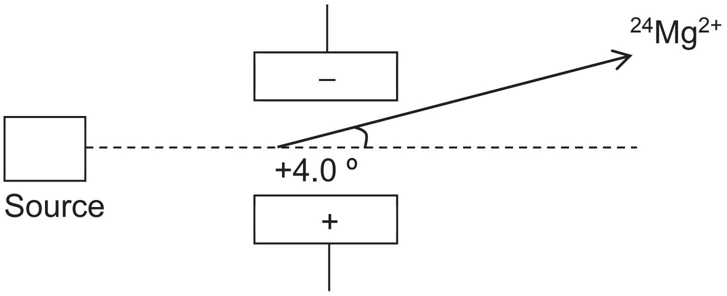
For each question there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

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

In an experiment, a sample containing 2 different species was vaporised, ionised and passed through an electric field. Analysis of the deflection occurring at the electric region revealed the following data for the sample. It was observed that a beam of $^{24}Mg^{2+}$ gives an angle of deflection of +4.0 °.



Which one of the following species will give the correct angle of deflection?

	isotope	no. of electrons	angle of deflection
A	^{16}O	6	–6.0 °
B	^{23}Na	10	+2.1 °
C	^{28}Si	10	–6.9 °
D	^{35}Cl	18	+1.4 °

2 Which one of the following corresponds to the electronic configuration of the 6 outermost electrons of a Group 6 element in its ground state?

A $3d^4 4s^2$

B $3d^5 4s^1$

C $4s^2 4p^4$

D $4p^6$

3 Which of the following have species arranged in increasing bond angle about the central atom?

1 ICl_4^- IO_3^-, I_3^-

2 XeF_4, XeO_3, XeF_2

3 N_2O, NO_3^-, NO_2^+

4 SO_4^{2-}, SO_3^{2-}, SO_2

A **1** and **2** only

B **1**, **2** and **4** only

C **1**, **3** and **4** only

D **2** and **3** only

4 The molar mass of ethanoic acid is 120.0 g mol^{-1} when dissolved in trichloromethane but 60.0 g mol^{-1} when dissolved in water.

Which one of the following statements best explains the phenomenon?

A Ethanoic acid is more soluble in trichloromethane than in water.

B Ethanoic acid molecules form strong covalent bonds with trichloromethane molecules.

C Ethanoic acid evaporates more readily in water.

D Ethanoic acid molecules form extensive hydrogen bonds with water molecules.

5 1.00 mol of gaseous molecules of a compound **A**, takes up a volume of 39 dm^3 when subjected to a pressure of 1.52 atm at a temperature of 70 ºC.

Which of the following statements explain the above observation?

1 Gaseous molecules of **A** experiences strong intermolecular forces of attractions.

2 Gaseous molecules of **A** have a significant molecular volume.

3 Gaseous molecules of **A** are in constant, rapid, random motion.

A **1**, **2** and **3**

B **1** and **2** only

C **2** and **3** only

D **1** only

6 **P**, **Q** and **R** are 3 consecutive elements in Period 3 of the Periodic Table.

- **R** has the highest melting point out of the 3 elements.
- The chloride of **P** gives a solution that is least acidic in water as compared to chlorides of **Q** and **R**.
- The 3rd ionisation energy of **Q** is much lower than that of **P**.

What can **P**, **Q** and **R** be?

A Na, Mg, A*l*

B Mg, A*l*, Si

C A*l*, Si, P

D Si, P, S

7 Which one of the following statements about Group 2 elements and their compounds is correct?

A Calcium hydroxide has a higher solubility than magnesium hydroxide.

B Calcium reacts with barium chloride to give calcium chloride.

C Strontium carbonate, on heating over a short period of time, decomposes to give more carbon dioxide gas than magnesium carbonate.

D Magnesium has a lower melting point than strontium.

8 10 cm^3 of gaseous $C_xH_yO_z$ was burnt in excess oxygen. There was a contraction of 20 cm^3. When the gaseous mixture was passed through aqueous sodium hydroxide, there was a further contraction of 30 cm^3. All gas volumes were measured at room temperature and pressure.

Which one of the following could be $C_xH_yO_z$?

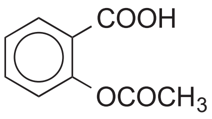
A $C_3H_2O_3$

B $C_3H_4O_4$

C $C_3H_6O_2$

D $C_3H_8O_2$

9 Aspirin is a medication used to treat pain, fever or inflammation.



Aspirin

25.0 cm^3 of 1.00 mol dm^{-3} NaOH was added to 25.0 cm^3 of solution containing aspirin. This resulting solution required 35.20 cm^3 of 0.325 mol dm^{-3} HC*l* to be fully neutralised.

What is the concentration of aspirin in the original 25.0 cm^3 solution?

A 0.229 mol dm^{-3}

B 0.271 mol dm^{-3}

C 0.458 mol dm^{-3}

D 0.542 mol dm^{-3}

10 Nitrogen monoxide, NO, is a pollutant that is formed in car exhausts and it can be oxidised as follows:

$$NO(g) + O(g) \rightarrow NO_2(g)$$

What is the enthalpy change of the above reaction given the following information?

$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$ $\Delta H = -199 \text{ kJ mol}^{-1}$

$O_3(g) \rightarrow \frac{3}{2} O_2(g)$ $\Delta H = -142 \text{ kJ mol}^{-1}$

$O_2(g) \rightarrow 2O(g)$ $\Delta H = +495 \text{ kJ mol}^{-1}$

A –94 kJ mol^{-1}

B –305 kJ mol^{-1}

C –552 kJ mol^{-1}

D –589 kJ mol^{-1}

11 A key step in the production of sulfuric acid is the oxidation of $SO_2(g)$ to $SO_3(g)$.

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

At 25 °C, $\Delta G = -142$ kJ mol^{-1}, $\Delta H = -198$ kJ mol^{-1}, $\Delta S = -188$ J K^{-1} mol^{-1}.

Assuming ΔH and ΔS are constant with temperature, which of the following statements about this reaction are correct?

1 The reaction becomes less spontaneous with increasing temperature.

2 The reaction becomes spontaneous at 780 °C.

3 The reaction is spontaneous at 900 °C.

A **1**, **2** and **3**

B **1** and **2** only

C **2** and **3** only

D **1** only

12 An experiment was carried out to investigate the initial rate of reaction between ammonium peroxodisulphate, $(NH_4)_2S_2O_8$, an oxidising agent, and potassium iodide, KI.

The initial concentrations of the $(NH_4)_2S_2O_8$ and KI solutions in the mixture together with the time taken for the mixture to darken for the various experimental runs are given below.

initial concentration of $(NH_4)_2S_2O_8$ / mol dm^{-3}	initial concentration of KI / mol dm^{-3}	time taken to darken / s
0.10	0.20	35
0.05	0.20	70
0.10	0.067	105
0.02	0.75	?

What is the expected time taken (in s) to darken when the experiment is repeated using initial concentrations of $(NH_4)_2S_2O_8$ and KI to be 0.02 mol dm^{-3} and 0.75 mol dm^{-3} respectively?

A 40 **B** 47 **C** 60 **D** 72

13 Ammonia is a raw material used in the manufacture of fertilisers, explosives and cleaning fluids. It is produced in the Haber process as shown:

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

- A closed system initially containing 2.00 mol of nitrogen, 6.00 mol of hydrogen, and 2.40 mol of ammonia at 448 °C is allowed to reach equilibrium in a sealed vessel of volume 1 dm^3. At equilibrium, there was 2.32 mol of nitrogen present.
- The vessel is subsequently expanded to 2 dm^3 under constant temperature, and equilibrium re-established.

Which of the following statements about this reaction are correct?

1 The equilibrium constant, K_c, is 3.96×10^{-3} mol^{-2} dm^6.

2 The equilibrium will shift to the left when vessel is expanded to double its initial volume.

3 The equilibrium concentration of $NH_3(g)$ is lower after the second equilibrium is established.

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

14 Common chlorine bleach is typically a 5 % sodium hypochlorite, NaC*l*O solution.

A solution, made by adding solid NaC*l*O to 2 dm^3 of water, has a pH of 10.5.

How many moles of NaC*l*O was added to the water, given that chloric(I) acid, HC*l*O has a K_a of 3.03×10^{-8} mol dm^{-3} at 25 °C?

A 0.25 mol **B** 0.31 mol **C** 0.55 mol **D** 0.62 mol

15 Hydroxyapatite, $Ca_5(PO_4)_3OH$, is the main constituent of tooth enamel. In the presence of saliva, which contains a buffer system, the following equilibria exist:

$$Ca_5(PO_4)_3OH(s) \rightleftharpoons 5Ca^{2+}(aq) + 3PO_4^{3-}(aq) + OH^-(aq)$$

$$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq)$$

Which one of the following statements does **not** help to explain why tooth enamel is dissolved more readily when saliva is acidic?

A The phosphate ion PO_4^{3-} accepts H^+.

B The hydroxide ions are neutralised by the acid.

C The calcium ions can precipitate to form $Ca(OH)_2$.

D The concentration of PO_4^{3-} decreases in this medium.

16 A solution contains three anions with the following concentrations:

anion	concentration / mol dm^{-3}
CrO_4^{2-}	0.20
CO_3^{2-}	0.10
Cl^-	0.010

A dilute $AgNO_3$ solution is slowly added to the solution.

Which is the first compound to precipitate and what concentration of Ag^+ is necessary to begin its precipitation?

[Given: K_{sp} (Ag_2CrO_4) = 1.2×10^{-12} mol^3 dm^{-9}, K_{sp} (Ag_2CO_3) = 8.1×10^{-12} mol^3 dm^{-9}, K_{sp} ($AgCl$) = 1.8×10^{-10} mol^2 dm^{-6}]

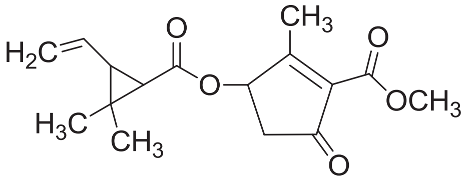
	first ppt	[Ag^+] to begin precipitation / mol dm^{-3}
A	Ag_2CrO_4	6.00×10^{-12}
B	Ag_2CrO_4	2.45×10^{-6}
C	Ag_2CO_3	9.06×10^{-6}
D	$AgCl$	1.80×10^{-8}

17 Species with the molecular formula CH_3 can act as an electrophile, a free radical or a nucleophile depending on the number of outer shell electrons on the central carbon atom.

How many outer shell electrons must be present for CH_3 to act in these different ways?

	as an electrophile	as a free radical	as a nucleophile
A	6	7	8
B	6	8	7
C	7	6	8
D	8	7	6

18 Pyrethrins such as jasmolin II, are a group of natural compounds synthesised by flowers of the genus Chrysanthemum to act as insecticides.



jasmolin II

How many stereoisomers are there for a molecule of jasmolin II?

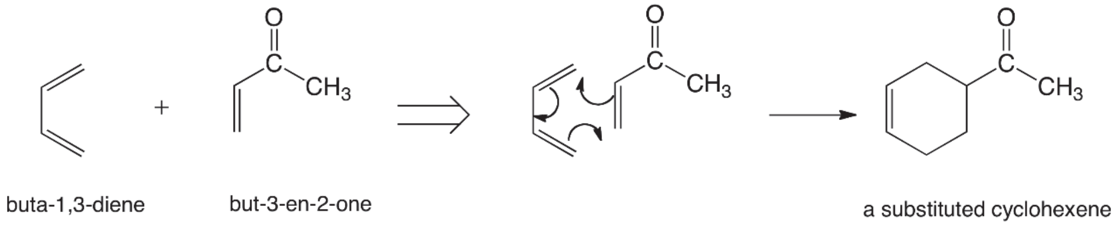
A 2 **B** 4 **C** 8 **D** 16

19 Compound **X** has molecular formula C_4H_{10}. **X** reacts with Cl_2(g) in the presence of sunlight to produce only two different monosubstituted products. Both of these products give the same Compound **Y**, and no other organic products, when they are reacted with hot ethanolic KOH.

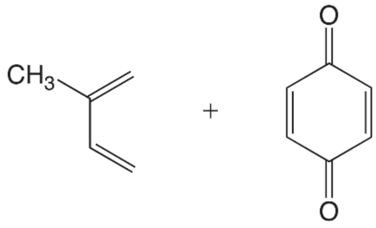
What is produced when **Y** is treated separately with hot acidified dichromate(VI) and cold alkaline manganate(VII)?

	hot acidified dichromate(VI)	cold alkaline manganate(VII)
A	CO_2 and $CH_3CH_2CO_2H$	$CH_2(OH)CH(OH)CH_2CH_3$
B	CO_2 and CH_3COCH_3	CH_3CO_2H only
C	$CH_2{=}CHCH_2CH_3$	$CH_2(OH)CH(OH)CH_2CH_3$
D	$CH_2{=}CHCH_2CH_3$	CO_2 and $CH_3CH_2CO_2H$

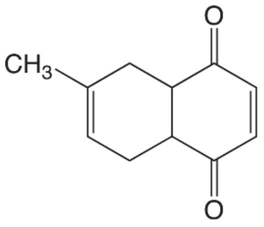
20 The Diels-Alder reaction is an organic reaction between a conjugated diene and a substituted alkene to form a substituted cyclohexene system. One such reaction between buta-1,3-diene and but-3-en-2-one is shown below:



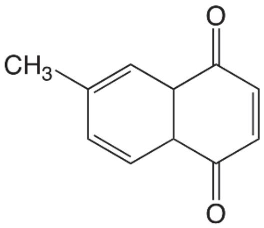
What would be the product formed when the following diene and substituted alkene reacts in a 1:1 ratio?



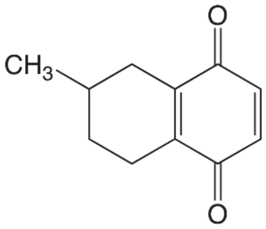
A



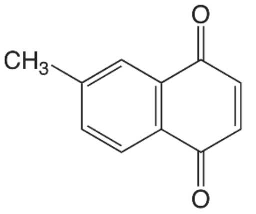
C



B

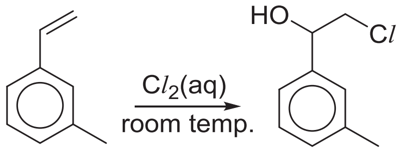


D

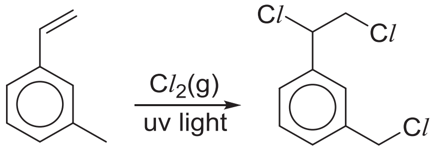


21 Which one of the following products is **unlikely** to be formed based on the given reagents and conditions?

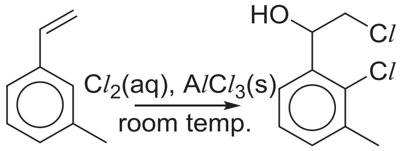
A



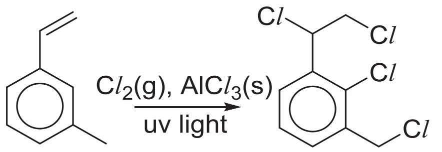
B



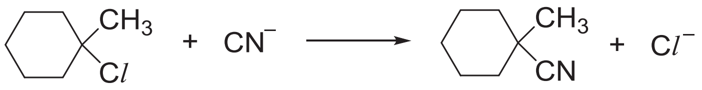
C



D



22 The reaction between 1–chloro–1–methylcyclohexane and alcoholic potassium cyanide is shown below:

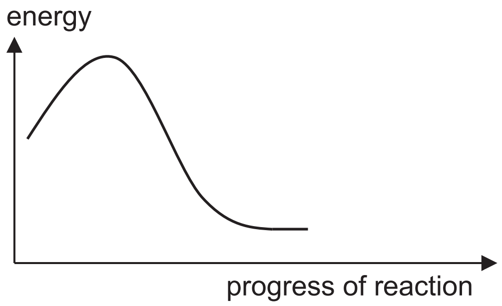


Which of the following statements regarding the reaction are likely to be true?

1 The rate equation of the reaction is overall first order.

2 The same mechanism will occur less readily if 1–chloro–1–methylhexane is used.

3 The energy profile diagram of the reaction is as shown below:



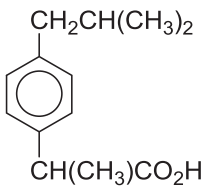
A **1**, **2** and **3**

B **1** and **2** only

C **2** and **3** only

D **3** only

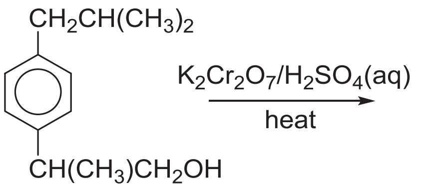
23 *Ibuprofen* is an anti-inflammatory drug.



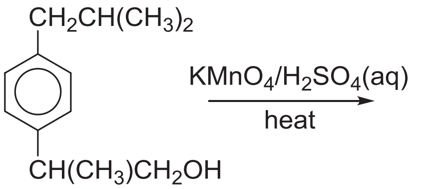
ibuprofen

Which one of the following reactions is **unlikely** to lead to its formation?

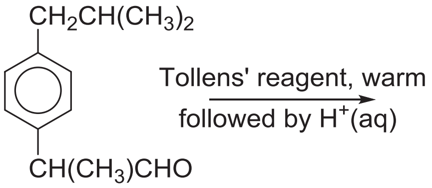
A



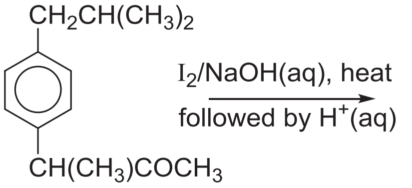
B



C

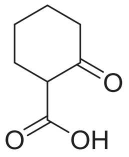
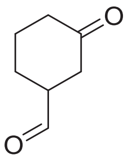
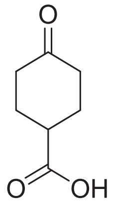


D



24 When compound **V** is first treated with an excess of a reducing agent, followed by heating with excess concentrated sulfuric acid, it gives **only one** final product with the molecular formula C_7H_{10}.

Which of the following options show a possible structure of compound **V** and the reducing agent?

	compound **V**	reducing agent
1		H_2/Ni
2		$NaBH_4$
3		$LiAlH_4$

A **1** and **2** only

B **2** and **3** only

C **1** only

D **3** only

25 The acid dissociation constants of ethanoic acid, peroxyethanoic acid, and ethanol are given in the table below.

name	formula	pK_a
ethanoic acid	CH_3CO_2H	4.8
peroxyethanoic acid	CH_3CO_3H	8.2
ethanol	CH_3CH_2OH	15.9

Which one of the following statements can best be inferred from the information given above?

A CH_3CO_3H can react with Na(s) but not with NaOH(aq).

B The K_b of the three conjugate bases decrease in the following order:

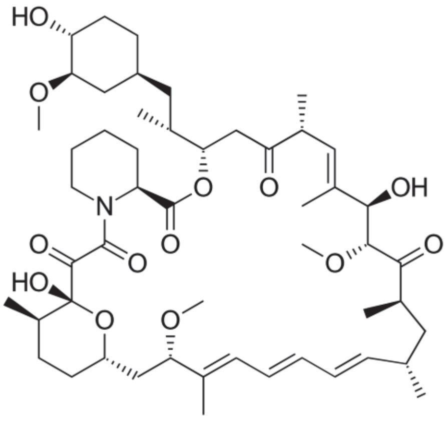
$$CH_3CO_2^- > CH_3CO_3^- > CH_3CH_2O^-$$

C The negative charge on $CH_3CO_2^-$ is less dispersed due to a smaller number of electron–withdrawing O atoms as compared to $CH_3CO_3^-$.

D The negative charge on $CH_3CO_2^-$ is stabilised by delocalisation of electrons over the C=O group but the negative charge on $CH_3CO_3^-$ is not.

26 *Use of Data Booklet is relevant to this question.*

The drug *Sirolimus* is used for treatment after kidney transplants.



Sirolimus

The reaction between *Sirolimus* and hot aqueous hydrochloric acid yields an equimolar mixture of two organic products.

What is the relative molecular mass of the nitrogen–containing organic product?

A 129.0	**B** 164.5	**C** 165.5	**D** 179.5

27 *Use of Data Booklet is relevant to this question.*

The calomel electrode was used extensively a reference electrode in the past. However, it has since been superseded by safer options such as the silver/silver chloride electrode and the standard hydrogen electrode (S.H.E.).

Calomel electrode: $\frac{1}{2}Hg_2Cl_2 + e^- \rightleftharpoons Hg + Cl^-$

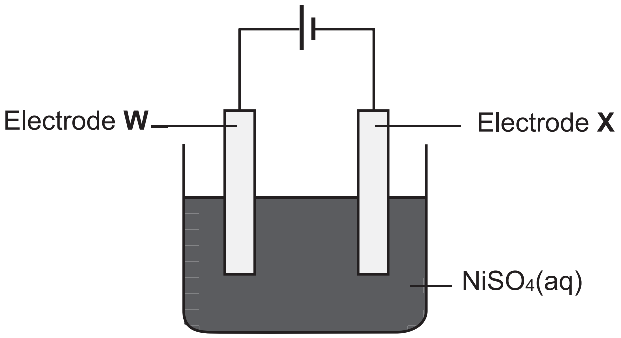
When measured with reference to the calomel electrode, a half–cell containing Zn^{2+}/Zn has a change in Gibbs' free energy of +199 kJ per mole of Zn^{2+}.

What is the standard electrode potential of the calomel electrode?

A +0.27 V	**B** +1.30 V	**C** –1.79 V	**D** –2.82 V

28 *Use of Data Booklet is relevant to this question.*

An electrolytic cell is set up to obtain pure nickel from a nickel–chromium alloy.



The mass of the anode changes by 25 g during the process.

Which one of the following statements best describes the electrolysis process?

A The mass of the cathode changes by 25 g during the process.

B Chromium can be collected as anode sludge at the end of the process.

C Electrode **W** is pure nickel and electrode **X** is nickel–chromium alloy.

D The concentration of $Ni^{2+}(aq)$ in the electrolyte will decrease during the process.

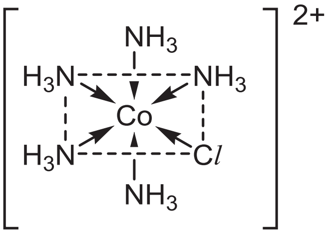
29 Two different complexes, **Y** and **Z**, can be obtained when aqueous cobalt(III) chloride undergoes ligand–exchange reaction with ammonia.

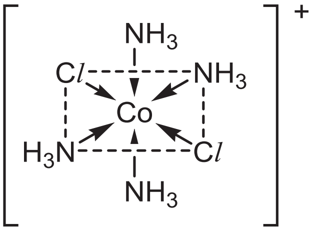
complex	co-ordination number	overall dipole moment	mole of AgC*l* ppt. per mole of complex
Y	6	yes	2
Z	6	no	1

Which one of the following is likely to be the correct cationic structures of **Y** and **Z**?

