

**2016 JC2 PRELIMINARY
EXAMINATIONS**

CHEMISTRY
Higher 2
Paper 1 Multiple Choice

9647/01
22 September 2016
1 hour

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.

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

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

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.

Multiple Choice Answer Sheet

Write your name, PDG and NRIC / FIN number, **including** the reference letter.

Shade the NRIC / FIN number.

Exam Title: JC2 Prelim

Exam Details: H2 Chemistry / Paper 1

Date: 22/09/2016

This document consists of **18** printed pages.

Section A

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

- 1 Antimony (Sb) can be produced in a two-stage process from its ore stibnite, Sb_2S_3 .

The ore is first roasted in oxygen, producing Sb_4O_6 and SO_2 .

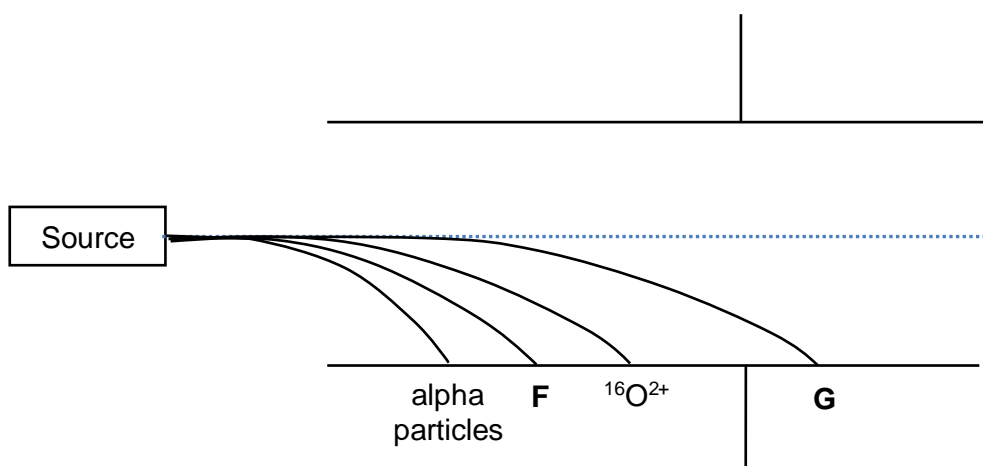
The Sb_4O_6 is then reduced by carbon, producing Sb and CO_2 .

What volume of CO_2 , measured at room temperature and pressure, is produced from 20 moles of Sb_2S_3 ?

- A** 360 dm^3 **B** 670 dm^3 **C** 720 dm^3 **D** 1440 dm^3

- 2 Alpha particles, ${}^4\text{He}^{2+}$, are commonly emitted by large radioactive nuclei.

The path of a mixture of ${}^{16}\text{O}^{2+}$ ions, alpha particles and two unknown ions, **F** and **G**, upon entering an electric field is shown below.



Which of the following represent **F** and **G**?

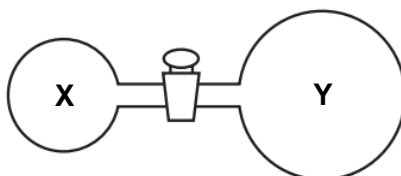
	F	G
A	${}^1\text{H}^+$	${}^9\text{Be}^{2+}$
B	${}^{12}\text{C}^{2+}$	${}^{27}\text{Al}^{3+}$
C	${}^9\text{Be}^{2+}$	${}^{14}\text{N}^{3+}$
D	${}^{12}\text{C}^+$	${}^1\text{H}^+$

- 3 In a research on the atomic nucleus, scientists have been comparing the stability of isotopes with the same neutron : proton ratio.

Which isotope has the same neutron : proton ratio as ^{10}B ?

- A ^{32}P B ^{32}S C ^{40}Ar D ^{40}K

- 4 Two glass vessels **X** and **Y** are connected by a closed valve.



X contains helium at $20\text{ }^{\circ}\text{C}$ at a pressure of $1 \times 10^5\text{ Pa}$. **Y** has been evacuated, and has three times the volume of **X**. In an experiment, the valve is opened and the temperature of the whole apparatus is raised to $100\text{ }^{\circ}\text{C}$.

What is the final pressure in the system?

- A $3.18 \times 10^4\text{ Pa}$
 B $4.24 \times 10^4\text{ Pa}$
 C $1.25 \times 10^5\text{ Pa}$
 D $5.09 \times 10^5\text{ Pa}$
- 5 The interhalogen compound BrF_3 is a volatile liquid which autoionises.



The electrical conductivity of BrF_3 decreases with increasing temperature.

Which statement is correct?

- A The autoionisation process is endothermic and the shape of the cation is linear.
 B The autoionisation process is endothermic and the shape of the cation is non-linear.
 C The autoionisation process is exothermic and the shape of the cation is linear.
 D The autoionisation process is exothermic and the shape of the cation is non-linear.

- 6 In an experiment, it was found that complete combustion of 10.0 g of an alcohol, **J**, raised the temperature of 100 g of water in a container from 25 °C to 75 °C.

Given that the process is only 65% efficient and the specific heat capacity of water is 4.18 J g⁻¹ K⁻¹, what is the total heat energy released per gram of **J** burnt?

- A** 2.09 kJ g⁻¹ **B** 3.22 kJ g⁻¹ **C** 13.5 kJ g⁻¹ **D** 20.8 kJ g⁻¹

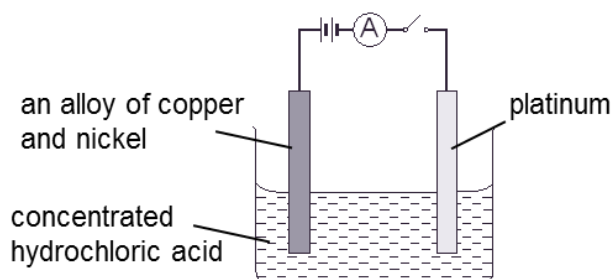
- 7 Limestone is a sedimentary rock largely made up of different crystal forms of calcium carbonate. At high temperatures, calcium carbonate decomposes to form calcium oxide and carbon dioxide.



What are the correct signs of ΔH and ΔS for this decomposition?

	ΔH	ΔS
A	-	-
B	-	+
C	+	-
D	+	+

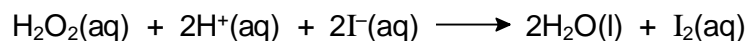
- 8 The circuit shown in the diagram was set up.



Which electrode reactions will occur on closing the switch?

- | | anode reaction | cathode reaction |
|----------|--|-------------------------|
| A | neither nickel nor copper is dissolved | hydrogen is evolved |
| B | copper is dissolved preferentially | copper is deposited |
| C | nickel is dissolved preferentially | hydrogen is evolved |
| D | nickel and copper are both dissolved | copper is deposited |

- 9 The reaction of hydrogen peroxide with iodide ions in acidic solution can be monitored by an initial rate method.



The following results were obtained for a series of experiments with different volumes of each reagent used.

experiment number	volume of $\text{H}_2\text{O}_2(\text{aq}) / \text{cm}^3$	volume of $\text{H}^+(\text{aq}) / \text{cm}^3$	volume of $\text{I}^-(\text{aq}) / \text{cm}^3$	volume of water / cm^3	time taken / s
1	40	40	20	0	33
2	20	40	20	20	66
3	40	20	30	10	22
4	20	40	30	10	44

What could be the mechanism of this reaction?

- A** $\text{H}_2\text{O}_2 + \text{H}^+ \longrightarrow \text{H}_2\text{O} + \text{OH}^+$ (fast)
 $\text{OH}^+ + 2\text{I}^- + \text{H}^+ \longrightarrow \text{H}_2\text{O} + \text{I}_2$ (slow)
- B** $\text{H}_2\text{O}_2 + \text{I}^- \longrightarrow \text{H}_2\text{O} + \text{IO}^-$ (slow)
 $\text{H}^+ + \text{IO}^- \longrightarrow \text{HIO}$ (fast)
 $\text{HIO} + \text{H}^+ + \text{I}^- \longrightarrow \text{I}_2 + \text{H}_2\text{O}$ (fast)
- C** $2\text{H}^+ + 2\text{I}^- \longrightarrow 2\text{HI}$ (fast)
 $2\text{HI} + \text{H}_2\text{O}_2 \longrightarrow \text{I}_2 + 2\text{H}_2\text{O}$ (slow)
- D** $\text{H}_2\text{O}_2 + \text{I}^- + \text{H}^+ \longrightarrow \text{H}_2\text{O} + \text{HIO}$ (fast)
 $\text{HIO} + \text{I}^- \longrightarrow \text{I}_2 + \text{OH}^-$ (slow)
 $\text{OH}^- + \text{H}^+ \longrightarrow \text{H}_2\text{O}$ (fast)

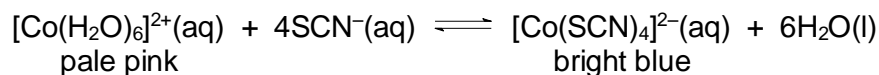
- 10 The same amount of electricity is passed through two electrolytic cells connected in series for 30 minutes. Cell 1 and Cell 2 contain aqueous solutions of $\text{Mn}(\text{NO}_3)_2$ and $\text{Au}(\text{NO}_3)_3$ respectively.

Given that 1.3 g of manganese is deposited on the cathode for Cell 1, what is the current used for electrolysis and the mass of the gold deposited on the cathode for Cell 2?

	current	mass of gold
A	1.3 A	3.1 g
B	1.3 A	4.7 g
C	2.5 A	3.1 g
D	2.5 A	4.7 g

11 Cobalt forms many coloured complexes with ligands such as H_2O and SCN^- .

A 100 cm^3 solution of $\text{Co}^{2+}(\text{aq})$ turns from pink to bright blue when 10 cm^3 of $\text{KSCN}(\text{aq})$ is added to the solution.



At equilibrium, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Co}(\text{SCN})_4]^{2-}$ are found to be present in a mole ratio of 1:10.

Given that $\lg K_c$ for the equilibrium is 3.00, which of the statements is **incorrect**?

- A The units of K_c is $\text{mol}^{-4} \text{ dm}^{12}$.
- B At equilibrium, $[\text{SCN}^-] = 3.16 \times 10^{-1} \text{ mol dm}^{-3}$.
- C $[\text{Co}(\text{SCN})_4]^{2-}$ is more stable than $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$.
- D Dilution of the reaction mixture decreases the proportion of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ at equilibrium.

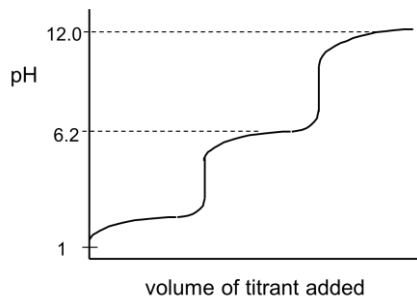
12 In which reaction is the underlined substance acting as a base?

- A $\text{HNO}_3 + \underline{\text{H}_2\text{SO}_4} \longrightarrow \text{H}_2\text{NO}_3^+ + \text{HSO}_4^-$
- B $\text{HSiO}_3^- + \underline{\text{HCN}} \longrightarrow \text{CN}^- + \text{H}_2\text{O} + \text{SiO}_2$
- C $\text{HNO}_2 + \underline{\text{HCO}_3^-} \longrightarrow \text{H}_2\text{O} + \text{CO}_2 + \text{NO}_2^-$
- D $\text{C}_6\text{H}_5\text{O}^- + \underline{\text{CH}_2\text{C}/\text{CO}_2\text{H}} \longrightarrow \text{C}_6\text{H}_5\text{OH} + \text{CH}_2\text{C}/\text{CO}_2^-$

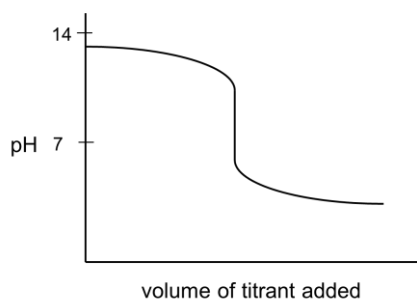
- 13 The change of colour for an indicator occurs over a limited range of pH that falls between ± 1.00 of the pK_a value of the indicator.

Which is the **most** suitable indicator that can be used to determine the end point of the corresponding titration?

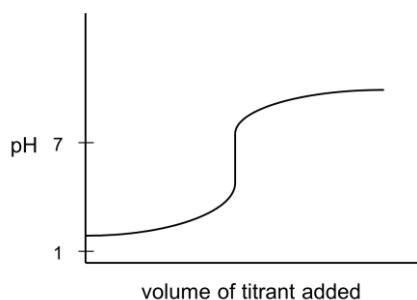
- A alizarin yellow
($pK_a = 11.0$)



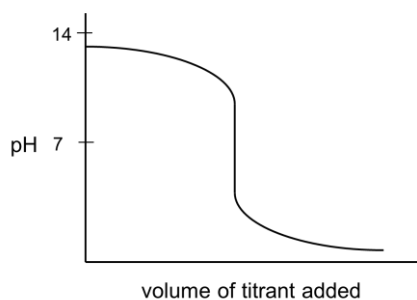
- B bromothymol blue
($pK_a = 7.1$)



- C methyl yellow
($pK_a = 3.3$)

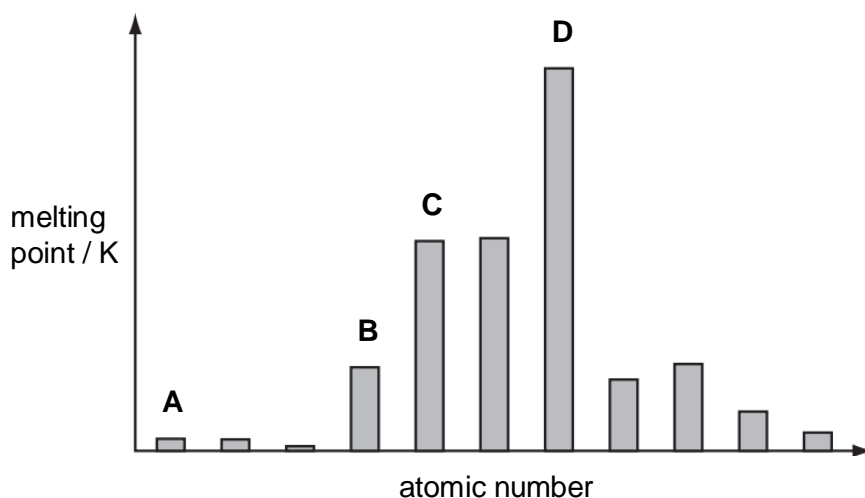


- D thymol blue
($pK_a = 1.6$)



- 14 The bar chart shows the melting points of a series of consecutive elements arranged in order of increasing atomic number. The elements sodium to chlorine form part of this series.

Which bar represents sodium?



- 15 Which oxide does **not** react with dilute sodium hydroxide to produce a salt?

A Al_2O_3 **B** P_4O_{10} **C** SO_2 **D** SiO_2

- 16 The three minerals below are obtained from mines around the world. Each one behaves as a mixture of two carbonate compounds. They can be used as fire retardants because they decompose in the heat, producing CO_2 . This gas smothers the fire.

Barytocite $BaCa(CO_3)_2$

Dolomite $CaMg(CO_3)_2$

Huntite $Mg_3Ca(CO_3)_4$

What is the order of effectiveness as fire retardant, from best to worst?

	best → worst		
A	dolomite	barytocite	huntite
B	dolomite	huntite	barytocite
C	huntite	barytocite	dolomite
D	huntite	dolomite	barytocite

- 17 Iodine is far less soluble in water than it is in aqueous potassium iodide, where it forms the complex ion I_3^- . For this reason, reactions involving aqueous iodine are often carried out in potassium iodide solution.

Which equation describes the quantitative determination of iodine in the presence of excess potassium iodide?

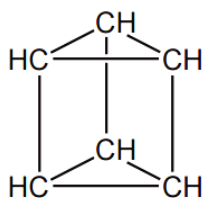
- A $I_2 + 2SO_4^{2-} \longrightarrow 2I^- + S_2O_8^{2-}$
 B $2I^- + 2S_2O_3^{2-} \longrightarrow I_2 + S_4O_6^{2-}$
 C $I_3^- + 2SO_4^{2-} \longrightarrow 3I^- + S_2O_8^{2-}$
 D $I_3^- + 2S_2O_3^{2-} \longrightarrow 3I^- + S_4O_6^{2-}$

- 18 Astatine, At, is below iodine in Group VII of the Periodic Table.

Which statement is most likely to be correct?

- A $AgAt(s)$ reacts with excess dilute aqueous ammonia to form a solution of a soluble complex.
 B At_2 and $KCl(aq)$ react to form $KAt(aq)$ and Cl_2 .
 C $KAt(aq)$ and dilute sulfuric acid react to form white fumes of $HAt(g)$.
 D $NaAt(s)$ and concentrated sulfuric acid react to form At_2 .

- 19 In 1869 Ladenburg suggested a structure for benzene, C_6H_6 , in which one hydrogen atom is attached to each carbon atom.



Ladenburg structure

A compound $C_6H_4Cl_2$ could be formed with the same carbon skeleton as the Ladenburg structure.

How many structural isomers would this compound have?

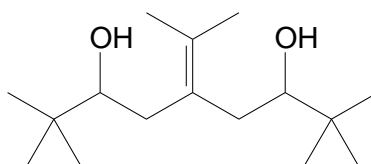
- A 3 B 4 C 5 D 6

- 20 High-energy irradiation in the stratosphere produces radicals from chlorofluoroalkanes, commonly known as CFCs.

Which radical could result from this irradiation of $\text{CHFCI/CF}_2\text{CI}$?

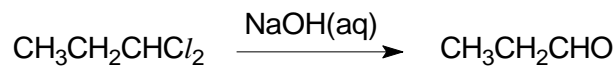
- A $\text{CHFCI}\dot{\text{C}}\text{FCI}$
 B $\dot{\text{C}}\text{HC/CF}_2\text{CI}$
 C $\dot{\text{C}}\text{HFCF}_2\text{CI}$
 D $\dot{\text{C}}\text{FC/CF}_2\text{CI}$

- 21 Compound L has the following structure.



What is the total number of geometrical isomers that can be formed from the product of the reaction of compound L with excess concentrated sulfuric acid at $170\text{ }^\circ\text{C}$?

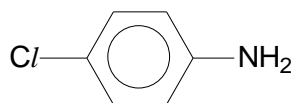
- A 8 B 7 C 4 D 3
- 22 1,1-dichloropropane reacts with excess hot aqueous sodium hydroxide in a series of steps to give propanal.



Which term describes the **second** step of this reaction?

- A addition
 B elimination
 C oxidation
 D substitution

- 23 4-chloroaniline is a pale yellow solid which is an important building block used for the production of pesticides, drugs and dyestuffs.

