

Name:		Centre/Index Number:		Class:	
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DUNMAN HIGH SCHOOL

Preliminary Examination

Year 6

H2 CHEMISTRY

Paper 3 Free Response Questions

9729/03

22 September 2021

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your centre number, index number, name and class at the top of this page.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A

Answer **all** questions.

Section B

Answer **one** question.

A Data Booklet is provided.

The use of an approved scientific calculator is expected, where appropriate.

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

For Examiner's Use	
Section A	
1	20
2	20
3	20
Section B	
4 / 5	20
Total	80

This document consists of **33** printed pages.

Section A

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

- 1 (a) Aqueous sodium hydroxide reacts with halogens, such as chlorine, under different conditions, to form NaCl/O and NaCl/O_3 .

At 10 °C, aqueous sodium hydroxide reacts with chlorine to produce NaCl and NaCl/O .

- (i) State the change(s) in oxidation state of chlorine when chlorine is reacted with aqueous sodium hydroxide at 10 °C. Hence, name the type of reaction that occurred.

[1]

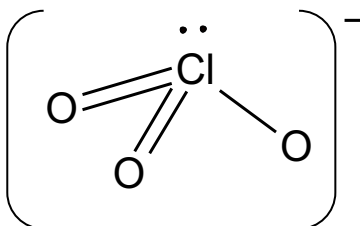
0 in Cl_2 to -1 in NaCl and $+1$ in NaCl/O
Disproportionation

- (ii) Write the balanced equation for the reaction occurring in (a)(i).

[1]



[2]



Shape: Trigonal pyramidal **AND** Bond angle: 107°

- (iv) Explain why fluorine does not undergo a similar reaction with aqueous sodium hydroxide to produce NaFO_3 .

[1]

Fluorine is a period 2 element and does not have vacant low-lying d orbitals to expand its octet structure to form FO_3^- .

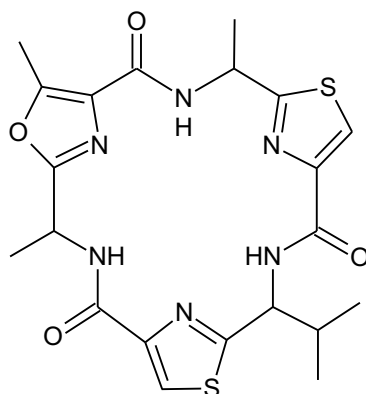
- (v) Describe and explain the relative volatility of Cl_2 and I_2 .

[2]

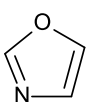
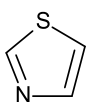
Both are simple molecular substances with weak instantaneous dipole-induced dipole interaction between molecules.

Cl_2 has smaller electron cloud size / smaller number of electrons and hence less polarisable electron cloud. Smaller amount of energy is needed to overcome these weaker id-id interactions in Cl_2 . Hence Cl_2 is more volatile than I_2 .

- (b) Venturamide A is a cyclic peptide with anti-malarial activity. It has the following structure.

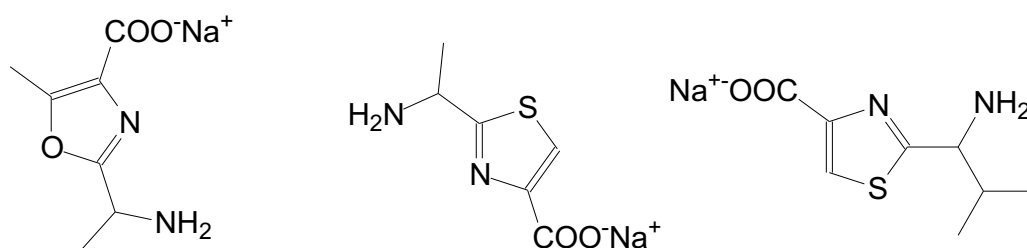


Suggest reagents and conditions for the basic hydrolysis of Venturamide A and draw the structures of the organic products.

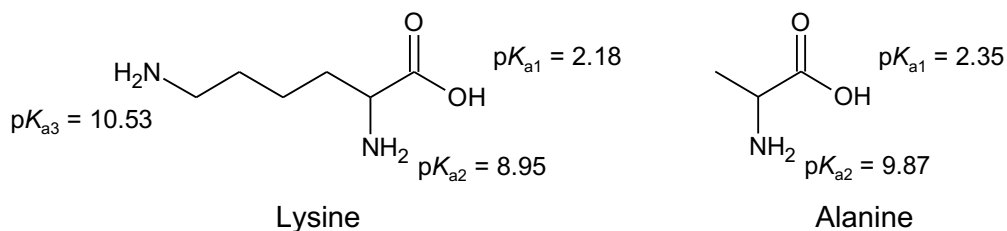
Assume that the 2 rings,  and , are inert in the reaction.

[3]

NaOH(aq), heat (under reflux)

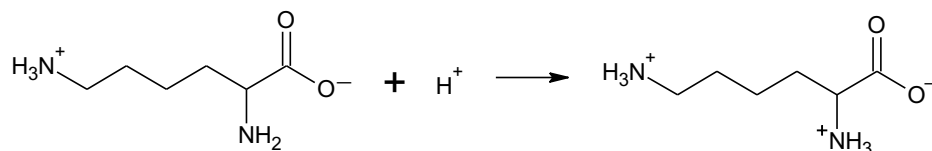


- (c) Lysine and alanine are naturally-occurring amino acids.



- (i) Write an equation to show how the zwitterionic form of lysine can remove small amounts of H⁺.

