YISHUN INNOVA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME

TEACHER'S COPY

CG | INDEX NO

CHEMISTRY 9729/01

Paper 1 Multiple Choice 14 September 2022

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, highlighters, glue or correction fluid/tape.
Write your name and class 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.

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BP~947

2

1 *Use of the Data Booklet is relevant to this question.*

The table shows the fifth, sixth, seventh, eighth and ninth ionisation energies of an element in the third period.

	5th	6th	7th	8th	9th
ionisation energy / kJ mol⁻¹	6270	21270	25430	29870	35920

Which element has these ionisation energy values?

A P   B S   C Cl   D Ar

Answer: A

The element is P as there is a large jump between the 5th and 6th ionisation energies as seen in this table.
The 6th electron for P is removed from an inner principal quantum shell.

2 Two elements X and Y have the following properties:
 • X and Y form ionic compounds Na₂X and Na₂Y respectively.
 • Element Y forms YF₆ molecule whereas X is not able to do so.

Which pair of electronic configurations for X and Y is correct?

	X	Y
A	[He] 2s² 2p⁴	[He] 2s² 2p²
B	[He] 2s² 2p²	[He] 2s² 2p⁶ 3s² 3p³
C	[He] 2s² 2p²	[He] 2s² 2p⁶ 3s² 3p²
D	[He] 2s² 2p⁴	[He] 2s² 2p⁶ 3s² 3p⁴

Answer: D

Compounds Na₂X and Na₂Y show that X and Y forms anions of –2 charge so it means that they have 6 electrons in their valence shell.

Y must be a period three element in order for YF₆ to exist as it has an expanded octet structure.

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3

Use of the Data Booklet is relevant to this question.

An element **G** forms an ionic nitrate with formula **G**(NO₃)₂.

In a sample of this compound, the ion **G** contains 80 electrons and 126 neutrons.

Which row describes:

- the Group where **G** is found,
- the nucleon number of **G** in this sample?

	Group	nucleon number
A	2	204
B	2	208
C	14	204
D	14	208

Answer: D

The formula **G**(NO₃)₂ shows that element **G** can form a +2 cation.

G atom has 82 electrons, 82 protons and 126 neutrons, so the nucleon number is 82 + 126 = 208.

Hence, **G** is Pb which is a Group 14 element with a mass number of 207.2 and a nucleon number of 208.

4   The table identifies the shape and polarity of four molecules.

Which rows are correct?

	molecule	molecular shape	polarity
1	beryllium chloride	bent	non-polar
2	nitrogen dioxide	bent	polar
3	sulfur trioxide	trigonal planar	non-polar
4	chlorine trifluoride	trigonal planar	polar

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

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[Turn over

4

Option 1 is incorrect as BeCl₂ is linear, not bent
Option 2 is correct as NO₂ is bent shaped and is polar
Option 3 is correct as SO₃ is trigonal planar and non-polar
Option 4 is incorrect as ClF₃ is T-shaped.

Answer: B

5   Hydrazine, N₂H₄, and hydrogen peroxide, H₂O₂, are both used as rocket propellants because they can produce large volumes of hot gases from a small volume of liquid.

Which statements about these two compounds are correct?

1   The bond angle in N₂H₄ is larger than that in H₂O₂.

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

3   N₂H₄ forms stronger intermolecular hydrogen bonds than H₂O₂.

4   There are σ bonds formed by sp³-s orbital overlap in both molecules.

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

Answer: A

1   Correct.
The bond angle in N₂H₄ is 107° (3 bp, 1 lp) and the bond angle in H₂O₂ is 105° (2 bp, 2 lp).

2   Incorrect.
The atomic radius of O is smaller than N so the effectiveness of the orbitals overlap is higher and the O-H bond is shorter.

3   Incorrect.
The dipole moment of the O-H bond is bigger, hence the hydrogen bonds between the H₂O₂ molecules are stronger

4   Correct.
The electron pairs around N and O are in a tetrahedral arrangement and hence the N and O atoms are sp³ hybridised and the H atoms consists of s orbitals. The N-H and O-H bonds are formed by sp³ – s orbital overlaps

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[Turn over

6

6 In an experiment, 0.100 g of a volatile liquid Q formed 0.0250 dm³ of vapour at 100 °C at 1 bar.

What is the relative molecular mass of Q?

A $\dfrac{0.100 \times 373}{0.0250 \times 22.7}$

B $\dfrac{0.0250 \times 273 \times 22.7}{0.100 \times 373}$

C $\dfrac{0.100 \times 273 \times 22.7}{0.0250 \times 373}$

D $\dfrac{0.100 \times 373 \times 22.7}{0.0250 \times 273}$

Answer: D

Using pV=nRT

$(100000)(0.0250 \times 10^{-3}) = \dfrac{0.100}{M_r}(R)(373)$

$M_r = \dfrac{0.100 \times 373 \times R}{100000 \times (0.0250 \times 10^{-3})}$

1 mol of any gas occupies 22.7 dm³ at standard temperature and pressure

$(100000)(22.7 \times 10^{-3}) = R (273)$

$R = \dfrac{100000 \times 22.7 \times 10^{-3}}{273}$

$M_r = \dfrac{0.100 \times 373 \times R}{100000 \times (0.0250 \times 10^{-3})} = \dfrac{0.100 \times 373 \times 100000 \times 22.7 \times 10^{-3}}{100000 \times (0.0250 \times 10^{-3}) \times 273} = \dfrac{0.100 \times 373 \times 22.7}{0.0250 \times 273}$
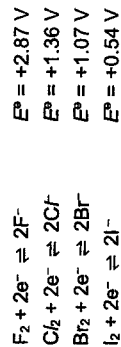
7 For the elements in Group 17, which trends down the Group are correct?

	volatility	oxidising power
A	decreases	decreases
B	decreases	increases
C	increases	decreases
D	increases	increases

Answer: A

Down Group 17,
- size of electron cloud of the halogens increases and more easily polarised
- stronger instantaneous dipole induced dipole interactions between molecules exists
- more energy needed to overcome the stronger intermolecular forces
- boiling point increases
- (Since boiling point is inversely proportional to volatility,) volatility of elements decreases down the group.

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

Down the group, the reactivity of the halogens as oxidising agents decreases as indicated by the less positive $E^{\ominus}$ values. The halogens have a lower tendency to be reduced.

8 Which statement about relative molecular mass is correct?

A It is the sum of the relative atomic masses of all the atoms within the molecule.

B It is the ratio of the average mass of a molecule to the mass of a ^{12}C atom.

C It is the ratio of the mass of 1 mol of molecules to the mass of 1 mol of ^1H atoms

D It is the average mass of all the atoms within the molecule.

Answer: A

A Correct.

B Incorrect.
Relative molecular mass is the ratio of the average mass of one molecule to **one twelfth of the mass of an atom of carbon-12**.

C Incorrect.
Relative molecular mass is the ratio of the average mass of one molecule to **one twelfth of the mass of an atom of carbon-12**.

D Incorrect.
Relative molecular mass is not the average mass alone.

9 The enthalpy change of reaction 1 is –114 kJ mol⁻¹.

$$2NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l) \quad \text{reaction 1}$$

By using this information, what is the most likely value for the enthalpy change of reaction 2?

$$NaOH(aq) + CH_3COOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l) \quad \text{reaction 2}$$
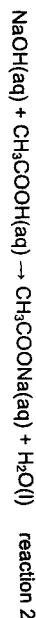
A –50 kJ mol⁻¹   **B** –57 kJ mol⁻¹   **C** –114 kJ mol⁻¹   **D** –228 kJ mol⁻¹

Answer: A

In reaction 1, when 2 mol of water is produced heat given out is = 114 kJ
In reaction 2, the neutralisation between CH₃COOH and NaOH produces 1 mol of water.
Thus, heat liberated = ½ × (114) = 57 kJ

Ethanoic acid is a weak acid which does not dissociate completely to give H⁺ ions. Hence some energy is required to for complete dissociation of H⁺ ions. Therefore ΔH is less exothermic for a weak acid and strong base compared to ΔH between a strong acid (H₂SO₄) and strong base (NaOH).

10 Which equations represent standard enthalpy changes at 298 K?

1   $H_2(g) + F_2(g) \rightarrow 2HF(g)$

2   $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

3   $\tfrac{1}{2}F_2(g) \rightarrow F(g)$

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

Answer: D

1   For equation 1, to represent the standard enthalpy change of formation of HF, 1 mol of HF should be formed.

2   For equation 2, to represent the standard enthalpy change of combustion of CH₄, water formed should be in the liquid state.

3   Equation 3 represents the standard enthalpy change of atomisation of fluorine.

11 Melphalan is a drug used to treat infections.

The breakdown of melphalan in the blood is a first-order reaction. An original concentration of melphalan of 15.00 mg dm⁻³ decreases to 1.875 mg dm⁻³ after 270 minutes.

What is the time taken, in minutes, for the concentration of melphalan to decrease from 10.0 mg dm⁻³ to 2.00 mg dm⁻³ in the blood?

A 105   **B** 180   **C** 209   **D** 360

Answer: C

$$15.00 \text{ mg dm}^{-3} \xrightarrow[\text{half-life}]{1^{st}} 7.50 \text{ mg dm}^{-3} \xrightarrow[\text{half-life}]{2^{nd}} 3.75 \text{ mg dm}^{-3} \xrightarrow[\text{half-life}]{3^{rd}} 1.875 \text{ mg dm}^{-3}$$
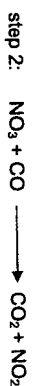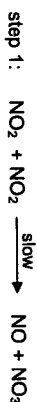
3 half-lives = 270 minutes, 1 half-life is 90 minutes

$$\frac{\text{final concentration of reactant}}{\text{initial concentration of reactant}} = \left(\frac{1}{2}\right)^n \text{ where n = number of half-lives.}$$

$$\frac{2}{10} = \left(\frac{1}{2}\right)^n$$

$$n = 2.3219$$

time taken = 2.3219 half-lives = 90 × 2.3219 = 209 minutes

12 The reaction between NO₂ and CO to produce NO and CO₂ is thought to occur in two steps:

step 1: $NO_2 + NO_2 \xrightarrow{\text{slow}} NO + NO_3$

step 2: $NO_3 + CO \longrightarrow CO_2 + NO_2$

Which statements are correct?

1   The rate constant has units of mol⁻² dm⁶ s⁻¹.

2   NO₂ is a catalyst.

3   The rate of reaction is independent on the concentration of CO.

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

Answer: B

1 Incorrect.

The rate equation is rate = $k[NO_2]^2$. Thus, the units for the rate constant $= \dfrac{\text{mol dm}^{-3}\,\text{s}^{-1}}{(\text{mol dm}^{-3})^2}$

$= \text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1}$.

2 Correct.

NO_2 is used up in step 1 and regenerated in step 2 so NO_2 is a catalyst.

3 Correct.

Since the order of reaction with respect to [CO] = 0, the rate of reaction is independent on the concentration of CO.

13 Each of the following equilibria is subjected to two changes which are carried out separately:

- the pressure is reduced at constant temperature;
- the temperature is increased at constant pressure.

Which equilibrium will both changes result in an increase in the proportion of products?

A $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $\Delta H = +53$ kJ mol^{-1}

B $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$ $\Delta H = -950$ kJ mol^{-1}

C $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta H = -92$ kJ mol^{-1}

D $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\Delta H = +57$ kJ mol^{-1}

Answer: D

For the proportion of products to increase, the equilibrium position will have to shift to the **right** when changes to pressure and temperature are made.

For the equilibrium position to shift to the **right** when pressure is reduced, the right hand side of the equilibrium must have more moles of gaseous particles.

For equilibrium position to shift to the right when temperature is increased, the forward reaction must be endothermic.

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14 At 25 °C, $K_w = 1.00 \times 10^{-14}$ mol^2 dm^{-6}.

At 62 °C, $K_w = 1.00 \times 10^{-13}$ mol^2 dm^{-6}.

Which row is correct?

	the ionisation of water is	at 62 °C, water with a pH of 7.0 is
A	endothermic	alkaline
B	endothermic	neutral
C	exothermic	alkaline
D	exothermic	neutral

Answer: A

As temperature increase from 25°C to 62°C, the value of K_w increased, this implies that the position of equilibrium shifted to the right (endothermic) to absorb excess heat. Hence, ionisation of water is endothermic.
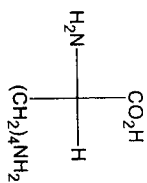
At 62°C, when pH =7, $[H^+] = 10^{-7}$,

$K_w = [H^+][OH^-]$,

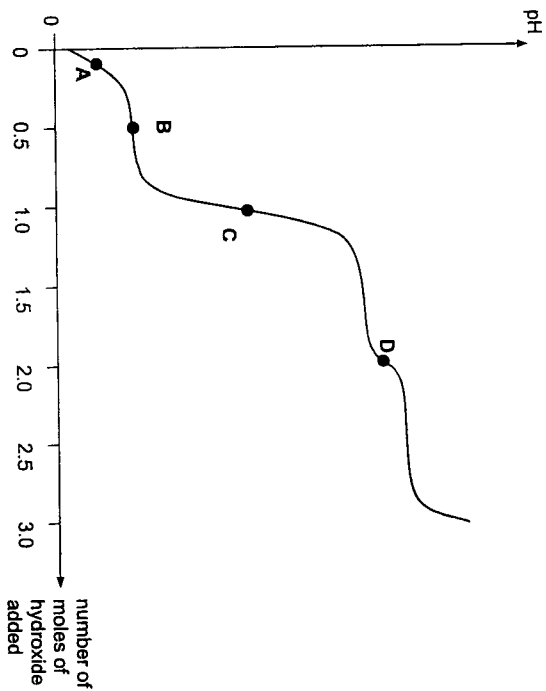$[OH^-] = \dfrac{1.00 \times 10^{-13}}{10^{-7}} = 1.00 \times 10^{-6}$ mol dm$^{-3} > 10^{-7}$ mol dm^{-3}

Since $[OH^-] > [H^+]$, solution is alkaline.

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15 Lysine is an essential amino acid found in the body. It has three pK_a values associated with it.

H_2N—CO_2H
$(CH_2)_4NH_2$—H

lysine

The pH curve below is obtained when one mole of the protonated lysine is titrated with hydroxide, OH^-, ions.

At which point on the graph does pH = pK_{a1} where K_{a1} is the first acid dissociation constant of lysine?

Answer: B

The buffer region will be formed before the equivalence point since the weak acid is present with the salt. At the maximum buffer capacity, pH = pK_a, and it will be at half equivalence point where the [salt] = [weak acid].

[Turn over

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16 Vehicles produce exhaust emissions when the engine is running. These emissions can include harmful pollutants such as carbon monoxide, oxides of nitrogen and unburnt hydrocarbons.

A catalytic converter is used to change the gases emitted through chemical reactions.

Which reactions between the stated compounds occur in the catalytic converter?

1   hydrocarbons + oxides of nitrogen → carbon dioxide + water + nitrogen

2   carbon monoxide + oxides of nitrogen → carbon dioxide + nitrogen

3   carbon monoxide + hydrocarbons → carbon dioxide + water
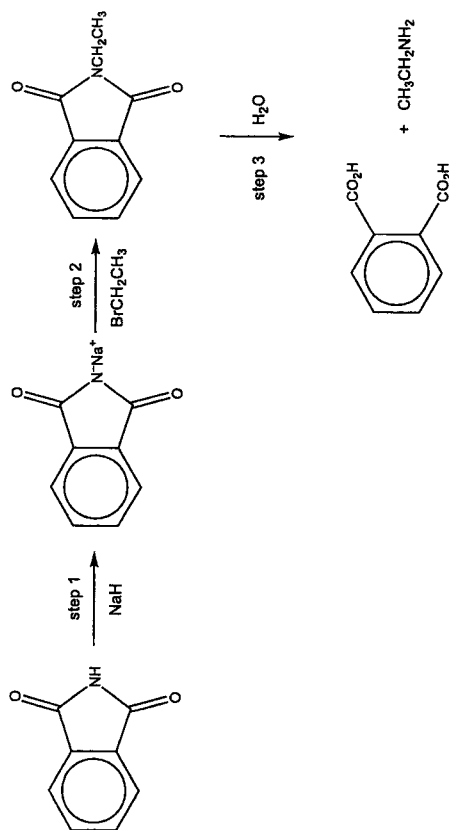
A	B	C	D
1, 2 and 3	1 and 2	2 and 3	1 only

Answer: B

The catalytic converter helps to oxidise carbon, carbon monoxide to carbon dioxide and water and reduce oxides of nitrogen to nitrogen.

Reaction 3 is incorrect as hydrocarbons do not contain oxygen and cannot oxidse CO to CO_2.

[Turn over

14

18 Benzene reacts with chloroethane to form ethylbenzene.

$$\text{benzene} + CH_3CH_2Cl \xrightarrow{AlCl_3} \text{ethylbenzene} (CH_2CH_3) + HCl$$
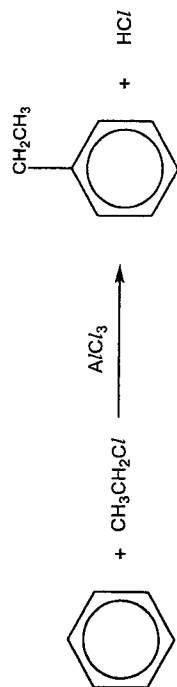
The reaction proceeds via several stages with two successive intermediates.

What could be the intermediates for this reaction?

A $[CH_3CH_2]^+$ and (structure with H, CH₂CH₃, +)

B $[CH_3CH_2]^-$ and (structure with H, CH₂CH₃, +)

C $[CH_3CH_2]^+$ and (structure with H, CH₂CH₃, +)

D $[CH_3CH_2]^-$ and (structure with H, CH₂CH₃, +)

Answer: **A**

$CH_3CH_2Cl + AlCl_3 \longrightarrow CH_3CH_2^+ + AlCl_4^-$

The positive charge in the arenium ion intermediate is delocalised over the 5 remaining sp² carbon atoms.