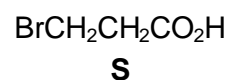
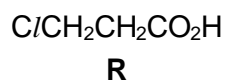
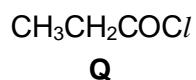
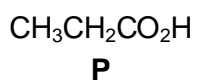


4-chloroaniline

Which of the following shows a suitable starting compound and sequence of steps to produce a good yield of 4-chloroaniline?

	starting compound	step 1	step 2
A		conc. HNO ₃ , conc. H ₂ SO ₄	Sn, conc. HCl followed by NaOH(aq)
B		dil. HNO ₃	LiAlH ₄
C		Cl ₂ , AlCl ₃	Sn, conc. HCl followed by NaOH(aq)
D		LiAlH ₄	Cl ₂ in CCl ₄

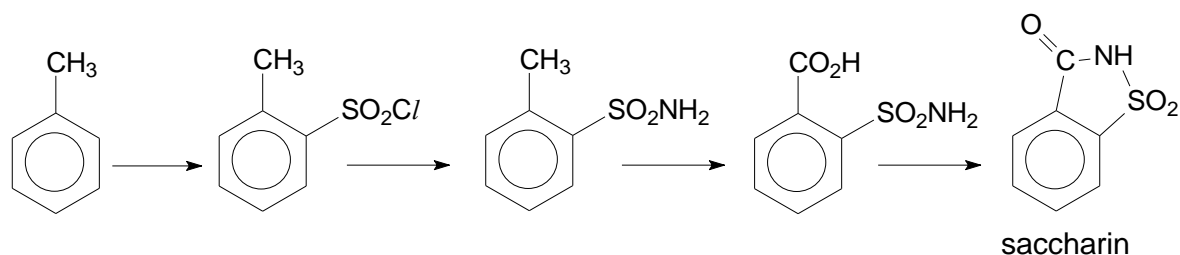
- 24 Why does hydrogen cyanide add to propanone but not to propene?
- A** Propanone is more susceptible to H⁺ attack than propene.
B Propanone is more susceptible to CN⁻ attack than propene.
C The C=C bond in propene is stronger than the C=O bond in propanone.
D The two methyl groups in propanone exert a stronger electron donating effect than the single methyl group in propene.
- 25 Equal amounts of compounds **P**, **Q**, **R** and **S** are separately shaken with 100 cm³ of water. The pH of each resultant solution is then measured.



Which of the following shows the correct order of **decreasing** pH of the solutions formed?

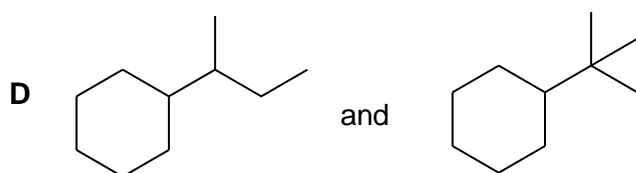
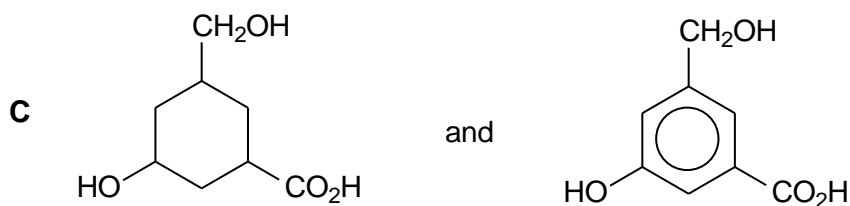
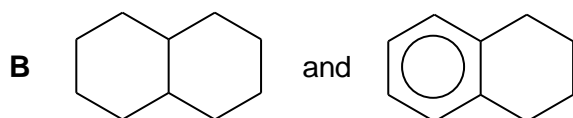
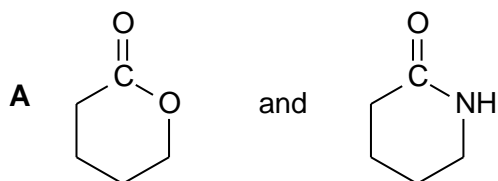
- A** P, R, S, Q
B P, S, R, Q
C Q, P, S, R
D Q, S, R, P

- 26 Saccharin is an artificial sweetening agent which can be synthesised from methylbenzene in the laboratory.

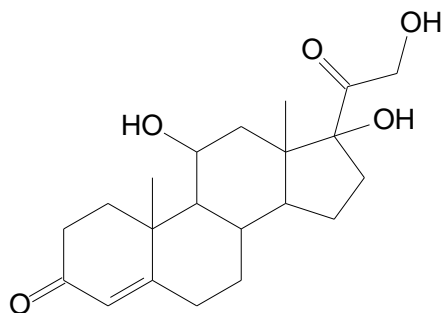


What type of reaction is **not** shown in this reaction scheme?

- A electrophilic substitution
 B elimination
 C nucleophilic substitution
 D oxidation
- 27 Which pair of organic compounds **cannot** be distinguished by a chemical test?



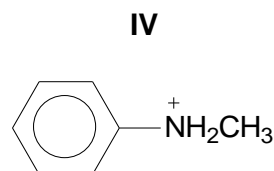
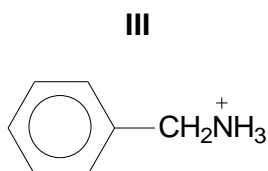
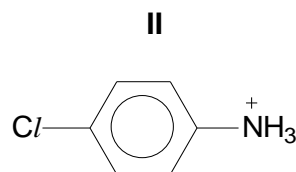
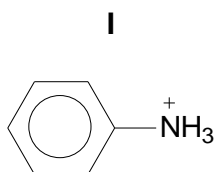
- 28 Cortisol is a steroid hormone which is released in response to stress and low blood glucose. Its structure is shown in the diagram below.



Cortisol is reduced with hydrogen in the presence of a platinum catalyst, and then oxidised by heating with acidified KMnO_4 . The product formed is further reacted with excess sodium to give an organic ion.

What is the charge on the organic ion produced?

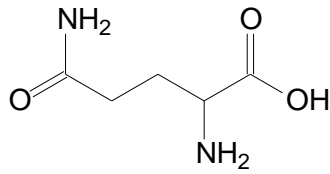
- A 1- B 2- C 3- D 5-
- 29 Consider the four species below.



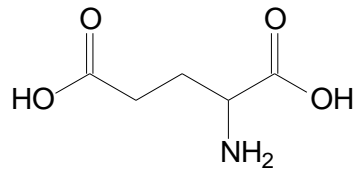
Which of the following shows the given species arranged in order of **decreasing** pK_a values?

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

- 30 The amino acids glutamine and glutamic acid can react with each other to form amide linkages.



glutamine



glutamic acid

What is the maximum number of different compounds, each containing one amide linkage, that can be formed from one molecule of glutamine and one molecule of glutamic acid?

- A 2
- B 3
- C 4
- D 5

Section B

For each of the questions in this section, one or more of the three numbered statements 1 to 3 may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct.)

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

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

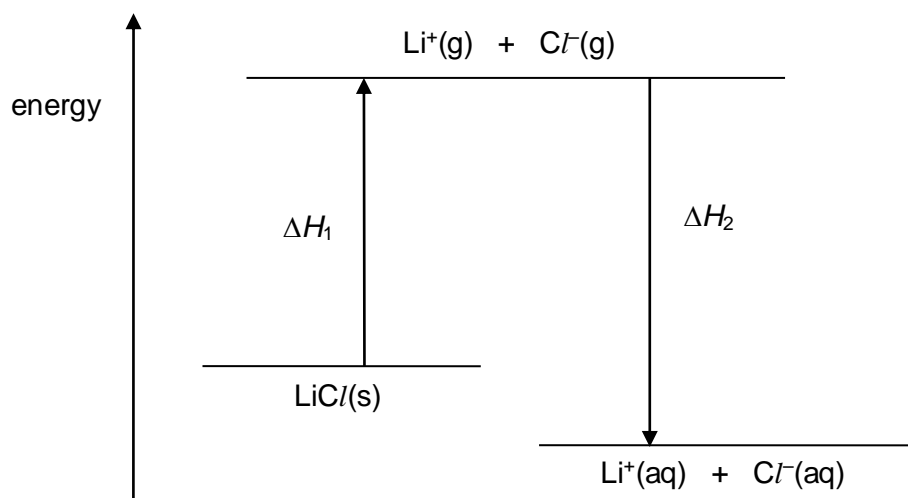
No other combination of statements is used as a correct response.

31 Which of the following ions has more electrons than protons and more protons than neutrons?

[$H = {}^1_1H$; $D = {}^2_1H$; $C = {}^{12}_6C$; $O = {}^{16}_8O$]

- 1 OH^-
- 2 HCO_3^-
- 3 DCO_3^-

32 An energy level diagram is shown below for the case of dissolving lithium chloride in water.



Which of the following about the enthalpy change of solution of lithium chloride is correct?

- 1 It is equal to $\Delta H_1 + \Delta H_2$.
- 2 It implies that dissolving lithium chloride is accompanied by an increase in temperature.
- 3 It is expected to be less exothermic than that of silver chloride.

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

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

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

33 Why does raising the pressure of a fixed mass of gaseous reactants at a constant temperature cause an increase in the rate of reaction?

- 1 More collisions occur per second when the pressure is increased.
- 2 More molecules have energy greater than the activation energy at the higher pressure.
- 3 Raising the pressure lowers the activation energy.

34 Use of the Data Booklet is relevant to this question.

Which ions contain one or more unpaired electrons?

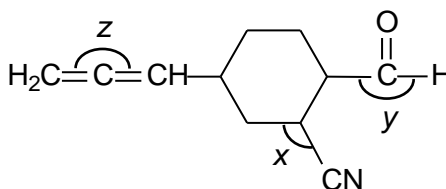
- 1 Cu^{2+}
- 2 Mn^{3+}
- 3 V^{3+}

35 When a hot glass rod is placed in a gas jar of hydrogen iodide, there is an immediate reaction as the hydrogen iodide decomposes.

Which statements about this reaction are correct?

- 1 Brown hydrogen iodide decolourises.
- 2 The hot rod provides the activation energy.
- 3 Purple fumes are observed.

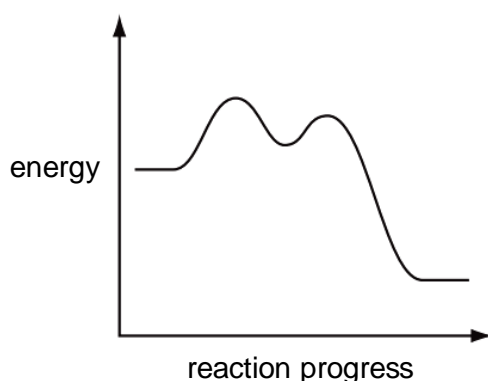
36 Which of the following statements are correct about compound **M**?



compound **M**

- 1 The bond angles in compound **M** increase in the order $x < y < z$.
- 2 There is only one sp hybridised carbon atom in compound **M**.
- 3 Compound **M** is planar.

37 A reaction pathway diagram is shown.



Which reactions would have this profile?

- 1 $(\text{CH}_3)_3\text{CBr} + \text{NaOH} \longrightarrow (\text{CH}_3)_3\text{COH} + \text{NaBr}$
- 2 $\text{CH}_3\text{CH}_2\text{Br} + \text{NaOH} \longrightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{NaBr}$
- 3 $(\text{CH}_3)_3\text{CCH}_2\text{CH}_2\text{Cl} + 2\text{NH}_3 \longrightarrow (\text{CH}_3)_3\text{CCH}_2\text{CH}_2\text{NH}_2 + \text{NH}_4\text{Cl}$

38 Which of the following reactions will produce a racemic mixture?

- 1 $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{Cl}$ heated under reflux with aqueous KOH.
- 2 CH_3CHO with HCN and a small amount of KOH.
- 3 $\text{CH}_3\text{CH}=\text{CHCH}_3$ with HBr dissolved in CCl_4 .

39 Compound **N** can react with alkaline aqueous iodine to form a yellow precipitate. When compound **N** reacts with hot acidified KMnO_4 , two products are obtained. Both products can also form a yellow precipitate with alkaline aqueous iodine.

What could be the identity of compound **N**?

- 1
- 2
- 3

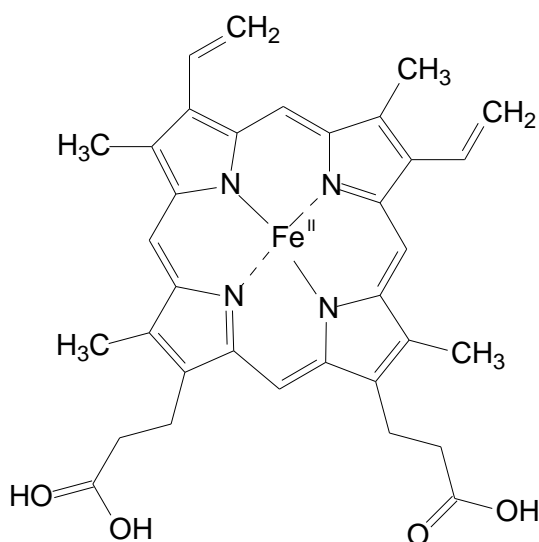
The responses **A** to **D** should be selected on the basis of

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

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

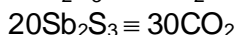
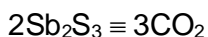
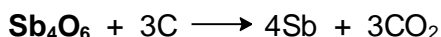
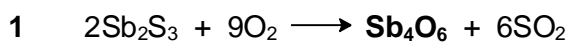
- 40** Haemoglobin is a type of protein found in red blood cells. It transports oxygen from the lungs to body tissues. A haemoglobin molecule is a tetramer made up of four globular protein subunits. Each subunit is composed of a protein chain tightly associated with a non-protein haem group.

The diagram below shows the structure of a haem group.



Which of the following is correct about haemoglobin?

- 1 Haemoglobin has higher affinity for carbon monoxide than oxygen.
- 2 Each haemoglobin molecule can carry four oxygen molecules.
- 3 The polypeptide chains in haemoglobin are held together by hydrogen bonding only.



Volume of CO_2 produced at r.t.p. = $30 \times 24 = \underline{720 \text{ dm}^3}$

2 Angle of deflection, $\theta \propto \frac{\text{ionic charge}}{\text{mass}}$ (i.e. z/m ratio) B

Arranging the species in order of **decreasing** angle of deflection, θ :

species	$^1\text{H}^+$	$^4\text{He}^{2+}$	$^9\text{Be}^{2+}$	$^{14}\text{N}^{3+}$	$^{12}\text{C}^{2+}$	$^{16}\text{O}^{2+}$	$^{27}\text{Al}^{3+}$	$^{12}\text{C}^+$
z/m	1.00	0.500	0.222	0.214	0.167	0.125	0.111	0.0833
identity	X		F	F	F		G	G

3

	no. of neutrons	no. of protons	ratio
^{10}B	5	5	1:1
^{32}P	17	15	
^{32}S	16	16	1:1
^{40}Ar	22	18	

B

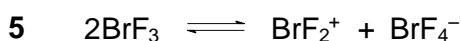
4 Using $\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$ A

$$p_2 = \frac{p_1 V_1 T_2}{V_2 T_1}$$

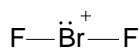
$$= \frac{1 \times 10^5 \times V_1 \times 373}{(3V_1 + V_1) \times 293}$$

$$= \frac{1 \times 10^5 \times 1 \times 373}{4 \times 293}$$

$$= \underline{3.18 \times 10^4 \text{ Pa}}$$



Since the electrical conductivity of BrF_3 decreases (i.e. the position of equilibrium shifts left) when temperature increases, the **reverse endothermic** process is favoured to absorb the extra heat. Hence, the **forward** autoionisation process is **exothermic**.



Since there are 2 bond pairs and 2 lone pairs around the central Br atom, BrF_2^+ has a **bent** (non-linear) shape.

- 6 Total heat released = $(\frac{100}{65} \times 100 \times 4.18 \times 50) = 32.2 \text{ kJ}$ B
 Total heat released per gram = $\frac{1}{10} (32.154) = \underline{3.22 \text{ kJ g}^{-1}}$

- 7 Since $\Delta n_{\text{gas}} = +1 \text{ mol}$; $\Delta S > 0$. D
 Since $\Delta G < 0$ only at high temperatures, $\Delta H > 0$.
 (Since reaction involves breaking of C–O bond during thermal decomposition, $\Delta H > 0$.)

- 8 At the positive electrode (anode): C

species	E^\ominus
$\text{Cl}_2/\underline{\text{Cl}^-}$	+1.36
$\text{Cu}^{2+}/\underline{\text{Cu}}$	+0.34
$\text{Ni}^{2+}/\underline{\text{Ni}}$	-0.25

Since $E^\ominus(\text{Ni}^{2+}/\text{Ni})$ is the least positive, **Ni will be oxidised to Ni^{2+} .**

At the negative electrode (cathode):

species	E^\ominus
$\underline{\text{H}^+}/\text{H}_2$	0.00

H^+ will be reduced to H_2 .

- 9 Comparing expt. 1 and 2, B
 When volume of H_2O_2 is halved, time taken is doubled (i.e. rate is halved).
 \Rightarrow **first order w.r.t. H_2O_2**

Comparing expt. 2 and 4,
 When volume of I^- increased 1.5 times, time taken decreased 1.5 times (i.e. rate increased 1.5 times).
 \Rightarrow **first order w.r.t. I^-**

Comparing expt. 3 and 4,
 When volume of H_2O_2 is halved and volume of H^+ is doubled, time taken is doubled (i.e. rate is halved).
 Since reaction is first order w.r.t. H_2O_2 , increasing $[\text{H}^+]$ has no effect on the time taken.
 \Rightarrow **zero order w.r.t. H^+**

Rate equation: **rate = $k [\text{H}_2\text{O}_2] [\text{I}^-]$**

\Rightarrow one molecule of H_2O_2 and one I^- ion are involved in the slow step (r.d.s) of the mechanism

- 10 $\text{Mn}^{2+} + 2\text{e}^- \longrightarrow \text{Mn}$ C

$$n(\text{Mn}) = 1.3 / 54.9 = 0.0237 \text{ mol}$$

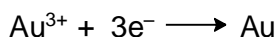
$$n(\text{e}^-) = 2 \times 0.0237 = 0.0474 \text{ mol}$$

$$\text{Using } Q = n_e F$$

$$Q = 0.0474 \times 96500 = 4574.1 \text{ C}$$

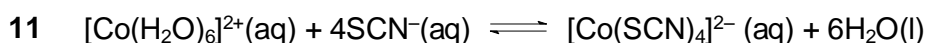
$$\text{Using } Q = It, I = Q/t$$

$$I = 4574.1 / (30 \times 60) = \underline{2.5 \text{ A}}$$



$$n(\text{Au}) = n(\text{e}^{-}) / 3 = 0.0474 / 3 = 0.0158 \text{ mol}$$

$$\text{mass of Au} = 0.0158 \times 197 = \underline{3.1 \text{ g}}$$



$$K_c = \frac{[\text{Co}(\text{SCN})_4]^{2-}}{[\text{Co}(\text{H}_2\text{O})_6]^{2+}[\text{SCN}^{-}]^4}$$

$$\text{Units of } K_c = \frac{\text{mol dm}^{-3}}{\text{mol dm}^{-3} \times (\text{mol dm}^{-3})^4}$$

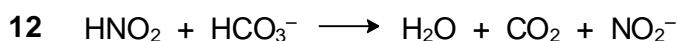
$$\text{Units of } K_c = \underline{\text{mol}^{-4} \text{ dm}^{12}} \quad \text{Hence, statement A is correct.}$$

$$10^3 = \frac{10}{1 \times [\text{SCN}^{-}]^4}$$

$$[\text{SCN}^{-}] = \underline{3.16 \times 10^{-1} \text{ mol dm}^{-3}} \quad \text{Hence, statement B is correct.}$$

Since K_c is more than 1, the position of equilibrium **lies to the right**. This indicates that $[\text{Co}(\text{SCN})_4]^{2-}$ is a more stable complex ion than $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$. Hence, statement **C** is correct.

