JURONG JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION 2018

CANDIDATE NAME			
CLASS	**18S**	EXAM INDEX	

CHEMISTRY
9729/01

Higher 2

Paper 1 Multiple Choice

13 September 2018
1 hour

Candidates answer on separate paper.

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, glue or correction fluid.
Write your name, class and exam index number on the Answer Sheet in the spaces provided unless this has been done for you.

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

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.
The use of an approved scientific calculator is expected, where appropriate.

This document consists of **13** printed pages and **1** blank page.

1 The successive ionisation energies (IE) of two elements, **E** and **J**, are given below:

IE/ kJ mol^{-1}	1st	2nd	3rd	4th	5th	6th	7th	8th
E	550	1065	4138	5500	6910	8760	10230	11800
J	1140	2103	3470	4560	5760	8550	9940	18600

What is the likely formula of the compound that is formed when **E** reacts with **J**?

A EJ_2

B EJ

C E_2J

D E_2J_3

2 Carbon, silicon and germanium are Group 14 elements and they all exist in a structure similar to diamond.

The given table shows the bond lengths in these structures.

Element **X**	C	Si	Ge
Bond length **X–X** / nm	0.154	0.234	0.244

Which of the following explain why the bond length increases down the group?

1 Degree of orbital overlap decreases down the group.
2 Atomic radius increases down the group.
3 Nuclear charge increases down the group.
4 Electronegativity decreases down the group.

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

3 Which of the following **cannot** be explained by hydrogen bonding?

A the existence of the hydrogen-difluoride anion, HF_2^-
B the difference in volatility between pentan-1-ol and hexan-1-ol
C the difference in melting point between 2-nitrophenol and 4-nitrophenol
D the higher than expected relative molecular mass of ethanoic acid in benzene

4 The percentage by mass of magnesium in a mixture of magnesium chloride and magnesium nitrate was found to be 21.25%.

What is the mass of magnesium chloride present in 100 g of the mixture?

A 47 g **B** 51 g

C 53 g **D** 56 g

5 When 10 cm^3 of a gaseous hydrocarbon **X** was burned in 70 cm^3 of oxygen, the final gaseous mixture contained 30 cm^3 of carbon dioxide and 20 cm^3 of unreacted oxygen.

What is the formula of hydrocarbon **X**?

[All gaseous volumes are measured under identical conditions.]

A C_2H_6 **B** C_3H_6

C C_3H_8 **D** C_4H_{10}

6 An ion of metal **L** can be oxidised by potassium manganate(VII) in acid solution to form **L**O_3^-. In an experiment, 1.25×10^{-3} mol of the ion of **L** required 37.5 cm^3 of 0.0200 mol dm^{-3} potassium manganate(VII) for complete reaction.

What is the initial oxidation state of the ion of **L** given that potassium manganate(VII) is reduced to Mn^{2+}?

A +1 **B** +2

C +3 **D** +4

7 Given the following standard enthalpy changes,

$C(s) + O_2(g) \rightarrow CO_2(g)$ –394 kJ mol^{-1}

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ –286 kJ mol^{-1}

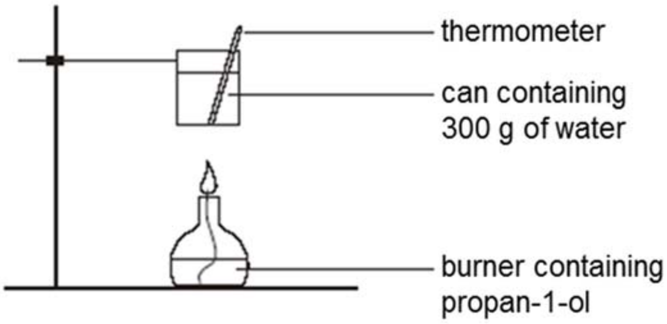
$2C(s) + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow C_2H_5OH(l)$ –278 kJ mol^{-1}

What is the standard enthalpy change of combustion of liquid ethanol, C_2H_5OH?

A –402 kJ mol^{-1} **B** –758 kJ mol^{-1}

C –1368 kJ mol^{-1} **D** –1924 kJ mol^{-1}

8 A student used the set–up below to heat a can containing 300 g of water.



The following data were recorded:

mass of propan–1–ol burnt = m g
change in temperature of water = ΔT °C

Given that:

relative molecular mass of propan–1–ol = 60.0
enthalpy change of combustion of propan–1–ol = –2021 kJ mol^{-1}
specific heat capacity of water = c J g^{-1} K^{-1}

What is the efficiency of this heating process?

A $\dfrac{m \times 2021 \times 1000}{300 \times c \times \Delta T \times 60.0} \times 100\%$

B $\dfrac{m \times c \times \Delta T \times 60.0}{300 \times 2021 \times 1000} \times 100\%$

C $\dfrac{300 \times c \times \Delta T \times 60.0}{m \times 2021} \times 100\%$

D $\dfrac{300 \times c \times \Delta T \times 60.0}{m \times 2021 \times 1000} \times 100\%$

9 The experimental results obtained for the reaction between **X** and **Y** at constant temperature are given in the table below.

Experiment	[**X**] / mol dm^{-3}	[**Y**] / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.3	0.2	4.00 x 10^{-4}
2	0.6	0.4	1.60 x 10^{-3}
3	0.6	1.2	1.44 x 10^{-2}

What is the rate equation for this reaction?

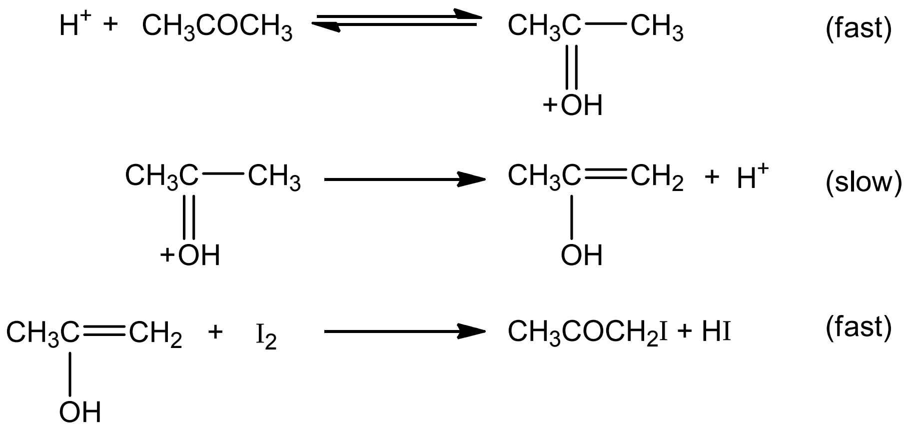
A Rate = k[**Y**]^2

B Rate = k[**X**]^2

C Rate = k[**X**]^2[**Y**]

D Rate = k[**X**][**Y**]^2

10 The mechanism for the iodination of propanone in aqueous acid involves the following steps.



$$H^+ + CH_3COCH_3 \rightleftharpoons CH_3C(=\overset{+}{O}H)CH_3 \qquad \text{(fast)}$$

$$CH_3C(=\overset{+}{O}H)CH_3 \longrightarrow CH_3C(OH){=}CH_2 + H^+ \qquad \text{(slow)}$$

$$CH_3C(OH){=}CH_2 + I_2 \longrightarrow CH_3COCH_2I + HI \qquad \text{(fast)}$$

Which of the following statements are true?

1 The overall order of the reaction is 1.

2 The acid acts as a catalyst.

3 The rate equation is rate = $k[CH_3COCH_3][H^+]$

4 The rate of the reaction is not affected by a change in the iodine concentration.

A 1, 2 and 4 only

B 2, 3 and 4 only

C 1 and 2 only

D 2 and 3 only

11 The rate of removal of *Aspirin*, a pain-killer drug, from the body is a first order reaction with a half-life of 2.0 h.

How long does it take for 87.5% of *Aspirin* to be removed from the body?

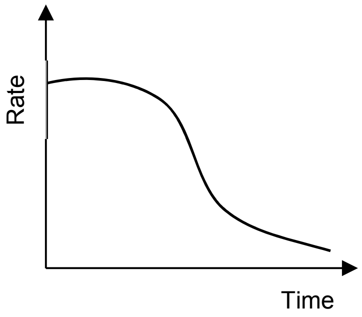
A	6.0 hours	**B**	2.0 hours
C	1.0 hours	**D**	0.4 hours

12 The reaction between potassium manganate(VII) and ethanedioic acid is an example of auto-catalytic reactions, in which one of the products catalyses the reaction.

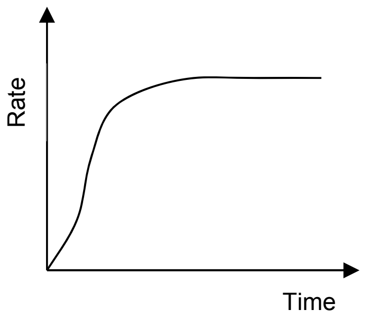
$$2MnO_4^-(aq) + 5H_2C_2O_4(aq) + 6H_3O^+(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 14\ H_2O(l)$$

Which graph correctly represents the kinetics of this reaction?

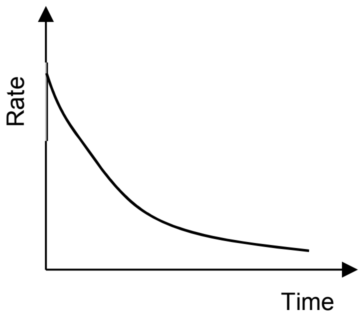
A



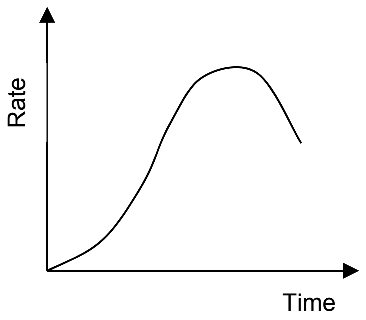
B



C



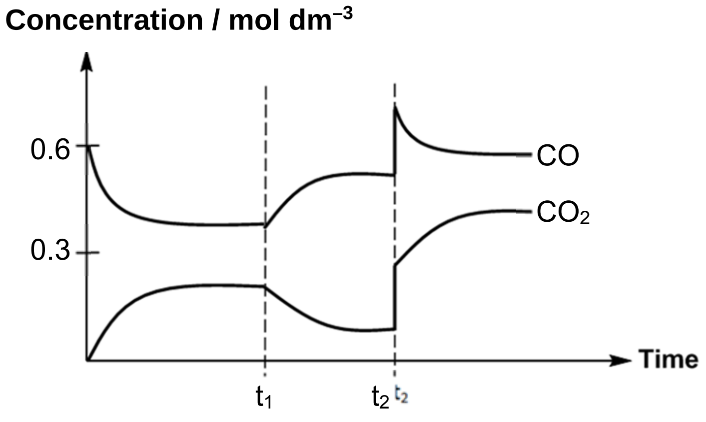
D



13 At a temperature *T* K, 0.60 mol dm^{-3} of CO and 0.30 mol dm^{-3} of O_2 were introduced into a 5 dm^3 vessel and allowed to reach equilibrium.

$$2\ CO\ (g) + O_2\ (g) = 2CO_2\ (g) \qquad \Delta H < 0$$

The graph below shows the changes in the concentration of CO and CO_2 in the system with time. A change was made to the system at time, t_1 and t_2.

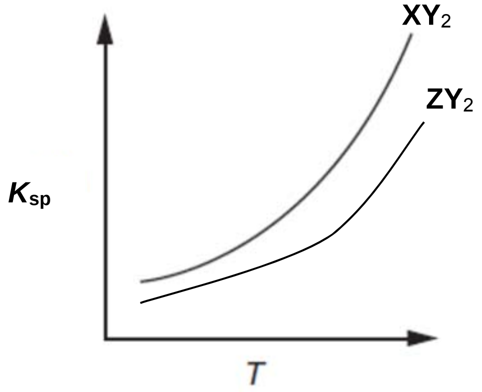


What were the changes made at time, t_1 and t_2?

	t_1	t_2
A	A catalyst was added	Volume of the system is increased
B	The temperature was increased	Volume of the system is decreased
C	Some O_2 was removed	An inert gas was added at constant volume
D	The temperature was decreased	More O_2 was added

14 $\mathbf{XY_2}$ and $\mathbf{ZY_2}$ are sparingly soluble salts containing $\mathbf{Z}^{2+}$, $\mathbf{X}^{2+}$ and $\mathbf{Y}^{-}$ ions.

The solubility product, K_{sp}, of both sparingly soluble salts varies with temperature as shown in the diagram below.



Which conclusions can be drawn from the information?

1 The enthalpy change of solution for both salts is endothermic.

2 Adding $\mathbf{Y}^{-}$ to the solution of $\mathbf{XY_2}$ decreases the K_{sp} of $\mathbf{XY_2}$.

3 Adding $\mathbf{Y}^{-}$ to the solution of $\mathbf{ZY_2}$ decreases the solubility of $\mathbf{ZY_2}$.

4 Given a solution with $[\mathbf{X}^{2+}] = [\mathbf{Z}^{2+}]$, $\mathbf{ZY_2}$ is precipitated out first on adding $\mathbf{Y}^{-}$.

A 1 and 3 only

B 3 and 4 only

C 1, 2 and 4 only

D 1, 3 and 4 only

15 A metal object was electroplated with chromium using an aqueous electrolyte of chromium(III) chloride and a graphite electrode. A current of 2.0 A was passed through the electroplating cell for 45 minutes.

What may be derived from the information given above?

1 The object to be electroplated was connected to the negative terminal of the battery.

2 The object increased in mass by 0.97 g.

3 Oxygen gas was evolved at the anode.

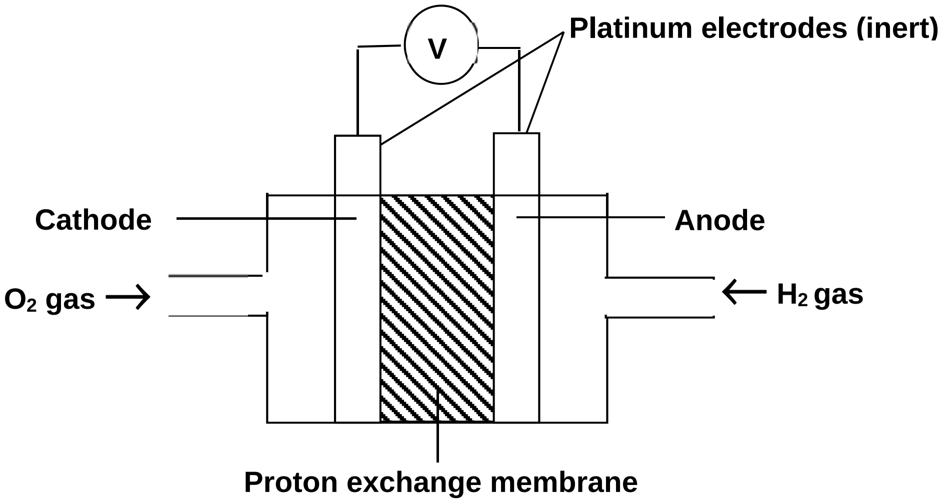
A 1, 2 and 3

B 1 and 2 only

C 2 and 3 only

D 1 only

16 A hydrogen fuel cell as illustrated below has a typical e.m.f. of 1.23 V.



Which of the following is true regarding the operation of this fuel cell?

1 The e.m.f can be increased by increasing the pressure of oxygen gas to 2 atm.

2 The electrode is platinised to increase the rate of reaction, but e.m.f. is not affected.

3 The proton exchange membrane allows the passage of H^+ ions in order to complete the circuit and maintains electrical neutrality.

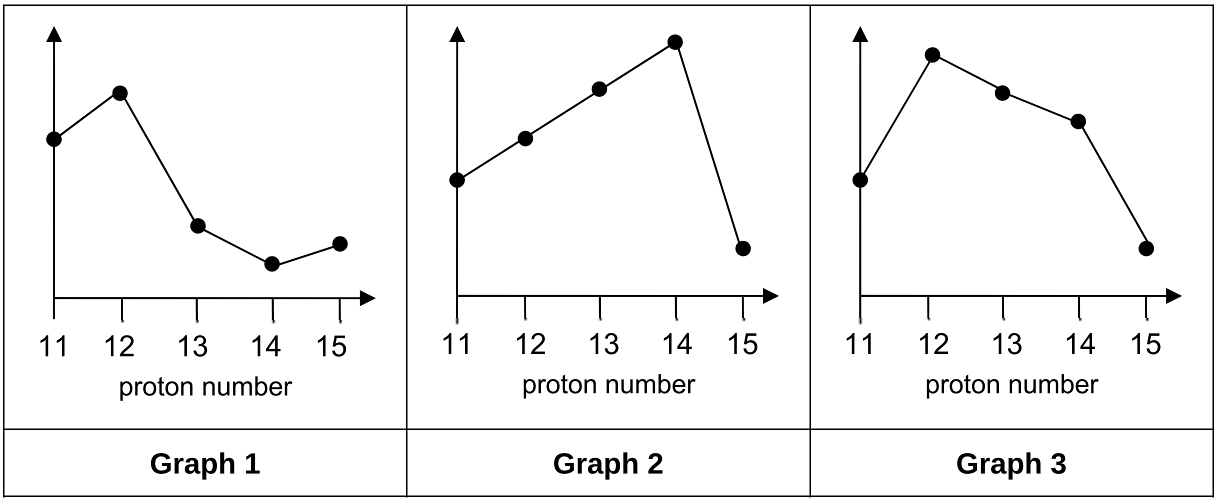
A 1, 2 and 3

B 1 and 2 only

C 2 and 3 only

D 1 only

17 The following graphs show how three properties of the elements, Na to P, and their compounds, vary with proton number.