©YJC   **[Turn over**

13

17 The Gabriel synthesis is a useful method of preparing primary amines.

(phthalimide, NH) $\xrightarrow[\text{NaH}]{\text{step 1}}$ (N⁻Na⁺) $\xrightarrow[\text{BrCH}_2\text{CH}_3]{\text{step 2}}$ (NCH₂CH₃)

$\xrightarrow[\text{H}_2\text{O}]{\text{step 3}}$ (benzene-1,2-dicarboxylic acid, CO₂H, CO₂H) + $CH_3CH_2NH_2$

What are the types of reactions occurring in each of the steps?

	step 1	step 2	step 3
A	acid-base	electrophilic substitution	hydrolysis
B	acid-base	nucleophilic substitution	hydrolysis
C	oxidation	electrophilic substitution	oxidation
D	oxidation	nucleophilic substitution	oxidation

Answer: **B**

Step 1: Amide acts as acid and donates a H⁺
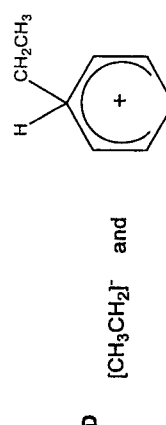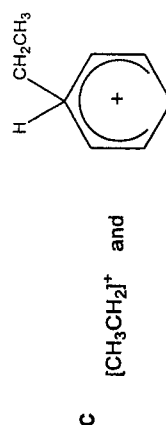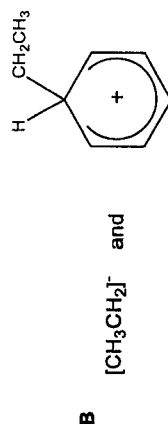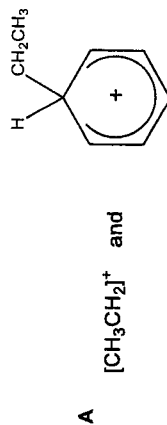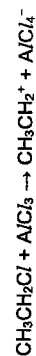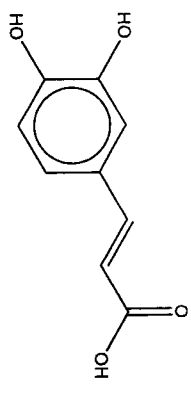Step 2: N⁻ acts as nucleophile and attacks the electron-deficient carbon bonded to bromine
Step 3: Amide undergoes hydrolysis

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B19 Caffeic acid is found at relatively high levels in spearmint and star anise. It shows antioxidant and anti-inflammatory activities.


caffeic acid

When treated with aqueous bromine, what is the maximum number of bromine atoms that can be incorporated into a molecule of caffeic acid?
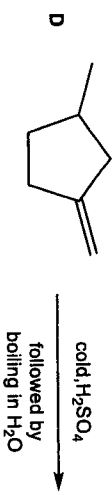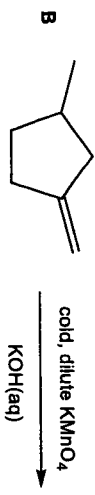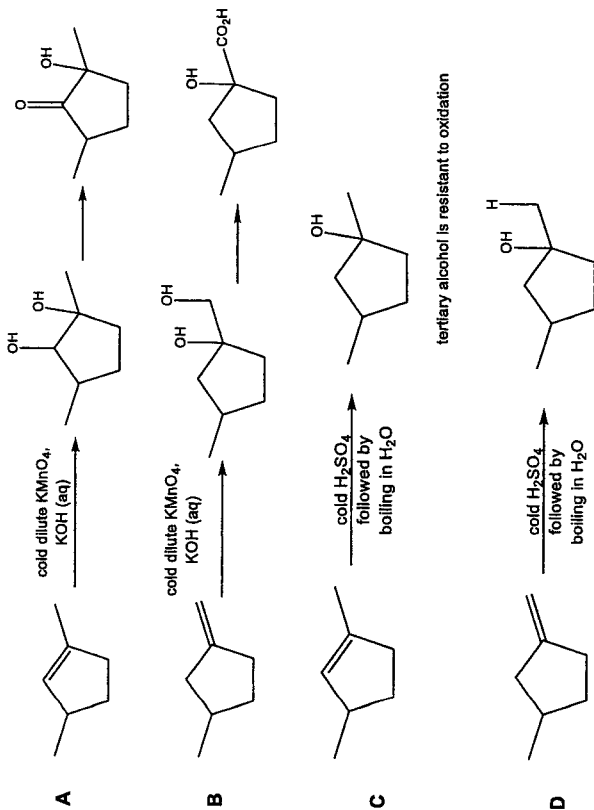
A 2   B 3   C 4   D 5

Answer: D

Phenol undergoes electrophilic substitution at carbon atoms 2, 4 and 6 relative to the carbon atom bonded to phenol, while the alkene group undergoes electrophilic addition to form bromoalcohol as the major product and 1,2-dibromoalkane as the minor product.
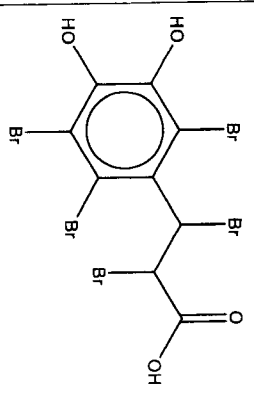
20 Which reaction forms a product which can be further oxidised to form a carboxylic acid?

A

$\xrightarrow{\text{cold, dilute KMnO}_4}$

B

$\xrightarrow{\text{cold, dilute KMnO}_4 \ \text{KOH(aq)}}$

$\xrightarrow[\text{KOH(aq)}]{}$

C

$\xrightarrow[\text{boiling in H}_2\text{O}]{\text{cold,H}_2\text{SO}_4 \ \text{followed by}}$

D

$\xrightarrow[\text{boiling in H}_2\text{O}]{\text{cold,H}_2\text{SO}_4 \ \text{followed by}}$

18

21 Cholecalciferol is a type of vitamin D that is made by the skin when exposed to sunlight. It can also be found in the flesh of fatty fish and fish liver oils.
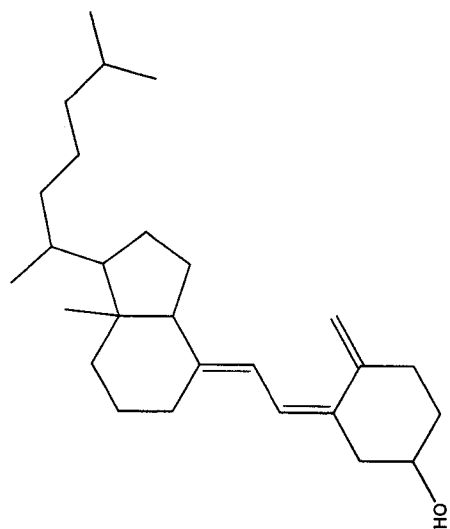

cholecalciferol

Which statements about cholecalciferol are correct?

1 There is a maximum of 128 stereoisomers.

2 Cholecalciferol can react with ethanoyl chloride to form a sweet-smelling product.

3 1 mole of cholecalciferol produces 3 moles of carbon dioxide when heated with acidified $KMnO_4$.

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

17

Answer: B

A cold dilute $KMnO_4$, KOH (aq)

B cold dilute $KMnO_4$, KOH (aq)

C cold H_2SO_4 followed by boiling in H_2O →   tertiary alcohol is resistant to oxidation

D cold H_2SO_4 followed by boiling in H_2O →   tertiary alcohol is resistant to oxidation

19

Answer: D

1
Correct.
There are 5 chiral centres and 2 alkenes that can exhibit cis-trans isomerism. $2^7 = 128$.
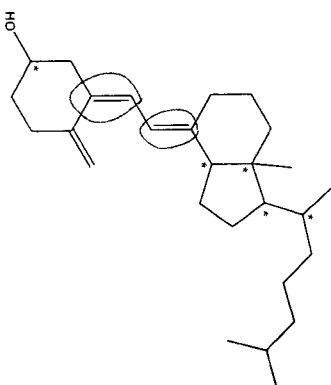
2
Correct.
The alcohol group can undergo condensation with ethanoyl chloride to form ester.

3
Correct.
The 3 alkene groups undergo strong oxidation. The terminal alkene gives 1 mole of CO_2 while ethanedioic acid undergoes further oxidation to give 2 moles of CO_2.

22 A comparison is made of the rate of hydrolysis of four halogenocompounds by hot aqueous NaOH.

$CH_3CH_2CH_2Cl$ CH_3CH_2COCl $C_6H_5CH_2Br$ C_6H_5Cl
E   F   G   H

How will the rates of hydrolysis compare?

	fastest ⟶			slowest
A	E	G	H	F
B	G	H	E	F
C	F	G	E	H
D	F	E	G	H

20

Answer: C
Acyl chloride (F) will undergo hydrolysis fastest, while chlorobenzene (H) will be resistant to hydrolysis.
Bromoalkane (G) will react faster than chloroalkane (E) due to C–Br bond being weaker than C–Cl bond.

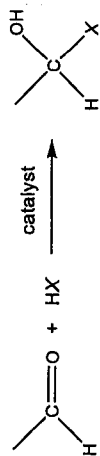**23** Which pairs of compounds can be distinguished using the stated reagents and conditions?

	compounds	reagents and conditions
1	$CH_3CH_2CO_2H$ and $CH_3CH_2CH_2OH$	Na, room temperature
2	$CH_3CO_2CH_2CH_3$ and $CH_3CONHCH_2CH_3$	NaOH(aq), I_2(aq), heat
3	$CH_3CON(CH_3)_2$ and $(CH_3)_2CHCONH_2$	NaOH(aq), heat

A 1, 2 and 3   **B** 1 and 2   **C** 2 and 3   **D** 3 only
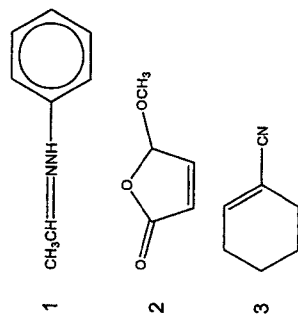
Answer: C

1
Incorrect.
Both carboxylic acid and alcohol will give effervescence of H_2 gas.

2
Correct.
Ester and amide undergo alkaline hydrolysis. Ethanol formed from hydrolysis of ester will give a pale yellow ppt with alkaline iodine.

3
Correct.
Primary amide undergoes alkaline hydrolysis to liberate NH_3 gas.

22

Answer: B

Working backwards, add in a H_2O followed by removal of the HX (where X is not necessarily a halogen; X can be –CN, –OCH$_3$, etc.) to obtain the C=O (i.e. HX is removed across the C-O bond) and hence the original reactant is obtained.

1   Correct.

$X = -NHNHC_6H_5$

2   Correct.

$X = -OCH_3$

3   Incorrect.

$X = -CN$

21

24   There is a range of reactions of the aldehyde group which have the pattern

of which the formation of a cyanohydrin (where X = CN) is one.

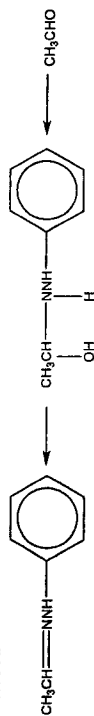Which compounds could be obtained by such an addition to an aldehyde group, followed by a dehydration?

A   1, 2 and 3   B   1 and 2   C   2 and 3   D   3 only
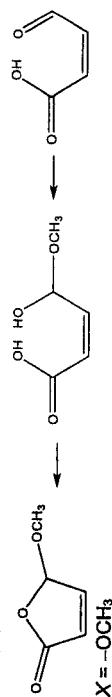
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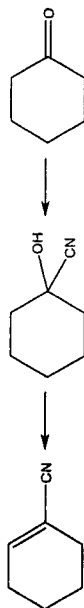
25 The compound $C_3H_7CO_2C_6H_5$ is an ester.

Which statement about this ester is correct?

A Its name is phenyl propanoate.

B When heated with NaOH(aq), phenol is one of the products formed.

C When heated with H_2SO_4(aq), butanoic acid is one of the products formed.

D It can be formed using butanoic acid and phenol.

Answer: C

A Incorrect.
Its name is phenyl butanoate.

B Incorrect.
$C_3H_7CO_2C_6H_5$ undergoes alkaline hydrolysis to form sodium butanoate and sodium phenoxide.

C Correct.
$C_3H_7CO_2C_6H_5$ undergoes acidic hydrolysis to form butanoic acid and phenol.

D Incorrect.
Phenol is too weak of a nucleophile to undergo condensation with carboxylic acid. Butanoyl chloride should be used instead.

26 A nonapeptide was hydrolysed partially using an enzyme to yield the following tripeptide fragments:

thr – ser –asn
pro – gly – his
asn – val – pro
pro –val –thr

What is the correct amino acid sequence in the nonapeptide?

A asn – val – pro – gly – his – thr – ser – asn – val

B thr – ser – asn – val – pro – gly – his – val – pro

C pro – val – thr – ser – asn – val – pro – gly – his
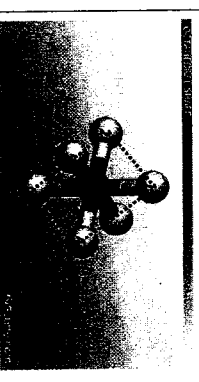
D his – gly – pro – val – asn – ser – thr – val – pro

Answer: C

pro –val –thr
thr – ser –asn
asn – val – pro
pro – gly – his

pro – val – thr – ser – asn – val – pro – gly – his

27 Which diagram correctly shows the arrangement of the six coordinate bonds in a regular octahedral complex of copper?
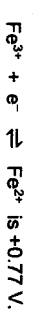
A   B   C   D

Answer: C

In the octahedral geometry, atoms 1,2,4 and 6 are in the same plane and bonds are represented as solid lines. Atom 5 is going out of the plane and the bond is represented by a wedge. Atom 3 is going into the plane and the bond is represented by a dash.

28 The standard redox potential for the half-cell reaction

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \text{ is } +0.77 \text{ V.}$$

Which cell would be used to determine this standard value?

A Fe electrode in 1 mol dm⁻³ Fe³⁺ against Fe electrode in 1 mol dm⁻³ Fe²⁺

B Pt electrode in 1 mol dm⁻³ Fe³⁺ against Pt electrode in 1 mol dm⁻³ Fe²⁺

C Fe electrode in a solution containing 1 mol dm⁻³ Fe³⁺ and 1 mol dm⁻³ Fe²⁺ against a standard hydrogen electrode

D Pt electrode in a solution containing 1 mol dm⁻³ Fe³⁺ and 1 mol dm⁻³ Fe²⁺ against a standard hydrogen electrode

23   24

Answer: D

The standard electrode potential of an element is the potential difference between the element and the aqueous solution of its ion at 1 mol dm^{-3} relative to that of the standard hydrogen electrode at 298 K and 1 bar. The electrode here is a platinum electrode as there is no iron metal present in the equation.

29   Use of the Data Booklet is relevant to this question.
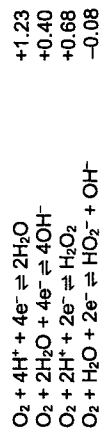   A hydrogen-oxygen fuel cell is shown.
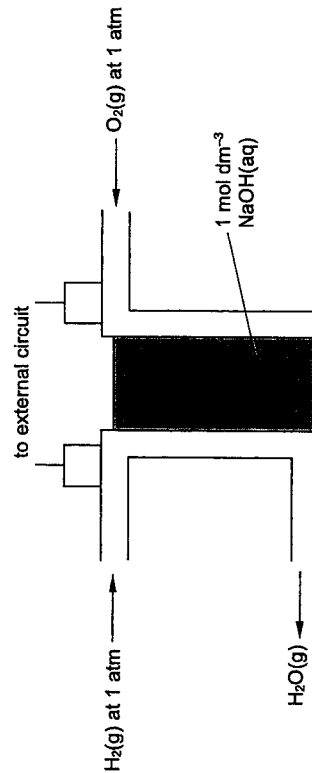
Which E° value should be used for the cathode?

A   −0.08 V

B   +0.40 V

C   +0.68 V

D   +1.23 V

Answer: B

Reduction of O₂ occurs at the cathode.

There are 4 equations in the Data Booklet that describes the reduction of O₂:

$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ +1.23
$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$ +0.40
$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$ +0.68
$O_2 + H_2O + 2e^- \rightleftharpoons HO_2^- + OH^-$ −0.08

We will select the half-equation with the most positive E° value that is in the alkaline medium, i.e. +0.40V.

30   Use of the Data Booklet is relevant to this question.
     An experiment is set up as shown to study the corrosion of iron.
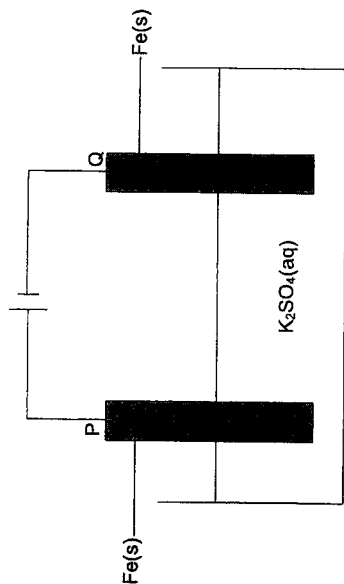
What will occur at electrodes P and Q?

	electrode P	electrode Q
A	no change in mass	decrease in mass and H₂ evolved
B	no change in mass	decrease in mass and SO₂ evolved
C	decrease in mass	no change in mass and SO₂ evolved
D	decrease in mass	no change in mass and H₂ evolved

Answer: D

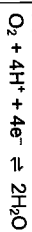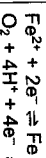Electrode P is the positive anode, while electrode Q is the negative cathode

Since oxidation occurs at the anode, while reduction occurs at the cathode,

At the anode:

$Fe^{2+} + 2e^- \rightleftharpoons Fe$ $\qquad E^\circ = -0.44$ V

$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ $\qquad E^\circ = +1.23$ V

Oxidation of the Fe anode will occur at electrode P since it has the most negative E° and causing a decrease in the mass of the Fe electrode.