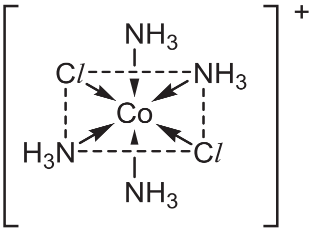
Y **Z**

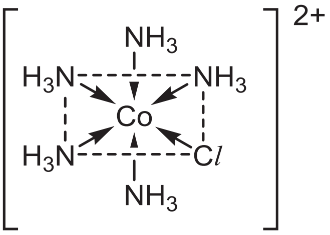
A



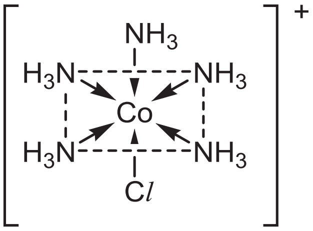


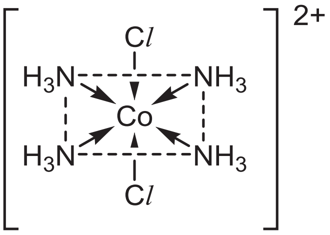
B



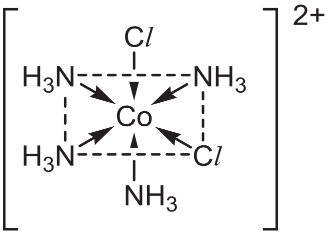


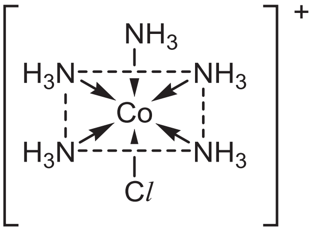
C





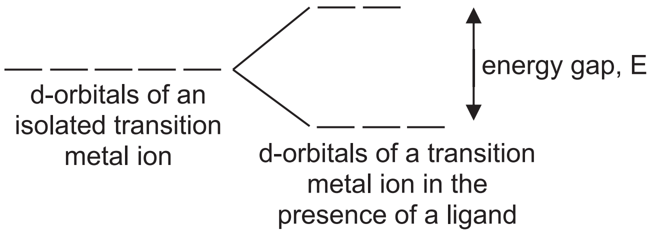
D





30 *Use of Data Booklet is relevant to this question.*

The following diagram shows how the d–orbitals are split in an octahedral environment.



Some transition metal ions exhibit the ability to change their electronic configuration from a 'high spin' state to a 'low spin' state.

In a 'high spin' state, the electrons occupy all the d–orbitals singly first, before starting to pair up in the lower energy d–orbitals.

In a 'low spin' state, the lower energy d–orbitals are first filled, by pairing up if necessary, before the higher energy d–orbitals are used.

Which one of the following transition metal ions is likely to be able to exhibit both spin states?

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

1 This question concerns some unusual nitrogen compounds.

(a) Heating monomer **X** to 150 °C produces the trimer, melamine, $C_3H_6N_6$. Melamine is a cyclic planar molecule and is symmetrical.

(i) Suggest a structure for melamine.

[1]

(ii) The average C–N bond length is 0.145 nm and the average C=N bond is 0.125 nm. Suggest why all the carbon-nitrogen bonds in melamine are intermediate in length between the given C–N and C=N values.

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

(iii) Deduce the structure of **X**. Calculate the number of protons, neutrons and electrons in a monomer of **X**.

[2]

(b) Group 1 metal azides, **M**N_3, can be formed by passing heated dinitrogen oxide, N_2O over their corresponding amines, **M**NH_2.

(i) Explain why lattice energies of Group 1 azides become less exothermic down the group.

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[1]

(ii) Suggest why the azides become thermally more stable down the group.

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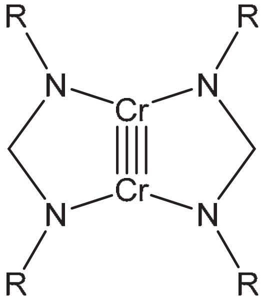
[2]

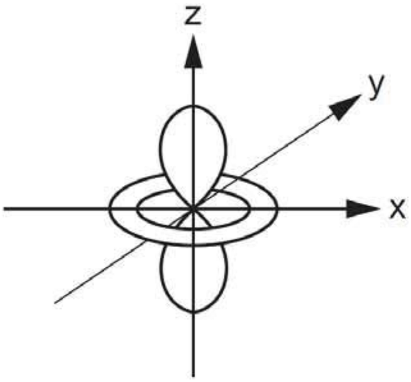
(c) Nitrogen has been used extensively in the research of compounds involving quadruple (bond order of 4) and quintuple (bond order of 5) bonds.

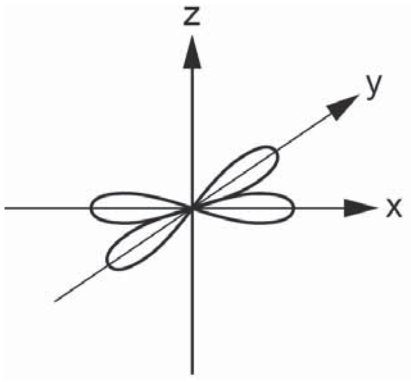
These compounds typically involve transition metal atoms that are able to form bonds between themselves using their d orbitals.

An example is given below:



(i) Sketches of the shapes of the atomic orbitals from the d subshells are shown below, in random order. Name and label **each** orbital.





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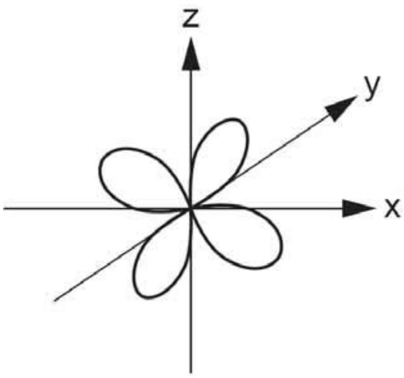

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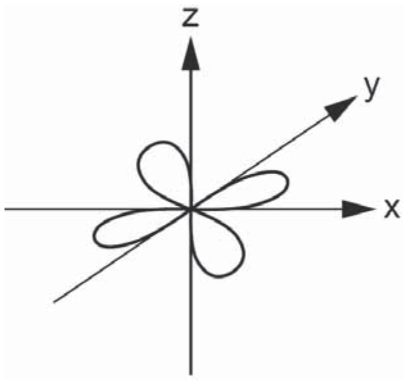

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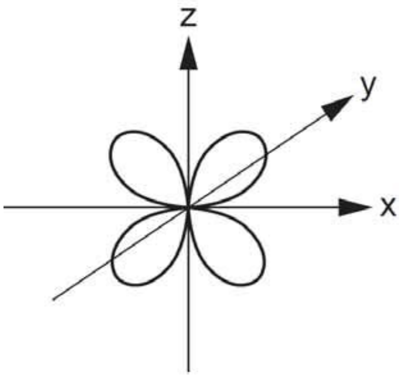

………………

[2]

(ii) The d orbitals of an atom can overlap with d orbitals of the same type to form pi (π) and delta (δ) bonds. While a single sigma (σ) bond involves the overlap of two orbital lobes in total, and a single pi (π) bond four lobes, a single delta (δ) bond involves the overlap of eight lobes in total. When two atoms overlap, the z-axis is used to define the internuclear axis.

Suggest two different d orbitals that could be involved in delta bonds (δ).

………………………………………………………………………………………………

[1]

[Total: 10]

2 *Use of Data Booklet is relevant to this question.*

Aerozine 50 is a 50/50 mix of UDMH, $(CH_3)_2N_2H_2$ and hydrazine, N_2H_4. It is used as a rocket fuel, and is typically mixed with dinitrogen tetroxide, N_2O_4, as the oxidising agent.

The equation for the reaction between UDMH and dinitrogen tetroxide under standard conditions is given as follows:

$(CH_3)_2N_2H_2(l) + 2N_2O_4(g) \rightarrow 2CO_2(g) + 3N_2(g) + 4H_2O(l)$ ---------- **reaction 1**

(a) Suggest an equation, including state symbols, for the reaction between hydrazine and dinitrogen tetroxide under standard conditions.

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[1]

(b) An experiment was set up such that hydrazine in a spirit burner was combusted beneath a copper can filled with water. It was found that 0.50 g of hydrazine was required to raise the temperature of 100 cm^3 of water in the can by 15 ºC.

Using relevant data from the *Data Booklet* and the information given below, calculate the efficiency of the system, expressed as a percentage.

- The heat capacity of the copper can be taken to be 96.0 J K^{-1}
- The density of water can be taken to be 1.00 g cm^{-3}.
- The standard enthalpy change of combustion of hydrazine, found using a bomb calorimeter, has a value of –628 kJ mol^{-1}.

[3]

Pure UDMH, $(CH_3)_2N_2H_2$, can be used as an alternative to *Aerozine 50* in thruster rockets.

(c) Using relevant data from the *Data Booklet* and the information given below, construct an energy cycle to calculate the enthalpy change for **reaction 1**.

$(CH_3)_2N_2H_2(l) + 4O_2(g) \rightarrow 2CO_2(g) + N_2(g) + 4H_2O(l)$	–1980 kJ mol^{-1}
$N_2O_4(g) \rightarrow 2N(g) + 4O(g)$	+1930 kJ mol^{-1}

[3]

(d) The total mass of propellant (UDMH and dinitrogen tetroxide, N_2O_4) used in the thruster rockets in the ascent stage of a lunar module was 366 kg.

Assuming that UDMH (M_r = 60.0) and dinitrogen tetroxide (M_r = 92.0) were mixed according to the stoichiometric ratio, calculate the mass of UDMH in the propellant mixture.

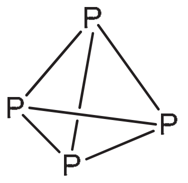
[1]

[Total: 8]

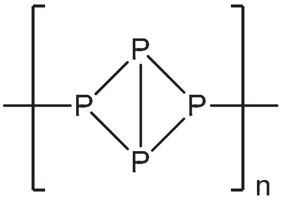
3 Use of the *Data Booklet* is relevant to this question.

Phosphorus and sulfur are elements in Period 3 in the Periodic Table and each can exist in various allotropic forms.

Phosphorus can exist as white phosphorus and red phosphorus. White phosphorus exists as a tetrahedron with bond angle 60° while red phosphorus exists as a polymeric chain of regular tetrahedrons.

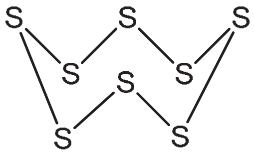


white phosphorus



red phosphorus

Sulfur, on the other hand is thermodynamically most stable at room temperature as rhombic sulfur, which consists of puckered S_8 rings.



Both elements form a wide range of compounds with the halogens.

(a) **(i)** By considering the bond angles involved, suggest why white phosphorus is less stable than red phosphorus.

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[1]

(ii) The phosphorus halides fume in air because of reaction with water vapour.

Explain briefly why phosphorus(V) chloride can react with water. Write a balanced equation for its reaction.

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[2]

(b) When sulfur is heated under pressure with chlorine, the major product is SCl_2.

$$S_8(g) + 8Cl_2(g) \rightarrow 8SCl_2(g)$$

(i) Using data from the *Data Booklet*, calculate the enthalpy change, ∆H, for this reaction.

[2]

Under suitable conditions, SCl_2 reacts with water to produce a yellow precipitate and a solution **X**. Solution **X** contains a mixture of SO_2(aq) and compound **Y**.

(ii) By constructing an equation for the hydrolysis of SCl_2, work out how the oxidation number of sulfur changes during the reaction.

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[2]

(iii) Hence, suggest a pH value of the resultant solution formed.

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[1]

(iv) Using relevant data from the *Data Booklet*, suggest what would be observed when acidified potassium dichromate is added to a sample of solution **X**.

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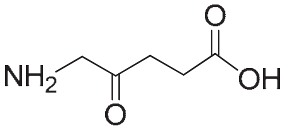
[2]

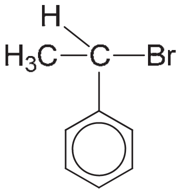
[Total: 10]

4 Aminolevulinic acid is involved in the synthesis of haemoglobin and chlorophyll.



aminolevulinic acid

(a) Aminolevulinic acid reacts readily with (1-bromoethyl)benzene.

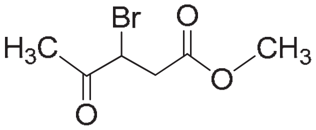


(1-bromoethyl)benzene

Name and outline the mechanism for the reaction of aminolevulinic acid with (1-bromoethyl)benzene.

[3]

(b) Compound **A** is a precursor in the synthesis of aminolevulinic acid.



compound **A**

Suggest a simple chemical test to distinguish between compound **A** and aminolevulinic acid. Include clearly the reagents, conditions and observations for each compound. Write a balanced equation for any positive test.

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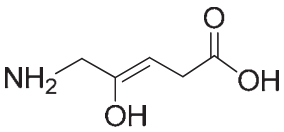
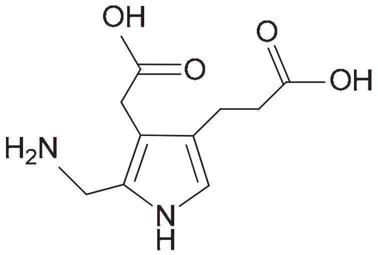
[3]

(c) Porphobilinogen is a pyrrole involved in porphyrin metabolism. It is generated from a reduced form of aminolevulinic acid, compound **B** by the enzyme ALA dehydratase.



compound **B**



porphobilinogen

Show how porphobilinogen may be formed from the condensation of two molecules of compound **B**, with the help of a balanced equation. Indicate clearly with dotted lines how the non-organic by-products are formed.

[2]

[Total: 8]

5 The formation of carbon-carbon bonds is important in the synthesis of large organic compounds. This question discusses the chemistry of some carbon-carbon bond forming reactions.

(a) Most of the starting reagents of such reactions typically involve a halogenoalkane. Halogenoalkanes can be obtained by reacting alkenes with hydrogen halides.

(i) Name and outline the mechanism of the reaction between 2-methylbut-2-ene and hydrogen chloride, showing the major product formed.

[2]

(ii) 2-methylbut-2-ene can also react with hydrogen bromide and hydrogen iodide to form its respective halogenoalkane.

Suggest and explain, with reference to the mechanism of the reaction, how the rate of reaction changes from HC*l* to HI.

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[2]

(b) Depending on the conditions of the reaction, a nitrile group can be introduced into an organic compound through either a halogenoalkane or a carbonyl, forming carbon-carbon bonds in the process.

(i) Suggest why alkenes are unable to react to form nitriles in the same way as carbonyls.

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[1]

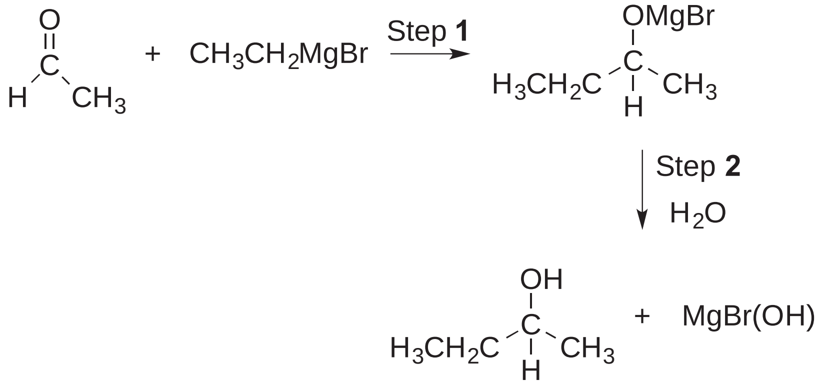
(ii) Propose a synthetic route that is **less than 5 steps** to convert butanal to pentanoic acid. State the reagents and conditions you would use for each step and draw the structures of the intermediate compounds.

[5]

(c) A classic carbon-carbon bond formation reaction is the Grignard reaction. First, the Grignard reagent, an alkylmagnesium halide, is formed by reacting a halogenoalkane with magnesium.

$$CH_3CH_2Br + Mg \rightarrow CH_3CH_2MgBr$$

The reaction then proceeds with a reaction between the alkylmagnesium halide with a carbonyl to give an alcohol in a 2-step reaction.



(i) Suggest the type of mechanism for step **1**.

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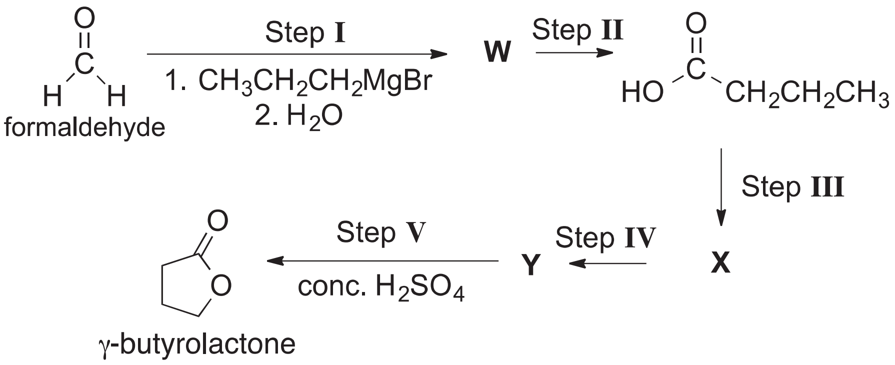
(ii) The synthesis of γ-butyrolactone, a common solvent from formaldehyde, involves the Grignard reaction as follows.



Propose structures of **W**, **X** and **Y**.

W	**X**

Y

[3]

(iii) State the reagents and conditions required for steps **II**, **III** and **IV**.

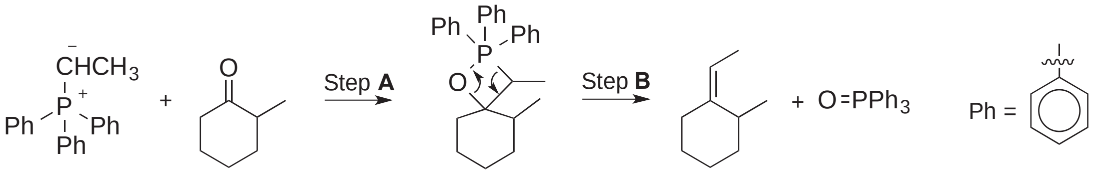
Step **II**: ……………………………………………………………………………….

Step **III**: ………………………………………………………………………………

Step **IV**: ………………………………………………………………………………

[3]

(d) Another common carbon-carbon bond formation reaction is the Wittig reaction. A phosphorus-containing reagent reacts with a carbonyl to form an intermediate, which then cleaves quickly to give an alkene.



(i) Identify, with the aid of a diagram, the type of stereoisomerism that the product can show.

[2]

(ii) By considering the hybridisation of relevant carbon atoms, suggest a reason why step **B** is a fast reaction.

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[2]

[Total: 21]

6 **(a)** 1.0 cm^3 of 0.10 mol dm^{-3} solution of sodium iodide was added to 1.0 cm^3 of 0.050 mol dm^{-3} $AgNO_3$(aq). 3.0 cm^3 of 1.0 mol dm^{-3} NH_3(aq) was then added. The resulting precipitate formed is virtually insoluble.

(i) Show that the number of moles of I^-(aq) that is **not** used to form the precipitate is 5.0 x 10^{-5} mol.

[1]

(ii) Show that under these conditions [I^-(aq)] = 0.010 mol dm^{-3} and hence [Ag^+(aq)] which would just allow the precipitate to dissolve.

K_{sp}(AgI) = 8.0 x 10^{-17} mol^2 dm^{-6}

[1]

(iii) Under the conditions of the experiment, [Ag^+(aq)] = 1.9 x 10^{-9} mol dm^{-3}. Use your answer in **(a)(ii)** to justify why the precipitate is virtually insoluble.

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(iv) When the above experiment is repeated using sodium chloride instead of sodium iodide, different observations were made. Briefly describe and explain the differences with the aid of equations. **No** calculations are required.

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[3]

(b) The standard electrode potential values for reactions **(I)** and **(II)** are +1.21 V and +0.54 V respectively.

$IO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2}I_2 + 3H_2O$ **(I)**

$\frac{1}{2}I_2 + e^- \rightleftharpoons I^-$ **(II)**

(i) Find the standard Gibbs free energy change for **each** of the reactions **(I)** and **(II).**

[1]

(ii) Use your answers from **(b)(i)** to find the standard Gibbs free energy change for the following reaction, and hence its standard electrode potential.

$IO_3^- + 6H^+ + 6e^- \rightleftharpoons I^- + 3H_2O$

[2]

(c) When 0.530 g of potassium iodide was completely reacted with an aqueous solution of XeF_2, all the iodide is converted into the iodate anion. A student proposed that the anion could be either iodate(V), IO_3^-, or iodate(VII), IO_4^-.

(i) Show that the number of moles of iodate that were involved in the reaction is 3.19×10^{-3} mol.

[1]

(ii) The equation involving the reaction of iodate(VII), IO_4^- with excess acidified potassium iodide is given below:

$IO_4^- + 8H^+ + 7I^- \rightarrow 4I_2 + 4H_2O$

For the reaction involving iodate(V), IO_3^- with excess acidified potassium iodide, write the corresponding half equations and hence the overall **ionic** equation.

Reduction: …………………………………………………………………………………...

Oxidation: ………………………………………………………………………………….

Overall ionic equation:

…………………………………………………………………………………………………

[3]

(iii) 3.19×10^{-3} mol of iodate anion, which is either iodate(V), IO_3^-, or iodate(VII), IO_4^- is acidified, and added to excess potassium iodide solution where iodine is formed. It is found that 28.40 cm^3 of 0.900 mol dm^{-3} of $Na_2S_2O_3$ is required to discharge the colour of iodine.

It is given that $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$.

By using the information and your answers in **(c)(ii)**, determine whether the anion is iodate(V), IO_3^-, or iodate(VII), IO_4^-.

[2]

(d) Nitrogen trifluoride was first prepared in the electrolysis of a molten mixture of ammonium fluoride and hydrogen fluoride using inert electrodes.

(i) It is given that at one of the electrodes, the following reaction occurs:
$NH_4^+ + 3F^- \rightarrow NF_3 + 4H^+ + 6e^-$

State the electrode that is involved in the above reaction and its polarity.

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

(ii) When the above electrolysis was set up using a current of 0.50 A, 0.276 g of nitrogen trifluoride was liberated. Calculate the time taken for the electrolysis to occur.

[2]

[Total: 18]

Section A

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

1 **(a)** Ethanoic acid and its salt, sodium ethanoate, is often used as an acid buffer to help extend the shelf-life of food products such as meat, fish and dairy.

A buffer solution of pH 5.5 was prepared by mixing 0.200 mol dm^{-3} of ethanoic acid and 0.200 mol dm^{-3} aqueous sodium ethanoate.

(K_a of ethanoic acid = 1.74 x 10^{-5} mol dm^{-3})

(i) What do you understand by the term *buffer solution*? [1]

(ii) Calculate the ratio of $\frac{\text{[ethanoate]}}{\text{[ethanoic acid]}}$ required to prepare the above buffer solution.

Hence deduce whether the above buffer is more effective in buffering against added acids or bases.

Write an equation to illustrate your answer. [3]

(iii) Calculate the volume of ethanoic acid and that of aqueous sodium ethanoate required to prepare 60 cm^3 of the above buffer. [1]

(iv) The boiling points of the components in the buffer are as shown.

Ethanoic acid	118 °C
Sodium ethanoate	881 °C

With reference to the structure and bonding present in the compounds, account for the difference in the boiling points. [3]

(b) The limestone that collects in kettles in hard water areas is mainly calcium carbonate. It can be removed fairly harmlessly by using a warm solution of vinegar, which contains ethanoic acid. The limestone dissolves with fizzing and a solution of calcium ethanoate remains.

(i) Write a balanced equation for the reaction between ethanoic acid and calcium carbonate. [1]

When the solution in **(b)** is evaporated and the resulting solid calcium ethanoate is heated strongly in a test-tube, an organic compound **Q** is formed, which condenses to a colourless liquid. The residue in the tube contains calcium carbonate.

When 0.10 g of compound **Q** was injected into a gas syringe at a temperature of 383 K and a pressure of 101 kPa, 55 cm^3 of vapour were produced.

(ii) Calculate the relative molecular mass of **Q**. [2]

(iii) Compound **Q** is neutral and water-soluble. **Q** does not react with sodium metal nor with Fehling's solution but it does react with alkaline aqueous iodine.

Suggest a structural formula for **Q.** Justify your answer by reference to these properties of **Q**. [4]

(iv) Construct a balanced equation for the formation of **Q** by the action of heat on calcium ethanoate. [1]

(v) The residue calcium carbonate can also undergo thermal decomposition when heated very strongly. Copper(II) carbonate behaves in a similar manner when heated.

State which carbonate, calcium or copper(II) will have a higher decomposition temperature. Explain your answer, with the help of relevant data from the *Data Booklet*. [3]

[Total: 19]

2 **(a)** In a closed reaction vessel maintained at a high temperature, 1 mol of Al_2Cl_6 dimers dissociate into $AlCl_3$ according to the following equation.

$$Al_2Cl_6(g) \rightleftharpoons 2AlCl_3(g)$$

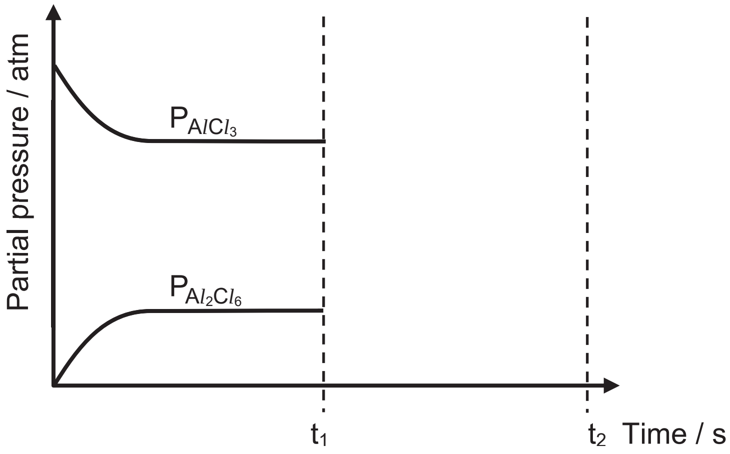
The average M_r of the equilibrium gas mixture is found to be 178.0.

(i) Given that the average M_r of the equilibrium gas mixture is the sum of the mole fractions of each gas, multiplied by the M_r of that gas, calculate the degree of dissociation of Al_2Cl_6, α. [3]

(ii) Write down the expression of K_p for the above equilibrium system. Hence, show that $K_p = K_cRT$. [2]

(iii) An experiment on the dissociation of Al_2Cl_6 was conducted in a closed container of a fixed volume and the partial pressures of all the components were plotted as shown in the figure below.

Copy and complete the diagram to show how the partial pressure of each gas changes when the volume of the container is halved at t_1 until t_2.



[2]

(b) Strontium chloride, $SrCl_2$ is a typical salt which forms neutral aqueous solutions. It emits a bright red colour in a flame and this allows it to be used as a source of redness in fireworks.

Use the data below to answer the questions that follow.

Standard Gibbs free energy change of solution of $SrCl_2(s)$	–41.6 kJ mol^{-1}
Standard enthalpy change of formation of $SrCl_2(s)$	–828.9 kJ mol^{-1}
Standard enthalpy change of formation of $Sr^{2+}(aq)$	–545.8 kJ mol^{-1}
Standard enthalpy change of formation of $Cl^-(aq)$	–167.5 kJ mol^{-1}
Standard enthalpy change of hydration of $Sr^{2+}(g)$	–1446 kJ mol^{-1}
Standard enthalpy change of hydration of $Cl^-(g)$	–378 kJ mol^{-1}

(i) Define the term *standard enthalpy change of formation* of strontium chloride. [1]

(ii) Calculate $\Delta H^\ominus_{sol}$ and $\Delta S^\ominus_{sol}$ of strontium chloride. [4]

(iii) Write an equation to show the relationship between the lattice energy of strontium chloride and $\Delta H^\ominus_{sol}$ of strontium chloride. Hence, calculate the lattice energy of strontium chloride. [2]

(iv) Predict with reasoning, how Gibbs free energy change of formation of strontium chloride, ΔG_f will change with increasing temperature. [2]

(c) Using the data given below, draw a labelled energy cycle to calculate the enthalpy change of combustion of solid carbon.

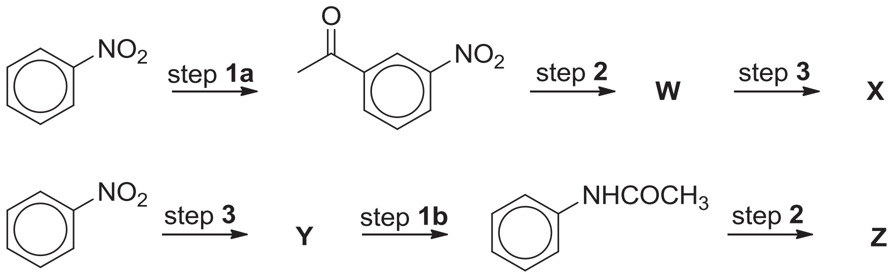
$2SrO(s) \rightarrow 2Sr(s) + O_2(g)$ $\Delta H = +1184\ kJ\ mol^{-1}$

$SrO(s) + CO_2(g) \rightarrow SrCO_3(s)$ $\Delta H = -234\ kJ\ mol^{-1}$

$2SrCO_3(s) \rightarrow 2Sr(s) + 2C(s) + 3O_2(g)$ $\Delta H = +2440\ kJ\ mol^{-1}$ [4]

[Total: 20]

3 **(a)** Consider the following synthesis pathways starting from nitrobenzene:



(i) Ethanoyl chloride (CH_3COCl) is used as a reactant for step **1a** and step **1b** but under different conditions. State the reaction mechanism that occurred for each step **1a** and **1b** and hence explain the difference in the conditions required. [3]

(ii) Identify the reagents and conditions required for **steps 2** and **3** and hence draw the structures of **W, X, Y** and **Z**.

[Note: **Steps 2** and **3** in both pathways each refers to the same set of reagents and conditions.] [6]

(iii) Compare the relative basicity of **Y** and **Z**. [2]

(b) In an isolated atom, the five d orbitals have the same energy. When a transition element ion is in an octahedral complex, the d orbitals are split into two groups of different energy levels.

(i) Draw an orbital energy diagram to show this, indicating the type of orbitals in each group. [2]

(ii) Use your diagram in **(b)(i)** to explain why transition element complexes like $Co(H_2O)_6^{2+}$ are often colored. [2]

(c) Aqueous cobalt(II) chloride, $CoCl_2$ is a pink solution which gives the following reactions.

$$CoCl_2(aq) \xrightarrow{NaOH(aq)} \text{blue ppt. insoluble in excess} \xrightarrow{H_2O_2} \text{blue ppt. turned brown}$$

$$CoCl_2(aq) \xrightarrow{HCl(aq)} \text{no observable change} \xrightarrow{H_2O_2} \text{no observable change}$$

(i) By using the data given below and appropriate values from the *Data Booklet*, calculate $E^\ominus_{cell}$ and explain the differences in the observations made between **acidic** and **alkaline** medium.

$$Co(OH)_3 + e^- \rightleftharpoons Co(OH)_2 + OH^- \qquad E^\ominus = +0.17\text{ V}$$

Write equations to account for the observations. [4]

(ii) When brine solution instead of HCl was added to $CoCl_2(aq)$, the solution turned from pink to blue. In this reaction, cobalt behaves like a transition element.
Suggest by means of an ionic equation, an explanation for this observation. [2]

[Total: 21]

Section B

Answer **one** question from this section.

4 **(a)** The kinetics of the acid–catalysed hydrolysis of ethyl ethanoate may be investigated by analysing samples of the reaction mixture at different times.

$$CH_3CO_2CH_2CH_3 + H_2O \xrightleftharpoons{H^+ \text{ (catalyst)}} CH_3CO_2H + CH_3CH_2OH$$

In one such experiment, the reaction mixture was prepared by mixing solutions of ethyl ethanoate and hydrochloric acid. The concentration of hydrochloric acid, which serves as the catalyst, can be assumed to stay constant throughout the reaction.

At different times, 10.0 cm^3 portions of the reaction mixture were pipetted, quenched and titrated with 0.200 mol dm^{-3} NaOH(aq).

After all necessary samples have been drawn, the remaining reaction mixture is then heated for ½ h to ensure complete reaction. The volume of NaOH required for titrating a 10.0 cm^3 sample of the resulting solution is 30.00 cm^3.

The following experimental data were obtained:

Time / min	Volume of NaOH required for titration, V / cm^3	$30.00 - V$ / cm^3
0	20.00	10.00
10	24.40	5.60
20	26.90	3.10
30	28.20	1.80
40	29.00	1.00
50	29.40	0.60

(i) State how each of the quantities, V and $(30 - V)$, is related to the concentration of the components of the reaction mixture at any point in time. [1]

(ii) Hence, choose appropriate data from the above table to plot a graph that will allow you to determine the order with respect to ethyl ethanoate. [2]

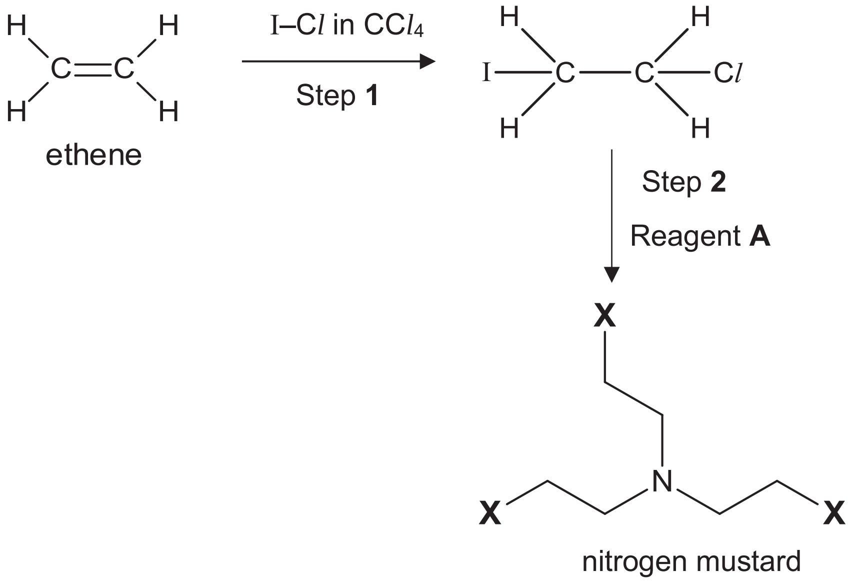
(iii) Deduce the order with respect to ethyl ethanoate, justifying your answer by showing construction lines clearly on your graph. [2]

(iv) Hydrolysis of $CH_3CO_2CH_2CH_3$ can also be catalysed by esterase, an enzyme found in the liver.

Sketch a graph to show how, for a constant [esterase], the rate of hydrolysis varies with $[CH_3CO_2CH_2CH_3]$ and explain the shape of the graph. [2]

(b) Nitrogen mustard gas is commonly used in chemotherapy.

It was suggested that the synthesis of nitrogen mustard can be carried out via the following pathway:

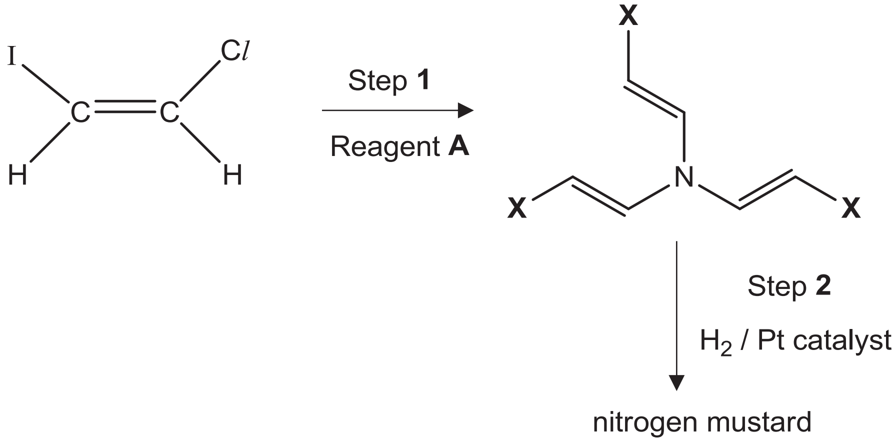


X in nitrogen mustard could be either C*l* or I.

(i) Suggest the identity of reagent **A** and the conditions necessary for an optimal yield in Step **2**. [1]

(ii) Is **X** in nitrogen mustard more likely to be C*l* or I? Explain your answer. [2]

(iii) Another reaction pathway was suggested for the synthesis of nitrogen mustard, with reagent **A** used for the first step:



Explain why this method of synthesis is likely to fail. [2]

(c) Compound **K** is a solid with the formula, $C_4H_9NO_3$. It dissolves in water to form a solution with high electrical conductivity. When **K** was warmed with aqueous sodium hydroxide, a colourless pungent gas was evolved. Acidification of the resulting solution gives **L**, $C_4H_6O_3$.

L gives an orange precipitate with 2,4-dinitrophenylhydrazine. When lithium aluminium hydride was added to **L**, **M**, $C_4H_{10}O_2$, was produced.
M can also be obtained from the oxidation of **N**, C_4H_8 by cold alkaline potassium manganate(VII).

Deduce the structures of compounds **K**, **L**, **M** and **N** and explain the reactions described. [8]

[Total: 20]

5 **(a)** The reaction between bromide and bromate(V) ions in acid solution is represented as follows:

$$5Br^- + BrO_3^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

The reaction between Br^- and BrO_3^- is relatively fast, with Br_2 produced almost immediately after the reactants are mixed.

To measure the initial rate of the reaction, aqueous Br^- is added to acidified BrO_3^- solution containing a small amount of compound **A** and methyl orange indicator. The initial colour of the methyl orange is pink as the solution is acidic. After some time, the pink colour disappears due to the bleaching action of Br_2 as shown:

$$\underset{\text{pink}}{Br_2 + \text{methyl orange (acid form)}} \rightarrow \underset{\text{colourless}}{\text{bleached methyl orange}} + 2Br^-$$

The time taken for the pink colour to disappear is an indication of the initial rate.

(i) Compound **A** is added to delay the disappearance of the pink colour, which would otherwise take place too quickly for effective measurement of time.

Given that compound **A** is an acidic organic compound containing only **one** functional group, suggest a suitable identity for compound **A**. [1]

(ii) Explain, with the aid of an equation, why the compound mentioned in your answer to **(i)** would be effective in delaying the disappearance of the pink colour. [2]

(iii) To find the order of reaction with respect to H^+, a total of five experiments are conducted.

In all the experiments, 10.0 cm^3 of KBr(aq), 10.0 cm^3 of $KBrO_3$(aq), 5.0 cm^3 of Compound **A** solution and 2 drops of methyl orange indicator are used, with water added to keep the total volume constant. The volume of H_2SO_4(aq) used and other experimental data for each experiment are shown in the table below:

Experiment No.	Volume of H_2SO_4(aq), V / cm^3	V^2 / cm^6	Time taken for colour to change from pink to colourless, t / s	$\frac{1}{t}$ / s^{-1}
1	30.0	900	10.0	0.100
2	25.0	625	14.4	0.069
3	20.0	400	22.5	0.044
4	15.0	225	40.0	0.025
5	10.0	100	90.0	0.011

Choose appropriate data from the table above to plot a graph that will enable you to determine the order of reaction with respect to H^+. [2]

(iv) State, with justification, the order of reaction with respect to H^+. [1]

(b) Champagne is an example of *sparkling wine*, a term referring to wine with significant levels of carbon dioxide in it, making it fizzy. In the traditional method of production, wine is allowed to undergo a natural fermentation after bottling, which involves conversion of the malic acid present into lactic acid:

$$\underset{\text{malic acid}}{HO_2CCH_2CH(OH)CO_2H} \rightarrow \underset{\text{lactic acid}}{CH_3CH(OH)CO_2H} + CO_2$$

(i) A bottle typically has a total capacity of 1.5 dm^3 and contains 1.3 dm^3 of wine with a malic acid concentration of 0.05 mol dm^{-3}.

By means of the ideal gas equation, calculate the pressure exerted inside the air gap of the bottle by the carbon dioxide produced when all the malic acid present undergoes fermentation.

Assume that the temperature inside the bottle is 25°C. [2]

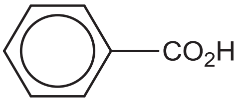
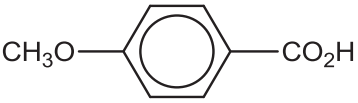
(ii) In fact, the pressure inside the bottle is much less under these conditions. Suggest why the actual pressure differs from the value calculated in **(i)**. [1]

(iii) Besides malic acid, many other organic acids also play an important role in our everyday life. For instance, acrylic acid, with the structure $CH_2{=}CHCO_2H$, is the starting material for the production of many plastics and adhesives industrially.

State the reagents and conditions that can be used to synthesize acrylic acid from lactic acid in the laboratory. [1]

(iv) Another example of an organic acid is benzoic acid which is commonly used as a food preservative.

The K_a values of benzoic acid and its substituted derivative, 4–methoxybenzoic acid are given below:

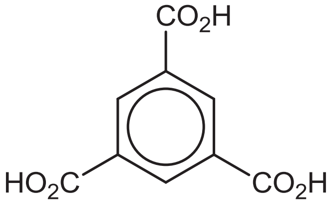
Compound	**K_a / mol dm^{-3}**
 Benzoic acid	6.5×10^{-5}
 4–methoxybenzoic acid	3.5×10^{-5}

Explain the difference in the K_a values of the two acids. [2]

(c) Compound **P** is an aromatic compound with molecular formula $C_{12}H_{15}O_3Cl$. It reacts with exactly 2 mol of PCl_5 to form an organic product **Q**. **P** also gives a brick–red precipitate with Fehling's solution.

Upon heating **P** with alcoholic NaOH, only one of the products formed, **R**, has the molecular formula $C_{12}H_{14}O_3$.

On oxidation with hot acidified potassium manganate(VII) solution, **R** gives **S**, $C_2H_4O_2$, and the following compound:



Suggest the structures of **P**, **Q**, **R** and **S**, explaining the reactions involved. [8]

[Total: 20]

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

1 Determination of the M_r of a carbonate salt

FA 1 is a solid carbonate, $\mathbf{X}CO_3$.

FA 2 is a solution containing 1.00 mol dm^{-3} of hydrochloric acid, HCl.

FA 3 is a solution of NaOH of concentration 0.100 mol dm^{-3}.

In this question, you will perform a titration. The data from this titration will be used to determine

- the amount of CO_3^{2-} ions in the mass of **FA 1** used,
- the M_r of $\mathbf{X}CO_3$ and hence the identity of the metal **X**.

(a) Titration of FA 4 against FA 3

(i) You are to determine the amount of carbonate ions, CO_3^{2-}, in **FA 1,** by back titration after some **FA 2** has been added to it. Carry out the procedure as listed below.

1. Weigh accurately between 1.25 – 1.35 g of **FA 1** into a clean and dry 150 cm^3 beaker. If you have used the TARE facility on the balance, indicate clearly in your recording.

2. Record your weighing in an appropriate format in the space provided on the next page.

3. Measure out 50 cm^3 of **FA 2** into a measuring cylinder. Pour this into the beaker containing **FA 1.** Stir thoroughly to ensure all of **FA 1** has dissolved.

4. Quantitatively transfer the mixture into a 250 cm^3 volumetric flask. Make up to the mark with distilled water. Shake to obtain a homogeneous solution. Label this solution **FA 4.**

5. Pipette 25.0 cm^3 of **FA 4** into a conical flask and add 2 drops of methyl orange indicator.

6. Fill the burette with **FA 3.**

7. Titrate **FA 4** with **FA 3.**

8. Repeat the titration as many times as you consider necessary to obtain accurate results.

9. Record your titration results in the space provided on the next page. Make certain that your recorded results show the precision of your working.

Results:

*For weighing of **FA 1***

Titration

[6]

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

volume of **FA 3** = ………………….. [1]

(b) **(i)** Calculate the amount of excess acid pipetted into the conical flask.

amount of excess acid in the conical flask = …………………… [1]

(ii) Calculate the total amount of excess acid in the volumetric flask.

amount of excess acid in the volumetric flask = …………………… [1]

(iii) Hence calculate the amount of acid that has reacted with the carbonate that you have weighed out.

amount of acid reacted = …………………….. [1]

(iv) Use your answer in **b(iii)** to calculate the M_r of $\mathbf{X}CO_3$.

M_r of $\mathbf{X}CO_3$ = ……………………..

Deduce the identity of metal **X**.
Show your working.

[A_r: C, 12.0; O, 16.0; H, 1.0; Be, 9.0; Mg, 24.3; Ca, 40.1; Sr, 87.6; Ba, 137.3]

X is ………………………………… [3]

(c) Planning

Sodium carbonate, Na_2CO_3, does **not** decompose on heating with a Bunsen burner. Sodium hydrogencarbonate, $NaHCO_3$, decomposes on heating.

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$$

You are to design an experiment in which the percentage by mass of $NaHCO_3$ in a mixture of $NaHCO_3$ and Na_2CO_3 can be determined by heating and weighing alone.

The only apparatus available consists of:

a boiling tube and holder
a chemical balance
a Bunsen burner
a heat proof mat

You are to show how you would use the results of this experiment to determine the percentage by mass of $NaHCO_3$ in the mixture.

(i) Outline, step by step, the practical sequence for the method you would use to:

- make appropriate weighings,
- decompose the sodium hydrogencarbonate in the mixture by heating,
- ensure that the decomposition was complete.

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…………………………………………………………………………………… [3]

(ii) By considering the products of the decomposition, suggest a reason why a crucible, without a lid, might be more appropriate than a boiling tube for this experiment.

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……………………………………………………………………………………… [1]

(iii) Prepare a table to show the masses you would measure and record during the experiment. Include in your table any other masses you would calculate from the experimental results to enable you to determine the percentage by mass of $NaHCO_3$ in the mixture.

Insert in your table the letters **A**, **B**, **C** etc. to represent each mass. Use these letters to show how your calculated masses are obtained e.g. **B** – **A**.

[2]

(iv) Use the letters you have entered in **(c)(iii)** to show how you would process the results to find:

- the mass of $NaHCO_3$ in the mixture,

[A_r: C, 12.0; H, 1.0; O, 16.0; Na, 23.0]

- the percentage by mass of $NaHCO_3$ in the mixture.

[2]

[Total: 21]

2 Determination of the concentration of a mixture of acids and the enthalpy change of neutralization

FA 5 is an aqueous solution prepared by mixing equal volumes of y mol dm^{-3} hydrochloric acid, HCl, and y mol dm^{-3} sulfuric acid, H_2SO_4.

FA 6 is 1.60 mol dm^{-3} sodium hydroxide, NaOH.

Take care as aqueous solutions of sodium hydroxide are corrosive.

When an acid is run into an alkali, an exothermic reaction takes place and the temperature of the mixture increases until the end–point is reached. If acid is added beyond the end–point, the temperature will decrease as no further reaction takes place and the acid is at a lower temperature than the mixture.

You are to follow the neutralisation of the acids in **FA 5** by measuring the temperature as volumes of **FA 5** are added in regular portions from a burette to a fixed volume of **FA 6** placed in a Styrofoam cup.

The data obtained will enable you to determine the value of y and the enthalpy change of neutralization, ΔH_{neut}, of this acid–base reaction.

In an appropriate format in the space provided on the next page, prepare a table in which you may record the following after each addition of **FA 5**:

- Total volume of **FA 5** added from the burette up to the point in time
- Total volume of solution in the cup (V_{cup})
- Temperature measured (T)

You also need to calculate the corresponding values of:

- $\Delta T = T - T_0$, where T_0 is the initial temperature of **FA 6**
- ($V_{\text{cup}} \times \Delta T$) to 3 significant figures

1. Fill the burette to 0.00 cm^3 with **FA 5**.
2. Place the Styrofoam cup in a 250 cm^3 beaker to provide support for the cup. Use the measuring cylinder to place 40.0 cm^3 of **FA 6** into the cup and measure the steady temperature of the alkali, T_0.
3. Run 5.00 cm^3 of **FA 5** from the burette into the cup, stir the solution with the thermometer and record the maximum temperature, T.
4. **Immediately** run a further 5.00 cm^3 of **FA 5** from the burette into the cup, stir and record the maximum temperature as before.
5. Continue the addition of **FA 5** in 5.00 cm^3 portions and record the maximum or minimum temperature reached after each addition. Do this until a total of 45.00 cm^3 of solution have been run from the burette.

(a) (i) Experimental results

[3]

(ii) On the grid provided below, plot (V_{cup} × ΔT) against the total volume of **FA 5** added.

Draw a line of best fit for the points before the maximum value of (V_{cup} × ΔT).

Draw a second line of best fit for the points after the maximum value.

Extrapolate both lines until they meet.

[2]

(iii) Read from your graph the maximum value of (V_{cup} × ΔT) and the end–point volume of the titration.

maximum value of (V_{cup} × ΔT) = ……………………..

end–point volume = …………………….. [3]

(b) **(i)** Calculate the concentration of hydrogen ions in **FA 5**.

concentration of hydrogen ions = …………………….. [1]

(ii) Hence, determine the value of y, which is the concentration of either HCl or H_2SO_4 used to prepare **FA 5**.

y = ……………………… [1]

(c) **(i)** Determine the enthalpy change of neutralization of this reaction, ΔH_{neut}.

You should assume that the specific heat capacity of the final solution is 4.18 J g^{-1} K^{-1}, and that its density is 1.00 g cm^{-3}.

ΔH_{neut} = …………………….. [3]

(ii) Student **A** carefully performed the same experiment and correctly processed the data using the same method. His calculated value of ΔH_{neut} is –65.0 kJ mol^{-1} while the published value for this enthalpy change is –57.7 kJ mol^{-1}.

The specific heat capacity of the Styrofoam cup has not been taken into consideration in calculating ΔH_{neut}. Explain whether this omission could have been the reason for the discrepancy between the value obtained by Student **A** and the one published.

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(iii) Student **B** performed the same experiment but chose to plot ΔT instead of ($V_{cup} \times \Delta T$) on the y–axis.

He also drew and extrapolated two straight lines through the plotted points to do the calculations.

Suggest why his method is likely to yield **less** accurate results.

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……………………………………………………………………………………… [1]

[Total: 16]

3 Inorganic Analysis

(a) You are provided with the solid **FA 7** which contains one cation and one anion from the ions listed in the **Qualitative Analysis Notes**, and the solution **FA 8**.

You are to perform the tests below to identify the ions present in **FA 7** and to suggest the nature of the compound in **FA 8**.

If the evolution of a gas is observed at any stage, the gas should be tested and identified. Details of the test carried out, the observations of the test and the identity of the gas should be given with the observations.

If it appears that no reaction has taken place this should be clearly recorded.

Carry out the following tests on **FA 7** and **FA 8** and complete the table to show your observations.

	Test	Observations
(i)	To a spatula–full of **FA 7** in a test–tube add 3 cm depth of dilute sulfuric acid. Warm, and when the reaction has stopped, filter the mixture. Retain the filtrate for tests **(iii)** and **(iv)**.	
(ii)	Place a spatula–full of **FA 7** in a test–tube and heat strongly. Leave the tube to cool. Retain the residue for test **(viii)**.	
(iii)	To a 1 cm depth of the filtrate from **(i)** in a test–tube, add aqueous sodium hydroxide drop by drop until 1 cm depth of the reagent has been added. Then add a further 1 cm depth of the aqueous sodium hydroxide.	
	Swirl the test-tube and leave to stand for 2–3 minutes.	
(iv)	To a 1 cm depth of the filtrate from **(i)** in a test–tube, add aqueous ammonia drop by drop until 1 cm depth of the reagent has been added. Then add a further 1 cm depth of the aqueous ammonia.	
	Then **cautiously** add 1 cm depth of **FA 8**.	

(v)	Place 2 cm depth of aqueous potassium iodide in a test–tube and add 2 cm depth of **FA 8**.	
	Then add 2 cm depth of dilute sulfuric acid.	
(vi)	To a 1 cm depth of **FA 8** in a test–tube, add 1 cm depth of dilute sulfuric acid and 2 cm depth of potassium manganate(VII). Observe for 2 minutes or until no further change occurs.	
(vii)	To a 1 cm depth of aqueous sodium sulfite in a test–tube, add a few drops of aqueous barium nitrate.	
	Then add 2 cm depth of dilute nitric acid.	
	Immediately add 1 cm depth of **FA 8**.	
(viii)	Transfer a portion of the residue from test **(ii)** into a test–tube and add 2 cm depth of **FA 8**.	

[9]

(b) **(i)** From your observations, identify the cation and anion present in **FA 7**. Quote evidence from the table to support your conclusions.

Cation ……………………………

Evidence ……………………………………………………………………..

……………………………………………………………………..

Anion ……………………………

Evidence ……………………………………………………………………..

…………………………………………………………………… [2]

(ii) In tests **(a)(v)** and **(vii)**, **FA 8** behaves as ……………………………………...

In test **(a)(vi)**, **FA 8** behaves as …………………………………………….. [1]

(c) **Planning**

One of the transition metals, vanadium, was named after the Scandinavian goddess of beauty and fertility, Vanadis (Freya) due to the wide range of colours found in vanadium compounds.

Starting with an aqueous solution of VO_2^+, you are to devise a plan which will enable you to determine the colour exhibited by two other ions containing vanadium, VO^{2+} and V^{3+}. Your plan should only involve simple test–tube reactions.

The standard electrode potentials of the following ions are as shown:

$VO_2^+ + 2H^+ + e^- \rightleftharpoons H_2O + VO^{2+}$ $E^\ominus = +1.00\ V$
$VO^{2+} + 2H^+ + e^- \rightleftharpoons H_2O + V^{3+}$ $E^\ominus = +0.34\ V$
$V^{3+} + e^- \rightleftharpoons V^{2+}$ $E^\ominus = -0.26\ V$

There are four reducing agents available as shown:

$Zn^{2+} + 2e^- \rightleftharpoons Zn$ $E^\ominus = -0.76\ V$
$Sn^{2+} + 2e^- \rightleftharpoons Sn$ $E^\ominus = -0.14\ V$
$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$ $E^\ominus = +0.68\ V$
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E^\ominus = +0.77\ V$

(i) Explain which reducing agent(s) will **not** be suitable for determining the colours exhibited by VO^{2+} and V^{3+}.

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…………………………………………………………………………………… [2]

(ii) Complete the table by choosing a suitable reducing agent for determining the colour exhibited by VO^{2+} and V^{3+} respectively. Justify your choice by calculating relevant $E^{\ominus}_{cell}$ values.

	Reducing agent	Justification
$VO_2^+ \rightarrow VO^{2+}$		
$VO_2^+ \rightarrow V^{3+}$		

[4]

[Total: 18]

VICTORIA JUNIOR COLLEGE
2017 JC2 PRELIMINARY EXAMINATIONS
H2 CHEMISTRY PAPER 1 ANSWERS

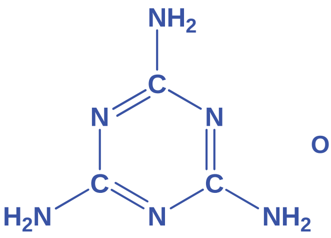
1	**B**	6	**B**	11	**B**	16	**D**	21	**C**	26	**C**
2	**B**	7	**A**	12	**B**	17	**A**	22	**B**	27	**A**
3	**A**	8	**D**	13	**A**	18	**C**	23	**B**	28	**D**
4	**D**	9	**D**	14	**D**	19	**C**	24	**D**	29	**A**
5	**C**	10	**B**	15	**C**	20	**A**	25	**D**	30	**C**

Victoria Junior College
2017 H2 Chemistry Prelim Exam 9729/2
Suggested Answers

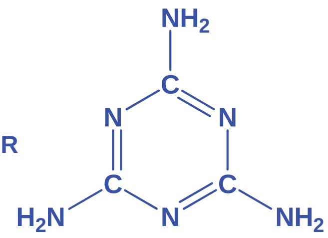
1 This question concerns some unusual nitrogen compounds.

(a) Heating monomer **X** to 150 °C produces the trimer, melamine, $C_3H_6N_6$. Melamine is a cyclic planar molecule and is symmetrical.

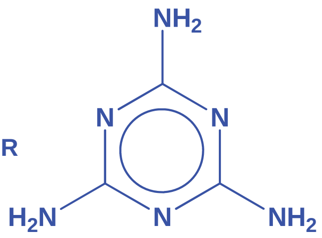
(i) Suggest a structure for melamine.



OR



OR



[1]

(ii) The average C–N bond length is 0.145 nm and the average C=N bond is 0.125 nm. Suggest why all the carbon-nitrogen bonds in melamine are intermediate in length between the given C–N and C=N values.

The structure of melamine is resonance–stabilised due to delocalisation of p orbital electrons between carbon and nitrogen atoms. Hence all carbon-nitrogen double bonds are partial double bonds.

[1]

(iii) Deduce the structure of **X**. Calculate the number of protons, neutrons and electrons in a monomer of **X**.

$H_2N-C\equiv N$

22p, 20n, 22e$^-$

[2]

(b) Group 1 metal azides, **M**N_3, can be formed by passing heated dinitrogen oxide, N_2O over their corresponding amines, **M**NH_2.

(i) Explain why lattice energies of Group 1 azides become less exothermic down the group.

Lattice energy $\propto |q^+.q^- / (r^+ + r^-)|$. Down Group 1, cationic radius increases, thus lattice energy becomes less exothermic.

[1]

(ii) Suggest why the azides become thermally more stable down the group.

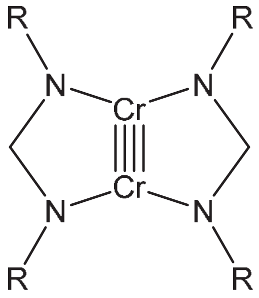
Down Group 1, cationic radius increases while charge remains the same. The charge density and polarising power of cations decrease. Extent of polarisation of anionic charge cloud N_3^- is less. More energy is required to decompose and break the N-N bonds within N_3^- down Group 1. Hence azides become more stable to heat.

[2]

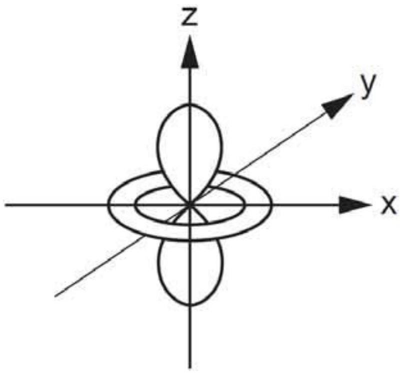
(c) Nitrogen has been used extensively in the research of compounds involving quadruple (bond order of 4) and quintuple (bond order of 5) bonds.

These compounds typically involve transition metal atoms that are able to form bonds between themselves using their d orbitals.

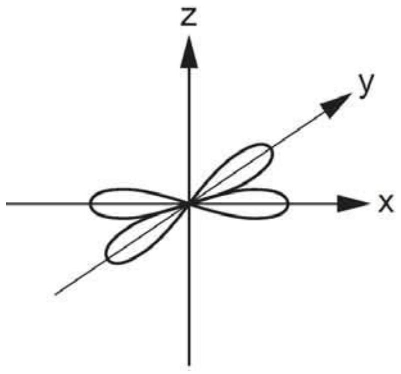
An example is given below:



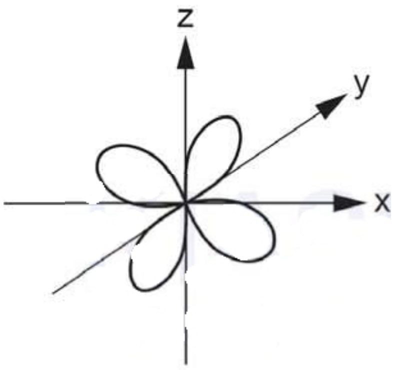
(i) Sketches of the shapes of the atomic orbitals from the d subshells are shown below, in random order. Name and label **each** orbital.



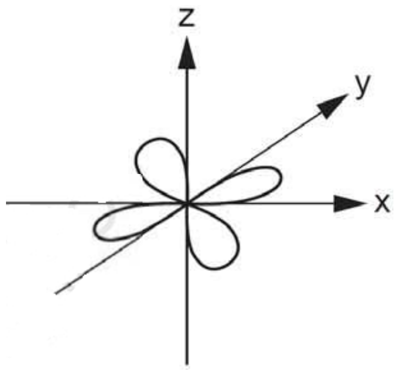
d_{z^2}



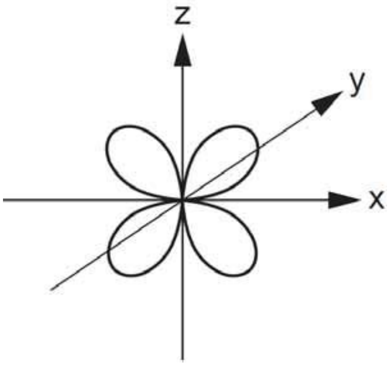
$d_{x^2-y^2}$



d_{yz}



d_{xy}



d_{xz}

[2]

(ii) The d orbitals of an atom can overlap with d orbitals of the same type to form pi (π) and delta (δ) bonds. While a single sigma (σ) bond involves the overlap of two orbital lobes in total, and a single pi (π) bond four lobes, a single delta (δ) bond involves the overlap of eight lobes in total. When two atoms overlap, the z-axis is used to define the internuclear axis.

Suggest two different d orbitals that could be involved in delta bonds (δ).

$d_{x^2-y^2}$ and d_{xy}

[1]

[Total: 10]

2 *Use of Data Booklet is relevant to this question.*

Aerozine 50 is a 50/50 mix of UDMH, $(CH_3)_2N_2H_2$ and hydrazine, N_2H_4. It is used as a rocket fuel, and is typically mixed with dinitrogen tetroxide, N_2O_4, as the oxidising agent.

The equation for the reaction between UDMH and dinitrogen tetroxide under standard conditions is given as follows:

$(CH_3)_2N_2H_2(l) + 2N_2O_4(g) \rightarrow 2CO_2(g) + 3N_2(g) + 4H_2O(l)$ ---------- **reaction 1**

(a) Suggest an equation, including state symbols, for the reaction between hydrazine and dinitrogen tetroxide under standard conditions.

$\mathbf{2N_2H_4(l) + N_2O_4(g) \rightarrow 3N_2(g) + 4H_2O(l)}$

[1]

(b) An experiment was set up such that hydrazine in a spirit burner was combusted beneath a copper can filled with water. It was found that 0.50 g of hydrazine was required to raise the temperature of 100 cm^3 of water in the can by 15 °C.

Using relevant data from the *Data Booklet* and the information given below, calculate the efficiency of the system, expressed as a percentage.

- The heat capacity of the copper can be taken to be 96.0 J K^{-1}
- The density of water can be taken to be 1.00 g cm^{-3}.
- The standard enthalpy change of combustion of hydrazine, found using a bomb calorimeter, has a value of –628 kJ mol^{-1}.

$Q_{aborbed}$ = (100)(4.18)(15) + (96.0)(15)
= 7710 J
$Q_{released}$ = 628000 x (0.5/32.0)
= 9813 J
Efficiency = 7710/9813 x 100 %
= 78.6 %

[3]

Pure UDMH, $(CH_3)_2N_2H_2$, can be used as an alternative to *Aerozine 50* in thruster rockets.

(c) Using relevant data from the *Data Booklet* and the information given below, construct an energy cycle to calculate the enthalpy change for **reaction 1**.

$(CH_3)_2N_2H_2(l) + 4O_2(g) \rightarrow 2CO_2(g) + N_2(g) + 4H_2O(l)$	–1980 kJ mol^{-1}
$N_2O_4(g) \rightarrow 2N(g) + 4O(g)$	+1930 kJ mol^{-1}

$$\begin{tikzcd}
4O_2(g) + (CH_3)_2N_2H_2(l) + 2N_2O_4(g) \arrow[r, "\Delta H_r"] \arrow[d, "-1980"'] & 2CO_2(g) + 3N_2(g) + 4H_2O(l) + 4O_2(g) \arrow[ddl, "{4BE(O{=}O) + 2BE(N{\equiv}N) = 4(496) + 2(944)}"] \\
2CO_2(g) + N_2(g) + 4H_2O(l) + 2N_2O_4(g) \arrow[d, "2(+1930)"'] & \\
2CO_2(g) + N_2(g) + 4H_2O(l) + 4N(g) + 8O(g) &
\end{tikzcd}$$

By Hess Law

$\Delta H_r + 4(496) + 2(944) = -1980 + 2(+1930)$

$\Delta H_r = -1990$ kJ mol^{-1}

[3]

(d) The total mass of propellant (UDMH and dinitrogen tetroxide, N_2O_4) used in the thruster rockets in the ascent stage of a lunar module was 366 kg.

Assuming that UDMH (M_r = 60.0) and dinitrogen tetroxide (M_r = 92.0) were mixed according to the stoichiometric ratio, calculate the mass of UDMH in the propellant mixture.

Let amount of UDMH be x mol and amount of N_2O_4 be 2x mol

$x(60.0) + 2x(92.0) = 366000$

$x = 1500$ mol

$m_{UDMH} = 1500 \times 60.0$

$= 90000$ g

$= 90$ kg

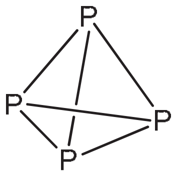
[1]

[Total: 8]

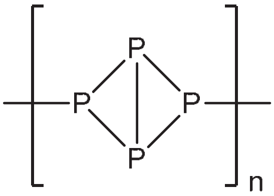
3 Use of the *Data Booklet* is relevant to this question.

Phosphorus and sulfur are elements in Period 3 in the Periodic Table and each can exist in various allotropic forms.

Phosphorus can exist as white phosphorus and red phosphorus. White phosphorus exists as a tetrahedron with bond angle 60° while red phosphorus exists as a polymeric chain of regular tetrahedrons.

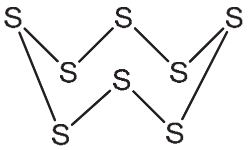


white phosphorus



red phosphorus

Sulfur, on the other hand is thermodynamically most stable at room temperature as rhombic sulfur, which consists of puckered S_8 rings.



Both elements form a wide range of compounds with the halogens.

(a) **(i)** By considering the bond angles involved, suggest why white phosphorus is less stable than red phosphorus.

The bond angle of 60° in white phosphorus, P_4 is smaller than 107° in red phosphorus. Hence there will be high angular strain in the bonding / strong electronic repulsion between the bond pairs. Thus, white phosphorus is less stable than red phosphorus.

[1]

(ii) The phosphorus halides fume in air because of reaction with water vapour.

Explain briefly why phosphorus(V) chloride can react with water. Write a balanced equation for its reaction.

PCl_5 undergoes hydrolysis in water due to the presence of energetically accessible vacant 3d orbitals on phosphorus which can accommodate lone pair of electrons from oxygen atoms of water molecules.

$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$

[2]

(b) When sulfur is heated under pressure with chlorine, the major product is SCl_2.

$$S_8(g) + 8Cl_2(g) \rightarrow 8SCl_2(g)$$

(i) Using data from the *Data Booklet*, calculate the enthalpy change, ΔH, for this reaction.

ΔH = Bonds broken – Bonds formed
= 8 x BE(S-S) + 8 x BE (Cl-Cl) – 16 x BE(S-Cl)
= (8 × 264) + (8 × 244) – (16 × 250)
= +64 kJ mol^{-1}

[2]

Under suitable conditions, SCl_2 reacts with water to produce a yellow precipitate and a solution **X**. Solution **X** contains a mixture of SO_2(aq) and compound **Y**.

(ii) By constructing an equation for the hydrolysis of SCl_2, work out how the oxidation number of sulfur changes during the reaction.

$2SCl_2 + 2H_2O \rightarrow S + SO_2 + 4HCl$
Oxidation number of sulfur increases from +2 (in SCl_2) to +4 (in SO_2), and also decreases from +2 (in SCl_2) to 0 (in S).

[2]

(iii) Hence, suggest a pH value of the resultant solution formed.

pH = 1 [OR 2]

[1]

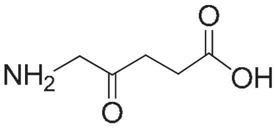
(iv) Using relevant data from the *Data Booklet*, suggest what would be observed when acidified potassium dichromate is added to a sample of solution **X**.

$E^\ominus(Cr_2O_7^{2-} | Cr^{3+}) = +1.33$ V > $E^\ominus(SO_4^{2-} | SO_2) = +0.17$ V
$E^\ominus_{cell} = +1.33 - 0.17 = +1.16$ V (spontaneous)
Thus $K_2Cr_2O_7$(aq), solution changes from orange to green.

[2]

[Total: 10]

4 Aminolevulinic acid is involved in the synthesis of haemoglobin and chlorophyll.

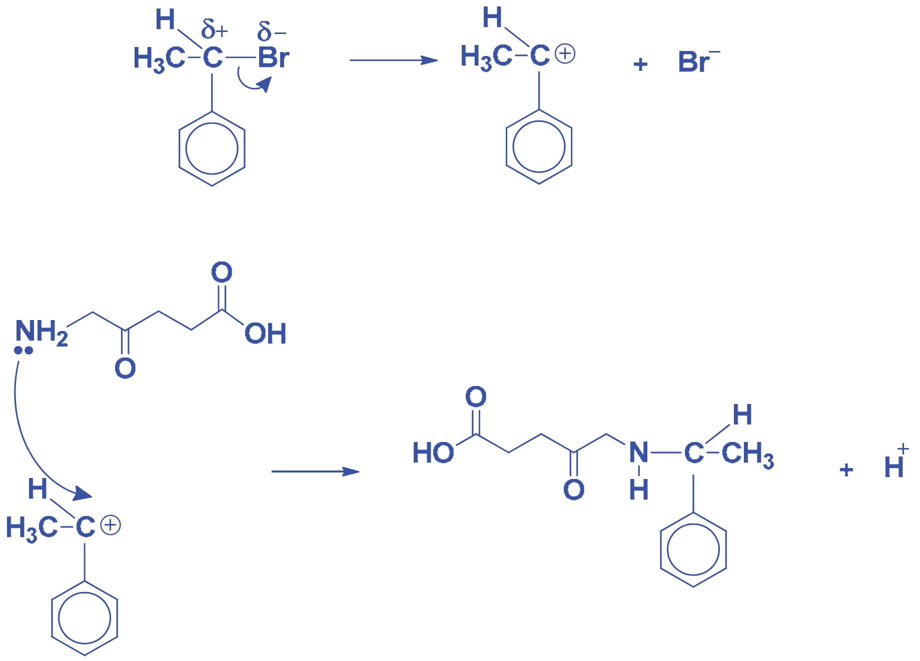


aminolevulinic acid

(a) Aminolevulinic acid reacts readily with (1-bromoethyl)benzene.

Name and outline the mechanism for the reaction of aminolevulinic acid with **(**1-bromoethyl**)**benzene.

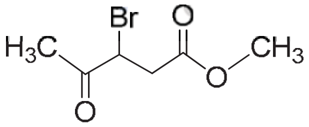
S_N1 mechanism



Note:
Dipole on C-Br and lone pair on N
Carbocation intermediate
Arrow drawn from lone pair on N to C+ AND arrow indicating heterolytic fission of C-Br bond
Product

[3]

(b) Compound **A** is a precursor in the synthesis of aminolevulinic acid.



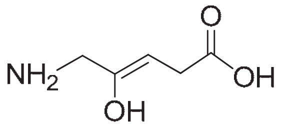
compound **A**

Suggest a simple chemical test to distinguish between compound **A** and aminolevulinic acid. Include clearly the reagents, conditions and observations for each compound. Write a balanced equation for any positive test.

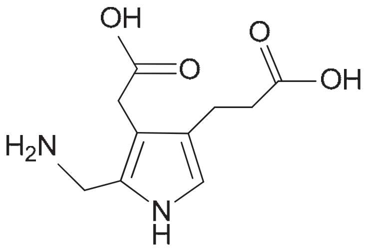
I_2(aq)/NaOH(aq), heat < 70°C
Observation for compound A: pale yellow ppt formed
$CH_3CO_2CH_2CH(Br)COCH_3 + 3I_2 + 6OH^- \rightarrow$
$^-O_2CCH_3CH_2CH(OH)CO_2^- + CHI_3 + 3I^- + 3H_2O + CH_3OH + Br^-$
Observation for aminolevulinic acid: no ppt formed
[Alternative tests accepted: Na_2CO_3 OR Na OR $KMnO_4/H_2SO_4$]

[3]

(c) Porphobilinogen is a pyrrole involved in porphyrin metabolism. It is generated from a reduced form of aminolevulinic acid, compound **B** by the enzyme ALA dehydratase.

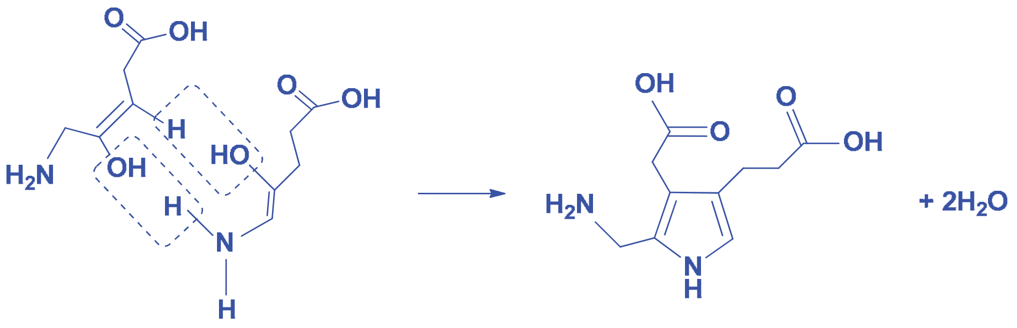


compound **B**



porphobilinogen

Show how porphobilinogen may be formed from the condensation of two molecules of compound **B**, with the help of a balanced equation. Indicate clearly with dotted lines how the non-organic by-products are formed.



Note:
2 molecules of A aligned as above
2 x dotted lines showing formation of $2H_2O$

[2]

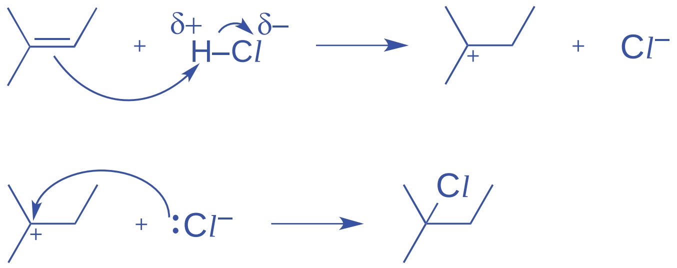
[Total: 8]

5 The formation of carbon-carbon bonds is important in the synthesis of large organic compounds. This question discusses the chemistry of some carbon-carbon bond forming reactions.

(a) Most of the starting reagents of such reactions typically involve a halogenoalkane. Halogenoalkanes can be obtained by reacting alkenes with hydrogen halides.

(i) Name and outline the mechanism of the reaction between 2-methylbut-2-ene and hydrogen chloride, showing the major product formed.

Electrophilic Addition



pair of arrows and partial charges (step 1)
correct intermediate & major product
balanced equations

[2]

(ii) 2-methylbut-2-ene can also react with hydrogen bromide and hydrogen iodide to form its respective halogenoalkane.

Suggest and explain, with reference to the mechanism of the reaction, how the rate of reaction changes from HC*l* to HI.

The **first step of the mechanism is the rate-determining step**.

From C*l* to I, **atomic radius increases**, **H–X bond length increases due to less effective overlap of orbitals**. **Bond strength decreases** and **less energy is required** to break H–X bond.

Hence rate of reaction increases in the following order.
Rate of reaction: HC*l* < HBr < HI

[2]

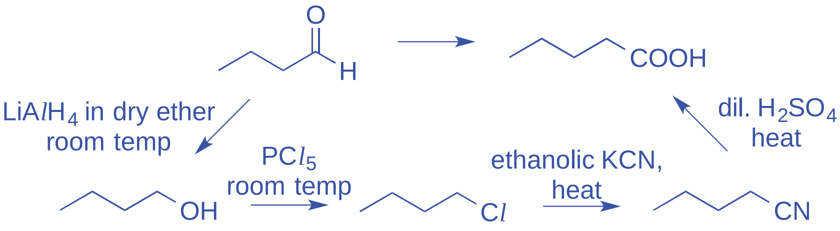
(b) Depending on the conditions of the reaction, a nitrile group can be introduced into an organic compound through either a halogenoalkane or a carbonyl, forming carbon-carbon bonds in the process.

(i) Suggest why alkenes are unable to react to form nitriles in the same way as carbonyls.

CN^- acts as a nucleophile due to the presence of a lone pair of electrons available for donation. **Alkenes have high electron density in the C=C** and hence **would repel CN^-**.

[1]

(ii) Propose a synthetic route that is **less than 5 steps** to convert butanal to pentanoic acid. State the reagents and conditions you would use for each step and draw the structures of the intermediate compounds.



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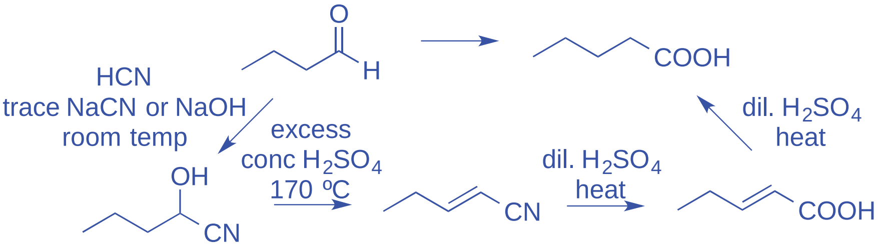


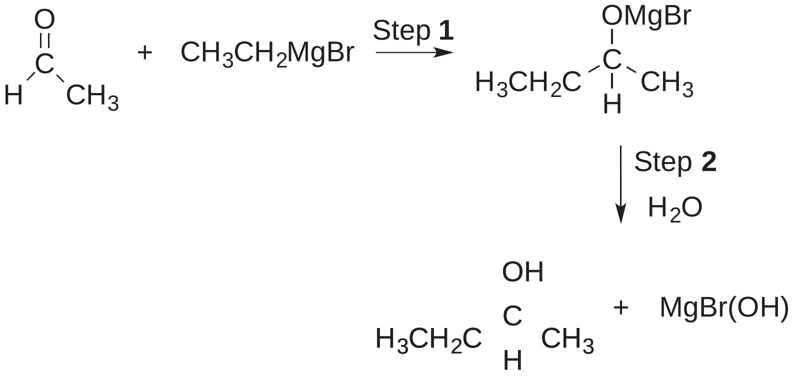
note: elimination of water and hydrolysis of nitrile are interchangeable

[5]

(c) A classic carbon-carbon bond formation reaction is the Grignard reaction. First, the Grignard reagent, an alkylmagnesium halide, is formed by reacting a halogenoalkane with magnesium.

$$CH_3CH_2Br + Mg \rightarrow CH_3CH_2MgBr$$

The reaction then proceeds with a reaction between the alkylmagnesium halide with a carbonyl to give an alcohol in a 2-step reaction.

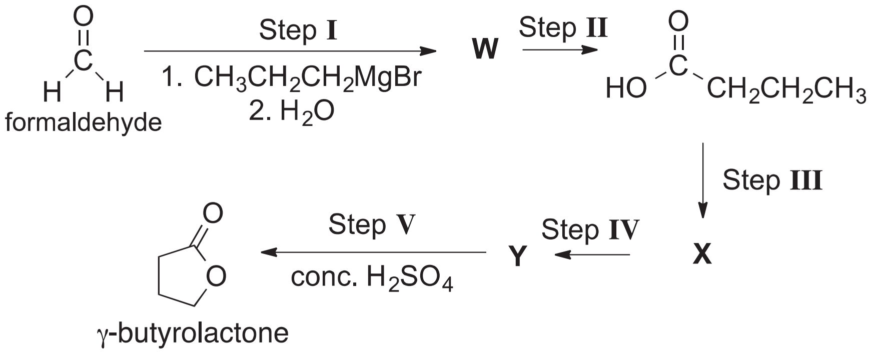


(i) Suggest the type of mechanism for Step **1**.

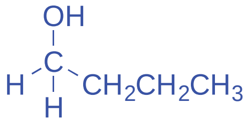
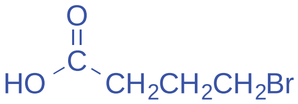
Nucleophilic addition

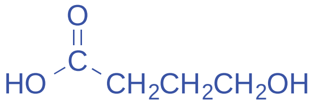
[1]

(ii) The synthesis of γ-butyrolactone, a common solvent from formaldehyde, involves the Grignard reaction as follows.



Propose structures of **W**, **X**, **Y** and **Z**.

 $HOCH_2CH_2CH_2CH_3$	 $HOOCCH_2CH_2CH_2Br$
W	**X**

 $HOOCCH_2CH_2CH_2OH$
Y

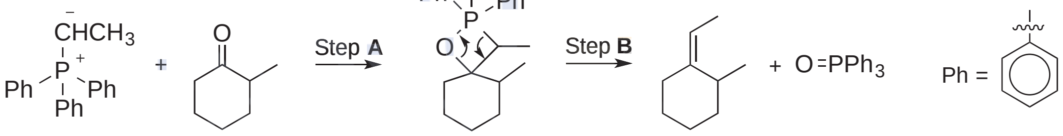
[3]

(iii) State the reagents and conditions required for steps **II**, **III** and **IV**.

Step **II**: **$KMnO_4$, H_2SO_4(aq), heat**
Step **III**: **Br_2, excess $CH_3CH_2CH_2CO_2H$, uv light**
Step **IV**: **NaOH(aq), heat**

[3]

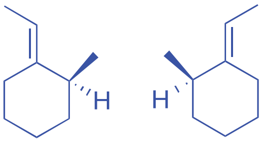
(d) Another common carbon-carbon bond formation reaction is the Wittig reaction. A phosphorus-containing reagent reacts with a carbonyl to form an intermediate, which then cleaves quickly to give an alkene.



(i) Identify, with the aid of a diagram, the type of stereoisomerism that the product can show.

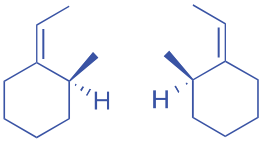
cis-trans isomerism (OR enantiomerism)

trans



(+) (–)

cis



Note: since the question asked for “can show”, students only need to identify one, even though there were 2

[2]

(ii) By considering the hybridisation of relevant carbon atoms, suggest a reason why step **B** is a fast reaction.

The carbon centres in the 4-membered cyclic ring are **sp^3 hybridised**. There is **high ring strain** due to angles being less than the ideal 109.5^{o}. This results in the ring being **unstable**, which will then collapse quickly.

[2]

[Total: 21]

6 **(a)** 1.0 cm^3 of 0.10 mol dm^{-3} solution of sodium iodide was added to 1.0 cm^3 of 0.050 mol dm^{-3} $AgNO_3$(aq). 3.0 cm^3 of 1.0 mol dm^{-3} NH_3(aq) was then added. The resulting precipitate formed is virtually insoluble.

(i) Show that the number of moles of I^-(aq) that is **not** used to form the precipitate is 5.0 x 10^{-5} mol.

Amount of I^- originally = 1.0 / 1000 x 0.10 = 1.0 x 10^{-4} mol
Amount of Ag^+ originally = 1.0 / 1000 x 0.050 = 5.0 x 10^{-5} mol
Amount of I^- left = 1.0 x 10^{-4} – 5.0 x 10^{-5} mol
= 5.0 x 10^{-5} mol (the rest of I^- has been precipitated as AgI)

[1]

(ii) Show that under these conditions [I^-(aq)] = 0.010 mol dm^{-3} and hence [Ag^+(aq)] which would just allow the precipitate to dissolve.

K_{sp}(AgI) = 8.0 x 10^{-17} mol^2 dm^{-6}

[I^-(aq)]
= (5.0 x 10^{-5}) / (1.0 + 1.0 + 3.0) x 1000 = 0.010 mol dm^{-3}

For AgI to just dissolve, ionic product < K_{sp}(AgI)
[Ag^+(aq)] = 8.0 x 10^{-17} / 0.010 = 8.0 x 10^{-15} mol dm^{-3}

[1]

(iii) Under the conditions of the experiment, [Ag^+(aq)] = 1.9 x 10^{-9} mol dm^{-3}. Use your answer in **(a)(ii)** to justify why the precipitate is virtually insoluble.

The value of [Ag^+] calculated in (a)(ii) is less than 1.9 x 10^{-9} mol dm^{-3}, Hence ionic product > K_{sp}(AgI), precipitation still occurs and will not be soluble.

[1]

(iv) When the above experiment is repeated using sodium chloride instead of sodium iodide, different observations were made. Briefly describe and explain the differences with the aid of equations. **No** calculations are required.

$Ag^+(aq) + X^-(aq) \rightleftharpoons AgX(s)$ X = Cl or I ……… (1)

$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$
Formation of white ppt of silver chloride and yellow ppt of silver iodide
Silver chloride will dissolve in aqueous NH_3 but silver iodide will not.
Aqueous NH_3 will form a complex with Ag^+ ions,
thus equilibrium (1) will shift left to restore the Ag^+ ions that were removed.
Hence ionic product of [Ag^+][Cl^-] < K_{sp} (AgCl) so ppt dissolves
AgI is less soluble with a much lower K_{sp} hence ionic product of [Ag^+][I^-] > K_{sp}(AgI) so ppt remains.

[3]

(b) The standard electrode potential values for reactions **(I)** and **(II)** are +1.21 V and +0.54 V respectively.

$IO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2}I_2 + 3H_2O$ **(I)**

$\frac{1}{2}I_2 + e^- \rightleftharpoons I^-$ **(II)**

(i) Find the standard Gibbs free energy change for **each** of the reactions **(I)** and **(II).**

For reaction (I),
$\Delta G^{\ominus} = -5 \times 96\,500 \times 1.21 = -5.84 \times 10^5$ J mol^{-1}
For reaction (II),
$\Delta G^{\ominus} = -1 \times 96\,500 \times 0.54 = -5.21 \times 10^4$ J mol^{-1}

[1]

(ii) Use your answers from **(b)(i)** to find the standard Gibbs free energy change for the following reaction, and hence its standard electrode potential.

$IO_3^- + 6H^+ + 6e^- \rightleftharpoons I^- + 3H_2O$

$\Delta G^{\ominus} = -5.21 \times 10^4 + (-5.84 \times 10^5) = -6.36 \times 10^5$ J mol^{-1}
$E^{\ominus}(IO_3^-/I^-) = -6.36 \times 10^5 / (-6 \times 96\,500) = +1.10$ V

[2]

(c) When 0.530 g of potassium iodide was completely reacted with an aqueous solution of XeF_2, all the iodide is converted into the iodate anion. A student proposed that the anion could be either iodate(V), IO_3^-, or iodate(VII), IO_4^-.

(i) Show that the number of moles of iodate that were involved in the reaction is 3.19×10^{-3} mol.

Amount of iodate = Amount of KI
= 0.530 / 166.0
= 3.19×10^{-3} mol

[1]

(ii) The equation involving the reaction of iodate(VII), IO_4^- with excess acidified potassium iodide is given below:

$IO_4^- + 8H^+ + 7I^- \rightarrow 4I_2 + 4H_2O$

For the reaction involving iodate(V), IO_3^- with excess acidified potassium iodide, write the corresponding half equations and hence the overall **ionic** equation.

Reduction: **$2IO_3^- + 12H^+ + 10e^- \rightarrow I_2 + 6H_2O$**
Oxidation: **$2I^- \rightarrow I_2 + 2e^-$**
Overall ionic equation: **$IO_3^- + 6H^+ + 5I^- \rightarrow 3I_2 + 3H_2O$**

[3]

(iii) 3.19 x 10^{-3} mol of iodate anion, which is either iodate(V), IO_3^-, or iodate(VII), IO_4^- is acidified, and added to excess potassium iodide solution where iodine is formed. It is found that 28.40 cm^3 of 0.900 mol dm^{-3} of $Na_2S_2O_3$ is required to discharge the colour of iodine.

It is given that $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$.

By using the information and your answers in **(c)(ii)**, determine whether the anion is iodate(V), IO_3^-, or iodate(VII), IO_4^-.

Since $I_2 : S_2O_3^{2-} = 1 : 2$,
assuming anion is IO_3^-, $IO_3^- : S_2O_3^{2-} = 1 : 6$
assuming anion is IO_4^-, $IO_4^- : S_2O_3^{2-} = 1 : 8$

If anion is IO_3^-,

volume of $S_2O_3^{2-}$ required = $\dfrac{6 \times 3.19 \times 10^{-3} \times 10^3}{0.900} = 21.30$ **cm^3**

If anion is IO_4^-,

volume of $S_2O_3^{2-}$ required = $\dfrac{8 \times 3.19 \times 10^{-3} \times 10^3}{0.900} = 28.40$ **cm^3**

(or any reasonable method of elimination is accepted)
Hence the anion is IO_4^-.

[2]

(d) Nitrogen trifluoride was first prepared in the electrolysis of a molten mixture of ammonium fluoride and hydrogen fluoride using inert electrodes.

(i) It is given that at one of the electrodes, the following reaction occurs:
$NH_4^+ + 3F^- \rightarrow NF_3 + 4H^+ + 6e^-$

State the electrode that is involved in the above reaction and its polarity.

Anode
positive

[1]

(ii) When the above electrolysis was set up using a current of 0.50 A, 0.276 g of nitrogen trifluoride was liberated. Calculate the time taken for the electrolysis to occur.

Amount of NF_3 collected = 0.276 / (14.0 + 19.0 x 3) = 3.89 x 10^{-3} mol
Amount of electrons needed to liberate NF_3
= 3.89 x 10^{-3} x 6 = 2.33 x 10^{-2} mol

Total quantity of charge used = 2.33 x 10^{-2} x 96 500 = 2250 C

Time taken = 2250 / 0.50 = 4500 s = 75 min

[2]

[Total: 18]

Victoria Junior College
2017 H2 Chemistry Prelim Exam 9729/3
Suggested Answers

Section A

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

1 **(a)** Ethanoic acid and its salt, sodium ethanoate, is often used as an acid buffer to help extend the shelf-life of food products such as meat, fish and dairy.

A buffer solution of pH 5.5 was prepared by mixing 0.200 mol dm^{-3} of ethanoic acid and 0.200 mol dm^{-3} aqueous sodium ethanoate.

(K_a of ethanoic acid = 1.74 x 10^{-5} mol dm^{-3})

(i) What do you understand by the term *buffer solution*? [1]

A buffer solution can <u>maintain a fairly constant pH</u> when a <u>small amount</u> of acid or base is added to it.

(ii) Calculate the ratio of $\frac{[\text{ethanoate}]}{[\text{ethanoic acid}]}$ required to prepare the above buffer solution.

Hence deduce whether the above buffer is more effective in buffering against added acids or bases.

Write an equation to illustrate your answer. [3]

K_a = $\frac{[H^+][A^-]}{[HA]}$ = 1.74 x 10^{-5} where A^- is ethanoate and HA is ethanoic acid.

$$\frac{[A^-]}{[HA]} = \frac{1.74\times10^{-5}}{10^{-5.5}} = \frac{1.74\times10^{-5}}{3.16\times10^{-6}} = \frac{5.51}{1}$$

As <u>higher [ethanoate]</u> is present, buffer is <u>better at removing added acids</u>.

$CH_3CO_2^- + H^+ \rightarrow CH_3CO_2H$

(iii) Calculate the volume of ethanoic acid and that of aqueous sodium ethanoate required to prepare 60 cm^3 of the above buffer. [1]

Let x cm^3 be volume of ethanoate and (60 – x) cm^3 to be volume of ethanoic acid.

$$\frac{x}{60-x} = \frac{5.51}{1}$$

x = 50.8 cm^3

Hence 50.8 cm^3 of sodium ethanoate and (60- 50.8) = 9.20 cm^3 of ethanoic acid will be required.

(iv) The boiling points of the components in the buffer are as shown.

Ethanoic acid	118°C
Sodium ethanoate	881°C

With reference to the structure and bonding present in the compounds, account for the difference in the boiling points. [3]

Ethanoic acid has a simple molecular structure with hydrogen bonding between the polar molecules.
Sodium ethanoate has a giant ionic structure with very strong electrostatic attractions between the oppositely charged ions. Hence a lot of heat energy is required to overcome the ionic attractions compared to the much weaker hydrogen bonding between acid molecules.

(b) The limestone that collects in kettles in hard water areas is mainly calcium carbonate. It can be removed fairly harmlessly by using a warm solution of vinegar, which contains ethanoic acid. The limestone dissolves with fizzing and a solution of calcium ethanoate remains.

(i) Write a balanced equation for the reaction between ethanoic acid and calcium carbonate. [1]

$2CH_3COOH + CaCO_3 \rightarrow Ca(CH_3COO)_2 + CO_2 + H_2O$

When the solution in **(b)** is evaporated and the resulting solid calcium ethanoate is heated strongly in a test-tube, an organic compound **Q** is formed, which condenses to a colourless liquid. The residue in the tube contains calcium carbonate.

When 0.10 g of compound **Q** was injected into a gas syringe at a temperature of 383 K and a pressure of 101 kPa, 55 cm^3 of vapour were produced.

(ii) Calculate the relative molecular mass of **Q**. [2]

$$PV = nRT = \frac{mRT}{M}$$

Rearranging gives $M = \frac{mRT}{PV} = \frac{0.10 \times 8.31 \times 383}{101 \times 10^3 \times 55 \times 10^{-6}}$

$= 57.3$

(iii) Compound **Q** is neutral and water-soluble. **Q** does not react with sodium metal nor with Fehling's solution but it does react with alkaline aqueous iodine.

Suggest a structural formula for **Q.** Justify your answer by reference to these properties of **Q**. [4]

Reaction	**Deduction**
Neutral	**Absence of acidic and basic groups**
No reaction with Na metal	**Absence of –OH group so not alcohol ad carboxylic acid**
No reaction with Fehling's solution	**Absence of aliphatic aldehyde**

Positive test with alkaline aqueous iodine	**Presence of $CH_3CO–$ group**

Mass of $CH_3CO–$ group = 43.0 hence remaining group has a mass of 57.9 – 43.0 = 14.9 ≈ 15.0
⇒ $–CH_3$ group present
Q is propanone CH_3COCH_3

(iv) Construct a balanced equation for the formation of **Q** by the action of heat on calcium ethanoate. [1]

$(CH_3COO)_2 \rightarrow CaCO_3 + CH_3COCH_3$

(v) The residue calcium carbonate can also undergo thermal decomposition when heated very strongly. Copper(II) carbonate behaves in a similar manner when heated.

State which carbonate, calcium or copper(II) will have a higher decomposition temperature. Explain your answer, with the help of relevant data from the *Data Booklet*. [3]

$CaCO_3$ will have a higher decomposition temperature.
Ionic radius of Ca^{2+} = 0.099 nm; Cu^{2+} = 0.073 nm

Size of Ca^{2+} is larger so its charge density is lower. Polarising power of Ca^{2+} is thus lower and less able to distort the electron cloud of CO_3^{2-} ion. Hence, $CaCO_3$ is more stable to heat and has a higher decomposition temperature.

[Total: 19]

2 **(a)** In a closed reaction vessel maintained at a high temperature, 1 mol of Al_2Cl_6 dimers dissociate into $AlCl_3$ according to the following equation.

$$Al_2Cl_6(g) \rightleftharpoons 2AlCl_3(g)$$

The average M_r of the equilibrium gas mixture is found to be 178.0.

(i) Given that the average M_r of the equilibrium gas mixture is the sum of the mole fractions of each gas, multiplied by the M_r of that gas, calculate the degree of dissociation of Al_2Cl_6, α. [3]

	$Al_2Cl_6(g)$ ⇌	$2AlCl_3(g)$
initial amt / mol	**1**	**0**
change	**–x**	**+2x**
eqm amt / mol	**1– x**	**2x**

Total amt of gases present at eqm
= 1– x + 2x
= (1 + x) mol

Average $M_r = [(1-x)/(1+x)]\,M_r(Al_2Cl_6) + [2x/(1+x)]\,M_r(AlCl_3)$
$= 178.0$

$178.0 = [(1-x)/(1+x)](267.0) + [2x/(1+x)](133.5)$
$x = 0.50$

Hence, $\alpha = x/1$
$= 0.50$

(ii) Write down the expression of K_p for the above equilibrium system. Hence, show that $K_p = K_cRT$. [2]

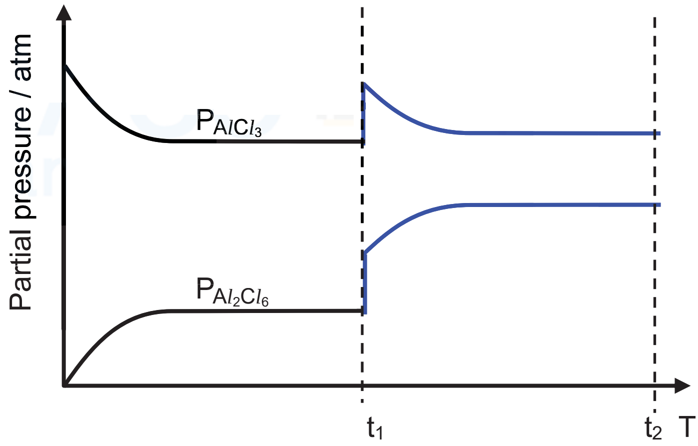
$K_p = (P_{AlCl_3})^2 / P_{Al_2Cl_6}$

Using PV = nRT; P = (n/V)RT = CRT

Hence, $K_p = ([AlCl_3]RT)^2 / [Al_2Cl_6]RT$
$= [AlCl_3]^2RT / [Al_2Cl_6]$
$= K_cRT$

(iii) An experiment on the dissociation of Al_2Cl_6 was conducted in a closed container of a fixed volume and the partial pressures of all the components were plotted as shown in the figure below.

Copy and complete the diagram to show how the partial pressure of each gas changes when the volume of the container is halved at t_1 until t_2.



[2]

Note:
Sudden increase in P of each gas at t_1
Increase in P_{Al2Cl6} and decrease in P_{AlCl3} after t_1 with eqm reached before t_2
Final eqm P_{AlCl3} is higher than the original eqm P before t_1

(b) Strontium chloride, $SrCl_2$ is a typical salt which forms neutral aqueous solutions. It emits a bright red colour in a flame and this allows it to be used as a source of redness in fireworks.

Use the data below to answer the questions that follow.

Standard Gibbs free energy change of solution of $SrCl_2(s)$	-41.6 kJ mol^{-1}
Standard enthalpy change of formation of $SrCl_2(s)$	-828.9 kJ mol^{-1}
Standard enthalpy change of formation of $Sr^{2+}(aq)$	-545.8 kJ mol^{-1}
Standard enthalpy change of formation of $Cl^{-}(aq)$	-167.5 kJ mol^{-1}
Standard enthalpy change of hydration of $Sr^{2+}(g)$	-1446 kJ mol^{-1}
Standard enthalpy change of hydration of $Cl^{-}(g)$	-378 kJ mol^{-1}

(i) Define the term *standard enthalpy change of formation* of strontium chloride. [1]

Standard enthalpy change of formation of $SrCl_2$ is the heat change when one mole of $SrCl_2(s)$ is formed from its constituent elements, Sr(s) and $Cl_2(g)$ under standard conditions of 298 K and 1 bar.

(ii) Calculate ΔH°_{sol} and ΔS°_{sol} of strontium chloride. [4]

$$\begin{aligned}\Delta H^{\circ}_{sol}(SrCl_2) &= \Delta H^{\circ}_f(Sr^{2+}{}_{(aq)}) + 2\Delta H^{\circ}_f(Cl^{-}{}_{(aq)}) - \Delta H^{\circ}_f(SrCl_{2(s)})\\ &= -545.8 + 2(-167.5) - (-828.9)\\ &= -51.9 \text{ kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta G^{\circ}_{sol} &= -41.6\\ &= \Delta H^{\circ}_{sol} - T\Delta S^{\circ}_{sol}\\ &= -51.9 - 298(\Delta S^{\circ}_{sol})\\ \Delta S^{\circ}_{sol} &= -34.6 \text{ J mol}^{-1}\text{ K}^{-1}\end{aligned}$$

(iii) Write an equation to show the relationship between the lattice energy of strontium chloride and ΔH°_{sol} of strontium chloride. Hence, calculate the lattice energy of strontium chloride. [2]

$$\Delta H^{\circ}_{sol}(SrCl_2) = -LE + \Delta H^{\circ}_{hyd}(Sr^{2+}{}_{(g)}) + 2\Delta H^{\circ}_{hyd}(Cl^{-}{}_{(g)})$$
$$-51.9 \text{ kJ mol}^{-1} = -LE + (-1446) + 2(-378)$$
$$LE = -2150 \text{ kJ mol}^{-1}$$

(iv) Predict with reasoning, how Gibbs free energy change of formation of strontium chloride, ΔG_f will change with increasing temperature. [2]

ΔS_f of strontium chloride is negative as there a decrease in number of gaseous molecules in the reaction. While ΔH_f of strontium chloride is negative, when temperature increases until $|T\Delta S_f| > |\Delta H_f|$ (or $-T\Delta S_f$ becomes more positive), based on $\Delta G_f = \Delta H_f - T\Delta S_f$, ΔG_f will become more positive at higher temperature and the reaction will become less spontaneous with increasing temperature.

(c) Using the data given below, draw a labelled energy cycle to calculate the enthalpy change of combustion of solid carbon.

$2SrO(s) \rightarrow 2Sr(s) + O_2(g)$ $\Delta H = +1184 \text{ kJ mol}^{-1}$
$SrO(s) + CO_2(g) \rightarrow SrCO_3(s)$ $\Delta H = -234 \text{ kJ mol}^{-1}$
$2SrCO_3(s) \rightarrow 2Sr(s) + 2C(s) + 3O_2(g)$ $\Delta H = +2440 \text{ kJ mol}^{-1}$ [4]

$$\begin{tikzcd}
2SrCO_3(s) \arrow[rr, "+2440"] & & 2Sr(s) + 2C(s) + 3O_2(g) \arrow[d, "2\Delta H_c(C(s))"] \\
& & 2Sr(s) + O_2(g) + 2CO_2(g) \arrow[dl, "-1184"] \\
& 2SrO(s) + 2CO_2(g) \arrow[uul, "2(-234)"] &
\end{tikzcd}$$

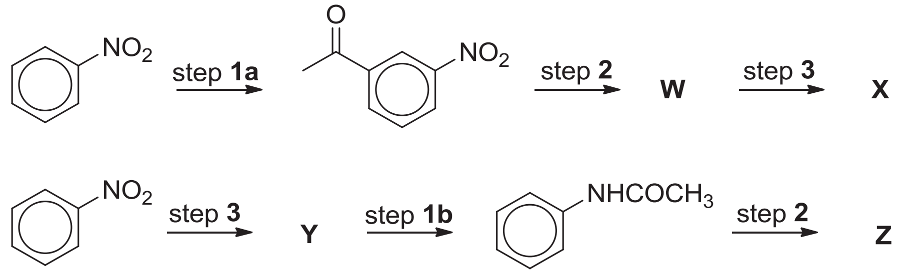
By Hess Law:

$+2440 + 2\Delta H_c(C(s)) + (-1184) = -2(-234)$

$\Delta H_c(C(s)) = -394 \text{ kJ mol}^{-1}$

[Total: 20]

3 **(a)** Consider the following synthesis pathways starting from nitrobenzene:



(i) Ethanoyl chloride (CH_3COCl) is used as a reactant for step **1a** and step **1b** but under different conditions. State the reaction mechanism that occurred for each step **1a** and **1b** and hence explain the difference in the conditions required. [3]

Step 1a: Electrophilic substitution

Step 1b: Nucleophilic substitution or condensation

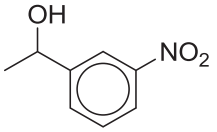
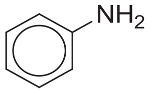
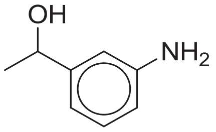
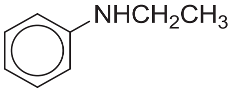
Lewis acid catalyst such as anhydrous $FeCl_3$ is required for step 1a to generate a strong electrophile for reaction.

(ii) Identify the reagents and conditions required for **steps 2** and **3** and hence draw the structures of **W, X, Y** and **Z**.

[Note: **Steps 2** and **3** in both pathways each refers to the same set of reagents and conditions.] [6]

Step 2: $LiAlH_4$ in dry ether, room temp

Step 3: Sn, conc. HCl, heat under reflux, followed by NaOH(aq), room temperature

 **W**	 **Y**
 **X**	 **Z**

(iii) Compare the relative basicity of **Y** and **Z**. [2]

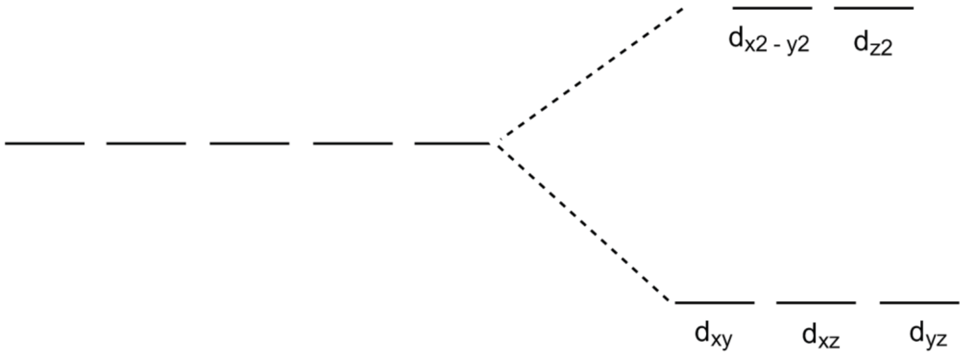
The basicity of a base depends on the availability of the lone pair of electrons on N for donation to acid.

Compound Z has an ethyl group which exerts an electron-donating inductive effect, causing the lone pair on electrons on N to be more available for donation to acid.

Hence compound Z is more basic than compound Y.

(b) In an isolated atom, the five d orbitals have the same energy. When a transition element ion is in an octahedral complex, the d orbitals are split into two groups of different energy levels.

(i) Draw an orbital energy diagram to show this, indicating the type of orbitals in each group. [2]



(ii) Use your diagram in **(b)(i)** to explain why transition element complexes like $Co(H_2O)_6^{2+}$ are often colored. [2]

For $Co(H_2O)_6^{2+}$, 3*d* electrons from the lower energy level are promoted to the upper energy level by absorbing a photon of light from the visible region of the electromagnetic spectrum. This effect is known as *d-d* transition which is possible due to partially filled d-subshell.
The colour seen is the complement of those absorbed in the visible region of the spectrum.

(c) Aqueous cobalt(II) chloride, $CoCl_2$ is a pink solution which gives the following reactions.

$$CoCl_2(aq) \xrightarrow{NaOH(aq)} \begin{array}{l}\text{blue ppt.}\\ \text{insoluble in excess}\end{array} \xrightarrow{H_2O_2} \begin{array}{l}\text{blue ppt.}\\ \text{turned brown}\end{array}$$

$$CoCl_2(aq) \xrightarrow{HCl(aq)} \begin{array}{l}\text{no observable}\\ \text{change}\end{array} \xrightarrow{H_2O_2} \begin{array}{l}\text{no observable}\\ \text{change}\end{array}$$

(i) By using the data given below and appropriate values from the *Data Booklet*, calculate $E^\ominus_{cell}$ and explain the differences in the observations made between **acidic** and **alkaline** medium.

$$Co(OH)_3 + e^- \rightleftharpoons Co(OH)_2 + OH^- \qquad E^\ominus = +0.17\ V$$

Write equations to account for the observations. [4]

In alkaline medium,
precipitation takes place as ionic product of blue ppt. $Co(OH)_2$, exceeds its K_{sp} value which is insoluble in excess.
$Co^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Co(OH)_2(s)$
$Co(OH)_2(s)$ undergoes redox reaction with H_2O_2 (HO_2^- in alkaline medium) to give brown ppt of $Co(OH)_3$.
$HO_2^- + H_2O + 2e^- \rightleftharpoons 3OH^- \qquad E^\ominus = +0.88\ V$
$Co(OH)_3 + e^- \rightleftharpoons Co(OH)_2 + OH^- \qquad E^\ominus = +0.17\ V$
$2Co(OH)_2 + HO_2^- + H_2O \rightarrow 2Co(OH)_3 + OH^-$
$E^\ominus_{cell} = +0.88 - (+0.17)$
$= 0.71\ V$ which is feasible

In acidic medium,

Co^{2+}(aq) does not undergo redox reaction with H_2O_2 and hence no observable change.

$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$ $\qquad E^\ominus = +1.77$ V

$Co^{3+} + e^- \rightleftharpoons Co^{2+}$ $\qquad E^\ominus = +1.89$ V

$2Co^{2+} + H_2O_2 + 2H^+ \rightarrow 2Co^{3+} + 2H_2O$

$E^\ominus_{cell} = +1.77 - (+1.89)$

$= -0.12$ V which is not feasible

(ii) When brine solution instead of HC*l* was added to $CoCl_2$(aq), the solution turned from pink to blue. In this reaction, cobalt behaves like a transition element.
Suggest by means of an ionic equation, an explanation for this observation.
[2]

When brine solution is added to an aqueous solution of Co^{2+}, ligand exchange occurs where Cl^- displaces H_2O ligands, forming the blue $[CoCl_4]^{2-}$.

$[Co(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CoCl_4]^{2-} + 6H_2O$

[Total: 21]

Section B

Answer **one** question from this section.

4 **(a)** The kinetics of the acid–catalysed hydrolysis of ethyl ethanoate may be investigated by analysing samples of the reaction mixture at different times.

$$CH_3CO_2CH_2CH_3 + H_2O \overset{H^+\text{ (catalyst)}}{\rightleftharpoons} CH_3CO_2H + CH_3CH_2OH$$

In one such experiment, the reaction mixture was prepared by mixing solutions of ethyl ethanoate and hydrochloric acid. The concentration of hydrochloric acid, which serves as the catalyst, can be assumed to stay constant throughout the reaction.

At different times, 10.0 cm^3 portions of the reaction mixture were pipetted, quenched and titrated with 0.200 mol dm^{-3} NaOH(aq).

After all necessary samples have been drawn, the remaining reaction mixture is then heated for ½ h to ensure complete reaction. The volume of NaOH required for titrating a 10.0 cm^3 sample of the resulting solution is 30.00 cm^3.

The following experimental data were obtained:

Time / min	Volume of NaOH required for titration, V / cm^3	30.00 – V / cm^3
0	20.00	10.00
10	24.40	5.60
20	26.90	3.10
30	28.20	1.80
40	29.00	1.00
50	29.40	0.60

(i) State how each of the quantities, V and (30 – V), is related to the concentration of the components of the reaction mixture at any point in time. [1]

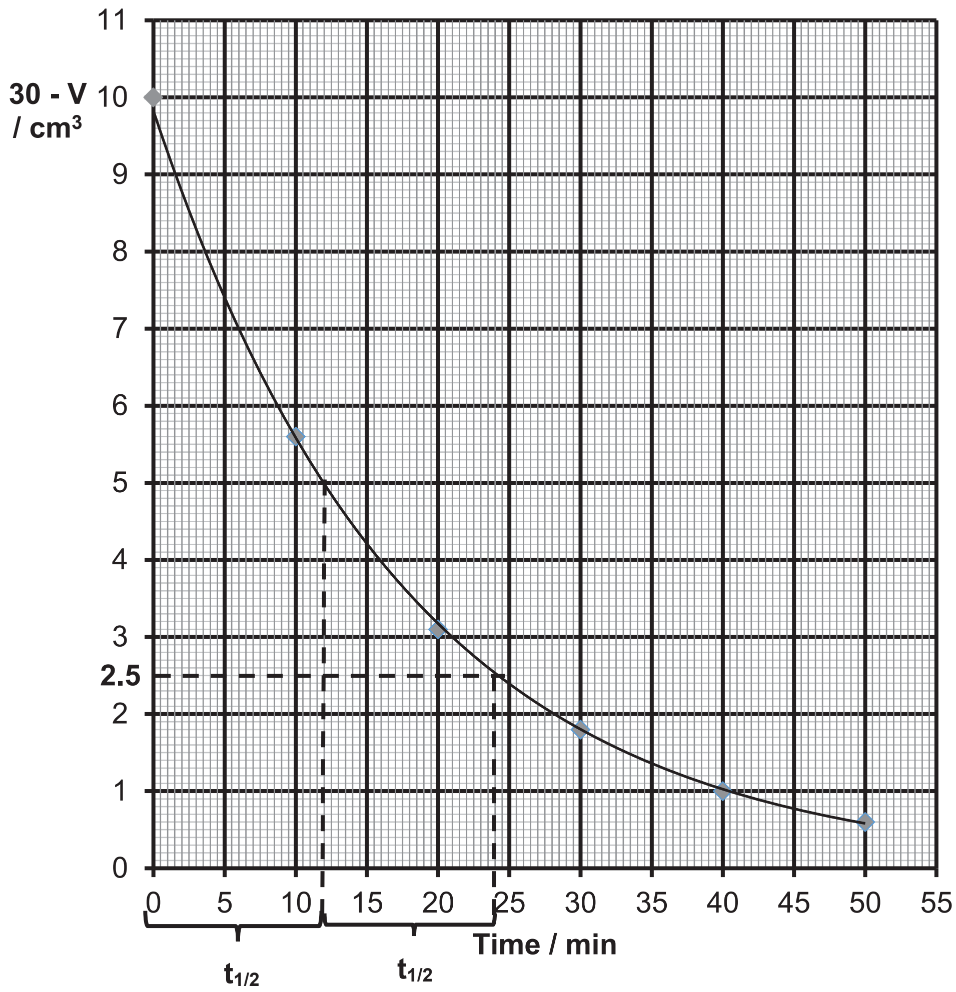
NaOH in titration neutralizes the CH_3CO_2H product and HC*l* catalyst. Hence, volume of NaOH, $\underline{V \propto [CH_3CO_2H] + [HCl]}$.

When hydrolysis reaction is completed, 30.00 cm^3 of NaOH is used to neutralize HC*l* and the maximum $[CH_3CO_2H]$ formed. Hence,

$$\begin{aligned} 30.00 - V &\propto [CH_3CO_2H]_{end} + [\cancel{HCl}] - \{[CH_3CO_2H] + [\cancel{HCl}]\} \\ &\propto [ester]_{initial} - [ester]_{reacted} = [ester] \end{aligned}$$

Hence $\underline{30.00 - V \propto [ester]}$

(ii) Hence, choose appropriate data from the above table to plot a graph that will allow you to determine the order with respect to ethyl ethanoate. [2]



Chooses to plot 30 – V against t
Large scale (at least ½ of grid) and axes properly labelled with units stated
All points correctly plotted
Smooth curve drawn through most of the points

(iii) Deduce the order with respect to ethyl ethanoate, justifying your answer by showing construction lines clearly on your graph. [2]

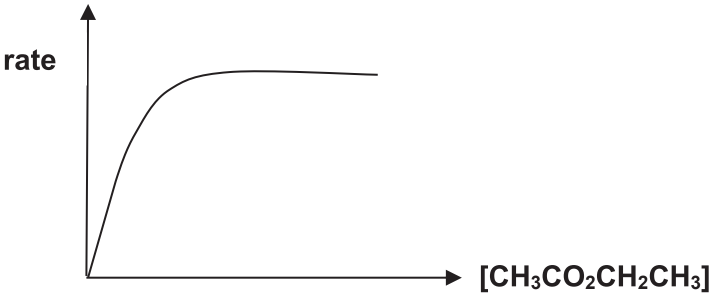
Show clearly two half–lives on graph

Since $t_{1/2}$ is constant at 12 min, reaction is first order w.r.t. ethyl ethanoate.

(iv) Hydrolysis of $CH_3CO_2CH_2CH_3$ can also be catalysed by esterase, an enzyme found in the liver.

Sketch a graph to show how, for a constant [esterase], the rate of hydrolysis varies with [$CH_3CO_2CH_2CH_3$] and explain the shape of the graph. [2]

Graph

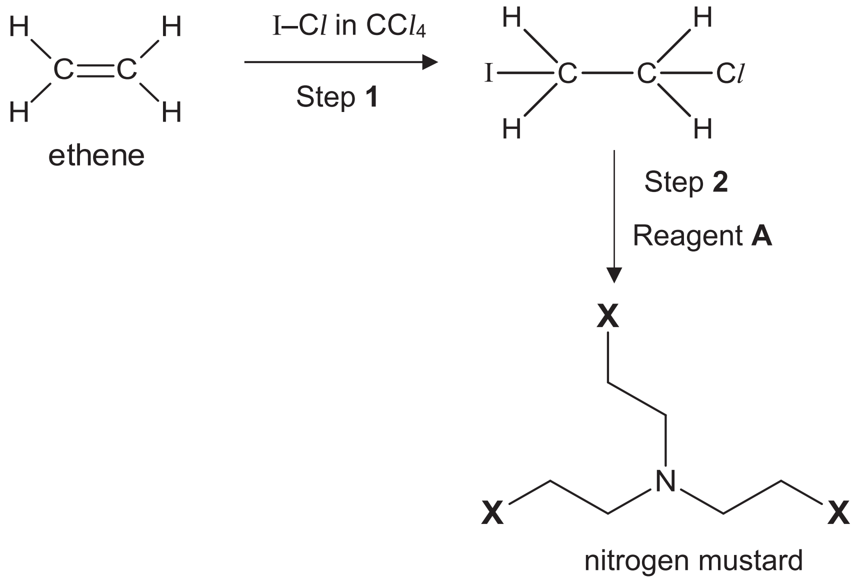


At low [substrate], rate is α [substrate] (OR 1st order rxn) since active sites are not fully occupied.

At high [substrate], rate becomes constant (OR zero order xn) since active sites fully occupied.

(b) Nitrogen mustard gas is commonly used in chemotherapy.

It was suggested that the synthesis of nitrogen mustard can be carried out via the following pathway:



X in nitrogen mustard could be either C*l* or I.

(i) Suggest the identity of reagent **A** and the conditions necessary for an optimal yield in Step **2**. [1]

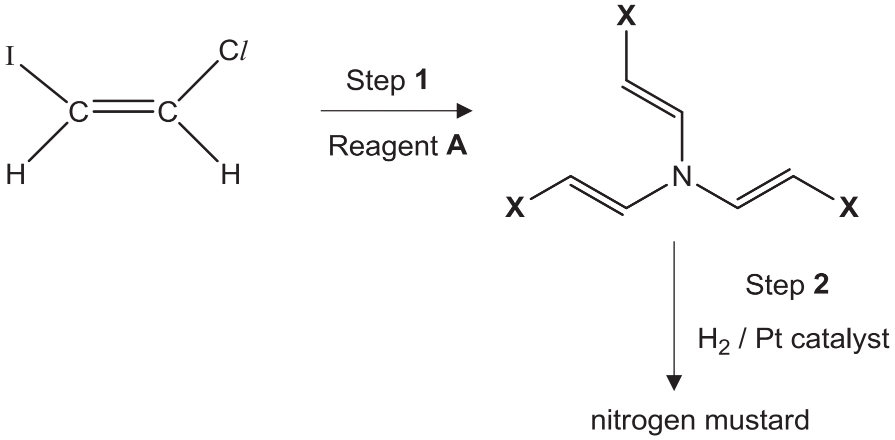
NH_3 dissolved in ethanol in limited amount, heat under pressure in a sealed tube

(ii) Is **X** in nitrogen mustard more likely to be C*l* or I? Explain your answer. [2]

X is likely to be C*l*.

In Step 2, iodine in CH_2ICH_2Cl is more likely to react with NH_3. As iodine atom is bigger than C*l*, the C–I bond is weaker and hence breaks more easily than C–C*l* bond.

(iii) Another reaction pathway was suggested for the synthesis of nitrogen mustard, with reagent **A** used for the first step:



Explain why this method of synthesis is likely to fail. [2]

Step 1 is not likely to occur as <u>$CH_2I=CH_2Cl$ is unreactive</u> towards reagent A. This is because the <u>p–orbital of the halogen atom overlaps with those of the C=C group</u> [OR lone pair on C*l* is delocalized into the ring], causing the C–halogen bond to acquire <u>partial double bond character</u> and hence <u>breaks less easily</u>.

(c) Compound **K** is a solid with the formula, $C_4H_9NO_3$. It dissolves in water to form a solution with high electrical conductivity. When **K** was warmed with aqueous sodium hydroxide, a colourless pungent gas was evolved. Acidification of the resulting solution gives **L**, $C_4H_6O_3$.

L gives an orange precipitate with 2,4-dinitrophenylhydrazine. When lithium aluminium hydride was added to **L**, **M**, $C_4H_{10}O_2$, was produced.

M can also be obtained from the oxidation of **N**, C_4H_8 by cold alkaline potassium manganate(VII).

Deduce the structures of compounds **K**, **L**, **M** and **N** and explain the reactions described. [8]

	Rxn type	**Structural feature**
High electrical conductivity of K	**---**	**K is an ionic compound.**
K + hot NaOH(aq)	**Acid–base reaction**	**Pungent gas is <u>NH_3</u>. This shows that <u>K contains NH_4^+</u>.** **Anion in solution is likely to be carboxylate which is acidified to give <u>carboxylic acid, L</u>.**
L + 2, 4–DNPH	**Condensation**	**<u>L is a carbonyl</u> compound.**
L + LiA*l*H$_4$ → M	**Reduction**	**Loss of one oxygen confirms carboxylic acid in L which is reduced to <u>primary alcohol</u> while carbonyl group is reduced to either <u>primary or secondary alcohol</u> in M.**

N + cold MnO_4^-/OH^- → M	Oxidation (given in qn)	The two alcohol groups in M are adjacent to one another. Since M contains a primary alcohol, N has a $=CH_2$ group (or terminal alkene). Since the other alcohol group in M is primary or secondary, the other alkene C has at least one H attached.

Hence, N is $CH_3CH_2CH=CH_2$.

M is $CH_3CH_2CH(OH)CH_2OH$.

L is $CH_3CH_2COCO_2H$.

K is $CH_3CH_2COCO_2^- NH_4^+$

[Total: 20]

5 **(a)** The reaction between bromide and bromate(V) ions in acid solution is represented as follows:

$$5Br^- + BrO_3^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

The reaction between Br^- and BrO_3^- is relatively fast, with Br_2 produced almost immediately after the reactants are mixed.

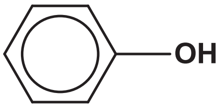
To measure the initial rate of the reaction, aqueous Br^- is added to acidified BrO_3^- solution containing a small amount of compound **A** and methyl orange indicator. The initial colour of the methyl orange is pink as the solution is acidic. After some time, the pink colour disappears due to the bleaching action of Br_2 as shown:

$$\underset{\text{pink}}{Br_2 + \text{methyl orange (acid form)}} \rightarrow \underset{\text{colourless}}{\text{bleached methyl orange}} + 2Br^-$$

The time taken for the pink colour to disappear is an indication of the initial rate.

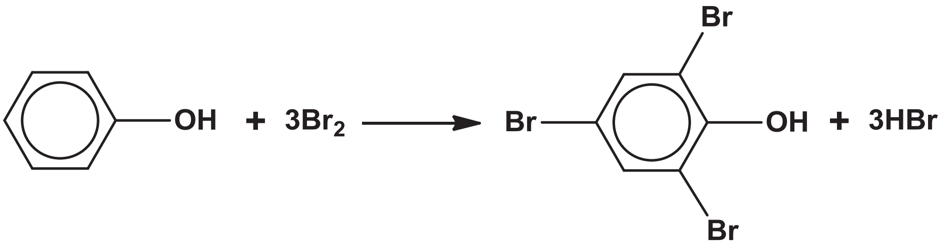
(i) Compound **A** is added to delay the disappearance of the pink colour, which would otherwise take place too quickly for effective measurement of time.

Given that compound **A** is an acidic organic compound containing only **one** functional group, suggest a suitable identity for compound **A**. [1]



(ii) Explain, with the aid of an equation, why the compound mentioned in your answer to **(i)** would be effective in delaying the disappearance of the pink colour. [2]

The lone pair on O of phenol is delocalized into the ring, causing the ring to be strongly activated. Hence, any Br_2 initially formed reacts readily with phenol in the following manner:



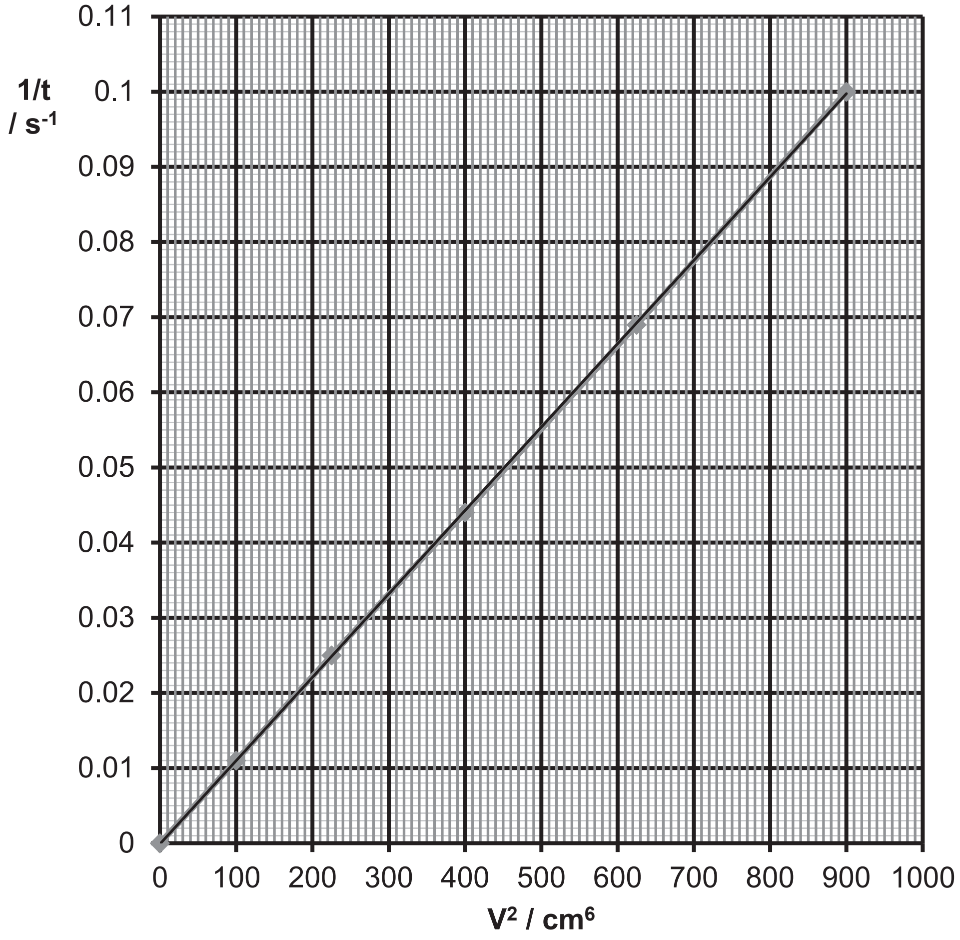
Br_2 is hence prevented from bleaching the methyl orange too soon.

(iii) To find the order of reaction with respect to H^+, a total of five experiments are conducted.

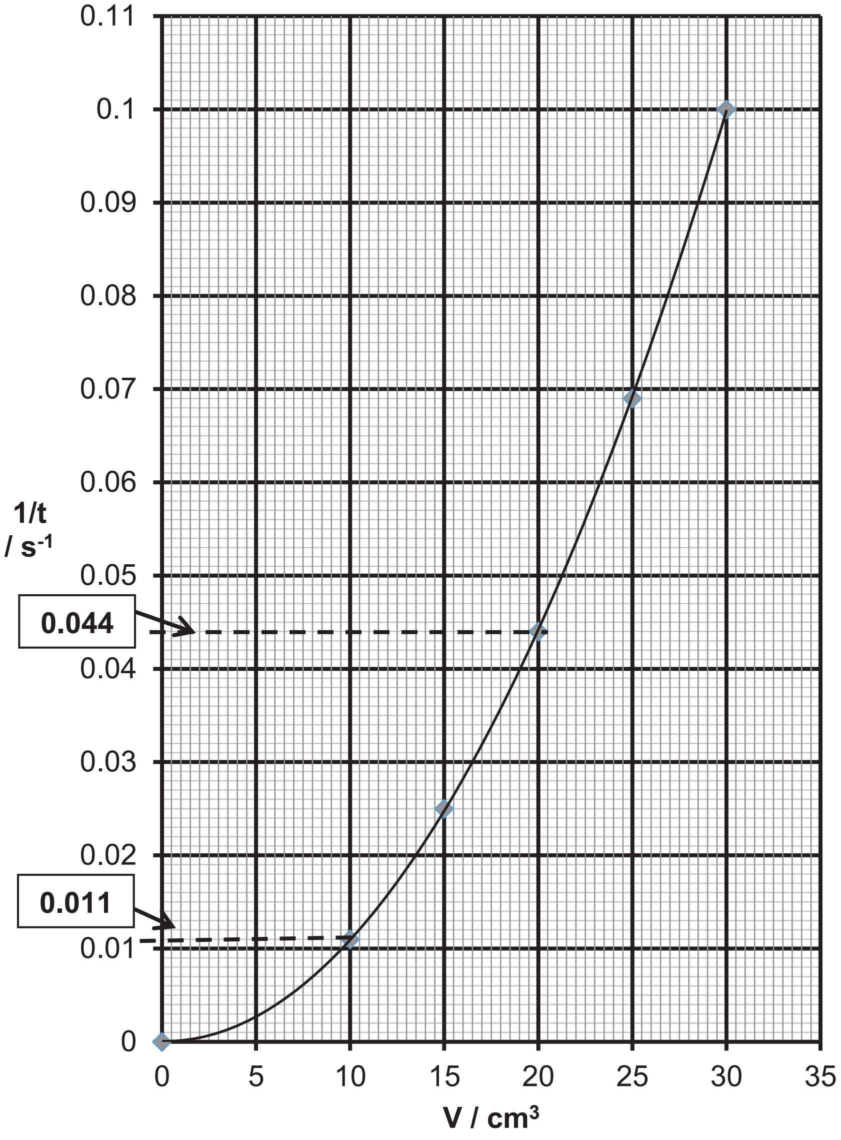
In all the experiments, 10.0 cm^3 of KBr(aq), 10.0 cm^3 of $KBrO_3$(aq), 5.0 cm^3 of Compound **A** solution and 2 drops of methyl orange indicator are used, with water added to keep the total volume constant. The volume of H_2SO_4(aq) used and other experimental data for each experiment are shown in the table below:

Experiment No.	Volume of H_2SO_4(aq), V / cm^3	V^2 / cm^6	Time taken for colour to change from pink to colourless, t / s	$\frac{1}{t}$ / s^{-1}
1	30.0	900	10.0	0.100
2	25.0	625	14.4	0.069
3	20.0	400	22.5	0.044
4	15.0	225	40.0	0.025
5	10.0	100	90.0	0.011

Choose appropriate data from the table above to plot a graph that will enable you to determine the order of reaction with respect to H^+. [2]


1/t / s^{-1}
0.11
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0
100
200
300
400
500
600
700
800
900
1000
V^2 / cm^6

OR



Chooses to plot 1/t vs V^2 or V
Large scale (at least ½ of grid) and axes properly labelled with units stated
All points correctly plotted
Straight line / smooth curve drawn through origin and most of the points

(iv) State, with justification, the order of reaction with respect to H^+. [1]

Using graph of 1/t vs V^2
Since the graph obtained is a <u>straight line passing through the origin</u>, rate $\propto [H^+]^2$. Hence, order with respect to H^+ is 2.

OR Using graph of 1/t vs V
A curve passing through the origin is obtained, whereby as $[H^+]$ (or V) increases by <u>*n* times</u>, rate (or 1/t) increases by <u>n^2 times</u>.
<u>[show any two points with co–ordinates on the graph</u> to illustrate this relationship]

Hence, order with respect to H^+ is <u>2</u>.

(b) Champagne is an example of *sparkling wine*, a term referring to wine with significant levels of carbon dioxide in it, making it fizzy. In the traditional method of production, wine is allowed to undergo a natural fermentation after bottling, which involves conversion of the malic acid present into lactic acid:

$$\underset{\text{malic acid}}{HO_2CCH_2CH(OH)CO_2H} \rightarrow \underset{\text{lactic acid}}{CH_3CH(OH)CO_2H} + CO_2$$

(i) A bottle typically has a total capacity of 1.5 dm^3 and contains 1.3 dm^3 of wine with a malic acid concentration of 0.05 mol dm^{-3}.

By means of the ideal gas equation, calculate the pressure exerted inside the air gap of the bottle by the carbon dioxide produced when all the malic acid present undergoes fermentation.

Assume that the temperature inside the bottle is 25°C. [2]

$n_{CO_2} = n_{\text{malic acid}}$
$= 1.3 \times 0.05$
$= 0.065$ mol

PV = nRT
$P = (0.065)(8.31)(25 + 273) / (0.2 \times 10^{-3})$
$= \underline{8.05 \times 10^5 \text{ Pa}}$

(ii) In fact, the pressure inside the bottle is much less under these conditions. Suggest why the actual pressure differs from the value calculated in **(i)**. [1]

Intermolecular attractive forces are not negligible. This causes the gas molecules to strike the walls of the container with less force, leading to lower pressure.

OR

Carbon dioxide can dissolve in aqueous solution. Thus less CO_2 occupies the empty space.

[Molecular volume not accepted as this would lead to actual pressure being higher.]

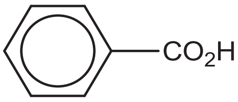
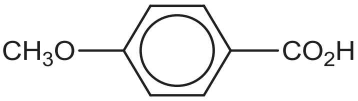
(iii) Besides malic acid, many other organic acids also play an important role in our everyday life. For instance, acrylic acid, with the structure $CH_2{=}CHCO_2H$, is the starting material for the production of many plastics and adhesives industrially.

State the reagents and conditions that can be used to synthesize acrylic acid from lactic acid in the laboratory. [1]

Excess concentrated H_2SO_4, heat to 170°C

(iv) Another example of an organic acid is benzoic acid which is commonly used as a food preservative.

The K_a values of benzoic acid and its substituted derivative, 4–methoxybenzoic acid are given below:

Compound	K_a / mol dm^{-3}
 Benzoic acid	6.5×10^{-5}
 4–methoxybenzoic acid	3.5×10^{-5}

Explain the difference in the K_a values of the two acids. [2]

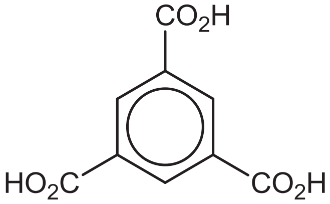
$RCO_2H \rightleftharpoons RCO_2^- + H^+$

4–methoxybenzoic acid is a weaker acid as shown by its lower K_a value. This is due to delocalization of the lone pair of O into the benzene ring, leading to intensification of the negative charge of the anion, which is hence destabilized.

(c) Compound **P** is an aromatic compound with molecular formula $C_{12}H_{15}O_3Cl$. It reacts with exactly 2 mol of PCl_5 to form an organic product **Q**. **P** also gives a brick–red precipitate with Fehling's solution.

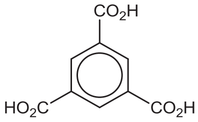
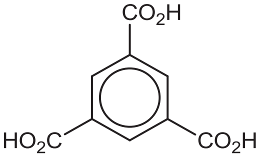
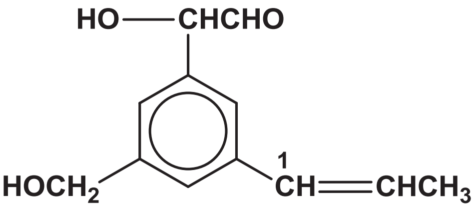
Upon heating **P** with alcoholic NaOH, only one of the products formed, **R**, has the molecular formula $C_{12}H_{14}O_3$.

On oxidation with hot acidified potassium manganate(VII) solution, **R** gives **S**, $C_2H_4O_2$, and the following compound:



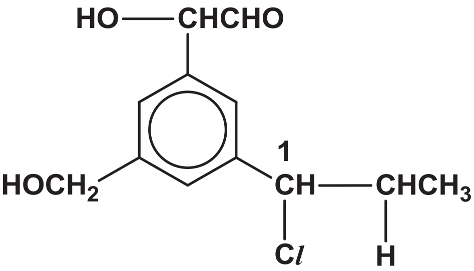
Suggest the structures of **P**, **Q**, **R** and **S**, explaining the reactions involved. [8]

	Rxn type	**Structural feature**
$P + 2PCl_5 \rightarrow Q$	**Nucleophilic substitution**	**P contains 2 alcohol or $-CO_2H$ groups. Hence, Q is a halogenoalkane or $-COCl$ group.**
P + Fehling's soln	**Oxidation**	**Brick red ppt is Cu_2O.** **P has an aliphatic aldehyde group.** **Since P has only 3 oxygen atoms, it cannot contain –COOH. Hence, P must be alcohol and Q is a halogenoalkane.**
P + NaOH(alc) → R	**Elimination**	**P has H and Cl atoms attached to adjacent C atoms.** **R is an alkene.**

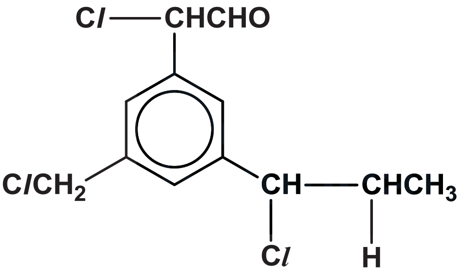
R + hot MnO_4^- / H^+ → S + 	Oxidative cleavage (given in qn)	Since S is an oxidation product, it must be a carboxylic acid or ketone. Based on its molecular formula, S is CH_3CO_2H. Hence, R has a $CH_3CH=$ group. The positions of the –COOH groups in  correspond to those of the side-chains in R. Hence, R is 

Since P only forms one alkene with alcoholic NaOH, Cl atom is on C1.

Hence, P is



and Q is



[Total: 20]

Victoria Junior College

2017 H2 Chemistry Prelim Exam 9729/4

Suggested Answers

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

1 Determination of the M_r of a carbonate salt

FA 1 is a solid carbonate, $\mathbf{X}CO_3$.

FA 2 is a solution containing 1.00 mol dm^{-3} of hydrochloric acid, HCl.

FA 3 is a solution of NaOH of concentration 0.100 mol dm^{-3}.

In this question, you will perform a titration. The data from this titration will be used to determine

- the amount of CO_3^{2-} ions in the mass of **FA 1** used,
- the M_r of $\mathbf{X}CO_3$ and hence the identity of the metal **X**.

(a) Titration of FA 4 against FA 3

(i) You are to determine the amount of carbonate ions, CO_3^{2-}, in **FA 1,** by back titration after some **FA 2** has been added to it. Carry out the procedure as listed below.

1. Weigh accurately between 1.25 – 1.35 g of **FA 1** into a clean and dry 150 cm^3 beaker. If you have used the TARE facility on the balance, indicate clearly in your recording.
2. Record your weighing in an appropriate format in the space provided on the next page.
3. Measure out 50 cm^3 of **FA 2** into a measuring cylinder. Pour this into the beaker containing **FA 1.** Stir thoroughly to ensure all of **FA 1** has dissolved.
4. Quantitatively transfer the mixture into a 250 cm^3 volumetric flask. Make up to the mark with distilled water. Shake to obtain a homogeneous solution. Label this solution **FA 4.**
5. Pipette 25.0 cm^3 of **FA 4** into a conical flask and add 2 drops of methyl orange indicator.
6. Fill the burette with **FA 3.**
7. Titrate **FA 4** with **FA 3.**
8. Repeat the titration as many times as you consider necessary to obtain accurate results.
9. Record your titration results in the space provided on the next page. Make certain that your recorded results show the precision of your working.

Results:

*For weighing of **FA 1***

Mass of beaker and FA 1 / g	5.125
Mass of empty beaker / g	3.825
Mass of FA 1 used / g	1.300

OR if TARE is used:

Mass of beaker only / g	TARE
Mass of FA1 / g	1.300

✓✓Table with appropriate headers / units
AND all readings to 3 dp
AND mass used within 1.25 – 1.35 g

Titration

Experiment	1	2
Final burette reading / cm^3	25.90	36.00
Initial burette reading / cm^3	0.00	10.00
Volume of FA 3 used / cm^3	25.90	26.00

✓✓Table with appropriate headers and units
✓✓Record all burette readings to 2 dp
✓✓At least two consistent readings ±0.10 cm^3
Accuracy:
[2m] M_r within ± 4 units of supervisor's answer (108)
[1m] M_r within ± 8 units of supervisor's answer (108)

[5m]

[6]

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

✓✓Average volume of FA 3 = (25.90 + 26.00) / 2 = 25.95 cm^3

volume of **FA 3** = 25.95 cm^3 [1]

(b) **(i)** Calculate the amount of excess acid pipetted into the conical flask.

✓✓Amount of acid pipetted in 25.0 cm^3
= (25.95 / 1000) x 0.100 = 2.60 x 10^{-3} mol

Amount of excess acid in conical flask =2.60 x 10^{-3} mol [1]

(ii) Calculate the total amount of excess acid in the volumetric flask.

✓✓Total amount of excess acid
= (250 / 25.0) x 2.60 x 10^{-3} mol = 2.60 x 10^{-2} mol

amount of excess acid in the volumetric flask = 2.60 x 10^{-2} mol [1]

(iii) Hence calculate the amount of acid that has reacted with the carbonate that you have weighed out.

✓✓Amount of acid reacted
= (1.00 x 50/1000) – 2.60 x 10^{-2} = 0.0240 mol

Amount of acid reacted = **0.0240 mol** [1]

(iv) Use your answer in **b(iii)** to calculate the M_r of **X**CO_3.

$XCO_3 + 2HCl \rightarrow XCl_2 + CO_2 + H_2O$

✓✓Amount of XCO_3 = (0.0240 / 2) = 0.0120 mol

✓✓M_r of XCO_3 = (1.30 / 0.0120) = 108.3

M_r of **X**CO_3 = **108.3**

Deduce the identity of metal **X**. Show your working.
[A_r: C, 12.0; O, 16.0; H, 1.0; Be, 9.0; Mg, 24.3; Ca, 40.1; Sr, 87.6; Ba, 137.3]

A_r of X + 12.0 + 3(16.0) = 108.3
A_r of X = 48.3

✓✓Hence X is Ca (calculated value closest to A_r of Ca)

X is **Ca** [3]

[Total: 13]

(c) **Planning**

Sodium carbonate, Na_2CO_3, does **not** decompose on heating with a Bunsen burner. Sodium hydrogencarbonate, $NaHCO_3$, decompose on heating.

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$$

You are to design an experiment in which the percentage by mass of $NaHCO_3$ in a mixture of $NaHCO_3$ and Na_2CO_3 can be determined by heating and weighing alone.

The only apparatus available consists of:

a boiling tube and holder
a chemical balance
a Bunsen burner
a heat proof mat

You are to show how you would use the results of this experiment to determine the percentage by mass of $NaHCO_3$ in the mixture.

(i) Outline, step by step, the practical sequence for the method you would use to:

- make appropriate weighings,
- decompose the sodium hydrogencarbonate in the mixture by heating,
- ensure that the decomposition was complete.

1. **Weigh the clean and dry boiling tube.**

2. **Add all the sample into the boiling tube. Weigh the mass of the boiling tube with the sample.**

3. **Heat the boiling tube gently at first (~1 min) and then strongly (~5 min) to decompose the sodium hydrogencarbonate. Heat the whole length of the tube to ensure even heating of the mixture and to prevent condensation.**

4. **Cool the boiling tube on a heat proof mat, and weigh the mass of the boiling tube and its residue.**

5. **Repeat heating, cooling and weighing steps [steps 3 and 4] until constant mass is achieved (OR consecutive mass difference within ±0.050 g is achieved) to ensure complete decomposition. Record all masses.**

Mark Scheme

[1m]: weigh empty boiling tube, sample and boiling tube before and after heating

[1m]: give details such as dry boiling tube, heat strongly, heat whole length of tube, use of heat proof mat for cooling

[1m]: heat until constant mass (OR within ±0.050 g) to ensure complete decomposition

[3]

(ii) By considering the products of the decomposition, suggest a reason why a crucible, without a lid, might be more appropriate than a boiling tube for this experiment.

The crucible has a ✓✓wider surface area for the volatile substances such as water vapour and carbon dioxide to escape more readily which lowers the risk of breakage due to condensation.

[OR It can withstand high temperature during heating which reduces the risk of breakage.]

[1]

(iii) Prepare a table to show the masses you would measure and record during the experiment. Include in your table any other masses you would calculate from the experimental results to enable you to determine the percentage by mass of $NaHCO_3$ in the mixture.

Insert in your table the letters **A**, **B**, **C** etc. to represent each mass. Use these letters to show how your calculated masses are obtained e.g. **B** – **A**.

Mass of empty boiling tube / g	**A**
Mass of boiling tube and sample before heating / g	**B**
Mass of boiling tube and residue after heating / g	**C**
Mass of sample used / g	**B – A**
Mass loss due to H_2O and CO_2 / g	**B – C**

Mark Scheme

[1m]: Tabulation with headers and units as well as raw data recorded (first 3 rows)

[1m]: Processed data of mass of sample used and mass loss due to heating (last 2 rows)

[2]

(iv) Use the letters you have entered in **(c)(iii)** to show how you would process the results to find:

- the mass of $NaHCO_3$ in the mixture,

[A_r: C, 12.0; H, 1.0; O, 16.0; Na, 23.0]

✓✓Mass of $NaHCO_3$ in the mixture

$= (B - C) \times \frac{168.0}{62.0}$ g = R g

- the percentage by mass of $NaHCO_3$ in the mixture.

✓✓Percentage of $NaHCO_3$ in the mixture = [R / (B – A)] x 100 %

[2]

[Total: 8]

2 Determination of the concentration of a mixture of acids and the enthalpy change of neutralization

FA 5 is an aqueous solution prepared by mixing equal volumes of y mol dm^{-3} hydrochloric acid, HC*l*, and y mol dm^{-3} sulfuric acid, H_2SO_4.

FA 6 is 1.60 mol dm^{-3} sodium hydroxide, NaOH.

Take care as aqueous solutions of sodium hydroxide are corrosive.

When an acid is run into an alkali, an exothermic reaction takes place and the temperature of the mixture increases until the end–point is reached. If acid is added beyond the end–point, the temperature will decrease as no further reaction takes place and the acid is at a lower temperature than the mixture.

You are to follow the neutralisation of the acids in **FA 5** by measuring the temperature as volumes of **FA 5** are added in regular portions from a burette to a fixed volume of **FA 6** placed in a Styrofoam cup.

The data obtained will enable you to determine the value of y and the enthalpy change of neutralization, ΔH_{neut}, of this acid–base reaction.

In an appropriate format in the space provided on the next page, prepare a table in which you may record the following after each addition of **FA 5**:

- Total volume of **FA 5** added from the burette up to the point in time
- Total volume of solution in the cup (V_{cup})
- Temperature measured (T)

You also need to calculate the corresponding values of:

- $\Delta T = T - T_0$, where T_0 is the initial temperature of **FA 6**
- ($V_{cup} \times \Delta T$) to 3 significant figures

1. Fill the burette to 0.00 cm^3 with **FA 5**.

2. Place the Styrofoam cup in a 250 cm^3 beaker to provide support for the cup. Use the measuring cylinder to place 40.0 cm^3 of **FA 6** into the cup and measure the steady temperature of the alkali, T_0.

3. Run 5.00 cm^3 of **FA 5** from the burette into the cup, stir the solution with the thermometer and record the maximum temperature, T.

4. **Immediately** run a further 5.00 cm^3 of **FA 5** from the burette into the cup, stir and record the maximum temperature as before.

5. Continue the addition of **FA 5** in 5.00 cm^3 portions and record the maximum or minimum temperature reached after each addition. Do this until a total of 45.00 cm^3 of solution have been run from the burette.

(a) (i) Experimental results

Total volume of FA 5 / cm^3	Total volume of solution in the cup (V_{cup}) / cm^3	Temperature (T) / °C	$\Delta T = T - T_0$ / °C	($V_{cup} \times \Delta T$) / cm^3 °C
0.00	40.0	31.0	0.0	0.00
5.00	45.0	35.0	4.0	180
10.00	50.0	38.5	7.5	375
15.00	55.0	41.0	10.0	550
20.00	60.0	43.0	12.0	720
25.00	65.0	44.0	13.0	845
30.00	70.0	45.0	14.0	980
35.00	75.0	44.0	13.0	975
40.00	80.0	43.0	12.0	960
45.00	85.0	42.0	11.0	935

✓✓Clear headers with units
AND table populated up to 45.00 cm^3 of FA 5
✓✓Correct computation of V_{cup}, ΔT and ($V_{cup} \times \Delta T$)
✓✓Correct precision: 2 d.p. for FA 5, 1 d.p. for V_{cup}, 1 d.p. for temperature and 3 s.f. for ($V_{cup} \times \Delta T$)

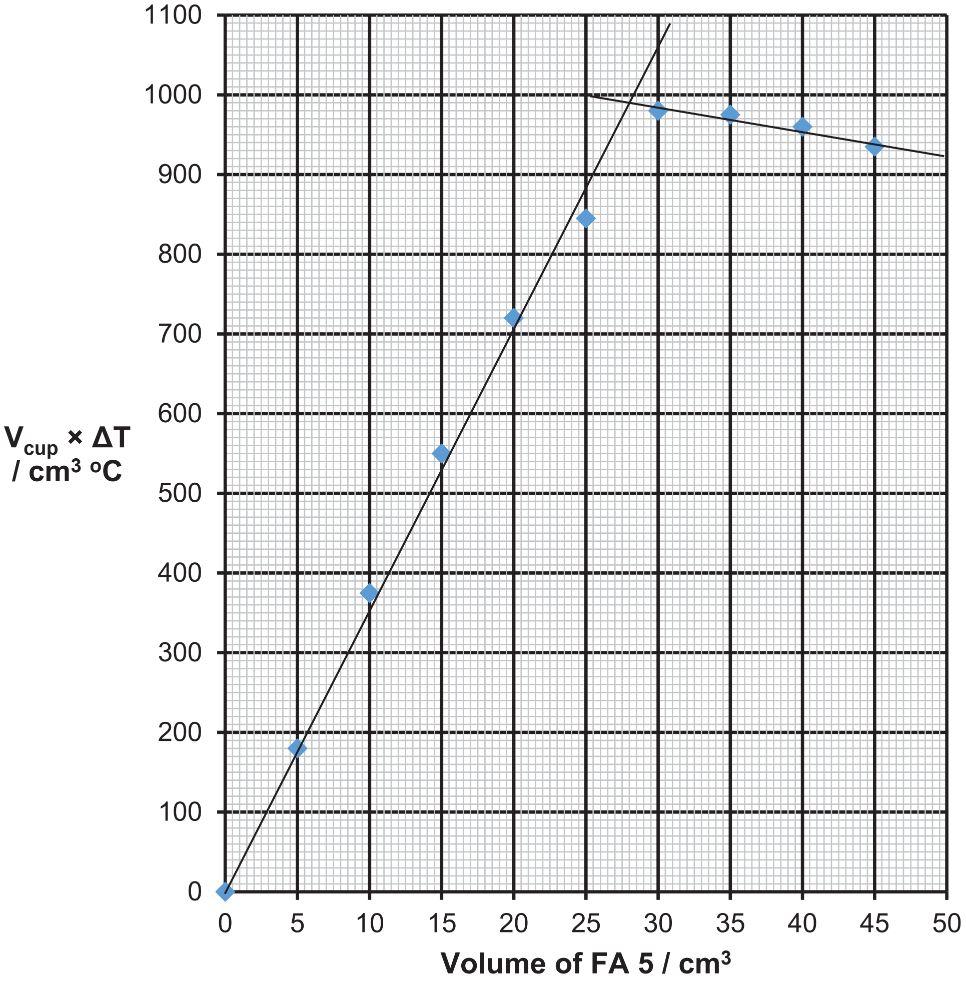
[3]

(ii) On the grid provided below, plot (V_{cup} × Δ*T*) against the total volume of **FA 5** added.

Draw a line of best fit for the points before the maximum value of (V_{cup} × Δ*T*).

Draw a second line of best fit for the points after the maximum value.

Extrapolate both lines until they meet.



✓✓Axes labelled with units AND scale large enough to cover at least ½ of given grid
✓✓Points correctly plotted to ± ½ a small square AND two lines of best fit drawn and extrapolated to meet

[2]

(iii) Read from your graph the maximum value of (V_{cup} × Δ*T*) and the end–point volume of the titration.

maximum value of (V_{cup} × Δ*T*) = **990 cm^3 °C**
end–point volume = **28.0 cm^3** [3]

✓✓Vol of FA5 AND V_{cup} × Δ*T* correctly read to ± ½ a small square
Accuracy:
Supervisor's value = 28.0 cm^3
[2m] End–point volume within 3.0 cm^3 of supervisor's value
[1m] End–point volume within 5.0 cm^3 of supervisor's value

(b) **(i)** Calculate the concentration of hydrogen ions in **FA 5**.

$H^+ + OH^- \rightarrow H_2O$
$n_{OH^-} = (40.0 / 1000) \times 1.60 = 0.0640 \text{ mol} = n_{H^+}$
✓✓ **$[H^+] = (0.0640 / \frac{28.0}{1000})$**
$= 2.29 \text{ mol dm}^{-3}$

concentration of hydrogen ions = **2.29 mol dm^{-3}** [1]

(ii) Hence, determine the value of *y*, which is the concentration of either HC*l* or H_2SO_4 used to prepare **FA 5**.

If V cm^3 of HC*l* and V cm^3 of H_2SO_4 were mixed to prepare FA 5,
$[H^+] = [n_{H^+}$ from HC*l* + n_{H^+} from $H_2SO_4] / 2V$
$2.29 = [V \times y + V \times 2y] / 2V$
$= 3y / 2$
✓✓ **y = 1.53** **[accept with or without mol dm^{-3}]**

y = **1.53** [1]

(c) **(i)** Determine the enthalpy change of neutralization of this reaction, ΔH_{neut}.

You should assume that the specific heat capacity of the final solution is 4.18 J g^{-1} K^{-1}, and that its density is 1.00 g cm^{-3}.

✓✓**Heat evolved = $(V_{cup} \times \Delta T) \times c = 990 \times 4.18 = 4140$ J**
$n_{H_2O} = n_{OH^-} = 0.0640$ mol
✓✓**$\Delta H_{neut} = -4140 / 0.0640 = -64700 \text{ J mol}^{-1} = -64.7 \text{ kJ mol}^{-1}$**

✓✓**Correct units for 1(a)(ii), 1(b), 2(a)(iii), 2(b) and 2(c)(i)**
AND
1 d.p. for *A*$_r$ / *M*$_r$, 3 sf for other answers, clear statements and working for 1(b), 2(b) and 2(c)(i)

ΔH_{neut} = **$-64.7 \text{ kJ mol}^{-1}$** [3]

(ii) Student **A** carefully performed the same experiment and correctly processed the data using the same method. His calculated value of ΔH_{neut} is –65.0 kJ mol^{-1} while the published value for this enthalpy change is –57.7 kJ mol^{-1}.

The specific heat capacity of the Styrofoam cup has not been taken into consideration in calculating ΔH_{neut}. Explain whether this omission could have been the reason for the discrepancy between the value obtained by Student **A** and the one published.

Omission of the specific heat capacity of the cup ✓✓could not have been the reason for the discrepancy because this would result in a ✓✓less exothermic ΔH_{neut} since the cup would also absorb heat.

[2]

(iii) Student **B** performed the same experiment but chose to plot ΔT instead of $(V_{cup} \times \Delta T)$ on the y–axis.

He also drew and extrapolated two straight lines through the plotted points to do the calculations.

Suggest why his method is likely to yield **less** accurate results.

$V_{cup} \times \Delta T \propto$ heat evolved
$\propto$ moles of limiting reagent
$\propto$ volume of FA 5 added before the end–point

✓✓However, total volume in the cup is not constant. Hence, ΔT is not proportional to volume of FA 5 added [OR vary less linearly with volume of FA 5]

[1]

[Total: 16]

3 Inorganic Analysis

(a) You are provided with the solid **FA 7** which contains one cation and one anion from the ions listed in the **Qualitative Analysis Notes**, and the solution **FA 8**.

You are to perform the tests below to identify the ions present in **FA 7** and to suggest the nature of the compound in **FA 8**.

If the evolution of a gas is observed at any stage, the gas should be tested and identified. Details of the test carried out, the observations of the test and the identity of the gas should be given with the observations.

If it appears that no reaction has taken place this should be clearly recorded.

Carry out the following tests on **FA 7** and **FA 8** and complete the table to show your observations.

	Test	Observations
(i)	To a spatula–full of **FA 7** in a test-tube add 3 cm depth of dilute sulfuric acid. Warm, and when the reaction has stopped, filter the mixture. Retain the filtrate for tests **(iii)** and **(iv)**.	**• Effervescence of CO_2 which** **• forms white ppt. in limewater** **• Colourless filtrate**
(ii)	Place a spatula–full of **FA 7** in a test-tube and heat strongly. Leave the tube to cool. Retain the residue for test **(viii)**.	**• CO_2 gas evolved which** **• forms white ppt. in limewater** **• Black residue (OR dark brown)**
(iii)	To a 1 cm depth of the filtrate from **(i)** in a test–tube, add aqueous sodium hydroxide drop by drop until 1 cm depth of the reagent has been added. Then add a further 1 cm depth of the aqueous sodium hydroxide.	**• Off-white ppt. insoluble in excess**
	Swirl the test-tube and leave to stand for 2–3 minutes.	**• Off-white ppt., rapidly turning brown on contact with air**
(iv)	To a 1 cm depth of the filtrate from **(i)** in a test-tube, add aqueous ammonia drop by drop until 1 cm depth of the reagent has been added. Then add a further 1 cm depth of the aqueous ammonia.	**• Off-white ppt. insoluble in excess**

	Then **cautiously** add 1 cm depth of **FA 8**.	**• Off-white ppt., rapidly turning (dark) brown** **• Effervescence of O_2** **• relights a glowing splint**
(v)	Place 2 cm depth of aqueous potassium iodide in a test–tube and add 2 cm depth of **FA 8**.	**• Solution turns (pale) yellow**
	Then add 2 cm depth of dilute sulfuric acid.	**• Yellow solution turns brown** **• Black solid forms**
(vi)	To a 1 cm depth of **FA 8** in a test–tube, add 1 cm depth of dilute sulfuric acid and 2 cm depth of potassium manganate(VII). Observe for 2 minutes or until no further change occurs.	**• Purple solution decolourises** **• Effervescence of O_2** **• relights a glowing splint**
(vii)	To a 1 cm depth of aqueous sodium sulfite in a test-tube, add a few drops of aqueous barium nitrate.	**• White ppt**
	Then add 2 cm depth of dilute nitric acid.	**• White ppt soluble in acid**
	Immediately add 1 cm depth of **FA 8**.	**• White ppt reforms**
(viii)	Transfer a portion of the residue from test **(ii)** into a test–tube and add 2 cm depth of **FA 8**.	**• Effervescence of O_2** **• relights a glowing splint**

[Mark Scheme: 20-23: 9m, 18-19: 8m, 16-17: 7m, 14-15: 6m, 12-13: 5m, 10-11: 4m, 8-9: 3m, 6-7: 2m, 4-5: 1m]

[9]

(b) **(i)** From your observations, identify the cation and anion present in **FA 7**. Quote evidence from the table to support your conclusions.

Cation **✓Mn^{2+}**

Evidence **✓Test (iii): off-white ppt., rapidly turning brown on contact with air, insoluble in excess [OR test (iv)]**

Anion **✓CO_3^{2-}**

Evidence **✓Test (i): Effervescence of CO_2 that forms white ppt. in limewater [OR test (ii)]**

[2]

(ii) In tests **(a)(v)** and **(vii)**, **FA 8** behaves as **✓oxidising agent**

In test **(a)(vi)**, **FA 8** behaves as **✓reducing agent** [1]

[Total: 12]

(c) Planning

One of the transition metals, vanadium, was named after the Scandinavian goddess of beauty and fertility, Vanadis (Freya) due to the wide range of colours found in vanadium compounds.

Starting with an aqueous solution of VO_2^+, you are to devise a plan which will enable you to determine the colour exhibited by two other ions containing vanadium, VO^{2+} and V^{3+}. Your plan should only involve simple test–tube reactions.

The standard electrode potentials of the following ions are as shown:

$$VO_2^+ + 2H^+ + e^- \rightleftharpoons H_2O + VO^{2+} \qquad E^\ominus = +1.00\text{ V}$$
$$VO^{2+} + 2H^+ + e^- \rightleftharpoons H_2O + V^{3+} \qquad E^\ominus = +0.34\text{ V}$$
$$V^{3+} + e^- \rightleftharpoons V^{2+} \qquad E^\ominus = -0.26\text{ V}$$

There are four reducing agents available as shown:

$$Zn^{2+} + 2e^- \rightleftharpoons Zn \qquad E^\ominus = -0.76\text{ V}$$
$$Sn^{2+} + 2e^- \rightleftharpoons Sn \qquad E^\ominus = -0.14\text{ V}$$
$$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2 \qquad E^\ominus = +0.68\text{ V}$$
$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \qquad E^\ominus = +0.77\text{ V}$$

(i) Explain which reducing agent(s) will **not** be suitable for determining the colours exhibited by VO^{2+} and V^{3+}.

✓✓Zinc will reduce VO_2^+ to V^{2+} and hence will not be able to observe the colour exhibited by VO^{2+} and V^{3+}.
✓✓Fe^{2+} is coloured and thus will affect the final colour observed.
[OR The reaction between Fe^{2+} and VO_2^+ is unlikely to occur as both reactants are positively charged and hence will not be kinetically feasible.]

[2]

(ii) Complete the table by choosing a suitable reducing agent for determining the colour exhibited by VO^{2+} and V^{3+} respectively. Justify your choice by calculating relevant $E^\ominus_{cell}$ values.

	Reducing agent	Justification
$VO_2^+ \rightarrow VO^{2+}$	**✓✓H_2O_2**	**$VO_2^+ + 2H^+ + e^- \rightleftharpoons H_2O + VO^{2+}$ $E^\ominus = +1.00$ V** **$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$ $E^\ominus = +0.68$ V** **$E^\ominus_{cell} = 1.00 - (0.68)$** **$=$ ✓✓$+0.32\text{ V} > 0$** **Reaction is feasible.** **$VO^{2+} + 2H^+ + e^- \rightleftharpoons H_2O + V^{3+}$ $E^\ominus = +0.34$ V** **$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$ $E^\ominus = +0.68$ V** **$E^\ominus_{cell} = 0.34 - (0.68)$** **$=$ ✓✓$-0.34\text{ V} < 0$** **Reaction is not feasible.** **H_2O_2 can only reduce VO_2^+ to VO^{2+}.**

$VO_2^+ \rightarrow V^{3+}$	✓✓Sn	**$VO_2^+ + 2H^+ + e^- \rightleftharpoons H_2O + VO^{2+}$ $E^\ominus = +1.00$ V** **$Sn^{2+} + 2e^- \rightleftharpoons Sn$ $E^\ominus = -0.14$ V** **$E^\ominus_{cell} = 1.00 - (-0.14)$** **$=$ ✓✓$+1.14$ V > 0** **Reaction is feasible.** **$VO^{2+} + 2H^+ + e^- \rightleftharpoons H_2O + V^{3+}$ $E^\ominus = +0.34$ V** **$Sn^{2+} + 2e^- \rightleftharpoons Sn$ $E^\ominus = -0.14$ V** **$E^\ominus_{cell} = 0.34 - (-0.14)$** **$=$ ✓✓$+0.48$ V > 0** **Reaction is feasible.** **$V^{3+} + e^- \rightleftharpoons V^{2+}$ $E^\ominus = -0.26$ V** **$Sn^{2+} + 2e^- \rightleftharpoons Sn$ $E^\ominus = -0.14$ V** **$E^\ominus_{cell} = -0.26 - (-0.14)$** **$=$ ✓✓-0.12 V < 0** **Reaction is not feasible.** **Sn can only reduce VO_2^+ to V^{3+}.**

[Mark Scheme: 6-7: 4m, 5: 3m, 3-4: 2m, 1-2: 1m]

[4]

[Total: 6]