What properties are shown by the three graphs?

	Graph 1	Graph 2	Graph 3
A	Melting point of oxide	Melting point of chloride	Electrical conductivity of element
B	Melting point of oxide	Melting point of element	Melting point of chloride
C	Melting point of chloride	Electrical conductivity of element	Melting point of oxide
D	Melting point of chloride	Melting point of element	Melting point of oxide

18 Which property of Group 2 elements (magnesium to barium) or their compounds increases with increasing proton number?

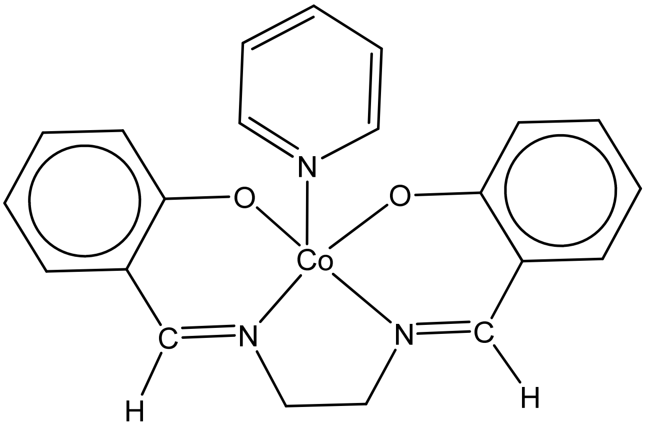
A the stability of the carbonates to heat
B the magnitude of the enthalpy change of hydration of the metal ions
C the acidity of aqueous solutions of the chlorides
D the melting points of the elements

19 For the sequence hydrogen iodide, hydrogen bromide and hydrogen chloride, which of the following properties show a decreasing trend?

1 thermal stability
2 acidity
3 ease of oxidation

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

20 The following cobalt complex is known to be the functional model for biological oxygen carrier.



What is the electronic configuration of the cobalt cation in the above complex?

A [Ar] $3d^6$

B [Ar] $3d^7$

C [Ar] $3d^5 4s^2$

D [Ar] $3d^7 4s^2$

21 Transition metals like platinum and rhodium are found in catalytic converters fitted into cars. Which of the following properties best explains the role of transition metals in this use?

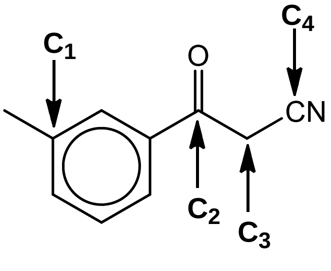
A Transition metals can exhibit variable oxidation states in their compounds as 3d and 4s electrons have similar energies.

B Transition metals form coloured ions due to absorption of energy in the visible light region to promote an electron from a lower to a higher energy 3d orbital.

C Transition metals have very high melting points because both 3d and 4s electrons are involved in forming strong metallic bond.

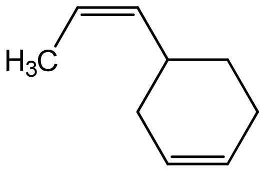
D Transition metals have partially filled 3d orbitals which are available for adsorption of reactant molecules.

22 What is the hybridisation of the various carbon atoms in the following molecule?



	C_1	C_2	C_3	C_4
A	sp^2	sp^3	sp	sp^2
B	sp^2	sp^2	sp^3	sp
C	sp^2	sp^2	sp	sp^3
D	sp^3	sp^2	sp^3	sp

23

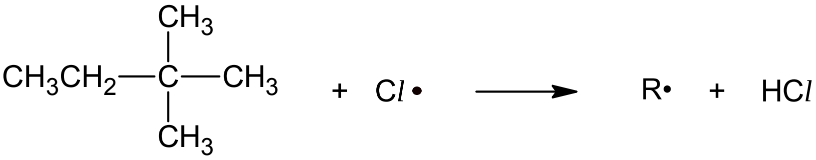


How many stereoisomers does the above molecule have?

A	2	**B**	4
C	6	**D**	8

24 When heated with chlorine, the hydrocarbon 2,2-dimethylbutane undergoes free radical substitution.

In a propagation step, the free alkyl radical R• is formed.



$CH_3CH_2C(CH_3)_2CH_3 + Cl\bullet \longrightarrow R\bullet + HCl$

How many different forms of R• are possible?

A	1	**B**	2
C	3	**D**	4

25 Which one of the following statements regarding organic reaction mechanisms is **correct**?

1 Electrophilic addition of alkenes involves a carbocation intermediate.

2 Electrophilic substitution of benzene involves an intermediate with 4 π electrons.

3 Nucleophilic substitution of tertiary halogenoalkanes involves a carbocation intermediate.

4 Nucleophilic addition of a carbonyl compound involves an alkoxide intermediate.

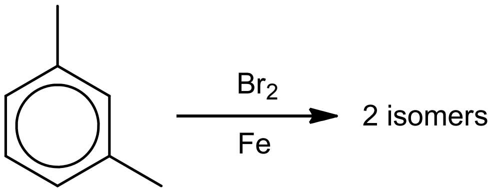
A 1, 2, 3 and 4

B 1 and 2 only

C 2 and 3 only

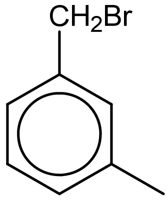
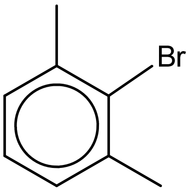
D 3 and 4 only

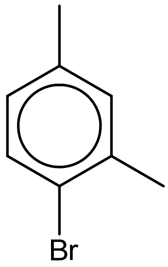
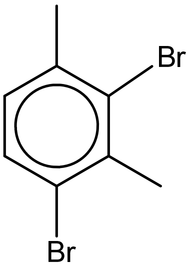
26 When 3-methyltoluene is treated with bromine in the presence of iron filings in the dark, a mixture of two mono-brominated isomers is formed.

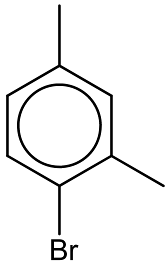
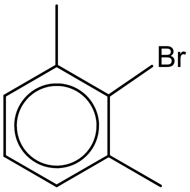


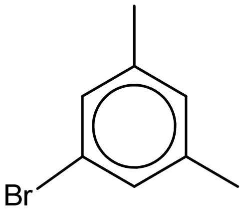
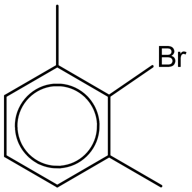
3-methyltoluene

What are the structures of these two isomers?

A  and 

B  and 

C  and 

D  and 

27 When ethyl ethanoate undergoes hydrolysis with dilute sulfuric acid in the presence of $H_2{}^{18}\mathbf{O}$, a mixture of two products is formed. Which of the following pairs correctly gives the structures of the two products?

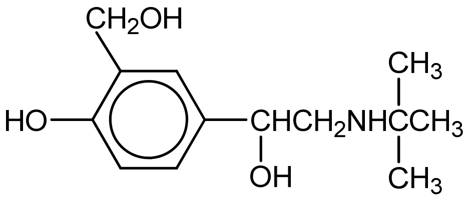
A $CH_3CO^{18}\mathbf{O}H$ and $CH_3CH_2{}^{18}\mathbf{O}H$

B CH_3COOH and $CH_3CH_2{}^{18}\mathbf{O}H$

C $CH_3C^{18}\mathbf{O}OH$ and CH_3CH_2OH

D $CH_3CO^{18}\mathbf{O}H$ and CH_3CH_2OH

28 Albuterol dilates the airways of the lung and is used for treating asthma and other conditions of the lung.



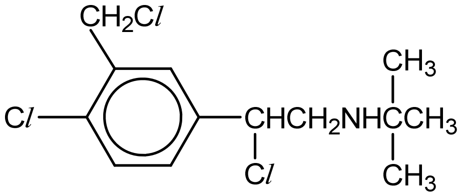
Albuterol

Which of the following statements is true about albuterol?

1 On addition of Na_2CO_3(aq), effervescence of CO_2 is produced.

2 On heating one mole of albuterol with NaOH(aq), one mole of NaOH is used up.

3 On reacting with phosphorus pentachloride,



is one of the products.

A 1 only

B 2 only

C 1 and 3 only

D 2 and 3 only

29 A sample of bromoethane was warmed with ethanolic silver nitrate, and a cream precipitate was observed after about 4 minutes.

Under similar reaction conditions, which one of the following compounds will result in precipitate formation only after 8 minutes?

A iodoethane

B ethanoyl bromide

C bromobenzene

D chloroethane

30 Which of the following gives the correct order of decreasing basic strength?

A $CH_3CH_2NH_2$, NH_3, $(CH_3CH_2)_2NH$

B $CH_3CH_2NH_2$, $(CH_3CH_2)_2NH$, $C_6H_5NH_2$

C $(CH_3CH_2)_2NH$, NH_3, $C_6H_5NH_2$

D $C_6H_5NH_2$, NH_3, $CH_3CH_2NH_2$

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2018 Paper 1 answer key

1	**A**	2	**B**	3	**B**	4	**C**	5	**C**
6	**B**	7	**C**	8	**D**	9	**A**	10	**B**
11	**A**	12	**D**	13	**B**	14	**D**	15	**A**
16	**A**	17	**D**	18	**A**	19	**C**	20	**B**
21	**D**	22	**B**	23	**B**	24	**C**	25	**A**
26	**C**	27	**D**	28	**B**	29	**D**	30	**C**

JURONG JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION 2018

CANDIDATE NAME

CLASS **18S**

EXAM INDEX

CHEMISTRY
Higher 2
9729/02

Paper 2 Structured Questions

29 August 2018
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and exam index number on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a HB pencil for any diagrams, graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
A *Data Booklet* is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	/**13**
2	/**13**
3	/**11**
4	/**10**
5	/**17**
6	/**11**
Penalty (delete accordingly)	
Lack **3sf** in final ans	**–1 / NA**
Missing/wrong **units** in final ans	**–1 / NA**
Bond linkages	**–1 / NA**
Total	

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

Answer **all** the questions.

For Examiner's Use

1 Nickel is an important transition metal used in the manufacture of stainless steel alloys. It is first isolated from the mineral ore niccolite by Swedish chemist Axel Fredrik Cronstedt in 1751.

(a) Nickel exists naturally as a mixture of five stable isotopes, each with their own relative isotopic mass. The information about four of these isotopes is given.

isotope	percentage abundance
^{58}Ni	68.1
^{61}Ni	1.14
^{62}Ni	3.63
^{64}Ni	0.93

The relative atomic mass of nickel is 58.7.

Calculate the relative isotopic mass of the fifth isotope of nickel.

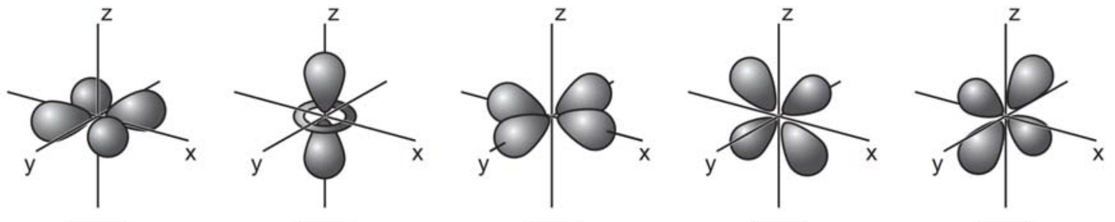
Give your answer to the **nearest whole number**.

[2]

(b) Nickel can form complexes with H_2O ligands.

In a $[Ni(H_2O)_6]^{2+}$ complex, the presence of the H_2O ligands causes the d orbitals to split into two groups at different energy levels.

(i) On the diagram below, tick the box under each of the orbitals of the higher energy level.



☐ ☐ ☐ ☐ ☐

[2]

(ii) Explain why a solution of $[Ni(H_2O)_6]^{2+}$ is coloured.

……………………………………………………………………………………..

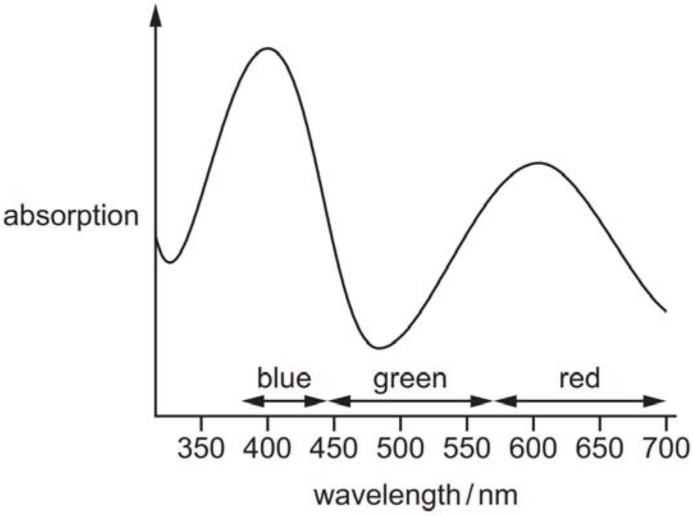
……………………………………………………………………………………..

……………………………………………………………………………………..

……………………………………………………………………………………..

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

(iii) The visible spectrum of a solution of $[Ni(H_2O)_6]^{2+}$ is shown below.



State and explain the colour of the solution.

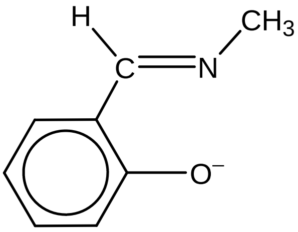
colour of the solution ……………………………….

explanation ……………………………………………………………………….

……………………………………………………………………………………..

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

(c) Nickel can form a complex with ligand **X**⁻, which has the structure shown below.



ligand **X**⁻

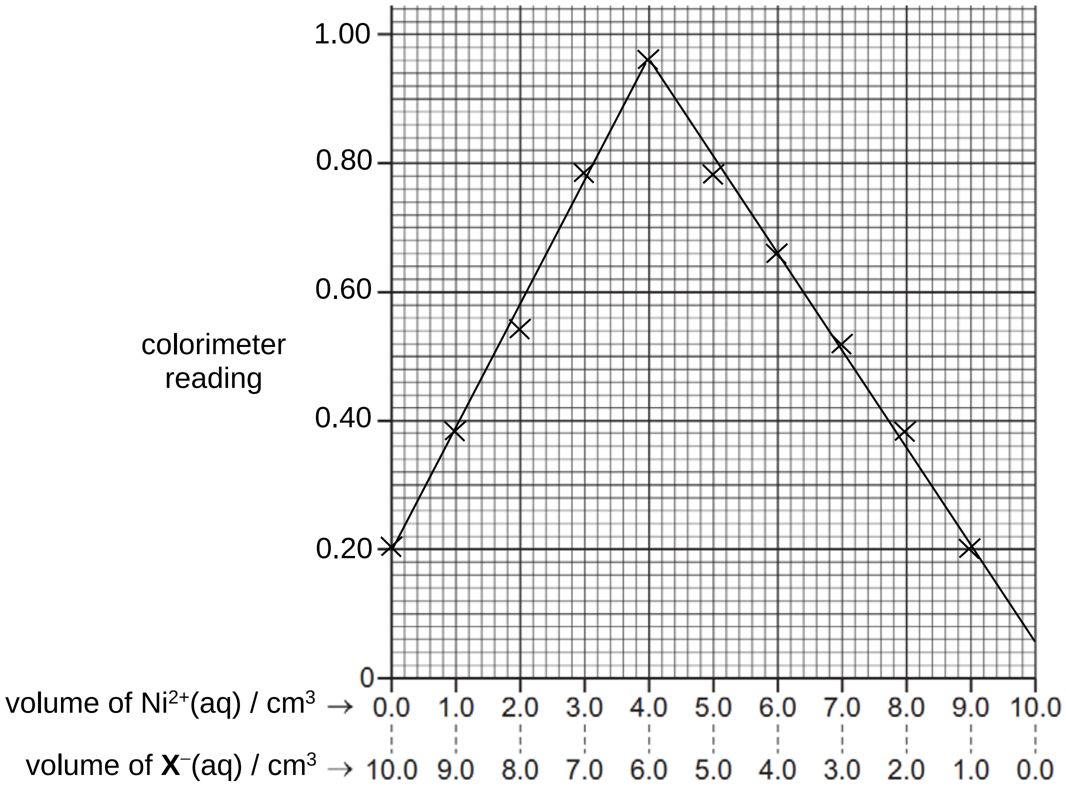
X⁻ is a bidentate ligand. On the structure above, draw circles around the atoms that bind to nickel when **X**⁻ behaves as a ligand. [1]

(d) The formula of a complex can be determined using colorimetry.

In colorimetry, light of a certain wavelength is passed through a complex ion solution. The absorbance of the light is proportional to the intensity of the colour of the solution. The more concentrated the complex ion solution, the more intense its colour and so the higher the absorbance.

An experiment is carried out to determine the formula of the complex formed between nickel and ligand **X**$^-$ having the structure given in **(c)**.

The following graph was obtained when the colour intensities of mixtures of a 3×10^{-3} mol dm^{-3} solution of nickel(II) chloride and a 4×10^{-3} mol dm^{-3} solution containing **X**$^-$ were measured using a colorimeter at room temperature.



Determine the stoichiometry of the complex and suggest its structural formula.

