NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CHEMISTRY 9729/01

Paper 1 Multiple Choice **24 September 2018**

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.
Write your name, class and tutor’s name on the Answer Sheet in the spaces provided unless this has been done for you.

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

Read the instructions on the Answer Sheet very carefully.

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

This document consists of **16** printed pages and **0** blank page.

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

1 Which of the following contains the smallest number of stated atoms at r.t.p.?

A oxygen atoms in 48 dm^3 of NO_2

B sulfur atoms in 48 dm^3 of SO_2

C carbon atoms in 44 g of CO_2

D nitrogen atoms in 44 g of N_2O

2 An isolated gaseous species has paired electrons in at least one of its 3d orbitals and a fully filled 4s subshell.

What could be the identity of the species?

A Cu **B** Fe^{3+} **C** Ni^{2+} **D** Sr^{2+}

3 Which one of the following species is **not** planar?

A BrF_3

B ICl_4^-

C PCl_4^+

D XeF_4

4 Hydrazine, N_2H_4, and hydrogen peroxide, H_2O_2, are both used as rocket propellants because they can produce large volumes of hot gases from a small volume of liquid.

Which of the following statements about these two compounds is correct?

1 The bond angle in N_2H_4 is larger than that in H_2O_2.

2 The N–H bond is shorter than the O–H bond.

3 Hydrazine forms stronger intermolecular hydrogen bonds than hydrogen peroxide.

4 There are σ bonds formed by sp^3 – s orbital overlap in both molecules.

A 1 and 4

B 2 and 3

C 1, 2 and 4

D 1, 3 and 4

5 Which factor is the most significant in explaining the non-ideal behaviour of the gases present in the reaction chamber in the Haber process?

A strong bonds between the atoms in the molecule

B the presence of a catalyst

C the high temperature of 450 °C

D the high pressure of 150 atm

6 A student mixed 25.0 cm^3 of 3.00 mol dm^{-3} hydrochloric acid with an equal volume of 6.00 mol dm^{-3} sodium hydroxide. The initial temperature of both solutions was 15.0 °C. The maximum temperature recorded was 24.5 °C. It was found that 15% of the heat produced during the experiment was lost to the surrounding.

Using these results, what is the enthalpy change of neutralisation?

A –15.6 kJ mol^{-1}

B –22.5 kJ mol^{-1}

C –31.1 kJ mol^{-1}

D –57.3 kJ mol^{-1}

7 A student calculated the lattice energy for calcium oxide using the data in the table below, and relevant data from the *Data Booklet*.

energy change	value / kJ mol^{-1}
standard enthalpy change of atomisation of calcium	+178
first electron affinity for oxygen	–141
second electron affinity for oxygen	+798
standard enthalpy change of formation of calcium oxide	–635

However, the value calculated by the student for the lattice energy was **more** exothermic than the correct value.

Which error could have been made in the calculation?

A omitting the second electron affinity for oxygen

B omitting the standard enthalpy change of formation of calcium oxide

C using the 1st and 2nd ionisation energies of magnesium instead of calcium

D using the standard enthalpy change of combustion of calcium rather than the standard enthalpy change of formation of calcium oxide

8 A student investigates the kinetics of the following reaction by using a spectrometer. The spectrometer is able to measure the concentration of iodine by measuring the absorbance of the solution.

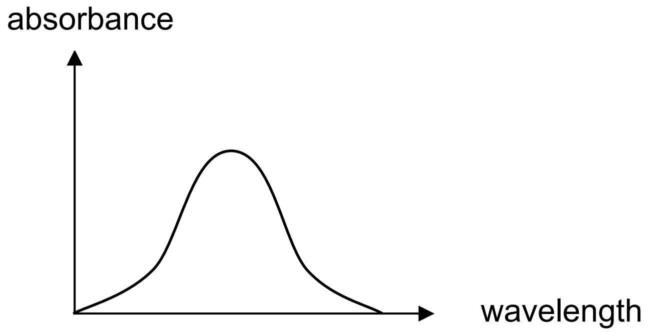
$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2H_2O(l)$$

The time taken for the absorbance of the reaction mixture to reach a fixed value is measured over a range of hydrogen peroxide concentrations.

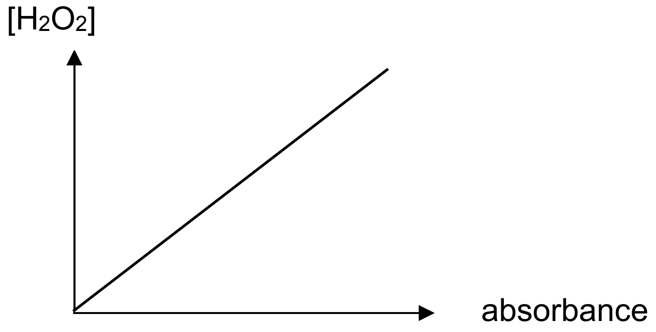
Based on the data obtained, the student correctly drew a graph to prove that order of reaction is one with respect to H_2O_2.

Which graph did the student draw?

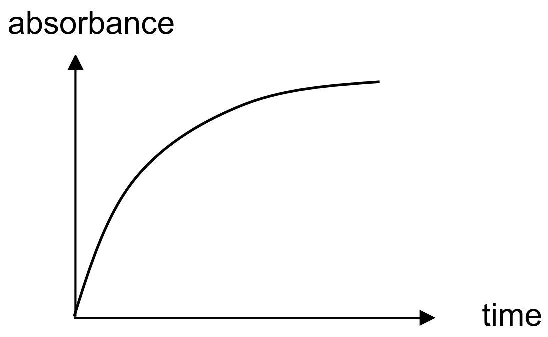
A



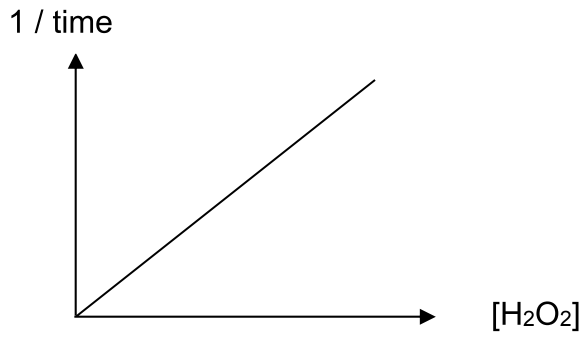
B



C



D



9 The decomposition of hydrogen peroxide follows first order kinetics. A certain solution of hydrogen peroxide undergoes complete decomposition to liberate 96 cm^3 of oxygen gas. It is found that at 25 °C, 48 cm^3 of oxygen was collected in 35 min.

How long will it take for 80 cm^3 of the gas to be produced?

A 87.5 min

B 90.5 min

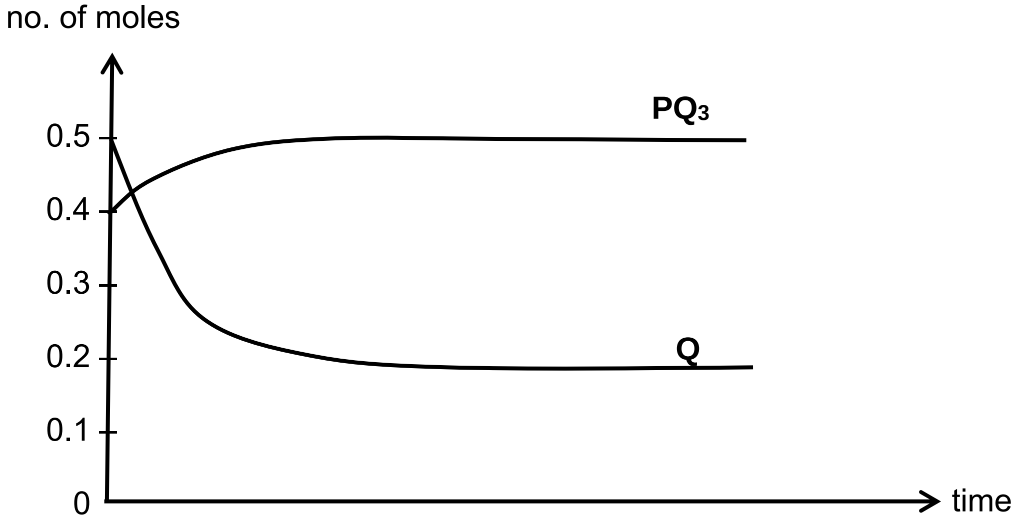
C 97.5 min

D 105 min

10 The system containing P, Q and PQ_3 is allowed to reach equilibrium in a 5 dm^3 vessel at a temperature of 1000 K.

$$P(g) + 3Q(g) \quad PQ_3(g)$$

The diagram below shows the change in number of moles of PQ_3 and Q with time. The initial number of moles of P was 0.2.



What is the equilibrium constant K_c for the reaction?

A $\frac{0.5}{0.1\times(0.2)^3}$ **B** $\frac{0.5}{0.2\times(0.2)^3}$ **C** $\frac{0.5\times5^3}{0.1\times(0.2)^3}$ **D** $\frac{0.5\times5^3}{0.2\times(0.2)^3}$

11 Which statement is correct about a reaction for which the equilibrium constant is independent of temperature?

1 The rate constants for the forward and reverse reactions are both independent of temperature.

2 Temperature has no effect on the position of equilibrium.

3 The forward and reverse reactions have equal activation energies.

4 The entropy change is zero.

A 1 and 2

B 2 and 3

C 3 and 4

D 2, 3 and 4

12 The two simplest carboxylic acids are formic acid and acetic acid. Formic acid is present in the venom of ant and bee stings while acetic acid is the major characterising component of vinegar. The pK_a values of the two acids is given in the table below.

Acid	**Formula**	**pK_a**
Formic acid	$HCOOH$	3.74
Acetic acid	CH_3COOH	4.76

Which solution has the lowest pH?

A 100 cm^3 of 0.10 mol dm^{-3} acetic acid

B 100 cm^3 of 0.10 mol dm^{-3} sodium acetate

C 100 cm^3 of 1.0 mol dm^{-3} formic acid and 50 cm^3 of 1.0 mol dm^{-3} aqueous sodium hydroxide

D 100 cm^3 of 1.0 mol dm^{-3} formic acid and 75 cm^3 of 1.0 mol dm^{-3} aqueous sodium hydroxide

13 Deuterium oxide, D_2O consists of an oxygen atom bonded to two atoms of the hydrogen isotope, deuterium ${}^{2}_{1}D$. It is known as 'heavy water' and is used for research into chemical reactions.

Like H_2O, pure D_2O is weakly ionised.

$$2D_2O \quad D_3O^+ + OD^-$$

For D_2O, we use the terms K_D instead of K_w and pD instead of pH.
At 25 °C, $pK_D = 14.8$

Which statements about D_2O at 25 °C is correct?

1 pD of D_2O is 7.4

2 D_2O is not a neutral liquid.

3 D_2O dissociates to a smaller extent than H_2O.

A 1 only

B 3 only

C 1 and 3

D 2 and 3

14 **W**, **X**, **Y** and **Z** are four consecutive elements in Period 3 but not necessarily in the order presented.

- Chloride of **W** dissolves in water and turns blue litmus red.
- **X** is a good conductor of electricity but is insoluble in water.
- Oxide of **Y** has the highest melting point.
- **Z** has the highest first ionisation energy and largest ionic radius.

Which of the following is the correct sequence of the four elements in order of increasing atomic number?

A **X, Y, Z, W**

B **X, Y, W, Z**

C **Y, X, W, Z**

D **Y, X, Z, W**

15 **M** is a Group 2 metal. The carbonate of **M** decomposes when heated in a Bunsen flame to give carbon dioxide and a white solid residue as the only products. This white solid residue is sparingly soluble in water. Even when large amounts of the solid residue are added to water the pH of the saturated solution is less than that of limewater.

What could be the identity of **M**?

A magnesium

B calcium

C strontium

D barium

16 A white powder is a mixture of sodium chloride and sodium iodide. It is dissolved in water in a test-tube. Excess aqueous silver nitrate is added to the test-tube. A precipitate, X, is observed.

Excess concentrated ammonia is then added to the test-tube containing X. After the test-tube has been shaken, a precipitate, Y, is observed.

Which statement about X or Y is correct?

A X is a pure white colour.

B X is pure silver iodide.

C Y is pure silver chloride.

D Y is yellow.

17 Which of the following statements is correct?

1 Enthalpy change of vaporisation of halogens increases down the group.

2 Bond energy of hydrogen halides increases down the group.

3 Oxidising power of halogens increases down the group.

4 Thermal stability of hydrogen halides increases down the group.

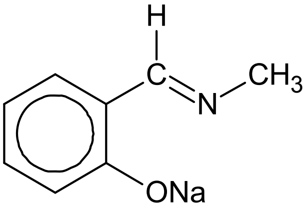
A 1 only

B 1 and 3

C 2 and 4

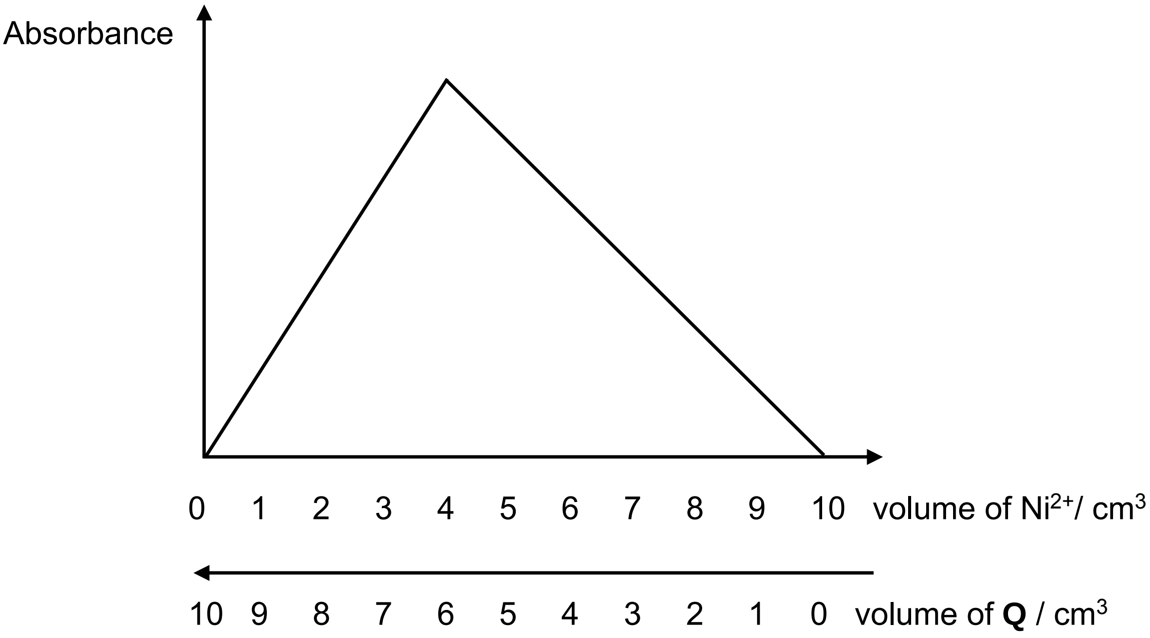
D 3 and 4

18 The complex of nickel with ligand **Q** (shown below) is thermochromic, being coloured red at room temperature but changing to yellow-green when heated to 170 °C.



Q

The following graph was obtained when the colour intensities of mixtures of a 4.0×10^{-3} mol dm^{-3} solution of **Q** and a 3.0×10^{-3} mol dm^{-3} solution of nickel(II) chloride were measured using a colorimeter at room temperature.



Which of the following statements is correct for the nickel(II) complex ion?

A The complex ion absorbs red light at room temperature.

B The co-ordination number of nickel(II) complex is 4.

C The overall charge of the nickel(II) complex is 2+.

D The shape of the nickel(II) complex ion is linear.

19 If a molecule contains two non-identical chiral carbon atoms, four optical isomers exist.

How many isomers are there with

- molecular formula $C_7H_{14}O$ **and**
- a five-membered ring **and**
- a tertiary alcohol group?

A 7 **B** 8 **C** 9 **D** 10

20 Which of the following trends are **incorrect**?

1 The boiling points of alcohols with the same molecular formula increases from primary to secondary to tertiary.

2 The pH values of the aqueous solutions increases from CH_3CH_2COCl to CH_3CH_2COOH to $CH_3CH_2CONH_2$ to $CH_3CHClCH_2NH_2$.

3 The ease of hydrolysis of the chlorine atoms decreases from chlorobenzene to chloroethane to ethanoyl chloride.

4 The pK_b values increases from ethanoate ion to phenoxide ion to ethoxide ion.

A 2 only

B 1 and 3 only

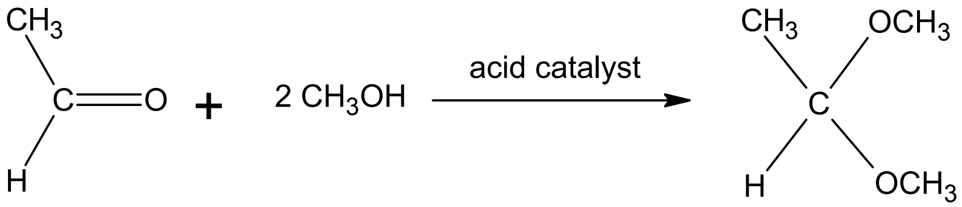
C 2 and 4 only

D 1, 3 and 4 only

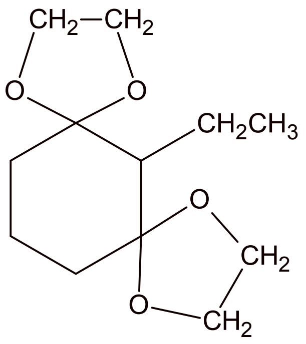
21 Alkenes undergo catalytic oxidation to produce aldehydes and ketones, for example

$$H_2C{=}CH_2 + 1/2\ O_2 \xrightarrow{\text{catalyst}} CH_3CHO$$

Acetals (molecules that contain 2 –OR groups bonded to the same carbon) can be formed from aldehydes and ketones in an acid catalysed process, for example

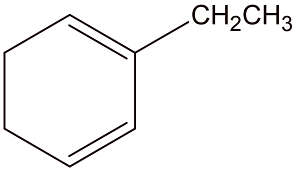


Compound **W** undergoes catalytic oxidation, followed by an acid catalysed reaction with $HOCH_2CH_2OH$ to produce the following as the only product.

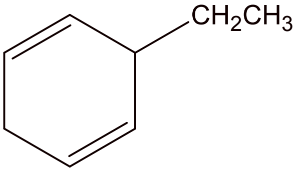


Which of the following best represents the structure of compound **W**?

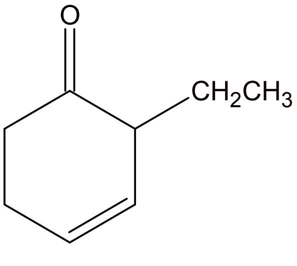
A



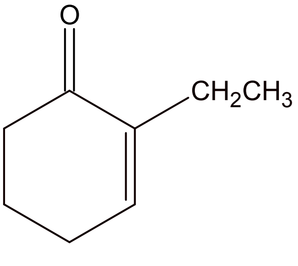
B



C



D



22 The molecular formula of compound **X** is $C_5H_{12}O$.

Compound **X**:

- reacts with alkaline aqueous iodine
- can be dehydrated to form two alkenes only.

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

A $CH_3CH_2CH(CH_3)CH_2OH$

B $(CH_3)_2C(OH)CH_2CH_3$

C $(CH_3)_2CHCH(OH)CH_3$

D $CH_3CH_2CH_2CH(OH)CH_3$

23 $H_2NNHC_6H_3(NO_2)_2$ is the structural formula of 2,4-DNPH.

Many but not all, organic reactions need to be heated before reaction occurs.

Which reaction cannot occur at a good rate at room temperature (20 °C)?

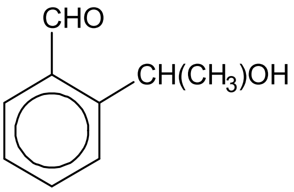
A $CH_3OH + PCl_5 \rightarrow CH_3Cl + POCl_3 + HCl$

B $CH_3CH_2OH + KBr \rightarrow CH_3CH_2Br + KOH$

C $CH_3COCl + CH_3CH_2OH \rightarrow CH_3COOCH_2CH_3 + HCl$

D $(CH_3)_2CO + H_2NNHC_6H_3(NO_2)_2 \rightarrow (CH_3)_2C{=}NNHC_6H_3(NO_2)_2 + H_2O$

24 Compound **X** is heated under reflux with an excess of acidified $K_2Cr_2O_7$ to form compound **Y**.



compound **X**

Both **X** and **Y** are separately warmed with Fehling's solution and the observations noted.

What are the observations?

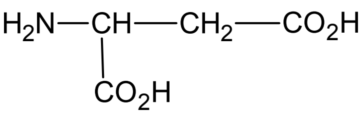
A Both **X** and **Y** give a red precipitate.

B Only **X** gives a red precipitate.

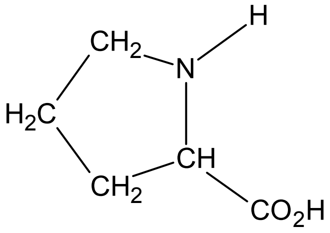
C Only **Y** gives a red precipitate.

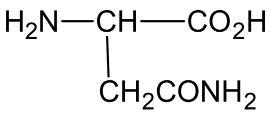
D Neither **X** nor **Y** gives a red precipitate.

25 The following are structures of 3 amino acids.



$H_2N-\underset{\displaystyle CO_2H}{\underset{|}{CH}}-CH_2-CO_2H$

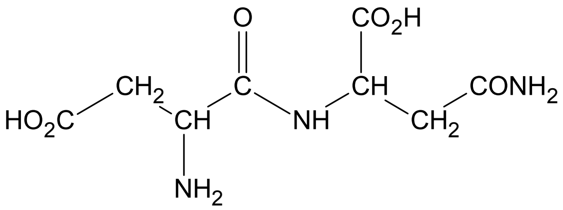




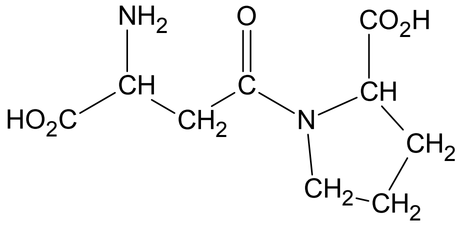
$H_2N-\underset{\displaystyle CH_2CONH_2}{\underset{|}{CH}}-CO_2H$

Which of the following represents dipeptides formed from these amino acids?

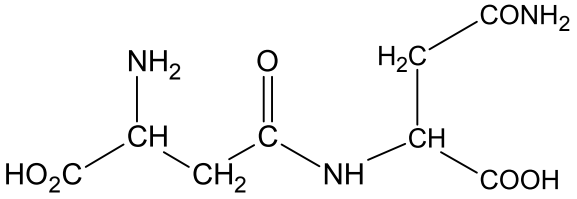
1



2



3



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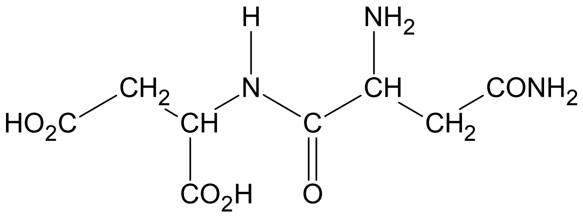


A 1 only

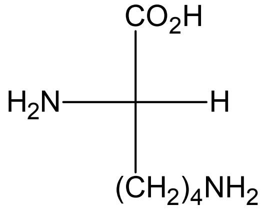
B 1 and 4 only

C 3 and 4 only

D All are correct

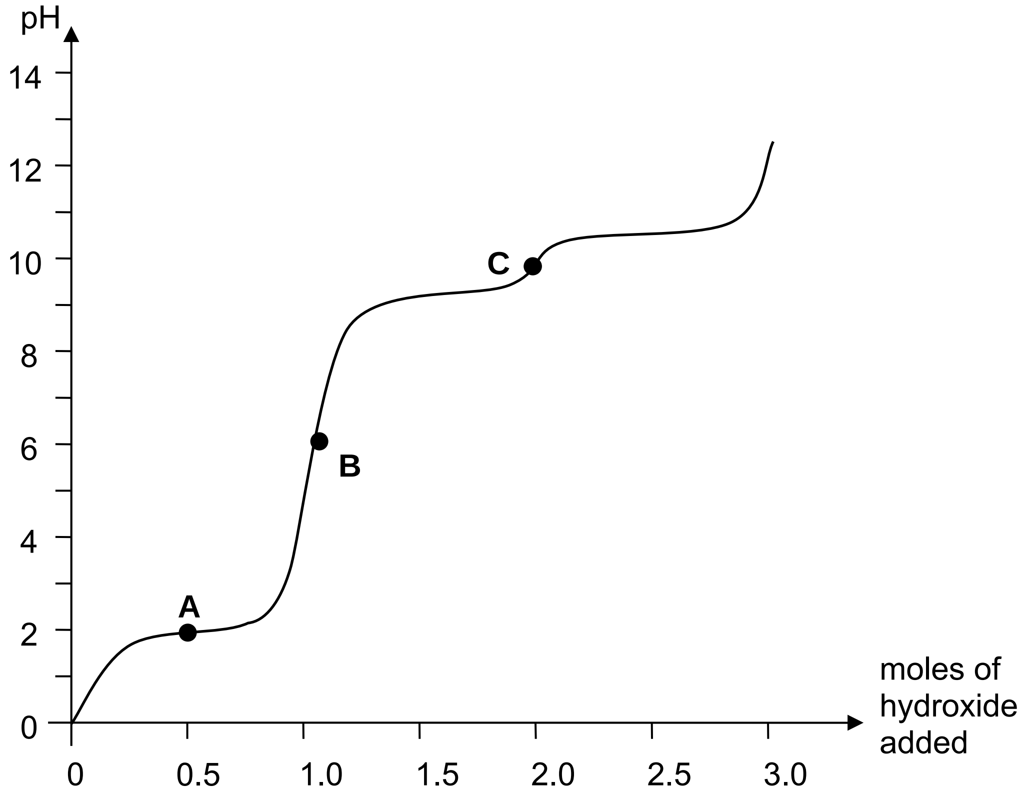
[Turn over

26 Lysine is an essential amino acid found in the body. It has three p*K*a values associated with it: 2.2, 9.0 and 10.5



lysine

When one mole of protonated lysine was titrated against hydroxide ions, the following pH curve is obtained:



Which of the following statements are true with respect to the curve above?

1 The α-amino group has a p*K*a value of 10.5.

2 Equal amounts of $H_3N^+CH(CO_2H)(CH_2)_4NH_3^+$ and $H_3N^+CH(CO_2H)(CH_2)_4NH_2$ are present at point **A**.

3 The major species present at point **C** has no net charge.

4 The major species present at point **B** will migrate towards the cathode of an electrolytic cell.

A 1 and 3 only

B 2 and 4 only

C 3 and 4 only

D All are correct

27 A carboxylic acid, **P**, has no possible chain isomers. It reacts with an alcohol, **Q**, that has only one other positional isomer.

What could be the ester formed from a reaction between **P** and **Q**?

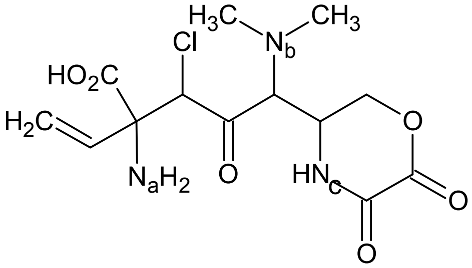
A butyl propanoate

B ethyl butanoate

C pentyl ethanoate

D propyl pentanoate

28 Which of the following statements about compound **W** is correct?



compound **W**

A In the gaseous phase, N_b is a stronger Lewis base than N_a but in the aqueous phase, N_b is a weaker Bronsted-Lowry base than N_a.

B When 96 dm^3 of H_2 gas was reacted with one mole of compound **W**, followed by excess sodium metal, at room conditions, the gas volume expanded by 48 dm^3.

C The reduction of **W** by $LiAlH_4$ will cause the oxidation state of any carbon involved in the reduction to decrease from +3 to −1.

D **W** will require 3 moles of NaOH(aq) for complete reaction if the reaction is to take place with heating.

29 Which of the following changes represent an oxidation process?

A CO_2 to $C_2O_4^{2-}$

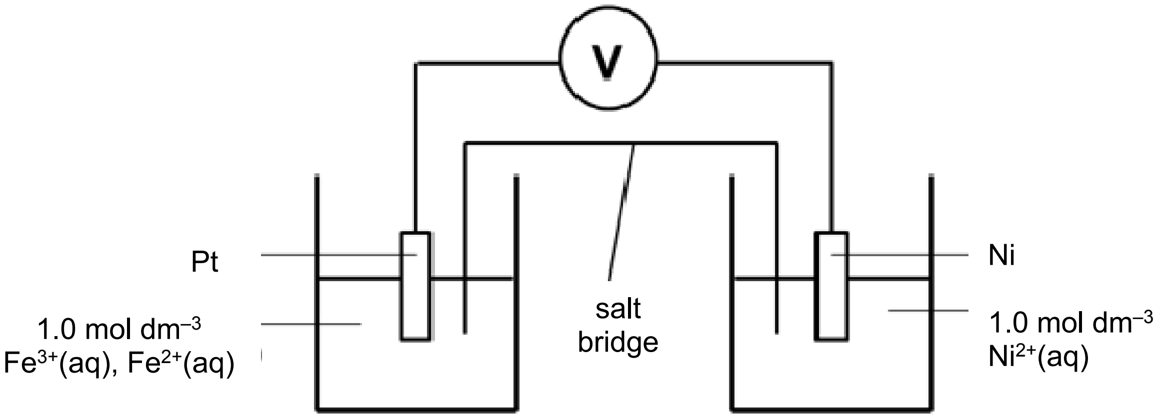
B CrO_4^{2-} to $Cr_2O_7^{2-}$

C Br_2 to BrF_3

D Cl_2 to ICl_3

30 *The use of Data booklet is relevant to this question.*

A Fe^{3+}/Fe^{2+} half-cell was connected to a Ni^{2+}/Ni half-cell as shown in the diagram below under standard conditions.



Which of the following statements is correct?

1 The solution in the Fe^{3+}/Fe^{2+} half-cell turns red-brown.

2 The cathode increases in size.

3 The electron flows from Fe^{3+}/Fe^{2+} half-cell to the Ni^{2+}/Ni half-cell.

4 The standard cell potential is +1.02 V.

A 4 only

B 1 and 3

C 2 and 3

D 1, 3 and 4

Nanyang JC J2 Preliminary Exam 2018
H2 Chemistry 9729/01
Paper 1 MCQ Answers and Comments

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

---

1 C

A: 2 mol of NO_2 gives 4 mol of O atoms
B: 2 mol of SO_2 gives 2 mol of S atoms
C: 1 mol of CO_2 gives 1 mol of C atoms
D: 1 mol of N_2O gives 2 mol of N atoms

---

2 D

Cu: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}4s^1$
Fe^{3+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$
Ni^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8$
Sr^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6$

---

3 C

A BrF_3 : T-shaped (3bp, 2 lp)
B ICl_4^- : square planar (4bp, 2 lp)
C PCl_4^+: tetrahedral (4 bp, 0 lp)
D XeF_4: square planar (4bp, 2 lp)

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4 A
(1 and 4 are correct)

1 True, bond angle in N_2H_4 is 107^{O} while bond angle in H_2O_2 is 105^{O}

2 False, the N–H bond is *longer* than the O–H bond as the O–H covalent bond in more polar. Students can also check the DB to compare the 2 bond energies.

3 False, hydrazine forms *weaker* intermolecular hydrogen bonds than hydrogen peroxide as N is less electronegative than O.

