Class	Reg Number
17	

Name ______________________________

MERIDIAN JUNIOR COLLEGE
JC2 Preliminary Examination
Higher 2

Calculator Model / No.

Chemistry 9729/01

Paper 1

21 September 2018
1 hour

Additional Material: *Data Booklet*
OMS

READ THESE INSTRUCTIONS FIRST

Write your name, class and register number in the spaces provided at the top of this page.

There are **thirty** questions in this paper. Answer **all** questions. For each question, there are four possible answers labelled **A**, **B**, **C** and **D**. Choose the **one** you consider correct and record your choice in soft pencil on the OMR answer sheet.

Read very carefully the instructions on the use of OMR answer sheet.

You are advised to fill in the OMR Answer Sheet as you go along; no additional time will be given for the transfer of answers once the examination has ended.

Use of OMR Answer Sheet

Ensure you have written your name, class register number and class on the OMR Answer Sheet.

Use a **2B** pencil to shade your answers on the OMR sheet; erase any mistakes cleanly. Multiple shaded answers to a question will not be accepted.

For shading of class register number on the ***OMR sheet***, please follow the given examples:
If your register number is **1**, then shade **01** in the index number column.
If your register number is **21**, then shade **21** in the index number column.

This document consists of **16** printed pages (including this cover page)

Answer all questions.

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

1 Zinc ethanoate, $(CH_3CO_2)_2Zn$ (M_r = 183.4) may be taken as a dietary supplement to prevent zinc deficiency.

What is the total number of ions present in a 5 cm^3 solution of aqueous zinc ethanoate given that the solution has a concentration of 10.64 g dm^{-3}?

A 1.7×10^{19} **B** 5.2×10^{20} **C** 3.5×10^{22} **D** 1.0×10^{23}

2 Gases given off during volcanic eruptions include H_2S and CS_2.

A 40 cm^3 gaseous sample of H_2S and CS_2, present in a 3 : 1 ratio respectively, was analysed by combustion using 100 cm^3 of oxygen. After measuring the volume of gas remaining, the product was treated with an excess of aqueous sodium hydroxide and the volume of gas measured again.

Any sulfur present is converted to SO_2 after combustion.

Given that all volume measurements were made under room conditions, what were the measured volumes?

	volume of gaseous mixture after burning / cm^3	volume of gaseous mixture after adding NaOH (aq) / cm^3
A	60	0
B	60	50
C	85	25
D	85	75

3 Consider the following reactions:

Reaction 1 $3\,F_2 + 4\,NH_3 \longrightarrow 3\,NH_4F + NF_3$

Reaction 2 $3\,Cl_2 + 8\,NH_3 \longrightarrow 6\,NH_4Cl + N_2$

Which of the following correctly shows the increasing order of reducing strength of the three species, Cl_2, F_2 and NH_3?

A $F_2 < Cl_2 < NH_3$

B $Cl_2 < F_2 < NH_3$

C $NH_3 < F_2 < Cl_2$

D $NH_3 < Cl_2 < F_2$

4 The successive ionization energies (I.E.) of two elements, **L** and **M**, are shown below:

IE / kJ mol^{-1}	**1st**	**2nd**	**3rd**	**4th**	**5th**	**6th**	**7th**	**8th**
L	1000	2252	3357	4556	7004	8496	27107	31719
M	578	1817	2745	11577	14842	18379	23326	27465

What is the likely formula of the compound formed when **L** and **M** reacts together?

A **L_3M_2** **B** **L_2M_3**

C **LM_3** **D** **L_3M**

5 Gaseous particle **X** has a charge of +1 and a proton number, n.

Gaseous particle **Y** has a proton number of (n+1) and is isoelectronic with **X**.

Which of the following statements correctly describes **X** and **Y**?

A **X** and **Y** are isotopes.

B **X** and **Y** atoms have same full electronic configurations.

C **Y** has a charge of +1 and same charge density as that of **X**.

D **Y** has a charge of +2 and smaller ionic radius than **X**.

6 Which of the following pairs of molecules satisfies both of the following conditions?

- Only one molecule is polar.
- The second molecule has a larger bond angle than the first molecule.

	First molecule	**Second molecule**
A	CO_2	F_2O
B	NF_3	SO_3
C	SF_6	XeF_4
D	SO_2	NO_2

7 Which of the following statements about A*l* is correct?

1 It has high melting point due to strong attraction between the delocalised electrons and residual cations.

2 It has stronger metallic bonding than Na.

3 It has high electrical conductivity due to the ability of its ions to carry the current.

A **1**, **2** and **3**

B **1** and **2** only

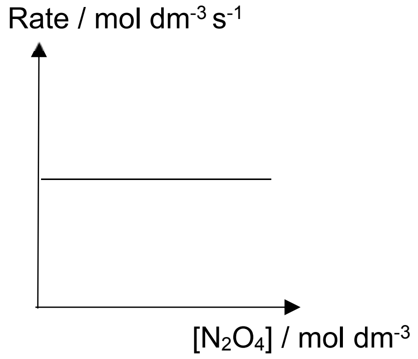
C **1** only

D **2** and **3** only

8 The decomposition of dinitrogen tetroxide, N_2O_4 is found to be first order with respect to the concentration of N_2O_4.

Which of the following graphs confirms the above finding?

A



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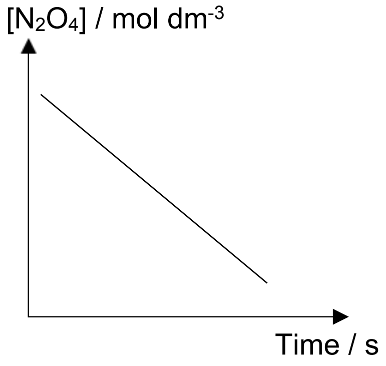

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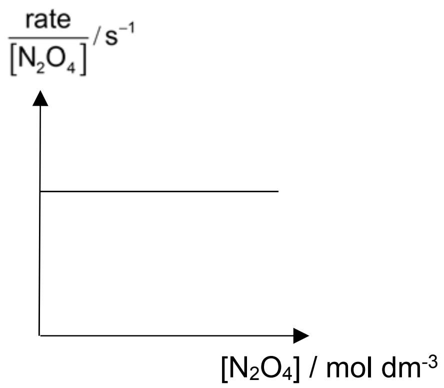
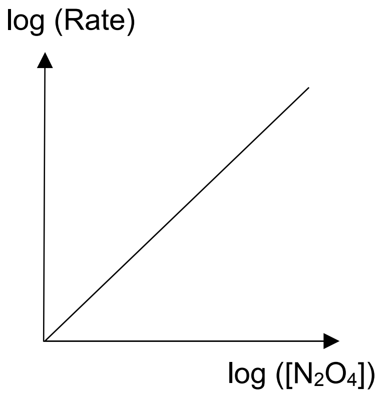


D



9 The hydrolysis of the anticancer drug *cis–platin* in water follows a first–order kinetics with a rate constant of 0.09 h^{-1} at 25 °C.

How long will it take for the concentration of a freshly prepared aqueous solution of *cis–platin* to decrease to 18% of its original concentration?

A 7.7 h

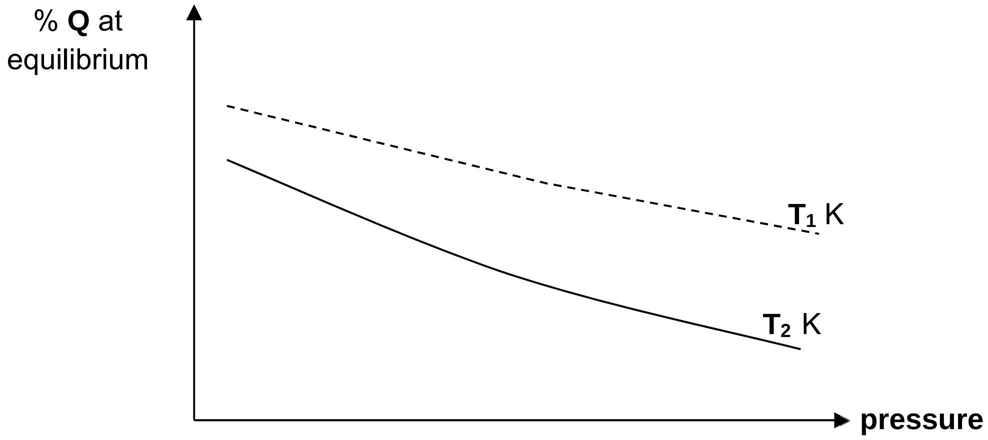
B 15.4 h

C 19.0 h

D 42.8 h

10 The graph below shows the variation of the percentage of **Q** present at equilibrium, with temperature and pressure.

$$3O_2(g) + 4NH_3(g) \rightleftharpoons 2N_2(g) + 6H_2O(g) \qquad \Delta H = -1248 \text{ kJ mol}^{-1}$$



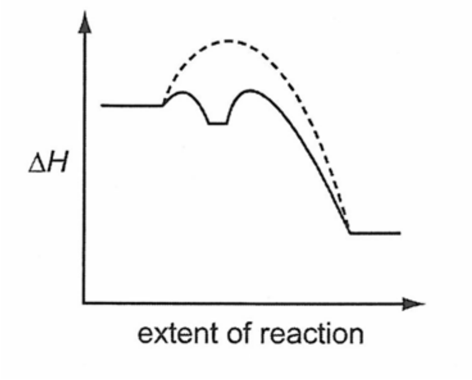
Which of the following systems could **Q** represent?

	Q	Temperature
A	O_2	$\mathbf{T_1 > T_2}$
B	NH_3	$\mathbf{T_2 > T_1}$
C	N_2	$\mathbf{T_1 > T_2}$
D	H_2O	$\mathbf{T_2 > T_1}$

11 The uncatalysed reaction between SO_2 and O_2 is slow.

$$2SO_2 + O_2 \longrightarrow 2SO_3$$

This reaction is speeded up in the presence of a suitable catalyst. The reaction profile diagram shows the energy changes involved during the catalyzed and uncatalysed reaction.



The uncatalysed reaction is shown as a dashed line.

Which of the following statements is true?

1 It involves a homogenous catalyst.

2 It involves a stable intermediate.

3 Both the activation energies of the forward and backward reaction are lowered in the presence of the catalyst.

A **1** only

B **3** only

C **2** and **3** only

D **1**, **2** and **3**

12 Water dissociates into ions according to the following equilibrium.

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad \Delta H^\ominus = +57 \text{ kJ mol}^{-1} \text{ at } 25°C$$

Which of the following is **incorrect** as temperature is increased to 50°C?

A The dissociation constant of water, K_w, increases

B pH of water remains at 7

C $[H^+]$ increases.

D $[H^+] = [OH^-]$

13 Which of the following pair of solutions will form an alkaline buffer solution that **best** resists pH changes when a small amount of acid or base is added.

A 10 cm^3 of 0.1 mol dm^{-3} NaOH and 20 cm^3 of 0.2 mol dm^{-3} $NH_4^+Cl^-$

B 25 cm^3 of 0.10 mol dm^{-3} NaOH added to 50 cm^3 0.10 mol dm^{-3} $CH_3CO_2^-Na^+$

C 10 cm^3 of 1 mol dm^{-3} H_2SO_4 and 20 cm^3 of 1 mol dm^{-3} $CH_3CH_2NH_2$

D 50 cm^3 of 0.05 mol dm^{-3} NaOH added to 50 cm^3 0.10 mol dm^{-3} $CH_3NH_3^+Cl^-$

14 The table shows some data of two acid–base indicators.

indicator	**approximate pH range of colour change**	**colour change**	
		acid	**alkali**
bromophenol–blue	3.0 – 4.6	yellow	purple
phenol–red	6.8 – 8.5	yellow	red

Which conclusion can be drawn about a solution when it turns bromophenol–blue purple and phenol–red yellow?

A The solution is weakly acidic.

B The solution is strongly acidic.

C The solution is weakly alkaline.

D The solution is strongly alkaline.

15 Below is one of the propagation steps in the reaction between CH_4 and Cl_2.

$$CH_4 + Cl\bullet \longrightarrow \bullet CH_3 + HCl \qquad \Delta H^\ominus_r = ?\ kJ\ mol^{-1}$$

Given the standard enthalpy changes of formation for CH_4, CH_3 radical and HC*l* are provided, which other enthalpy value is required to calculate $\Delta H^\ominus_r$?

A Standard enthalpy change of atomisation of chlorine

B Standard enthalpy change of formation of HC*l* (aq)

C Standard enthalpy change of formation of Cl_2 gas

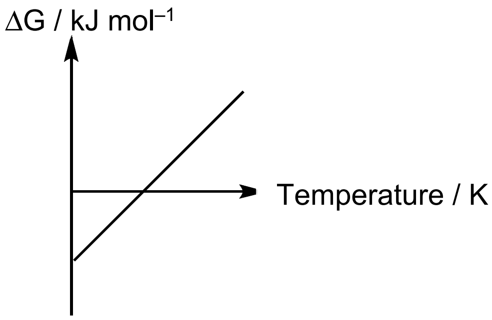
D Bond dissociation value for C–H bond

16 The combustion of gaseous hydrogen is a strongly exothermic process with equation as follows:

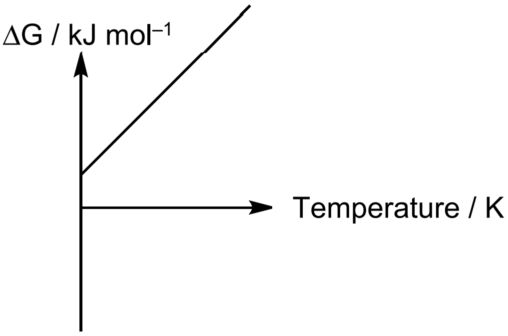
$$H_2\,(g) + \tfrac{1}{2}O_2\,(g) \longrightarrow H_2O\,(g)$$

Which of the following graphs best illustrates how ΔG varies with temperature?

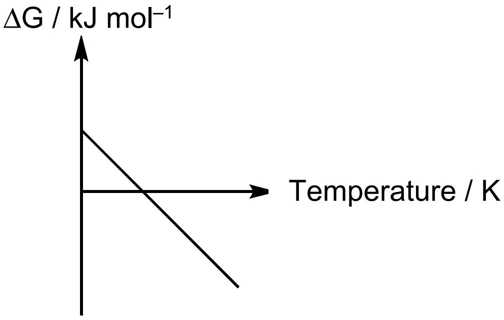
A



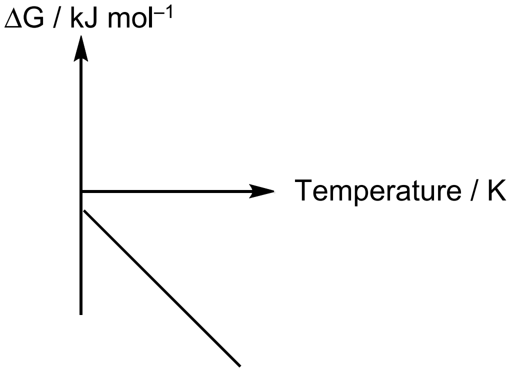
B



C



D



17 A student wanted to predict the solubility of barium chloride using calculation based on the following values.

Enthalpy change	Numerical value / kJ mol^{-1}
Lattice energy of barium chloride	2053
$\Delta H^{\ominus}_{hydration}$ for Ba^{2+}	1309
$\Delta H^{\ominus}_{hydration}$ for Cl^{-}	378

The student wrongly concluded that “barium chloride has $\Delta H^{\ominus}_{solution}$ of 366 kJ mol^{-1}, hence it is insoluble.”

Which of the following should be the correct conclusion?

A Barium chloride is insoluble. However, $\Delta H^{\ominus}_{solution}$ should be +366 kJ mol^{-1}, the positive sign needs to be shown.

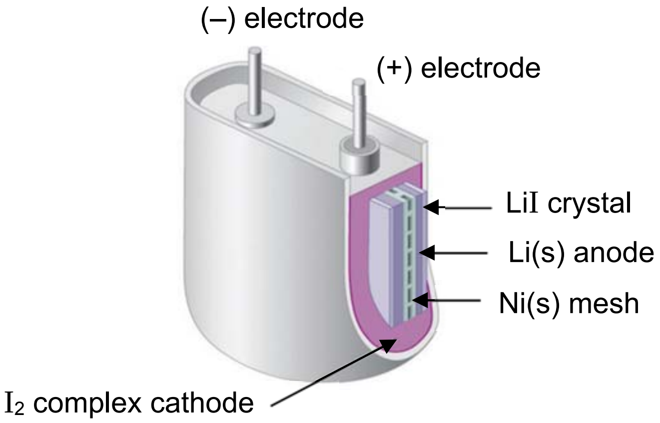
B Barium chloride is insoluble. However, $\Delta H^{\ominus}_{solution}$ should be +12 kJ mol^{-1}.

C $\Delta H^{\ominus}_{solution}$ should be –366 kJ mol^{-1}, hence barium chloride is soluble

D $\Delta H^{\ominus}_{solution}$ should be –12 kJ mol^{-1}, hence barium chloride is soluble

18 *Use of the Data Booklet is relevant for this question.*

Artificial pace makers are used to regulate the heartbeat of cardiac patients. The device is powered by a water–free lithium iodide battery as shown below.



Which of the following statements about the lithium iodide battery is correct?

A The I_2 complex cathode carries a negative charge.

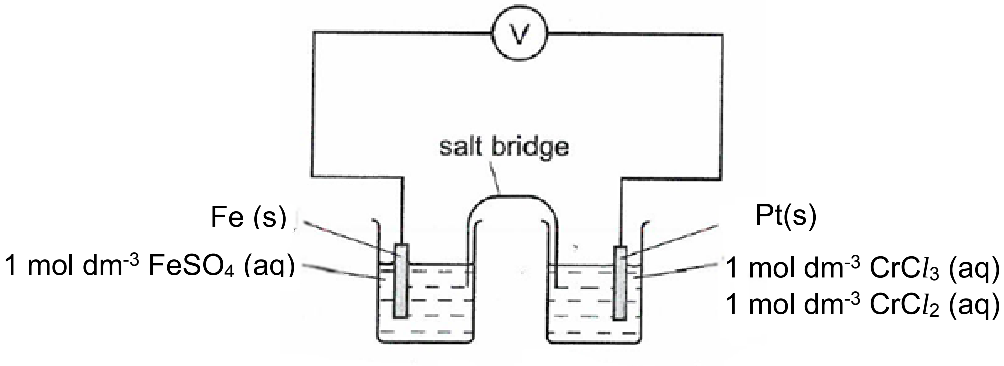
B The cell potential of the lithium iodide battery has a value of +2.50 V.

C The Ni mesh provides a medium for Li^+ ions to flow from Li (s) to I_2 complex.

D The pacemaker will last for less than 3 years if it contains 5 g of reactive Li(s) and operates at 0.8 mA.

19 *Use of the Data Booklet is relevant for this question.*

The following electrochemical cell was set up.



Which change to the half–cells could result in a cell potential of 0.00 V?

1 increase [$FeSO_4$]

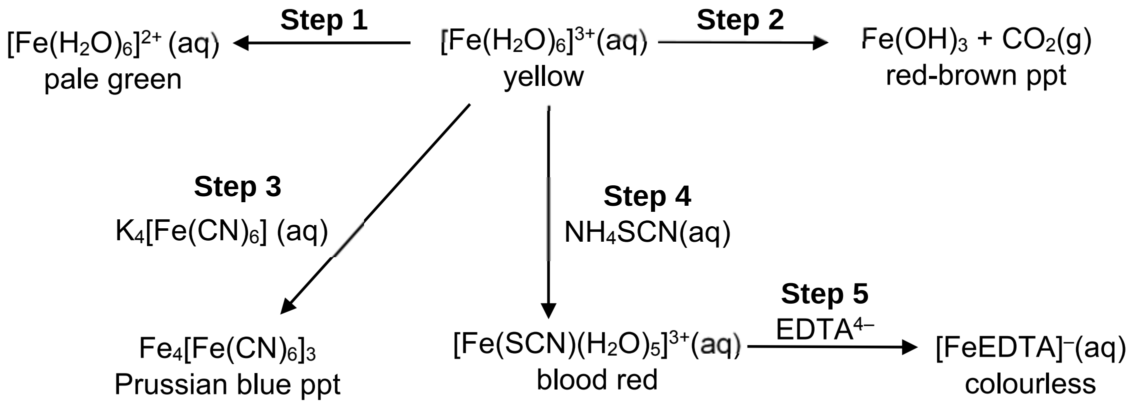
2 decrease [$CrCl_2$]

3 decrease [$CrCl_3$]

4 increase the surface area of the Fe electrode

A	**1** and **2** only	**B**	**1** and **3** only
C	**1**, **2** and **3** only	**D**	**3** and **4** only

20 The following shows a reaction scheme involving aqueous Fe(III) ions.



Which of the following statements regarding the reaction scheme shown above is correct?

A Step **1** and Step **4** are ligand exchange reactions.

B The increasing order of ligand strength is $H_2O < CN^- < SCN^- < EDTA^{4-}$.

C NaOH (aq) can be used as a reagent in Step **2**.

D Both Fe(II) and Fe(III) ions exist in the $Fe_4[Fe(CN)_6]_3$.

21 *Use of the Data Booklet is relevant for this question.*

Vanadyl (IV) sulfate, $VOSO_4(H_2O)_5$, is a hygroscopic blue solid and is a common source of vanadium in the laboratory.

Which of the following statements is true for an aqueous solution of $VOSO_4$?

1 VO^{2+}(aq) can serve as a homogeneous catalyst in the reaction between iodide ions and peroxodisulfate ions.

2 The solution appears blue as the d–orbitals are split by the presence of the sulfate ions.

3 Zn metal can reduce VO^{2+}(aq) to V^{2+}(aq).

A **1** and **2** only

B **1** and **3** only

C **2** and **3** only

D **1**, **2** and **3**

22 The properties of the oxides of four elements in Period 3, **E, F, G** and **H** are given below.

1 The oxide of **E** is amphoteric.

2 The oxide of **F** dissolves in water to form a strongly alkaline solution.

3 The oxide of **G** reacts with dilute sodium hydroxide at room temperature.

4 The oxide of **H** is insoluble in water but is soluble in concentrated sodium hydroxide.

Which of the following shows the correct sequence of the four elements in order of increasing proton number?

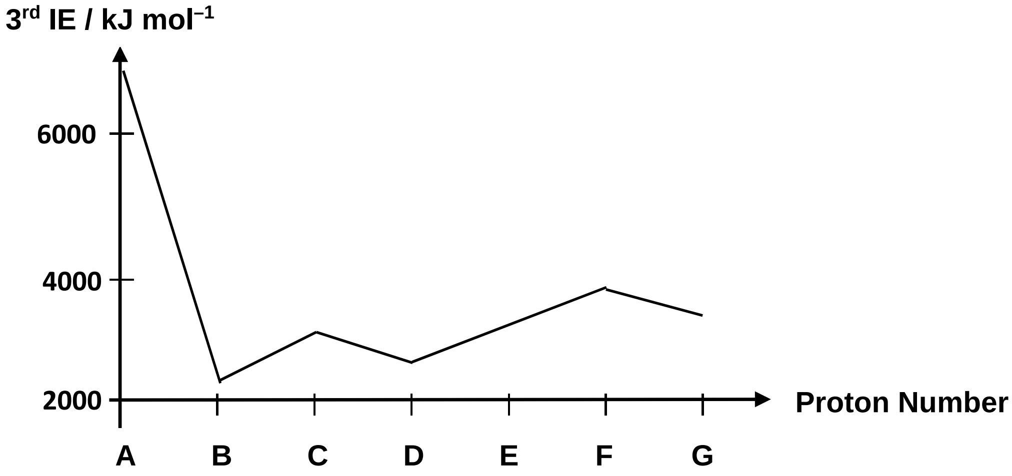
A **F**, **E**, **G**, **H**

B **F**, **E**, **H**, **G**

C **G**, **F**, **E**, **H**

D **G**, **F**, **H**, **E**

23 The diagram shows the third ionisation energy of seven consecutive elements, **A** to **G** in the Periodic Table. Their atomic numbers lie between 3 and 20.



Which of the following statements is correct?

1 Element **A** is strongly oxidising.

2 Oxide of **B** is soluble in water.

3 Oxide of **C** is acidic.

4 Element **E** forms a hydride of general formula H_2**E**.

A **1** and **4** only

B **1, 3** and **4** only

C **2, 3** and **4** only

D **3** and **4** only

24 A student conducted the following experiment using the setup below and recorded his observations.

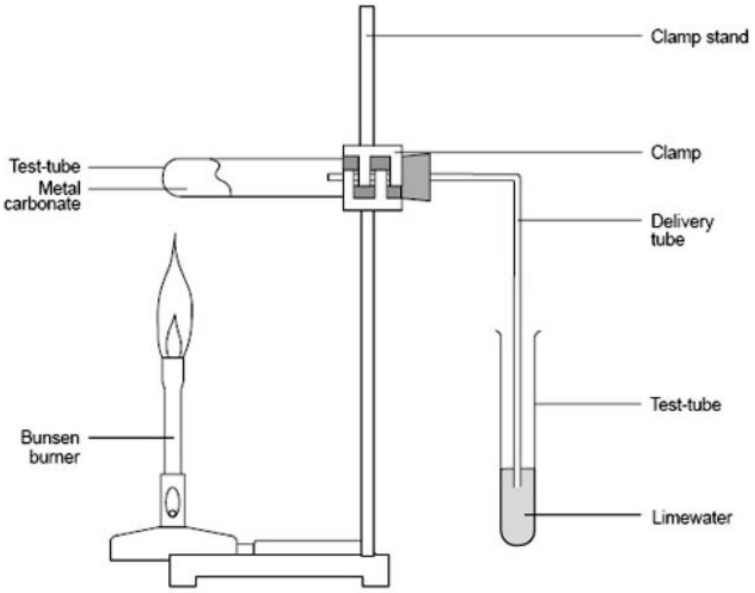


Fig 1: Setup of experiment

Carbonate	***Colour before heating***	***Colour after heating***	***Observations***
$CaCO_3$	white	white	white ppt formed with limewater
$BaCO_3$	white	white	white ppt formed with limewater
$CuCO_3$	green	black	white ppt formed with limewater

Using the above data and relevant data from the *Data Booklet*, which of the following statements concerning the metal carbonates is correct?

1 Lattice energy of calcium carbonate is more exothermic than that of barium carbonate.

2 Carbon dioxide is produced at a lower temperature from calcium carbonate than from barium carbonate.

3 The oxide from the copper carbonate is formed more readily than that from calcium carbonate.

A **1**, **2** and **3**

B **1** and **2** only

C **1** and **3** only

D **2** only

25 3–ethylpentane can react with bromine in the presence of sunlight to give a mixture of three possible monosubstituted halogenoalkanes, 1–bromo–3–ethylpentane, 2–bromo–3–ethylpentane and 3–bromo–3–ethylpentane.

Given the relative rates of abstracting H atoms are:

Type of H atom	Primary	Secondary	Tertiary
Relative rate of abstraction	1	4	6

What is the expected ratio of 1–bromo–3–ethylpentane, 2–bromo–3–ethylpentane and 3–bromo–3–ethylpentane formed?

