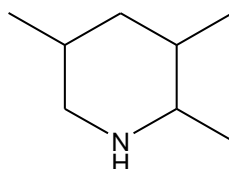


piperidine

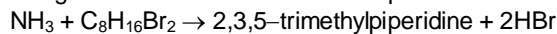


pyridine

- (a) The structure of 2,3,5-trimethylpiperidine is shown below.

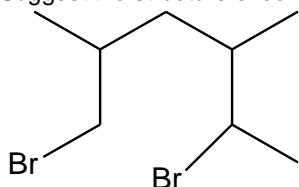


It can be synthesised by reacting ammonia with a dibromo compound **G**.



G

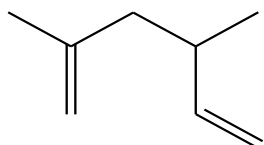
- (i) Suggest the structure of compound **G**.



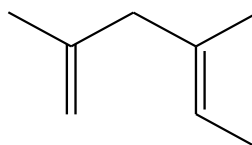
- (ii) When compound **G** is reacted with NaOH in ethanol, a mixture of isomeric alkenes with molecular formula C_8H_{14} is formed.

Suggest the structures of all the isomers.

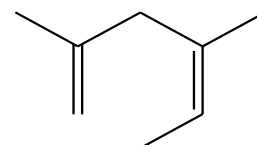
You may use skeletal representations in your answers.



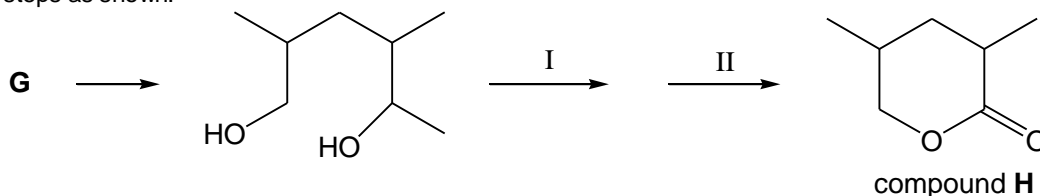
2,4-dimethylhexa-1,5-diene



geometric isomers of 2,4-dimethylhexa-1,4-diene



- (iii) Compound **G** can be converted to compound **H** by first converting it to a diol, followed by two more steps as shown.



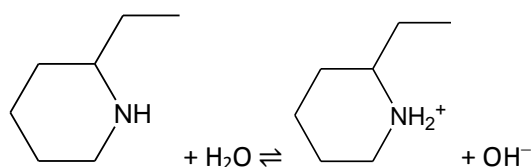
Complete the table below.

Step	Reagents and Conditions	Type of reaction
I	aqueous alkaline iodine / I_2 , NaOH(aq) / I_2 (aq), NaOH(aq); warm (not heat)	Oxidation
II	concentrated sulfuric acid (trace amount); heat under reflux	Condensation

- (b) The table below shows the $\text{p}K_b$ values of three monoprotic bases, ammonia, 2-ethylpiperidine and 2,3-dimethylpyridine.

	NH_3 ammonia	 2-ethylpiperidine	 2,3-dimethylpyridine
$\text{p}K_b$	4.74	3.55	7.43

- (i) Give an equation which represents the reaction of 2-ethylpiperidine with water.



- (ii) Explain why 2-ethylpiperidine has a lower pK_b value than ammonia.

2-ethylpiperidine: 2° **aliphatic amine** with **2 electron-donating alkyl** groups, **lone ep of N is readily available** to be donated to H^+
 Ammonia does not have any electron-donating alkyl group.

A 10.0 cm^3 sample of **J**, a solution containing 2-ethylpiperidine and 2,3-dimethylpyridine, was titrated against $0.50\text{ mol dm}^{-3}\text{ HCl(aq)}$ in the presence of two indicators, bromothymol blue and methyl orange. It was found that 12.20 cm^3 of HCl(aq) were needed to change the colour of the first indicator and a **further 7.80 cm^3** were needed to change the colour of the second indicator.

- (iii) Use the data to calculate the concentration of each of the two bases in **J**.

In titrating a mixture of bases, the stronger or strongest base will be neutralised first.

$$\begin{aligned} \eta_{2\text{-ethylpiperidine in J}} &= \eta_{\text{HCl to reach 1st eq pt}} \\ &= \frac{12.20}{1000} \times 0.50 = 6.10 \times 10^{-3}\text{ mol} \end{aligned}$$

$$[2\text{-ethylpiperidine}] \text{ in J} = \frac{12.20}{1000} \times 0.50 \div \frac{10.0}{1000} = 0.610\text{ mol dm}^{-3}$$

$$\begin{aligned} \eta_{2,3\text{-dimethylpyridine in J}} &= \eta_{\text{HCl to reach 2nd eq pt}} \\ &= \frac{7.80}{1000} \times 0.50 = 3.90 \times 10^{-3}\text{ mol} \end{aligned}$$

$$[2,3\text{-dimethylpyridine}] \text{ in J} = \frac{7.80}{1000} \times 0.50 \div \frac{10.0}{1000} = 0.390\text{ mol dm}^{-3}$$

- (iv) Calculate the initial pH of **J**.

$K_b(2\text{-ethylpiperidine})$ is $= 10^{3.88}$ (≈ 7600) $\times K_b(2,3\text{-dimethylpyridine})$, \therefore 2-ethylpiperidine is a much stronger base)

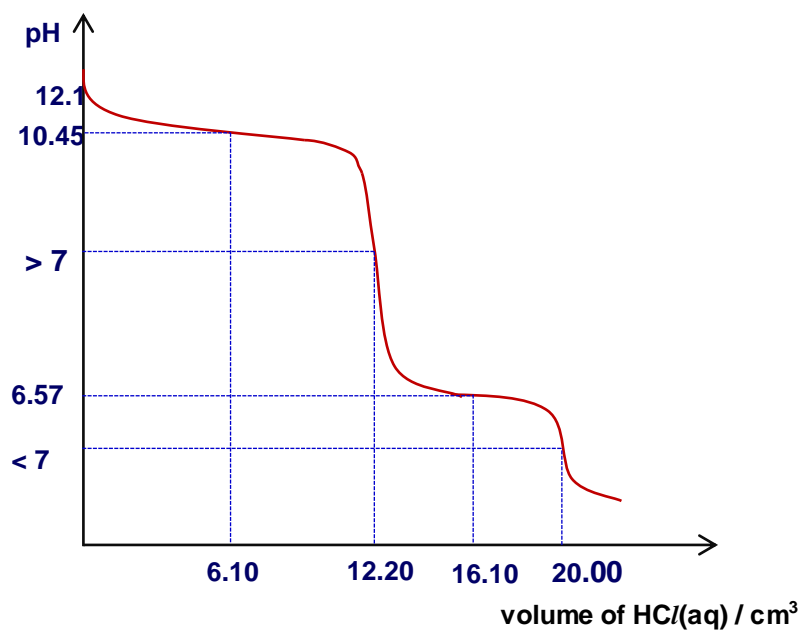
initial pH of solution **J** = pH of 2-ethylpiperidine in solution

$$\begin{aligned} [\text{OH}^-] &= \sqrt{[\text{base}] \times K_b} = \sqrt{(0.610 \times 10^{-3.55})} \\ &= 1.31 \times 10^{-2}\text{ mol dm}^{-3} \end{aligned}$$

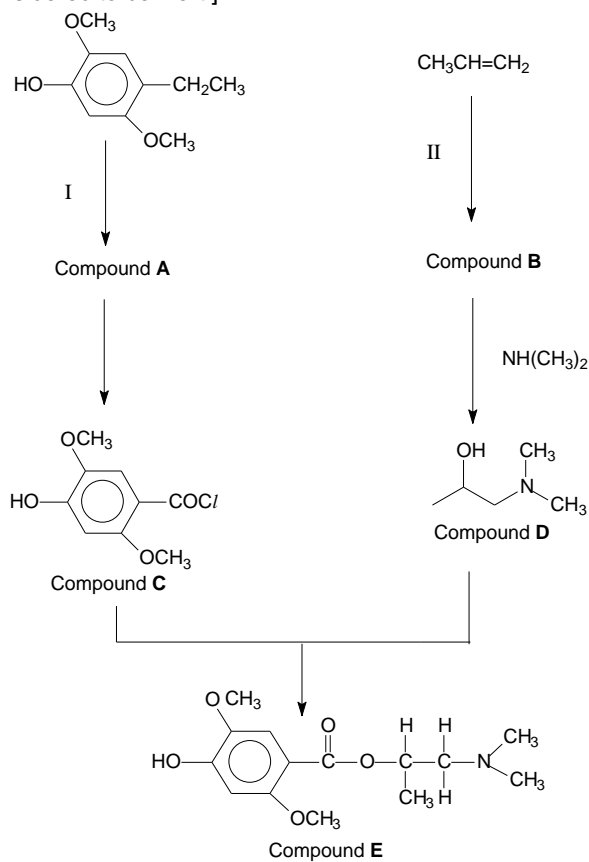
$$\therefore \text{pOH} = 1.88, \text{ pH} = 12.1$$

- (v) Hence, sketch the shape of the pH curve during this titration, showing the pH values and volumes of HCl(aq) at significant points.

- initial pH = **12.1**
- pH at 1st max buffer capacity = **10.45** ($= 14 - 3.55$), **$6.10\text{ cm}^3\text{ HCl(aq)}$**
- pH at 2nd max buffer capacity = **6.57** ($= 14 - 7.43$), **$16.10\text{ cm}^3\text{ HCl(aq)}$**
- 1st eq pt **$12.20\text{ cm}^3\text{ HCl(aq)}$**
- 2nd eq pt **$20.00\text{ cm}^3\text{ HCl(aq)}$**
- correct shape (2-steps)



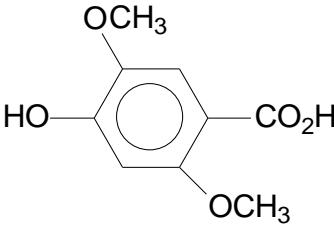
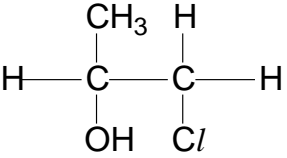
- 6 The reaction scheme below shows the synthesis of compound **E** starting from an alkene and a phenol derivative. [The CH_3O group can be considered to be inert.]