4 True, both N and O are sp^3 hybridised, and form σ bonds by overlapping with the s orbital of H.

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5 D

Gases deviate from non-ideal behaviour at low temperature or high pressure hence option D is true.

Explanation for option D: At high pressure, volume of container decreases hence volume of gas particles is more significant compared to volume of container, therefore gas behave less ideally.

Note for option A, it should be the significant <u>intermolecular</u> hydrogen bonds between molecules that result in deviation from ideal gas behaviour (not the <u>intramolecular</u> covalent bonds between atoms).

6 C

amount of water formed
$= \frac{25.0}{1000}$ x 3.00 = 0.07500 mol

heat produced
= (25.0 + 25.0) x 4.18 x 9.5 x $\frac{100}{85}$
= 2335 J mol^{-1}

$$\Delta H_n = -\frac{2335\times10^{-3}}{0.07500}$$
$$= -31.14$$
$$= -31.1 \text{ kJ mol}^{-1}$$

---

7 C

$\Delta H^{e}_{lattice\ energy}$ CaO
= – ($\Delta H^{e}_{atomisation}$ Ca + 1st and 2nd ionisation energies of calcium + $\Delta H^{e}_{atomisation}$ O + first and second electron affinity for oxygen) + $\Delta H^{e}_{formation}$ CaO

Option A: Less exothermic
Option B: Less exothermic
Option C: More exothermic since 1st and 2nd ionisation energies of magnesium are more endothermic than calcium
Option D: No change since standard enthalpy change of combustion of calcium is equal to the standard enthalpy change of formation of calcium oxide.

---

8 D

1/ time presents rate of reaction
Since first order wrt H_2O_2, hence
$[H_2O_2] \alpha 1 / \text{time}$

---

9 B

$$\frac{96-80}{96} = \left(\frac{1}{2}\right)^{t/35}$$

t = 90.5 min

---

10 C

$[Q]_{eqm} = 0.2 / 5 \text{ mol dm}^{-3}$
$[PQ_3]_{eqm} = 0.5 / 5 \text{ mol dm}^{-3}$
Initial P = 0.2 mol

Since P and PQ_3 have the same mole ratio in the equation,
|change in P| = |change in PQ_3| = 0.1
(read off from graph)

Alternatively, you can also find change in P = 1/3 change in Q.

Hence $[P]_{eqm} = (0.2 - 0.1) = 0.1 / 5 \text{ mol dm}^{-3}$

$$K_c = \frac{[PQ_3]}{[Q]^3[P]} = \frac{(\frac{0.5}{5})}{(\frac{0.2}{5})^3(\frac{0.1}{5})} = \frac{0.5 \times 5^3}{0.2^3 \times 0.1}$$

---

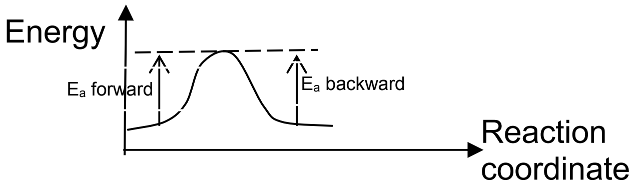
11 B

If equilibrium constant is independent of temperature, it means when temperature changes, neither forward nor backward reaction is favoured and this is only possible if ΔH is zero.

1. All rate constants are affected by temperature according to Arrhenius equation: $k = A^{-Ea/RT}$.

2. Temperature would have no effect on POE if ΔH is zero.

3. When ΔH is zero, activation energies for forward and backward reaction are equal as shown in the energy profile diagram below:



4. We cannot deduce any information about ΔS unless some information about how value of equilibrium constant changes with pressure is provided.

---

12 A

A pH of 0.010 mol dm^{-3} acetic acid = - lg ($\sqrt{10^{-4.76}(0.10)}$) = 2.88
B The solution contains a basic salt hence pH > 7.
C A buffer at maximum buffering capacity of formic acid and its salt is formed. pH = pKa = 3.74
D As more hydroxide is added compared to option C, pH of D > C but pH D < 7 as it is an acidic buffer.

---

13 C

1: $K_D = 10^{-14.8}$
$[D^+] = \sqrt{10^{-14.8}} = 3.98 \times 10^{-8}$
pD = 7.4

2: Since $[H^+]=[OH^-]$, D_2O is netural.

3: $K_D = 10^{-14.8} < K_w = 10^{-14}$ hence D_2O dissociates to a smaller extent than H_2O.

---

14 C

Chloride of **W** dissolves in water and turns blue litmus red: **W** is not Na (NaCl is neutral)

X is a good conductor of electricity but insoluble in water. **X** can be Mg or Al (However, since **Y** is Mg, **X** must be Al)

Oxide of **Y** has the highest melting point: MgO (**Y** is Mg)

Z has the highest first ionisation energy and largest ionic radius. (**Z** is P)

Since the four elements in Period 3 must be consecutive, **W** must be Si.

Hence the order is **Y**, **X**, **W**, **Z**.
(Mg, Al, Si, P)

---

15 A

$\mathbf{M}CO_3 \rightarrow \mathbf{M}O + CO_2$
Down the group, solubility of oxides increases and pH of the solution increases.
$MgO + H_2O \quad Mg(OH)_2$
$BaO + H_2O \rightarrow Ba(OH)_2$
MgO dissolves sparingly in water to form weak base $Mg(OH)_2$ whereas BaO dissolves readily in water to form strong base, $Ba(OH)_2$.
Since pH of the saturated solution is less than that of limewater, $Ca(OH)_2$, **M** must be Mg.

---

16 D

$Ag^+(aq) + Cl^-(aq) \quad AgCl(s)$ – white ppt
$Ag^+(aq) + I^-(aq) \quad AgI(s)$ – yellow ppt
$Ag^+(aq) + 2NH_3 \quad [Ag(NH_3)_2]^+$
Only AgCl dissolves in conc NH_3, AgI remains insoluble in conc NH_3. Hence Y is AgI(s) – yellow ppt.

---

17 A

Enthalpy change of vaporisation is inversely proportional to boiling point.

Halogens have simple molecular structure with weak instantaneous dipole-induced dipole forces (id-id) between molecules.

As the number of electrons or size of electron cloud increases, the electron cloud gets more polarised, id-id forces increases down the group. More energy required to overcome id-id forces. Boiling point increases and hence ΔH_{vap} decreases down the group.

Thermal stability of HX decreases down group 17 due to decreasing bond strength of H–X (increasing H–X bond length)

Electrode reaction	$E^{\ominus}$ / V
$F_2 + 2e^- \quad 2F^-$	+2.87
$Cl_2 + 2e^- \quad 2Cl^-$	+1.36
$Br_2 + 2e^- \quad 2Br^-$	+1.07
$I_2 + 2e^- \quad 2I^-$	+0.54

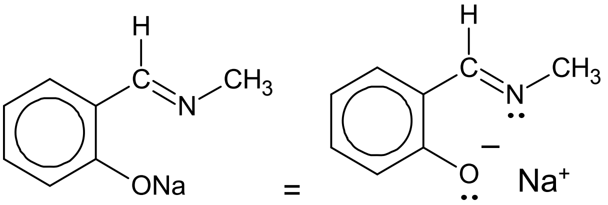
$E^{\ominus}(X_2|X^-)$ becomes less positive down the group, oxidising power of elements decreases down the group.

---

18 B

A The red complex ion absorbs complementary colour (green) at room temperature.

B



$$n(Ni^{2+}) = 3.0\times10^{-3}\times\frac{4}{1000} = 1.2\times10^{-3} \text{ mol}$$

$$n(Q) = 4.0\times10^{-3}\times\frac{6}{1000} = 2.4\times10^{-3} \text{ mol}$$

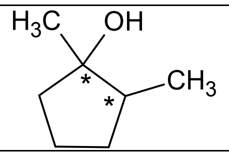
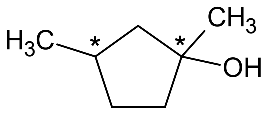
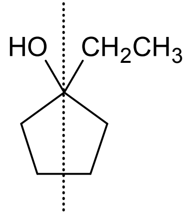
$$\frac{n(Ni^{2+})}{n(Q)} = \frac{1.2\times10^{-3}}{2.4\times10^{-3}} = \frac{1}{2}$$

Since **Q** is a bidentate ligand (lone pair on N and lone pair on O^- for dative bonding), the co-ordination number of nickel(II) complex is 4.

C The overall charge of the nickel(II) complex is 0 as there are 2 ligands of **Q** to one nickel(II) ion.

D The shape of the nickel(II) complex ion is not linear as the co-ordination number is not 2.

19 C

	
4 optical isomers	4 optical isomers
	
no cis-trans isomer no optical isomer as contains an internal line of symmetry	

20 D (1,3 and 4)

Option 1 (incorrect)

The surface area decreases from primary (elongated) to secondary to tertiary alcohol (spherical). Hence strength of id-id forces of attraction decreases from primary to secondary to tertiary.

Option 2 (correct)

CH_3CH_2COCl hydrolyses in water to produce a strong acid, HCl. Hence the pH of its aqueous solution is the lowest. $CH_3CH_2CONH_2$ contains an amide functional group which is neutral. $CH_3CH(Cl)CH_2NH_2$ contains an amine functional group which is basic and hence its pH value is the highest.

Option 3 (incorrect)

The ease of hydrolysis of the chlorine atoms ~~decreases~~ increases from chlorobenzene to chloroethane to ethanoyl chloride.

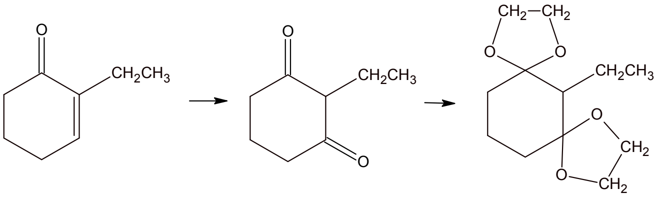
Option 4 (incorrect)

Acidity decreases from ethanoic acid to phenol to ethanol.

Ethanoic acid is the strongest among the three, hence its conjugate base, ethanoate ion will be the weakest, with the largest pK_b value.

Ethanol is the weakest among the three, hence its conjugate base, ethoxide ion will be the strongest, with the smallest pK_b value.

21 D

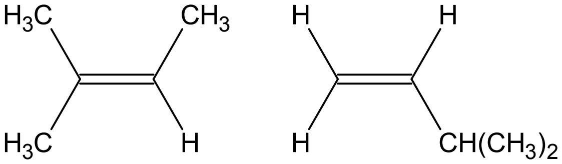


22 C

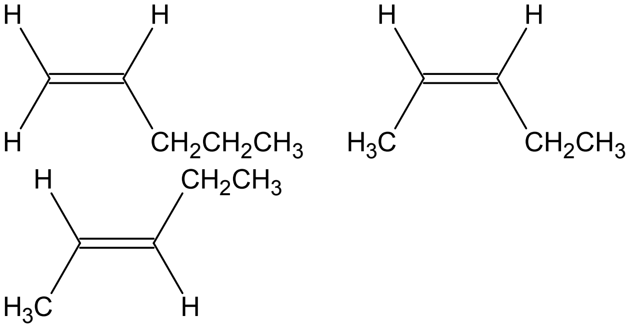
A and **B** do not contain methyl alcohol, hence will not be able to react with alkaline aqueous iodine.

C, $(CH_3)_2CH\mathbf{CH(OH)CH_3}$ and **D**, $(CH_3CH_2CH_2\mathbf{CH(OH)CH_3})$ contain methyl alcohol, hence will react with alkaline aqueous iodine.

When **C** undergoes dehydration, it produces two alkenes only as shown below.



When **D** undergoes dehydration, it produces three alkenes as shown below.



23 B

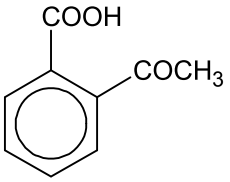
All can occur at a good rate at room temperature (20 °C) except

$CH_3CH_2OH + KBr \rightarrow CH_3CH_2Br + KOH$ as conc. H_2SO_4 needs to be added to react with KBr with heating to produce HBr which will then reacts with CH_3CH_2OH to produce CH_3CH_2OH.

24 D

X contains an aromatic aldehyde that does **not** give a red ppt when warmed with Fehling's solution.

X reacts with acidified $K_2Cr_2O_7$ to give **Y** as shown below.

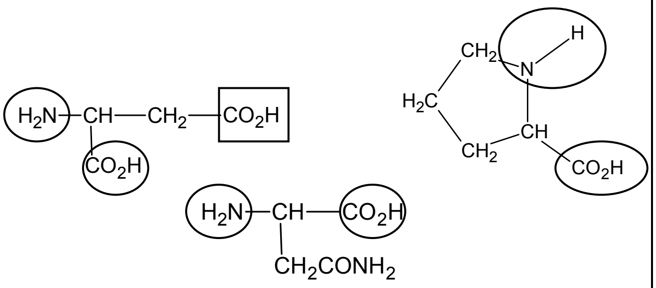


So **Y** also does **not** give a red ppt when warmed with Fehling's solution.

---

25 B

A dipeptide (formed in the body) should be formed between the carboxylic acid and amino group bonded directly to the α C i.e. see circles in black



Hence, only Option 1 and 4 is correct. Option 2 and 3 show structures that are bonded by the carboxylic acid group in the side chain of the 1st amino acid (look at the –COOH in the rectangle box) and are not classified as dipeptides formed in the body. Option 3 is incorrect.

---

26 C (3 and 4)

Option 1:

The α–amino group should have a pK_a value of 9.0 because it is closer to the –COOH group which is withdrawing in nature.

Option 2:

Equal amounts of $H_3N^+CH(CO_2H)(CH_2)_4NH_3^+$ and $H_3N^+CH(CO_2^-)(CH_2)_4NH_3^+$ are present at point **A**.

Option 3:

At point C, $H_2NCH(CO_2^-)(CH_2)_4NH_3^+$ is present, which is a zwitterion with no net charge

Option 4:

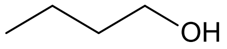
At point B, $H_3N^+CH(CO_2^-)(CH_2)_4NH_3^+$ is present which has net positive charge, hence will migrate to cathode

---

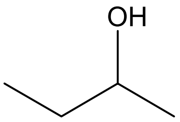
27 A

A butyl propanoate is formed by butan-1-ol and propanoic acid

The positional isomer of butan-1-ol is butan-2-ol as shown below.



butan-1-ol



butan-2-ol

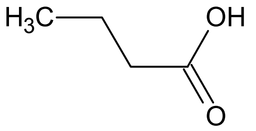
Propanoic acid has no chain isomerism.

Both conditions fulfilled.

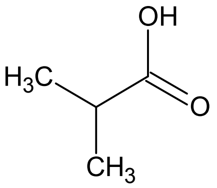
B ethyl butanoate is formed by ethanol and butanoic acid

Ethanol has no positional isomer.

Butanoic acid has 1 chain isomer as shown below.



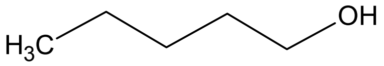
butanoic acid



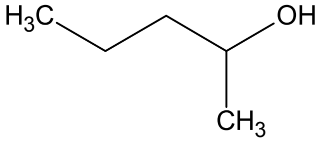
2-methylpropanoic acid

C pentyl ethanoate is formed by pentan-1-ol and ethanoic acid

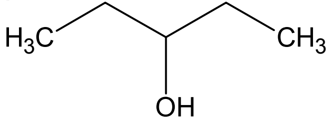
Pentan-1-ol has 2 positional isomers as shown below.



pentan-1-ol



pentan-2-ol

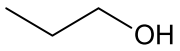


pentan-3-ol

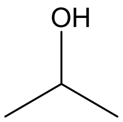
Ethanoic acid has no chain isomerism.

D Propyl pentanoate is formed by propan-1-ol and pentanoic acid

Propan-1-ol has 1 positional isomer.

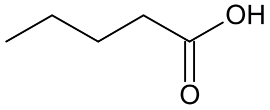


propan-1-ol

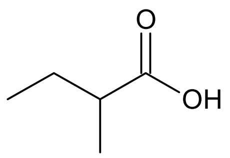


propan-2-ol

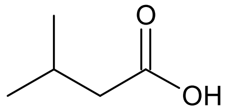
Pentanoic acid has 3 chain isomers as shown below.



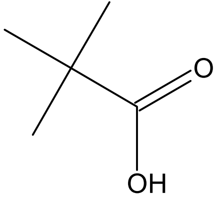
pentanoic acid



2-methylbutanoic acid



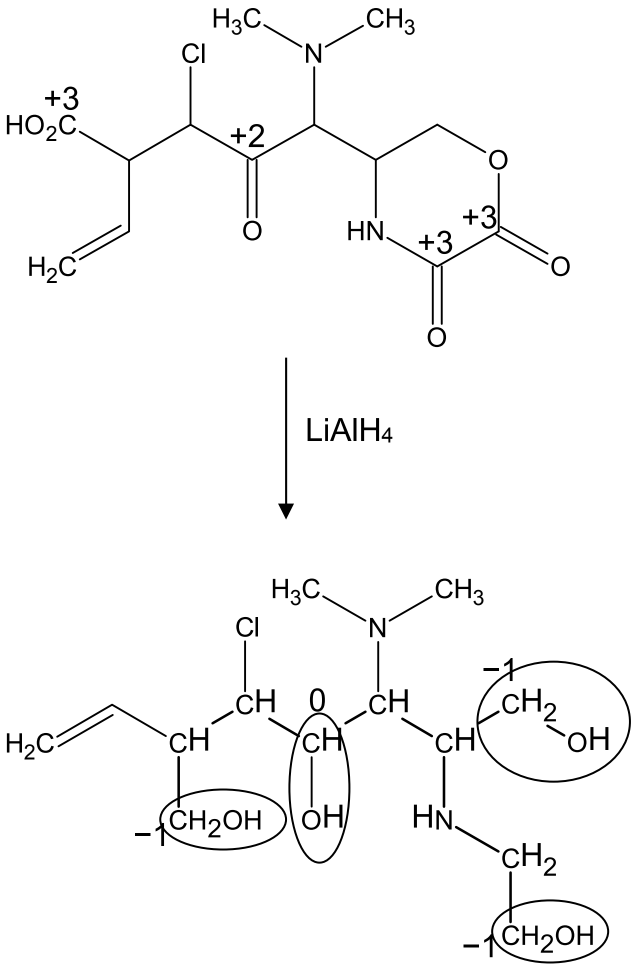
3-methylbutanoic acid



2,2-dimethylpropanoic acid

---

28 A



A (Correct) As a Lewis base, N_b has more electron-donating grps than N_a which increases the electron density on the N atom and hence the availability of the lone pair of electrons for donation to a Lewis acid. So N_b is a stronger Lewis base than N_a.

As a Bronsted-Lowry base, N_b experiences steric hindrance from the presence of 3 bulky alkyl grps, hence protons from the aq soln will have difficulty going near the lone pairs to form dative bond. So N_b is a weaker Bronsted-Lowry base than N_a.

B (Incorrect) When 96 dm^3 of H_2 gas was reacted with one mole of compound **W**, followed by excess sodium metal, at room conditions, the gas volume ~~expanded~~ contracted by ~~48~~24 dm^3.

96 dm^3 is equivalent to 4 mol of H_2 gas. Only the alkene and ketone function grp will be reduced by H_2(g) using up 2 out of the 4 mol of H_2(g) present.

Alkene will be reduced to alkane while ketone will be reduced to 2° alcohol. The 2° alcohol and –COOH grp present will then react with Na to produce 1 mol of H_2(g).

The final volume of H_2(g) is 72 dm^3.

The gas volume contracted by 24 dm^3.

C Incorrect. The numbers written beside the C atom (as shown above) shows the oxidation state of the carbon before and after the reduction by $LiAlH_4$.

D Functional groups in **W** that will react with NaOH with heating are –COOH, RCl, amide and ester. So will need 4 mol of NaOH.

Functional groups in **W** that will react with NaOH without heating is –COOH. So will need 1 mol of NaOH.

---

29 C

A: O.S. of C changes from +4 to +3 (reduction)

B: O.S. of Cr remains unchanged at +6

C: O.S. of Br changes from 0 to +3 (oxidation)

D: O.S. of Cl changes from 0 to –1 (reduction)

---

30 A

$Fe^{3+} + e \rightarrow Fe^{2+}$ +0.77V → +ve → [R]

$Ni + 2e \rightarrow Ni^{2+}$ -0.25V → -ve → [O]

Fe^{3+} is yellow and Fe^{2+} is pale green.

Reduction occurs at the Fe^{3+}/Fe^{2+} half-cell.

E_{cell} = +0.77 – (-0.25) = +1.02 V.

Electrons flow from the anode (Ni^{2+}/Ni half-cell) to the cathode (Fe^{3+}/Fe^{2+} half-cell).

Pt cathode size remains unchanged.

NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME

CLASS

TUTOR'S NAME

CHEMISTRY

9729/02

Paper 2 Structured

11 September 2018

2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

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

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

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

For Examiner's Use	
1	**/24**
2	**/11**
3	**/9**
4	**/13**
5	**/18**
Total	**/75**

This document consists of **17** printed pages and **1** blank page.

Answer **all** questions in the spaces provided.

1(a) An unknown sample was found to contain the anions, Cl^-, ClO_3^- and NO_3^-. A student weighed a sample into a beaker and recorded the following data.

mass of beaker and sample / g	68.962
mass of empty beaker / g	67.620

The sample was dissolved and diluted in a 250 cm^3 volumetric flask to obtain solution **L**.

In **experiment 1**, a 50 cm^3 portion of solution **L** was reacted with excess silver nitrate solution. The AgCl precipitated was transferred onto a dry filter paper and was placed under an infra-red lamp. The dry AgCl precipitate was weighed and the following data was obtained.

<u>Experiment 1</u>

mass of dry filter paper and AgCl / g	0.737
mass of dry filter paper / g	0.620

In **experiment 2**, a gas was bubbled into another 50 cm^3 portion of solution **L** to convert ClO_3^- to Cl^- before the addition of excess silver nitrate solution. The AgCl precipitated was also dried and weighed. The following data was obtained.

<u>Experiment 2</u>

mass of dry filter paper and AgCl / g	0.799
mass of dry filter paper / g	0.651

(i) Write the half equation for the reduction of ClO_3^- to Cl^-.

.... [1]

(ii) Determine the mass of Cl^- in 50 cm^3 of solution **L**.

[1]

(iii) Determine the mass of Cl^- converted from ClO_3^- in **experiment 2**.

[2]

(iv) Hence, determine the percentage mass of ClO_3^- in the unknown sample.

[3]

(v) The *E* ((ClO_3^-/Cl^-) has a value of +1.47 V. From the list of standard electrode potentials in the *Data Booklet*, identify a gas that would reduce ClO_3^- to Cl^-. Explain your answer.

....

....

....

.... [2]

(b) **(i)** An aqueous solution of HCl has a density of 1.15 g cm^{-3} and is 30% by mass of HCl.

Calculate the concentration in mol dm^{-3} of this solution of HCl.

[2]

(ii) Calculate the volume of this solution required to prepare 5 dm^3 of 0.20 mol dm^{-3} HCl by dilution with water.

[1]

(c) The gelatin silver process is the photographic process used with black-and-white films. The following information pertains to the process of taking photographs and developing films.

Taking photographs

- A 35 mm cartridge of black-and-white print film contains a long strip of plastic that has layered coatings on each side.
- On the front side of the film, the layers are made of gelatin which contain grains of silver chloride crystals.
- When the shutter of the camera is opened for a fraction of a second to allow the film to be exposed to light, these crystals undergo decomposition thereby producing an image on the film.

Developing films

- After the photographs have been taken, the film is developed in a dark room under a light source that emits low energy light.
- Firstly, the film is soaked in water before adding phenidone. Phenidone makes the image more visible by reacting with the exposed silver chloride crystals to produce silver atoms and two other by-products.
- This reaction can only proceed at high pH.
- After some time, the reaction will then be quenched.
- Finally, the film will be soaked in ammonium thiosulfate, $(NH_4)_2S_2O_3$, which is used as a fixer to make the image permanent and light resistant. This is done through the reaction between the unexposed silver chloride crystals and the fixer.

(i) Write the balanced equation for the decomposition of silver chloride crystals when it is exposed to light.

.... [1]

(ii) Suggest a suitable colour of the light source that is used in a dark room.

.... [1]

(iii) Complete the equation for the reaction between the developing agent, phenidone, and the exposed silver chloride crystals. Hence, state the role of phenidone in this reaction.

phenidone

role of phenidone .... [2]

(iv) Suggest a suitable reagent, other than excess cold water, that can be used to quench the development of the film. Explain.

....

....

....

.... [2]

(v) When the non-exposed silver chloride crystals react with the fixer, $(NH_4)_2S_2O_3$, a silver complex compound **M** is formed together with a chloride salt, **N**. Both **M** and **N** have the same cation. The silver-containing complex ion has a coordination number of 2 and is chlorine-free.

Suggest the formulae of compounds **M** and **N**.

compound **M**: .... compound **N**: .... [2]

(vi) State the shape of the silver-containing ion in compound **M**.

.... [1]

(vii) Complete the electronic configuration of silver in compound **M**. Hence, deduce the colour of compound **M**.

compound **M** $[Ar]3d^{10}4s^2$ ....

....

....

....

....

.... [2]

(viii) Explain why the fixer, $(NH_4)_2S_2O_3$, is able to make the image permanent and light resistant on the film.

....

....

.... [1]

[Total: 24]

2 Dinitrogen tetroxide, commonly referred to as nitrogen tetroxide, is the chemical compound N_2O_4. It is a useful reagent in chemical synthesis.

(a) Colourless N_2O_4 readily dissociates to form brown NO_2 and the following equilibrium is reached fairly quickly in the gaseous phase.

$$N_2O_4(g) \qquad 2NO_2(g) \qquad\qquad \Delta H > 0$$

(i) When 4.60 g of N_2O_4 is placed in an evacuated 1.48 dm^3 flask at 27 °C, the equilibrium pressure is 1 atm.

Calculate the value of K_p at 27 °C.

[3]

(ii) Describe and explain what you would observe when the stoppered flask is placed into a basin of boiling water.

....

....

....

....

.... [1]

(b) N_2O_4 is also used in the large scale manufacture of nitric acid. It reacts with water to give both nitrous acid and nitric acid.

$$N_2O_4 + H_2O \rightarrow HNO_2 + HNO_3$$

The two acids have different acid strengths. To determine the acid strength of the two acids, two separate solutions containing 0.10 mol dm^{-3} of each acid were prepared. The pH was found to be 2.17 and 1.00 for the solutions containing nitrous acid and nitric acid respectively.

(i) Use the data provided to prove nitrous acid is a weak acid and hence, determine its K_a value.

[2]

(ii) Suggest a reason why nitrous acid is a weaker acid than nitric acid.

....

....

....

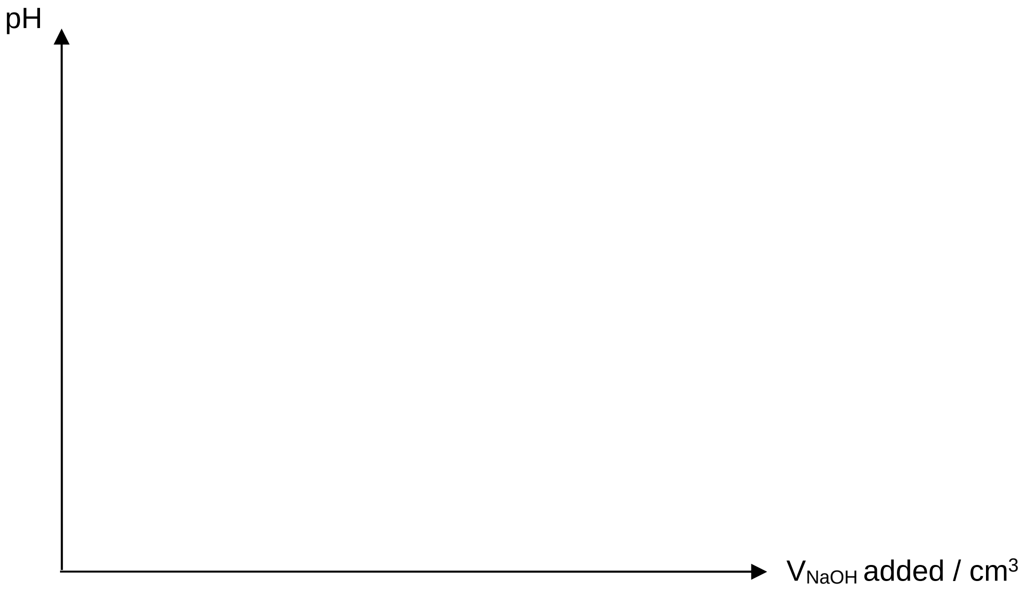
.... [1]

25.0 cm^3 of the prepared 0.10 mol dm^{-3} nitrous acid was titrated with 0.10 mol dm^{-3} aqueous sodium hydroxide.

(iii) Using your value of K_a calculated in part **(i)**, calculate the pH when 25.00 cm^3 of aqueous sodium hydoxide has been added.

[2]

(iv) On the given axes below, sketch the pH-volume added graph you would expect to obtain when the above titration was performed. Label the appropriate pH at various key points on the graph.



[2]

[Total: 11]

3 The equation for the reaction between bromine and methanoic acid is as follows:

$$Br_2(aq) + HCOOH(aq) \rightarrow 2HBr(aq) + CO_2(g)$$

It is hypothesised that the reaction is elementary. To prove this hypothesis, volumes of the two reactants were varied and the rate of the reaction is measured in terms of the rate at which the bromine concentration changes. When the total volume is kept constant, the following relationship is true.

$$\text{rate of reaction } \alpha \ \frac{\text{volume of bromine used}}{\text{time for color of bromine to disappear}}$$

The temperature of the reaction mixture was maintained at 25 °C.

The following results were obtained in three repeated experiments:

Expt	Volume of 1.0 mol dm^{-3} Br_2 / cm^3	Volume of 10.0 mol dm^{-3} HCOOH / cm^3	Volume of water added / cm^3	Relative time for colour of bromine to disappear
1	10	10	0	1.4
2	40	20	20	2.8
3	5	10	5	1.4

(a) By comparing the rates of reactions, explain how the results of the three experiments support the hypothesis that the reaction is elementary.

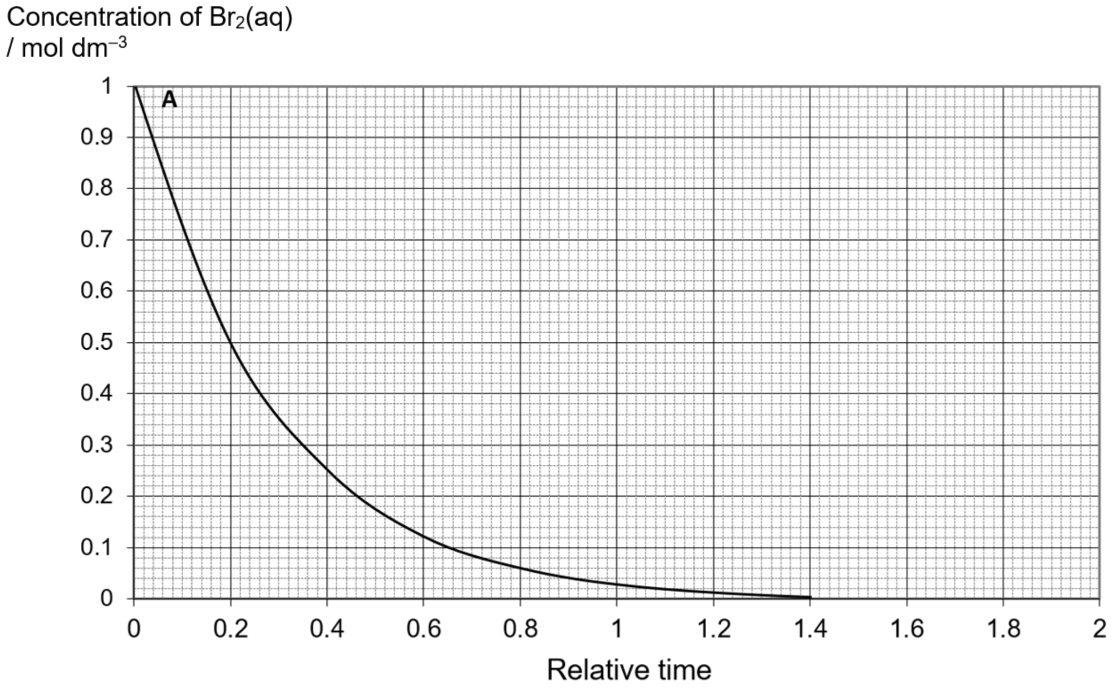
....