At the cathode:

$K^+ + e^- \rightleftharpoons K$ $\qquad E^\circ = -2.92$ V
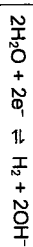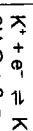
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ $\qquad E^\circ = -0.83$ V

The Fe electrode will not dissolve since Fe cannot be reduced and thus no change in mass of the Fe electrode.

H_2 gas will be evolved since it has the most positive E°.

ANSWER KEY

A	D	D	B	A
D	C	A	A	D
C	C	A	A	B
B	C	C	D	B
C	B	A	B	C
D	C	B	C	D

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CHEMISTRY

9729/02

Paper 2 Structured Questions

29 August 2022

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class in the spaces at the top of this page.
Write in dark blue or black pen on both sides of the paper.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, highlighters, glue or correction fluid/tape.

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.

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

For Examiner's Use	
1	/ 14
2	/ 17
3	/ 12
4	/ 16
5	/ 16

	units	significant figures
Penalty		

Overall	/ 75

2

Answer all the questions in the spaces provided.

1 Gallium, chromium and iron are metals that are found in Period 4 of the Periodic Table.

(a) (i) Naturally occurring gallium, Ga, is a mixture of two isotopes.

Table 1.2 shows the relative percentage abundance of the two isotopes.

relative mass	relative % abundance
68.9256	60.11
70.9247	39.89

Table 1.2

Calculate the relative atomic mass of Ga to four significant figures.
Show your working. [2]

Relative atomic mass of Ga = $\dfrac{(68.9256 \times 60.11) + (70.9247 \times 39.89)}{100}$ = **69.72**

(ii) Gallium reacts with nitrogen to form gallium nitride, GaN.

Calculate the volume of nitrogen gas needed to react with 10 kg of gallium at s.t.p.. [2]

$Ga(s) + \tfrac{1}{2}N_2(g) \rightarrow GaN(s)$

Amount of Ga = 10000 ÷ 69.7 = 143.47 mol
Amount of N_2 needed = 0.5 × 143.47 = **71.736 mol**
Volume of N_2 needed = 71.736 × 22.7 = **1630 dm³**

(b) Chromium(III) hydroxide, $Cr(OH)_3$, is sparingly soluble in water.

$Cr(OH)_3(s) \rightleftharpoons Cr^{3+}(aq) + 3OH^-(aq)$
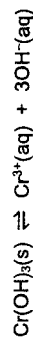
(i) Write an expression for the solubility product, K_{sp}, of chromium(III) hydroxide, stating its units. [2]

$K_{sp} = [Cr^{3+}][OH^-]^3$, units: $mol^4\ dm^{-12}$

This document consists of **28** printed pages.

(ii) Calculate the concentration of $OH^-(aq)$ in a saturated solution of chromium(III) hydroxide, given the value of K_{sp} is 6.7×10^{-31}. [2]

Let the solubility of $Cr(OH)_3$ be x mol dm⁻³

$[Cr^{3+}] = x$ mol dm⁻³, $[OH^-] = 3x$ mol dm⁻³
$K_{sp} = [Cr^{3+}][OH^-]^3 = (x)(3x)^3$
$6.7 \times 10^{-31} = 27x^4$
$x = \mathbf{1.2550 \times 10^{-8}}$ **mol dm⁻³**
$[OH^-] = 3 \times (1.2550 \times 10^{-8}) = \mathbf{3.77 \times 10^{-8}}$ **mol dm⁻³**

(iii) Describe and explain how the solubility of chromium(III) hydroxide is affected by adding $Cr_2(SO_4)_3(aq)$. [1]

When $Cr_2(SO_4)_3(aq)$ is added, it **increases the concentration of Cr^{3+}**. This cause the **position of equilibrium to shift to the left** to **decrease $[Cr^{3+}]$**, hence **solubility of $Cr(OH)_3$ decreases.**

(c) Iron(II) oxide, FeO, is used to form Fe_3O_4 as shown.

$$4FeO(s) \rightarrow Fe(s) + Fe_3O_4(s)$$
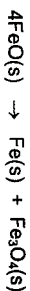
Each formula unit of Fe_3O_4 contains one Fe^{2+} and two Fe^{3+} ions.

(i) Using oxidation number, show how the reaction can be described as a *disproportionation reaction*. [1]

The oxidation number of Fe is simultaneously decreased from +2 in FeO to 0 in Fe and +2 in FeO to +3 in Fe_3O_4.

$Fe_3O_4(l)$ can be electrolysed using inert electrodes to form Fe.

(iii) Write the half-equation for the reaction that occurs at the anode during the electrolysis of $Fe_3O_4(l)$. [1]

$$2O^{2-}(l) \rightarrow O_2(g) + 4e^-$$

[Turn over
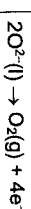
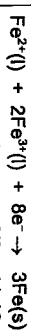
(iii) Calculate the maximum mass of iron metal formed when $Fe_3O_4(l)$ is electrolysed for 6 hours using a current of 50 A.

Assume that one Fe^{2+} and two Fe^{3+} ions are discharged at the same rate. [3]

$Q = I \times t = 50 \times (6 \times 60 \times 60) = 1.08 \times 10^6$ C = n_eF
$n_e = (1.08 \times 10^6) \div (96500) = 11.19$ mol

$Fe^{2+}(l) + 2Fe^{3+}(l) + 8e^- \rightarrow 3Fe(s)$
Amount of Fe formed = 3/8 × 11.19 = 4.20 mol
Mass of Fe formed = 4.20 × 55.8 = **234 g**

[Total: 14]

2 (a)   An organic compound **A**, C_5H_yO, undergoes complete combustion to produce CO_2 and H_2O.

The value of y in the molecular formula of **A** can be determined by exploding it with an excess oxygen and analysing the products of the combustion.

(i) Balance the following equation, in terms of y, for the complete combustion of one mole of compound **A** at 300 °C and 1 atm.

$C_5H_yO(g)$ + ... $O_2(g)$ → .... $CO_2(g)$ + ... $H_2O(g)$ [1]

$$C_5H_yO(g) + \left(\frac{18+y}{4}\right)O_2(g) \rightarrow 5CO_2(g) + \left(\frac{y}{2}\right)H_2O(g)$$

(ii) When 10 cm³ of gaseous compound **A** was mixed with an excess oxygen at 300 °C and 1 atm, there is an expansion of volume by 25 cm³.

Determine the value of y. [2]

Using Avogadro's Law where mole ratio = volume ratio,

$$C_5H_yO(g) + \left(\frac{18+y}{4}\right)O_2(g) \rightarrow 5CO_2(g) + \left(\frac{y}{2}\right)H_2O(g)$$

	$C_5H_yO(g)$	$\left(\frac{18+y}{4}\right)O_2(g)$	$5CO_2(g)$	$\left(\frac{y}{2}\right)H_2O(g)$
Mole	1	$\left(\frac{18+y}{4}\right)$	5	$\left(\frac{y}{2}\right)$
Volume	10	$\left(\frac{18+y}{4}\right) \times 10$	50	$\left(\frac{y}{2}\right) \times 10$

Volume of gases produced = Volume of CO_2 + Volume of H_2O = $50 + \left(\frac{y}{2}\right) \times 10 = (50 + 5y)$ cm³

Volume of gases used up = Volume of **A** + Volume of O_2 reacted = $10 + \left(\frac{18+y}{4}\right) \times 10 = \left(\frac{110+5y}{2}\right)$ cm³

[Turn over

6

(ii) Table 2.1 gives the melting points of $CaCN_2$ and NH_2CN.

Table 2.1

compound	melting point / °C
$CaCN_2$	1340
NH_2CN	44

Explain, in terms of structure and bonding, the difference in melting point between $CaCN_2$ and NH_2CN. [2]

- $CaCN_2$ has a higher melting point than NH_2CN.
- NH_2CN has a **simple molecular structure with hydrogen bonds** between its molecules.
- $CaCN_2$ has a **giant ionic lattice** held together by the **electrostatic attractions between Ca^{2+} and CN_2^{2-} ions.**
- As the **ionic bonds in $CaCN_2$ is stronger than the hydrogen bonds between NH_2CN molecules, more energy** is required to overcome them during melting.

(d) When CO_2 reacts with H_2, methanol, CH_3OH, is produced according to equation.

$$CO_2(g) + 3H_2(g) \rightarrow CH_3OH(l) + H_2O(l)$$

Table 2.2 shows the standard enthalpy and entropy changes of reaction for this process at 298K.

Table 2.2

ΔH° at 298 K	-131 kJ mol^{-1}
ΔS° at 298 K	-410 J K^{-1} mol^{-1}

(i) Explain why the process shows an overall negative value for ΔS°. [1]

The ΔS° **is negative** as there is a **decrease in number of moles of gaseous molecules.** There is a **decrease in the number of ways to arrange the gaseous molecules.** Hence the **disorder of the system decreases.**

(ii) Calculate the standard Gibbs free energy change, ΔG°, for this reaction at 298 K. [1]

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
$\Delta G^\circ = -131 - (298)(-0.41) = -8.82$ kJ mol^{-1}

5

Expansion in volume = Volume of gases produced − Volume of gases used up
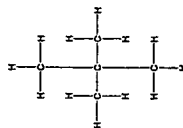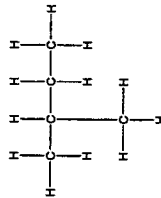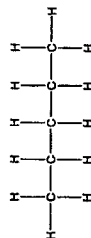
$25 = (50 + 5y) - \left(\dfrac{110 + 5y}{2}\right)$

$y = 12$

(iii) Draw the arrangement of the hybridised orbitals of one of the carbon atoms in Compound **A**. [1]
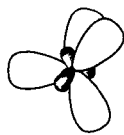
(b) Draw the displayed formula of all the constitutional (structural) isomers with the formula C_5H_{12}. [1]

(c) Cyanamide, NH_2CN, is an organic compound used in agriculture and in the synthesis of pharmaceuticals.
The carbon atom is bonded to both nitrogen atoms in the cyanamide molecule.

Cyanamide can be produce by the hydrolysis of calcium cyanamide in the presence of carbon dioxide.

$$CaCN_2 + H_2O + CO_2 \rightarrow CaCO_3 + NH_2CN$$

(i) Draw a 'dot-and-cross' diagram of the cyanamide molecule.
You should distinguish carefully between electrons originating from the central atom and those from the other atoms. [1]

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7

(iii) Predict the effect of increasing the temperature on the spontaneity of this reaction.
Explain your answer. [2]

$\Delta H^\ominus$ is negative, $\Delta S^\ominus$ is negative
$\Delta G = \Delta H - T\Delta S$

As temperature increases, **magnitude of** $T\Delta S^\ominus$ **> magnitude of** $\Delta H^\ominus$
$\Delta G > 0$ reaction become **less spontaneous** as temperature increases.

or

As temperature increases, $-T\Delta S$ **becomes more positive**, hence ΔG **becomes more positive** (ΔH is negative). So reaction become **less spontaneous** as temperature increases.

(e) (i) Define the term *standard enthalpy change of combustion*. [1]

Standard enthalpy change of combustion is the heat evolved when 1 mole of a substance is completely burnt in excess oxygen at 298 K and 1 bar.

(ii) Use of the *Data Booklet* is relevant to this question.

In an experiment to determine the standard enthalpy change of combustion of ethanol, CH_3CH_2OH, 0.230 g of ethanol was burned, and the heat given off raised the temperature of 100 g of water by 16.3 °C.

Calculate the enthalpy change of combustion, $\Delta H^\ominus_c$, of ethanol. [2]

Heat transferred = $100 \times 4.18 \times 16.3$ = **6813.4 J**
Amount of ethanol burnt = $0.230 \div 46.0$ = **0.00500 mol**
$\Delta H^\ominus_c = -(6813.4 \div 0.00500)$ = **−1360 kJ mol⁻¹**

(iii) Suggest one reason why the value for the enthalpy change of combustion of ethanol determined by a simple laboratory calorimetry experiment is likely to be lower than the true value. [1]

- Heat loss to the surrounding
- Incomplete combustion of the ethanol
- Some ethanol evaporated before weighing
- Heat capacity of the calorimeter is not accounted for

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(f) The equation below represents the standard enthalpy change of formation of propan-1-ol.

$$3C(s) + 4H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow CH_3CH_2CH_2OH(l)$$

Calculate the standard enthalpy change of formation, $\Delta H^\ominus_f$, of liquid propan-1-ol using the data given in Table 2.3.

Table 2.3

standard enthalpy change of combustion of $CH_3CH_2CH_2OH(l)$	−2021 kJ mol⁻¹
standard enthalpy change of combustion of C(s)	−393.5 kJ mol⁻¹
standard enthalpy change of formation of $H_2O(l)$	−285.8 kJ mol⁻¹

$\Delta H^\ominus_f$ of $H_2O(l) = \Delta H^\ominus_c$ of $H_2(g)$
$\Delta H^\ominus_f$ of $CH_3CH_2CH_2OH(l)) = 3(-393.5) + 4(-285.8) - (-2021.0)$ = **−303 kJ mol⁻¹**

[1]

[Total: 17]

3 Iodide ions react with peroxodisulfate ions to form iodine and sulfate ions as shown in the equation.

$$2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$$

The rate of the reaction can be determined by mixing 50.0 cm³ of 0.200 mol dm⁻³ of aqueous potassium iodide with 50.0 cm³ of 2.00 mol dm⁻³ aqueous potassium peroxodisulfate. At various time intervals, a portion of the reaction mixture would be drawn, quenched and titrated against a standard solution of aqueous sodium thiosulfate, $Na_2S_2O_3(aq)$.

The volume of sodium thiosulfate used is directly proportional to the volume of iodine produced.

(a) Outline how you would collect sufficient data to allow a graph of volume of sodium thiosulfate against time to be drawn. You are provided with the same solutions which were used in the experiment described.

No details regarding use of specific glassware are required. [3]

Step 1: Using a measuring cylinder, add 50 cm³ of KI(aq) into a beaker.
Step 2: Using another measuring, add 50 cm³ of $K_2S_2O_8(aq)$ into the beaker.
Step 3: Start the stopwatch immediately.
Step 4: At $t = 2$ minute, pipette 10.0 cm³ of the reaction mixture into a conical flask.
Step 5: Pour ice/cold water into the conical flask immediately to quench the reaction.
Step 6: Titrate the solution in the conical flask with $Na_2S_2O_3(aq)$. When the solution turns pale yellow, add a few drops of starch and continue to titrate the blue-black solution decolourises.
Step 7: Repeat step 4 to 6 for $t = 4$, 6, 8 and 10 mins

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(c) The concentration of peroxodisulfate ions was halved and a new series of experiments carried out at the same temperature. When a similar graph was plotted, the gradient at each point was half that obtained from **(b)**.

What is the order of reaction with respect to peroxodisulfate ions? Explain your answer. [2]

When the **concentration of peroxodisulfate is halved, the rate of the reaction is halved.**

Since **rate of reaction is directly proportional to the concentration of peroxodisulfate**, order of reaction is one.

or

rate = $k[I^-][S_2O_8^{2-}]^x$ where x is the order of reaction with respect to $[S_2O_8^{2-}]$

When $[S_2O_8^{2-}]$ is halved, the new gradient = $k[\,½ × S_2O_8^{2-}]^x$.

Since the new gradient is half of the old gradient,

$$\frac{k(\tfrac{1}{2})^x[S_2O_8^{2-}]^x}{k[S_2O_8^{2-}]^x} = \frac{1}{2}$$

$(½)^x = ½$

$x = 1$

(d) The reaction between iodide and peroxodisulfate ions is very slow. If a small amount of aqueous iron(II) ions is added to the mixture, the rate of reaction increases.

(i) Explain why the iron(II) ions can be described as a *homogeneous catalyst*. [2]

Fe^{2+} is described as a homogeneous catalyst because it is in the **same physical state as the two reactants** and it is **not being consumed/used up by the reaction/amount left at the end as the same as the beginning.**

(ii) State the property, typical of transition metals, which allows iron(II) ions to behave as a catalyst in this reaction.

Include relevant chemical equations to support you answer. [3]

Transition elements are able to exhibit variable oxidations state and hence they can gain or lose electrons readily.

$2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \rightarrow 2Fe^{3+}(aq) + 2SO_4^{2-}(aq)$
$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$

[Total: 12]

9

(b) The order of reaction with respect to [KI] is one.