- (a) (i) State reagents and conditions for steps I and II.

Step I: KMnO_4 , dil H_2SO_4 , heat
 Step II: $\text{Cl}_2(\text{aq})$ or $\text{Br}_2(\text{aq})$

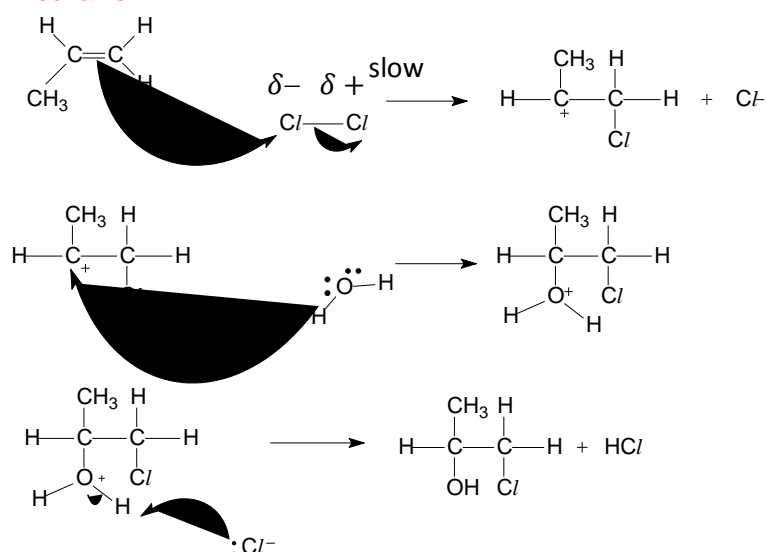
(ii) Suggest the identities of compounds **A** and **B**.

A	Compound B
	

(iii) Describe a mechanism for the reaction taking place in step II. In your answers, include all necessary curly arrows, lone pairs and relevant dipoles.

Electrophilic Addition

Detailed mechanism:

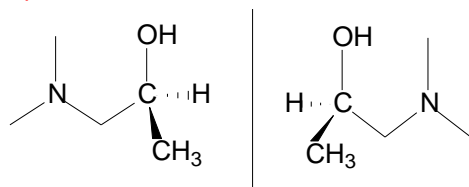


Penalty:

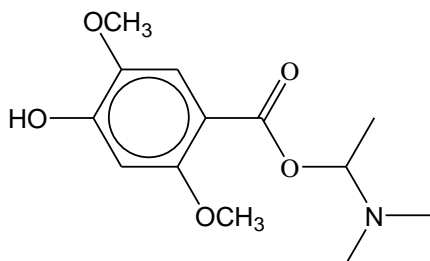
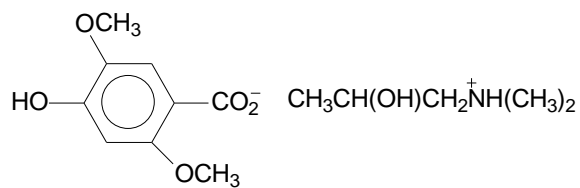
- any missing arrow/ wrong direction of arrow/arrow pointing to wrong atoms (for 1st and 2nd step)
- missing partial charge
- OH⁻ instead of H₂O attack in 2nd step
- missing slow step in 1st step
- missing lone pair on nucleophile

(iv) State the type of stereoisomerism exhibited by **D**. Draw appropriate structures to illustrate your answer.

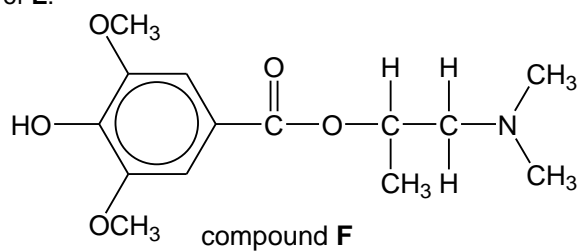
Optical Isomerism



(v) Draw the organic product formed when compound **A** reacts with compound **D**.



(b) Compound **F** is an isomer of **E**.



Describe a simple chemical test to distinguish between compounds **E** and **F**.

Add aqueous bromine:

E: yellow brown / orange bromine decolourises

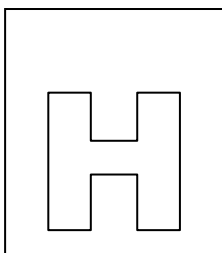
F: yellow brown / orange colour remains

Or

Add liquid bromine:

E: reddish brown bromine decolourises

F: reddish brown colour remains



SH2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE
NAME

SUBJECT
CLASS

REGISTRATION
NUMBER

CHEMISTRY

Paper 3 Free response

9647/03

Monday 29 Aug 2016
2 hour

READ THESE INSTRUCTIONS FIRST

Answer any **four** questions.

A Data Booklet is provided.

The use of an approved scientific calculator is expected, where appropriate.

You are reminded of the need for good English and clear presentation in your answers.

At the end of the examination, fasten all your work securely behind the cover page.

The number of marks is given in brackets [] at the end of each question or part question.

This paper consists of **11** printed pages.

Answer any **four** questions.

- 1 (a) Alums are salts formed when a monovalent cation with a large radius (e.g. K^+ or NH_4^+) and a trivalent cation with a small radius (e.g. Al^{3+} , Fe^{3+} or Cr^{3+}) combine with sulfate ions.

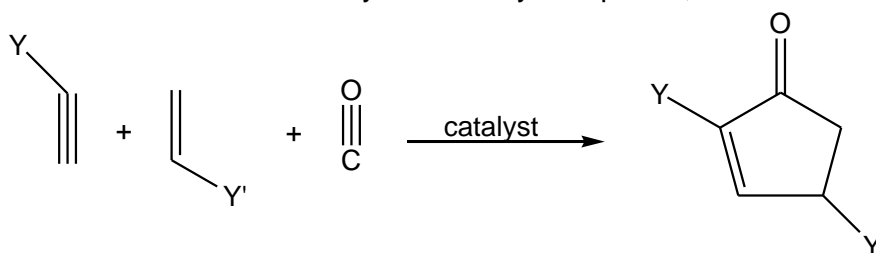
An ammonium iron alum has the formula $(NH_4)_aFe(SO_4)_b \cdot 12H_2O$.

To determine the chemical formula of the alum, two separate samples of **0.500 g** of the alum were each dissolved in 100 cm^3 of water.

An excess of $NaOH(aq)$ was added to the first alum solution and the mixture was boiled. The ammonia gas evolved exactly neutralised 5.2 cm^3 of $0.200 \text{ mol dm}^{-3} HCl(aq)$.

An excess of zinc was added to the second alum solution, which reduced Fe^{3+} to Fe^{2+} , and the resulting solution was filtered. The filtrate collected required 10.4 cm^3 of $0.0200 \text{ mol dm}^{-3}$ acidified $KMnO_4(aq)$ for complete reaction.

- (i) Calculate the amount of NH_4^+ ions present in **0.500 g** of the alum. [1]
- (ii) Write an equation for the reaction between the filtrate and acidified $KMnO_4$. Hence, calculate the amount of Fe^{3+} ions present in **0.500 g** of the alum. [2]
- (iii) Using your answers in (i) and (ii), determine the values of **a** and **b**. [2]
- (b) The Pauson-Khan reaction is a gas phase reaction between an alkyne, an alkene and carbon monoxide to form a cyclic carbonyl compound, as shown below.



where Y and Y' can be Cl or H.

An organic compound **A** was produced from the Pauson-Khan reaction. The compound has the following composition by mass; 51.5 % C, 13.7% O, 30.5% Cl and 4.3% H. M_r of **A** is 116.5.

Upon heating with ethanolic $AgNO_3$, **A** gave a white precipitate.

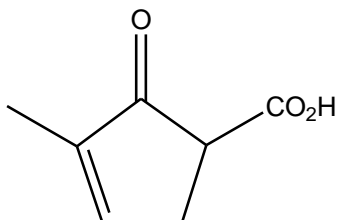
- (i) Determine the molecular formula of **A** and draw its structural formula. [3]

(ii) By quoting relevant data from the *Data Booklet* and given that the bond energy of $\text{C}\equiv\text{O}$ is 1079 kJ mol^{-1} , prove that the enthalpy change of reaction in the Pauson-Khan reaction to form **A** is -221 kJ mol^{-1} . [2]

(iii) Predict the sign of the entropy change for the formation of **A** in the above reaction. Hence, deduce if the reaction is feasible at a high or low temperature. [2]

(iv) With the aid of a Boltzmann diagram, predict and explain the effect on the rate of the Pauson-Khan reaction without a catalyst. [3]

(c) Another possible product of the Pauson-Khan reaction is shown below:



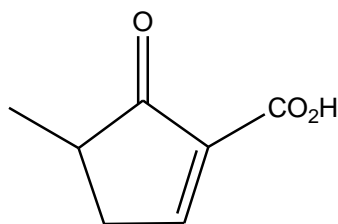
B

(i) Draw the product formed when **B** reacts with each of the following.

- I. cold $\text{KMnO}_4(\text{aq})$ in $\text{KOH}(\text{aq})$
- II. H_2 , Pt
- III. LiAlH_4

[3]

(ii) Compound **C** is an isomer of **B**, and has the structure shown below:



C

Deduce which compound, **B** or **C**, is more acidic.

[2]

[Total: 20]

- 2 Bovine serum albumin (BSA) is a serum albumin protein which is a main constituent of cow milk. It is often used as a protein concentration standard in laboratory experiments. The BSA molecule is a single chain of 607 amino acids, 66% of which are incorporated into β -pleated sheets. It is a globular protein and takes up a roughly spherical shape in water.

Six of the most common amino acids in the BSA molecule are listed below.