[2]

For Examiner's Use

(e) Like nickel, platinum can also forms complexes in which the central atom is surrounded by four ligands.

A and **B** are isomeric complexes of the same shape with the formula of $Pt(PR_3)_2I_2$.
[The PR_3 ligand has the same shape as NH_3. R is a phenyl group.]

Given that isomer **A** has a dipole moment, draw the structures of **A** and **B**.

isomer **A**

isomer **B** [2]

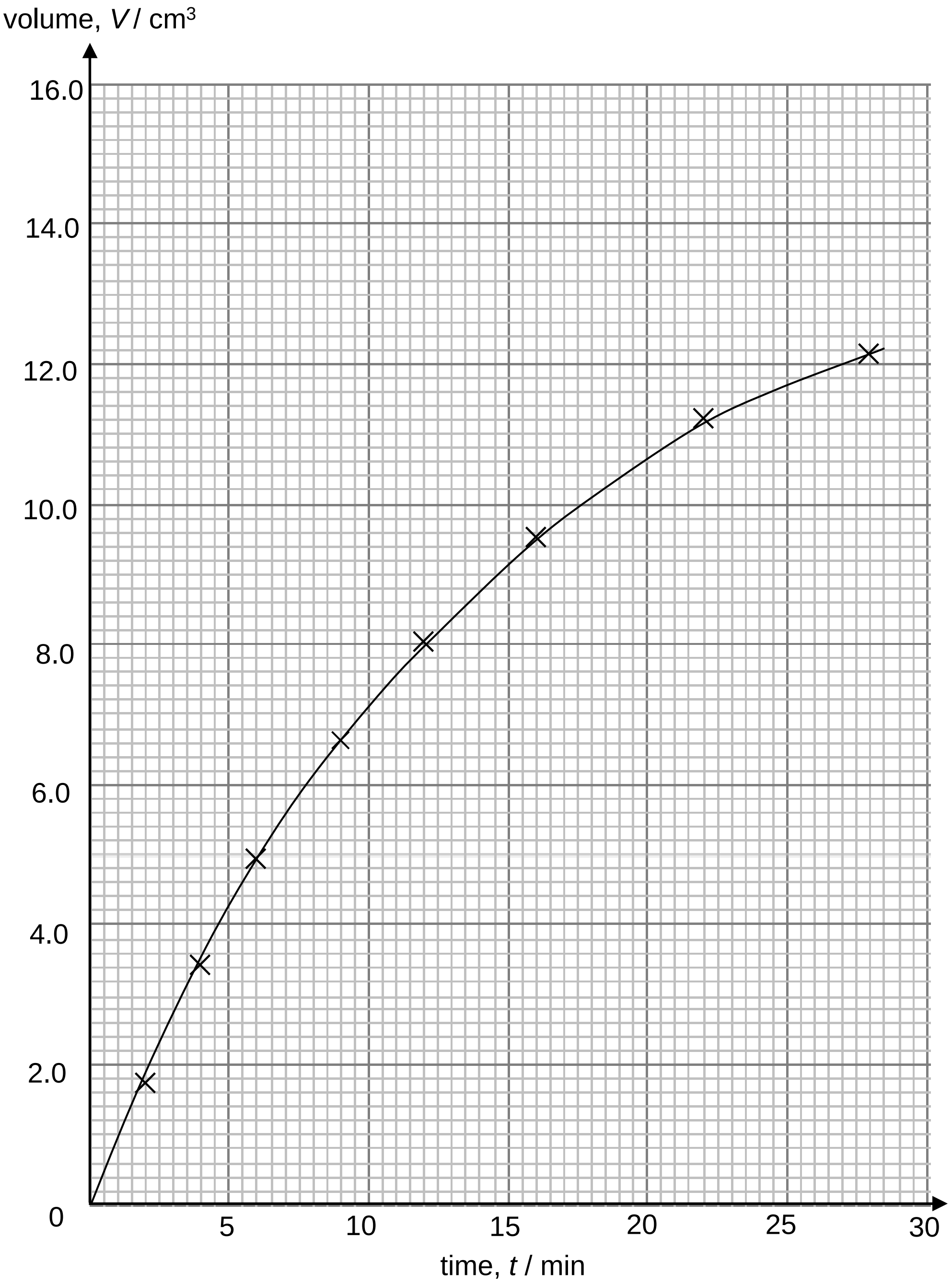
[Total: 13]

2 **(a)** Benzenediazonium chloride, $C_6H_5N_2Cl$, decomposes at 50 °C and 101 kPa, according to the equation below.

$$C_6H_5N_2Cl(aq) \rightarrow C_6H_5Cl(aq) + N_2(g)$$

The progress of the decomposition reaction of a 500 cm^3 sample of $C_6H_5N_2Cl(aq)$ solution was studied by measuring the volume of gas produced over time.

The volume of gas produced, V, after time, t, is proportional to the amount of benzenediazonium chloride that has decomposed. The final volume of gas produced, V_{final}, is 14.6 cm^3 and it is directly proportional to the original concentration of benzenediazonium chloride. The results are recorded in the graph below.



(i) Use the graph to determine the order of the reaction with respect to benzenediazonium chloride.

Show all your working, and draw clearly any construction lines on your graph.

Order of reaction with respect to benzenediazonium chloride: …………….

explanation ……………………………………………………………………….

……………………………………………………………………………….. [2]

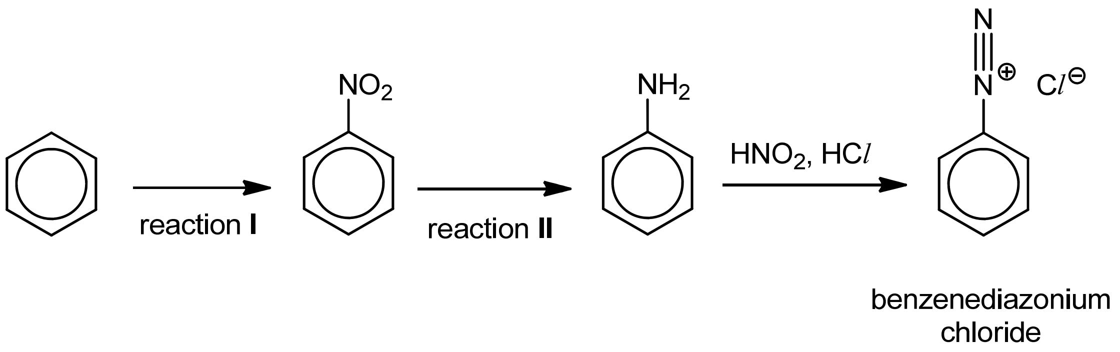
(ii) Calculate the rate constant, stating its units.

[2]

(iii) Assuming nitrogen behaves ideally, calculate the original concentration, in mol dm^{-3}, of benzenediazonium chloride.

[3]

(b) Benzenediazonium chloride is an important intermediate for the production of dyes. The following scheme shows the synthesis of benzenediazonium chloride from benzene.



(i) State the type of reaction and suggest the reagents and conditions for reaction **I**.

type of reaction: ……………………………………………….

reagents: ……………………………………………………..

conditions: ………………………………………………….. [3]

In reaction **II**, nitrobenzene is reduced to phenylamine via two steps.

During step 1, granulated Sn and concentrated HC*l* are added to nitrobenzene and the mixture is heated under reflux in a hot water bath for about half an hour. Sn, which acts as the reducing agent, is converted to Sn^{4+} ions.

(ii) Balance the following half-equation for the reduction of nitrobenzene in acid solution to give $C_6H_5NH_3^+$ in step 1.

.... $C_6H_5NO_2$ + ... H^+ + …. e^- → …………………………………………... [1]

(iii) Hence, by considering electron transfer, write a balanced overall equation for the reaction of nitrobenzene, Sn and concentrated HC*l* in step 1.

…. $C_6H_5NO_2$ + …. Sn + …. HC*l* → ……………………………………………. [1]

Step 2 involves the addition of aqueous sodium hydroxide to the resulting mixture.

(iv) Suggest the purpose of this stage.

……………………………………………………………………………………..

……………………………………………………………………………………..

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

[Total: 13]

For Examiner's Use

3 Metals have properties that make them well suited to serve as battery anodes.

They are easily oxidised from their metallic state to produce ions and electrons, where the electrons liberated are conducted throughout the external circuit. The fact that metals are physically strong and easily fashioned into any desired shape adds to their attractiveness as anodes.

Metals commonly employed as anodes in commercial batteries are listed in **Table 3.1**. The tabulated properties give clues as to the ability of each metal to play this role.

Metal	relative atomic mass	density / g cm^{-3}	standard electrode potential, $E^{\ominus}$ / V	electrochemical capacity / A h g^{-1}
lithium	6.9	0.53	–3.04	3.86
sodium	23.0	0.97	–2.71	1.17
magnesium	24.3	1.74	–2.38	2.21
iron	55.8	7.86	–0.44	0.96
zinc	65.4	7.14	–0.76	0.82
lead	207.2	11.3	–0.13	0.26

Table 3.1

(a) Suggest **two** reasons why lithium is the best choice among the metals in **Table 3.1** to be used as a battery anode.

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

……………………………………………………………………………………………… [2]

(b) A schematic diagram of a lithium-ion battery is shown below. Lithium is the anode whereas a paste of iron disulfide (FeS_2) powder mixed with powdered graphite serves as the cathode.

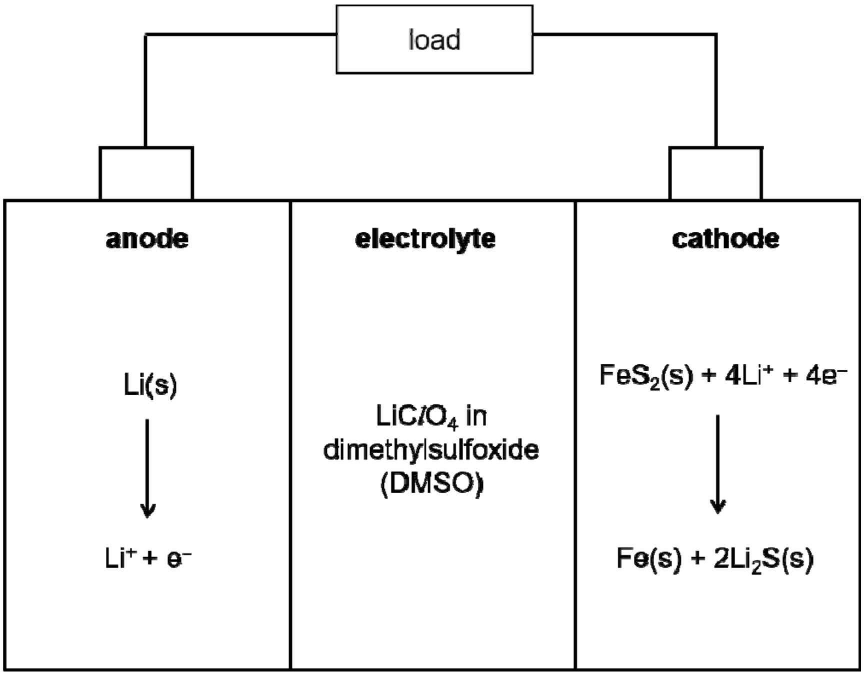


Figure 3.1

(i) On **Figure 3.1**, indicate clearly the direction of electron flow. [1]

(ii) Most batteries use aqueous solutions of ionic salts or ionisable molecules as electrolytes. However, the electrolyte used in this lithium-ion battery must be non-aqueous such as dissolving $LiClO_4$ in dimethylsulfoxide (DMSO), which is an organic solvent. Suggest why.

……………………………………………………………………………………

……………………………………………………………………………………

…………………………………………………………………………………… [1]

(c) Like enthalpy, Gibbs free energy *G* is a state function. Thus, Hess' Law can likewise be applied to calculate the standard Gibbs free energy change of a reaction, ΔG°, from relevant data such as the standard Gibbs free energy changes of formation.

Table 3.2 below lists the standard Gibbs free energy change of formation, ΔG_f°, for some compounds.

species	ΔG_f° / kJ mol^{-1}
FeS_2(s)	–160
Li_2S(s)	–439

Table 3.2

(i) Use the data in **Table 3.2** above to show that the standard Gibbs free energy change, ΔG_r°, of the overall cell reaction in the lithium-ion battery is –718 kJ mol^{-1}.

$$4Li(s) + FeS_2(s) \rightarrow Fe(s) + 2Li_2S(s)$$

[1]

(ii) Use the ΔG_r° value given in **(c)(i)** to calculate the E°_{cell} of this battery.

[2]

(iii) Use your answer in **(c)(ii)** and relevant $E^{\ominus}$ value in **Table 3.1** to calculate the standard electrode potential of the $FeS_2(s)/Fe(s)$ half-cell at the cathode.

[1]

(iv) By using **one** of the phrases *more positive*, *more negative* or *no change*, deduce the effect of increasing $[Li^+]$ on the electrode potential of

- the left-hand electrode (anode) …………………………………….
- The right-hand electrode (cathode) ………………………………….

[2]

(v) Hence deduce whether the overall $E^{\ominus}_{cell}$ is likely to *increase*, *decrease* or *remain the same*, when $[Li^+]$ increases.

…………………………………………………………………………………. [1]

[Total: 11]

For Examiner's Use

4 **(a)** **Figure 4.1** is an incomplete sketch showing the melting points of some of the elements of the Period 3 (sodium to argon). Estimate and indicate, on **Figure 4.1**, the melting points of the four other elements: Mg, A*l*, S and C*l*.

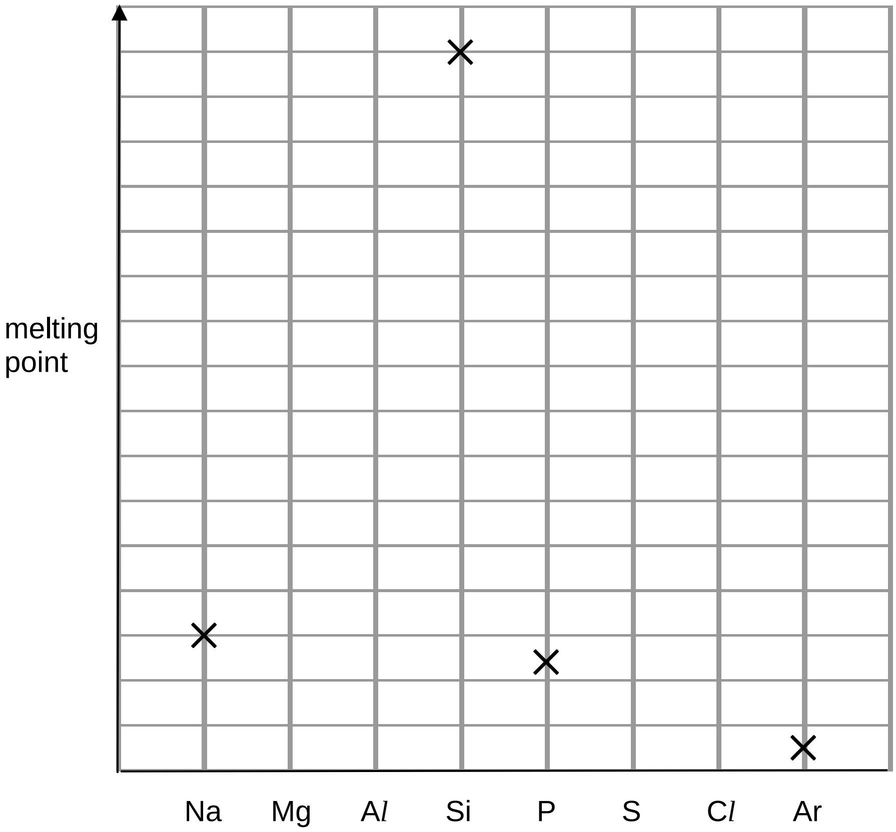
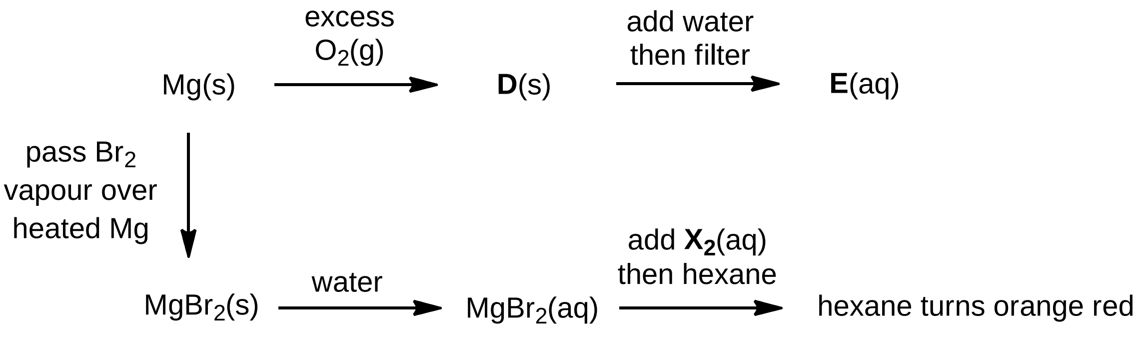


Figure 4.1 [2]

(b) Some reactions of magnesium and its compounds are shown below.



(i) Identify compounds **D** and **E**.

D: ………………….. **E**: ……………………. [2]

(ii) Use appropriate data in the *Data Booklet* to deduce whether $\mathbf{X_2}$ is Cl_2 or I_2.

……………………………………………………………………………………..

……………………………………………………………………………………..

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

(c) Sodium reacts with water to form aqueous sodium hydroxide.