Use this information and the procedure given in **(a)** to sketch a graph on Fig. 3.1 showing the relationship between the time taken to draw out the reaction mixture and the volume of sodium thiosulfate added.
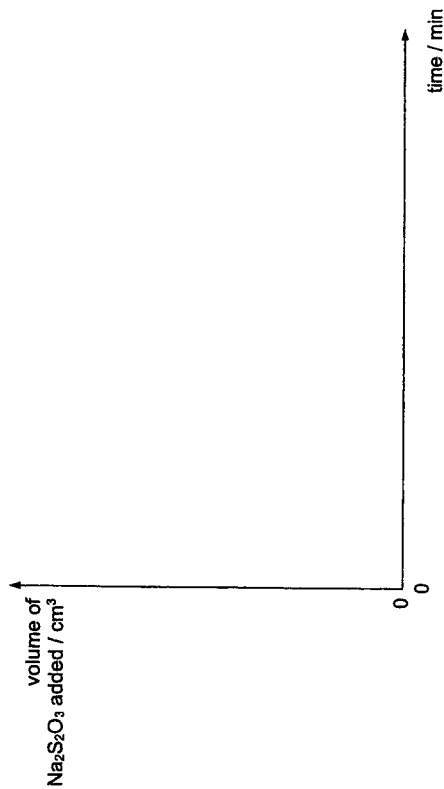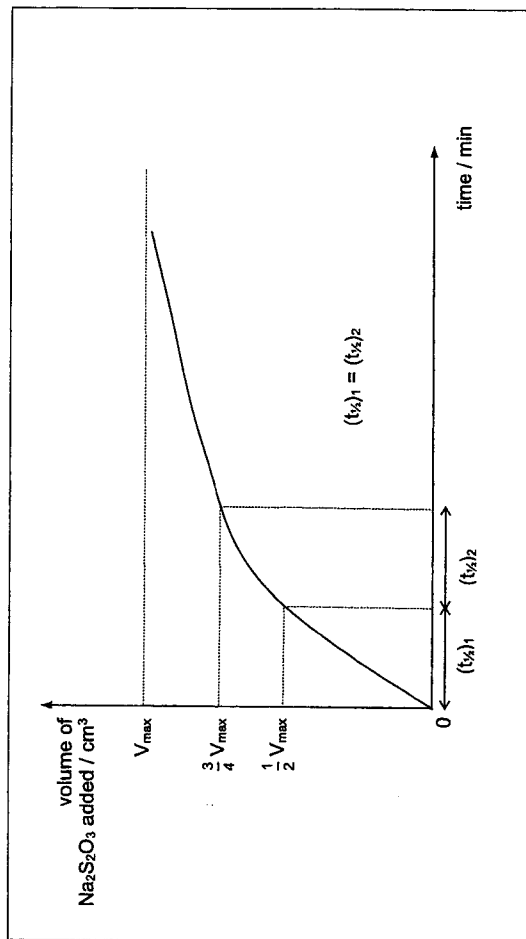No calculations for volume of sodium thiosulfate are required. [2]

Fig. 3.1

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4 **(a)** Amphetamine is a synthetic stimulant drug that stimulates the nervous system. It is used for treatment of attention-deficit hyperactivity disorder (ADHD).

Amphetamine can be synthesised from phenylpropanone as shown in Fig. 4.1.

phenylpropanone

step 1
+ NH₃

step 2

step 3
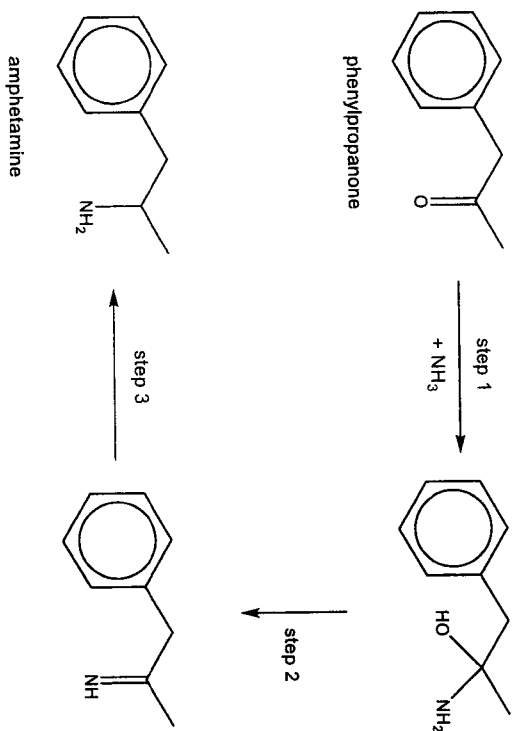
amphetamine

Fig. 4.1

(i) State the *type of reactions* that occur during each of the steps 1, 2 and 3.

step	type of reaction
1	
2	
3	

[3]

step	type of reaction
1	nucleophilic addition
2	elimination
3	reduction

[Turn over

12

(ii) Amphetamine can be also synthesised from (2-bromopropyl)benzene with ammonia as shown in Fig. 4.2.

(2-bromopropyl)benzene

NH₃
heat

amphetamine

Fig. 4.2

When plane-polarised light is passed through the amphetamine that is synthesised using this reaction, there is no effect.

Draw a mechanism that can explain the above observation. Show relevant lone pairs and dipole, and use curly arrows to indicate the movement of electrons pairs.
Use R to represent - $CH_2C_6H_5$.

[3]

Name of mechanism: Nucleophilic substitution, S_N1

step 1

step 2

slow

+ HBr

[Turn over

13

The building blocks of proteins are α-amino acids that have the general structure as shown.

$$H_2N-\underset{R}{\overset{H}{\underset{|}{\overset{|}{C}}}}-COOH$$

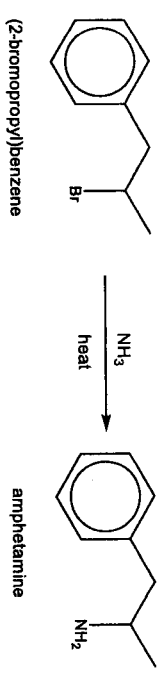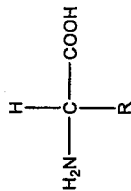Table 4.1 shows the pKa values of the different functional groups present in three α-amino acids.

Table 4.1

amino acid	R group	pKa of α-carboxyl group	pKa of α-amino group	pKa of side chain
aspartic acid	-CH$_2$CO$_2$H	2.09	9.82	3.86
lysine	-(CH$_2$)$_4$NH$_2$	2.15	9.16	10.67
glutamine	-(CH$_2$)$_2$CONH$_2$	2.20	9.10	-

(b) Mixtures of α-amino acids can be separated by ion-exchange chromatography.
This technique involves pouring the mixture of α-amino acids dissolved in water at pH 7.0 down a column containing an ion-exchange resin called DEAE-cellulose.

The structure of the DEAE-cellulose can be presented as shown below.
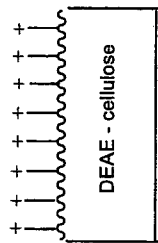
DEAE - cellulose

The '+' signs on the diagram show that the DEAE-cellulose is positively charged at pH 7.0.

The separation of the α-amino acids from the mixture is based on their net charge of their predominant species at pH 7.0.

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(i) A mixture of aspartic acid, lysine, and glutamine are dissolved in water and poured down the ion-exchange column as shown in Fig. 4.1.

mixture of aspartic acid, lysine and glutamine
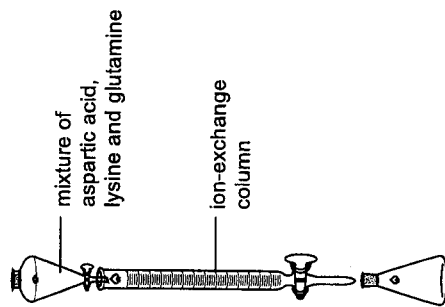
ion-exchange column

Fig. 4.1

Draw the structure of the predominant species of the three α-amino acids at pH 7.0 and suggest the order in which the α-amino acids will be collected.
Explain your answer.

order of α-amino acids collected	structure of predominant species of α-amino acid at pH 7.0	explanation
first		
second		
last		

[4]

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order of α-amino acids washed off the column	structure of predominant species of α-amino acid at pH 7.0	explanation
first	$^+H_3N-\overset{H}{\underset{(CH_2)_4NH_3^+}{C}}-CO_2^-$	At pH 7, lysine is **positively charged** and there will be **repulsion** with the positively charged DEAE-cellulose.
second	$^+H_3N-\overset{H}{\underset{(CH_2)_2CONH_2}{C}}-CO_2^-$	At pH 7, glutamine is **electrically neutral**.
last	$^+H_3N-\overset{H}{\underset{CH_2CO_2^-}{C}}-CO_2^-$	At pH 7, aspartic acid will be **negatively charged** and there will be **attraction** with the positively charged DEAE-cellulose.

(ii) Alanine and leucine are also α-amino acids.

$$H_2N-\overset{H}{\underset{CH_3}{C}}-COOH$$

alanine

$$H_2N-\overset{H}{\underset{CH_2CH(CH_3)_2}{C}}-COOH$$
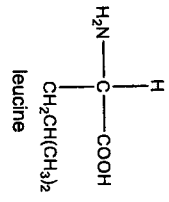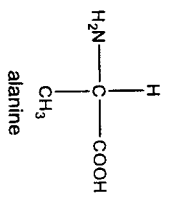
leucine

Explain why DEAE-cellulose cannot be used to separate a mixture of these two α-amino acids.

[1]

At pH 7, both alanine and leucine will be electrically neutral. R groups in both alanine and leucine are **not charged**. Both will not be attracted to DEAE cellulose and **will be washed off together at the same rate**.

(c) A tripeptide can be made by reacting aspartic acid, lysine and glutamine.

amino acid	R group
aspartic acid	-CH_2CO_2H
lysine	-(CH_2)_4NH_2
glutamine	-(CH_2)_2CONH_2

16
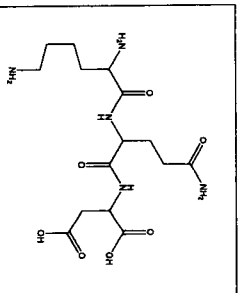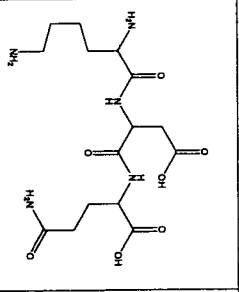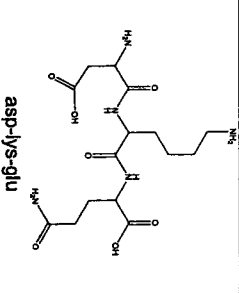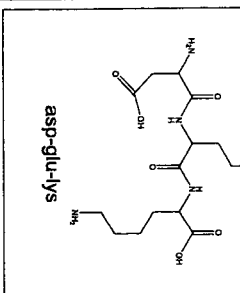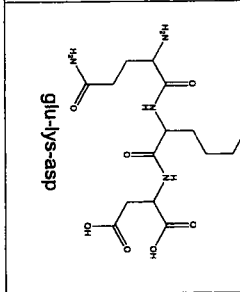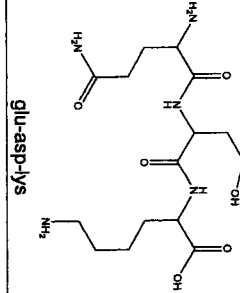
(i) Name the type of reaction occurring when a tripeptide in formed from the three amino acids.

[1]

condensation reaction

(ii) State the maximum number of different tripeptides that can be formed from the three amino acids.

[1]

Maximum number of different tripeptides = 3! = 6

(iii) Draw the skeletal formula of one of the possible tripeptides that can be formed from the three amino acids.

[2]

lys-glu-asp

asp-glu-lys

lys-asp-glu

glu-lys-asp

asp-lys-glu

glu-asp-lys

[Total: 15]

(iii) State a reagent you could use to convert ethanoic acid into ethanol. [1]

LiAlH₄ (in dry ether)

(b) Alcohol dehydrogenase enzyme combines with ethanol to form an enzyme-substrate complex which will then be converted into ethanal.

Fig. 5.2 shows the relationship between the [ethanol] and the rate of reaction, using a fixed amount of the alcohol dehydrogenase enzyme.
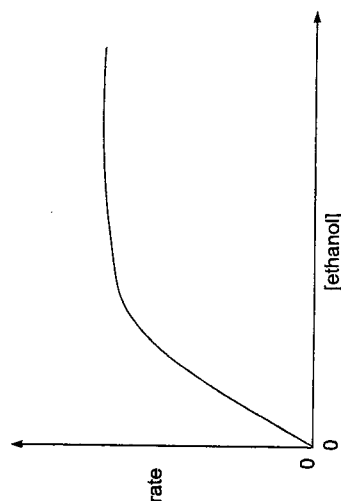
Fig. 5.2

Explain the relationship between [ethanol] and the rate of the enzyme catalysed reaction. [2]

For a fixed amount of enzyme, there are a finite number of active sites on the enzyme.

- At low [ethanol], **not all of the active sites are occupied**.
  rate ∝ [ethanol]
  reaction is **first order** with respect to the [ethanol].

- At high [ethanol], **all the active sites are occupied**.
  At this point, any increase in [ethanol] will not have any effect on the reaction rate.
  The reaction is **zero order** with respect to the [ethanol].

---

5 The alcoholic drinks industry produces a vast range of products every year. Alcohol in the body depressed the activity of the central nervous system and so drinking alcohol reduces vigilance, slows reaction times and impair judgement. Most countries in the world have introduced laws to control the use of alcohol, particularly in relation to operating machines and driving.

Blood alcohol concentration (BAC) is a good measure of the extent to which the activity of the central nervous system is depressed. It is usually defined as follows.

BAC = mg of ethanol per 100 cm³ of blood

After the consumption of too much alcoholic beverage, people sometimes experience a hangover the following day. There are a variety of causes of a hangover, one of these is the accumulation of the toxic metabolites of ethanol in the body.

Ethanol is removed from the blood by enzymes in a two-step process as shown in Fig. 5.1.
Ethanol first converted to ethanal by a group of enzymes known as alcohol dehydrogenase, and the ethanal formed is then converted to ethanoic acid by another enzyme, acetaldehyde dehydrogenase.

Fig. 5.1

Ethanal is relatively toxic and it is responsible for alcohol-related facial flushing, headaches, nausea and increased heart rate.

(a) In step 1 of Fig. 5.1, ethanol reacts with nicotinamide adenine dinucleotide, NAD⁺, a coenzyme, to form ethanal, H⁺ and a compound called NADH.

(i) State the type of reaction that has occurred for NAD⁺ in this reaction. [1]

reduction

(ii) Both ethanal and ethanoic acid can be obtained from ethanol in the laboratory.
State the reagents you could use to carry out these reactions. How would you ensure that the main product was ethanal rather than ethanoic acid. [1]

K₂Cr₂O₇, dilute H₂SO₄, heat with immediate distillation

(c) The rate equation for the conversion of ethanol to ethanal by the alcohol dehydrogenase enzyme is

$$\text{rate} = \frac{k_{cat}[AD][S]}{K_M + [S]}$$

Where:
[AD] is the concentration of the alcohol dehydrogenase enzyme,
[S] is the concentration of the substrate, ethanol,
k_{cat} is the rate constant,
K_M is a constant that measures the ease of dissociation of the enzyme-substrate complex back to the reactants.

Table 5.1 gives the values of k_{cat} and K_M for ethanol.

Table 5.1

k_{cat} / s^{-1}	K_M / mol dm^{-3}
1.33	1.00 × 10^{-3}

(i) The concentration of ethanol at the Singapore legal limit to drive a car, when expressed in mol dm^{-3}, is 1.74 × 10^{-2} mol dm^{-3}.

Using the information above, show that the rate equation of this reaction is

$$\text{rate} = k_{cat}[AD]$$

when [ethanol] is at the Singapore's legal limit to drive a car. [1]

At present in Singapore the legal limit to drive a car is 80 mg of ethanol per 100 cm^3 of blood.

Since the [ethanol] at the legal limit of 1.74 × 10^{-2} mol dm^{-3} is larger than K_M value of 1.00 × 10^{-3} mol dm^{-3}, K_M < [S] the rate equation becomes

$$\text{rate} = \frac{k_{cat}[AD][S]}{K_M + [S]} \approx \frac{k_{cat}[AD][S]}{[S]} = k[AD]$$

(ii) Calculate the rate loss of ethanol, in mol dm^{-3} s^{-1}, when a person is sobering up. [3]

The rate of loss of ethanol per 100 cm^3 of blood is 18.33 mg hr^{-1} and is a constant value.

Drivers who consume too much alcoholic beverages will need to wait for the BAC in their blood to fall below the legal limit. This process of waiting is known as sobering up.

rate loss of ethanol in g per 100 cm^3 of blood per hour = 18.333 × 10^{-3} g
rate loss of ethanol in g per 1 dm^3 of blood per hour = 0.18333 g
rate loss of ethanol in mol per 1 dm^3 of blood per hour = 0.18333 ÷ 46.0 = 3.9854 × 10^{-3} mol
rate loss of ethanol in mol per 1 dm^3 of blood per sec = 3.9854 × 10^{-3} ÷ (60 × 60) = 1.11 × 10^{-6} mol

(iii) Use your answer to (c)(i) and (c)(ii) to calculate the concentration of alcohol dehydrogenase enzyme in this person. [1]

rate = k[AD]
[AD] = rate ÷ k = (1.107 × 10^{-6}) ÷ 1.33 = 8.32 × 10^{-3} mol dm^{-3}

(iv) Calculate the time, in hours, required for the person with a BAC of 345 mg of ethanol per 100 cm^3 of blood to fall to the Singapore's legal limit to drive a car immediately after he has stopped consuming any more alcoholic beverages. [1]

Let t = time required
rate of loss of ethanol per 100 cm^3 of blood = 18.33 mg hr^{-1} = $\dfrac{345-80}{\Delta t}$ = $\dfrac{345-80}{t-0}$
t = 14.45 = 14.5 hours

(d) Methanol and ethane-1,2-diol are poisonous chemicals. When ingested, alcohol dehydrogenase metabolises these alcohols to form acidic metabolites that are highly toxic.

(i) Write an equation of the oxidation of ethane-1,2-diol to its corresponding acid. Use [O] to present the formula of the oxidising agent. [1]

$$HOCH_2CH_2OH + 4[O] \rightarrow (CO_2H)_2 + 2H_2O$$

(ii) Ethanol is used to treat victims of methanol or ethane-1,2-diol poisoning. This is because ethanol is a better substrate for alcohol dehydrogenase, and it will be metabolised preferentially by the enzyme.