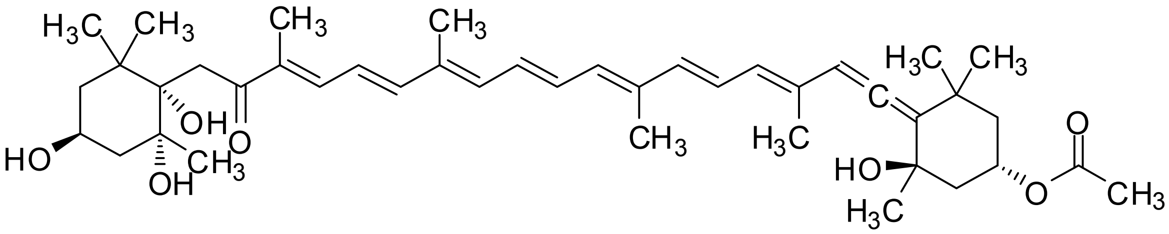
A 1 : 1 : 1

B 1 : 4 : 6

C 3 : 8 : 2

D 9 : 6 : 1

26 *Fucoxanthin* is a carotenoid which is found as an accessory pigment in the chloroplasts of brown algae and most other heterokonts, giving them a brown or olive–green colour.



Fucoxanthin

How many organic compounds will be formed when *Fucoxanthin* reacts with hot acidified $KMnO_4$?

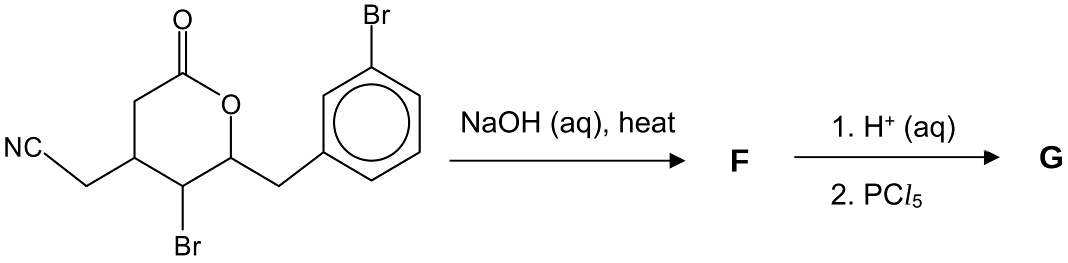
A 3

B 4

C 5

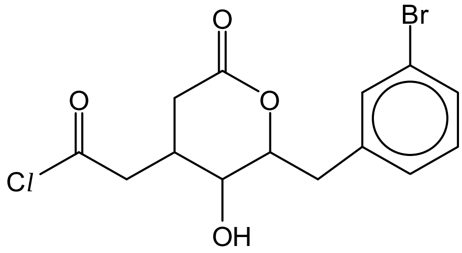
D 6

27 The reaction scheme below shows the formation of compound **G:**



What is the structure of compound **G**?

A



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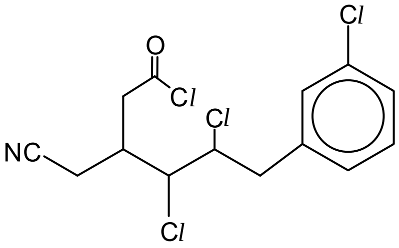
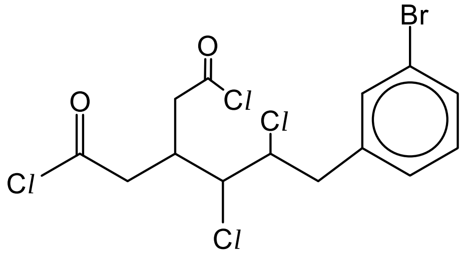
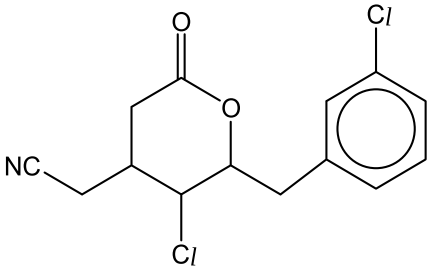


C

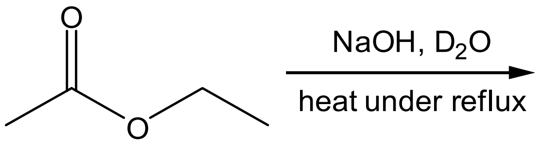


D

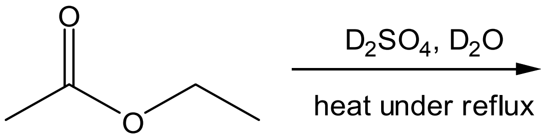


28 Which of the following reactions will **not** incorporate deuterium (D) into any of the organic products formed? (D= ${}^{2}_{1}H$, an isotope of hydrogen)

A



B



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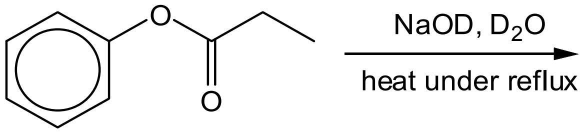
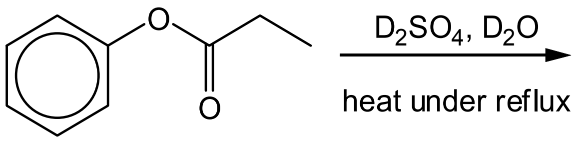
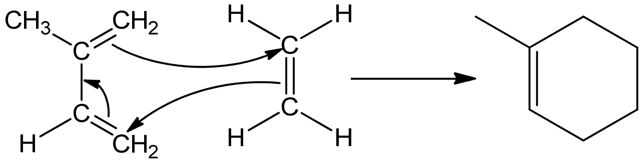


D

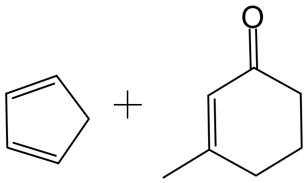


29 *Limonene* can be obtained via a series of organic reactions involving the *Diels–Alder* reaction.

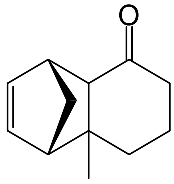
The *Diels–Alder* reaction involves a concerted cycloaddition mechanism.



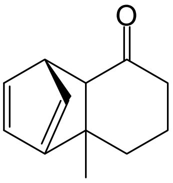
What would be the product form when the following diene and alkene reacts in a 1:1 ratio?



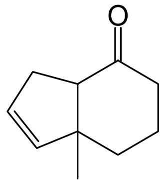
A



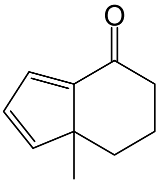
B



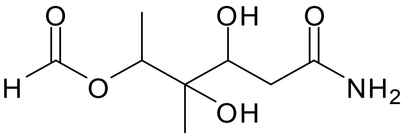
C



D



30 Which of the following statements is true of compound **A**, shown below?



Compound **A**

1 Upon reaction with hot acidified $KMnO_4$, an organic compound containing 5 oxygen atoms is formed.

2 Compound **A** has a total of 6 stereoisomers.

3 On reacting with $LiAlH_4$, one molecule with one –OH group is formed together with another molecule that has 4 –OH groups.

A	**1** and **2** only	**B**	**2** and **3** only
C	**1** only	**D**	**3** only

END OF PAPER

Class	Reg Number
17	

Name **Suggested Solutions**

Calculator Model / No.

MERIDIAN JUNIOR COLLEGE
JC2 Preliminary Examination
Higher 2

Chemistry

9729/01

Paper 1

21 September 2018
1 hour

Additional Material: *Data Booklet*
OMS

READ THESE INSTRUCTIONS FIRST

Write your name, class and register number in the spaces provided at the top of this page.

There are **thirty** questions in this paper. Answer **all** questions. For each question, there are four possible answers labelled **A**, **B**, **C** and **D**. Choose the **one** you consider correct and record your choice in soft pencil on the OMR answer sheet.

Read very carefully the instructions on the use of OMR answer sheet.

You are advised to fill in the OMR Answer Sheet as you go along; no additional time will be given for the transfer of answers once the examination has ended.

Use of OMR Answer Sheet

Ensure you have written your name, class register number and class on the OMR Answer Sheet.

Use a **2B** pencil to shade your answers on the OMR sheet; erase any mistakes cleanly. Multiple shaded answers to a question will not be accepted.

For shading of class register number on the ***OMR sheet***, please follow the given examples:
If your register number is **1**, then shade **01** in the index number column.
If your register number is **21**, then shade **21** in the index number column.

This document consists of **13** printed pages (including this cover page)

Qn	Ans
1	B
2	C
3	A
4	A
5	D
6	B
7	B
8	C
9	C
10	D

Qn	Ans
11	D
12	B
13	D
14	A
15	A
16	A
17	D
18	D
19	B
20	D

Qn	Ans
21	B
22	B
23	D
24	A
25	C
26	B
27	C
28	C
29	A
30	C

1 **Answer: B**

$[(CH_3CO_2)_2Zn] = \frac{10.64}{183.4} = 0.0580 \text{ mol dm}^{-3}$

Amount of $(CH_3CO_2)_2Zn = \frac{5}{1000} \times 0.0580 = 2.90 \times 10^{-4}$ mol

$(CH_3CO_2)_2Zn \equiv 2CH_3CO_2^- \equiv Zn^{2+}$

Total amount of ions = $3 \times 2.90 \times 10^{-4} = 8.70 \times 10^{-4}$ mol

Total number of ions = $8.70 \times 10^{-4} \times 6.02 \times 10^{23}$ = 5.2×10^{20} ions

2 **Answer: C**

Explanation:

volume of $H_2S = \frac{3}{4} \times 40$ = 30 cm^3 and volume of $CS_2 = \frac{1}{4} \times 40$ = 10 cm^3

Combustion equations:

$H_2S\,(g) + \frac{3}{2}O_2\,(g) \rightarrow SO_2\,(g) + H_2O\,(l)$ and

30 cm^3 45 cm^3 30 cm^3

$CS_2\,(g) + 3O_2\,(g) \rightarrow CO_2\,(g) + 2SO_2$

10 cm^3 30 cm^3 10 cm^3 20 cm^3

Total volume of SO_2 formed = 30 + 20 = **50 cm^3**

Volume of CO_2 formed = **10 cm^3**

volume of O_2 remaining = 100 – (45 + 30) = **25 cm^3**

Volume of gaseous mixture after burning = 50 + 10 + 25 = **85 cm^3**

Since CO_2 and SO_2 are acidic gases, they will be removed by NaOH (aq) therefore, **Volume of gaseous mixture after adding NaOH (aq)** = 85 – 60 = **25 cm^3**

3 **Answer: A**

By considering change in oxidation number of element:

Reaction 1 $3F_2 + 4NH_3 \longrightarrow 3NH_4F + NF_3$

0 –3 –1 +3

NH_3 acts as reducing agent hence it is a stronger reducing agent than F_2.

Reaction 2 $3Cl_2 + 8NH_3 \longrightarrow 6NH_4Cl + N_2$

0 –3 –1 0

NH_3 acts as reducing agent hence it is a stronger reducing agent than Cl_2.

F_2 oxidises N to a larger extent (from –3 in NH_3 to +3 in NF_3) as compared to Cl_2 (from –3 in NH_3 to 0 in N_2). **F_2 is a stronger oxidising agent and hence a weaker reducing agent as compared to Cl_2.**

NH_3 is the **strongest reducing agent** whereas **F_2** is the **weakest reducing agent**.

4 **Answer: A**

For element **L**: biggest increase between 6th and 7th ionisation energy.
(Largest difference in IE between 6th and 7th I.E.)
7th electron is removed from the inner quantum shell which is closer to the nucleus.
Thus the element has 6 valence electrons.
Element **L** belongs to **Group 16.**

For element **M**: biggest increase between 3rd and 4th ionisation energy.
(Largest difference in IE between 3rd and 4th I.E.)
4th electron is removed from the inner quantum shell which is closer to the nucleus.
Thus the element has 3 valence electrons.
Element M belongs to **Group 13**.

So the likely formula of the compound formed is **L_3M_2.**

5 **Answer: D**

	X	**Y**
Proton number, n	n	n + 1
No of electrons	n + 1	n
Charge	+1	+2

Option A is wrong
X and **Y** have different number of protons. Hence they can't be isotopes.

Option B is wrong
X and **Y** have different number of protons. **X** atom has n electrons while **Y** has (n + 1) electrons. Hence **X** and **Y** atoms have different full electronic configurations.

Option C is wrong
Y has charge of +2 while it has same number of electrons as that of **X**. Hence, **Y** has smaller ionic radius. This leads to higher charge density.

Option D is correct
Y has charge of +2 while it has same number of electrons as that of **X**. Hence, **Y** has smaller ionic radius.

6 **Answer: B**

	First molecule	**Second molecule**
A	CO_2 *(2 bond pairs)* Shape: Linear Polarity: Non–polar Bond angle: 180°	F_2O *(2 bond pairs, 2 lone pair)* Shape: Bent Polarity: Polar Bond angle: 104.5°
B	NF_3 *(3 bond pairs, 1 lone pair)* Shape: Trigonal Pyramidal Polarity: Polarity: Polar Bond angle: 107°	SO_3 *(3 bond pairs, 0 lone pair)* Shape: Trigonal Planar Polarity: Non–polar Bond angle: 120°
C	SF_6 *(6 bond pairs, 0 lone pair)* Shape: Octahedral Polarity: Non–polar Bond angle: 90°	XeF_4 *(4 bond pairs, 2 lone pair)* Shape: Square Planar Polarity: Non–polar Bond angle: 90°
D	SO_2 *(2 bond pairs, 1 lone pair)* Shape: Bent Polarity: Polar Bond angle: 118°	NO_2 *(2 bond pairs, 1 lone electron)* Shape: Bent Polarity: Polar Bond angle: > 118 °
	Lone pair – bond pair repulsion > 1 unpaired electron – bond pair repulsion.	

7 **Answer: B**

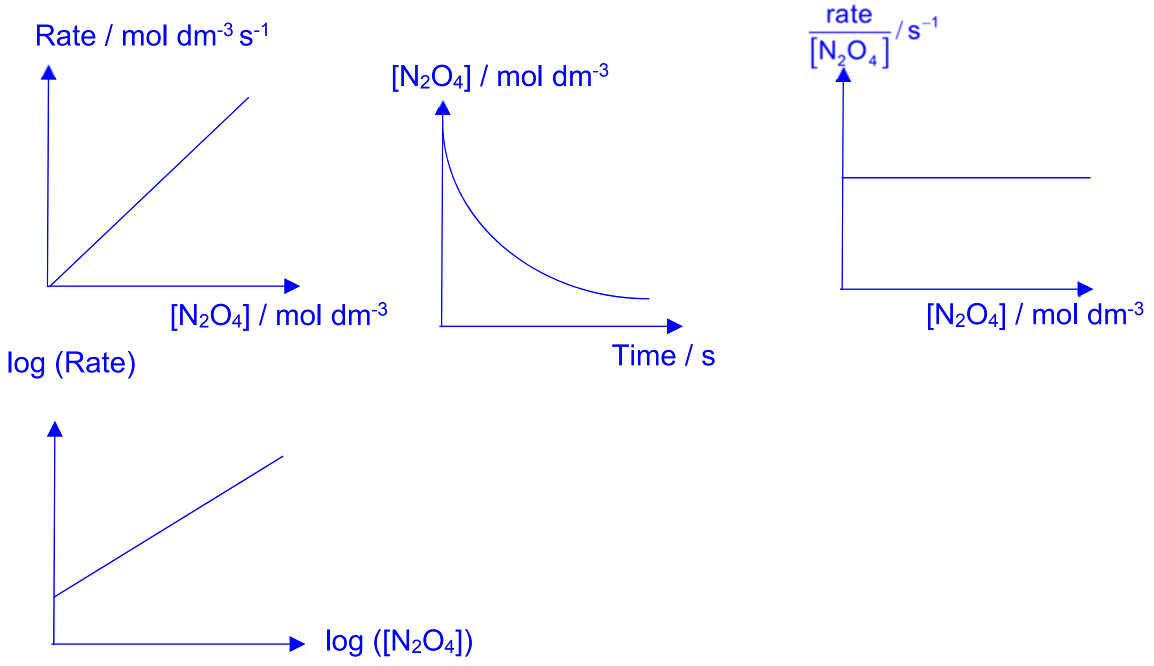
Statement **1** is correct as melting involves overcoming of the strong metallic bonds arising from the strong electrostatic forces attraction between the delocalised electrons and the residual metallic cations.

Statement **2** is correct as A*l* contribute more delocalised electrons than Na and this contributes to stronger metallic bonds.

Statement **3** is incorrect as electrical conductivity in metals is due to the delocalised electrons, not mobile ions.

8 **Answer: C**

The graphs for first order reaction are shown as below:



9 **Answer: C**

$$\text{Half–life, } t_{\frac{1}{2}} = \frac{\ln 2}{k} = \frac{\ln 2}{0.09} = 7.7 \text{ h}$$

$$\frac{C_t}{C_o} = \left(\frac{1}{2}\right)^n$$

$$\frac{18}{100} = \left(\frac{1}{2}\right)^n \Rightarrow n = 2.47$$

Time taken = half–life × n = 7.7 × n = **19.0 h**

10 **Answer: D**

$3O_2(g) + 4NH_3(g) \rightleftharpoons 2N_2(g) + 6H_2O(g) \qquad \Delta H = -1248\ \text{kJ mol}^{-1}$

When pressure increases, by Le Chatelier's Principle, the equilibrium position shifts **left** to **reduce the number of moles of gas** to **decrease pressure**.

Therefore, Q represents products since the graphs show **decreasing %Q** when **pressure increases.**

Since forward reaction is exothermic, **$T_2 > T_1$**. By Le Chatelier's Principle, the equilibrium position shifts **left** towards the **endothermic** reaction to **absorb heat.**
T_2 has lower %Q than T_1

11 **Answer: D**

Option 1 is correct as it involves the formation of an intermediate.

Option 2 is correct as the potential energy of the intermediate is lower than that of the starting material.

Option 3 is correct as the catalyst will lower both E_a and E_a'

12 **Answer: B**

When temperature increases, based on Le Chatelier's principle, equilibrium position will shift right towards the endothermic reaction to absorb heat.

$[H^+]$ & $[OH^-]$ increases in magnitude

Since $K_w = [H^+][OH^-]$, K_w increases in magnitude.

$[H^+] = [OH^-]$ as 1 mol of water molecule dissociates to form 1 mol of H^+ and 1 mol of OH^-.

pH will decrease to a value below 7, as $[H^+]$ increases. ($pH = -\log[H^+]$)

13 **Answer: D**

Alkaline buffer consists of a weak base and its conjugate acid.

$$pOH = pK_b + \lg \frac{[salt]}{[acid]}$$

Maximum buffer capacity occurs when pOH = pK_b, where $\frac{[salt]}{[acid]} = 1$

A → 0.003 mol NH_4^+ and 0.001 mol of NH_3
B → acidic buffer
C → 0.02 mol of $CH_3CH_2NH_3^+$
D → 0.0025 mol $CH_3NH_3^+$ and 0.0025 mol of CH_3NH_2

14 **Answer: A**

Bromophenol–blue appears purple (**pH > 4.6)** ⇒ Option **A** is **incorrect**
Phenol–red appears yellow (**pH < 6.8)** ⇒ Options **C and D** are **incorrect**.
The solution must be **weakly acidic and with $4.6 < pH < 6.8$**.

15 **Answer: A**

The calculation could be completed using $\Delta H^\ominus_f$ of all compounds if $\Delta H^\ominus_f$ of C*l*• is provided. Atomisation of C*l*–C*l* molecule involves homolysis of the bond, forming C*l* atoms with one unpaired electron each, i.e. C*l* radicals.

16 **Answer: A**

$\Delta G = \Delta H - T\Delta S$
Reaction is exothermic ⇒ $\Delta H < 0$ ⇒ y–intercept is negative
Less gaseous products than reactants ⇒ $\Delta S < 0$ ⇒ $(-\Delta S) > 0$ ⇒ gradient of graph is positive

17 **Answer: D**

Explanation:
$BaCl_2$
$\Delta H^\ominus_{solution}$ = |Lattice energy| – $|\Delta H^\ominus_{hydration}\ Ba^{2+}|$ – $2|\Delta H^\ominus_{hydration}\ Cl^-|$
= 2053 – 1309 – 2(378) = –12 kJ mol^{-1}

18 **Answer: D**

Option A is incorrect.
Cathode is a positive electrode and accept electrons.

Option B is incorrect.

$E_{cell} = E_{red} - E_{ox} = 0.54 - (-3.04) = +3.58$ V

Option C is incorrect.
Ni is a metal which allows **electrons** to pass through and connect Li to I_2 complex.

Option D is correct.

Amount of Li^+, $\frac{5}{6.9} = \frac{0.8 \times 10^{-3} \times t}{1 \times 96500}$ ➔ $t = 8.73 \times 10^7$ s ➔ Time = 2.77 years

19 **Answer: B**

$Cr^{3+}(aq) + e \rightleftharpoons Cr^{2+}(aq)$ $Fe^{2+}(aq) + 2e \rightleftharpoons Fe(s)$

$E^\ominus_{red} = E^\ominus_{(Cr^{3+} | Cr^{2+})} = -0.41$ V $E^\ominus_{ox} = E^\ominus_{(Fe^{2+} | Fe)} = -0.44$ V
$E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{ox} = -0.41 - (-0.44) = \underline{\mathbf{+0.03\ V}}$

For E_{cell} to be 0.00 V, E_{red} should decrease (more negative) ***OR***
E_{ox} should increase (more positive)

Change	*Effect*
increase [$FeSO_4$]	increase in [Fe^{2+} (aq)], $Fe^{2+} + 2e \rightleftharpoons Fe$ eqm position shifts right, $\underline{\boldsymbol{E_{ox}}\uparrow}$
decrease [$CrCl_2$]	decrease in [Cr^{2+} (aq)], $Cr^{3+} + e \rightleftharpoons Cr^{2+}$ eqm position shifts right, $E_{red}\uparrow$
decrease [$CrCl_3$]	decrease in [Cr^{3+} (aq)], $Cr^{3+} + e \rightleftharpoons Cr^{2+}$ eqm position shifts right, $\underline{\boldsymbol{E_{red}}\downarrow}$
increase surface area of Fe electrode	no effect to E_{red} value

20 **Answer: D**

Option **A** is wrong. Step 1 is reduction.

Option **B** is inconclusive. While the relative strength of H_2O, SCN^- and $EDTA^{4-}$ ligands can be concluded from the ligand exchange reactions in Step **4** and **5**, nothing can be concluded about the relative strength of H_2O and CN^- ligands.

Option **C** is incorrect. While $Fe(OH)_3$ can be formed, CO_2 (g) cannot be produced from this reaction. The correct reagent to be used in Step **2** should be Na_2CO_3.

Option **D** is correct.

21 **Answer: B**

Option 1 is correct.
$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$
$E^\ominus_{(S_2O_8^{2-}/SO_4^{2-})} = +2.01V$; $E^\ominus_{(I_2/I^-)} = +0.54V$
Hence, any transition metal ions catalyst with **$E^\ominus$ values between + 2.01 V and +0.54 V**
$E^\ominus_{(VO_2^+/VO^{2+})} = +1.00V$

Option 2 is incorrect.
When $VOSO_4(H_2O)_5$ dissolve in water to form an aqueous solution. $[VO(H_2O)_6]^{2+}$ is formed. The blue colour of the solution observed is due to the d-d transition caused by the splitting of the d-orbitals by the water ligands.

Option 3 is correct.
Zinc metal is functioning as a reducing agent. Assuming Zn is in excess,

$E^\ominus_{(Zn^{2+}/Zn)} = -0.76V$ (Oxidation) $E^\ominus_{(VO^{2+}/V^{2+})} = +0.34V$ (Reduction)	$Zn + 2VO^{2+} + 4H^+ \rightarrow Zn^{2+} + 2V^{3+} + 2H_2O$ $E^\ominus_{cell} = +0.34 - (-0.76) = +1.10\ V > 0$ (feasible)
$E^\ominus_{(Zn^{2+}/Zn)} = -0.76V$ (Oxidation) $E^\ominus_{(V^{3+}/V^{2+})} = -0.26V$(Reduction)	$Zn + 2V^{3+} \rightarrow Zn^{2+} + 2V^{2+}$ $E^\ominus_{cell} = -0.26 - (-0.76) = +0.50\ V > 0$ (feasible)
$E^\ominus_{(Zn^{2+}/Zn)} = -0.76V$ (Oxidation) $E^\ominus_{(V^{2+}/V)} = -1.20V$(Reduction)	$E^\ominus_{cell} = -1.20 - (-0.76) = -0.55\ V < 0$ (not feasible)

22 **Answer: B**

1	The oxide of **E** is amphoteric.	**E** is **aluminum**.
2	The oxide of **F** dissolves in water to form a strongly alkaline solution.	**F** is **sodium**.
3	The oxide of **G** reacts with dilute sodium hydroxide at room temperature.	**G** could either be **phosphorus or sulfur**.
4	The oxide of **H** is insoluble in water but is soluble in concentrated sodium hydroxide.	**H** is **silicon**.

In **increasing proton number**,
sodium, aluminium, silicon, phosphorus/sulfur

Option **B**: **F, E, H, G**

23 **Answer: D**

Element **A** has the **highest 3rd IE** ⇒ element **A** is in Group **2**.