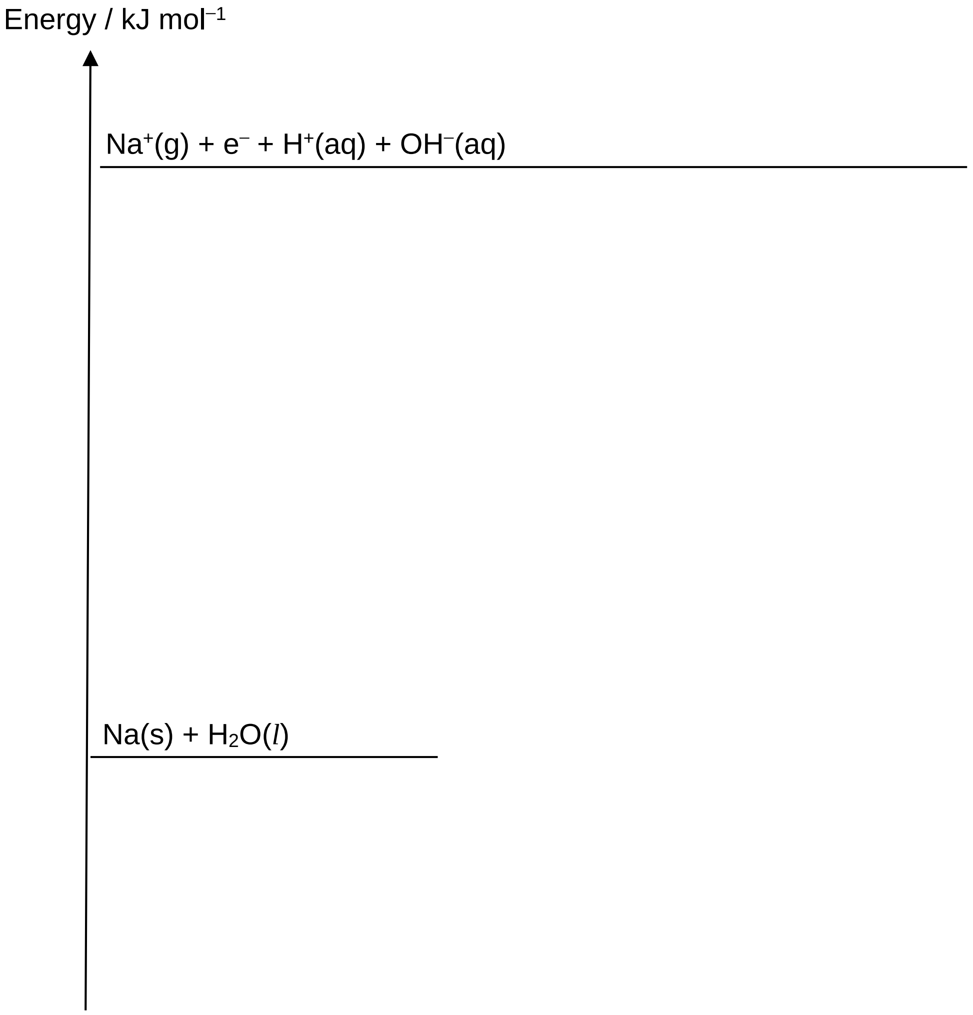
$$Na(s) + H_2O(l) \rightarrow Na^+(aq) + OH^-(aq) + \tfrac{1}{2}H_2(g) \qquad \Delta \boldsymbol{H}_r$$

On the grid below, draw an energy cycle which can be used to calculate $\Delta \boldsymbol{H}_r$, by incorporating the enthalpy changes in **Table 4.1** and any relevant data from the *Data Booklet*.

Hence, calculate $\Delta \boldsymbol{H}_r$.

	value / kJ mol^{-1}
enthalpy change of atomisation of Na(s)	+107
enthalpy change for $Na^+(g) + H^+(aq) + e^- \rightarrow Na^+(aq) + \tfrac{1}{2}H_2(g)$	–850
enthalpy change for $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$	–58

Table 4.1



[4]

[Total: 10]

5 **(a)** But-1-ene reacts with hydrogen bromide to give 2-bromobutane as the major product.

(i) Name and describe the mechanism for this reaction. Show all charges, relevant lone pairs and the movement of electron pairs by using curly arrows.

Name of mechanism: ………………………………………………….

[3]

(ii) With reference to the mechanism you have drawn in **(a)(i)**, explain why the major product is 2-bromobutane rather than 1-bromobutane.

……………………………………………………………………………………..

……………………………………………………………………………………..

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

(iii) 2-bromobutane is chiral. However, the product mixture from this reaction does not rotate plane-polarised light.

With reference to the mechanism you have drawn in **(a)(i)**, explain why this is so.

……………………………………………………………………………………..

……………………………………………………………………………………..

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

(b) **Figure 5.1** shows a reaction scheme involving 4-bromobutanone.

Compounds **J** and **K** have the following properties:

- Effervescence is seen when reacted with sodium metal.
- No yellow precipitate is formed when mixed with alkaline aqueous iodine.
- A pale cream precipitate slowly forms when excess HNO_3(aq) is added, followed by $AgNO_3$(aq).

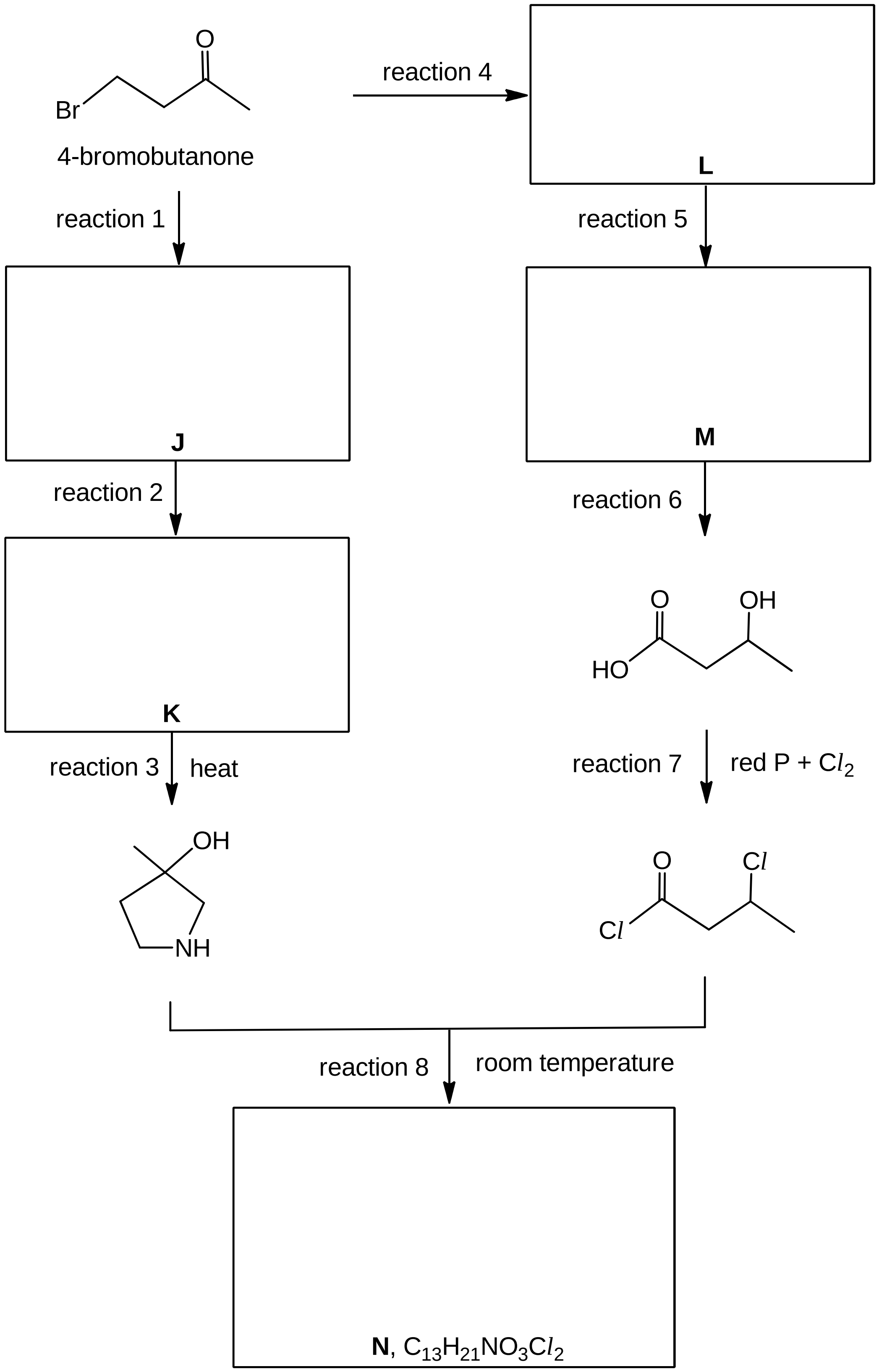


Figure 5.1

(i) Work out the structures for compounds **J**–**N**. Draw their structural formulae in the boxes on the reaction scheme shown in **Figure 5.1**. [5]

(ii) Suggest reagents and conditions for reactions 1, 2, 4, 5 and 6.

reaction 1: …………………………………………………

reaction 2: …………………………………………………

reaction 4: …………………………………………………

reaction 5: …………………………………………………

reaction 6: ………………………………………………… [5]

(iii) State the types of reaction for reactions 7 and 8.

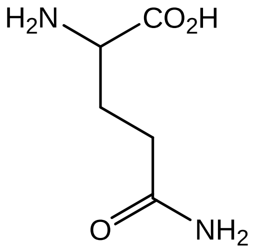
reaction 7: …………………………………………………

reaction 8: ………………………………………………… [2]

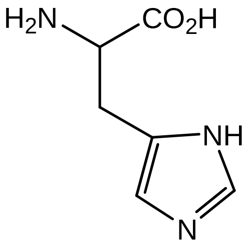
[Total: 17]

For Examiner's Use

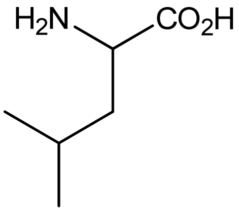
6 A pentapeptide comprises the following five amino acids.



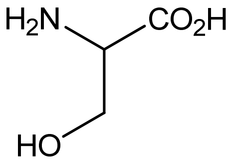
glutamine (gln)
M_r = 146



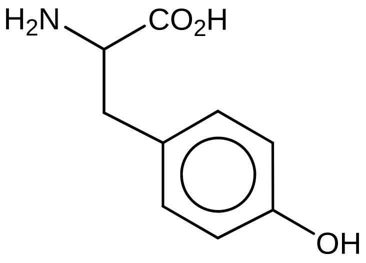
histidine (his)
M_r = 155



leucine (leu)
M_r = 131



serine (ser)
M_r = 105



tyrosine (tyr)
M_r = 181

(a) Calculate the M_r of this pentapeptide. Show your working clearly.

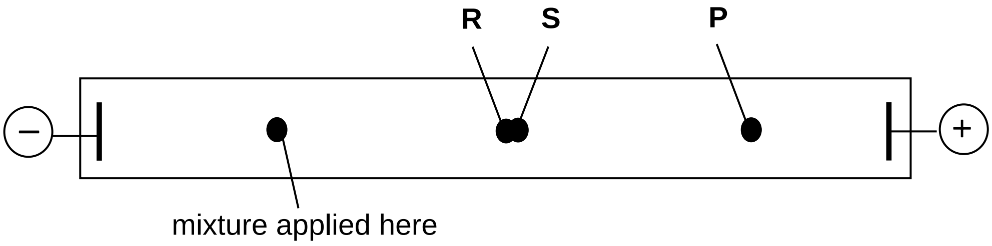
[1]

(b) The pentapeptide was broken down by enzymes to form shorter peptides and individual amino acids. One of the peptides is a dipeptide with the sequence **gln-tyr**.

(i) Draw the structure of the dipeptide at pH 12.

[2]

A mixture of this dipeptide (gln-tyr) and its two constituent amino acids (gln and tyr) was subjected to electrophoresis in a buffer at pH = 12. At the end of the experiment, the following results were seen. Spots **R** and **S** remained very close together.



The three spots are due to the three species gln, tyr and gln-tyr.

(ii) Which species is responsible for spot **P**? Explain your answer

spot **P**: …………………….

explanation ……………………………………………………………………

………………………………………………………………………………….

………………………………………………………………………………….

…………………………………………………………………………………. [2]

(iii) Suggest why the other two species give spots **R** and **S** that are so close together.

……………..……………………………………………………………………

………………………………………………………………………………….

…………………………………………………………………………………. [1]

(c) State a reagent you would use and the observations you would make to distinguish tyrosine (tyr) from glutamine (gln).

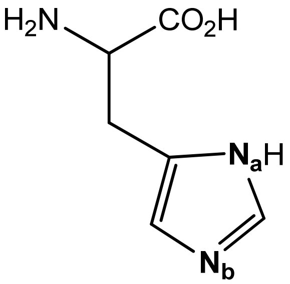
test ………………………………………….

observations ………………………………………………………………………..

…………………………………………………………………………………………..

………………………………………………………………………………………… [2]

(d) There are two nitrogen atoms, **N**$_a$ and **N**$_b$, in the side chain of histidine. However, only one of the nitrogen atoms can act as a Bronsted base.



(i) **N**$_a$ and **N**$_b$ have the same state of hybridisation. State their state of hybridisation.

……………………………… [1]

(ii) Predict which nitrogen atom, **N**$_a$ or **N**$_b$, can act as a Bronsted base. Explain your answer.

……………………………………………………………………………………..

……………………………………………………………………………………..

……………………………………………………………………………………..

……………………………………………………………………………………..

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

[Total: 11]

END OF PAPER

Suggested Answers for 2018 H2 Chemistry Preliminary Examination Paper 2

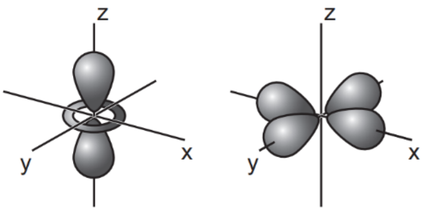
1 **(a)** % abundance of 5th isotope = 100 – (68.1 + 1.14 + 3.63 + 0.93) = 26.2 %

Let relative isotopic mass of 5th isotope be x.

$58.7 = 0.262x + (58 \times 0.681) + (61 \times 0.0114) + (62 \times 0.0363) + (64 \times 0.0093)$

$\therefore\ x = 60$

(b) **(i)**



☑ ☑

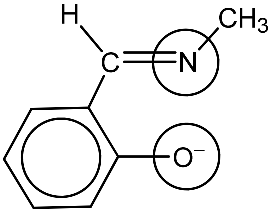
(ii) Visible light is absorbed when an electron transits from a lower energy d orbital to a higher energy d orbital that is partially filled.

Colour seen is the complement of the colours that are absorbed.

(iii) Colour: Green

Wavelengths corresponding to the blue and red regions are most absorbed (or green region is least absorbed).

(c)



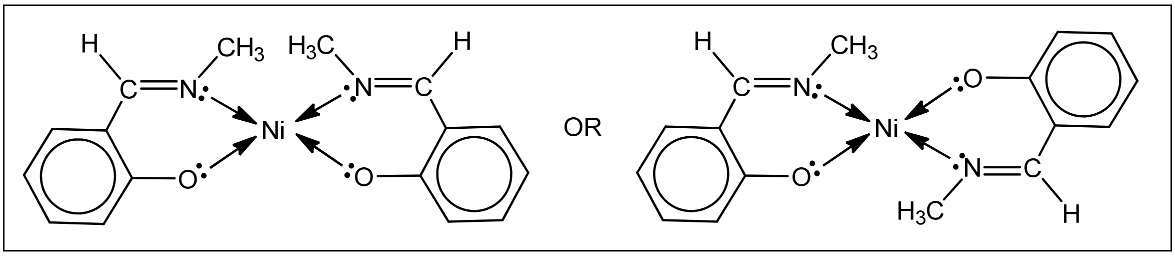
(d) $n(Ni^{2+}) = 4.0 \times 10^{-3} \times 3 \times 10^{-3} = 1.2 \times 10^{-5}$ mol

$n(X^{-}) = 6.0 \times 10^{-3} \times 4 \times 10^{-3} = 2.4 \times 10^{-5}$ mol

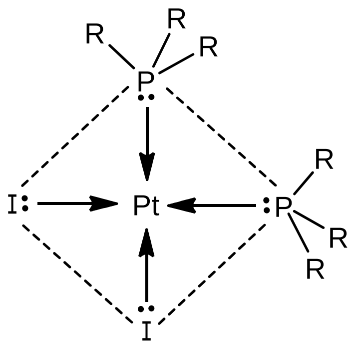
$n(Ni^{2+}) : n(X^{-}) = 1.2 \times 10^{-5} : 2.4 \times 10^{-5} = 1 : 2$

Empirical formula is NiX_2.