....

....

.... [3]

(b) During another experiment, the concentration of Br_2 was monitored over time and the following graph (Run **A**) was obtained. The concentration of HCOOH used was 10.0 mol dm^{-3}.



(i) Define the term "half-life".

....

.... [1]

(ii) The experiment was repeated using 0.8 mol dm^{-3} of Br_2(aq) and 10.0 mol dm^{-3} of HCOOH. On the axes above, draw the concentration-time graph of Br_2(aq) for the new experiment and label it 'Run **B'**.

On your graph, clearly state and label the half-life of Br_2(aq). [1]

(iii) The experiment was repeated again using 1.0 mol dm^{-3} of Br_2(aq) and 5.0 mol dm^{-3} of HCOOH (Run **C**). In comparison to Run **A**, state how the half-life of the experiment will change.

....

....

.... [1]

(c) By drawing a suitable illustration, estimate and explain the change in rate of reaction when temperature is increased to 35 °C.

....

....

....

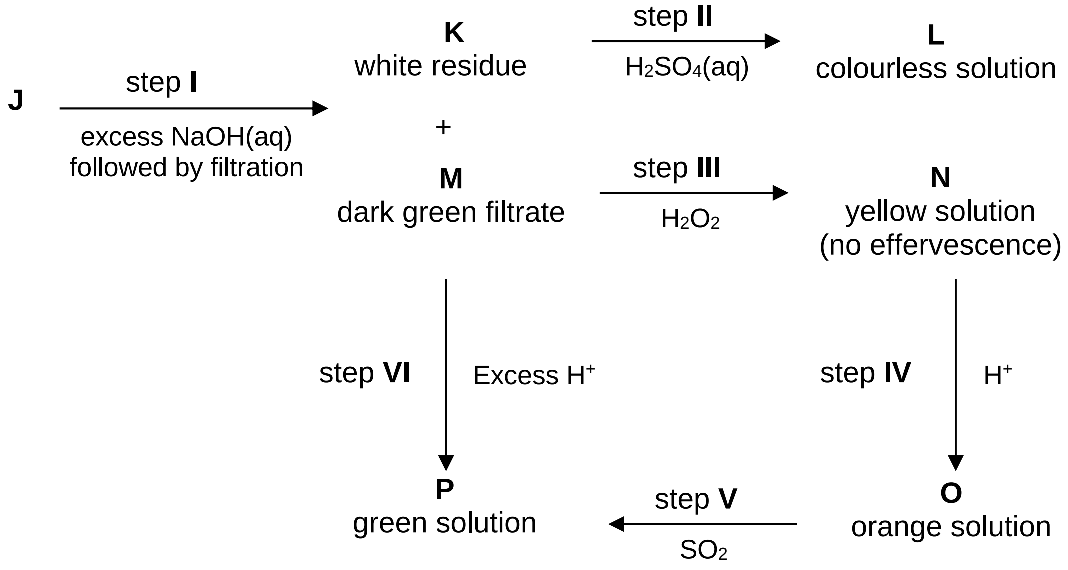
....

....

.... [3]

[Total: 9]

4(a) Solution **J** contains a Group 2 ion and a transition metal ion. The following reaction scheme shows how **J** reacts with some common reagents in the laboratory.



(i) State the identities of **K**, **L**, **M**, **N**, **O** and **P.**

K.. **L**..

M .... **N**..

O.. **P**..

[3]

(ii) State the roles of H_2O_2 and SO_2 in steps **III** and **V** respectively.

H_2O_2 in step **III**: ....

SO_2 in step **V**: .... [1]

(iii) Write an ionic equation to explain the formation of solution **P** in step **V**.

.... [1]

(iv) Explain how solution **P** can be formed in step **VI**.

....

....

....

....

....

....

.... [2]

(b) Among the elements of Group 14, those towards the top, carbon to germanium, have very different properties from those at the bottom, tin and lead.
For example, the melting points show a marked change after germanium.

element	C	Si	Ge	Sn	Pb
mp / °C	>3550	1410	937	232	327

Carbon, silicon and germanium each form a solid with the same type of structure.

(i) Explain why the melting points of these elements decrease from carbon to germanium.

....

....

....

....

....

.... [2]

(ii) Explain how first ionisation energy changes from carbon to germanium.

....

....

....

....

....

.... [2]

Carbon and silicon each form a tetrachloride. CCl_4 has no reaction with water; $SiCl_4$ reacts violently with water.

(iii) Write a balanced equation for the reaction of $SiCl_4$ with water.

.... [1]

(iv) Suggest an explanation for the inertness of CCl_4 to water.

....

....

.... [1]

[Total: 13]

5 Azo dyes are made in large quantites from benzene, C_6H_6, via nitrobenzene, $C_6H_5NO_2$ (density = 1.20 g cm^{-3}), and phenylamine, $C_6H_5NH_2$.

(a) The preparation of nitrobenzene requires benzene to be warmed under reflux at about 55 °C with a mixture of concentrated nitric and sulfuric acids. Some information about these substances is given below:

Benzene: immiscible with water; highly flammable; extremely toxic by ingestion or inhalation; known carcinogen.

Concentrated nitric acid: miscible with water; causes severe burns to eyes and skin; strong oxidising agent. The acid contains about 30 % water by volume.

Concentrated sulfuric acid: miscible with water; causes severe burns to eyes and skin; strong oxidising agent; dilution with water is very exothermic and can be dangerous.

(i) Nitric acid is placed in a suitable flask and sulfuric acid is added slowly with cooling of the flask. Explain why cooling is necessary.

....

.... [1]

(ii) Benzene is added slowly to the acid mixture, which is then warmed at 55 °C for 45 minutes under reflux with vigorous stirring of the reaction mixture.

Explain why the reflux condenser is necessary and also why the mixture is vigorously stirred.

....

....

.... [2]

(iii) State, with a reason, **one** other precaution (other than wearing protective wear) that would be necessary when carrying out the experiment.

....

.... [1]

(iv) The reaction mixture is then poured into a large excess of cold water, the liquid nitrobenzene layer is separated and *washed* with sodium carbonate solution.
Explain why this washing is necessary.

....

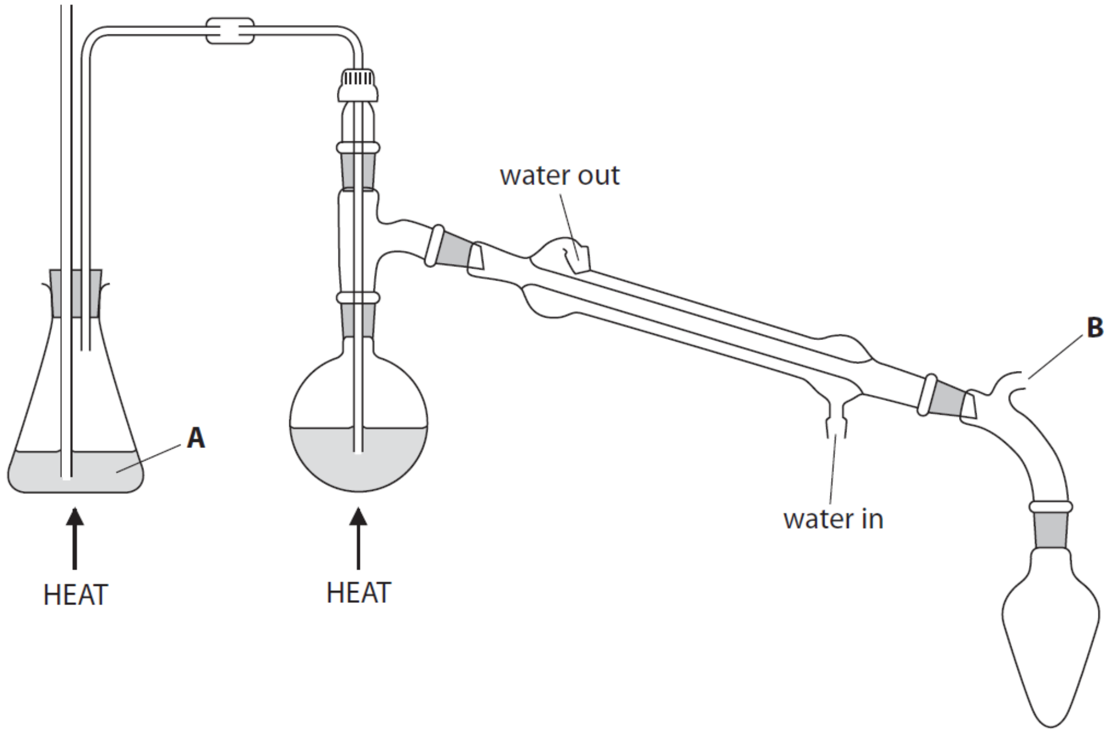
.... [1]

(v) The nitrobenzene layer is dried before being distilled to purify it.
Identify a suitable drying agent.

.... [1]

(b) Steam distillation is a purification process to separate nitrobenzene from the reaction mixture. During the process of steam distillation, a current of steam is blown through a mixture containing the desired organic substance to be distilled. This caused the desired organic substance to vaporise. The vapour containing the desired organic substance can then be condensed and collected. This method is used predominantly to purify liquids that are not very volatile and are immiscible with water.

The diagram below shows a steam distillation apparatus used to extract nitrobenzene from the reaction mixture.



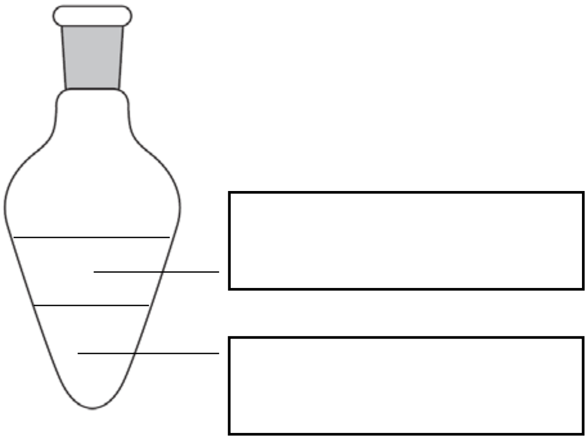
(i) Identify substance **A**.

.... [1]

(ii) Explain the purpose of the part of the apparatus labelled **B**.

.... [1]

(iii) On the diagram below, state the contents of the receiver at the end of the steam distillation.

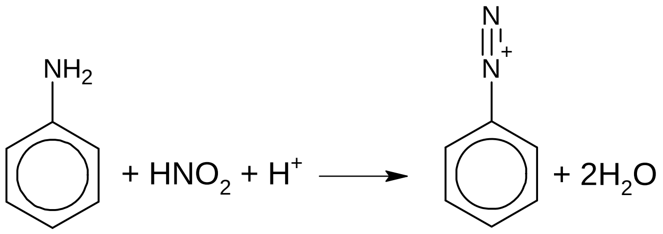


[1]

(c) The purified nitrobenzene is then reduced to phenylamine, $C_6H_5NH_2$.

The phenylamine is diazotised by reaction with nitrous acid at a temperature between 0 °C and 10 °C. Nitrous acid is generated in the reaction mixture from sodium nitrite and hydrochloric acid.

The ionic equation for the diazotisation of phenylamine to produce benzenediazonium ion is as shown below.

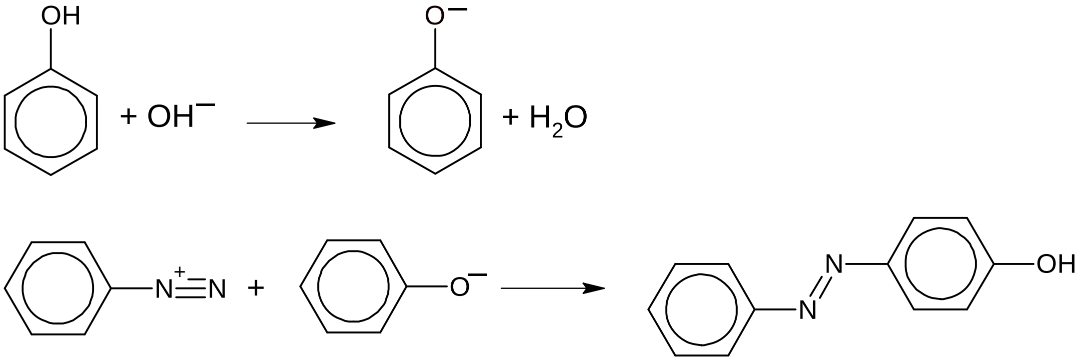


benzenediazonium ion

If the above reaction is warmed, benzenediazonium ion will undergo hydrolysis to give phenol. A gas will also be produced and the resulting mixture is acidic.

Reaction of the benzenediazonium compound with an alkaline solution of a phenol, C_6H_5OH, will produce a solid azo dye, which is purified by recrystallisation.

The equations for the reaction between benzenediazonium ion and phenol to produce the solid azo dye are shown below.



azo dye

(i) State the reagents and conditions needed to reduce nitrobenzene to phenylamine.

.... [1]

(ii) Explain why the temperature for diazotization to phenylamine must **not** be lower than 0 °C.

.... [1]

(iii) Write an equation to show benzenediazonium ion undergoing hydrolysis upon warming.

.... [1]

(d) Purification by recrystallisation requires the following steps:

1. The azo dye is dissolved in a minimum volume of hot solvent.
2. The solution is filtered through a pre-heated funnel.
3. The solution is cooled and filtered using a Buchner funnel.
4. The solid is washed with a small amount of cold solvent.
5. The solid is dried in a desiccator.

(i) Explain why a **minimum** volume of hot solvent is used in step 1.

....

.... [1]

(ii) Explain why the funnel must be pre-heated.

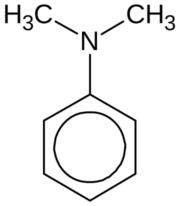
.... [1]

(iii) Suggest a reason why it is preferable to dry the solid in a desiccator rather than in an oven.

.... [1]

(e) This question compares the acidity and basicity of some organic compounds.

(i) Explain why an aqueous solution of of N,N-dimethylphenylamine is more basic than an aqueous solution of phenylamine.



N,N-dimethylphenylamine

....

....

....

.... [1]

(ii) Explain why an aqueous solution of azo dye is more acidic than an aqueous solution of phenol.

....

....

....

.... [2]

[Total: 18]

[End of Paper]

NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME: Teachers’ Mark Scheme

CLASS:

TUTOR’S NAME:

CHEMISTRY

9729/02

Paper 2 Structured

11 September 2018

2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

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

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

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

For Examiner’s Use	
1	/24
2	/11
3	/9
4	/13
5	/18
Total	/75

This document consists of **17** printed pages and **1** blank page.

[Turn over

Answer **all** questions in the spaces provided.

1(a) An unknown sample was found to contain the anions, Cl^-, ClO_3^- and NO_3^-. A student weighed a sample into a beaker and recorded the following data.

mass of beaker and sample / g	68.962
mass of empty beaker / g	67.620

The sample was dissolved and diluted in a 250 cm^3 volumetric flask to obtain solution **L**.

In **experiment 1**, a 50 cm^3 portion of solution **L** was reacted with excess silver nitrate solution. The AgCl precipitated was transferred onto a dry filter paper and was placed under an infra-red lamp. The dry AgCl precipitate was weighed and the following data was obtained.

Experiment 1

mass of dry filter paper and AgCl / g	0.737
mass of dry filter paper / g	0.620

In **experiment 2**, a gas was bubbled into another 50 cm^3 portion of solution **L** to convert ClO_3^- to Cl^- before the addition of excess silver nitrate solution. The AgCl precipitated was also dried and weighed. The following data was obtained.

Experiment 2

mass of dry filter paper and AgCl / g	0.799
mass of dry filter paper / g	0.651

(i) Write the half equation for the reduction of ClO_3^- to Cl^-.

$ClO_3^- + 6H^+ + 6e^- \rightarrow Cl^- + 3H_2O$ [1] ....[1]

(ii) Determine the mass of Cl^- in 50 cm^3 of solution **L**.

mass of AgCl precipitate in expt 1 = 0.737 – 0.620 = 0.117 g

mass of Cl^- present in 50 cm^3 portion

$= \frac{35.5}{35.5+107.9} \times 0.117 = 0.02896 \text{ g} \approx 0.0290 \text{ g}$ [1]

[1]

(iii) Determine the mass of Cl^- converted from ClO_3^- in **experiment 2**.

mass of AgCl precipitate in expt 2 = 0.799 – 0.651 = 0.148 g

mass of Cl^- present in 50 cm^3 portion $= \frac{35.5}{35.5+107.9} \times 0.148 = 0.03663 \text{ g}$ [1]

mass of Cl^- from ClO_3^- in 50 cm^3 = 0.03663 – 0.02896

= 0.007674 g ≈ 0.00767 g [1]

[2]

(iv) Hence, determine the percentage mass of ClO_3^- in the unknown sample.

Since n(ClO_3^-) : n(Cl^-) is 1 : 1,

mass of ClO_3^- present in 50 cm^3 = $0.007674 \times \frac{35.5+3(16)}{35.5}$ = 0.01805 g [1]

mass of ClO_3^- present in 250 cm^3 = $0.01805 \times \frac{250}{50}$ = 0.1805 g [1]

% ClO_3^- present in unknown compound = $\frac{0.1805}{68.962-67.620}$ x 100%
= 13.45% ≈ 13.5% [1]

[3]

(v) The E (ClO_3^-/Cl^-) has a value of +1.47 V. From the list of standard electrode potentials in the *Data Booklet*, identify a gas that would reduce ClO_3^- to Cl^-. Explain your answer.

E (H^+/H_2) = 0.00 V
H_2 gas is an appropriate reducing agent. [1]
(also accept E (NO_3^-/NO_2) or E (SO_4^{2-}/SO_2) as their E < +1.47V)

E_{cell} = (+1.47) – (0.oo) = +1.47 V > 0

Since, E_{cell} > 0, the reaction is feasible. [1]

....

.... [2]

(b) **(i)** An aqueous solution of HCl has a density of 1.15 g cm^{-3} and is 30% by mass of HCl.

Calculate the concentration in mol dm^{-3} of this solution of HCl.

mass of HCl in 1 cm^3 = $\frac{30}{100}$ x 1.15 = 0.3450 g [1]

[HCl] = $\frac{0.3450}{1.0+35.5}$ x 1000 = 9.45 mol dm^{-3} [1]

[2]

(ii) Calculate the volume of this solution required to prepare 5 dm^3 of 0.20 mol dm^{-3} HCl by dilution with water.

volume of HCl required = $\frac{5 \times 0.20}{9.452}$ = 0.106 dm^{-3} = 106 cm^3 [1]

[1]

(c) The gelatin silver process is the photographic process used with black-and-white films. The following information pertains to the process of taking photographs and developing films.

Taking photographs

- A 35 mm cartridge of black-and-white print film contains a long strip of plastic that has layered coatings on each side.
- On the front side of the film, the layers are made of gelatin which contain grains of silver chloride crystals.
- When the shutter of the camera is opened for a fraction of a second to allow the film to be exposed to light, these crystals undergo decomposition thereby producing an image on the film.

Developing films

- After the photographs have been taken, the film is developed in a dark room under a light source that emits low energy light.
- Firstly, the film is soaked in water before adding phenidone. Phenidone makes the image more visible by reacting with the exposed silver chloride crystals to produce silver atoms and two other by-products.
- This reaction can only proceed at high pH.
- After some time, the reaction will then be quenched.
- Finally, the film will be soaked in ammonium thiosulfate, $(NH_4)_2S_2O_3$, which is used as a fixer to make the image permanent and light resistant. This is done through the reaction between the unexposed silver chloride crystals and the fixer.

(i) Write the balanced equation for the decomposition of silver chloride crystals when it is exposed to light.

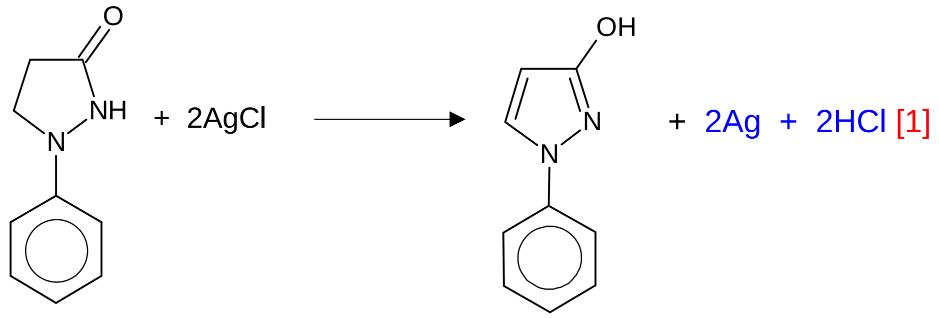
$2AgCl \xrightarrow{\text{light}} 2Ag + Cl_2$ [1]

.... [1]

(ii) Suggest a suitable colour of the light source that is used in a dark room.

Red. (Also accept orange or yellow) [1] .... [1]

(iii) Complete the equation for the reaction between the developing agent, phenidone, and the exposed silver chloride crystals. Hence, state the role of phenidone in this reaction.



phenidone

role of phenidone reducing agent [1]... [2]

(iv) Suggest a suitable reagent, other than excess cold water, that can be used to quench the development of the film. Explain.

Acetic acid / Citric acid / Any plausible acids. e.g. HCl, HNO_3, H_2SO_4 [1]

When acid is added, the pH will be lowered. Hence, the reaction will not proceed at lower pH. [1]

.... [2]

(v) When the non-exposed silver chloride crystals react with the fixer, $(NH_4)_2S_2O_3$, a silver complex compound **M** is formed together with a chloride salt, **N**. Both **M** and **N** have the same cation. The silver-containing complex ion has a coordination number of 2 and is chlorine-free.

Suggest the formulae of compounds **M** and **N**.

compound **M**: $(NH_4)_3[Ag(S_2O_3)_2]$ [1]....... compound **N**: NH_4Cl [1] ....[2]

(vi) State the shape of the silver-containing ion in compound **M**.

Linear [1]..[1]

(vii) Complete the electronic configuration of silver in compound **M**. Hence, deduce the colour of compound **M**.

compound **M** [Ar]$3d^{10}4s^{2}4p^{6}4d^{10}$ [1] ....

Since the 4d orbitals are fully occupied, d–d transition cannot occur. [1]

Hence, compound **M** is colourless. [1]

....

.... [2]

(viii) Explain why the fixer, $(NH_4)_2S_2O_3$, is able to make the image permanent and light resistant on the film.

The fixer is able to remove any remaining unexposed AgCl. Hence, there is no AgCl remaining on the film to undergo decomposition through the exposure of light to change the image on the film. [1]

....

....

.... [1]

[Total: 24]

2 Dinitrogen tetroxide, commonly referred to as nitrogen tetroxide, is the chemical compound N_2O_4. It is a useful reagent in chemical synthesis.

(a) Colourless N_2O_4 readily dissociates to form brown NO_2 and the following equilibrium is reached fairly quickly in the gaseous phase.

$$N_2O_4(g) \qquad 2NO_2(g) \qquad\qquad \Delta H > 0$$

(i) When 4.60 g of N_2O_4 is placed in an evacuated 1.48 dm^3 flask at 27 °C, the equilibrium pressure is 1 atm.

Calculate the value of K_p at 27 °C.

- Initial no of moles of N_2O_4 = 4.60 / (14.0 × 2 + 16.0 × 4) = 0.0500 mol

ICE table/eqm amounts:

$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$$

Initial / mol	0.0500	0
Eqm / mol	0.0500 – x	+2x

- PV = nRT

$(101325)(1.48 \times 10^{-3}) = n\ (8.31)(300)$

n(gases at eqm) = 0.06015 = 0.0602 mol

- Solve for x and find eqm amts

0.0500 – x + 2x = 0.06015

x = 0.01015

$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$$

Eqm / mol	0.03985	0.0203

- $K_p = \dfrac{(P_{NO_2})^2}{P_{N_2O_4}} = \dfrac{\left(\dfrac{0.02030}{0.06015} \times 1\right)^2}{\dfrac{0.03985}{0.06015} \times 1}$ =0.172 atm

4 points 3 marks; 3 points: 2 marks; 2 points: 1 mark

<u>Alternative solution in terms of partial pressure ICE table.</u>

$$P(N_2O_4 \text{ initial}) = \frac{0.05(8.314)(300)}{1.48 \times 10^{-3}} = 84220Pa = 0.08312atm$$

ICE table/eqm partial pressures:

$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$$

Initial / atm	0.08312	0
Eqm / atm	0.08312 – x	+2x

0.08312 – x + 2x = 1

x =0.1687 atm

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}} = \frac{(0.1687\times 2)^2}{0.8312-0.1687} = 0.172 \text{ atm}$$

[3]

(ii) Describe and explain what you would observe when the stoppered flask is placed into a basin of boiling water.

Temperature of system increases and by Le Chatelier's Principle, the forward endothermic reaction is favoured. Position of equlibrium shifts to the right to absorb added heat and more NO_2 is formed. Hence the reaction mixture becomes more brown. **[1]**

....

.... [1]

(b) N_2O_4 is also used in the large scale manufacture of nitric acid. It reacts with water to give both nitrous acid and nitric acid.

$$N_2O_4 + H_2O \rightarrow HNO_2 + HNO_3$$

The two acids have different acid strengths. To determine the acid strength of the two acids, two separate solutions containing 0.10 mol dm^{-3} of each acid were prepared. The pH was found to be 2.17 and 1.00 for the solutions containing nitrous acid and nitric acid respectively.

(i) Use the data provided to prove nitrous acid is a weak acid and hence, determine its K_a value.

$[H^+]$ in solution of HNO_2 = $10^{-2.17}$ = 0.00676 $moldm^{-3}$
which is less than $[HNO_2]$ = 0.10 $moldm^{-3}$.
Hence HNO_2 only dissociates partially and it is a weak acid. **[1]**

OR for the same concentration of acid, HNO_2 dissociates to produce a lower $[H^+]$ (as shown by the higher pH of the solution). Hence, it dissociates to a smaller extent and is a weak acid. ☒ higher pH so weaker acid.

(FYI. Not required in answer: $[H^+]$ in solution of HNO_3 = $10^{-1.00}$ = 0.100 mol dm^{-3} = $[HNO_3]$ hence Not required it is completely dissociated and HNO_3 is a strong acid.)

$$K_a = \frac{[NO_2^-][H^+]}{[HNO_2]} = \frac{(0.00676)^2}{0.10 - 0.00676} = 4.90 \times 10^{-4} \text{ mol dm}^{-3} \quad \textbf{[1]}$$

[Note if students use $[H^+] = \sqrt{K_a . c}$ or $K_a = \frac{(0.00676)^2}{0.10} = 4.57 \times 10^{-4}$]

[2]

(ii) Suggest a reason why nitrous acid is a weaker acid than nitric acid.

Nitric acid is a stronger acid as NO_3^- is a more stable conjugate base than NO_2^- as the negative charge is more effectively dispersed over a greater number of electronegative oxygen atoms (or vice versa). **[1]**

....

....

....

.... [1]

25.0 cm^3 of the prepared 0.10 mol dm^{-3} nitrous acid was titrated with 0.10 mol dm^{-3} aqueous sodium hydroxide.

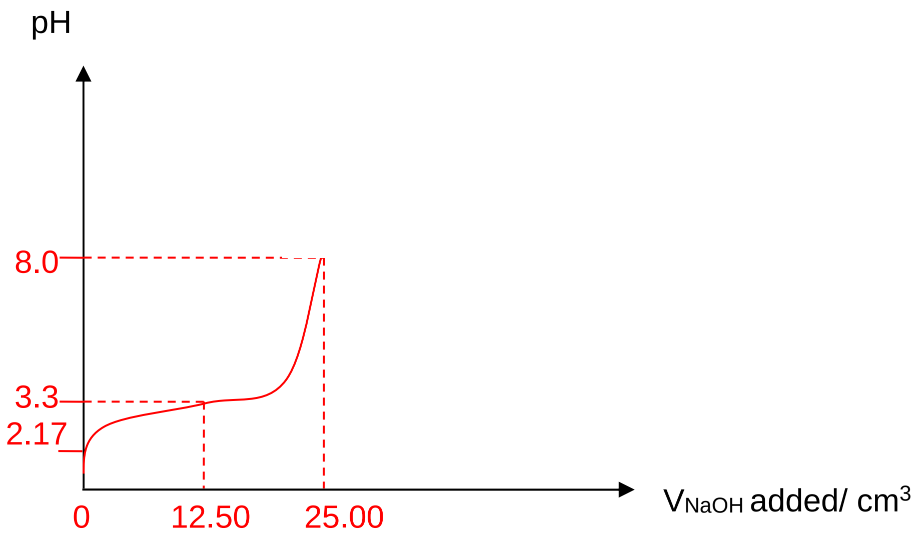
(iii) Using your value of K_a calculated in part **(i)**, calculate the pH when 25.00 cm^3 of aqueous sodium hydoxide has been added.

Equivalence volume = 25.00 cm^3
At equivalence point, solution contains basic salt only.

$K_b = 10^{-14} / 4.90 \times 10^{-4} = 2.040 \times 10^{-11}$
[salt] = 25.0 x 0.1 / 50.0 = 0.05 $moldm^{-3}$
$[OH^-] = \sqrt{K_b.c} = \sqrt{2.040\times10^{-11}(0.05)} = 1.010\times10^{-6}$
pH = 14 **–** pOH = 14 – (–lg(1.010×10^{-6})) = 8.0
4 points [2], 2 points [1] ecf K_a value

[2]

(iv) On the given axes below, sketch the pH-volume added graph you would expect to obtain when the above titration was performed. Label the appropriate pH at various key points on the graph.



Label following values

- Initial pH (given in question)
- Maximum buffering capacity occurs at 12.50 cm^3: pH = pK_a (–lg(4.90×10^{-4}) = 3.3)
- Equivalence point (calculated in iii)

Correct shape (relatively flat at buffer region)
*don't penalize if students sketch graph beyond 25.00 cm^3
4 points [2], 2-3 points [1]

[2]

[Total: 11]

3 The equation for the reaction between bromine and methanoic acid is as follows:

$$Br_2(aq) + HCOOH(aq) \rightarrow 2HBr(aq) + CO_2(g)$$

It is hypothesised that the reaction is elementary. To prove this hypothesis, volumes of the two reactants were varied and the rate of the reaction is measured in terms of the rate at which the bromine concentration changes. When the total volume is kept constant, the following relationship is true.

$$\text{rate of reaction } \alpha \ \frac{\text{volume of bromine used}}{\text{time for color of bromine to disappear}}$$

The temperature of the reaction mixture was maintained at 25 °C.

The following results were obtained in three repeated experiments:

Expt	Volume of 1.0 mol dm^{-3} Br_2 / cm^3	Volume of 10.0 mol dm^{-3} HCOOH / cm^3	Volume of water added / cm^3	Relative time for colour of bromine to disappear
1	10	10	0	1.4
2	40	20	20	2.8
3	5	10	5	1.4

(a) By comparing the rates of reactions, explain how the results of the three experiments support the hypothesis that the reaction is elementary.