Amino acid	Formula of side chain (R in $RCH(NH_2)CO_2H$)
Isoleucine	$-CH(CH_3)CH_2CH_3$
Methionine	$-CH_2CH_2SCH_3$
Tyrosine	$-CH_2C_6H_4OH$
Asparagine	$-CH_2CONH_2$
Lysine	$-CH_2(CH_2)_3NH_2$
Asparate	$-CH_2CO_2H$

Table 1

- (a) (i) There are three pK_a values associated with lysine: 2.17, 9.04, 12.48.

Make use of these pK_a values to suggest the major species present in aqueous solutions of lysine with the following pH values:

- pH 1
- pH 3
- pH 10
- pH 14

[4]

- (ii) Suggest **two** positive tests (stating reagents, conditions and observations) that could be used to confirm the identity of two amino acids: asparagine and tyrosine.

[2]

- (b) (i) Describe the conditions needed to hydrolyse a protein non-enzymatically.

[1]

- (ii) Briefly describe what is meant by the *primary structure of proteins*.

[1]

- (iii) Describe how a polypeptide chain is held in the shape of a β -pleated sheet.

[1]

- (iv) With the aid of a diagram and using suitable amino acids from *Table 1*, describe how hydrogen bonding maintains the tertiary structure of proteins.

[2]

- (v) The following recipe illustrates how a lemon sponge cake can be made.

Steps:

1. Cream butter and sugar until light and fluffy.
2. Beat in eggs.
3. Sift over the flour, add lemon juice and rind.
4. Bake for 10 minutes at 180 °C.

Suggest how any of the **two** steps described above can cause denaturation, making specific reference to suitable pairs of amino acids present in BSA.

[4]

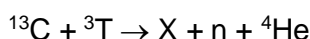
- (c) When a beam of ${}^3_1\text{T}^+$ particles is passed through an electric field, the angle of deflection is found to be $+5.00^\circ$. You may assume that all the ${}^3_1\text{T}^+$ particles travel at the same speed through an electric field of constant strength.
- (i) Calculate the angles of deflection if ${}^3_1\text{T}^+$ is replaced with the following, leaving your answers to 2 decimal places:

- ${}^{32}\text{S}^{2-}$
- ${}^{56}\text{Fe}^{3+}$

[2]

The mass of particle **D** is 25 times that of ${}^3_1\text{T}^+$. When a beam of **D** is passed through the same electric field as that used for ${}^3_1\text{T}^+$, the angle of deflection is found to be $+0.60^\circ$.

- (ii) Determine the overall charge on a particle of **D**. [1]
- (iii) A particle of **D** contains 27 protons. Deduce the number of electrons in this particle and hence write its electronic configuration. [1]
- (iv) A nuclear reaction is a reaction in which there is a change in the atomic nucleus.
An experimental nuclear reactor uses ${}^{13}\text{C}$ and tritium, ${}^3_1\text{T}$, as fuel. A nuclear reaction between these two atoms are described below (n is a neutron).

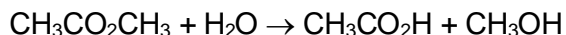


Suggest the identity of **X** with the aid of the *Data Booklet*.

[1]

[Total: 20]

- 3 (a) The kinetics of the hydrolysis of methyl ethanoate may be investigated by determining the concentration of ethanoic acid produced.



In a 1 dm³ vessel, 0.350 mol of CH₃CO₂CH₃ was heated with dilute hydrochloric acid which acted as a catalyst. The following results were obtained.

Time / s	[CH ₃ CO ₂ H] / mol dm ⁻³
0	0
340	0.105
680	0.185
1080	0.243
1440	0.278

- (i) What is meant by the term *order of reaction*? [1]
- (ii) By drawing a suitable graph using the data given above, determine the order of reaction with respect to methyl ethanoate. [3]
- (iii) Given that the hydrolysis reaction is first order with respect to hydrochloric acid, write the rate equation for this reaction. [1]
- (b) Esters can also undergo reduction in the presence of a strong reducing agent such as lithium aluminium hydride, LiAlH₄. The reaction produces two alcohols.

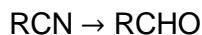


Using this information, and that provided below, draw out the full mechanism for the formation of ethanol from methyl ethanoate.

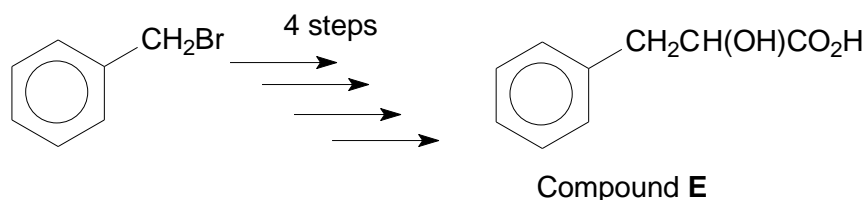
- There is an initial nucleophilic attack by hydride ion, H⁻, on the ester to generate a negatively charged ion.
- The C=O π bond reforms and the –OR' group is eliminated from the ester, forming an aldehyde.
- A second hydride ion attacks the aldehyde to generate an alkoxide ion.
- The alkoxide ion is then protonated to form the alcohol.

[3]

- (c) Besides esters, nitriles can also undergo reduction to give aldehydes in the presence of another strong reducing agent, diisobutyl aluminium hydride (DIBAL).



- (i) By considering the change in oxidation states of the reacting carbon, suggest why the conversion of a nitrile to an aldehyde is a reduction reaction. [1]

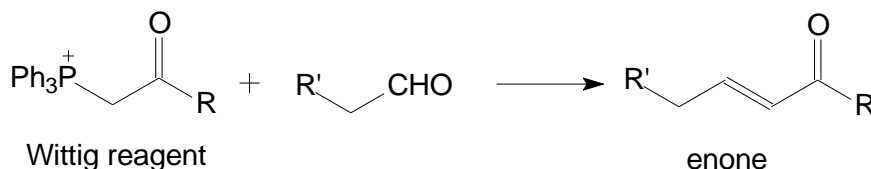


- (ii) Compound E can be synthesised using DIBAL as a reducing agent in one of the steps above.

Suggest the reagents and conditions required for each step of synthesis and identify all the intermediate compounds.

[5]

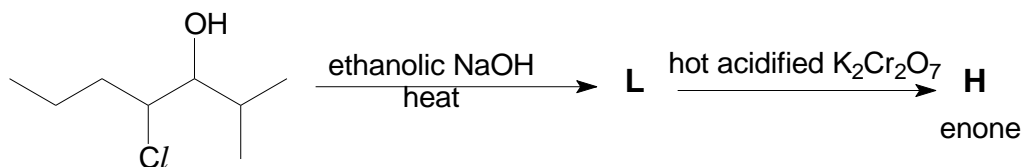
- (d) A Wittig reagent can convert an aldehyde to an enone, a ketone with an adjacent double bond.



(where 'Ph' represents $-\text{C}_6\text{H}_5$)

Wittig reagent **F** was reacted with an aldehyde **G** to give an enone **H**. **H** was then reacted with hot acidified potassium manganate(VII) to give two different compounds, **J** and **K**.

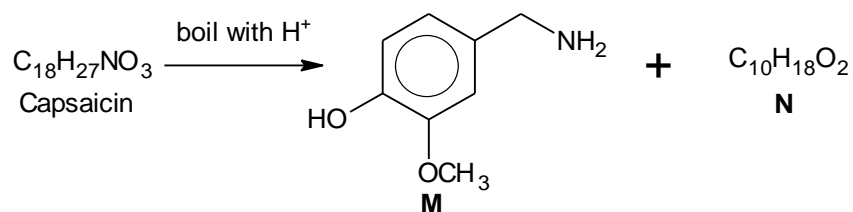
H can also be synthesised by the following route.



- (i) Suggest the identities of compounds **H**, **J**, **K** and **L**. [4]
- (ii) Suggest the identities of compounds **F** and **G**. [2]

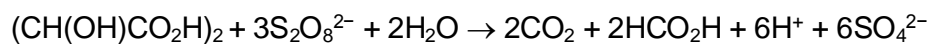
[Total: 20]

- 4 (a) The question below is related to some compounds of Group II elements.
- Write an equation, with state symbols, for the thermal decomposition of strontium nitrate. [1]
 - Use the *Data Booklet* to explain how the thermal stability of zinc nitrate might compare to strontium nitrate. [3]
 - The chemical properties of beryllium and its compounds show similarity to those of aluminium. Beryllium form complexes of coordination number 4.
 - Aluminium chloride, $AlCl_3$, dimerises to form Al_2Cl_6 .
Draw the displayed formula of Al_2Cl_6 , showing clearly the bond angle about Al . [1]
 - Explain why $AlCl_3$ dimerises. [1]
 - Explain, using a relevant equation, why a solution of beryllium chloride is acidic. [2]
 - Beryllium oxide, similar to aluminium oxide, is amphoteric. Suggest the nature of bonding in beryllium oxide. [1]
 - Write equations for the reaction of beryllium oxide with $HCl(aq)$ and $NaOH(aq)$. [2]
- (b) Capsaicin is a slightly acidic compound responsible for the burning sensation of chilli peppers. Its molecular structure can be deduced by the following reaction scheme.
[Assume that $-OCH_3$ group is inert.]



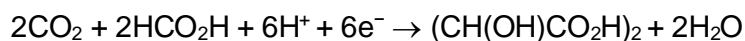
- When **N** is heated with concentrated acidified potassium manganate(VII), **P**, $C_6H_{10}O_4$, and **Q**, C_4H_8O , are formed.
P is formed from the reaction of $Br(CH_2)_4Br$ with hot ethanolic KCN followed by hydrolysis. **Q** can be reduced to an alcohol, **R**, which is optically active.
Deduce the structures of **N**, **P**, **Q**, **R** and capsaicin. [5]
- Draw the organic compound formed when **M** reacts with CH_3CH_2COCl . [1]

- (c) Peroxodisulfate(VI) ion, $S_2O_8^{2-}$, is capable of oxidising tartaric acid, $(CH(OH)CO_2H)_2$, to carbon dioxide and methanoic acid. The E°_{cell} of the reaction is +0.99 V.



The reaction is very slow, even when temperature is increased. However, the reaction rate can be increased by adding a suitable catalyst.