Describe a simple chemical test that could be used to distinguish ethanol from methanol and state your observations clearly [2]

chemical test	ethanol	methanol
To each unknown in separate test-tubes, add I$_2$(aq), NaOH(aq) and warm	(pale) yellow precipitate	no precipitate
To each unknown in separate test-tubes, add KMnO$_4$(aq), H$_2$SO$_4$(aq) and warm	purple KMnO$_4$ decolourises	purple KMnO$_4$ decolourises and effervescence. Gas evolved gives a white precipitate with limewater

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(iii) Ethane-1,2-diol dissolves in water readily.

Draw a diagram to show how water molecules interact with the ethane-1,2-diol molecule.
Label the diagram to show the interaction involved. [1]
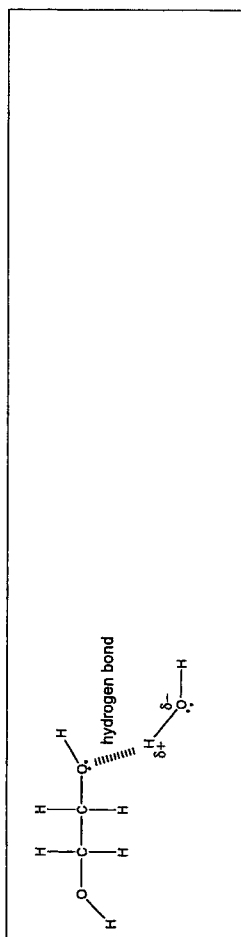
(e) The first four members of the series of carboxylic acids represented by the general formula $H-(CH_2)_n-CO_2H$ ($n = 0, 1, 2, 3...$) are fully soluble in water, but as the value of n increases from 4 upwards, the acids become increasingly insoluble.

By considering the relevant interactions between the molecules of the carboxylic acids with each other, and also with the solvent, suggest reason for this decreasing solubility.

As the value of n increases, the **instantaneous dipole-induced dipole interactions between RCO_2H molecules becomes increasingly significant and interferes with the hydrogen bonding between themselves and with H_2O molecules.**

The energy released by forming **the more predominant instantaneous dipole-induced dipole interactions** with water molecules is insufficient to overcome the **hydrogen bonding between water molecules and the more predominant instantaneous dipole-induced dipole interactions between the long chain carboxylic acid molecules.**

[Total: 17]

YISHUN INNOVA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME	SUGGESTED ANSWERS
CG	INDEX NO

CHEMISTRY

9729/03

Paper 3 Free Response

12 September 2022

2 hours

Candidates answer on the Question Paper.
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and index number on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use 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. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A
Answer all the questions.

Section B
Answer one question.

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

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

For Examiner's Use	
Section A	
1	/ 17
2	/ 18
3	/ 25
Section B	
4 or 5	/ 20
Penalty	units
	significant figures
Overall	/ 80

This document consists of **26 printed pages** and **6 blank pages**

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2

Section A

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

1 (a) Describe and explain the trend in the thermal stability of the hydrogen halides, HCl, HBr and HI. Include an equation for the thermal decomposition reaction in your answer. [3]

$$HX(g) \rightarrow \tfrac{1}{2}H_2(g) + \tfrac{1}{2}X_2(g)$$
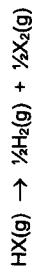
The thermal stabilities of the hydrogen halides **decrease** down the Group from HCl to HI.

This is because
- **the size of the halogens increases** from Cl to I and the valence orbital used for bonding is larger and more diffuse;
- **the effectiveness of the orbitals overlap decreases;**
- this result in **the weaker covalent bond formed between the hydrogen and halogen atoms** or quoting **H–X bond energies;**
- **lesser amount of energy** is required to overcome the covalent bond between the hydrogen and halogen atoms.

(b) Alkanes are generally considered to be unreactive compounds, showing an inertness to common reagents such as NaOH, H_2SO_4, and $K_2Cr_2O_7$.

(i) Suggest a reason why these reagents do not react with an alkane such as propane. [1]

The C–H bond is non-polar.
The C–H bond does not break heterolytically, only homolytically.

Propane can be converted into 2-chloropropane when it reacts with chlorine in ultraviolet (UV) light.

(ii) Describe the mechanism of the reaction between propane and chlorine in UV light. [3]

Free radical substitution

initiation   Cl—Cl $\xrightarrow{\text{UV}}$ 2C$l\cdot$

propagation $CH_3CH_2CH_3 + Cl\cdot \longrightarrow \dot{C}H_3CHCH_3 + HCl$

  $CH_3\dot{C}HCH_3 + Cl_2 \longrightarrow CH_3CH(Cl)CH_3 + Cl\cdot$

termination $2Cl\cdot \longrightarrow Cl_2$

  $CH_3\dot{C}HCH_3 + Cl\cdot \longrightarrow CH_3CH(Cl)CH_3$

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3

2 CH₃CHCH₃ ⟶ $H_3C-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_3$
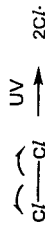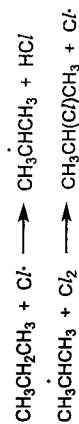
(c) (i) Define the term *lattice energy*. [1]

Lattice energy is the heat evolved when 1 mole of a solid ionic compound is formed from its constituent gaseous ions.

(ii) Use the data in Table 1.1, together with data from the *Data Booklet*, to calculate a value for the lattice energy of silver iodide, AgI(s). Show your working.

Table 1.1

	value / kJ mol⁻¹
electron affinity of iodine, I(g) + e⁻ → I⁻(g)	−295
enthalpy change of sublimation of iodine molecules, I₂(s) → I₂(g)	+62
standard enthalpy change of atomisation of Ag(s)	+285
standard enthalpy change of formation of AgI(s)	−62

[3]

Ag(s) + ½I₂(s) → [ΔH$_f$(AgI) = −62] → AgI(s)

Ag(s) + ½I₂(g)   ½ × ΔH$_{sub}$(I₂) = 31

Ag(s) + I(g)   ΔH$_{atm}$(I) = ½ BE (I-I) = 75.5

Ag(g) + I(g)   ΔH$_{atm}$(Ag) = +285

Ag⁺(g) + I(g)   1st I.E.'(Ag) = +731

Ag⁺(g) + I⁻(g)   E.A.(I) = −295

L.E. → AgI(s)
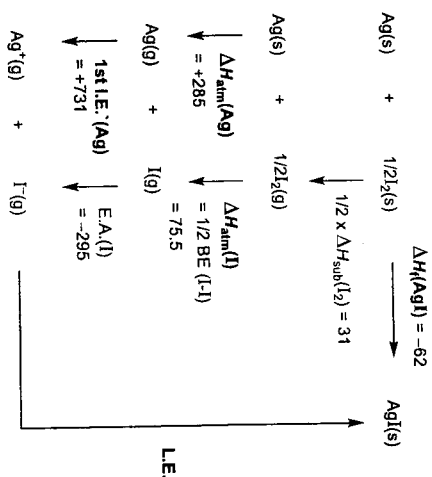
Lattice energy = −62 − [31 + 75.5 + (−295) + 285 + 731] = −889.5 = −890 kJ mol⁻¹

4

(d) Air bags in car inflate rapidly during an accident to protect the front passengers. The air bag contains sodium azide, NaN₃, silicon dioxide, SiO₂, and potassium nitrate, KNO₃.

On impact, three reactions take place.

The sodium azide first decomposes to sodium and nitrogen.

2NaN₃(s) → 2Na(s) + 3N₂(g)
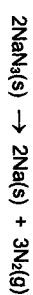
The nitrogen formed inflates the air bag while the sodium formed reacts with potassium nitrate to form sodium oxide, potassium oxide and additional nitrogen gas, which may be used to fill the air bag.

Potassium oxide and sodium oxide then react with silicon dioxide to form harmless metal silicates.

K₂O(s) + Na₂O(s) + SiO₂(s) → K₂Na₂SiO₄(s)
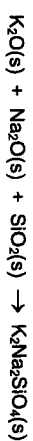
(i) Write an equation, with state symbols, for the reaction between sodium and potassium nitrate. [1]

10Na(s) + 2KNO₃(s) → 5Na₂O(s) + K₂O(s) + N₂(g)
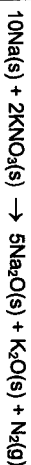
(ii) Calculate the mass of sodium azide needed to inflate an air bag of capacity 60 dm³ at room temperature and pressure. [2]
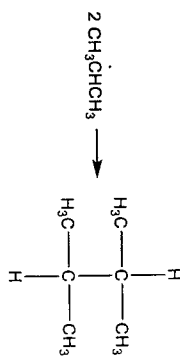
Amount of N₂ needed to fill a 60 dm³ air bag = 60 ÷ 24 = 2.50 mol

2 mol of NaN₃ produces 3 mol of N₂ and 2 mol of Na;

10 mol of Na produces 1 mol of N₂ in its reaction with KNO₃ which means 2 mol of Na produces 0.2 mol of N₂

Hence 2 mol of NaN₃ produces a total of 3.2 mol of N₂.

Amount of NaN₃ needed to produce 2.5 mol of N₂ = $\frac{2.5}{3.2} × 2$ = **1.5625 mol**

Mass of NaN₃ required = 1.5625 × (23.0 + 14.0 × 3) = **102 g**

(iii) A plant is designed to convert, at equilibrium, 50% of the reactants into ammonia. Assuming that the reactants are a mixture of N_2 and H_2 in a 1 : 3 ratio by volume, calculate the total equilibrium pressure necessary to bring about a 50% conversion at

- 600 K, and
- 750 K.

[2]

Let the number of moles of N_2 be x

	$N_2(g)$	+	$3H_2(g)$	⇌	$2NH_3(g)$
initial / mol	x		$3x$		0
change / mol	$-0.5x$		$-1.5x$		$+x$
equilibrium / mol	$0.5x$		$1.5x$		x

Total amount of gases at equilibrium = $3x$ mol

Let P = equilibrium pressure

$p(N_2) = (0.5x/3x) \times P = 1/6P$; $p(H_2) = (1.5x/3x) \times P = 1/2P$; $p(NH_3) = (x/3x) \times P = 1/3P$

$$K_p = \frac{(1/3P)^2}{(1/6P)(1/2P)^3} = \frac{16}{3P^2}$$

At 600 K,

$1.33 \times 10^{-2} = \dfrac{16}{3P^2}$

$P = 20$ atm

At 750 K,

$1.33 \times 10^{-4} = \dfrac{16}{3P^2}$

$P = 200$ atm

(iii) Discuss the relative advantage and disadvantage of using plants designed to run at 600 K instead of 750 K. [2]

The advantages of running at 600 K as compared to 750K,

- high yield as the forward reaction is exothermic and thus a lower temperature will favour the forward reaction; or
- low cost (or more safe) as the pressure required is not too high

The disadvantage of running at 600K as compared to 750K,

- the rate of the reaction is slower.

Theory shows that K_p varies with temperature according to the equation below.

$$\log_{10} \frac{K_p \,(\text{at temperature } T_1)}{K_p \,(\text{at temperature } T_2)} = \frac{-\Delta H}{2.30R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where: T_1 and T_2 are the temperatures in Kelvins,

ΔH is the enthalpy change of the reaction,

R is the molar gas constant.

(iii) To determine the amount of sodium azide in an impure sample, the azide present is first reacted with excess iodine.

$$2N_3^- + I_2 \rightarrow 3N_2 + 2I^-$$
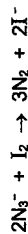
The amount of unreacted iodine is then titrated with a standard solution of sodium thiosulfate.

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

0.120 g of an impure sample of sodium azide was dissolved in water. The mixture was reacted with 25.0 cm³ of 0.050 mol dm⁻³ of aqueous iodine. The excess iodine was found to require 23.10 cm³ of 0.040 mol dm⁻³ aqueous sodium thiosulfate for reaction. Calculate the percentage purity of sodium azide in the sample. [3]

$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

Amount of $S_2O_3^{2-}$ used = $0.040 \times (23.10 \times 10^{-3}) = 9.240 \times 10^{-4}$ mol

Amount of excess $I_2 = 0.5 \times (9.240 \times 10^{-4}) = \mathbf{4.620 \times 10^{-4}}$ **mol**

Initial amount of I_2 used = $0.050 \times 0.0250 = 1.250 \times 10^{-3}$ mol

Amount of I_2 reacted with $N_3^- = (1.250 \times 10^{-3}) - (4.620 \times 10^{-4}) = \mathbf{7.880 \times 10^{-4}}$ **mol**

Amount of $NaN_3 = 2 \times (7.880 \times 10^{-4}) = 1.576 \times 10^{-3}$ mol

Mass of $NaN_3 = (1.576 \times 10^{-3}) \times (23.0 + 14.0 \times 3) = 0.1024$ g

Percentage purity of NaN_3 in the sample $= \dfrac{0.1024}{0.120} \times 100\% = \mathbf{85.4\%}$

[Total: 17]

2 (a) Ammonia is manufactured by the following reaction.

equation 2.1 $\qquad N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

The value of the equilibrium constant, K_p, measured at two different temperatures is shown in Table 2.1.

Table 2.1

temperature / K	K_p / atm⁻²
600	1.33×10^{-2}
750	1.33×10^{-4}

(i) Write the expression for the equilibrium constant, K_p, for this reaction. [1]

$$K_p = \frac{(p_{NH_3})^2}{(p_{N_2})(p_{H_2})^3}$$

(iv) Use the data in Table 2.1, together with data from the *Data Booklet*, and to calculate the enthalpy change, ΔH, in kJ mol⁻¹, for the reaction in equation 2.1. **[1]**

$$\log_{10}\frac{K_p \text{ (at temperature } T_1)}{K_p \text{ (at temperature } T_2)} = \frac{-\Delta H}{2.30R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\log_{10}\frac{1.33 \times 10^{-4}}{1.33 \times 10^{-2}} = \frac{-\Delta H}{2.30(8.31)}\left(\frac{1}{600} - \frac{1}{750}\right)$$

$\Delta H = -114678$ J mol⁻¹ = **–115 kJ mol⁻¹**

(v) The standard enthalpy change of formation of ammonia is –46 kJ mol⁻¹, given that ΔH for the reaction in equation 2.1 to be –92 kJ mol⁻¹.

Suggest one reason why this differs from the value calculated in **(iv)**. **[1]**

- The calculated ΔH from enthalpy change of formation is based on standard conditions of 298 K and 1 bar. **or**
- The calculated ΔH in **(iv)** is based on 50% conversion of the reactants.

(b) The K_b values of three bases, at 25 °C, are shown in Table 2.2.

Table 2.2

base	formula	K_b / mol dm⁻³
ammonia	NH_3	1.8×10^{-5}
ethylamine	$CH_3CH_2NH_2$	4.5×10^{-4}
phenylamine	(benzene ring with NH_2)	7.4×10^{-10}

(i) Calculate the pH of 0.25 mol dm⁻³ solution of ethylamine.

pOH = $-\log_3\sqrt{K_b \times c}$
= $-\log\sqrt{4.5 \times 10^{-4} \times 0.25}$
= **1.9744**
pH = 14 – 1.9744 = **12.0**

[2]

(ii) Explain the relative magnitudes of the K_b values in Table 2.2. **[2]**

Increasing order of base strength: **phenylamine < ammonia < ethylamine**

Ethylamine has the largest K_b value and is the strongest base as the lone pair on N is more available to accept a proton, as the electron donating –CH₂CH₃ group increases the electron density at the N atom making the lone pair of electrons on N atom more available to accept a proton.

Phenylamine has a smaller K_b value and is a weaker base than ammonia as the lone pair of electrons on the N atom is delocalised into the benzene ring. This decreases the electron density on nitrogen atom, making the lone pair of electrons on N atom less available to accept a proton.

(iii) Explain why amides, RCONH₂, are neutral, rather than basic. **[1]**

Amides are neutral because the lone pair of electrons on the N atom in the –CONH₂ group is not available for donation to H⁺ as it is delocalised into the C=O group.

(c) Nitrous acid, HNO₂, can be used to react with aminoalcohol to form an enlarged cycloketone via the Tiffeneau-Demjanov Rearrangement, as shown below.

cyclic aminoalcohol $\xrightarrow{\text{HNO}_2}$ cycloketone

Methylenecyclopentane can be used to synthesise cyclohexanone by the four-step route shown in Fig. 2.1.

methylenecyclopentane $\xrightarrow{\text{step 1}}$ **L** $\xrightarrow{\text{step 2}}$ **M** $\xrightarrow{\text{step 3}}$ **N** $\xrightarrow[\text{+ HNO}_2]{\text{step 4}}$ cyclohexanone

Fig. 2.1

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(b) (i) Draw a fully labelled diagram of the experimental set-up used to measure the standard electrode potential of the Ni²⁺(aq)/Ni(s) half-cell. Indicate clearly the positive and negative electrodes. **[3]**

$H_2(g)$ at 298K & 1 bar — Pt(s) — $[H^+] = 1$ mol dm⁻³ — + (cathode)
salt bridge
Ni(s) — $[Ni^{2+}] = 1$ mol dm⁻³ — – (anode)

Another cell composing of a standard Ni²⁺(aq)/Ni half-cell and a standard Cr₂O₇²⁻(aq)/Cr³⁺(aq) half-cell was set up.