[2]

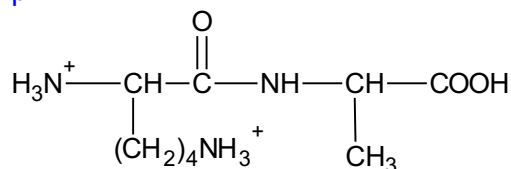


(ii) Draw the structures of the major species present in a solution of the lys–ala dipeptide at **each** of the following pH values at room temperature.

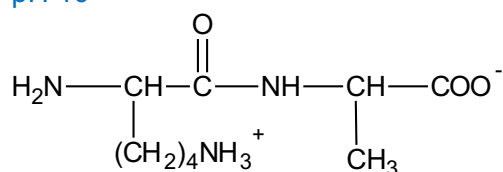
- pH 1
- pH 10

[2]

pH 1



pH 10



(iii) Briefly explain why the α -NH₂ group of lysine is less basic than its side-chain -NH₂ group.

[1]

The α -NH₂ group of lysine is less basic because it is nearer to the electron-withdrawing carboxylic acid group.

(d) Compound **X**, C₈H₁₆Cl₂, is a symmetrical molecule which has two chiral carbon centres.

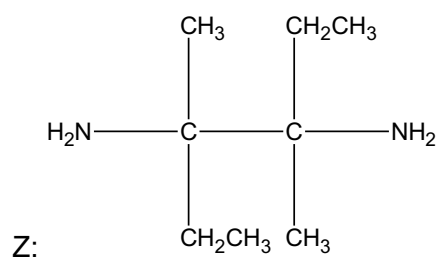
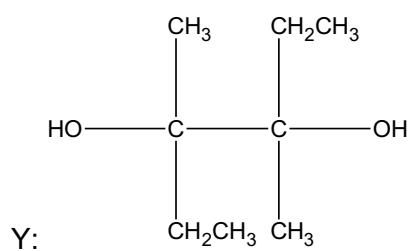
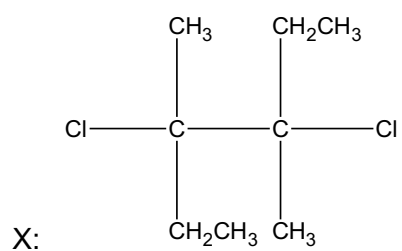
When compound **X** is heated under reflux with excess aqueous sodium hydroxide, compound **Y**, C₈H₁₈O₂, is formed. The reaction kinetics follows the rate equation, rate = $k[\text{X}]$.

Upon heating **Y** with acidified potassium manganate(VII), no decolourisation is observed. When compound **X** is heated in a sealed tube in excess ammonia gas, compound **Z** with the molecular formula C₈H₂₀N₂ is produced.

Deduce the structures of compounds **X** to **Z**, giving your reasoning.

[5]

- X undergoes nucleophilic substitution with aqueous NaOH to give Y
⇒ Y contains 2 alcohol groups / Y is a diol
- Reaction is 1st order with respect to X
⇒ X contains 2 tertiary chloroalkane that undergoes S_N1
- Y does not undergo oxidation with acidified potassium manganate(VII)
⇒ Y contains 2 tertiary alcohol groups
- X undergo nucleophilic substitution with ammonia to give Z
⇒ Z contains 2 (primary) amines

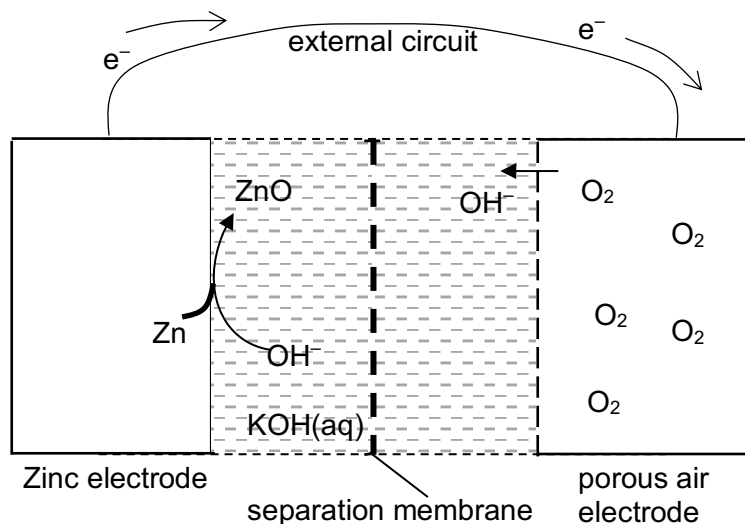


[Total: 20]

- 2 (a) Zinc–air batteries have received revived interest recently due to its higher energy density, larger storage capacity and lower production cost as compared to the commonly–used conventional lithium–ion batteries.

A zinc–air battery comprises zinc electrode, porous carbon–containing air electrode, an electrolyte and a separation membrane. The electrolyte used is aqueous potassium hydroxide.

The zinc–air battery has a standard cell potential of +1.59 V.

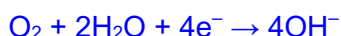


During discharging, zinc is oxidised to zinc oxide, ZnO, at the zinc electrode according to the following reaction:



- (i) Write the half-equation for the reaction that occurred at the air electrode during discharging.

[1]



- (ii) Using suitable data from the *Data Booklet*, calculate the $E^\ominus$ value for the ZnO / Zn electrode.