Dilution of the reaction mixture decreases the concentration of ions in the solution. Hence, the **position of equilibrium shifts to the left** to increase the concentration of ions. This **increases** the proportion of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$. Hence, statement **D** is incorrect.



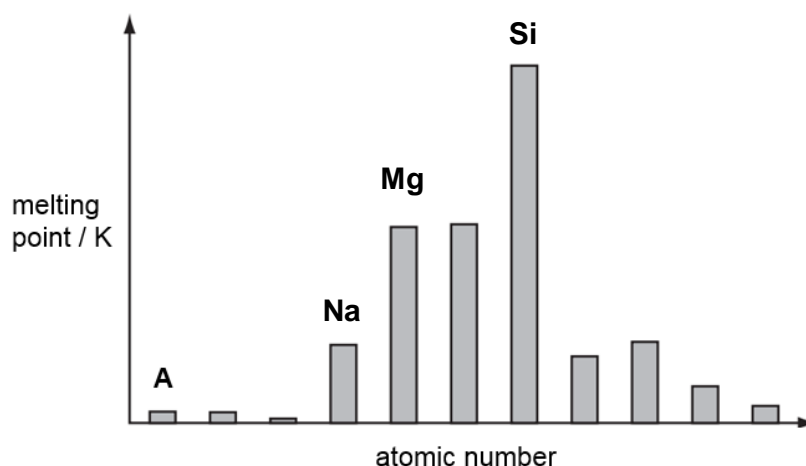
HCO_3^{-} acts as a *Bronsted base* which **accepts a proton** from HNO_2 , a *Bronsted acid*. The H_2CO_3 formed is unstable and decomposes to H_2O and CO_2 .

13 The working pH range of an indicator is between $\text{p}K_a - 1.00$ and $\text{p}K_a + 1.00$. **B**

A suitable indicator will be one where the working pH range of the indicator lies within the range of rapid pH change at the end-point of the titration.

Hence, only the indicator in **B** fulfils the condition.

14



B

oxide	nature of oxide	reacts with dil. NaOH	remarks
Al ₂ O ₃	amphoteric	yes	–
P ₄ O ₁₀	acidic	yes	–
SO ₂	acidic	yes	–
SiO ₂	acidic	no	only reacts with hot and concentrated strong alkalis to form silicates

D

16 Each mineral behaves as a mixture of two carbonate compounds.

D

mineral	formula	behaves as a mixture of
barytocalcite	BaCa(CO ₃) ₂	1 mol BaCO ₃ and 1 mol CaCO ₃
dolomite	CaMg(CO ₃) ₂	1 mol CaCO ₃ and 1 mol MgCO ₃
huntite	Mg ₃ Ca(CO ₃) ₄	3 mol MgCO ₃ and 1 mol CaCO ₃

The effectiveness of each of the three minerals as fire retardant is dependent on its **ease of thermal decomposition** to produce CO₂, which smothers the fire.

The ease of thermal decomposition of the minerals is dependent on the charge density and hence the polarising power of the respective Group II metal ions (Ba²⁺, Ca²⁺ and Mg²⁺).

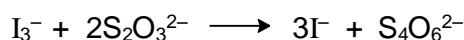
The order of effectiveness as fire retardant, from best to worst, corresponds to the order of decreasing polarising power of the Group II metal ions: Mg²⁺, Ca²⁺, Ba²⁺.

Huntite is a more effective fire retardant than dolomite as huntite contains more MgCO₃ and hence it produces more CO₂ upon complete thermal decomposition.

17 I₂ undergoes a redox reaction with S₂O₃²⁻, forming I⁻ and S₄O₆²⁻. (Recall from 'Group VII')

D

In the presence of excess KI, I₂ forms the complex ion I₃⁻. Hence, the overall equation is as shown:



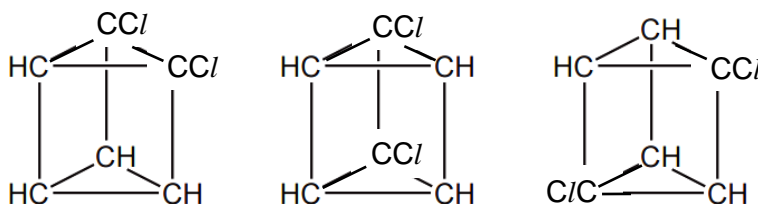
18 Since At is below I in Group VII,

D

- Similar to AgI, AgAt is likely to be **insoluble** in excess dilute aqueous NH₃
- At₂ is a weaker oxidising agent than Cl₂ and hence, At₂ is **unable** to oxidise Cl⁻ to form At⁻ and Cl₂
- KAt and **concentrated** sulfuric acid react to form **At₂** (HAt formed initially is oxidised by the sulfuric acid)

19 The compound C₆H₄Cl₂ has the following **three** structural isomers:

A



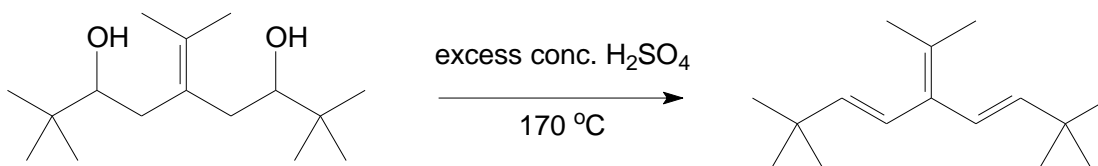
20

bond	bond energy / kJ mol ⁻¹
C–F	> 410
C–H	410
C–Cl	340

C

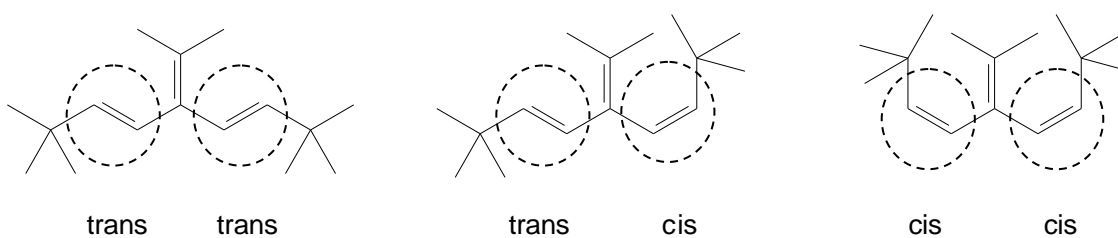
Irradiation of **CHFC/CF₂Cl** results in **homolytic fission** of the weakest C–Cl bond, forming the **•CHFCF₂Cl** radical.

21

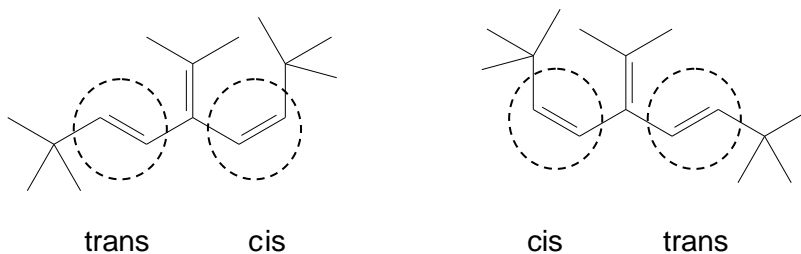


D

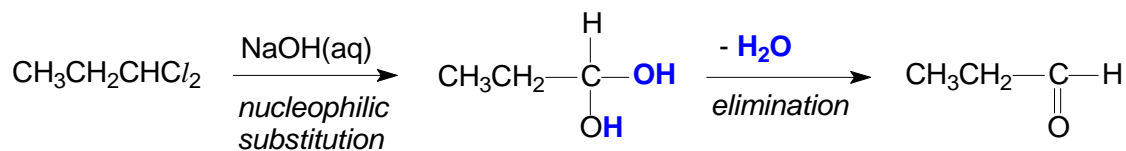
The **three** geometrical isomers of the product are as follows:



Note: The following two structures are equivalent.

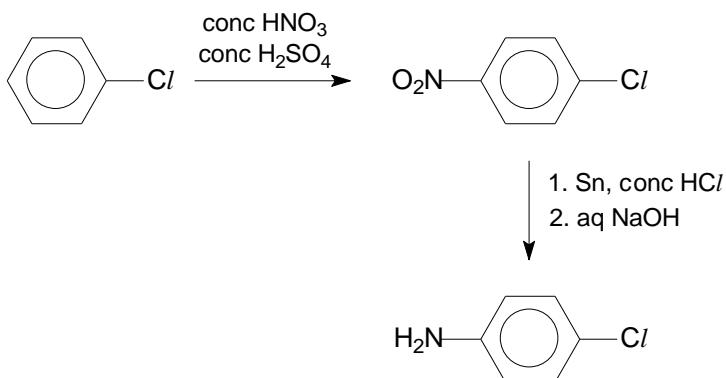


22



B

23



A

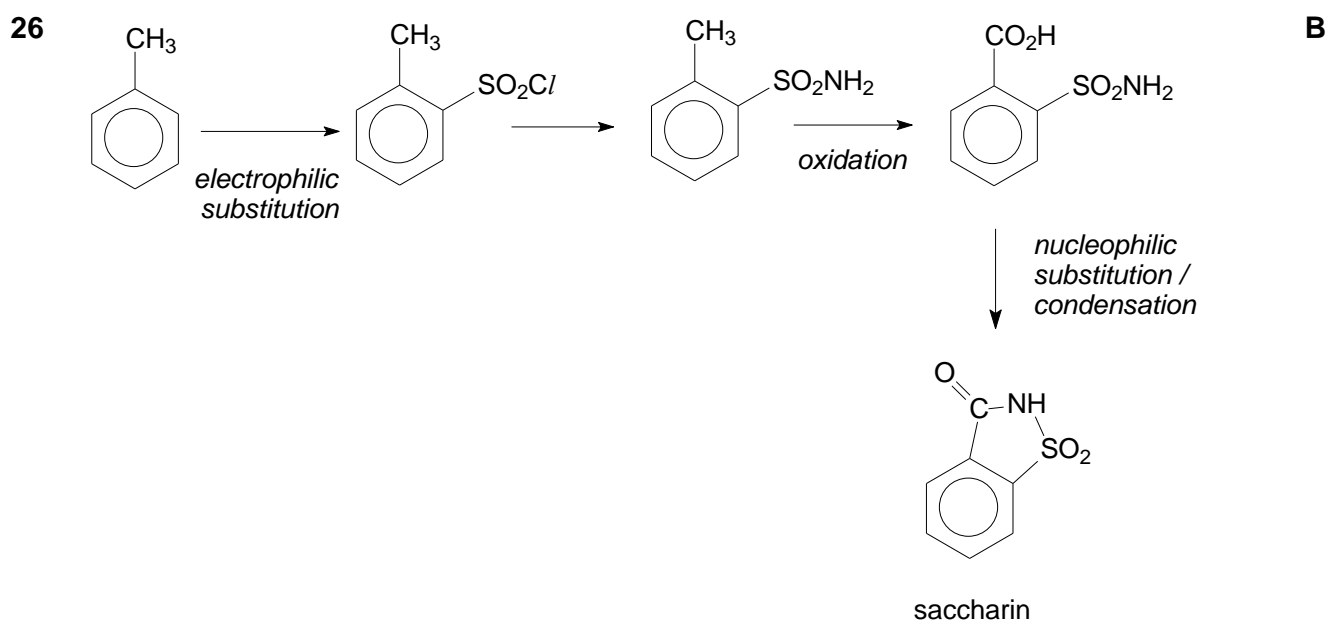
Note that $-\text{NO}_2$ is 3-directing and cannot be reduced using LiAlH₄.

- 24 The CN^- nucleophile attacks the **electron deficient** carbon in propanone in the **nucleophilic addition** mechanism. **B**
- 25 **Q hydrolyses** in water to produce a strongly acidic solution of $\text{CH}_3\text{CO}_2\text{H}$ and **HCl**. Hence, the resulting solution formed has the lowest pH. **B**

P, R and **S** are weak acids which ionise partially in water.

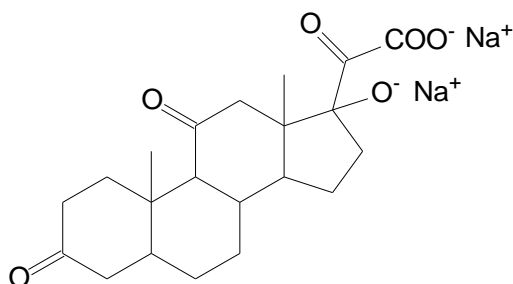
The presence of electronegative atoms (*Cl* and *Br*) on **R** and **S** exerts an electron-withdrawing effect on $\text{ClCH}_2\text{CH}_2\text{COO}^-$ and $\text{BrCH}_2\text{CH}_2\text{COO}^-$ respectively, which disperses the negative charge and stabilises the anion. Hence, the dissociation of $\text{CH}_3\text{CH}_2\text{COOH}$ to give H^+ ions is least favourable. The resulting solution from **P** has the highest pH.

Since *Cl* is more electronegative than *Br*, it exerts a stronger electron-withdrawing effect on $\text{ClCH}_2\text{CH}_2\text{COO}^-$ and hence $\text{ClCH}_2\text{CH}_2\text{COOH}$ is more acidic than $\text{BrCH}_2\text{CH}_2\text{CO}_2\text{H}$. Hence, the resulting solution from **R** has a lower pH than **S**.



- 27 **A:** aqueous KMnO_4 , dilute H_2SO_4 , heat **D**
 For the compound on the left, purple solution decolourises.
 (hydrolysis of ester + oxidation of primary alcohol)
 For the compound on the right, purple solution remains.
- B:** aqueous KMnO_4 , dilute H_2SO_4 , heat
 For the compound on the left, purple solution remains.
 For the compound on the right, purple solution decolourises.
 (side-chain oxidation on benzene ring)
- C:** aqueous Br_2 / neutral FeCl_3
 For the compound on the left, orange solution remains / no violet colouration observed.
 For the compound on the right, orange solution decolourises / violet colouration observed.

28



B

29 The four species given are conjugate acids of their corresponding amines.

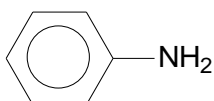
A

A low $\text{p}K_{\text{a}}$ value for its conjugate acid will indicate a high $\text{p}K_{\text{b}}$ value for the amine.

A decreasing $\text{p}K_{\text{a}}$ value for the conjugate acids of the amines also indicates an increasing $\text{p}K_{\text{b}}$ value for the amines.

Hence, the species can be arranged in the **order of decreasing basicity** of the corresponding amine.

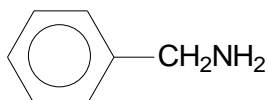
amine of I



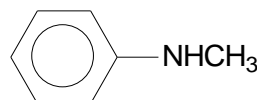
amine of II



amine of III



amine of IV



Amine of **III** is the most basic as the electron-donating alkyl group ($\text{C}_6\text{H}_5\text{CH}_2-$) increases the availability of lone pair on N.

Amines **I**, **II** and **IV** are less basic than that of **III** since the lone pair on N can be delocalised into the π electron cloud of the benzene ring, decreasing the availability of the lone pair.

Amine of **IV** is more basic than that of **I** and **II** as it is a secondary amine. The presence of the electron-donating alkyl group ($-\text{CH}_3$) increases the availability of the lone pair as compared to amines of **I** and **II**.

Amine of **II** is less basic than that of **I** as the presence of electron-withdrawing Cl decreasing the availability of the lone pair on N to a greater extent.

30 Possible combinations:

B

Glutamine	-NH ₂	-CO ₂ H
Glutamic acid		
-NH ₂	×	√
-CO ₂ H (1)	√	×
-CO ₂ H (2)	√	×

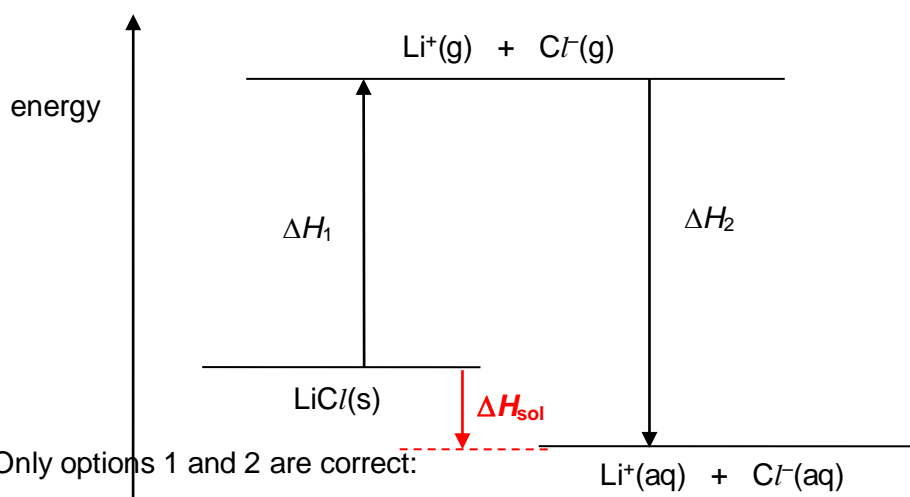
∴ 3 different compounds can be formed

31

	no. of protons	no. of electrons	no. of neutrons
OH ⁻	9	10	8
HCO ₃ ⁻	31	32	30
DCO ₃ ⁻	31	32	31

B

32



B

Only options 1 and 2 are correct:

1. By Hess' law, $\Delta H_{\text{sol}}(\text{LiCl}) = \Delta H_1 + \Delta H_2$.
2. From the energy level diagram, $\text{LiCl}(\text{s}) \longrightarrow \text{Li}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ is an exothermic process. Hence, the process is accompanied by an increase in temperature.
3. Silver chloride is sparingly soluble while lithium chloride is soluble. Hence, $\Delta H_{\text{sol}}(\text{LiCl})$ is expected to be MORE exothermic than $\Delta H_{\text{sol}}(\text{AgCl})$.