(ii) Calculate $\Delta G^\ominus$, in kJ mol⁻¹, for the reaction that occurs **[2]**

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$ $\quad E^\ominus = +1.33$ V

$Ni^{2+} + 2e^- \rightleftharpoons Ni$ $\quad E^\ominus = -0.25$ V

Overall equation: $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O + 3Ni^{2+}$
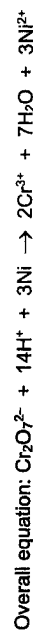
$E^\ominus_{cell} = +1.33 - (-0.25) =$ **1.58 V**

$\Delta G^\ominus = -nFE^\ominus_{cell} = -6 \times 96500 \times 1.58 = -914820$ J mol⁻¹ = **−915 kJ mol⁻¹**

(iii) Predict how the voltage of this cell would change, if at all, if the pH of the Cr₂O₇²⁻(aq)/Cr³⁺(aq) half-cell was increased. Explain your answer. **[1]**

When the pH of the Cr₂O₇²⁻(aq)/Cr³⁺(aq) half-cell was increased, the **[H⁺] decreased.**

As such the **$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$ equilibrium shifts to the left and the $E^\ominus_{cell}$ ($Cr_2O_7^{2-}$/Cr³⁺(aq)) becomes less positive. Hence, the voltage will be less positive.**
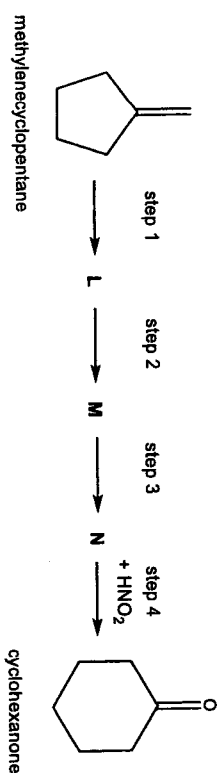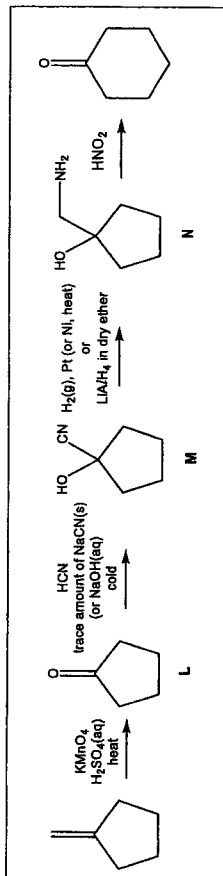

9

State the reagents and conditions required for step 1, 2 and 3 and suggest structures for the organic compounds **L**, **M** and **N**. **[6]**

$KMnO_4$, $H_2SO_4(aq)$ heat

HCN, trace amount of NaCN(s) (or NaOH(aq)) cold

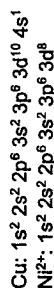$H_2(g)$, Pt (or Ni, heat) or LiAlH₄ in dry ether

HNO₂

[Total: 18]

3 (a) (i) Explain what is meant by the term *transition element*. **[1]**

A transition element is a **d-block element that forms at least one or more stable ions with a partially filled d-subshell.**

(ii) State the electronic configuration of the Cu atom and Ni²⁺ ion. **[2]**

Cu: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$

Ni²⁺: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8$

(iii) Explain why transition element complexes are usually coloured. **[3]**

In a complex,
- in the presence of ligands, the **3d orbitals of transition metal are split into two groups of orbitals with small energy difference**, ΔE, which falls within the energy (wavelength) range of visible light.
- Due to the **partially filled 3d orbitals, an electron from the lower energy 3d orbitals can absorb certain wavelengths of visible light and promotes to the higher energy 3d orbitals when exposed to light.**
- The colour seen is the **complement of the colour absorbed.**

(c) Table 3.1 give data about some physical properties of the elements calcium, iron and copper.

Table 3.1

property	calcium	iron	copper
relative atomic mass	40.1	55.8	63.5
atomic radius (metallic) / nm	0.197	0.126	0.128
ionic radius (2+) / nm	0.099	0.076	0.069
melting point / K	1112	1808	1358
density / g cm^{-3}	1.54	7.86	8.92
electrical conductivity / × 10^6 S cm^{-1}	0.298	0.100	0.596

(i) Explain why the atomic radii of iron and copper are similar to each other. [2]

Nuclear charge of copper is higher than iron as copper has higher number of protons.

Shielding effect of copper is higher than iron as the **additional electrons are added to the inner 3d subshell.**

The increase in nuclear charge is to a large extent **cancelled out by the increase in shielding effect** leading to **relatively constant nuclear charge.** Hence, the atomic radius of iron and copper are similar.

(ii) Explain why the densities of iron and copper are significantly greater than that of calcium using relevant data from Table 3.1. (No calculations are required.) [2]

Density = mass ÷ volume

Iron and copper have **greater relative atomic mass and smaller atomic / ionic radius than** calcium.

Hence, iron and copper have greater relative atomic mass to atomic radius ratio than calcium and therefore a higher density.

(iii) Write an equation, with state symbols, for the decomposition of the carbonate ion, CO_3^{2-}. [1]

When solid copper(II) carbonate is heated, it behaves in a similar way to the Group 2 carbonates.

$$CO_3^{2-}(s) \rightarrow CO_2(g) + O^{2-}(s)$$

(iv) Copper(II) carbonate decomposes at 300 °C while calcium carbonate decomposes at 830 °C.

Suggest an explanation for the difference in the temperature at which the two metal carbonates will decompose. [2]

While the charge of Cu^{2+} is the same as that of Ca^{2+}, the ionic radii of Cu^{2+} is **smaller than that of Ca^{2+}** [✓]. Hence the **charge density and polarising power of Cu^{2+} is higher than Ca^{2+}** [✓] resulting in the charge cloud of the large CO_3^{2-} anion is distorted (or polarised) to a **greater extent and a bigger weakening effect on the C–O bond within the CO_3^{2-}** [✓] by the Cu^{2+}. Thus, **less amount of energy is required to break the C–O bond** [✓] in the CO_3^{2-}.

Therefore, $CuCO_3$ decomposes at a lower temperature than $CaCO_3$.

(d) Describe and explain what you would see when NH_3(aq) is added slowly to a solution containing Cu^{2+}(aq) ions, until the NH_3(aq) is in excess.

Write equations for any reactions that occur. [4]

As a weak **Brønsted-Lowry base**, ammonia undergoes partial dissociation in aqueous medium to form hydroxide ions.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

A **blue precipitate**, $Cu(OH)_2$, is first formed when a **small amount of NH_3(aq) is added to** Cu^{2+}(aq), a blue solution.

$$[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Cu(OH)_2(s) + 6H_2O(l)$$

When excess NH_3(aq) is added, **NH_3 acts as a ligand**, the **blue precipitate dissolves to give a deep blue solution** due to the formation of the complex ion, $[Cu(NH_3)_4(H_2O)_2]^{2+}$.

$$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$$
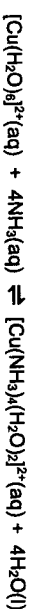
NH_3 is a stronger ligand than H_2O and displaces water via **ligand exchange reaction.**

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Section B

Answer **one** question in this section.

4 (a) Table 4.1 shows the melting points of these four elements found in Period 3 of the Periodic Table.

Table 4.1

element	melting point / °C
sodium	97
silicon	1410
sulfur	112
chlorine	–100

These four elements differ greatly in their melting points. Explain this variation. [4]

Silicon has the highest melting point due to its **giant covalent structure**. A large amount of energy is required to break the **strong electrostatic attraction between the two positive nuclei of Si atoms and shared pair of electrons** in the three-dimensional tetrahedral network.

Sodium has **giant metallic lattice structure**. A large amount of energy is required to break the strong **electrostatic forces of attraction between the 'sea of delocalised electrons' and the Na⁺ cations.**

Sodium has a lower melting point than silicon because the **metallic bonds in sodium is weaker than the covalent bonds in silicon.**
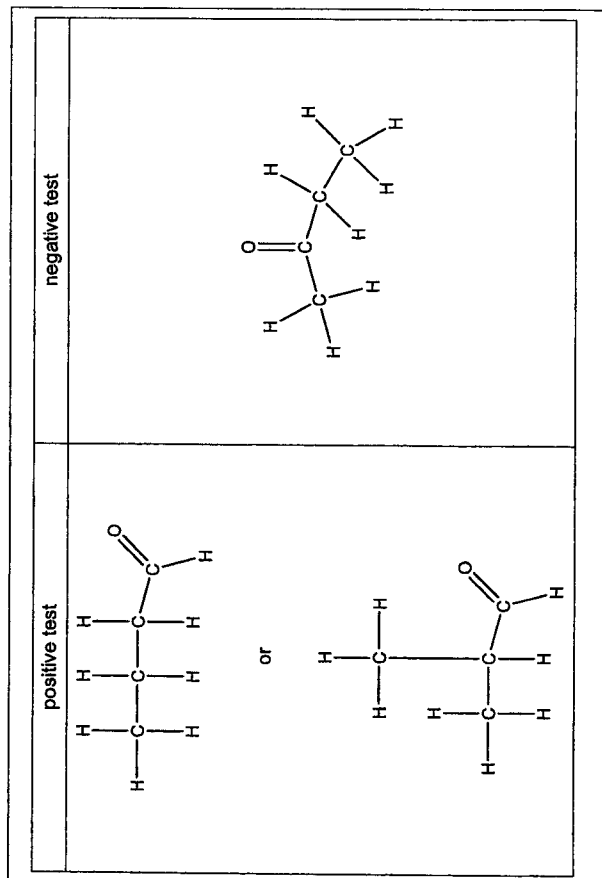
Sulfur and chlorine have lower melting points than silicon since they are **simple molecular molecules with weak instantaneous-dipole induced-dipole between the molecules.** A lower amount of energy is required to overcome the weak intermolecular instantaneous-dipole induced-dipole attractions.

Sulfur has a higher melting point than chlorine as it has a larger electron cloud and hence its electron cloud is more easily polarised **and the strength of instantaneous-dipole induced-dipole between S₈ molecules are stronger.**

The **instantaneous-dipole induced-dipole between the sulfur molecules is stronger than the metallic bonds in sodium** and hence the melting point of sulfur is higher than that of sodium.

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(e) An alkaline solution of complexed Cu^{2+}(aq) is used in organic chemistry to test for a particular functional group.

Draw the displayed formulae of **one** compound with the molecular formula C_4H_8O that would show a positive result in this test, and the displayed formulae of **one** compound with the same molecular formula that would not. Label your structures clearly. [2]

positive test	negative test
or	

[Total: 25]

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(b) Beams of charged particles are deflected by an electric field.

(i) State two ways in which the behaviour of electrons in an electric field differs from that of protons. [1]

> The deflection of electrons will be toward the positive pole whereas the deflection of protons will be toward the negative pole.
>
> The angle of deflection of electrons occurs with a greater magnitude as an electron is much lighter than a proton.

(ii) In a particular experimental set-up, protons are deflected through an angle of +15°.

Assuming an identical set of experimental conditions, by what angles will the following particles be deflected?

- $^2H^-$
- $^3He^{2+}$

[2]

angle of deflection ∝ charge/mass ratio

The charge/mass ratio of a proton is 1.

- charge/mass ratio of $^2H^- = \frac{-1}{2}$ and angle of deflection = −7.5°

- charge/mass ratio of $^3He^{2+} = \frac{+2}{3}$ and angle of deflection = +10°

(c) (i) State three basic assumptions of the kinetic theory as applied to an ideal gas. [2]

- molecules of ideal gas take up zero (or negligible) volume as compared to the volume of the container
- molecules of ideal gas have negligible intermolecular forces of attraction
- intermolecular collisions between molecules of ideal gas are perfectly elastic

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(ii) Diving tanks store a mixture of oxygen, nitrogen and helium gas at high pressures for deep-water diving for long periods of time.

When air bubbles are released underwater, they expand in size. A 10 cm³ bubble was released from a diver, 120 m below the water surface at a pressure of 1300 kPa and temperature of 10 °C.
It was estimated that pressure increases by 101 kPa with each 10 m depth.

Calculate the volume of the air bubble when it ascends towards the water surface by 60 m where the water temperature is 20 °C. [1]

Using pV = nRT and since the number of moles of the gas in the bubble

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{(1300000 - (6 \times 101000))V_1}{(273 + 20)} = \frac{(1300000)(10 \times 10^{-6})}{(273 + 10)}$$

$V_1 = 1.94 \times 10^{-5}$ m³

(d) Buttercups contain a poisonous cyclic compound called protoanemonin, $C_5H_4O_2$.

On catalytic hydrogenation, protoanemonin gives compound A, $C_5H_8O_2$. When A is heated with an acid, compound B, $C_5H_{10}O_3$, is formed. On standing, B slowly loses water and is converted back to A again.
Compound B gives a yellow precipitation with aqueous alkaline iodine and compound C, $C_4H_6O_4$, can be isolated.

Protoanemonin is an unstable oil which when treated with an acid or alkali, it is converted to compound D, $C_5H_6O_3$. Unlike protoanemonin, D effervesces with aqueous sodium hydrogencarbonate and gives a precipitate with 2,4-dinitrophenylhydrazine but does not react with Tollens' reagent.

Suggest possible structures for A, B, C, D and protoanemonin. For each reaction, state the type of reaction described and explain what the information tells you about the functional group present in each compound. [10]

5 (a) (i) Describe the reactions, if any, of the chlorides NaCl, AlCl₃ and SiCl₄ with water. Write equations for all reactions that occur, and suggest the pH of the resulting solutions. [3]
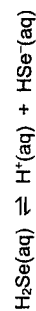
	NaCl	AlCl₃	SiCl₄
reactivity and observation	NaCl which is ionic **dissolves in water** with no further reaction to give a **colourless solution**	AlCl₃ which is covalent **dissolves in water** with partial hydrolysis to give a colourless solution	SiCl₄ which is covalent undergoes complete hydrolysis in water **vigorously to give a colourless solution, a white solid and steamy white fumes**
equation	$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$	$AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$ $[Al(H_2O)_6]^{3+}(aq) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H^+(aq)$	$SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(g)$
pH of resulting solution	7	3	1 – 2

(ii) Aluminium oxide is amphoteric.

Write equations to illustrate the acid-basic behaviour of aluminium oxide. [2]

$Al_2O_3(s) + 3H_2O(l) + 2NaOH(aq) \rightarrow 2NaAl(OH)_4(aq)$

$Al_2O_3(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2O(l)$
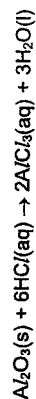
(b) Hydrogen selenide can act as a weak acid.

$$H_2Se(aq) \rightleftharpoons H^+(aq) + HSe^-(aq)$$

NaHSe is a weak base. The pH of a solution of 0.10 mol dm⁻³ NaHSe is 8.45.

Calculate the pKₐ of H₂Se. [3]

$pOH = 14 - 8.45 = 5.55$

$[OH^-] = 10^{-5.55} = 2.8183 \times 10^{-6} \text{ mol dm}^{-3}$

$K_b = \dfrac{[OH^-]^2}{c} = \dfrac{(2.8183 \times 10^{-6})^2}{0.10} = 7.9428 \times 10^{-11} \text{ mol dm}^{-3}$

$pK_b = -\log K_b = -\log (7.9428 \times 10^{-11}) = 10.1$

$pK_a = 14 - 10.1 = \textbf{3.90}$

[Total: 20]

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information	type of reaction	functional group present
On catalytic hydrogenation, *protoanemonin* gives compound **A**, C₅H₈O₂.	reduction [√]	*Protoanemonin* contains (two) alkene [√]
When **A** is heated with an acid, compound **B**, C₅H₁₀O₃, is formed.	hydrolysis [√]	A contains an ester. [√] B contains a **carboxylic acid** and an alcohol. [√]
On standing, **B** slowly loses water and is converted back to **A** again.	condensation [√]	
Compound **B** gives a yellow precipitation with aqueous alkaline iodine and compound **C**, C₄H₆O₄, can be isolated.	oxidation [√]	B contains the methyl carbinol, CH₃CH(OH)-, group. [√]
Protoanemonin is an unstable oil which when treated with an acid or alkali, it is converted to compound **D**, C₅H₆O₃.	hydrolysis [√]	*Protoanemonin* contains an ester [√]
D effervesce with aqueous sodium hydrogencarbonate	acid-carbonate [√]	D contains a **carboxylic acid** [√]
D gives a precipitate with 2,4-dinitrophenylhydrazine but does not react with Tollens' reagent.	condensation [√]	D contains a **ketone** [√]

[Turn over]

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(c) The Gattermann-Koch reaction is used to produce benzaldehyde as shown in Fig. 5.1.
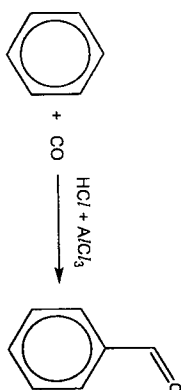

Fig. 5.1

(i) Name the *type of reaction* in the Gattermann-Koch reaction. [1]

electrophilic substitution

Fig. 5.2 shows the synthesis of compound U, which involves the Gattermann-Koch reaction.
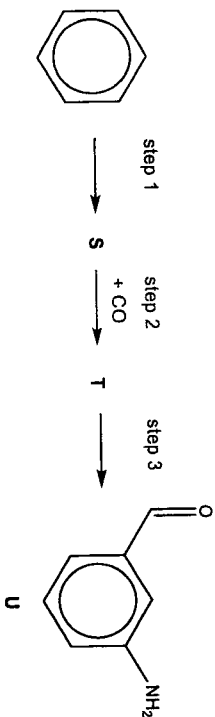
Fig. 5.2

(ii) Suggest the structures of the intermediate organic products S and T. [2]

S	T
NO$_2$	NO$_2$ CHO
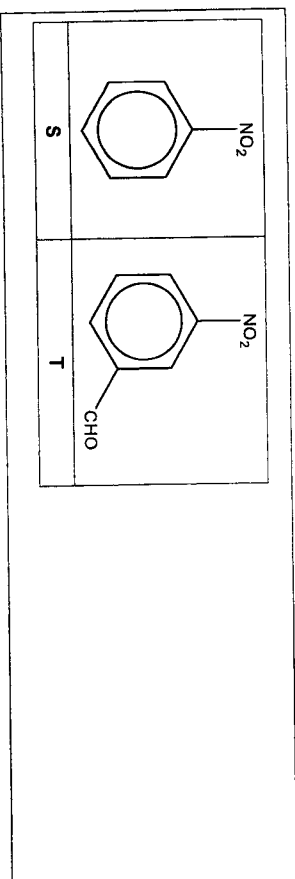
(iii) Suggest the reagents and conditions for step 1 and step 3. [2]

step 1: concentrated HNO$_3$, concentrated H$_2$SO$_4$, 55 °C
step 3: Sn, concentrated HCl, heat, followed by NaOH(aq)

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(d) Table 5.1 lists the pK$_a$ values for some other weak acids.