The half equation for the reduction of carbon dioxide to tartaric acid is

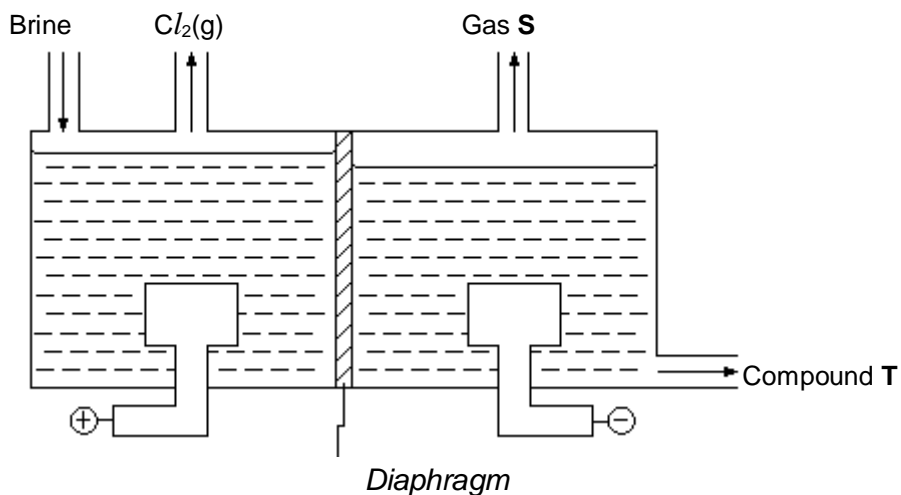


Using the *Data Booklet*, show how cobalt(III) ion can act as a homogenous catalyst.

[3]

[Total: 20]

- 5 (a) Chlorine is manufactured from brine (concentrated NaCl) by electrolysis using inert electrodes at room temperature. The anode and cathode compartments are separated by a diaphragm which is a permeable membrane.



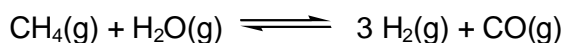
- (i) Suggest the identities of gas **S** and compound **T**. [1]
- (ii) Using relevant E^\ominus data from the *Data Booklet*, suggest a reason why the electrolysis of dilute $\text{NaCl}(\text{aq})$ produces mainly oxygen at the anode, whereas the electrolysis of brine produces mainly chlorine gas. [2]
- (iii) Suggest the products that might be formed if the diaphragm is removed and the solution is stirred. Write an equation for any reaction that occurs. [1]
- (b) Orchids can be made into jewellery that gleams with either a reddish tint of copper or shiny gold. In copper-plating, orchids are coated with a thin layer of graphite paste before placing them in a bath of aqueous copper(II) sulfate and electroplating.
- (i) Suggest a reason why orchids are first coated with graphite. [1]
- (ii) To ensure high standards of electroplated orchids, the copper coating must be at least 0.5 mm thick. Given that the total surface area of a typical orchid is 10 cm^2 and the operating current is 20 A, calculate the time required to electroplate an orchid. [Density of copper = 8.96 g cm^{-3}] [3]

- (c) The use of *Data Booklet* is relevant to this question.

When iron is heated with bromine, FeBr₃ is produced. However, when heated with iodine, FeI₂ is produced instead.

- (i) Write the **two** equations for the formation of FeBr₃. [2]
- (ii) Hence explain why when iron is heated with iodine, FeI₂ is produced but not FeI₃. [2]
- (iii) An unknown element **U** is diatomic and is below iodine in Group VII of the Periodic Table. The hydride of **U**, **HU**, and hydride of iodine, HI, differ in their physical properties and reactivities.
- (I) Suggest and explain how the polarities of H-**U** and H-I bonds differ.
- (II) Suggest and explain how the boiling points of **HU** and HI differ.
- (III) Suggest and explain how the acidities of **HU** and HI differ when dissolved in water.
- [4]

- (d) Methane and steam react to give hydrogen and carbon monoxide as follows.



A mixture of 3.0 mol of CO and 8.0 mol of H₂ is heated in a closed container of 2 dm³ and allowed to reach dynamic equilibrium at 300 K. The amount of hydrogen at equilibrium was found to be 6.5 mol.

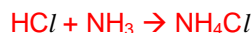
- (i) Determine the amounts of methane and steam at equilibrium. [2]
- (ii) Write the expression for the equilibrium constant, K_c , for the above equilibrium and calculate the K_c at 300 K. [2]

[Total: 20]

Suggested answers for 2016 SH2 Chemistry Paper 3

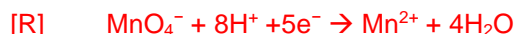
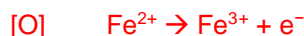
- 1 (a) Alums are salts formed when a monovalent cation with a large radius (e.g. K^+ or NH_4^+) and a trivalent cation with a small radius (e.g. Al^{3+} , Fe^{3+} or Cr^{3+}) combine with sulfate ions.
An ammonium iron alum has the formula $(NH_4)_aFe(SO_4)_b \cdot 12H_2O$.
To determine the chemical formula of the alum, two separate samples of 0.5 g of the alum were each dissolved in 100 cm^3 of water.
An excess of $NaOH(aq)$ was added to the first alum solution and the mixture was boiled. The ammonia gas evolved exactly neutralised 5.2 cm^3 of 0.200 $mol\ dm^{-3}$ $HCl(aq)$.
An excess of zinc was added to the second alum solution, which reduced Fe^{3+} to Fe^{2+} , and the resulting solution was filtered. The filtrate collected required 10.4 cm^3 of 0.0200 $mol\ dm^{-3}$ acidified $KMnO_4(aq)$ for complete reaction.

(i) Calculate the amount of NH_4^+ ions present in 0.5 g of the alum. [1]



$$\text{Amount of } NH_4^+ = \frac{5.2}{1000} \times 0.200 = \underline{1.04 \times 10^{-3} \text{ mol}} \quad [1]$$

(ii) Write an equation for the reaction between the filtrate and acidified $KMnO_4$. Hence, calculate the amount of Fe^{3+} ions present in 0.5 g of the alum. [2]



$$\text{Amount of } MnO_4^- = \frac{10.4}{1000} \times 0.0200 = 2.08 \times 10^{-4} \text{ mol} \quad [1/2]$$

$$\text{Amount of } Fe^{3+} = 2.08 \times 10^{-4} \times 5 = \underline{1.04 \times 10^{-3} \text{ mol}} \quad [1]$$

(iii) Using your answers in (i) and (ii), determine the values of **a** and **b**. [2]

There is 1 Fe^{3+} per formula unit of $(NH_4)_aFe(SO_4)_b \cdot 12H_2O$

$$\frac{\text{Amount of } Fe^{3+}}{\text{Amount of } NH_4^+} = \frac{1.04 \times 10^{-3}}{1.04 \times 10^{-3}} = \frac{1}{1}$$

$$\text{Hence, } \mathbf{a} = \underline{1} \quad [1]$$

Comparing the charges of the ions:

$$+1 + 3 - 2(\mathbf{b}) = 0$$

$$\mathbf{b} = \underline{2} \quad [1]$$

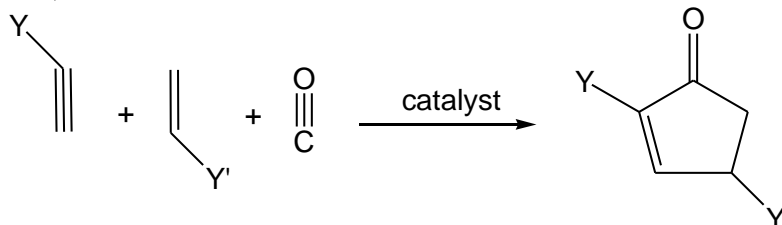
or

$$M_r \text{ of compound} = \frac{0.5}{1.04 \times 10^{-3}} = 480.77$$

$$\text{Given that } \mathbf{a} = 1, 14.0 + 1.0 \times 4 + 55.8 + (32.1 + 16.0 \times 4) \mathbf{b} + 12 \times (16.0 + 2.0) = 480.77$$

$$\mathbf{b} = 1.987 \approx 2$$

- (b) The Pauson-Khan reaction is a gas phase reaction between an alkyne, an alkene and carbon monoxide to form a cyclic carbonyl compound, as shown below.



where Y and Y' can be Cl or H.

An organic compound **A** was produced from the Pauson-Khan reaction. The compound has the following composition by mass; 51.5% C, 13.7% O, 30.5% Cl and 4.3% H. M_r of **A** is 116.5.

Upon heating with ethanolic $AgNO_3$, **A** gave a white precipitate.

- (i) Determine the molecular formula of **A** and draw its structural formula. [3]

	C	O	Cl	H
% by mass	51.5	13.7	30.3	4.3
Relative amount / mol	4.29	0.856	0.853	4.3
Simplest ratio	5	1	1	5

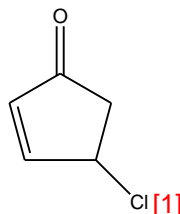
[1] for table

Empirical formula of **A**: C_5H_5OCl

Let molecular formula of **A** be $(C_5H_5OCl)_n$

$$\therefore n(12.0 \times 5 + 1.0 \times 5 + 16.0 + 35.5) = 116.5$$

$$n = 1$$



Molecular formula of **A** = C_5H_5OCl

[1]

- (ii) By quoting relevant data from the *Data Booklet* and given that the bond energy of $C\equiv O$ is 1079 kJ mol^{-1} , prove that the enthalpy change of reaction in the Pauson-Khan reaction to form **A** is -221 kJ mol^{-1} . [2]

Bonds broken: 1 $C\equiv O$, 1 $C\equiv C$, 1 $C=C$

Bonds formed: 4 $C-C$, $C=C$, $C=O$ [1]

$$\Delta H = \Sigma BE(\text{bonds broken}) - \Sigma BE(\text{bonds formed})$$

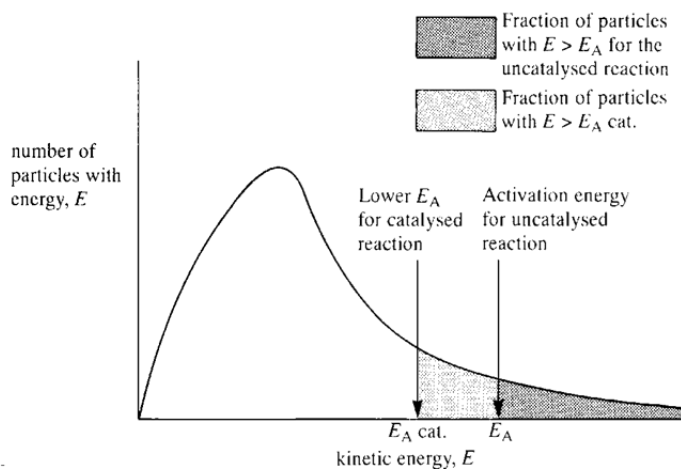
$$= 1079 + 840 + 610 - (4 \times 350 + 610 + 740) = -221 \text{ kJ mol}^{-1} \quad [1]$$

- (iii) Predict the sign of the entropy change for the formation of **A** in the above reaction. Hence, deduce if the reaction is feasible at a high or low temperature. [2]

There is a **decrease** in the number of **gaseous particles**, hence there is a decrease in the degree of disorderliness; entropy **decreases** or ΔS is **negative**. [1]

Both ΔH and ΔS are of negative values; temperature must **be low** enough for $|-T\Delta S| < |\Delta H|$ **such that $\Delta G < 0$** . [1]

- (iv) With the aid of a Boltzmann diagram, predict and explain the effect on the rate of the Pauson-Khan reaction without a catalyst. [3]



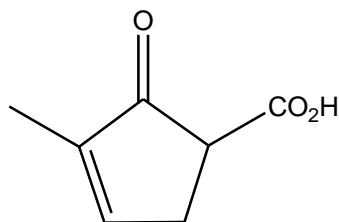
Marking points

- y-axis: proportion / number of particles; x-axis: energy / kinetic energy
- start from zero (origin)
- peak of the graph lies on the left half
- graph plateaus off towards the end

- labelling of particles with energies above E_a and E_a'
 Total marks for graph: [1½]; each point missing: [-½]

Without a catalyst, the activation energy will be higher, thus there are **fewer particles** [½] with energy greater than or equal to the activation energy, resulting in **lower frequency of effective collisions** [½] and **rate of the reaction decreases**. [½]

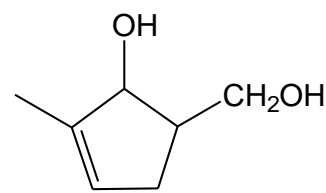
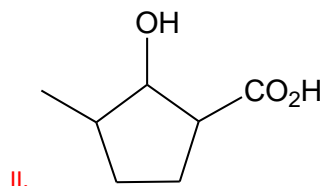
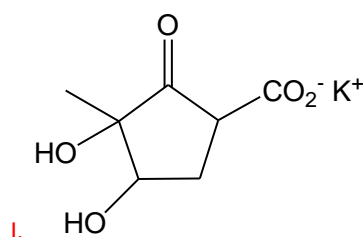
(c) Another possible product of the Pauson-Khan reaction is shown below:



(i) Draw the product formed when **B** reacts with each of the following.

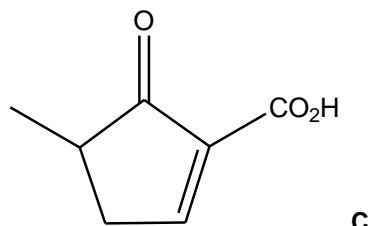
- I. cold $\text{KMnO}_4(\text{aq})$ in $\text{KOH}(\text{aq})$
- II. H_2 , Pt
- III. LiAlH_4

[3]



[1] each

(ii) Compound **C** is an isomer of **B**, and has the structure shown below:

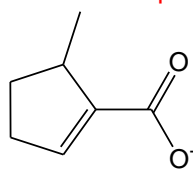


Deduce which compound, **B** or **C**, is more acidic.

[2]

C is a stronger acid than **B**. [1]

The **delocalisation** of lone pair of electrons from O^- in $-\text{CO}_2^-$ to the overlapped p orbitals in $\text{C}=\text{O}$ and $\text{C}=\text{C}$ helps to **disperse the negative charge** on the conjugate base (carboxylate anion) of **C**,



, to a **greater extent than** that of **B**, making the anion of **C** **more stable**. [1]

[Total: 20]

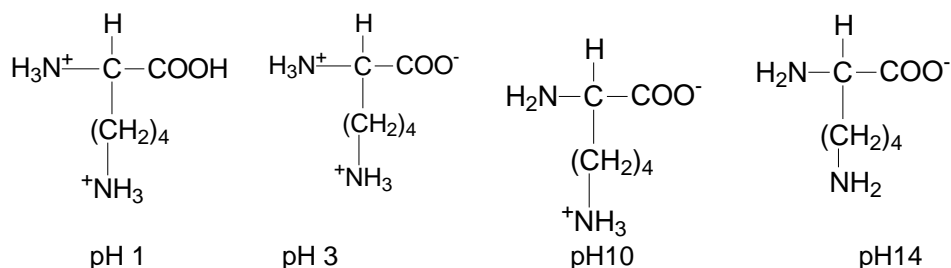
- 2 **Bovine serum albumin, BSA** is a serum albumin protein which is a main constituent of cow milk. It is often used as a protein concentration standard in lab experiments. The BSA molecule is a single chain of 607 amino acids, 66% of which are incorporated into a β -pleated sheet. It is a globular protein and takes up a roughly spherical shape in water. Six of the most common amino acids in the BSA molecule are listed below.

Amino acid	Formula of side chain (R in $\text{RCH}(\text{NH}_2)\text{CO}_2\text{H}$)
Isoleucine	$-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$
Methionine	$-\text{CH}_2\text{CH}_2\text{SCH}_3$
Tyrosine	$-\text{CH}_2\text{C}_6\text{H}_4\text{OH}$
Asparagine	$-\text{CH}_2\text{CONH}_2$
Lysine	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$
Aspartate	$-\text{CH}_2\text{COOH}$

Table 1: Types of amino acid

- (a) (i) There are three pK_a values associated with lysine: 2.17, 9.04, 12.48.
Make use of these pK_a values to suggest the major species present in solutions of lysine with the following pH values:
- pH 1
 - pH 3
 - pH 10
 - pH 14

[4]



- (ii) Suggest two positive tests (stating reagents and observations) that would enable the amino acids asparagine and tyrosine to confirm their identities. [2]

[1 each]

Test 1: Add NaOH(aq), warm

Observations: Tyrosine: no evolution of alkaline gas which turns red litmus paper blue;

Asparagine: alkaline gas evolves, turns red litmus paper blue.

Test 2a: Add neutral FeCl_3 (aq)

Observations: Tyrosine: purple complex forms; Asparagine: no purple complex forms.

Test 2b: Add Br_2 (aq)

Observations: Tyrosine: yellow / orange solution decolourised; Asparagine: yellow / orange solution remains.

- (b) (i) Describe the conditions needed to hydrolyse a protein non-enzymatically. [1]

HCl (aq)/ H_2SO_4 (aq); prolonged heating

or

NaOH (aq)/ KOH (aq); prolonged heating

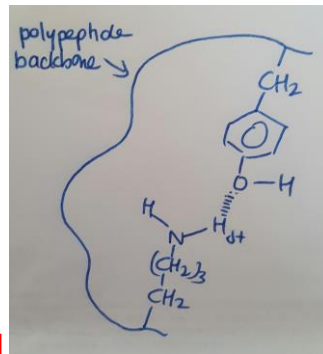
- (ii) Briefly describe what is meant by the *primary structure of proteins*. [1]

Primary protein structure is a **unique sequence of amino acids** joined by peptide bonds in a polypeptide chain.

- (iii) Describe how a polypeptide chain is held in the shape of a β -pleated sheet. [1]

The polypeptide backbone (polypeptide chain) is **folded** into **β -pleated sheet**. It is maintained through **hydrogen bonding** found at **regular intervals** between **N-H group of one peptide and C=O group of another peptide** of the polypeptide backbone.

- (iv) Using suitable amino acids in Table 1, describe hydrogen bonding interaction in the tertiary structure of proteins with the aid of a diagram. [2]



Tyrosine / Lysine / Aspartate / Asparagine

[1]

[1]

- (v) The following recipe illustrates how a lemon sponge cake can be made.
1. Cream butter and sugar until light and fluffy.
 2. Beat in eggs.
 3. Sift over the flour, add lemon juice and rind.
 4. Bake for 10 minutes at 180 °C

Suggest how the above changes can cause denaturation, making specific reference to suitable pairs of amino acids present in BSA. [2]

Beat in eggs: Mechanical agitation can break the weak interactions (van der Waals and Hydrogen bonding) that hold the configuration of the protein together. (Isoleucine, Methionine, Tyrosine, Asparagine) [2]

Add lemon juice: Destruction of ionic bonds occurs extensively at extreme pH conditions.

Adding acids: $H^+ + -COO^- \rightarrow -COOH$

H^+ from acids reacts with $-COO^-$ on R groups of amino acid residues to form $-COOH$. Ionic bonds present are broken. (Lysine and Aspartate) [2]

Bake for 10 minutes at 180 °C: Energy supplied is sufficient to overcome the intermolecular interactions / ionic bonds which hold the configuration of the protein together. (any pairs of amino acids) [2]

[2]

- (c) When a beam of ${}^3_1T^+$ particles is passed through an electric field, the angle of deflection is found to be +5.00 °. You may assume that all the ${}^3_1T^+$ particles travel at the same speed through an electric field of constant strength.

Calculate the angles of deflection if ${}^3_1T^+$ is replaced with the following, leaving your answers to 2 decimal places.

- (i) ${}^{32}_{16}S^{2-}$

[1]

Angle of deflection $\propto \frac{\text{charge}}{\text{size}}$

$$\text{Angle of deflection for } {}^{32}_{16}S^{2-} = -\frac{\frac{2}{16}}{\frac{3}{1}} \times 5^\circ = -0.94^\circ [1]$$

${}^{56}_{26}Fe^{3+}$

[1]

Angle of deflection $\propto \frac{\text{charge}}{\text{size}}$

$$\text{Angle of deflection} = +\frac{\frac{3}{26}}{\frac{56}{1}} \times 5^\circ = +0.80^\circ [1]$$

The mass of particle **Q** is 25 times that of ${}^3_1T^+$. When a beam of **Q** is passed through the same electric field as in (a), the angle of deflection is found to be +0.60°.

- (ii) Determine the overall charge on a particle of **Q**.

[1]

Q is positively charged

Angle of deflection $\propto \frac{\text{charge}}{\text{size}}$

$$+0.60^\circ = \frac{x}{\frac{25}{1}} \times 5^\circ$$

$$x = +3 [1]$$

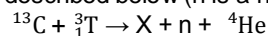
- (iii) A particle of **Q** contains 27 protons. Deduce the number of electrons in this particle and hence write its electronic configuration. [1]

No of proton = 27

No of electron = 27-3 = 24

Electronic configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$

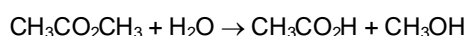
- (iv) A nuclear reaction is a reaction in which is a change to an atomic nucleus.
An experimental nuclear reactor use ^{13}C and Tritium, ^3_1T , as fuel. A nuclear reaction between these two atoms are described below (n is a neutron).



Suggest the identities of **X** with the use of the *Data Booklet*. [1]

X: $^{11}_5\text{B}$ or boron or B

- 3 (a) The kinetics of the hydrolysis of methyl ethanoate may be investigated by determining the concentration of ethanoic acid produced.



In a 1 dm^3 mixture, 0.350 mol of $\text{CH}_3\text{CO}_2\text{CH}_3$ was heated with dilute hydrochloric acid which acts as the catalyst. The following results were obtained.

Time / s	$[\text{CH}_3\text{CO}_2\text{H}] / \text{mol dm}^{-3}$	$[\text{CH}_3\text{CO}_2\text{CH}_3] / \text{mol dm}^{-3}$
0	0	0.350
340	0.105	0.245
680	0.185	0.165
1080	0.243	0.107
1440	0.278	0.072

- (i) What is meant by the term *order of reaction*? [1]

Rate = $k [\text{A}]^m [\text{B}]^n$ where

m = *order of reaction with respect to A*

n = *order of reaction with respect to B*

m + n = *overall order of reaction*

or

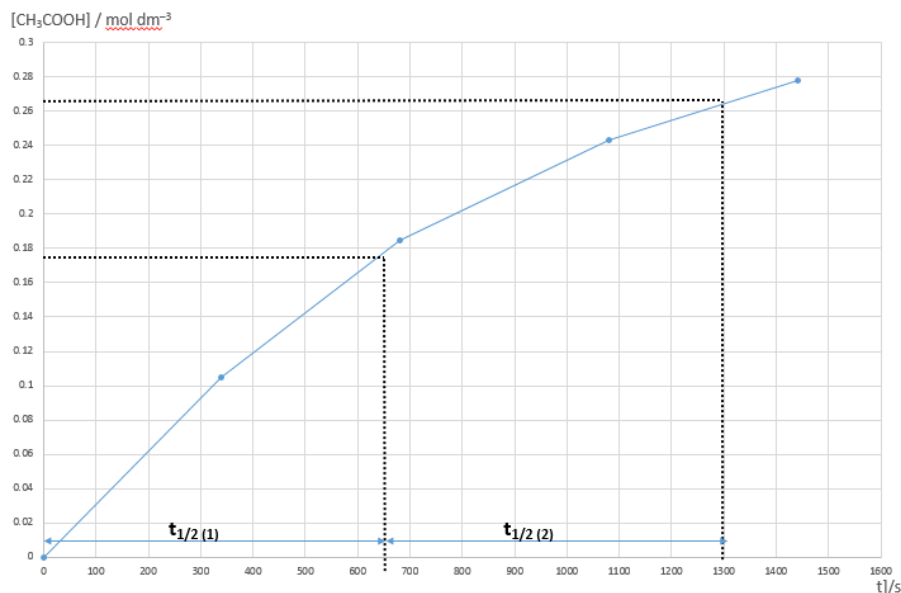
The order of reaction is the power to which the concentration of a reactant is raised in an experimentally determined rate equation.

- (ii) By drawing a suitable graph using the data given above, determine the order of reaction with respect to methyl ethanoate. [3]

Since $\text{CH}_3\text{CO}_2\text{CH}_3 \equiv \text{CH}_3\text{CO}_2\text{H}$, 0.350 mol of $\text{CH}_3\text{CO}_2\text{H}$ must be formed with 100% yield as 0.350 mol of $\text{CH}_3\text{CO}_2\text{CH}_3$ was used.

50% yield, $[\text{CH}_3\text{CO}_2\text{H}]$ formed = 0.175 mol (1st half-life)

75% yield, $[\text{CH}_3\text{CO}_2\text{H}]$ formed = 0.263 mol (2nd half-life)



Correctly plotted of all points [1]

Correctly labelled axes and 2 half-lives

Correctly identified 2 half-lives:

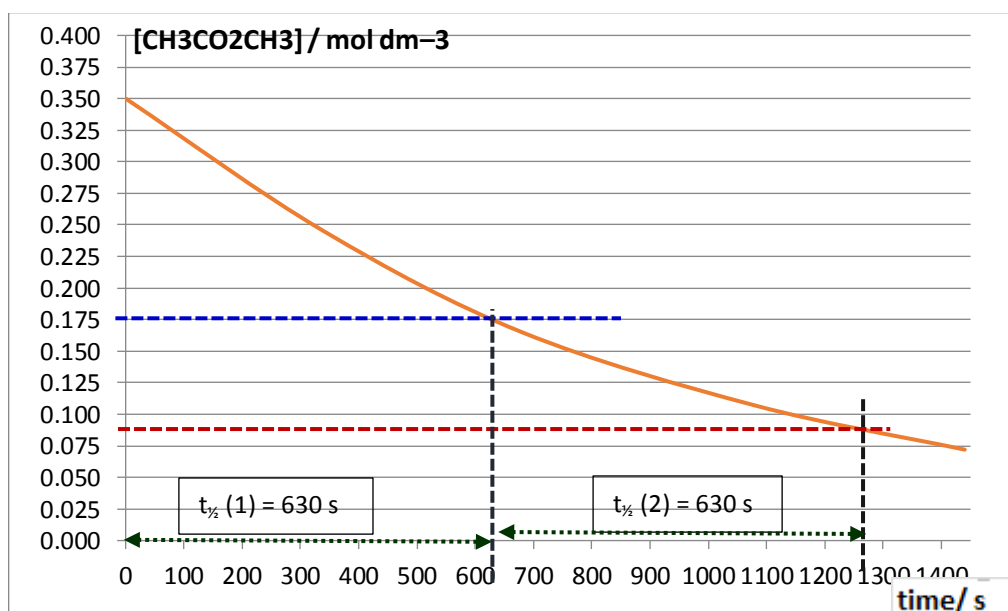
$$t_{1/2}(1) = t_{1/2}(2) \text{ [1]}$$

order of reaction wrt methyl ethanoate is 1. [1]

(stating order is 1 wo correct reasoning will not score this mark)

- (iii) Given that the hydrolysis reaction is first order with respect to hydrochloric acid, write down the rate equation for this reaction. [1]

$$\text{Rate} = k[\text{CH}_3\text{CO}_2\text{CH}_3] [\text{H}^+]$$

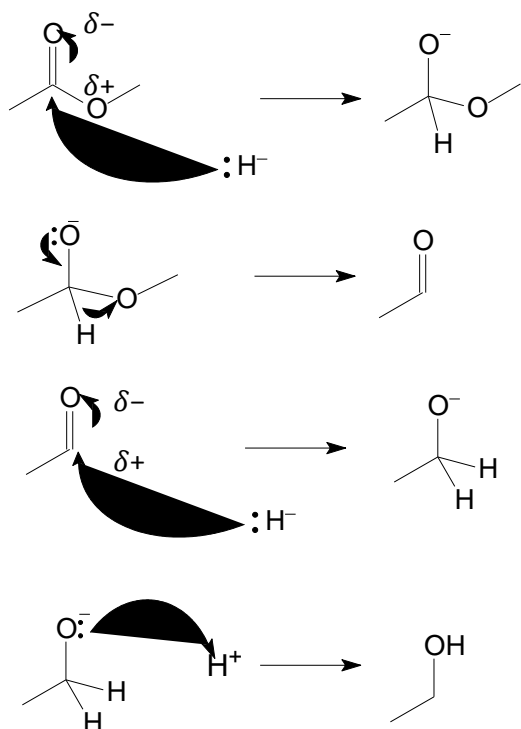


- (b) Esters can also undergo reduction in the presence of a strong reducing agent such as lithium aluminium hydride, LiAlH_4 . The reaction produces two alcohols.



Using this information, and that provided below, suggest a mechanism for the formation of ethanol from methyl ethanoate.

- There is an initial nucleophilic attack by hydride ion, H^- , on the ester to generate a negatively charged ion.
- The $\text{C}=\text{O}$ π bond reforms and the $-\text{OR}'$ group is eliminated from the ester, forming an aldehyde.
- A second hydride ion attacks the aldehyde to generate an alkoxide ion.
- The alkoxide ion is then protonated to form the alcohol.



Mark Scheme:

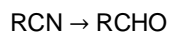
Penalise 1 m if wrong starting cpd given.

Penalise 0.5m for every following mistakes:

- Each missing/wrong arrows (up to 2 m)
- Missing any partial charge on ester and aldehyde
- Missing lone pairs on hydride

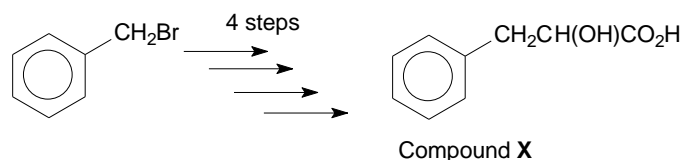
[3]

- (c) Besides esters, nitriles can also undergo reduction to give aldehyde in the presence of another strong reducing agent, diisobutyl aluminium hydride (DIBAL).

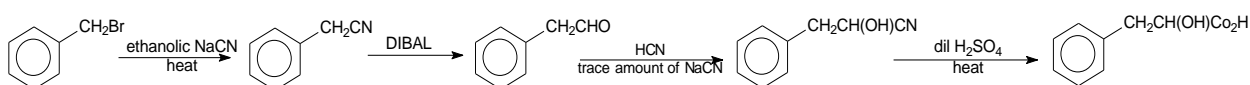


- (i) By considering the change in oxidation states of the reacting carbon, suggest why the conversion of a nitrile to an aldehyde is a reduction reaction. [1]

The oxidation state of carbon changes from +3 in nitrile to +1 in aldehyde.



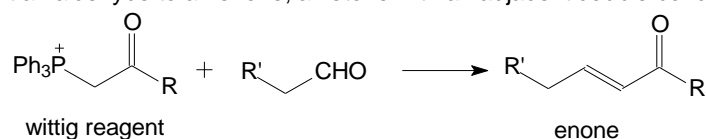
- (ii) Compound X can be synthesised using DIBAL as a reducing agent in one of the steps above. Suggest the reagents and conditions required for each step of synthesis and identify all the intermediate compounds. [5]



[1]: each intermediate product (total 3m)

[½]: each reagent and condition (total 2m)

- (d) A Wittig reagent can convert an aldehyde to an enone, a ketone with an adjacent double bond.

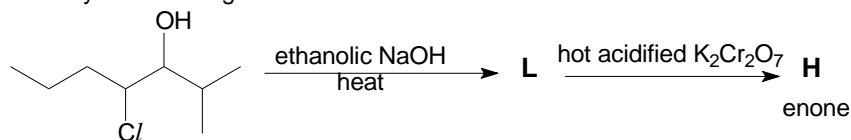


(Where 'Ph' represents $-\text{C}_6\text{H}_5$)

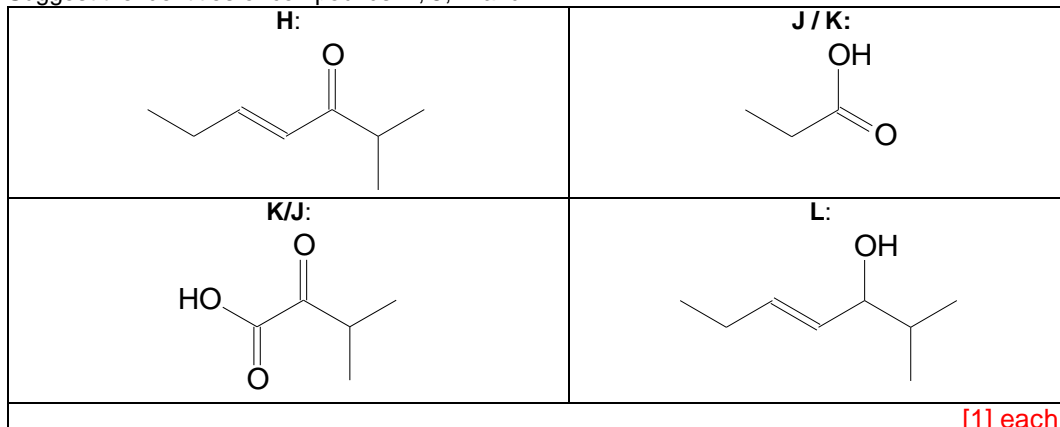
8

Wittig reagent **F** was reacted with an aldehyde **G** to give an enone **H**. **H** was then reacted with hot acidified potassium manganate (VII) to give two different compounds, **J** and **K**.

H can also be synthesised by the following route.



(i) Suggest the identities of compounds **H**, **J**, **K** and **L**. [4]



(iii) Suggest the identities of compounds **F** and **G**.
1 each [2]

F: $\text{Ph}_3\text{PCH}_2\text{COCH}(\text{CH}_3)_2$

G: $\text{CH}_3\text{CH}_2\text{CHO}$

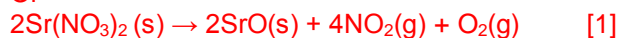
[1] each

4 (a) The question below is related to some Group II compounds.

(i) Write an equation, with state symbols, for the thermal decomposition of strontium nitrate. [1]



Or



(ii) Use the *Data Booklet* to explain how the thermal stability of zinc nitrate might compare to strontium nitrate. [3]

From *Data Booklet*,

ionic radius of $\text{Zn}^{2+} = 0.074 \text{ nm}$; ionic radius of $\text{Sr}^{2+} = 0.113 \text{ nm}$ [$\frac{1}{2}$]

Zn^{2+} has a higher $\frac{\text{charge}}{\text{size}}$ ratio / charge-density and hence a higher polarizing power. [$\frac{1}{2}$]

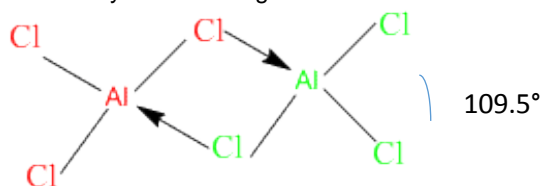
Hence Zn^{2+} will polarise/distort the electron cloud of NO_3^- to a greater extent; N–O bond is weakened more [$\frac{1}{2}$]

Easier/requires less energy to overcome the N–O bond in zinc nitrate. [$\frac{1}{2}$]

Thus, **$\text{Zn}(\text{NO}_3)_2$ is thermally less stable** than $\text{Sr}(\text{NO}_3)_2$. [1].

(iii) The chemical properties of beryllium and its compounds show similarity to that of aluminium. Beryllium complexes have coordinate number 4.

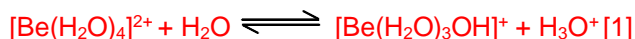
I. Aluminium chloride, AlCl_3 , dimerises to form Al_2Cl_6 . Draw the displayed formula of Al_2Cl_6 , showing clearly the bond angle about Al. [1]



II. Explain why AlCl_3 dimerises. [1]

Al is electron deficient/has one vacant p orbital/has not achieved octet and hence can accept a lone pair from Cl.

III. Explain, using relevant equations, why a solution of beryllium chloride is acidic. [2]

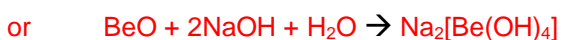
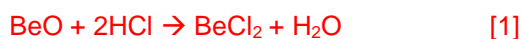


Be^{2+} has high charge density (or $\frac{\text{charge}}{\text{size}}$ ratio) and is able to polarise O-H bond of water, weakening and breaking the O-H bond to give H^+ . [1]

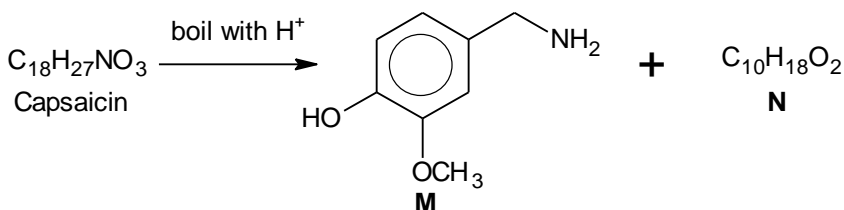
IV. Beryllium oxide, similar to aluminium oxide, is amphoteric. Suggest the nature of bonding in beryllium oxide. [1]

Beryllium oxide is ionic with covalent character. [1]

V. Write equations for the reaction of beryllium oxide with $\text{HCl}(\text{aq})$ and with $\text{NaOH}(\text{aq})$. [2]



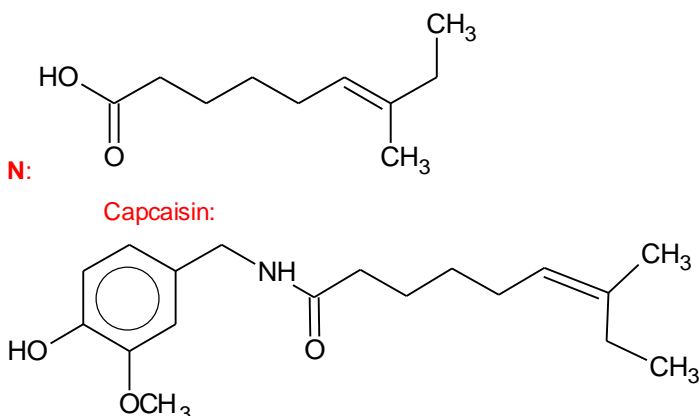
(b) The compound responsible for the hot taste of chilli peppers is capsaicin. Its molecular structure can be deduced by the following reaction scheme. Capsaicin is slightly acidic.



(i) When N is heated with concentrated acidified potassium manganate(VII), P, $\text{C}_6\text{H}_{10}\text{O}_4$ and Q, $\text{C}_4\text{H}_8\text{O}$, are formed.

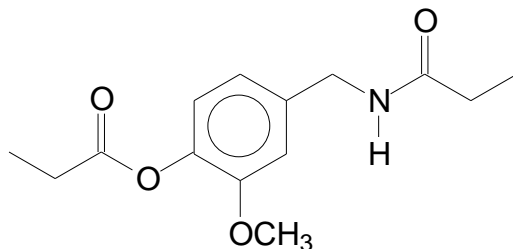
P is formed from the reaction of $\text{Br}(\text{CH}_2)_4\text{Br}$ with hot ethanolic KCN followed by hydrolysis. Q can be reduced to an alcohol, R, which is optically active.

Deduce the structures of N, P, Q, R and capsaicin. [5]



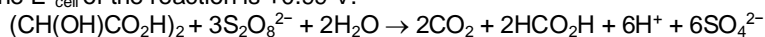
[1] each

- (ii) Assuming that $-\text{OCH}_3$ is inert, draw the organic compound formed when **M** reacts with $\text{CH}_3\text{CH}_2\text{COCl}$.