[1]

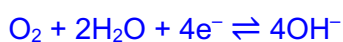
$$E^\ominus_{\text{cell}} = E^\ominus_{\text{cathode}} - E^\ominus_{\text{anode}}$$

$$+1.59 = 0.40 - E^\ominus(\text{ZnO} / \text{Zn})$$

$$E^\ominus(\text{ZnO} / \text{Zn}) = -1.19 \text{ V}$$

- (iii) With reference to your answer in (a)(i), predict how the operating cell potential of the zinc–air batteries will be affected when the atmospheric pressure is lowered.

[1]



Partial pressure of O_2 decreases, hence the equilibrium position shifts left.

$E^\ominus_{(\text{O}_2/\text{OH}^-)}$ will be less positive than 0.40 V hence E_{cell} becomes less positive than 1.59 V.

- (iv) A polymer in the porous air electrode controls the passage of carbon dioxide into the electrolyte.

Given that the separation membrane allows Zn^{2+} ions to pass through, suggest a reason why there is a need to control the passage of carbon dioxide into the electrolyte.

[1]

Alkaline aqueous KOH may react with CO_2 from the air to form carbonate anions. Zinc carbonate formed is insoluble and may clog the surface of the porous air electrode, hindering the normal operation of the battery.

- (b) An organic polymer, which is used as the separation membrane in the zinc–air battery, can be synthesised from compound **X**.

Compound **X** has molecular formula $\text{C}_3\text{H}_3\text{N}$. On heating with dilute sulfuric acid, **X** forms compound **Y**, $\text{C}_3\text{H}_4\text{O}_2$. Both **X** and **Y** decolourise aqueous bromine but only **Y** reacts with sodium carbonate to form a gas which forms white precipitate in $\text{Ca}(\text{OH})_2(\text{aq})$.

- (i) Suggest structures for compounds **X** and **Y**, giving reasons for your answers.

[3]

Observation	Deduction
Both X and Y decolourise aqueous bromine	Both X and Y undergoes electrophilic addition. Both X and Y contain alkene group.
Y reacts with sodium carbonate to form gas which forms white precipitate in $\text{Ca}(\text{OH})_2(\text{aq})$.	Y undergoes acid-carbonate /neutralisation reaction with sodium carbonate to give $\text{CO}_2(\text{g})$. Y contains carboxylic acid group.
On heating with dilute sulfuric acid, X forms compound Y , $\text{C}_3\text{H}_4\text{O}_2$.	X undergoes acidic hydrolysis to form Y . X contains nitrile group (since N has a N atom in its molecular formula.)

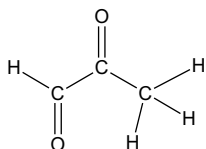
X: $\text{CH}_2=\text{CHCN}$

Y: $\text{CH}_2=\text{CHCOOH}$

- (ii) Compound **Z** is a constitutional isomer of **Y**. They can be distinguished using Fehling's solution or alkaline aqueous iodine.

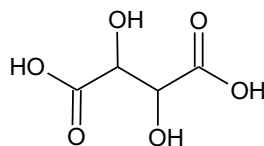
Draw the displayed formula for **Z**.

[1]



Fehling's solution is made by adding equal volumes of aqueous copper(II) sulfate and potassium sodium tartrate in sodium hydroxide.

Potassium sodium tartrate is a double salt of tartaric acid.



Tartaric acid

Table 2.1 below lists some properties of three stereoisomers of tartaric acid.

Table 2.1

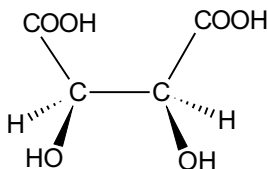
Isomer	Effect on plane-polarised light	Melting point/ °C
A	Rotate to the right	170
B	Rotate to the left	170
C	No effect	140

- (iii) Explain why isomers **A** and **B** behave differently towards plane-polarised light. [1]

Isomers A and B are the enantiomers/non-superimposable mirror images of each other. Hence A and B behave rotate plane-polarised light in opposite directions.

- (iv) Draw the structural formula of isomer **C**. Explain why
- it has a lower melting point from **A** and **B**
 - it does not rotate plane-polarised light.

[3]



The packing of tartaric acid molecules in C is not as regular (not as effectively packed/closely packed) as the packing of tartaric acid molecules in A or B where only one enantiomer isomer of tartaric acid is present. Hence melting point of sample C is lower than that of A. (accept that C is not an enantiomer of A and B)

Isomer C is a meso compound of tartaric acid. The molecule has an internal plane of symmetry.

- (c) Mazak is an alloy of magnesium, aluminium, zinc and copper which is widely used to make die-cast toys.

Magnesium and aluminium are adjacent elements in the third Period of the Periodic Table; copper and zinc are next to each other in the first row of transition elements.

The densities of the four metals present in Mazak, in ascending numerical order, are given below.

	metal 1	metal 2	metal 3	metal 4
density/ g cm^{-3}	1.74	2.70	7.13	8.94

Suggest which two of the metals, Mg, Al, Zn and Cu are metals 1 and 2. Explain your answer.

[2]

Metals 1 and 2 are main group elements whereas metals 3 and 4 are transition elements as densities of transition elements are generally higher due to relatively larger atomic mass and smaller atomic radii.

Therefore, in transition elements, more atoms can be packed per unit volume, giving rise to relatively higher densities than main group elements.

Metal 1 is Mg and metal 2 is Al since Al has relatively higher atomic mass and a smaller atomic radius than Mg.