Table 5.1

acid	formula	pK$_a$
benzoic acid	CO$_2$H	4.20
2-chlorobenzoic acid	Cl CO$_2$H	2.89
2-hydroxybenzoic acid	OH CO$_2$H	2.97
4-hydroxybenzoic acid	HO CO$_2$H	4.54
thiobenzoic acid	C O SH	3.61

(i) Explain the difference in the pK$_a$ values between 2-chlorobenzoic acid and benzoic acid. [1]

pK$_a$: benzoic acid > 2-chlorobenzoic acid
acid strength: benzoic acid < 2-chlorobenzoic acid
stability of conjugate base: benzoate ion < 2-chlorobenzoate ion

2-chlorobenzoic acid is the strongest acid as the **negative charge on the O atom of its conjugate base (2-chlorobenozate ion) is dispersed due to the electron-withdrawing Cl atom**. This dispersion of charge stabilises the 2-chlorobenozate ion to a larger extent than the benzoate ion and 2-hydroxybenzoate ion. Hence, 2-chlorobenzoic acid **dissociates to a larger extent than** benzoic acid and 2-hydroxybenzoic acid.

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(ii) Suggest a reason why the pK_a value of 2-hydroxybenzoic acid is so much less than the pK_a of 4-hydroxybenzoic acid. [1]

2-hydroxybenzoic acid is a stronger acid than 4-hydroxybenzoic acid as the presence of –OH, stabilises its conjugate base (2-hydroxybenzoate ion) through **intra-molecular hydrogen bonding**. Hence, 2-hydroxybenzoic acid dissociates to a larger extent than 4-hydroxybenzoic acid.
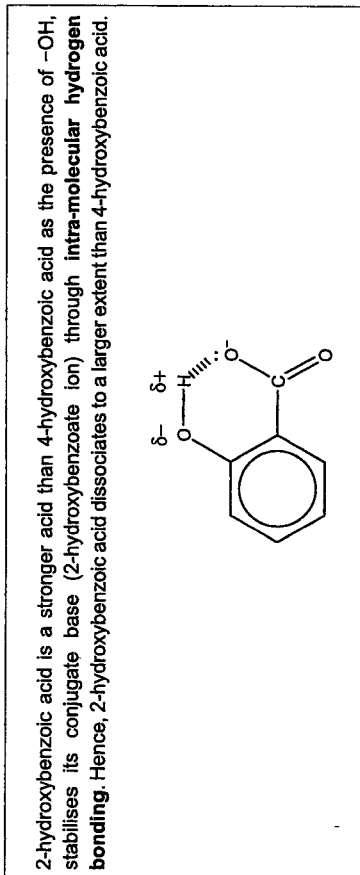
(iii) Thiobenzoic acid is related to benzoic acid by the replacement of one of the oxygen atoms with a sulfur atom.

Suggest a reason why the pK_a for thiobenzoic acid is lower than benzoic acid. [1]

Thiobenzoic acid is a stronger acid than benzoic acid because
• the S–H bond is weaker than the O–H and thus it can be broken more easily, or
• $C_6H_5COS^-$ is more stable than $C_6H_5COO^-$ because S atom is bigger so can accommodate the negative charge better.

(e) Enones are ketones having a neighbouring C=C double. Enones undergoes a reaction called conjugate addition, a type of nucleophillic addition reaction, with a primary amine.

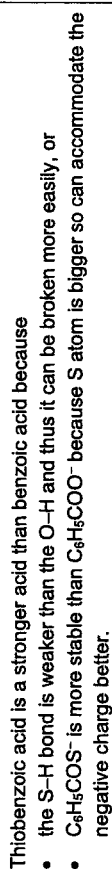The reaction of 3-butene-2-one, an enone, with ethylamine via conjugate addition is as shown.

3-butene-2-one $+$ CH₃CH₂NH₂ $\xrightarrow{\text{ethanol}}$ 4-N-ethylamino-2-butanone

ethylamine
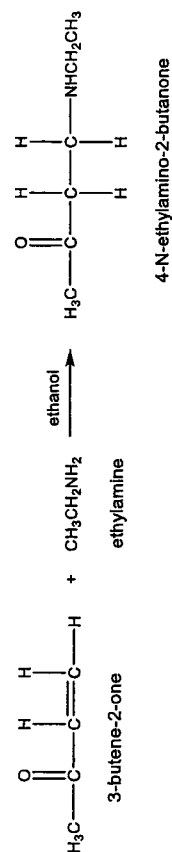
In this reaction, an amine is added directly to an alkene carbon.

The reaction takes place in 3 steps.

step 1   The amine attacks the terminal alkene carbon to form an enolate ion intermediate.

enolate ion
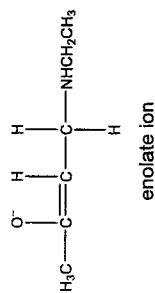
step 2   The intermediate will undergo rearrangement to form back the ketone and a carbanion.

step 3   The carbanion is then protonated to form the product.

(i) Suggest the mechanism for the conjugate addition reaction between 3-butene-2-one and ethylamine to form 4-N-ethylamino-2-butanone.

Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [3]

step 1

step 2

step 3

23
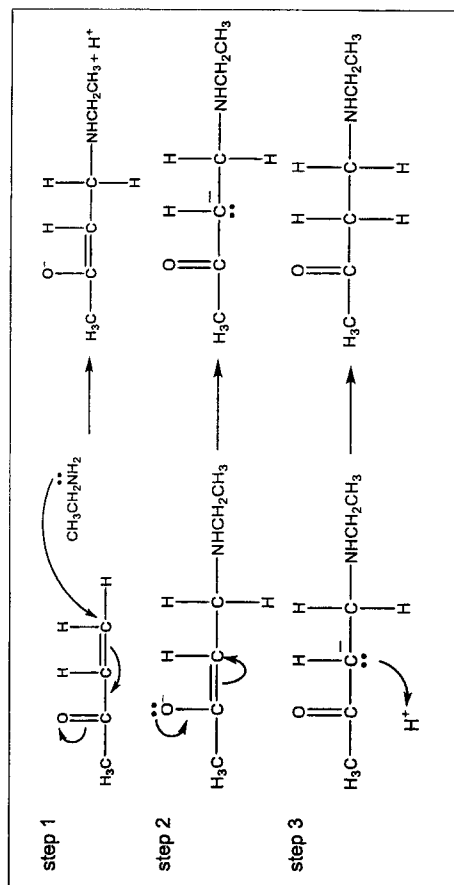
(ii) In the absence of the carbonyl group, there will be no reaction between butene and ethylamine.

Suggest why this is so.

[1]

Conjugate addition between butene and ethylamine does not occur because the **carbon atoms in the C=C have the same electronegativity**, thus the **carbon atoms do not have a partial positive charge** and thus are **not electron deficient** and therefore will not be approach by the NH₃ nucleophile.

[Total: 20]

24

Additional Answer Space

If you use the following pages to complete the answer to any question, the question number must be clearly shown.

[Turn over

25

Page 1

YISHUN INNOVA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION

CANDIDATE NAME	SUGGESTED ANSWERS

CLASS		DATE	

H2 CHEMISTRY

9729/04

Paper 4 Practical Paper

23 August 2022
2 hours 30 minutes

Candidates answer on question paper.
Additional Materials: As listed in the Confidential Instructions
Insert

READ THESE INSTRUCTIONS FIRST

Write your name and class in the spaces at the top of this page.
Give details of the practical shift and laboratory where appropriate, in the boxes provided.
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.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 23 and 24.

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.

Shift	
Laboratory	

For Examiner's use	
1	
2	
3	
4	
Total	**55**

This document consists of **24** printed pages.

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[Turn over

Page 2

2

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

1 **Determination of a value for the solubility product, K_{sp}, of calcium iodate(V), Ca(IO₃)₂**

The solubility in water of solid calcium iodate(V), Ca(IO₃)₂, is low. When a sample of this salt is mixed with water, a small amount dissolves and an equilibrium between the solid salt and its aqueous ions is established.

$$Ca(IO_3)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2IO_3^-(aq)$$
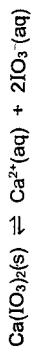
If separate aqueous solutions containing Ca²⁺ ions and IO₃⁻ ions are mixed, some of the solid salt is formed and, again an equilibrium is established.

When specified volumes of potassium iodate and calcium nitrate are mixed, some calcium iodate(V) is formed as a white solid. The mixture should be left to stand for some time.

After the solid is removed by filtration, the amount of iodate(V) ions left in the filtrate is determined as described below.

When excess potassium iodide, KI, is added to an acidified solution containing iodate(V) ions, iodine is liberated as follows.

reaction 1 $IO_3^-(aq) + 5I^-(aq) + 6H^+ \rightarrow 3I_2(aq) + 3H_2O(l)$
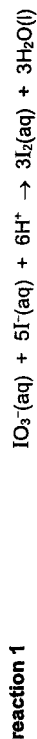
The liberated iodine is then titrated with a standard solution of sodium thiosulfate.

reaction 2 $2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$
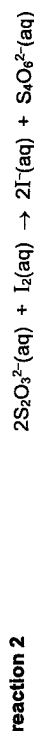
In this question, you will perform a titration to determine the solubility product, K_{sp}, of calcium iodate(V).

You are provided with:

• **FA 1**, 0.200 mol dm⁻³ potassium iodate, KIO₃
• **FA 2**, 1.00 mol dm⁻³ calcium nitrate, Ca(NO₃)₂
• **FA 3**, 0.0400 mol dm⁻³ sodium thiosulfate, Na₂S₂O₃
• **FA 4**, aqueous solution of potassium iodide, KI
• **FA 5**, dilute hydrochloric acid, HCl

You are also provided with starch solution.

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[Turn over

(a) Preparation of the reaction mixture

1. Use a measuring cylinder to transfer 50 cm³ of **FA 1** to the beaker labelled **reaction mixture**.
2. Use a measuring cylinder to transfer 20 cm³ of **FA 2** to the same beaker.
3. A precipitate will form, stir the mixture thoroughly. Leave this mixture to stand for 15 minutes to allow equilibrium to be reached.

While you are waiting for the mixture to reach equilibrium, proceed with Question 2(a).

(b) (i) **Analysing the filtrate**

1. Filter the reaction mixture through a **dry** filter paper into a **dry** conical flask, labelled **FA 6**. This is the filtrate, **FA 6**. Do not wash the white precipitate with water.
2. Fill a burette with **FA 3**.
3. Use a pipette to transfer 10.0 cm³ of **FA 6** into a 250 cm³ conical flask.
4. Use a measuring cylinder to add about 10 cm³ of **FA 4** to the conical flask.
5. Use a measuring cylinder to add about 2 cm³ of **FA 5** to the conical flask.
6. Run **FA 3** from the burette into the conical flask until the brown colour of the iodine fades to a pale yellow colour.
7. Add about 5 drops of starch solution to the conical flask. Continue adding **FA 3** until the blue-black colour **just disappears**.
8. Record your titration results, to an appropriate level of precision, in the space provided below.
9. Repeat points 3 to 7 until consistent results are obtained. Rinse the conical flask thoroughly between each titration.

Titration results

initial burette reading	/ cm³	0.00	2.00
final burette reading	/ cm³	36.50	38.50
volume of FA 3 used	/ cm³	36.50	36.50

[3]

(ii) From your titrations, obtain a suitable volume of **FA 3** to be used in your calculations. Show clearly how you obtained this volume. [3]

Volume of **FA 3** used = (36.50 + 36.50) ÷ 2 = 36.50 cm³

(c) (i) Calculate the amount of $S_2O_3^{2-}$ ions present in the volume of **FA 3** recorded in (b)(ii). [1]

Amount of $S_2O_3^{2-}$ ions = $(36.50 \times 10^{-3}) \times 0.0400 = 1.46 \times 10^{-3}$ **mol**

(ii) Calculate the amount of IO_3^- ions present in 10.0 cm³ of the filtrate, **FA 6**. [1]

$2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

Amount of I_2 = ½ × Amount of $S_2O_3^{2-}$ = ½ × (1.46 × 10⁻³) = 7.30 × 10⁻⁴ mol

$IO_3^-(aq) + 5I^-(aq) + 6H^+ \rightarrow 3I_2(aq) + 3H_2O(l)$

Amount of IO_3^- in 10.0 cm³ = 1/3 × Amount of I_2 = 1/3 × 7.30 × 10⁻⁴ = **2.4333 × 10⁻⁴ mol**

(iii) Calculate the total amount of IO_3^- ions present in the filtrate, **FA 6**. [1]

Amount of IO_3^- in 70.0 cm³ = (2.4333 × 10⁻⁴) × 7 = **1.70 × 10⁻³ mol**

(d) (i) Using the initial amount of IO_3^- ions in the reaction mixture prepared in (a), and your answer from (c)(iii), calculate the amount of IO_3^- ions precipitated as $Ca(IO_3)_2$. [1]

Initial amount of IO_3^- ions in the reaction mixture prepared = 0.200 × 50.0 × 10⁻³ = 0.0100 mol

Amount of IO_3^- precipitated = 0.0100 − 1.70 × 10⁻³ = **8.30 × 10⁻³ mol**

Page 5

(ii) Deduce the amount of Ca^{2+} ions removed by precipitation in **(a)**, point 3, and hence, calculate the amount of Ca^{2+} ions left in **FA 6**. [2]

$Ca(IO_3)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2IO_3^-(aq)$

Amount of Ca^{2+} removed by precipitation
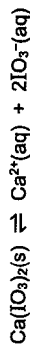
Amount of Ca^{2+} removed by precipitation = $\frac{1}{2}$ × Amount of IO_3^- precipitated
= $\frac{1}{2}$ × 8.2966 × 10⁻³ mol
= **4.15 × 10⁻³ mol**

Initial amount of Ca^{2+} added = 1.00 × 20.0 × 10⁻³ = 0.0200 mol
Amount of Ca^{2+} left in **FA 6** = 0.0200 − (4.15 × 10⁻³) = **0.0159 mol**

(e) (i) Write an expression for the solubility product, K_{sp}, of calcium iodate(V). [1]

$K_{sp} = [Ca^{2+}][IO_3^-]^2$

(ii) Use this expression, together with your answers to parts **(c)(iii)** and **(d)(ii)** to calculate a value for this solubility product. Include units in your answer. [1]

$[Ca^{2+}]$ = 0.0159 ÷ (70 ÷ 1000) = 0.227 mol dm⁻³
$[IO_3^-]$ = (1.70 × 10⁻³) ÷ (70 ÷ 1000) = 0.024285 mol dm⁻³
K_{sp} = 0.227 × (0.024285)² = **1.34 × 10⁻⁴ mol³ dm⁻⁹**

(f) A student added solid calcium nitrate to his filtrate, **FA 6**.

Predict, qualitatively, the effect of such an addition on the filtrate, and on the magnitude of the mean titre, in part **(b)(ii)**. Explain your answer. [2]

Predictions:
More precipitate will form and the titre value will be lower.

Explanation:
The addition of $Ca(NO_3)_2$ increases the concentration of Ca^{2+} and to remove some of the Ca^{2+}, the equilibrium moves towards the solid.
Hence, IO_3^- ions are removed from the solution causing the concentration of IO_3^- to be lower so less $S_2O_3^{2-}$ needed.

Page 6

(g) In part **(b)(i)**, point **1**, you are told to use **dry** apparatus and to avoid washing the residue with water. Suggest and explain the likely consequences on your mean titre value in part **(b)(ii)** if you failed to follow these instructions. [1]

Water would be added to the filtrate, causing **FA 6** to be diluted and the mean titre value would be lower.

(h) A teacher performed this experiment and obtained a value for the solubility product, K_{sp}, of 2.77 × 10⁻⁵. A literature value for this solubility product is 6.71 × 10⁻⁶ at 20 °C.

You should assume that apparatus of the same precision was used in each case.

Give a possible explanation for the higher value of K_{sp} obtained by the teacher. Suggest an improvement which might allow a value closer to the literature value to be obtained. [1]

Not all precipitate has had time to form/reaction has not reached equilibrium, so $[Ca^{2+}]$ and $[IO_3^-]$ too high.
Allow precipitate to form/equilibrium to establish by leaving the reaction mixture for a considerable time before filtering it.
or
The teacher's experiment is not carried out at 20 °C, so equilibrium position is displaced towards the aqueous ions/to the right (as the K_{sp} value is higher than actual).
Equilibrate the reaction mixture in a water bath at 20 °C for a considerable time before filtering it.

[Total: 18]

2 Qualitative Analysis

In this question, you will perform tests to
• investigate reactions involving vanadate(V) ion, VO_3^-
• deduce the functional groups present in four organic compounds.

You are provided with:
• **FA 7**, ammonium vanadate(V), NH_4VO_3
• zinc, Zn

Unless otherwise stated, the volumes given below are approximate and should be estimated rather than measured.

Keep the reaction mixture for use in 2(a)(ii).

(a) (i) To a 2 cm depth of **FA7** in a test-tube, add a small spatula of zinc. Leave for approximately 4 minutes with occasional shaking. Record all your observations.

[2]

Effervescence which pops a lighted splint.   Yellow solution turns blue and then to green finally to lilac/violet/purple.

