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**

Candidates answer on the Question Paper. **2 hours**
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

Section A

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

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

$HX(g) \rightarrow \frac{1}{2}H_2(g) + \frac{1}{2}X_2(g)$

The thermal stabilities of the hydrogen halides **decrease** down the Group from HC*l* to HBr to HI.

This is because
- the **size of the halogens increases** from C*l* 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

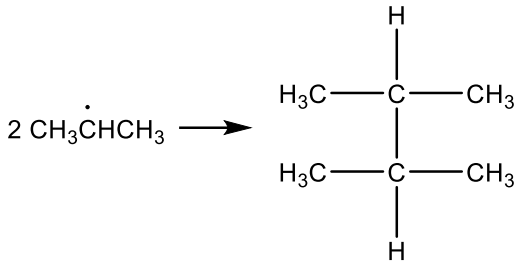
initiation $Cl-Cl \xrightarrow{UV} 2Cl\cdot$

propagation $CH_3CH_2CH_3 + Cl\cdot \longrightarrow CH_3\dot{C}HCH_3 + HCl$

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

termination $2Cl\cdot \longrightarrow Cl_2$

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



(c) (i) Define the term *lattice energy*. [1]

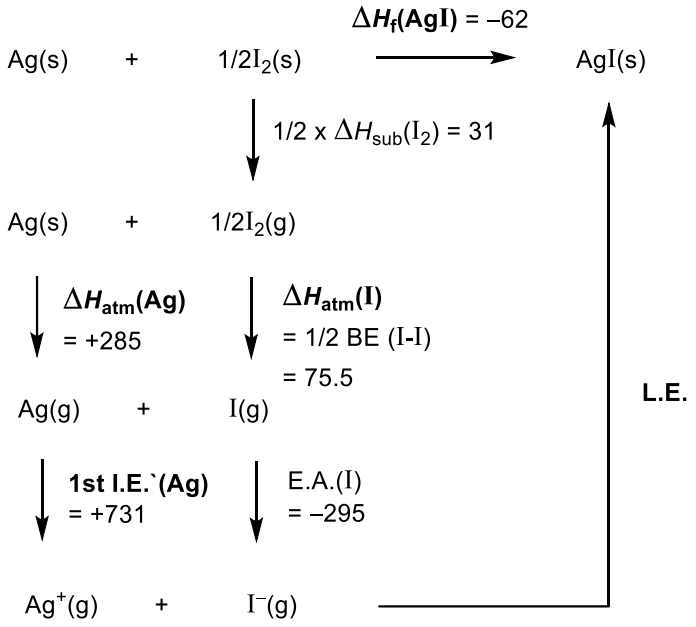
Lattice energy is the **heat evolved when 1 mole of a solid ionic compound is formed from its constituent gaseous ions**.

(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, $I(g) + e^- \rightarrow I^-(g)$	–295
enthalpy change of sublimation of iodine molecules, $I_2(s) \rightarrow I_2(g)$	+62
standard enthalpy change of atomisation of Ag(s)	+285
standard enthalpy change of formation of AgI(s)	–62

[3]



Lattice energy = –62 – [31 + 75.5 + (–295) + 285 + 731] = –889.5 = –890 kJ mol^{-1}

(d) Air bags in car inflate rapidly during an accident to protect the front passengers. The air bag contains sodium azide, NaN_3, silicon dioxide, SiO_2, and potassium nitrate, KNO_3.

On impact, three reactions take place.

The sodium azide first decomposes to sodium and nitrogen.

$$2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g)$$

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.

$$K_2O(s) + Na_2O(s) + SiO_2(s) \rightarrow K_2Na_2SiO_4(s)$$

(i) Write an equation, with state symbols, for the reaction between sodium and potassium nitrate. [1]

$10Na(s) + 2KNO_3(s) \rightarrow 5Na_2O(s) + K_2O(s) + N_2(g)$

(ii) Calculate the mass of sodium azide needed to inflate an air bag of capacity 60 dm^3 at room temperature and pressure. [2]

Amount of N_2 needed to fill a 60 dm^3 air bag = 60 ÷ 24 = 2.50 mol

2 mol of NaN_3 produces 3 mol of N_2 and 2 mol of Na;

10 mol of Na produces 1 mol of N_2 in its reaction with KNO_3 which means 2 mol of Na produces 0.2 mol of N_2

Hence 2 mol of NaN_3 produces a total of 3.2 mol of N_2.

Amount of NaN_3 needed to produce 2.5 mol of $N_2 = \frac{2.5}{3.2} \times 2 =$ **1.5625 mol**

Mass of NaN_3 required = 1.5625 × (23.0 + 14.0 × 3) = **102 g**

(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 cm^3 of 0.050 mol dm^{-3} of aqueous iodine. The excess iodine was found to require 23.10 cm^3 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 $I_2 = 0.5 \times (9.240 \times 10^{-4}) =$ **4.620×10^{-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^- = $(1.250 \times 10^{-3}) - (4.620 \times 10^{-4}) =$ **7.880×10^{-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 = $\frac{0.1024}{0.120} \times 100\% =$ **85.4%**

[Total: 17]

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

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

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]

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

(ii) 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,

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

P = 20 atm

At 750 K,

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

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.

(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]

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

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

$\Delta H = -114678$ J mol^{-1} = -115 kJ mol^{-1}

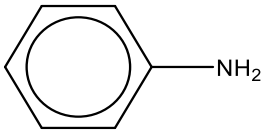
(v) The standard enthalpy change of formation of ammonia is -46 kJ mol^{-1}, given that ΔH for the reaction in equation 2.1 to be -92 kJ mol^{-1}.

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		7.4×10^{-10}

(i) Calculate the pH of 0.25 mol dm^{-3} solution of ethylamine. [2]

pOH = $-\log\sqrt{K_b \times c}$

= $-\log\sqrt{4.5 \times 10^{-4} \times 0.25}$

= **1.9744**

pH = 14 – 1.9744 = **12.0**

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

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

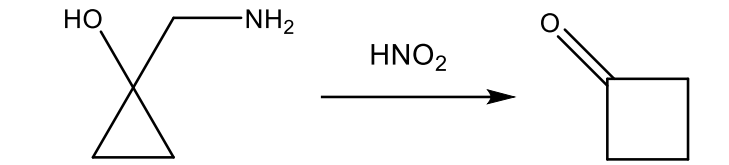
Ethylamine has the largest K_b value and is the strongest base as the **lone pair on N is more available to accept a proton,** as **the electron donating $-CH_2CH_3$ group increases the electron density at the N atom** making the **lone pair of electrons on N atom more available to accept a proton.**

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, $RCONH_2$, are neutral, rather than basic. [1]

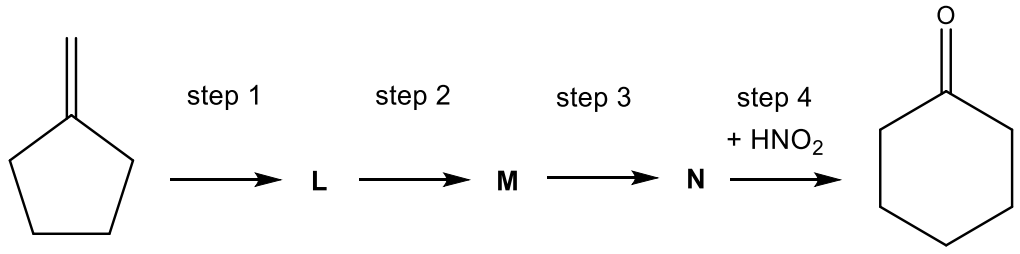
Amides are neutral because the **lone pair of electrons on the N atom in the $-CONH_2$ group is not available for donation to H^+ as it is delocalised into the C=O group**.

(c) Nitrous acid, HNO_2, can be used to react with aminoalcohol to form an enlarged cycloketone via the Tiffeneau-Demjanov Rearrangement, as shown below.



cyclic aminoalcohol cycloketone

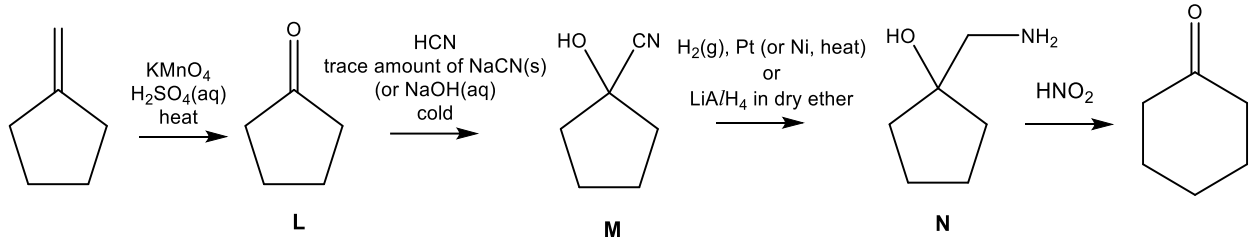
Methylenecyclopentane can be used to synthesise cyclohexanone by the four-step route shown in Fig. 2.1.



methylenecyclopentane cyclohexanone

Fig. 2.1

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



[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 Ni^{2+} ion. [2]

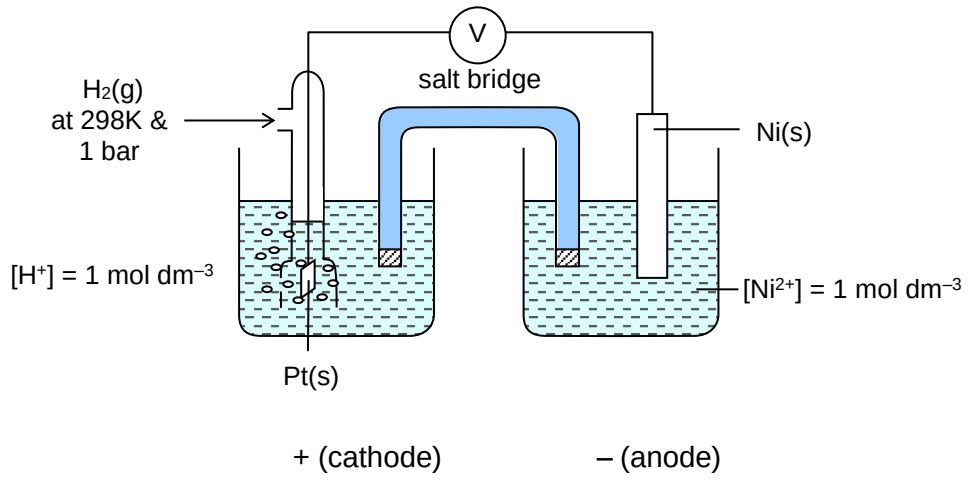
Cu: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$
Ni^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8$

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

In a complex,

- in the **presence of ligands**, the **3*d* 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**.

(b) (i) Draw a fully labelled diagram of the experimental set-up used to measure the standard electrode potential of the $Ni^{2+}(aq)/Ni(s)$ half-cell. Indicate clearly the positive and negative electrodes. [3]



Another cell composing of a standard $Ni^{2+}(aq)/Ni$ half-cell and a standard $Cr_2O_7^{2-}(aq)/Cr^{3+}(aq)$ 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: $Cr_2O_7^{2-} + 14H^+ + 3Ni \rightarrow 2Cr^{3+} + 7H_2O + 3Ni^{2+}$

$E^{\ominus}_{cell} = +1.33 - (-0.25) =$ **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 $Cr_2O_7^{2-}(aq)/Cr^{3+}(aq)$ half-cell was increased. Explain your answer. [1]

When the pH of the $Cr_2O_7^{2-}(aq)/Cr^{3+}(aq)$ 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 **$E^{\ominus}_{cell}$ ($Cr_2O_7^{2-}(aq)/Cr^{3+}(aq)$) becomes less positive**. Hence, the **voltage will be less positive**.

(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 3*d* 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.

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

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

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

(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 **electron 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.

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

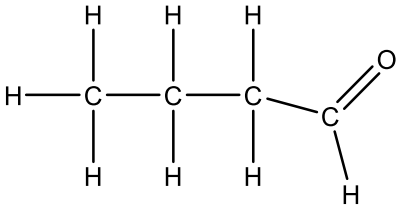
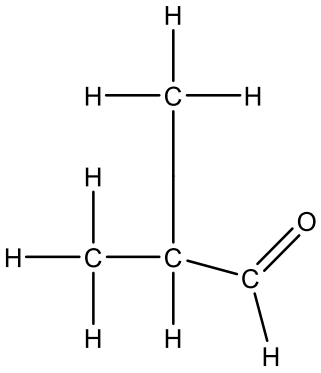
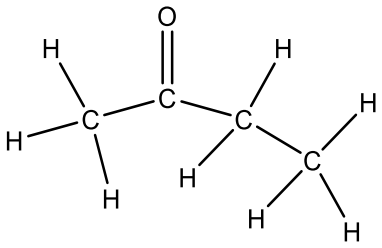
When excess $NH_3(aq)$ is added, **NH_3 acts as a ligand**, the **blue precipitate dissolves to give a deep blue solution** due to the formation of the complex ion, $[Cu(NH_3)_4(H_2O)_2]^{2+}$.

$$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$$

NH_3 is a stronger ligand than H_2O and displaces water via **ligand exchange reaction**.

(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]

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 / ^{o}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 S_8 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.

(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 $+15^{o}$.

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

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

angle of deflection $\propto$ charge/mass ratio

The charge/mass ratio of a proton is 1.

- charge/mass ratio of $^{2}H^{-} = \frac{-1}{2}$ and angle of deflection = -7.5^{o}
- charge/mass ratio of $^{3}He^{2+} = \frac{+2}{3}$ and angle of deflection = $+10^{o}$

(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

(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 cm^3 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

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

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

$V_1 = 1.94 \times 10^{-5}\ m^3$

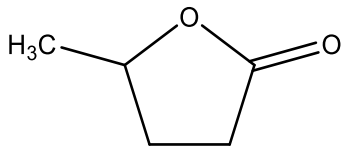
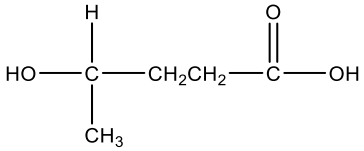
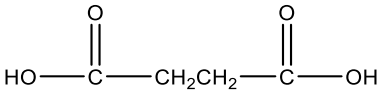
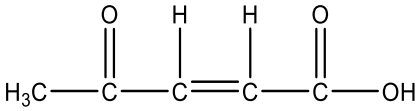
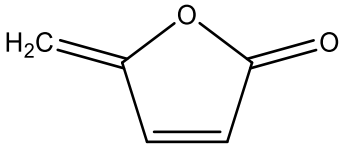
(d) Buttercups contain a poisonous cyclic compound called *protoanemonin*, $C_5H_4O_2$.

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]

information	type of reaction	functional group present
On catalytic hydrogenation, *protoanemonin* gives compound **A**, $C_5H_8O_2$.	**reduction** [√]	*Protoanemonin* contains (two) **alkene** [√]
When **A** is heated with an acid, compound **B**, $C_5H_{10}O_3$, 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**, $C_4H_6O_4$, can be isolated.	**oxidation** [√]	**B** contains the methyl carbinol, $CH_3CH(OH)$-, group. [√]
Protoanemonin is an unstable oil which when treated with an acid or alkali, it is converted to compound **D**, $C_5H_6O_3$.	**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** [√]

A	**B**	**C**
		
D	*protoanemonin*	
		

[Total: 20]

5 (a) (i) Describe the reactions, if any, of the chlorides NaC*l*, A*l*C*l*$_3$ and SiC*l*$_4$ with water. Write equations for all reactions that occur, and suggest the pH of the resulting solutions. [3]

	NaC*l*	A*l*C*l*$_3$	SiC*l*$_4$
reactivity and observation	NaC*l* which is ionic **dissolves in water** with no further reaction to give a **colourless solution**	A*l*C*l*$_3$ which is covalent **dissolves in water** with partial hydrolysis to give a **colourless solution**	SiC*l*$_4$ which is covalent undergoes complete hydrolysis in water **vigorously to give a colourless solution, a white solid and steamy white fumes**
equation	NaC*l*(s) → Na^+(aq) + Cl^-(aq)	A*l*C*l*$_3$(s) + 6H_2O(l) → $[Al(H_2O)_6]^{3+}$(aq) + 3Cl^-(aq) $[Al(H_2O)_6]^{3+}$(aq) ⇌ $[Al(H_2O)_5(OH)]^{2+}$(aq) + H^+(aq)	SiC*l*$_4$(l) + 2H_2O(l) → SiO_2(s) + 4HC*l*(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]

A*l*$_2O_3$(s) + 3H_2O(l) + 2NaOH(aq) → 2NaA*l*(OH)$_4$(aq)

A*l*$_2O_3$(s) + 6HC*l*(aq) → 2A*l*C*l*$_3$(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 pK_a of H_2Se. [3]

pOH = 14 – 8.45 = 5.55

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

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

pK_b = – log K_b = –log (7.9428×10^{-11}) = 10.1

pK_a = 14 – 10.1 = **3.90**

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

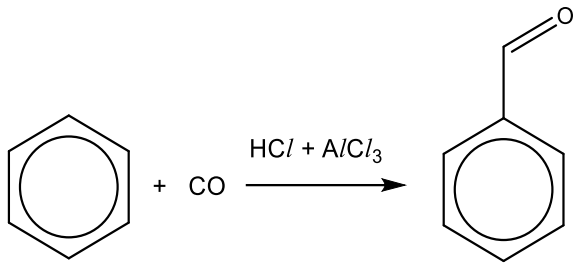
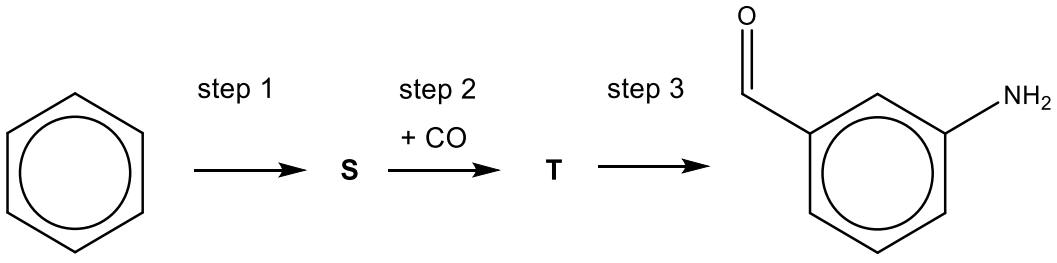


Fig. 5.1

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

electrophilic substitution

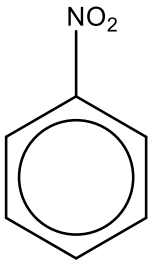
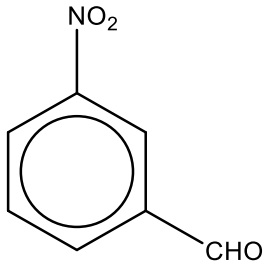
Fig. 5.2 shows the synthesis of compound **U**, which involves the Gattermann-Koch reaction.



U

Fig. 5.2

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

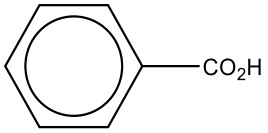
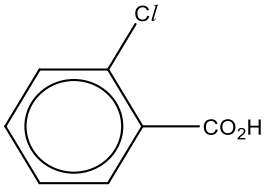
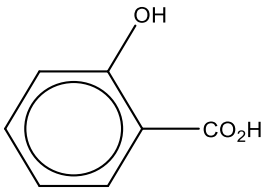
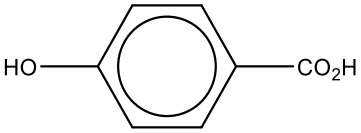
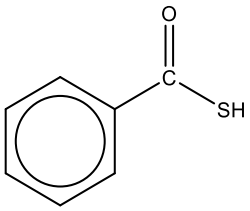
	
S	**T**

(iii) Suggest the reagents and conditions for step 1 and step 3. [2]

step 1: concentrated HNO_3, concentrated H_2SO_4, 55 ^oC
step 3: Sn, concentrated HC*l*, heat, followed by NaOH(aq)

(d) Table 5.1 lists the pK_a values for some other weak acids.

Table 5.1

acid	formula	pK_a
benzoic acid		4.20
2-chlorobenzoic acid		2.89
2-hydroxybenzoic acid		2.97
4-hydroxybenzoic acid		4.54
thiobenzoic acid		3.61

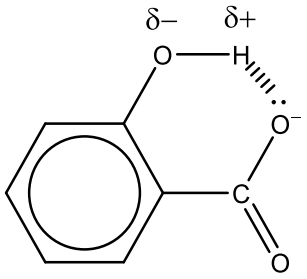
(i) Explain the difference in the pK_a values between 2-chlorobenzoic acid and benzoic acid. [1]

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 C*l* 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.

(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.

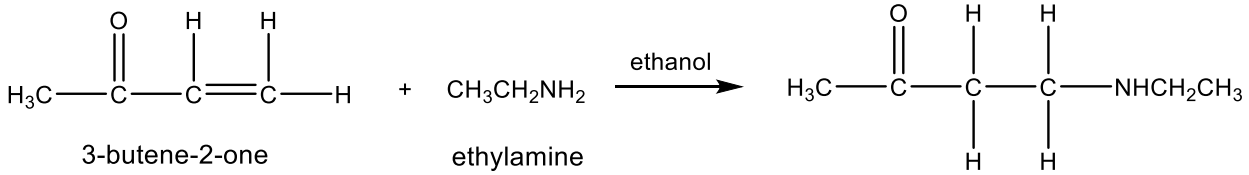


(iii) Thiobenzoic acid is related to benzoic acid by the replacement of one of the oxygen atoms with a sulfur atom.
Suggest a reason why the pK_a for thiobenzoic acid is lower than benzoic acid. [1]

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 nucleophilic addition reaction, with a primary amine.

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

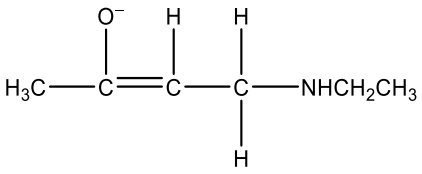


3-butene-2-one ethylamine 4-N-ethylamino-2-butanone

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.



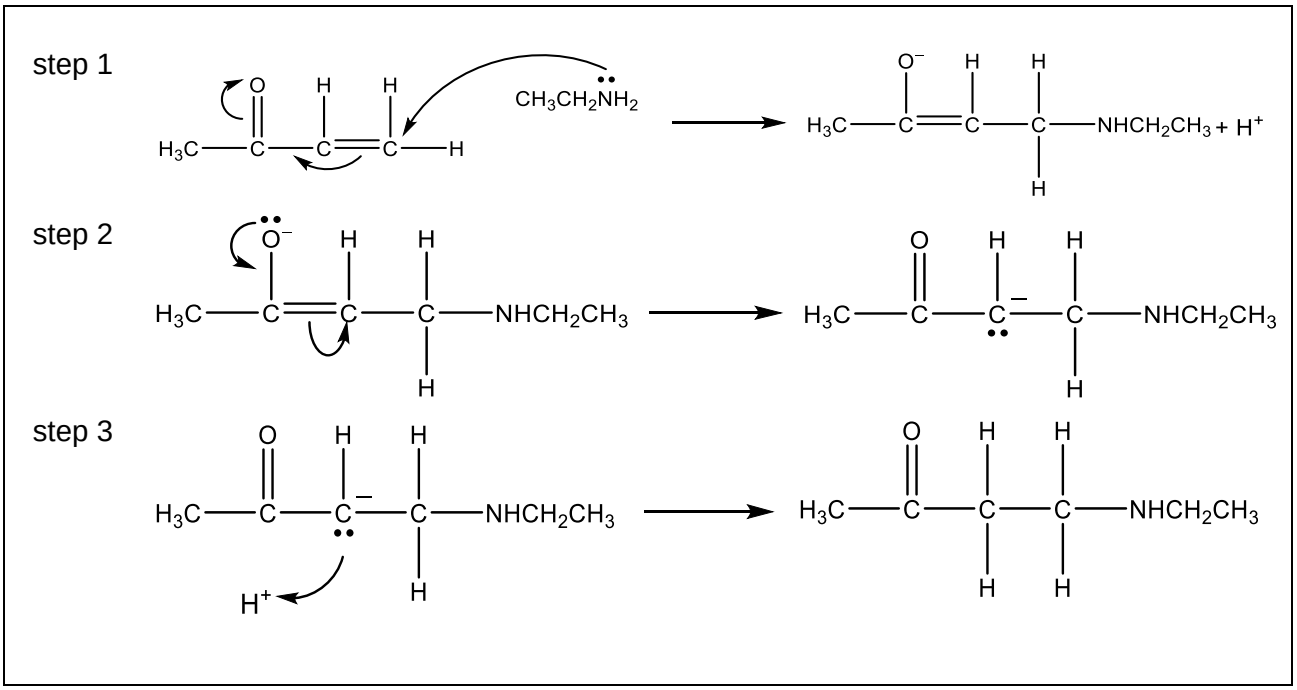
enolate ion

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]



(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 NH_3 nucleophile.

[Total: 20]

Additional Answer Space

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