Expt	Vol. of 1.0 mol dm^{-3} Br_2 / cm^3	Vol. of 10.0 mol dm^{-3} HCOOH / cm^3	Vol. of water added / cm^3	Relative time for colour of bromine to disappear	Rate
1	10	10	0	1.4	10/1.4=7.14
2	40	20	20	2.8	
2a	40/4=10	20/4=5	20/4=5	2.8	10/2.8=3.57
3	5	10	5	1.4	5/1.4=3.57

Using expt 1 and 3,

When vol of Br_2 halved i.e. 10/5, the rate halved i.e. 7.14/3.57. Hence rate is directly proportional to Br_2, 1st order wrt Br_2.

Using expt 1 and 2a,

When vol of HCOOH halved i.e. 10/5, the rate halved i.e. 7.14/3.57. Hence rate is directly proportional to HCOOH, 1st order wrt HCOOH.

Since orders of reaction correspond to stoichiometric ratio of the overall equation, the reaction is elementary.

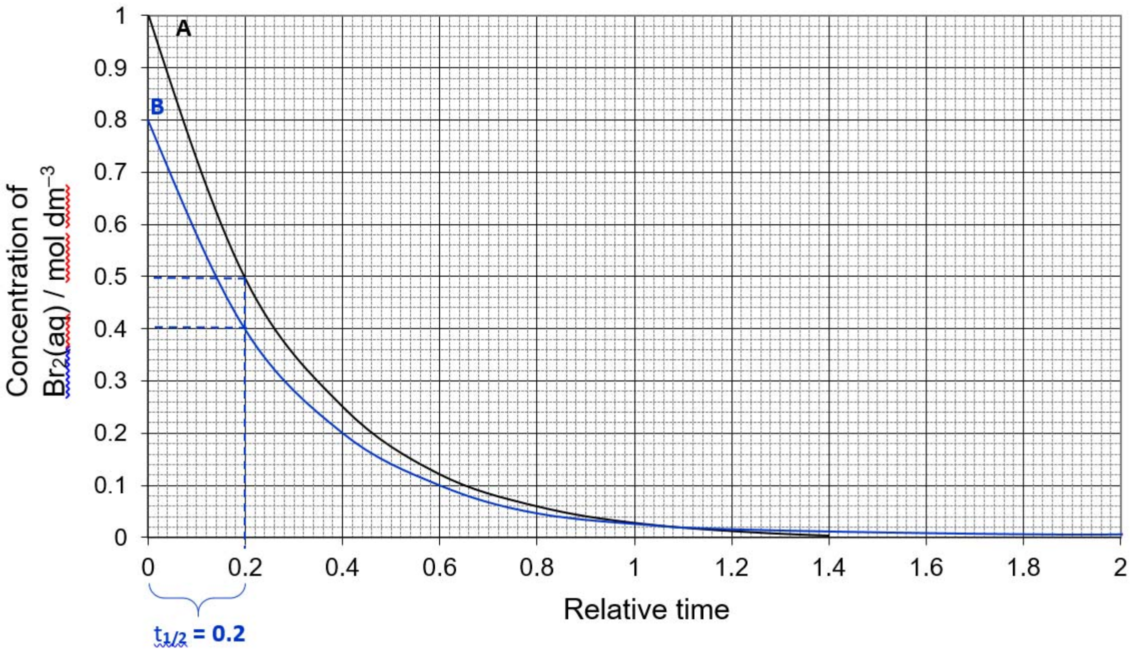
1 mark for finding order wrt Br_2

1 mark for finding order wrt HCOOH and deducing the hypothesis correctly

....

.... [3]

(b) During another experiment, the concentration of Br_2 was monitored over time and the following graph (Run **A**) was obtained. The concentration of HCOOH used was 10.0 mol dm^{-3}.



(i) Define the term "half-life".

Time taken for concentration of reactant to reach half its original concentration.

.... [1]

(ii) The experiment was repeated using 0.8 mol dm^{-3} of $Br_2(aq)$ and 10.0 mol dm^{-3} of HCOOH. On the axes above, draw the concentration-time graph of $Br_2(aq)$ for the new experiment and label it 'Run **B**'.

On your graph, clearly state and label the half-life of $Br_2(aq)$. [1]

Curve must show at least 2 constant half-lives. Only one half-life needs to be clearly labelled.

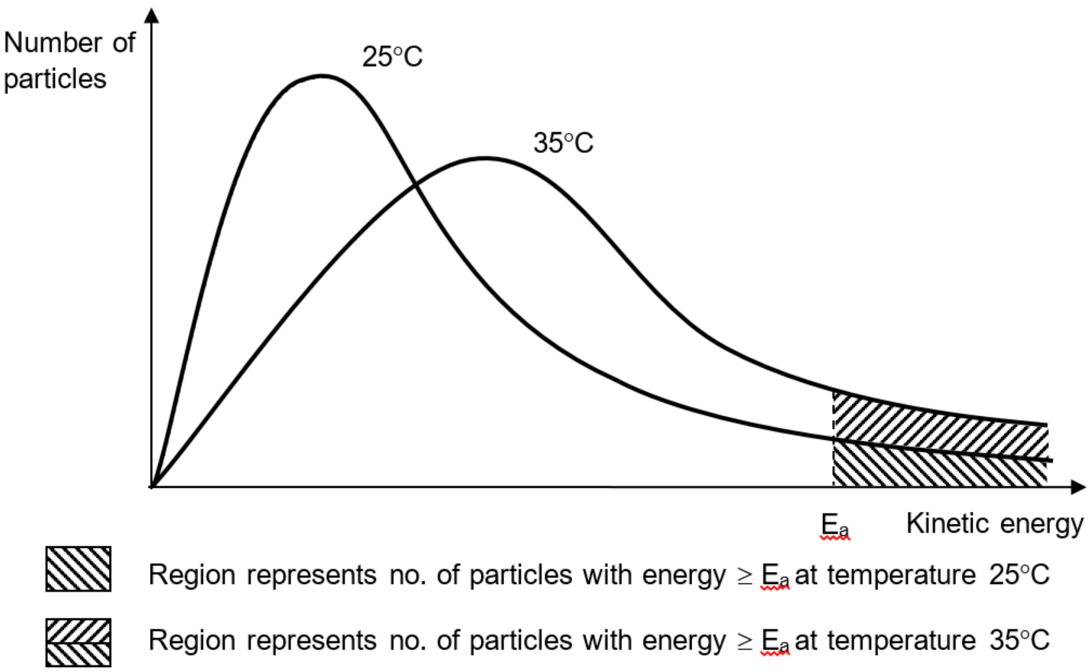
(iii) The experiment was repeated again using 1.0 mol dm^{-3} of $Br_2(aq)$ and 5.0 mol dm^{-3} of HCOOH (Run **C**). In comparison to Run **A**, state how the half-life of the experiment will change.

The reaction is a pseudo-first order reaction in which $\mathbf{t}_{1/2} = \dfrac{\ln 2}{k[HCOOH]}$

Hence if [HCOOH] halves, $t_{1/2}$ will double from 0.2 to 0.4.

.... [1]

(c) By drawing a suitable illustration, estimate and explain the change in rate of reaction when temperature is increased to 35 °C.



When the temperature increases by 10 °C,

⇒ the average kinetic energy of particles doubles

⇒ the shape of the Maxwell-Boltzmann curve flattens out such that double the number particles have energy ≥ E_a

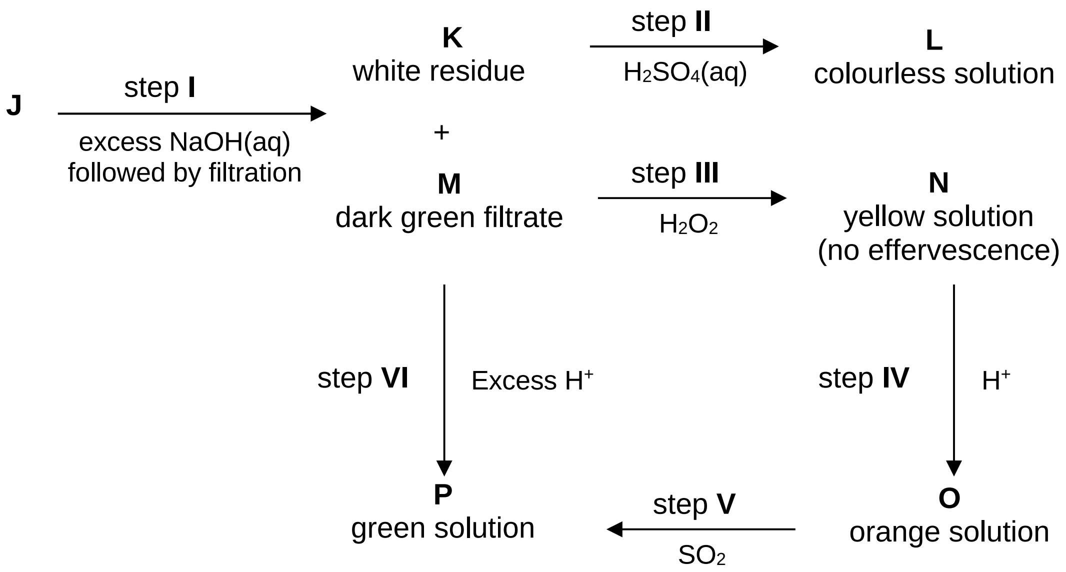
⇒ the frequency of effective collisions doubles

⇒ Rate constant doubles, hence rate doubles

.... [3]

[Total: 9]

4(a) Solution **J** contains a Group 2 ion and a transition metal ion. The following reaction scheme shows how **J** reacts with some common reagents in the laboratory.



(i) State the identities of **K**, **L**, **M**, **N**, **O** and **P.**

K $Mg(OH)_2$... **L** $MgSO_4$ or Mg^{2+}..........................

M $[Cr(OH)_6]^{3-}$.. **N** CrO_4^{2-} ....

O $Cr_2O_7^{2-}$ .... **P** Cr^{3+} or $[Cr(H_2O)_6]^{3+}$....................

[3]

6 correct [3]; 4, 5 correct [2]; 2, 3 correct [1] (Note: also accept Be for K & L)

[3]

(ii) State the roles of H_2O_2 and SO_2 in steps **III** and **V** respectively.

H_2O_2 in step **III**: oxidising agent ....

SO_2 in step **V**: reducing agent .... [1]

(iii) Write an ionic equation to explain the formation of solution **P** in step **V**.

$Cr_2O_7^{2-} + 3SO_2 + 2H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O$ [1] .... [1]

(iv) Explain how solution **P** can be formed in step **VI**.

$Cr^{3+}(aq) + 3OH^-(aq) \quad Cr(OH)_3(s)$ (1)
or $[Cr(H_2O)_6]^{3+}(aq) + 3OH^-(aq) \quad Cr(H_2O)_3(OH)_3(s) + 3H_2O$
$Cr(OH)_3(s) + 3OH^-(aq) \quad Cr(OH)_6^{3-}(aq)$ (2)
When H^+ is added, it removes the excess $OH^-(aq)$ which was added. Position of equilibrium (2) will shift to the left to form grey-green ppt of $Cr(OH)_3$. [1]
When excess H^+ is added, it removes all the $OH^-(aq)$ in the solution. Position of equilibrium (1) will shift to the left forming green solution of Cr^{3+}. [1]

....

.... [2]

(b) Among the elements of Group 14, those towards the top, carbon to germanium, have very different properties from those at the bottom, tin and lead.
For example, the melting points show a marked change after germanium.

element	C	Si	Ge	Sn	Pb
mp / °C	>3550	1410	937	232	327

Carbon, silicon and germanium each form a solid with the same type of structure.

(i) Explain why the melting points of these elements decrease from carbon to germanium.

They have giant covalent structures with strong covalent bonds between atoms in a 3-dimensional network. [1] From carbon to germanium, the atomic radius increase and the bond length increase (C–C bond length < Si–Si bond length < Ge–Ge bond length), hence the covalent bond strength decrease from carbon to silicon to germanium. [1] Since the melting of these elements require breaking the covalent bonds between the respective atoms, the melting point decreases since less energy is required to break the weaker covalent bonds.

.... [2]

(ii) Explain how first ionisation energy changes from carbon to germanium.

Down the group from carbon to germanium,

- the number of protons increases, nuclear charge increases.
- As the number of electron shells increases, shielding effect increases significantly.
- The outermost electron is further away from the nucleus, hence attraction between the nucleus and outermost electron decreases
- The first ionisation energy decreases down a group.

4 points – [2]; 2,3 points – 1

.... [2]

Carbon and silicon each form a tetrachloride. CCl_4 has no reaction with water; $SiCl_4$ reacts violently with water.

(iii) Write a balanced equation for the reaction of $SiCl_4$ with water.

$SiCl_4 + H_2O \rightarrow SiO_2 + 4HCl$ [1] .... [1]

(iv) Suggest an explanation for the inertness of CCl_4 to water.

Water molecules could not form co-ordinate/dative bonds with the central carbon atom of CCl_4 because carbon is in period 2 and does not have energetically accessible low lying orbitals to accommodate lone pair of electrons from O atom in H_2O. [1]

....

.... [1]

[Total: 13]

5 Azo dyes are made in large quantites from benzene, C_6H_6, via nitrobenzene, $C_6H_5NO_2$ (density = 1.20 g cm^{-3}), and phenylamine, $C_6H_5NH_2$.

(a) The preparation of nitrobenzene requires benzene to be warmed under reflux at about 55 °C with a mixture of concentrated nitric and sulfuric acids. Some information about these substances is given below:

Benzene: immiscible with water; highly flammable; extremely toxic by ingestion or inhalation; known carcinogen.

Concentrated nitric acid: miscible with water; causes severe burns to eyes and skin; strong oxidising agent. The acid contains about 30 % water by volume.

Concentrated sulfuric acid: miscible with water; causes severe burns to eyes and skin; strong oxidising agent; dilution with water is very exothermic and can be dangerous.

(i) Nitric acid is placed in a suitable flask and sulfuric acid is added slowly with cooling of the flask. Explain why cooling is necessary.

To avoid the temperature rising too much OR the reaction between sulfuric acid and water is exothermic as the sulfuric acid is diluted by the water in nitric acid

....

.... [1]

(ii) Benzene is added slowly to the acid mixture, which is then warmed at 55 °C for 45 minutes under reflux with vigorous stirring of the reaction mixture.

Explain why the reflux condenser is necessary and also why the mixture is vigorously stirred.

Prevents escape of benzene / volatile liquids [1]
reactants are immisicible/do not mix/form separate layers so they need to be stirred to make reaction rate acceptable or increase frequency of effective collisions or increase the surface area of contact between the two immiscible layers or to enable the reactant molecules to collide with the correct orientation [1]

....

.... [2]

(iii) State, with a reason, **one** other precaution (other than wearing protective wear) that would be necessary when carrying out the experiment.

EITHER
benzene is toxic so use fume cupboard
OR
benzene/nitrobenzene is flammable so use heating mantle/water bath

....

.... [1]

(iv) The reaction mixture is then poured into a large excess of cold water, the liquid nitrobenzene layer is separated and *washed* with sodium carbonate solution. Explain why this washing is necessary.

sodium carbonate removes/neutralises (residual) acid [1]

.... [1]

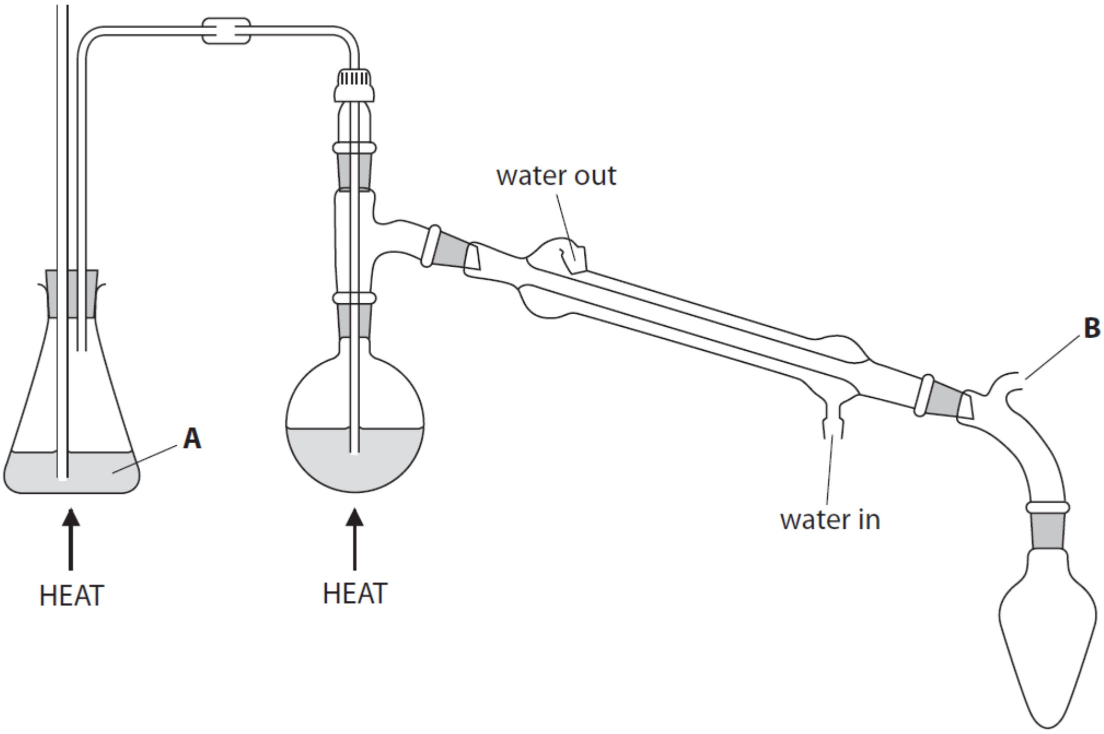
(v) The nitrobenzene layer is dried before being distilled to purify it. Identify a suitable drying agent.

(anhydrous) sodium sulfate / magnesium sulfate OR
(anhydrous) calcium chloride OR silica gel

.... [1]

(b) Steam distillation is a purification process to separate nitrobenzene from the reaction mixture. During the process of steam distillation, a current of steam is blown through a mixture containing the desired organic substance to be distilled. This caused the desired organic substance to vaporise. The vapour containing the desired organic substance can then be condensed and collected. This method is used predominantly to purify liquids that are not very volatile and are immiscible with water.

The diagram below shows a steam distillation apparatus used to extract nitrobenzene from the reaction mixture.



(i) Identify substance **A**.

water (to produce steam) .... [1]

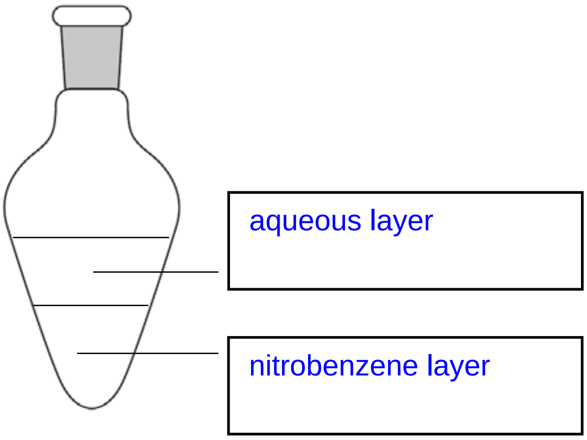
(ii) Explain the purpose of the part of the apparatus labelled **B**.

prevents pressure building up (by allowing gases/vapour to escape)
allow to prevent explosion

reject to allow gases/vapours to escape only
ignore the reference to 'air' for gases / vapours

.... [1]

(iii) On the diagram below, state the contents of the receiver at the end of the steam distillation.



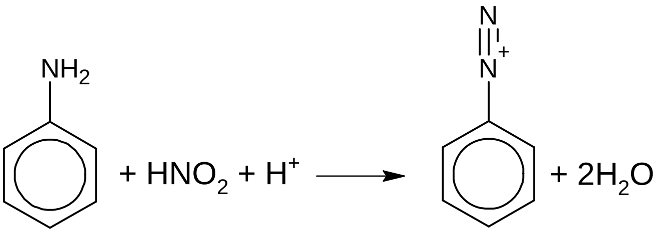
[1]

aqueous layer on top while nitrobenzene on bottom [1]

(c) The purified nitrobenzene is then reduced to phenylamine, $C_6H_5NH_2$.

The phenylamine is diazotised by reaction with nitrous acid at a temperature between 0 °C and 10 °C. Nitrous acid is generated in the reaction mixture from sodium nitrite and hydrochloric acid.

The ionic equation for the diazotisation of phenylamine to produce benzenediazonium ion is as shown below.

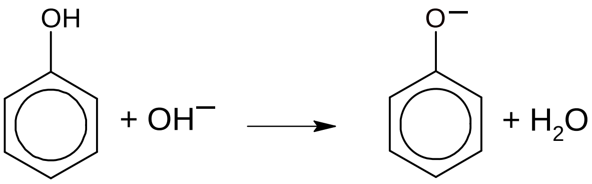


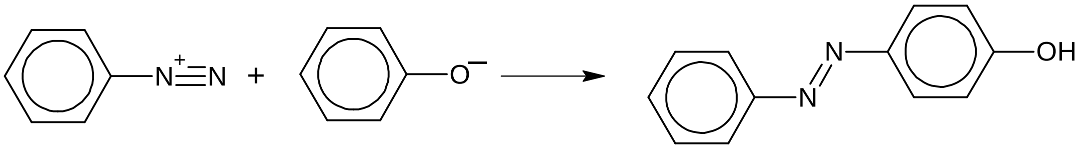
benzenediazonium ion

If the above reaction is warmed, benzenediazonium ion will undergo hydrolysis to give phenol. A gas will also be produced and the resulting mixture is acidic.

Reaction of the benzenediazonium compound with an alkaline solution of a phenol, C_6H_5OH, will produce a solid azo dye, which is purified by recrystallisation.

The equations for the reaction between benzenediazonium ion and phenol to produce the solid azo dye are shown below.





azo dye

(i) State the reagents and conditions needed to reduce nitrobenzene to phenylamine.

Sn, conc. HCl, under under reflux (followed by addition of NaOH(aq) [1]

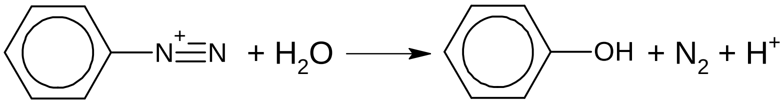
.... [1]

(ii) Explain why the temperature for diazotization to phenylamine must **not** be lower than 0 °C.

< 0 °C reaction is too slow [1]
allow mixture freezes

.... [1]

(iii) Write an equation to show benzenediazonium ion undergoing hydrolysis upon warming.



.... [1]

(d) Purification by recrystallisation requires the following steps:

1. The azo dye is dissolved in a minimum volume of hot solvent.
2. The solution is filtered through a pre-heated funnel.
3. The solution is cooled and filtered using a Buchner funnel.
4. The solid is washed with a small amount of cold solvent.
5. The solid is dried in a desiccator.

(i) Explain why a **minimum** volume of hot solvent is used in step 1.

To prevent (much of the) azo dye remaining in solution on cooling
OR
Gives a saturated solution

....

.... [1]

(iii) Explain why the funnel must be pre-heated.

To prevent crystallization (of the azo dye) [1]

.... [1]

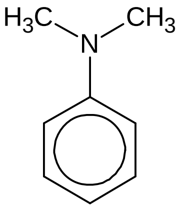
(iv) Suggest a reason why it is preferable to dry the solid in a desiccator rather than in an oven.

Decomposition could occur if the compound were to be heated
OR
Compound might melt

.... [1]

(e) This question compares the acidity and basicity of some organic compounds.

(i) Explain why an aqueous solution of N,N-dimethylphenylamine is more basic than an aqueous solution of phenylamine.



N,N-dimethylphenylamine

There are <u>2 electron-donating $-CH_3$ groups</u> [pt 1] attached to the N atom in N,N-dimethylphenylamine. Hence the <u>electron density on the N atom in N,N-dimethylphenylamine is higher</u> [pt 2] than that in phenylamine. The <u>lone pair of electrons on the N atom in N,N-dimethylphenylamine is more available</u> [pt 3] for dative bonding with a H^+.

....

.... [1]

(ii) Explain why an aqueous solution of azo dye is more acidic than an aqueous solution of phenol.

This group, <u>$C_6H_5N=N-$</u> is an <u>electron-withdrawing</u> [pt 4] group which <u>further disperses the negative charge on the O atom</u> [pt 5] in the conjugate base of azo dye. The <u>conjugate base formed by the azo dye is further stabilized</u> [pt 6]. <u>The azo dye donates proton more readily</u> [pt 7].

....

.... [2]

7 pts – 3 marks
5 – 6 pts – 2 marks
3 – 4 pts – 1 mark

[Total: 18]

[End of Paper]

NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CHEMISTRY

9~~64~~729/03

Paper 3 Free Response

~~21~~ 18 September 2018~~6~~

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2 hours

Additional Materials: Writing Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

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

Section A
Answer **all** questions.

Section B
Answer **one** question.

A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.
~~Answer any **four** questions.~~
~~A Data Booklet is provided.~~
~~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.

[Turn over

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Section A

Answer **all** questions in this section.

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1 Cobalt is a typical transition element which is commonly used as a catalyst and metal for electroplating. Cobalt also forms complex ions with ligands such as H_2O and NH_3 to give various coloured octahedral complexes such as $[Co(H_2O)_6]^{2+}$ and $[Co(NH_3)_6]^{2+}$ which are pink and yellow respectively.

(a) The ligand exchange in octahedral complexes is one of the most extensively studied reactions in transition metals.

An example of a ligand exchange reaction involving cobalt~~-~~(II) ions is:

$$[Co(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+} + 6H_2O$$

(i) Explain why cobalt forms coloured complexes. [3]

(ii) Suggest why $[Co(NH_3)_6]^{2+}$ is of a different colour from $[Co(H_2O)_6]^{2+}$. [1]

(iii) A student wishes to investigate the kinetics of the ligand exchange reaction of $[Co(H_2O)_6]^{2+}$ to form $[Co(NH_3)_6]^{2+}$ by using a spectrometer. This machine measures the amount of light that is absorbed when a specific wavelength of visible light is shone through a few cm^3 of the coloured solution. It does this by comparing the amount of light passing through the sample with the amount of light passing through the pure solvent.

The spectrometer is set to use the wavelength of light that is absorbed most strongly by the complex ion. The amount of light absorbed is expressed as an absorbance value. The more concentrated the solution, the higher the absorbance value. The temperature of the sample in the spectrometer can be thermostatically controlled for reaction rate analysis for which the sample has to be kept at a constant temperature.

Outline the experimental procedure on how the student would accurately determine the initial rate of the ligand exchange reaction at 5 °C. ~~[3]~~

The details of the use of ~~No details regarding use of~~ specific glassware for measurement are **not** required. [3]

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(iv) When $[Co(H_2O)_6]^{2+}$ is mixed with an excess of NH_3~~–~~(aq), each H_2O molecule is replaced by a NH_3 molecule one at a time. Given that the stepwise formation of $[Co(NH_3)_6]^{2+}$ from $[Co(H_2O)_6]^{2+}$ undergoes a dissociative mechanism which resembles a S_N1 mechanism in organic chemistry.

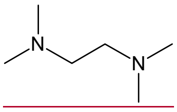
Suggest a possible mechanism for the formation of $[Co(H_2O)_5NH_3]^{2+}$ from $[Co(H_2O)_6]^{2+}$ and show clearly how the shape of the complex ion changes.

In ~~-~~your mechanism, show appropriate curly arrows, lone pairs and dipoles. [3]

(v) State the rate equation for the above ligand exchange reaction. [1]

(vi) Hence, predict and explain the effect on the rate of reaction, if any, when the ammonia ligand is replaced ~~by~~with a fluoride ion. [1]

(b) $[Co(H_2O)_6]^{2+}$ can also undergo ligand exchange reactions with TMEDA to form $[Co(TMEDA)_3]^{2+}$.



TMEDA

By considering the entropy and enthalpy changes during the formation of $[Co(TMEDA)_3]^{2+}$ from $[Co(H_2O)_6]^{2+}$ and that of $[Co(NH_3)_6]^{2+}$ from $[Co(H_2O)_6]^{2+}$, suggest how the standard Gibbs free energy change of the two reactions will compare in sign and in magnitude.

Hence, predict which reaction will be ~~the~~ more spontaneous. Explain your reasoning.
[3]

(c) **(i)** Draw a fully labelled diagram of an electrochemical cell composed of a standard Cl_2|~~/~~Cl^- electrode and a standard Co^{2+}~~/~~|Co electrode. Indicate the direction of the electron flow. [3]

(ii) Calculate the $E^{\ominus}_{cell}$ of the electrochemical cell and write a balanced equation for the cell reaction.
[~~1~~2]

(iii) Using your answer in **(ii)**, calculate ΔG for the cell reaction. [1]

(iv) Use the *Data Booklet* to suggest the effect on the cell potential of this cell of adding excess aqueous ammonia to the Co^{2+}|~~/~~Co half cell. Explain your answer. [1]

[Total: 2~~1~~2]

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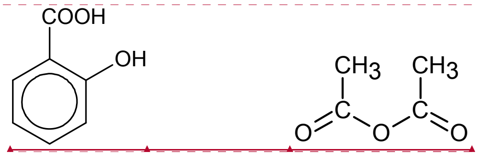
~~**Answer any four questions.**~~

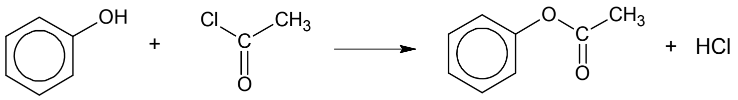
~~1~~2**(a)** Aspirin is one of the most widely used drug in the world. It is a powerful analgesic (pain reliever), antipyretic (fever reducer) and anti-inflammatory drug.

It is synthesised using 2-hydroxybenzoic acid and ethanoic anhydride. 8 – 10 drops of 85% phosphoric acid which catalyses the reaction is added. The reaction mixture is then heated under reflux for around fifteen minutes. The other product of this reaction is ethanoic acid.



2-hydroxybenzoic acid ethanoic anhydride

Ethanoyl chloride and phenol can undergo condensation reaction.



Ethanoic anhydride and 2-hydroxybenzoic acid can undergo a similar reaction to form aspirin.

(i) Draw the structure of aspirin. [1]

(ii) Draw a labelled diagram of the assembled apparatus for the synthesis of aspirin. [3]

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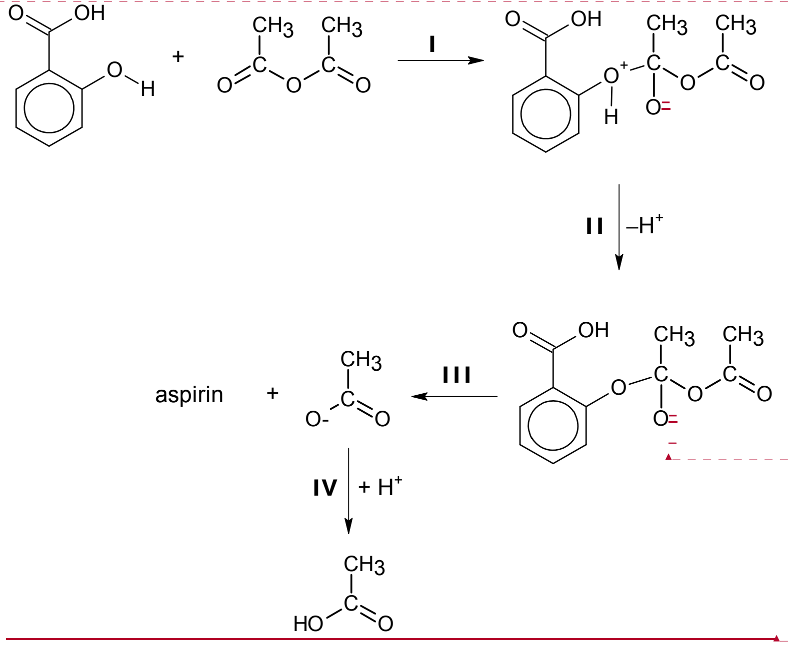
The mechanism for the reaction between 2-hydroxybenzoic acid and ethanoic anhydride involves four steps. It is proposed as below:



(iii) Using the information given above, state the type of mechanism in step **I**. [1]

(iv) Copy and complete the whole mechanism above by showing any relevant charges, lone pairs of electrons and movement of electrons in your answer. [3]

(v) State a reason why ethanoic anhydride is used rather than ethanoyl chloride for the synthesis of aspirin. [1]

(b) In 1911, the French chemist F.A.V. Grignard reacted small pieces of magnesium with a warm solution of bromoethane in a dry, non-polar solvent and obtained a solution containing ethylmagnesium bromide, C_2H_5MgBr. Many Grignard reagents, with different alkyl or aryl groups, have now been prepared and are widely used in organic syntheses. A typical example of the use of a Grignard reagent is the two-step reaction of C_2H_5MgBr with propanone, CH_3COCH_3, to form 2-methylbutan-2-ol.

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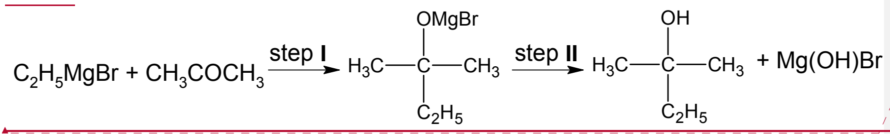
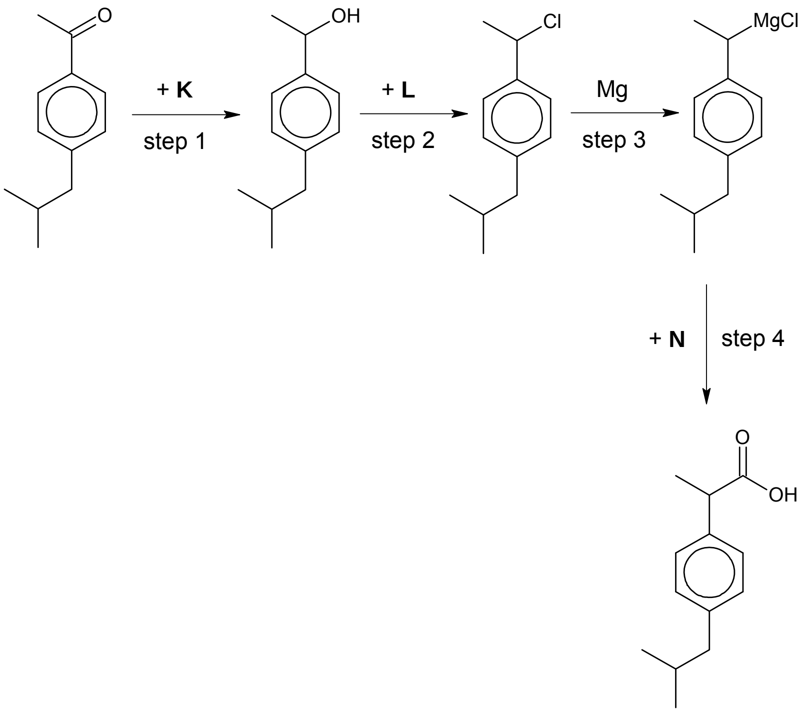


$$C_2H_5MgBr + CH_3COCH_3 \xrightarrow{\text{step I}} H_3C\text{—}\underset{C_2H_5}{\overset{OMgBr}{C}}\text{—}CH_3 \xrightarrow{\text{step II}} H_3C\text{—}\underset{C_2H_5}{\overset{OH}{C}}\text{—}CH_3 + Mg(OH)Br$$

Suggest the type of reaction which occurs in step **II**. [1]

(c) The following scheme shows the synthesis of ibuprofen which is an alternative medication to aspirin. In step 4, the Grignard reagent readily converts into a carboxylic acid.



ibuprofen

(i) Suggest the identity of the reagent **K** in step 1. [1]

(ii) Suggest the identity of the reagent **L** in step 2. [1]

(iii) Suggest the identity of the reagent **N** in step 4. [1]

(d) Suggest a simple chemical test that could be used to distinguish between aspirin and ibuprofen. You should state what you would observe for **each** compound. [3]

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~~Copper(I) sulfate, Cu_2SO_4, can be made from copper(I) oxide under non-aqueous conditions. On adding this salt to water, it immediately undergoes a disproportionation reaction.~~

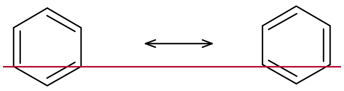
~~(i) Suggest, with a reason, the colour of copper(I) sulfate. [2]~~

~~(ii) Using suitable data from the *Data Booklet*, explain why the disproportionation reaction occurs, and write an equation for it. [3]~~

~~**(b)** Palladium(II) salts can form square planar complexes. Successive addition of ammonia and hydrogen chloride to an aqueous palladium(II) salt produces, under different conditions, three compounds with empirical formula $PdN_2H_6Cl_2$. Two of these, **A** and **B**, are non-ionic, with M_r = 211. **A** has a dipole moment, whereas **B** has none. The third compound, **C**, is ionic, having M_r = 422, and contains palladium in both its cation and anion.~~

~~For each **A**, **B** and **C**, deduce a structure that fits the above data, explaining your reasons fully. [6]~~

~~**(c)** Benzene ring is often represented as a structure that has a ring within the hexagon. Alternatively, chemists have also represented the structure of benzene in the following forms, known as resonance structures.~~

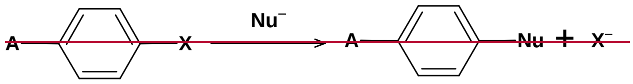


Benzene (two resonance forms)

~~The resonance relationship is indicated by the double headed arrow between them. The only difference between resonance forms is the placement of the pi electrons and non-bonding electrons.~~

~~Most aromatic compounds undergo electrophilic substitution. However aryl halides undergo a limited number of substitution reactions with strong nucleophiles.~~

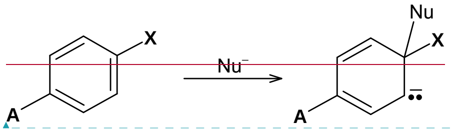
~~An example of a reaction is as follows:~~



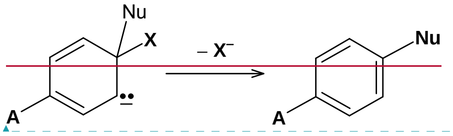
~~where **A** is an electron withdrawing group and **X** is a halogen~~

~~The mechanism of this reaction has two steps:~~
- ~~addition of the nucleophile~~
- ~~elimination of the halogen leaving group~~

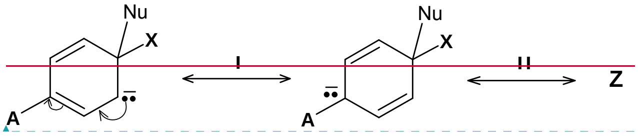
3 ~~**Step 1** involves the addition of the nucleophile (Nu^-). The Nu^- attacks the carbon atom bonded to a halogen, causing the pi bond to break. A resonance stabilised carbanion with a new C–Nu bond is formed. The aromatic ring is destroyed in this step.~~



~~**Step 2** involves the loss of the halogen **X**, reforming the aromatic ring.~~

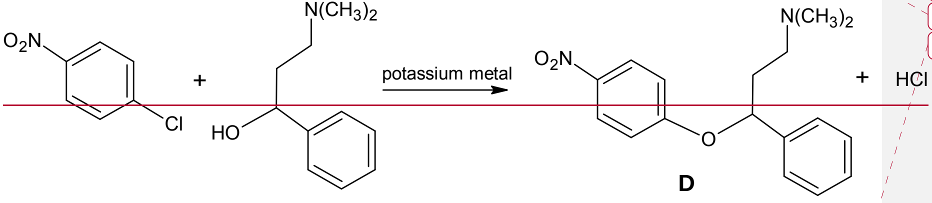


~~Two other resonance structures of the intermediate in **Step 1** are shown below:~~



~~**(i)** Copy the above diagram and draw the resonance structure, **Z**. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons in forming **Z**.~~ ~~[2]~~

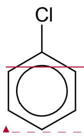
~~The reaction below shows the synthesis of compound, **D**.~~

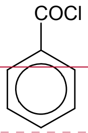


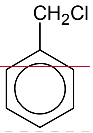
~~**(ii)** Suggest the role of potassium metal in the reaction.~~ ~~[1]~~

~~**(iii)** Use the information given above to draw out the full mechanism for the reaction that forms **D**, labelling the slow and fast steps. In your answer, showing any relevant charges, lone pair of electrons and movement of electrons.~~ ~~[3]~~

~~**(d)** Describe and explain the relative ease of hydrolysis of the following three chloro-compounds.~~ ~~[3]~~







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~~**2** Sulfuric acid, H_2SO_4, can behave as an acid, an oxidising agent or as a dehydrating agent in various reactions.~~

~~**(a)** Draw a diagram to illustrate the shape of pure sulfuric acid and indicate the bond angle about the sulfur atom. [2]~~

~~**(b)** The Contact Process is used for the manufacture of sulfuric acid. One of the reactions that takes place is the following reversible reaction:~~

~~$2SO_2(g) + O_2(g)$ Ý $2SO_3(g)$ $\Delta H = -197$ kJ mol^{-1}~~

~~Sulfur dioxide and oxygen in a 2:1 molar ratio at a total initial pressure of 3 atm is passed over a catalyst in a fixed volume vessel at 400 °C. When equilibrium is established, the percentage of sulfur trioxide in the mixture of gases is found to be 30%.~~

~~**(i)** Write an expression for the equilibrium constant, K_p, of the reaction. [1]~~

~~**(ii)** Calculate the value of K_p at 400 °C, stating its units. [3]~~

~~**(iii)** How would the percentage conversion of SO_2 into SO_3 be affected when the pressure is raised? Explain. [2]~~

~~**(c)** Dilute sulfuric acid takes part in typical acid-base reactions and it can be used to distinguish the following solids: MgO, BaO and SiO_2.~~

~~State the observations, if any, to indicate the differences in their reaction when water is added to each solid followed by dilute sulfuric acid. [4]~~

~~**(d)** Sulfur dioxide is a major pollutant from sulfuric acid plants. The SO_2 emitted into the atmosphere is oxidised in the air, which then reacts with water to form sulfuric acid, hence causing acid rain:~~

~~$2SO_2(g) + O_2(g) + 2H_2O(l) \longrightarrow 2H_2SO_4(l)$ ΔH_1~~

~~Using the data below and data from **(b)**, construct an energy cycle to calculate~~

~~**(i)** the enthalpy change of formation of $SO_2(g)$, and hence~~

~~**(ii)** the enthalpy change of reaction, ΔH_1 for the above reaction.~~

~~Enthalpy change of formation of $H_2O(l)$ = –286 kJ mol^{-1}~~
~~Enthalpy change of formation of $H_2SO_4(l)$ = –811 kJ mol^{-1}~~
~~Enthalpy change of formation of $SO_3(g)$ = –493 kJ mol^{-1}~~
~~[4]~~

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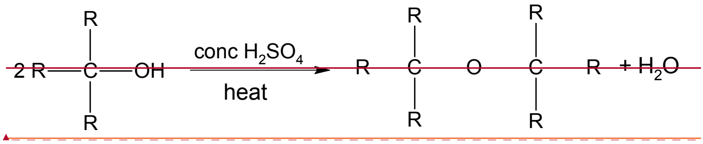
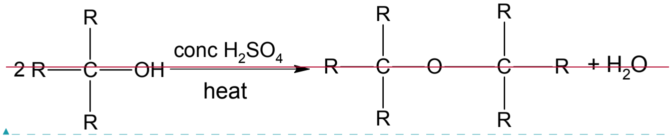
~~**(e)** Alcohols react with concentrated sulfuric acid at high temperatures to form alkenes. A common side reaction that can happen is the formation of ethers, which is also catalysed by concentrated sulfuric acid.~~

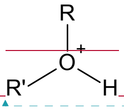




~~The mechanism occurs via 3 steps:~~

~~**Step 1:**~~
~~An acid base reaction in which H^+ from H_2SO_4 protonates the oxygen atom in alcohol. This step is very fast and reversible.~~

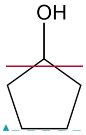
~~**Step 2:**~~
~~A second alcohol molecule functions as the nucleophile and attacks the product from **step 1**. The C–O bond is cleaved and a water molecule leaves the molecule. This creates an oxonium ion~~



~~intermediate.~~

~~**Step 3:**~~
~~Another acid base reaction in which the proton in the oxonium ion is removed by a suitable base (in this case a water molecule) to give the ether product. This step is very fast and reversible.~~

~~**(i)** Draw the ether formed when cyclopentanol undergoes the above reaction.~~



~~cyclopentanol~~

~~[1]~~

~~**(ii)** Draw out the full mechanism for the reaction between two cyclopentanol molecules to form an ether. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons. [3]~~

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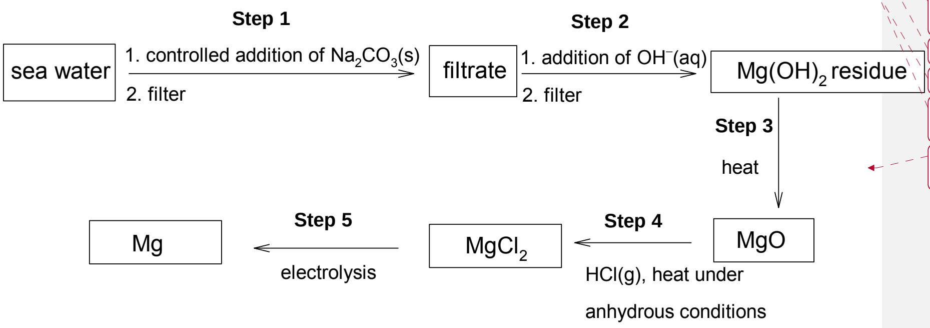
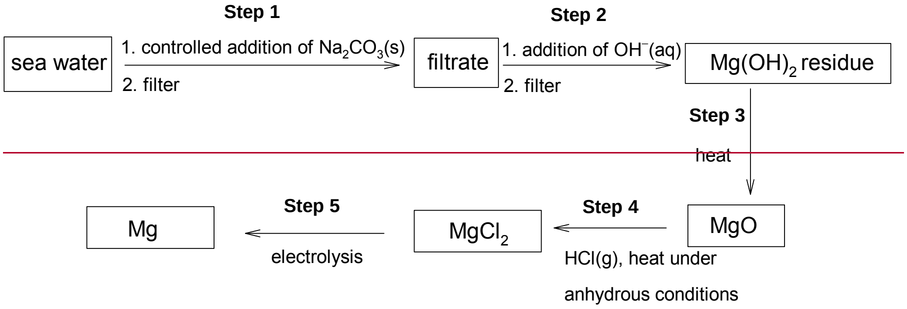
3 Magnesium is present as dissolved magnesium ions in sea water and is the only metal directly extracted from sea water. There is enough magnesium dissolved in the Earth's oceans to supply all of our magnesium needs for the next 1000 years.

~~Garlic contains many amino acids, minerals and enzymes. Garlic also contains at least 33 sulfur compounds like alliin, allicin and ajoene. The sulfur compounds are responsible for both garlic's pungent odour and many of its medical effects.~~

(a) Apart from magnesium ions, the two other most abundant cations found in sea water are sodium and calcium ions.

Magnesium can be extracted from sea water by the following steps:





Concentration of common ions in sea water:

ion	**concentration / mol dm^{-3}**
magnesium	0.056
calcium	0.010
sodium	0.457
chloride	0.535

The numerical values of solubility products are given below:

compound	**value of solubility product**
magnesium carbonate	1.00×10^{-5}
calcium carbonate	8.70×10^{-9}

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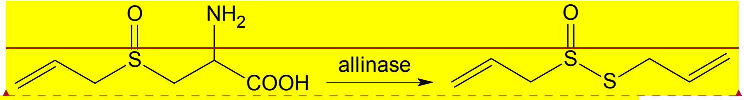
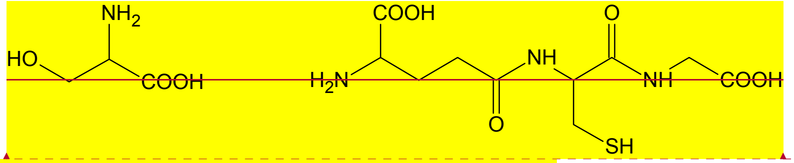
magnesium hydroxide	5.61 × 10^{-12}
calcium hydroxide	5.50 × 10^{-6}

~~When raw garlic is chopped or crushed, the enzyme allinase converts alliin into allicin, which is responsible for the odour of fresh garlic.~~



~~alliin~~ ~~allicin~~

~~Allicin can also be biosynthesised by using serine and glutathione.~~



~~serine~~ ~~glutathione~~

~~**(i)** Explain why raw chopped garlic has a stronger odour than when it is cooked. [1]~~

(i) Explain why the addition of sodium carbonate ~~ions~~ in **step 1** has to be controlled. [1]

(ii) Hence, state the cations present in the filtrate after **step 1** is carried out. [1]

(iii) What is the maximum mass of solid sodium carbonate that can be added to 1 dm^3 of sea water in **step 1**? [2]

(iv) Use the data provided to explain the following:

- Solid sodium carbonate was added to sea water (under controlled conditions) **before** the hydroxide ions.
- The reverse order (i.e. adding hydroxide ions before sodium carbonate) is **not** preferred over the extraction of magnesium.

~~(under controlled conditions)~~

~~sodium~~

[2]

(v) Calculate the minimum pH of the hydroxide solution required for precipitation of magnesium hydroxide in **step 2** if an equal volume of hydroxide ions was added to the filtrate. Give your answer to 2 decimal places. [2]

(b) **(i)** Write the equations that occur during the electrolysis of magnesium chloride in ~~S~~**step 5**. State clearly the reactions that occur at the cathode and the anode, and include state symbols. [2]

(ii) In a factory, a current of 95 kA was passed through a suitable setup for 24 hours. Assuming that the procedure is 90% efficient, calculate the mass of Mg that can be produced. [2]

(iii) Give a reason why electrolysis of magnesium chloride is preferred to that of magnesium oxide in this industrial process. [1]

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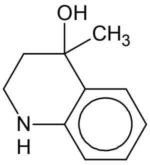
(c) ~~A is an organic compound.~~ When 0.46~~7~~8 g of an organic compound **A** was evaporated in a syringe, the volume of the vapour produced after correction to s.t.p was 60 cm^3. On heating with aqueous sodium hydroxide, **A** gives a compound that dissolves in water.

A reacts with aluminium oxide to give two products **B** and **C**. Both **B** and **C** react with HBr to give the same product **D**. **D** exhibits enantiomerism and exists as a pair of enantiomers.

A gives **E** when reacted with lithium aluminium hydride in dry ether.



E

(i) Prove that the molar~~ecular~~ mass of **A** is 177 g mol^{-1}. [1]

(ii) Hence, d~~D~~educe the structural formulae of all the above structures, and explain the chemistry involved. [6]

(iii) State the type of isomerism exhibited by **B** and **C**. Explain why **B** and **C** both give the same product **D** when reacted with HBr. [2]

[Total: 22]

~~**(ii)** When one molecule of serine reacts with one molecule of glutathione, it is possible to form two esters with different structural formulae.~~
~~Draw the structural formula of **each** of these esters. [2]~~

~~**(iii)** Draw the structural formulae of the products when glutathione is hydrolysed. [3]~~

~~Alliin has pK_a values of 1.84 and 8.45.~~

~~**(iv)** Make use of these pK_a values to suggest the major species present in solutions of alliin with the following pH values. [3]~~

- ~~pH 1~~
- ~~pH 7~~
- ~~pH 11~~

~~v) Calculate the pH of 0.10 mol dm^{-3} solution of alliin. [1]~~

~~**(vi)** With reference to the pK_a values, identify the major species formed when 10 cm^3 of 0.10 mol dm^{-3} NaOH is added to 10 cm^3 of 0.10 mol dm^{-3} protonated alliin. Hence, deduce whether the solution is acidic, neutral or alkaline. [2]~~

~~**(vii)** Sketch the pH-volume added curve you would expect to obtain when 30 cm^3 of 0.10 mol dm^{-3} NaOH is added to 10 cm^3 of 0.10 mol dm^{-3} protonated alliin.~~
~~Briefly describe how you have calculated the various key points on the curve. [4]~~

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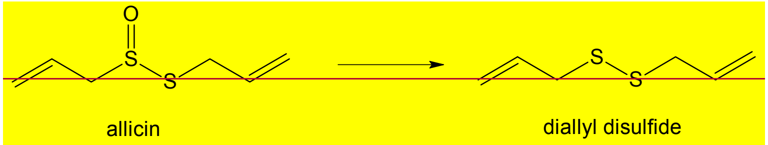
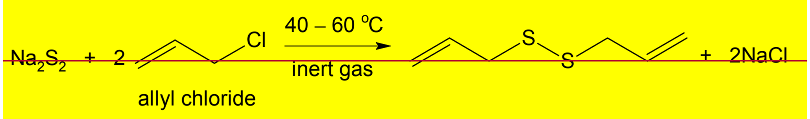
~~(b)~~ ~~Diallyl disulfide is one of the principal components of the distilled oil of garlic. It is a yellowish liquid which is insoluble in water and has a strong garlic odour. It is produced during the decomposition of allicin.~~



~~Diallyl disulfide can be produced industrially from sodium disulfide and allyl chloride at temperatures of 40 – 60 ¼C in an inert atmosphere.~~



~~**(i)** Give the *IUPAC* name of allyl chloride.~~ ~~[1]~~

~~**(ii)** Explain, in thermodynamic terms, suggest why diallyl disulfide is insoluble in water.~~ ~~[2]~~

~~**(iii)** State the type of reaction when diallyl disulfide is converted back to allicin.~~ ~~[1]~~

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Section B

Answer **one** question from this section.

4 Cycloalkanes are a homologous series of cyclic saturated hydrocarbons with the general formula C_nH_{2n} while n-alkanes are a homologous series of straight-chain saturated hydrocarbons with the general formula C_nH_{2n+2}.

n-alkanes	Boiling point / °C	Enthalpy change of combustion / kcal mol^{-1}	cycloalkanes	Boiling point / °C	Enthalpy change of combustion / kcal mol^{-1}
ethane	–89	–373.0	-	-	-
propane	–42	–530.4	cyclopropane	–33	–499.8
butane	–1	–687.8	cyclobutane	12	–656.0
pentane	36	–845.2	cyclopentane	49	–793.5
hexane	69	–1002.6	cyclohexane	81	–944.6
heptane	98	–1160.0	cycloheptane	119	–1108.3

(a) Explain the term "homologous series". [1]

(b) Explain the increase in magnitudes of both boiling point and enthalpy change of combustion from ethane to heptane. [3]

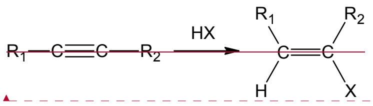
~~Alkynes are organic molecules which contain carbon-carbon triple bonds and are part of the homologous series with formula of C_nH_{2n-2} i.e.~~

~~$R_1-C\equiv C-R_2$~~

~~where R_1 and R_2 = H or alkyl or aryl groups~~

~~Alkynes exhibit similar chemical properties to alkenes.~~

~~e.g. addition reactions with electrophiles i.e. X_2 or HX to form alkenes~~



~~e.g. oxidation by hot concentrated $KMnO_4$ to form mixture of carboxylic acids~~

~~$R_1-C\equiv C-R_2 \xrightarrow{KMnO_4} R_1COOH + R_2COOH$~~

~~However, unlike alkenes, terminal alkynes are able to react with strong bases like sodium amide.~~

~~$RC\equiv CH + NaNH_2 \longrightarrow RC\equiv C^-Na^+ + NH_3$~~

~~**(a)** Ethyne, C_2H_2, is heated with excess sodium bromide and concentrated sulfuric acid to produce a dihalide, $C_2H_4Br_2$. The overall reaction may be considered to take place in two stages, the first between inorganic reagents only and the second involving the organic reagent.~~

~~**(i)** Write an equation for the first stage. [1]~~

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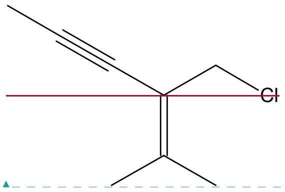
~~**(ii)** Suggest a structure for the dihalide formed. [1]~~

~~**(iii)** When the concentrated sulfuric acid is added to the reaction mixture, cooling is necessary to prevent the formation of inorganic by-products.~~
~~Write an equation to explain the formation of these inorganic by-products. [1]~~

~~**(b)** Compound **A**, is an enyne chloride (i.e. compounds that contains chloro, alkyne and alkene functional groups).~~



~~Compound **A**~~

~~One mole of compound **A** reacts with two moles of Br_2 to produce a mixture of 4 stereoisomers. Draw structures of the stereoisomers formed. [3]~~

(c) ~~Compound **B**, which is an isomer of Compound **A** and also an enyne chloride, is treated with sodium amide, $NaNH_2$ followed by heating under reflux to form compound **C**, C_8H_{10}. Compound **C** reacts with hot concentrated $KMnO_4$ to produce butane-1,4-dioic acid only.~~Suggest why combustion tends to be incomplete as the alkane increases in molecular mass. [1]

Cyclopropane is a colourless gas with a "petroleum-like" odour. Unlike its straight-chain counterpart, it is considered to be highly strained and unstable. The instability of cyclic alkanes can be measured by calculating its "ring strain energy" using the formula below:

Ring strain energy =

$$\begin{matrix}\text{number of}\\ \text{carbon atoms}\\ \text{in cyclic alkane, A}\end{matrix} \times \left(\left| \begin{matrix}\text{enthalpy change of combustion}\\ \text{of a } CH_2 \text{ group in the}\\ \text{cyclic alkane, A}\end{matrix} \right| - \left| \begin{matrix}\text{enthalpy change of combustion}\\ \text{of a } CH_2 \text{ group in an}\\ \text{unstrained n-alkane}\end{matrix} \right| \right)$$

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~~number of carbon atoms in cyclic alkane, A × (|enthalpy change of combustion of a CH_2 group in the cyclic alkane, A| − |enthalpy change of combustion of a CH_2 group in an unstrained n-alkane|)~~

number of carbon atoms in cyclic alkane, A × (|enthalpy change of combustion of a CH_2 group in the cyclic alkane, A| −
|enthalpy change of combustion of a CH_2 group in an unstrained n-alkane|)

number of carbon atoms in cyclic alkane, A

× (|enthalpy change of combustion of a CH_2 group in the cyclic alkane, A| − |enthalpy change of combustion of a CH_2 group in an unstrained n-alkane|)

number of carbon atoms in cyclic alkane, A

× (|enthalpy change of combustion of a CH_2 group in the cyclic alkane, A| − |enthalpy change of combustion of a CH_2 group in an unstrained n-alkane|)

~~number of carbon atoms in cyclic alkane × (|enthalpy change of combustion of a CH_2 group in the cyclic alkane| − |enthalpy change of combustion of a CH_2 group in an unstrained n-alkane|)~~

(d) Given that the ΔH_f of CO_2 is −94.05 kcal mol^{-1} and ΔH_f of water is −68.3 kcal mol^{-1}, write an equation showing the formation of cyclopropane, and hence calculate the enthalpy change of formation of cyclopropane. ~~calculate the enthalpy change of formation of cyclopropane.~~ [2~~1~~]

(e) Using the formula above, prove that the ring strain energy in cyclopropane is +27.6 kcal mol^{-1}. [2]

(f) Due to the presence of ring strain, cyclopropane undergoes an addition reaction with bromine in the absence of ultraviolet radiation.

(i) Suggest the skeletal structure of the molecule formed after reaction with Br_2. [1]

(ii) Hence, using VSEPR theory, explain why the presence of ring strain causes cyclopropane to undergo addition reactions. [1]

(g) Cyclopropane rings can be formed using a technique called "cyclopropanation".

One such cyclopropanation technique involves the 2 mechanistic steps stated below:

Step 1: Dissociation of diazomethane, CH_2N_2 to form methylene, CH_2, and N_2.~~Formation of methylene, CH_2, and N_2 from diazomethane, CH_2N_2.~~

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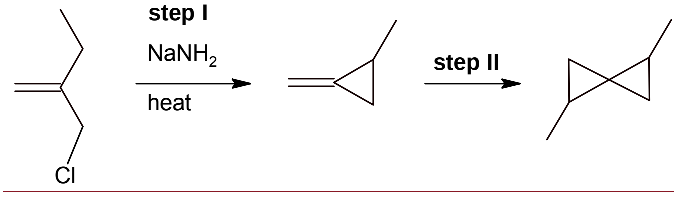
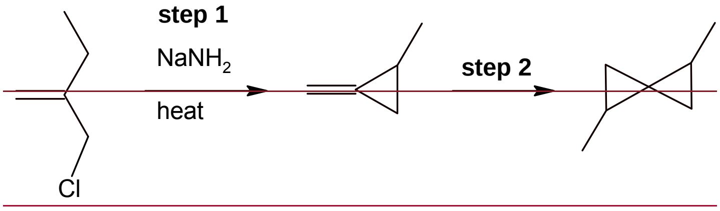
Step 2: Addition of methylene, CH_2, to trans-but-2-ene to form the cyclic ring. The reaction leaves the stereochemistry of the molecule unchanged.

(i) It is observed that the diazomethane molecule is trigonal planar in shape. By considering the shape, d~~D~~raw a dot-and-cross diagram of diazomethane, CH_2N_2, clearly showing the type of bonds formed within the molecule. [1]

(ii) Draw the structure of the cyclic molecule formed in ~~s~~**Step 2**, showing the stereochemical arrangement clearly. State and explain if the molecule can rotate plane-polarised light. [2]

~~**(h)**~~ Cyclopropane rings are a precursor for many types of fatty acids. The following shows part of the synthetic route for fatty acids.





A **B**

(iii~~i~~) **Step I~~1~~** involves the reaction of molecule **A** with $NaNH_2$ to form NH_3 and a negatively-charged~~n~~ organic intermediate which eventually formed molecule **B** upon heating.

State the type of reactions that took place in **step I~~1~~** and draw the organic intermediate that was formed. [2]

(iv~~i~~) By considering the reactivity of the Cl atom, explain why~~if~~ molecule **C** cannot be used to replace molecule **A** in the synthesis above. [1~~2~~]

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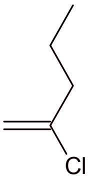
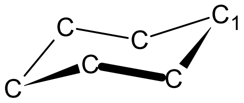


C

(v) Using the above information, s~~S~~uggest a suitable reagent for **step II~~2~~**. [1]

(h) Unlike the cyclic alkanes smaller than cyclohexane, cyclohexane does not experience ring strain due to the “chair shape” arrangement adopted by the six carbons as seen below:



chair shape arrangement of carbon atoms

By copying out the chair shape arrangement above and drawing ~~in~~ the 3-D arrangement of hydrogen atoms bonded to~~for~~ C_1, explain why cyclohexane does not experience ring strain.

[2~~2~~]

~~**(i)** Explain the reaction with $NaNH_2$. [1]~~

~~**(ii)** Hence, explain the formation of compound **C**. [1]~~

~~**(iii)** Suggest skeletal structures for compounds **B** and **C**. [2]~~

~~When a current of 1.0 A was passed through aqueous potassium maleate ($KO_2CCH{=}CHCO_2K$) for 15 minutes, it was found that 110 cm^3 H_2, measured at r.t.p, was collected at the cathode. The following reaction took place.~~

$$\cancel{2H_2O + 2e^- \longrightarrow H_2 + 2OH^-}$$

~~**(d)** State the relationship between the Faraday constant, *F* and the Avogadro’s constant, *L*. [1]~~

~~**(e)** Using the data above and the *Data Booklet*, calculate a value for Avogadro’s constant. [3]~~

~~**(f)** Ethyne and CO_2 gas were produced at the anode. In order to determine the stoichiometry of the anode reaction, the volume of the gases collected at the anode was measured. The anode gas was first passed through aqueous NaOH before being collected in a gas syringe. The following data was collected:~~

- ~~mass of NaOH before experiment = 10.501 g~~
- ~~mass of NaOH after experiment = 10.904 g~~
- ~~initial reading on syringe = 10.0 cm^3~~
- ~~final reading on syringe = 120.0 cm^3~~

~~**(i)** State the oxidation state of carbon in ethyne. [1]~~

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~~**(ii)** With the help of an equation, explain the purpose of passing the anode gas through NaOH. [1]~~

~~**(iii)** Calculate the volume of CO_2 produced, assuming r.t.p conditions. [1]~~

~~**(iv)** Hence, suggest an ionic equation for the reaction that occurred at the anode. [1]~~

~~**(g)** When aqueous potassium maleate was acidified, maleic acid, $HO_2CCH=CHCO_2H$ (pK_{a1} = 1.90 and pK_{a2} = 6.07) was liberated. Fumaric acid (pK_{a1} = 3.03 and pK_{a2} = 4.44) is a stereoisomer of maleic acid.~~

~~With a suitable illustration, suggest a reason why maleic acid has a lower pK_{a1} but higher pK_{a2} than fumaric acid.~~

~~[2]~~

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5(a) ~~Dopamine is an organic compound of the catecholamine and phenethylamine families that plays several important roles in the brain and body. Its name is derived from its chemical structure: it is an amine synthesised by removing a carboxyl group from a molecule of its precursor compound, L-DOPA.~~

The halogens and their compounds, show many similarities and trends in their properties. Some data are given for the elements fluorine, chlorine and iodine.

Element	Bond Energy / kJ mol^{-1}	Standard enthalpy change of atomisation / kJ mol^{-1}
Fluorine	158	79
Chlorine	242	121
Bromine	193	112
Iodine	151	107

(i) For fluorine and chlorine, their enthalpy changes of atomisation are half the value of their respective bond energies. For bromine and iodine, their enthalpy changes of atomisation are much more than half the value of their respective bond energies.

Explain in detail ~~for~~ this difference. [1]

(ii) The standard enthalpy change of formation of iodine monochloride, I–Cl, is –24.0 kJ mol^{-1}.

Use this information and the data from the table above to calculate the I–Cl bond energy. [1]

~~Below is a synthetic route involving L-DOPA and dopamine:~~

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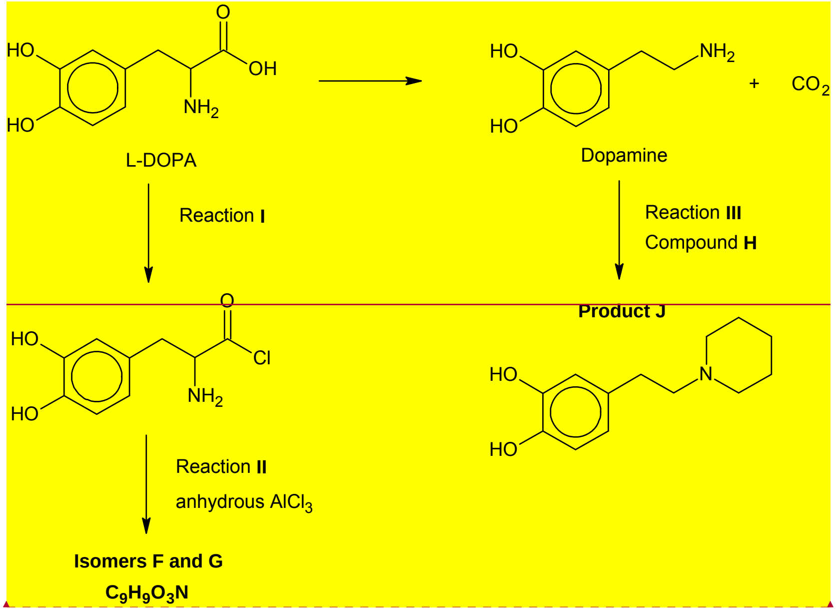
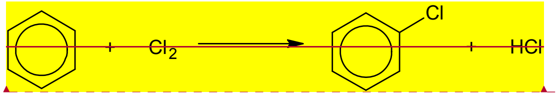


~~(i) State the reagents and conditions and any observations in Reaction **I**. [1]~~

~~(ii) Aluminium chloride is used as a catalyst in electrophilic substitution reactions. The chlorination of benzene is represented by the following overall equation.~~



~~The reaction occurs in several steps.~~

~~• The first step is the reaction between Cl_2 and $AlCl_3$.~~

~~$Cl_2 + AlCl_3 \longrightarrow Cl^+ + AlCl_4^-$~~

~~• The benzene ring is then attacked by the Cl^+ cation in the second step.~~

~~$AlCl_3$ reacts in a similar way with acyl chlorides, producing a carbocation that can then attack a benzene ring.~~

~~Predict the structures of isomers **F** and **G** in Reaction **II**. [2]~~

~~(iii) In Reaction **III**, dopamine was reacted with alkyl halide **H** to give the final product **J**. Draw the displayed formula of **H**. [2]~~

(iii) Explain why your answer in **(ii)** ~~does not correspond~~is larger in value compared to the average of the bond energies of I–I and Cl–Cl. [1]

(b) ICl reacts with pure water to form HCl and HI:

$$2ICl(l) + 2H_2O(l) \rightarrow 2HCl(aq) + 2HI(aq) + O_2(g) \qquad \Delta H_r = +171.2\ kJ\ mol^{-1}$$

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Using ΔH_r, the following data, as well as relevant data from **a(ii)**, draw an energy level diagram to calculate the enthalpy change of formation of aqueous HI.

Label your diagram ~~,~~ and draw arrows representing the energy terms involved. Use words or symbol to represent these energy terms.

	ΔH / kJ mol^{-1}
Standard enthalpy change of formation of H_2O	–285.8
Standard enthalpy change of formation of gaseous HCl	–92.3
Standard enthalpy change of reaction: $HCl(g) \rightarrow HCl(aq)$	–75.1
Standard enthalpy change of vaporisation of liquid ICl	+41.4

[4]

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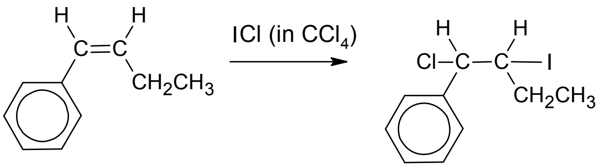
(~~b~~c) ICl is a useful reagent in organic synthesis. It is used in the following reaction to form compound **E**.

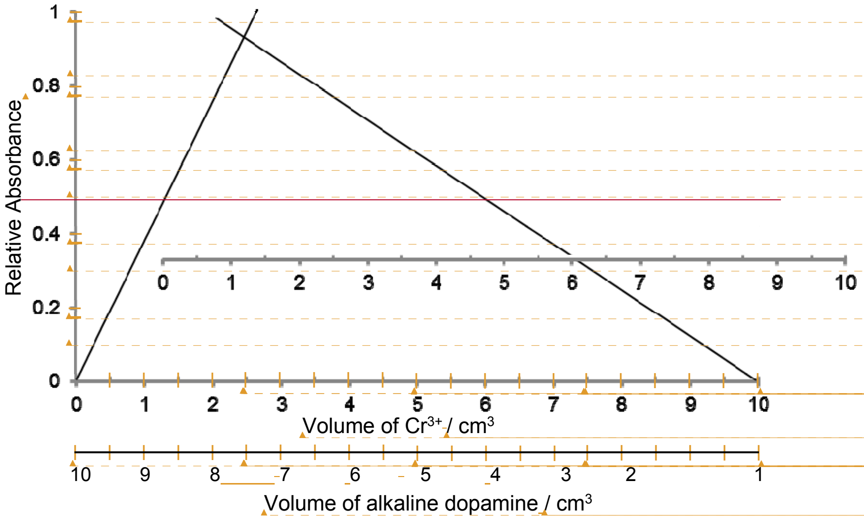


E

(i) Describe the mechanism for the formation of **E**. [3]

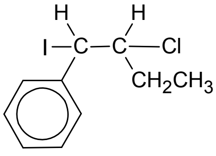
(ii) ~~Dopamine is a bidentate ligand. When different volumes of 0.0030 mol dm⁻³ of aqueous Cr(III) and 0.0020 mol dm⁻³ of alkaline dopamine solution were mixed, a complex R is formed. Analysis of R shows that its formula is~~ ~~$[Cr(C_8H_9NO_2)_x(H_2O)_y]^{z}$~~~~, where x, y and z are integers.~~

~~To determine the stoichiometry of the complex ion formed, the colour intensities of these different mixtures were measured using a colorimeter. The following absorption spectrum was obtained.~~



~~**(i)** Use the graph and the information given to determine the formula of complex R. Show your workings clearly.~~ ~~[3]~~

With the aid of a diagram, explain why **E** is formed and not **F**. [2]



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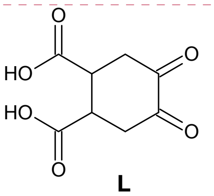
(d) Compound **J**, $C_{11}H_{16}O_2$, decolourises bromine water. 1 mole of **J** reacts with sodium metal to produce 22.7 dm^3 of hydrogen gas at s.t.p. On heating with acidified $KMnO_4$, **K**, $C_9H_{10}O_5$, is the only organic product formed.

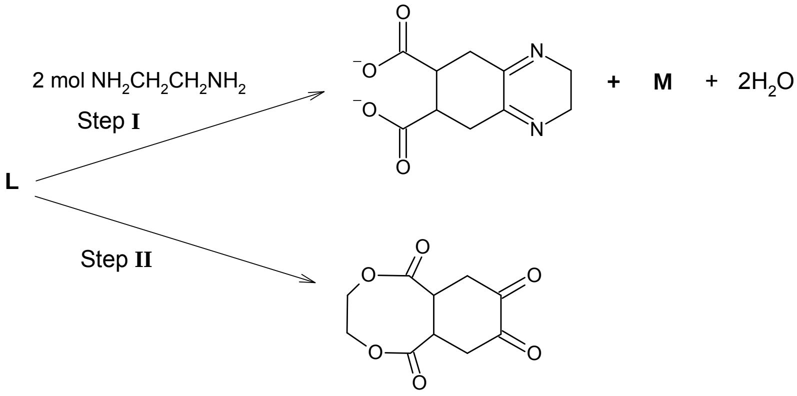
K reacts with sodium carbonate and 2,4-DNPH. When **K** reacts with alkaline aqueous iodine, **L** is formed upon acidification.



L

Suggest structures for **J** and **K** and explain the reactions described. [5]

(e) In the following reaction scheme, compounds **M** and **N** can be obtained from **L**.



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(i) Draw the structure of **M**. State the type(s) of reaction in Step **I**. [2]

(ii) Suggest reagents and conditions to synthesise product **N** from **L**. [1]

~~**(ii)** The crystal field describes the breaking of orbital degeneracy in transition metal complexes due to the presence of ligands. When the d-orbitals split into high energy and low energy orbitals, the difference in energy of the two levels is denoted as Δ_o. The relationship between Δ_o and colours of complexes can be described in the equation below:~~

~~$\Delta_o = \frac{hc}{\lambda}$~~

~~where h is Planck's constant, *c* is the speed of light and λ is the wavelength of light absorbed~~

~~colour~~	~~absorbed λ / nm~~
~~violet~~	~~410~~
~~indigo~~	~~430~~
~~blue~~	~~480~~
~~blue-green~~	~~500~~
~~green~~	~~530~~
~~yellow~~	~~580~~
~~orange~~	~~610~~
~~red~~	~~680~~

~~Given that Δ_o for complex **R** is 4.125 x 10^{-22} kJ and using relevant data from the *Data Booklet*, calculate the wavelength of light. Deduce the colour of complex **R**. [2]~~

~~**(c)** Iodine is not very soluble in water, it is freely soluble in KI(aq), according to the following equilibrium:~~

~~$I^-(aq) + I_2(s)$ — $I_3^-(aq)$~~

~~**(i)** Draw a fully labelled experimental set-up for a voltaic cell made up of a $Cr_2O_7^{2-}$ / Cr^{3+} half-cell and a I_2/I^- half-cell under standard conditions. Indicate clearly the anode and cathode and show the flow of electrons. [3]~~

~~**(ii)** By using appropriate values from the *Data Booklet*, predict what, if anything, will happen when a small amount of acidified vanadium(II) chloride is added to the I_2/I^- half-cell. [3]~~

~~**(d)** Explain the following statements.~~

~~**(i)** BrF_3 is a covalent compound which exhibits electrical conductivity in liquid state at room temperature. With the aid of an equation, suggest an explanation for its electrical conductivity. [2]~~

~~**(ii)** $SiCl_4$ reacts violently in water but CCl_4 has no reaction with water. [1]~~

~~**(iii)** Compounds NeF_2 and NeF_4 do not exist but XeF_2 and XeF_4 exist. [1]~~

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NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CHEMISTRY

9~~64~~729/03

Paper 3 Free Response

~~21~~ 18 September 2018~~6~~

2 hours

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Additional Materials: Writing Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

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

Section A
Answer **all** questions.

Section B
Answer **one** question.

A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.
~~Answer any **four** questions.~~
~~A Data Booklet is provided.~~
~~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.

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Section A

Answer **all** questions in this section.

1 Cobalt is a typical transition element which is commonly used as a catalyst and metal for electroplating. Cobalt also forms complex ions with ligands such as H_2O and NH_3 to give various coloured octahedral complexes such as $[Co(H_2O)_6]^{2+}$ and $[Co(NH_3)_6]^{2+}$ which are pink and yellow respectively.

(a) The ligand exchange in octahedral complexes is one of the most extensively studied reactions in transition metals.

An example of a ligand exchange reaction involving cobalt(II) ions is:

$$[Co(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+} + 6H_2O$$

(i) Explain why cobalt forms coloured complexes. [3]

- The presence of ligands causes the energy level of the five 3d orbitals to be split into two different levels (crystal field splitting).
- The energy difference, ΔE, corresponds to wavelengths in the visible spectrum.
- When light energy is absorbed by the substance, an electron is promoted from a d orbital of lower to one of higher energy (d-d transition)
- Unabsorbed wavelengths are transmitted and the colour of the complex is complementary to the colour absorbed.

[3] for 4 marking points
[2] for 3 marking points
[1] for 2 marking points

(ii) Suggest why $[Co(NH_3)_6]^{2+}$ is of a different colour from $[Co(H_2O)_6]^{2+}$. [1]

- Different ligands give rise to a difference in the splitting of the *d*-orbitals, cause a different energy gap (Δ*E*).
- A different wavelengths of visible light is absorbed and thus a different wavelength of light is observed.

[1] for 2 marking points

(iii) A student wishes to investigate the kinetics of the ligand exchange reaction of $[Co(H_2O)_6]^{2+}$ to form $[Co(NH_3)_6]^{2+}$ by using a spectrometer. This machine measures the amount of light that is absorbed when a specific wavelength of visible light is shone through a few cm^3 of the coloured solution. It does this by comparing the amount of light passing through the sample with the amount of light passing through the pure solvent.

The spectrometer is set to use the wavelength of light that is absorbed most strongly by the complex ion. The amount of light absorbed is expressed as an absorbance value. The more concentrated the solution, the higher the absorbance value. The temperature of the sample in the spectrometer can be thermostatically controlled for reaction rate analysis for which the sample has to be kept at a constant temperature.

Outline the experimental procedure on how the student would accurately determine the initial rate of the ligand exchange reaction at 5 °C.

~~[3]~~

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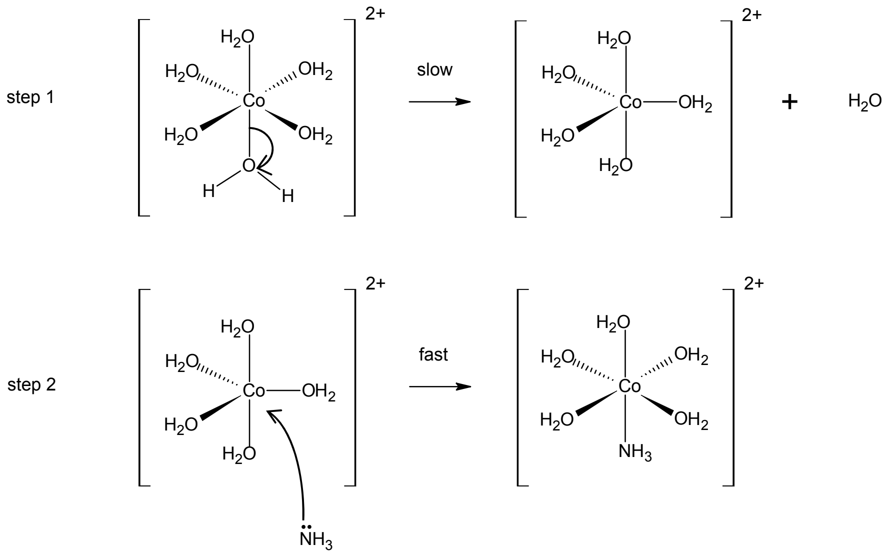
The details of the use of ~~No details regarding use of~~ specific glassware for measurement are **not** required. [3]

- Spectrometer is set up to absorb the wavelength of violet (monitoring product) or green (monitoring reactant) and maintain the temperature of the sample at 5 °C.
- Separate solutions of $[Co(H_2O)_6]^{2+}$ and NH_3 are cooled to 5 °C in an ice-water bath.
- Stoichiometric amounts of $[Co(H_2O)_6]^{2+}$ and NH_3 (or excess NH_3) are mixed and swirled. A few cm^3 of the coloured solution is quickly placed into the spectrometer.
- A stop watch is started.
- The concentration of $[Co(H_2O)_6]^{2+}$ (or $[Co(NH_3)_6]^{2+}$) is then determined by measuring the absorbance of the reaction mixture at time = 0 minute and then at regular time intervals (e.g. every 5 minutes), to obtain at least 5 measurements.
- A graph of absorbance value against time is plotted.
- The initial rate is found by drawing a tangent at time = 0 minute.

7 marking points
[1] for 2 marking points

(iv) When $[Co(H_2O)_6]^{2+}$ is mixed with an excess of NH_3~~–~~(aq), each H_2O molecule is replaced by a NH_3 molecule one at a time. Given that the stepwise formation of $[Co(NH_3)_6]^{2+}$ from $[Co(H_2O)_6]^{2+}$ undergoes a dissociative mechanism which resembles a S_N1 mechanism in organic chemistry.
Suggest a possible mechanism for the formation of $[Co(H_2O)_5NH_3]^{2+}$ from $[Co(H_2O)_6]^{2+}$ and show clearly how the shape of the complex ion changes.
In -your mechanism, show appropriate curly arrows, lone pairs and dipoles.
[3]



Square pyramidal intermediate is accepted as well.

[1] for correct shapes
[1] for arrows and lone pair on NH_3

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[1] for intermediate and side product

(v) State the rate equation for the above ligand exchange reaction. [1]

rate = k [$[Co(H_2O)_6]^{2+}$] [1]

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(vi) Hence, predict and explain the effect on the rate of reaction, if any, when the ammonia ligand is replaced ~~by~~with a fluoride ion. [1]

The rate of reaction remains constant as the rate is independent of the incoming ligand. [1]

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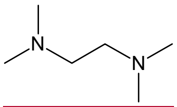
(b) $[Co(H_2O)_6]^{2+}$ can also undergo ligand exchange reactions with TMEDA to form $[Co(TMEDA)_3]^{2+}$.



TMEDA

By considering the entropy and enthalpy changes during the formation of $[Co(TMEDA)_3]^{2+}$ from $[Co(H_2O)_6]^{2+}$ and that of $[Co(NH_3)_6]^{2+}$ from $[Co(H_2O)_6]^{2+}$, suggest how the standard Gibbs free energy change of the two reactions will compare in sign and in magnitude.

Hence, predict which reaction will be ~~the~~ more spontaneous. Explain your reasoning. [3]

$[Co(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+} + 6H_2O$

$[Co(H_2O)_6]^{2+} + 3TMEDA \rightleftharpoons [Co(TMEDA)_3]^{2+} + 6H_2O$

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ΔH for formation of $[Co(NH_3)_6]^{2+}$ and $[Co(TMEDA)_3]^{2+}$ is similar in magnitude and sign due to the breaking of 6 similar Co—O bonds and forming of 6 similar Co—N bonds. [1]

ΔS for formation of $[Co(TMEDA)_3]^{2+}$ would be more positive than that of $[Co(NH_3)_6]^{2+}$ because there is an increase in number of aqueous particles when $[Co(TMEDA)_3]^{2+}$ is formed, allowing more ways of arranging the particles. [1]

Since ΔH for formation of $[Co(NH_3)_6]^{2+}$ and $[Co(TMEDA)_3]^{2+}$ are similar in magnitude and sign and ΔS for formation of $[Co(TMEDA)_3]^{2+}$ is more positive than that of $[Co(NH_3)_6]^{2+}$, ΔG for formation of $[Co(TMEDA)_3]^{2+}$ would be more negative than that of $[Co(NH_3)_6]^{2+}$ and hence more spontaneous. [1]

~~ΔH for formation of $[Co(NH_3)_6]^{2+}$ and $[Co(TMEDA)_3]^{2+}$ is similar in magnitude due to breaking of similar Co—O bonds and forming of similar Co—N bonds. [1]~~

~~ΔS for formation of $[Co(TMEDA)_3]^{2+}$ would be more positive than that of $[Co(NH_3)_6]^{2+}$ because there is an increase in number of aqueous particles as $[Co(TMEDA)_3]^{2+}$ is formed, allowing more ways of arranging the particles. [1]~~

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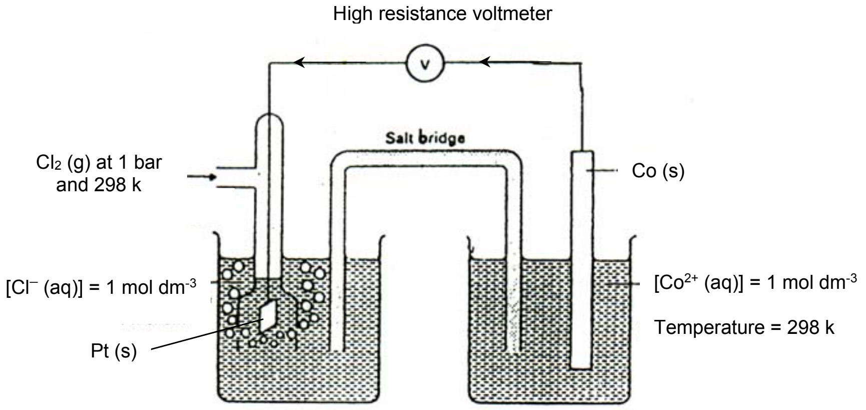
~~Since ΔH for formation of $[Co(NH_3)_6]^{2+}$ and $[Co(TMEDA)_3]^{2+}$ are similar in magnitude and ΔS for formation of $[Co(TMEDA)_3]^{2+}$ is more positive than that of $[Co(NH_3)_6]^{2+}$, ΔG for formation of $[Co(TMEDA)_3]^{2+}$ would be more negative than that of $[Co(NH_3)_6]^{2+}$ and hence more spontaneous. [1]~~

(c) **(i)** Draw a fully labelled diagram of an electrochemical cell composed of a standard $Cl_2|Cl^-$ electrode and a standard $Co^{2+}|Co$ electrode. Indicate the direction of the electron flow. [3]



[1] correct set-up
[1] concentration of ions, 298 and 1 bar
[1] electron flow

(ii) Calculate the $E^\ominus_{cell}$ of the electrochemical cell and write a balanced equation for the cell reaction.
[~~1~~2]

E_{cell} = +1.36 – (–0.28) = +1.64 V [1]

$Co + Cl_2 \rightarrow Co^{2+} + 2Cl^-$
~~$Co^{2+} + 2Cl^- \rightarrow Co + Cl_2$~~ [1]

(iii) Using your answer in **(ii)**, calculate ΔG for the cell reaction. [1]

Overall 2 mol of electrons are transferred.

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$\Delta G = -nFE_{cell} = -2 \times 96500 \times 1.64 = -317\,000\ J\ mol^{-1} = -317\ kJ\ mol^{-1}$

(iv) Use the *Data Booklet* to suggest the effect on the cell potential of this cell of adding excess aqueous ammonia to the Co^{2+}|~~/~~Co half cell. Explain your answer. [1]

$Co^{2+} + 2e \rightleftharpoons Co$ $E^{\ominus} = -0.28\ V$

$[Co(NH_3)_6]^{2+} + 2e \rightleftharpoons Co + 6NH_3$ $E^{\ominus} = -0.43\ V$

In the presence of ammonia ligands, Co^{2+} undergoes ligand exchange to form a more stable complex ion of $[Co(NH_3)_6]^{2+}$. The $E^{\ominus}(Co^{2+}|Co)$ becomes more negative and the Ecell becomes more positive.

Or

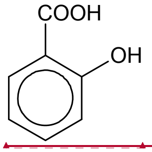
The formation of $[Co(NH_3)_6]^{2+}$ decreases the concentration of Co^{2+}. This caused the position of equilibrium for $Co^{2+} + 2e \rightleftharpoons Co$ to shift left. The $E^{\ominus}(Co^{2+}|Co)$ becomes more negative and the Ecell becomes more positive.

[Total: 2~~1~~2]

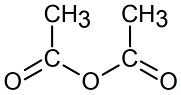
~~**Answer any four questions.**~~

~~1~~2(a) Aspirin is one of the most widely used drug in the world. It is a powerful analgesic (pain reliever), antipyretic (fever reducer) and anti-inflammatory drug.

It is synthesised using 2-hydroxybenzoic acid and ethanoic anhydride. 8 – 10 drops of 85% phosphoric acid which catalyses the reaction is added. The reaction mixture is then heated under reflux for around fifteen minutes. The other product of this reaction is ethanoic acid.

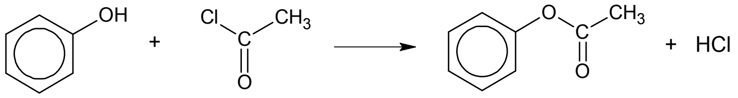


2-hydroxybenzoic acid



ethanoic anhydride

Ethanoyl chloride and phenol can undergo condensation reaction.



Ethanoic anhydride and 2-hydroxybenzoic acid can undergo a similar reaction to form aspirin.

(i) Draw the structure of aspirin. [1]

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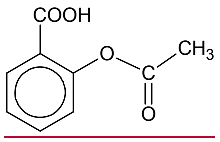
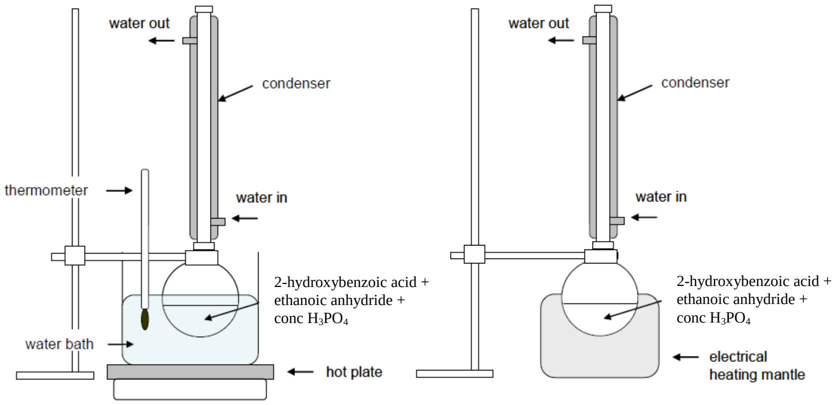


(ii) Draw a labelled diagram of the assembled apparatus for the synthesis of aspirin. [3]



[1] flask fitted with Liebig condenser
[1] clear label of water entering and leaving the condenser in a correct manner
[1] correct heat source (thermostated water bath if thermometer is not drawn)

The mechanism for the reaction between 2-hydroxybenzoic acid and ethanoic anhydride involves four steps. It is proposed as below:

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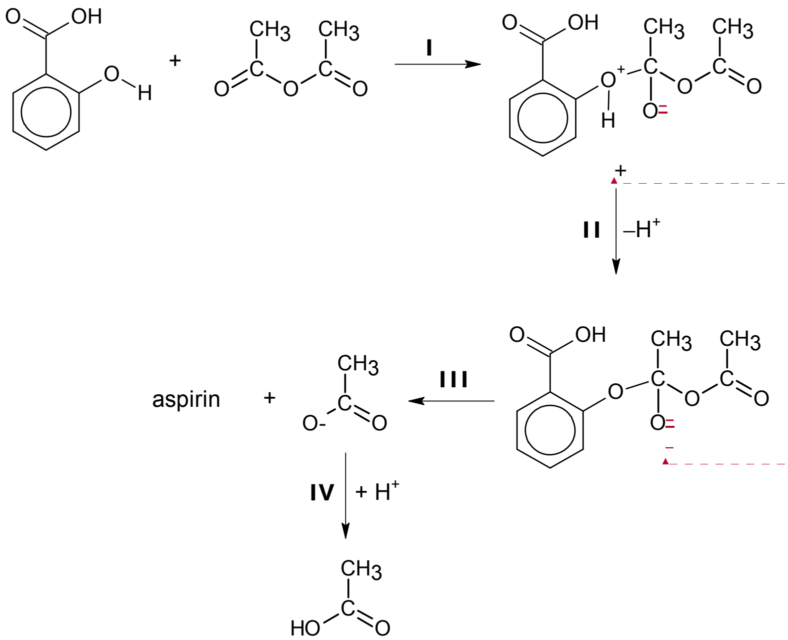

(iii) Using the information given above, state the type of mechanism in step **I**. [1]

Nucleophilic addition [1]

(iv) Copy and complete the whole mechanism above by showing any relevant charges, lone pairs of electrons and movement of electrons in your answer. [3]

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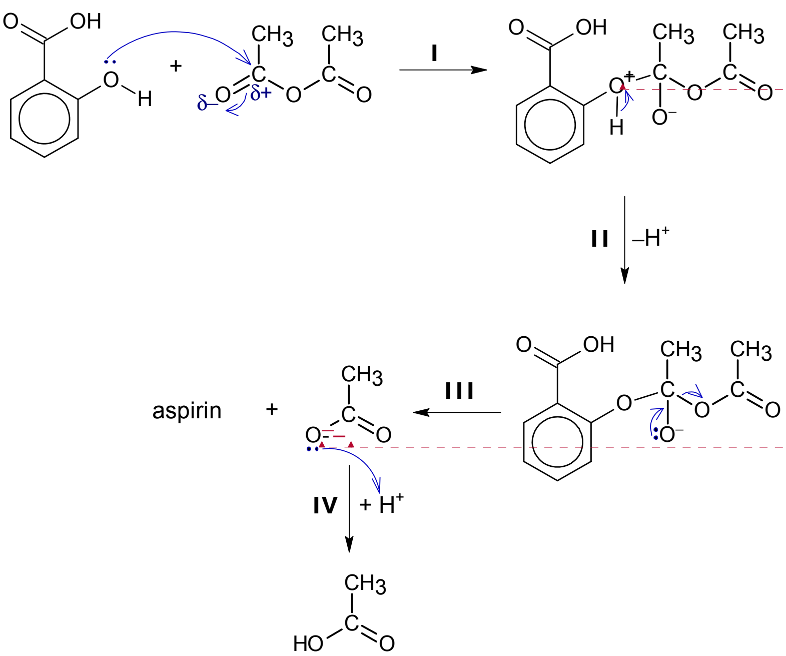
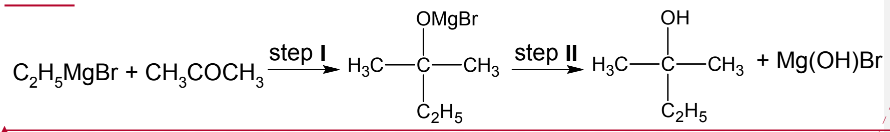


4 steps: 3 marks; 3 steps: 2 mark; 2 steps: 1 mark

(v) State a reason why ethanoic anhydride is used rather than ethanoyl chloride for the synthesis of aspirin. [1]

Safer because ethanoic anhydride is less corrosive as it does not produce corrosive and poisoning / toxic fumes of HCl [1] and less readily hydrolysed.

(b) In 1911, the French chemist F.A.V. Grignard reacted small pieces of magnesium with a warm solution of bromoethane in a dry, non-polar solvent and obtained a solution containing ethylmagnesium bromide, C_2H_5MgBr. Many Grignard reagents, with different alkyl or aryl groups, have now been prepared and are widely used in organic syntheses. A typical example of the use of a Grignard reagent is the two-step reaction of C_2H_5MgBr with propanone, CH_3COCH_3, to form 2-methylbutan-2-ol.



$$C_2H_5MgBr + CH_3COCH_3 \xrightarrow{\text{step I}} H_3C-\overset{\overset{OMgBr}{|}}{\underset{\underset{C_2H_5}{|}}{C}}-CH_3 \xrightarrow{\text{step II}} H_3C-\overset{\overset{OH}{|}}{\underset{\underset{C_2H_5}{|}}{C}}-CH_3 + Mg(OH)Br$$

Suggest the type of reaction which occurs in step **II**. [1]

Hydrolysis [1]

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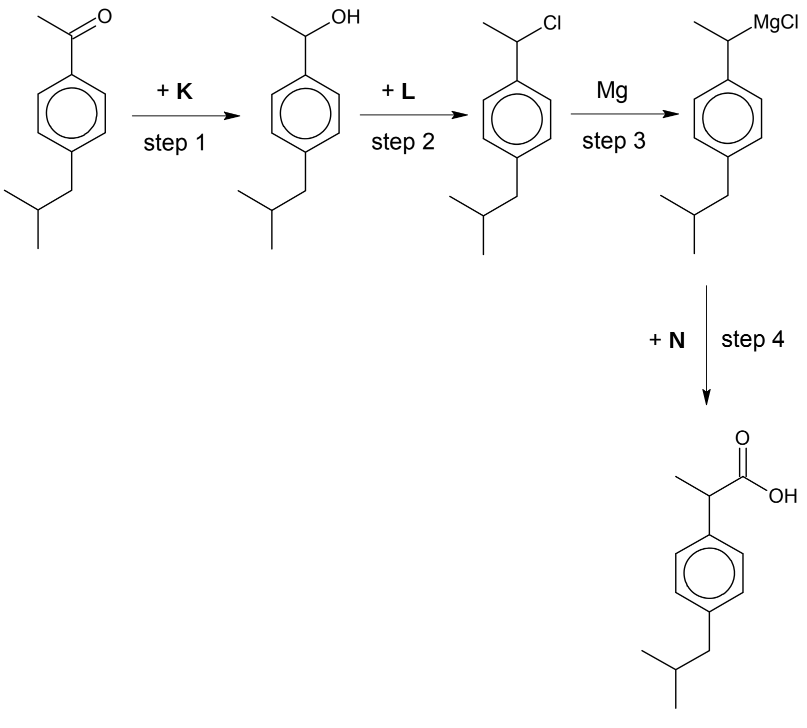
(c) The following scheme shows the synthesis of ibuprofen which is an alternative medication to aspirin. In step 4, the Grignard reagent readily converts into a carboxylic acid.



ibuprofen

(i) Suggest the identity of the reagent **K** in step 1. [1]

NaBH$_4$ [1]

(ii) Suggest the identity of the reagent **L** in step 2. [1]

PCl$_5$ or SOCl$_2$ [1]

(iii) Suggest the identity of the reagent **N** in step 4. [1]

CO$_2$ [1]

(d) Suggest a simple chemical test that could be used to distinguish between aspirin and ibuprofen. You should state what you would observe for **each** compound. [3]

1. Add H$_2$SO$_4$(aq), heat [1] – test
2. Distill

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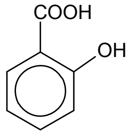


Product obtained from aspirin: CH_3COOH,

3. Add $Br_2(aq)$.

Orange Br_2 decolourises with aspirin; Orange Br_2 remains for ibuprofen. [1]

[Total: 16]

~~Copper(I) sulfate, Cu_2SO_4, can be made from copper(I) oxide under non-aqueous conditions. On adding this salt to water, it immediately undergoes a disproportionation reaction.~~

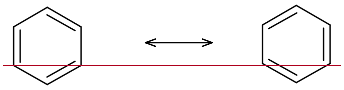
~~**(i)** Suggest, with a reason, the colour of copper(I) sulfate. [2]~~

~~**(ii)** Using suitable data from the *Data Booklet*, explain why the disproportionation reaction occurs, and write an equation for it. [3]~~

~~**(b)** Palladium(II) salts can form square planar complexes. Successive addition of ammonia and hydrogen chloride to an aqueous palladium(II) salt produces, under different conditions, three compounds with empirical formula $PdN_2H_6Cl_2$. Two of these, **A** and **B**, are non-ionic, with M_r = 211. **A** has a dipole moment, whereas **B** has none. The third compound, **C**, is ionic, having M_r = 422, and contains palladium in both its cation and anion.~~

~~For each **A**, **B** and **C**, deduce a structure that fits the above data, explaining your reasons fully. [6]~~

~~**(c)** Benzene ring is often represented as a structure that has a ring within the hexagon. Alternatively, chemists have also represented the structure of benzene in the following forms, known as resonance structures.~~

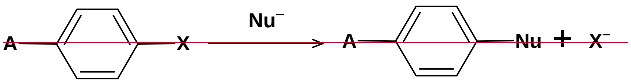


Benzene (two resonance forms)

~~The resonance relationship is indicated by the double headed arrow between them. The only difference between resonance forms is the placement of the pi electrons and non-bonding electrons.~~

~~Most aromatic compounds undergo electrophilic substitution. However aryl halides undergo a limited number of substitution reactions with strong nucleophiles.~~

~~An example of a reaction is as follows:~~



~~where **A** is an electron withdrawing group and **X** is a halogen~~

~~The mechanism of this reaction has two steps:~~
- ~~addition of the nucleophile~~
- ~~elimination of the halogen leaving group~~

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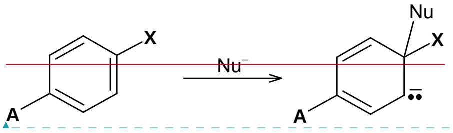
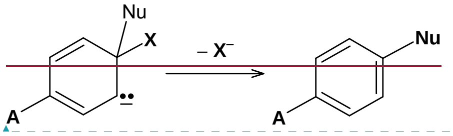
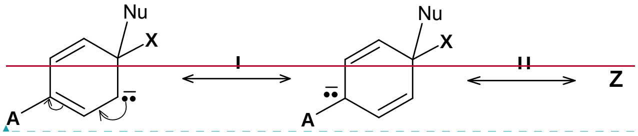
~~3 **Step 1** involves the addition of the nucleophile (Nu⁻). The Nu⁻ attacks the carbon atom bonded to a halogen, causing the pi bond to break. A resonance stabilised carbanion with a new C–Nu bond is formed. The aromatic ring is destroyed in this step.~~



~~**Step 2** involves the loss of the halogen **X**, reforming the aromatic ring.~~

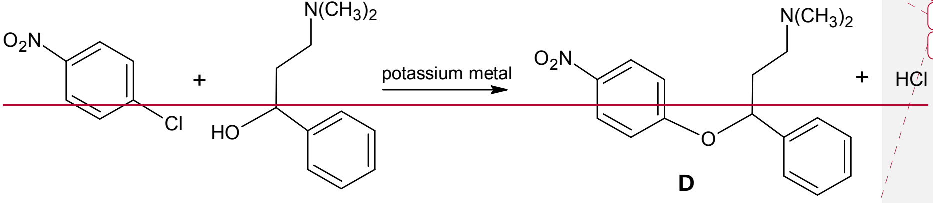


~~Two other resonance structures of the intermediate in **Step 1** are shown below:~~



~~**(i)** Copy the above diagram and draw the resonance structure, **Z**. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons in forming **Z**.~~ ~~[2]~~

~~The reaction below shows the synthesis of compound, **D**.~~

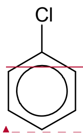


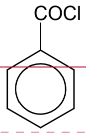
D

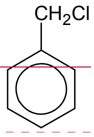
~~**(ii)** Suggest the role of potassium metal in the reaction.~~ ~~[1]~~

~~**(iii)** Use the information given above to draw out the full mechanism for the reaction that forms **D**, labelling the slow and fast steps. In your answer, showing any relevant charges, lone pair of electrons and movement of electrons.~~ ~~[3]~~

~~**(d)** Describe and explain the relative ease of hydrolysis of the following three chloro-compounds.~~ ~~[3]~~







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~~[Total: 20]~~

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~~**2** Sulfuric acid, H_2SO_4, can behave as an acid, an oxidising agent or as a dehydrating agent in various reactions.~~

~~**(a)** Draw a diagram to illustrate the shape of pure sulfuric acid and indicate the bond angle about the sulfur atom. [2]~~

~~**(b)** The Contact Process is used for the manufacture of sulfuric acid. One of the reactions that takes place is the following reversible reaction:~~

~~$2SO_2(g) + O_2(g)$ Ý $2SO_3(g)$ $\Delta H = -197$ kJ mol^{-1}~~

~~Sulfur dioxide and oxygen in a 2:1 molar ratio at a total initial pressure of 3 atm is passed over a catalyst in a fixed volume vessel at 400 °C. When equilibrium is established, the percentage of sulfur trioxide in the mixture of gases is found to be 30%.~~

~~**(i)** Write an expression for the equilibrium constant, K_p, of the reaction. [1]~~

~~**(ii)** Calculate the value of K_p at 400 °C, stating its units. [3]~~

~~**(iii)** How would the percentage conversion of SO_2 into SO_3 be affected when the pressure is raised? Explain. [2]~~

~~**(c)** Dilute sulfuric acid takes part in typical acid-base reactions and it can be used to distinguish the following solids: MgO, BaO and SiO_2 .~~

~~State the observations, if any, to indicate the differences in their reaction when water is added to each solid followed by dilute sulfuric acid. [4]~~

~~**(d)** Sulfur dioxide is a major pollutant from sulfuric acid plants. The SO_2 emitted into the atmosphere is oxidised in the air, which then reacts with water to form sulfuric acid, hence causing acid rain:~~

~~$2SO_2(g) + O_2(g) + 2H_2O(l) \longrightarrow 2H_2SO_4(l)$ ΔH_1~~

~~Using the data below and data from **(b)**, construct an energy cycle to calculate~~

~~**(i)** the enthalpy change of formation of $SO_2(g)$, and hence~~

~~**(ii)** the enthalpy change of reaction, ΔH_1 for the above reaction.~~

~~Enthalpy change of formation of $H_2O(l)$ = –286 kJ mol^{-1}~~
~~Enthalpy change of formation of $H_2SO_4(l)$ = –811 kJ mol^{-1}~~
~~Enthalpy change of formation of $SO_3(g)$ = –493 kJ mol^{-1}~~
~~[4]~~

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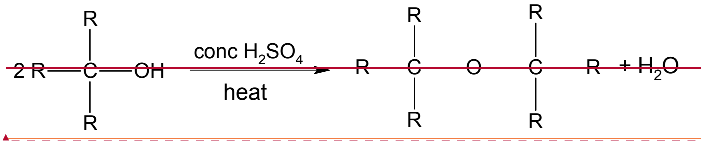
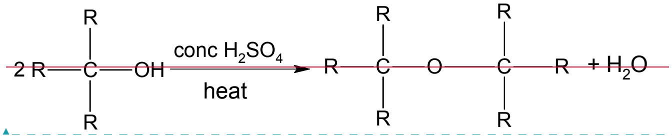
~~**(e)** Alcohols react with concentrated sulfuric acid at high temperatures to form alkenes. A common side reaction that can happen is the formation of ethers, which is also catalysed by concentrated sulfuric acid.~~

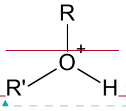




~~The mechanism occurs via 3 steps:~~

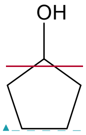
~~**Step 1:**~~
~~An acid base reaction in which H^+ from H_2SO_4 protonates the oxygen atom in alcohol. This step is very fast and reversible.~~

~~**Step 2:**~~
~~A second alcohol molecule functions as the nucleophile and attacks the product from **step 1**. The C–O bond is cleaved and a water molecule leaves the molecule. This creates an oxonium ion~~ ~~intermediate.~~



~~**Step 3:**~~
~~Another acid base reaction in which the proton in the oxonium ion is removed by a suitable base (in this case a water molecule) to give the ether product. This step is very fast and reversible.~~

~~**(i)** Draw the ether formed when cyclopentanol undergoes the above reaction.~~



~~cyclopentanol~~
~~[1]~~

~~**(ii)** Draw out the full mechanism for the reaction between two cyclopentanol molecules to form an ether. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons. [3]~~

~~[Total: 20]~~

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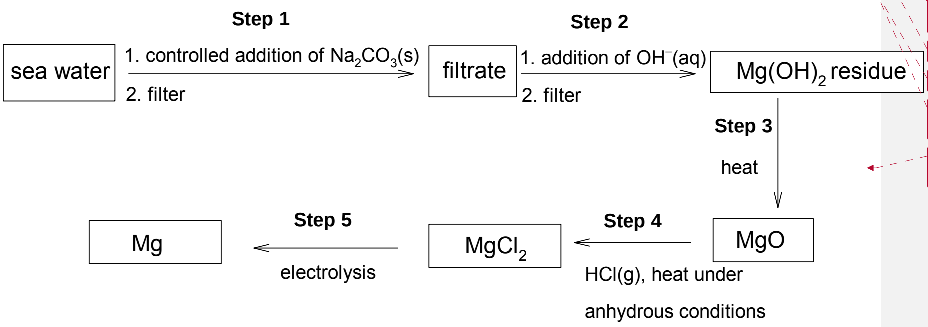
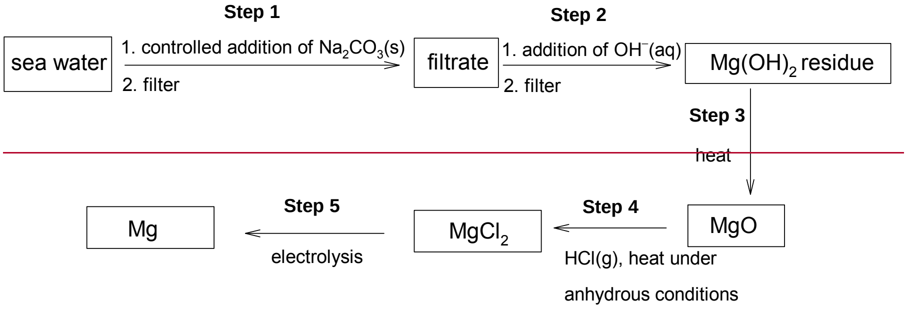
3 Magnesium is present as dissolved magnesium ions in sea water and is the only metal directly extracted from sea water. There is enough magnesium dissolved in the Earth's oceans to supply all of our magnesium needs for the next 1000 years.

~~Garlic contains many amino acids, minerals and enzymes. Garlic also contains at least 33 sulfur compounds like alliin, allicin and ajoene. The sulfur compounds are responsible for both garlic's pungent odour and many of its medical effects.~~

(a) Apart from magnesium ions, the two other most abundant cations found in sea water are sodium and calcium ions.

Magnesium can be extracted from sea water by the following steps:





Concentration of common ions in sea water:

ion	**concentration / mol dm^{-3}**
magnesium	0.056
calcium	0.010
sodium	0.457
chloride	0.535

The numerical values of solubility products are given below:

compound	**value of solubility product**
magnesium carbonate	1.00×10^{-5}
calcium carbonate	8.70×10^{-9}

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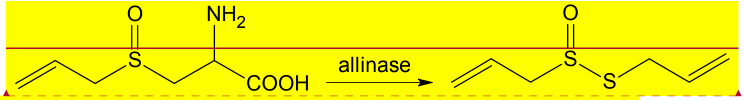
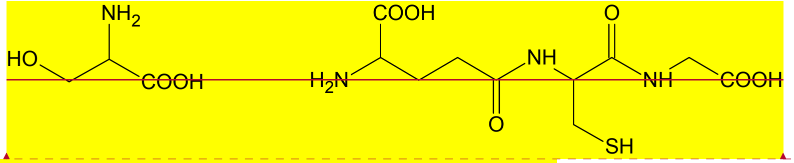
magnesium hydroxide	5.61×10^{-12}
calcium hydroxide	5.50×10^{-6}

~~When raw garlic is chopped or crushed, the enzyme allinase converts alliin into allicin, which is responsible for the odour of fresh garlic.~~



~~alliin~~ ~~allicin~~

~~Allicin can also be biosynthesised by using serine and glutathione.~~



~~serine~~ ~~glutathione~~

~~**(i)** Explain why raw chopped garlic has a stronger odour than when it is cooked. [1]~~

(i) Explain why the addition of sodium carbonate ~~ions~~ in **step 1** has to be controlled. [1]

If too much carbonate ions was added, both $MgCO_3$ and $CaCO_3$ will be precipitated.

(ii) Hence, state the cations present in the filtrate after **step 1** is carried out. [1]

Na^+ and Mg^{2+}

(iii) What is the maximum mass of solid sodium carbonate that can be added to 1 dm^3 of sea water in **step 1**? [2]

The $[CO_3^{2-}]$ must be controlled such that only calcium carbonate precipitates out, leaving MgCO$_3$ in the solution.

$$K_{sp} = [Mg^{2+}][CO_3^{2-}]$$

$$\text{maximum}[CO_3^{2-}] = \frac{K_{sp}}{[Mg^{2+}]} = \frac{1.0\times10^{-5}}{0.056} = 1.785\times10^{-4} \quad [1]$$

$$m_{CaCO_3} = 1.785\times10^{-4}\times100.1 = 0.0179 \text{ g} \quad [1]$$

(iv) Use the data provided to explain the following:

- Solid sodium carbonate was added to sea water (under controlled conditions) **before** the hydroxide ions.
- The reverse order (i.e. adding hydroxide ions before sodium carbonate) is **not** preferred over the extraction of magnesium.

~~(under controlled conditions)~~

~~sodium~~

[2]

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Comparing the K_{sp} of the 2 carbonates, $CaCO_3$ is less soluble and will be precipitated out first, leaving the Mg^{2+} ions in solution, and can be further purified via other steps. [1]

If hydroxide ions was added before carbonate ions, $Mg(OH)_2$ having a smaller K_{sp} value than $Ca(OH)_2$ will be less soluble and precipitate out first, together with other solid impurities in sea water, leading to an impure product. [1]

(v) Calculate the minimum pH of the hydroxide solution required for precipitation of magnesium hydroxide in **step 2** if an equal volume of hydroxide ions was added to the filtrate. Give your answer to 2 decimal places. [2]

Assume $[Mg^{2+}] = 0.056$ mol dm^{-3} *(from table)*

After adding equal volume of hydroxide ions, $[Mg^{2+}]_{new} = \dfrac{0.056}{2} = 0.028$ mol dm^{-3}

$$K_{sp} = [Mg^{2+}][OH^-]^2$$

$$[OH^-] = \sqrt{\frac{K_{sp}}{[Mg^{2+}]}} = \sqrt{\frac{5.61\times10^{-12}}{0.028}} = 1.415\times10^{-5} \quad [1]$$

$$[OH^-]\text{required} = 1.415\times10^{-5} \text{ x } 2$$

$$\text{pOH}=-\log(1.415\times10^{-5} \text{ x } 2) = 4.55$$

$$\text{pH} = 9.45 \ [1] \text{ 2dp ans}$$

(b) **(i)** Write the equations that occur during the electrolysis of magnesium chloride in ~~S~~**step 5**. State clearly the reactions that occur at the cathode and the anode, and include state symbols. [2]

Cathode: Mg^{2+} (l) + 2e → Mg (l) [1]

Anode : $2Cl^-$ (l) → Cl_2(g) + 2e [1]

(ii) In a factory, a current of 95 kA was passed through a suitable setup for 24 hours. Assuming that the procedure is 90% efficient, calculate the mass of Mg that can be produced. [2]

$$Q = It = nzF$$

$$\frac{95\times1000\times24\times60\times60}{100}\times90 = n\times2\times96500$$

$$n = 38.28 \times10^4 \quad [1]$$

$$m = 38.28\times10^4\times24.3 = 930{,}000g = 930kg \quad [1]$$

(iii) Give a reason why electrolysis of magnesium chloride is preferred to that of magnesium oxide in this industrial process. [1]

$MgCl_2$ has a lower melting point than MgO, hence the electrolysis can be carried out at a lower temperature, saving operation costs. [1]

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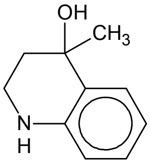
(c) ~~**A** is an organic compound.~~ When 0.46~~7~~8 g of an organic compound **A** was evaporated in a syringe, the volume of the vapour produced after correction to s.t.p was 60 cm^3. On heating with aqueous sodium hydroxide, **A** gives a compound that dissolves in water.

A reacts with aluminium oxide to give two products **B** and **C**. Both **B** and **C** react with HBr to give the same product **D**. **D** exhibits enantiomerism and exists as a pair of enantiomers.

A gives **E** when reacted with lithium aluminium hydride in dry ether.



E

(i) Prove that the molar~~ecular~~ mass of **A** is 177 g mol$^{-/}$. [1]

From Data Booklet, at s.t.p, V_m = 22.7 dm^3 mol^{-1} at 10^5 Pa and 273 K

Either

$$10^5 \times 60 \times 10^{-6} = \frac{0.468}{M} \times 8.31 \times 273$$

$$M = 176.9 = 177 \text{ g mol}^{-1} \text{ [1]}$$

Or

n(A) = 60 / 22700 = 2.643 × 10^{-7} mol

M_r(A) = 0.468 / 2.643 × 10^{-7} = 177.06 ≈ 177 g mol^{-1}

Comments

- Generally well-done.

- Common mistake include:
  Using incorrect V_m such as V_m = 24 dm^3 or V_m = 22.4 dm^3

- A small number of students did not use the numerical data of 0.468 g and 60 cm^3 to prove the molar mass of **A**. These students used the following approach, which is NOT acceptable for this question.

  1 mol of **A** undergoes reduction to give 1 mol of **E**.
  molar mass of **E** = 163.0 g mol^{-1}
  A has amide.
  molar mass of **A** = 163.0 – 2(1.0) + 16.0 = 177.0 g mol^{-1}

  Note that you are expected to use the numerical data of 0.468 g and 60 cm^3 to prove the molar mass of **A**.

(ii) Hence, ~~d~~Deduce the structural formulae of all the above structures, and explain the

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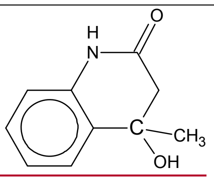
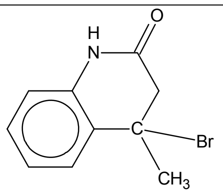
chemistry involved. [6]



A



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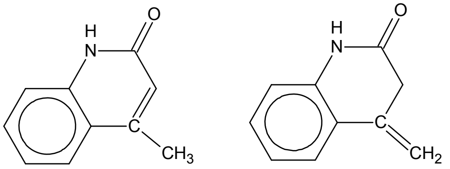

B & C

1 mk for each structure [4]

1/2 mk for each point (max of 2 mks):

1) From the molar mass of 177 g mol^{-1}, the molecular formula is likely to be $C_{10}H_{11}O_2N$.

2) **A** undergoes basic hydrolysis with NaOH (aq) to give –COO⁻ (–COOH + NaOH) and $–NH_2$. –COO⁻ is an ionic salt that ~~is soluble in~~dissolves in water by forming ion-dipole interactions with water. ⇒ **A** contains an amide group to give an amine and carboxylic salt when hydrolysed.

Some students wrote that the compounds form from the hydrolysis of **A** dissolves in water to via formation of hydrogen bonds with water. It may seem correct, but note that **A** contains an amide in a cyclic structure, hence after hydrolysis, there will be only one single product.

3) **A** undergoes elimination with Al_2O_3 to give alkenes **B** and **C** ⇒ **A** contains an alcohol group

4) The amide group in **A** undergoes reduction with $LiAlH_4$ to give an amine in **E**

5) Alkenes **B** and **C** undergo electrophilic addition with HBr to give halogenoalkane/alkyl halide/bromoalkane **D**.

6) **D** contains a chiral carbon and hence exists as a pair of enantiomers.

Comments

Out of the above 6 statements, the following key points are expected to gain credit.

- **A** undergoes (basic) hydrolysis with NaOH ⇒ **A** contains an amide group
- **A** undergoes elimination with Al_2O_3 to give alkenes **B** and **C** ⇒ **A** contains an alcohol group
- The amide group in **A** undergoes **reduction** with $LiAlH_4$ to give an amine in **E**
- Alkenes **B** and **C** undergo **electrophilic addition** with HBr to give **halogenoalkane/alkyl halide/bromoalkane D**

OR

- **D contains a chiral carbon** and hence exists as a pair of enantiomers.

4 bullet pts correct – 2 marks
2 bullet pts correct (minimum) – 1 mark

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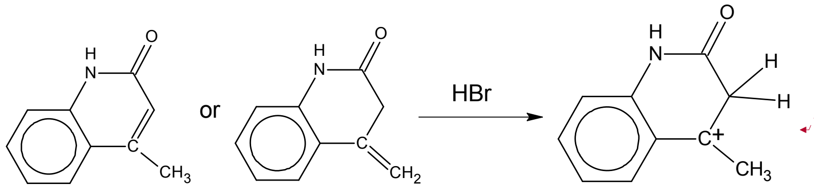
(iii) State the type of isomerism exhibited by **B** and **C.** Explain why **B** and **C** both give the same product **D** when reacted with HBr. [2]

Constitutional isomerism. [1]

When alkenes B and C undergo electrophilic addition with HBr, both form the same carbocation. The carbocation will be attacked by Br⁻ , which leads to the formation of D.



B **or** **C** **carbocation**

---

[1] for explanation & structure of carbocation

[Total: 22]

~~**(ii)** When one molecule of serine reacts with one molecule of glutathione, it is possible to form two esters with different structural formulae.~~
~~Draw the structural formula of **each** of these esters. [2]~~

~~**(iii)** Draw the structural formulae of the products when glutathione is hydrolysed. [3]~~

~~Alliin has pK_a values of 1.84 and 8.45.~~

~~**(iv)** Make use of these pK_a values to suggest the major species present in solutions of alliin with the following pH values. [3]~~

- ~~pH 1~~
- ~~pH 7~~
- ~~pH 11~~

~~**v)** Calculate the pH of 0.10 mol dm^{-3} solution of alliin. [1]~~

~~**(vi)** With reference to the pK_a values, identify the major species formed when 10 cm^3 of 0.10 mol dm^{-3} NaOH is added to 10 cm^3 of 0.10 mol dm^{-3} protonated alliin. Hence, deduce whether the solution is acidic, neutral or alkaline. [2]~~

~~**(vii)** Sketch the pH-volume added curve you would expect to obtain when 30 cm^3 of 0.10 mol dm^{-3} NaOH is added to 10 cm^3 of 0.10 mol dm^{-3} protonated alliin.~~
~~Briefly describe how you have calculated the various key points on the curve. [4]~~

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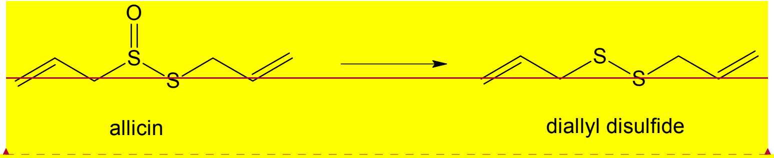
~~**(b)** Diallyl disulfide is one of the principal components of the distilled oil of garlic. It is a yellowish liquid which is insoluble in water and has a strong garlic odour. It is produced during the decomposition of allicin.~~



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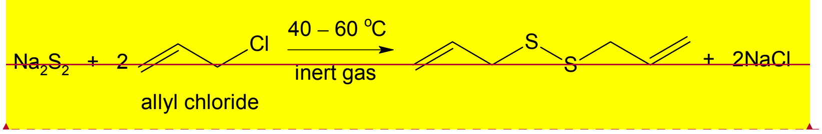
~~Diallyl disulfide can be produced industrially from sodium disulfide and allyl chloride at temperatures of 40 – 60 ¼C in an inert atmosphere.~~



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~~**(i)** Give the *IUPAC* name of allyl chloride. [1]~~

~~**(ii)** Explain, in thermodynamic terms, suggest why diallyl disulfide is insoluble in water. [2]~~

~~**(iii)** State the type of reaction when diallyl disulfide is converted back to allicin. [1]~~

~~[Total: 20]~~

Section B

Answer **one** question from this section.

4 Cycloalkanes are a homologous series of cyclic saturated hydrocarbons with the general formula C_nH_{2n} while n-alkanes are a homologous series of straight-chain saturated hydrocarbons with the general formula C_nH_{2n+2}.

n-alkanes	Boiling point / °C	Enthalpy change of combustion / kcal mol^{-1}	cycloalkanes	Boiling point / °C	Enthalpy change of combustion / kcal mol^{-1}
ethane	–89	–373.0	-	-	-
propane	–42	–530.4	cyclopropane	–33	–499.8
butane	–1	–687.8	cyclobutane	12	–656.0
pentane	36	–845.2	cyclopentane	49	–793.5
hexane	69	–1002.6	cyclohexane	81	–944.6
heptane	98	–1160.0	cycloheptane	119	–1108.3

(a) Explain the term “homologous series”. [1]

Group of organic compounds with

- Same functional group
- Differ by a CH_2 group

(b) Explain the increase in magnitudes of both boiling point and enthalpy change of combustion from ethane to heptane. [3]

- Alkanes have simple molecular structure with weak instantaneous dipole-induced dipole (id-id) forces between molecules
- From ethane to heptane, the electron cloud gets bigger and more easily polarised, hence id-id forces become stronger.
- More energy needed to break the id-id forces, hence boiling point increases
- From ethane to heptane, the molecule increases by a CH_2 group
- This results in more C – C bonds and C – H bonds to break and more C=O and O – H bonds to form, hence more heat given off during combustion.

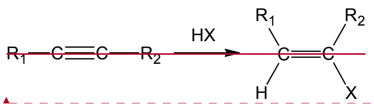
✓✓✓

~~Alkynes are organic molecules which contain carbon-carbon triple bonds and are part of the homologous series with formula of C_nH_{2n-2} i.e.~~

~~$R_1—C\equiv C—R_2$~~

~~where R_1 and R_2 = H or alkyl or aryl groups~~

~~Alkynes exhibit similar chemical properties to alkenes.~~
~~e.g. addition reactions with electrophiles i.e. X_2 or HX to form alkenes~~



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~~e.g. oxidation by hot concentrated KMnO$_4$ to form mixture of carboxylic acids~~

~~$R_1—C\equiv C—R_2 \xrightarrow{KMnO_4} R_1COOH + R_2COOH$~~

~~However, unlike alkenes, terminal alkynes are able to react with strong bases like sodium amide.~~

~~$RC\equiv CH + NaNH_2 \longrightarrow RC\equiv C^-\,Na^+ + NH_3$~~

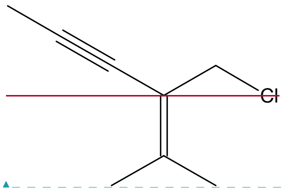
~~**(a)** Ethyne, C_2H_2, is heated with excess sodium bromide and concentrated sulfuric acid to produce a dihalide, $C_2H_4Br_2$. The overall reaction may be considered to take place in two stages, the first between inorganic reagents only and the second involving the organic reagent.~~

~~**(i)** Write an equation for the first stage. [1]~~

~~**(ii)** Suggest a structure for the dihalide formed. [1]~~

~~**(iii)** When the concentrated sulfuric acid is added to the reaction mixture, cooling is necessary to prevent the formation of inorganic by-products.~~
~~Write an equation to explain the formation of these inorganic by-products. [1]~~

~~**(b)** Compound **A**, is an enyne chloride (i.e. compounds that contains chloro, alkyne and alkene functional groups).~~



~~Compound **A**~~

~~One mole of compound **A** reacts with two moles of Br_2 to produce a mixture of 4 stereoisomers. Draw structures of the stereoisomers formed. [3]~~

(c) ~~Compound **B**, which is an isomer of Compound **A** and also an enyne chloride, is treated with sodium amide, $NaNH_2$ followed by heating under reflux to form compound **C**, C_8H_{10}. Compound **C** reacts with hot concentrated $KMnO_4$ to produce butane-1,4-dioic acid only.~~Suggest why combustion tends to be incomplete as the alkane increases in molecular mass. [1]

As the alkane increases in molecular mass, the alkane becomes liquid and liquid phase reactions are slower than gas phase reactions. Hence combustion tends to be incomplete.

Cyclopropane is a colourless gas with a “petroleum-like” odour. Unlike its straight-chain counterpart, it is considered to be highly strained and unstable. The instability of cyclic alkanes can be measured by calculating its “ring strain energy” using the formula below:

Ring strain energy =

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$$\begin{array}{c}\text{number of}\\ \text{carbon atoms}\\ \text{in cyclic alkane, A}\end{array} \times \left(\left| \begin{array}{c}\text{enthalpy change of combustion}\\ \text{of a CH}_2\text{ group in the}\\ \text{cyclic alkane, A}\end{array} \right| - \left| \begin{array}{c}\text{enthalpy change of combustion}\\ \text{of a CH}_2\text{ group in an}\\ \text{unstrained n-alkane}\end{array}\right| \right)$$

~~$\begin{array}{c}\text{number of}\\ \text{carbon atoms}\\ \text{in cyclic alkane, A}\end{array} \times \left(\left| \begin{array}{c}\text{enthalpy change of combustion}\\ \text{of a CH}_2\text{ group in the}\\ \text{cyclic alkane, A}\end{array} \right| - \left| \begin{array}{c}\text{enthalpy change of combustion}\\ \text{of a CH}_2\text{ group in an}\\ \text{unstrained n-alkane}\end{array}\right| \right)$~~

$$\begin{array}{c}\text{number of}\\ \text{carbon atoms}\\ \text{in cyclic alkane, A}\end{array} \times \left(\left| \begin{array}{c}\text{enthalpy change of combustion}\\ \text{of a CH}_2\text{ group in the}\\ \text{cyclic alkane, A}\end{array} \right| - \right.$$

$$\left. \left| \begin{array}{c}\text{enthalpy change of combustion}\\ \text{of a CH}_2\text{ group in an}\\ \text{unstrained n-alkane}\end{array}\right| \right)$$

$$\begin{array}{c}\text{number of}\\ \text{carbon atoms}\\ \text{in cyclic alkane, A}\end{array}$$

$$\times \left(\left| \begin{array}{c}\text{enthalpy change of combustion}\\ \text{of a CH}_2\text{ group in the}\\ \text{cyclic alkane, A}\end{array} \right| - \left| \begin{array}{c}\text{enthalpy change of combustion}\\ \text{of a CH}_2\text{ group in an}\\ \text{unstrained n-alkane}\end{array}\right| \right)$$

$$\begin{array}{c}\text{number of}\\ \text{carbon atoms}\\ \text{in cyclic alkane, A}\end{array}$$

$$\times \left(\left| \begin{array}{c}\text{enthalpy change of combustion}\\ \text{of a CH}_2\text{ group in the}\\ \text{cyclic alkane, A}\end{array} \right| - \left| \begin{array}{c}\text{enthalpy change of combustion}\\ \text{of a CH}_2\text{ group in an}\\ \text{unstrained n-alkane}\end{array}\right| \right)$$

~~$\begin{array}{c}\text{number of}\\ \text{carbon atoms}\\ \text{in cyclic alkane}\end{array} \times \left(\left| \begin{array}{c}\text{enthalpy change of combustion}\\ \text{of a CH}_2\text{ group in the}\\ \text{cyclic alkane}\end{array} \right| - \left| \begin{array}{c}\text{enthalpy change of combustion}\\ \text{of a CH}_2\text{ group in an}\\ \text{unstrained n-alkane}\end{array}\right| \right)$~~

(d) Given that the ΔH_f of CO_2 is –94.05 kcal mol^{-1} and ΔH_f of water is –68.3 kcal mol^{-1}, write an equation showing the formation of cyclopropane, and hence calculate the enthalpy change of formation of cyclopropane. ~~calculate the enthalpy change of formation of cyclopropane.~~ [2~~1~~]

$3C(s) + 3H_2(g) \rightarrow C_3H_6(g)$

ΔH_f = [3(–94.05) + 3(–68.3)] – (–499.8) = +12.75 kcal mol^{-1}

(e) Using the formula above, prove that the ring strain energy in cyclopropane is +27.6 kcal mol^{-1}. [2]

Enthalpy change of combustion of CH_2 group in unstrained molecule

= –530.4 – (–373.0) = –157.4 kcal mol^{-1} (can use other values to subtract)

Enthalpy change of combustion of CH_2 group in cyclopropane

= 1/3 (–499.8) = –166.6 kcal mol^{-1}

Strain energy of cyclopropane = 3 × (166.6 – 157.4) = +27.6 kcal mol^{-1}

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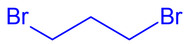
(f) Due to the presence of ring strain, cyclopropane undergoes an addition reaction with bromine in the absence of ultraviolet radiation.

(i) Suggest the skeletal structure of the molecule formed after reaction with Br_2. [1]



(ii) Hence, using VSEPR theory, explain why the presence of ring strain causes cyclopropane to undergo addition reactions. [1]

Cyclopropane has a C – C – C angle of 60° which is smaller than the optimal angle of 109.5° in sp^3 carbons. As a result, bond pairs are much closer to each other and experience greater repulsion, hence weakening the C – C bonds, which breaks easily during addition.

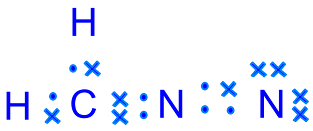
(g) Cyclopropane rings can be formed using a technique called "cyclopropanation".

One such cyclopropanation technique involves the 2 mechanistic steps stated below:

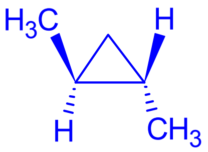
Step 1: Dissociation of diazomethane, CH_2N_2 to form methylene, CH_2, and N_2.~~Formation of methylene, CH_2, and N_2 from diazomethane, CH_2N_2.~~

Step 2: Addition of methylene, CH_2, to trans-but-2-ene to form the cyclic ring. The reaction leaves the stereochemistry of the molecule unchanged.

(i) It is observed that the diazomethane molecule is trigonal planar in shape. By considering the shape, d~~D~~raw a dot-and-cross diagram of diazomethane, CH_2N_2, clearly showing the type of bonds formed within the molecule.
[1]



(ii) Draw the structure of the cyclic molecule formed in s~~S~~tep 2, showing the stereochemical arrangement clearly. State and explain if the molecule can rotate plane-polarised light. [2]



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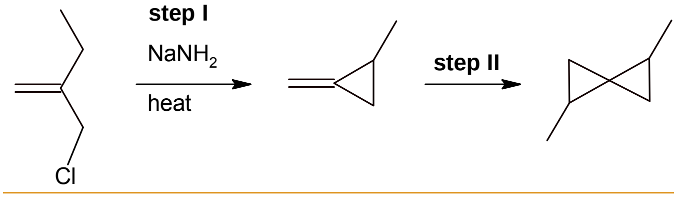
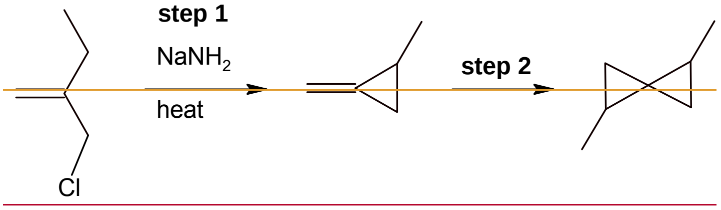
Yes, the molecule contains two chiral centres and does not have an internal plane of symmetry.

(~~h~~) Cyclopropane rings are a precursor for many types of fatty acids. The following shows part of the synthetic route for fatty acids.

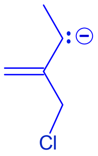




A **B**

(iii~~i~~) **Step I~~1~~** involves the reaction of molecule **A** with NaNH$_2$ to form NH$_3$ and a negatively-charged~~n~~ organic intermediate which eventually formed molecule **B** upon heating.

State the type of reactions that took place in **step I~~1~~** and draw the organic intermediate that was formed. [2]

- Molecule A reacted with NaNH$_2$ in an acid base reaction
- 

- (Intramolecular) nucleophilic substitution

*✓✓

(iv~~i~~) By considering the reactivity of the Cl atom, explain why~~if~~ molecule **C** cannot be used to replace molecule **A** in the synthesis above.

[1~~2~~]

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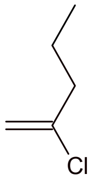


C

The chloro group is directly bonded to the double bond.

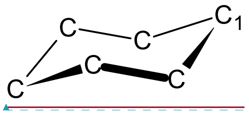
- The p orbital of Cl overlaps with the π orbital of the C=C bond,
- hence lone pair on Cl delocalises into the C=C bond,
- strengthening the C – Cl bond.

Hence, the Cl atom is resistant to nucleophilic substitution.

(v) Using the above information,
~~s~~Suggest a suitable reagent for **step II~~2~~**. [1]

$CH(CH_3)N_2$

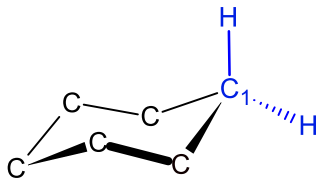
(h) Unlike the cyclic alkanes smaller than cyclohexane, cyclohexane does not experience ring strain due to the “chair shape” arrangement adopted by the six carbons as seen below:



chair shape arrangement of carbon atoms

By copying out the chair shape arrangement above and drawing ~~in~~ the 3-D arrangement of hydrogen atoms bonded to~~for~~ C_1, explain why cyclohexane does not experience ring strain.

[2~~2~~]



- Cyclohexane does not experience ring strain as cyclohexane bond angles are close to 109.5° due to the chair shape formation.

~~**(i)** Explain the reaction with $NaNH_2$. [1]~~

~~**(ii)** Hence, explain the formation of compound **C**. [1]~~

~~**(iii)** Suggest skeletal structures for compounds **B** and **C**. [2]~~

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~~When a current of 1.0 A was passed through aqueous potassium maleate ($KO_2CCH{=}CHCO_2K$) for 15 minutes, it was found that 110 cm^3 H_2, measured at r.t.p, was collected at the cathode. The following reaction took place.~~

~~$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$~~

~~**(d)** State the relationship between the Faraday constant, *F* and the Avogadro's constant, *L*. [1]~~

~~**(e)** Using the data above and the *Data Booklet*, calculate a value for Avogadro's constant. [3]~~

~~**(f)** Ethyne and CO_2 gas were produced at the anode. In order to determine the stoichiometry of the anode reaction, the volume of the gases collected at the anode was measured. The anode gas was first passed through aqueous NaOH before being collected in a gas syringe. The following data was collected:~~

- ~~mass of NaOH before experiment = 10.501 g~~
- ~~mass of NaOH after experiment = 10.904 g~~
- ~~initial reading on syringe = 10.0 cm^3~~
- ~~final reading on syringe = 120.0 cm^3~~

~~**(i)** State the oxidation state of carbon in ethyne. [1]~~

~~**(ii)** With the help of an equation, explain the purpose of passing the anode gas through NaOH. [1]~~

~~**(iii)** Calculate the volume of CO_2 produced, assuming r.t.p conditions. [1]~~

~~**(iv)** Hence, suggest an ionic equation for the reaction that occurred at the anode. [1]~~

~~**(g)** When aqueous potassium maleate was acidified, maleic acid, $HO_2CCH{=}CHCO_2H$ (pK_{a1} = 1.90 and pK_{a2} = 6.07) was liberated. Fumaric acid (pK_{a1} = 3.03 and pK_{a2} = 4.44) is a stereoisomer of maleic acid.~~
~~With a suitable illustration, suggest a reason why maleic acid has a lower pK_{a1} but higher pK_{a2} than fumaric acid.~~
~~[2]~~

[Total: 20]

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5(a) ~~Dopamine is an organic compound of the catecholamine and phenethylamine families that plays several important roles in the brain and body. Its name is derived from its chemical structure: it is an amine synthesised by removing a carboxyl group from a molecule of its precursor compound, L-DOPA.~~

The halogens and their compounds, show many similarities and trends in their properties. Some data are given for the elements fluorine, chlorine and iodine.

Element	Bond Energy / kJ mol^{-1}	Standard enthalpy change of atomisation / kJ mol^{-1}
Fluorine	158	79
Chlorine	242	121
Bromine	193	112
Iodine	151	107

(i) For fluorine and chlorine, their enthalpy changes of atomisation are half the value of their respective bond energies. For bromine and iodine, their enthalpy changes of atomisation are much more than half the value of their respective bond energies.

Explain in detail ~~for~~ this difference. [1]

Fluorine and chlorine are gases but bromine is a liquid and iodine is a solid at room temperature. The enthalpy change of atomisation includes the energy required to change $Br_2(l) \rightarrow Br_2(g)$ and $I_2(s) \rightarrow I_2(g)$ [to vapourise bromine and iodine to the gaseous state].

(ii) The standard enthalpy change of formation of iodine monochloride, I–Cl, is –24.0 kJ mol^{-1}.

Use this information and the data from the table above to calculate the I–Cl bond energy. [1]

$\Delta H_r = \sum \text{Bonds broken} - \sum \text{Bonds formed}$

–24.0 = ½ BE(Cl–Cl) + ½ BE(I–I) – BE(I–Cl)

BE(I–Cl) = +220.5

= +221 kJmol^{-1}

~~Below is a synthetic route involving L-DOPA and dopamine:~~

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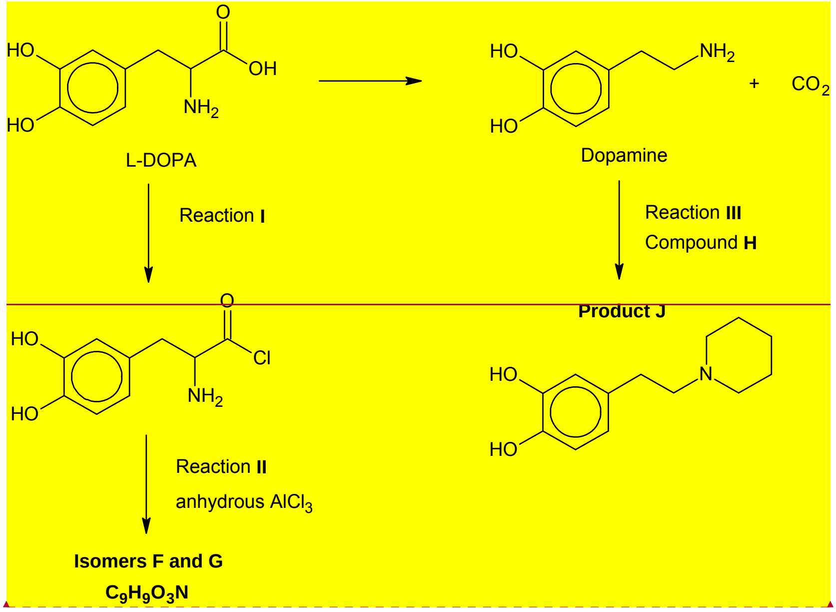
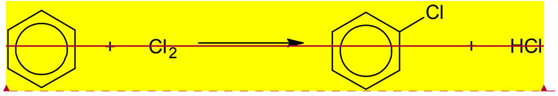


~~**(i)** State the reagents and conditions and any observations in Reaction **I**. [1]~~

~~**(ii)** Aluminium chloride is used as a catalyst in electrophilic substitution reactions. The chlorination of benzene is represented by the following overall equation.~~



~~The reaction occurs in several steps.~~

- ~~The first step is the reaction between Cl_2 and $AlCl_3$.~~

~~$Cl_2 + AlCl_3 \longrightarrow Cl^+ + AlCl_4^-$~~

- ~~The benzene ring is then attacked by the Cl^+ cation in the second step.~~

~~$AlCl_3$ reacts in a similar way with acyl chlorides, producing a carbocation that can then attack a benzene ring.~~

~~Predict the structures of isomers **F** and **G** in Reaction **II**. [2]~~

~~**(iii)** In Reaction **III**, dopamine was reacted with alkyl halide **H** to give the final product **J**. Draw the displayed formula of **H**. [2]~~

(iii) Explain why your answer in **(ii)** ~~does not correspond~~is larger in value compared to the average of the bond energies of I–I and Cl–Cl. [1]

I–Cl is polar while I–I and Cl–Cl are non-polar molecules. There is additional electrostatic attraction between $I^{\delta+}$ and $Cl^{\delta-}$. Hence, the actual bond energy of I–Cl is greater than the average bond energies of I–I and Cl–Cl.

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(b) ICl reacts with pure water to form HCl and HI:

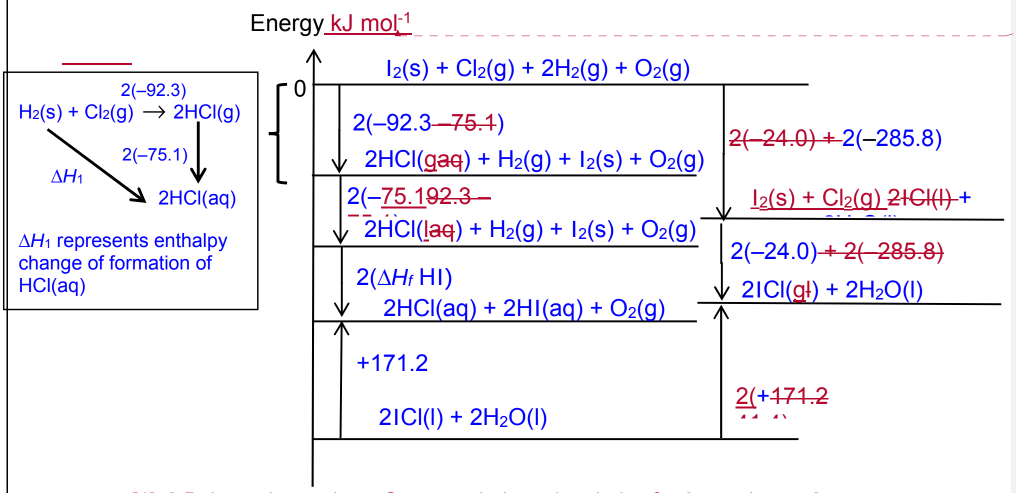
$2ICl(l) + 2H_2O(l) \rightarrow 2HCl(aq) + 2HI(aq) + O_2(g)$ ΔH_r = +171.2 kJ mol^{-1}

Using ΔH_r, the following data, as well as relevant data from **a(ii)**, draw an energy level diagram to calculate the enthalpy change of formation of aqueous HI.

Label your diagram ~~,~~ and draw arrows representing the energy terms involved. Use words or symbol to represent these energy terms.

	ΔH / kJ mol^{-1}
Standard enthalpy change of formation of H_2O	–285.8
Standard enthalpy change of formation of gaseous HCl	–92.3
Standard enthalpy change of reaction: $HCl(g) \rightarrow HCl(aq)$	–75.1
Standard enthalpy change of vaporisation of liquid ICl	+41.4

[4]



[1]x2 Balanced equations, State symbols and enthalpy for 3 reactions x 2

[1] ~~Label energy terms on diagram, arrows correctly~~

~~[1] Recognise the enthalpy change of formation~~ Energy level diagram (energy axis, ‘0’ at elements level, correct direction of arrows)

By Hess’ Law:

2(–24.0) + 2(–285.8) + (+171.2) = 2(41.4) + 2(–92.3) + 2(–75.1~~167.4~~) + 2ΔH_f(HI(aq))

2ΔH_f(HI(aq)) = – 2(–75.1) – 2(–92.3) + 2(–285.8) + 2(–24.0) – 2(41.4) + (+171.2)

~~–48.0 –571.6 + 171.2 + 334.8~~

ΔH_f(HI(aq)) = – 98~~56~~.2~~8~~ kJ mol^{-1} [1]

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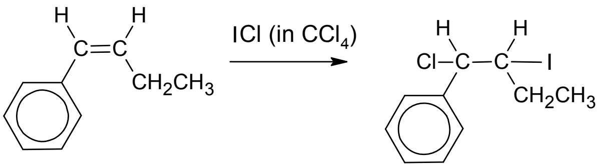
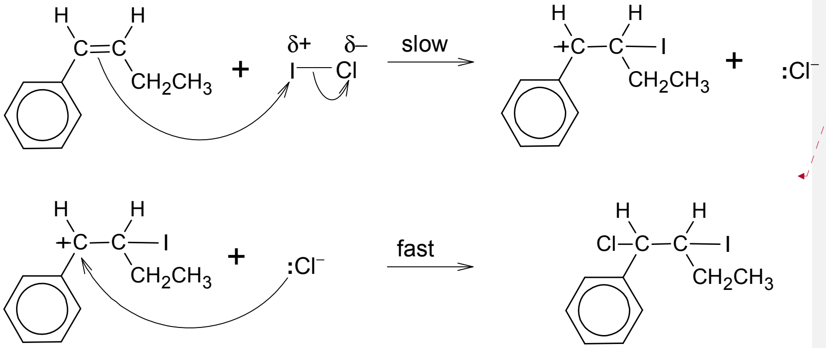
(~~b~~c) ICl is a useful reagent in organic synthesis. It is used in the following reaction to form compound **E**.



E

(i) Describe the mechanism for the formation of **E**. [3]

Electrophilic Addition



- Name of mechanism
- Correct arrows indicated
- Correct carbocation drawn
- Balanced equations
- Slow/ fast steps
- Charges on the atoms, lone pairs of electrons on Cl$^-$

Every 2 points – 1 mark

~~**(ii)** Dopamine is a bidentate ligand. When different volumes of 0.0030 mol dm^{-3} of aqueous Cr(III) and 0.0020 mol dm^{-3} of alkaline dopamine solution were mixed, a complex R is formed. Analysis of R shows that its formula is $[Cr(C_8H_9NO_2)_x(H_2O)_y]^{z□}$, where x, y and z are integers.~~

~~To determine the stoichiometry of the complex ion formed, the colour intensities of these different mixtures were measured using a colorimeter. The following absorption spectrum was obtained.~~

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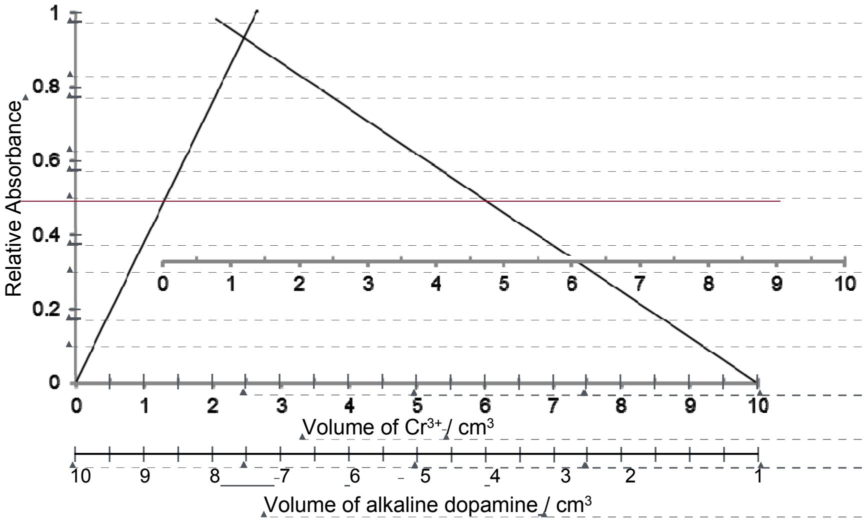
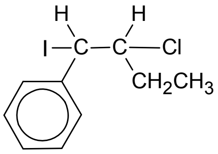


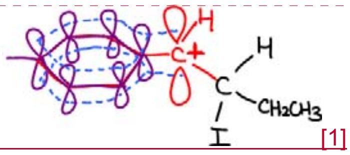
~~**(i)** Use the graph and the information given to determine the formula of complex R. Show your workings clearly. [3]~~

With the aid of a diagram, explain why **E** is formed and not **F**. [2]



F

The carbocation and the C atoms in benzene ring are sp^2 hybridised. The (+) charge on carbocation is dispersed over the neighbouring benzene ring. Due to the effective overlap between the unhybridised p-orbitals of benzene and the empty p-orbital on the carbocation, the delocalised electrons makes the (+) charge on the carbocation less (+). [1]



[1]

(d) Compound **J**, $C_{11}H_{16}O_2$, decolourises bromine water. 1 mole of **J** reacts with sodium metal to produce 22.7 dm^3 of hydrogen gas at s.t.p. On heating with acidified $KMnO_4$, **K**, $C_9H_{10}O_5$, is the only organic product formed.

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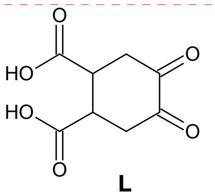
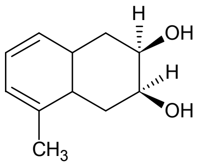
K reacts with sodium carbonate and 2,4-DNPH. When **K** reacts with alkaline aqueous iodine, **L** is formed upon acidification.



L

Suggest structures for **J** and **K** and explain the reactions described. [5]



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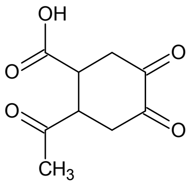

K

Observations	Deductions
J,$C_{11}H_{16}O_2$ decolourises bromine water	**J** could be alkene or phenol. An alkene undergoes electrophilic addition reaction with Br_2(aq) to form halogenoalkane.
22.7 dm^3 of hydrogen is formed at s.t.p when **J** is reacted with sodium metal	n(H_2) = $\frac{22.7}{22.7}$ = 1 mol of H_2 is formed. $ROH + Na \rightarrow RO^-Na^+ + ½H_2$ Since 1 FG produces ½ mole of H_2, there must be 2 –OH groups present. –COOH group is absent as it will only produce only ½ mole of H_2 and 2 –COOH groups or 1 –OH & 1 –COOH groups cannot be present as it will not correspond to the molecular formula of **J**.
On heating with acidified $KMnO_4$, **K**, $C_9H_{10}O_5$, is the only organic product formed	Secondary alcohol and the alkene in **J** undergoes oxidation with $KMnO_4$ to form ketones and carboxylic acid. There is a decrease in 2C atoms – which suggest that ethane-1,2-dioc acid was oxidised to form CO_2. From the given structure of **L**, it can be seen that **K** is unlikely a phenol and should not contain benzene as there will not be oxidation that leads to a reduction of 2 C atoms.
K reacts with sodium carbonate and 2,4 DNPH	**K** undergoes acid-base with Na_2CO_3 → –$COCH_3$ present. **K** undergoes condensation with 2,4 DNPH → –confirms presence of ketones.
K reacts with alkaline aqueous iodine to form **L**	**K** undergoes mild oxidation with alkaline I_2(aq) → –$COCH_3$ present. **K** undergoes acid-base reaction with alkali to form salt → –COOH present.

1 mark for each correct structure
3 marks for explanation
5 points – 3 marks
3 to 4 points – 2 marks
2 points – 1 mark

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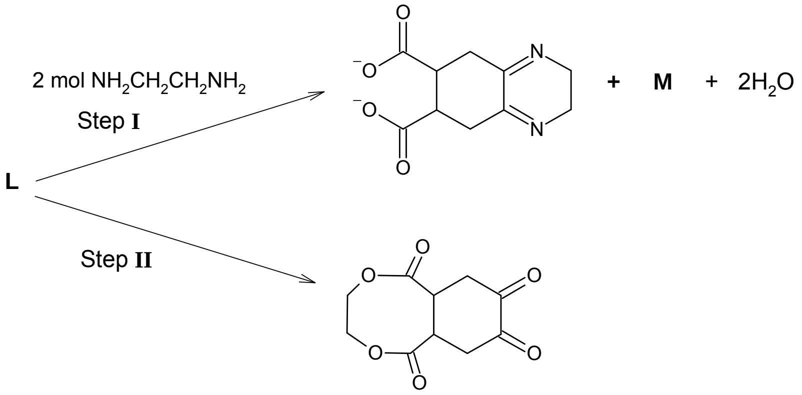
(e) In the following reaction scheme, compounds **M** and **N** can be obtained from **L**.



N

(i) Draw the structure of **M**. State the type(s) of reaction in Step **I**. [2]

$^+NH_3CH_2CH_2NH_3^+$ [1] Types of reaction: Condensation, Acid – Base [1]

(ii) Suggest reagents and conditions to synthesise product **N** from **L**. [1]

~~**(ii)** The crystal field describes the breaking of orbital degeneracy in transition metal complexes due to the presence of ligands. When the d orbitals split into high energy and low energy orbitals, the difference in energy of the two levels is denoted as Δ_o. The relationship between Δ_o and colours of complexes can be described in the equation below:~~

$$\cancel{\Delta_o = \frac{hc}{\lambda}}$$

~~where h is Planck's constant, c is the speed of light and λ is the wavelength of light absorbed~~

~~colour~~	~~absorbed λ / nm~~
~~violet~~	~~410~~
~~indigo~~	~~430~~
~~blue~~	~~480~~
~~blue-green~~	~~500~~
~~green~~	~~530~~
~~yellow~~	~~580~~
~~orange~~	~~610~~
~~red~~	~~680~~

$CH_2(OH)CH_2(OH)$, concentrated H_2SO_4 heat under reflux.

OR
1) PCl_5 at rtp 2) $CH_2(OH)CH_2(OH)$, rtp

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~~Given that Δ_o for complex **R** is 4.125 x 10^{-22} kJ and using relevant data from the *Data Booklet*, calculate the wavelength of light. Deduce the colour of complex **R**.~~ ~~[2]~~

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~~**(c)** Iodine is not very soluble in water, it is freely soluble in KI(aq), according to the following equilibrium:~~

$$\cancel{I^-(aq) + I_2(s) \rightleftharpoons I_3^-(aq)}$$

~~**(i)** Draw a fully labelled experimental set-up for a voltaic cell made up of a $Cr_2O_7^{2-}$ / Cr^{3+} half-cell and a I_2/I^- half-cell under standard conditions. Indicate clearly the anode and cathode and show the flow of electrons.~~ ~~[3]~~

~~**(ii)** By using appropriate values from the *Data Booklet*, predict what, if anything, will happen when a small amount of acidified vanadium(II) chloride is added to the I_2/I^- half-cell.~~ ~~[3]~~

~~**(d)** Explain the following statements.~~

~~**(i)** BrF_3 is a covalent compound which exhibits electrical conductivity in liquid state at room temperature. With the aid of an equation, suggest an explanation for its electrical conductivity.~~ ~~[2]~~

~~**(ii)** $SiCl_4$ reacts violently in water but CCl_4 has no reaction with water.~~ ~~[1]~~

~~**(iii)** Compounds NeF_2 and NeF_4 do not exist but XeF_2 and XeF_4 exist.~~ ~~[1]~~

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