33

1. When pressure is increased, the gaseous reactant particles become closer together. Hence, the frequency of effective collisions increases.
2. More molecules have energy greater than the E_a at a higher **temperature**.
3. Raising the pressure has no effect on the E_a . The E_a is lowered only in the presence of a catalyst.

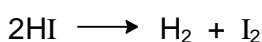
D

34

	electronic config.	no. of unpaired electrons
1. Cu ²⁺	[Ar] 3d ⁹	1
2. Mn ³⁺	[Ar] 3d ⁴	4
3. V ³⁺	[Ar] 3d ²	2

A

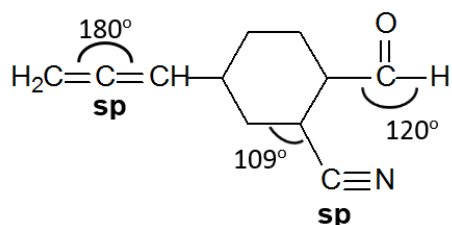
35



C

1. Gaseous hydrogen iodide appears as **white fumes** NOT brown
2. The hot rod provides the activation energy to break the H-I bond
3. The I₂ formed appears as purple fumes (violet black I₂ solids are also observed)

36



D

37 The reaction pathway diagram illustrates a **two-step** reaction mechanism. **D**

1. Tertiary RX undergoes a two-step S_N1 mechanism
2. Primary RX undergoes a single step S_N2 mechanism
3. Same as option 2

38 The nucleophile (OH^- , CN^- , Br^-) can attack the carbocation / planar molecule from either side with equal probability in the S_N1 / nucleophilic addition / electrophilic addition mechanism. **C**

A racemic mixture will not be formed in (1) since the product is not even chiral.

39 Compound 1 will undergo oxidative cleavage and compound 2 will undergo hydrolysis when reacted with hot acidified KMnO_4 . **B**

Compounds with the structure $\text{CH}_3-\overset{\text{H}}{\underset{\text{OH}}{\text{C}}}-$ or $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-$ will form a yellow ppt with alkaline aqueous iodine.

- 40 Option 1: Fe^{2+} in haemoglobin forms a stronger dative covalent bond with carbon monoxide than oxygen. **B**
- Option 2: Each haemoglobin molecule contains 4 haem groups. One molecule of oxygen binds to the Fe^{2+} on each haem group.
- Option 3: The polypeptide chains in haemoglobin are held together by R group interactions.

**2016 JC2 PRELIMINARY
EXAMINATIONS**

NAME: _____ **PDG:** _____/15 **Register No:** _____

CHEMISTRY

9647/02

Higher 2

16 September 2016

Paper 2 Structured Questions

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

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

Answer **all** questions.

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				
Paper 2	1		Total	/ 72
	2			
	3			
	4			
	5			
	6			

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

1 Planning (P)

Group II nitrates decompose on heating to form metal oxide, nitrogen(IV) oxide and oxygen.

Group II nitrates and their oxides are solids that can be easily weighed to determine the amount present. Nitrogen(IV) oxide is an acidic gas and can be absorbed by a known amount of excess strong alkali such as sodium hydroxide.



The amount of strong alkali remaining can then be determined by titrating against a standard solution of strong acid.

The oxygen produced from the decomposition can be trapped by a simple gas collection set-up to measure the volume collected.

You are to plan an experiment to confirm that the molar quantities of magnesium oxide, nitrogen(IV) oxide and oxygen produced agree with the equation for the thermal decomposition of magnesium nitrate.

- (a) Write an equation for the thermal decomposition of magnesium nitrate. You should include state symbols in your equation.

..... [1]

- (b) Suggest the capacity of the apparatus to be used to collect the oxygen gas.

Hence calculate the mass of magnesium nitrate to be heated to produce a stated volume of oxygen gas appropriate for the apparatus.

You should assume that one mole of any gas occupies 24.0 dm^3 under room conditions.

capacity of apparatus:

mass of magnesium nitrate to be heated: [2]

- (c) Use your answer to (b) to calculate the minimum volume of 1.00 mol dm^{-3} aqueous sodium hydroxide needed to absorb the nitrogen(IV) oxide produced from the thermal decomposition of magnesium nitrate.

volume of sodium hydroxide needed: [1]

- (d) You may assume that you are provided with:

- solid magnesium nitrate
- 1.00 mol dm^{-3} sodium hydroxide
- 0.20 mol dm^{-3} hydrochloric acid
- the apparatus and chemicals normally found in a school or college laboratory

Your plan should include:

- a diagram of the assembled apparatus capable of absorbing the nitrogen(IV) oxide and collecting the oxygen separately and in sequence;
- an outline of how the results would be obtained, including the essential details of the titration procedure;
- measures to ensure reliability of results;
- brief, but specific, details of how the results will be used to
 - determine the amounts in moles of reactant and all products at the end of complete thermal decomposition
 - confirm that the decomposition had occurred according to the molar ratios in the equation.

- 2 (a) Ethoxyethane, $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$, may be regarded as a water molecule in which each of the hydrogen atoms has been replaced by an ethyl group.

At room temperature, boron trifluoride is a gas and ethoxyethane is a liquid. When boron trifluoride is mixed in a 1 : 1 molar ratio with ethoxyethane, a liquid with a boiling point of 127°C is formed.

- (i) Suggest what type of bond is formed between boron trifluoride and ethoxyethane, explaining your answer.

.....

 [2]

- (ii) Draw a diagram to illustrate the shape of and bonding in the product.

(You may represent the $-\text{CH}_2\text{CH}_3$ group with $-\text{R}$)

[1]

Often in the preparation of an organic compound the product is obtained as an aqueous solution. The chemist needs to separate the organic compound from water by using solvent extraction method. Organic compounds are more soluble in organic solvents than in water.

Ethoxyethane is a good solvent for many organic compounds. It is immiscible with water and has a low boiling point (35°C). When an aqueous solution containing an organic compound is shaken with ethoxyethane in a separating funnel, the compound distributes itself between the two layers, in accordance with its partition coefficient between ethoxyethane and water, until equilibrium is reached.

The partition coefficient, $K_{\text{partition}}$, of an organic compound, **J**, between ethoxyethane and water is given by the following expression.

$$K_{\text{partition}} = \frac{\text{concentration of J in ethoxyethane (organic layer)}}{\text{concentration of J in water (aqueous layer)}}$$

where the concentration of **J** can be expressed in g cm^{-3} .

The partition coefficient is a constant at a constant temperature.

(b) When 20 cm³ of ethoxyethane were shaken with 75 cm³ of an aqueous solution containing 5.00 g of **J**, it was found that 2.14 g of **J** were extracted into the ethoxyethane.

(i) Calculate the partition coefficient, $K_{\text{partition}}$, of **J** between ethoxyethane and water.

[1]

(ii) In another experiment

- 10 cm³ of ethoxyethane were shaken with 75 cm³ of an aqueous solution containing 5.00 g of **J** and the layers were separated.
- The aqueous layer was shaken with a second 10 cm³ portion of ethoxyethane and the layers were separated.
- The two organic layers were combined.

Use the value of $K_{\text{partition}}$ you calculated in **(b)(i)** to calculate the total mass of **J** extracted by this procedure.

[2]

(iii) Hence comment whether it is more efficient to use one 20 cm³ portion of ethoxyethane or two successive portions of 10 cm³ ethoxyethane for extraction.

..... [1]

(c) Anhydrous calcium chloride was then added to the combined organic layers obtained in **(b)(ii)**.

Suggest the reason for the addition of anhydrous calcium chloride.

..... [1]

[Total: 8]

- 3 Nitrogen and phosphorus are both Group V elements. Nitrogen exists in its elemental form as simple molecules, N_2 , while phosphorus occurs in one of the many forms, including 'white' phosphorus and 'red' phosphorus. Some data about these two forms of phosphorus are shown in **Table 1.1**.

Table 1.1

	'white' phosphorus	'red' phosphorus
appearance at room temperature	creamy white solid	red solid
melting point / °C	44	590
solubility in methylbenzene	soluble	insoluble

- (a) Suggest the type of structure and bonding in 'red' phosphorus. Explain your reasoning.

.....

.....

.....

..... [2]

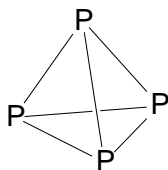
- (b) The 2s and 2p orbitals of nitrogen atoms can hybridise in the same way as the 2s and 2p orbitals of carbon atoms.

Suggest the type of hybridisation in N_2 and draw the arrangement of the hybrid orbital(s) around each nitrogen atom.

type of hybridisation

[2]

- (c) The corresponding form of phosphorus, P_2 , is not stable under standard conditions. Instead, 'white' phosphorus consists of molecules with a tetrahedral structure as shown.



'white' phosphorus

- (i) Unlike N_2 , P_2 is not stable under standard conditions. Suggest a reason for this.

.....
 [1]

- (ii) Using the data in **Table 1.2**, construct an appropriate energy cycle and use it to determine the enthalpy change for the conversion of 'white' phosphorus to the gaseous diatomic molecule, P_2 .

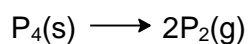


Table 1.2

P–P bond energy	200 kJ mol ⁻¹
P≡P bond energy	485 kJ mol ⁻¹
enthalpy change of vaporisation of $P_4(s)$	+12 kJ mol ⁻¹

[3]

- (iii) The formation of $P_2(g)$ from 'white' phosphorus is not spontaneous under standard conditions.

Suggest how the conditions would need to be changed to make it spontaneous. Explain your reasoning.

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

- (d) Although nitrogen gas makes up about 79% of the atmosphere, it does not easily form compounds.

- (i) Explain why the conditions in a car engine lead to the production of oxides of nitrogen.

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

- (ii) Give an equation for a reaction involved in the removal of nitrogen monoxide, NO, from a car's exhaust gases, in the catalytic converter.

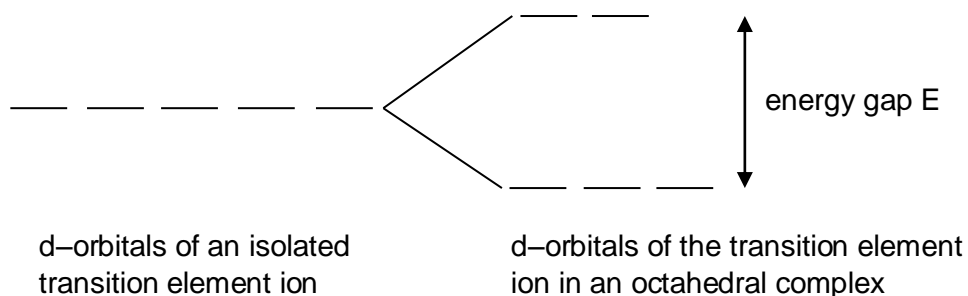
..... [1]

[Total: 12]

4 (a) (i) What is meant by the term *ligand* in the context of transition element chemistry?

.....
 [1]

(ii) Although the five d-orbitals are at the same energy in an isolated atom, when a transition element ion is in an octahedral complex the orbitals are split into two groups, as shown in the following diagram.



Use this diagram as an aid in explaining the following.

- Transition element complexes are often coloured.

.....

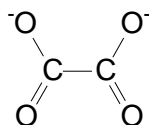
- The colour of a complex of a given transition element often changes when the ligands around it are changed.

.....

 [5]

- (b) Heating a solution containing potassium ethanedioate, iron(II) ethanedioate and hydrogen peroxide produces the light green complex $K_3Fe(C_2O_4)_3$, which contains the ion $[Fe(C_2O_4)_3]^{3-}$.

The structure of the ethanedioate ion is as follows.



- (i) Determine the oxidation number of carbon in this ion.
 [1]
- (ii) Determine the oxidation number of iron in $[Fe(C_2O_4)_3]^{3-}$.
 [1]
- (iii) The iron atom in the $[Fe(C_2O_4)_3]^{3-}$ ion is surrounded octahedrally by six oxygen atoms. Draw a three-dimensional diagram to show the shape of this ion.

[2]

- (c) Kidney stones are usually made up of an inorganic salt of calcium with ethanedioate. Thus, people who are prone to kidney stones have to limit or avoid eating foods with high ethanedioate content such as spinach, peanuts and sweet potatoes.

- (i) Write the expression for the solubility product of calcium ethanedioate.
 [1]
- (ii) The value of K_{sp} for calcium ethanedioate is 2.3×10^{-9} . Calculate $[C_2O_4^{2-}]$ in a saturated solution of calcium ethanedioate.

[1]

(iii) A solution **W** is saturated with both calcium ethanedioate and calcium chloride.

The concentration of ethanedioate ions in solution **W** is less than that calculated in (c)(ii). Explain why this is so.

.....
 [1]

(d) By quoting relevant data from the *Data Booklet*, explain the following observations:

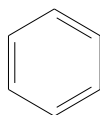
compound	pH of a 1.0 mol dm ⁻³ solution in water
NaCl	7.0
MgCl ₂	6.5
AlCl ₃	3.0

.....

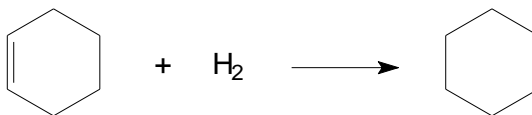
 [2]

[Total: 15]

- 5 (a) Kekulé proposed the following structure for benzene.



The enthalpy change of hydrogenation of cyclohexene, as shown, is -121 kJ mol^{-1} .



Based on this value for cyclohexene it is possible to calculate the enthalpy change of hydrogenation of benzene, based on Kekulé's structure, to be -363 kJ mol^{-1} .

Explain the difference between this calculated value and the actual value for the enthalpy change of hydrogenation of benzene of -209 kJ mol^{-1} .

.....
 [1]

- (b) Benzene undergoes electrophilic substitution reactions.

Nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$, can be formed from benzene. Give the reagents and conditions necessary for this process and identify the electrophile.

reagents

conditions

electrophile [2]

(c) Fig. 5.1 shows a reaction scheme starting from nitrobenzene.

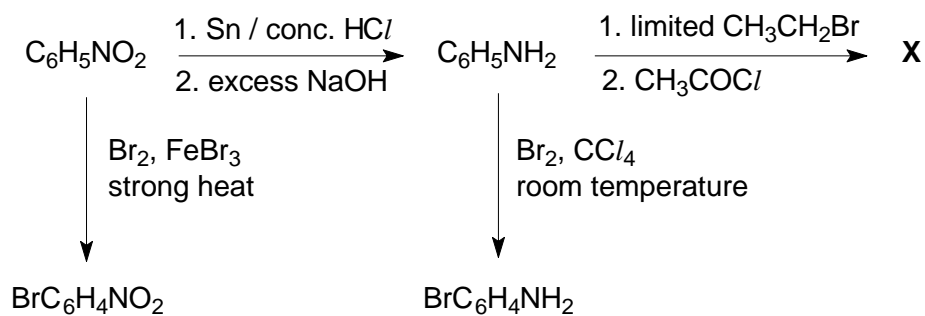


Fig. 5.1

- (i) Explain why the bromination of phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$, is possible with the milder conditions shown in Fig. 5.1.

.....

 [2]

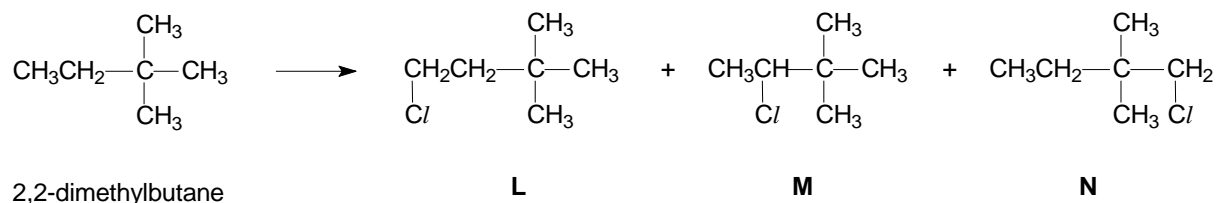
- (ii) Write an equation for the reaction between nitrobenzene and the reducing mixture, Sn / conc. HCl. Use [H] to represent the formula of the reducing agent in your equation.

..... [1]

- (iii) Draw the structural formula of X.

[1]

- (d) When heated with chlorine, the hydrocarbon 2,2-dimethylbutane produces compounds **L**, **M** and **N**.



It is observed that the rate of substitution of a hydrogen atom in 2,2-dimethylbutane by a chlorine atom is dependent on the type of hydrogen substituted – *primary*, *secondary* or *tertiary*.

The table below shows the relative rate of substitution by chlorine.

Reaction	Type of hydrogen substituted	Relative rate
$\text{RCH}_3 \longrightarrow \text{RCH}_2\text{Cl}$	<i>primary</i>	1
$\text{R}_2\text{CH}_2 \longrightarrow \text{R}_2\text{CHCl}$	<i>secondary</i>	7
$\text{R}_3\text{CH} \longrightarrow \text{R}_3\text{CCl}$	<i>tertiary</i>	21

Using the information from the table and by considering the number of hydrogen atoms of each type (*primary*, *secondary* or *tertiary*) within 2,2-dimethylbutane, predict the ratio of the three products **L**, **M** and **N**.

Explain how you arrived at your answer.

ratio of **L** to **M** to **N**:

explanation:

.....
 [2]

[Total: 9]

6 (a) The interhalogen compound ICl reacts with alkenes in an addition reaction. ICl reacts faster with alkenes than the pure halogens.

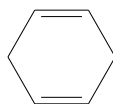
(i) Describe the mechanism of the reaction between ICl and propene.

[3]

(ii) Suggest why ICl reacts with alkenes faster than the pure halogens, Cl_2 , Br_2 and I_2 .