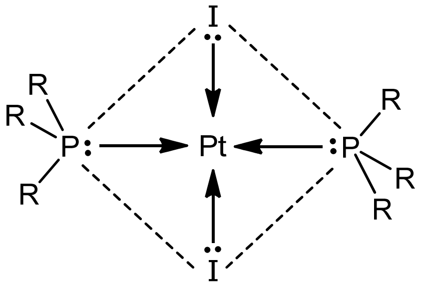
Structural formula of the complex:



(e)

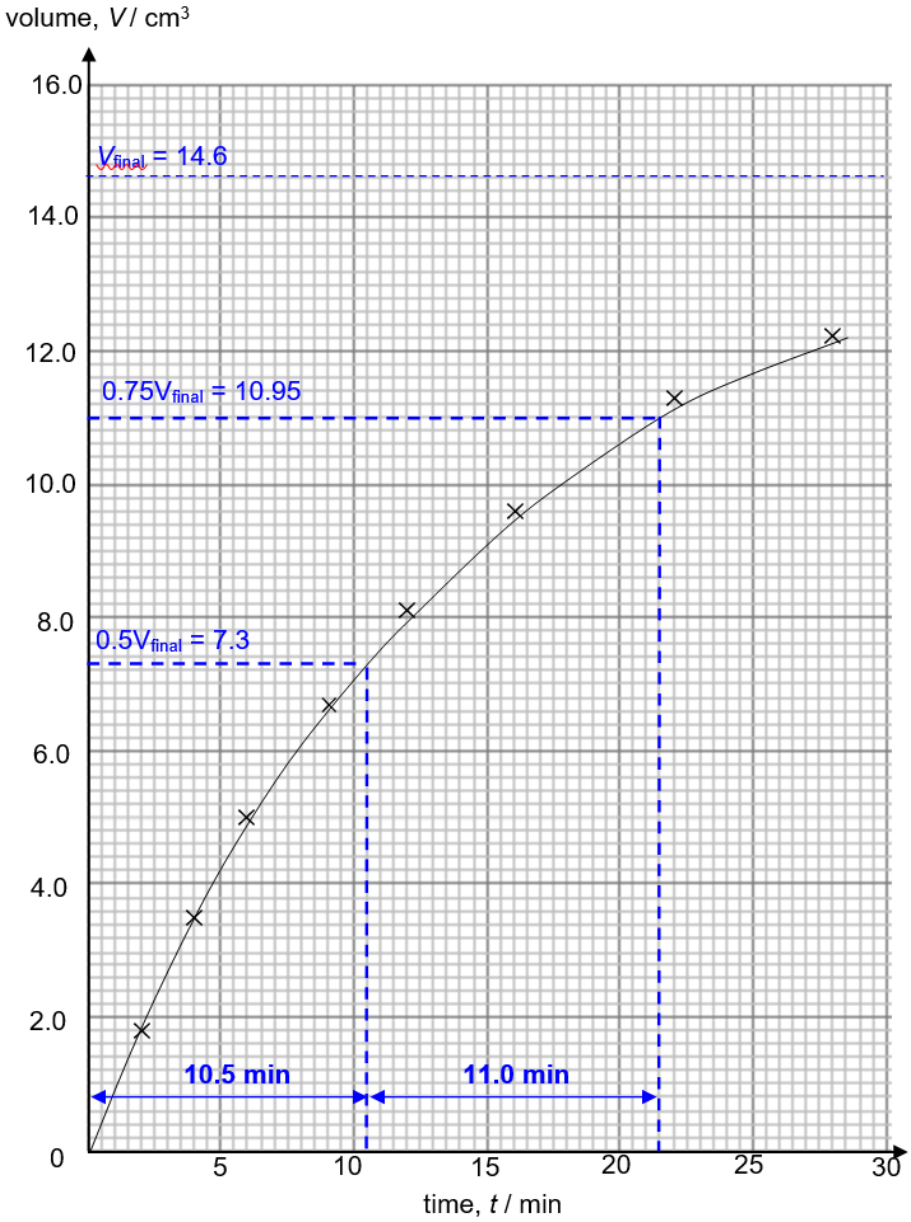


Isomer **A**



Isomer **B**

2 **(a)**



(i) Order of reaction with respect to benzenediazonium chloride: 1

1st $t_{½}$ = 10.5 min; 2nd $t_{½}$ = 11.0 min ⇒ Half-lives are relatively constant.

(ii) Average $t_{½}$ = 0.5 (10.5 + 11.0) = 10.75 min

For overall 1st order reaction, $k = \dfrac{\ln 2}{10.75}$ = 0.0645 min^{-1}

(iii) $n(N_2) = \dfrac{(101000)(14.7\times10^{-6})}{(8.31)(50+273)}$ = 0.000549 mol

= $n(C_6H_5N_2Cl)$ in 500 cm^3 solution

Original [benzenediazonium chloride] = $0.000549\times\dfrac{1000}{500}$ = 0.00110 mol dm^{-3}

(b) **(i)** type of reaction: electrophilic substitution

reagents: concentrated HNO_3

conditions: concentrated H_2SO_4, 50 °C

(ii) $1C_6H_5NO_2 + 7H^+ + 6e^- \rightarrow C_6H_5NH_3^+ + 2H_2O$

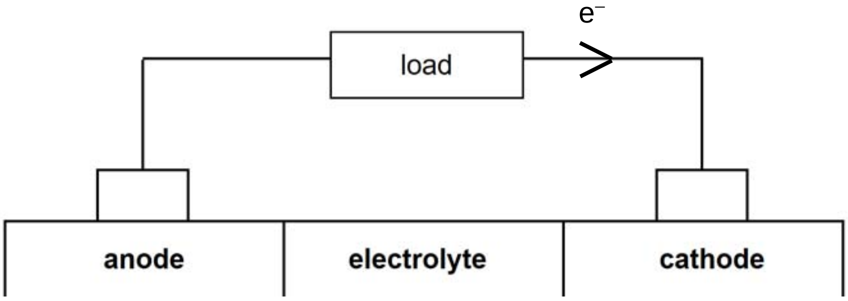
(iii) $2C_6H_5NO_2 + 3Sn + 14HCl \rightarrow 2C_6H_5NH_3Cl + 3SnCl_4 + 4H_2O$

(iv) NaOH will undergo acid-base reaction with $C_6H_5NH_3^+$ (or deprotonate $C_6H_5NH_3^+$) to give $C_6H_5NH_2$.

3 **(a)** Any 2 of the following:

- Li is the lightest/has the lowest density so lithium battery is most portable.
- Li has the most negative $E^\ominus$/ is most easily oxidised among the metals and thus gives the largest e.m.f./$E^\ominus_{cell}$.
- Li has the largest electrochemical capacity so it can produce the largest amount of electrical charge per unit mass of the metal.

(b) **(i)**



(ii) Li is a reactive metal and will undergo redox reaction with water to produce H_2 gas which may cause explosion.

(c) **(i)**

$$\begin{tikzcd}
4Li(s) + FeS_2(s) \arrow[rr, "\Delta G_r^\ominus"] & & Fe(s) + 2Li_2S(s) \\
& 4Li(s) + Fe(s) + 2S(s) \arrow[ul, "\Delta G_f^\ominus(FeS_2)"] \arrow[ur, "2\Delta G_f^\ominus(Li_2S)"'] &
\end{tikzcd}$$

$\Delta G_r^\ominus$ = $\Sigma\,(a_i \times \Delta G_f^\ominus(\text{products})) - \Sigma\,(a_i \times \Delta G_f^\ominus(\text{reactants}))$

= 2(–439) – (–160)

= –718 kJ mol^{-1} (shown)

(ii) $\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$

$-718 \times 10^3 = -(4)(96500)(E^{\ominus}_{cell})$

$E^{\ominus}_{cell} = +1.86$ V

(iii) $Li^+ + e^- \rightleftharpoons Li \quad E^{\ominus} = -3.04$ V ---[O]

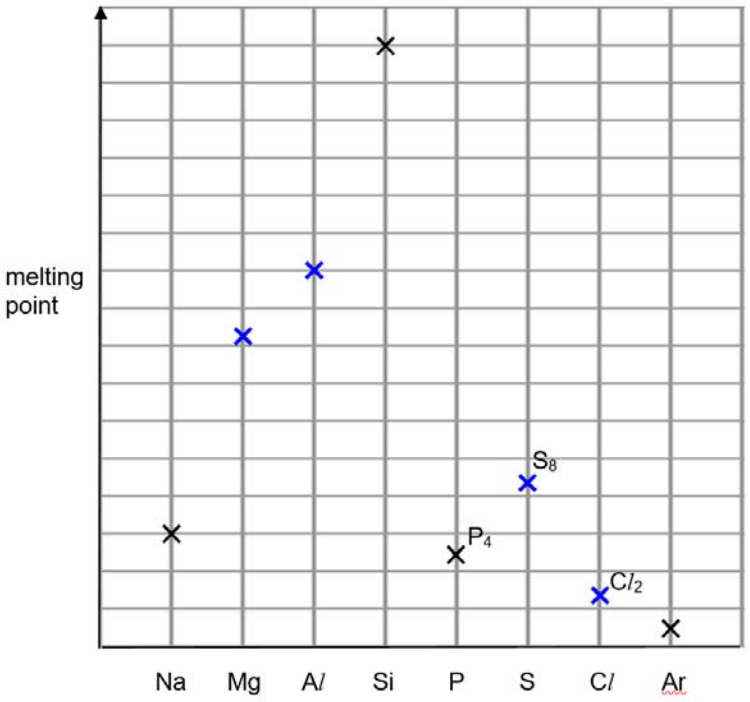
$+1.86 \;= E^{\ominus}(FeS_2/Fe) - (-3.04)$

$(FeS_2/Fe) = -1.18$ V

(iv)
- the left-hand electrode (anode): more positive
- The right-hand electrode (cathode): more positive

(v) $E^{\ominus}_{cell}$ will remain the same.

4 **(a)**



(b) **(i)** **D**: MgO **E**: $Mg(OH)_2$

(ii) X_2 is Cl_2.

$E^{\ominus}_{cell}$ for reaction of Cl_2 and Br^- = (+1.36) – (+1.07) = +0.29 V > 0 (energetically feasible).

OR

$E^{\ominus}_{cell}$ for reaction of I_2 and Br^- = (+0.54) – (+1.07) = –0.53 V < 0 (energetically not feasible).

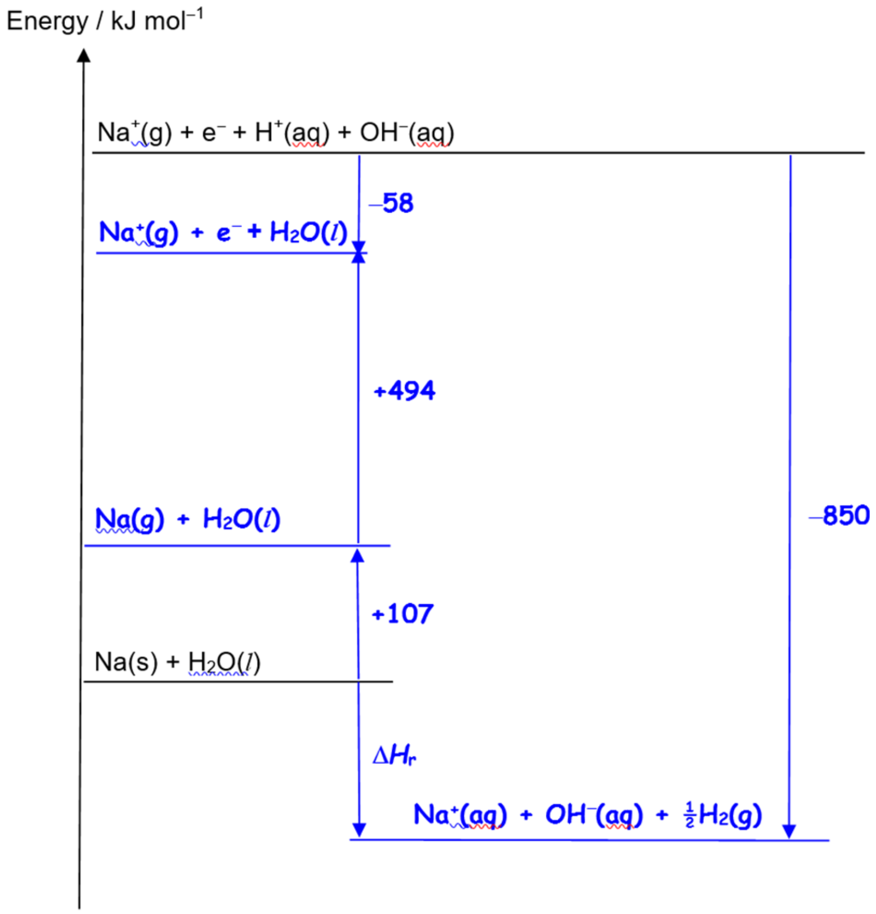
OR

$E^{\ominus}(Cl_2/Cl^-) > E^{\ominus}(Br_2/Br^-)$ so Cl_2 is a stronger oxidising agent than Br_2 and thus can oxidise Br^- to Br_2.

OR

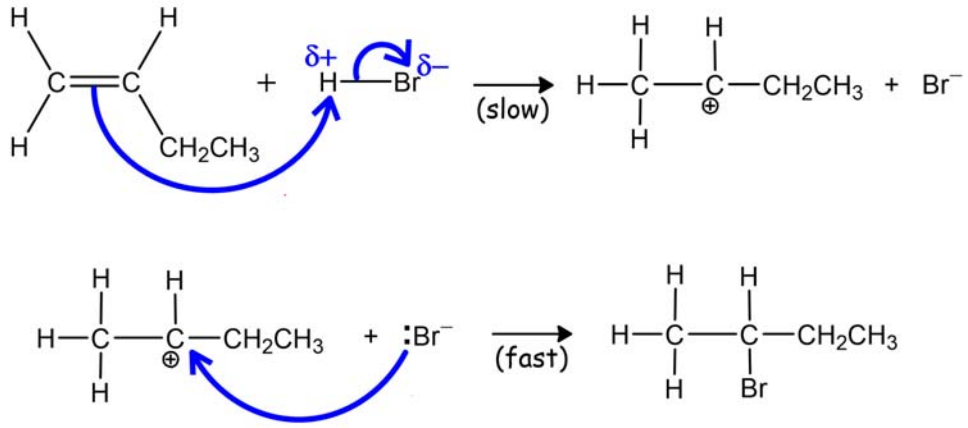
$E^{\ominus}(Br_2/Br^-) > E^{\ominus}(I_2/I^-)$ so I_2 is a weaker oxidising agent than Br_2 and thus cannot oxidise Br^- to Br_2.

(c)



$\Delta H_r = (+107) + (+494) - (-58) + (-850) = -191\ \text{kJ mol}^{-1}$

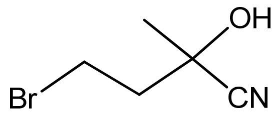
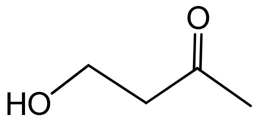
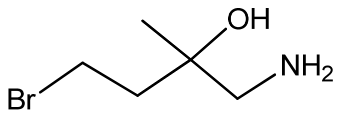
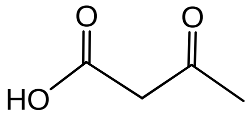
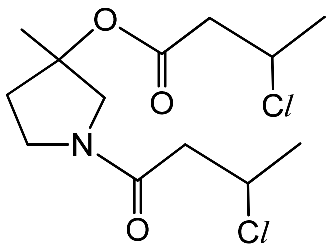
5 **(a)** **(i)** Name of mechanism: electrophilic addition



(ii) In the first step, secondary carbocation, $^+CH(CH_3)CH_2CH_3$, (which yields 2-bromobutane) is more stable and thus more readily formed than primary carbocation, $^+CH_2CH_2CH_2CH_3$, (which yields 1-bromobutane) as it has one more electron-donating alkyl group which disperses its positive charge more.

(iii) There is equal probability for Br^- to attack either side of the trigonal planar C^+ of carbocation in step 2, forming a racemic mixture.

(b) **(i)**

J: 	**L:** 
K: 	**M**: 
N: 	

(ii) reaction 1: HCN, trace amount of KCN/NaCN

reaction 2: $LiAlH_4$, dry ether OR H_2, Ni, heat

reaction 4: aqueous NaOH/KOH, heat

reaction 5: acidified $K_2Cr_2O_7$/$KMnO_4$, heat

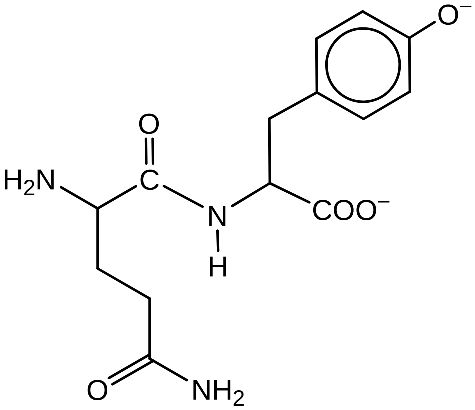
reaction 6: $NaBH_4$, methanol OR H_2, Ni, heat

(iii) reaction 7: nucleophilic substitution

reaction 8: condensation

6 **(a)** $M_r = 146 + 155 + 131 + 105 + 181 - (4 \times 18.0) = 646$

(b) **(i)**



(ii) spot **P**: tyr

Tyrosine has a charge of 2– at pH = 12 and a smaller mass/M_r than gln-tyr. It has the highest $\frac{\text{charge}}{\text{mass}}$ ratio compared to the other two species so it moves the fastest and thus furthest from original position.

(iii) Charge of gln-tyr is twice that of gln and its mass/Mr of is about twice that of gln.

OR

gln and gln-tyr have similar $\frac{\text{charge}}{\text{mass}}$ ratios ($\frac{\text{charge}}{\text{mass}}$ of gln is $\frac{1}{146} = 0.00685$ whereas $\frac{\text{charge}}{\text{mass}}$ of gln-tyr is $\frac{2}{309} = 0.00647$).

(c) test: Br_2(aq)

observations: Tyr decolourises orange Br_2(aq) and forms a white precipitate while gln will not.

OR

test: neutral $FeCl_3$(aq)

observations: Tyr will give a violet colouration while glu will not.

OR

test: NaOH(aq), heat

observations: Gln will give NH_3 gas which turns damp red litmus paper blue while tyr will not.

(d) **(i)** sp^2

(ii) N_b can act as a Bronsted base.

This is because the lone pair of electron on N_a is in an unhybridised p orbital which is parallel to the adjacent π electron systems so it is delocalised into C=C and C=N_b due to p-p orbital overlap. Hence, the lone pair of electrons is not available for protonation.

However, the lone pair (of electron) on N_b is in a sp^2 orbital which is on the same plane as the ring (or not parallel to adjacent π electron system) and hence it will not be delocalised into the adjacent C=C. Thus, the lone pair of electron is available for protonation.

JURONG JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION 2018

CANDIDATE NAME			
CLASS	**18S**	EXAM INDEX	

CHEMISTRY **9729/03**

Higher 2

Paper 3 Free Response

11 September 2018
2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and exam index number on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a HB pencil for any diagrams, graphs.
Do not use staples, paper clips, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

The use of an approved scientific calculator is expected, where appropriate.
A *Data Booklet* is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **11** printed pages and **1** blank page.

Section A

Answer **all** the questions in this section.

1 **(a)** Peroxides refer to a class of compounds with an oxygen-oxygen single bond.

Hydrogen peroxide, H_2O_2, is the simplest peroxide. It is commonly used in laboratories for both its oxidising and reducing properties.

Sodium peroxide, Na_2O_2, is prepared by burning sodium in air. This reaction also produces sodium oxide, Na_2O.

Compound	Melting point / °C
hydrogen peroxide, H_2O_2	−11
sodium peroxide, Na_2O_2	675
sodium oxide, Na_2O	920

(i) Draw the ‘dot-and-cross’ diagrams for

- hydrogen peroxide, H_2O_2
- sodium peroxide, Na_2O_2. [2]

(ii) Explain the difference in the melting points between

- sodium peroxide (Na_2O_2) and hydrogen peroxide (H_2O_2)
- sodium peroxide (Na_2O_2) and sodium oxide (Na_2O). [2]

(b) The peroxides of the Group 2 elements, MO_2, decompose on heating to produce a single gas and the solid oxide, MO, only.

(i) Write an equation for the thermal decomposition of strontium peroxide, SrO_2. [1]

(ii) Suggest how the temperature at which thermal decomposition of MO_2 occurs varies down Group 2.

Explain your answer. [3]

1 **(c)** Dicarboxylic acids dissociate in stages.

$$HO_2C(CH_2)_nCO_2H \overset{\text{stage 1}}{\rightleftharpoons} HO_2C(CH_2)_nCO_2^- + H^+ \overset{\text{stage 2}}{\rightleftharpoons} {}^-O_2C(CH_2)_nCO_2^- + 2H^+$$

The pK_a values for stage 1 and stage 2 for some dicarboxylic acids are listed below.

n in $HO_2C(CH_2)_nCO_2H$	pK_a(1) for stage 1	pK_a(2) for stage 2
1	2.83	5.69
2	4.16	5.61
3	4.31	5.41

For comparison, the pK_a value of ethanoic acid, CH_3CO_2H, is 4.76.

(i) With reference to the table given, suggest why the pK_a(1) values

- are all smaller than the pK_a of ethanoic acid,
- become larger as n increases. [3]

(ii) Suggest why all the pK_a(2) values in the table above are larger than the pK_a of ethanoic acid. [1]

(iii) Calculate the pH of a 0.10 mol dm^{-3} solution of $HO_2CCH_2CO_2H$. Ignore the effect of pK_a(2) on the pH. [1]

(iv) Sketch the pH-volume added curve you would expect to obtain when 20 cm^3 of 0.10 mol dm^{-3} NaOH is added to 10 cm^3 of 0.10 mol dm^{-3} $HO_2CCH_2CO_2H$.

Mark clearly the initial pH and the point(s) of maximum buffering capacity. Indicate the volume at equivalence point(s). [3]

(v) The monosodium salts of edible dicarboxylic acids can act as buffers.

Write two equations to show how monosodium butanedioate, $HO_2C(CH_2)_2CO_2Na$, acts as a buffer. [2]

(vi) A solution containing both $HO_2C(CH_2)_2CO_2Na$ and $NaO_2C(CH_2)_2CO_2Na$ forms a buffer solution. The following equilibrium is present in the solution.

$$HO_2C(CH_2)_2CO_2^-(aq) \rightleftharpoons {}^-O_2C(CH_2)_2CO_2^-(aq) + H^+(aq)$$

By choosing the correct pK_a value given in the table, calculate the pH of a buffer solution made by mixing 100 cm^3 of 0.5 mol dm^{-3} $HO_2C(CH_2)_2CO_2Na$ and 50 cm^3 of 0.3 mol dm^{-3} $NaO_2C(CH_2)_2CO_2Na$. [2]

[Total: 20]

2 Sulfur is the second member of Group 16 in the Periodic Table.

(a) Explain why sulfur has a lower first ionisation energy than phosphorus. [1]

(b) Natural gas, consisting primarily of methane, is available in large amounts and is used as a fuel. However, direct conversion of alkanes such as methane into useful products is challenging owing to their unreactivity.

(i) Give a reason why alkanes are unreactive. [1]

In 2013, scientists discovered that they could selectively convert methane to alkenes using gaseous sulfur, S_2, over a suitable catalyst. This conversion takes place at over 1000 K, where sulfur exists as S_2(g), as shown in **reaction 1**.

(ii) **reaction 1** $2CH_4(g) + S_2(g) \rightarrow C_2H_4(g) + 2H_2S(g)$

Calculate the enthalpy change of **reaction 1** by drawing an energy cycle using the following information.

$CH_4(g) + 2S_2(g) \rightarrow CS_2(g) + 2H_2S(g)$ $\Delta H_r^{\circ} = +96.0\ \text{kJ mol}^{-1}$

$C_2H_4(g) + 3S_2(g) \rightarrow 2CS_2(g) + 2H_2S(g)$ $\Delta H_r^{\circ} = +91.0\ \text{kJ mol}^{-1}$ [2]

(c) The key stage in the manufacture of sulfuric acid is the reaction between sulfur dioxide and oxygen over a catalyst.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

(i) When an equimolar mixture of SO_2 and O_2 is passed over a catalyst at T °C at an initial total pressure of 200 kPa, the percentage conversion of SO_2(g) is 98%.

Calculate the equilibrium partial pressure of each of the three gases and hence, the value of K_p at temperature T °C. [3]

(ii) The table below shows values of K_p for this equilibrium at different temperatures.

temperature / °C	K_p / kPa^{-1}
25	4.0×10^{22}
200	2.5×10^{8}
800	1.3×10^{-3}

Using relevant data from the given table, explain in terms of the position of equilibrium,

- the sign of ΔG° at 25 °C and
- the sign of ΔH for the forward reaction. [4]

2 **(d)** **(i)** Which of the two gases, SO_2 and O_2, is less ideal? Explain your answer. [1]

(ii) Sketch a graph of volume (V) against temperature (T/ K) for a given mass of an ideal gas at constant pressure. [1]

(e) In the atmosphere, the oxidation of SO_2 to SO_3 can be catalysed by NO_2.

The mechanism for this catalysed oxidation of SO_2 to SO_3 occurs in two steps.

$$\textit{step 1}: \ NO_2(g) + SO_2(g) \xrightarrow{\textit{slow}} NO(g) + SO_3(g) \qquad \Delta H_{1'} = -88 \text{ kJ mol}^{-1}$$

$$\textit{step } 2: \ NO(g) + \frac{1}{2}O_2(g) \xrightarrow{\textit{fast}} NO_2(g) \qquad \Delta H_{2'} = -57 \text{ kJ mol}^{-1}$$

Use this information to construct a fully-labelled reaction pathway diagram for the catalysed oxidation of SO_2 to SO_3. Indicate on your diagram, the 'reactants', 'products', $\Delta H_{1'}$, $\Delta H_{2'}$ and the activation energy, E_a, of the reaction. [3]

(f) Oxides of nitrogen are also used in other applications.

One such oxide is N_2O_5, which exists as $[NO_2^+][NO_3^-]$ in solution.

When benzene is added to a solution of N_2O_5 in CCl_4, an excellent yield of nitrobenzene is obtained in the absence of any added catalyst.

(i) Write a balanced equation for the reaction of benzene and N_2O_5. [1]

(ii) Suggest a mechanism for this reaction, showing all charges and using curly arrows to show the movement of electron pairs. [2]

(iii) Compounds **H** has the molecular formula, C_9H_{12}. Mononitration of **H** produces only one organic product. Suggest the structure of **H**. [1]

[Total: 20]

3 **(a)** Copper has the highest electrical conductivity rating among the non-precious metals. The high conductivity of copper is a consequence of its electronic configuration.

(i) State the electronic configuration of Cu atom. [1]

(ii) Explain why copper is regarded as a *transition element*. [1]

(iii) Suggest why copper is **not** usually used for overhead electrical cables despite its superior conductivity. [1]

(b) Electrical wiring is the most important market for the copper industry. To be used in wiring, copper must be at least 99.9% pure. Chalcopyrite, $CuFeS_2$, is the most common copper ore being used to obtain pure copper in a two-step process.

The first step occurs in a furnace where chalcopyrite is heated strongly with silica, SiO_2, and air. The furnace reduces the copper(II) in chalcopyrite to copper.

The reaction occurring in the blast furnace can be represented by the following **unbalanced** equation.

$$CuFeS_2 + SiO_2 + O_2 \rightarrow Cu + FeSiO_3 + SO_2$$

The copper obtained is nowhere near 99.9% pure as it contains nickel and silver as minor impurities to form an alloy.

The second step occurs in an electrolytic cell where the alloy undergoes electrolysis to produce copper at or above 99.9% purity.

(i) Identify the element that undergoes oxidation in the furnace and state the initial and final oxidation numbers of this element. [1]

(ii) In the furnace, the element O is reduced alongside with the element Cu. Using oxidation numbers or otherwise, write a **balanced** equation for the reaction occurring in the furnace. [1]

(iii) Draw a fully labelled diagram of the electrolytic cell where copper purification occurs. [2]

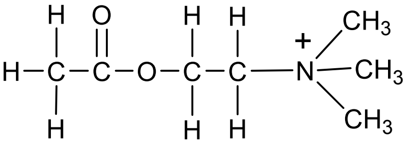
(iv) Explain, by quoting relevant $E^{\ominus}$ values, what happens to the nickel and silver impurities during this purification procedure. [4]

(c) When dilute aqueous ammonia was added to copper(II) sulfate solution, a pale blue precipitate was first observed which dissolved to give a dark blue solution when aqueous ammonia was added in excess. In these reactions, the ammonia can act as a *Bronsted-Lowry base* and as a *Lewis base*.

Illustrate the meaning of *Bronsted-Lowry base* and *Lewis base* using the reactions of aqueous copper(II) ions with ammonia. Write equations to account for the observations noted in these reactions. [4]

3 **(d)** In 2013, scientists suggested that too much copper in our diet may contribute to Alzheimer's disease, a neurological disorder in which death of brain cells causes memory loss and cognitive decline. In patients with Alzheimer's disease, the concentration of acetylcholine, a neurotransmitter essential for processing memory and learning, is found to be lower.

The structure of acetylcholine is shown below.

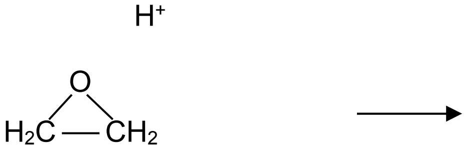


When acetylcholine undergoes hydrolysis in the presence of an enzyme, two products are formed; one of which is a charged species called choline.

(i) Draw the structures of these **two** products. [2]

(ii) As a precursor to the synthesis of acetylcholine, choline is an essential nutrient in our diet. Choline can be produced in a sealed reaction vessel by the reaction of anhydrous trimethylamine, $N(CH_3)_3$, with epoxyethane and HC*l* under moderate pressure.

Copy and complete the diagram below to suggest a mechanism to show how choline is formed. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows.



epoxyethane

[3]

[Total: 20]

Section B

Answer **one** question from this section.

4 **(a)** Thionyl chloride, $SOCl_2$, is a colourless liquid that is primarily used in the chlorination of organic compounds.

(i) Draw the shape of $SOCl_2$. [1]

(ii) Explain which molecule, $SOCl_2$ or $COCl_2$, is expected to have a larger bond angle. [1]

(b) When $SOCl_2$ is reacted with a carboxylic acid to produce an acyl chloride, two acidic gases are formed.

$$SOCl_2(l) + RCO_2H \rightarrow RCOCl + SO_2(g) + HCl(g)$$

A 1.00 g sample of a carboxylic acid RCO_2H was treated in this way, and the gases were absorbed in 60.0 cm^3 of 0.500 mol dm^{-3} NaOH(aq). The excess NaOH was titrated with 0.500 mol dm^{-3} HCl(aq). It required 10.8 cm^3 of the HCl(aq) solution to reach the end-point.

(i) Write equations for the complete reactions between

- NaOH and HCl,
- NaOH and SO_2. [2]

(ii) Calculate the total number of moles of NaOH that reacted with the acidic gases, SO_2 and HCl. [1]

(iii) Calculate the number of moles of RCO_2H that produced the SO_2 and HCl. [1]

(iv) Hence calculate the M_r of the carboxylic acid, RCO_2H. [1]

(v) The R group contains carbon and hydrogen only.

Suggest the structure of RCO_2H. [1]

(c) Using $SOCl_2$ in the initial step, carboxylic acids can be converted into primary amines by the following sequence of reactions.

$$RCO_2H \xrightarrow[\text{step 1}]{SOCl_2} RCOCl \xrightarrow[\text{step 2}]{} \mathbf{D} \xrightarrow[\text{step 3}]{} RCH_2NH_2$$

(i) Identify the structure of **D**. [1]

(ii) Suggest the reagents needed for step 2 and step 3. [2]

(iii) State the *types of reaction* for step 2 and step 3. [1]

4 **(d)** Angelic acid, $C_5H_8O_2$, is a natural product isolated from the roots of the angelica plant.

- Angelic acid reacts with H_2 + Ni to form **T**, $C_5H_{10}O_2$.
- Both angelic acid and **T** exhibit stereoisomerism.
- On treatment with hot acidic $KMnO_4$, angelic acid produces two acidic compounds, **U** and **V**.
- Only **U** gives yellow precipitate with alkaline aqueous iodine.

(i) Suggest structures for **T**, **U**, **V** and angelic acid. Explain the reactions. [6]

(ii) State the types of stereoisomerism shown by angelic acid and compound **T**. [2]

[Total: 20]

5 **(a)** **(i)** Describe the reaction of $SiCl_4$ with water and include any observations you can make. Write an equation for the reaction that occurs. [2]

(ii) Carbon is in the same group as silicon. However, CCl_4 does not react with water. Explain why. [1]

(b) Chlorine-containing organic compounds can also differ in their reactivity towards hydrolysis reactions.

Compounds **A** and **B** are isomers with the molecular formula, C_7H_7Cl. Compound **A** reacts with aqueous NaOH on heating but compound **B** does not.

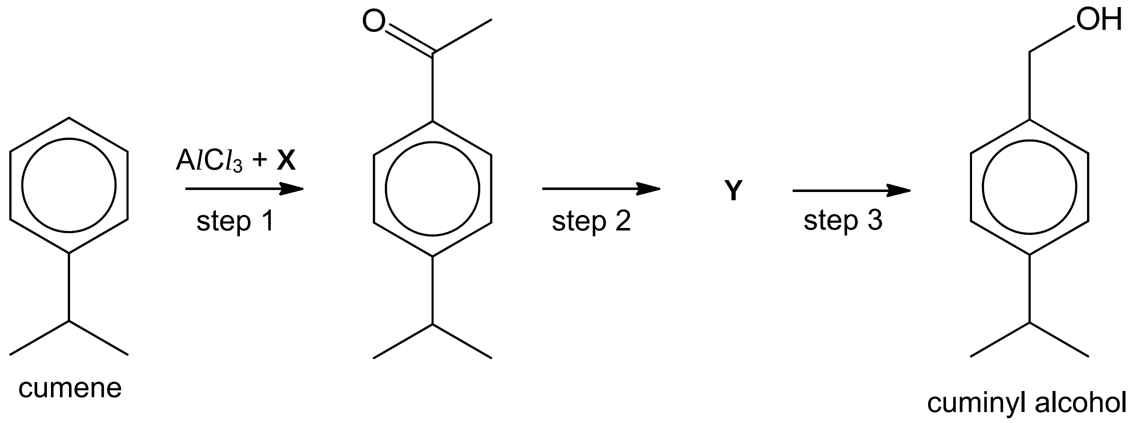
Draw the structures of compounds **A** and **B** and explain the difference in their reactivity towards aqueous NaOH. [2]

(c) Heating tin with hydrochloric acid produces hydrogen gas. Careful removal of water from the resulting product produces white solid $SnCl_2$.

In contrast, passing chlorine gas over heated tin produces colourless liquid $SnCl_4$ as the only product.

Using relevant $E^{\ominus}$ from the *Data Booklet*, explain the above observations. [2]

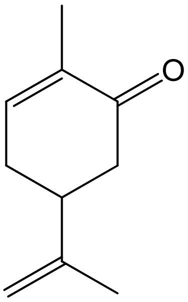
(d) Cumin is a spice used to flavour food. One of the key organic compounds responsible for the smell of cumin is cuminyl alcohol. It can be synthesised from cumene as shown below. Aluminium chloride is used as a catalyst with reagent **X** in step 1.



(i) Suggest the identity of reagent **X**. [1]

(ii) Suggest reagents and conditions for steps 2 and 3 and draw the structure of the intermediate compound **Y**. [3]

5 **(e)** Carvone, an isomer of cuminyl alcohol, is most responsible for the flavour of caraway, dill and spearmint.



carvone

(i) When carvone is treated with $NaBH_4$, compound **M**, $C_{10}H_{16}O$, is produced. Draw the structure of **M** and write an equation to represent this reaction. [2]

(ii) Compound **N** is isomeric with compound **M**.

On treatment with hot concentrated $KMnO_4$, **N** gives two compounds, **P**, C_3H_6O, and **Q**, $C_4H_4O_5$. **P** and **Q** are formed in the mole ratio of 2 : 1.

All three compounds, **N**, **P** and **Q** give an orange precipitate with 2,4-dinitrophenylhydrazine but only **N** forms a silver mirror with Tollens' reagent. One mole of **Q** reacts with two moles of aqueous sodium hydrogencarbonate.

Suggest structures for **N**, **P** and **Q** and explain the observations described above. [7]

[Total: 20]

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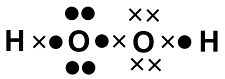
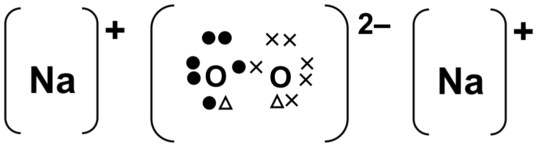
Suggested Answers for 2018 H2 Chemistry Preliminary Examination Paper 3

1 **(a)** **(i)** H_2O_2 :



[1m]

Na_2O_2 :



Accept:
1) 2 $[Na]^+$
Reject:
1) $[Na]_2^+$
2) electrons are drawn around Na^+

[1m]

(ii) Sodium peroxide has a giant ionic structure while hydrogen peroxide has a simple molecular structure.

More energy is needed to overcome the **strong ionic bonds between Na^+ and O_2^{2-}/oppositely charged ions** (✓)

compared to the **weak intermolecular force in H_2O_2/ hydrogen bonds between H_2O_2 molecules**. (✓)

Hence, sodium peroxide has a higher boiling point than hydrogen peroxide.

Both sodium peroxide and sodium oxide have a giant ionic structure.

While O_2^{2-} and O^{2-} have the same ionic charge, **O_2^{2-}** has a **larger radius/ bigger size than O^{2-}** (✓).

Less energy is needed to overcome the **weaker ionic bonds between Na^+ and O_2^{2-} than that between Na^+ and O^{2-}** . (✓)

Hence, sodium peroxide has a lower boiling point than sodium oxide.

4(✓) : **[2m]** ; 2-3(✓) : **[1m]**

Minus 1m if no comparison of the strength of bonds is made.

(b) **(i)** $SrO_2 \rightarrow SrO + \frac{1}{2} O_2$ or $2SrO_2 \rightarrow 2SrO + O_2$ **[1m]**

(ii) Down the Group, **decomposition temperature increases**. **[1m]**

Down the Group,

① **radius of M^{2+}/cation increases**
② **charge density** of M^{2+} **decreases**
[1m]

③ **polarising power** of M^{2+} **decreases** / **polarisation of O_2^{2-} anion occurs to smaller extent**
④ **less weakening of O–O bond**
⑤ MO_2 becomes **thermally more stable**, higher temperature is needed to decompose.
[1m]

1 (c) (i) pK_a(1) values are all smaller than the pK_a of ethanoic acid

[1m] smaller pK_a implies larger K_a, indicating **dicarboxylic acids are more acidic/ stronger acids** than ethanoic acid

[1m] **–CO_2H group is electron-withdrawing**, **disperse the negative charge** and **stabilise** mono**anion**/ $HO_2C(CH_2)_nCO_2^-$

Or mono**anion**/ $HO_2C(CH_2)_nCO_2^-$ is **stabilised by hydrogen bonding** (especially for malonic acid when n=1)

pK_a(1) values become larger as n increases

[1m] electron-withdrawing **–CO_2H group** is **further away from –CO_2^- / ionising –CO_2H / the other –CO_2H group**

Or intervening **additional electron-donating alkyl groups destabilise anion**

(ii) larger pK_a implies smaller K_a with $HO_2C(CH_2)_nCO_2^-$ being a weaker acid than CH_3CO_2H; it is **more difficult to remove** a positively charged **H^+ from a negatively charged** species/ mono**anion** (electrostatically not favourable) [1m]

(iii) $[H^+] = \sqrt{K_a \times c}$

$= \sqrt{10^{-2.83} \times 0.10}$

$= \mathbf{0.0122\ mol\ dm^{-3}}$

pH = $-\lg [H^+]$ = **1.92** [1m]

(iv)

The following should be clearly marked and labelled:

(✓) Both axes are labelled with units stated for x-axis.

(✓) Curve starts at pH 1.92 (ecf)

(✓) First maximum buffering capacity at 5 cm^3 and pH 2.83.

(✓) Second maximum buffering capacity at 15 cm^3 and pH 5.69.

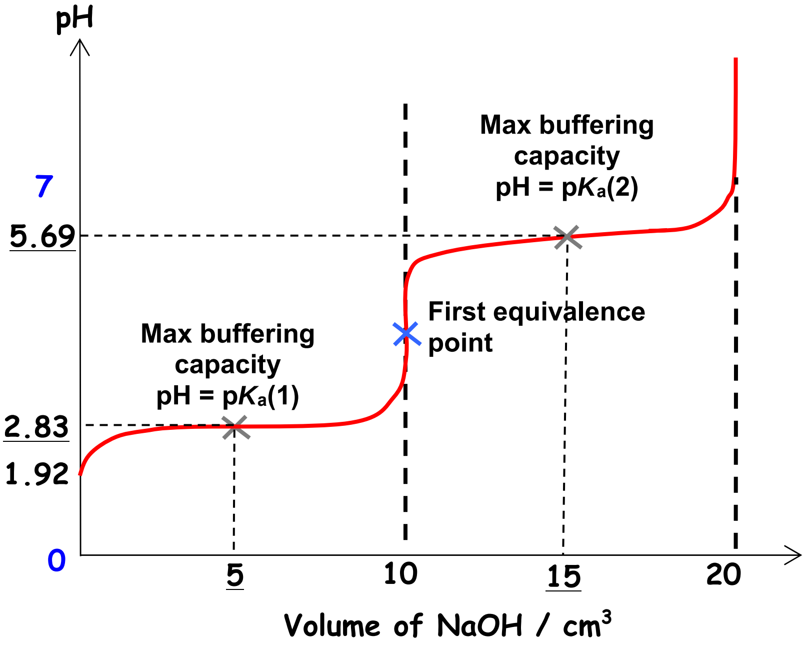
(✓) First equivalence point at 10 cm^3 and graph ends at 20 cm^3

(✓) 2 points of inflection

6(✓) – [3m]

4–5(✓) – [2m]

2–3(✓) – [1m]



(v) [1m] $HO_2C(CH_2)_2CO_2Na + H^+ \rightarrow HO_2C(CH_2)_2CO_2H + Na^+$

[1m] $HO_2C(CH_2)_2CO_2Na + OH^- \rightarrow {}^-O_2C(CH_2)_2CO_2Na + H_2O$

allow ionic eqns; reject =

1 (c) (vi) System: <u>Acidic Buffer</u>

$$pH = pK_a + \lg\frac{[salt]}{[acid]} = pK_a + \lg\frac{n(salt)}{n(acid)}$$

$$= 5.61 + \lg\left(\frac{\frac{50}{1000}\times 0.3}{\frac{100}{1000}\times 0.5}\right)$$

$$= \underline{5.09}$$

[1m] quote the correct pK_a (5.61) in working
[1m] pH calculation (ecf from wrong pK_a)

2 (a) Inter-electronic **<u>repulsion between paired 3p</u>** **<u>electrons</u>** makes it **<u>easier to remove one of the paired</u>** 3p **<u>electrons</u>** than to remove the unpaired 3p electron from phosphorus. [1m]

(b) (i) [1m] Either one of the following:

<u>Very strong</u> C–C and C–H <u>bonds</u> / **<u>high bond energies</u>**

<u>Non-polar</u> / **<u>C and H have similar electronegativities</u>**

(ii)

$$\begin{tikzcd}
2CH_4(g) + S_2(g) \arrow[rr] \arrow[dr, "+3S_2(g)"', "+2(96.0)"] & & C_2H_4(g) + 2H_2S(g) \arrow[dl, "+91.0"', "+3S_2(g)"] \\
& 2CS_2(g) + 4H_2S(g) &
\end{tikzcd}$$

[1m] energy cycle

ΔH for reaction 1 = +2(96.0) – 91.0 = +**<u>101 kJ mol^{-1}</u>** [1m]

(c) (i)

	$2SO_2(g)$	+ $O_2(g)$ =	$2SO_3(g)$	
initial partial pressure /kPa	100	100	0	
	−0.98(100)	**−½(98)**		
eqm partial pressure /**<u>kPa</u>**	**2** (✓)	**51** (✓)	**98** (✓)	2 (✓): [1m] 3(✓): [2m]

$$K_p = \frac{(P_{SO_3})^2}{(P_{SO_2})^2(P_{O_2})} = \frac{(98)^2}{(2)^2(51)}$$

$$= \underline{\mathbf{47.1}}\ \text{kPa}^{-1}$$ [1m]

(ii) Since **<u>K_p at 25 °C</u>** is much **<u>larger than 1</u>**, the **<u>position of equilibrium</u>** in $2SO_2(g) + O_2(g) = 2SO_3(g)$ **<u>lies</u>** very much **<u>to the right</u>** [1m], so the **<u>forward reaction is spontaneous</u>** and **<u>$\Delta G^{\ominus}$ is negative</u>**. [1m]

As **<u>K_p decreases with increasing temperature</u>**, it implies that the **<u>position of equilibrium shifts to the left</u>** [1m] with increasing temperature to absorb some heat. Hence, the backward reaction is endothermic and the **<u>forward reaction is exothermic</u>**, so **<u>ΔH has a negative sign</u>**. [1m]

2 (d) (i) **SO_2** is less ideal.

Either:

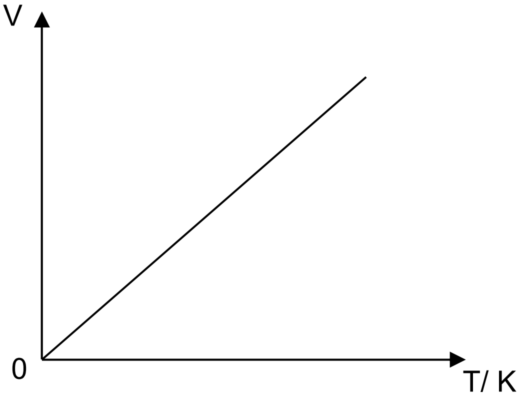
SO_2 has stronger intermolecular forces of attraction between its molecules as it is a **polar molecule / has greater number of electrons per molecule**.

OR

SO_2 is a **larger molecule** than O_2, so the **volume of SO_2 molecules is less negligible compared to the volume of the container/gas**.

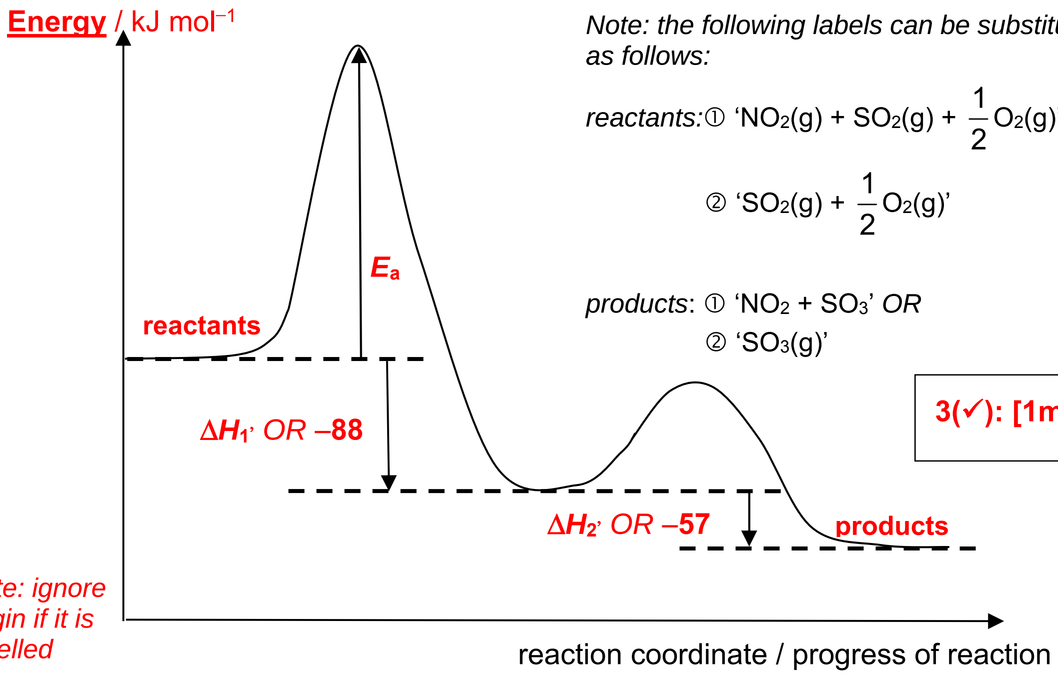
[1m]

(ii)



[1m]

(e)



Note: the following labels can be substituted as follows:

reactants: ① '$NO_2(g) + SO_2(g) + \frac{1}{2}O_2(g)$' *OR*

② '$SO_2(g) + \frac{1}{2}O_2(g)$'

products: ① '$NO_2 + SO_3$' *OR*

② '$SO_3(g)$'

3(✓): [1m]

Note: ignore origin if it is labelled

(✓): *2 humps.*

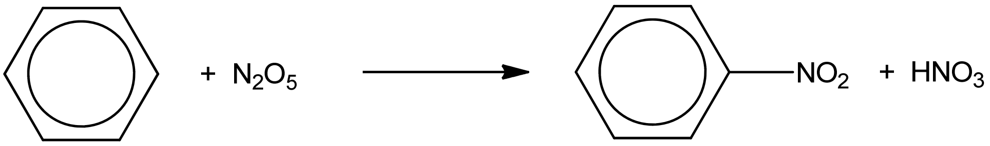
(✓): *label 'reactants', 'products' OR using appropriate formulae (with balanced species)*

(✓): *label y-axis. Ignore x-axis label. Reject if reactants are labelled at '0' level*

[1m] : *Both $\Delta H_{1'}$ and $\Delta H_{2'}$ shown. Ignore direction of arrows.*

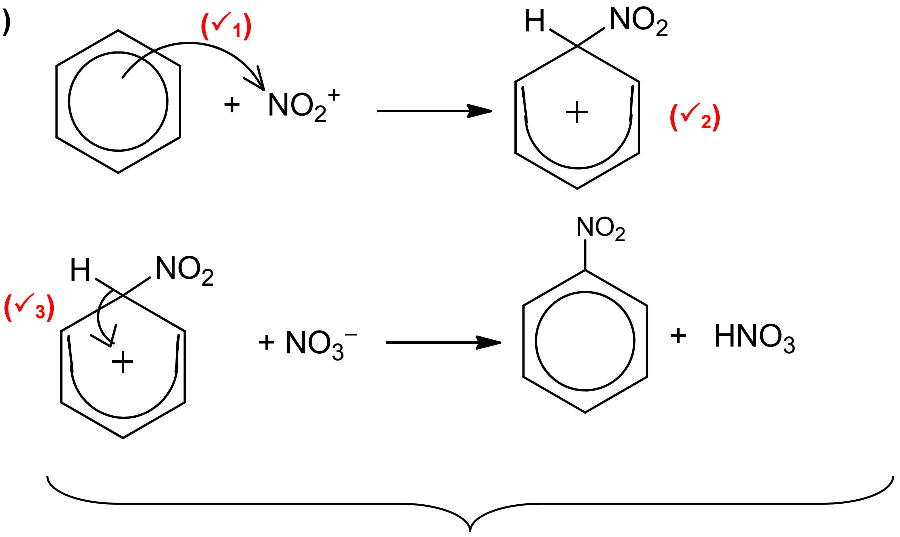
[1m] : *correct labelling of E_a, with $E_{a1} > E_{a2}$. Ignore direction of arrows.*

2 **(f)** **(i)**



[1m]

(ii)



(✓4): correct products and balanced equation

(✓1) – *full arrow from π–electron ring of benzene to the N atom of* NO_2^+.

(✓2) – *correct arenium ion with delocalisation of positive charge over the other 5 carbons.*

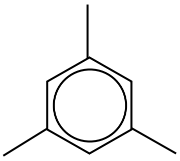
(✓3) – *full arrow from C–H bond to the (+)ve charge of arenium ion*

(✓4) – *correct products formed with* ***balanced equation*** *with* HNO_3 *as the other product*

Note: *Labelling of* ***"slow/fast"*** *step is* ***not*** *required.*

4(✓): [2m]; 2–3(✓): [1m]

(iii) Structure of **H**:



[1m]

3 (a) (i) Cu: **$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$** [1m]

(**not $3d^9\ 4s^2$** due to the extra stability of $3d^{10}$ and the similar energies of 3d and 4s electron)

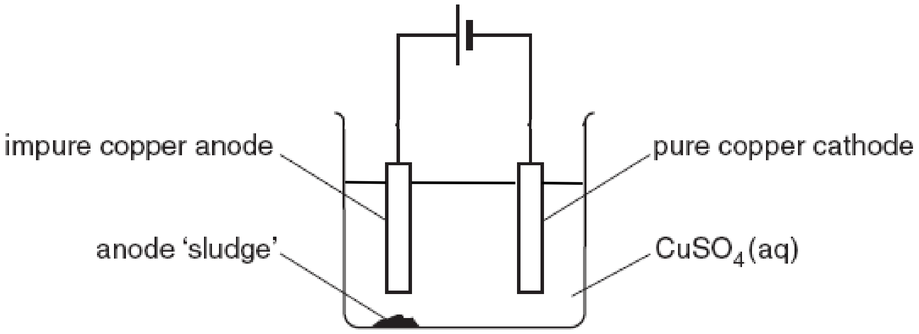
(ii) Copper is a **d-block element** that **forms** one or more **stable ions with incompletely filled d-orbitals**. [1m]

(iii) Copper has **high density/** is **too heavy** for overhead use. [1m]

(b) (i) **S** is oxidised from **–2 to +4** [1m]

(ii) $\underline{2}\,CuFeS_2 + \underline{2}\,SiO_2 + \underline{5}\,O_2 \rightarrow \underline{2}\,Cu + \underline{2}\,FeSiO_3 + \underline{4}\,SO_2$ [1m]

(iii)



[1m] these labels on the diagram: **impure copper, pure copper, $CuSO_4$(aq)**

[1m] battery with 2 electrodes dipped in a common electrolyte;
battery must show the correct polarity with respect to the impure copper.

(iv) species present:

Cu^{2+}(aq), SO_4^{2-}(aq), $H_2O(l)$, impure Cu (anode) and impurities such as Ag, Ni

$O_2 + 4H^+ + 4e^- \;=\; \mathbf{2H_2O}$ $E^\ominus = +1.23$ V
$Cu^{2+} + 2e^- \;=\; \mathbf{Cu}$ $E^\ominus = +0.34$ V
$Ni^{2+} + 2e^- \;=\; \mathbf{Ni}$ $E^\ominus = -0.25$ V
$Ag^+ + e^- \;=\; \mathbf{Ag}$ $E^\ominus = +0.80$ V

Note:
The species is more easily oxidised when the $E^\ominus$ is more negative (*or* less positive).

[1m] **quote $E^\ominus$ values for Cu^{2+}/Cu, Ni^{2+}/Ni and Ag^+/Ag**

At the **anode**,
Cu(s) is oxidised to Cu^{2+}(aq) in preference over H_2O as $E^\ominus(Cu^{2+}/Cu)$ is more negative than $E^\ominus(O_2/H_2O)$.
Ni(s) is also **oxidised to Ni^{2+}**(aq) (which goes into the solution) as **$E^\ominus(Ni^{2+}/Ni)$ is more negative than $E^\ominus(Cu^{2+}/Cu)$**. [1m]
Ag(s) **is not oxidised** to Ag^+ as **$E^\ominus(Ag^+/Ag)$ is more positive than $E^\ominus(Cu^{2+}/Cu)$**.
∴ **Ag**(s) **is collected as "anode sludge"**. [1m]

$\mathbf{2H_2O} + 2e^- \;=\; H_2 + 2OH^-$ $E^\ominus = -0.83$V
$\mathbf{Cu^{2+}} + 2e^- \;=\; Cu$ $E^\ominus = +0.34$ V
$\mathbf{Ni^{2+}} + 2e^- \;=\; Ni$ $E^\ominus = -0.25$ V

Note:
The species is more easily reduced when the $E^\ominus$ is more positive (*or* less negative).

At the **cathode**,
Cu^{2+}(aq) is reduced to Cu(s) in preference over H_2O as $E^\ominus(Cu^{2+}/Cu)$ is more positive than $E^\ominus(H_2O/H_2)$.

Ni^{2+}(aq) **is not reduced** to Ni(s) **as $E^\ominus(Ni^{2+}/Ni)$ is more negative than $E^\ominus(Cu^{2+}/Cu)$**.
∴ **Ni^{2+}**(aq) **remains in the solution**. [1m]

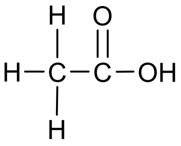
3 **(c)** [1m] ***Bronsted-Lowry base*** is a **proton/H$^+$ acceptor** as illustrated by **NH$_3$ accepting a proton/H$^+$ from H$_2$O to form OH$^-$**.
Or $NH_3(aq) + H_2O(l) = NH_4^+(aq) + OH^-(aq)$

[1m] $Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s)$
pale blue soln → pale blue ppt

[1m] $Cu(OH)_2(s) + 4NH_3(aq) + 2H_2O(l) \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 2OH^-(aq)$
Or $[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$
dark blue soln

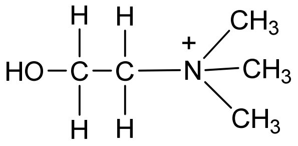
When added in excess, NH$_3$ acts as a *Lewis base* where N in NH$_3$ ligand **donates a lone pair** of electrons **to Cu^{2+}**, forming strong dative bonds with Cu^{2+} to give the stable $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex. [1m]

(d) **(i)**



CH_3COOH

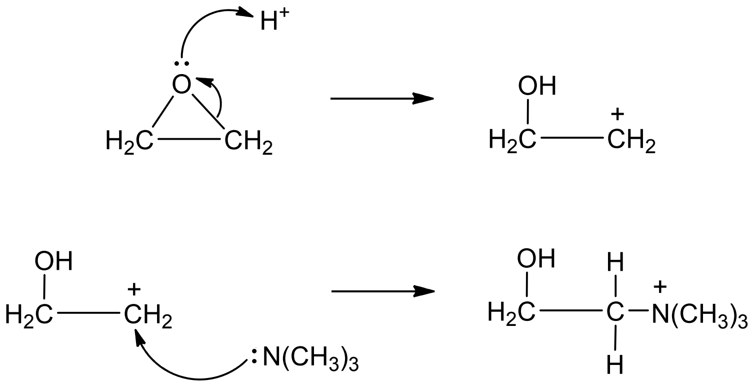
[1m] and



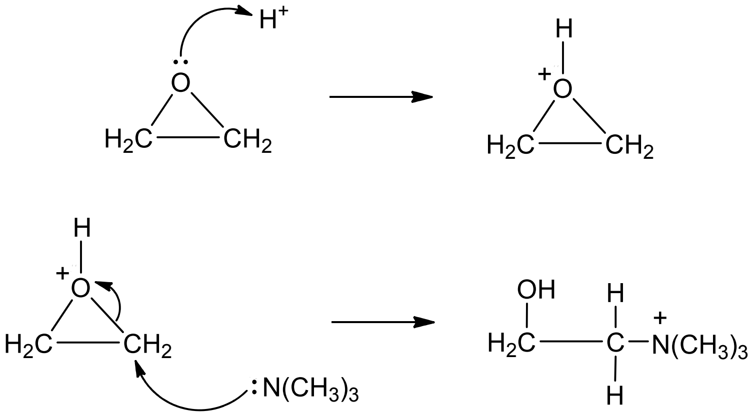
$HOCH_2CH_2N^+(CH_3)_3$

[1m]

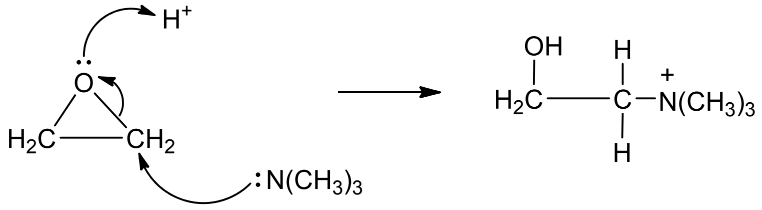
(ii) **Option 1**:



Option 2:

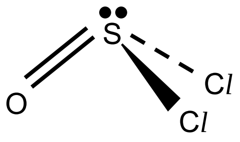


Option 3:

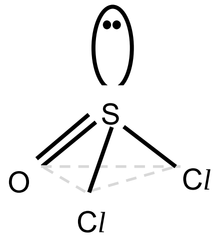


[1m] for each curly arrow with the associated lone pair and any positive charge

4 **(a)** **(i)**



or



[1m] illustrate trigonal pyramidal shape.

(ii) **$COCl_2$** will have a larger bond angle. **[1m] bonus**

$COCl_2$ has lesser number/ 3 sets of **electron pairs** (or state **3 bp, 0 lp**) which can be **further apart to minimise repulsion** compared to **$SOCl_2$** that **has 4 electron pairs** (or state **3 bp, 1 lp**). **[1m]**

(b) **(i)** $NaOH + HCl \rightarrow NaCl + H_2O$ **[1m]**

$2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$ **[1m]**

Allow if 2nd eqn is split into 2 eqns: $SO_2 + H_2O \rightarrow H_2SO_3$
$2NaOH + H_2SO_3 \rightarrow Na_2SO_3 + 2H_2O$

Reject: $NaOH + SO_2 \rightarrow NaHSO_3$ for NaOH is added in excess

(ii)

$$n(NaOH)\ \text{reacted} = \frac{60.0-10.8}{1000}\times 0.500$$

= **0.0246** mol **[1m]**

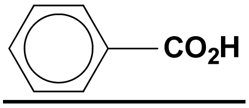
(iii) RCO_2H : $SO_2 + HCl$: NaOH
1 : 1 : 3

$$n(RCO_2H) = \frac{0.0246}{3} = \mathbf{0.00820}\ \text{mol}$$ **[1m]**

(iv) $$M_r\,(RCO_2H) = \frac{1.00}{0.0082} = \mathbf{122}$$ **[1m] no units, 3 s.f., ecf**

(v) RCO_2H: mass units of $-CO_2H$ = 45
mass units of –R = 122 – 45 = 77
estimated number of C in –R = 77/12 = 6.4 (⇒ R contains 6 carbon atoms)

RCO_2H is



[1m]

(c) **(i)** **$RCONH_2$** **[1m]**

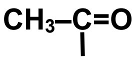
(ii) Step 2: **NH_3**(g) **[1m]** reject (aq)

Step 3: **$LiAlH_4$**, dry ether **[1m]** reject (aq); ignore 'heat'

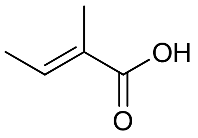
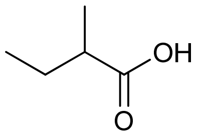
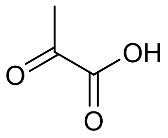
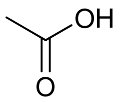
(iii) Step 2: **condensation/ nucleophilic acyl substitution**
Step 3: **reduction**

allow nucleophilic substitution
[1m] each, bonus

4 **(d)** **(i)**

Observation	Type of Reaction	Deduction
Angelic acid + H_2 → **T** $C_5H_8O_2$ $C_5H_{10}O_2$	**reduction** (✓)	**Angelic acid** is an **alkene**. (✓)
Angelic acid + $KMnO_4$ → **U** and **V**	**Oxidative cleavage of C=C** /**oxidation** (✓)	**U** and **V** are **carboxylic acids.** (✓)
U + I_2/OH^- → yellow ppt	**Iodoform test/ oxidation** (✓)	**U** has the structure  $CH_3\text{–}\underset{\vert}{C}\text{=O}$ (✓)

5-6(✓): [2m]; 3-4(✓): [1m]

angelic acid	**T**	**U**	**V**
			

[1m] for each structure

(ii) angelic acid : **cis-trans isomerism** **[1m]**

compound **T** : **enantiomerism** **[1m]**

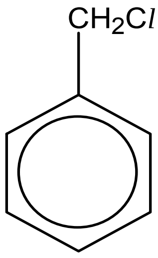
5 **(a)** **(i)** **$SiCl_4$ reacts with water / hydrolyses** completely in water **to give** a strongly **acidic solution**. **[1m] bonus**

A **white solid/ppt** of SiO_2 will be observed/ **white (or steamy) fumes** of HC*l* will be observed. **[1m]**

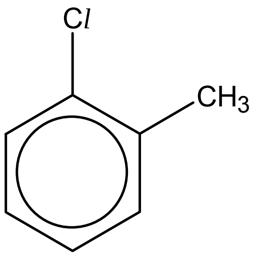
$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$ **[1m]**

(ii) Unlike silicon, **carbon does not have energetically accessible empty 3d orbitals to accept** a lone pair of **electrons from water** molecules. **[1m]**

(b)



A



B (-CH_3 and C*l* groups can be in any position)

[1m] for both structures of **A** and **B**

For compound **B**, **delocalisation of the lone pair** of electrons **on C*l* into the** π-electron cloud of **benzene ring** **imparts double bond character to the C–C*l*, strengthening the C–C*l* bond**. Hence, **B** does not react with NaOH(aq). **[1m]**

5 (c) $2H^+ + 2e^- \rightleftharpoons H_2$ $E^\ominus = 0.00\ V$

$Sn^{2+} + 2e^- \rightleftharpoons Sn$ $E^\ominus = -0.14\ V$

$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$ $E^\ominus = +0.15\ V$

$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ $E^\ominus = +1.36\ V$

Reaction between H^+ and Sn:

$E^\ominus_{cell}$ = 0.00 – (–0.14) = +0.14 V > 0 (reaction is energetically feasible) [1m]

Reaction between H^+ and Sn^{2+}:

$E^\ominus_{cell}$ = 0.00 – (+0.15) = –0.15 V < 0

Oxidation of Sn^{2+} to Sn^{4+} by H^+ is NOT energetically feasible.

Reaction between Cl_2 and Sn:

$E^\ominus_{cell}$ = 1.36 – (–0.14) = +1.50 V > 0

Oxidation of Sn to Sn^{2+} by Cl_2 is energetically feasible. [1m]

Reaction between Cl_2 and Sn^{2+}:

$E^\ominus_{cell}$ = 1.36 – (+0.15) = +1.21 V > 0

Oxidation of Sn^{2+} to Sn^{4+} by Cl_2 is energetically feasible. [1m] bonus

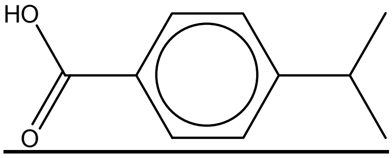
Award max [1m] if three $E^\ominus_{cell}$ values are calculated without any comment.

(d) (i) **CH_3COCl** [1m]

(ii) Step **2**: **alkaline I_2(aq), heat,** followed by H^+(aq) [1m]

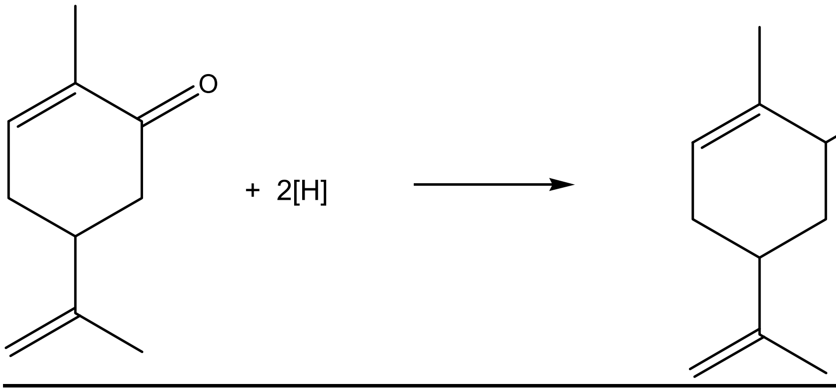
Step **3**: **$LiAlH_4$, dry ether** [1m]

Y:



[1m]

(e) (i)



M [1m]

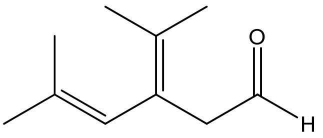
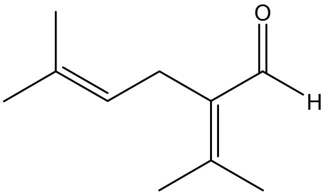
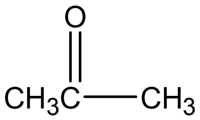
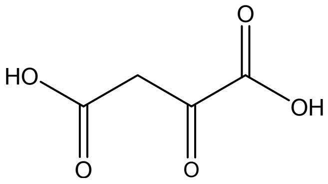
[1m]

5 (e) (ii)

Information from question	Type of reaction	Deduction
N reacts with hot concentrated $KMnO_4$ to give **P** and **Q**	**oxidation** (✓)	**C=C bond in N cleaves** (✓)
N, **P**, **Q** react with 2,4-DNPH	**condensation** (✓)	**N, P and Q contains carbonyl group** / **contains either aldehyde or ketone groups** (✓)
Only **N** gives silver mirror with Tollens' reagent	**oxidation** (✓)	**N contains** aliphatic **aldehyde group** (✓) **P and Q contain ketone group** (✓)
One mole of **Q** reacts with two moles of $NaHCO_3$(aq)	**acid-carbonate reaction** / **acid – hydrogen carbonate reaction** (✓)	**Q contains 2 –CO_2H groups** (✓)

8-9(✓): [4m]
6-7(✓): [3m]
4-5(✓): [2m]
2-3(✓): [1m]

[1m] for each correct structure

 or 	 $CH_3\overset{\overset{O}{\|}}{C}-CH_3$	
N	**P**	**Q**