- (d) A solution contains $4.40 \times 10^{-3} \text{ mol dm}^{-3}$ of $\text{Al}^{3+}(\text{aq})$ and 1.00 mol dm^{-3} of $\text{Cu}^{2+}(\text{aq})$.

Aqueous NaOH was then added slowly to 1 cm depth of the solution in a test-tube.

- (i) Using numerical values of K_{sp} given below, show that the addition of NaOH will **not** allow for the separation of the Al^{3+} and Cu^{2+} metal cation in the above solution.

compound	K_{sp}
$\text{Cu}(\text{OH})_2$	2.20×10^{-20}
$\text{Al}(\text{OH})_3$	4.60×10^{-33}

[3]

When precipitation occurs, ionic product of the hydroxide = K_{sp}

For precipitation of $\text{Cu}(\text{OH})_2$:

$$[\text{Cu}^{2+}][\text{OH}^-]^2 = K_{\text{sp}}$$

$$(1.00)[\text{OH}^-]^2 = 2.20 \times 10^{-20}$$

$$[\text{OH}^-] = 1.48 \times 10^{-10} \text{ mol dm}^{-3}$$

For precipitation of $\text{Al}(\text{OH})_3$:

$$[\text{Al}^{3+}][\text{OH}^-]^3 = K_{\text{sp}}$$

$$(0.0044)[\text{OH}^-]^3 = 4.60 \times 10^{-33}$$

$$[\text{OH}^-] = 1.01 \times 10^{-10} \text{ mol dm}^{-3}$$

Since the $[\text{OH}^-]$ required for both precipitates to form is similar, it does not allow for the separation of the two metal ions.

- (ii) Suggest how the separation of the two aqueous ions can be effectively carried out. Use *Le Chatelier's Principle* to explain your observations and include relevant equations in your answer.

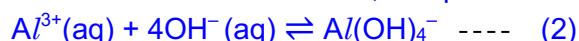
[3]

Add aqueous NaOH until in excess to both solutions. White ppt of $Al(OH)_3$ formed dissolves and pale blue ppt $Cu(OH)_2$ remains insoluble.

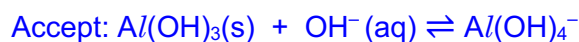
$Al(OH)_3$ formed when a little NaOH is added is sparingly soluble. In aqueous solution, there is a small concentrations of Al^{3+} and OH^- .



When excess OH^- is added, complex formation takes place.



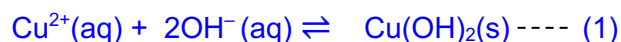
The $[Al^{3+}]$ falls shifting the position of equilibrium of (1) to the left, causing the precipitate to dissolve.



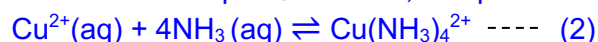
OR

Add aq NH_3 until in excess to both solutions. Blue ppt $Cu(OH)_2$ dissolves to give a dark blue solution while white ppt of $Al(OH)_3$ remains insoluble.

$Cu(OH)_2$ formed when a little aq NH_3 is added is sparingly soluble. In aqueous solution, there is a small concentration of Cu^{2+} and OH^- .



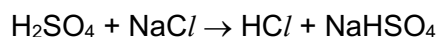
When excess aq NH_3 is added, complex formation takes place.



The $[Cu^{2+}]$ falls shifting the position of equilibrium of (1) to the left, causing the precipitate to dissolve.

[Total: 20]

- 3 (a) Concentrated sulfuric acid reacts with solid sodium chloride to produce hydrogen chloride according to the equation shown.



- (i) Explain what is meant by the term *Brønsted-Lowry acid*.

[1]

A Brønsted-Lowry acid is a proton donor.

- (ii) Identify the two different conjugate acid-base pairs in the reaction, stating clearly which is the acid and base in each pair.

[1]

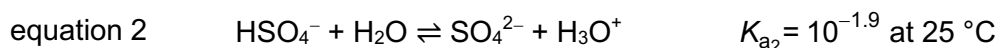
acid: H_2SO_4

conjugate base: HSO_4^-

base: Cl^-

conjugate acid: HCl

When mixed with water, sulfuric acid dissociates in two steps.



- (iii) Explain the difference in the K_a values.

[1]

K_{a2} is smaller than K_{a1} because it is more difficult to lose a proton from the negatively charged HSO_4^- than the uncharged H_2SO_4 molecule as energy is required to overcome the electrostatic attractions between oppositely charged ions.

- (iv) Use equations 1 and 2 to write expressions for the acid dissociation constants, K_{a1} and K_{a2} .

[1]

$$K_{a1} = \frac{[\text{HSO}_4^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{SO}_4]}$$

$$K_{a2} = \frac{[\text{SO}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{HSO}_4^-]}$$

- (v) A sample of dilute sulfuric acid at 25 °C was found to have a pH value of 1.2. Use your answer in (a)(iv) to calculate the $[\text{SO}_4^{2-}]/[\text{H}_2\text{SO}_4]$ ratio and hence show that the amount of H_2SO_4 in the sample is negligible.

[2]

$$K_{a1} \times K_{a2} = \frac{[\text{HSO}_4^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{SO}_4]} \times \frac{[\text{SO}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{HSO}_4^-]} = \frac{[\text{SO}_4^{2-}][\text{H}_3\text{O}^+]^2}{[\text{H}_2\text{SO}_4]}$$

$$\frac{[\text{SO}_4^{2-}]}{[\text{H}_2\text{SO}_4]} = \frac{K_{a1} \times K_{a2}}{[\text{H}_3\text{O}^+]^2} = \frac{10^3 \times 10^{-1.9}}{(10^{-1.2})^2} = 3160$$

Since $\frac{[\text{SO}_4^{2-}]}{[\text{H}_2\text{SO}_4]} \gg 1$, the amount of H_2SO_4 in the sample is negligible.

- (vi) 10 cm³ of 0.500 mol dm⁻³ sulfuric acid is diluted to 100 cm³ with deionised water. Calculate the pH of the diluted solution.

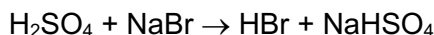
[1]

dilution factor = 100 / 10 = 10

[H⁺] in diluted solution = 0.500 / 10 × 2 = 0.100 mol dm⁻³

pH = -log₁₀(10⁻¹) = 1.0

- (b) Concentrated sulfuric acid also reacts with solid sodium bromide to produce hydrogen bromide.



In addition, the hydrogen bromide produced further reacts with concentrated sulfuric acid to give a reddish brown gas.

- (i) Suggest the identity of the reddish brown gas and use relevant data from the *Data Booklet* to explain why HBr further reacts with H₂SO₄ whereas HCl does not.

[2]

The reddish brown gas is Br₂.

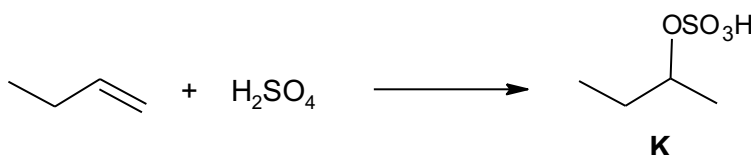
Since $E^\ominus(\text{Br}_2/\text{Br}^-) = +1.07 \text{ V}$ is less positive than $E^\ominus(\text{Cl}_2/\text{Cl}^-) = +1.36 \text{ V}$, HBr is a stronger reducing agent/ has a greater tendency to be oxidised than HCl. Thus HBr is able to reduce H₂SO₄ to SO₂ while itself is oxidised to Br₂ whereas HCl does not.

- (ii) Explain the difference in thermal stability of HBr and HCl.

[2]

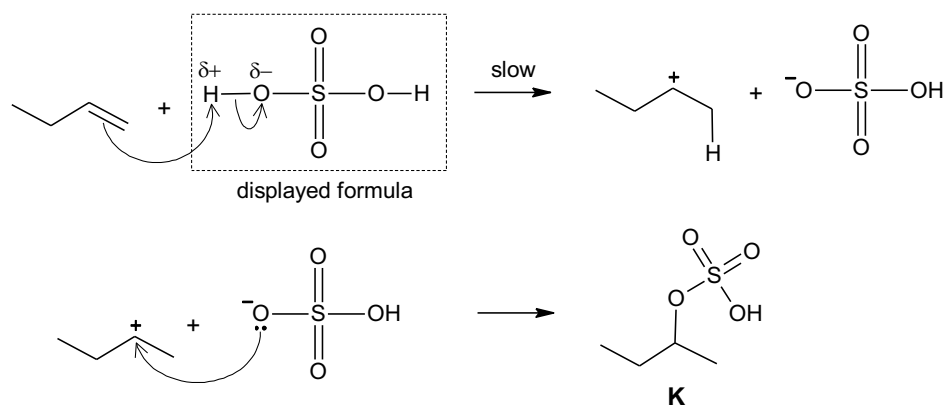
H-Br bond has a lower bond energy / weaker bond strength than the H-Cl bond. The weaker H-Br bond requires less energy to break and thus HBr is less thermally stable.

- (c) But-1-ene reacts with cold concentrated sulfuric acid to produce an alkyl hydrogen sulfate, **K**.



- (i) Suggest a mechanism for the formation of **K** from but-1-ene. Show the displayed formula of the sulfuric acid molecule, the structure of the intermediate and the movement of electron pairs by using curly arrows.

[3]

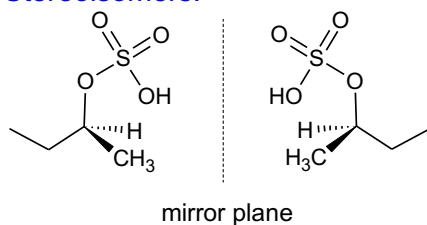


- (ii) State the type of stereoisomerism shown by compound **K** and draw its stereoisomers.

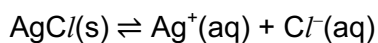
[1]

Enantiomerism.

Stereoisomers:



- (d) Silver chloride exists in equilibrium with its ions.



- (i) Using relevant data from the *Data Booklet* together with the following data, construct a fully labelled energy cycle to calculate the enthalpy change for the dissociation of silver chloride in water.

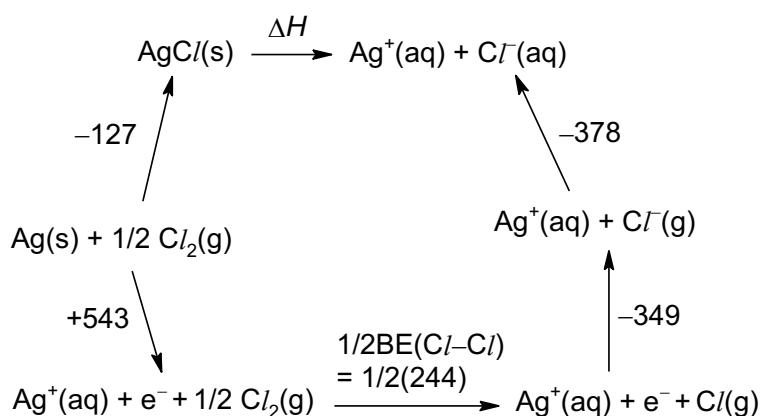
standard enthalpy change of formation of AgCl(s) $= -127 \text{ kJ mol}^{-1}$

first electron affinity of chlorine $= -349 \text{ kJ mol}^{-1}$

standard enthalpy change of hydration of chloride ion $= -378 \text{ kJ mol}^{-1}$

standard enthalpy change of reaction of $\text{Ag(s)} \rightarrow \text{Ag}^+(\text{aq}) + \text{e}^-$ $= +543 \text{ kJ mol}^{-1}$

[3]



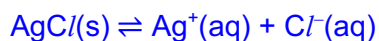
By Hess' law,

$$\Delta H = 127 + 543 + \frac{1}{2}(244) - 349 - 378 = +65 \text{ kJ mol}^{-1}$$

- (ii) State and explain the effect of adding concentrated hydrochloric acid on the solubility of silver chloride.

[2]

As $[\text{Cl}^-]$ increases with the addition of concentrated HCl , by Le Chatelier's Principle, the position of the following equilibrium will shift to the left to decrease $[\text{Cl}^-]$, favouring the precipitation of AgCl(s) and thus solubility of AgCl(s) decreases.



[Total: 20]

Section B

Answer **one** question from this section.

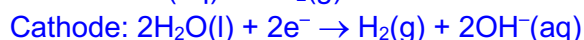
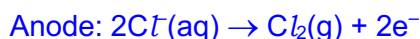
- 4 (a) A saltwater chlorine generator (SWG) is an alternative method of disinfecting swimming pools as opposed to the direct addition of hypochlorite salts into water.

The SWG uses electrolysis to produce chlorine gas.

- (i) The working principle of a SWG can be understood by the electrolysis of concentrated aqueous NaCl using inert titanium electrodes.

Write equations to illustrate the reactions taking place at each electrode in the SWG.

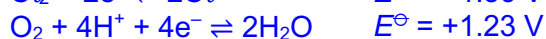
[2]



- (ii) With reference to relevant half-equations and their $E^\ominus$ values from the *Data Booklet*, explain the reaction occurring at the anode.

[2]

From the *Data Booklet*,



At high $[\text{Cl}^-]$, position of the Cl_2/Cl^- equilibrium lies to the left to reduce $[\text{Cl}^-]$. $E_{\text{Cl}_2/\text{Cl}^-}$ is less positive such that it becomes less positive than $E_{\text{O}_2/\text{H}_2\text{O}}^\ominus$. Hence, Cl^- is preferentially oxidised to Cl_2 at the anode.

- (iii) A current of 2.08 A was passed through a SWG prototype for 4 h 30 min. Calculate the volume of chlorine gas that is expected to be liberated at room temperature and pressure.

[2]

$$\begin{aligned} Q &= 2.08 \times [(4 \times 3600) + (30 \times 60)] \\ &= 33\,696 \text{ C} \end{aligned}$$

$$n(\text{e}^-) = \frac{33\,696}{96\,500} = 0.34918 \text{ mol}$$



$$n(\text{Cl}_2) = 0.17459 \text{ mol}$$

$$\begin{aligned} V(\text{Cl}_2) &= 0.17459 \times 24.0 \\ &= 4.19 \text{ dm}^3 \end{aligned}$$

- (b) The distinctive smell of swimming pool water is attributed to a by-product known as chloramines.

Ammonia, which originates from bodily sources such as perspiration and urine, reacts with hypochlorous acid, HClO , to produce various types of chloramines, namely NH_2Cl , NHC_2 and NC_3 .

- (i) At a temperature of 70°C and a pressure of 1.2 atm , 0.400 g of a gaseous mixture containing NH_2Cl , NHC_2 and NC_3 takes up a volume of 150 cm^3 .

Calculate the average M_r of the sample.

[2]

$$\begin{aligned}
 pV &= nRT \\
 pV &= \left(\frac{m}{M}\right)RT \\
 M &= \frac{mRT}{pV} \\
 &= \frac{0.400 \times 8.31 \times (273 + 70)}{1.2 \times 101\,325 \times (150 \times 10^{-6})} \\
 &= 62.512 \\
 &= 62.5\text{ g mol}^{-1}
 \end{aligned}$$

$$M_r = 62.5$$

- (ii) NC_3 gas behaves less ideally than NH_3 gas. Explain this observation.

[1]

NC_3 has a larger electron cloud size than NH_3 and hence stronger instantaneous dipole-induced dipole intermolecular interaction.

- (iii) NC_3 can be removed by channelling swimming pool water through an Ultraviolet (UV) disinfection system, producing chlorine gas as shown by the equation below.



Predict, with reasoning, the sign of the entropy change.

[1]

Entropy change is positive as there is an increase in moles (or amount) of gaseous molecules and hence an increase in disorderliness of the system.

- (iv) Using your answer in (b)(iii), suggest whether the removal of NC_3 in swimming pool water is easier on a hotter or colder day. Explain your answer.

[2]

Removal of NC_3 is easier on a hotter day.

With an increase in temperature T and $\Delta S > 0$, $-T\Delta S$ becomes more negative. Since $\Delta H > 0$, $\Delta G = \Delta H - T\Delta S$ becomes more negative when T increases. Reaction becomes more spontaneous.

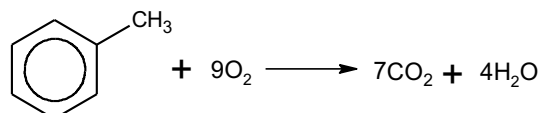
- (v) A student determined $\Delta G^\ominus$ of the reaction in (b)(iii) to be -154 kJ mol^{-1} .

State a limitation of this value in predicting the spontaneity of this reaction.

[1]

$\Delta G^\ominus$ predicts the spontaneity of a reaction only under standard conditions (at 298 K, 1 bar). The spontaneity of this reaction may change at other temperatures.

- (c) Methylbenzene can be used as an additive in unleaded petrol. It has a boiling point of 111°C . The combustion of methylbenzene is shown below.



- (i) Using bond energy data from the *Data Booklet*, calculate the standard enthalpy change of combustion, ΔH_c , of methylbenzene.

[2]

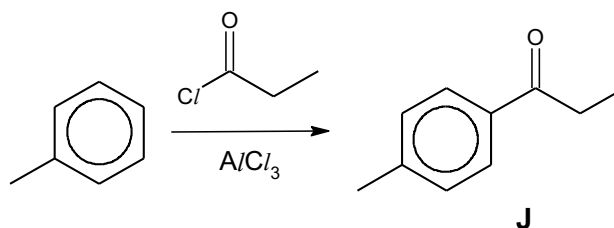
$$\begin{aligned}\Delta H_c &= [8(410) + 350 + 6(520) + 9(496)] - [14(805) + 8(460)] \\ &= 11214 - 14950 \\ &= -3736 \text{ kJ mol}^{-1} \\ &= -3740 \text{ kJ mol}^{-1} \text{ (3 s.f.)}\end{aligned}$$

- (ii) The ΔH_c calculated in (c)(i) is more exothermic than its experimental value. Other than the use of average bond energy values in the calculation, suggest a reason for the discrepancy between the two values.

[1]

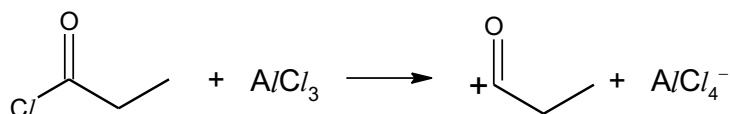
The calculation in (c)(i) using bond energy values excludes the energy required to vapourise methylbenzene from the liquid to gaseous state. Hence, it is more exothermic than the expected.

Methylbenzene undergoes a reaction with propanoyl chloride as shown below.

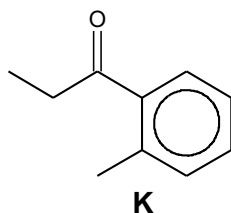


- (iii) Write an equation to show the generation of the electrophile.

[1]



- (iv) Compound **K** is another possible product of the reaction.



Suggest why **K** is likely to be formed in smaller quantities compared to **J**.

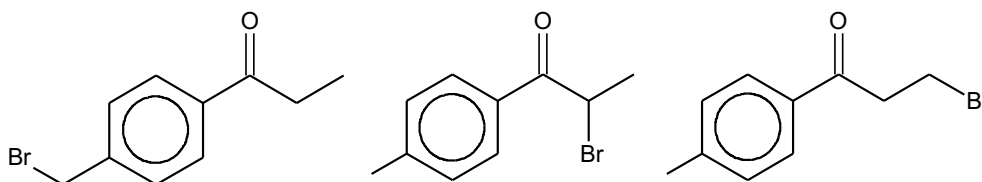
[1]

The approach of electrophile is sterically hindered by the adjacent -CH_3 group when it approaches the 2-position of methylbenzene.

- (v) Compound **J** is reacted with bromine gas in the presence of UV light.

Draw all possible monobrominated products formed and suggest their relative ratios.

[2]



Ratio = 3 : 2 : 3

[Total: 20]

5 Addition and substitution reactions are common reactions in organic chemistry.

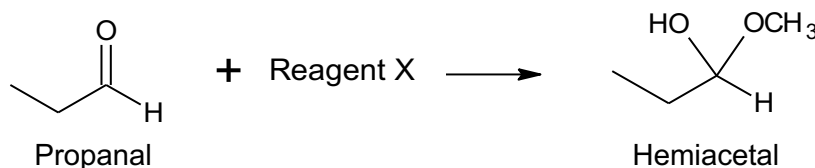
- (a) Alkenes and carbonyl compounds can undergo addition reactions. However, carbonyl compounds undergo nucleophilic addition reactions while alkenes do not.

Explain why alkenes do not undergo nucleophilic addition reactions.

[1]

The C=C in alkenes is electron-rich and will repel the electron-rich nucleophiles.

- (b) One example of a nucleophilic addition reaction that carbonyl compounds can undergo is the conversion of the carbonyl group to a hemiacetal. An example involving propanal is shown below.

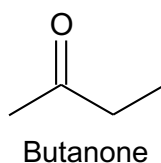


- (i) Suggest the identity of reagent X.

[1]

Methanol, CH₃OH

Butanone can undergo the same nucleophilic addition reaction using the reagent X.



Observations were made about the reactions as shown in Table 5.1.

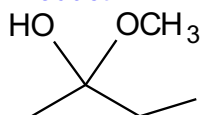
Table 5.1

	Reaction between propanal and reagent X	Reaction between butanone and reagent X
Relative Rate	Faster	Slower
Optical activity of product	Optically inactive	Optically inactive

- (ii) Suggest the structure of the product formed when butanone reacts with reagent X, and explain the observations made about the two reactions in Table 5.1.

