1 The Avogadro constant is *L*. How many neutrons are present in 24 dm^3 of chlorine gas, measured at r.t.p?

A	17*L*	**B**	18.5*L*	**C**	37*L*	**D**	71*L*

2 A carbon sample contains a mixture of ^{12}C and ^{14}C isotopes. When 1.000 g of this sample is burned completely in $^{16}O_2$. The mass of CO_2 formed is 3.629 g.

What is the percentage by mass of the ^{12}C isotope in this sample?

A	85.0%	**B**	88.6%	**C**	90.0%	**D**	91.4%

3 When phosphoryl chloride, $POCl_3$, dissolves in water, it gives a mixture of phosphoric acid and hydrochloric acid. How many moles of sodium hydroxide would be needed to neutralise the solution formed by adding one mole of $POCl_3$ to excess water?

A	3	**B**	4	**C**	5	**D**	6

4 Which of the following pairs have similar shapes and the first species has a smaller bond angle than the second species?

1 $SiCl_4$, PF_4^+

2 PH_3, NH_3

3 SO_3^{2-}, CO_3^{2-}

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

5 But-2-enedioic acid, $HC(CO_2H)=C(CO_2H)H$, exists as a pair of *cis*-*trans* isomers. The *cis* isomer has a lower melting point than the *trans* isomer.

Which of the following statements is correct about but-2-enedioic acid?

1 In the solid state, both the *cis* and *trans* isomers have the same density.

2 Intramolecular hydrogen bonding is present in the *cis* isomer.

3 The *cis* isomer is less polar than the *trans* isomer.

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

6 Which of the following statements about prop-1,2-diene, $H_2C=C=CH_2$, is **not** correct?

A The C=C in prop-1,2-diene is stronger than the C=C in ethene.

B The two π-bonds in prop-1,2-diene are perpendicular to each other.

C There are only two sp^2 hybridised carbon atoms in a prop-1,2-diene molecule.

D Prop-1,2-diene is a planar molecule.

7 Which of the following statements is **not** correct?

A Under very high pressure, HC*l* gas behaves more ideally than Cl_2 gas.

B Ideal gas molecules have zero size.

C Real gas molecules behave more ideally under low pressure and high temperature.

D There are no collisions between ideal gas molecules.

8 The lattice energies of the compounds, magnesium oxide, magnesium bromide, sodium oxide and sodium bromide are given below.

Which of the following values corresponds to the lattice energy of magnesium bromide?

A –752 kJ mol^{-1} **B** –2440 kJ mol^{-1}

C –2481 kJ mol^{-1} **D** –3790 kJ mol^{-1}

9 The enthalpy changes of formation of gaseous ethene and ethane are +52 kJ mol^{-1} and –85 kJ mol^{-1} respectively at 298 K.

Consider the following reaction.

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$

Which of the following statements is correct?

A $\Delta S_{\text{reaction}}$ is positive.

B The enthalpy change of the reaction is –137 kJ mol^{-1}.

C If ethene is converted to ethane via four stages instead of one as shown above, the enthalpy change of the reaction will be less exothermic.

D The addition of a catalyst will cause the enthalpy change of reaction to be more exothermic.

10 Ammonium chloride readily dissolves in water at room temperature. During the process, the temperature of the solution decreases.

Which of the following statements is correct?

1 Dissolution of ammonium chloride is favoured due to the entropy change.

2 Dissolution of ammonium chloride is not spontaneous at very low temperature.

3 The sum of the hydration energies of ammonium ion and chloride ion is less exothermic than the lattice energy of ammonium chloride.

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

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

11 Three experiments are conducted to determine the rate equation for a reaction between sulfuric acid and sodium thiosulfate. The volumes used and the time taken for the precipitate to form are shown below.

Experiment	Volume of H_2SO_4 / cm^3	Volume of $Na_2S_2O_3$ / cm^3	Volume of water / cm^3	Time / s
1	20	20	20	30
2	40	20	0	15
3	x	20	0	15

What could be a suitable value for x?

A 5 **B** 10 **C** 20 **D** 30

12 Lead is the final product formed by a series of changes in which the rate-determining stage is the radioactive decay of uranium-238. This radioactive decay is a first-order reaction with a half-life of 4.5×10^9 years.

What would be the age of a rock sample, originally lead-free, in which the molar ratio of uranium to lead is now 1:7?

A 1.5×10^9 years

B 2.25×10^9 years

C 9.0×10^9 years

D 1.35×10^{10} years

13 A reversible reaction is catalysed.

Which of the following statements about this reaction are correct?

1 The catalyst alters the mechanism of the reaction.

2 The catalyst reduces the activation energy for both the forward and the backward reaction.

3 The catalyst alters the composition of the equilibrium mixture.

A 1, 2 and 3

B 1 and 2 only

C 2 and 3 only

D 1 only

14 Pure nitrosyl chloride gas, NOC*l*, was heated at 320 °C in a 2.0 dm^3 vessel. At equilibrium, 30% of the NOC*l* gas has dissociated according to the equation below and the total pressure was p atm.

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

What is the numerical value of the equilibrium constant, K_p, at 320 °C?

A $\frac{17.9}{p}$ **B** $\frac{41.7}{p}$ **C** $0.0240p$ **D** $0.0276p$

15 What is the pH of the resultant solution when 100 cm^3 of 0.10 mol dm^{-3} aqueous NH_4Cl and 40 cm^3 of 0.15 mol dm^{-3} aqueous NaOH are mixed at 25 °C? (pK_b of NH_3 = 4.75)

A 4.57 **B** 4.93 **C** 9.07 **D** 9.43

16 The value of the solubility product, K_{sp}, of silver chromate(VI), Ag_2CrO_4, is 2.5×10^{-22} at 25 °C.

Which statement about silver chromate(VI) is correct?

A The units for K_{sp} of silver chromate(VI) are $mol^2\ dm^{-6}$.

B Addition of nitric acid will cause K_{sp} value of silver chromate(VI) to increase.

C Addition of nitric acid will cause the solubility of silver chromate(VI) to increase.

D The solubility of silver chromate(VI) in water is 1.58×10^{-11} mol dm^{-3}.

17 Which of the following changes does not alter the reduction potential measured for a Cl_2/Cl^- half-cell?

A Adding water into the half-cell.

B Placing the half-cell in an ice-water bath.

C Adding silver ions into the half-cell.

D Introducing an additional 1 bar of inert gas into the half-cell.

18 When a large current was passed through an aqueous copper(II) sulfate solution with two inert electrodes, there was liberation of x mol of copper and y dm^3 of oxygen, measured at r.t.p.

How many moles of electrons passed through the circuit?

A $x+\frac{y}{12}$ **B** $x+\frac{y}{6}$ **C** $2x+\frac{y}{12}$ **D** $2x+\frac{y}{6}$

19 Which of the following statements concerning the chlorine-containing compounds of period 3 elements is correct?

A PCl_3 and Cl_2O_7 are both acidic in nature due to their reactions with water.

B NaC*l* dissolves easily in water due to the favourable ion-dipole interactions and the compounds with the highest electrical conductivity in molten state is $AlCl_3$.

C The low boiling points of PCl_3 and Cl_2O_7 are due to the weak P–C*l* and C*l*–O bond energies.

D Both CCl_4 and $SiCl_4$ can dissolve in excess water completely to give an acidic solution.

20 When aqueous ammonia is added to a solution containing hexaaquairon(III) ions, $[Fe(H_2O)_6]^{3+}$, a red-brown precipitate is formed which does not dissolve in excess ammonia.

What is the role of the ammonia molecule in this reaction?

A Bronsted-Lowry base

B Lewis acid

C Ligand

D Reducing agent

21 Which types of stereoisomerism are shown by 2,4-dimethylhex-2-ene?

A enantiomerism only

B *cis-trans* isomerism only

C both *cis-trans* isomerism and enantiomerism

D neither *cis-trans* isomerism nor enantiomerism

22 A sample of ethene was added to a solution containing both Br_2(aq) and $NaCl$(aq). Which of the following products is **not** likely to be found in the reaction mixture?

A	$CH_2(OH)CH_2Br$	**B**	CH_2BrCH_2Cl
C	$CH_2(OH)CH_2Cl$	**D**	CH_2BrCH_2Br

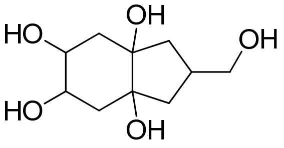
23 Organic compound **X** gives a precipitate when warmed with aqueous silver nitrate. This precipitate dissolves when concentrated aqueous ammonia is added.

What could **X** be?

1 1-bromopropane
2 1-chloropropane
3 chlorobenzene

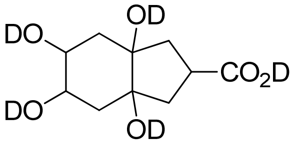
A	1, 2 and 3	**B**	1 and 2 only
C	2 and 3 only	**D**	1 only

24 Deuterium, D, is an isotope of hydrogen. Which of the following is the product formed when the compound **Y** is distilled with $K_2Cr_2O_7$ in aqueous D_2SO_4?

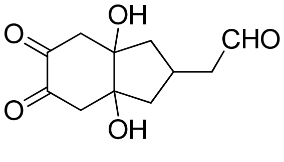


Compound **Y**

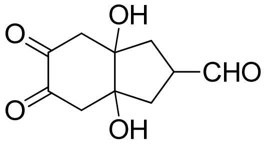
A



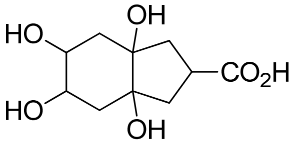
B



C



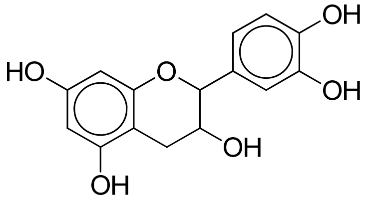
D



25 Starting with $C_6H_5COCH_3$, which two-stage process does **not** involve a condensation reaction?

	stage 1	**stage 2**
A	HCN with trace NaCN	NaOH
B	NH_2NH_2	NaOH
C	I_2 with NaOH	C_2H_5OH with conc. H_2SO_4
D	$NaBH_4$	CH_3COCl

26 Catechin is an antioxidant found in tea leaves, chocolates and red wine. It is often studied for its function as an inhibitor to the growth of cancer cells, amongst other health benefits.



catechin

Which of the following statements about catechin is correct?

A 1 mol of catechin reacts with 5 mol of NaOH.

B It can undergo electrophilic substitution with 2.5 mol of $Br_2(aq)$.

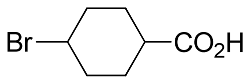
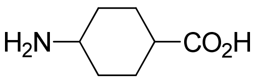
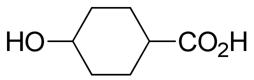
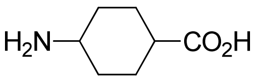
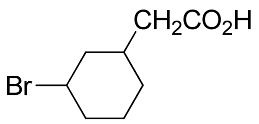
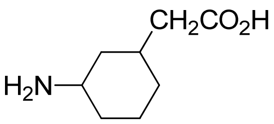
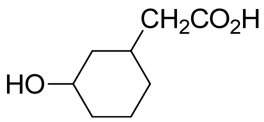
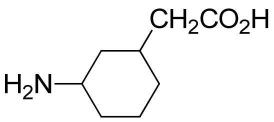
C It can undergo oxidation with hot alkaline $KMnO_4(aq)$.

D 1 mol of catechin reacts with 2 mol of Na_2CO_3.

27 The diagram below shows a reaction scheme for the formation of compound **Z**.

Compound **Z**

Which combination could be **X** and **Y**?

	X	**Y**
A		
B		
C		
D		

28 Equal amounts of two organic compounds, **P** and **Q**, were separately added to 100 cm^3 of water and the pH values of both solutions were determined. It was found that the pH of the aqueous solution of **P** is higher.

Which pairs of compounds could be **P** and **Q**?

	P	**Q**
1	CH_3CH_2OH	CH_3CO_2H
2	$CH_3CH_2NH_2$	$C_6H_5NH_2$
3	C_6H_5ONa	$C_6H_5CO_2Na$

A 1, 2 and 3

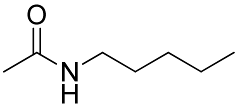
B 1 and 2 only

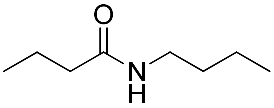
C 2 and 3 only

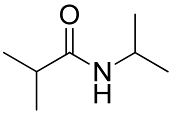
D 1 only

29 An amide, **M**, has the empirical formula $C_7H_{15}ON$. When **M** is hydrolysed by heating under reflux with dilute hydrochloric acid, a carboxylic acid with empirical formula C_2H_4O is obtained as one of the products.

What could be the skeletal formula of **M**?

1 

2 

3 

A 1, 2 and 3

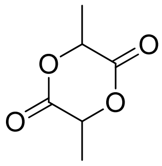
B 1 only

C 2 and 3 only

D 3 only

30 Which ester might be formed when lactic acid, $CH_3CH(OH)CO_2H$, is heated?

1 $CH_3CH(OH)CO_2CH(CH_3)CO_2H$

2 

3 $CH_3CH(OH)CO_2CH(OH)CH_3$

A 1, 2 and 3

B 1 and 2 only

C 2 and 3 only

D 1 only

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

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

1 **(a)** Bromine exists naturally as a mixture of two stable isotopes, ^{79}Br and ^{81}Br, in a 1:1 ratio.

(i) Write down the full electronic configuration of $^{79}Br^{2+}$.

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

(ii) Define the term *relative isotopic mass*.

…………………………………………………………………………………………

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

(b) Chlorine atom exists naturally as two isotopes, ^{35}Cl and ^{37}Cl, in a 3:1 ratio. When equimolar amounts of bromine and chlorine were mixed together, an interhalogen compound, BrC*l*, is formed. The product mixture contains four species with three different mass numbers 114, 116 and 118. $^{79}Br^{35}Cl$ is one of the four species.