.....
 [1]

Cyclohexa-1,4-diene behaves as a typical alkene.



cyclohexa-1,4-diene

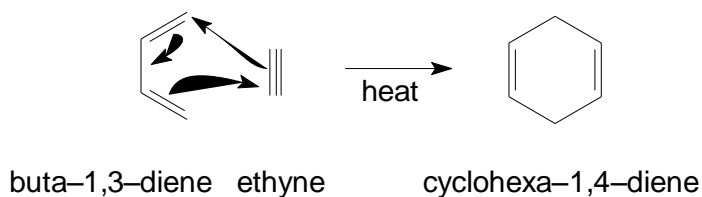
(b) State the total numbers of σ bonds and π bonds in a molecule of cyclohexa-1,4-diene.

number of σ bonds

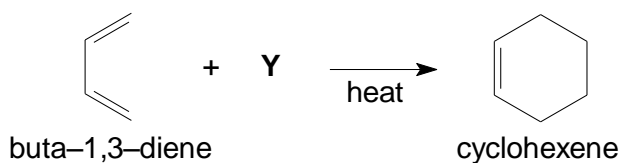
number of π bonds

[1]

- (c) Cyclohexa-1,4-diene can be made by heating buta-1,3-diene with ethyne in the Diels-Alder reaction. The diagram below shows the movement of electron pairs, represented by curly arrows, needed to generate the cyclohexa-1,4-diene in a single step.



- (i) In a similar type of reaction, cyclohexene can be formed from buta-1,3-diene and another alkene, **Y**.



Suggest the **name** of the alkene, **Y**, that would react with buta-1,3-diene to form cyclohexene in this type of reaction.

..... [1]

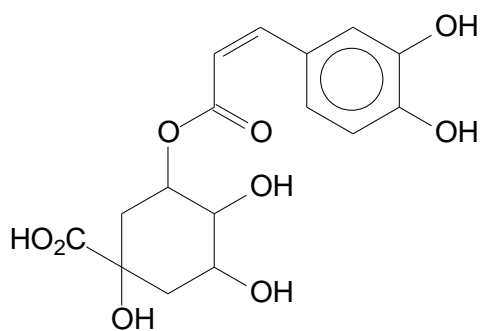
- (ii) In another similar reaction, penta-1,3-diene reacts with propene to form two products that are structural isomers.

Deduce the structures of these two isomers.

--	--

[2]

(d) Chlorogenic acid occurs naturally in coffee and an edible species of bamboo.

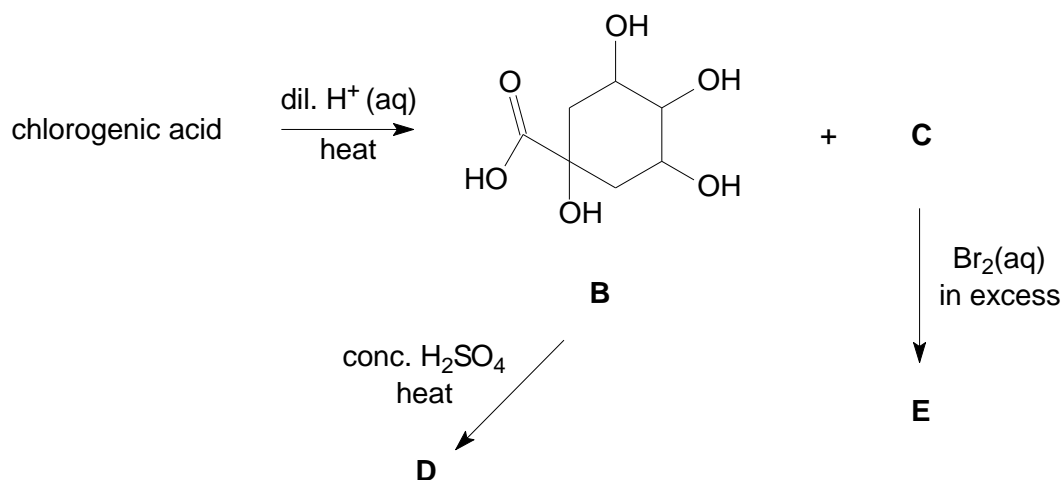


chlorogenic acid

(i) Draw the structural formula of the compound formed when chlorogenic acid is treated with an excess of sodium metal.

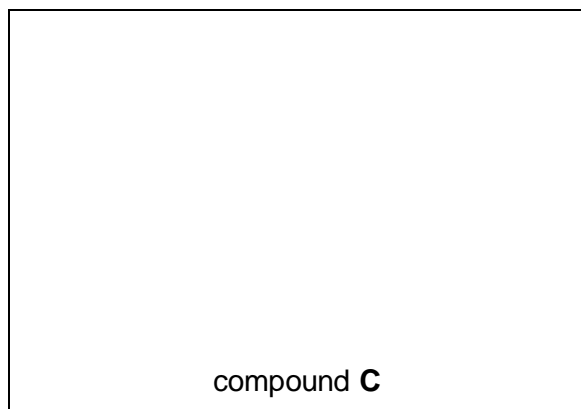
[1]

On heating with dilute acid, chlorogenic acid produces two compounds, **B** and **C**.



- (ii) State the *type of reaction* undergone by chlorogenic acid when **B** and **C** are formed. Draw the displayed formula of compound **C**.

type of reaction



[2]

When compound **B** is heated with concentrated H_2SO_4 , compound **D**, $\text{C}_7\text{H}_6\text{O}_3$, is formed.

CO_2 is evolved when compound **D** is treated with $\text{Na}_2\text{CO}_3(\text{aq})$. Compound **D** decolourises $\text{Br}_2(\text{aq})$ giving a white precipitate, but does not react with cold, alkaline KMnO_4 .

When compound **C** is treated with an excess of $\text{Br}_2(\text{aq})$, compound **E** is produced.

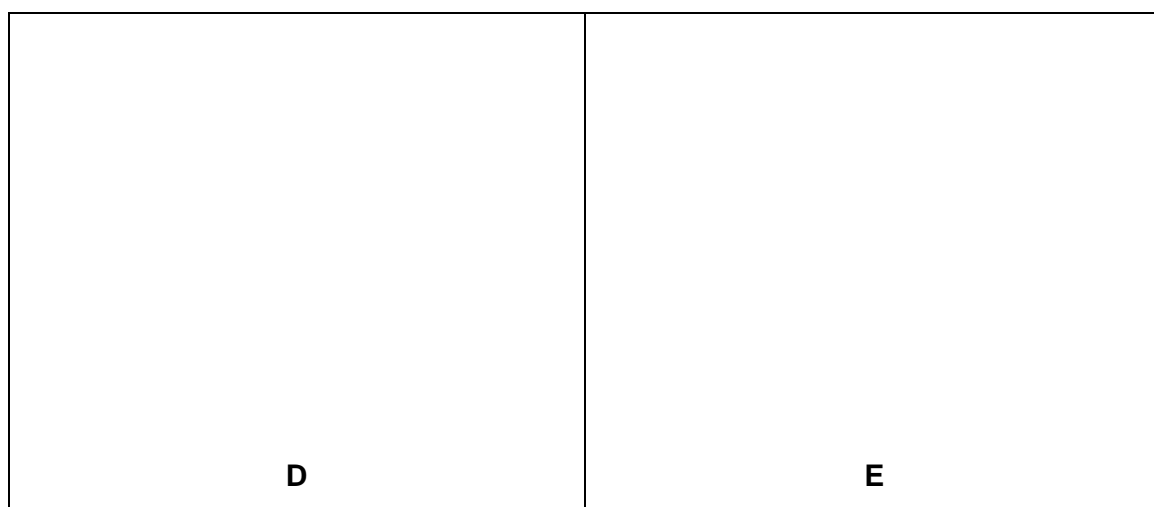
- (iii) Identify the functional group that would have been shown to be present in **D** if the test with cold, alkaline KMnO_4 had been positive.

..... [1]

- (iv) Name the functional groups in compound **D** that react with the following.

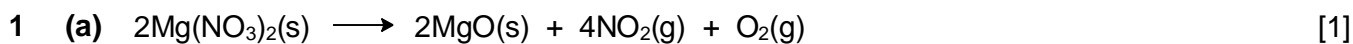
$\text{Na}_2\text{CO}_3(\text{aq})$ $\text{Br}_2(\text{aq})$ [2]

- (v) Suggest structures for compounds **D** and **E**.

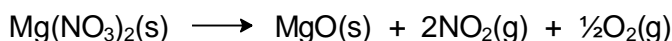


[2]

[Total: 16]



OR



- (b) Correctly stated volume, with units, of apparatus to be used for gas collection.
E.g. 100 ml or 100 cm³ gas syringe [1]

AND

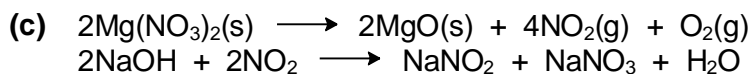
Correctly calculated mass of magnesium nitrate to produce a stated volume of O₂ gas that would be appropriate for the stated volume of apparatus.

E.g. for 60 cm³ of O₂,

$$n(\text{O}_2) = 60/24000 = 2.50 \times 10^{-3} \text{ mol}$$

$$n[\text{Mg}(\text{NO}_3)_2] = 2 \times n(\text{O}_2) = 5.00 \times 10^{-3} \text{ mol}$$

$$\text{mass of Mg}(\text{NO}_3)_2 = 5.00 \times 10^{-3} \times [24.3 + 2(14.0) + 6(16.0)] = \underline{0.742 \text{ g}}$$
 [1]



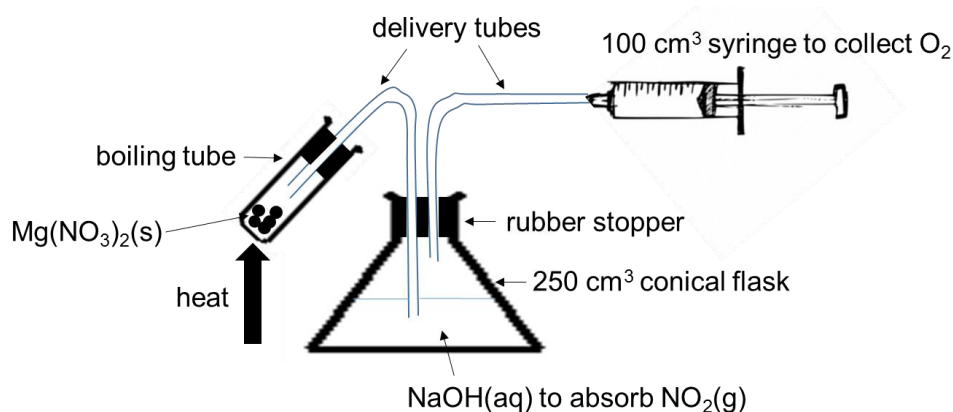
$$n(\text{NO}_2) = 2 \times n[\text{Mg}(\text{NO}_3)_2] = 2 \times 5.00 \times 10^{-3} = 0.0100 \text{ mol}$$

$$n(\text{NaOH}) = n(\text{NO}_2) = 0.0100 \text{ mol}$$

$$\text{min. volume of } 1.00 \text{ mol dm}^{-3} \text{ NaOH needed} = 0.0100 / 1.00 \times 1000 = \underline{10.00 \text{ cm}^3}$$
 [1]

- (d) A diagram of the assembled apparatus capable of absorbing the nitrogen(IV) oxide and collecting the oxygen separately and in sequence [2]

- Directly heated vessel (boiling tube) labelled magnesium nitrate with tube at exit
- Gas stream led into a liquid labelled (1.00 mol dm⁻³) NaOH which will absorb the nitrogen(IV) oxide / NO₂
- Collects a gas in a syringe or over a liquid, provided it is properly connected
- All parts of the apparatus are connected and air-tight AND nitrogen(IV) oxide absorption precedes oxygen collection



An outline of how the results would be obtained and measures to ensure reliability of results

[4]

1. Record the mass of the empty boiling tube.
2. Weigh accurately about 0.75 g of magnesium nitrate into a boiling tube.
3. Using a burette, add 20.00 cm³ of 1.00 mol dm⁻³ sodium hydroxide into the chamber collecting nitrogen(IV) oxide / NO₂.
4. Set up the apparatus according to the diagram above.
5. After ensuring that all the connections are properly sealed, start heating the magnesium nitrate in the boiling tube. Heat strongly for about 5 minutes, moving the boiling tube to ensure even heating of the solid. Continue heating until no further bubbling is seen in the sodium hydroxide solution and the syringe shows no further change in volume of oxygen gas collected.
6. Remove the delivery tube from the alkali before taking the boiling tube off the flame. *(To prevent back flow of liquid into the boiling tube due to cooling of air)*
7. Allow all the apparatus and chemicals to cool to room temperature before taking measurements.
8. Weigh the boiling tube and residue. Subtract the mass of the empty boiling tube to determine the mass of magnesium oxide produced.
9. Transfer all the sodium hydroxide solution into a 100 cm³ volumetric flask. Top up to the mark with distilled water. Stopper the flask and shake well to obtain a homogeneous solution.
10. Pipette 25.0 cm³ of the solution into a 250 cm³ conical flask for titration.
11. Add a few drops of methyl orange indicator. Titrate with the 0.20 mol dm⁻³ hydrochloric acid from the 50.00 cm³ burette until the solution turns from yellow to orange.
12. Repeat the titration until consistent results within ± 0.10 cm³ are obtained.
13. Record the volume of oxygen gas collected in the syringe.

Brief, but specific, details of how results will be used to determine the amounts in moles of reactant and all products at the end of complete thermal decomposition AND confirm that the decomposition had occurred according to the molar ratios in the equation

$$n(\text{MgO}) = \text{mass of MgO} / M_r \text{ of MgO} = x \text{ mol}$$

$$\begin{aligned} n(\text{NO}_2) &= n(\text{NaOH that reacted with NO}_2) \\ &= (20/1000 \times 1) - [(\text{vol. of HCl}/1000 \times 0.20) \times 100/25.0] = y \text{ mol} \end{aligned}$$

$$n(\text{O}_2) = \text{volume of O}_2/24000 = z \text{ mol}$$

}

[1]

Compare each of the values x , y and z with $n[\text{Mg}(\text{NO}_3)_2]$ used ($\approx 5.00 \times 10^{-3}$ mol) to check if the decomposition has occurred according to the molar ratios in the equation. [1]

[Total: 12]

- 2 (a) (i) B atom in BF_3 molecule is electron-deficient as it has only 6 electrons around it. Hence, the B atom can accept another 2 electrons from the lone pair of O atom in ethoxyethane molecule. By forming a dative bond with the O atom of $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$, the B atom achieves the octet configuration. [2]



(b) (i)
$$K_{\text{partition}} = \frac{\text{concentration of J in ethoxyethane (organic layer)}}{\text{concentration of J in water (aqueous layer)}}$$

$$= \frac{2.14 / 20}{(5 - 2.14) / 75} = \underline{2.81}$$
 [1]

- (ii) 1st extraction [2]

$$2.81 = (x / 10) / [(5 - x) / 75]$$

$$2.81 (5 - x) = 7.5 x$$

$$x = 1.36 \text{ g}$$

2nd extraction

Mass of **J** remaining in aqueous layer after 1st extraction = $5.00 - 1.36 = 3.64 \text{ g}$

$$2.81 = (y / 10) / [(3.64 - y) / 75]$$

$$2.81 (3.64 - y) = 7.5 y$$

$$y = 0.992 \text{ g}$$

\therefore total mass of **J** extracted = $1.36 + 0.992 = \underline{2.35 \text{ g}}$

- (iii) It is more efficient to use two successive portions of 10 cm^3 ethoxyethane than one 20 cm^3 portion of ethoxyethane since total mass of **J** extracted is greater using two successive portions. [1]

- (c) Anhydrous calcium chloride (drying agent) was added to remove water present in the organic layer. [1]

[Total: 8]

3 (a) Giant covalent structure with strong covalent bonds between P atoms. [1]

Relatively high melting point **OR** insolubility in organic solvent (methylbenzene) suggests strong bonding throughout the structure. [1]

(b) type of hybridisation: sp [1]

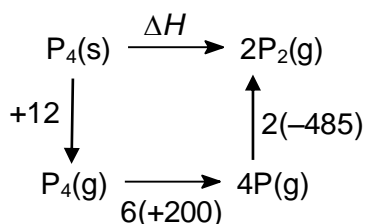


(c) (i) Phosphorus-phosphorus triple bonds are much weaker than nitrogen-nitrogen triple bonds as phosphorus atoms are too big to come close enough together to form strong bonds. [1]

OR

Orbitals of P are larger and more diffused hence overlap of orbitals is less effective.

(ii) [2]



$$\begin{aligned} \Delta H &= +12 + 6(+200) + 2(-485) \\ &= \underline{+242 \text{ kJ mol}^{-1}} \end{aligned} \quad [1]$$

(iii) Increase temperature [1]

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

Since $\Delta H > 0$, $\underline{\Delta S > 0}$ (as there is an increase in no. of moles of gas), for ΔG to be negative (i.e. spontaneous), magnitude of $T\Delta S$ must be greater than that of ΔH . Hence, T must be large. [1]

(d) (i) High temperature (needed for reaction between N_2 and O_2) [1]



[Total: 12]

4 (a) (i) A ligand is a neutral molecule or an anion which possesses at least one lone pair of electrons which can be used to form dative bonds with the central atom or ion. [1]

(ii) *Transition element complexes are often coloured:*

In the presence of ligands, the d orbitals of transition metal ion are split into two levels.

The energy gap E between the non-degenerate orbitals is small and corresponds to that in the visible light region. [1]

Energy is absorbed from the visible region when an electron is promoted from a lower level d orbital to a vacant higher level d orbital (d-d transition). [1]

The colour of the transition metal complex is the complement of the colour absorbed. [1]

The colour of a complex of a given transition element often changes when the ligands around it are changed:

The size / magnitude of the energy gap E depends on the ligand. [1]

(Since $E = hc / \lambda$),

When the ligand changes, E changes, λ (absorbed) also changes (hence colour of the complex changes). [1]

(b) (i) Let O.N. of C in $C_2O_4^{2-}$ be x

$$2(x) + 4(-2) = -2$$

$$x = \underline{\underline{+3}}$$

[1]

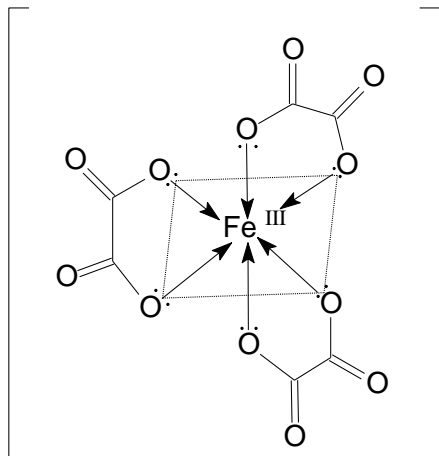
(ii) Let O.N. of Fe in $[Fe(C_2O_4)_3]^{3-}$ be y

$$y + 3(-2) = -3$$

$$y = \underline{\underline{+3}}$$

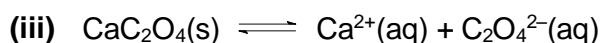
[1]

(iii) []³⁻ [2]



(c) (i) $K_{sp} = [Ca^{2+}][C_2O_4^{2-}]$ [1]

(ii) $[C_2O_4^{2-}] = (2.3 \times 10^{-9})^{1/2} = \underline{\underline{4.80 \times 10^{-5} \text{ mol dm}^{-3}}}$ [1]



Increase in $[\text{Ca}^{2+}]$ due to the presence of the common ion Ca^{2+} (from CaCl_2) in solution **W** shifts the position of the above equilibrium to the left. Hence, $[\text{C}_2\text{O}_4^{2-}]$ in solution **W** is less than that calculated in **(c)(i)**. [1]

(d)

cation	ionic radius / nm
Na^+	0.095
Mg^{2+}	0.065
Al^{3+}	0.050

} [1]

The charge density of the cation increases from Na^+ to Mg^{2+} to Al^{3+} . Thus, the polarising power of the cation increases in the same order.