[4]

Product:



Explanation for relative rate:

Butanone has an additional electron-donating alkyl group. This means that the electrophilic/carbonyl carbon has a smaller δ^+ and is less reactive towards nucleophiles. Hence, the nucleophilic addition occurs at a slower rate.

Explanation for optical activity of product:

Both propanal and butanone have a trigonal planar geometry around their electrophilic/carbonyl carbon. Hence, the nucleophile has equal chance of attacking this carbon from the top or bottom of the plane. This results in a mixture of two enantiomers of equal proportions (i.e. racemic mixture). Hence, the resultant mixture is optically inactive.

- (iii) Describe two chemical tests that would be able to distinguish propanal and butanone.

The two tests must include:

- Test 1 that gives a positive test with propanal but not butanone
- Test 2 that gives a positive test with butanone but not propanal

You should include the positive observation of each test in your answer.

[3]

Test 1 (Positive test with propanal but not butanone):

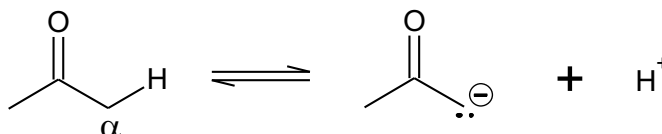
KMnO₄, H₂SO₄(aq), heat (in a water bath) + Purple KMnO₄ decolourises

Test 2 (Positive test with butanone and not propanal):

I₂, NaOH(aq), warm (in a water bath) + pale yellow ppt forms

- (c) Ketones can undergo electrophilic substitution because the hydrogen atom on the alpha (α) carbon of a ketone is considered to be weakly acidic. The alpha carbon is the carbon atom that is next to the carbonyl group.

The deprotonation of ketones at the alpha carbon results in the formation of a resonance-stabilised conjugate base, which can then react with electrophiles.



- (i) Suggest why the conjugate base of the ketone is resonance-stabilised.

[1]

The lone pair of electrons on the negatively charged carbon / the negative charge can be delocalised into the π bond of the carbonyl group, reducing the intensity of the negative charge.

- (ii) Suggest why ketones are much less acidic than carboxylic acids.

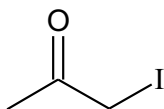
[2]

For the carboxylate anion, the negative charge can be delocalised over 2 highly electronegative oxygen atoms, as compared to just 1 oxygen atom in the conjugate base of ketones.

There is a higher intensity of the negative charge on the conjugate base of the ketone, and hence it is less stabilised. The ketone would dissociate to a lesser extent, making it a weaker acid.

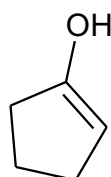
- (iii) Suggest the structure of the organic product formed when the conjugate base of propanone reacts with a molecule of iodine.

[1]



- (d) Phosphorus trichloride, PCl_3 , and phosphorus pentachloride, PCl_5 , are commonly used in the substitution reactions involving carboxylic acids and alcohols.

- (i) Cyclopenten-1-ol does not undergo substitution with PCl_3 or PCl_5 . Suggest a reason for this.



Cyclopenten-1-ol

[1]

The p orbital of O atom overlaps with the π electron cloud of the $\text{C}=\text{C}$ bond, resulting in the $\text{C}-\text{O}$ bond having partial double bond character.

A large amount of energy is required to break the $\text{C}-\text{O}$ bond and hence substitution of the alcohol group does not happen.

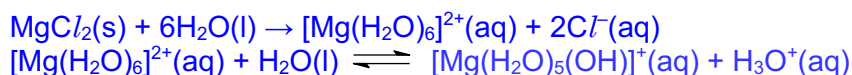
Phosphorus pentachloride, silicon chloride and magnesium chloride were added separately to three beakers of water. A few drops of universal indicator were added to each beaker and the colour of the solution in each beaker was recorded in Table 5.2.

Table 5.2

Beaker	Colour of solution
A	Red
B	Red
C (to which MgCl_2 was added)	Yellow

- (ii) With the aid of a chemical equation, account for the colour of the solution observed in beaker C.

[2]



MgCl_2 dissolves in water to produce Mg^{2+} which partially hydrolyses in water to give a weakly acidic solution.

- (iii) A precipitate was observed in beaker A.

State the identity of this precipitate.

[1]



- (iv) Write an equation that describes the reaction that happens when phosphorus pentachloride dissolves in excess water.

[1]



- (v) A unknown mass of phosphorus pentachloride was completely dissolved in 500 cm³ of water. A 10 cm³ aliquot of the resultant solution required 16.00 cm³ of 0.2 mol dm⁻³ aqueous KOH for complete neutralisation.

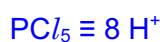
Calculate the mass of phosphorus pentachloride that was dissolved in 500 cm³ of water.

[2]

$$\text{Moles of KOH used} = \frac{16.00}{1000} \times 0.2 = 0.0032 \text{ mol}$$

$$\text{Moles of H}^+ \text{ present in } 10 \text{ cm}^3 = 0.0032 \text{ mol}$$

$$\text{Moles of H}^+ \text{ present in } 500 \text{ cm}^3 = 0.0032 \times \frac{500}{10} = 0.16 \text{ mol}$$



$$\text{Moles of PCl}_5 \text{ dissolved in } 500 \text{ cm}^3 \text{ of water} = 0.16 \div 8 = 0.02 \text{ mol}$$

$$\text{Mass of PCl}_5 \text{ dissolved} = 0.02 \times (31 + 35.5 \times 5) = 4.17 \text{ g}$$

[Total: 20]