(ii) To 1 cm depth of the **solution** from (a)(i) in a test-tube, add 1 cm depth of sulfuric acid. Then add potassium manganate(VII) a few drops at a time until no further reaction occurs. At this stage, the solution is pink because unreacted $KMnO_4$ is present.

Record all the changes you observe.

[2]

Solution turns from violet to blue then to green and finally to yellow   Purple $KMnO_4$ decolorises.

(iii) State the type of reaction occurring in the test in (a)(ii).

[1]

Redox

(b) You are provided with samples of **FA 8, FA 9, FA 10** and **FA 11**, each of which is an aqueous solution containing a different one of the following:

a carboxylic acid
a ketone
an alcohol
an aldehyde

You will perform the tests described in Table 2.1.

In addition to having access to the usual bench reagents, you are also provided with the following:
• iodine solution,
• solid sodium carbonate.

Perform the tests described in Table 2.1. Some of the observations have been completed for you. There is no need to carry those tests. Record your observations in Table 2.1.

Test and identify any gases evolved. If there is no observable change write **no observation change.**

Use a fresh sample of each solution in each test.

Table 2.1

	observations with FA 8	observations with FA 9	observations with FA 10	observations with FA 11
1. Add about 1 cm depth of **FA 8** in a test-tube. To this test-tube, add 6 drops of sodium hydroxide solution, followed by iodine solution, dropwise, until a permanent orange/red colour is present.	no observable change	no observable change	pale yellow precipitate formed	pale yellow precipitate formed
Warm the mixture in a beaker of hot water for two minutes.				
Add sodium hydroxide solution using a teat pipette until no further change is seen.				
Repeat using FA 10 instead of FA 8.				
Place about 2 cm depth of aqueous silver nitrate in a boiling tube. Then slowly add 1 cm depth of aqueous sodium hydroxide. Add aqueous ammonia slowly, with shaking, until the precipitate just dissolves. You can use a clean glass rod to stir the mixture and help dissolve the precipitate. Use this solution for test 2.				

2.	Place about 1 cm depth of FA 8 in a test–tube.	Effervescence observed.	No effervescence observed.	No effervescence observed.
	To this test tube, add a small spatula of sodium carbonate power.	White ppt formed with limewater.		
	Repeat using FA 10 and FA 11.			

[4]

(iv) Complete Table 2.2 with the functional groups present in FA 8, FA 10 and FA 11.

Give evidence from the observations in Table 2.1 and (b)(ii) to support your conclusions.

Table 2.2

	functional group present	evidence
FA 8	carboxylic acid	Effervescence with sodium carbonate which give white ppt with limewater shows that CO_2 is present. Only carboxylic acid is able to react with sodium carbonate.
FA 10	ketone	Pale yellow ppt formed show that $-COCH_3$ or $-CH(CH_3)OH$ is present but purple solution remains which shows that it cannot be oxidised so it must be ketone.
FA 11	alcohol	Pale yellow ppt formed show that $-COCH_3$ or $-CH(CH_3)OH$ is present and purple solution decolourise which shows that it can be oxidised so it must be alcohol.

[3]

[Total: 15]

2.	Add about 1 cm depth of the solution prepared in a test-tube.	no observable change	silver mirror formed	no observable change
	Add 1 cm depth of FA 8 to the test-tube, shake the tube and place it in the test-tube rack to stand.			
	Repeat using FA 9, instead of FA 8.			

[2]

(ii) The observations in Table 2.1 are sufficient to identify the functional group present in FA 9.

State the functional group present in FA 9 and give evidence to support your answer.

functional group in FA 9 aldehyde ....

evidence silver mirror formed shows that FA 9 is an aldehyde ....

[1]

(iii) Devise and perform simple tests to identify the functional groups in FA 8, FA 10 and FA 11. Your test should use only the reagents provided. Record your test and observations in the space below.

Any test requiring heating MUST be performed using a beaker of hot water.

|	FA 8	FA 10	FA 11
Place about 1 cm depth of FA 8 in a test–tube.	Purple solution remains.	Purple solution remains.	Purple solution decolourised.
To this test – tube, add a few drops of potassium manganate and dilute sulfuric acid and place the test- tube in the hot water bath. Leave for a few minutes.			
Repeat using FA 10 and FA 11.			

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3 Determination of a value for the activation energy of a reaction

FA 12 is 0.1 mol dm^{-3} solution of hydrated sodium thiosulfate, Na$_2$S$_2$O$_3$.5H$_2$O.

FA 13 is 2.0 mol dm^{-3} hydrochloric acid.

Solid sulfur is one of the products formed in the reaction between sodium thiosulfate and a strong acid, as shown in the equation 3.1. The presence of sulfur causes the solution to be opaque.

reaction 3   S$_2$O$_3^{2-}$(aq) + 2H$^+$(aq) → S(s) + SO$_2$(g) + H$_2$O(l)
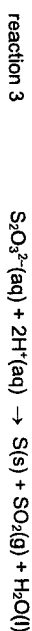
In order to determine the activation energy for this experiment, you will need to investigate the effect of temperature on its rate. The rate of this reaction is studied by measuring the time taken for the reaction to become opaque.

The activation energy, E_a, can be determined from the Arrhenius Equation, where T is the reaction temperature in Kelvin and k is the rate constant at temperature T. The frequency factor, A, can be regarded as a constant under the conditions of this experiment.

$$k = Ae^{-\frac{E_a}{RT}}$$

In this question, you will perform a series of five experiments, at different temperatures, T_K, each using the same volumes of **FA 12** and **FA 13**. Then, you will determine the value for the activation energy of the reaction graphically by plotting values of ln(1/t) on the y-axis against 1/T_K on the x-axis, a straight line of best fit may be drawn. The gradient of this line is $-E_a$/R, where R is the ideal gas constant.

For each experiment, you will note the temperature of the reaction, T, and the time taken, t, for the reaction mixture to become opaque.

You will then calculate values, to 3 significant figures, for

- 1/t,
- ln(1/t),
- T in Kelvin, T_K (0.0 °C = 273.0 K)
- 1/T_K

(a) Prepare a table in the space provided on page 16 in which to record, to an appropriate level of precision:

- all temperatures,
- all values of t,
- all calculated values of 1/t, ln(1/t), T_K and 1/T_K.

Notes: In each of these experiments, you will need to place the conical flask containing the reaction mixture on the printed page on page 2 of the insert. You will view the page by looking vertically down through the mixture. You will stop the stopwatch when the mixture **first** becomes opaque. This will be the first instant when you can no longer see the printed numbers on the page.

Under no circumstances should the equipment used to measure one solution be used to measure another solution.

Before you prepare your experimental solutions,

- rinse the inside of the two boiling tubes labelled '1' with about 2 cm^3 of **FA 12**. Pour this **FA 12** into the waste bottle and place the boiling tubes in the test-tube rack until you need them.

- rinse the inside of the two boiling tubes labelled '2' with about 2 cm^3 of **FA 13**. Pour this **FA 13** into the waste bottle and place the boiling tubes in the test-tube rack until you need them.

Experiment 1 is performed at room temperature. This is the lowest temperature you will carry out. Experiment 2 is performed at 70 °C. This is the highest temperature you will carry out. The other three experiments are performed at different temperatures. You will use water baths to change the temperature of these reaction mixtures.

To prepare a hot water bath, you will mix tap water with the hot water provided until an appropriate temperature is reached.

1. Use a measuring cylinder to transfer 10 cm^3 of **FA 12** into the boiling tube labelled '1'. Place the boiling tube into a 250 cm^3 beaker containing hot water. This will be the hot water bath.

2. Use another measuring cylinder to transfer 20 cm^3 of **FA 13** into the boiling tube labelled '2'. Place the boiling tube into the hot water bath.

3. Leave the boiling tubes in the hot water bath for use in **Experiment 2** and start **Experiment 1**.

13

Experiment 1

1. Use a measuring cylinder to transfer 20 cm³ of **FA 13** into a 100 cm³ conical flask.

2. Measure and record the temperature of **FA 13**.

3. Use another measuring cylinder to measure 10 cm³ of **FA 12**.

Note: Small amounts of SO_2 will be produced during the reaction. Minimise inhalation of SO_2.

4. Pour **FA 12** rapidly into the same conical flask. Start the stopwatch when about half of the **FA 12** solution has been added.

5. Swirl the conical flask once to mix the solutions. Then place the flask on the printed page of page 2 of the insert.

6. Stop the stopwatch when the solution **first** becomes opaque.

7. Record the time taken, t, to the nearest second in your table.

8. Discard the reaction mixture **immediately** down the sink. Wash out the conical flask and stand it upside down on a paper towel to drain.

Experiment 2

1. Measure and record the temperature of **FA 13** in boiling tube 2.

2. Remove the thermometer and carefully transfer the hot content of boiling tube 2 into a 100 cm³ conical flask.

3. Pour rapidly the hot content of boiling tube 1 into the same conical flask. Start the stopwatch when about half of the **FA 12** solution has been added.

4. Swirl the conical flask once to mix the solutions. Then place the flask on the printed page of page 2 of the insert.

5. Stop the stopwatch when the solution **first** becomes opaque.

6. Record the time taken, t, to the nearest second in your table.

7. Discard the reaction mixture **immediately** down the sink. Wash out the conical flask and stand it upside down on a paper towel to drain.

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Experiment 3, 4 and 5

Repeat **Experiment 2** but at three different temperatures. Keep the temperature of **FA 13** between room temperature and 70 °C. Do not exceed 70 °C. You will use water baths to change the temperature of these reaction mixtures.

Results

experiment	t / s	$1/t$ / s^{-1}	$\ln(1/t)$	T / °C	T_K / K	$1/T_K$ / K^{-1}
1	44	0.0228	−3.78	30.0	303	0.00330
2	37	0.0270	−3.61	38.0	311	0.00322
3	30	0.0333	−3.40	44.0	317	0.00315
4	22	0.0455	−3.09	53.0	326	0.00307
5	17	0.0588	−2.83	60.0	333	0.00300

[4]

(b) (i) Plot a graph of $\ln(1/t)$ on the y-axis against $1/T_K$ on the x-axis. Draw the best-fit straight line taking into account all of your plotted points.

$y = -3223.5x + 6.8057$

[3]

15
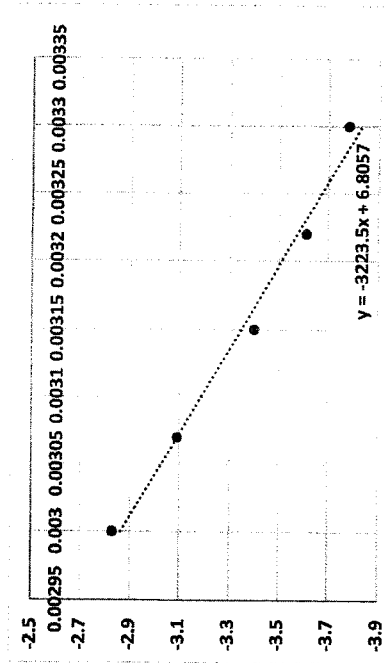
(ii) Calculate the value of the gradient of the line to three significant figures, showing clear how you did this.

[1]

Taking two points which are more than 3 big squares apart in both horizontal and vertical directions,

Gradient = $\frac{\Delta y}{\Delta x}$ = −2950

(iii) Calculate the activation energy, E_a, for reaction 3.
[$R = 8.314$ J K^{-1} mol^{-1}]

[4]

$-E_a/R$ = gradient
E_a = −2950 × (−8.314) = **2.45 × 10⁴ J mol^{-1}**

(c) In **Experiment 1**, you are told to start the stopwatch when about half of the **FA 12** solution has been added.

Suggest why this method is likely to be more accurate than starting the stopwatch after all the **FA 12** has been added.

[1]

The experiment time will be longer which results in a smaller percentage error.

(d) When you performed this experiment, you were instructed to wash and drain the conical flask before using it again.

State and explain the likely effect on **t** of not draining a flask before it is reused.

[1]

effect on **t**:
t will increase

explanation:
Presence of undrained water left in the conical flask would result in dilution of the reactants and hence rate of reaction decreases, resulting in a longer **t**.

16

(e) A student repeated the experiment but chose to use burettes to measure the volumes of **FA 12** and **FA 13**.

State and explain, in terms of percentage error, whether the student was wise to use a burette, rather than a 100 cm³ measuring cylinder, to measure the volume of **FA 12**.

[1]

% error with burette = $\frac{2 \times 0.05}{10}$ × 100 = 1.00%

% error with measuring cylinder = $\frac{0.5}{10}$ × 100 = 5.00%

The student was wise as the use of a burette gives a smaller percentage error.

[Total: 15]

17

4 Planning

(a) Relative atomic mass of an element is the the average mass of one atom of that element as compared to $\frac{1}{12}$ of the mass of a ^{12}C atom.

Magnesium is a reactive metal and appears dull because the metal on the surface is oxidised by air. The metal reacts with hydrochloric acid according to the following equation.

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

Plan an investigation to determine the relative atomic mass of magnesium.

You should make use of the water displacement method for collection of gas in your plan. In addition, you should plan to prepare a solution of hydrochloric acid of a suitable concentration and to collect a suitable volume of gas in your investigation.

You may assume that you are provided with:
- one piece of magnesium strip
- 0.50 mol dm⁻³ hydrochloric acid
- a piece of sandpaper
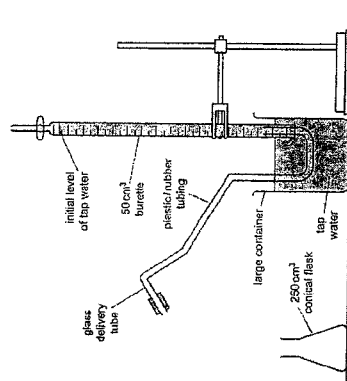- the equipment normally found in a school or college laboratory

Your plan should include brief details of:
- the apparatus you would use
- the quantities of the reactants and conditions that you would use
- the procedure that you would follow
- the measurements you would make (you may find it useful to label measurements in your plan as M1, M2 etc)
- an outline of how you would use your results to determine the *relative atomic mass* of magnesium.

[A_r: H, 1.0; Cl: 35.5]

You may assume that 1 mole of a gas has a volume of approximately 24 dm³ at 293 K and 1 atm.

[Turn over

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1. Assuming 40 cm³ of $H_2(g)$ is to be collected,
   Amount of H_2 produced = $40 \div 24000 = 1.6666 \times 10^{-3}$ mol
   Amount of HCl needed = $1.6666 \times 10^{-3} \times 2 = 3.333 \times 10^{-3}$ mol
   Volume of HCl needed = $(3.333 \times 10^{-3}) / 0.50 = 6.6666 \times 10^{-3}$ dm³
   = 6.67 cm³

2. Using a 25.0 cm³ pipette (or 50.00 cm³ burette), transfer 25.0 cm³ of the 0.50 mol dm⁻³ hydrochloric acid into a 250 cm³ volumetric flask. Make up the solution to 250 cm³ with deionised water and mix thoroughly.

3. Set up the experiment as shown below and place the beaker of tap water in a thermostatically controlled water bath at 20 °C.

Labels: initial level of tap water; 50cm³ burette; plastic/rubber tubing; glass delivery tube; large container; 250cm³ conical flask; tap water

4. Using a 100 cm³ measuring cylinder, transfer 70 cm³ of the diluted hydrochloric acid into a 250 cm³ conical flask.

5. Remove the layer of oxide on the Mg strip using the sandpaper and weigh the Mg strip (M1)

6. Add the Mg strip into the conical flask and insert the bung into the conical flask.

7. Read and record the initial water level (M2) in the burette. Hold the flask by its neck and gently swirl it continuously.

8. Read and record the final water level (M3) in the burette when no more $H_2(g)$ is produced.

9. *Wipe dry and reweigh the Mg strip if there's leftover when no more effervescence is present.*

10. Volume of $H_2(g)$ collected = M2 – M3 (initial burette reading – final burette reading) = M4
    Amount of H_2 = (M4 ÷ 24 × 10⁻³) mol
    Amount of Mg = (M4 ÷ 24 × 10⁻³) mol
    A_r of Mg = M1 ÷ (M4 ÷ 24 × 10⁻³) (Assuming that Mg is the limiting reagent)

(b) Identify one safety issue, relating to the properties of chemicals used or produced, in this procedure. Explain the precaution you would take to minimise the issue. **[1]**

Keep naked flame away from the apparatus as hydrogen is flammable.

[Total: 7]

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	reaction with	
	NaOH(aq)	NH₃(aq)
aluminium, Al³⁺(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH₄⁺(aq)	ammonia produced on heating	–
barium, Ba²⁺(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca²⁺(aq)	white ppt. with high [Ca²⁺(aq)]	no ppt.
chromium(III), Cr³⁺(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu²⁺(aq),	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe²⁺(aq)	green ppt. turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess
iron(III), Fe³⁺(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg²⁺(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn²⁺(aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn²⁺(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

ions	reaction
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, $Cl^-(aq)$	gives white ppt. with $Ag^+(aq)$ (soluble in $NH_3(aq)$)
bromide, $Br^-(aq)$	gives pale cream ppt. with $Ag^+(aq)$ (partially soluble in $NH_3(aq)$)
iodide, $I^-(aq)$	gives yellow ppt. with $Ag^+(aq)$ (insoluble in $NH_3(aq)$)
nitrate, $NO_3^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and Al foil
nitrite, $NO_2^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and Al foil; NO liberated by dilute acids (colourless $NO \rightarrow$ (pale) brown NO_2 in air)
sulfate, $SO_4^{2-}(aq)$	gives white ppt. with $Ba^{2+}(aq)$ (insoluble in excess dilute strong acids)
sulfite, $SO_3^{2-}(aq)$	SO_2 liberated with dilute acids; gives white ppt. with $Ba^{2+}(aq)$ (soluble in dilute strong acids)

(c) Test for gases

ions	reaction
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	colour of element	colour in aqueous solution	colour in hexane
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple