2019 VJC H2 Chem Prelim P1

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

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

Which of the following statements are **incorrect**?

1 Both isotopes of $^{56}_{22}Ti$ and $^{58}_{22}Ti$ have more neutrons than electrons.

2 The first ionisation energy increases continuously from sodium to phosphorus as the number of protons increases but number of inner quantum shells remains the same.

3 The second ionisation energy of chromium is lower than the second ionisation energy of manganese as manganese has one more proton than chromium.

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

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

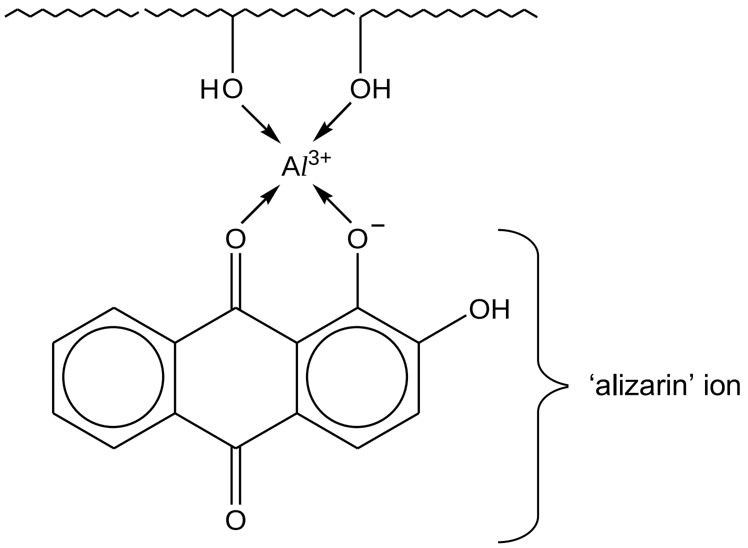
C **2** only

D **3** only

2 In which of the following pairs does the first substance have a higher melting point than the second substance?

	first substance	second substance
A	$CH_3CH_2OCH_3$	$CH_3CH_2NHCH_3$
B	$CH_3CH_2CH_2CH_2OH$	$CH_3CHClCH_2CH_2OH$
C	RbC*l*	KC*l*
D	$H_2NCH_2COCO_2H$	$H_2NCH_2CH_2CO_2H$

3 The dye 'alizarin' sticks fast to cotton when a 'mordant' containing aluminium ion is used. Under alkaline conditions, the aluminium ions become bonded to the hydroxyl groups of cotton. The dye 'alizarin' can then bond with the aluminium ions, giving the structure below which dyes cotton red.



Which statement is correct?

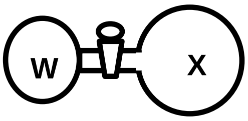
A The formula for 'alizarin' ion is $C_{14}H_9O_4^-$.

B There are 12 carbon atoms in the 'alizarin' ion that are sp^2 hybridised.

C In the absence of a mordant, alizarin can bind to cotton via hydrogen bonding.

D There is a decrease in the bond angles about the oxygen atoms of the cotton hydroxyl groups upon binding to aluminium ions.

4 Two vessels **W** and **X** are connected by a closed valve. Vessel **X** contains three times the volume of **W**.



W contains argon gas at 20 °C at a pressure of 1.00×10^5 Pa while **X** has been evacuated. In an experiment, the valve is opened and the temperature of the whole system is raised to T °C. The final pressure in the system decreases by 6.82×10^4 Pa.

What is the final temperature in the system?

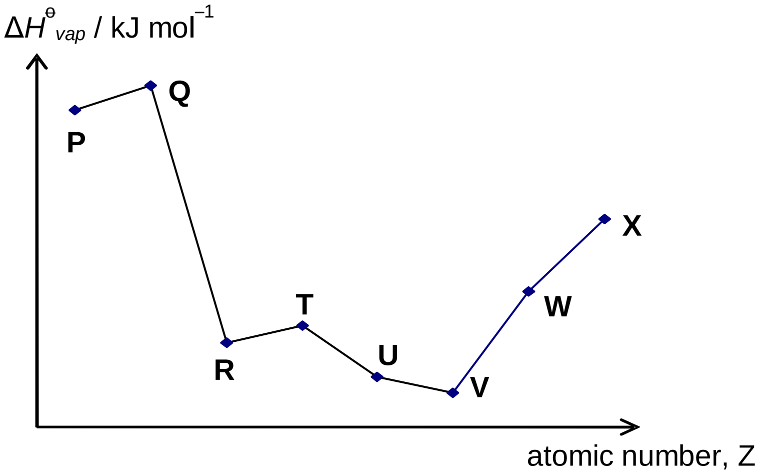
A 99.7 °C

B 373 °C

C 526 °C

D 799 °C

5 The graph below shows the variation in the standard enthalpy change of vaporisation, $\Delta H^{\ominus}_{vap}$, for eight consecutive elements in the Periodic Table, all with atomic number, $10 \leq Z \leq 20$.



Which one of the following statements is **incorrect**?

A Effervescence of hydrogen gas is observed when sodium is added to the solution containing chloride of element **P**.

B Element **U** is the most electronegative element among all the eight elements.

C When a mixture of the oxides of element **R** and element **W** is dissolved in water, the solution is approximately neutral.

D The oxide of element **Q** has a lower melting point than the oxide of element **T**.

6 Given a sample of strontium carbonate that was mixed with strontium nitrate, two separate experiments using the same mass of the solid mixture were conducted.

Experiment **1**: Excess dilute hydrochloric acid was added to the sample and volume of gas evolved was found to be 75 cm^3.

Experiment **2**: The sample was heated strongly to constant mass and the volume of gas evolved was found to be 200 cm^3.

All volumes were measured at the same temperature and pressure.

What is the mole ratio of strontium nitrate to strontium carbonate in the sample?

A 2 : 3

B 5 : 3

C 5 : 6

D 9 : 5

7 When H_2SO_4 is used to make an aqueous solution, the solution is found to contain H_2SO_4 molecules, H^+ ions, HSO_4^- ions and SO_4^{2-} ions.

Which one of the following statements best describes the system?

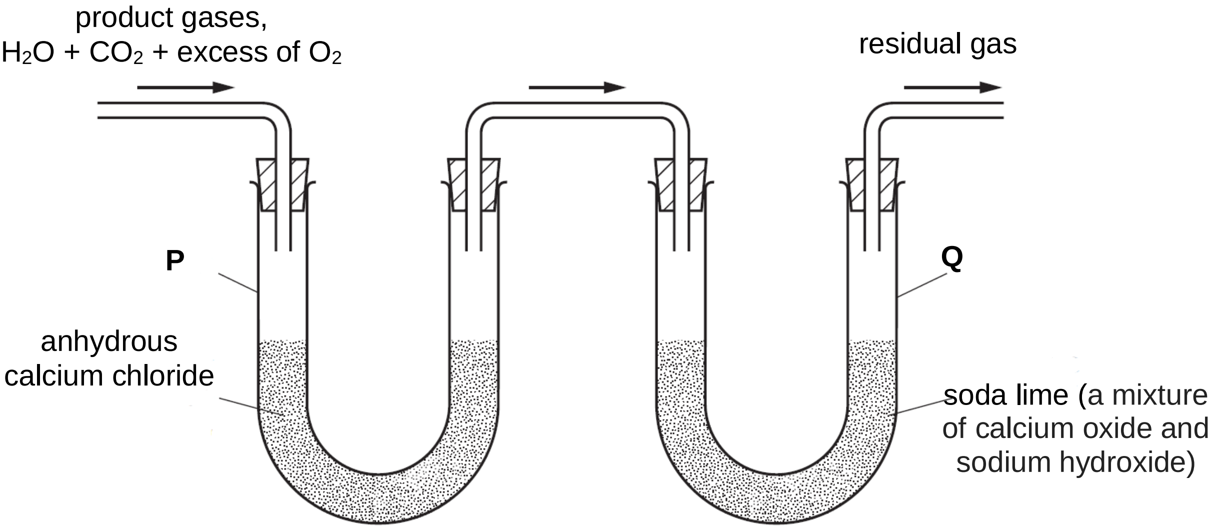
A The solution contains equal number of moles of H^+ ions and HSO_4^- ions.

B The solution contains equal number of moles of HSO_4^- ions and SO_4^{2-} ions.

C The number of moles of H_2SO_4 dissociated is equal to the sum of the number of moles of H^+ ions and HSO_4^- ions.

D The number of moles of H_2SO_4 dissociated is equal to the sum of the number of moles of HSO_4^- ions and SO_4^{2-} ions.

8 A 10 cm^3 sample of the hydrocarbon C_3H_8 is burned in excess oxygen and the product gases are collected as follows.



The increase in mass of the collecting vessels **P** and **Q** are $M_{\mathbf{P}}$ and $M_{\mathbf{Q}}$ respectively and the volume of the residual gas is V_R.

Which one of the following statements is **incorrect**?

A The ratio $\frac{V_R}{10}$ is equal to 5.

B The ratio $\frac{M_{\mathbf{Q}}}{M_{\mathbf{P}}}$ is equal to 1.8.

C The volume of residual gas, V_R, only contains excess O_2.

D The increase in mass in vessel **P**, $M_{\mathbf{P}}$, is smaller than the increase in vessel **Q**, $M_{\mathbf{Q}}$.

9 Which one of the following pairs contains identical enthalpy change values?

A	first ionisation energy of oxygen	–1 x first electron affinity of oxygen
B	standard enthalpy change of combustion of C(graphite)	standard enthalpy change of formation of CO_2(g)
C	standard enthalpy change of neutralization between H_2SO_4(aq) and NaOH(aq)	standard enthalpy change of neutralization between H_2SO_4(aq) and NH_3(aq)
D	bond energy of F_2(g)	standard enthalpy change of atomisation of F_2(g)

10 The table below gives the enthalpy changes and entropy changes for the dissolution of sodium chloride and magnesium chloride.

		$\Delta H^{\ominus}_{sol}$, kJ mol^{-1}	$\Delta S^{\ominus}_{sol}$, J mol^{-1} K^{-1}
I	$NaCl(s) + (aq) \rightarrow Na^+(aq) + Cl^-(aq)$	+3.87	+43.0
II	$MgCl_2(s) + (aq) \rightarrow Mg^{2+}(aq) + 2Cl^-(aq)$	–155	–97.1

Which one of the following statements can be supported by the information given?

A Reaction **II** is more spontaneous than reaction **I** at higher temperatures.

B The hydration energy of Mg^{2+} is more exothermic than the hydration energy of Na^+.

C The system becomes more disordered when there is greater number of product particles.

D The lattice energy of $MgCl_2$ is more exothermic than the sum of the hydration energies of its ions.

11 When 10 g of calcium carbonate was added to 100 cm^3 of 0.10 mol dm^{-3} hydrochloric acid, the volume of CO_2 produced was recorded as follows:

time / s	0	50	75	100	125	150	175	200	225	250
total volume of CO_2 given off / cm^3	0	60	78	90	99	105	108	114	120	120

Which one of the following statements **cannot** be deduced from these results?

A The rate constant is around 0.02 s^{-1}.

B The rate of the reaction decreases with time

C The half-life of the reaction is around 50 seconds.

D The reaction is first order with respect to hydrochloric acid.

12 In the upper atmosphere, nitrogen oxides participate in the decomposition of ozone, O_3, via the following elementary steps:

reaction **I** : $O_3 \rightarrow O_2 + O$
reaction **II** : $O + NO_2 \rightarrow O_2 + NO$
reaction **III** : $O_3 + NO \rightarrow O_2 + NO_2$

Which of the following statements can be deduced from the information given?

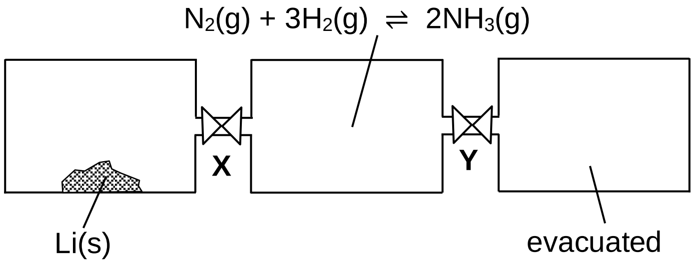
1 The overall equation for the decomposition of ozone is $2O_3 \rightarrow 3O_2$.

2 Reaction **II** must take place before reaction **III** can occur.

3 Both NO and NO_2 can behave as a catalyst for the decomposition of ozone.

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

13 Three vessels of equal volume are connected by taps, **X** and **Y**, as shown:



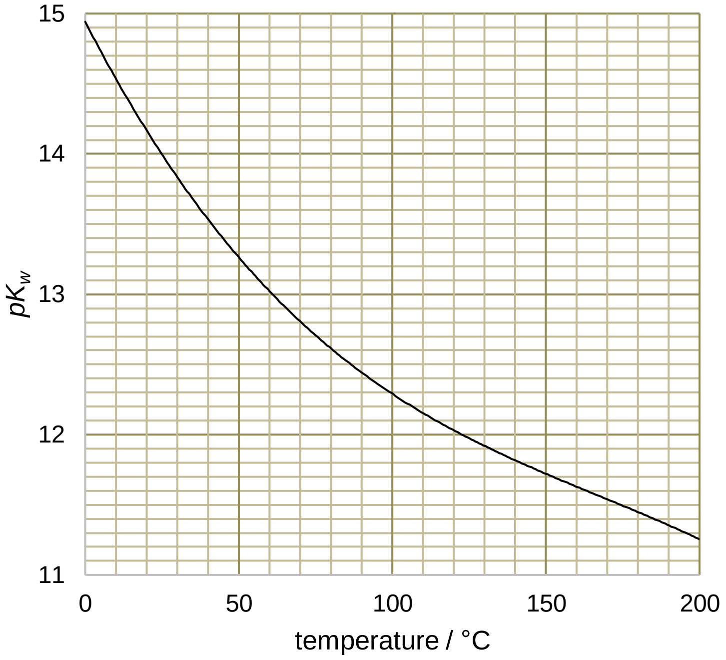
At the start, both taps are closed. The left-hand vessel contains lithium only, the middle vessel has the indicated reaction at equilibrium and the right-hand vessel is evacuated.

Lithium reacts with nitrogen at room temperature to form solid Li_3N.

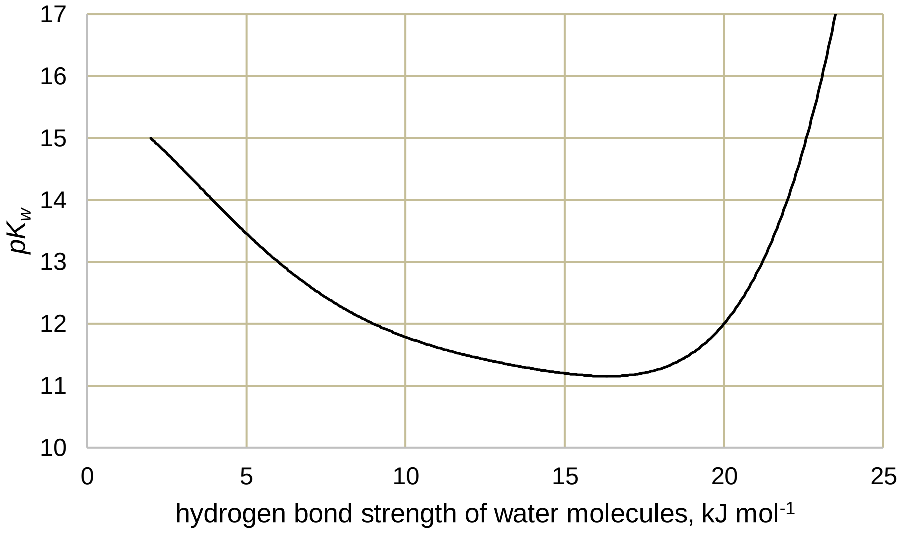
Which one of the following actions will result in the most ammonia in the equilibrium mixture?

A open **X** only
B open **Y** only
C open **X** and **Y**
D keep both **X** and **Y** closed

14 The graphs of pK_w against temperature and pK_w against strength of hydrogen bond of water molecules are given below.



graph 1: pK_w against temperature



graph 2: pK_w against hydrogen bond strength of water molecules

Which one of the following statements can be deduced from the graphs?

A The formation of extremely strong hydrogen bonds favours the dissociation of water molecules.

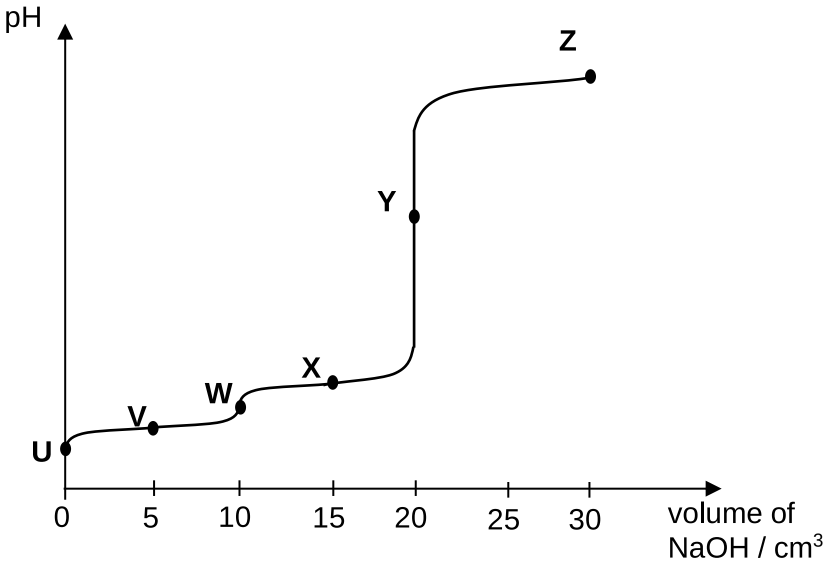
B There is more H^+ than OH^- present with increasing temperature.

C The pH of water increases with increasing temperature.

D The pH of water at 100 °C is 6.2.

15 Oxalic acid, $H_2C_2O_4$, is a relatively strong acid despite being an organic acid. The two pK_a values for oxalic acid is 1.23 and 4.19.

The titration curve between 0.10 mol dm^{-3} $H_2C_2O_4$ and 0.20 mol dm^{-3} NaOH is given below.



Which of the following statements are correct?

1 The volume of $H_2C_2O_4$ used in the titration is 20.0 cm^3.

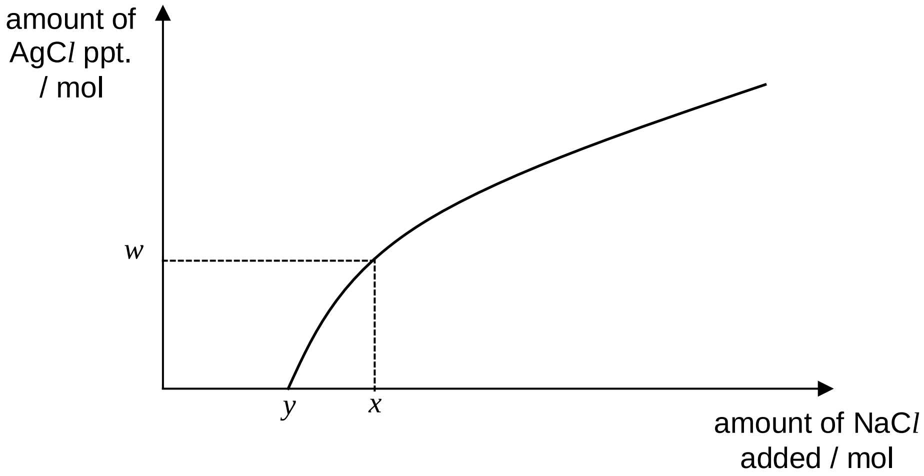
2 The initial pH of $H_2C_2O_4$ is 1.1 [Ignore the effects of the second pK_a].

3 The points **V**, **X** and **Z** are made up of conjugate acid–base pairs.

4 The first end-point can be followed by using methyl orange indicator and the second end-point can be followed by using phenolphthalein indicator.

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

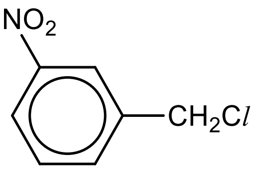
16 When solid NaC*l* was added to a 1 dm^3 solution containing z mol of Ag$^+$ ions, the amount of AgC*l* precipitated was found to change as follows:



Which one of the following gives the correct expression for the solubility product of AgC*l*?

A	$(z–w).(x–w)$	**C**	$(z).(x)$
B	$(w).(x–y)$	**D**	$(y).(y)$

17 Which one of the following types of reaction is compound **K** **not** likely to undergo?



compound **K**

A	electrophilic addition	**C**	nucleophilic substitution
B	electrophilic substitution	**D**	reduction

18 The hydride ion, H$^–$, is a strong reducing agent, a good nucleophile and a good base.

Which one of the following conversions would the hydride ion **not** be expected to bring about?

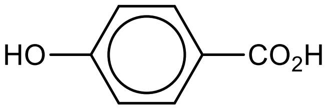
A C_2H_5Br to C_2H_6

B CH_3CH_3 to $CH_2=CH_2$

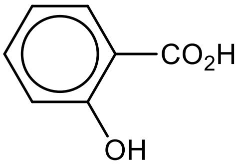
C CH_3CHO to CH_3CH_2OH

D CH_3CO_2H to $CH_3CO_2^–$

19 Which option correctly describes the comparison of the melting point and the first pK_a between 4–hydroxybenzoic acid and 2–hydroxybenzoic acid?



4–hydroxybenzoic acid



2–hydroxybenzoic acid

	melting point of 4–hydroxybenzoic acid	first pK_a of 4–hydroxybenzoic acid
A	lower	lower
B	lower	higher
C	higher	higher
D	higher	lower

20 In which one of the following processes is the organic product a gas at room temperature and pressure?

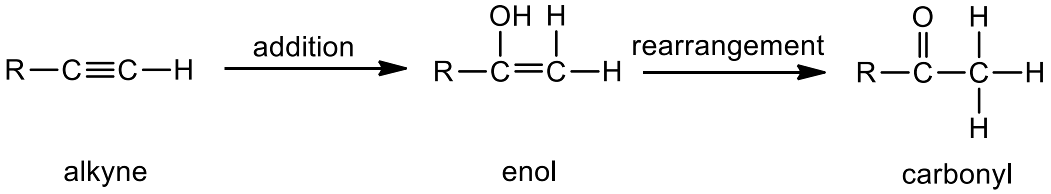
A substitution of ethanol by hydrogen bromide

B dehydration of ethanol

C esterification of ethanoic acid by ethanol

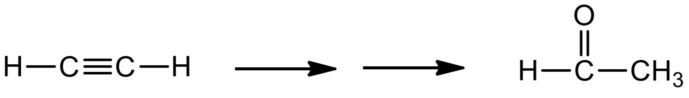
D oxidation of ethanal by acidified potassium dichromate(VI)

21 An alkyne (C≡C) undergoes addition of water in a similar mechanism as an alkene. However, the enol (C=C-OH) that is formed is unstable and would undergo rearrangement to form a carbonyl compound.



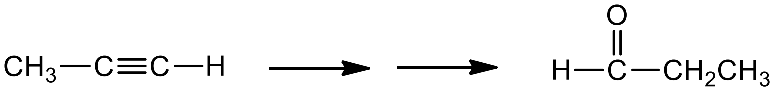
Which compound is **unlikely** to be formed when the following alkynes undergo addition of water?

A



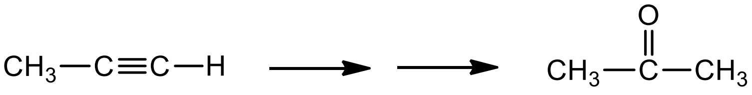
$H-C\equiv C-H \longrightarrow \longrightarrow H-\overset{O}{\overset{\|}{C}}-CH_3$

B



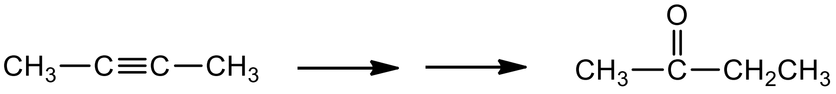
$CH_3-C\equiv C-H \longrightarrow \longrightarrow H-\overset{O}{\overset{\|}{C}}-CH_2CH_3$

C



$CH_3-C\equiv C-H \longrightarrow \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

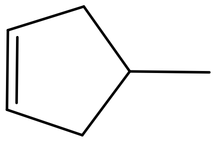
D



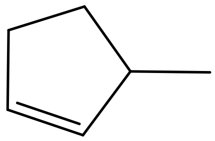
$CH_3-C\equiv C-CH_3 \longrightarrow \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_3$

22 Which one of the following compounds react with hot acidified $KMnO_4$ and the resultant product formed will give a positive test with **both** 2,4–dinitrophenylhydrazine and PCl_5?

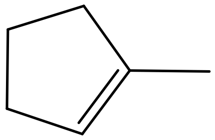
A



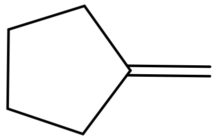
C



B

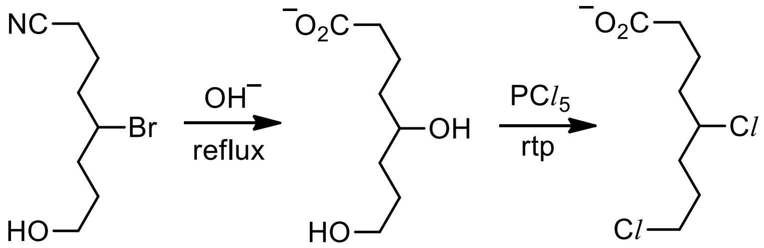


D

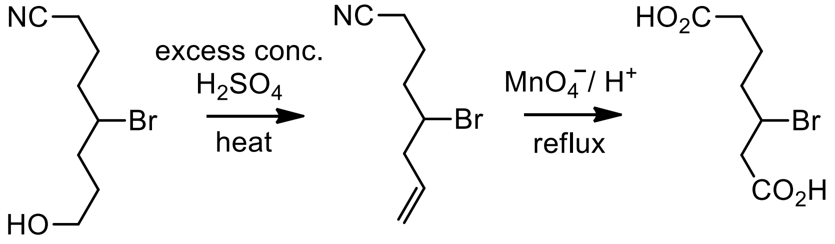


23 Which one of the following 2-stage processes will **not** yield the final product as shown?

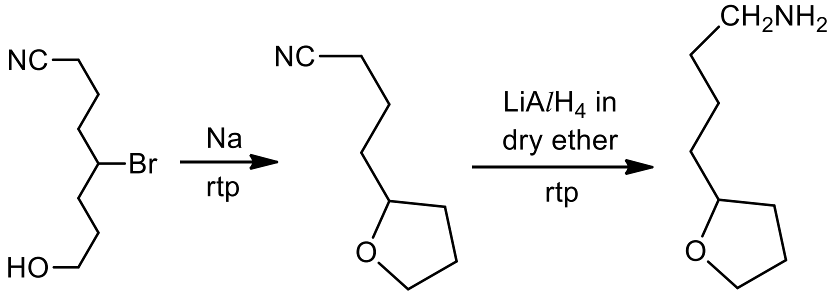
A



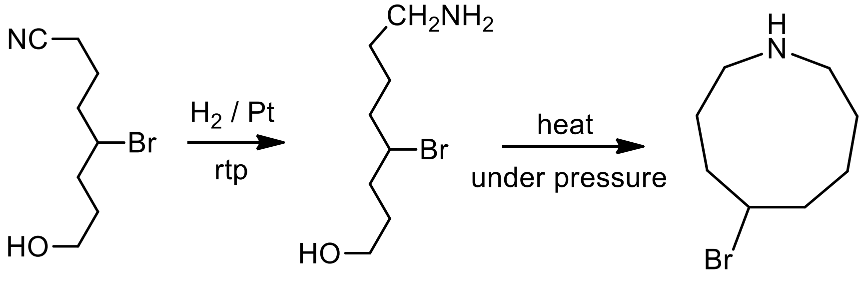
B



C



D



24 Compound **Z** releases a gas that turns damp red litmus paper blue upon addition of hot aqueous NaOH. Which compounds could be **Z**?

1 $CH_3CH_2CH_2CN$

2 $CH_3CH_2CONHCH_3$

3 $CH_3CH_2CO_2NH_4$

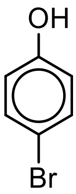
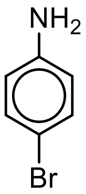
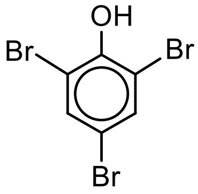
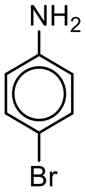
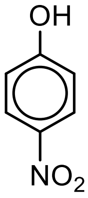
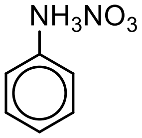
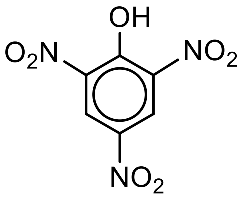
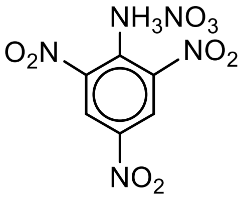
A **1**, **2** and **3**

B **1** and **3** only

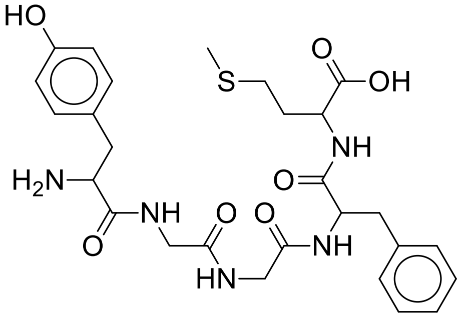
C **1** only

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

25 Which one of the following options shows the correct products when phenol and phenylamine react with the reagents and conditions indicated?

	reagents and conditions	product of phenol	product of phenylamine
A	$Br_2(aq)$ room temperature		
B	Br_2 in CCl_4 room temperature		
C	$HNO_3(aq)$ room temperature		
D	HNO_3(concentrated) room temperature		

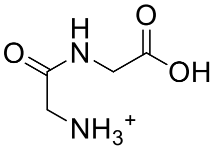
26 To reduce pain during stress, animals generate their own opiates. One such opiate is called *encephalin*, a pentapeptide as shown below:



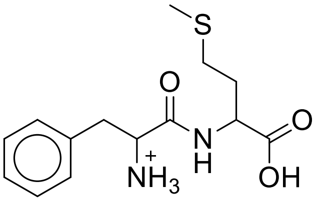
encephalin

Which one of the following dipeptides is **not** a product of the partial hydrolysis of *encephalin* with 6 mol dm^{-3} HC*l*?

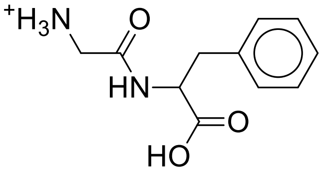
A



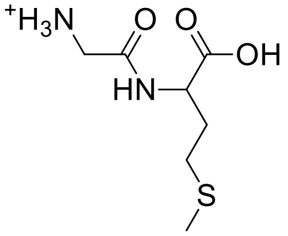
C



B



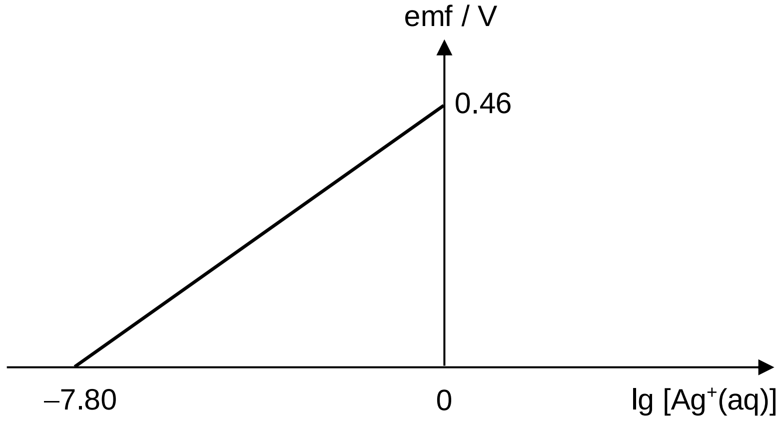
D



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

An electrochemical cell is made up of **X**$^{2+}$(aq)|**X**(s) and Ag^{+}(aq)|Ag(s) half-cells. **X**(s) is the negative electrode and the concentration of **X**$^{2+}$(aq) is kept at 1.00 mol dm^{-3} throughout.

The graph below shows the variation in electromotive force (emf) of the above electrochemical cell with lg [Ag^{+}(aq)] at 298 K.



Which of the following statements are correct?

1 The direction of electron flow in the external circuit will be reversed when the concentration of Ag^{+}(aq) is 1.00 x 10^{-6} mol dm^{-3}.

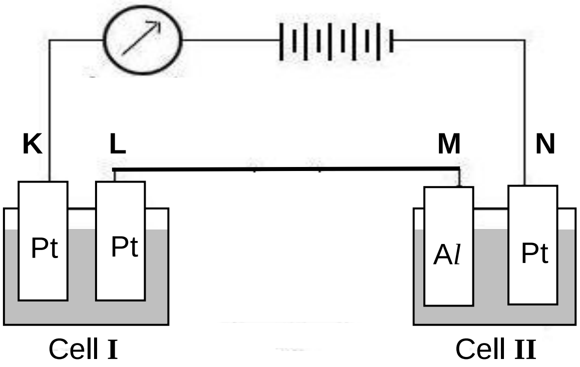
2 The standard electrode potential of the **X**$^{2+}$(aq)|**X**(s) half-cell is +0.34 V.

3 The emf of the given cell under standard conditions will be +0.46 V.

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

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

An experiment involving the electrolysis of aqueous copper(II) sulfate in Cell **I** and aqueous sulfuric acid in Cell **II** was carried out.



Given that relative formula mass of Al_2O_3 is 102.0 and the mass of Al_2O_3 formed at electrode **M** is 0.142 g.

What is the maximum mass of copper deposited at electrode **L** after complete electrolysis?

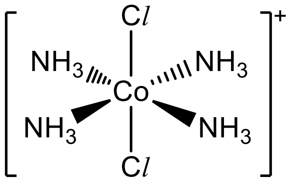
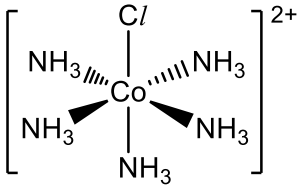
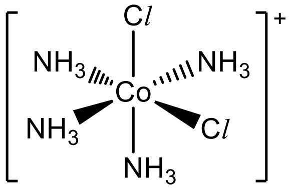
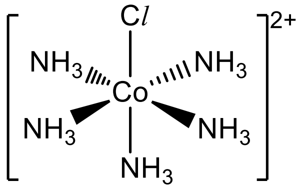
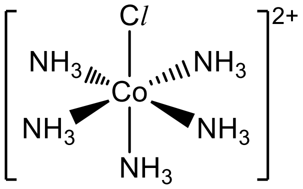
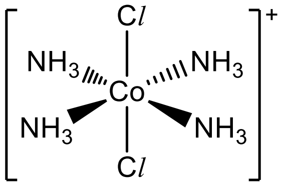
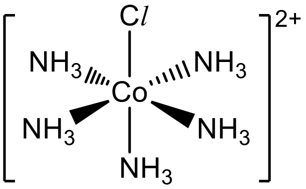
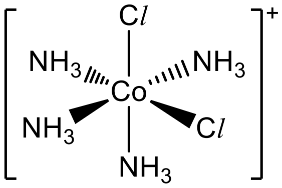
[Note: Assume that all the O_2 produced at electrode **M** completely reacted to form Al_2O_3.]

A	0.133 g	**C**	0.265 g
B	0.236 g	**D**	0.530 g

29 Two different complexes, **K** and **L**, can be obtained by reacting aqueous cobalt(III) chloride with ammonia under various conditions. Different proportions of chloride are precipitated when each of the complexes is treated with aqueous silver nitrate.

	Formula	Number of moles of AgC*l* precipitated per mole of complex	Does the complex have a dipole moment?
K	$CoCl_3(NH_3)_5$	2	yes
L	$CoCl_3(NH_3)_4$	1	no

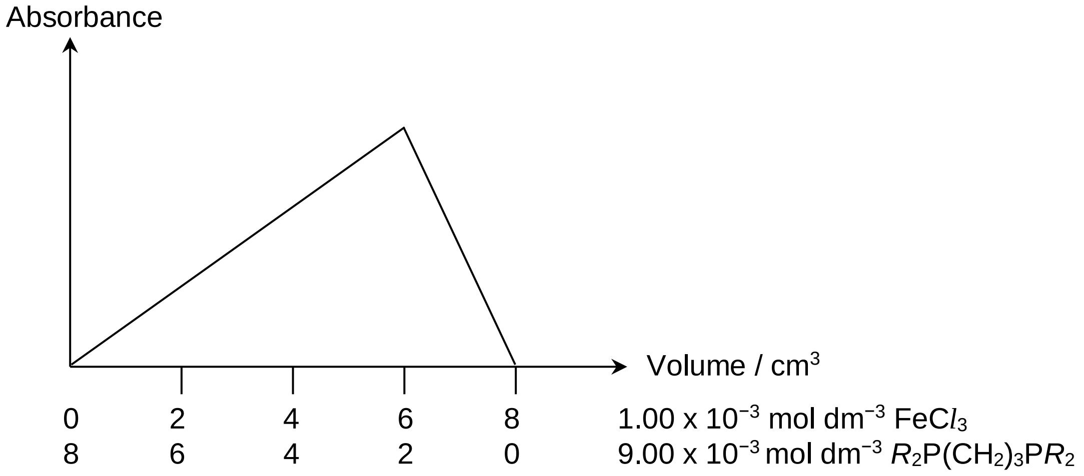
Which one of the following options shows the correct structures of **K** and **L**?

	K	**L**
A		
B		
C		
D		

30 In this question, '*R*' represents a phenyl group.

2-bis(diphenylphosphino)propane, $R_2P(CH_2)_3PR_2$, is a commonly used ligand which forms a complex ion with many metal ions.

In the graph below, the intensity of visible light absorbance for different mixtures containing 1.00 x 10^{-3} mol dm^{-3} $FeCl_3(aq)$ and 9.00 x 10^{-3} mol dm^{-3} $R_2P(CH_2)_3PR_2$ are shown.



Which one of the following statements is **not** true?

A The formula of the complex ion formed is $[Fe(R_2P(CH_2)_3PR_2)_3]^{3+}$.

B Each $R_2P(CH_2)_3PR_2$ can form three dative covalent bonds with Fe^{3+} ion

C The coordination number of the complex ion formed is 6.

D H_2O molecule is a weaker ligand than $R_2P(CH_2)_3PR_2$.

H2 CHEMISTRY PAPER 1 ANSWERS

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

1 **(a)** An unknown solid sample, with a mass of 1.50 g, contains three sodium salts, $NaCl$, $NaClO_3$ and $NaNO_3$. The sample was completely dissolved in water and diluted in a 250 cm^3 volumetric flask to obtain solution **L**.

In one experiment, a 50 cm^3 portion of solution **L** was reacted with excess silver nitrate solution. The $AgCl$ precipitate formed was removed by filtration, dried and weighed. The $AgCl$ precipitate was found to have a mass of 0.240 g.

In another experiment, a gas was bubbled into a new 50.0 cm^3 portion of solution **L** to convert ClO_3^- to Cl^-. Excess silver nitrate was then added to the resulting mixture. The $AgCl$ precipitated formed was treated similarly as before and found to have a mass of 0.285 g.

(i) Determine the amount of ClO_3^- ions present in 50 cm^3 of solution **L**.

[2]

(ii) Hence, determine the percentage by mass of $NaClO_3$ present in the original solid sample.

[2]

(b) Suggest whether $NaCl$ or $NaClO_3$ has a lower melting point. Explain your answer.

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[2]

(c) **(i)** Draw a dot-and-cross diagram of the ClO_3^- anion.

[1]

(ii) Chlorine forms a number of oxides, one of which is Cl_2O_7. Cl_2O_7 is a symmetrical molecule, with a central oxygen atom bonded to two chlorine atoms.

Draw the structure of Cl_2O_7.

[1]

(iii) The bonds in Cl_2O_7 exhibit two different bond lengths, namely, 0.141 nm and 0.171 nm. However, all the bonds in the ClO_3^- ion have the same bond length of 0.149 nm.

Suggest why the bond length in ClO_3^- is intermediate between those present in Cl_2O_7.

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....
[2]

(iv) The bond angle formed between the central oxygen atom and its two surrounding chlorine atoms is larger than expected with a value of 118.6°.

Suggest a possible reason why.

....

....

[1]

[Total: 11]

2 **(a)** Use of the *Data Booklet* is necessary for this part of the question.

The sub–atomic makeup of certain ions formed from isotopes of cobalt and lead is given below:

	number of neutrons	number of electrons
Co ion	33	25
Pb ion	122	▨

In a particular experimental set–up, a beam containing the above ions of cobalt was passed through an electric field and was deflected by an angle of +10.2°.

Under identical conditions, another beam containing the above ions of lead was deflected by an angle of +6.0°.

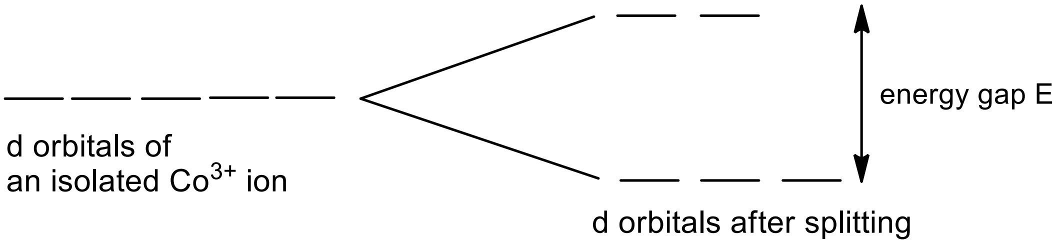
What is the overall charge of the lead ions?

[2]

(b) Many transition metals and their complexes are paramagnetic. Paramagnetism is a property of a substance which allows it to be weakly attracted to a magnet. This property is due to the presence of unpaired electrons in the substance.

CoF_6^{3-} and $[Co(NH_3)_6]^{3+}$ are both complexes with cobalt in the +3 oxidation state. However, only CoF_6^{3-} displays paramagnetism while $[Co(NH_3)_6]^{3+}$ does not. This is determined by whether the electronic configuration of the Co^{3+} ion in the complex displays a "high spin" or a "low spin" state.

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



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

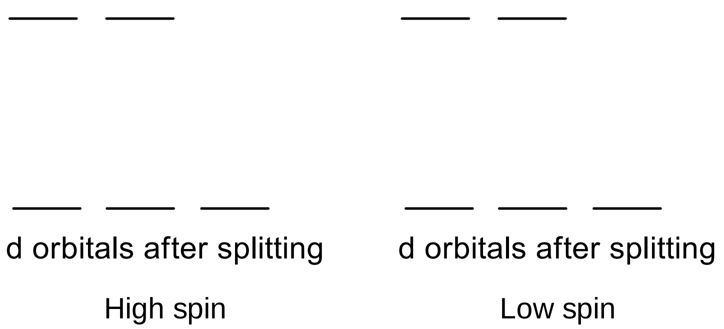
In a 'low spin' state, the lower energy d–orbitals are filled first, by pairing up if necessary, before the higher energy d–orbitals are used.

(i) Draw the shapes of the d_{xy} and d_{z^2} orbitals. Label your drawings clearly.

[2]

(ii) Using ↑ or ↓ to represent electrons, show, on the two diagrams below, the electronic distribution of a Co^{3+} ion in a high spin state, and in a low spin state.

Hence, identify the cobalt complex that corresponds to each particular spin state.



Complex: ....

[2]

(iii) Suggest why electrons usually prefer to occupy orbitals singly rather than in pairs.

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[1]

(iv) Using the explanation in **(b)(iii)**, together with the information given above, state and explain which of the two cobalt complexes contains the larger energy gap, E, between its d orbitals.

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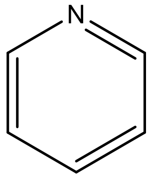
[1]
[Total: 8]

3 Frederick Thomas Trouton was an Irish physicist who observed a relationship between boiling points and enthalpy changes of vaporisation after studying many liquids. He published his findings and formulated Trouton's rule which states that the molar *entropy* of vaporisation, ΔS_{vap}, for most liquids is about 85 J K^{-1} mol^{-1}.

The boiling points and enthalpy changes of vaporisation of several organic liquids are as follows:

substance	boiling point / °C	ΔH_{vap} / kJ mol^{-1}	ΔS_{vap} / J K^{-1} mol^{-1}
propanone, $(CH_3)_2CO$	56.1	29.1	
dimethyl ether, $(CH_3)_2O$	–24.8	21.5	86.6
ethanol, CH_3CH_2OH	78.4	38.6	
octane, $CH_3(CH_2)_6CH_3$	125.6	34.4	86.3
pyridine, 	115.3	35.1	90.4

(a) Explain the term *entropy* and why ΔS_{vap} at constant pressure is positive.

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[2]

(b) Complete the above table by calculating the ΔS_{vap} for propanone and ethanol. Show your working for the calculation of ΔS_{vap} for propanone.

[2]

(c) By considering the structure and bonding of the various substances in this question, state and explain the relationship between strength of intermolecular forces of attraction and the entropy of a substance in the liquid state.

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[2]

(d) **(i)** With the aid of a diagram, show and label the bonding between two methanoic acid molecules in the **gaseous** phase.

[1]

(ii) Hence, predict if ΔS_{vap} for methanoic acid is more or less positive than predicted by Trouton's rule. Explain your reasoning.

[No marks will be awarded if a prediction has no reasoning.]

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[2]
[Total: 9]

4 Ozone, O_3, is fairly stable but rapidly decomposes, with the release of heat, to form oxygen in the presence of silver catalyst. A silver catalyst was added to 800 cm^3 of a mixture of oxygen and ozone. The volume increased as follows and the reaction is complete at 1800 s.

total volume of gas mixture, V_{total} / cm^3	800	805	810	815	818	819
volume of O_3(g) /cm^3						0
time, t / s	0	210	420	860	1350	1800

(a) **(i)** Write a chemical equation to represent the overall process of the decomposition of ozone to form oxygen.

.... [1]

(ii) By considering the stoichiometry of the reaction, calculate the initial volume of ozone and initial volume of oxygen in the mixture.

[1]

(iii) Given that volume of O_3 reacted = 2 (V_{total} – 800), complete the above table by calculating the volume of ozone in the mixture at the various times stated. Fill in the volume of O_3 at t = 0 s using your answer in **a(ii)**.

[1]

(iv) The decomposition of ozone is a *first order* reaction.

Write down the rate equation and explain the term *first order*.

[2]

(v) Show, by means of a suitable graph, that these data are consistent with a first order reaction.

[If you are unable to solve **(iii)**, sketch the graph without data points and indicate clearly how it can be used to verify the order of reaction.]

[2]

(b) **(i)** Silver is a heterogeneous catalyst in this reaction. Outline how a heterogeneous catalyst works.

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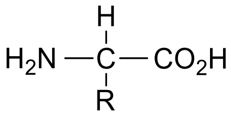
[2]

(ii) Draw a labelled energy profile diagram for the decomposition of ozone, with and without the use of a catalyst.

[2]
[Total: 11]

5 **(a)** Nitrogen is one of the key elements present in α-amino acids, the building block of proteins. α-amino acids have the following general formula.



$$H_2N-\overset{\displaystyle H}{\underset{\displaystyle R}{C}}-CO_2H$$

The table below shows the R groups of the α-amino acids present in a polypeptide, **J**.

α–amino acid	M_r	R group
asp	133.0	$-CH_2CO_2H$
lys	146.0	$-CH_2CH_2CH_2CH_2NH_2$
gln	146.0	$-CH_2CH_2CONH_2$

You have to refer to the table above when answering **a(i)** and **a(ii)**.

(i) When polypeptide **J** undergoes hydrolysis, three aspartic acid, two lysine and one glutamine molecules were formed as shown in the following reaction:

$$\mathbf{J} \longrightarrow 3\ \text{asp} + 2\ \text{lys} + 1\ \text{gln}$$

Calculate the M_r of polypeptide **J**.

[1]

(ii) A dipeptide, *gln–lys*, is obtained upon hydrolysis of polypeptide **J** by an enzyme. Draw the structural formula of this dipeptide at pH 1.

[1]

(iii) A sample of lysine, extracted from the hydrolysis of polypeptide **J** rotated plane polarised light anticlockwise. However, a second sample of lysine obtained from laboratory synthesis had no effect on plane polarised light.

Suggest an explanation for these observations.

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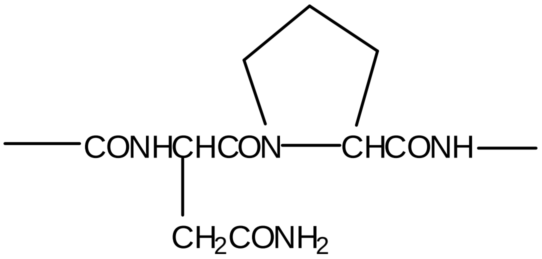
[2]

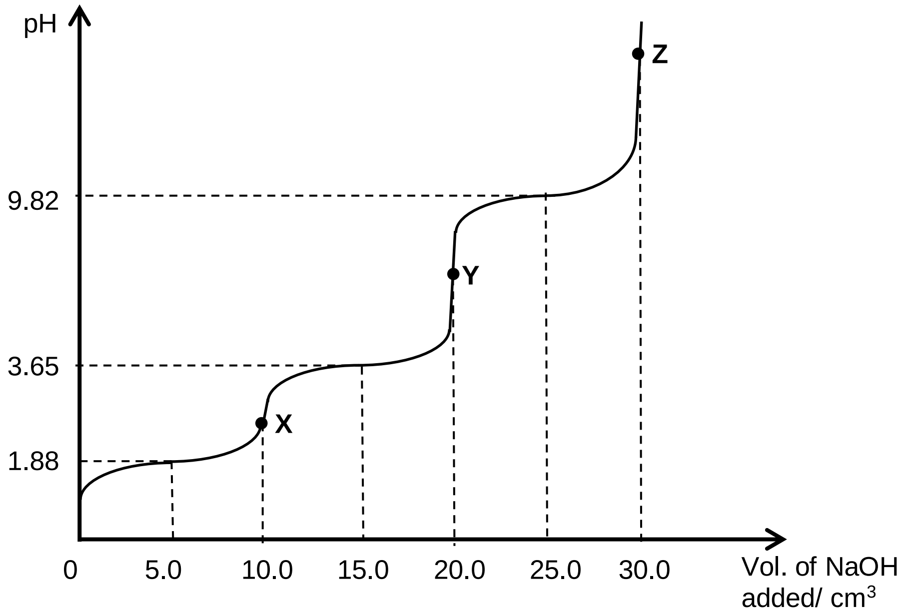
(iv) Part of the chain of another polypeptide **K** is shown below.



Draw the structure of the organic products formed when polypeptide **K** is treated with excess aqueous KOH under prolonged heating.

[2]

(b) The following titration curve is obtained when a solution of fully protonated aspartic acid, $H_3N^+CH(CH_2CO_2H)CO_2H$ is titrated with NaOH(aq). **X**, **Y** and **Z** denote the first, second and third equivalence point respectively.



(i) Identify the species present at **X** and **Z**.

[1]

(ii) Hence, explain why there is a sharp increase in pH when a small amount of NaOH(aq) is added to solution at **Z**.

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[1]

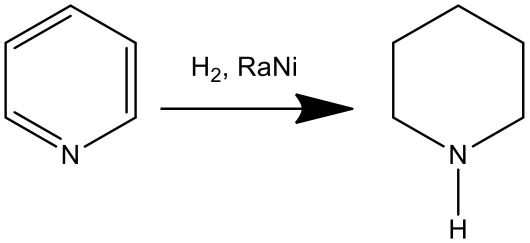
(iii) At pH 10.0, the mixture can act as a buffer. Identify the two species present in this buffer. With the aid of an equation, show how the buffer works when a small amount of acid is added to it.

[2]

(iv) Calculate the ratio of the concentrations of the two species in the buffer required to maintain the pH in **(b)(iii)**.

[2]

(c) Pyridine is a cyclic structure containing nitrogen and is analogous to that of benzene. It can be reduced to piperidine with Raney nickel (RaNi) as shown in the following reaction:



(i) State the type of hybrid orbital occupied by the lone pair of electrons on the N atom in pyridine and piperidine.

Pyridine: ……………………………

Piperidine: …………………………

[1]

(ii) Hence, suggest how the basicity of pyridine might compare to that of piperidine. Give reasons for your answers.

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[2]

(iii) In an attempt to form a quaternary amine salt, a student treated piperidine with excess iodomethane under acidic condition. Explain why this synthesis will **not** be successful.

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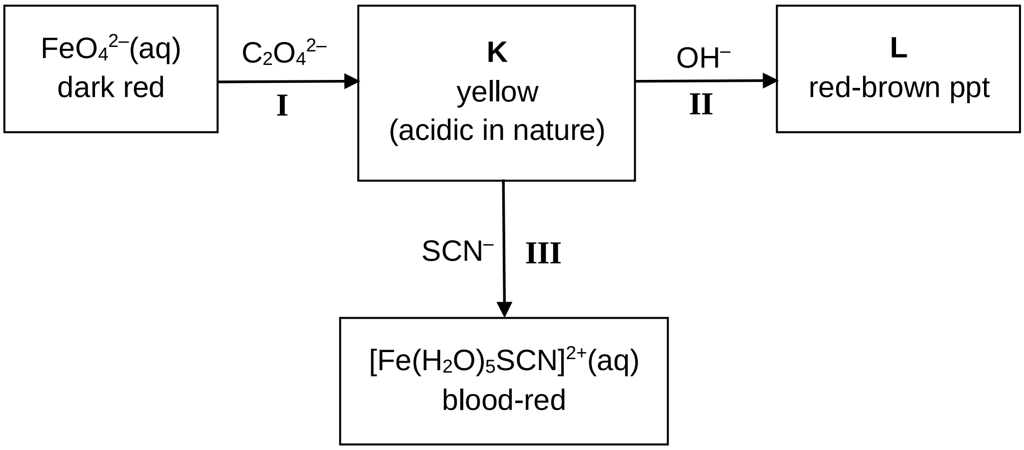
[2]
[Total: 17]

6 **(a)** In most of its compounds, iron has the oxidation state +2 or +3. However, other oxidation states of iron are possible. For example, potassium ferrate(VI), K_2FeO_4, contains iron in the +6 oxidation state. Reflecting its high oxidation state, FeO_4^{2-} is a powerful oxidising agent.

The following scheme illustrates a series of reactions involving various oxidation states of iron.



(i) Iron is considered to be a transition metal. Justify the statement.

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[1]

(ii) Explain why FeO_4^{2-}(aq) is coloured.

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[2]

(iii) State the type of reaction that occurred in reactions **I** to **III**.

I …………………………………………….

II …………………………………………….

III …………………………………………….

[3]

(iv) Write an equation to illustrate the acidic nature of **K**.

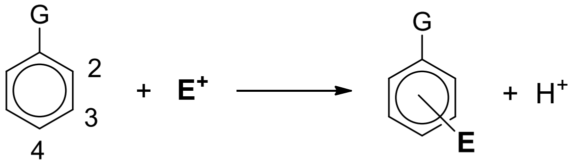
…………………………………………………………………………………………..

[1]

(v) Using relevant data from the *Data Booklet,* predict whether a reaction will occur when iodide ions are mixed with **K** and **L** separately. Write an equation for any reaction that occurs.

[2]

(b) In an aromatic substitution reaction, the position of the incoming group, **E**, is determined by the nature of the group, **G**, already bonded to the ring, and not by the nature of the incoming group **E**.



(i) Name the type of reaction mechanism between phenol and the incoming group, **E**.

…………………………………………………………………………………………..

[1]

(ii) Both phenylamine, $C_6H_5NH_2$, and phenol, activate the benzene ring in a similar manner so that the ring becomes highly susceptible to the incoming group, **E**. Comparing the difference in electronegativity between oxygen in phenol and nitrogen in phenylamine, explain the relative rate of phenol and phenylamine with the incoming group, **E**.

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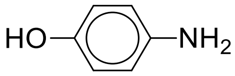
[2]

(iii) From your answers in **(b)(ii)**, outline the reaction mechanism for the mono-substitution of 4-aminophenol with the incoming group, $\mathbf{E}^+$.



4-aminophenol

[3]

(c) The choice of solvent used in the bromination of phenol can greatly affect the type of product formed.

(i) Draw the structure of the product formed when phenol undergoes reaction with Br_2 in water and with Br_2 in a non-polar organic solvent like CS_2 separately.

[1]

(ii) By considering the nature of the incoming group, **E**, suggest an explanation for the difference in the reaction between phenol and bromine dissolved in the two different types of solvent mentioned in **(c)(i)**.

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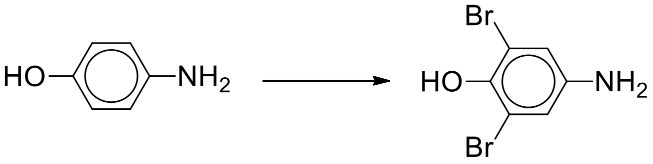
[1]

(d) Suggest the reagents and conditions required to carry out the following transformation and explain the rationale for the choice.



Reagents and conditions: ....

Explanation: ....

....
[2]
[Total: 19]

Victoria Junior College
2019 H2 Chemistry Prelim Exam 9729/2
Suggested Answers

1 **(a)** An unknown solid sample, with a mass of 1.50 g, contains three sodium salts, NaC*l*, NaC*l*O$_3$ and NaNO$_3$. The sample was completely dissolved in water and diluted in a 250 cm^3 volumetric flask to obtain solution **L**.

In one experiment, a 50 cm^3 portion of solution **L** was reacted with excess silver nitrate solution. The AgC*l* precipitate formed was removed by filtration, dried and weighed. The AgC*l* precipitate was found to have a mass of 0.240 g.

In another experiment, a gas was bubbled into a new 50.0 cm^3 portion of solution **L** to convert C*l*O$_3^-$ to C*l*$^-$. Excess silver nitrate was then added to the resulting mixture. The AgC*l* precipitated formed was treated similarly as before and found to have a mass of 0.285 g.

(i) Determine the amount of C*l*O$_3^-$ ions present in 50 cm^3 of solution **L**.

From 1st experiment, $n_{AgCl} = \dfrac{0.240}{107.9 + 35.5} = 1.674 \times 10^{-3}$ mol $= n_{Cl^-}$

From 2nd experiment, $n_{AgCl} = \dfrac{0.285}{107.9 + 35.5} = 1.987 \times 10^{-3}$ mol $= n_{Cl^-} + n_{ClO_3^-}$

$n_{ClO_3^-}$ **in 50.0 cm^3 of L** $= 1.987 \times 10^{-3} - 1.674 \times 10^{-3}$
$= 3.13 \times 10^{-4}$ mol [2]

(ii) Hence, determine the percentage by mass of NaC*l*O$_3$ present in the original solid sample.

$n_{ClO_3^-}$ **in 250.0 cm^3 of L** $= (250 / 50) \times 3.13 \times 10^{-4}$
$= 1.565 \times 10^{-3}$ mol $= n_{NaClO_3}$

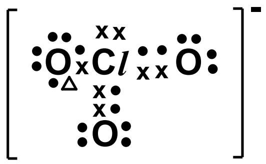
Percentage by mass of NaC*l*O$_3$

$= \dfrac{1.565 \times 10^{-3} \times (23.0 + 35.5 + 3 \times 16.0)}{1.50} \times 100\% = 11.1\%$ [2]

(b) Suggest whether NaC*l* or NaC*l*O$_3$ has a lower melting point. Explain your answer.

NaC*l*O$_3$ has a lower melting point. Both NaC*l* and NaC*l*O$_3$ have giant ionic structure with electrostatic attraction between ions of opposite charges. $|\text{Lattice energy}| \propto \dfrac{q_+ \times q_-}{r_+ + r_-}$. Since C*l*O$_3^-$ is larger than C*l*$^-$, NaC*l*O$_3$ has a lower magnitude of lattice energy. Hence, less energy is required to break the ionic bonds. [2]

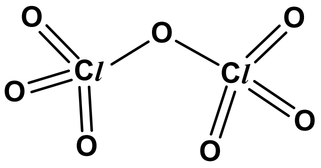
(c) **(i)** Draw a dot-and-cross diagram of the ClO_3^- anion.



[1]

(ii) Chlorine forms a number of oxides, one of which is Cl_2O_7. Cl_2O_7 is a symmetrical molecule, with a central oxygen atom bonded to two chlorine atoms.

Draw the structure of Cl_2O_7.



[1]

(iii) The bonds in Cl_2O_7 exhibit two different bond lengths, namely, 0.141 nm and 0.171 nm. However, all the bonds in the ClO_3^- ion have the same bond length of 0.149 nm.

Suggest why the bond length in ClO_3^- is intermediate between those present in Cl_2O_7.

Resonance arising from the overlapping of p orbitals of C*l* atom with those of the surrounding O atoms. This leads to delocalization of the lone pair on O^- into the C*l*=O double bonds, causing all bonds to have partial double bond character. [2]

(iv) The bond angle formed between the central oxygen atom and its two surrounding chlorine atoms is larger than expected with a value of 118.6°.

Suggest a possible reason why.

Repulsion between the electron clouds (or steric hindrance) of the two bulky –C*l* atoms [1]

[Total: 11]

2 **(a)** Use of the *Data Booklet* is necessary for this part of the question.

The sub–atomic makeup of certain ions formed from isotopes of cobalt and lead is given below:

	Number of neutrons	Number of electrons
Co ion	33	25
Pb ion	122	

In a particular experimental set–up, a beam containing the above ions of cobalt was passed through an electric field and was deflected by an angle of +10.2°.

Under identical conditions, another beam containing the above ions of lead was deflected by an angle of +6.0°.

What is the overall charge of the lead ions?

From the Data Booklet,
Proton number: Co = 27, Pb = 82

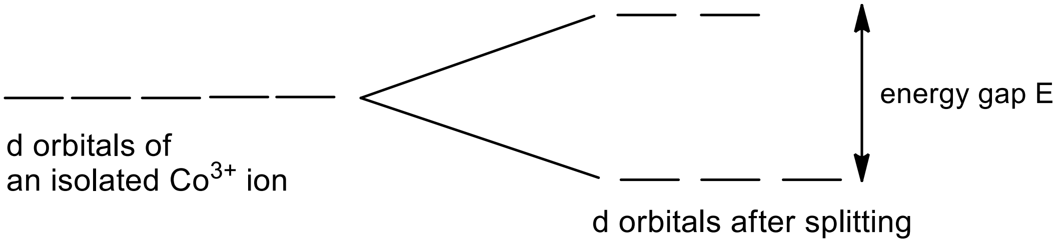
Charge of Co ion = +27 – 25 = +2
Nucleon number of Co = 33 + 27 = 60
Nucleon number of Pb = 122 + 82 = 204
Angle of deflection of Co ion = $+10.2 = k\left(\frac{2}{60}\right) \Rightarrow k = 306$
Let charge of Pb be x.
Angle of deflection of Pb ion = $+6.0 = 306\left(\frac{x}{204}\right)$
$x = +4$ ***(+ve sign must be included)***

[2]

(b) Many transition metals and their complexes are paramagnetic. Paramagnetism is a property of a substance which allows it to be weakly attracted to a magnet. This property is due to the presence of unpaired electrons in the substance.

CoF_6^{3-} and $[Co(NH_3)_6]^{3+}$ are both complexes with cobalt in the +3 oxidation state. However, only CoF_6^{3-} displays paramagnetism while $[Co(NH_3)_6]^{3+}$ does not. This is determined by whether the electronic configuration of the Co^{3+} ion in the complex displays a "high spin" or a "low spin" state.

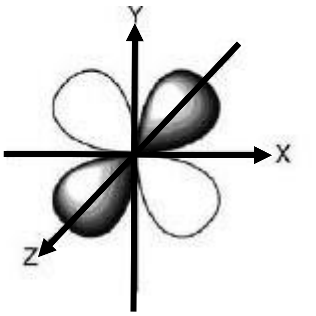
The following diagram shows how the d–orbitals are split in an octahedral environment.



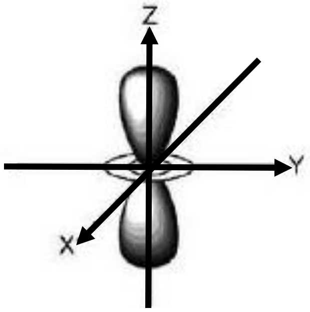
In a 'high spin' state, the electrons occupy all the d–orbitals singly, before starting to pair up in the lower energy d–orbitals.

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

(i) Draw the shapes of the d_{xy} and d_{z^2} orbitals. Label your drawings clearly.



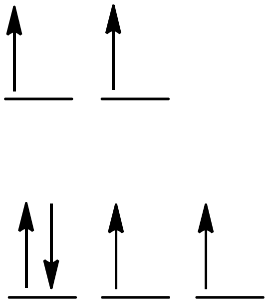
d_{xy}



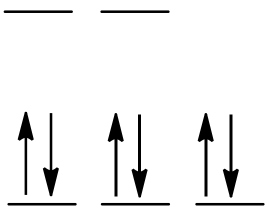
d_{z^2}

[2]

(ii) Using ↑ or ↓ to represent electrons, show, on the two diagrams below, the electronic distribution of a Co^{3+} ion in a high spin state, and in a low spin state. Hence, identify the cobalt complex that corresponds to each particular spin state.



d orbitals after splitting



d orbitals after splitting

	High spin	Low spin
Complex:	**CoF_6^{3-}**	**$[Co(NH_3)_6]^{3+}$**

[2]

(iii) Suggest why electrons usually prefer to occupy orbitals singly rather than in pairs.

To <u>minimize repulsion</u> between <u>negatively (OR similarly) charged electrons</u>. [1]

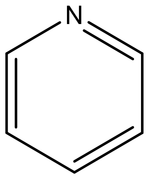
(iv) Using the explanation in **(b)(iii)**, together with the information given above, state and explain which of the two cobalt complexes contains the larger energy gap, E, between its d orbitals.

The <u>low spin complex</u>, $[Co(NH_3)_6]^{3+}$, contains the larger energy gap. Electrons pair up only if the <u>energy gap is larger than the energy required to overcome</u> the interelectronic <u>repulsion</u>. [1]

[Total: 8]

3 Frederick Thomas Trouton was an Irish physicist who observed a relationship between boiling points and enthalpy changes of vaporisation after studying many liquids. He published his findings and formulated Trouton's rule which states that the molar *entropy* of vaporisation, ΔS_{vap}, for most liquids is about 85 J K^{-1} mol^{-1}.

The boiling points and enthalpy changes of vaporisation of several organic liquids are as follows:

substance	boiling point / °C	ΔH_{vap} / kJ mol^{-1}	ΔS_{vap} / J K^{-1} mol^{-1}
propanone, $(CH_3)_2CO$	56.1	29.1	**88.4**
dimethyl ether, $(CH_3)_2O$	-24.8	21.5	86.6
ethanol, CH_3CH_2OH	78.4	38.6	**109.8**
octane, $CH_3(CH_2)_6CH_3$	125.6	34.4	86.3
pyridine, 	115.3	35.1	90.4

(a) Explain the term *entropy* and why ΔS_{vap} at constant pressure is positive.

Entropy is a measure of the dispersal of energy / disorderliness / randomness in a system.
Vapourisation involves the phase/state of a substance from liquid to gas at constant pressure, the same number of particles can move more freely and in greater volume in gaseous phase as compared to liquid phase resulting in greater entropy of a substance in gas phase as compared to liquid phase. [2]

(b) Complete the above table by calculating the ΔS_{vap} for two propanone and ethanol. Show your working for the calculation of ΔS_{vap} for propanone.

$\Delta G = \Delta H - T\Delta S$; phase change $\therefore$ $\Delta G = 0$

$$\Delta S = \frac{\Delta H}{T} = \frac{29.1\times10^3}{56.1+273} = 88.4 \text{ J K}^{-1}\text{ mol}^{-1}$$

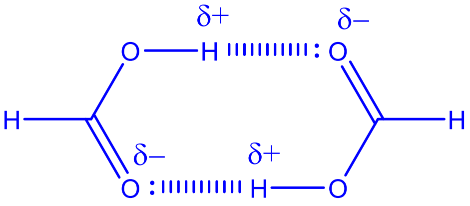
[2]

(c) By considering the structure and bonding of the various substances in this question, state and explain the relationship between strength of intermolecular forces of attraction and the entropy of a substance in the liquid state.

Octane is non-polar and has instantaneous dipole-induced dipole interactions between molecules.

Propanone, dimethyl ether and pyridine are polar and have stronger permanent dipole-permanent dipole attraction between molecules.
Ethanol is the most polar and has strongest hydrogen bonds between molecules.
The stronger the intermolecular forces of attraction between molecules, the lower the entropy of a substance in liquid state. [2]

(d) **(i)** With the aid of a diagram, show and label the bonding between two methanoic acid molecules in the **gaseous** phase.



[1]

(ii) Hence, predict if ΔS_{vap} for methanoic acid is more or less positive than predicted by Trouton's rule. Explain your reasoning carefully.

[No marks will be awarded if a prediction has no reasoning.]

ΔS_{vap} is less positive.
In gaseous phase, methanoic acid molecules exist as <u>dimers</u> which decrease the total number of molecules in the sample/show greater structure/lower randomness/reduce dispersal of energy leading to a smaller change in entropy during phase change. [2]

[Total: 9]

4 Ozone, O_3, is fairly stable but rapidly decomposes, with the release of heat, to form oxygen in the presence of silver catalyst. A silver catalyst was added to 800 cm^3 of a mixture of oxygen and ozone. The volume increased as follows and the reaction is complete at 1800 s.

Total volume of gas mixture, V_{total} / cm^3	800	805	810	815	818	819
volume of O_3(g) / cm^3	**38**	**28**	**18**	**8**	**2**	0
time, t / s	0	210	420	860	1350	1800

(a) **(i)** Write a chemical equation to represent the overall process of the decomposition of ozone to form oxygen.

$2O_3(g) \rightarrow 3O_2(g)$ [1]

(ii) By considering the stoichiometry of the reaction, calculate the initial volume of ozone and initial volume of oxygen in the mixture.

For every 2 mol of O_3 reacted, there is a net increase of 1 mol of gas particles. Since there is a net increase of 19 cm^3 of gas at the end of the reaction, by Avogadro's Law,
no. of moles of $O_3(g)$ = 19.0 × 2 = 38.0 cm^3
no. of moles of $O_2(g)$ = 800 – 38 = 762 cm^3 [1]

(iii) Given that volume of O_3 reacted = 2 (V_{total} – 800), complete the above table by calculating the volume of ozone in the mixture at the various times stated. Fill in the volume of O_3 at t = 0 s using your answer in **a(ii)**.

At 210 s, there is a net increase in gas volume of 5 cm^3. This means 10 cm^3 of $O_3(g)$ has reacted.

Amount of $O_3(g)$ left = 38 – 10 = 28 cm^3 [1]

(iv) The decomposition of ozone is a *first order* reaction.

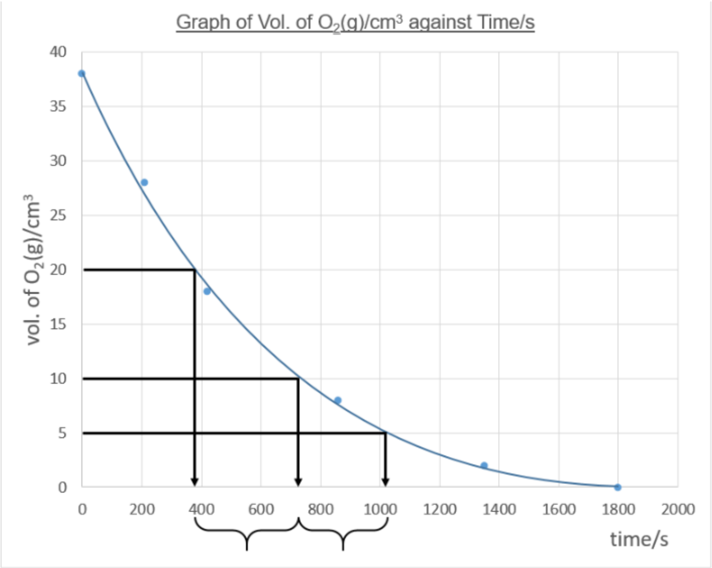
Write down the rate equation and explain the term *first order*.

rate = $k[O_3]$

The order of reaction refers to the power to which the O_3 concentration term is being raised in the rate equation. [2]

(v) Show, by means of a suitable graph, that these data are consistent with a first order reaction.

[If you are unable to solve (iii), sketch the graph without data points and indicate clearly how it can be used to verify the order of reaction.]



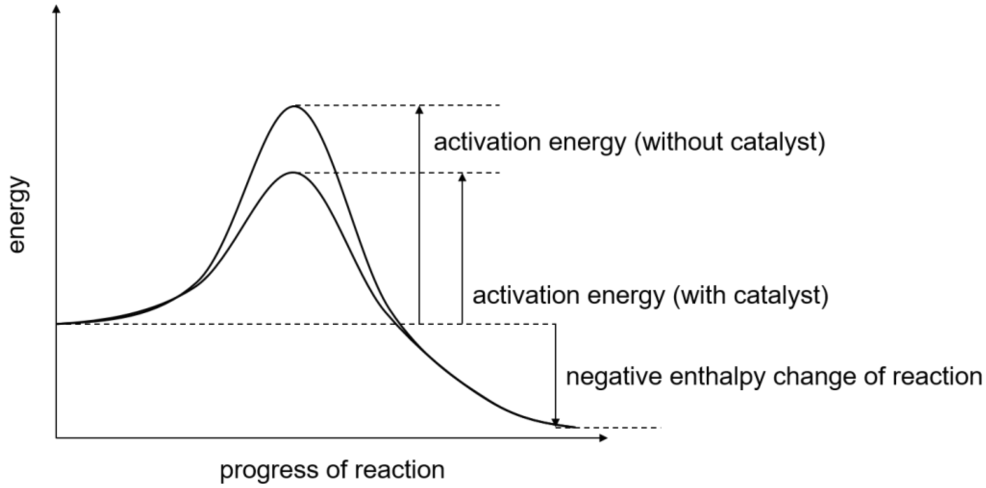
constant $t_{1/2} \approx 300$ s

[2]

(b) (i) Silver is a heterogeneous catalyst in this reaction. Outline how a heterogeneous catalyst work.

Reactant molecules are adsorbed on the surface of the catalyst. Concentration of reactants at the catalyst surface is increased and bonds in reactant molecules are weakened resulting in lowering of activation energy. Products formed subsequently desorb from the surface. [2]

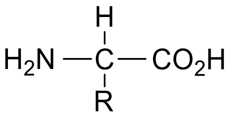
(ii) Draw a labelled energy profile diagram for the decomposition of ozone, with and without the use of a catalyst.



[2]

[Total: 11]

5 **(a)** Nitrogen is one of the key elements present in α-amino acids, the building block of proteins. α-amino acids have the following general formula.



$$H_2N-\overset{H}{\underset{R}{C}}-CO_2H$$

The table below shows the R groups of the α-amino acids present in a polypeptide, **J**.

α–amino acid	M_r	R group
asp	133.0	$-CH_2CO_2H$
lys	146.0	$-CH_2CH_2CH_2CH_2NH_2$
gln	146.0	$-CH_2CH_2CONH_2$

You have to refer to the table above when answering **a(i)** and **a(ii)**.

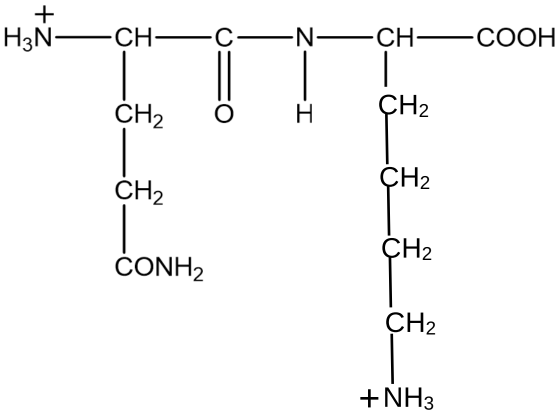
(i) When polypeptide **J** undergoes hydrolysis, three aspartic acid, two lysine and one glutamine molecules were formed as shown in the following reaction:

$$\mathbf{J} \longrightarrow 3\text{ asp} + 2\text{ lys} + 1\text{ gln}$$

Calculate the M_r of polypeptide **J**.

M_r of J = 3(133.0) + 2(146.0) + 1(146.0) – 5(18.0) = 747.0 [1]

(ii) A dipeptide, *gln–lys*, is obtained upon hydrolysis of polypeptide **J** by an enzyme. Draw the structural formula of this dipeptide at pH 1.



[1]

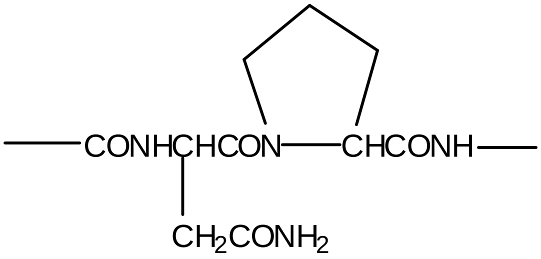
(iii) A sample of lysine, extracted from the hydrolysis of polypeptide **J** rotated plane polarised light anticlockwise. However, a second sample of lysine obtained from laboratory synthesis had no effect on plane polarised light.

Suggest an explanation for these observations.

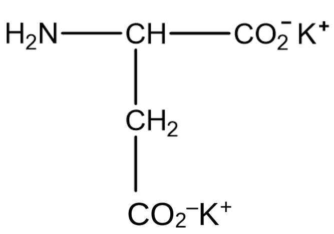
The sample of aspartic acid extracted from the hydrolysis of polypeptide J contains only one enantiomer. However, the one obtained from laboratory synthesis is a racemic mixture, in which each

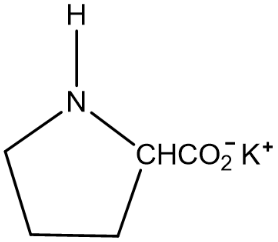
of the both enantiomers rotating plane polarised light by an equal angle but in opposite directions. [2]

(iv) Part of the chain of another polypeptide **K** is shown below.



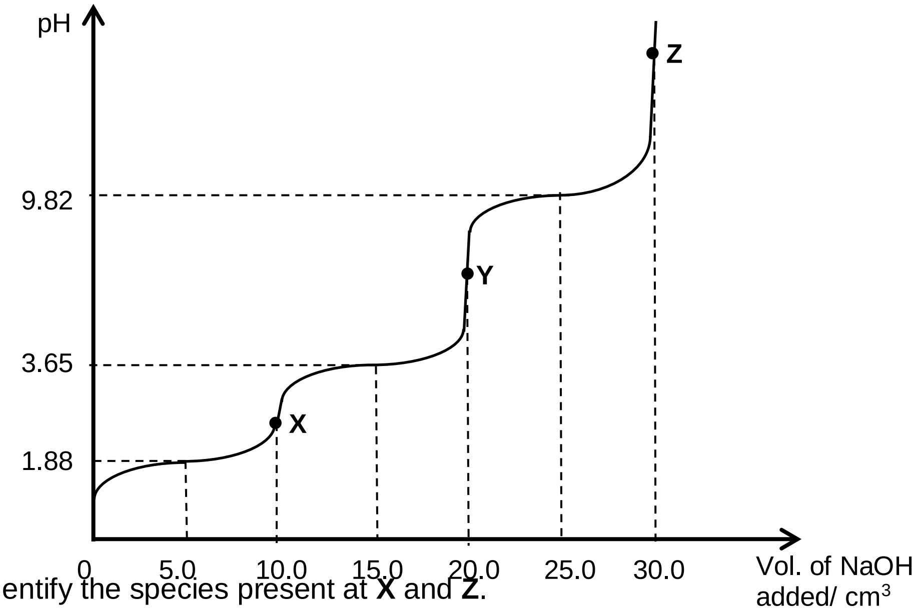
Draw the structure of the organic products formed when polypeptide **K** is treated with excess aqueous KOH under prolonged heating.





[2]

(b) The following titration curve is obtained when a solution of fully protonated aspartic acid, $H_3N^+CH(CH_2CO_2H)CO_2H$ is titrated with NaOH(aq). **X**, **Y** and **Z** denote the first, second and third equivalence point respectively.



(i) Identify the species present at **X** and **Z**.

X: $H_3N^+CH(CH_2CO_2H)CO_2^-$
Z: $H_2NCH(CH_2CO_2^-)CO_2^-$

[1]

(ii) Hence, explain why there is a sharp increase in pH when a small amount of NaOH(aq) is added to solution at **Z**.

The solution at Z is basic. It <u>does not have any H^+ to neutralise OH^- from NaOH</u>. Hence, there is a large increase in pH with the addition of small amount of NaOH(aq). [1]

(iii) At pH 10.0, the mixture can act as a buffer. Identify the two species present in this buffer. With the aid of an equation, show how the buffer works when a small amount of acid is added to it.

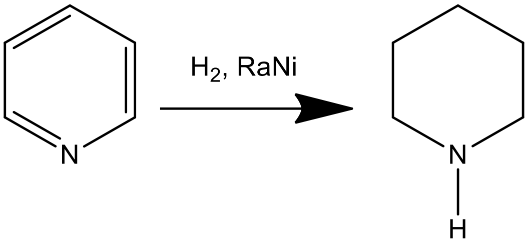
$H_3N^+CH(CH_2CO_2^-)CO_2^-$ and $H_2NCH(CH_2CO_2^-)CO_2^-$
$H^+ + H_2NCH(CH_2CO_2^-)CO_2^- \rightarrow H_3N^+CH(CH_2CO_2^-)CO_2^-$

[2]

(iv) Calculate the ratio of the concentrations of the two species in the buffer required to maintain the pH in **(b)(iii)**.

$pH = pK_{a3} + \lg([salt] / [acid])$
$10.0 = 9.82 + \lg([salt] / [acid])$
$[salt] / [acid] = 1.51$ [2]

(c) Pyridine is a cyclic structure containing nitrogen and is analogous to that of benzene. It can be reduced to piperidine with Raney nickel (RaNi) as shown in the following reaction:



(i) State the type of hybrid orbital occupied by the lone pair of electrons on the N atom in pyridine and piperidine.

Pyridine: **sp^2**

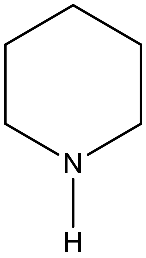
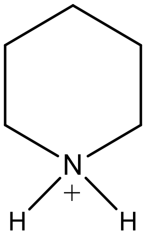
Piperidine: **sp^3**

[1]

(ii) Hence, suggest how the basicity of pyridine might compare to that of piperidine. Give reasons for your answers.

Pyridine is a weaker base than piperidine. Lone pair electrons in sp^2 orbitals is closer to the nucleus / more strongly attracted by the nucleus due to greater s character. Hence, lone pair electrons is less available for donation to acid in pyridine. [2]

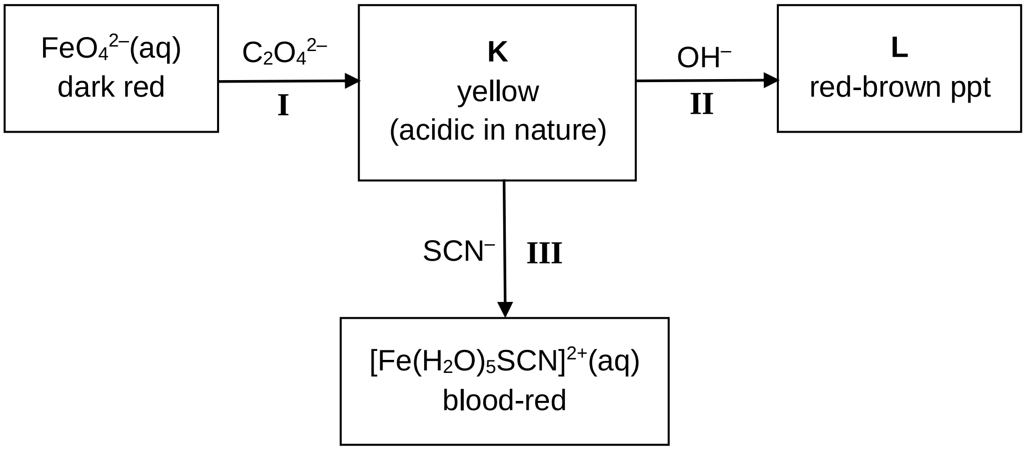
(iii) In an attempt to form a quaternary amine salt, a student treated piperidine with excess iodomethane under acidic condition. Explain why this synthesis will not be successful.

Under acidic conditions,  **is neutralised to form** . **Hence, the protonated piperidine will not be able to act as a nucleophile since the lone pair on the N is not available for the nucleophilic substitution to form the quaternary amine salt.** [2]

[Total: 17]

6 **(a)** In most of its compounds, iron has the oxidation state +2 or +3. However, other oxidation states of iron are possible. For example, potassium ferrate(VI), K_2FeO_4, contains iron in the +6 oxidation state. Reflecting its high oxidation state, FeO_4^{2-} is a powerful oxidising agent.

The following scheme illustrates a series of reactions involving various oxidation states of iron.



(i) Iron is considered to be a transition metal. Justify the statement.

Iron is a d-block element that forms one or more stable ions [Fe^{2+}, Fe^{3+} or Fe(VI)] with partially filled d subshell and therefore considered to be a transition element. [1]

(ii) Explain why FeO_4^{2-}(aq) is coloured.

In the presence of ligands, the degenerate 3d orbitals are split into 2 different energy levels (d-d splitting).
A 3d e from the lower energy level is promoted to the upper energy level by absorbing energy from the visible region of the electromagnetic spectrum, known as d-d transition (which is possible only with partially-filled d subshell configuration).
The complement of the colour absorbed is seen. [2]

(iii) State the type of reaction that occurred in reactions **I** to **III**.

I – Redox reaction
II – Precipitation
III – Ligand exchange [3]

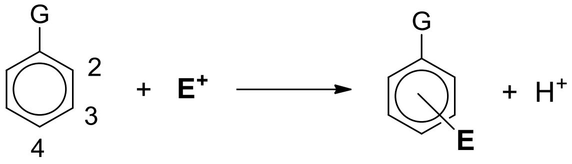
(iv) Write an equation to illustrate the acidic nature of **K**.

$$[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5OH]^{2+} + H_3O^+$$ [1]

(v) Using relevant data from the *Data Booklet,* predict whether a reaction will occur when iodide ions are mixed with **K** and **L** separately. Write an equation for any reaction that occurs.

K – $[Fe(H_2O)_6]^{3+}$
L – $Fe(OH)_3$
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E^\ominus = +0.77$ V
$I_2 + 2e^- \rightleftharpoons 2I^-$ $E^\ominus = +0.54$ V
c $= E^\ominus_{red} - E^\ominus_{ox}$
$= +0.77 - (+0.54)$
$= +0.23$ V
$E^\ominus_{cell} > 0$ V, spontaneous
$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$
The reaction is likely to occur because the reactants are oppositely charged and can attract each other.
$Fe(OH)_3 + e^- \rightleftharpoons Fe(OH)_2 + OH^-$ $E^\ominus = -0.56$ V
$I_2 + 2e^- \rightleftharpoons 2I^-$ $E^\ominus = +0.54$ V
$E^\ominus_{cell}$ $= E^\ominus_{red} - E^\ominus_{ox}$
$= -0.56 - (+0.54)$
$= -1.10$ V
$E^\ominus_{cell} < 0$ V, not spontaneous
Reaction is unlikely to occur. [2]

(b) In an aromatic substitution reaction, the position of the incoming group, **E**, is determined by the nature of the group, **G**, already bonded to the ring, and not by the nature of the incoming group **E**.



(i) Name the type of reaction mechanism between phenol and the incoming group, **E**.

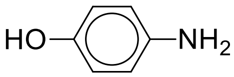
Electrophilic (aromatic) substitution [1]

(ii) Both phenylamine, $C_6H_5NH_2$, and phenol, activate the benzene ring in a similar manner so that the ring becomes highly susceptible to the incoming group, **E**. Comparing the difference in electronegativity between oxygen in phenol and nitrogen in phenylamine, explain the relative rate of phenol and phenylamine with the incoming group, **E**.

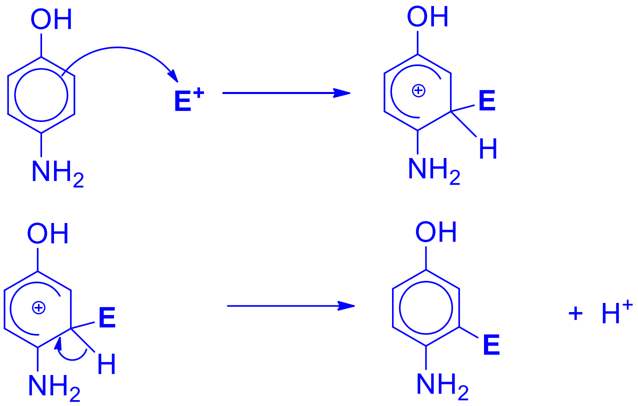
Oxygen is more electronegative than nitrogen. Oxygen in phenol therefore has less tendency to donate the lone pair of electrons to benzene ring compared to nitrogen in phenylamine. This results in lower electron density in benzene and less electron rich to attract electrophile E. Hence

phenol is less reactive towards electrophilic substitution compared to phenylamine. [2]

(iii) From your answers in **(b)(ii)**, write the mechanism for the mono-substitution of 4-aminophenol with the incoming group, **E**$^+$.



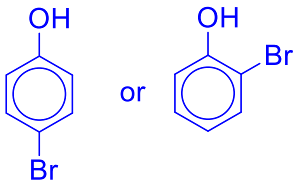
4-aminophenol



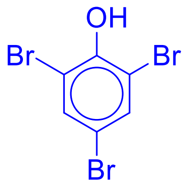
[3]

(c) The choice of solvent used in the bromination of phenol can greatly affect the type of product formed.

(i) Draw the structure of the product formed when phenol undergoes reaction with Br_2 in water and with Br_2 in a non-polar organic solvent like CS_2 separately.



with Br_2 in CS_2



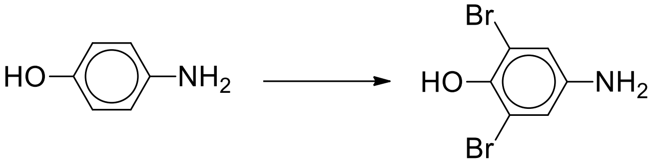
with Br_2 (aq) [1]

(ii) By considering the nature of the incoming group, **E**, suggest an explanation for the difference in the reaction between phenol and bromine dissolved in the two different types of solvent mentioned in **(c)(i)**.

Polar solvent like water can interact and stabilise the partial charge in $Br^{\delta+}$–$Br^{\delta-}$ molecule and therefore results in a higher concentration of polarised Br_2 molecule for multiple substitution in the benzene ring.
OR
Non-polar solvent like CS_2 is unable to interact and stabilise the partial charge in $Br^{\delta+}$–$Br^{\delta-}$ molecule and results in a lower concentration of polarised Br_2 molecule. Hence only mono-substitution can take place.
OR

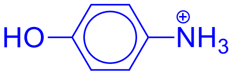
Phenol dissociates in water to form phenoxide carrying negatively charged O which is more electron-donating than –OH group, hence, ring is more activated for multiple substitution. [1]

(d) Suggest the reagents and conditions required to carry out the following transformation and explain the rationale for the choice.



Reagents: Add aqueous bromine with dilute HC*l*

Conditions: room temperature

Rationale: Addition of acid is to form  **that makes $–NH_3^+$ a deactivating group. Being deactivating in nature, the –OH group will now determine the electrophilic substitution at 2- & 6- position with respect to phenol group.** [2]

[Total: 19]

Section A

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

1 **(a)** Account for the reactions that occur when $MgCl_2$ and PCl_5 are separately dissolved in water. Predict the pH of the resulting solutions formed and write equations for the reactions that occur. [4]

(b) A sample consists of a solid mixture of MgO and Al_2O_3. Describe briefly an experimental procedure that will enable you to separate the mixture and recover each of the oxides in its pure form. [3]

(c) The highest fluoride of xenon, XeF_6, can be obtained by heating the octafluoroxenates of the Group 1 metals, M_2XeF_8, where M represents the Group 1 metal.

$$M_2XeF_8 \rightarrow 2MF + XeF_6$$

Suggest reasons why the sodium salt (M = Na) decomposes below 100 °C, whereas the caesium salt (M = Cs) requires a temperature of 400 °C. Hence explain why $MgXeF_8$ is not known to exist. [3]

(d) Suggest identities for the following substances **A** to **D**, writing equations where appropriate.

When magnesium is heated with nitrogen under inert conditions, an ionic compound, **A** is produced. When water is added to **A**, a colourless gas **B** which turns damp red litmus paper blue is produced. **B** reacts with chlorate(I) ion, ClO^- in a 2 : 1 mole ratio to form a colourless liquid **C** with empirical formula NH_2. The reaction of **C** with sulfuric acid in a 1:1 mole ratio produces a salt **D**, $N_2H_6SO_4$, which contains one cation and one anion per formula unit. [4]

(e) Real gases do not obey the ideal gas equation exactly. Many chemists have tried to come up with gas equations that describe the behaviour of real gases. In 1873 J D van der Waals introduced an approximate gas equation that is applicable for all real gases. The van der Waals equation is

$$P = \frac{nRT}{V-n\mathbf{b}} - \mathbf{a}\frac{n^2}{V^2}$$

where **a** and **b** are constants which are characteristic of each gas. The other symbols carry their usual meaning and units as in the ideal gas equation.

(i) Using what you have learnt about the differences between ideal and real gases, suggest what the constants **a** and **b** represent. [2]

(ii) The values of the constants **a** and **b** for CO_2 are **a** = 0.3658 Pa m^6 mol^{-2} and **b** = 4.29 x 10^{-5} m^3 mol^{-1}.

Use your answer in **(e)(i)** to suggest how the value of the constant **a** for xenon (Xe) will compare with CO_2. Explain your answer briefly. [1]

(iii) Use the

- ideal gas equation and
- van der Waals equation

to calculate the pressure exerted by 1 mol of CO_2 at a temperature of 30 °C and volume of 1 dm^3.

[3]

[Total: 20]

2 (a) Malonic acid, $CH_2(CO_2H)_2$ is an organic *weak dibasic acid*. It is a building block chemical to produce numerous valuable compounds, including the flavour and fragrance compound, cinnamic acid, and the pharmaceutical compound, valproate. The two *pK_a* values of $CH_2(CO_2H)_2$ are 2.83 and 5.69.

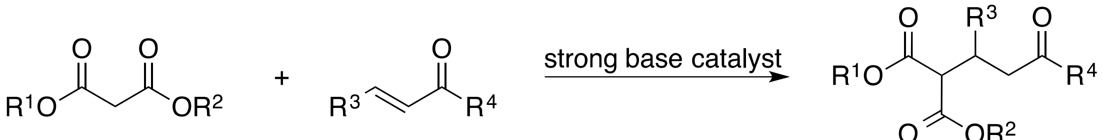
(i) Define the term *weak acid*. [1]

(ii) Calculate the pH of 25.0 cm^3 solution of 0.100 mol dm^{-3} $CH_2(CO_2H)_2$. [1]

(iii) Calculate pH of the resulting solution when 50 cm^3 of 0.100 mol dm^{-3} NaOH was added to the solution in **(a)(ii)**. [2]

(iv) Using your answers in **(a)(ii)** and **(a)(iii)**, as well as the *pK_a* values provided, sketch a graph to show how the pH of the solution changes as 50 cm^3 of 0.100 mol dm^{-3} NaOH is gradually added to 25.0 cm^3 of 0.100 mol dm^{-3} $CH_2(CO_2H)_2$. Clearly indicate the corresponding volumes of NaOH in your graph. [2]

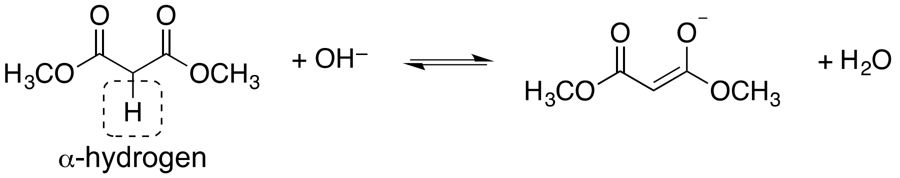
(b) Malonic acid can be converted to its corresponding β–diester. β–diesters are commonly used as starting compounds in the Michael addition reaction, where they react with α,β-unsaturated ketones. It is one of the most useful methods for the formation of C–C bonds.



β–diester α,β–unsaturated ketone

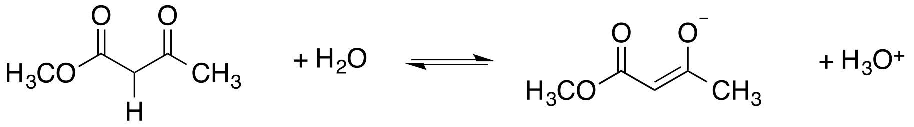
(i) Suggest reagents and conditions to convert malonic acid to dimethyl malonate, $CH_2(COOCH_3)_2$. State the type of reaction. [2]

(ii) The first step in the mechanism of Michael addition involves an acid–base reaction where the strong base catalyst extracts an α-hydrogen from the β–diester.



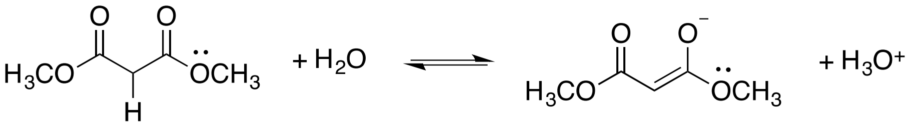
Reagents similar to the malonate ester can undergo the same type of reaction. The *pK_a* values of malonate ester and another similar reagent are as follows:

pK_a



β-ketoester

11



β-diester

13

Explain the difference in *pK_a* values between the two compounds. [2]

(iii) Compound **A**, C_8H_9ClO, contains a non-aromatic six-membered ring. **A** reacts with 2,4-dinitrophenylhydrazine to form an orange precipitate but does not react with Tollen's reagent. 1 mole of **A** reacts with 3 moles of H_2 gas in the presence of solid platinum. When **A** is warmed with aqueous sodium hydroxide, compound **B**, $C_8H_{10}O_2$ is formed. **B** gives a pale yellow precipitate when warmed with alkaline aqueous iodine. When **B** is warmed with acidified potassium permanganate, compounds **C**, $C_3H_2O_5$ and **D**, $C_5H_6O_5$ are formed. **D** also gives a pale yellow precipitate when warmed with alkaline aqueous iodine. **A** is able to undergo Michael addition with dimethyl malonate, $CH_2(COOCH_3)_2$, to form **E**, a compound with 18 carbons.

Deduce the structural formulae of compounds **A**, **B**, **C**, **D** and **E**, explaining clearly your reasoning for all reactions described.

[10]
[Total: 20]

3 **(a)** A Latimer diagram provides a concise way of representing large amount of information about the different oxidation states of an element. In a Latimer diagram, the most highly oxidised form of an element is written on the left, with successively lower oxidation states to the right. The different species are connected by arrows, and the standard electrode potential in volts is written above each arrow.

The Latimer diagrams for chlorine in acidic and alkaline medium are shown below.

In acidic medium:

$$ClO_4^- \xrightarrow{+1.19\ V} ClO_3^- \xrightarrow{+1.21\ V} ClO_2^- \xrightarrow{+1.66\ V} ClO^- \xrightarrow{+1.64\ V} Cl_2 \xrightarrow{+1.36\ V} Cl^-$$

In alkaline medium:

$$ClO_4^- \xrightarrow{+0.36\ V} ClO_3^- \xrightarrow{+0.35\ V} ClO_2^- \xrightarrow{+0.65\ V} ClO^- \xrightarrow{+0.40\ V} Cl_2 \xrightarrow{+1.36\ V} Cl^-$$

(i) Define the term *standard electrode potential*. [1]

(ii) The standard electrode potentials in a Latimer diagram are not additive. For example, the standard electrode potential for converting ClO_4^- to ClO^- in acidic medium is **not** the sum of +1.19 V and +1.21 V and +1.66 V. However, their respective standard Gibbs' free energy changes are additive.