A : Mg Group 2, **B : A*l*** Group 13,
C : Si Group 14, **E : S** Group 16

1 Mg is a strong reducing agent ($E^{\ominus}_{Mg^{2+}/Mg} = -2.38V$). (False)
2 Al_2O_3 does not dissolve in water, because of its extremely high lattice energy. Large amount of energy is required to break the strong ionic bonds. (False)
3 SiO_2 is an acidic oxide, even though it doesn't dissolve in water to form an acid. It reacts with hot conc. NaOH to from Na_2SiO_3. (True)
4 Sulfur is in Group 16, hence it can form a hydride of H_2S. (True)

24 **Answer: A**

Option 1 – *Comparing $BaCO_3$ and $CaCO_3$:*
Ionic radius: Ba^{2+} (0.135 nm) > Ca^{2+} (0.099 nm)

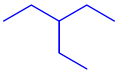
$$\boxed{|\text{Lattice energy}| \propto \frac{q_+q_-}{r_+ + r_-}}$$

Magnitude of lattice energy: $CaCO_3 > BaCO_3$

Option 2 & 3 – *Comparing $BaCO_3$, $CuCO_3$ and $CaCO_3$:*

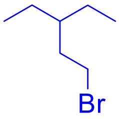
- Ionic radius: Cu^{2+} (0.073 nm) < Ca^{2+} (0.099 nm) < Ba^{2+} (0.135 nm)
- Charge density & polarising power of cation: $Cu^{2+} > Ca^{2+} > Ba^{2+}$
- Ability of cation to distort the CO_3^{2-} electron cloud, weakening and break the C–O bond for: $Cu^{2+} > Ca^{2+} > Ba^{2+}$
- Thermal Stability: $BaCO_3 > CaCO_3 > CuCO_3$

25 **Answer: C**



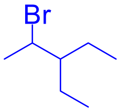
3-ethylpentane

9 Primary H atoms
6 Secondary H atoms
1 Tertiary H atom



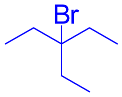
1-bromo-3-ethylpentane

9 x 1 = 9



2-bromo-3-ethylpentane

6 x 4 = 24

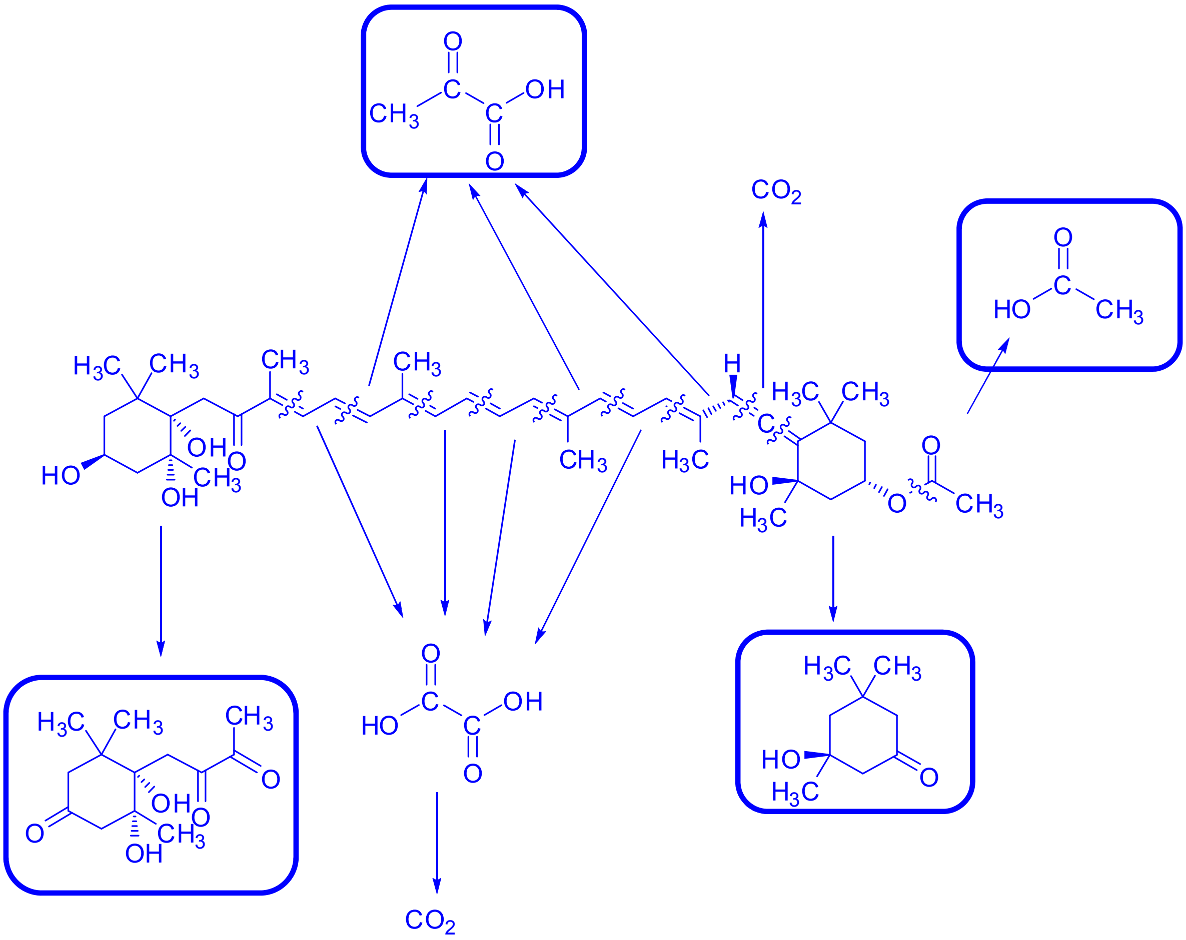


3-bromo-3-ethylpentane

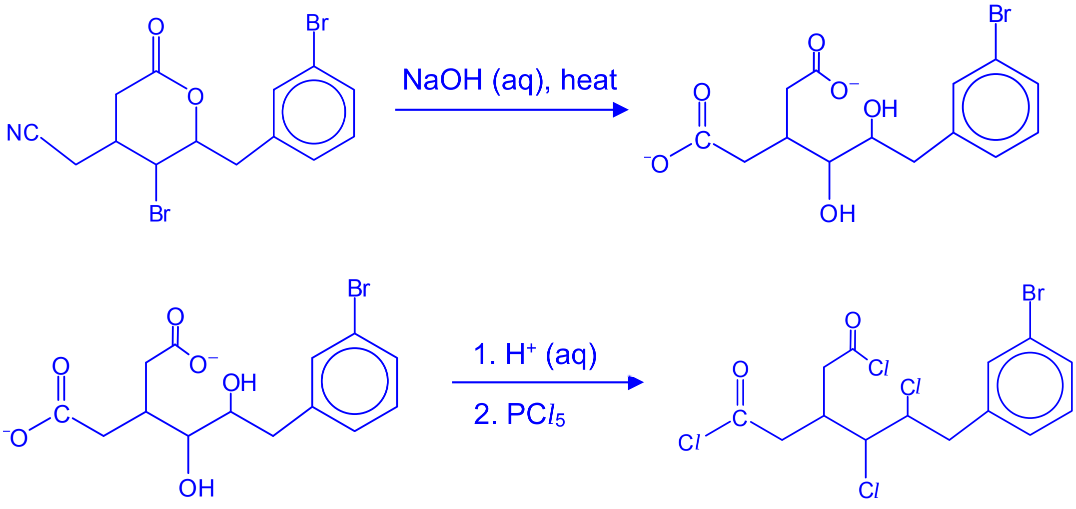
1 x 6 = 6

Ratio is 9 : 24 : 6
= 3 : 8 : 2

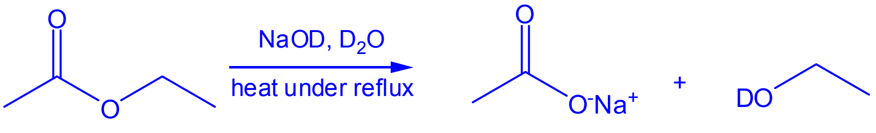
26 **Answer: B**

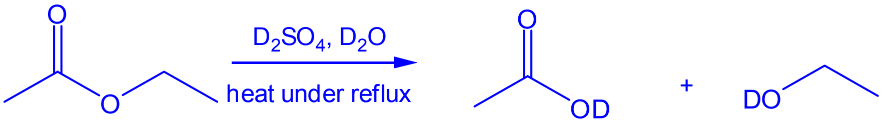


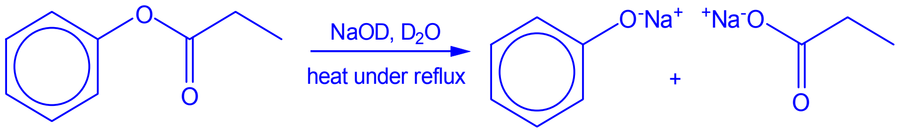
27 **Answer: C**

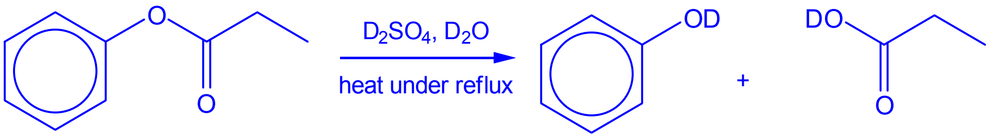


28 **Answer: C**

A


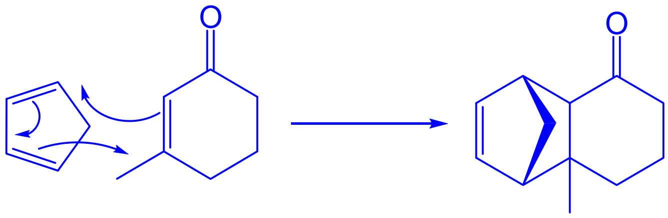
B


C


D


29 Answer: A

Explanation:

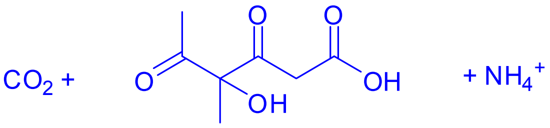


30 Answer: C

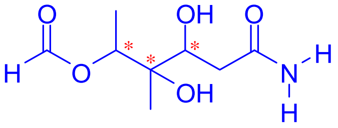
Explanation:

Option 1 is true: Compound A undergoes acidic hydrolysis (amide and ester) as well as oxidation.

Products are

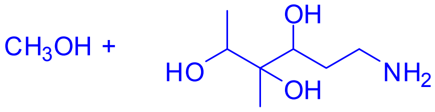


Option 2 is false: Compound A has 3 chiral carbon atoms with no internal plane of symmetry. Total number of stereoisomers should be $2^3 = 8$ (not 2 × 3 = 6)



Option 3 is false:

The products after reacting with LiA*l*H₄ are



END OF PAPER

Class	Reg Number
17	

Name: ____________________

Calculator Model / No.

MERIDIAN JUNIOR COLLEGE
JC2 Preliminary Examination
Higher 2

Chemistry

9729/02

Paper 2 Structured Questions

18 September 2018

2 hours

Additional Materials: *Data Booklet*

INSTRUCTIONS TO CANDIDATES

Write your name, class and register number in the spaces provided at the top of this page.

Write your calculator brand and model/number in the box provided above.

Answer **all** questions in the spaces provided on the question paper.

All working must be shown clearly.

INFORMATION FOR CANDIDATES

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

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

Examiner's Use			
Paper 1	**MCQ**	**/ 30**	**/ 15 %**
Paper 2	**Q1**	**/ 13**	
	Q2	**/ 19**	
	Q3	**/ 14**	
	Q4	**/ 15**	
	Q5	**/14**	
	Total	**/ 75**	**/ 30%**
Paper 3	**Total**	**/ 80**	**/ 35%**
Paper 4	**Total**	**/ 55**	**/ 20%**
Total			**/ 100 %**
Grade			

This document consists of **17** printed pages (including this cover page).

1 Ammonia is one of the most highly produced inorganic chemicals. Modern chemical plants depend on Haber Process whereby hydrogen derived from natural gas reacts with atmospheric nitrogen using a catalyst under high pressure and temperature to produce anhydrous ammonia.

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$$

(a) For the above reaction, a 1:3 ratio of N_2 and H_2 is passed over a catalyst. The resulting mixture is allowed to reach dynamic equilibrium. At equilibrium, 20% of the N_2 has reacted and the total pressure is 2.0 atm.

(i) Explain what is meant by the term *dynamic equilibrium*.

[1]

(ii) Calculate the partial pressures of N_2 and H_2 at equilibrium.

[2]

(iii) Write an expression for the equilibrium constant, K_p, and calculate its value.

[2]

(b) **(i)** Using relevant data in the *Data Booklet,* calculate the enthalpy change of reaction, ΔH_{rxn} of the Haber Process.

[2]

(ii) The enthalpy change of reaction calculated above in **(b)(i)** differs slightly from the actual value of –92.0 kJ mol^{-1}. Suggest a reason for this.

[1]

(c) Explain whether the formation of ammonia is favoured with

I high or low pressure,
II high or low temperature.

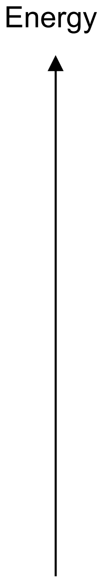
[3]

(d) Ammonium chloride, NH_4Cl is typically used in instant ice–packs. A crushing action activates the ice–pack as this mixes NH_4Cl with water. The ice–pack cools as the dissolution of NH_4Cl is endothermic.

Draw an energy level diagram to determine the standard enthalpy change of solution of ammonium chloride given the following information.

Lattice energy of ammonium chloride	–705 kJ mol^{-1}
Enthalpy change of hydration of NH_4^+	–307 kJ mol^{-1}
Enthalpy change of hydration of Cl^-	–381 kJ mol^{-1}

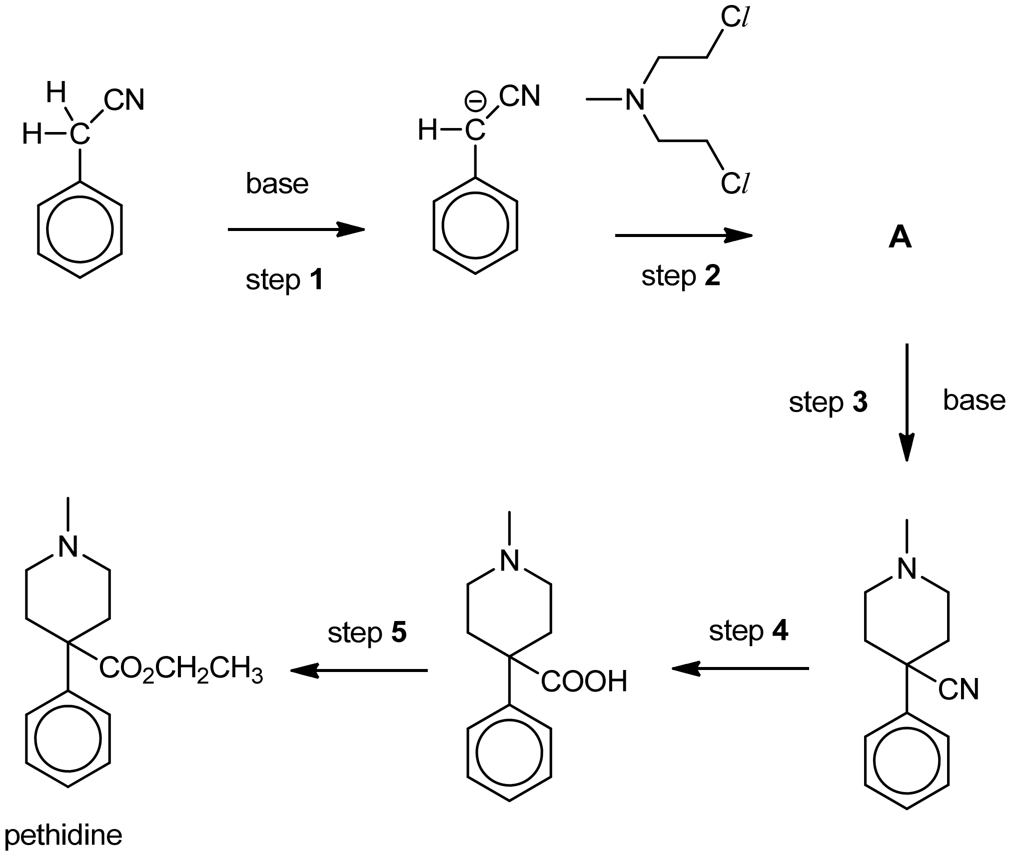
[2]



[Total: 13]

2 Nitrogen is an element commonly found in various major classes of drugs.

(a) The following is a reaction scheme for the synthesis of pethidine, a powerful painkilling drug.



(i) State the type of reaction for step **1** and step **2**.

[2]

Step 1: ....

Step 2: ....

(ii) Suggest the structure of intermediate **A**

[1]

(iii) State the reagents and conditions needed for step **4** and step **5**.

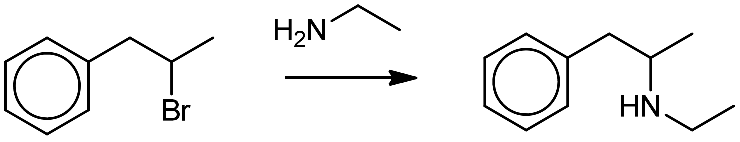
[2]

Step 4: ....

Step 5: ....

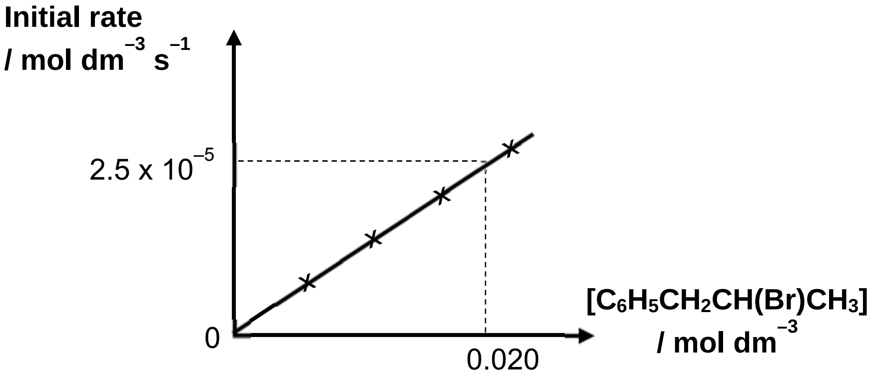
(b) Kinetics studies of organic reactions provide strong evidence in supporting the postulated mechanisms.

The results from the kinetics study of the nucleophilic substitution reaction involved in the synthesis of N–ethylamphetamine, a discontinued weight–loss drug, are presented below.



(2-bromopropyl)benzene N-ethylamphetamine

The graph was plotted based on data obtained from repeating the experiment several times by varying the concentration of $C_6H_5CH_2CH(Br)CH_3$ while maintaining that of $CH_3CH_2NH_2$ to be at 2.5 mol dm^{-3}.



(i) The rate equation for the reaction was found to be

$$\text{rate} = k\,[C_6H_5CH_2CH(Br)CH_3][CH_3CH_2NH_2]$$

Using the graph provided, justify why the order of reaction with respect to $C_6H_5CH_2CH(Br)CH_3$ is one.

[2]

....

....

....

....

....

(ii) Calculate the rate constant, k and state its units.

[2]

(iii) Given that this is a bimolecular reaction, outline the mechanism for this reaction. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons.

[3]

(iv) Suggest why the rate of reaction decreases when $(CH_3)_3CNH_2$ is used instead of $CH_3CH_2NH_2$.

[1]

(v) Explain how the reactivity of (2–chloropropyl)benzene will differ towards $CH_3CH_2NH_2$ as compared to (2–bromopropyl)benzene.

[1]

(vi) With the aid of a Maxwell–Boltzmann Distribution curve, explain how heating the reaction mixture will increase the rate of the reaction.

[3]

(c) Investigating the optical activity of the product of a nucleophilic substitution reaction can also provide evidence on how the reaction may proceed.

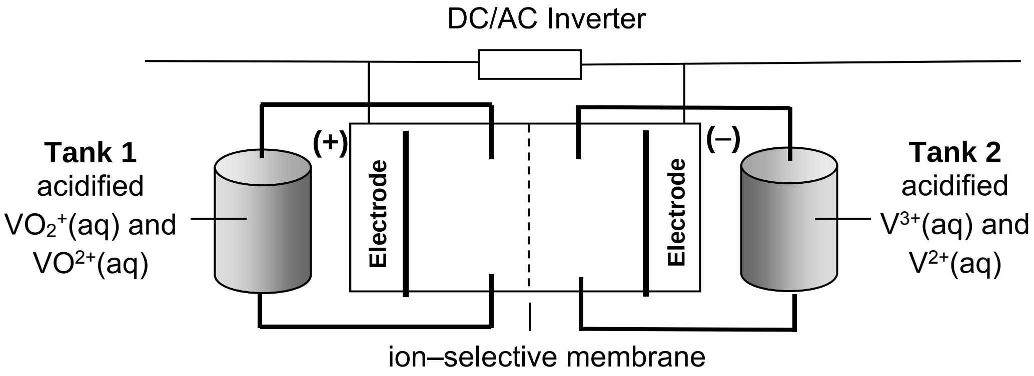
Consider the reaction between the (+) enantiomer of 2–bromobutane and hot NaOH (aq).

State the expected optical activity of the product if this reaction proceeds via S_N1 mechanism. Provide reasoning for your answer.

[2]

[Total: 19]

3 The vanadium flow battery (VFB) is a type of rechargeable battery that employs electrolyte containing vanadium ions in different oxidation states.



(a) Electricity is generated from the battery by half–cell reactions of these electrolytes that were pumped into the cell from separate storage tanks. The two electrolytes in the cell are separated by an ion selective membrane, which only allows H^+ ions to pass through.

(i) Write the two half equations for the reaction occurring at the anode and the cathode when the battery discharges. Hence, write the overall cell reaction.

[2]

Anode: ....

Cathode: ....

Overall: ....

(ii) Calculate the e.m.f of the battery.

[1]

(iii) Explain how the ion–selective membrane in VFB maintains electrical neutrality.

[1]

....

....

....

....

(iv) State and explain what happens to the overall e.m.f when a small amount of OH^-(aq) ions were added to the electrolyte in **Tank 1**.

[2]

(b) The total concentration of vanadium ions in the 20 dm^3 electrolyte in **Tank 1** is 5.00 mol dm^{-3}. During the charging of the VFB, the percentage composition of VO_2^+ has to be increased from 5% to 90%.

(i) Calculate the amount of VO_2^+ that needs to be converted during this charging process.

[1]

(ii) Find the time taken, in hours, if a 120 A current is used in the charging process.

[2]

(c) Anodising of aluminum is an electrolytic process to increase the thickness of the alumnium oxide layer on the surface of aluminium, by passing a direct current through dilute sulfuric acid.

(i) Draw a labelled diagram of an electrolysis set–up during the anodising of aluminium. **[2]**

(ii) Write the half–equations for the reactions taking place at the anode, cathode and hence write the overall equation. **[2]**

Anode: ....

Cathode: ....

Overall: ....

(iii) State and explain any observations if copper(II) sulfate was used as the electrolyte instead. **[1]**

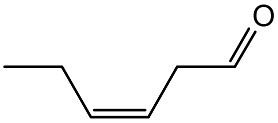
....

....

....

[Total: 14]

4(a) *cis*–3–hexenal, $CH_3CH_2CH=CHCH_2CHO$ is a compound with an intense smell of freshly cut grass and leaves.



cis–3–hexenal

Two isomers, **P** and **Q**, with the same molecular formula, $C_6H_{10}O$, as *cis*–3–hexenal show different types of isomerism. Both isomers decolourises aqueous bromine in the dark and both gives a positive test with Fehling's reagent.

Draw their structures and state their isomeric relationship to *cis*–3–hexenal.

[2]

isomer **P**	isomer **Q**
isomeric relationship to *cis*–3–hexenal:	isomeric relationship to *cis*–3–hexenal:

(b) Aldehydes and ketones (broadly classified as carbonyl compounds) can be reduced to alcohols using metal hydride reagents such as lithium aluminium hydride ($LiAlH_4$) and sodium borohydride ($NaBH_4$). These metal hydride reagents provide a source of hydride, H^- ions.

(i) The reaction between *cis*–3–hexenal, $CH_3CH_2CH{=}CHCH_2CHO$ and sodium borohydride in methanol is a nucleophilic addition reaction.

Draw the mechanism for this reaction, showing all charges, dipoles and curly arrows to represent the movement of electron pairs.

[3]

(ii) BH_3 is a side product of the earlier reaction in **(b)(i)**. BH_3 can form an addition product with Lewis bases, for example, with the alkoxide ion generated in the mechanism.

Draw the structure of this adduct formed and explain why the formation of the adduct is likely to happen.

[2]

(c) Both $LiAlH_4$ and $NaBH_4$ are sources of H^-. Hydride ions react vigorously with Bronsted–Lowry acids, releasing H_2 (g) and heat.

$LiAlH_4$ reacts violently with water or alcohols. When carrying out reactions with $LiAlH_4$, chemists often use solvents like anhydrous diethyl ether that has been treated to remove traces of water. On the other hand, $NaBH_4$ does not react that vigorously with water or alcohol.

Using the information provided or otherwise, suggest why $LiAlH_4$ is a better source of H^- than $NaBH_4$.

	Pauling Electronegativity
aluminium	1.61
boron	2.04
hydrogen	2.20

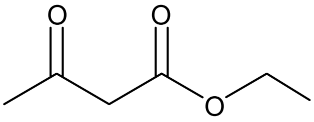
[1]

....

....

....

(d) A student proposed the following procedure to reduce ethyl acetoacetate ($C_6H_{10}O_3$),



using $NaBH_4$.

Procedures

1. Add 0.70 g of $NaBH_4$ to 25 cm^3 ethanol solvent in a 100 cm^3 round–bottomed flask. Cool the resulting mixture to 0 °C using an ice–bath.
2. To this mixture, slowly add 30 cm^3 of 40.8 g dm^{-3} ethyl acetoacetate solution. Stir the resulting solution at 0 °C for 15 minutes, then allow to warm to room temperature and stir for an additional 15 minutes.
3. Evaporate the solvent. Dissolve the resulting white solid in 30 cm^3 dichloromethane solvent, CH_2Cl_2.
4. Cool the flask in an ice–bath. Then, add 30 cm^3 of 1 mol dm^{-3} hydrochloric acid dropwise, while stirring, to quench the reaction by destroying any unreacted hydride. **Safety note*: The addition of HCl will release H_2 gas.*
5. Separate the organic layer from the aqueous layer.
6. Add powdered magnesium sulfate to the organic layer in excess, till no clumping of magnesium sulfate powder is observed. Filter off the magnesium sulfate and evaporate the dichloromethane solvent.
7. Weigh the product and record the actual yield.

(i) Explain why $NaBH_4$ is soluble in ethanol (in **step 1**) in terms of structure and bonding. **[2]**

(ii) One mole of $NaBH_4$ can reduce a maximum of four moles of carbonyl groups. Generally, in an experimental procedure, the reducing agent $NaBH_4$ should be used in excess.

Determine with relevant calculations, whether the student is correct with the quantities proposed in his procedures (**step 1 – 2**). **[2]**

(iii) In **step 4**, hydrochloric acid is added to quench the reaction, producing hydrogen gas and sodium boron chloride. Write an equation for the reaction that took place. **[1]**

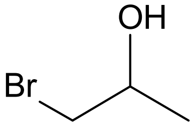
(iv) Draw the **skeletal** formula of the product isolated in the organic layer at the end of the experiment. **[1]**

(v) Suggest the function of magnesium sulfate in **step 6**. **[1]**

[Total: 15]

5 Organic reactions can lead to increased variation due to the direction–specific nature of covalent bonds, giving rise to much complexity from using only a small range of elements such as carbon, hydrogen and oxygen.

(a) Propene reacts with aqueous bromine to form a mixture of products, including molecule **A**.



Molecule **A**

(i) State the IUPAC name of molecule **A**.

[1]

....

(ii) Draw a mechanism for the reaction between propene and aqueous bromine to form Molecule **A** and hydrogen bromide. Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs.

[3]

(iii) Molecule **A** is the major product of this reaction. Suggest the structure of two other organic by–products.

[2]

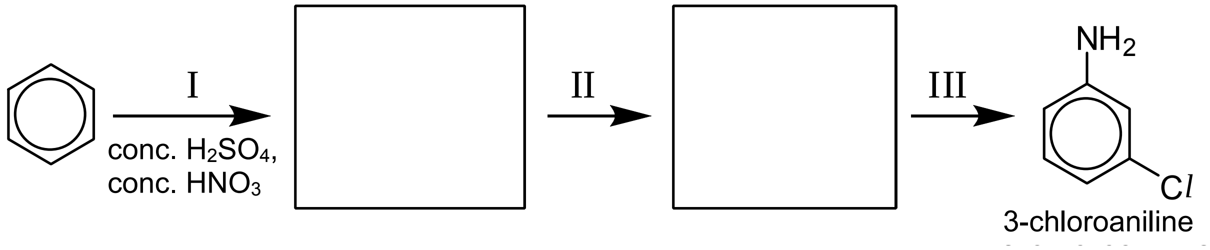
(iv) In the mechanism outlined in **(a)(ii)**, two stereoisomers of **A** are formed in equal amounts. Draw these two stereoisomers and name the type of isomerism displayed.

[2]

(b) 3–chloroaniline can be synthesised from benzene in a 3–step synthesis.

(i) Propose a synthetic route by suggesting the two intermediates compounds and state the reagents and conditions used for steps **II** and **III**.

[4]



Step II: ....

Step III: ....

(ii) One of the by–products from the synthesis in **(b)(i)** is HC*l*, which is a strong acid. The acid dissociation constant values, K_a of several hydrogen halides are shown below.

Compound	**K_a / mol dm^{-3}**
HC*l*	1.3×10^6
HBr	1.0×10^9
HI	3.2×10^9

Account for the relative K_a values.

[2]

....

....

....

....

[Total: 14]

END OF PAPER

Class	Reg Number
17	

Name: Suggested Solutions

Calculator Model / No.

MERIDIAN JUNIOR COLLEGE
JC2 Preliminary Examination
Higher 2

Chemistry **9729/02**

Paper 2 Structured Questions **18 September 2018**

2 hours

Additional Materials: *Data Booklet*

INSTRUCTIONS TO CANDIDATES

Write your name, class and register number in the spaces provided at the top of this page.

Write your calculator brand and model/number in the box provided above.

Answer **all** questions in the spaces provided on the question paper.

All working must be shown clearly.

INFORMATION FOR CANDIDATES

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

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

Examiner's Use			
Paper 1	**MCQ**	**/ 30**	**/ 15 %**
Paper 2	**Q1**	**/ 13**	
	Q2	**/ 19**	
	Q3	**/ 14**	
	Q4	**/ 15**	
	Q5	**/14**	
	Total	**/ 75**	**/ 30%**
Paper 3	**Total**	**/ 80**	**/ 35%**
Paper 4	**Total**	**/ 55**	**/ 20%**
Total			**/ 100 %**
Grade			

This document consists of **17** printed pages (including this cover page).

1 Ammonia is one of the most highly produced inorganic chemicals. Modern chemical plants depend on Haber Process whereby hydrogen derived from natural gas reacts with atmospheric nitrogen using a catalyst under high pressure and temperature to produce anhydrous ammonia.

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$$

(a) For the above reaction, a 1:3 ratio of N_2 and H_2 is passed over a catalyst. The resulting mixture is allowed to reach dynamic equilibrium. At equilibrium, 20% of the N_2 has reacted and the total pressure is 2.0 atm.

(i) Explain what is meant by the term *dynamic equilibrium*.

[1]

A dynamic equilibrium is a chemical equilibrium where the rate of forward reaction is equal to the rate of backward reaction and the substances are still reacting together although the concentrations of the reactants and products remain constant.

(ii) Calculate the partial pressures of N_2 and H_2 at equilibrium.

[2]

	$N_2(g)$ +	**$3H_2(g)$ $\rightleftharpoons$**	**$2NH_3(g)$**
Initial no. of mole	x	$3x$	0
Change in no. of mole	$-0.2x$	$-0.6x$	$+0.4x$
No. of mole at equilibrium	$0.8x$	$2.4x$	$0.4x$

Total no. of moles at equilibrium = $0.8x + 2.4x + 0.4x = 3.6x$

Mole fraction at equilibrium	$0.8x / 3.6x$ = 0.222	$2.4x / 3.6x$ = 0.667	$0.4x / 3.6x$ = 0.111
Partial Pressure at equilibrium/ atm	0.222 x 2.0 = 0.444	0.667 x 2.0 = 1.33	0.111 x 2.0 = 0.222

Partial pressure of N_2 at equilibrium = 0.444 atm
Partial pressure of H_2 at equilibrium = 1.33 atm

(iii) Write an expression for the equilibrium constant, K_p, and calculate its value.

[2]

$$K_p = \frac{\left(P_{NH_3}\right)^2}{\left(P_{N_2}\right)\left(P_{H_2}\right)^3} = \frac{(0.222)^2}{(0.444)(1.33)^3} = 0.0472\ \text{atm}^{-2}$$

(b) **(i)** Using relevant data in the *Data Booklet,* calculate the enthalpy change of reaction, ΔH_{rxn} of the Haber Process.

[2]

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

ΔH_{rxn} = [BE(N≡N) + 3BE(H–H) – [6BE(N–H)]
= [(944) + 3(436)] – [6(390)]
= – 88.0 kJ mol^{-1}

(ii) The enthalpy change of reaction calculated above in **(b)(i)** differs slightly from the actual value of –92.0 kJ mol^{-1}. Suggest a reason for this.

[1]

The bond energy calculation is an approximation method as the N–H bond energy value / bond energy values for polyatomic molecules from the *Data Booklet* are average values.

(c) Explain whether the formation of ammonia is favoured with

I high or low pressure,
II high or low temperature.

[3]

I High pressure favours ammonia formation.
By Le Chatelier's Principle, with an increase in pressure, the equilibrium position will shift right to decrease the number of moles of gas to decrease pressure.

New equilibrium mixture contains less reactants, N_2 and H_2 and more products, NH_3. Yield of ammonia increases.

II Low temperature favours ammonia formation.
By Le Chatelier's Principle, with a decrease in temperature, the equilibrium position will shift right towards exothermic reaction to release heat.

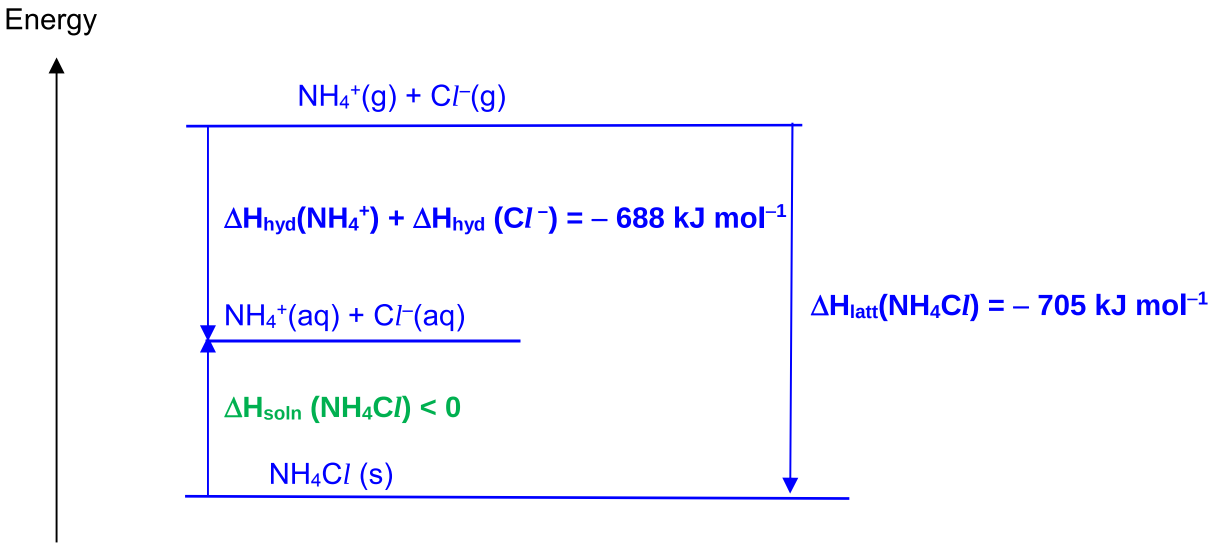
New equilibrium mixture contains less reactants, N_2 and H_2 and more products, NH_3. Yield of ammonia increases.

(d) Ammonium chloride, NH_4Cl is typically used in instant ice–packs. A crushing action activates the ice–pack as this mixes NH_4Cl with water. The ice–pack cools as the dissolution of NH_4Cl is endothermic.

Draw an energy level diagram to determine the standard enthalpy change of solution of ammonium chloride given the following information.

Lattice energy of ammonium chloride	–705 kJ mol^{-1}
Enthalpy change of hydration of NH_4^+	–307 kJ mol^{-1}
Enthalpy change of hydration of Cl^-	–381 kJ mol^{-1}

[2]



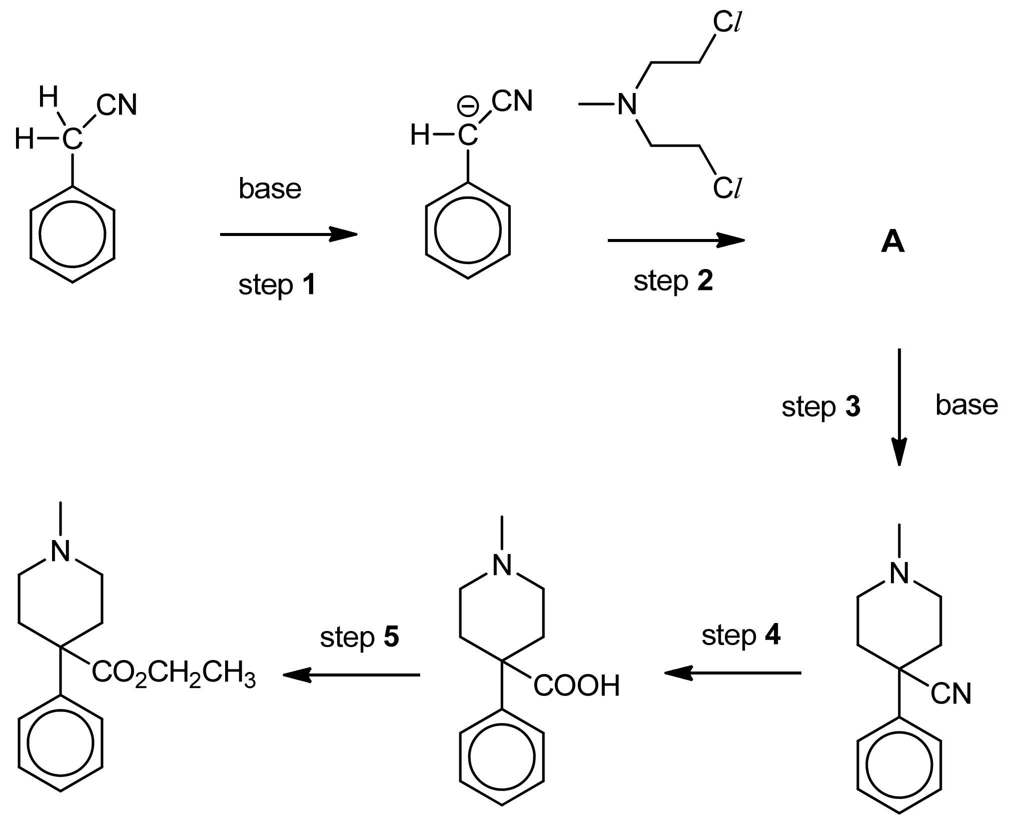
By Hess' Law,

$$\begin{aligned}\Delta H_{soln}(NH_4Cl) &= -\Delta H_{latt}(NH_4Cl) + \Delta H_{hyd}(NH_4^+) + \Delta H_{hyd}(Cl^-)\\ &= -(-705) + (-307) + (-381)\\ &= +17.0 \text{ kJ mol}^{-1}\end{aligned}$$

[Total: 13]

2 Nitrogen is an element commonly found in various major classes of drugs.

(a) The following is a reaction scheme for the synthesis of pethidine, a powerful painkilling drug.



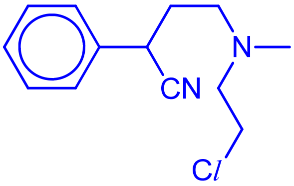
pethidine

(i) State the type of reaction for step **1** and step **2**. **[2]**

Step 1: acid–base reaction / neutralisation

Step 2: nucleophilic substitution

(ii) Suggest the structure of intermediate **A** **[1]**



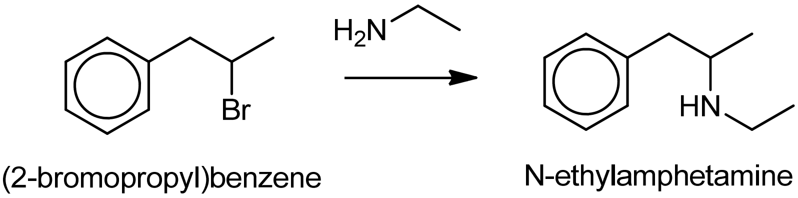
(iii) State the reagents and conditions needed for step **4** and step **5**. **[2]**

Step 4: HC*l* (aq) / H_2SO_4 (aq), heat under reflux

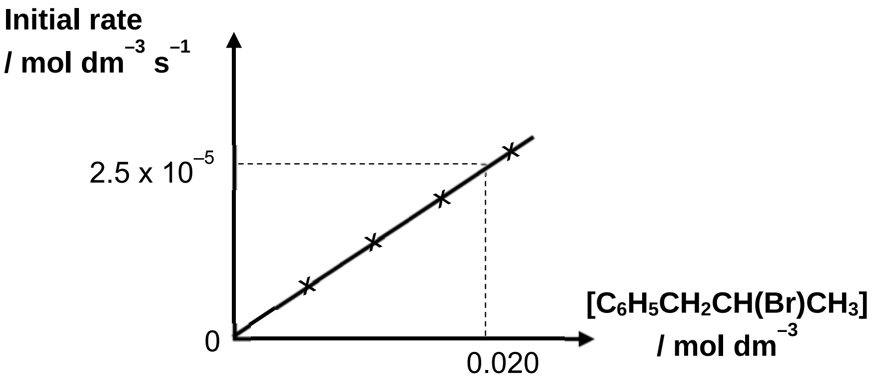
Step 5: CH_3CH_2OH, conc. H_2SO_4, heat OR PCl_5 followed by CH_3CH_2OH

(b) Kinetics studies of organic reactions provide strong evidence in supporting the postulated mechanisms.

The results from the kinetics study of the nucleophilic substitution reaction involved in the synthesis of N–ethylamphetamine, a discontinued weight–loss drug, are presented below.



The graph was plotted based on data obtained from repeating the experiment several times by varying the concentration of $C_6H_5CH_2CH(Br)CH_3$ while maintaining that of $CH_3CH_2NH_2$ to be at 2.5 mol dm^{-3}.



(i) The rate equation for the reaction was found to be

$$\text{rate} = k\,[C_6H_5CH_2CH(Br)CH_3][CH_3CH_2NH_2]$$

Using the graph provided, justify why the order of reaction with respect to $C_6H_5CH_2CH(Br)CH_3$ is one.

[2]

The graph of rate against $[C_6H_5CH_2CH(Br)CH_3]$ is a positively sloped straight line passing through the origin hence the initial rate is directly proportional to $[C_6H_5CH_2CH(Br)CH_3]$.

(ii) Calculate the rate constant, k and state its units.

[2]

Using data from the graph,

$\text{Rate} = k\,[C_6H_5CH_2CH(Br)CH_3]\,[CH_3CH_2NH_2]$

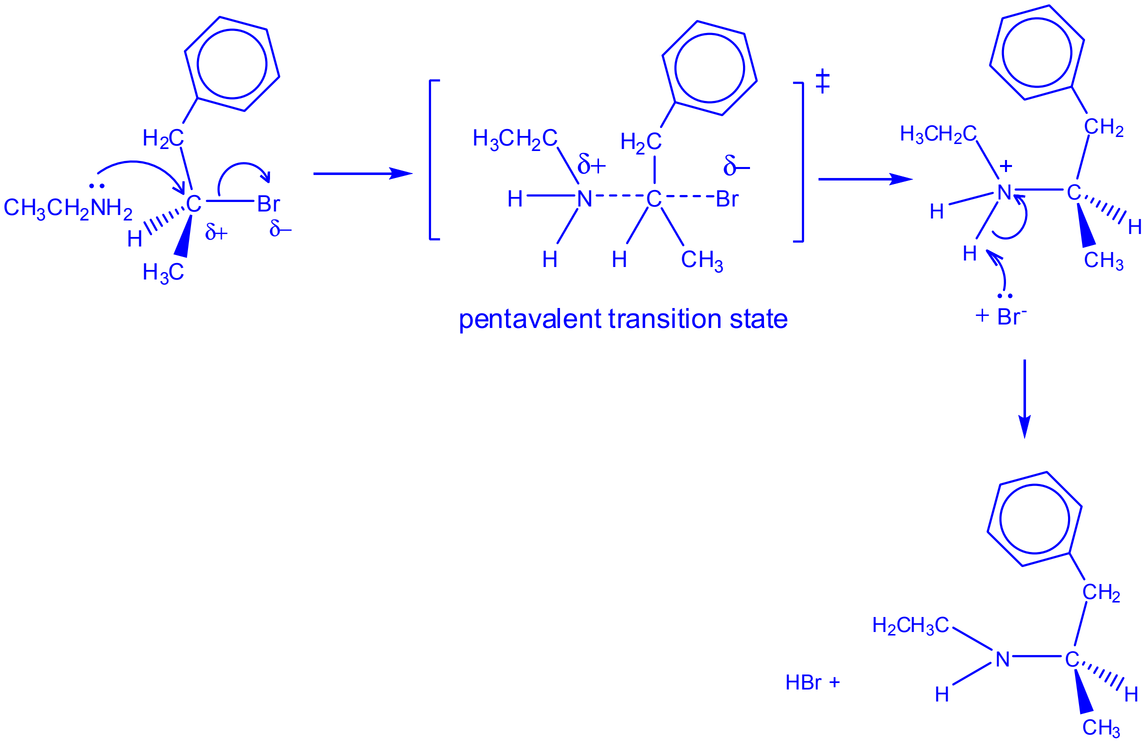
$2.5 \times 10^{-5} = k\,(0.020)(2.5)$

$k = 5.00 \times 10^{-4}$ mol^{-1} dm^{3} s^{-1}

(iii) Given that this is a bimolecular reaction, outline the mechanism for this reaction. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons.

[3]

Nucleophilic Substitution (**S_N2**)



(iv) Suggest why the rate of reaction decreases when $(CH_3)_3CNH_2$ is used instead of $CH_3CH_2NH_2$.

[1]

The alkyl group of $(CH_3)_3CNH_2$ is bulkier than that of $CH_3CH_2NH_2$ hence there will be steric hindrance. The rate of reaction will decrease.

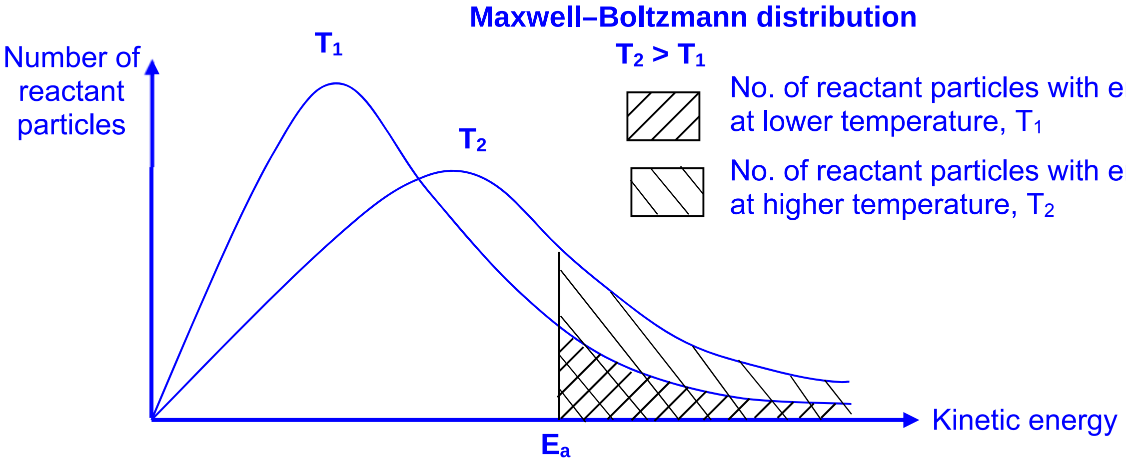
(v) Explain how the reactivity of (2–chloropropyl)benzene will differ towards $CH_3CH_2NH_2$ as compared to (2–bromopropyl)benzene.

[1]

C–C*l* bond is stronger than C–Br. Hence (2–chloropropyl)benzene will be less reactive towards $CH_3CH_2NH_2$.

(vi) With the aid of a Maxwell–Boltzmann Distribution curve, explain how heating the reaction mixture will increase the rate of the reaction.

[3]



- When temperature is increased, number of reactant particles with energy ≥ E_a increases,
- Frequency of effective collisions increases.
- Since rate of reaction is proportional to the frequency of effective collisions, rate of reaction increases.

(c) Investigating the optical activity of the product of a nucleophilic substitution reaction can also provide evidence on how the reaction may proceed.

Consider the reaction between the (+) enantiomer of 2–bromobutane and hot NaOH (aq).

State the expected optical activity of the product if this reaction proceeds via S_N1 mechanism. Provide reasoning for your answer.

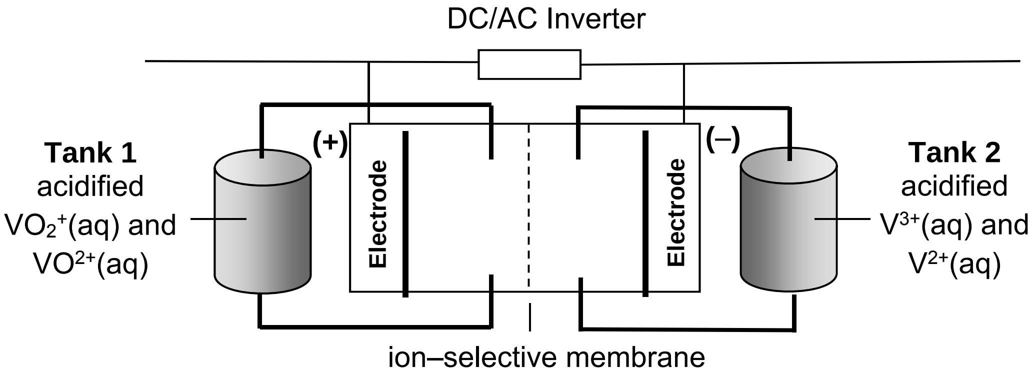
[2]

If the reaction proceeds via a S_N1 mechanism, the product obtained is likely going to be optically inactive.

Since S_N1 mechanism involves the formation of a carbocation intermediate, the nucleophile (OR OH^-) can attack the sp^2 hybridised (OR trigonal planar) carbocation (OR $[CH_3CH(CH_2CH_3)]^+$) intermediate from either top and bottom of the plane with equal probability giving rise to equal amount of both enantiomers of the product (OR racemic mixture).

[Total: 19]

3 The vanadium flow battery (VFB) is a type of rechargeable battery that employs electrolyte containing vanadium ions in different oxidation states.



(a) Electricity is generated from the battery by half–cell reactions of these electrolytes that were pumped into the cell from separate storage tanks. The two electrolytes in the cell are separated by an ion selective membrane, which only allows H^+ ions to pass through.

(i) Write the two half equations for the reaction occurring at the anode and the cathode when the battery discharges. Hence, write the overall cell reaction.

[2]

Anode: $V^{2+}(aq) \longrightarrow V^{3+}(aq) + e$

Cathode: $VO_2^{+}(aq) + 2H^{+}(aq) + e \longrightarrow VO^{2+}(aq) + H_2O(l)$

Overall: $V^{2+}(aq) + VO_2^{+}(aq) + 2H^{+}(aq) \longrightarrow V^{3+}(aq) + VO^{2+}(aq) + H_2O(l)$

(ii) Calculate the e.m.f of the battery.

[1]

Cathode (Tank 1): $VO_2^{+}(aq) + 2H^{+}(aq) + e \longrightarrow VO^{2+}(aq) + H_2O(l)$ $E^\ominus_{ox} = +1.00\ V$

Anode (Tank 2): $V^{2+}(aq) \longrightarrow V^{3+}(aq) + e$ $E^\ominus_{ox} = -0.26\ V$

$$E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{oxid} = +1.00 - (-0.26)$$
$$= +1.26\ V$$

(iii) Explain how the ion–selective membrane in VFB maintains electrical neutrality.

[1]

As the reaction proceeds, the anode/Tank 2 becomes more positively charged (formation of more positively charged ion) whilst the cathode/Tank 1 becomes more negatively charged (due to consumption of H^+).

The membrane allows H^+ ions to migrate from Tank 2/anode to Tank 1/cathode so as to maintain electrical neutrality.

(iv) State and explain what happens to the overall e.m.f when a small amount of OH^-(aq) ions were added to the electrolyte in **Tank 1**.

[2]

When OH^-(aq) ions were added, $[H^+]$ decreases in electrolyte in Tank 1

$$VO_2^+ (aq) + 2H^+ (aq) + e \rightleftharpoons VO^{2+} (aq) + H_2O (l) —— (1) E^{\ominus}_{red}$$

By Le Chatelier's Principle, the equilibrium position in (1) will shift left to increase $[H^+]$. Hence, E_{red} becomes less positive

Since, $E_{cell} = E_{red} - E_{oxid}$; E_{cell} becomes less positive/more negative.

(b) The total concentration of vanadium ions in the 20 dm^3 electrolyte in **Tank 1** is 5.00 mol dm^{-3}. During the charging of the VFB, the percentage composition of VO_2^+ has to be increased from 5% to 90%.

(i) Calculate the amount of VO_2^+ that needs to be converted during this charging process.

[1]

Change in amount of VO_2^+ required = $\left(\frac{90}{100} - \frac{5}{100}\right) \times 20.0 \times 5.00 = 85.0$ mol

(ii) Find the time taken, in hours, if a 120 A current is used in the charging process.

[2]

$VO_2^+(aq) + 2H^+(aq) + e^- \longrightarrow VO^{2+} (aq) + H_2O (l)$

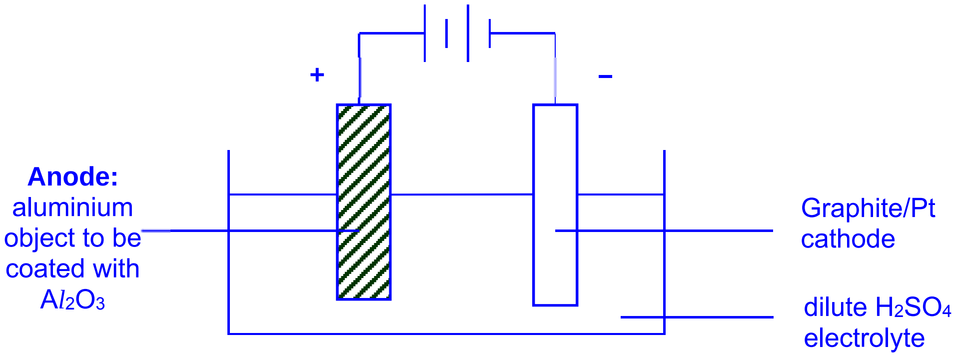
Amount of VO_2^+ = $\frac{It}{nF}$

$85.0 = \frac{120 \times t}{1 \times 96500}$ ➔ t = 68354 s = 19.0 h

(c) Anodising of aluminum is an electrolytic process to increase the thickness of the alumnium oxide layer on the surface of aluminium, by passing a direct current through dilute sulfuric acid.

(i) Draw a labelled diagram of an electrolysis set–up during the anodising of aluminium.

[2]



(ii) Write the half–equations for the reactions taking place at the anode, cathode and hence write the overall equation.

[2]

Anode: $2Al\,(s) + 3H_2O(l) \longrightarrow Al_2O_3\,(s) + 6H^+\,(aq) + 6e$

Cathode: $2H^+\,(aq) + 2e \longrightarrow H_2\,(g)$

Overall: $2Al\,(s) + 3H_2O(l) \longrightarrow Al_2O_3\,(s) + 3H_2\,(g)$

(iii) State and explain any observations if copper(II) sulfate was used as the electrolyte instead.

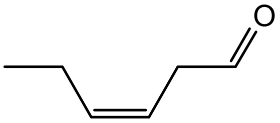
[1]

Pink Cu solid will be deposited on the cathode; blue $CuSO_4$ solution/electrolyte fades.

Cu^{2+} will be preferentially reduced/discharged at the cathode instead of H^+, as $E^{\theta}_{Cu^{2+}/Cu}$ is more positive compared to $E^{\theta}_{H_2/H^+}$

[Total: 14]

4(a) *cis*–3–hexenal, $CH_3CH_2CH{=}CHCH_2CHO$ is a compound with an intense smell of freshly cut grass and leaves.

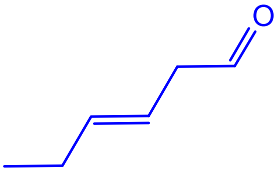


cis–3–hexenal

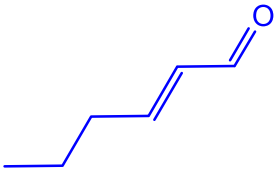
Two isomers, **P** and **Q**, with the same molecular formula, $C_6H_{10}O$, as *cis*–3–hexenal show different types of isomerism. Both isomers decolourises aqueous bromine in the dark and both gives a positive test with Fehling's reagent.

Draw their structures and state their isomeric relationship to *cis*–3–hexenal.

[2]



isomer **P**



isomer **Q**

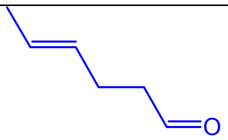
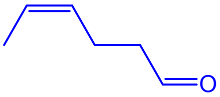
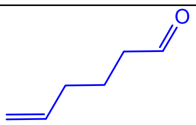
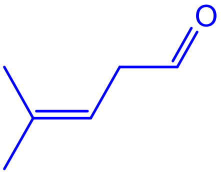
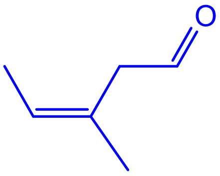
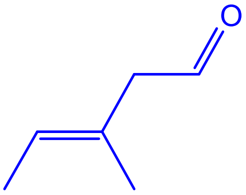
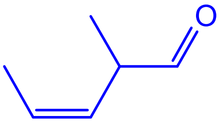
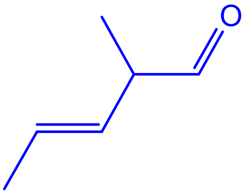
isomeric relationship to *cis*–3–hexenal:

cis–trans isomerism

isomeric relationship to *cis*–3–hexenal:

constitutional isomerism

Other possible answers

 *trans*–4–hexenal	 *cis*–4–hexenal	 5–hexenal
 5–methyl–4–hexenal	 *trans–3–methyl–4–hexenal*	 *cis–3–methyl–4–hexenal*
 cis–2–methyl–4–hexenal	 *trans–2–methyl–4–hexenal*	

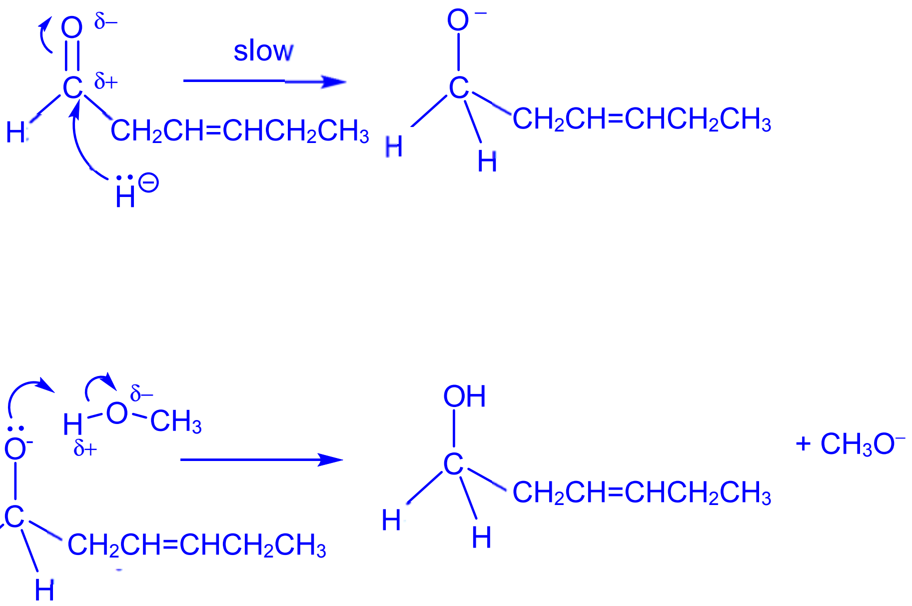
(b) These metal hydride reagents provide a source of hydride, H^- ions.

(i) The reaction between *cis*–3–hexenal, $CH_3CH_2CH=CHCH_2CHO$ and sodium borohydride in methanol is a nucleophilic addition reaction.

Draw the mechanism for this reaction, showing all charges, dipoles and curly arrows to represent the movement of electron pairs.

[3]

Nucleophilic addition

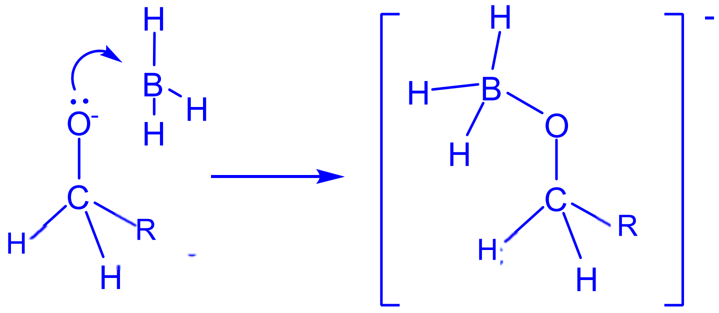


(ii) BH_3 is a side product of the earlier reaction in **(b)(i)**. BH_3 can form an addition product with Lewis bases, for example, with the alkoxide ion generated in the mechanism.

Draw the structure of this adduct formed and explain why the formation of the adduct is likely to happen.

[2]

- B in BH_3 is electron deficient or B has only 6 electrons.
- B readily accepts lone pair of electron from Lewis bases to form complexes to attain stable octet structure / configuration.



(c) Both LiAlH_4 and $NaBH_4$ are sources of H^-. Hydride ions react vigorously with Bronsted–Lowry acids, releasing H_2 (g) and heat.

LiAlH_4 reacts violently with water or alcohols. When carrying out reactions with LiAlH_4, chemists often use solvents like anhydrous diethyl ether that has been treated to remove traces of water. On the other hand, $NaBH_4$ does not react that vigorously with water or alcohol.

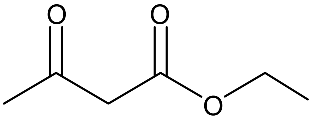
Using the information provided or otherwise, suggest why LiAlH_4 is a better source of H^- than $NaBH_4$.

	Pauling Electronegativity
aluminium	1.61
boron	2.04
hydrogen	2.20

[1]

The difference between the electronegativities of B and H is smaller than the difference between the electronegativities of A*l* and H, so there is a greater degree of ionic character in A*l*–H bonds than in B–H bonds

(d) A student proposed the following procedure to reduce ethyl acetoacetate ($C_6H_{10}O_3$),



using $NaBH_4$.

Procedures

1. Add 0.70 g of $NaBH_4$ to 25 cm^3 ethanol solvent in a 100 cm^3 round–bottomed flask. Cool the resulting mixture to 0 °C using an ice–bath.
2. To this mixture, slowly add 30 cm^3 of 40.8 g dm^{-3} ethyl acetoacetate solution. Stir the resulting solution at 0 °C for 15 minutes, then allow to warm to room temperature and stir for an additional 15 minutes.
3. Evaporate the solvent. Dissolve the resulting white solid in 30 cm^3 dichloromethane solvent, CH_2Cl_2.
4. Cool the flask in an ice–bath. Then, add 30 cm^3 of 1 mol dm^{-3} hydrochloric acid dropwise, while stirring, to quench the reaction by destroying any unreacted hydride. **Safety note*: The addition of HCl will release H_2 gas.*
5. Separate the organic layer from the aqueous layer.
6. Add powdered magnesium sulfate to the organic layer in excess, till no clumping of magnesium sulfate powder is observed. Filter off the magnesium sulfate and evaporate the dichloromethane solvent.
7. Weigh the product and record the actual yield.

(i) Explain why $NaBH_4$ is soluble in ethanol (in **step 1**) in terms of structure and bonding.

[2]

- $NaBH_4$ has a giant ionic lattice structure.
- The formation of ion–dipole interactions between polar ethanol molecules and the ions results in the release of energy causes the detachment of ions from the crystal lattice for solvation/hydration.
- Hence, $NaBH_4$ is soluble in ethanol.

(ii) One mole of $NaBH_4$ can reduce a maximum of four moles of carbonyl groups. Generally, in an experimental procedure, the reducing agent $NaBH_4$ should be used in excess.

Determine with relevant calculations, whether the student is correct with the quantities proposed in his procedures (**step 1 – 2**).

[2]

Amount of $NaBH_4$ available = $\frac{0.70}{23.0+10.8+4.0}$ = 0.01852 mol

Amount of ethyl acetoacetate available = $\frac{40.8\times\frac{30}{1000}}{12.0\times6+10.0+16.0\times3}$ = 9.415×10^{-3} mol

Since $NaBH_4$ can reduced a maximum of 4 carbonyl groups,
mole ratio could be $NaBH_4 \equiv$ 4 carbonyl groups

Theoretical amount of $NaBH_4$ required if all carbonyl groups are used up
= $9.415 \times 10^{-3} / 4$ = 0.00235 mol

Amount of $NaBH_4$ available > Amount of $NaBH_4$ required
$\Rightarrow$ $NaBH_4$ is in large excess; the student is correct.

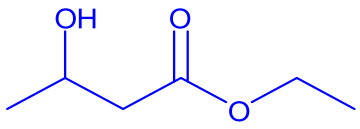
(iii) In **step 4**, hydrochloric acid is added to quench the reaction, producing hydrogen gas and sodium boron chloride. Write an equation for the reaction that took place.

[1]

$NaBH_4 + 4HCl \longrightarrow NaBCl_4 + 4H_2$

(iv) Draw the **skeletal** formula of the product isolated in the organic layer at the end of the experiment.

[1]



(v) Suggest the function of magnesium sulfate in **step 6**.

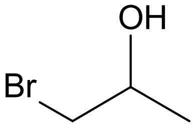
[1]

$MgSO_4$: drying agent to remove water in the organic layer

[Total: 15]

5 Organic reactions can lead to increased variation due to the direction–specific nature of covalent bonds, giving rise to much complexity from using only a small range of elements such as carbon, hydrogen and oxygen.

(a) Propene reacts with aqueous bromine to form a mixture of products, including molecule **A**.



Molecule **A**

(i) State the IUPAC name of molecule **A**.

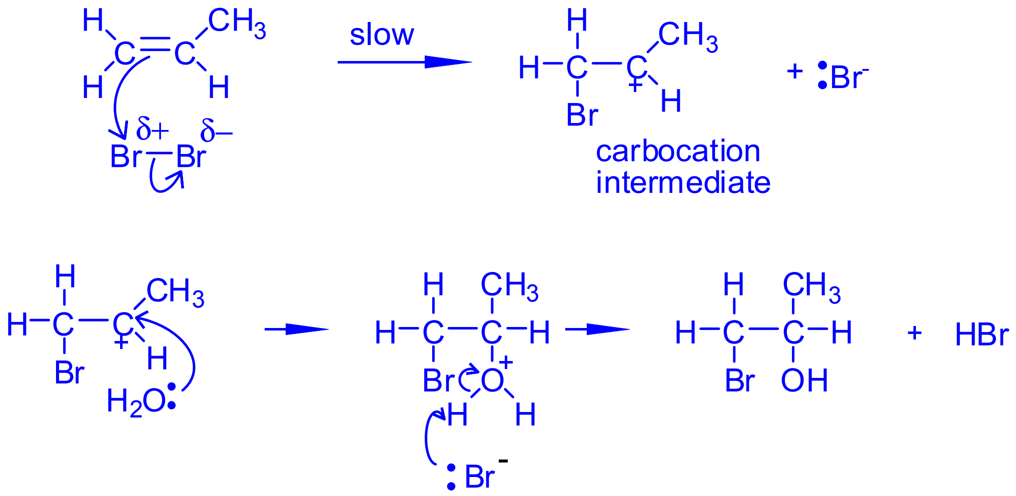
[1]

1–bromopropan–2–ol or 1-bromo-2-propanol

(ii) Draw a mechanism for the reaction between propene and aqueous bromine to form Molecule **A** and hydrogen bromide. Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs.

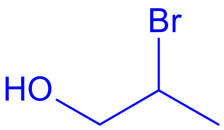
[3]

Electrophilic Addition

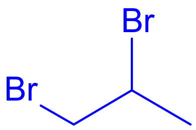


(iii) Molecule **A** is the major product of this reaction. Suggest the structure of two other organic by–products.

[2]

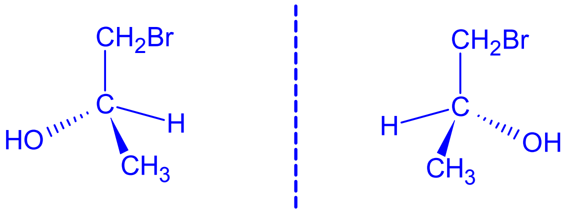


and



(iv) In the mechanism outlined in **(a)(ii)**, two stereoisomers of **A** are formed in equal amounts. Draw these two stereoisomers and name the type of isomerism displayed.

[2]

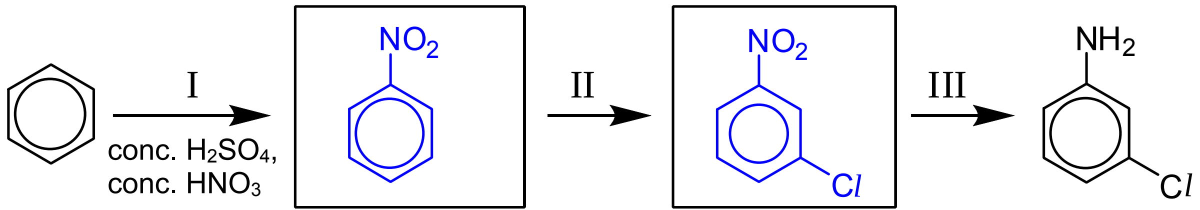


Enantiomerism

(b) 3–chloroaniline can be synthesised from benzene in a 3–step synthesis.

(i) Propose a synthetic route by suggesting the two intermediates compounds and state the reagents and conditions used for steps **II** and **III**.

[4]



3-chloroaniline

Step II: Cl_2, anhydrous $AlCl_3$, heat

Step III: Sn, in excess conc HCl, heat followed by NaOH (aq)

(ii) One of the by–products from the synthesis in **(b)(i)** is HCl, which is a strong acid. The acid dissociation constant values, K_a of several hydrogen halides are shown below.

Compound	**K_a / mol dm^{-3}**
HCl	1.3×10^6
HBr	1.0×10^9
HI	3.2×10^9

Account for the relative K_a values.

[2]

Down the group, the K_a value of HX increases. This means HX dissociates more readily to give H^+. This is because H–X bond strength decreases and becomes easier to break.

[Total: 14]

Name ________________________ **Class: 17S**_______ **Reg Number:** _____

MERIDIAN JUNIOR COLLEGE
JC 2 Preliminary Examination
Higher 2

Chemistry **9729/03**

Paper 3 Free Response **13 September 2018**

2 hour

Additional Materials: *Data Booklet*
Writing Paper

INSTRUCTIONS TO CANDIDATES

Write your name, class and register number in the spaces provided at the top of this page.

Answer all questions in Section A and one question from Section B.

Begin each question on a fresh page of writing paper.

Fasten the writing papers behind the given **Cover Page for Questions 1 & 2** and **Cover Page for Questions 3 & 4 or 5** respectively.

Hand in Questions **1 & 2** and **3 & 4 or 5** **separately**.

You are advised to spend about 30 minutes per question only.

INFORMATION FOR CANDIDATES

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

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

This document consists of **17** printed pages (including this cover page).

Section A

Answer **all** questions in this section.

1(a) Explain the variation in melting point of the oxides of the elements in Period 3 (sodium to sulfur), using oxides of three different structure as examples.

Indicate clearly the type of structure and bonding present in the examples you have selected.

[3]

(b) With the aid of the *Data Booklet*, explain the difference in observed melting points of Na*Cl* (801 °C) and MgO (2852 °C).

[2]

(c) Instead of melting like chlorides or oxides, Group 2 nitrates decompose upon heating.

(i) Write an equation, including state symbols, for the thermal decomposition of magnesium nitrate, $Mg(NO_3)_2$.

[1]

(ii) Predict, with reasoning, whether barium nitrate, $Ba(NO_3)_2$, is more or less thermally stable compared with $Mg(NO_3)_2$.

[2]

(d) Chlorides of Period 3 elements dissolve in water to form solutions of differing pH values.

(i) Sketch a graph to illustrate how the pH of the resultant solutions vary across the period (from sodium to phosphorus).

[1]

(ii) Write an equation to illustrate the reaction of PCl_5 with water.

[1]

(iii) Lithium is a Group 1 element. Its chloride, Li*Cl* however behaves similarly to that of a chloride of a Group 2 element when dissolved in water.

Suggest a reason why this would be so.

[1]

(e) Disulfur dichloride, S_2Cl_2 is one of three chlorides of sulfur. It is a liquid at room temperature with a pungent odour. It has a structure in which the central sulfur atoms are bonded by a single covalent bond.

Draw clear diagrams of two possible molecular arrangements of S_2Cl_2, showing clearly the electron pairs around the sulfur atoms. Apply the principles of the VSEPR theory to suggest which arrangement would result in a molecule which could be more stable.

[3]

(f) CCl_4, an important commercial solvent is prepared by the reaction of Cl_2 gas with a sulfur–containing carbon compound. S_2Cl_2 is produced as a by–product. The reaction for the production is shown below.

$$CS_2\,(l) + 3Cl_2\,(g) \longrightarrow CCl_4\,(l) + S_2Cl_2\,(l)$$

(i) Using appropriate data in **Table 1.2** and the energy cycle provided, determine the enthalpy change, $\Delta H^{\ominus}_{rxn}$ for the above reaction.

Table 1.2

	$\Delta H^{\ominus}$ / kJ mol^{-1}
Standard enthalpy change of formation of $CCl_4\,(l)$	–135.4
Standard enthalpy change of combustion of C (s)	–393.5
Standard enthalpy change of formation of $S_2Cl_2\,(l)$	–58.2
Standard enthalpy change of formation of $SO_2\,(g)$	–296.8
$CS_2\,(l) + 3O_2\,(g) \longrightarrow CO_2\,(g) + 2SO_2\,(g)$	–1077.0
$SO_2\,(g) + Cl_2\,(g) \longrightarrow SO_2Cl_2\,(l)$	+97.3

[2]

$$\begin{tikzcd}
CS_2\,(l) + 3Cl_2\,(g) \arrow[rr, "\Delta H^{\ominus}_{rxn}"] \arrow[d] & & CCl_4\,(l) + S_2Cl_2\,(l) \arrow[ddl] \\
CO_2\,(g) + 2SO_2\,(g) + 3\,Cl_2\,(g) & & \\
 & 2S\,(s) + 3Cl_2\,(g) + C\,(s) \arrow[ul] &
\end{tikzcd}$$

(ii) CCl_4 could be reacted with limited oxygen according to the following reaction.

$$CCl_4\,(l) + O_2\,(g) \longrightarrow COCl_2\,(g) + Cl_2O\,(g) \qquad \Delta H^{\ominus} = -5.2 \text{ kJ mol}^{-1}$$

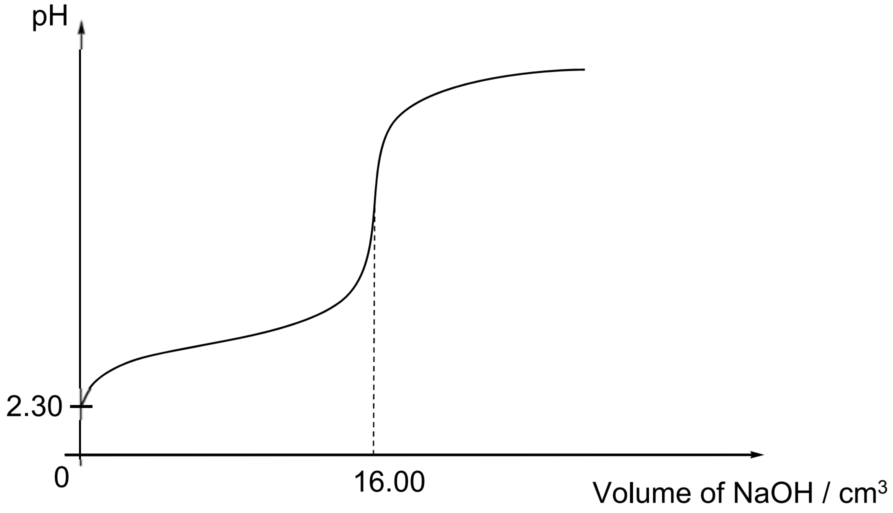
Predict the sign of entropy change, $\Delta S^{\ominus}$ for this reaction and explain whether the reaction would be spontaneous at all temperatures.

[2]

[Total: 18]

2 In analytical chemistry, both quantitative and qualitative information about chemical reactions are established through the use of various chemical methods.

(a) Glycolic acid, $HOCH_2COOH$ is a weak acid used in many cosmetic skin–care products. When a student titrated 25.0 cm^3 of a glycolic acid against 0.250 mol dm^{-3} NaOH, the following titration curve was obtained.



(i) Suggest an appropriate indicator for the titration, giving a reason for your choice.

[1]

(ii) Use the above titration data to calculate the K_a value of glycolic acid.

[2]

(b) The pH levels of skin–care products need to be regulated to prevent degradation of the active ingredients. A buffer solution containing ethanoic acid and its sodium salt, sodium ethanoate can be added to control the pH. The pK_a of ethanoic acid is 4.76.

(i) With the aid of a balanced equation, briefly explain how a solution of ethanoic acid and sodium ethanoate can maintain a fairly constant pH when a small amount of acid is added to this solution.

[1]

(ii) Determine the resulting pH of a 100.0 cm^3 solution containing 0.10 mol dm^{-3} of ethanoic acid and 0.10 mol dm^{-3} of sodium ethanoate when 5.0×10^{-4} mol of H_2SO_4 is added to this solution.

[2]

(c) Another student performed a series of thermometric experiments to determine the enthalpy change of neutralisation involving several acids and sodium hydroxide. Her experimental results are summarised in the table below.

Acid	**Enthalpy change of neutralisation, $\Delta H^{\ominus}_{n}$ / kJ mol^{-1}**
hydrochloric acid, HC*l*	– 57.2
hydrofluoric acid, HF	– 68.6
glycolic acid, $HOCH_2COOH$	– 53.2

(i) Explain why the neutralisation reaction involving glycolic acid is less exothermic than that involving hydrochloric acid.

[1]

Deducing the strength of acids solely from the enthalpy change of neutralisation may not be appropriate as there are exceptions. For instance, the neutralisation reaction between HF, a weak acid and NaOH is significantly more exothermic than that of HC*l* and NaOH.

(ii) Suggest why the neutralisation reaction between HF and NaOH is unexpectedly more exothermic.

[1]

(d) Argentometric titration can be used to determine the amount of sodium chloride present in skin–care products by titrating the sample against silver nitrate, $AgNO_3$. A suitable indicator is one that forms a precipitate of a different colour after all the chloride ions have reacted.

The following are relevant K_{sp} values of some sparingly soluble silver compounds.

	K_{sp}
AgC*l*	1.8×10^{-10} mol^2 dm^{-6}
AgI	7.7×10^{-17} mol^2 dm^{-6}
Ag_3PO_4	1.3×10^{-20} mol^4 dm^{-12}

(i) Write an expression for the solubility product, K_{sp} of Ag_3PO_4.

[1]

(ii) Given that Ag_3PO_4 precipitate is yellow in appearance, by means of suitable calculations, suggest whether potassium phosphate, K_3PO_4 can be used as an indicator in the argentometric titration for the determination of chloride content.

[2]

(iii) With the aid of appropriate equations, explain why silver chloride, AgC*l* is soluble in excess aqueous ammonia.

[3]

(iv) Hence, briefly explain why silver iodide, AgI remains insoluble even in concentrated ammonia solution.

[1]

(e) The distinctive reactions of solid halides with hot concentrated sulfuric acid also provide useful basis for further analysis.

These halides react with hot concentrated sulfuric acid to form white fumes of hydrogen halides.

$$\mathrm{Na\mathbf{X}\,(s)} + \mathrm{H_2SO_4\,(\mathit{l})} \longrightarrow \mathrm{H\mathbf{X}\,(g)} + \mathrm{NaHSO_4\,(s)}$$

where **X** = C*l*, Br or I

However, only HBr and HI formed will further react with concentrated H_2SO_4. The main products for these reactions are recorded in the table below.

HC*l*	HBr	HI
no further reaction	red–brown gas	violet fumes
	acidic gas that decolourises acidified purple $KMnO_4$	pungent H_2S gas

(i) Suggest an identity for both the red–brown gas and the acidic gas formed when HBr further reacts with concentrated H_2SO_4.

[1]

(ii) Hence, write an equation for the reaction between HBr and concentrated H_2SO_4.

[1]

(iii) By considering the reactions of HC*l* and HI with concentrated sulfuric acid and the change in oxidation number of sulfur, explain which halide ion is a stronger reducing agent.

[2]

[Total: 19]

3 Transition elements show typical properties that distinguish them from s–block elements such as calcium. The following table gives data about some physical properties of the elements calcium, iron, copper and cadmium.

property	**calcium**	**iron**	**copper**	**cadmium**
relative atomic mass	40.1	55.8	63.5	112.4
atomic radius (metallic) / nm	0.197	0.126	0.128	0.151
ionic radius (2+) / nm	0.099	0.076	0.069	0.097
melting point / °C	839	1535	1085	322
density / g cm^{-3}	1.54	7.86	8.92	8.65

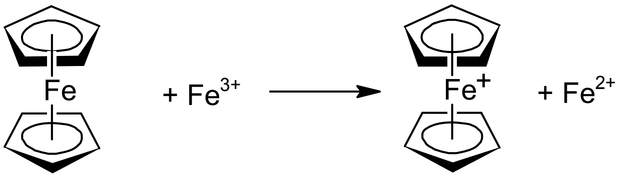
(a) **(i)** Explain why the atomic radii of iron and copper are similar to each other.

[2]

(ii) The melting point of iron is significantly higher than that of calcium and cadmium. Explain this using relevant data from the table and in terms of the structure and bonding in each metal.

[3]

(b) Ferrocene, $Fe(C_5H_5)_2$, is an orange organometallic solid. In this complex, $C_5H_5^-$ is the ligand and it donates π electrons from the ring to the vacant 3*d* orbitals of Fe. A chemist suggested that ferrocene would react with aqueous iron(III) ions to form iron(II) ions as shown below.



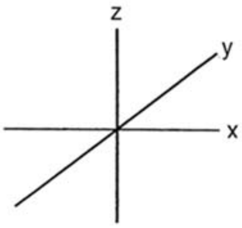
ferrocene

(i) The chemist found the reduction potential of ferrocene, $E^\ominus_{Fe(C_5H_5)_2^+ / Fe(C_5H_5)_2}$ to be +0.63V. Predict if the reaction between ferrocene and iron(III) ions will occur. Calculate $\Delta G^\ominus$ for this reaction.

[2]

(ii) Iron(II) ion forms octahedral complexes, the orbitals are split into two energy levels. Using the Cartesian axes shown below, draw separate labelled diagrams of

1. one of the *d* orbitals at the **lower** energy level in an octahedral complex,
2. one of the *d* orbitals at the **higher** energy level in an octahedral complex.



[2]

(iii) Using your diagrams in **(b)(ii)**, explain why the *d* subshell of a transition metal ion is split into two energy levels in an octahedral complex.

[2]

Most transition element complexes are coloured.

(iv) Explain why ferrocene is orange in colour.

[2]

(v) Aqueous Fe^{2+} ion is green in colour, suggest and explain if water causes a larger or smaller split between the two groups of 3*d* orbitals as compared to $C_5H_5^-$.

[2]

(vi) The reaction between $S_2O_8^{2-}$ and I^- is slow in the absence of catalyst. Fe^{2+}(aq) can be used as catalyst for the reaction between $S_2O_8^{2-}$ and I^-.

Explain with the aid of equations how it works.

[3]

(c) Cadmium ions form complexes with primary amines and with 1,2–diaminoethane.

(1) $Cd(H_2O)_6^{2+}(aq) + 4CH_3NH_2(aq) \rightleftharpoons [Cd(CH_3NH_2)_4]^{2+}(aq) + 6H_2O(l)$

$K_{stab} = 3.6 \times 10^6$

(2) $Cd(H_2O)_6^{2+}(aq) + 2H_2NCH_2CH_2NH_2(aq) \rightleftharpoons [Cd(H_2NCH_2CH_2NH_2)_2]^{2+}(aq) + 6H_2O(l)$

$K_{stab} = 4.2 \times 10^{10}$

K_{stab} is an equilibrium constant that accounts for the formation of a complex. It is a measure of the strength of the interactions between the ligands and the metal centre that come together to form the complex.

The values for $\Delta H^\ominus$ and $\Delta G^\ominus$ for equilibria **(1)** and **(2)**, and the value of $\Delta S^\ominus$ for equilibrium **(1)**, are given in the table below. All values are determined at a temperature of 298 K.

Equilibrium	**$\Delta H^\ominus$ / kJ mol^{-1}**	**$\Delta G^\ominus$ / kJ mol^{-1}**	**$\Delta S^\ominus$ / J mol^{-1} K^{-1}**
(1)	– 57.3	– 37.4	– 66.8
(2)	– 56.5	– 60.7	**–**

(i) Suggest a reason why the $\Delta H^\ominus$ values for the two equilibria are very similar.

[1]

(ii) Calculate the standard entropy change of reaction, $\Delta S^\ominus$ in equilibrium **(2)**.

[2]

(iii) Suggest a reason for the difference between the $\Delta S^\ominus$ you have calculated for equilibrium **(2)** and that for equilibrium **(1)** given in the table.

[1]

(iv) Which of the two complexes is more stable? Give a reason for your answer.

[1]

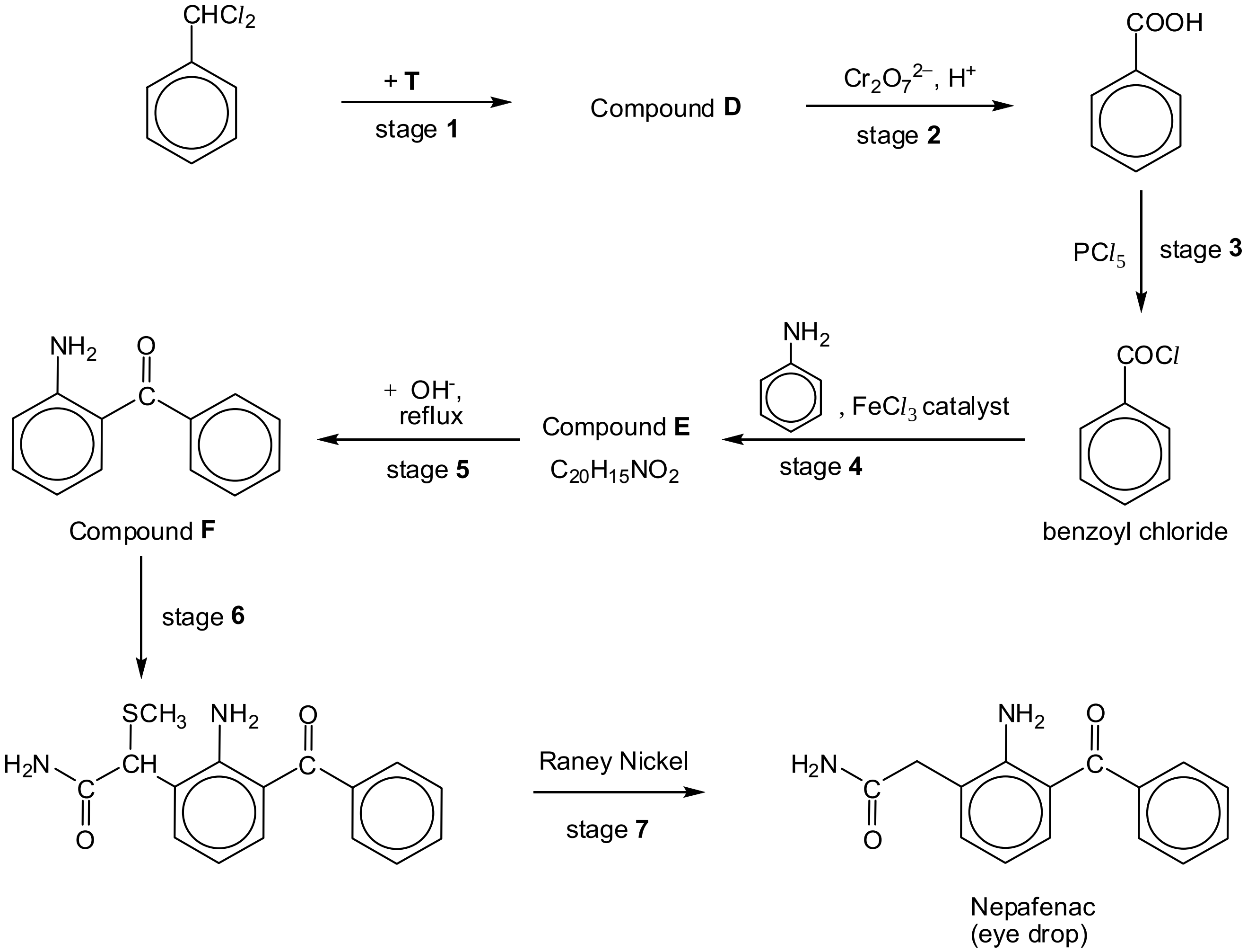
[Total: 23]

Section B

Answer **one** question from this section.

4(a) *Nepafenac* is a prescription eye drop that is used to treat pain and inflammation associated with eye surgery.

The following scheme shows a synthesis of *Nepafenac*.



(i) State the type of reaction occurring in stage **3** and stage **7**.

[2]

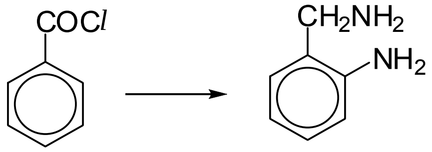
(ii) Draw the structure of compound **D**. Suggest the reagent and conditions required in stage **1**.

[2]

(iii) In stage **4**, two reactions are involved. Draw the structure of compound **E** and state the reactions that occurred.

[2]

(iv) Benzoyl chloride can be converted into 2–aminobenzylamine, an important starting material in the synthesis of quinazoline, a source of useful pharmacophores for new drug development.

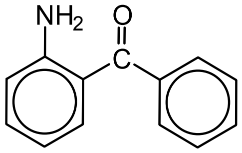


benzoyl chloride 2-aminobenzylamine

Suggest a 4–step synthesis of 2–aminobenzylamine from benzoyl chloride. You should state the reagents and conditions needed for each step, and show clearly the structures of any intermediate compounds.

[4]

(v) A student made a statement regarding a reaction with compound **F**: *"Cyanide, CN^-, is acting as a **Bronsted–Lowry base** to attack the carbonyl group of compound **F** to form a cyanohydrin."*

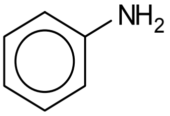
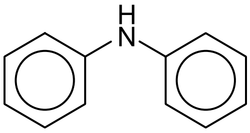


Compound **F**

Based on your understanding of a *Bronsted–Lowry* base, explain why the student's statement is wrong.

[1]

(vi) Data about phenylamine and diphenylamine are given in the table below.

Compound	 phenylamine	 diphenylamine
pK_b value	9.39	13.21

Give **two** reasons, why pK_b of phenylamine is lower than that of diphenylamine.

[2]

(b) Compound **J**, $C_{10}H_8O_3$, does not decolourise bromine water nor give effervescence with magnesium strip. **J** gives a silver mirror with Tollens' reagent but does not give a precipitate with hot alkaline Cu^{2+} solution.

On prolonged heating with acidified $KMnO_4$, **J** gives benzene–1,2–3–tricarboxylic acid as the only organic product. When heated with dilute H_2SO_4, **J** forms compound **K**, $C_{10}H_{10}O_4$. **K** gives a yellow precipitate with alkaline aqueous iodine.

J reacts with $LiAlH_4$ to form compound **L** (with an internal plane of symmetry), $C_{10}H_{14}O_3$. However, **J** forms compound **M**, $C_{10}H_{10}O_3$ with $NaBH_4$.

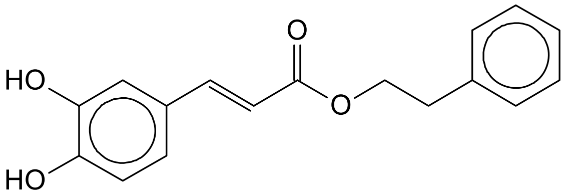
All compounds are optically active but only **K** reacts with sodium carbonate.

Suggest the structure for **J**, **K**, **L** and **M** and explain the reactions described.

[7]

[Total: 20]

5 Caffeic acid phenethyl ester (CAPE) is a natural occurring compound, found in propolis from honeybee hives. It is currently being studied for its anti–carcinogenic and anti–inflammatory properties. It is the ester of caffeic acid and 2–phenylethanol.



caffeic acid phenethyl ester (CAPE)

(a) Till date, there has been two well–established reaction schemes to synthesise CAPE. Study **Fig. 2.1** and **Fig 2.2** carefully and answer the questions that follow.

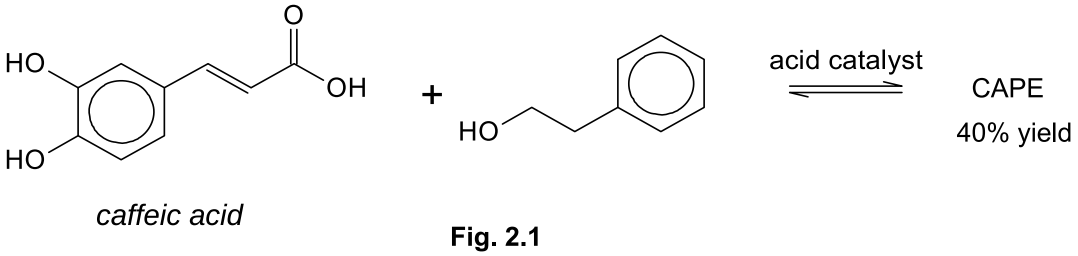


Fig. 2.1

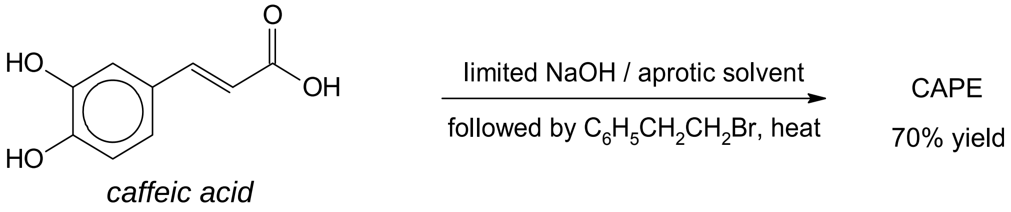


Fig. 2.2

(i) State the type of reaction occurring in each of the above synthesis method.

[2]

(ii) To improve the yield of CAPE in **Fig 2.1**, a student suggested using the acyl chloride derivative of caffeic acid instead. Comment on the validity of his suggestion.

[2]

(iii) Explain why NaOH has to be added in limited amount rather than in large excess in **Fig 2.2**.

[1]

(iv) A protic solvent is one that has labile proton(s) and readily donates its proton(s). Conversely an aprotic solvent does not have any labile proton. Suggest why is it important to use an aprotic solvent in **Fig 2.2**.

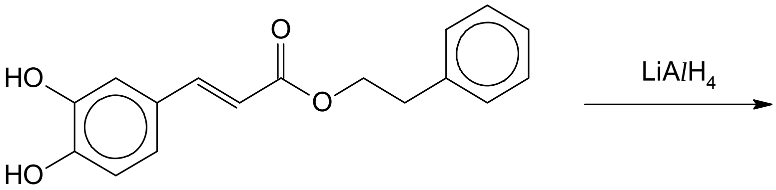
[1]

(v) The reported yield in **Fig. 2.2** is only 70%, as there are other by–products. Draw the skeletal formula of one possible by–product, assuming that caffeic acid reacts with $C_6H_5CH_2CH_2Br$ in a 1:1 ratio.

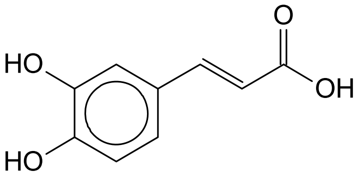
[1]

(vi) Draw the structure of the resultant product(s) when CAPE is reacted with $LiAlH_4$.

[1]



(b) The structure of *caffeic acid* is shown below.



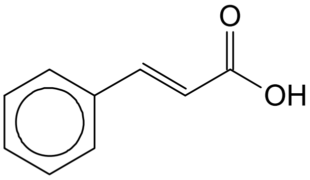
caffeic acid

(i) *Caffeic acid* contains two organic functional groups with pK_a values lower than that of an alcohol. Identify these functional groups.

Compare and account for the relative pK_a values of these two organic groups.

[3]

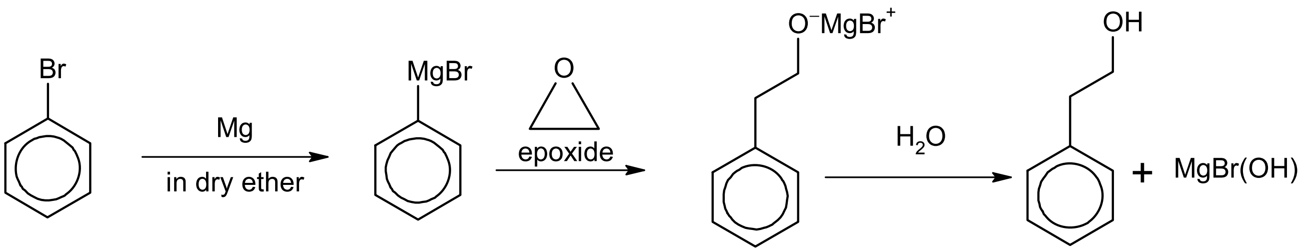
(ii) Suggest a chemical test that can be carried out to distinguish between a sample of *caffeic acid* and *cinnamic acid.*



cinnamic acid

[2]

(c) The synthesis of 2–phenylethanol from bromobenzene is shown below.



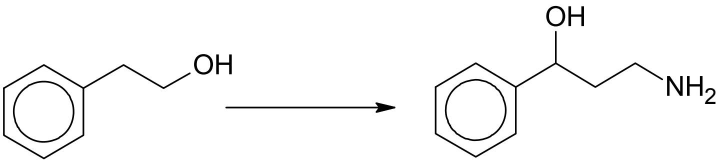
In the above synthesis, a Grignard reagent, C_6H_5MgBr is generated. Once generated, the Grignard reagent behaves as a nucleophile. The C_6H_5 in C_6H_5MgBr behaves like an anion, $C_6H_5^-$ and is a strong Lewis base. The Grignard reagent is useful for the formation of carbon–carbon bonds.

The reaction between the Grignard reagent, C_6H_5MgBr and the epoxide, C_2H_4O is a bimolecular reaction and the intermediate formed will subsequently react with water to form 2–phenylethanol.

From the information provided, outline the mechanism to account for this reaction. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons by curly arrows.

[2]

(d) Suggest a 4–step synthesis of 3–amino–1–phenylpropan–1–ol from 2–phenylethanol.



3-amino-1-phenylpropan-1-ol

The synthesis involves an intermediate compound that decolourises aqueous bromine in the dark. You should state the reagents and conditions needed for each step, and show clearly the structures of any intermediate compounds.

[3]

(e) A 0.460 g sample of gaseous methanoic acid, HCOOH was found to only occupy a volume of 173 cm^3 at a temperature of 160°C and a pressure of 1.04×10^5 Pa.

Using the ideal gas equation and the above information, determine the molar mass of this gaseous sample. Hence, draw a possible structure at this temperature.

[2]

[Total: 20]

END OF PAPER

Cover Page for P3 Q1 & 2

Name ________________________ **Class: 17S_______** **Reg Number: _____**

MERIDIAN JUNIOR COLLEGE
JC 2 Preliminary Examination
Higher 2

13 September 2018

INSTRUCTION TO CANDIDATES

Write your name, class and register number in the spaces provided at the top of this page.

Answer **all** questions in Section **A.**

Answer **only ONE** question in Section **B.**

Begin each question on a ***fresh page*** of writing paper.

Fasten your answers for Q1 & 2 behind this Cover Page.

You are advised to spend about **30 min each question.**

INFORMATION FOR CANDIDATES

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

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

Examiner's Use		
Paper 3	**Q1**	**/ 18**
	Q2	**/ 19**

Cover Page for P3 Q3 & 4 or 5

Name __________________________ **Class: 17S**_______ **Reg Number:** _____

MERIDIAN JUNIOR COLLEGE
JC 2 Preliminary Examination
Higher 2

13 September 2018

INSTRUCTION TO CANDIDATES

Write your name, class and register number in the spaces provided at the top of this page.

Answer **all** questions in Section **A.**

Answer **only ONE** question in Section **B. CIRCLE the question that you have attempted.**

Begin each question on a ***fresh page*** of writing paper.

Fasten your answers for Q 3, 4 & 5 behind this Cover Page.

You are advised to spend about **30 min each question.**

INFORMATION FOR CANDIDATES

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

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

Examiner's Use		
Paper 3	**Q3**	**/ 23**
	Q4	**/ 20**
	Q5	**/ 20**

Name Suggested Solutions Class: 17S______ Reg Number: _____

MERIDIAN JUNIOR COLLEGE
JC 2 Preliminary Examination
Higher 2

Chemistry **9729/03**

Paper 3 Free Response **13 September 2018**

2 hour

Additional Materials: *Data Booklet*
Writing Paper

INSTRUCTIONS TO CANDIDATES

Write your name, class and register number in the spaces provided at the top of this page.

Answer all questions in Section A and one question from Section B.

Begin each question on a fresh page of writing paper.

Fasten the writing papers behind the given **Cover Page for Questions 1 & 2** and **Cover Page for Questions 3 & 4 or 5** respectively.

Hand in Questions **1 & 2** and **3 & 4 or 5** **separately**.

You are advised to spend about 30 minutes per question only.

INFORMATION FOR CANDIDATES

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

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

This document consists of **15** printed pages (including this cover page).

Section A

Answer **all** questions in this section.

1(a) Explain the variation in melting point of the oxides of the elements in Period 3 (sodium to sulfur), using oxides of three different structure as examples.

Indicate clearly the type of structure and bonding present in the examples you have selected.

[3]

High melting point for NaO_2, MgO_2 (or Al_2O_3)
– giant ionic lattice structure with strong electrostatic forces of attraction between oppositely charged ions

High melting point (intermediate between that of NaO_2 and MgO) for SiO_2
– giant (3D) molecular structure with strong covalent bonds between (Si and O) atoms

Low melting point (lower than that of NaO_2) for P_4O_{10}, SO_3
– simple molecular structure with weak instantaneous dipole – induced dipole attractive forces between molecules.

(b) With the aid of the *Data Booklet*, explain the difference in observed melting points of NaC*l* (801 °C) and MgO (2852 °C)

[2]

$$\text{Lattice energy} \propto \frac{q_+ \times q_-}{r_+ + r_-}$$

Charge of cation, q_+: $Na^+ < Mg^{2+}$
Radius of cation, r_+: Na^+ (0.095 nm) > Mg^{2+} (0.065 nm)

Charge of anion, q_-: $Cl^- < O^{2-}$
Radius of anion, r_-: Cl^- (0.181 nm) > O^{2-} (0.140 nm)

Lattice energy of NaC*l* is less exothermic than that of MgO ⇒ Melting point: NaC*l* < MgO

(c) Instead of melting like chlorides or oxides, Group 2 nitrates decompose upon heating.

(i) Write an equation, including state symbols, for the thermal decomposition of magnesium nitrate, $Mg(NO_3)_2$.

[1]

$$Mg(NO_3)_2\,(s) \longrightarrow MgO\,(s) + 2NO_2\,(g) + \frac{1}{2}O_2\,(g)$$

(ii) Predict, with reasoning, whether barium nitrate, $Ba(NO_3)_2$, is more or less thermally stable compared with $Mg(NO_3)_2$.

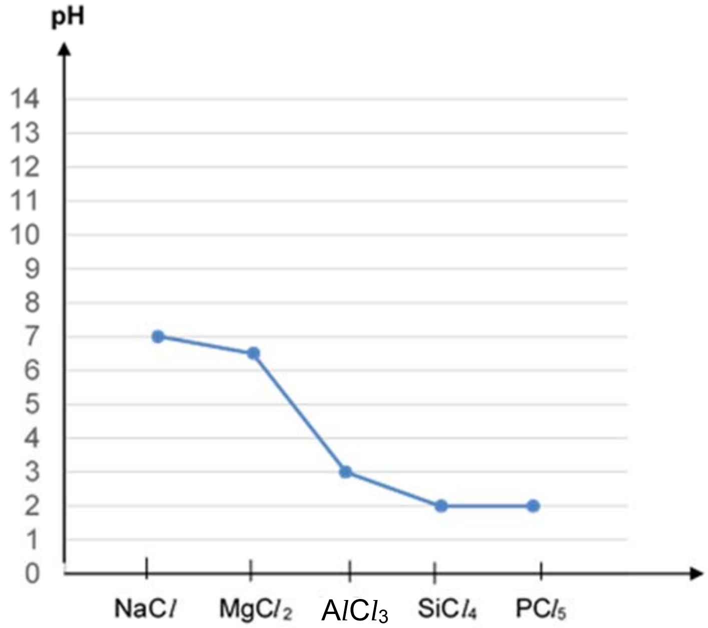
[2]

$Ba(NO_3)_2$ is more thermally stable compared with $Mg(NO_3)_2$.
Ba^{2+} is less polarising due to lower charge density than Mg^{2+}, hence it is less able to polarise electron cloud of NO_3^- to a significant extent.

(d) Chlorides of Period 3 elements dissolve in water to form solutions of differing pH values.

(i) Sketch a graph to illustrate how the pH of the resultant solutions vary across the period (from sodium to phosphorus).

[1]



(ii) Write an equation to illustrate the reaction of PCl_5 with water.

[1]

(iii) Lithium is a Group 1 element. Its chloride, LiC*l* however behaves similarly to that of a chloride of a Group 2 element when dissolved in water.

Suggest a reason why this would be so.

[1]

Similar to $MgCl_2$ as the metal cations have similar charge densities (hence diagonal relationship)

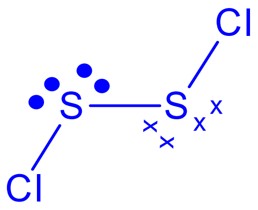
(e) Disulfur dichloride, S_2Cl_2 is one of three chlorides of sulfur. It is a liquid at room temperature with a pungent odour. It has a structure in which the central sulfur atoms are bonded by a single covalent bond.

Draw clear diagrams of two possible molecular arrangements of S_2Cl_2, showing clearly the electron pairs around the sulfur atoms. Apply the principles of the VSEPR theory to suggest which arrangement would result in a molecule which could be more stable.

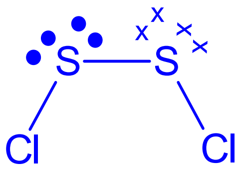
[3]

To minimise repulsion and maximise stability, the 4 electron pairs are directed to corners of a regular tetrahedron. Since lone pair – lone pair repulsion > lone pair – bond pair repulsion > bond pair – bond pair repulsion, the shape is bent about each S atom.

Arrangement 1 is more stable over arrangement 2 as the lone pairs of electrons are pointed away from each other (in opposite directions), which minimises the repulsion.



Arrangement 1



Arrangement 2

(f) CCl_4, an important commercial solvent is prepared by the reaction of Cl_2 gas with a sulfur–containing carbon compound. S_2Cl_2 is produced as a by–product. The reaction for the production is shown below.

$$CS_2\,(l) + 3Cl_2\,(g) \longrightarrow CCl_4\,(l) + S_2Cl_2\,(l)$$

(i) Using appropriate data in **Table 1.2** and the energy cycle provided, determine the enthalpy change, $\Delta H^\ominus_{rxn}$ for the above reaction.

Table 1.2

	$\Delta H^\ominus$ / kJ mol^{-1}
Standard enthalpy change of formation of $CCl_4\,(l)$	–135.4
Standard enthalpy change of combustion of C (s)	–393.5
Standard enthalpy change of formation of $S_2Cl_2\,(l)$	–58.2
Standard enthalpy change of formation of SO_2 (g)	–296.8
$CS_2\,(l) + 3O_2\,(g) \longrightarrow CO_2\,(g) + 2SO_2\,(g)$	–1077.0
$SO_2\,(g) + Cl_2\,(g) \longrightarrow SO_2Cl_2\,(l)$	+97.3

[2]

$$\begin{tikzcd}
CS_2\,(l) + 3Cl_2\,(g) \arrow[rr, "\Delta H^\ominus_{rxn}"] \arrow[d, "{+\,3O_2\,(g)}"', "\Delta H^\ominus_1"] & & CCl_4\,(l) + S_2Cl_2\,(l) \arrow[dl, "{-\Delta H^\ominus_f\,(CCl_4\,(l)) - \Delta H^\ominus_f\,(S_2Cl_2\,(l))}"] \\
CO_2\,(g) + 2SO_2\,(g) + 3\,Cl_2\,(g) & & \\
& 2S\,(s) + 3Cl_2\,(g) + C\,(s) \arrow[ul, "{+\,3O_2\,(g)}", "{\Delta H^\ominus_c\,(C(s)) + 2\Delta H^\ominus_f\,(SO_2(g))}"'] &
\end{tikzcd}$$

By Hess' Law,

$$\Delta H^\ominus_{rxn} = \Delta H^\ominus_1 - \Delta H^\ominus_c\,(C(s)) - 2\Delta H^\ominus_f\,(SO_2(g)) \;-\Delta H^\ominus_f\,(CCl_4\,(l)) - \Delta H^\ominus_f\,(S_2Cl_2\,(l))$$

$$\Delta H^\ominus_{rxn} = (-1077) - (-393.5) - 2(-296.8) + (-135.4) + (-58.2)$$

$$= -283.5 \text{ kJ mol}^{-1}$$

(ii) CCl_4 could be reacted with limited oxygen according to the following reaction.

$$CCl_4\,(l) + O_2\,(g) \longrightarrow COCl_2\,(g) + Cl_2O\,(g) \qquad \Delta H^\ominus = -5.2 \text{ kJ mol}^{-1}$$

Predict the sign of entropy change, $\Delta S^\ominus$ for this reaction and explain whether the reaction would be spontaneous at all temperatures.

[2]

ΔS is positive as there is to an increase in number of moles of gas (from 1 to 2), hence an increase in the entropy / disorder of the system.

$\Delta G = \Delta H - T\Delta S$

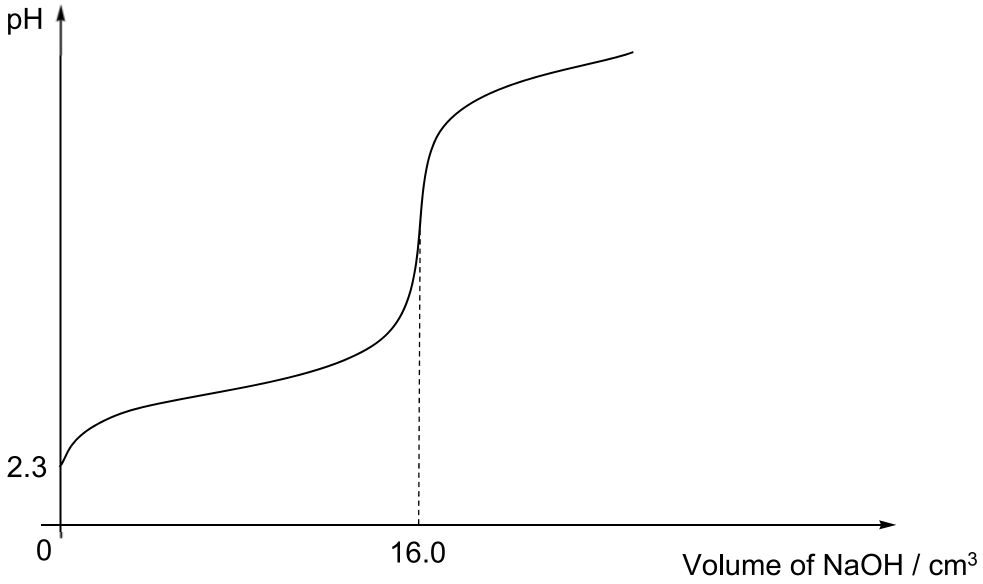
When $\Delta S = +ve$, then $-T\Delta S = -ve$, ➔ Both ΔH and $-T\Delta S$ are negative

$\Delta G < 0$ (–ve) ⇒ spontaneous for all temperature.

[Total: 18]

2 In analytical chemistry, both quantitative and qualitative information about chemical reactions are established through the use of various chemical methods.

(a) Glycolic acid, $HOCH_2COOH$ is a weak acid used in many cosmetic skin–care products. When a student titrated 25.0 cm^3 of a glycolic acid against 0.250 mol dm^{-3} NaOH, the following titration curve was obtained.



(i) Suggest an appropriate indicator for the titration, giving a reason for your choice.

[1]

Phenolphthalein
The pH transition range of the indicator lies within the rapid pH change over the equivalence point

(ii) Use the above titration data to calculate the K_a value of glycolic acid.

[2]

$HA \equiv OH^-$
Amount of NaOH = Amount of HA in 25.0 cm^3 of solution

$$= \frac{16.0}{1000} \times 0.250 = 4.00 \times 10^{-3} \text{ mol}$$

$$[HA] = \frac{4.00\times10^{-3}}{\frac{25.0}{1000}} = 0.160 \text{ mol dm}^{-3}$$

$$[H^+] = 10^{-2.3} = 5.01 \times 10^{-3} \text{ mol dm}^{-3}$$

$$K_a = \frac{\left(5.01\times10^{-3}\right)^2}{0.160} = 1.57 \times 10^{-4} \text{ mol dm}^{-3}$$

(b) The pH level of skin–care products need to be regulated to prevent degradation of the active ingredients. A buffer solution containing ethanoic acid and its sodium salt, sodium ethanoate can be added to control the pH. The pK_a of ethanoic acid is 4.76.

(i) With the aid of a balanced equation, briefly explain how a solution of ethanoic acid and sodium ethanoate can maintain a fairly constant pH when a small amount of acid is added to this solution.

[1]

When a small amount of H^+ is added, $CH_3COO^- + H^+ \longrightarrow CH_3COOH$

H^+ added is removed as CH_3COOH. $[H^+]$ slightly changed and pH remains fairly constant

(ii) Determine the resultant pH of a 100.0 cm^3 solution containing 0.10 mol dm^{-3} of ethanoic acid and 0.10 mol dm^{-3} of sodium ethanoate when 5.0 x 10^{-4} mol of H_2SO_4 is added to this solution.

[2]

$H_2SO_4 \equiv 2H^+$
Amount of H^+ added = 1.0 x 10^{-3} mol

$[H^+]$ = 1.0 x 10^{-2} mol dm^{-3}

$[CH_3COOH]_{new}$ = 0.10 + 0.010 = 0.110 mol dm^{-3}
$[CH_3COO^-]_{new}$ = 0.10 – 0.010 = 0.09000 mol dm^{-3}

$$pH = pK_a + \log_{10}\frac{[CH_3COO^-]_{new}}{[CH_3COOH]_{new}} = 4.76 + \log_{10}\left(\frac{0.0900}{0.110}\right) = 4.67 \text{ (2 d.p.)}$$

(c) Another student performed a series of thermometric experiments to determine the enthalpy change of neutralisation involving several acids and sodium hydroxide. Her experimental results are summarised in the table below.

Acid	**Enthalpy change of neutralisation, $\Delta H^\ominus_n$ / kJ mol^{-1}**
hydrochloric acid, HC*l*	– 57.2
hydrofluoric acid, HF	– 68.6
glycolic acid, $HOCH_2COOH$	– 53.2

(i) Explain why the neutralisation reaction involving glycolic acid is less exothermic than that involving hydrochloric acid.

[1]

Glycolic acid is a weak acid and is only slightly dissociated in aqueous solution. Some of the energy evolved from the neutralisation process is used to further dissociate the weak acid completely.

Deducing the strength of acids solely from the enthalpy change of neutralisation may not be appropriate as there are exceptions. For instance, the neutralisation reaction between HF, a weak acid and NaOH is significantly more exothermic than that of HC*l* and NaOH.

(ii) Suggest why the neutralisation reaction between HF and NaOH is unexpectedly more exothermic.

[1]

On dissociation, the small F^- ions can form strong ion–dipole interactions with water molecules that releases high amount of heat.

OR

The enthalpy change of hydration of F^- ions is very exothermic.

(d) Argentometric titration can be used to determine the amount of sodium chloride present in skin–care products by titrating the sample against silver nitrate, $AgNO_3$. A suitable indicator is one that forms a precipitate of a different colour after all the chloride ions have reacted.

The following are relevant K_{sp} values of some sparingly soluble silver compounds.

	K_{sp}
$AgCl$	1.8×10^{-10} mol^2 dm^{-6}
AgI	7.7×10^{-17} mol^2 dm^{-6}
Ag_3PO_4	1.3×10^{-20} mol^4 dm^{-12}

(i) Write an expression for the solubility product, K_{sp} of Ag_3PO_4.

[1]

K_{sp} of $Ag_3PO_4 = [Ag^+]^3\,[PO_4^{3-}]$

(ii) Given that Ag_3PO_4 precipitate is yellow in appearance, by means of suitable calculations, suggest whether potassium phosphate, K_3PO_4 can be used as an indicator in the argentometric titration for the determination of chloride content.

[2]

Let the solubility of AgC*l* be *s*.

$AgCl\,(s) \rightleftharpoons Ag^+\,(aq) + Cl^-\,(aq)$

$K_{sp}\,(AgCl) = [Ag^+][Cl^-] = s^2$

$$\text{Solubility of AgCl} = [Ag^+] = \sqrt{1.8\times10^{-10}} = 1.34 \times 10^{-5}\ \text{mol dm}^{-3}$$

Let the solubility of Ag_3PO_4 be *s*.

$Ag_3PO_4\,(s) \rightleftharpoons 3Ag^+\,(aq) + PO_4^{3-}\,(aq)$

$K_{sp}\,(Ag_3PO_4) = [Ag^+]^3\,[PO_4^-] = (3s)^3\,(s) = 27s^4$

$$\text{Solubility of } Ag_3PO_4 = \sqrt[4]{\frac{1.3\times10^{-20}}{27}} = 4.68 \times 10^{-6}\ \text{mol dm}^{-3}$$

Since solubility of Ag_3PO_4 is lower, it has the tendency to precipitate out first before most Cl^- has been precipitated therefore it is not suitable to be used as an indicator.

(iii) With the aid of appropriate equations, explain why silver chloride, Ag*Cl* is soluble in excess aqueous ammonia.

[3]

When aqueous ammonia is added, a soluble complex cation $[Ag(NH_3)_2]^+(aq)$ is formed, hence decreasing $[Ag^+(aq)]$.

$Ag^+(aq) + 2NH_3(aq) \longrightarrow [Ag(NH_3)_2]^+(aq)$ ——— (1)

By Le Chatelier's Principle, the equilibrium position in (2) shifts right to increase $[Ag^+(aq)]$ but Ag^+ will be used to form more $[Ag(NH_3)_2]^+$.

$AgCl\,(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ ——— (2)

Overall, $[Ag^+(aq)]$ decreases and ionic product of $[Ag^+][Cl^-]$ decreases to a value lower than its relatively higher K_{sp}. Hence white ppt of Ag*Cl* dissolves.

(iv) Hence, briefly explain why silver iodide, AgI, remains insoluble even in concentrated ammonia solution.

[1]

K_{sp} of AgI is relatively much lower than that of Ag*Cl*. AgI remains insoluble in concentrated NH_3 as its ionic product, $[Ag^+][I^-]$ which decreases will still be higher than its K_{sp} value.

(e) The distinctive reactions of solid halides with hot concentrated sulfuric acid also provide useful basis for further analysis.

These halides react with hot concentrated sulfuric acid to form white fumes of hydrogen halides.

$$Na\mathbf{X}\,(s) + H_2SO_4\,(l) \longrightarrow H\mathbf{X}\,(g) + NaHSO_4\,(s)$$

where **X** = C*l*, Br or I

However, only HBr and HI formed will further react with concentrated H_2SO_4. The main products for these reactions are recorded in the table below.

HC*l*	HBr	HI
no further reaction	red–brown gas	violet fumes
	acidic gas that decolourises acidified purple $KMnO_4$	pungent H_2S gas

(i) Suggest an identity for both the red–brown gas and the acidic gas formed when HBr further reacts with concentrated H_2SO_4.

[1]

Red–brown gas is Br_2 and acidic gas is SO_2.

(ii) Hence, write an equation for the reaction between HBr and concentrated H_2SO_4.

[1]

$2HBr\,(g) + H_2SO_4\,(l) \longrightarrow Br_2\,(g) + SO_2\,(g) + 2H_2O\,(l)$

(iii) By considering the reactions of HC*l* and HI with concentrated sulfuric acid and the change in oxidation number of sulfur, explain which halide ion is a stronger reducing agent.

[2]

Cl^- is a weaker reducing agent OR I^- is a stronger reducing agent.

Cl^- does not react with H_2SO_4 so there is no change in oxidation number of sulfur.

I^- is able to reduce H_2SO_4 to H_2S. There is a decrease in the oxidation number of S from +6 in H_2SO_4 to –2 in H_2S.

[Total: 19]

3 Transition elements show typical properties that distinguish them from s–block elements such as calcium. The following table gives data about some physical properties of the elements calcium, iron, copper and cadmium.

property	**calcium**	**iron**	**copper**	**cadmium**
relative atomic mass	40.1	55.8	63.5	112.4
atomic radius (metallic) / nm	0.197	0.126	0.128	0.151
ionic radius (2+) / nm	0.099	0.076	0.069	0.097
melting point / °C	839	1535	1085	322
density / g cm^{-3}	1.54	7.86	8.92	8.65

(a) **(i)** Explain why the atomic radii of iron and copper are similar to each other.

[2]

- Nuclear charge increases from Fe to Cu. The electrons in Cu are added to the inner 3d orbitals and provide more shielding for the 4s electrons.

- Increase in nuclear charge slightly outweighs the increase in shielding effect. Effective nuclear charge increases only slightly.

- Hence, atomic radius of Fe and Cu are similar.

(ii) The melting point of iron is significantly higher than that of calcium and cadmium. Explain this using relevant data from the table and in terms of the structure and bonding in each metal.

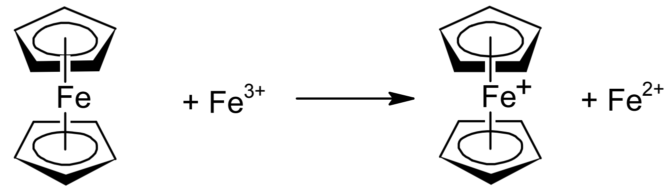
[3]

Fe, Cd and Ca have giant metallic structure. Both 3d and 4s electrons of Fe and Cd are involved in the delocalized in metallic bonding while only the 4s electrons for Ca is involved.

The ionic radius of Fe^{2+} is also smaller than that of Ca^{2+} and Cd^{2+} resulting in higher charge density. This results in stronger electrostatic forces of attraction between the Fe^{2+} cations and sea of delocalised electrons.

Hence, Fe has a higher melting point than Ca and Cd.

(b) Ferrocene, $Fe(C_5H_5)_2$, is an orange organometallic solid. In this complex, $C_5H_5^-$ is the ligand and it donates π electrons from the ring to the vacant 3*d* orbitals of Fe. A chemist suggested that ferrocene would react with aqueous iron(III) ions to form iron(II) ions as shown below.



ferrocene

(i) The chemist found the reduction potential ferrocene, $E^{\ominus}_{Fe(C_5H_5)_2^+ / Fe(C_5H_5)_2}$ to be +0.63V. Predict if the reaction between ferrocene and iron(III) ions will occur. Calculate $\Delta G^{\ominus}$ for this reaction.

(ii) **[2]**

$Fe(C_5H_5)_2^+ + e \rightleftharpoons Fe(C_5H_5)_2$ $E^{\ominus} = +0.63$ V (Oxidation)

$Fe^{3+} + e \rightleftharpoons Fe^{2+}$ $E^{\ominus} = +0.77$ V (Reduction)

Overall: $Fe^{3+} + Fe(C_5H_5)_2 \longrightarrow Fe^{2+} + Fe(C_5H_5)_2^+$

$E^{\ominus}_{cell} = E^{\ominus}_{red} - E^{\ominus}_{oxid}$
$= 0.77 - 0.63$
$= +0.14$ V

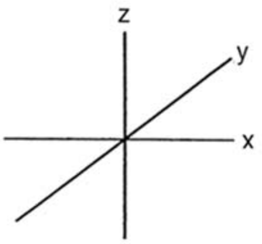
Since $E^{\ominus}_{cell} > 0 \Rightarrow$ Reaction is spontaneous

$\Delta G^{\theta} = -nFE^{\theta}_{cell}$
$= -(1 \times 96500 \times 0.14) = -13.51$ kJ mol^{-1}

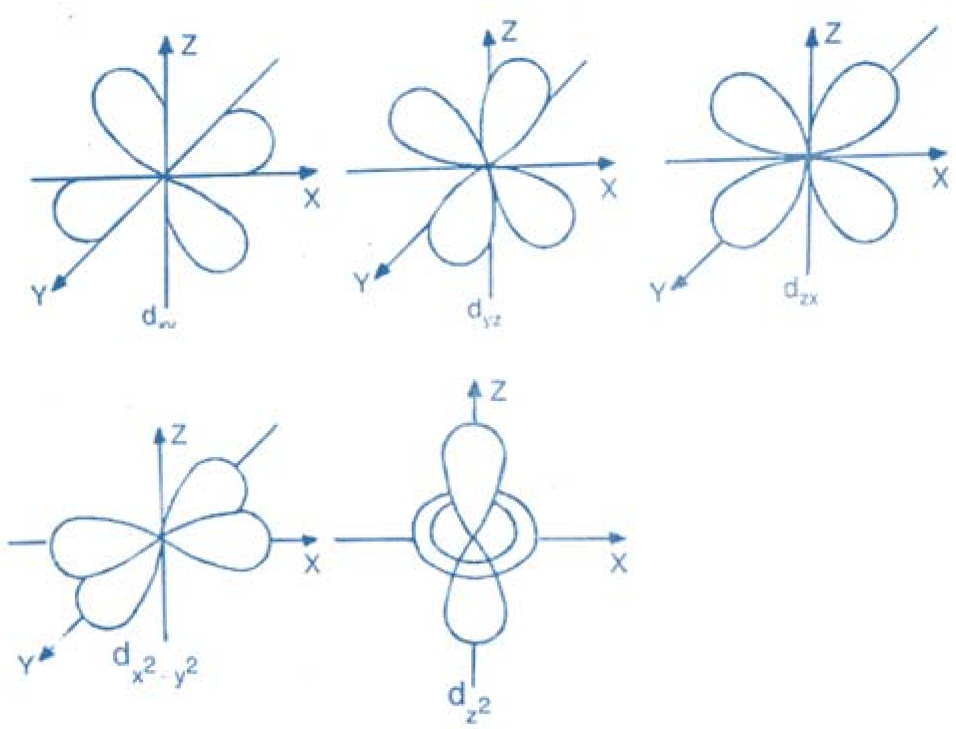
(iii) Iron(II) ion forms octahedral complexes, the orbitals are split into two energy levels. Using the Cartesian axes shown below, draw separate labelled diagrams of

1. one of the *d* orbitals at the **lower** energy level in an octahedral complex,

2. one of the *d* orbitals at the **higher** energy level in an octahedral complex.



[2]



(iii) Using your diagrams in **(b)(ii)**, explain why the *d* subshell of a transition metal ion is split into two energy levels in an octahedral complex.

- The $d_{x^2-y^2}$ orbital and the d_{z^2} orbitals have their lobes pointing at the ligands along the x and y axes, and z axis respectively, hence they experience greater repulsion from the ligands. On the other hand, the d_{xy}, d_{xz} and d_{yz} orbitals experienced less repulsion as their lobes are in between the coordinate axes.

- As a result, the five d orbitals are split into 2 energy levels, with the $d_{x^2-y^2}$ and d_{z^2} orbitals having the higher energy level and the d_{xy}, d_{xz} and d_{yz} orbitals having the lower energy level.

Most transition element complexes are coloured.

(iv) Explain why ferrocene is orange in colour.

[2]

Fe^{2+} ion has partially filled *d* orbitals. In the presence of $C_2H_5^-$ ligands, the *d* orbitals are split into two groups with an energy gap, ΔE. This effect is known as *d* orbital splitting.

During the d–d transition, the *d* electrons from the lower energy d orbitals absorb a blue wavelength of light from the visible spectrum and gets promoted to a *higher* energy *d* orbital. The orange colour observed in ferrocene is complementary of the blue colour absorbed.

(v) Aqueous Fe^{2+} ion is green in colour, suggest and explain if water causes a larger or smaller split between the two groups of 3*d* orbitals as compared to $C_5H_5^-$.

[2]

With H_2O ligands, the green $Fe^{2+}(aq)$ ion absorbed red which has a longer wavelength and lower ΔE than the blue absorbed when $C_5H_5^-$ is the ligand.

Hence, H_2O ligands causes a smaller splitting of the 3*d* orbitals of Fe^{2+}.

(vi) The reaction between $S_2O_8^{2-}$ and I^- is slow in the absence of catalyst. $Fe^{2+}(aq)$ can be used as catalyst for the reaction between $S_2O_8^{2-}$ and I^-.

Explain with the aid of equations how it works.

[3]

With Fe^{2+} (aq) catalyst:
Step 1: Fe^{2+} intermediate reacts with $S_2O_8^{2-}$

Equation 1 : $2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \longrightarrow 2SO_4^{2-}(aq) + 2Fe^{3+}(aq)$

$E^{\ominus}_{cell} = 2.01 - 0.77 = +1.24\ V > 0 \Rightarrow$ reaction is spontaneous

Step 2: Fe^{3+} reacts with I^-.

Equation 2 : $2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2\,Fe^{2+}(aq) + I_2(aq)$

$E^{\ominus}_{cell} = 0.77 - 0.54 = +0.23\ V > 0 \Rightarrow$ reaction is spontaneous

Overall equation : $S_2O_8^{2-}(aq) + 2I^-(aq) \longrightarrow 2SO_4^{2-}(aq) + I_2(aq)$

Both steps are spontaneous since oppositely charged ions are involved and attract each other. Activation energy is lowered and thus reaction is faster (or kinetically feasible).

(c) Cadmium ions form complexes with primary amines and with 1,2–diaminoethane.

(1) $Cd(H_2O)_6^{2+}(aq) + 4CH_3NH_2(aq) \rightleftharpoons [Cd(CH_3NH_2)_4]^{2+}(aq) + 6H_2O(l)$

$K_{stab} = 3.6 \times 10^6$

(2) $Cd(H_2O)_6^{2+}(aq) + 2H_2NCH_2CH_2NH_2(aq) \rightleftharpoons [Cd(H_2NCH_2CH_2NH_2)_2]^{2+}(aq) + 6H_2O(l)$

$K_{stab} = 4.2 \times 10^{10}$

K_{stab} is an equilibrium constant that accounts for the formation of a complex. It is a measure of the strength of the interactions between the ligands and the metal centre that come together to form the complex.

The values for $\Delta H^\ominus$ and $\Delta G^\ominus$ for equilibria **(1)** and **(2)**, and the value of $\Delta S^\ominus$ for equilibrium **(1)**, are given in the table below. All values are determined at a temperature of 298 K.

Equilibrium	**$\Delta H^\ominus$ / kJ mol^{-1}**	**$\Delta G^\ominus$ / kJ mol^{-1}**	**$\Delta S^\ominus$ / J mol^{-1} K^{-1}**
(1)	– 57.3	– 37.4	– 66.8
(2)	– 56.5	– 60.7	**–**

(i) Suggest a reason why the $\Delta H^\ominus$ values for the two equilibria are very similar.

[1]

Each complex is formed by making four N–Cd bonds and breaking six O–Cd bonds
OR
same types of / similar bonds forming / breaking
OR
same number of bonds forming / breaking

(ii) Calculate the standard entropy change of reaction, $\Delta S^\ominus$ in equilibrium **(2)**.

[2]

$\Delta S = (\Delta H - \Delta G) / T$

$= (60.7 - 56.5) \times 1000 / 298$

$= +14.1$ J mol^{-1} K^{-1}

(iii) Suggest a reason for the difference between the $\Delta S^\ominus$ you have calculated for equilibrium **(2)** and that for equilibrium **(1)** given in the table.

[1]

For equilibrium (1), 5 moles of reactants react to form 7 moles of products while equilibrium (2), 3 moles of reactants react to form 7 moles of products. Hence, there is more disorder in equilibrium (2) than equilibrium (1) and hence ΔS^θ for equilibrium (2) is more positive.

(iv) Which of the two complexes is more stable? Give a reason for your answer.

[1]

The $[Cd(H_2NCH_2CH_2NH_2)_2]^{2+}$ in equilibrium 2 is more stable because either K_{stab} is larger in magnitude or $\Delta G^{\ominus}$ is more negative.

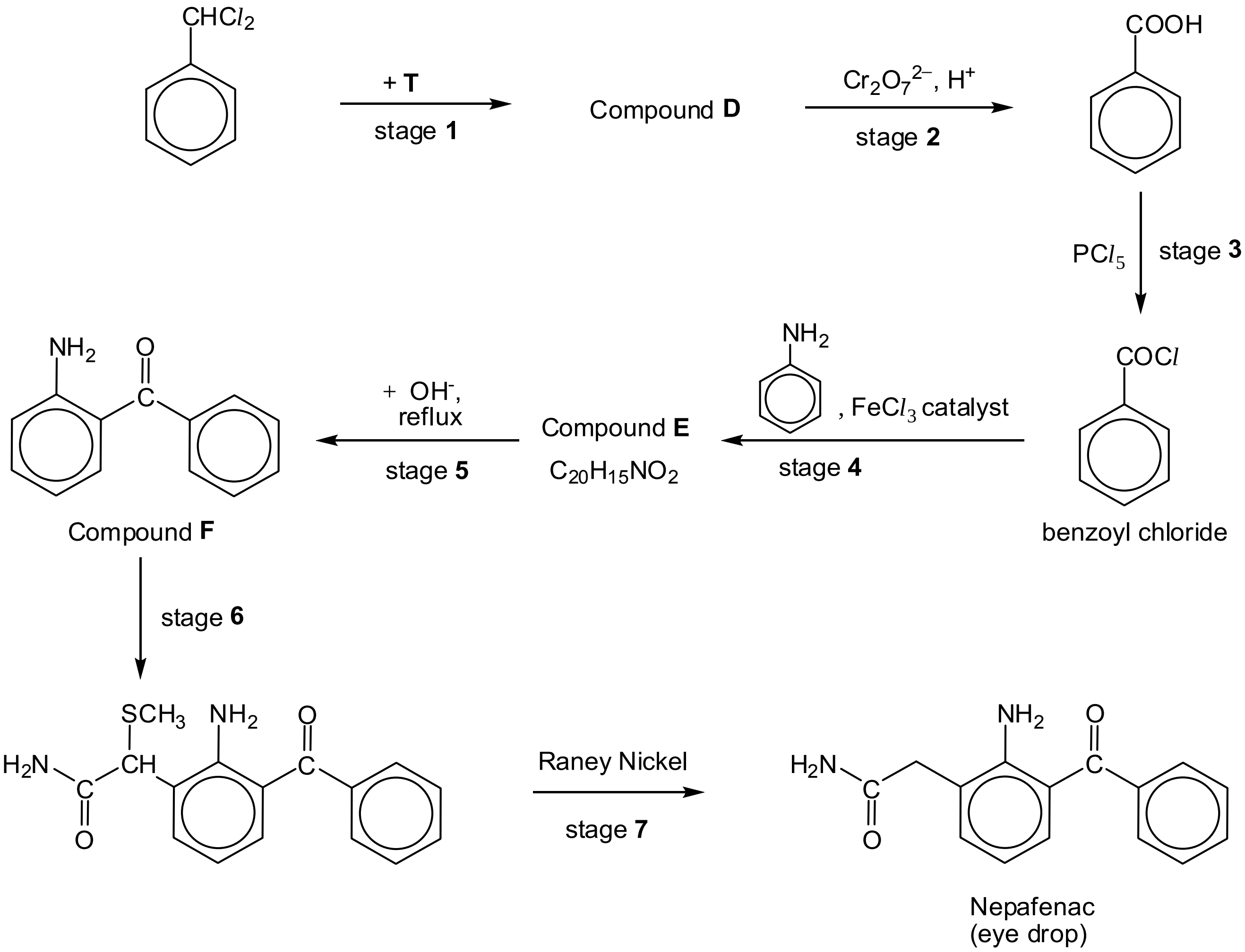
[Total: 23]

Section B

Answer **one** question from this section.

4(a) *Nepafenac* is a prescription eye drop that is used to treat pain and inflammation associated with eye surgery.

The following scheme shows a synthesis of *Nepafenac*.



(i) State the type of reaction occurring in stage **3** and stage **7**.

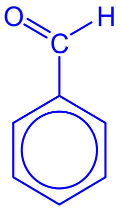
[2]

Stage 3: Nucleophilic acyl substitution

Stage 7: Reduction

(ii) Draw the structure of compound **D**. Suggest the reagent and conditions required in stage **1**.

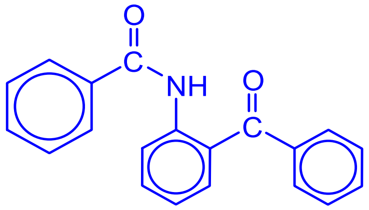
[2]



NaOH (aq), heat

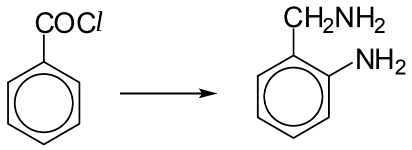
(iii) In stage **4**, two reactions are involved. Draw the structure of compound **E** and state the reactions that occurred.

[2]



Electrophilic substitution and Condensation / Nucleophilic acyl substitution

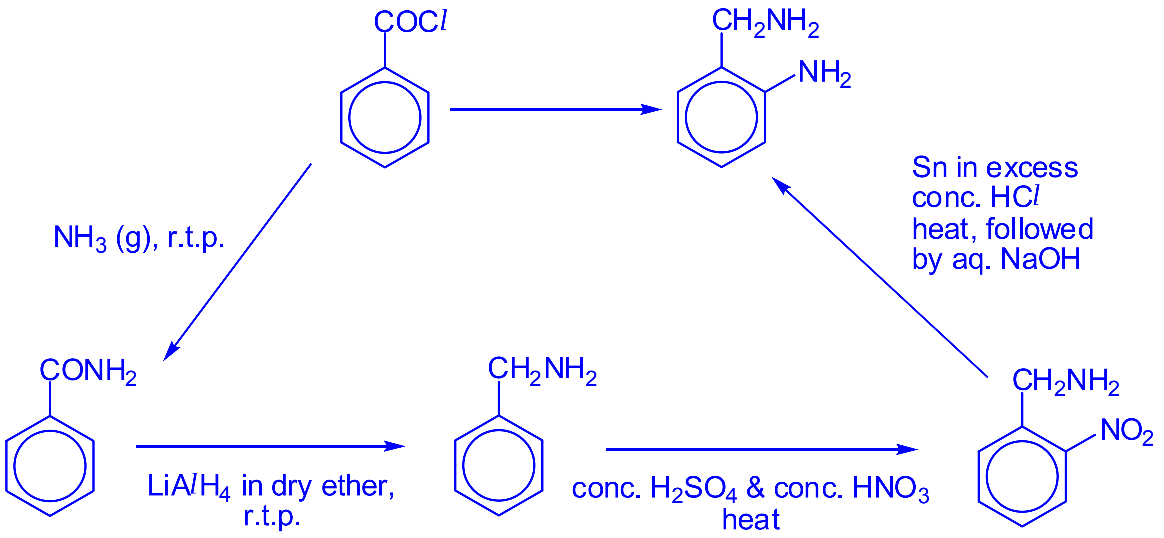
(iv) Benzoyl chloride can be converted into 2–aminobenzylamine, an important starting material in the synthesis of quinazoline, a source of useful pharmacophores for new drug development.



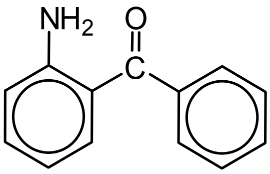
benzoyl chloride 2-aminobenzylamine

Suggest a 4–step synthesis of 2–aminobenzylamine from benzoyl chloride. You should state the reagents and conditions needed for each step, and show clearly the structures of any intermediate compounds.

[4]



(v) A student made a statement regarding a reaction with compound **F**: *"Cyanide, CN^-, is acting as a **Bronsted–Lowry base** to attack the carbonyl group of compound **F** to form a cyanohydrin."*



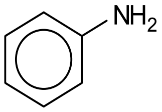
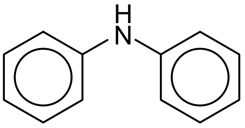
Compound **F**

Based on your understanding of a *Bronsted–Lowry* base, explain why the student's statement is wrong.

[1]

A *Bronsted–Lowry* base is a proton acceptor. In this reaction, the cyanide is behaving as a Lewis base that act as an electron–pair donor.

(vi) Data about phenylamine and diphenylamine are given in the table below.

Compound	 phenylamine	 diphenylamine
pK_b value	9.39	13.21

Give **two** reasons, why pK_b of phenylamine is lower than that of diphenylamine.

[2]

Phenylamine is a stronger base than diphenylamine. There is greater delocalisation of lone pair of electrons on N atom into the two benzene ring of diphenylamine as compare to phenylamine.

There is also greater steric hindrance of the 2 R group of diphenylamine.
The lone pair on N atom of diphenylamine is less available to accept a proton.

(b) Compound **J**, $C_{10}H_8O_3$, does not decolourise bromine water nor give effervescence with magnesium strip. **J** gives a silver mirror with Tollens' reagent but does not give a precipitate with hot alkaline Cu^{2+} solution.

On prolonged heating with acidified $KMnO_4$, **J** gives benzene–1,2–3–tricarboxylic acid as the only organic product. When heated with dilute H_2SO_4, **J** forms compound **K**, $C_{10}H_{10}O_4$. **K** gives a yellow precipitate with alkaline aqueous iodine.

J reacts with $LiAlH_4$ to form compound **L** (with an internal plane of symmetry), $C_{10}H_{14}O_3$. However, **J** forms compound **M**, $C_{10}H_{10}O_3$ with $NaBH_4$.

All compounds are optically active but only **K** reacts with sodium carbonate.

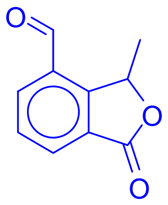
Suggest the structure for **J**, **K**, **L** and **M** and explain the reactions described.

[7]

- J has comparable number of C and H atoms and no. of carbon atoms > 6 ➔ J contains a benzene ring.
- J does not undergo electrophilic substitution (or electrophilic addition) with aqueous bromine. J *does not contain* phenol (or alkene group).
- J does not undergo acid metal displacement with Mg. J does not contain alcohol/phenol/carboxylic acid group.
- J undergoes oxidation with Tollens' reagent but does not undergoes oxidation with Fehling's reagent. ➔ J contains an aromatic aldehyde.
- J undergoes oxidation with hot acidified $KMnO_4$ to give benzene–1,2,3–tricarboxylic acid as the only organic product. Substituents the on benzene ring are on 1, 2 and 3 position.
- When heated with dilute H_2SO_4, J undergoes acidic hydrolysis to form K. Since only one compound is formed / no decrease in no. of carbon atoms.
    - J contains cyclic ester.
    - K contains carboxylic acid and alcohol group.
- K undergoes oxidation with alkaline aqueous iodine. ➔ K contains $RCHOH(CH_3)$
- J undergoes reduction with $LiAlH_4$ to form compound L and 6 H atoms are added to L.
    - J contains aldehyde and cyclic ester.
    - L contains 3 alcohol groups
- J undergoes reduction with $NaBH_4$ to form compound L and only 2 H atoms are added to M.
    - J contains aldehyde and cyclic ester.
    - L contains 1 alcohol group
- K undergoes acid–base / neutralisation with sodium carbonate. ➔ K contains carboxylic acid group.

- All compound contains chiral carbon and does not an internal plane of symmetry.

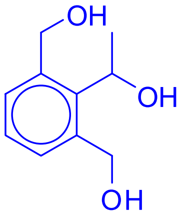
Compound **J:**



Chemical Formula: $C_{10}H_8O_3$

- No phenol, carboxylic acid, alcohol FGs
- Aromatic aldehyde
- Cyclic ester
- Forms benzene–1,2,3–tricarboxylic acid on strong oxidation
- Undergoes reduction to form **L** (gain of 6 H atoms)

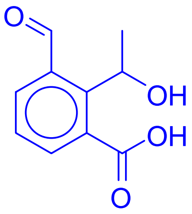
Compound **L**:



Chemical Formula: $C_{10}H_{14}O_3$

- Product of reduction of **J** (using $LiAlH_4$)
- Reduction of ester in **J** to alcohols in **L** (gain of 4 H)
- Reduction of aldehyde in **J** to primary alcohol in **L** (gain of 2H)
- Internal plane of symmetry

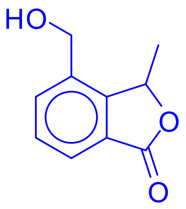
Compound **K**:



Chemical Formula: $C_{10}H_{10}O_4$

- Contains carboxylic acid
- Acidic hydrolysis product of **J** (ester linkage)
- Contains a $CH_3CH(OH)$–

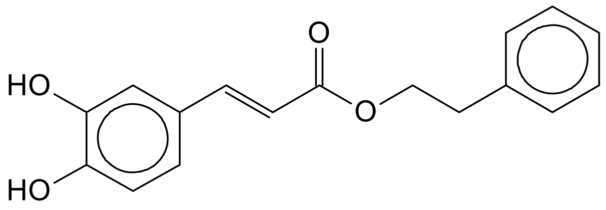
Compound **M**:



Chemical Formula: $C_{10}H_{10}O_3$

- Product of reduction of **J** (using $NaBH_4$)
- Reduction of aldehyde in **J** to primary alcohol in **L** (gain of 2 H)

5 Caffeic acid phenethyl ester (CAPE) is a natural occurring compound, found in propolis from honeybee hives. It is currently being studied for its anti–carcinogenic and anti–inflammatory properties. It is the ester of caffeic acid and 2–phenylethanol.



caffeic acid phenethyl ester (CAPE)

(a) Till date, there has been two well–established reaction schemes to synthesise CAPE. Study **Fig. 2.1** and **Fig 2.2** carefully and answer the questions that follow.

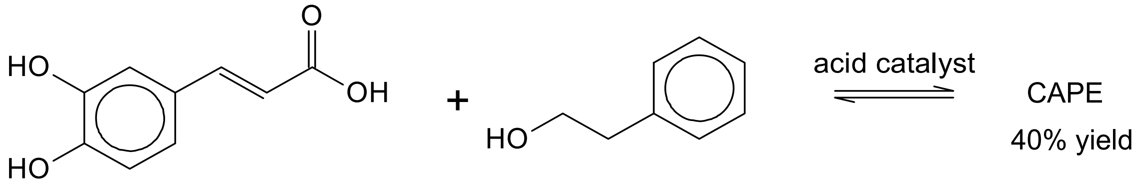


Fig. 2.1

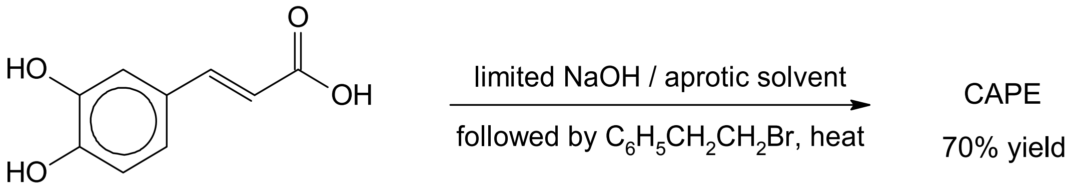


Fig. 2.2

(i) State the type of reaction occurring in each of the above synthesis method. **[2]**

Fig 2.1: Condensation / Nucleophilic Acyl Substitution
Fig 2.2: Nucleophilic substitution

(ii) To improve the yield of CAPE in **Fig 2.1**, a student suggested using the acyl chloride derivative of caffeic acid instead. Comment on the validity of his suggestion. **[2]**

Yes, his suggestion is valid. The reaction between an acyl chloride and an alcohol to form ester is irreversible, hence a higher yield is expected. There are two very electronegative atoms O and C*l* bonded to highly electron deficient carbonyl C atom in an acyl chloride. Hence, the carbonyl C atom in an acyl chloride is more susceptible to nucleophilic acyl substitution.

OR

No, his suggestion is invalid.An acyl chloride functional groups can undergo condensation / nucleophilic acyl substitution with the phenol functional groups to form other esters (side products), hence a lower yield is expected.

(iii) Explain why NaOH has to be added in limited amount rather than in large excess in **Fig 2.2**.

[1]

This is to prevent the halogenoalkane from undergoing nucleophilic substitution with NaOH to form the corresponding alcohols.

(iv) A protic solvent is one that has labile proton(s) and readily donates its proton(s). Conversely an aprotic solvent does not have any labile proton. Suggest why is it important to use an aprotic solvent in **Fig 2.2**.

[1]

This is to prevent the carboxylate anion from being protonated to form carboxylic acid, hence reducing its ability to function as the nucleophile for nucleophilic substitution with the halogenoalkane.

OR

This is to prevent the generation of phenoxide, another nucleophile which can undergo nucleophilic substitution with $C_6H_5CH_2CH_2Br$ to form the corresponding ether.

(v) The reported yield in **Fig. 2.2** is only 70%, as there are other by–products. Draw the skeletal formula of one possible by–product, assuming that caffeic acid reacts with $C_6H_5CH_2CH_2Br$ in a 1:1 ratio.

[1]

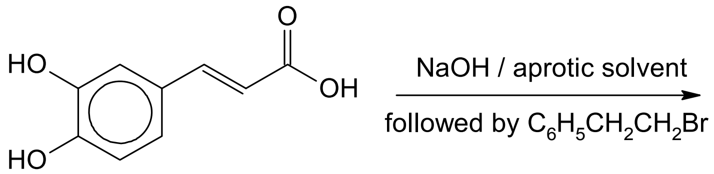
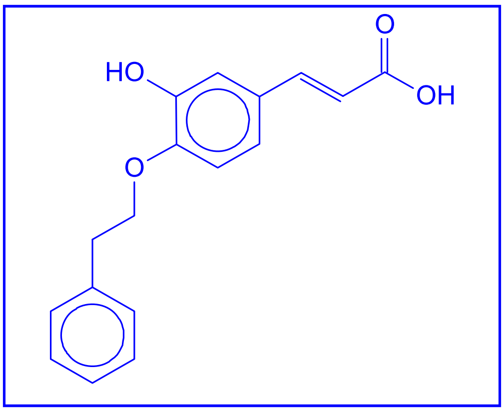
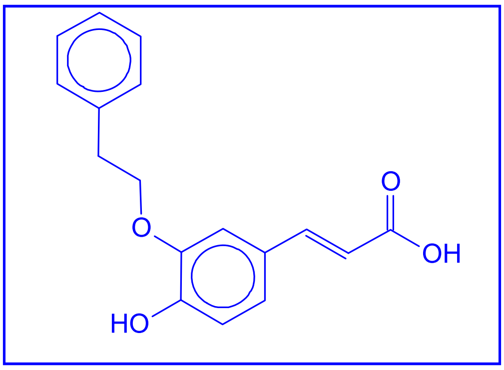


Fig. 2.2

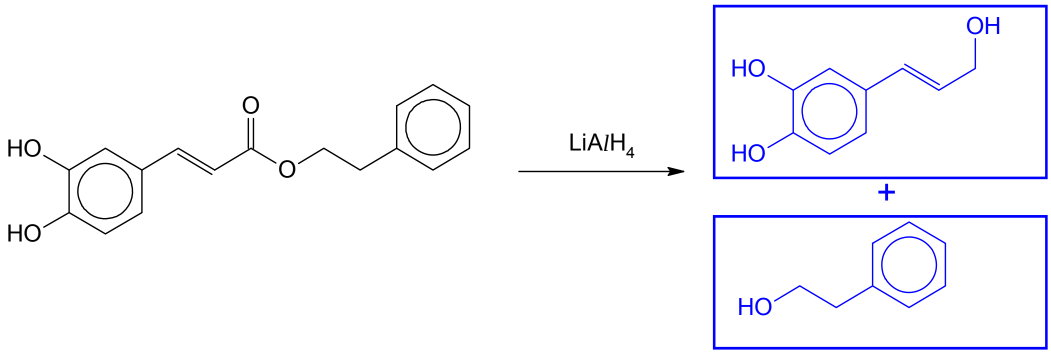


OR

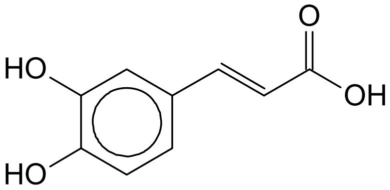


(vi) Draw the structure of the resultant product(s) when CAPE is reacted with $LiAlH_4$.

[1]



(b) The structure of *caffeic acid* is shown below.



caffeic acid

(i) *Caffeic acid* contains two organic functional groups with pK_a values lower than that of an alcohol. Identify these functional groups.

Compare and account for the relative pK_a values of these two organic groups.

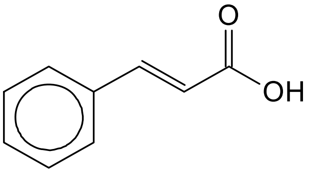
[3]

The carboxylic acid functional group has a lower pK_a value than the phenol functional group. Carboxylic acid is a stronger acid than phenol.

The phenoxide ion is stabilised by charge delocalisation, where the lone pair of electrons on the oxygen atom of the phenoxide ion is delocalised into the benzene ring. This reduces the intensity of the negative charge on the oxygen atom of the phenoxide ion, hence stabilising the phenoxide ion. Phenol is stronger acid than alcohol with a higher tendency to dissociate in aqueous medium to give H^+.

The carboxylate anion ($RCOO^-$) is resonance stabilised by the delocalisation of the negative charge over the C atom and both electronegative oxygen atoms in the carboxylate anion. Hence, the carboxylate anion is more stable than phenoxide ion. There is a greater tendency for the carboxylic acid to dissociate in aqueous medium to give H^+ as compared to phenol.

(ii) Suggest a chemical test that can be carried out to distinguish between a sample of *caffeic acid* and *cinnamic acid.*



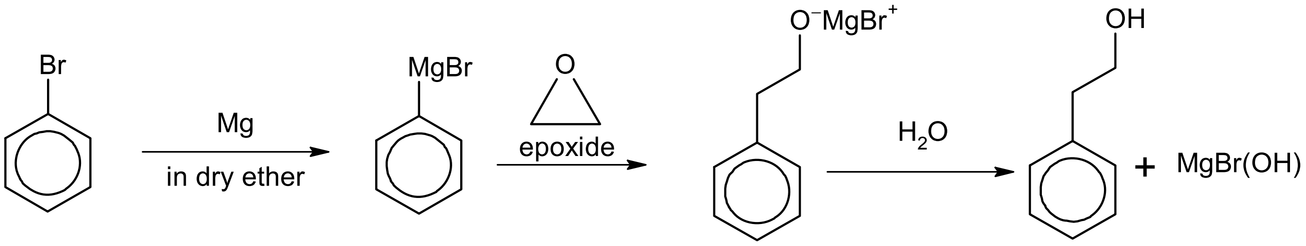
cinnamic acid

[2]

Test: Add aqueous neutral $FeCl_3$ to each compound separately at r.t.p.

Observations:
Caffeic acid: Violet complex / colouration will be formed.
Cinnamic acid: No violet complex will be formed.

(c) The synthesis of 2–phenylethanol from bromobenzene is shown below.

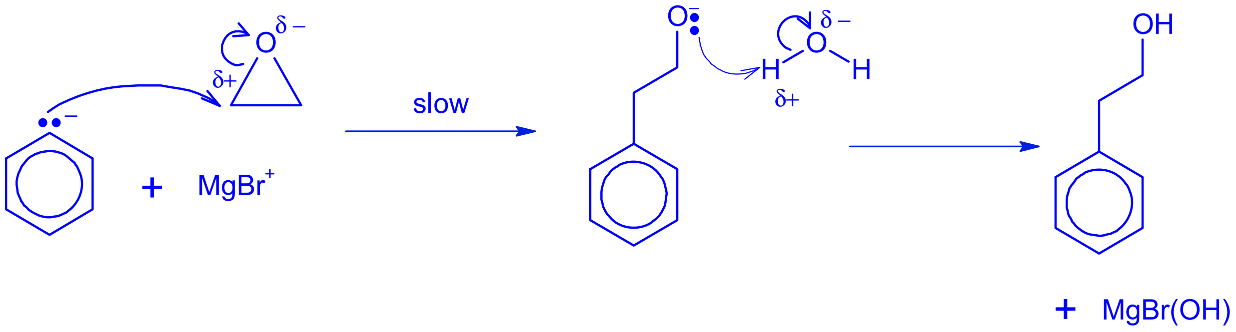


In the above synthesis, a Grignard reagent, C_6H_5MgBr is generated. Once generated, the Grignard reagent behaves as a nucleophile. The C_6H_5 in C_6H_5MgBr behaves like an anion, $C_6H_5^-$ and is a strong Lewis base. The Grignard reagent is useful for the formation of carbon–carbon bonds.

The reaction between the Grignard reagent, C_6H_5MgBr and the epoxide, C_2H_4O is a bimolecular reaction and the intermediate formed will subsequently react with water to form 2–phenylethanol.

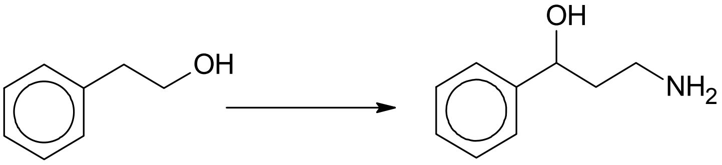
From the information provided, outline the mechanism to account for this reaction. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons by curly arrows.

[2]



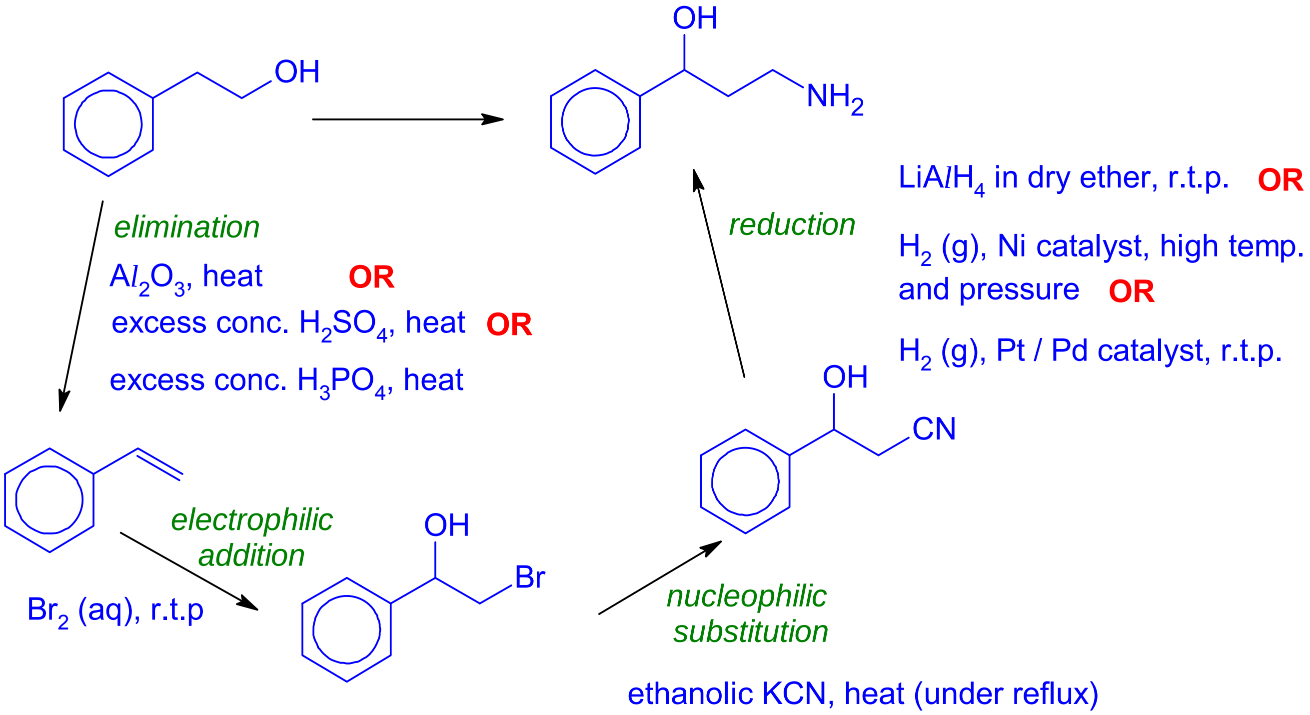
(d) Suggest a 4–step synthesis of 3–amino–1–phenylpropan–1–ol from 2–phenylethanol.

The synthesis involves an intermediate compound that decolourises aqueous bromine in the dark. You should state the reagents and conditions needed for each step, and show clearly the structures of any intermediate compounds.



3-amino-1-phenylpropan-1-ol

[3]



Al_2O_3, heat **OR**
excess conc. H_2SO_4, heat **OR**
excess conc. H_3PO_4, heat

Br_2 (aq), r.t.p

ethanolic KCN, heat (under reflux)

$LiAlH_4$ in dry ether, r.t.p. **OR**
H_2 (g), Ni catalyst, high temp. and pressure **OR**
H_2 (g), Pt / Pd catalyst, r.t.p.

(e) A 0.460 g sample of gaseous methanoic acid, HCOOH was found to only occupy a volume of 173 cm^3 at a temperature of 160°C and a pressure of 1.04×10^5 Pa.

Using the ideal gas equation and the above information, determine the molar mass of this gaseous sample. Hence, draw a possible structure at this temperature.

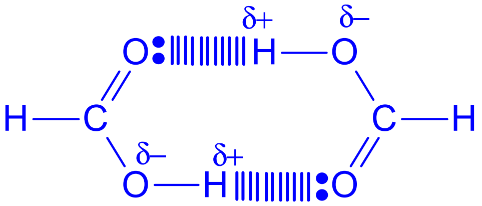
[2]

Applying $\mathbf{pV = nRT}$

$$\mathbf{pV} = \frac{m}{M}\mathbf{RT}$$

Molar mass, $\mathbf{M} = \frac{mRT}{pV} = \frac{0.460 \times 8.31 \times (160+273)}{(1.04 \times 10^5)(173 \times 10^{-6})} = 92.0\ g\ mol^{-1}$

The molar mass of 92.0 g mol^{-1} is **doubled** of the expected molar mass of HCOOH (46.0 g mol^{-1})



|||||||||| hydrogen bonds

[Total: 20]

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