[1]

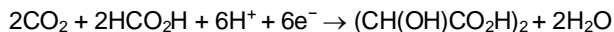
- (iii) Peroxodisulfate(VI) ion, $\text{S}_2\text{O}_8^{2-}$, is capable of oxidising tartaric acid, $(\text{CH}(\text{OH})\text{CO}_2\text{H})_2$, to carbon dioxide and methanoic acid. The E°_{cell} of the reaction is +0.99 V.



The reaction is very slow, even when temperature is increased.

However, the reaction rate can be increased by adding a suitable catalyst.

The half equation for the reduction of carbon dioxide to tartaric acid is



Using the *Data Booklet*, show how cobalt(III) ion can act as a homogenous catalyst.



$$\text{Since } E^\circ_{\text{cell}} = E^\circ_{\text{red}} (\text{S}_2\text{O}_8^{2-} / \text{SO}_4^{2-}) + E^\circ_{\text{ox}} ((\text{CH}(\text{OH})\text{CO}_2\text{H})_2 / \text{HCO}_2\text{H}, \text{CO}_2)$$

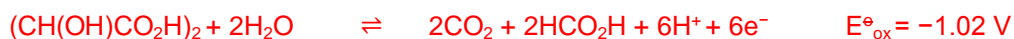
$$+0.99 = +2.01 + E^\circ_{\text{ox}} ((\text{CH}(\text{OH})\text{CO}_2\text{H})_2 / \text{HCO}_2\text{H}, \text{CO}_2)$$

$$E^\circ_{\text{ox}} ((\text{CH}(\text{OH})\text{CO}_2\text{H})_2 / \text{HCO}_2\text{H}, \text{CO}_2) = -1.02 \text{ V}$$

$$\text{Hence } E^\circ_{\text{red}} (\text{HCO}_2\text{H}, \text{CO}_2 / (\text{CH}(\text{OH})\text{CO}_2\text{H})_2) = +1.02 \text{ V [1]}$$

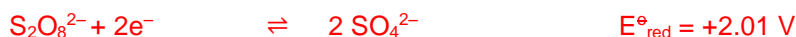
With Co^{3+} catalyst,

Step 1



$$E^\circ_{\text{cell}} = +0.80 \text{ V} > 0, \text{ reaction is feasible. [1]}$$

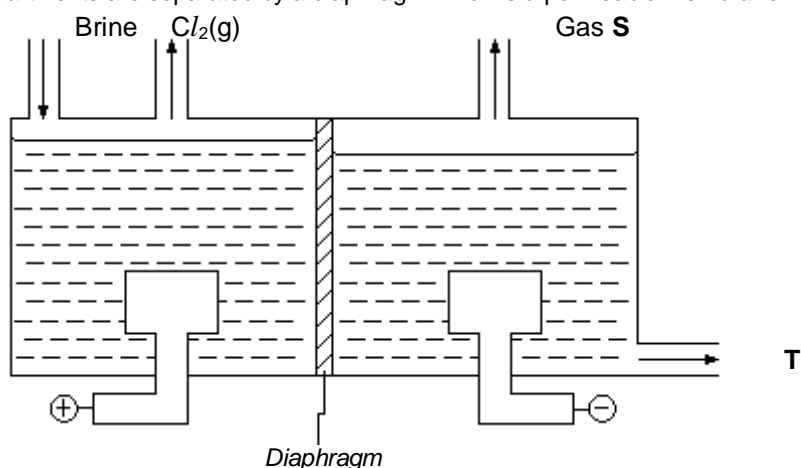
Step 2



$$E^\circ_{\text{cell}} = +0.19 \text{ V} > 0, \text{ reaction is feasible. [1]}$$

Co^{3+} oxidises tartaric acid to give CO_2 and HCOOH and itself is reduced to Co^{2+} . Co^{2+} then reduces $\text{S}_2\text{O}_8^{2-}$ to SO_4^{2-} and Co^{3+} is regenerated. Hence Co^{3+} acts as a homogeneous catalyst.

- 5 (a) Chlorine is manufactured from brine, concentrated NaCl, by electrolysis using inert electrodes at room temperature. The anode and cathode compartments are separated by a diaphragm which is a permeable membrane.



- (i) Suggest the identities of gas **S** and compound **T**. [1]

S: Hydrogen / H₂ [½] **T:** NaOH [½]

- (ii) Using relevant E° data from the *Data Booklet*, suggest the reason why the electrolysis of dilute NaCl(aq) produces mainly oxygen at the anode, whereas the electrolysis of brine produces mainly chlorine gas. [2]

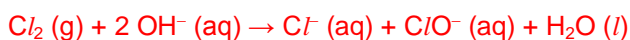
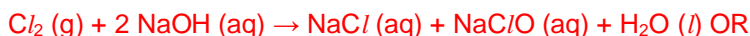


When dilute NaCl is used, E°_{ox} H₂O is more positive/less negative than E°_{ox} of Cl⁻, hence water is preferentially oxidised to O₂. [½]

When brine is used, concentration of Cl⁻ is high, eqm (2) shifts right and

E_{ox}(Cl⁻) is more positive/less negative than E°_{ox} of H₂O [½] (due the small initial difference between the E°_{ox} values) hence Cl⁻ is preferentially oxidised to Cl₂. [½]

- (iii) Suggest what the products might be if the diaphragm is removed and the solution is stirred, by writing an equation for any reaction that occurs. [1]



No need for state symbols. [1] or [0]

- (b) Orchids can be made into jewellery that gleams with either a reddish tint of copper or shiny gold. In copper-plating, orchids are coated with a thin layer of graphite paste before placing them in a bath of aqueous copper(II) sulfate and electroplating.

- (i) Suggest a reason why orchids are first coated with graphite. [1]

To conduct electricity

- (ii) To ensure high standards, the copper coating must be at least 0.5 mm thick. Given that the total surface area of a typical orchid is 10 cm² and the operating current is 20 A, calculate the time required to plate an orchid. [Density of copper = 8.96 g cm⁻³] [3]

$$\text{Volume of Cu layer} = 10 \times \frac{0.5}{10} = 0.5 \text{ cm}^3$$

$$\text{Mass of Cu layer} = 8.96 \times 0.5 = 4.48 \text{ g}$$

$$\text{Amt of Cu in the layer} = \frac{4.48}{63.5} = 0.07055 \text{ mol [1]}$$

$$\text{Amt of electrons required} = 2(0.07055) = 0.14110 \text{ mol [1]}$$

$$\text{Amt of charge required} = 0.14110 \times 96500 = 13616 \text{ C}$$

$$\text{Time required to plate an orchid} = \frac{13616}{20} = 680.81 = 681 \text{ s [1]}$$

- (c) The use of *Data Booklet* is relevant to this question.
When iron is heated with bromine, FeBr₃ is produced. However, when heated with iodine, FeI₂ is produced instead.

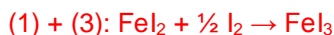
- (i) Write the **two** equations for the formation of FeBr₃. [2]



- (ii) Hence explain why when iron is heated with iodine, FeI₂ is produced but not FeI₃. [2]



$$E^\circ_{\text{cell}} = +0.54 + 0.44 = +0.98 \text{ V} > 0, \text{ reaction is feasible [1]}$$



$$E^\circ_{\text{cell}} = +0.54 - 0.77 = -0.23 \text{ V} < 0, \text{ reaction is not feasible}$$

Iodine can only oxidise iron to Fe²⁺, not Fe³⁺. [1]

- (iii) An unknown element, **U**, which exists as diatomic molecules, is said to be positioned below iodine in Group VII. The hydride of **U**, **HU**, and of iodine, **HI**, differ in their physical properties and reactivities.

- (i) Suggest and explain how the polarities of H-**U** and H-I bonds differ. [1]

H-U bond is less polar [½] as U is less electronegative [½].

- (ii) Suggest and explain how the boiling points of **HU** and **HI** differ. [2]

HU molecules have a larger electron cloud [½] than **HI** molecules, hence a greater ease of distortion of electron cloud [½; temporary dipole-induced dipole interactions (td-id) are more readily induced.

More energy is required to overcome the stronger td-id interactions between **HU** molecules [½].

- (iii) Suggest and explain how the acidities of **HU** and **HI** differ when each is dissolved in water. [1]

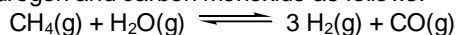
HU is a stronger acid [½]

H-U bond is weaker than H-I bond [½].

OR

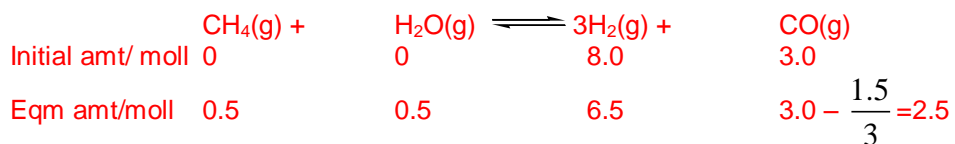
H-U bond is **longer** than H-I bond, hence is **easier to break** H-U bonds to give H⁺. [½]

- (d) Methane and steam react to give hydrogen and carbon monoxide as follows.



A mixture of 3.0 mol of CO and 8.0 mol of H₂ is heated in a closed container of 2 dm³ and allowed to reach dynamic equilibrium at 300 K. The amount of hydrogen at equilibrium was found to be 6.5 mol.

- (i) Determine the amounts of methane and steam at equilibrium. [2]



0.500 mol each for methane and steam

- (ii) Write the expression for the equilibrium constant, K_c , for the above equilibrium and calculate K_c at 300 K. [2]

$$\begin{aligned}
 k_c &= \frac{[\text{H}_2]^3[\text{CO}]}{[\text{CH}_4][\text{H}_2\text{O}]} \\
 &= \frac{\left(\frac{6.5}{2.0}\right)^3 \left(\frac{2.5}{2.0}\right)}{\left(\frac{0.5}{2.0}\right)^2} \\
 &= 687 \text{ mol}^2 \text{ dm}^{-6}
 \end{aligned}$$

Expression [1] answer with units [1]