As a result, NaCl does not hydrolyse in water ($\text{pH} = 7$); MgCl_2 hydrolyses only to a small extent ($\text{pH} = 6.5$) and AlCl_3 hydrolyses to a larger extent ($\text{pH} = 3.0$). [1]

[Total: 15]

- 5 (a) The actual value for the enthalpy of hydrogenation of benzene is less exothermic as more energy is needed to break the bonds in benzene due to delocalisation of the π electrons. [1]

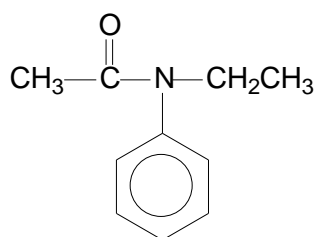
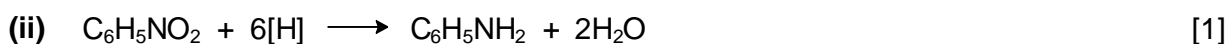
OR

Benzene is resonance-stabilised and hence has a lower energy level.

- (b) reagents: conc. HNO_3 + conc. H_2SO_4 } [1]
 conditions: 55 – 60 °C }
 electrophile: NO_2^+ [1]

- (c) (i) In phenylamine, the lone pair on the N atom is delocalised into the benzene ring, making the ring more electron-rich. [1]

Hence, the ring is more susceptible to (electrophilic) attack and hence does not require the strong electrophile Br^+ generated by the reaction between Br_2 and FeBr_3 . [1]



X

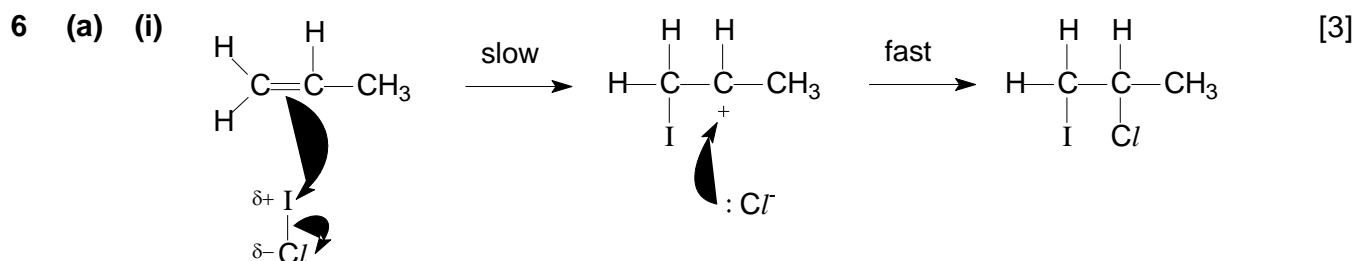
(d) 3 : 14 : 9

[1]

Relative rate suggests 1 : 7 : 1, but there are 3 primary to 2 secondary to 9 primary hydrogen atoms in L, M and N respectively. Hence, this ratio becomes 3 : 14 : 9.

[1]

[Total: 9]



[3]

(ii) ICl is polar while pure halogens are not.

[1]

(b) number of σ bonds: 14
number of π bonds: 2 }

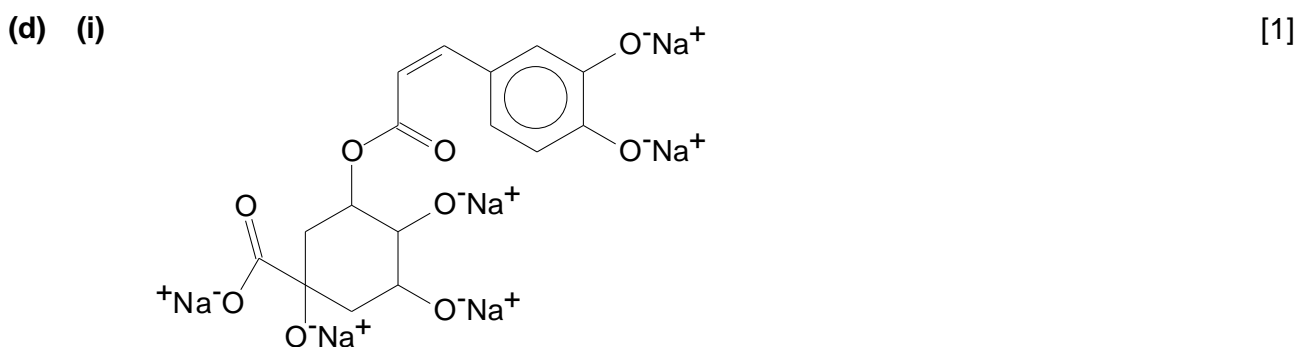
[1]

(c) (i) ethene

[1]



[2]



[1]

(ii) (acid) hydrolysis

[1]



[1]

C

(iii) alkene **OR** C=C

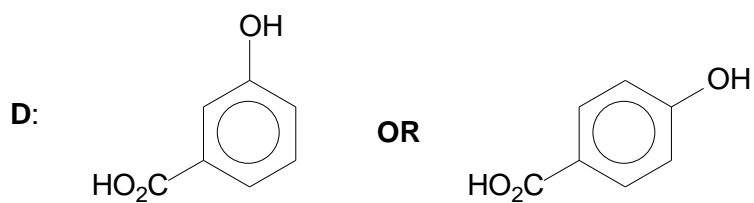
[1]

(iv) $\text{Na}_2\text{CO}_3(\text{aq})$: carboxylic acid
 $\text{Br}_2(\text{aq})$: phenol

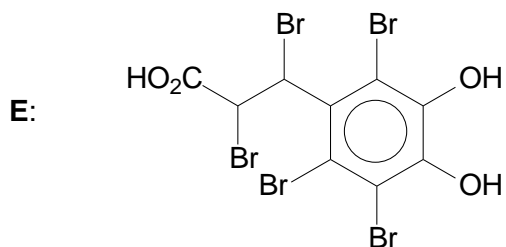
[1]

[1]

(v)



[1]



[1]

[Total: 16]

Name _____ Index No. _____

Subject _____ Class _____ Date _____

partial pressure, P_1 of N_2O / kPa



20 cm x 24 cm 1000 2000 3000 4000 5000 6000 7000 8000 time t/s

AJCP3INSERT $t_{1/2} = 3200s$ $t_{1/2} = 3200s$ 146

2016 JC2 PRELIMINARY

EXAMINATIONS

CHEMISTRY

9647/03

Higher 2

21 September 2016

Paper 3 Free Response

2 hours

Candidates answer on separate paper.

Additional Materials: Writing Paper
 Data Booklet
 Graph Paper

READ THESE INSTRUCTIONS FIRST

Write your name, PDG and register 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 pencil for any diagrams or graphs.

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

Answer any **four** questions.

Start each question on a fresh sheet of paper.

A Data Booklet is provided.

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

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

At the end of the examination, fasten all your work securely together.

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

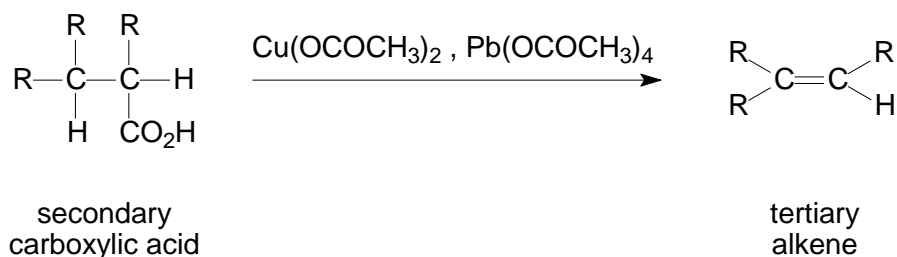
This document consists of **12** printed pages.

- 1 (a) 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 and copper.

property	calcium	iron	copper
relative atomic mass	40.1	55.8	63.5
atomic radius (metallic) / nm	0.197	0.126	0.128
ionic radius (2+) / nm	0.099	0.076	0.069
melting point / °C	839	1535	1085
density / g cm ⁻³	1.54	7.86	8.92
electrical conductivity / x 10 ⁶ S cm ⁻¹	0.298	0.100	0.596

- (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. Explain this in terms of the type and strength of bonding in each metal. [3]
- (iii) Using relevant data from the table, explain why the densities of iron and copper are significantly greater than that of calcium. (No calculations are required.) [2]
- (b) Cu(I) ions are unstable and readily undergo disproportionation in aqueous solution. Write an ionic equation showing the disproportionation of Cu⁺(aq) ions, and choose relevant E^\ominus values from the *Data Booklet* to calculate E_{cell}^\ominus for the reaction. [2]
- (c) Cu(I) is stable in insoluble salts and in some complexes. Complexes of Cu(I) are colourless whereas complexes of Cu(II) are coloured. Use these facts to explain the following observations, writing equations for all reactions.
- (i) The addition of KI(aq) to CuSO₄(aq) produces a white precipitate, CuI, and a brown solution. The brown solution turns colourless when aqueous sodium thiosulfate, Na₂S₂O₃, is added, and the white precipitate remains. [2]
- (ii) On boiling with copper foil, the colour of a solution of CuCl₂ in concentrated hydrochloric acid changes from blue to colourless. The colourless solution contains a linear complex ion of copper and chlorine. After filtering off the excess copper metal and diluting the solution with water, a white precipitate is formed, which contains 35.9 % of chlorine by mass. [3]

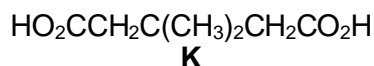
- (d) Some copper compounds have found a use as reagents for unusual organic reactions. An example is the use of a mixture of copper(II) ethanoate and lead(IV) ethanoate for the conversion of carboxylic acids into alkenes containing one less carbon atom. This reaction is known as oxidative decarboxylation.



When a secondary carboxylic acid **G**, $\text{C}_9\text{H}_{16}\text{O}_2$, was treated in this way, alkene **H**, C_8H_{14} , was formed. On treatment with hot acidified concentrated KMnO_4 , **H** produced a single compound **J**, $\text{C}_8\text{H}_{14}\text{O}_3$.

Compound **J** evolved CO_2 with $\text{Na}_2\text{CO}_3(\text{aq})$, gave an orange precipitate with 2,4-dinitrophenylhydrazine reagent, and gave a yellow precipitate with alkaline aqueous iodine.

When the yellow precipitate had been filtered off, acidification of the aqueous solution produced 3,3-dimethylpentan-1,5-dioic acid, **K**.

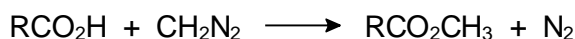


Use the information above to deduce the structures for compounds **G**, **H** and **J**, explaining all the reactions involved.

[6]

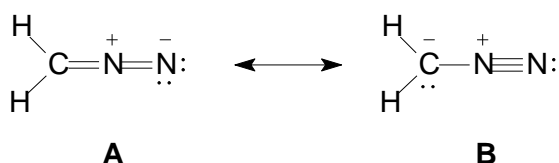
[Total: 20]

- 2 (a) One frequently used method for preparing methyl esters is by reaction of carboxylic acids with diazomethane, CH_2N_2 .



The reaction of a carboxylic acid with diazomethane occurs via a two-step mechanism.

- Protonation of diazomethane by the carboxylic acid to yield methyldiazonium ion, CH_3N_2^+ , and carboxylate ion in the first step.
 - Reaction of the carboxylate ion with CH_3N_2^+ to form N_2 in the second step.
- (i) **A** and **B** are two possible resonance structures of diazomethane, CH_2N_2 .



Suggest which resonance structure of diazomethane, **A** or **B**, is likely to be involved in the first step of the mechanism.

[1]

- (ii) Using your answer from (a)(i), suggest the mechanism for the reaction between RCO_2H and diazomethane. Show any relevant lone pairs, dipoles and charges, and indicate the movement of electron pairs with curly arrows.

[3]

- (b) (i) Write an equation for the complete combustion of methyl ethanoate, $\text{CH}_3\text{CO}_2\text{CH}_3$.

[1]

- (ii) Define the term *standard enthalpy change of formation*.

[2]

- (iii) Use the standard enthalpy changes of combustion, ΔH_c^\ominus in **Table 2.1** to calculate the standard enthalpy change of formation of methyl ethanoate.

Table 2.1

	$\Delta H_c^\ominus / \text{kJ mol}^{-1}$
carbon	-393.5
hydrogen	-285.8
methyl ethanoate	-1592.1

[3]

- (c) Describe one simple chemical test to distinguish between $\text{HCO}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CO}_2\text{CH}_3$. State clearly how each compound behaves in the test. [3]
- (d) Consecutive elements **W**, **X**, **Y** and **Z** are in the third period of the Periodic Table. Element **Y** has the highest first ionisation energy and the lowest melting point of these four elements.
- (i) Describe what you would see when elements **W** and **Z** are separately burned in air or oxygen. [2]
- (ii) The oxides of elements **X** and **Y** can be obtained when the elements are burned in excess oxygen. The oxides of **X** and **Y** have melting points of $1720\text{ }^\circ\text{C}$ and $580\text{ }^\circ\text{C}$ respectively.
- Briefly relate these melting points to the structure of and bonding in each of these oxides. [2]
- (iii) Describe the reactions, if any, of the oxides of elements **X** and **Y** with water. Include the approximate pH value of any resulting solutions, and write equations for any reactions that occur. [3]

[Total: 20]

- 3 (a) Nickel–metal hydride (Ni–MH) batteries are the most common rechargeable batteries used for devices that require large amounts of energy such as digital cameras and MP3 players. Most Ni–MH batteries use an alloy containing mainly lanthanum and nickel.

In one such battery, one of the electrodes is LaNi_5H_6 and the other is $\text{NiO}(\text{OH})$. The electrolyte is aqueous KOH . During discharge, an electrochemical reaction takes place to produce $\text{LaNi}_5(\text{s})$ and $\text{Ni}(\text{OH})_2(\text{s})$ and releases electrical energy.

- (i) Construct the two half–equations for the reactions that take place at each electrode during **discharge**. Indicate the polarity of the electrodes in your answer. [2]

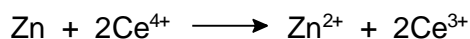
- (ii) During **recharge**, an electrical potential is applied across the electrodes to reverse the electrochemical reaction.

Using your answer in (a)(i), write the overall equation for the reaction that occurs during **recharge**. [1]

- (iii) Overcharging the Ni–MH battery may result in the electrolyte being discharged at the electrodes. A safety vent is thus incorporated in the battery to release the excess pressure.

With reference to the *Data Booklet*, suggest a relevant half–equation for the formation of one product at the electrode of the Ni–MH battery. [1]

- (b) Zinc–cerium battery is another type of rechargeable battery using a two–electrolyte system. The overall equation for the discharging process is given below.



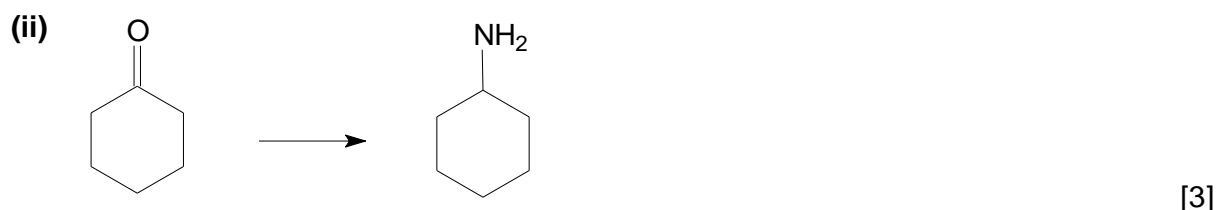
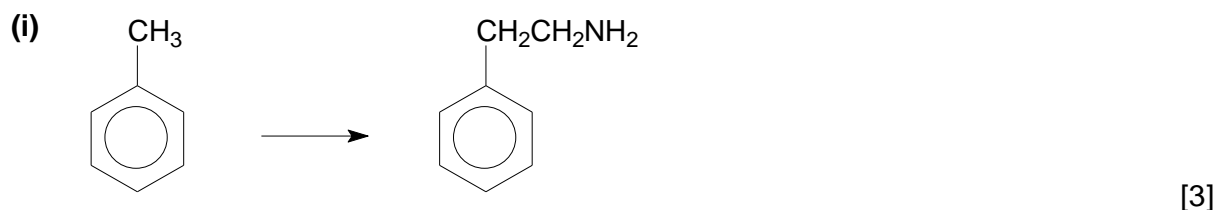
- (i) Given that the typical cell voltage for the cell is 2.2 V, calculate the standard electrode potential of the cerium half–cell, using relevant data from the *Data Booklet*. [1]

- (ii) Using relevant data from the *Data Booklet*, deduce if the $\text{Ce}^{4+}/\text{Ce}^{3+}$ half–cell can be replaced with Br_2/Br^- half–cell. [1]

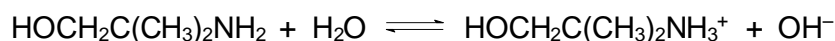
- (c) Amines can be made from a variety of compounds.

Suggest, **in no more than three steps**, how each of the following transformations can be achieved.

For each transformation, draw the structures of the intermediate compounds and indicate reagents and conditions for each of the steps.



- (d) The buffer of 2-amino-2-methylpropan-1-ol (AMP) has been shown to be well suited for the determination of the activity of enzymes like alkaline phosphatase and lactate dehydrogenase. It hydrolyses in water with a pK_b value of 4.3.



- (i) A 100 cm³ solution containing 0.500 mol dm⁻³ of HOCH₂C(CH₃)₂NH₂ is mixed with a 100 cm³ solution containing 0.800 mol dm⁻³ HOCH₂C(CH₃)₂NH₃⁺.

Calculate the pH of the buffer solution formed.

[2]

- (ii) State the ratio of $\frac{[\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{NH}_2]}{[\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{NH}_3^+]}$ when the pH of the buffer solution is 9.7.

Hence calculate the mass of solid NaOH to be added to the buffer solution in (d)(i) to achieve this ratio.

[2]

- (e) Proteins are long-chain molecules made by linking together amino acids.

Myoglobin is one such protein that stores and releases oxygen in vertebrate muscle cells. The table below shows some of the amino acids in a molecule of myoglobin.