Using relevant data given below, show that the standard electrode potential for converting ClO_4^- to ClO^- in acidic medium is 1.34 V.

electrode reaction	$E^\ominus$ / V	$\Delta G^\ominus$ / kJ mol^{-1}
$ClO_4^- + 2H^+ + 2e^- \rightleftharpoons ClO_3^- + H_2O$	+1.19	–220.7
$ClO_3^- + 2H^+ + 2e^- \rightleftharpoons ClO_2^- + H_2O$	+1.21	–233.5
$ClO_2^- + 2H^+ + 2e^- \rightleftharpoons ClO^- + H_2O$	+1.66	–320.4
$ClO^- + 2H^+ + e^- \rightleftharpoons \frac{1}{2}Cl_2 + H_2O$	+1.64	–158.3
$\frac{1}{2}Cl_2 + e^- \rightleftharpoons Cl^-$	+1.36	–131.2

[2]

(iii) With the exception of the conversion of Cl_2 to Cl^-, the standard electrode potentials in alkaline medium are less positive than their corresponding conversions in the acidic medium.

Suggest why this is so. [2]

(iv) A disproportionation reaction is a redox reaction in which a chemical species undergo reduction and oxidation simultaneously.

In hot alkaline medium, Cl_2 undergoes disproportionation to form two chlorine-containing species according to the following equation.

$$3Cl_2(g) + xOH^-(aq) \longrightarrow 5Cl^-(aq) + ClO_y^-(aq) + zH_2O(l)$$

By considering the number of moles of electrons transferred and using the Latimer diagram for chlorine in alkaline medium, first solve for y. Then, use it to solve for x and z. [2]

(b) Besides the standard hydrogen electrode, other reference electrodes have also been employed in electrochemistry. An example is the silver chloride electrode, which involves dipping silver metal coated with solid silver chloride into a solution of sodium chloride. The solubility product for AgC*l* is 2.0×10^{-10} mol^2 dm^{-6}.

(i) The standard electrode potential of a silver chloride electrode is +0.230 V. However, when 1.0 mol dm^{-3} sodium chloride is used to set up the silver chloride electrode, this value cannot be achieved.

Explain why this is so. [1]

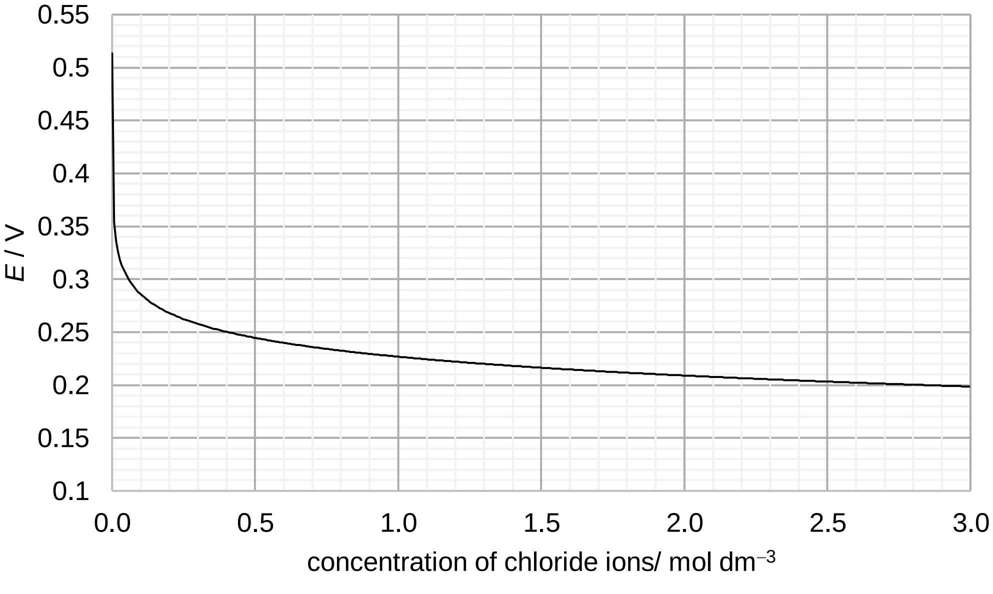
At 298 K, the electrode potential of the silver chloride electrode, *E*, can be estimated from the concentration of silver ions present using formula (1):

$$E = 0.80 - 0.0591 \log \frac{1}{[\mathrm{Ag^+}]} \text{ .....formula (1)}$$

(ii) Using the expression given, calculate the value of *E* in each of the following cases:

- in pure water and
- when the addition of sodium chloride results in a chloride ion concentration of 2.5 mol dm^{-3}. [3]

(iii) Using the graph given below, suggest why sodium chloride solution ranging from 1.0 mol dm^{-3} to 3.0 mol dm^{-3} is typically used in the setting up of a silver chloride electrode rather than pure water.



[1]

(iv) A student attempted to study the validity of formula (1) by adding aqueous ammonia to vary the concentration of silver ions in solution. This is due to the ability of ammonia to form a complex with the silver ions, thus decreasing its concentration in solution.

Explain a potential problem that may arise with this method of analysis. [1]

(v) The silver chloride electrode is used in many medical equipment. In a particular device used for electrocardiography, a layer of silver metal with a thickness of 1mm is plated onto an electrode with a surface area of 0.12 cm^2 before coating it with solid silver chloride.

If a current of 15.0 mA is used for the electroplating process, calculate the time required to completely plate the silver metal onto the electrode from a solution containing $Ag^+(aq)$.

[The density of silver metal is 10.5 g cm^{-3}]

[2]

(c) When sodium halides react with concentrated sulfuric acid, an acid-base reaction takes place resulting in the formation of white fumes of hydrogen halides.

$$Na\mathbf{X}(s) + H_2SO_4(l) \longrightarrow H\mathbf{X}(g) + NaHSO_4(s), \text{ where } \mathbf{X} = Cl, Br \text{ or } I$$

Subsequently, depending on the reducing strength of the hydrogen halides, a further reaction might take place with concentrated sulfuric acid, resulting in the formation of halogens, a sulfur-containing product and water.

The observations for the reaction of the different sodium halides with concentrated sulfuric acid are shown below:

sodium halide	observations
$NaCl$	white fumes of HCl
NaBr	white fumes of HBr red-brown Br_2 gas which condenses to form a red-brown liquid colourless and pungent SO_2 gas
NaI	white fumes of HI violet I_2 gas which condenses to form a black solid colourless and pungent H_2S gas

(i) Write a balanced molecular equation for each of the following reactions:

- between gaseous HBr and concentrated H_2SO_4
- between gaseous HI and concentrated H_2SO_4 [2]

(ii) Arrange the hydrogen halides in order of increasing reducing strength. Explain your answer, using relevant information from the *Data Booklet* to support the difference in observations. [3]

[Total: 20]

Section B

Answer **one** question from this section.

4 Sulfur forms many cyclic allotropes with different ring sizes. In the gas phase, all ring sizes from S_3 to S_{12} have been detected.

When a 1.00 g sample of sulfur was dissolved in 1 dm^3 of an organic solvent, the following equilibrium was established:

$$8S_7(g) \rightleftharpoons 7S_8(g)$$

The percentages by mass of S_7 and S_8 at equilibrium are:

ring size	S_7	S_8
percentage by mass	0.76	98.92

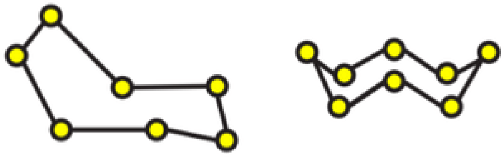
(a) **(i)** Calculate the amount, in moles, of S_7 and S_8 at equilibrium. [2]

(ii) Write an expression for the equilibrium constant, K_C, and calculate its value for the above reaction between S_7 and S_8. [2]

(iii) The amount of S_8 is increased by 0.01 mol at time t_1. Sketch, on the same axes, two graphs to show how $[S_7]$ and $[S_8]$ vary from t_1 to t_2, the time when equilibrium is re-established at the same temperature.
[You are only required to label the concentrations at t_1.] [2]

(iv) An inert gas is then added at constant pressure. State and explain how the position of equilibrium would change. [2]

The shape of the S_7 and S_8 molecules are as follows.



(b) **(i)** Define the term bond energy with reference to the S–S bonds in S_8. [1]

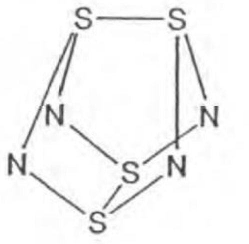
(ii) Given that the S–S bond energy in S_7 is 260.0 kJ mol^{-1} and that in S_8 is 263.3 kJ mol^{-1}, calculate the enthalpy change for the forward reaction between S_7 and S_8. [1]

(iii) Using your answers in **(a)(ii)** and **(b)(ii)**, and given that:

$$\Delta G^{\ominus} = -RT \ln K_c$$

where T is in Kelvins and ΔG is in J mol^{-1}, calculate the standard entropy change of the reaction. [2]

(c) Sulfur also forms an 8-membered ring in a compound with nitrogen, S_4N_4. In S_4N_4, nitrogen and sulfur atoms alternate in the ring. The four nitrogen atoms are arranged in a plane, with two sulfur atoms above the plane, and two sulfur atoms below the plane. The shape of a molecule of S_4N_4 is as shown.



S_4N_4

Using the data provided below, construct an energy cycle to calculate the average S–N bond energy in S_4N_4.

enthalpy change of formation of S_4N_4	+460 kJ mol^{-1}
enthalpy change of atomisation of sulfur	+297 kJ mol^{-1}
enthalpy change of atomisation of nitrogen	+497 kJ mol^{-1}
S–S bond energy in S_4N_4	+204 kJ mol^{-1}

[3]

(d) Sulfur and tungsten has certain similarities since both atoms have a total of six valence electrons, even though sulfur is a main group element and tungsten is a transition metal. Both elements reach their maximum +6 oxidation state when combined with electronegative elements such as fluorine and oxygen.

(i) Sulfur trioxide, SO_3 and tungsten(VI) oxide, WO_3 differ markedly in their physical properties. While SO_3 is a gaseous pollutant used in industrial preparation of sulfuric acid, WO_3 is used in electrochromic windows, allowing the windows to change colour when an electrical voltage is applied. Their boiling points are 44.9 ^{o}C and 1700 ^{o}C respectively.

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

(ii) Most tungsten occurs naturally in the tungsten anion, WO_4^{2-}, analogous to the sulfate ion, SO_4^{2-}.

Draw the structure of WO_4^{2-}. State the shape and bond angle of the O–W–O bond. [2]

[Total: 20]

5 **(a)** The Mars Curiosity rover's landing in August 2012 was achieved using hydrazine rocket thrusters. Hydrazine, N_2H_4, is popular with NASA as it produces no carbon dioxide.

N_2H_4 has a boiling point of 114 ^oC and decomposes to its elements when passed over a suitable catalyst. The rapid production of hot gaseous products is what provides the thrust.

(i) With the aid of a balanced equation, define the term standard enthalpy change of formation for hydrazine. [2]

(ii) Hydrazine may be obtained from the reaction between ammonia and hydrogen peroxide.

$$2NH_3(g) + H_2O_2(l) \rightarrow N_2H_4(l) + 2H_2O(l) \qquad \Delta H_r^\ominus = -241.0 \text{ kJ mol}^{-1}$$

Calculate the standard enthalpy change for the decomposition of 1 mol of hydrazine to its elements using data below.

compound	$\Delta H_f^\ominus$ / kJ mol^{-1}
NH_3	–46.1
H_2O_2	–187.8
H_2O	–285.8

[2]

(b) The first ever rocket-powered fighter plane, the Messerschmitt Me 163, was powered by the reaction between a hydrazine-methanol mixture, known as 'C-Stoff', and hydrogen peroxide ('T-Stoff'). The standard enthalpy change of combustion of hydrazine and methanol are −622.2 kJ mol^{-1} and −726.0 kJ mol^{-1}.

The fighter plane would hold 225 dm^3 of hydrazine and 862 dm^3 of methanol. The densities of hydrazine and methanol are 1.021 g cm^{-3} and 0.7918 g cm^{-3} respectively.

Calculate the heat energy evolved under standard conditions for the combustion of this quantity of rocket fuel, assuming that all the hydrazine and methanol are fully combusted.

[2]

(c) Hydrazine is also commonly combined with dinitrogen tetroxide, N_2O_4, in rocket fuels. This forms a hypergolic mixture, that is, the reactants ignite spontaneously on contact.

(i) Suggest the reaction products that are formed in the reaction between N_2H_4 and N_2O_4. Briefly explain why. [2]

(ii) Draw the structure of N_2O_4, indicating clearly the shape and bond angle around each nitrogen atom. [2]

(iii) At room temperature, N_2O_4 exists as a gas while N_2H_4 is a liquid. With reference to their structure and bonding, account for this difference. [3]

(d) At 46 °C, N_2O_4 (colourless gas) exists in equilibrium with nitrogen dioxide, NO_2 (brown gas) with an equilibrium constant, K_p of 0.66 atm. The equation for the equilibrium is

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

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

(ii) A certain amount of N_2O_4 is allowed to dissociate in a vessel. At equilibrium, the partial pressure of NO_2 is found to be 0.332 atm.

Calculate the partial pressure of N_2O_4 and total pressure at equilibrium. [2]

(iii) Hence, determine the percent dissociation of N_2O_4 at 46 °C. [2]

(iv) State and explain what may be observed when the vessel containing the gases is expanded. [2]

[Total: 20]

Victoria Junior College
2019 H2 Chemistry Prelim Exam 9729/3
Suggested Answers

Section A

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

1 (a) Account for the reactions that occur when $MgCl_2$ and PCl_5 are separately dissolved in water. Predict the pH of the resulting solutions formed and write equations for the reactions that occur. [4]

Mg^{2+} has high charge density due to small ionic radius (and high charge). Mg^{2+} has high polarising power and hence $MgCl_2$ undergoes hydration and partial hydrolysis, producing a slightly acidic solution.

$MgCl_2 + 6H_2O \rightarrow [Mg(H_2O)_6]^{2+} + 2Cl^-$ hydration
$[Mg(H_2O)_6]^{2+} + H_2O \rightleftharpoons [Mg(H_2O)_5OH]^+ + H_3O^+$ hydrolysis
pH of resulting solution = 6.5

PCl_5 undergoes complete hydrolysis due to the presence of energetically accessible vacant 3d orbitals on phosphorus which can accommodate lone pair from water molecules. The solution produced is strongly acidic.

$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$
pH of resulting solution = 2

(b) A sample consists of a solid mixture of MgO and Al_2O_3. Describe briefly an experimental procedure that will enable you to separate the mixture and recover each of the oxides in its pure form. [3]

1. Add excess NaOH(aq) to the sample.
2. Filter the resulting mixture. The residue collected is mainly MgO.
3. Wash the residue with distilled water and press between pieces of filter paper to obtain dry solid MgO.
4. To the filtrate, add HCl(aq) dropwise till the maximum mass of precipitate is formed.
5. Filter the resulting mixture. The residue collected is mainly $Al(OH)_3$.
6. Wash the residue with distilled water and press between pieces of filter paper to obtain dry solid $Al(OH)_3$.
7. Heat the residue till constant mass to obtain dry solid Al_2O_3.
[Note: $Al(OH)_3$ is expected to decompose on heating to form Al_2O_3, similar to Group 2 hydroxides.]

(c) The highest fluoride of xenon, XeF_6, can be obtained by heating the octafluoroxenates of the Group 1 metals, M_2XeF_8, where M represents the Group 1 metal.

$$M_2XeF_8 \rightarrow 2MF + XeF_6$$

Suggest reasons why the sodium salt (M = Na) decomposes below 100 °C, whereas the caesium salt (M = Cs) requires a temperature of 400 °C. Hence explain why $MgXeF_8$ is not known to exist. [3]

Down group 1, as ionic radius increases, charge density of cations decreases, polarising power of cations decreases, which polarises the XeF_8^{2-} anion to a lesser extent. The anion becomes more thermally stable and hence higher temperature is required to decompose caesium salt compared to sodium salt.

Mg^{2+} has higher charge density than Na^+, making $MgXeF_8$ very unstable and hence does not exist.

(d) Suggest identities for the following substances **A** to **D**, writing equations where appropriate.

When magnesium is heated with nitrogen under inert conditions, an ionic compound, **A** is produced. When water is added to **A**, a colourless gas **B** which turns damp red litmus paper blue is produced. **B** reacts with chlorate(I) ion, ClO^- in a 2 : 1 mole ratio to form a colourless liquid **C** with empirical formula NH_2. The reaction of **C** with sulfuric acid in a 1 : 1 mole ratio produces a salt **D**, $N_2H_6SO_4$, which contains one cation and one anion per formula unit. [4]

A: Mg_3N_2
B: NH_3
C: N_2H_4
D: $[N_2H_5^+][HSO_4^-]$ (accept $[N_2H_6^{2+}][SO_4^{2-}]$)

$3Mg + N_2 \rightarrow Mg_3N_2$
$Mg_3N_2 + 3H_2O \rightarrow 3MgO + 2NH_3$ (Accept $Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$)
$2NH_3 + ClO^- \rightarrow N_2H_4 + Cl^- + H_2O$
$N_2H_4 + H_2SO_4 \rightarrow [N_2H_5^+][HSO_4^-]$ (accept $[N_2H_6^{2+}][SO_4^{2-}]$)

(e) Real gases do not obey the ideal gas equation exactly. Many chemists have tried to come up with gas equations that describe the behaviour of real gases. In 1873 J D van der Waals introduced an approximate gas equation that is applicable for all real gases. The van der Waals equation is

$$P = \frac{nRT}{V - n\mathbf{b}} - \mathbf{a}\frac{n^2}{V^2}$$

where **a** and **b** are constants which are characteristic of each gas. The other symbols carry their usual meaning and units as in the ideal gas equation.

(i) Using what you have learnt about the differences between ideal and real gases, suggest what the constants **a** and **b** represent. [2]

The constant a takes into account real gas particles have intermolecular forces of attraction, hence the pressure would be lower than expected if assuming ideal gas behaviour (the equation involves subtracting an^2/V^2)

The constant b takes into account real gas particles are of finite size and occupy a significant volume compared to the volume of the container, hence the volume in which the gas particles can freely move about would be lower than expected if assuming ideal gas behaviour (the equation involves subtracting nb from V)

(ii) The values of the constants **a** and **b** for CO_2 are **a** = 0.3658 Pa m^6 mol^{-2} and **b** = 4.29 x 10^{-5} m^3 mol^{-1}.

Use your answer in **(e)(i)** to suggest how the value of the constant **a** for xenon (Xe) will compare with CO_2. Explain your answer briefly. [1]

Xe will have larger value of a, since it will have stronger instantaneous dipole-induced dipole interactions and have larger particle size than CO_2.

(iii) Use the

- ideal gas equation and
- van der Waals equation

to calculate the pressure exerted by 1 mol of CO_2 at a temperature of 30 °C and volume of 1 dm^3.

[3]

Using ideal gas equation,
pressure = $1 \times 8.31 \times (30 + 273) / (1 \times 10^{-3}) = 2.52 \times 10^6$ Pa

Using van der Waals equation,
pressure
$= [1 \times 8.31 \times (30 + 273)] / (1 \times 10^{-3} - 1 \times 4.29 \times 10^{-5}) - 0.3658 [1^2 / (1 \times 10^{-3})^2]$
$= 2.26 \times 10^6$ Pa

[Total: 20]

2 **(a)** Malonic acid, $CH_2(CO_2H)_2$ is an organic *weak dibasic acid*. It is a building block chemical to produce numerous valuable compounds, including the flavour and fragrance compound, cinnamic acid, and the pharmaceutical compound, valproate. The two pK_a values of $CH_2(CO_2H)_2$ are 2.83 and 5.69.

(i) Define the term *weak acid*. [1]

Weak acid **partially dissociates** in water to give **H^+ ions**.

(ii) Calculate the pH of 25.0 cm^3 solution of 0.100 mol dm^{-3} $CH_2(CO_2H)_2$. [1]

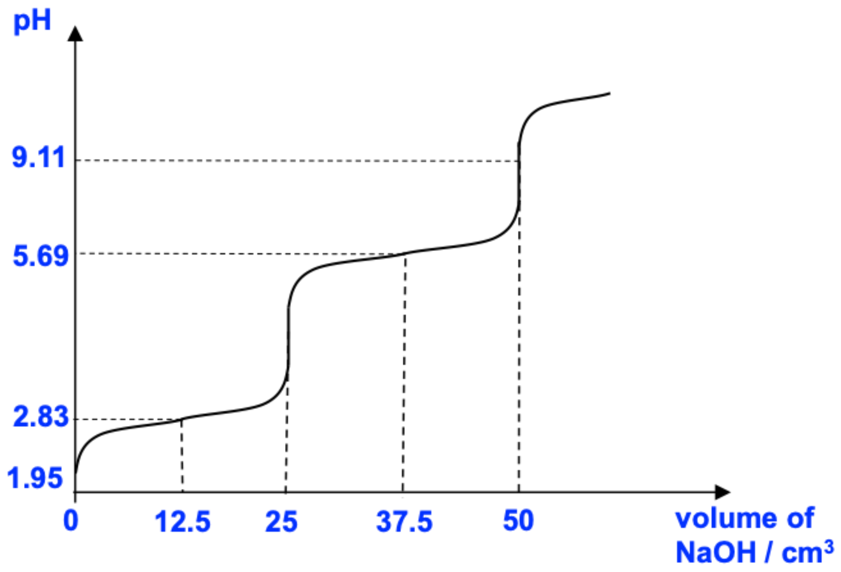
$$K_a = \frac{[H^+][CH_2(COOH)(COO^-)]}{[CH_2(COOH)_2]}$$

$$pH = -\lg\sqrt{K_a \times [CH_2(COOH)_2]} = -\lg\sqrt{10^{-2.83} \times 0.100} = \underline{\mathbf{1.92}}$$

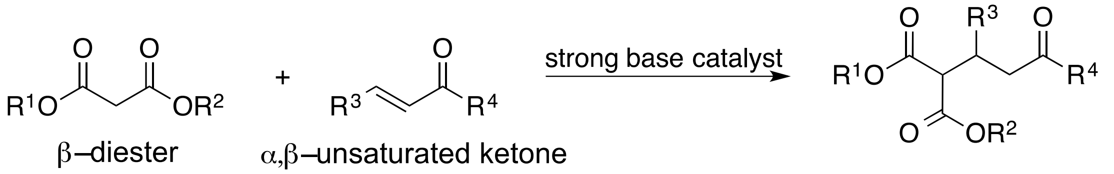
(iii) Calculate pH of the resulting solution when 50 cm^3 of 0.100 mol dm^{-3} NaOH was added to the solution in **(a)(ii)**. [2]

When 50 cm^3 of NaOH added, complete neutralisation has taken place, product is $CH_2(COO^-)_2$.
$[CH_2(COO^-)_2] = 25 \div 75 \times 0.100 = 0.0333$ mol dm^{-3}
pK_b of $(CH_2COO^-)_2 = 14 - 5.69 = 8.31$
$pOH = -\lg\sqrt{K_b \times [CH_2(COO^-)_2]} = -\lg\sqrt{10^{-8.31} \times 0.0333} = 4.89$
$pH = 14 - pOH = \underline{\mathbf{9.11}}$

(iv) Using your answers in **(a)(ii)** and **(a)(iii)**, as well as the pK_a values provided, sketch a graph to show how the pH of the solution changes as 50 cm^3 of 0.100 mol dm^{-3} NaOH is gradually added to 25.0 cm^3 of 0.100 mol dm^{-3} $CH_2(CO_2H)_2$. Clearly indicate the corresponding volumes of NaOH in your graph. [2]



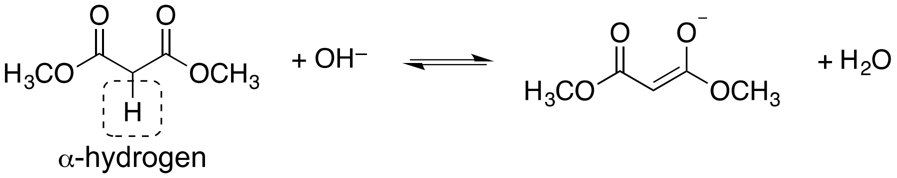
(b) Malonic acid can be converted to its corresponding β–diester. β–diesters are commonly used as starting compounds in the Michael addition reaction, where they react with α,β-unsaturated ketones. It is one of the most useful methods for the formation of C–C bonds.



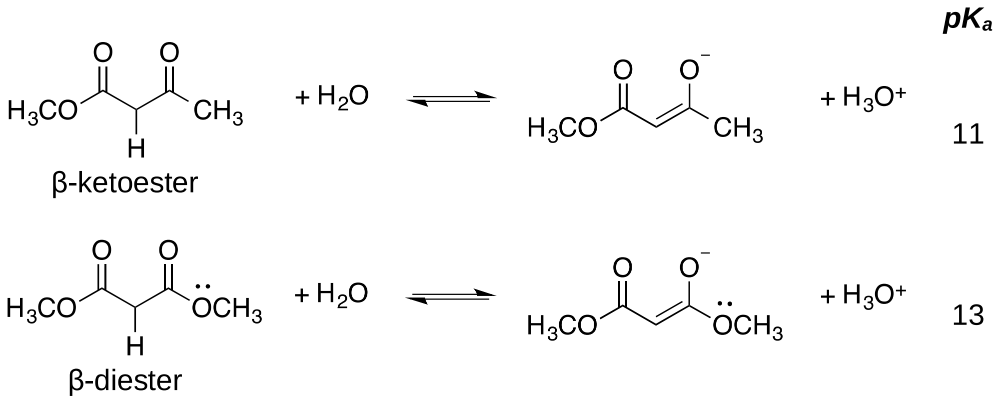
(i) Suggest reagents and conditions to convert malonic acid to dimethyl malonate, $CH_2(COOCH_3)_2$. State the type of reaction. [2]

CH_3OH, conc H_2SO_4, heat
condensation

(ii) The first step in the mechanism of Michael addition involves an acid–base reaction where the strong base catalyst extracts an α-hydrogen from the β–diester.



Reagents similar to the malonate ester can undergo the same type of reaction. The *pK* values of malonate ester and another similar reagent are as follows:



Explain the difference in pK_a values between the two compounds. [2]

β-ketoester has a **lower pKa** than β-diester, suggesting that it is a **stronger acid** than β-diester.

Strength of acid is dependent on the **stability of anion** formed.

The anion of β-diester is attached to an **$-OCH_3$ group**. **Lone pair in oxygen atom overlaps with p orbitals** of the adjacent unsaturated carbon, and is **delocalized** into the system, increasing the electron density. The negative charge is **intensified to a larger extent**, cause it be less stable and thus a weaker acid.

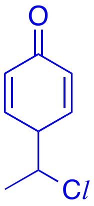
(iii) Compound **A**, C_8H_9ClO, contains a non-aromatic six-membered ring. **A** reacts with 2,4-dinitrophenylhydrazine to form an orange precipitate but does not react with

Tollen's reagent. 1 mole of **A** reacts with 3 moles of H_2 gas in the presence of solid platinum. When **A** is warmed with aqueous sodium hydroxide, compound **B**, $C_8H_{10}O_2$ is formed. **B** gives a pale yellow precipitate when warmed with alkaline aqueous iodine. When **B** is warmed with acidified potassium permanganate, compounds **C**, $C_3H_2O_5$ and **D**, $C_5H_6O_5$ are formed. **D** also gives a pale yellow precipitate when warmed with alkaline aqueous iodine. **A** is able to undergo Michael addition with dimethyl malonate, $CH_2(COOCH_3)_2$, to form **E**, a compound with 18 carbons.

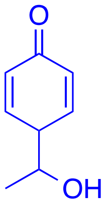
Deduce the structural formulae of compounds **A**, **B**, **C**, **D** and **E**, explaining clearly your reasoning for all reactions described. [10]

Observations	**Deductions**
A, C_8H_9ClO reacts with 2,4-dinitrophenylhydrazine to form an orange precipitate.	**A** undergoes **condensation**. **A** contains a **carbonyl**.
A, C_8H_9ClO does not react with Tollen's reagent.	**A** does not contain aldehyde. **A** is a **ketone**.
1 mole of **A** reacts with 3 moles of H_2 gas in the presence of solid platinum.	**A** undergoes **reduction**. **3 degrees of unsaturation**. Ketone reduced A contains **alkene.**
When **A** is warmed with aqueous sodium hydroxide, compound **B**, $C_8H_{10}O_2$ is formed.	**A** undergoes **nucleophilic substitution**. **aliphatic –Cl** substituted to form **–OH** in **B**.
B gives a pale yellow precipitate when warmed with alkaline aqueous iodine.	**B** undergoes **oxidative cleavage** to give **CHI_3.** **B** contains either **$-CH(CH_3)(OH)$ or $-COCH_3$ structural unit**.
B is warmed with acidified potassium permanganate, compounds **C**, $C_3H_2O_5$ and **D**, $C_5H_6O_5$ are formed.	**B** undergoes **oxidative cleavage** of **C=C**
D also gives a pale yellow precipitate when warmed with alkaline aqueous iodine.	**D** undergoes oxidative cleavage. **D** contains either **$-COCH_3$ structural unit**.
A is able to undergo Michael addition with dimethyl malonate, $CH_2(COOCH_3)_2$, to form **E**, a compound with 18 carbons.	**A** contains **α,β-unsaturated ketones**.

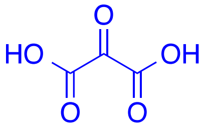
A



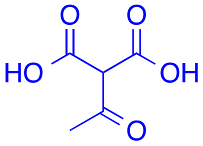
B



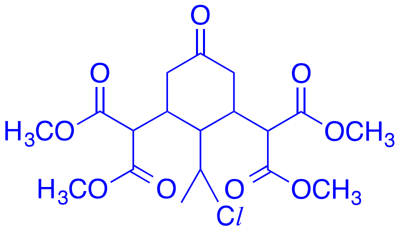
C



D



E



3 **(a)** A Latimer diagram provides a concise way of representing large amount of information about the different oxidation states of an element. In a Latimer diagram, the most highly oxidised form of an element is written on the left, with successively lower oxidation states to the right. The different species are connected by arrows, and the standard electrode potential in volts is written above each arrow.

The Latimer diagrams for chlorine in acidic and alkaline medium are shown below.

In acidic medium:

$$\mathrm{C}l\mathrm{O_4^-} \xrightarrow{+1.19\ \mathrm{V}} \mathrm{C}l\mathrm{O_3^-} \xrightarrow{+1.21\ \mathrm{V}} \mathrm{C}l\mathrm{O_2^-} \xrightarrow{+1.66\ \mathrm{V}} \mathrm{C}l\mathrm{O^-} \xrightarrow{+1.64\ \mathrm{V}} \mathrm{C}l_2 \xrightarrow{+1.36\ \mathrm{V}} \mathrm{C}l^-$$

In alkaline medium:

$$\mathrm{C}l\mathrm{O_4^-} \xrightarrow{+0.36\ \mathrm{V}} \mathrm{C}l\mathrm{O_3^-} \xrightarrow{+0.35\ \mathrm{V}} \mathrm{C}l\mathrm{O_2^-} \xrightarrow{+0.65\ \mathrm{V}} \mathrm{C}l\mathrm{O^-} \xrightarrow{+0.40\ \mathrm{V}} \mathrm{C}l_2 \xrightarrow{+1.36\ \mathrm{V}} \mathrm{C}l^-$$

(i) Define the term *standard electrode potential*. [1]

The term standard electrode potential refers to the potential of a half–cell relative to that of a standard hydrogen electrode, measured at 298 K, 1 bar for each gas and 1 mol dm^{-3} for each aqueous ion .

(ii) The standard electrode potentials in a Latimer diagram are not additive. For example, the standard electrode potential for converting $\mathrm{C}l\mathrm{O_4^-}$ to $\mathrm{C}l\mathrm{O^-}$ in acidic medium is **not** the sum of +1.19 V and +1.21 V and +1.66 V. However, their respective standard Gibbs' free energy changes are additive.

Using relevant data given below, show that the standard electrode potential for converting $\mathrm{C}l\mathrm{O_4^-}$ to $\mathrm{C}l\mathrm{O^-}$ in acidic medium is 1.34 V. [2]

electrode reaction	$E^\ominus$ / V	$\Delta G^\ominus$ / kJ mol^{-1}
$\mathrm{C}l\mathrm{O_4^-} + 2\mathrm{H^+} + 2e^- \rightleftharpoons \mathrm{C}l\mathrm{O_3^-} + \mathrm{H_2O}$	+1.19	–220.7
$\mathrm{C}l\mathrm{O_3^-} + 2\mathrm{H^+} + 2e^- \rightleftharpoons \mathrm{C}l\mathrm{O_2^-} + \mathrm{H_2O}$	+1.21	–233.5
$\mathrm{C}l\mathrm{O_2^-} + 2\mathrm{H^+} + 2e^- \rightleftharpoons \mathrm{C}l\mathrm{O^-} + \mathrm{H_2O}$	+1.66	–320.4
$\mathrm{C}l\mathrm{O^-} + 2\mathrm{H^+} + e^- \rightleftharpoons \tfrac{1}{2}\mathrm{C}l_2 + \mathrm{H_2O}$	+1.64	–158.3
$\tfrac{1}{2}\mathrm{C}l_2 + e^- \rightleftharpoons \mathrm{C}l^-$	+1.36	–131.2

$\Delta G^\ominus$ for $\mathrm{C}l\mathrm{O_4^-}$ to $\mathrm{C}l\mathrm{O^-}$ = (–220.7) + (–233.5) + (–320.4)
= –774.6 kJ mol^{-1}

Since $\Delta G^\ominus = -nFE^\ominus$

$$E^\ominus \text{ for } \mathrm{C}l\mathrm{O_4^-} \text{ to } \mathrm{C}l\mathrm{O^-} = -\frac{(\Delta G^\ominus \text{ for } \mathrm{C}l\mathrm{O_4^-} \text{ to } \mathrm{C}l\mathrm{O^-})}{n \times F}$$

$$= -\frac{(-774.6 \times 1000)}{6 \times 96500}$$

= +1.34 V (shown)

(iii) With the exception of the conversion of Cl_2 to Cl^-, the standard electrode potentials in alkaline medium are less positive than their corresponding conversions in the acidic medium.

Suggest why this is so. [2]

Other than the conversion of Cl_2 to Cl^-, all other conversions have H^+ on the left hand side of the electrode equations. The addition of OH^- will cause $[H^+]$ to decrease . By Le Chatelier's Principle, the equilibrium position will shift to the left to counteract the decrease in $[H^+]$. Hence reduction of each electrode reaction becomes less favoured .

(iv) A disproportionation reaction is a redox reaction in which a chemical species undergo reduction and oxidation simultaneously.

In hot alkaline medium, Cl_2 undergoes disproportionation to form two chlorine-containing species according to the following equation.

$$3Cl_2(g) + xOH^-(aq) \longrightarrow 5Cl^-(aq) + ClO_y^-(aq) + zH_2O(l)$$

By considering the number of moles of electrons transferred and using the Latimer diagram for chlorine in alkaline medium, first solve for y. Then, use it to solve for x and z. [2]

Total electrons gained (Cl_2 to Cl^-) = 5 x 1
= 5 mol

Total electrons lost (Cl_2 to ClO_y^-) = 5 mol

Based on the Latimer diagram, the oxidation state of Cl in ClO_y^- has to be +5 . Thus the other chlorine-containing specie is ClO_3^- i.e. $y = 3$.

[R]: $Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$
[O]: $Cl_2(g) + 12OH^-(aq) \longrightarrow 2ClO_3^-(aq) + 6H_2O(l) + 10e^-$

Balancing redox equation, 5[R] +1[O]:
$6Cl_2(g) + 12OH^-(aq) \longrightarrow 10Cl^-(aq) + 2ClO_3^-(aq) + 6H_2O(l)$
$3Cl_2(g) + 6OH^-(aq) \longrightarrow 5Cl^-(aq) + ClO_3^-(aq) + 3H_2O(l)$

$x = 6, z = 3$

(b) Besides the standard hydrogen electrode, other reference electrodes have also been employed in electrochemistry. An example is the silver chloride electrode, which involves dipping silver metal coated with solid silver chloride into a solution of sodium chloride. The solubility product for AgCl is 2.0×10^{-10} $mol^2\ dm^{-6}$.

(i) The standard electrode potential of a silver chloride electrode is +0.230 V. However, when 1.0 $mol\ dm^{-3}$ sodium chloride is used to set up the silver chloride electrode, this value cannot be achieved.

Explain why this is so. [1]

The sparingly soluble AgCl can also contribute Cl^- to the electrolyte. Hence, $[Cl^-]$ will be more than 1 $mol\ dm^{-3}$, which means that the electrode potential value achieved will be non–standard.

At 298 K, the electrode potential of the silver chloride electrode, *E*, can be estimated from the concentration of silver ions present using formula (1):

$$E = 0.80 - 0.0591 \log \frac{1}{[\mathrm{Ag}^+]} \quad \text{.....formula (1)}$$

(ii) Calculate the value of *E* in each of the following cases:

- in pure water and
- when the addition of sodium chloride results in a chloride ion concentration of 2.5 mol dm^{-3}. [3]

In pure water

K_{sp} of AgC*l* = $[\mathrm{Ag}^+].[\mathrm{C}l^-]$
2.0×10^{-10} = x^2
$[\mathrm{Ag}^+]$ = x
= 1.41×10^{-5} mol dm^{-3}

$$E = 0.80 - 0.0591 \log \frac{1}{(1.41 \times 10^{-5})}$$

= +0.513 V

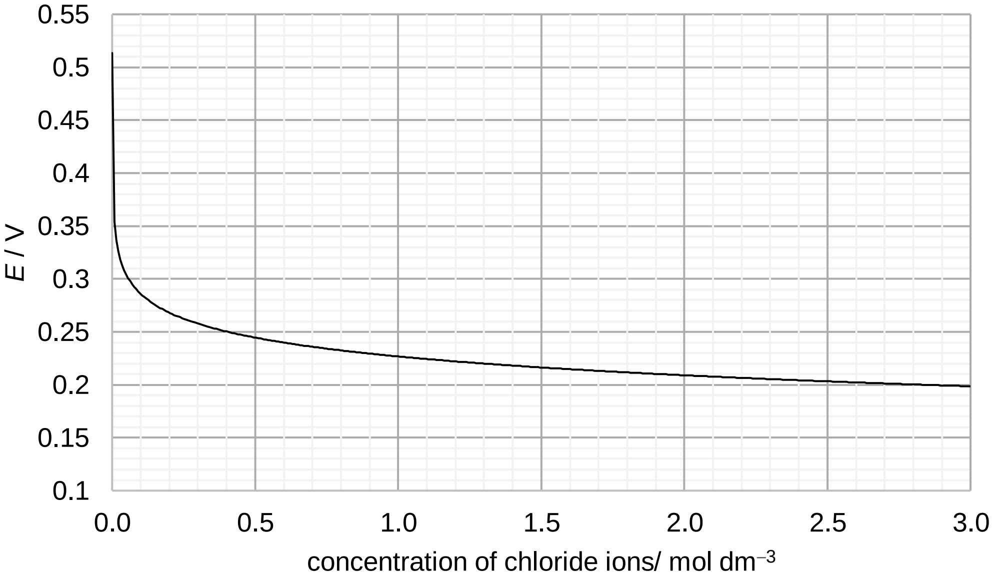
When $[\mathrm{C}l^-]$ = 2.5 mol dm^{-3}

K_{sp} of AgC*l* = $[\mathrm{Ag}^+].[\mathrm{C}l^-]$
2.0×10^{-10} = $[\mathrm{Ag}^+].[2.5]$
$[\mathrm{Ag}^+]$ = 8.00×10^{-11} mol dm^{-3}

$$E = 0.80 - 0.0591 \log \frac{1}{(8.00 \times 10^{-11})}$$

= +0.203 V

(iii) Using the graph given below, suggest why sodium chloride solution ranging from 1.0 mol dm^{-3} to 3.0 mol dm^{-3} is typically used in the setting up of a silver chloride electrode rather than pure water. [1]



The value of *E* when using 1.0 mol dm^{-3} to 3.0 mol dm^{-3} sodium chloride solution is less affected by change in concentration compared to using pure water. This makes the silver chloride electrode more suitable for use as a reference electrode.

(iv) A student attempted to study the validity of formula (1) by adding aqueous ammonia to vary the concentration of silver ions in solution. This is due to the ability of ammonia to form a complex with the silver ions, thus decreasing its concentration in solution.

Explain a potential problem that may arise with this method of analysis. [1]

$\mathbf{Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)}$
$\mathbf{Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)}$ **…..(I)**

By Le Chatelier's Principle, equilibrium position of (I) will shift to the left to counteract the decrease in [Ag$^+$] , causing AgC*l*(s), which is needed for the silver chloride reference electrode, to dissolve.

OR

The decrease in [Ag$^+$] will cause ionic product of AgC*l* to fall below its K_{sp} value, thus causing AgC*l*(s), which is needed for the silver chloride reference electrode, to dissolve.

(vi) The silver chloride electrode is used in many medical equipment. In a particular device used for electrocardiography, a layer of silver metal is plated with a thickness of 1 mm onto an electrode with a surface area of 0.12 cm^2 before coating it with solid silver chloride.

If a current of 15.0 mA is used for the electroplating process, calculate the time required to completely plate the silver metal onto the electrode from a solution containing Ag$^+$(aq).

[The density of silver metal is 10.5 g cm^{-3}] [2]

Volume of Ag needed = 0.12 x 0.1
= 0.012 cm^3

Mass of Ag needed = 10.5 x 0.012
= 0.126 g

Amount of Ag needed = 0.126 / 107.9
= 1.17 x 10^{-3} mol

Amount of e$^-$ needed, n_e = 1.17 x 10^{-3} mol

Q = n_e F
= (1.17 x 10^{-3}) (96500)
= 112.9 C

t = Q / I
= (112.9) / (15.0 x 10^{-3})
= 7.53 x 10^3 s

(c) When sodium halides react with concentrated sulfuric acid, an acid-base reaction takes place resulting in the formation of white fumes of hydrogen halides.

$$NaX(s) + H_2SO_4(l) \longrightarrow HX(g) + NaHSO_4(s), \text{ where } X = Cl, Br \text{ or } I$$

Subsequently, depending on the reducing strength of the hydrogen halides, a further reaction might take place with concentrated sulfuric acid, resulting in the formation of halogens, a sulfur-containing product and water.

The observations for the reaction of the different sodium halides with concentrated sulfuric acid are shown below:

sodium halide	observations
Na*Cl*	white fumes of HC*l*
NaBr	white fumes of HBr red-brown Br_2 gas which condenses to form a red-brown liquid colourless and pungent SO_2 gas
NaI	white fumes of HI violet I_2 gas which condenses to form a black solid colourless and pungent H_2S gas

(i) Write a balanced molecular equation for each of the following reactions:

- between gaseous HBr and concentrated H_2SO_4
- between gaseous HI and concentrated H_2SO_4

[2]

$$2HBr(g) + H_2SO_4(l) \longrightarrow Br_2(l) + SO_2(g) + 2H_2O(l)$$
$$8HI(g) + H_2SO_4(l) \longrightarrow 4I_2(s) + H_2S(g) + 4H_2O(l)$$

[state symbols not required]

(ii) Arrange the hydrogen halides in order of increasing reducing strength. Explain your answer, using relevant information from the *Data Booklet* to support the difference in observations. [3]

In order of increasing reducing strength: HC*l* < HBr < HI

From *Data Booklet*, – for quoting $E^\ominus$ values

$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ $\quad E^\ominus = +1.36$ V

$Br_2 + 2e^- \rightleftharpoons 2Br^-$ $\quad E^\ominus = +1.07$ V

$I_2 + 2e^- \rightleftharpoons 2I^-$ $\quad E^\ominus = +0.54$ V

From C*l* to I, $E^\ominus(X_2/X^-)$ becomes less positive . Thus oxidation of half-equation is more favoured and reducing strength of halides increases.

HC*l*, the weakest reducing agent, cannot reduce S.
HBr, a stronger reducing agent, can reduce S from +6 (H_2SO_4) to +4 (SO_2).
HI, the strongest reducing agent, can reduce S from +6 (H_2SO_4) to –2 (H_2S).

[Total: 20]

Section B

Answer **one** question from this section.

4 Sulfur forms many cyclic allotropes with different ring sizes. In the gas phase, all ring sizes from S_3 to S_{12} have been detected.

When a 1.00 g sample of sulfur was dissolved in 1 dm^3 of an organic solvent, the following equilibrium was established:

$$8S_7(g) \rightleftharpoons 7S_8(g)$$

The percentages by mass of S_7 and S_8 at equilibrium are:

ring size	S_7	S_8
percentage by mass	0.76	98.92

(a) **(i)** Calculate the amount, in moles, of S_7 and S_8 at equilibrium. [2]

No. of moles of S_7 $= \dfrac{\frac{0.76}{100} \times 1.00}{7 \times 32.1}$

$= \dfrac{0.0076}{224.7}$

$= 3.38 \times 10^{-5}$ mol

No. of moles of S_8 $= \dfrac{\frac{98.92}{100} \times 1.00}{8 \times 32.1}$

$= \dfrac{0.9892}{256.8}$

$= 3.85 \times 10^{-3}$ mol

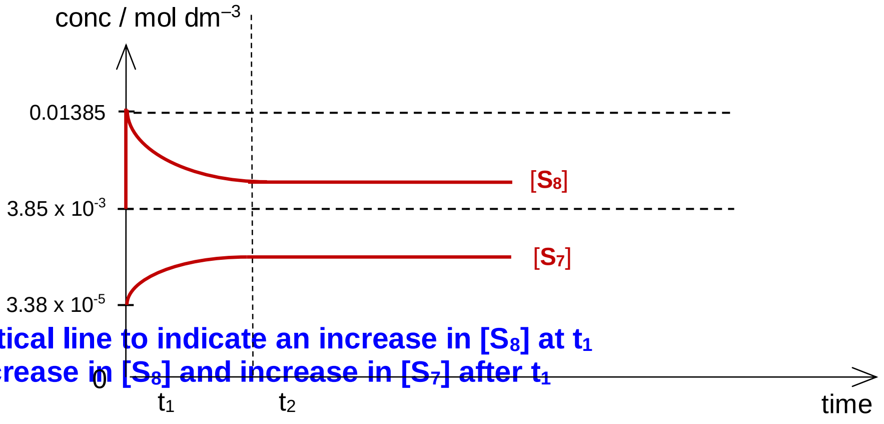
(ii) Write an expression for the equilibrium constant, K_C, and calculate its value for the above reaction between S_7 and S_8. [2]

$$K_c = \frac{[S_8]^7}{[S_7]^8}$$

$$= \frac{\left[\frac{3.85 \times 10^{-3}}{1}\right]^7}{\left[\frac{3.38 \times 10^{-5}}{1}\right]^8}$$

$= 7.36 \times 10^{18}$ mol^{-1} dm^3 (ecf from (b)(i))

(iii) The amount of S_8 is increased by 0.01 mol at time t_1. Sketch, on the same axes, two graphs to show how $[S_7]$ and $[S_8]$ vary from t_1 to t_2, the time when equilibrium is re-established at the same temperature.
[You are only required to label the concentrations at t_1.] [2]



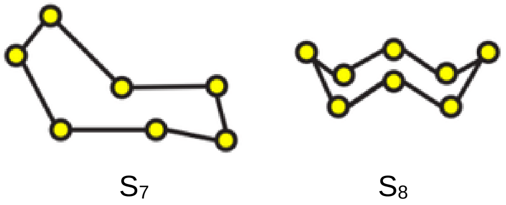
Vertical line to indicate an increase in $[S_8]$ at t_1
Decrease in $[S_8]$ and increase in $[S_7]$ after t_1

Horizontal line to indicate equilibrium re-established at t_2, new equilibrium $[S_8]$ still higher than previous equilibrium

(iv) An inert gas is then added at constant pressure. State and explain how the position of equilibrium would change. [2]

To keep total pressure constant when the inert gas is added, the volume of the system must increase. Hence, the partial pressures of S_7 and S_8 decrease. By Le Chatelier's Principle, the equilibrium will shift left where there are more gas particles, so as to increase the pressure of the system.

The shape of the S_7 and S_8 molecules are as follows.



(b) **(i)** Define the term bond energy with reference to the S–S bonds in S_8. [1]

The energy required to break 1 mole of covalent bonds between 2 sulfur atoms in a gaseous S_8 molecule.

(ii) Given that the S–S bond energy in S_7 is 260.0 kJ mol^{-1} and that in S_8 is 263.3 kJ mol^{-1}, calculate the enthalpy change for the forward reaction between S_7 and S_8. [1]

Enthalpy change of reaction = (8 x 7 x 260.0) – (7 x 8 x 263.3)
= 14560 – 14744.8
= –185 kJ mol^{-1}

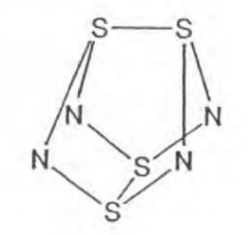
(iii) Using your answers in **(a)(ii)** and **(b)(ii)**, and given that:

$$\Delta G^{\ominus} = -RT \ln K_c$$

where T is in Kelvins and ΔG is in J mol^{-1}, calculate the standard entropy change of the reaction. [2]

$$\Delta G^{\ominus} = -RT \ln K_c$$
$$= -8.31 \times 298 \times \ln(7.36 \times 10^{18})$$
$$= -1.08 \times 10^{5} \text{ J mol}^{-1}$$
$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$
$$\Delta S^{\ominus} = (\Delta H^{\ominus} - \Delta G^{\ominus})/T$$
$$= \frac{-185 \times 10^{3} - (-1.08 \times 10^{5})}{298}$$
$$= -258 \text{ J mol}^{-1} \text{ K}^{-1}$$

(c) Sulfur also forms an 8-membered ring in a compound with nitrogen, S_4N_4. In S_4N_4, nitrogen and sulfur atoms alternate in the ring. The four nitrogen atoms are arranged in a plane, with two sulfur atoms above the plane, and two sulfur atoms below the plane. The shape of a molecule of S_4N_4 is as shown.



S_4N_4

Using the data provided below, construct an energy cycle to calculate the average S–N bond energy in S_4N_4. [3]

enthalpy change of formation of S_4N_4	+460 kJ mol^{-1}
enthalpy change of atomisation of sulfur	+297 kJ mol^{-1}
enthalpy change of atomisation of nitrogen	+497 kJ mol^{-1}
S–S bond energy in S_4N_4	+204 kJ mol^{-1}

By

$$\begin{tikzcd}
\frac{1}{2}S_8(s) \arrow[dr, "4(+297)"'] & + & 2N_2(g) \arrow[r, "+460"] \arrow[dr, "4(+497)"] & S_4N_4(g) \arrow[d, "2(+204) + 8BE(S\text{-}N)"] \\
& 4S(g) & + & 4N(g)
\end{tikzcd}$$

Hess' law,

$+460 + 8BE(S–N) + 2(+204) = 4(+297) + 4(+497)$

$Be(S–N) = +289$ kJ mol^{-1}

(d) Sulfur and tungsten has certain similarities since both atoms have a total of six valence electrons, even though sulfur is a main group element and tungsten is a transition metal. Both elements reach their maximum +6 oxidation state when combined with electronegative elements such as fluorine and oxygen.

(i) Sulfur trioxide, SO_3 and tungsten(VI) oxide, WO_3 differ markedly in their physical properties. While SO_3 is a gaseous pollutant used in industrial preparation of sulfuric acid, WO_3 is used in electrochromic windows, allowing the windows to change colour when an electrical voltage is applied. Their boiling points are 44.9 ^oC and 1700 ^oC respectively.

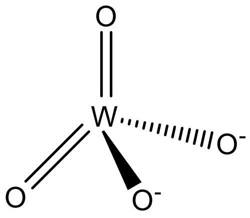
With reference to the structure and type of bonding, account for the difference in boiling points. [3]

SO_3 has a simple molecular structure. Weak instantaneous dipole-induced dipole interactions exist between SO_3 molecules. A small amount of energy is required to overcome the weak intermolecular forces, hence the boiling point of SO_3 is low.

WO_3 has a giant ionic structure. Strong electrostatic forces of attraction exist between the W^{6+} and O^{2-} ions. A large amount of energy is required to overcome the strong ionic bonds, hence the boiling point of WO_3 is very high.

(ii) Most tungsten occurs naturally in the tungsten anion, WO_4^{2-}, analogous to the sulfate ion, SO_4^{2-}.

Draw the structure of WO_4^{2-}. State the shape and bond angle of the O–W–O bond. [2]



Dotted and wedge bonds shown
Overall –2 charge shown
Tetrahedral
Bond angle 109.5^o

[Total: 20]

5 **(a)** The Mars Curiosity rover's landing in August 2012 was achieved using hydrazine rocket thrusters. Hydrazine, N_2H_4, is popular with NASA as it produces no carbon dioxide.

N_2H_4 has a boiling point of 114 °C and decomposes to its elements when passed over a suitable catalyst. The rapid production of hot gaseous products is what provides the thrust.

(i) With the aid of a balanced equation, define the term standard enthalpy change of formation for hydrazine. [2]

$N_2(g) + 2H_2(g) \rightarrow N_2H_4(l)$
The enthalpy change when one mole of N_2H_2 is formed from its constituent elements N_2 and H_2 under standard conditions of 298 K and 1 bar.

(ii) Hydrazine may be obtained from the reaction between ammonia and hydrogen peroxide.

$$2NH_3(g) + H_2O_2(l) \rightarrow N_2H_4(l) + 2H_2O(l) \qquad \Delta H_r^\ominus = -241.0 \text{ kJ mol}^{-1}$$

Calculate the standard enthalpy change for the decomposition of 1 mol of hydrazine to its elements using data below. [2]

compound	$\Delta H_f^\ominus$ / kJ mol^{-1}
NH_3	–46.1
H_2O_2	–187.8
H_2O	–285.8

$$\Delta H_r^\ominus = \sum\Delta H_f^\ominus{}_{(products)} - \sum\Delta H_f^\ominus{}_{(reactants)}$$
$$-241.0 = [\Delta H_f^\ominus{}_{(N2H4)} + 2(-285.8)] - [2(-46.1) + (-187.8)]$$
$$\Delta H_f^\ominus{}_{(N2H4)} = 50.6 \text{ kJ mol}^{-1}$$

Hence, decomposition enthalpy = – 50.6 kJ mol^{-1}

(b) The first ever rocket-powered fighter plane, the Messerschmitt Me 163, was powered by the reaction between a hydrazine-methanol mixture, known as ‘C-Stoff’, and hydrogen peroxide (‘T-Stoff’). The standard enthalpy change of combustion of hydrazine and methanol are −622.2 kJ mol^{-1} and −726.0 kJ mol^{-1}.

The fighter plane would hold 225 dm^{3} of hydrazine and 862 dm^{3} of methanol. The densities of hydrazine and methanol are 1.021 g cm^{-3} and 0.7918 g cm^{-3} respectively.

Calculate the heat energy evolved under standard conditions for the combustion of this quantity of rocket fuel, assuming that all the hydrazine and methanol are fully combusted. [2]

Amount of hydrazine = $\frac{225000 \times 1.021}{32.0}$

= 7.18×10^{2} **mol**

Amount of methanol = $\frac{862000 \times 0.7918}{32.0}$

= 2.13×10^{4} **mol**

Total heat energy evolved = $7.18 \times 10^{2} \times 622.2 + 2.13 \times 10^{4} \times 726.0$

$= 4.46 \times 10^{6} + 1.55 \times 10^{7}$

$= 2.0 \times 10^{7}$ **kJ**

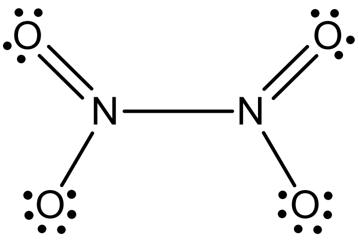
(c) Hydrazine is also commonly combined with dinitrogen tetroxide, N_2O_4, in rocket fuels. This forms a hypergolic mixture, that is, the reactants ignite spontaneously on contact.

(i) Suggest the reaction products that are formed in the reaction between N_2H_4 and N_2O_4. Briefly explain why. [2]

N_2 and H_2O.

The products formed should be chemically stable with strong bonds, e.g. N≡N and O−H bonds, making the reaction exothermic. They should also be formed as gases which provide thrust.

(ii) Draw the structure of N_2O_4, indicating clearly the shape and bond angle around each nitrogen atom. [2]



Trigonal planar wrt each N
Bond angle 120° indicated

(iii) At room temperature, N_2O_4 exists as a gas while N_2H_4 is a liquid. With reference to their structure and bonding, account for this difference. [3]

Both N_2O_4 and N_2H_4 have a simple molecular structure. Weak permanent dipole-permanent dipole interactions exist between N_2O_4 molecules while stronger hydrogen bonding exist between N_2H_4 molecules. A larger amount of energy is required to overcome these stronger intermolecular forces in N_2H_4, hence the boiling point of N_2O_4 is lower than that of N_2H_4.

(d) At 46 °C, N_2O_4 (colourless gas) exists in equilibrium with nitrogen dioxide, NO_2 (brown gas) with an equilibrium constant, K_p of 0.66 atm. The equation for the equilibrium is

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

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

$$K_p = \frac{P^2_{NO_2}}{P_{N_2O_4}}$$

(ii) A certain amount of N_2O_4 is allowed to dissociate in a vessel. At equilibrium, the partial pressure of NO_2 is found to be 0.332 atm.

Calculate the partial pressure of N_2O_4 and total pressure at equilibrium. [2]

	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$
Equilibrium partial pressure / atm	**p**		**0.332**

$$K_p = \frac{P^2_{NO_2}}{P_{N_2O_4}}$$

$$= \frac{0.332^2}{p} = 0.66$$

Solving,

$$P_{N_2O_4} = 0.167 \text{ atm}$$

$$\text{Total } P_{eqm} = 0.332 + 0.167$$

$$= 0.499 \text{ atm}$$

(iii) Hence, determine the percent dissociation of N_2O_4 at 46 ^{o}C. [2]

Since each mole of N_2O_4 dissociates to give 2 moles of NO_2,

Percent dissociation = $\frac{\frac{0.332}{2}}{\frac{0.332}{2}+0.167} \times 100$

= 49.9%

(iv) State and explain what may be observed when the vessel containing the gases is expanded. [2]

The mixture is seen to darken in colour / become more brown in colour. By expansion (i.e. increasing volume), the partial pressures of both gases will decrease. By Le Chatelier's Principle, the system will counteract the decrease in pressure by favouring the forward reaction that will increase the number of gas particles. Position of equilibrium shifts to the right where there is more brown NO_2 gas.

[Total: 20]

H2 CHEMISTRY PAPER 1 ANSWERS

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

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

1 Determination of the dependence of the rate of reaction between glucose and acidified potassium manganate(VII) on temperature

Read through the whole method before starting any practical work. Where appropriate, prepare a table for your results in the space provided.

Show your working and appropriate significant figures in the final answer to **each** step of your calculations.

Glucose, $C_6H_{12}O_6$, is a sugar that can act as a reducing agent. You will investigate how an increase in temperature affects the rate of the redox reaction between glucose and acidified potassium manganate(VII).

FA 1 is 0.020 mol dm^{-3} acidified potassium manganate(VII), $KMnO_4$.
FA 2 is 1.0 mol dm^{-3} sulfuric acid, H_2SO_4.
FA 3 is an aqueous solution containing 32.8 g dm^{-3} glucose, $C_6H_{12}O_6$.
FA 4 is a solid mixture containing an unknown percentage of glucose.

You will measure the time it takes for the purple colour to disappear. Your table of results on the following page should include the rate of reaction for each experiment.

(a) Method

Experiment 1

1. Fill the burette with **FA 1**.
2. Add 5.00 cm^3 of **FA 1** into the 250 cm^3 beaker.
3. Use the 50 cm^3 measuring cylinder to transfer 50.0 cm^3 of **FA 2** into the beaker containing **FA 1**.
4. Use the same measuring cylinder to transfer 50.0 cm^3 of distilled water into the same beaker.
5. Place the beaker on the tripod and heat its contents to between 75 °C and 80 °C.
6. While the solution in the beaker is being heated, pour 25.0 cm^3 of **FA 3** into the 25 cm^3 measuring cylinder.
7. When the temperature of the contents of the beaker has reached between 75 °C and 80 °C, turn off the Bunsen burner and **carefully** hold the top of the hot beaker with a paper towel and place it onto the white tile.
8. Record the temperature of the solution in the beaker.
9. Add the 25.0 cm^3 of **FA 3** and **immediately** start timing.
10. Stir the contents of the beaker once and stop timing as soon as the solution turns colourless. Record the time to the nearest second.
11. Record the temperature of the solution as soon as it is colourless.
12. Calculate and record the average temperature of the reaction mixture to one decimal place.
13. Empty, rinse and dry the beaker so it is ready for use in **Experiment 2**.

Experiment 2

1. Add 5.00 cm^3 of **FA 1** into the 250 cm^3 beaker.
2. Use the 50 cm^3 measuring cylinder to transfer 50.0 cm^3 of **FA 2** into the beaker containing **FA 1**.
3. Use the same measuring cylinder to transfer 50.0 cm^3 of distilled water into the same beaker.
4. Place the beaker on the tripod and heat its contents to between 35 °C and 40 °C.
5. While the solution in the beaker is being heated, pour 25.0 cm^3 of **FA 3** into the 25 cm^3 measuring cylinder.
6. When the temperature of the contents of the beaker has reached between 35 °C and 40 °C, turn off the Bunsen burner and **carefully** hold the top of the hot beaker with a paper towel and place it onto the white tile.
7. Record the temperature of the solution in the beaker.
8. Add the 25.0 cm^3 of **FA 3** and **immediately** start timing.
9. Stir the contents of the beaker once and stop timing as soon as the solution turns colourless. Record the time to the nearest second.
10. Record the temperature of the solution as soon as it is colourless.
11. Calculate and record the average temperature of the reaction mixture to one decimal place.
12. Empty, rinse and dry the beaker so it is ready for use in **Experiment 3**.

Experiments 3, 4 and 5

1. Repeat the method for **Experiment 2** at three different temperatures.
2. Keep the temperature of the contents of the beaker between room temperature and 80 °C.
3. Record all your results in your table.

Results:

The rate of reaction can be calculated as shown.

$$\text{rate} = \frac{1000}{\text{reaction time}}$$

Calculate the rate of reaction for each experiment and include this in your table.

[5]

(b) Plot a graph of rate (*y*-axis) against average temperature (*x*-axis) on the grid below. Select a scale on the *x*-axis to include an average temperature of 30.0 °C. Label any points you consider anomalous.

Draw the most appropriate best-fit curve taking into account all of your plotted points and extrapolate it to 30.0 °C.

[3]

(c) **Use your graph** to calculate the **time** to the nearest second that the reaction would have taken if the average temperature had been 52.5°C.
Show **on the grid** how you obtained your answer.

time =……………… [2]

(d) Explain, by referring to your graph or your table of results, how the rate of reaction is affected by an increase in temperature.

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(e) (i) Calculate the maximum percentage error in the reaction time recorded for **Experiment 1**. Assume the error of the timer is ±1 s.

maximum percentage error in **Experiment 1** =……………… [1]

(ii) You have carried out experiments at five different temperatures.

Identify an experiment, if any, you should have repeated. Give a reason for your answer.

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(iii) Suggest one way to improve the accuracy of the results for this investigation.

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(f) (i) Calculate the concentration of glucose in **FA 3** in mol dm^{-3}.

concentration of glucose in **FA 3** =……………… [1]

(ii) Calculate the volume of 0.020 mol dm^{-3} acidified $KMnO_4$ that would react with **all** the glucose present in 25.0 cm^3 of **FA 3**.

$$5C_6H_{12}O_6 + 24MnO_4^- + 72H^+ \rightarrow 30CO_2 + 24Mn^{2+} + 66H_2O$$

Volume of acidified $KMnO_4$ required =……………… [2]

(iii) Comment on the feasibility of conducting a redox titration between the given concentration of glucose and acidified $KMnO_4$.

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(g) **Determination of the percentage of glucose in FA 4 by titration**

1. Weigh accurately 1.5 g of **FA 4** in a weighing bottle. Record your weighing appropriately in the space below. If you use **TARE** facility of the balance, please indicate clearly in your recording.
2. Dissolve the solid in a beaker and quantitatively transfer into a 250 cm^3 volumetric flask. Make up to the mark with distilled water. Label this **FA 4 solution**.
3. Pipette 25.0 cm^3 of **FA 4 solution** into a conical flask.
4. Using a measuring cylinder add 50.0 cm^3 of **FA 2** into the conical flask.
5. Place the conical flask on the tripod and heat its contents to between 75 °C and 80 °C.
6. When the temperature of the contents of the conical flask has reached between 75 °C and 80 °C, turn off the Bunsen burner and **carefully** hold the neck of the conical flask with a paper towel.
7. Titrate with **FA 1** until a permanent colour change is observed.
8. Record the burette readings in the suitable format. Repeat titration to achieve consistent results.

Results:

*Weighing of **FA 4***

Titration

[5]

(h) **(i)** From your titrations, obtain a suitable volume of **FA 1** to be used in your calculations. Show clearly how you obtained this volume.

volume of **FA 1** = ………………….. [1]

(ii) Calculate the amount of **FA 1** required for titration.

$5C_6H_{12}O_6 + 24MnO_4^- + 72H^+ \rightarrow 30CO_2 + 24Mn^{2+} + 66H_2O$

amount of **FA 1** = ………………….. [1]

(iii) Hence, calculate the amount of glucose in **FA 4**.

amount of glucose in **FA 4** = ………………….. [1]

(iv) Use your answer in **(h)(iii)** to determine the percentage of glucose in the mixture.
[A_r: C, 12.0; O, 16.0; H, 1.0]

percentage of glucose in the mixture = ………………….. [1]

[Total: 27]

2 Planning

An electroplating process uses an electric current to coat an object with a thin layer of metal. An example is *copper plating*. In this process, copper metal is made the anode and is allowed to undergo oxidation. The copper is then reformed at the cathode, coating the object to the plated. The mass of copper plated at the end of the process can be calculated by taking relevant mass measurements.

In the following, you will use the *copper plating* process to determine the Faraday constant, which is the charge in coulombs, C, carried by 1 mole of electrons.

(a) Show that the mass of copper plated onto an object is related to the duration of the *copper plating* process by the following expression:

$$m_{Cu} = \frac{I \times M_{Cu}}{2F} t$$

where

m_{Cu} : mass of copper plated onto an object in grams, g

M_{Cu} : molar mass of copper, g mol^{-1}

I : current in amperes, A

F : Faraday constant

t : duration of the *copper plating* process in seconds, s

[2]

(b) A series of experiments can be carried out, in which the duration of each experiment is varied and the corresponding mass of copper plated onto the object is determined. The data obtained is then to be used for plotting a suitable graph to determine the value of the Faraday constant.

You are required to write a plan, describing how such a series of experiments can be carried out for an appreciable mass of copper to be plated. The duration of each experiment should be at least 5 min but not exceeding 50 min.

You may assume that you are provided with:

- 1.0 mol dm^{-3} copper(II) sulfate solution;
- five equal pieces of clean, dry copper metals;
- five equal pieces of clean, dry objects to be plated (the object is electrically conductive but is inert during the *copper plating* process);
- an electrical power source that supplies a constant current of 0.50 A (the electrical power source can be switched on and off);
- connecting wires;
- stopwatch;
- the apparatus and chemicals normally found in a school laboratory.

Your plan should include the following:

- a clearly labelled diagram of the *copper plating* setup, including the direction of electron flow;
- the procedure you would follow;
- the measurements you would make and how you would determine the mass of copper plated accurately and reliably to allow a suitable graph to be drawn.

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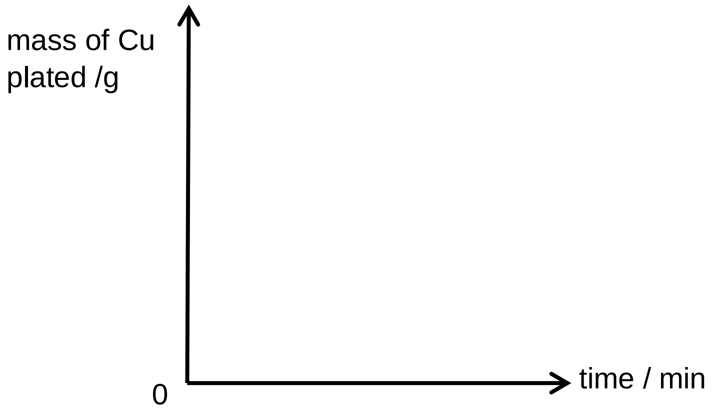
…………………………………………………………………………………………………[6]

(c) Sketch, on the axes below, the graph you would expect and describe how it could be used to determine the value of Faraday constant.



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

(d) During the *copper plating* process, the mass lost at the anode should ideally be the same as the mass gained at the cathode. However, the presence of impurities can cause the mass change at one electrode to be numerically larger than the other electrode.

For each of the following, deduce, with explanation, the electrode that will have a numerically larger mass change.

You may find the following information useful:

$Ag^+ + e^- \rightleftharpoons Ag$ $E^\ominus = +0.80$ V
$Cu^{2+} + 2e^- \rightleftharpoons Cu$ $E^\ominus = +0.34$ V
$Pb^{2+} + 2e^- \rightleftharpoons Pb$ $E^\ominus = -0.13$ V

[A_r: Ag, 107.9; Cu, 63.5; Pb, 207.2]

(i) Presence of Pb impurity at the anode.

Electrode with numerically larger mass change: ………………..

Explanation:

……………………………………………………………………………………………..

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

(ii) Presence of Ag^+ impurity in the electrolyte.

Electrode with numerically larger mass change: ………………..

Explanation:

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…………………………………………………………………………………………[1]

(e) It is important to ensure that the cathode is dry at the start and at the end of each experiment.

Explain the effect, if any, on the calculated value of the Faraday constant if the cathode is dry at the beginning but wet at the end of each experiment.

Effect on calculated value of the Faraday constant: ………………..

Explanation:

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

(f) The Faraday constant obtained from the *copper plating* process can be used to provide an estimate for Avogadro's constant.

A student who conducted the *copper plating* process obtained a value of 96480 C mol^{-1} for the Faraday constant. Using this value, calculate Avogadro's constant.

[Note: The charge of an electron has a numerical value of 1.60×10^{-19} C.]

[1]

[Total: 14]

3 (a) Investigation of some inorganic reactions

FA 5 is an aqueous solution of $CuSO_4$.

FA 6 is a reducing agent.

FA 7 is a solution of ammonium vanadate(V), NH_4VO_3.

You will also need access to the **FA 2** solution you used earlier.

You are to perform the tests described in **Table 3.1** and record your observations in the table.

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

Table 3.1

	tests	observations
(i)	Using a measuring cylinder, add 10 cm^3 of **FA 5** into a boiling tube. Add 4 spatulas of **FA 6**. Warm the mixture cautiously till boiling. Leave to cool for 5 minutes. Filter the mixture and keep the filtrate for tests **(ii)** and **(iii)**.	
(ii)	To 1 cm depth of the filtrate from **(i)**, add aqueous ammonia.	
(iii)	To another 1 cm depth of the filtrate from **(i)**, add 1 spatula of solid ammonium chloride. Stir to ensure all the solid ammonium chloride dissolves. Then add aqueous ammonia.	

Table 3.1

	tests	observations
(iv)	Using a measuring cylinder, transfer 2 cm^3 of **FA 7** and 10 cm^3 of **FA 2** into a boiling tube. Swirl the mixture gently. The resultant yellow solution is **FA 8**, which is an acidified solution of VO_2^+.	
(v)	Transfer about 2 spatulas of **FA 6** into a **dry** weighing bottle. From this sample in the weighing bottle, add a **very small** quantity of **FA 6** to the boiling tube containing **FA 8** solution from test **(iv)**. Swirl the mixture gently and record your observations. Continue to add more **FA 6** in **small** quantities with swirling, until all the **FA 6** in the weighing bottle is used up. Record all colour changes observed.	
	Filter the mixture and retain the filtrate for test **(vi)**.	
(vi)	To 1 cm depth of the filtrate from test **(v)**, add an equal volume of aqueous hydrogen peroxide.	

[6]

(b) **(i)** Suggest an identity for **FA 6**. Explain your answer with reference to evidence from relevant tests above.

identity of **FA 6**

…………………………………………………………………………………………

explanation

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…………………………………………………………………………………………[2]

(ii) Explain the difference in observations between tests **(a)(ii)** and **(a)(iii)**.

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…………………………………………………………………………………………[2]

(iii) The half equations that represent the stepwise reduction of VO_2^+ ions are shown below.

Electrode reaction	$E^\ominus$ / V
$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$	+1.00
$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O$	+0.34
$V^{3+} + e^- \rightleftharpoons V^{2+}$	–0.26
$V^{2+} + 2e^- \rightleftharpoons V$	–1.20

When excess aqueous ammonia is added to 1 cm depth of the filtrate obtained in test **(a)(v)**, a grey precipitate is observed.

Given that the $E^\ominus$ value for **FA 6** is between −1.00 V to –0.50 V, state the identity of the grey precipitate.

…………………………………………………………………………………………[1]

(c) Planning

There are three unlabelled bottles of aqueous solutions. Each bottle contains a different solution from the other two.

The possible identities of the solutions are:

$Na_2CO_3(aq)$ $Al_2(SO_4)_3(aq)$ $Mg(NO_3)_2(aq)$

Plan an investigation, using test–tube reactions, which would allow you to identify each of these three solutions.

Other than the three solutions, the only reagent available is the **FA 5** solution used in **3(a)**, which contains $CuSO_4$.

Your plan should include:

- an outline of the sequence of steps you would follow,
- the expected observations at each step, and
- an explanation of how you would analyse your results in order to identify each solution.

You are **not** required to carry out the plan.

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…………………………………………………………………………………………….[3]

[Total: 14]

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

1 Determination of the dependence of the rate of reaction between glucose and acidified potassium manganate(VII) on temperature

Read through the whole method before starting any practical work. Where appropriate, prepare a table for your results in the space provided.

Show your working and appropriate significant figures in the final answer to **each** step of your calculations.

Glucose, $C_6H_{12}O_6$, is a sugar that can act as a reducing agent. You will investigate how an increase in temperature affects the rate of the redox reaction between glucose and acidified potassium manganate(VII).

FA 1 is 0.020 mol dm^{-3} acidified potassium manganate(VII), $KMnO_4$.
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FA 3 is an aqueous solution containing 32.8 g dm^{-3} glucose, $C_6H_{12}O_6$.
FA 4 is a solid mixture containing an unknown percentage of glucose.

You will measure the time it takes for the purple colour to disappear. Your table of results on the following page should include the rate of reaction for each experiment.

(a) Method

Experiment 1

1. Fill the burette with **FA 1**.
2. Add 5.00 cm^3 of **FA 1** into the 250 cm^3 beaker.
3. Use the 50 cm^3 measuring cylinder to transfer 50.0 cm^3 of **FA 2** into the beaker containing **FA 1**.
4. Use the same measuring cylinder to transfer 50.0 cm^3 of distilled water into the same beaker.
5. Place the beaker on the tripod and heat its contents to between 75 °C and 80 °C.
6. While the solution in the beaker is being heated, pour 25.0 cm^3 of **FA 3** into the 25 cm^3 measuring cylinder.
7. When the temperature of the contents of the beaker has reached between 75 °C and 80 °C, turn off the Bunsen burner and **carefully** hold the <u>top of the hot beaker with either a cloth or paper towel</u> and place it onto the white tile.
8. Record the temperature of the solution in the beaker.
9. Add the 25.0 cm^3 of **FA 3** and **immediately** start timing.
10. Stir the contents of the beaker once and stop timing as soon as the solution turns colourless. Record the time to the nearest second.
11. Record the temperature of the solution as soon as it is colourless.
12. Calculate and record the average temperature of the reaction mixture to one decimal place.
13. Empty, rinse and dry the beaker so it is ready for use in **Experiment 2**.

Experiment 2

1. Add 5.00 cm^3 of **FA 1** into the 250 cm^3 beaker.
2. Use the 50 cm^3 measuring cylinder to transfer 50.0 cm^3 of **FA 2** into the beaker containing **FA 1**.
3. Use the same measuring cylinder to transfer 50.0 cm^3 of distilled water into the same beaker.
4. Place the beaker on the tripod and heat its contents to between 35 °C and 40 °C.
5. While the solution in the beaker is being heated, pour 25.0 cm^3 of **FA 3** into the 25 cm^3 measuring cylinder.
6. When the temperature of the contents of the beaker has reached between 35 °C and 40 °C, turn off the Bunsen burner and **carefully** hold the top of the hot beaker with either a cloth or paper towel and place it onto the white tile.
7. Record the temperature of the solution in the beaker.
8. Add the 25.0 cm^3 of **FA 3** and **immediately** start timing.
9. Stir the contents of the beaker once and stop timing as soon as the solution turns colourless. Record the time to the nearest second.
10. Record the temperature of the solution as soon as it is colourless.
11. Calculate and record the average temperature of the reaction mixture to one decimal place.
12. Empty, rinse and dry the beaker so it is ready for use in **Experiment 3**.

Experiments 3, 4 and 5

1. Repeat the method for **Experiment 2** at three different temperatures.
2. Keep the temperature of the contents of the beaker between room temperature and 80 °C.
3. Record all your results in your table.

Results:

The rate of reaction can be calculated as shown.

$$\text{rate} = \frac{1000}{\text{reaction time}}$$

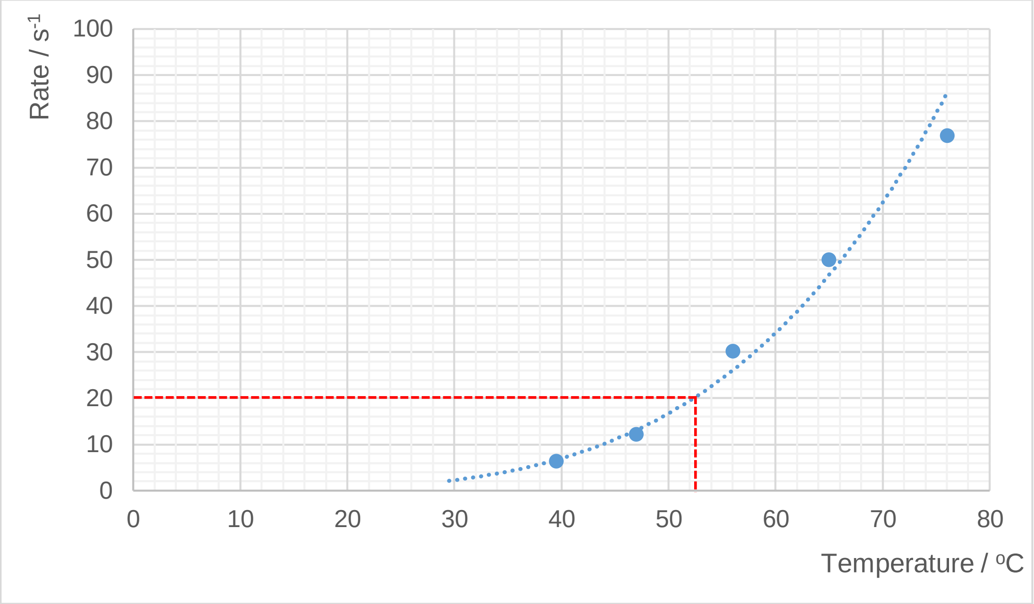
Calculate the rate of reaction for each experiment and include this in your table.

Experiment	**T_{initial} / °C**	**T_{final} / °C**	**T_{average} / °C**	**time / s**	**rate / s^{-1}**
1	**80.0**	**72.0**	**76.0**	**12**	**76.9**
2	**40.0**	**39.0**	**39.5**	**155**	**6.45**
3	**49.0**	**45.0**	**47.0**	**82**	**12.2**
4	**59.0**	**53.0**	**56.0**	**33**	**30.3**
5	**69.0**	**61.0**	**65.0**	**20**	**50.0**

[5]

(b) Plot a graph of rate (*y*-axis) against average temperature (*x*-axis) on the grid below. Select a scale on the *x*-axis to include an average temperature of 30.0 °C. Label any points you consider anomalous.

Draw the most appropriate best-fit curve taking into account all of your plotted points and extrapolate it to 30.0 °C.



[3]

(c) **Use your graph** to calculate the **time** to the nearest second that the reaction would have taken if the average temperature had been 52.5°C.
Show **on the grid** how you obtained your answer.

From the graph, at 52.5 °C,

$$\textbf{rate} = \frac{1000}{\text{reaction time}} = 20\ \text{s}^{-1}$$

$$\textbf{Hence, reaction time} = \frac{1000}{20} = 50\ \text{s}$$

time = **50 s** [2]

(d) Explain, by referring to your graph or your table of results, how the rate of reaction is affected by an increase in temperature.

The <u>rate of reaction increases with increase in temperature</u>. The <u>gradient increases with temperature / graph is exponential / acceleration of rate with temperature increase</u>.

[1]

(e) **(i)** Calculate the maximum percentage error in the reaction time recorded for **Experiment 1**. Assume the error of the timer is ±1 s.

Maximum percentage error = 1 / 12 x 100
= 8.33%

maximum percentage error in **Experiment 1** = **8.33** % [1]

(ii) You have carried out experiments at five different temperatures.

Identify an experiment, if any, you should have repeated. Give a reason for your answer.

Identifies no anomaly as all points are near line of best fit.

[1]

(iii) Suggest one way to improve the accuracy of the results for this investigation.

Use thermostatically controlled water bath to heat both reagents and keep them at constant temperature.

[1]

(f) **(i)** Calculate the concentration of glucose in **FA 3** in mol dm^{-3}.

$$\textbf{Concentration of glucose} = \frac{32.8}{180.0} = 0.182 \text{ mol dm}^{-3}$$

concentration of glucose in **FA 3** = **0.182** mol dm^{-3} [1]

(ii) Calculate the volume of 0.020 mol dm^{-3} acidified $KMnO_4$ that would react with **all** the glucose present in 25.0 cm^3 of **FA 3**.

$$5C_6H_{12}O_6 + 24MnO_4^- + 72H^+ \rightarrow 30CO_2 + 24Mn^{2+} + 66H_2O$$

Amount of glucose in 25.0 cm^3 = 0.182 x 25.0/1000
= 4.55 x 10^{-3} mol

Amount of $KMnO_4$ reduced = 4.55 x 10^{-3} x $\frac{24}{5}$
= 2.18 x 10^{-2} mol

Volume of $KMnO_4$ reduced = 2.18 x 10^{-2}/0.020
= 1.09 dm^3

Volume of acidified $KMnO_4$ required = **1.09 dm^3** [2]

(iii) Comment on the feasibility of conducting a redox titration between the given concentration of glucose and acidified $KMnO_4$.

It is <u>not feasible</u> as the <u>volume</u> required for acidified $KMnO_4$ is <u>too large</u>.

[1]

(g) **Determination of the percentage of glucose in FA 4 by titration**

1. Weigh accurately 1.5 g of **FA 4** in a weighing bottle. Record your weighing appropriately in the space below. If you use **TARE** facility of the balance, please indicate clearly in your recording.
2. Dissolve the solid in a beaker and quantitatively transfer into a 250 cm^3 volumetric flask. Make up to the mark with distilled water. Label this **FA 4 solution**.
3. Pipette 25.0 cm^3 of **FA 4 solution** into a conical flask.
4. Using a measuring cylinder add 50.0 cm^3 of **FA 2** into the conical flask.
5. Place the conical flask on the tripod and heat its contents to between 75 °C and 80 °C.
6. When the temperature of the contents of the conical flask has reached between 75 °C and 80 °C, turn off the Bunsen burner and **carefully** hold the <u>neck of conical flask with either a cloth or paper towel</u>.
7. Titrate with **FA 1** until a permanent colour change is observed.

8. Record the burette readings in the suitable format. Repeat titration to achieve consistent results.

Results:

Weighing of ***FA 4***

Mass of weighing bottle and FA 4 / g	**1.825**
Mass of empty weighing bottle / g	**0.325**
Mass of FA 4 used / g	**1.500**

OR

Mass of weighing bottle only / g	**TARE**
Mass of FA 4 / g	**1.500**

Tabulation with ALL readings recorded, clear headers and units for mass table 3 d.p. correct subtraction and mass of solid within stated range (1.450 – 1.550 g)

Titration

Experiment	**1**	**2**
Final burette reading / cm^3	**22.40**	**42.40**
Initial burette reading / cm^3	**0.00**	**20.00**
Volume of FA 1 used / cm^3	**22.40**	**22.40**

Tabulation with ALL readings recorded, clear headers and units for titration table
2 d.p. for titration reading
At least two consistent readings ±0.10 cm^3

[5]

(h) **(i)** From your titrations, obtain a suitable volume of **FA 1** to be used in your calculations. Show clearly how you obtained this volume.

Average volume of FA 1 used = (22.40 + 22.40) ÷ 2
= 22.40 cm^3

volume of **FA 1** = **22.40 cm^3** [1]

(ii) Calculate the amount of **FA 1** required for titration.

$$5C_6H_{12}O_6 + 24MnO_4^- + 72H^+ \rightarrow 30CO_2 + 24Mn^{2+} + 66H_2O$$

Amount of FA 1 used = 22.40/1000 x 0.020
= 4.48 x 10^{-4} mol

amount of **FA 1** = **4.48 x 10^{-4} mol** [1]

(iii) Hence, calculate the amount of glucose in **FA 4**.

Amount of glucose in 25.0 cm^3 of FA 4 solution = 4.48 x 10^{-4} x $\frac{5}{24}$
= 9.33 x 10^{-5} mol

Amount of glucose in 250 cm^3 of FA 4 solution = $9.33 \times 10^{-5} \times \frac{250}{25.0}$
$= 9.33 \times 10^{-4}$ mol

amount of glucose in **FA 4** = **9.33×10^{-4} mol** [1]

(iv) Use your answer in **(h)(iii)** to determine the percentage of glucose in the mixture.
[A_r: C, 12.0; O, 16.0; H, 1.0]

Mass of glucose in 250 cm^3 of FA 4 solution = $9.33 \times 10^{-4} \times 180.0$
= 0.168 g
Percentage of glucose in FA 4 = 0.168/1.500 x 100 %
= 11.2 %

percentage of glucose in the mixture = **11.2 %** [1]

[Total: 27]

2 Planning

An electroplating process uses an electric current to coat an object with a thin layer of metal. An example is *copper plating*. In this process, copper metal is made the anode and is allowed to undergo oxidation. The copper is then reformed at the cathode, coating the object to the plated. The mass of copper plated at the end of the process can be calculated by taking relevant mass measurements.

In the following, you will use the *copper plating* process to determine the Faraday constant, which is the charge in coulombs, C, carried by 1 mole of electrons.

(a) Show that the mass of copper plated onto an object is related to the duration of the *copper plating* process by the following expression:

$$m_{Cu} = \frac{I \times M_{Cu}}{2F}\, t$$

where

m_{Cu} : mass of copper plated onto an object in grams, g

M_{Cu} : molar mass of copper, g mol^{-1}

I : current in amperes, A

F : Faraday constant

t : duration of the *copper plating* process in seconds, s

$Cu^{2+} + 2e^- \rightarrow Cu$

$Q = I\,t$ ....(1)

$Q = n_e F$ ....(2)

From (1) and (2)

$I\,t = n_e F$

$I\,t = (2n_{cu}) F$

$I\,t = (\frac{2m_{Cu}}{M_{Cu}}) F$

$m_{Cu} = (\frac{I \times M_{Cu}}{2F})\, t$ **(shown)**

[2]

(b) A series of experiments can be carried out, in which the duration of each experiment is varied and the corresponding mass of copper plated onto the object is determined. The data obtained is then to be used for plotting a suitable graph to determine the value of the Faraday constant.

You are required to write a plan, describing how such a series of experiments can be carried out for an appreciable mass of copper to be plated. The duration of each experiment should be at least 5 min but not exceeding 50 min.

You may assume that you are provided with:

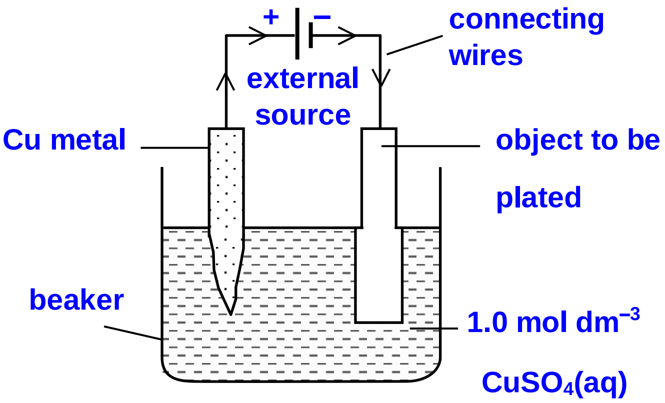
- 1.0 mol dm^{-3} copper(II) sulfate solution;
- five equal pieces of clean, dry copper metals;
- five equal pieces of clean, dry objects to be plated (the object is electrically conductive but is inert during the *copper plating* process);
- an electrical power source that supplies a constant current of 0.50 A (the electrical power source can be switched on and off);

- connecting wires;
- stopwatch;
- the apparatus and chemicals normally found in a school laboratory.

Your plan should include the following:

- a clearly labelled diagram of the *copper plating* setup, including the direction of electron flow;
- the procedure you would follow;
- the measurements you would make and how you would determine the mass of copper plated accurately and reliably to allow a suitable graph to be drawn.

Experimental setup:

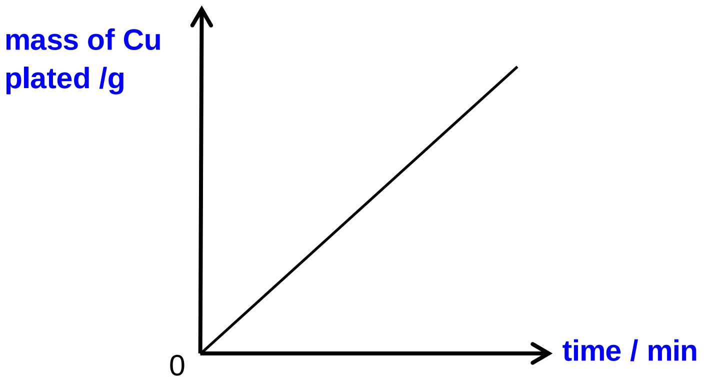


Procedure:

1. **Weigh one of the objects to be plated.**
2. **Set up according to the diagram shown above. Ensure that the electrical power source is switched off.**
3. **Switch on the electrical power source and start the stopwatch simultaneously.**
4. **After 5 min, switch off the electrical power source.**
5. **Remove the plated object, wash the plated object with distilled water and dry it between pieces of filter paper.**
6. **Weigh the plated object. Then calculate the mass of copper plated by taking the difference between the mass of the plated object and the original mass of the object.**
7. **Repeat steps 1 to 6 with durations of 15 min, 25 min, 35 min, 45 min.**

[6]

(c) Sketch, on the axes below, the graph you would expect and describe how it could be used to determine the value of Faraday constant.



Results analysis:

Let the gradient of the graph be k

$$k = \left(\frac{I \times M_{Cu}}{2F}\right)$$

$$F = \left(\frac{I \times M_{Cu}}{2k}\right)$$

[2]

(d) During the *copper plating* process, the mass lost at the anode should ideally be the same as the mass gained at the cathode. However, the presence of impurities can cause the mass change at one electrode to be numerically larger than the other electrode.

For each of the following, deduce, with explanation, the electrode that will have a numerically larger mass change.

You may find the following information useful:

$Ag^+ + e^- \rightleftharpoons Ag$ $\qquad E^\ominus = +0.80\ V$

$Cu^{2+} + 2e^- \rightleftharpoons Cu$ $\qquad E^\ominus = +0.34\ V$

$Pb^{2+} + 2e^- \rightleftharpoons Pb$ $\qquad E^\ominus = -0.13\ V$

[A_r: Ag, 107.9; Cu, 63.5; Pb, 207.2]

(i) Presence of Pb impurity at the anode.

Electrode with numerically larger mass change: **Anode**

Explanation:

Pb gets preferentially oxidised at the anode but Cu^{2+} gets preferentially reduced at the cathode. For every 1 mol of Pb (1 x 207.2 = 207.2 g) oxidised at the anode, 1 mol of Cu (1 x 63.5 g= 63.5 g) is formed at the cathode. Thus the mass change at the anode will be numerically larger.

[1]

(ii) Presence of Ag^+ impurity in the electrolyte.

Electrode with numerically larger mass change: **Cathode**

Explanation:

Cu gets oxidised at the anode but Ag^+ gets preferentially reduced at the cathode. For <u>every 1 mol of Cu (1 x 63.5 = 63.5 g) oxidised at the anode</u>, <u>2 mol of Ag (2 x 107.9 g= 215.8 g) is formed at the cathode</u>. Thus the mass change at the cathode will be numerically larger.

[1]

(e) It is important to ensure that the cathode is dry at the start and at the end of each experiment.

Explain the effect, if any, on the calculated value of the Faraday constant if the cathode is dry at the beginning but wet at the end of each experiment.

Effect on calculated value of the Faraday constant: **<u>Smaller</u>**

Explanation:

If the cathode is dry at the beginning but wet at the end of each experiment, the <u>mass of copper plated calculated for each experiment will be higher than actual</u>. This will lead to a <u>steeper gradient</u> for the graph plotted. Thus calculated Faraday constant will be smaller than actual. [1]

(f) The Faraday constant obtained from the *copper plating* process can be used to provide an estimate for Avogadro's constant.

A student who conducted the *copper plating* process obtained a value of 96480 C mol^{-1} for the Faraday constant. Using this value, calculate Avogadro's constant.

[Note: The charge of an electron has a numerical value of 1.60×10^{-19} C.]

Avogadro's constant = $96480 / 1.60 \times 10^{-19}$

$= 6.03 \times 10^{23}$ electrons mol^{-1}

[1]

[Total: 14]

3 (a) **Investigation of some inorganic reactions**

FA 5 is an aqueous solution of $CuSO_4$.

FA 6 is a reducing agent.

FA 7 is a solution of ammonium vanadate(V), NH_4VO_3.

You will also need access to the **FA 2** solution you used earlier.

You are to perform the tests described in **Table 3.1** and record your observations in the table.

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

Table 3.1

	tests	observations
(i)	Using a measuring cylinder, add 10 cm^3 of **FA 5** into a boiling tube. Add 4 spatulas of **FA 6**. Warm the mixture cautiously till boiling. Leave to cool for 5 minutes.	**Blue FA 5 turns colourless** **(OR award below for filtrate colour)**
	Filter the mixture and keep the filtrate for tests **(ii)** and **(iii)**.	**Red-brown/brown/black/ residue** **colourless filtrate**
(ii)	To 1 cm depth of the filtrate from **(i)**, add aqueous ammonia.	**White ppt formed, soluble in excess NH_3 to give a colourless solution.**

(iii)	To another 1 cm depth of the filtrate from **(i)**, add 1 spatula of solid ammonium chloride. Stir to ensure all the solid ammonium chloride dissolves. Then add aqueous ammonia.	No observable change (OR no ppt)

Table 3.1

tests		observations
(iv)	Using a measuring cylinder, transfer 2 cm^3 of **FA 7** and 10 cm^3 of **FA 2** into a boiling tube. Swirl the mixture gently. The resultant yellow solution is **FA 8**, which is an acidified solution of VO_2^+.	
(v)	Transfer about 2 spatulas of **FA 6** into a **dry** weighing bottle. From this sample in the weighing bottle, add a **very small** quantity of **FA 6** to the boiling tube containing **FA 8** solution from test **(iv)**. Swirl the mixture gently and record your observations. Continue to add more **FA 6** in **small** quantities with swirling, until all the **FA 6** in the weighing bottle is used up. Record all colour changes observed.	**Yellow solution turns green [mixture of yellow VO_2^+ and blue VO^{2+}]** **Green solution turns blue (OR bluish-green OR greenish blue) [more VO^{2+} formed]** **Blue solution turns green (OR dark green) [V^{3+} formed]** **Green solution turns purple (OR violet OR blue) [V^{2+} formed]** **Effervescence of H_2 gas which** **extinguished lighted splint with a 'pop sound**.
	Filter the mixture and retain the filtrate for test **(vi)**.	

(vi)	To 1 cm depth of the filtrate from test **(v)**, add an equal volume of aqueous hydrogen peroxide.	**Violet solution turns brown (OR orange OR red)** **Effervescence of O_2 gas which** **relighted glowing splint.**

[6]

(b) **(i)** Suggest an identity for **FA 6**. Explain your answer with reference to evidence from relevant tests above.

identity of **FA 6**
Zn

explanation

In test (i), decolourisation of blue $CuSO_4$ suggests reduction of Cu^{2+} to Cu and oxidation of FA 6

In test (ii), formation of white ppt soluble in excess $NH_3(aq)$ suggests presence of Zn^{2+} in filtrate from test (i).

[2]

(ii) Explain the difference in observations between tests **(a)(ii)** and **(a)(iii)**.

$NH_4Cl \rightarrow NH_4^+ + Cl^-$

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ ----(1)

Presence of additional NH_4^+ from NH_4Cl (OR NH_4^+ is a common ion) shifts position of equilibrium (1) to the left.

$[OH^-]$ is lowered and ionic product is lesser than K_{sp}. Hence, no ppt is formed in (a)(iii).

[2]

(iii) The half equations that represent the stepwise reduction of VO_2^+ ions are shown below.

Electrode reaction	$E^\ominus$ / V
$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$	+1.00
$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O$	+0.34
$V^{3+} + e^- \rightleftharpoons V^{2+}$	–0.26
$V^{2+} + 2e^- \rightleftharpoons V$	–1.20

When excess aqueous ammonia is added to 1 cm depth of the filtrate obtained in test **(a)(v)**, a grey precipitate is observed.

Given that the $E^\ominus$ value for **FA 6** is between −1.00 V to –0.50 V, state the identity of the grey precipitate.

$E^\ominus$ values suggest that FA 6 reduces VO_2^+ to V^{2+}. Hence, the grey ppt is $\underline{V(OH)_2}$.

[1]

(c) Planning

There are three unlabelled bottles of aqueous solutions. Each bottle contains a different solution from the other two.

The possible identities of the solutions are:

$Na_2CO_3(aq)$ $Al_2(SO_4)_3(aq)$ $Mg(NO_3)_2(aq)$

Plan an investigation, using test–tube reactions, which would allow you to identify each of these three solutions.

Other than the three solutions, the only reagent available is the **FA 5** solution used in **3(a)**, which contains $CuSO_4$.

Your plan should include:

- an outline of the sequence of steps you would follow,
- the expected observations at each step, and
- an explanation of how you would analyse your results in order to identify each solution.

You are **not** required to carry out the plan.

	$Na_2CO_3(aq)$	**$Al_2(SO_4)_3(aq)$**	**$Mg(NO_3)_2(aq)$**
FA 5 (aq $CuSO_4$)	**Blue (OR green) ppt**	**no ppt**	**no ppt**
$Na_2CO_3(aq)$	**---**	**White ppt** **CO_2 effervescence**	**White ppt** **No effervescence**

Add FA 5 to each of the three solutions in separate test–tubes. The solution that gives a blue (OR green) ppt can be identified as $\underline{Na_2CO_3}$ while the other two solutions give no ppt.

Add $\underline{Na_2CO_3(aq)}$ to fresh samples of the two remaining unidentified solutions in separate test–tubes.

The solution that gives white ppt and CO_2 effervescence can be identified as $\underline{Al_2(SO_4)_3}$ while the solution that gives white ppt with no effervescence is $\underline{Mg(NO_3)_2}$.

[3]

[Total: 14]