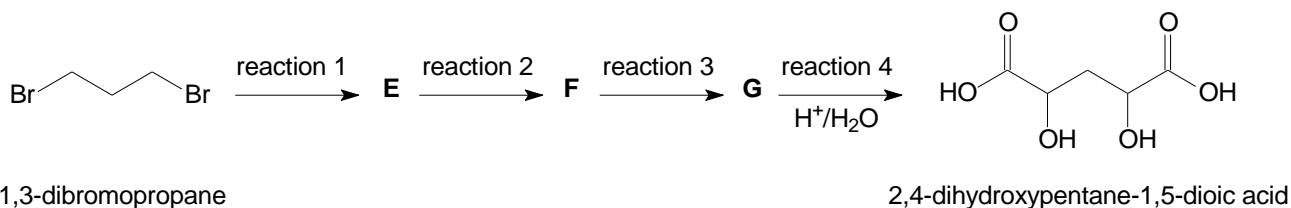
amino acid	aspartic acid	serine	alanine	lysine
abbreviation	asp	ser	ala	lys
formula of side chain	$-\text{CH}_2\text{CO}_2\text{H}$	$-\text{CH}_2\text{OH}$	$-\text{CH}_3$	$-(\text{CH}_2)_4\text{NH}_2$

- (i) Given that asp-lys-ala is a particular **section** of the protein chain of myoglobin, draw the displayed formula for this **section** at pH 7. [1]
- (ii) Describe **two** types of side-chain interaction that would occur between the amino acids residues of myoglobin. Illustrate your answer with suitable pairs of amino acids from the table above. [2]
- (iii) Casein is the predominant protein found in milk. The conversion of milk to cheese is a denaturation process involving the addition of the *Lactobacillus* bacterium which produces lactic acid.

Explain this phenomenon by considering the types of side-chain interaction that are affected during the denaturation of casein. [1]

[Total: 20]

- 4 (a) 1,3-dibromopropane is the starting material for a four-step reaction sequence which produces 2,4-dihydroxypentane-1,5-dioic acid. The four reactions are shown.



Compound **F** has the molecular formula $C_3H_4O_2$. On treatment with Tollens' reagent, it gives a silver mirror.

- (i) Draw the structures of **E** and **F**. [2]

- (ii) When preparing compound **F** from **E** it is important that the product is distilled off rather than continually refluxed.

State which unwanted product is avoided by distilling off compound **F**.

[1]

- (iii) In an experiment, 9.0 g of 1,3-dibromopropane was converted into compound **F** with an overall yield of 67 %. Calculate the mass of **F** that was obtained.

[2]

- (iv) Compound **G** is converted into the final product by reaction with dilute acid. Suggest the structure of **G**.

[1]

- (b) The oxides of Group I and II metals have many uses. Beryllium oxide, BeO , is used in many high-performance semiconductor parts for applications such as radio equipment, while sodium oxide, Na_2O , is a significant component of glasses and windows.

- (i) Using the given data and other relevant data from the *Data Booklet*, construct an energy level diagram and use it to calculate the lattice energy of beryllium oxide. Label each energy level in your diagram and draw arrows representing the energy terms involved. Use symbols or numbers to represent these energy terms.

enthalpy change of formation of beryllium oxide	-609 kJ mol^{-1}
enthalpy change of atomisation of beryllium	$+324 \text{ kJ mol}^{-1}$
first electron affinity of oxygen	-141 kJ mol^{-1}
second electron affinity of oxygen	$+798 \text{ kJ mol}^{-1}$

[3]

- (ii) The theoretical lattice energy of beryllium oxide is $-4293 \text{ kJ mol}^{-1}$. Suggest a reason why this value is different from your answer in (b)(i).

[1]

- (iii) Explain how you would expect the numerical magnitude of the lattice energy of beryllium oxide to compare with that of sodium oxide.

[2]

- (iv) Explain the reaction(s) that occur(s) when chlorine gas is bubbled into a flask containing water, at room temperature, to which sodium oxide has been added. Write equation(s) where appropriate.

[2]

- (c) Soluble chromates(VI) in the soil are toxic at low concentrations for plants.

In water treatment to remove the chromate(VI) ions, $\text{CrO}_4^{2-}(\text{aq})$, from a sample of soil water, aqueous acidified iron(II) sulfate is first added to the water sample to convert the chromate(VI) ions to chromium(III) ions, $\text{Cr}^{3+}(\text{aq})$. This is followed by adding aqueous sodium carbonate to the resultant solution to produce effervescence and an insoluble compound.

- (i) Construct an equation for the reaction between aqueous acidified iron(II) sulfate and chromate(VI) ions.

[1]

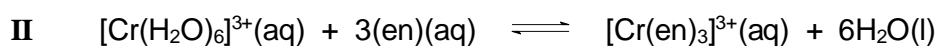
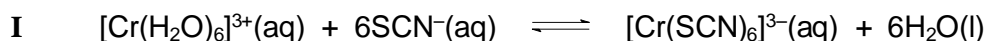
- (ii) Identify the insoluble compound formed upon adding aqueous sodium carbonate.

With the aid of an appropriate ionic equation, explain its formation.

[2]

- (d) Chromium(III) ions coordinate with both monodentate and polydentate ligands.

Consider the following complex formation reactions with thiocyanate, SCN^- , and ethylenediamine, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, ligands:



where (en) is ethylenediamine

- (i) Explain what is meant by *entropy*.

[1]

- (ii) Explain how you would expect the entropy change, ΔS_r^\ominus , for reaction II to compare with that for reaction I.

[2]

[Total: 20]

5 Nitrogen forms numerous oxides, two of which are dinitrogen monoxide, N_2O , and dinitrogen tetroxide, N_2O_4 .

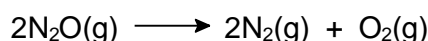
- (a) Dinitrogen monoxide, N_2O , is a non-toxic gas that is used commercially as the propellant in cans of whipped cream.

Given that N_2O is a linear molecule, draw a 'dot-and-cross' diagram showing the electrons (outer shells only) in N_2O .

You should distinguish carefully between electrons originating from each of the nitrogen atoms.

[1]

- (b) At 1200 K and in the presence of a gold wire, N_2O decomposes as follows.



The kinetics of this reaction can be followed by measuring the total pressure, P , as it changes with time, t . In one such experiment, the total pressure changes as follows.

total pressure, P / kPa	25.0	27.5	30.0	32.5	34.0	35.0
time, t / s	0	1030	2360	4230	5870	7420
partial pressure, p , of N_2O / kPa	25.0					

- (i) What is the total pressure when the reaction is complete? [1]

- (ii) Show that the partial pressure of N_2O at any time, t , is equal to $(75.0 - 2P)$ kPa. [2]

- (iii) Hence calculate the partial pressures of N_2O after 1030 s, 2360 s, 4230 s, 5870 s and 7420 s. [1]

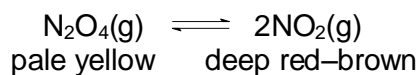
- (iv) Using your answers from (b)(iii) and the data above, plot these data on suitable axes and use your graph to determine the order of reaction with respect to N_2O .

You should show all your working and draw clearly any construction lines on your graph.

[3]

- (v) The rate of reaction is expressed in kPa s^{-1} . Write the rate equation for the reaction, and calculate a value for the rate constant. Include units in your answer. [3]

At a temperature of 27 °C, gaseous N₂O₄ and NO₂ are in dynamic equilibrium according to the following equation.



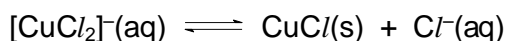
- (c)** When 4.60 g of N₂O₄ is placed in an evacuated 1.48 dm³ flask at 27 °C, the equilibrium pressure is 1.00 atm (101 kPa).
- (i)** Calculate the number of moles of N₂O₄ at the start. [1]
- (ii)** Calculate the number of moles of gas at equilibrium, assuming the gases behave ideally. [1]
- (iii)** Hence calculate the percentage of the N₂O₄ that has been dissociated. [2]
- (iv)** Write an expression for the equilibrium constant, K_p , for the reaction and show it has a value of 0.17 atm at 27 °C. [3]
- (d)** When the equilibrium mixture from **(c)** at 27 °C is suddenly compressed in a gas syringe, the mixture immediately darkens and then slowly becomes paler. Suggest why the mixture behaves in this way. [2]

[Total: 20]

- 1 (a) (i) Nuclear charge / proton number increases from Fe to Cu. } [1]
 However, additional electrons are being added to the inner 3d subshell. As such, there is an increase in shielding effect caused by the increasing number of d electrons from Fe to Cu. } [1]
- Hence, effective nuclear charge remains fairly constant from Fe to Cu. [1]
- (ii) Fe uses both the 3d and 4s electrons while Ca only uses the 4s electrons for metallic bonding. [1]
- The ionic radius of Fe is also smaller than that of Ca, resulting in higher charge density. [1]
- This results in stronger metallic bonding between Fe ions and the valence electrons. [1]
- (iii) density = mass / volume } [1]
 Fe and Cu have greater atomic mass } [1]
 and smaller atomic radius. [1]
- (b) $2\text{Cu}^+(\text{aq}) \longrightarrow \text{Cu}(\text{s}) + \text{Cu}^{2+}(\text{aq})$ [1]
- State symbols not required*
- $E^\ominus(\text{Cu}^+/\text{Cu}) = +0.52 \text{ V}$
 $E^\ominus(\text{Cu}^{2+}/\text{Cu}^+) = +0.15 \text{ V}$
- $E_{\text{cell}}^\ominus = +0.52 - (+0.15) = \underline{+0.37 \text{ V}}$ [1]
- (c) (i) I^- and Cu^{2+} undergo a redox reaction to produce the white precipitate copper(I) iodide, CuI, and brown solution I_2 . } [1]
 $2\text{I}^-(\text{aq}) + \text{Cu}^{2+}(\text{aq}) \longrightarrow \text{CuI}(\text{s}) + \text{I}_2(\text{aq})$ } [1]
- $\text{S}_2\text{O}_3^{2-}$ then reduces I_2 to I^- (colourless solution), itself oxidises to $\text{S}_4\text{O}_6^{2-}$ (redox reaction). } [1]
 $2\text{S}_2\text{O}_3^{2-}(\text{aq}) + \text{I}_2(\text{aq}) \longrightarrow 2\text{I}^-(\text{aq}) + \text{S}_4\text{O}_6^{2-}(\text{aq})$ } [1]
- State symbols not required*
- (ii) Cu and Cu^{2+} undergo a redox reaction (or comproportionation) to form a colourless Cu(I) complex, $[\text{CuCl}_2]^-$. } [1]
 $\text{Cu}(\text{s}) + \text{Cu}^{2+}(\text{aq}) + 4\text{Cl}^-(\text{aq}) \longrightarrow 2[\text{CuCl}_2]^- (\text{aq})$ } [1]

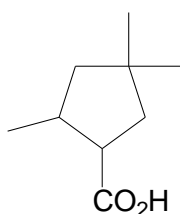
Element	Cu	Cl
% by mass	64.1	35.9
A_r	63.5	35.5
No. of moles	$64.1/63.5$ $= 1.009$	$35.9/35.5$ $= 1.011$
Simplest whole no. ratio	1	1

The white precipitate is CuCl.

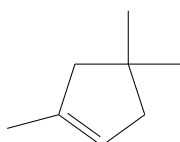


State symbols not required

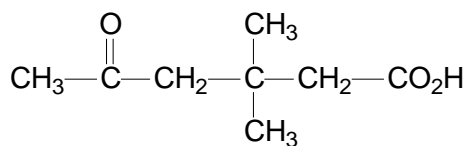
Information	Type of reaction	Deduction(s)
On treatment with hot acidified concentrated KMnO_4 , H produced a single compound J , $\text{C}_8\text{H}_{14}\text{O}_3$.	Oxidative cleavage	H contains a <u>C=C / alkene</u> . Since a single compound is formed (without loss of C), H is a <u>cycloalkene</u> .
J evolved CO_2 with $\text{Na}_2\text{CO}_3(\text{aq})$,	Acid-base	J contains <u>RCO_2H / carboxylic acid</u> .
J gave an orange precipitate with 2,4-DNPH,	Condensation	J contains a <u>ketone</u> . (J cannot contain an aldehyde since J is produced from strong oxidation of H with KMnO_4)
J and gave a yellow precipitate with alkaline aqueous iodine.	Oxidation / tri-iodomethane reaction	J has a <u>$\text{CH}_3\text{CO}-$</u> structure (J cannot have a $\text{CH}_3\text{CH}(\text{OH})-$ structure since J is produced from strong oxidation of H with KMnO_4)



G



H

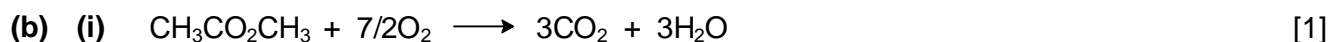
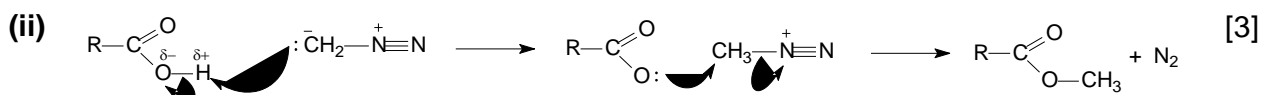


J

Do not accept  *for structure of G as G is a secondary carboxylic acid*

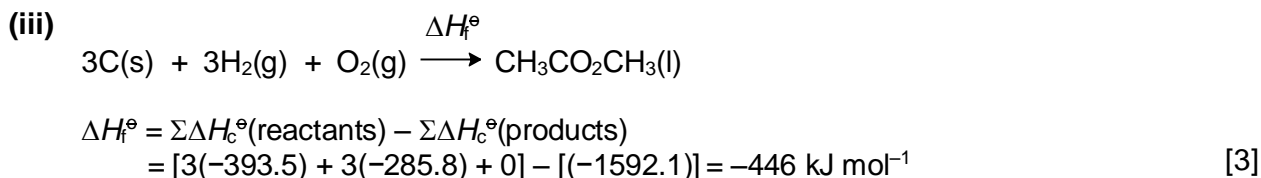
[Total: 20]

2 (a) (i) B [1]



Accept equation multiplied through by 2

(ii) The amount of heat absorbed or evolved when one mole of substance is formed from its constituent elements in their standard states at 298 K and 1 atm. [2]



(c) Heat each compound separately with NaOH(aq), and then add I₂(aq) to the resulting solution. [1]

A yellow precipitate (CHI_3) is observed for HCO₂CH₂CH₃. [1]

No (yellow) precipitate is observed for CH₃CO₂CH₃. [1]

(d) (i) **W** (aluminium) burns in O_2 with an intense white flame to give a white solid of Al_2O_3 . [1]

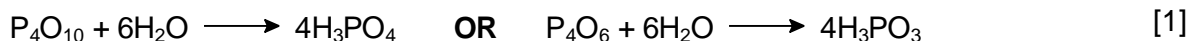
Z (sulfur) burns in O_2 on gentle heating with a pale blue flame to give a colourless gas of SO_2 . [1]

(ii) The oxide of **X** (SiO_2) has a giant molecular structure. Large amount of energy is required to break the strong covalent bonds between Si and O atoms. [1]

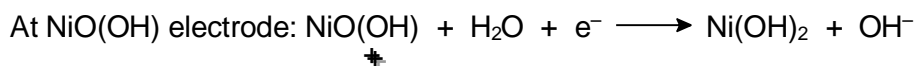
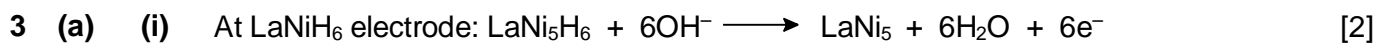
The oxide of **Y** (P_4O_{10} or P_4O_6) has a simple molecular structure. Less energy is required to break the weak van der Waal's forces of attraction between the molecules. [1]

(iii) The oxide of **X** (SiO_2) is insoluble in water. Hence, the pH of the resulting solution is 7. [1]

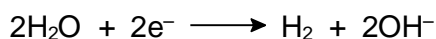
The oxide of **Y** (P_4O_{10} or P_4O_6) reacts readily in water to produce a strongly acidic solution of pH 2. [1]



[Total: 20]

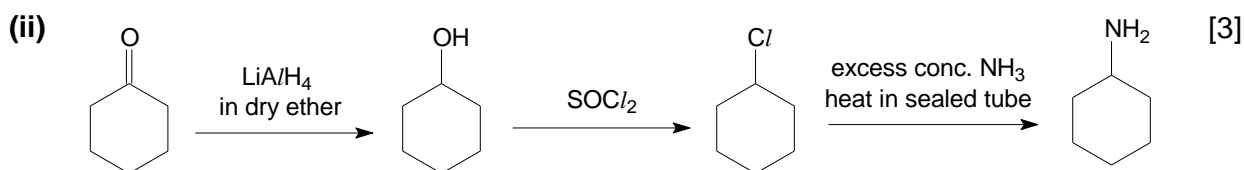
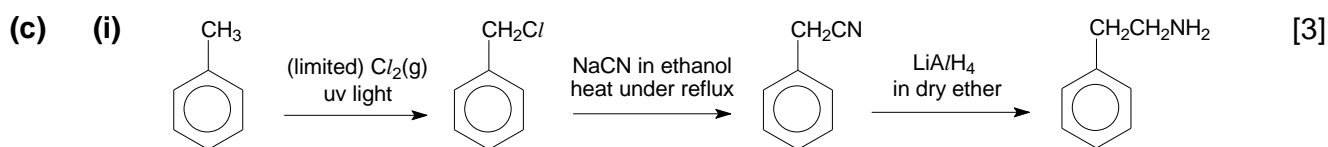


OR



$E^\ominus_{\text{cell}} = +1.07 - (-0.76)$
 $= \underline{+1.83 \text{ V} > 0}$ (feasible)

Since it is feasible for the battery to discharge electricity, the Ce⁴⁺/Ce³⁺ half-cell can be replaced with Br₂/Br⁻ half-cell. [1]



(d) (i) Since equal volume of HOCH₂C(CH₃)₂NH₂ and HOCH₂C(CH₃)₂NH₃⁺ are mixed, concentration of both species are halved.

$$K_b = \frac{[\text{HOCH}_2\text{C(CH}_3)_2\text{NH}_3^+][\text{OH}^-]}{[\text{HOCH}_2\text{C(CH}_3)_2\text{NH}_2]}$$

$$10^{-4.3} = \frac{(0.400)[\text{OH}^-]}{0.250}$$
 [1]

$$[\text{OH}^-] = 3.13 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\text{pOH} = -\log(3.13 \times 10^{-5}) = 4.5$$

$$\text{pH} = \underline{9.5}$$
 [1]

- (ii) Since $pK_b(\text{AMP}) = 4.3$, $pK_a(\text{conjugate acid of AMP}) = 9.7$.

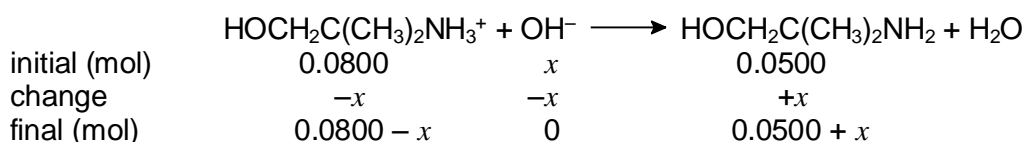
When pH of the buffer = 9.7, the buffer solution is at its maximum buffering capacity.

$$\text{Hence } \frac{[\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{NH}_2]}{[\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{NH}_3^+]} = 1. \quad [1]$$

$$\text{initial } n(\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{NH}_3^+) = 100/1000 \times 0.800 = 0.0800 \text{ mol}$$

$$\text{initial } n(\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{NH}_2) = 100/1000 \times 0.500 = 0.0500 \text{ mol}$$

Let x be $n(\text{OH}^-)$ added



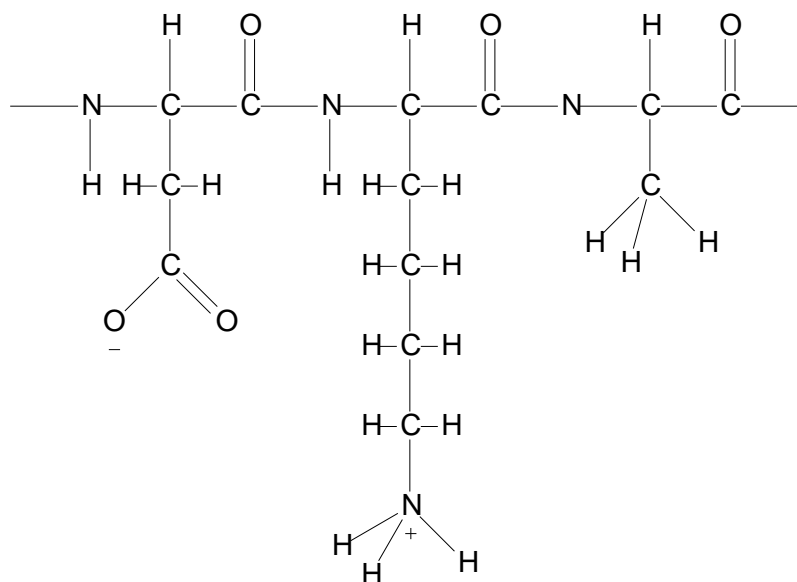
$$\text{Since } \frac{[\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{NH}_2]}{[\text{HOCH}_2\text{C}(\text{CH}_3)_2\text{NH}_3^+]} = 1,$$

$$0.0800 - x = 0.0500 + x$$

$$x = 0.015 \text{ mol}$$

$$\text{mass of NaOH added} = 0.015 \times (23.0 + 16.0 + 1.0) = \underline{0.600 \text{ g}} \quad [1]$$

(e) (i)



- (ii)
- Ionic bonding between charged R groups containing the $-\text{CO}_2^-$ groups, $-\text{NH}_3^+$ groups. [1]
Example: Between lysine (containing $-\text{NH}_3^+$) and aspartic acid (containing $-\text{CO}_2^-$)
 - Hydrogen bonding between polar R groups containing the carboxyl groups ($-\text{CO}_2\text{H}$), amino groups ($-\text{NH}_2$) or hydroxyl ($-\text{OH}$) groups. [1]
Example: Between aspartic acid and serine or between lysine and serine.

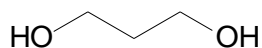
- (iii) Lactic acid dissociates to give H^+ which may protonate the carboxylate group (in glutamic acid) or the amine group (in lysine), disrupting ionic bonds between the charged R groups. [1]

OR

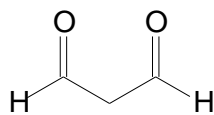
disrupting the hydrogen bonding between the polar R groups (e.g. lysine and serine, leading to denaturation).

[Total: 20]

4 (a) (i)



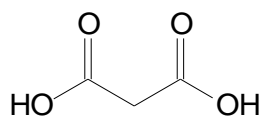
E



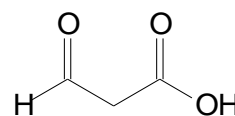
F

[2]

(ii)



OR



[1]

Accept "propanedioic acid"

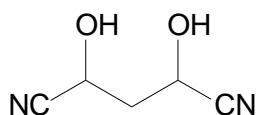
Accept "3-oxopropanoic acid"

(iii) $n(1,3\text{-dibromopropane}) = 9.0 / 201.8 = 0.0446 \text{ mol}$
 mass of F = $0.67 \times 0.0446 \times 72.0 = \underline{2.15 \text{ g}}$

[1]

[1]

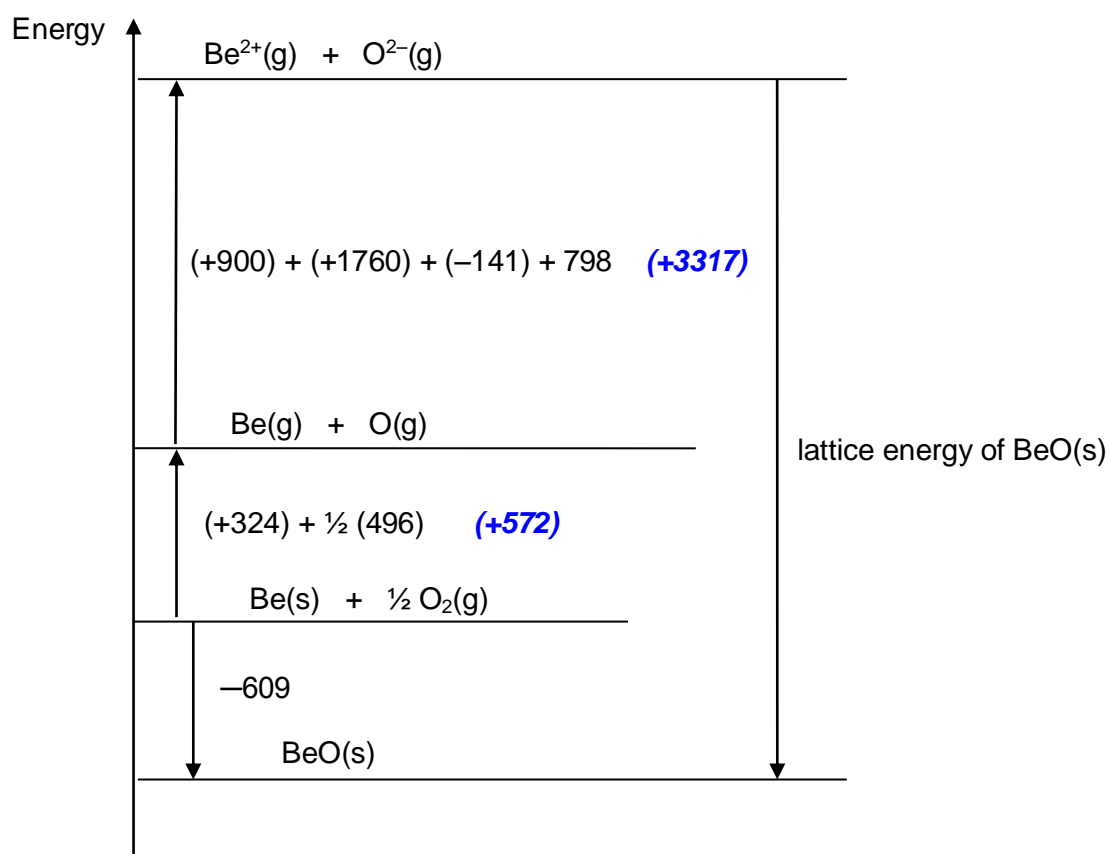
(iv)



G

[1]

(b) (i)



[2]

$$\begin{aligned} \text{Lattice energy of BeO(s)} &= -(3317 + 572 + 609) \\ &= \underline{-4498 \text{ kJ mol}^{-1}} \end{aligned}$$

[1]

(ii) Theoretical calculation assumes pure ionic character.
 But Be^{2+} ion is small and highly charged, hence it has high polarising power
 $\Rightarrow \text{BeO}$ exhibits covalent character
 \Rightarrow Attraction is stronger, so observed value is more exothermic. } [1]

(iii) Given $\text{LE} \propto \frac{q_+q_-}{r_+ + r_-}$
 ionic charge of $\text{Be}^{2+} >$ ionic charge of Na^+ }
 ionic radius of $\text{Be}^{2+} <$ ionic radius of Na^+ } [1]

Stronger attraction between oppositely charged ions in BeO }
 \Rightarrow LE (BeO) $>$ of LE (Na_2O) in magnitude } [1]

(iv) $\text{Na}_2\text{O}(\text{s}) + \text{H}_2\text{O}(\text{l}) \longrightarrow 2\text{NaOH}(\text{aq})$ }
 Sodium oxide dissolves in water to produce sodium hydroxide } [1]

$\text{Cl}_2(\text{g}) + 2\text{NaOH}(\text{aq}) \longrightarrow \text{NaCl}(\text{aq}) + \text{NaClO}(\text{aq}) + \text{H}_2\text{O}(\text{l})$ }
 Chlorine undergoes disproportionation reaction when reacted with NaOH . } [1]

State symbols not required

(c) (i) $\text{CrO}_4^{2-} + 8\text{H}^+ + 3\text{e} \longrightarrow \text{Cr}^{3+} + 4\text{H}_2\text{O}$
 $\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + \text{e}$

 $\text{CrO}_4^{2-} + 3\text{Fe}^{2+} + 8\text{H}^+ \longrightarrow \text{Cr}^{3+} + 3\text{Fe}^{3+} + 4\text{H}_2\text{O}$ [1]

(ii) chromium(III) hydroxide **OR** $\text{Cr}(\text{OH})_3(\text{H}_2\text{O})_3$ **OR** $\text{Cr}(\text{OH})_3$
 $2[\text{Cr}(\text{H}_2\text{O})_6]^{3+} + 3\text{CO}_3^{2-} \longrightarrow 2[\text{Cr}(\text{OH})_3(\text{H}_2\text{O})_3] + 3\text{CO}_2 + 3\text{H}_2\text{O}$ [1]

$\text{Cr}^{3+}(\text{aq})$ undergoes hydrolysis with water liberating $\text{H}^+(\text{aq})$ }
 Undergoes acid-base reaction with $\text{Na}_2\text{CO}_3(\text{aq})$ } [1]

(d) (i) • a state function that measures the degree of disorder / randomness in a system [1]
OR
 • gives a measure of the extent to which particles and energy are distributed within the system **OR**
 • the greater the disorder / randomness, the larger is the entropy.

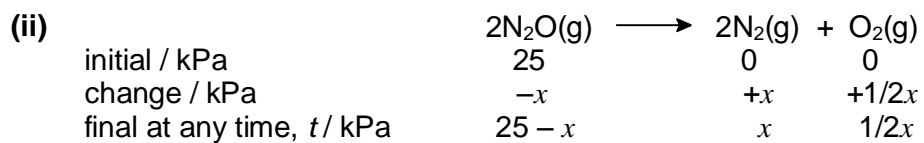
(ii) In reaction I, there is no change in number of particles in aqueous solution, } [1]
 whereas in reaction II, there is an increase of 3 particles. }

\Rightarrow Increase in number of ways of arrangement and energy distribution of the particles
 $\Rightarrow \Delta S_r^\ominus$ is more positive [1]

[Total: 20]



(b) (i) total pressure, P , when reaction is complete = $3/2 \times 25 = \underline{37.5 \text{ kPa}}$ [1]



$$25 - x + x + 1/2x = P$$

$$25 + 1/2x = P$$

$$x = 2P - 50$$

[1]

Hence, partial pressure of N_2O at any time, t , is

$$25 - x = 25 - (2P - 50)$$

$$= 25 - 2P + 50$$

$$= \underline{75.0 - 2P \text{ (shown)}}$$

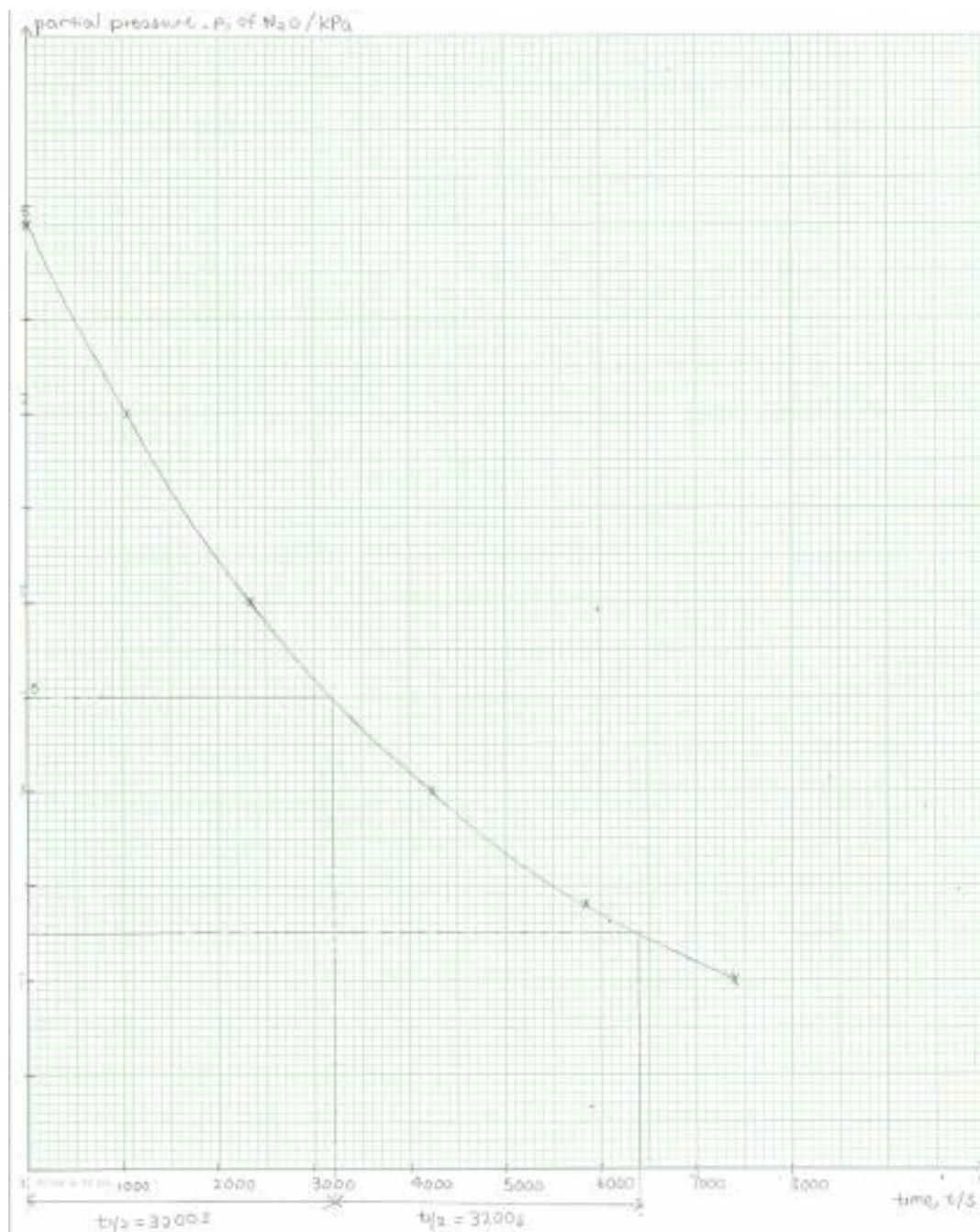
[1]

(iii)

P / kPa	27.5	30.0	32.5	34.0	35.0
t / s	1030	2360	4230	5870	7420
p of $\text{N}_2\text{O} / \text{kPa}$	<u>20</u>	<u>15</u>	<u>10</u>	<u>7</u>	<u>5</u>

[1]

(iv)



[2]

Since $t_{1/2}$ is constant at 3200 s, the order of reaction w.r.t. N_2O is 1.

[1]

(v) rate = $k p_{N_2O}$

[1]

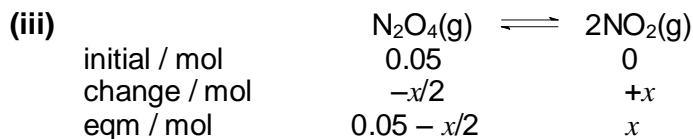
$$\begin{aligned} t_{1/2} &= \frac{\ln 2}{k} \\ k &= \frac{\ln 2}{t_{1/2}} \\ &= \frac{\ln 2}{3200} = \underline{2.17 \times 10^{-4} \text{ s}^{-1}} \end{aligned}$$

[1]

[1]

(c) (i) $n(\text{N}_2\text{O}_4) = 4.60 / 92.0 = \underline{0.0500 \text{ mol}}$ [1]

(ii) $pV = nRT$
 $n = pV / RT$
 $= \frac{101 \times 10^3 \times 1.48 \times 10^{-3}}{8.31 \times 300} = \underline{0.0600 \text{ mol}}$ [1]



$0.05 - x/2 + x = 0.06$
 $x = 0.02$ [1]

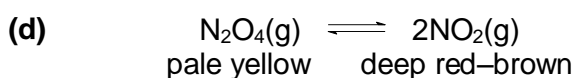
$n(\text{N}_2\text{O}_4) \text{ dissociated} = x/2 = 0.02/2 = 0.01$
 $\% \text{ of } \text{N}_2\text{O}_4 \text{ dissociated} = 0.01 / 0.05 \times 100 = \underline{20.0 \%}$ [1]

(iv) $K_p = \frac{p_{\text{NO}_2}^2}{p_{\text{N}_2\text{O}_4}}$ [1]

$p(\text{NO}_2) = 0.02/0.06 \times 1.00$
 $= 1/3 \text{ atm}$

$p(\text{N}_2\text{O}_4) = 0.04/0.06 \times 1.00$
 $= 2/3 \text{ atm}$

$K_p = \frac{(1/3)^2}{2/3} = 1/6 \approx \underline{0.17 \text{ (shown)}}$ [1]



When the equilibrium mixture is suddenly compressed in a gas syringe, $[\text{N}_2\text{O}_4]$ and $[\text{NO}_2]$ increase due to the reduced volume. [1]

Compression of the gas also results in an increase in pressure. The position of the above equilibrium shifts left to decrease pressure by producing fewer gas molecules. The mixture becomes paler as $[\text{N}_2\text{O}_4]$ increases. [1]

[Total: 20]