(i) With the help of the information given in **(a)**, state the species that corresponds to each mass number. Hence, calculate the relative abundance for each mass number.

mass number	species	relative abundance
114	$^{79}Br^{35}Cl$	
116		
118		

[3]

(ii) Explain whether BrC*l* or Cl_2 has a greater enthalpy change of vaporisation.

…………………………………………………………………………………………

…………………………………………………………………………………………

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

(iii) Suggest with a reason how the first ionisation energy of ^{79}Br is compared to ^{81}Br.

…………………………………………………………………………………………

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

(c) Bromine reacts with an element **A** to form a compound with empirical formula **A**Br_3. The percentage by mass of **A** in **A**Br_3 is 4.31%. Calculate the relative atomic mass of **A**.

[1]

(d) Bromine and fluorine react to form the pale yellow liquid, bromine trifluoride, as shown in **Reaction 1**.

Reaction 1 $Br_2(l) + 3F_2(g) \rightarrow 2BrF_3(l)$

Some thermochemical data are given below.

Standard enthalpy change of formation of $BrF_3(l)$ / kJ mol^{-1}	–301
Standard Gibbs free energy change of formation of $BrF_3(l)$ / kJ mol^{-1}	–241
Standard entropy of $Br_2(l)$, $S^{\ominus}(Br_2)$ / J mol^{-1} K^{-1}	152
Standard entropy of $BrF_3(l)$, $S^{\ominus}(BrF_3)$ / J mol^{-1} K^{-1}	178

(i) The above reaction is spontaneous at 298 K even though $\Delta S^{\ominus}$ is negative. Explain qualitatively why $\Delta H^{\ominus}$ is the predominant factor that causes the reaction to be spontaneous.

……………………………………………………………………………………………

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

(ii) Sketch a graph to show how $\Delta G^{\ominus}$ varies with temperature in K for **Reaction 1**. Label the y–intercept.

[1]

(iii) Given that $\Delta S^\ominus = 2 \times S^\ominus(BrF_3) - [S^\ominus(Br_2) + 3 \times S^\ominus(F_2)]$ for **Reaction 1**, calculate the standard entropy of $F_2(g)$, $S^\ominus(F_2)$, at 298 K.

[2]

(e) Similar to water, liquid BrF_3 can be used as a solvent and it undergoes minimal self–ionisation.

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$
$$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

When $(BrF_2^+)_2(SnF_6^{2-})$ and $Ag^+(BrF_4^-)$ react in BrF_3, an insoluble Ag_2SnF_6 is formed.

(i) Construct an equation for the reaction between $(BrF_2^+)_2(SnF_6^{2-})$ and $Ag^+(BrF_4^-)$.

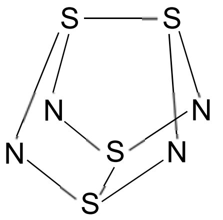
………………………..…………………………………….………………………… [1]

(ii) State and draw the shapes of BrF_2^+ and BrF_4^-, including lone pairs of electrons.

BrF_2^+	BrF_4^-

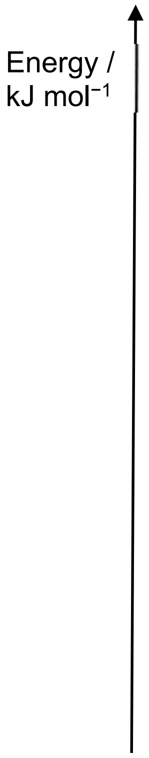
[2]

(f) One of the most readily prepared sulfur nitrides is S_4N_4, which can be made by passing dry $NH_3(g)$ into a solution of SCl_2 in an organic solvent. A proposed structure of the molecule of S_4N_4 is shown below.



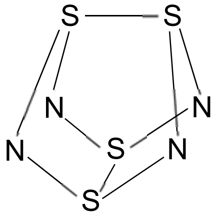
(i) Using the data given below, construct a suitable energy level diagram to calculate the S–N bond energy in S_4N_4.

$\Delta H_f^\ominus[S_4N_4(g)] = +460\ kJ\ mol^{-1}$
$\Delta H_{at}^\ominus[S(s)] = +279\ kJ\ mol^{-1}$
$\Delta H_{at}^\ominus$[nitrogen] $= +497\ kJ\ mol^{-1}$
Bond energy of (S–S) in $S_4N_4 = +204\ kJ\ mol^{-1}$



[3]

(ii) The nitrogen atoms in S_4N_4 show their usual valency of 3. All four sulfur atoms have the same oxidation number. Add to the structure below to show which sulfur–nitrogen bonds are single bonds and which are double bonds.



[1]

(iii) Hence, explain why the calculated bond energy of sulfur–nitrogen bond in S_4N_4 from **(f)(i)** is between that of a S−N bond and a S=N bond.

………………………………………………………………………………………………

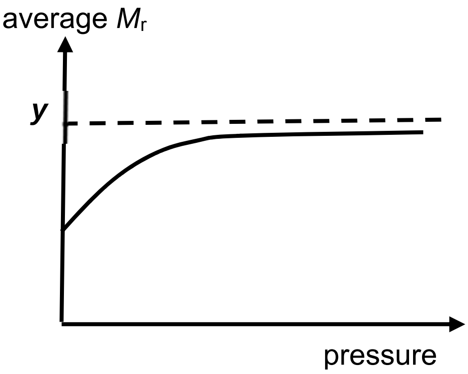
……………………………..………………………………………………………………… .[1]

[Total: 20]

2 **(a)** Dinitrogen tetraoxide, N_2O_4, and nitrogen dioxide, NO_2, exist in dynamic equilibrium with each other as shown below.

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

(i) The diagram below shows the variation of the average molecular mass of the equilibrium mixture with pressure.



Predict a value for ***y*** and account for the shape of the graph.

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....

....

.... [2]

0.0100 mol of inert N_2 with a partial pressure of 0.27 bar and 0.0500 mol of N_2O_4 were placed in a sealed vessel of volume 1.00 dm^3 and temperature of 50 °C. When equilibrium was established, the total pressure of all gases was 1.95 bar.

(ii) With reference to the *Data Booklet*, calculate the average molecular mass, M_r, of the N_2O_4/NO_2 equilibrium mixture. Give your answer to **three** significant figures.

[2]

(iii) Use your answer in **(a)(ii)** to calculate the mole fraction of NO_2 in the N_2O_4/NO_2 equilibrium mixture.

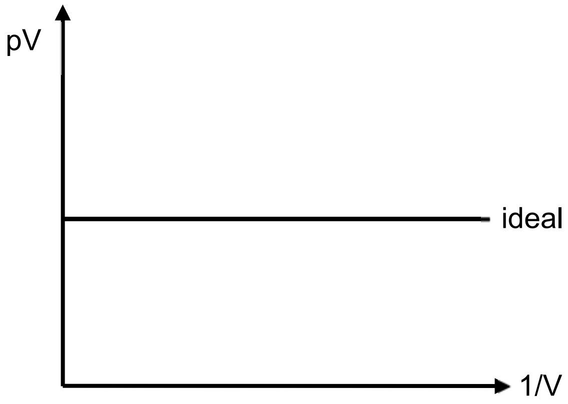
[1]

(iv) Write an expression for the equilibrium constant, K_c, for this N_2O_4/NO_2 equilibrium. Calculate the value of K_c and give its units.

[2]

(v) Sketch and label on the same axes, a graph of variation of pV against 1/V at constant temperature for 1 mol of

(I) N_2O_4, and
(II) NO_2.

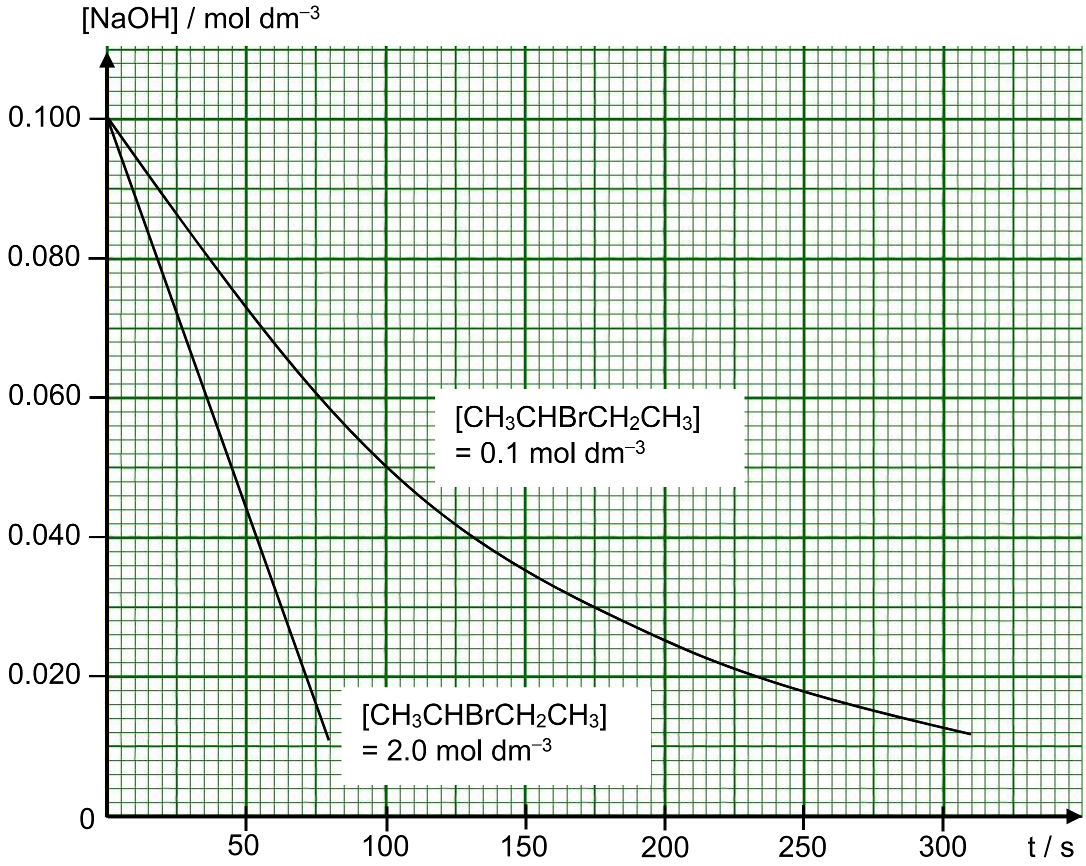


[1]

(b) 2–bromobutane, $CH_3CHBrCH_2CH_3$, is hydrolysed by aqueous sodium hydroxide. The kinetics of the reaction was determined by monitoring the change in concentration of sodium hydroxide with time.

Two sets of experiments were performed using different initial concentrations of 2–bromobutane while the initial concentration of sodium hydroxide was kept at 0.100 mol dm^{-3}.

The following graphs are obtained.



(i) Explain the terms *order of reaction* and *half–life*.

…………………………………………………………………………………………

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

(ii) Use the graphs to determine the order of reaction with respect to

(I) NaOH, and

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(II) $CH_3CHBrCH_2CH_3$

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[2]

(iii) By determining the half–life for the graph of [$CH_3CHBrCH_2CH_3$] = 0.1 mol dm^{-3}, calculate the initial rate at t = 0 min, including its units.

[2]

(iv) Write two elementary equations to show how $CH_3CHBrCH_2CH_3$ and NaOH react.

……………………………………………………………………………………

…………………………………………………………………………………… [1]

(v) $C_6H_5CH_2Br$ reacts with NaOH(aq) via an S_N1 mechanism. Suggest why this may be so.

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…………………………………………………………………………………… [1]

(c) 2–iodobutane, $CH_3CHICH_2CH_3$, exists as two enantiomers, **A** and **B**, which rotate plane–polarised light in opposite directions.

An optically pure sample containing only isomer **A** rotates plane–polarised light by an angle of +15.0°. It reacts with a solution of radioactive iodide, $^{131}I^-$, dissolved in a mixture of ethanol and water. The product mixture is found to rotate plane–polarised light by an angle of −6.4°. The reaction is found to proceed by both the S_N1 and S_N2 mechanisms. If S_N1 and S_N2 mechanisms proceed in a ratio of 1:1, the percentage composition of **B** is 75%.

(i) Determine the percentage composition of **B** in the product mixture. Hence, deduce the predominant mechanism for the above reaction.

[2]

(ii) Describe the S_N2 mechanism for the reaction of $CH_3CHICH_2CH_3$ with $^{131}I^-$.

[2]

[Total: 20]

3 Nickel is widely used as components of fuel cells and batteries. It often occurs in ores along with iron as metal oxides. After the initial reduction of the ore with carbon, a nickel–iron alloy is formed. It can then be purified by an electrolysis technique.

(a) On the other hand, Group 2 metal oxides such as magnesium oxide, are not reduced by carbon. Use relevant data from the *Data Booklet* to explain why carbon can reduce oxides of nickel and iron but not magnesium oxide.

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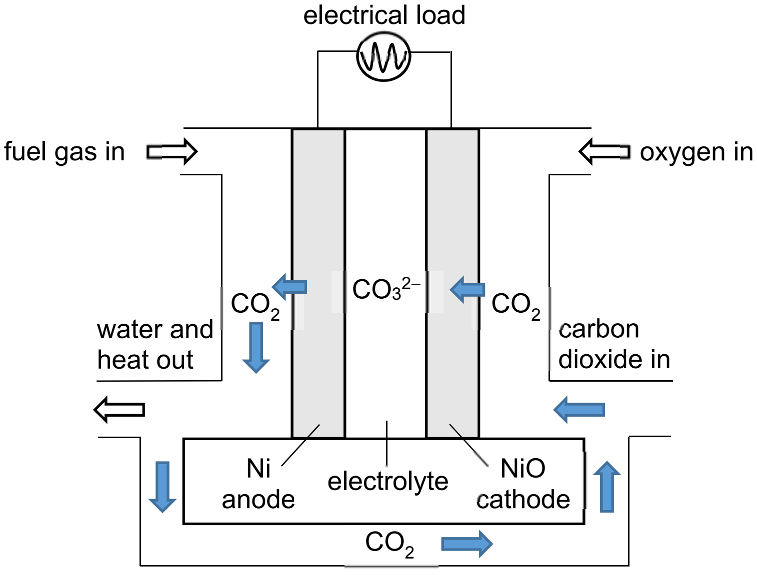
.... [2]

(b) Nickel and nickel(II) oxide are used as electrodes in molten carbonate fuel cells (MCFC).

MCFC operates at temperatures above 650 °C to ensure ionic conductivity of its electrolyte, which is a mixture of lithium carbonate and potassium carbonate.

The high temperature also allows fuel reforming which produces hydrogen gas at the anode for the electrochemical reaction. Fuel gases, such as natural gas and other higher hydrocarbons derived from biomass, could be used with MCFC. The CO_2 generated at the anode is recycled to the cathode where it is consumed as shown in the schematic diagram of MCFC below.



(i) When a hydrocarbon C_xH_y is used as the fuel gas, it undergoes fuel reforming with H_2O at the anode to produce hydrogen gas and carbon monoxide.

Write a balanced equation for the fuel reforming of the hydrocarbon, C_xH_y.

.... [1]

(ii) The fuel reforming is catalysed by the nickel. Explain the mode of action of the nickel catalyst.

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……………………………………………………………………………………… [2]

(iii) Carbonates are generated at the cathode by the reaction between oxygen and carbon dioxide. The carbonate ions then diffuse across the electrolyte to the anode and react with hydrogen gas, generating steam and carbon dioxide.

Write the half–equations at both electrodes and hence give the overall equation for the MCFC.

Cathode: ……………………………………………………………………………..

Anode: ……………………………………………………………………………..

Overall: ……………………………………………………………………………..

[2]

(iv) The temperature of MCFC is kept constant.

With reference to your answer from **(b)(iii)**, state and explain the effect of increasing the partial pressure of oxygen on the cell potential of this MCFC.

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……………………………………………………………………………………… [2]

(c) Biomass from farms could be used to produce fuel gases for MCFC to power an ammonia–making plant for the farming community. The ammonia is manufactured in the following three–step process.

Step 1: Electrolysis of molten lithium hydroxide at 750 K to form lithium metal.

$$4LiOH \rightarrow 4Li + 2H_2O + O_2$$

Step 2: Reaction of lithium metal with nitrogen to form lithium nitride.

$$3Li + \tfrac{1}{2}N_2 \rightarrow Li_3N$$

Step 3: Reaction of lithium nitride with water to re–form lithium hydroxide and ammonia.

$$Li_3N + 3H_2O \rightarrow 3LiOH + NH_3$$

Thus, the lithium hydroxide formed in **Step 3** can be re–used in **Step 1** and the process can be repeated.

(i) The electrolysis will only proceed at an appreciable rate when the applied potential exceeds the cell potential by 0.60 V.

Use appropriate $E^\ominus$ values from the *Data Booklet* to calculate the minimum potential that should be applied in **Step 1**.

[2]

(ii) State the ratio between the lithium produced in **Step 1** and the ammonia produced in **Step 3**.

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

(iii) A farm requires 0.0770 tonnes of ammonia per acre annually.

If the lithium hydroxide was not recycled at the end of the process, calculate the total mass of lithium (in tonnes) that would have to be produced to generate the required mass of ammonia for a farm of 100 acres in a year.

[1 tonne = 10^6 g]

[2]

(d) Unlike lithium carbonate and potassium carbonate, a mixture of Group 2 carbonates consisting of magnesium carbonate and barium carbonate is **not** a suitable electrolyte for the molten carbonate fuel cell (MCFC) in **(b)**. For each of the carbonates, suggest a reason why it is not a suitable electrolyte.

Magnesium carbonate:

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……………………………………………………………………………………………...

Barium carbonate:

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[2]

(e) A solution contains 0.100 mol dm^{-3} magnesium nitrate and 0.100 mol dm^{-3} barium nitrate. Solid sodium carbonate is added slowly to 100 cm^3 of this solution.
[$K_{sp}(MgCO_3) = 3.5 \times 10^{-8}$ mol^2 dm^{-6}; $K_{sp}(BaCO_3) = 5.1 \times 10^{-9}$ mol^2 dm^{-6}]

(i) State which metal ion is first precipitated. Calculate the concentration of carbonate ions in the solution needed for the first trace of precipitate to be seen.

[1]

(ii) Determine the concentration of the metal ion stated in **(e)(i)** when the other metal ion just begins to precipitate.

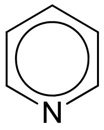
[2]

(iii) The separation is considered effective when less than 1% of the metal ion remains in the solution. Hence, deduce if the above separation is effective.

[1]

[Total: 20]

4 **(a)** Pyridine is an aromatic planar molecule similar to benzene. Unlike benzene, pyridine can act as a Bronsted–Lowry base and a nucleophile.



pyridine

(i) State the type of hybridisation of the nitrogen atom in pyridine.

.... [1]

(ii) Hence, explain why pyridine has a higher pK_b than ethylamine, $CH_3CH_2NH_2$.

....

....

.... [1]

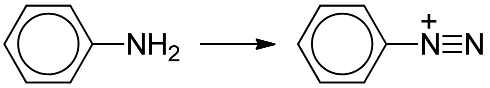
(iii) Write a balanced equation to show that pyridine is acting as

a Bronsted–Lowry base

a Lewis base but not a Bronsted–Lowry base

[2]

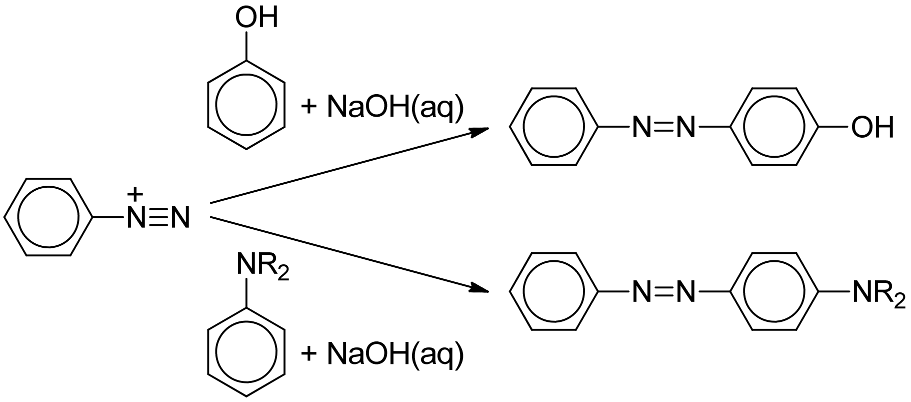
(b) Phenylamine and subsituted phenylamines are used to make dyes and food colourants. The first step in this process is the production of a diazonium ion as shown.



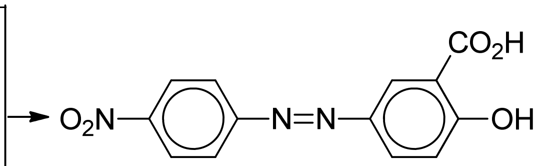
(i) State the type of reaction.

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

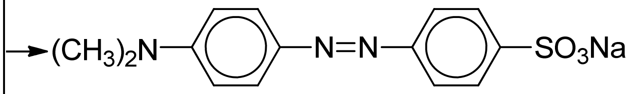
The diazonium ion is then reacted with a phenol or an arylamine in alkaline solution.



(ii) Suggest the starting compounds needed to synthesise the following dyes. Draw their full structural formulae in the boxes provided.



alizarin yellow R



methyl orange

[4]

(iii) The benzene ring containing the NaO_3S- group in methyl orange is less reactive towards bromine than the other benzene ring. Suggest **two** reasons.

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………………………………………………………………………………………………

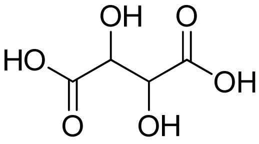
……………………………………………………………………………………… [2]

(iv) Alizarin yellow R exhibits stereoisomerism and is a common indicator for acid−base titrations.

Draw the stereoisomers of alizarin yellow R.

[1]

(c) Tartaric acid is present in many plants.

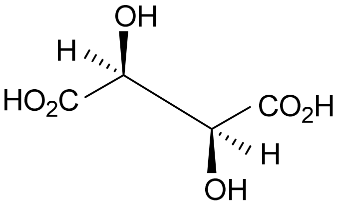


tartaric acid

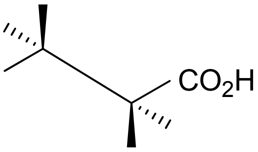
(i) Tartaric acid has two acid dissociation constants, K_{a1} and K_{a2}, for which the pK_a values are 2.99 and 4.40. Draw the species present at pH 4.40.

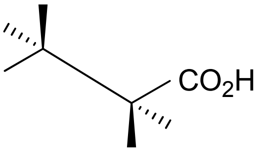
[1]

(ii) One stereoisomer of tartaric acid is shown below.



Complete the diagrams below to show two other stereoisomers of tartaric acid.





[2]

[Total: 15]

End of Paper

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

1 **(a)** Bromine exists naturally as a mixture of two stable isotopes, ^{79}Br and ^{81}Br, in a 1:1 ratio.

(i) Write down the full electronic configuration of $^{79}Br^{2+}$.

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

[1]

(ii) Define the term *relative isotopic mass*.

Mass of an atom of isotope relative to $\frac{1}{12}$ the mass of an atom of carbon–12 isotope.

[1]

(b) Chlorine atom exists naturally as two isotopes, ^{35}Cl and ^{37}Cl, in a 3:1 ratio. When equimolar amounts of bromine and chlorine were mixed together, an interhalogen compound, BrC*l*, is formed. The product mixture contains four species with three different mass numbers 114, 116 and 118. $^{79}Br^{35}Cl$ is one of the four species.

(i) With the help of the information given in **(a)**, state the species that corresponds to each mass number. Hence, calculate the relative abundance for each mass number.

mass number	species	relative abundance
114	$^{79}Br^{35}Cl$	$\frac{1}{2} \times \frac{3}{4} = \frac{3}{8}$
116	$^{79}Br^{37}Cl$ and $^{81}Br^{35}Cl$	$(\frac{1}{2} \times \frac{1}{4}) + (\frac{1}{2} \times \frac{3}{4}) = \frac{1}{2}$
118	$^{81}Br^{37}Cl$	$\frac{1}{2} \times \frac{1}{4} = \frac{1}{8}$

[3]

(ii) Explain whether BrC*l* or Cl_2 has a greater enthalpy change of vaporisation.

BrC*l* has a greater enthalpy change of vaporisation as it has stronger instantaneous dipole–induced dipole interactions due to the greater number of electrons in the larger BrC*l* molecule.

OR
BrC*l* has a greater enthalpy change of vaporisation as it is polar with stronger permanent dipole–permanent dipole interactions than the instantaneous dipole–induced dipole interactions in Cl_2.

[1]

(iii) Suggest with a reason how the first ionisation energy of ^{79}Br is compared to ^{81}Br.

First ionisation energy of ^{79}Br is the same as that of ^{81}Br because they have the same number of protons.

[1]

(c) Bromine reacts with an element **A** to form a compound with empirical formula **A**Br_3. The percentage by mass of **A** in **A**Br_3 is 4.31%. Calculate the relative atomic mass of **A**.

Let A_r of A be y.

Element	**A**	**Br**
No. of moles/mol	$\frac{4.31}{y}$	$\frac{100-4.31}{79.9}$

Mole ratio of A : Br = 1 : 3 = $\frac{4.31}{y} : \frac{100-4.31}{79.9}$

No. of moles of Br atoms = 3 × no. of moles of A atoms

$\frac{100-4.31}{79.9} = 3 \times \frac{4.31}{y}$

y = 10.8

[1]

(d) Bromine and fluorine react to form the pale yellow liquid, bromine trifluoride, as shown in **Reaction 1**.

Reaction 1 $Br_2(l) + 3F_2(g) \rightarrow 2BrF_3(l)$

Some thermochemical data are given below.

Standard enthalpy change of formation of $BrF_3(l)$ / kJ mol^{-1}	–301
Standard Gibbs free energy change of formation of $BrF_3(l)$ / kJ mol^{-1}	–241
Standard entropy of $Br_2(l)$, $S^⦵(Br_2)$ / J mol^{-1} K^{-1}	152
Standard entropy of $BrF_3(l)$, $S^⦵(BrF_3)$ / J mol^{-1} K^{-1}	178

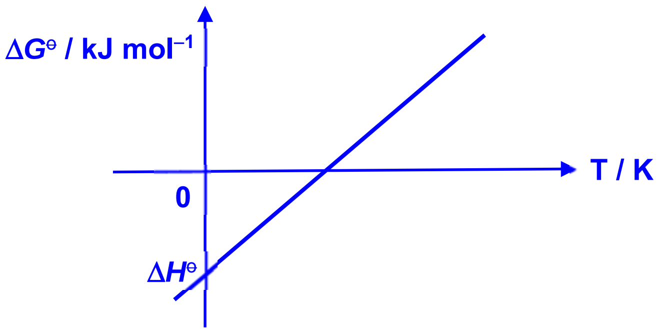
(i) The above reaction is spontaneous at 298 K even though $\Delta S^⦵$ is negative. Explain qualitatively why $\Delta H^⦵$ is the predominant factor that causes the reaction to be spontaneous.

$\Delta G^⦵ = \Delta H^⦵ - T\Delta S^⦵ < 0$ at 298 K

$\Delta H^⦵$ is the predominant factor as it is exothermic (or negative) and drives the reaction.

[1]

(ii) Sketch a graph to show how $\Delta G^⦵$ varies with temperature in K for **Reaction 1**. Label the y–intercept.



[1]

(iii) Given that $\Delta S^\ominus = 2 \times S^\ominus(BrF_3) - [S^\ominus(Br_2) + 3 \times S^\ominus(F_2)]$ for **Reaction 1**, calculate the standard entropy of $F_2(g)$, $S^\ominus(F_2)$, at 298 K.

$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$
$\Delta S^\ominus = (\Delta H^\ominus - \Delta G^\ominus) / T$
$= 2(-301 + 241) \times 10^3 / 298$
$= -403 \text{ J mol}^{-1} \text{ K}^{-1}$

$-403 = 2(178) - [152 + 3S^\ominus(F_2)]$
$S^\ominus(F_2) = 202 \text{ J mol}^{-1} \text{ K}^{-1}$

[2]

(e) Similar to water, liquid BrF_3 can be used as a solvent and it undergoes minimal self–ionisation.

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$
$$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

When $(BrF_2^+)_2(SnF_6^{2-})$ and $Ag^+(BrF_4^-)$ react in BrF_3, an insoluble Ag_2SnF_6 is formed.

(i) Construct an equation for the reaction between $(BrF_2^+)_2(SnF_6^{2-})$ and $Ag^+(BrF_4^-)$.

$(BrF_2^+)_2(SnF_6^{2-}) + 2Ag^+(BrF_4^-) \rightarrow 4BrF_3 + Ag_2SnF_6$

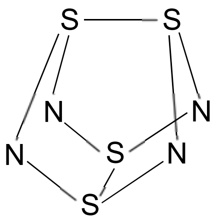
[1]

(ii) State and draw the shapes of BrF_2^+ and BrF_4^-, including lone pairs of electrons.

bent	square planar
BrF_2^+	BrF_4^-

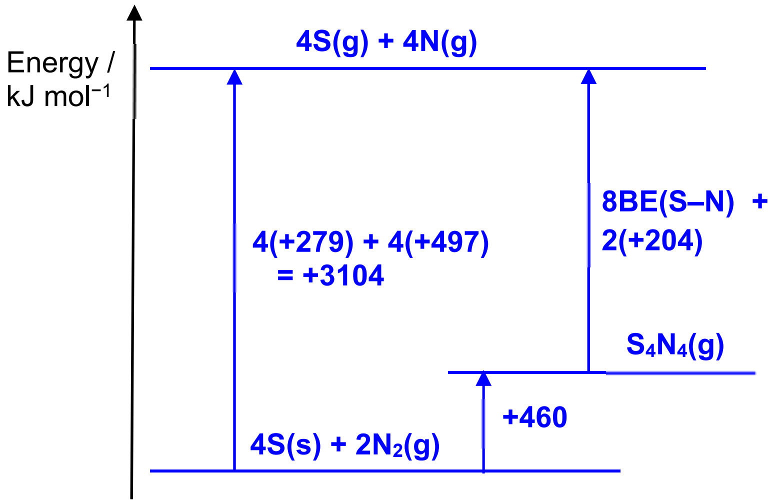
[2]

(f) One of the most readily prepared sulfur nitrides is S_4N_4, which can be made by passing dry $NH_3(g)$ into a solution of SCl_2 in an organic solvent. A proposed structure of the molecule of S_4N_4 is shown below.



(i) Using the data given below, construct a suitable energy level diagram to calculate the S–N bond energy in S_4N_4.

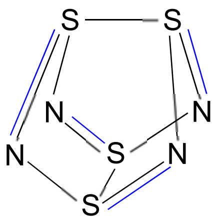
$\Delta H_f^\ominus [S_4N_4(g)] = +460\ kJ\ mol^{-1}$
$\Delta H_{at}^\ominus [S(s)] = +279\ kJ\ mol^{-1}$
$\Delta H_{at}^\ominus [\text{nitrogen}] = +497\ kJ\ mol^{-1}$
Bond energy of (S–S) in S_4N_4 = +204 kJ mol^{-1}



By Hess's Law,
$8BE(S\text{–}N) + 2(+204) = -(+460) + 3104$
$BE(S\text{–}N) = +279.5\ kJ\ mol^{-1}$

[3]

(ii) The nitrogen atoms in S_4N_4 show their usual valency of 3. All four sulfur atoms have the same oxidation number. Add to the structure below to show which sulfur–nitrogen bonds are single bonds and which are double bonds.



[1]

(iii) Hence, explain why the calculated bond energy of sulfur–nitrogen bond in S_4N_4 from **(f)(i)** is between that of a S−N bond and a S=N bond.

This is due to the delocalisation of pi electrons / formation of resonance structures between the two sulfur−nitrogen bonds in S−N−S / N−S−N.

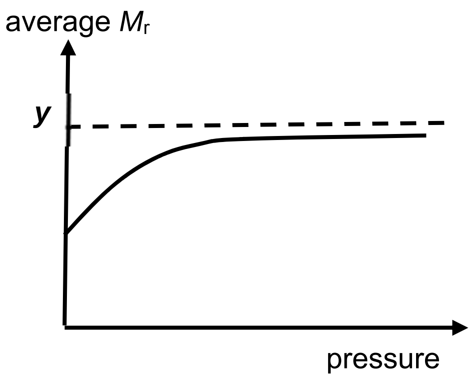
[1]

[Total: 20]

2 **(a)** Dinitrogen tetraoxide, N_2O_4, and nitrogen dioxide, NO_2, exist in dynamic equilibrium with each other as shown below.

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

(i) The diagram below shows the variation of the average molecular mass of the equilibrium mixture with pressure.



Predict a value for ***y*** and account for the shape of the graph.

y = 2(14.0) + 4(16.0) = 92.0
By Le Chatelier's Principle, as pressure increases, the position of equilibrium would shift left to decrease the amount of gaseous molecules. Hence, more N_2O_4 will be produced and average M_r increases.

[2]

0.0100 mol of inert N_2 with a partial pressure of 0.27 bar and 0.0500 mol of N_2O_4 were placed in a sealed vessel of volume 1.00 dm^3 and temperature of 50 °C. When equilibrium was established, the total pressure of all gases was 1.95 bar.

(ii) With reference to the *Data Booklet*, calculate the average molecular mass, M_r, of the N_2O_4/NO_2 equilibrium mixture. Give your answer to **three** significant figures.

Mass of N_2O_4 initially = Total mass of N_2O_4 and NO_2 at equilibrium
= 0.0500 × 92.0
= 4.60 g

Total pressure of N_2O_4 and NO_2 at equilibrium
= 1.95 – 0.27
= 1.68 bar

$$pV = nRT = \frac{m}{M_r}RT$$
$$1.68 \times 10^5 \times 1.00 \times 10^{-3} = \frac{4.60}{M_r} \times 8.31 \times (273 + 50)$$
$$M_r = 73.5$$

[2]

(iii) Use your answer in **(a)(ii)** to calculate the mole fraction of NO_2 in the N_2O_4/NO_2 equilibrium mixture.

Let the mole fraction of NO_2 be z. Then the mole fraction of N_2O_4 is $(1 – z)$.

$$46z + 92(1 - z) = 73.5$$
$$z = 0.402$$

[1]

(iv) Write an expression for the equilibrium constant, K_c, for this N_2O_4/NO_2 equilibrium. Calculate the value of K_c and give its units.

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

Total number of moles of N_2O_4 and NO_2 at equilibrium
= 4.60 ÷ 73.5
= 0.0626 mol

n_{NO_2}
$= 0.402 \times 0.0626$
= 0.0252 mol

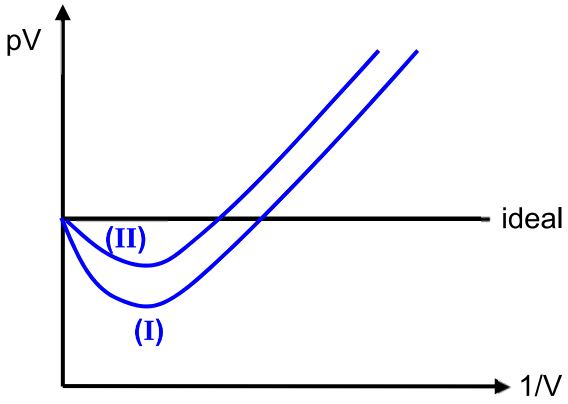
$n_{N_2O_4}$
= 0.0626 – 0.0252
= 0.0374 mol

$$K_c = \frac{(0.0252)^2}{0.0374}$$
$$= 0.0170 \text{ mol dm}^{-3}$$

[2]

(v) Sketch and label on the same axes, a graph of variation of pV against 1/V at constant temperature for 1 mol of

(I) N_2O_4, and
(II) NO_2.

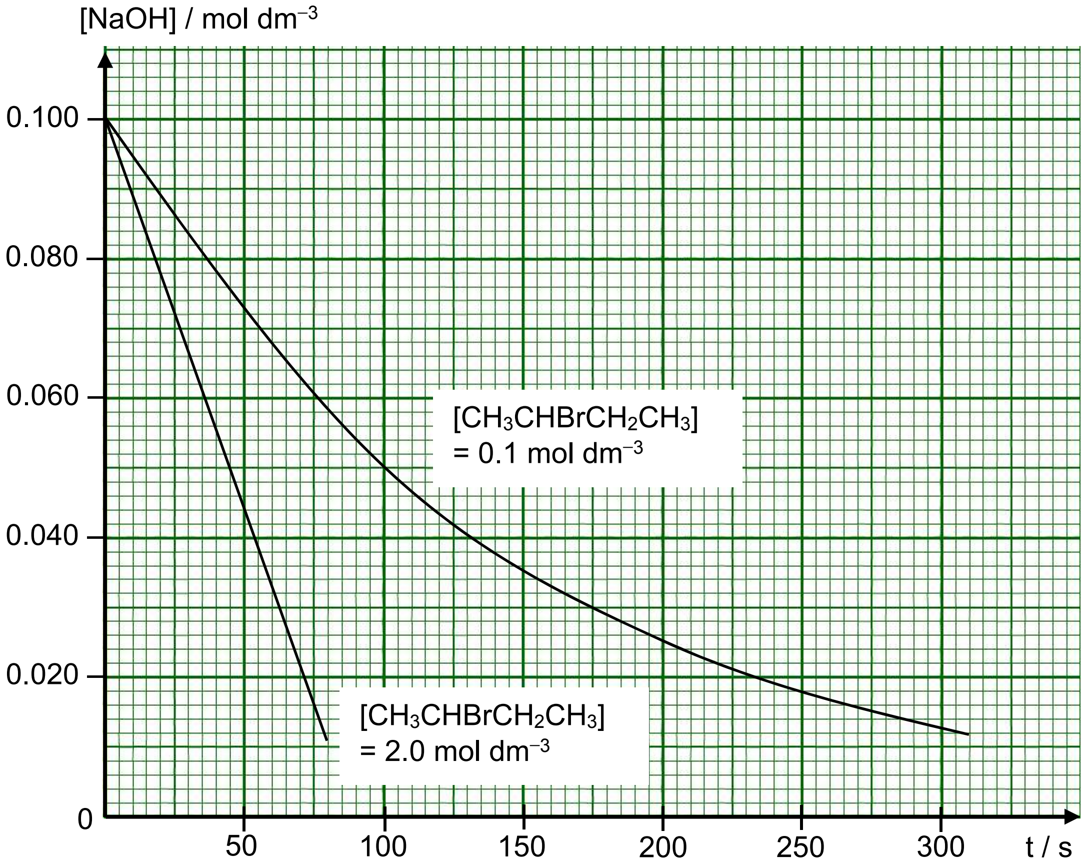


[1]

(b) 2–bromobutane, $CH_3CHBrCH_2CH_3$, is hydrolysed by aqueous sodium hydroxide. The kinetics of the reaction was determined by monitoring the change in concentration of sodium hydroxide with time.

Two sets of experiments were performed using different initial concentrations of 2–bromobutane while the initial concentration of sodium hydroxide was kept at 0.100 mol dm^{-3}.

The following graphs are obtained.



(i) Explain the terms *order of reaction* and *half–life*.

The order of reaction with respect to a given reactant is the power to which the concentration of that reactant is raised to in the rate equation.

The half–life ($t_{1/2}$) of a reaction is the time taken for the concentration of a reactant to decrease to half its initial value.

[2]

(ii) Use the graphs to determine the order of reaction with respect to

(I) NaOH, and

When [$CH_3CHBrCH_2CH_3$] = 2.0 mol dm^{-3}, $CH_3CHBrCH_2CH_3$ is in excess and has pseudo zeroth order. From the graph of [$CH_3CHBrCH_2CH_3$] = 2.0 mol dm^{-3}, rate is a constant as seen from the constant gradient.

Thus, order of reaction wrt NaOH is zero.

(II) $CH_3CHBrCH_2CH_3$

From the graph of [$CH_3CHBrCH_2CH_3$] = 0.1 mol dm^{-3}, $t_{1/2}$ is constant.

Thus, order of reaction wrt $CH_3CHBrCH_2CH_3$ is one.

[2]

(iii) By determining the half–life for the graph of $[CH_3CHBrCH_2CH_3] = 0.1$ mol dm^{-3}, calculate the initial rate at t = 0 min, including its units.

$t_{1/2} = 100$ s
$k = \ln 2 \div 100$
$k = 6.93 \times 10^{-3}$ s^{-1}

Rate $= k\,[CH_3CHBrCH_2CH_3]$
$= 6.93 \times 10^{-3} \times 0.1$
$= 6.93 \times 10^{-4}$ mol dm^{-3} s^{-1}

[2]

(iv) Write two elementary equations to show how $CH_3CHBrCH_2CH_3$ and NaOH react.

$CH_3CHBrCH_2CH_3 \rightarrow CH_3\overset{+}{C}HCH_2CH_3 + Br^-$ slow

$CH_3\overset{+}{C}HCH_2CH_3 + OH^- \rightarrow CH_3CH(OH)CH_2CH_3$ fast

[1]

(v) $C_6H_5CH_2Br$ reacts with NaOH(aq) via an S_N1 mechanism. Suggest why this may be so.

The carbocation from $C_6H_5CH_2Br$ is resonance–stabilised as the positive charge can delocalise into the benzene ring.

[1]

(c) 2–iodobutane, $CH_3CHICH_2CH_3$, exists as two enantiomers, **A** and **B**, which rotate plane–polarised light in opposite directions.

An optically pure sample containing only isomer **A** rotates plane–polarised light by an angle of +15.0°. It reacts with a solution of radioactive iodide, $^{131}I^-$, dissolved in a mixture of ethanol and water. The product mixture is found to rotate plane–polarised light by an angle of −6.4°. The reaction is found to proceed by both the S_N1 and S_N2 mechanisms. If S_N1 and S_N2 mechanisms proceed in a ratio of 1:1, the percentage composition of **B** is 75%.

(i) Determine the percentage composition of **B** in the product mixture. Hence, deduce the predominant mechanism for the above reaction.

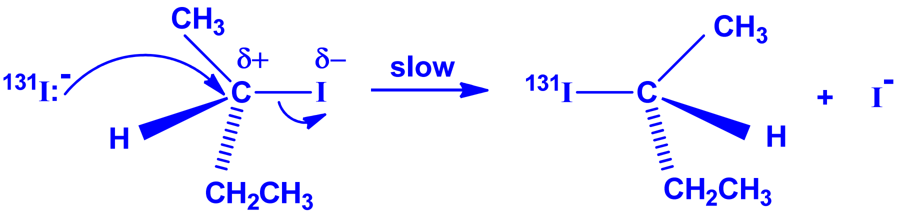
Let the percentage composition of B be *z*% and the percentage composition of A be (100 – *z*)%.

$$(-15.0^\circ)\left(\frac{z}{100}\right) + (+15.0^\circ)\left(\frac{100 - z}{100}\right) = -6.4^\circ$$
$z = 71.3\%$

Since percenatge composition of B is less than 75 %, the predominant mechanism is <u>S_N1</u>.

[2]

(ii) Describe the S$_N$2 mechanism for the reaction of $CH_3CHICH_2CH_3$ with $^{131}I^-$.



[2]

[Total: 20]

3 Nickel is widely used as components of fuel cells and batteries. It often occurs in ores along with iron as metal oxides. After the initial reduction of the ore with carbon, a nickel–iron alloy is formed. It can then be purified by an electrolysis technique.

(a) On the other hand, Group 2 metal oxides such as magnesium oxide, are not reduced by carbon. Use relevant data from the *Data Booklet* to explain why carbon can reduce oxides of nickel and iron but not magnesium oxide.

From *Data Booklet*,
$E^\ominus(Mg^{2+}|Mg) = -2.38$ V
$E^\ominus(Ni^{2+}|Ni) = -0.25$ V
$E^\ominus(Fe^{2+}|Fe) = -0.44$ V
$E^\ominus(Fe^{3+}|Fe) = -0.04$ V

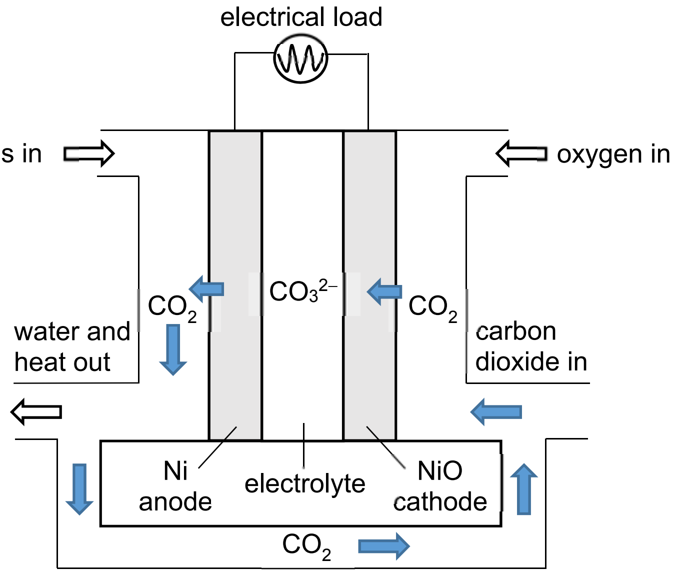
Standard reduction potential, $E^\ominus$, for nickel and iron are both much less negative than that of magnesium.

[2]

(b) Nickel and nickel(II) oxide are used as electrodes in molten carbonate fuel cells (MCFC).

MCFC operates at temperatures above 650 °C to ensure ionic conductivity of its electrolyte, which is a mixture of lithium carbonate and potassium carbonate.

The high temperature also allows fuel reforming which produces hydrogen gas at the anode for the electrochemical reaction. Fuel gases, such as natural gas and other higher hydrocarbons derived from biomass, could be used with MCFC. The CO_2 generated at the anode is recycled to the cathode where it is consumed as shown in the schematic diagram of MCFC below.



(i) When a hydrocarbon C_xH_y is used as the fuel gas, it undergoes fuel reforming with H_2O at the anode to produce hydrogen gas and carbon monoxide.

Write a balanced equation for the fuel reforming of the hydrocarbon, C_xH_y.

$C_xH_y + xH_2O \rightarrow (x + y/2)H_2 + xCO$

[1]

(ii) The fuel reforming is catalysed by the nickel. Explain the mode of action of the nickel catalyst.

Nickel is a heterogeneous catalyst.
Gaseous reactants are adsorbed on the Ni surface through forming weak bonds with the active sites of the catalyst.
This weakens the covalent bonds within the reactant molecules.
High concentration of reactants on the catalyst surface come into close contact with proper orientation for reaction to occur.
Products desorb from the surface of the catalyst.

[2]

(iii) Carbonates are generated at the cathode by the reaction between oxygen and carbon dioxide. The carbonate ions then diffuse across the electrolyte to the anode and react with hydrogen gas, generating steam and carbon dioxide.

Write the half–equations at both electrodes and hence give the overall equation for the MCFC.

Cathode: $O_2(g) + 2CO_2(g) + 4e^- \rightarrow 2CO_3^{2-}(l)$
Anode: $H_2(g) + CO_3^{2-}(l) \rightarrow H_2O(g) + CO_2(g) + 2e^-$
Overall: $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$

[2]

(iv) The temperature of MCFC is kept constant.

With reference to your answer from **(b)(iii)**, state and explain the effect of increasing the partial pressure of oxygen on the cell potential of this MCFC.

Higher partial pressure of O_2 would cause the position of equilibrium of the overall reaction to shift to the right to decrease the amount of gaseous oxygen.
The cell potential becomes more positive. [2]

(c) Biomass from farms could be used to produce fuel gases for MCFC to power an ammonia–making plant for the farming community. The ammonia is manufactured in the following three–step process.

Step 1: Electrolysis of molten lithium hydroxide at 750 K to form lithium metal.

$$4LiOH \rightarrow 4Li + 2H_2O + O_2$$

Step 2: Reaction of lithium metal with nitrogen to form lithium nitride.

$$3Li + \tfrac{1}{2}N_2 \rightarrow Li_3N$$

Step 3: Reaction of lithium nitride with water to re–form lithium hydroxide and ammonia.

$$Li_3N + 3H_2O \rightarrow 3LiOH + NH_3$$

Thus, the lithium hydroxide formed in **Step 3** can be re–used in **Step 1** and the process can be repeated.

(i) The electrolysis will only proceed at an appreciable rate when the applied potential exceeds the cell potential by 0.60 V.

Use appropriate $E^\ominus$ values from the *Data Booklet* to calculate the minimum potential that should be applied in **Step 1**.

$E^\ominus(Li^+|Li) = -3.04$ V
$E^\ominus(O_2|OH^-) = +0.40$ V

$E^\ominus_{cell}$
$= |-3.04 - (+0.40)|$
$= 3.44$ V

Minimum potential
$= 3.44 + 0.60$
$= 4.04$ V

[2]

(ii) State the ratio between the lithium produced in **Step 1** and the ammonia produced in **Step 3**.

Ratio of Li : NH_3 = 3 : 1

[1]

(iii) A farm requires 0.0770 tonnes of ammonia per acre annually.

If the lithium hydroxide was not recycled at the end of the process, calculate the total mass of lithium (in tonnes) that would have to be produced to generate the required mass of ammonia for a farm of 100 acres in a year.

[1 tonne = 10^6 g]

Mass of NH_3 needed for 100 acres in a year
= $0.0770 \times 10^6 \times 100$
= 7.70×10^6 g

Amount of NH_3
= $7.70 \times 10^6 \div 17.0$
= 4.53×10^5 mol

Amount of Li required
= $3 \times 4.53 \times 10^5$
= 1.36×10^6 mol

Mass of Li required
= $1.36 \times 10^6 \times 6.9$
= 9.38×10^6 g
= 9.38 tonnes

[2]

(d) Unlike lithium carbonate and potassium carbonate, a mixture of Group 2 carbonates consisting of magnesium carbonate and barium carbonate is **not** a suitable electrolyte for the molten carbonate fuel cell (MCFC) in **(b)**. For each of the carbonates, suggest a reason why it is not a suitable electrolyte.

Magnesium carbonate:

Mg^{2+} ion has greater charge density than Group 1 ion and hence polarising the electron cloud of CO_3^{2-} to a greater extent. This causes lower thermal stability.

$MgCO_3$ may undergo thermal decomposition at the high operating temperature of the fuel cell, forming CO_2, depleting the source of CO_3^{2-}.

Barium carbonate:

$BaCO_3$ may have a higher melting point than the operating temperature.

There will be no charge carriers in the electrolyte if the carbonate does not melt.

[2]

(e) A solution contains 0.100 mol dm^{-3} magnesium nitrate and 0.100 mol dm^{-3} barium nitrate. Solid sodium carbonate is added slowly to 100 cm^3 of this solution.
[$K_{sp}(MgCO_3) = 3.5 \times 10^{-8}$ mol^2 dm^{-6}; $K_{sp}(BaCO_3) = 5.1 \times 10^{-9}$ mol^2 dm^{-6}]

(i) State which metal ion is first precipitated. Calculate the concentration of carbonate ions in the solution needed for the first trace of precipitate to be seen.

Since K_{sp} of $BaCO_3$ is smaller (lower solubility), Ba^{2+} is precipitated first.

$K_{sp} = [Ba^{2+}][CO_3^{2-}] = 5.1 \times 10^{-9}$
$0.100 \times [CO_3^{2-}] = 5.1 \times 10^{-9}$
$[CO_3^{2-}] = 5.1 \times 10^{-8}$ mol dm^{-3}

[1]

(ii) Determine the concentration of the metal ion stated in **(e)(i)** when the other metal ion just begins to precipitate.

$[CO_3^{2-}]$ when Mg^{2+} starts to precipitate
$= 3.5 \times 10^{-8} \div 0.100$
$= 3.5 \times 10^{-7}$ mol dm^{-3}

Using K_{sp} of $BaCO_3$,
$[Ba^{2+}] \times 3.5 \times 10^{-7} = 5.1 \times 10^{-9}$
$[Ba^{2+}] = 0.0146$ mol dm^{-3}

[2]

(iii) The separation is considered effective when less than 1% of the metal ion remains in the solution. Hence, deduce if the above separation is effective.

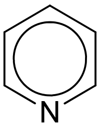
Percentage of Ba^{2+} ions remained
$= \frac{0.0146}{0.100} \times 100\%$ (ecf)
$= 14.6\% >> 1\%$

The above separation is not effective.

[1]

[Total: 20]

4 **(a)** Pyridine is an aromatic planar molecule similar to benzene. Unlike benzene, pyridine can act as a Bronsted–Lowry base and a nucleophile.



pyridine

(i) State the type of hybridisation of the nitrogen atom in pyridine.

sp^2 hybridisation

[1]

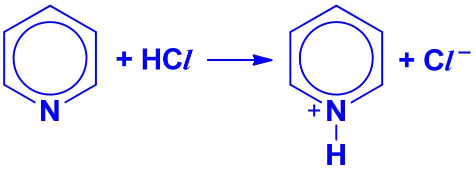
(ii) Hence, explain why pyridine has a higher pK_b than ethylamine, $CH_3CH_2NH_2$.

The nitrogen atom in pyridine is sp^2 hybridised while that in ethylamine is sp^3 hybridised.
Hence, the lone pair of electrons in pyridine is less available for donation as it is more strongly attracted by / closer to the nucleus.

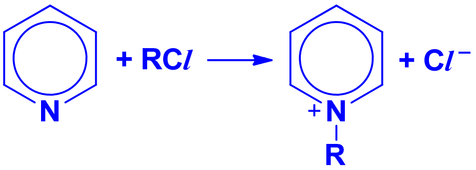
[1]

(iii) Write a balanced equation to show that pyridine is acting as

a Bronsted–Lowry base

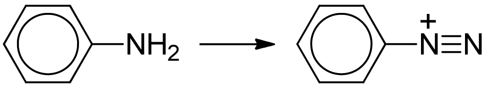


a Lewis base but not a Bronsted–Lowry base



[2]

(b) Phenylamine and subsituted phenylamines are used to make dyes and food colourants. The first step in this process is the production of a diazonium ion as shown.

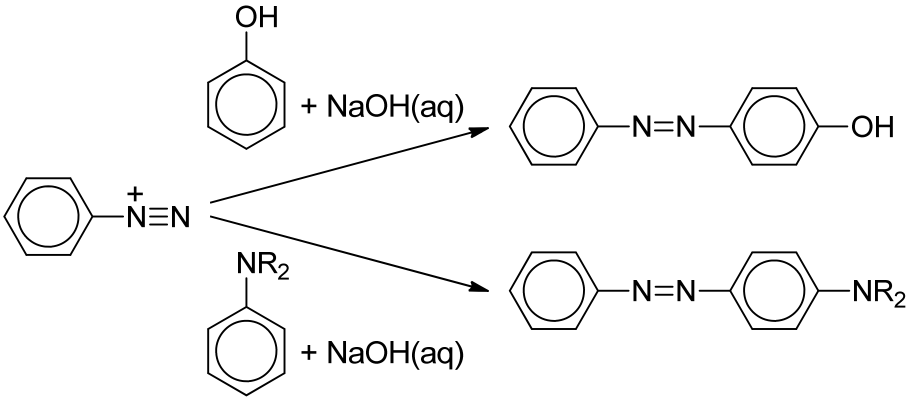


(i) State the type of reaction.

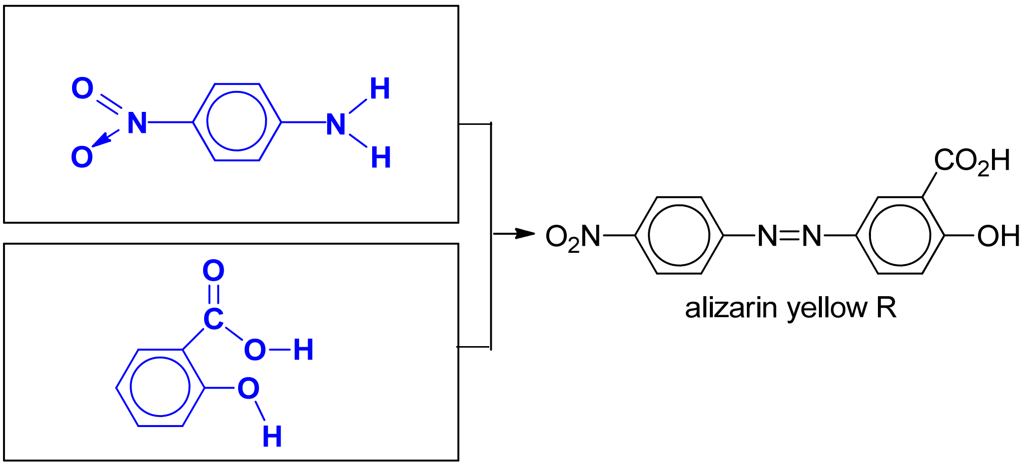
Oxidation

[1]

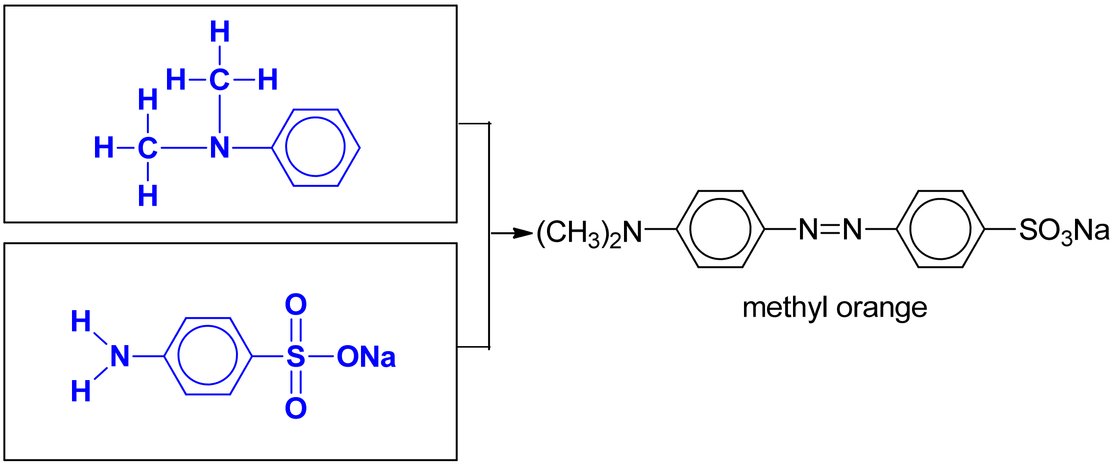
The diazonium ion is then reacted with a phenol or an arylamine in alkaline solution.



(ii) Suggest the starting compounds needed to synthesise the following dyes. Draw their full structural formulae in the boxes provided.



alizarin yellow R



methyl orange

[4]

(iii) The benzene ring containing the NaO_3S- group in methyl orange is less reactive towards bromine than the other benzene ring. Suggest **two** reasons.

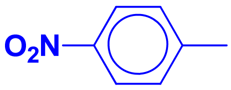
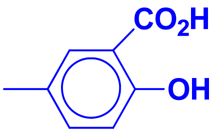
NaO_3S- group is an electron withdrawing group, making the benzene ring less electron–rich and less susceptible to electrophilic attack.

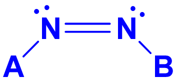
Lone pair of electrons on $-N(CH_3)_2$ can delocalise into the benzene ring, making the benzene ring more electron–rich and more susceptible to electrophilic attack.

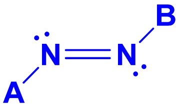
[2]

(iv) Alizarin yellow R exhibits stereoisomerism and is a common indicator for acid−base titrations.

Draw the stereoisomers of alizarin yellow R.

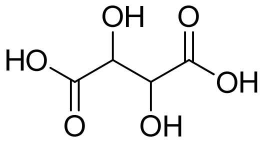
Let A be . **Let B be** .





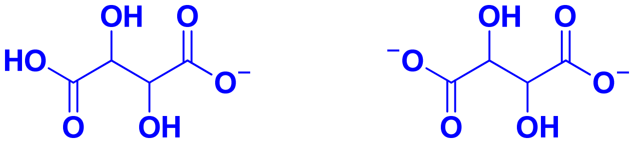
[1]

(c) Tartaric acid is present in many plants.



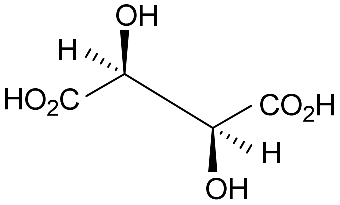
tartaric acid

(i) Tartaric acid has two acid dissociation constants, K_{a1} and K_{a2}, for which the pK_a values are 2.99 and 4.40. Draw the species present at pH 4.40.

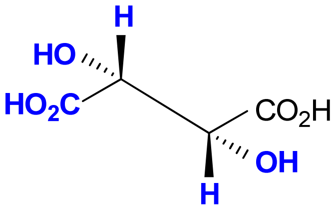


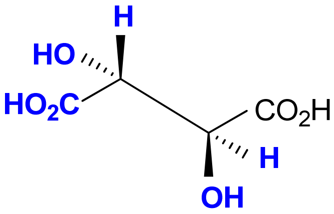
[1]

(ii) One stereoisomer of tartaric acid is shown below.



Complete the diagrams below to show two other stereoisomers of tartaric acid.





[2]

[Total: 15]

Section A

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

1 **(a)** All the elements in the third period of the Periodic Table, sodium to sulfur, form chlorides by direct combination with chlorine. Aluminium chloride may be produced by passing a stream of chlorine over heated aluminium metal in a long hard–glass tube.

(i) With the aid of equations, explain the following observations when different amounts of water were added to solid aluminium chloride.

(I) When a limited amount of water was added, a white solid was formed together with steamy fumes.

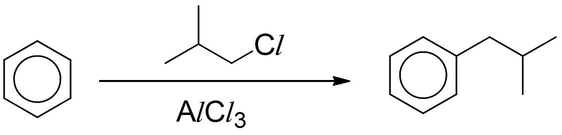
(II) When excess water was added, a solution of pH 3 was obtained. [2]

(ii) Both aluminium chloride and copper(I) complex solutions are colourless whereas a solution of copper(II) sulfate appears blue.
Explain these observations. [3]

(iii) Briefly describe the process of anodisation of aluminium. Write ion-electron equations for the reactions occurring at the anode and the cathode. [2]

(b) Compound **A** can be synthesised from benzene using aluminium chloride via a simple Friedel–Crafts alkylation as shown in **Reaction 1**. In addition, compound **B**, an isomer of compound **A** is also formed.

Reaction 1:



\+ compound **B**

compound **A**

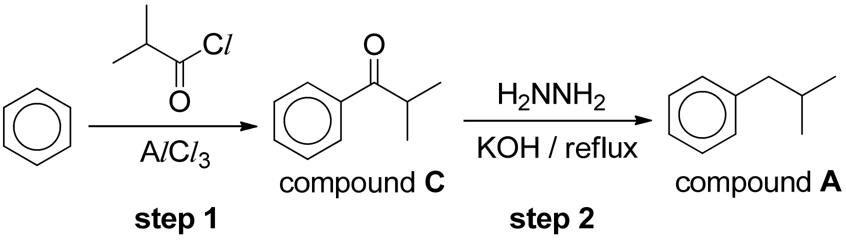
(i) Compound **B** rotates plane-polarised light. It is formed after the carbocation intermediate undergoes rearrangement through the movement of an alkyl group to an adjacent carbon atom bearing the positive charge.

Draw the structure of compound **B**. Explain why the rearrangement of the carbocation is favoured. [2]

(ii) Explain why multi-substituted product is more favoured over mono-substituted product in **Reaction 1**. [1]

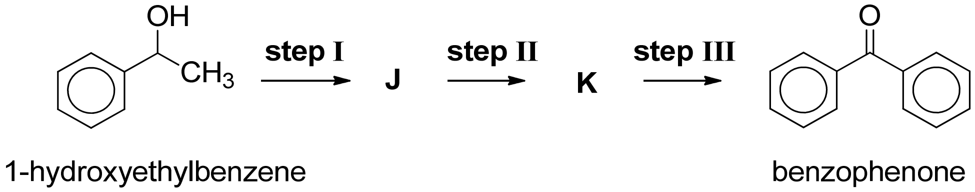
(c) Compound **A** can be formed via compound **C** as shown in **Reaction 2** below. **Step 1** involves Friedel–Crafts acylation, which have similar reaction conditions and mechanism as Friedel-Crafts alkylation.

Reaction 2:



(i) Draw the mechanism for **step 1**. In your answer, show relevant charges, lone pairs of electrons and movement of electrons. [3]

(ii) Hence, suggest reagents and conditions for **steps I** to **III** in the following synthesis of benzophenone from 1-hydroxyethylbenzene. Give the structural formulae of **J** and **K**.



[4]

(d) A student wants to synthesise benzophenone using the reaction pathway illustrated in **(c)(ii)**. However, the solid sample of 1-hydroxyethylbenzene is contaminated with phenylamine. Briefly explain how you can separate 1-hydroxyethylbenzene from phenylamine via extraction. You are provided with

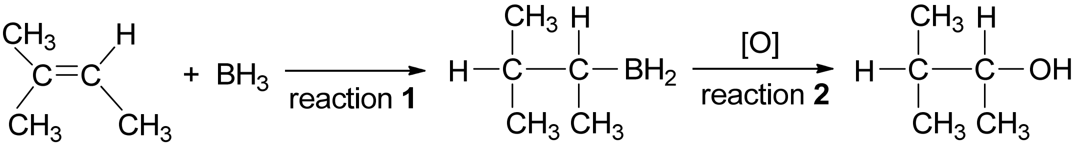
- ethanol, hexane, HC*l*(aq), NaOH(aq),
- separating funnel, and
- apparatus commonly found in a college laboratory.

[3]

[Total: 20]

2 **(a)** Borane, BH_3, is used to synthesise alcohols from alkenes as shown in the reaction sequence below.

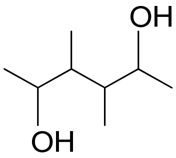
In reaction **1**, the BH_2 group from BH_3 is bonded to the **less** substituted carbon atom of the double bond. The remaining H atom from BH_3 is bonded to the other carbon atom.



(i) Name and show the mechanism of reaction **1**. In your answer, show relevant charges, lone pairs of electrons and movement of electrons. [3]

(ii) The product formed in reaction **1** contains a chiral centre. Explain whether the product formed rotates plane-polarised light. [2]

(iii) The diol **W** can be prepared by the same method as shown above.

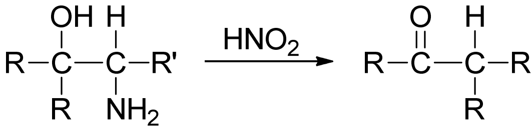


W

Draw the skeletal structure of the diene which could be used to prepare diol **W**. [1]

(b) A carbonyl compound, **Y**, $C_6H_{10}O$, can be synthesised from aminoalcohol, **X**, $C_6H_{13}ON$, in the presence of nitrous acid, HNO_2, via Tiffeneau-Demjanov Rearrangement.

The simplified illustration of the rearrangement is shown below.

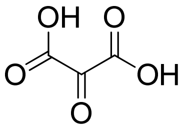


Y produces a yellow precipitate with iodine in alkaline solution. Treatment of **Y** with hot acidified solution of potassium manganate(VII) produces **Z,** $C_5H_8O_3$, along with a gas that forms a white precipitate in limewater. **Y** was also observed to decolourise bromine in tetrachloromethane readily.

(i) Explain the chemistry of the reactions described and deduce the structural formulae of **X**, **Y** and **Z**. [5]

(ii) With reference to the *Data Booklet*, identify an infra-red absorption range that will be shown by the functional group in **Y** but **not** in **X**. [1]

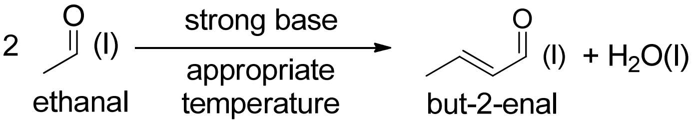
(c) Devise a three–step synthesis to obtain compound **V** from the carbonyl compound, $ClCH_2CHO$.



V

Give the reagents and conditions for each step. Draw the structural formulae of all the intermediates. [4]

(d) By either adjusting the reaction temperature or using a stronger base, ethanal can undergo Aldol Condensation reaction to form but-2-enal as shown below.



(i) With reference to the *Data Booklet*, calculate the enthalpy change for this Aldol Condensation reaction. [2]

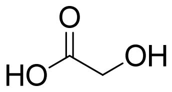
(ii) Explain why the actual enthalpy change for the Aldol Condensation reaction is different from that calculated in **(d)(i)**. [1]

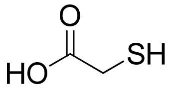
(iii) Suggest a simple chemical test to confirm the presence of but-2-enal in the product mixture. [1]

[Total: 20]

3 This question is about acids, bases and their derivatives.

(a) Glycolic acid and thioglycolic acid have very similar structures as shown below.


glycolic acid


thioglycolic acid

Glycolic acid has only one measurable pK_a value of 3.38. Thioglycolic acid has two measurable pK_a values of 3.67 and 10.31 respectively.

(i) Both oxygen and sulfur are Group 16 elements. Hence, suggest why the alcohol functional group of glycolic acid is a weaker acid than the –SH group of thioglycolic acid. [1]

(ii) Compare the first pK_a values of glycolic acid and thioglycolic acid. Explain its significance. [2]

(iii) Suggest the major species present in solutions of thioglycolic acid with the following pH values.

- pH 0
- pH 7
- pH 14 [2]

(iv) Assuming thioglycolic acid to be H_2A, calculate the percentage of each of the ionic species of thioglycolic acid present at pH 9.0. [3]

(v) Hence, calculate the volume of 0.100 mol dm^{-3} aqueous sodium hydroxide needed to form the solution in **(iv)** when added to 25.0 cm^3 of 0.100 mol dm^{-3} thioglycolic acid. [2]

(b) The hydroxide ion is the strongest possible base in aqueous solution, but in organic solvents it is possible to have other stronger bases. In 2016, Australian researchers announced the formation of an organic gas-phase di-anion, DEB^{2-}. It is the strongest base known.

DEB^{2-} is produced from compound **A** which is a disubstituted benzene, $C_6H_4R_2$, where R− is the same substituent.

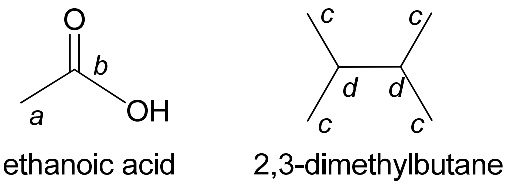
(i) Draw all the possible structures of $C_6H_4R_2$. [1]

(ii) Compound **A** has the molecular formula $C_{12}H_6O_4$ and effervesces on addition of sodium hydrogen carbonate.

Suggest the functional group present in the substituent R− that is responsible for the effervescence. Hence, deduce a structure for R−. [1]

^{13}C nuclear magnetic resonance (NMR) spectroscopy is an analytical method. In simplistic use, it allows different types of carbon atoms to be deduced from the corresponding signals in the spectrum.

For example, the ^{13}C NMR spectra for the ethanoic acid and 2,3-dimethylbutane would both show two distinct signals since each molecule has only two different carbon environments. This is shown in the diagram below where equivalent carbon environments are labelled with the same letter.



(iii) Compound **A** is found to have six signals in its ^{13}C NMR spectrum. Using your answers to **(b)(i)**, **(b)(ii)** and the information provided above, deduce the structure of compound **A**. [1]

(iv) Compound **A** forms DEB^{2-} via intermediates **B**$^{2-}$ and **C**$^{2-}$ through the removal of positive ions or neutral molecule from the substituent R−.

$$\begin{array}{ccccccc} \text{Compound } \mathbf{A} & \longrightarrow & \mathbf{B}^{2-} & \longrightarrow & \mathbf{C}^{2-} & \longrightarrow & \text{DEB}^{2-} \\ C_{12}H_6O_4 & & M_r = 212 & & M_r = 168 & & M_r = 124 \end{array}$$

Determine the skeletal structures of **B**$^{2-}$, **C**$^{2-}$ and DEB^{2-}. [2]

(c) An organic acid **D**, $C_7H_{10}O_2$, is refluxed with acidified $KMnO_4$ to produce only one organic compound **E**, $C_4H_6O_4$. Compound **D** decolourises bromine water. Gentle heating of the anhydrous crystals of compound **E** produces a neutral compound **F**, $C_4H_4O_3$, which does not react with sodium metal or give a precipitate with 2,4–dinitrophenylhydrazine.

Compound **F** reacts with ethanol in the presence of a catalyst to form compound **G**, $C_6H_{10}O_4$.

Compound **F** also reacts with methylamine, CH_3NH_2, to give a compound **H**, $C_5H_9NO_3$, which gives a salt on reaction with NaOH but not with HC*l*. Compound **H** does not display enantiomerism.

Both compounds, **G** and **H**, produce **E** on heating with dilute sulfuric acid.

Suggest the structures of **D**, **E**, **F**, **G** and **H**. [5]

[Total: 20]

Section B

Answer **one** question from this section.

4 **(a)** Chlorine dioxide, ClO_2, is a reddish-yellow gas that does not occur naturally in the environment. When added to aqueous hydroxide, chlorine dioxide undergoes the following reaction producing chlorate(III) and chlorate(V) ions.

$$2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O$$

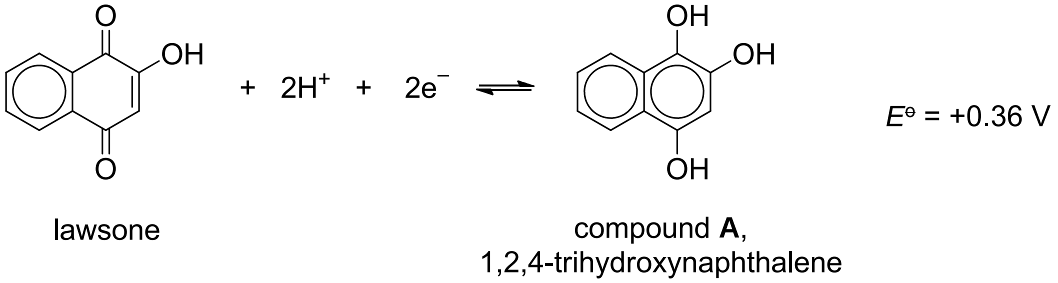
Unlike ClO_2, bromine dioxide is less stable and react with aqueous hydroxide to produce bromide and bromate(V) ions. Bromate(V) ion is formed more readily than chlorate(V) ion.

(i) Write a balanced equation for the reaction of bromine dioxide with sodium hydroxide. Hence, state the type of reaction. [2]

(ii) Explain why bromate(V) ion is formed more readily than the chlorate(V) ion in aqueous hydroxide. [1]

Lawsone is a dye that is extracted from the henna plant, *Lawsonia inermis*. Although its natural colour is yellow, lawsone reacts with the proteins in hair and skin to produce the characteristic brown henna colour.

Lawsone can be readily reduced to a colourless compound **A**, 1,2,4-trihydroxynaphthalene. However, the hair dye containing lawsone is relatively resistant to the decolourisation by chlorine water in swimming pools.



(iii) With reference to the *Data Booklet*, explain why chlorine water cannot spontaneously decolourise lawsone. [2]

(iv) The Gibb's free energy change, $\Delta G^\ominus$, is related to the equilibrium constant, K_c, through the following equation:

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

where $\Delta G^\ominus$ is in J mol^{-1}.

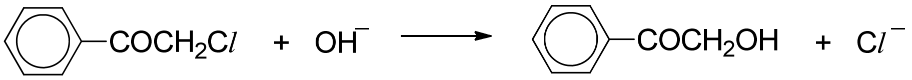
Using the answer from **(a)(iii)** and the *Data Booklet*, calculate K_c. Hence, deduce whether the position of equilibrium lies more on the left or right hand side of the equilibrium under standard conditions. [2]

(v) Suggest a reagent that could be used to convert lawsone into compound **A** in the laboratory. [1]

(vi) When lawsone is reacted with Br_2(aq), compound **B** with molecular formula, $C_{10}H_5O_3Br$, is formed. **B** reacts with 3 mol of 2,4-DNPH. Reaction of **B** with NaOH(aq) gives **C**. Compound **C** reacts with HCl and $ZnCl_2$ to produce **D**. The reaction of **D** with methylamine gives **E** with molecular formula, $C_{11}H_9O_3N$, which further reacts with CH_3COCl to give a neutral compound **F**.

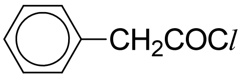
Suggest the skeletal formulae of compounds **B**, **C**, **D**, **E** and **F**. [5]

(b) Chloroacetophenone was formerly the most widely used tear gas, under the codename *CN*. It was used in warfare and in riot control. Residues of *CN* can be destroyed by the hydrolysis of alkali.

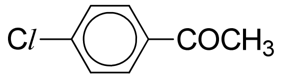


chloroacetophenone

G and **H** are isomers of chloroacetophenone.



G



H

(i) Arrange the isomers, chloroacetophenone, **G** and **H**, in increasing ease of hydrolysis. Explain your choice. [3]

(ii) Iodoacetophenone is even more reactive than chloroacetophenone towards alkaline hydrolysis. Briefly explain why it is so. [1]

(iii) Suggest a suitable experimental technique for studying the rate of hydrolysis. [1]

(iv) Compound **H** reacts with alkaline aqueous iodine to give a yellow solid, CHI_3. Similar reaction occurs between compound **H** and alkaline aqueous chlorine.

Write a balanced equation for the reaction of compound **H** with alkaline aqueous chlorine. State the observation. [2]

[Total: 20]

5 **(a)** Copper can be extracted from a double salt, $CuFeS_2$ by reacting it with oxygen and silicon dioxide. In this reaction, copper, iron(II) silicate, $FeSiO_3$, and an oxide of sulfur are produced. The oxide of sulfur does not decolourise acidified potassium manganate(VII).

(i) Draw a dot-and-cross diagram for $CuFeS_2$. [1]

(ii) Write a balanced equation for the overall reaction. Deduce the reducing agent in the reaction. [2]

(iii) Copper(I) sulfide is one of the reaction intermediate. Write the full electronic configuration of copper(I). [1]

(iv) The crude copper obtained contains trace amount of silver and nickel. With relevant data from the *Data Booklet* and a labelled diagram, describe how the crude copper can be purified through electrolysis. [4]

(v) 5.0 g of crude copper containing 0.1 g of silver and 0.1 g of nickel is purified through electrolysis as in **(a)(iv)**. During electrolysis, 80% of the current is used to oxidise the metals. With reference to the *Data* Booklet, determine the time needed to purify the copper completely using a current of 2 A. [2]

(vi) A student accidentally added some iron(III) nitrate into a solution of copper(II) nitrate. You are provided with

- NH_3(aq), NaOH(aq), HNO_3(aq) and
- apparatus commonly found in a college laboratory.

Describe how the student could separate these two metal ions in the mixture. Give relevant equations and state the types of reactions that have occurred. [3]

(b) Compounds **W**, **X**, **Y** and **Z** are constitutional isomers with molecular formula $C_9H_{10}O_2$ and none of them shows *cis-trans* isomerism. All four isomers can form intra-molecular hydrogen bonding. The results of seven tests carried out on the four isomers are shown below.

	Test	**W**	**X**	**Y**	**Z**
1	Rotate plane-polarised light	Yes	No	Yes	Yes
2	Add dilute NaOH at room temperature	Soluble	Soluble	Soluble	Insoluble
3	Heat with acidified $K_2Cr_2O_7$	Orange solution turned green	Orange solution did not turn green	Orange solution turned green	Orange solution turned green
4	Add 2,4-DNPH	Orange precipitate	Orange precipitate	No orange precipitate	Orange precipitate
5	Warm with Fehling's solution	Brick-red precipitate	No brick-red precipitate	No brick-red precipitate	No brick-red precipitate
6	Warm with Tollens' reagent	Grey ppt	No grey ppt	No grey ppt	Grey ppt
7	Warm with I_2(aq) and NaOH(aq)	No pale yellow precipitate	Pale yellow precipitate	No pale yellow precipitate	Pale yellow precipitate

(i) Use the information in the table above to suggest a skeletal formula for each of these four isomers. [4]

(ii) Write a balanced equation for the reaction between **W** and 2,4-DNPH. [1]

(iii) Explain why **W** is soluble in NaOH(aq) at room temperature. [2]

[Total: 20]

End of Paper

Section A

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

1 **(a)** All the elements in the third period of the Periodic Table, sodium to sulfur, form chlorides by direct combination with chlorine. Aluminium chloride may be produced by passing a stream of chlorine over heated aluminium metal in a long hard–glass tube.

(i) With the aid of equations, explain the following observations when different amounts of water were added to solid aluminium chloride.

(I) When a limited amount of water was added, a white solid was formed together with steamy fumes.

(II) When excess water was added, a solution of pH 3 was obtained. [2]

For **(I)**: $AlCl_3$ reacts with a limited amount of water to give $Al(OH)_3(s)$ and $HCl(g)$:

$AlCl_3(s) + 3H_2O(l) \rightarrow Al(OH)_3(s) + 3HCl(g)$

For **(II)**:

$AlCl_3$ undergoes hydrolysis as Al^{3+} has high charge density / strong polarising power. Polarisation of H_2O molecules favours the loss of H^+, and hence, acidity of the solution increases (pH ≈ 3).

$AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$

$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(H_2O)_5OH]^{2+}(aq) + H_3O^+(aq)$

(ii) Both aluminium chloride and copper(I) complex solutions are colourless whereas a solution of copper(II) sulfate appears blue. Explain these observations. [3]

$AlCl_3$ solution is colourless because the energy gap between the n=2 and n=3 electronic shells is not within the visible light region. Hence, visible light is not absorbed.

Cu(I) complex is colourless because the 3d subshell is fully filled. Hence, no d-d /electronic transition can occur.

$CuSO_4$ solution appears blue because partially-filled 3d subshell is split into two different energy levels in the presence of ligands.

Electron from the lower energy level absorb a wavelength of light complementary to the observed colour and get promoted to the higher energy level. Thus, d-d transition can take place.

(iii) Briefly describe the process of anodisation of aluminium. Write ion-electron equations for the reactions occurring at the anode and the cathode. [2]

The aluminium is made the anode in the electrolysis of dilute sulfuric acid.

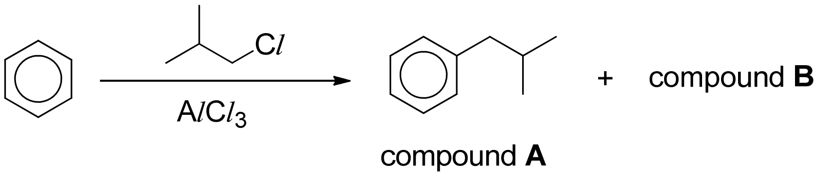
The oxygen released at the anode reacts with the aluminium surface to build up a thicker layer of aluminium oxide.

Anode: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

Cathode: $2H^+(aq) + 2e^- \rightarrow H_2(g)$

(b) Compound **A** can be synthesised from benzene using aluminium chloride via a simple Friedel–Crafts alkylation as shown in **Reaction 1**. In addition, compound **B**, an isomer of compound **A** is also formed.

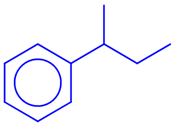
Reaction 1:



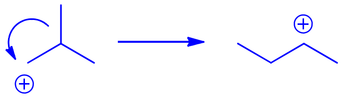
(i) Compound **B** rotates plane-polarised light. It is formed after the carbocation intermediate undergoes rearrangement through the movement of an alkyl group to an adjacent carbon atom bearing the positive charge.

Draw the structure of compound **B**. Explain why the rearrangement of the carbocation is favoured. [2]

B:



A primary carbocation rearranges into a secondary carbocation that is more stable because more electron-donating alkyl groups help dispersed the positive charge and stabilised the carbocation:

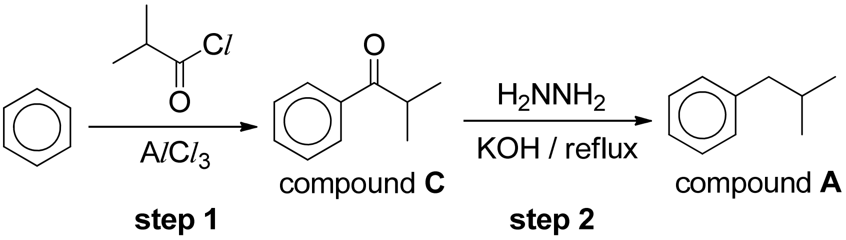


(ii) Explain why multi-substituted product is more favoured over mono-substituted product in **Reaction 1**. [1]

The alkyl group that is bonded to the benzene ring exerts electron–donating inductive effect.
This activates the benzene ring, making it even more susceptible towards electrophilic attack / reactive with respect to electrophilic substitution, thus forming multi-substituted product.

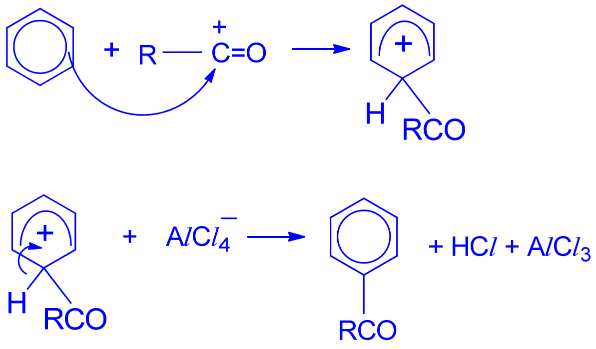
(c) Compound **A** can be formed via compound **C** as shown in **Reaction 2** below. **Step 1** involves Friedel–Crafts acylation, which have similar reaction conditions and mechanism as Friedel-Crafts alkylation.

Reaction 2:

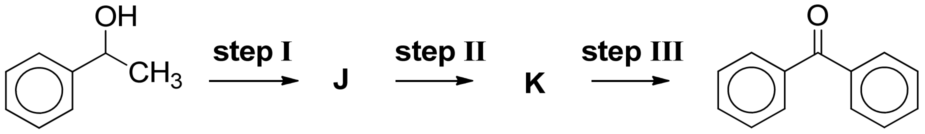


(i) Draw the mechanism for **step 1**. In your answer, show relevant charges, lone pairs of electrons and movement of electrons. [3]

Mechanism: Electrophilic substitution
Let R be $(CH_3)_2CH–$
$RCOCl + AlCl_3 \rightarrow RCO^+ + AlCl_4^-$



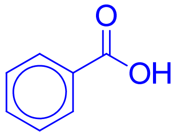
(ii) Hence, suggest reagents and conditions for **steps I** to **III** in the following synthesis of benzophenone from 1-hydroxyethylbenzene. Give the structural formulae of **J** and **K**.

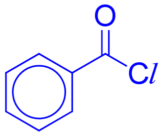


1-hydroxyethylbenzene

benzophenone

[4]

J: 

K: 

step I: $\mathrm{KMnO_4}$, $\mathrm{H_2SO_4}$, reflux
step II: $\mathrm{PC}l_5$, room temperature OR $\mathrm{PC}l_3$, reflux OR $\mathrm{SOC}l_2$, reflux
step III: $\mathrm{C_6H_6}$, anhydrous $\mathrm{A}l\mathrm{C}l_3$, room temperature

(d) A student wants to synthesise benzophenone using the reaction pathway illustrated in **(c)(ii)**. However, the solid sample of 1-hydroxyethylbenzene is contaminated with phenylamine. Briefly explain how you can separate 1-hydroxyethylbenzene from phenylamine via extraction. You are provided with

- ethanol, hexane, $\mathrm{HC}l$(aq), NaOH(aq),
- separating funnel and
- apparatus commonly found in a college laboratory.

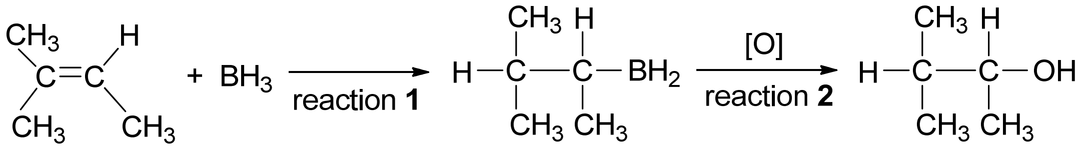
[3]

(i) Dissolve the solid sample in hexane.
(ii) Transfer the mixture to a separating funnel.
(iii) Add $\mathrm{HC}l$(aq) to the mixture to convert phenylamine to the salt.
(iv) Shake the separating funnel and then drain off the bottom aqueous layer to get the organic layer.
(v) Evaporate the organic layer to obtain 1-hydroxyethylbenzene.

[Total: 20]

2 **(a)** Borane, $\mathrm{BH_3}$, is used to synthesise alcohols from alkenes as shown in the reaction sequence below.

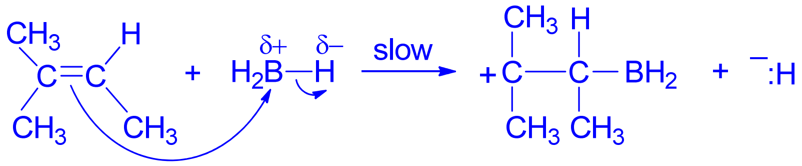
In reaction **1**, the $\mathrm{BH_2}$ group from $\mathrm{BH_3}$ is bonded to the **less** substituted carbon atom of the double bond. The remaining H atom from $\mathrm{BH_3}$ is bonded to the other carbon atom.



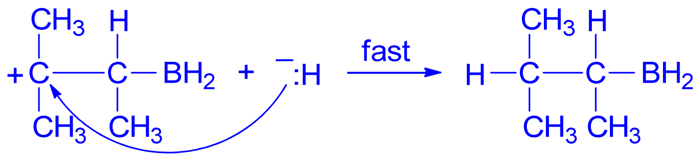
(i) Name and show the mechanism of reaction **1**. In your answer, show relevant charges, lone pairs of electrons and movement of electrons. [3]

Mechanism: Electrophilic addition

Step 1:



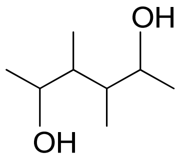
Step 2:



(ii) The product formed in reaction **1** contains a chiral centre. Explain whether the product formed rotates plane-polarised light. [2]

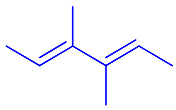
The product does not rotate plane-polarised light.
The alkene carbon atom is sp^2 hybridised (or trigonal planar).
Electrophile can attack from either the top or bottom plane of the $C=C$ with equal probability. Hence, a racemic mixture is formed.

(iii) The diol **W** can be prepared by the same method as shown above.



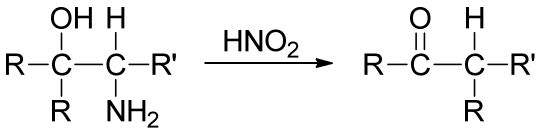
W

Draw the skeletal structure of the diene which could be used to prepare diol **W**. [1]



(b) A carbonyl compound, **Y**, $C_6H_{10}O$, can be synthesised from aminoalcohol, **X**, $C_6H_{13}ON$, in the presence of nitrous acid, HNO_2, via Tiffeneau-Demjanov Rearrangement.

The simplified illustration of the rearrangement is shown below.

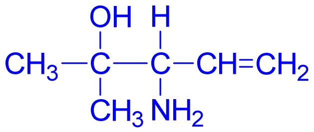


$$R-\overset{OH}{\underset{R}{C}}-\overset{H}{\underset{NH_2}{C}}-R' \xrightarrow{HNO_2} R-\overset{O}{\overset{\|}{C}}-\overset{H}{\underset{R}{C}}-R'$$

Y produces a yellow precipitate with iodine in alkaline solution. Treatment of **Y** with hot acidified solution of potassium manganate(VII) produces **Z,** $C_5H_8O_3$, along with a gas that forms a white precipitate in limewater. **Y** was also observed to decolourise bromine in tetrachloromethane readily.

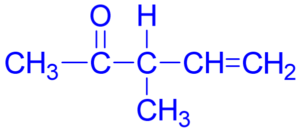
(i) Explain the chemistry of the reactions described and deduce the structural formulae of **X**, **Y** and **Z**. [5]

X is



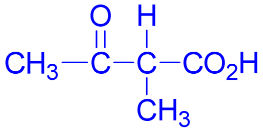
$$CH_3-\overset{OH}{\underset{CH_3}{C}}-\overset{H}{\underset{NH_2}{C}}-CH=CH_2$$

Y is



$$CH_3-\overset{O}{\overset{\|}{C}}-\overset{H}{\underset{CH_3}{C}}-CH=CH_2$$

Z is



$$CH_3-\overset{O}{\overset{\|}{C}}-\overset{H}{\underset{CH_3}{C}}-CO_2H$$

Y undergoes oxidative cleavage with iodine in alkaline solution to give yellow ppt., CHI_3. Y has CH_3CO- group.

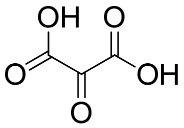
Y undergoes oxidative cleavage with hot acidified $KMnO_4(aq)$ to produce $CO_2(g)$ which forms white ppt. in limewater. Y is a terminal alkene (OR has $=CH_2$ group).

Y undergoes electrophilic addition with Br_2 in CCl_4. Y is an alkene.

(ii) With reference to the *Data Booklet*, identify an infra-red absorption range that will be shown by the functional group in **Y** but **not** in **X**. [1]

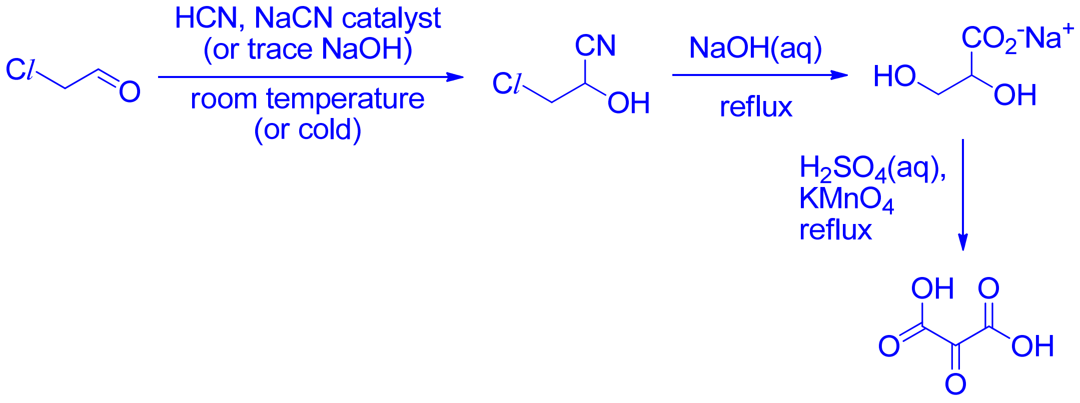
1670 – 1740 cm^{-1} due to ketone functional group.

(c) Devise a three–step synthesis to obtain compound **V** from the carbonyl compound, C*l*CH₂CHO.

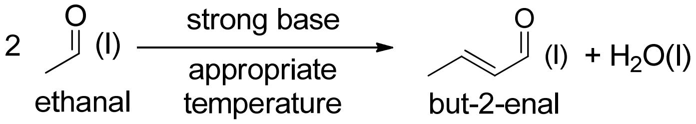


V

Give the reagents and conditions for each step. Draw the structural formulae of all the intermediates. [4]



(d) By either adjusting the reaction temperature or using a stronger base, ethanal can undergo Aldol Condensation reaction to form but-2-enal as shown below.



(i) With reference to the *Data Booklet*, calculate the enthalpy change for this Aldol Condensation reaction. [2]

bonds broken	
one C=O	+740
two C–H	2(+410)
Total	+1560

bonds formed	
one C=C	+610
two O–H	2(+460)
Total	+1530

$\Delta H = +1560 - (+1530) = +30 \text{ kJ mol}^{-1}$

(ii) Explain why the actual enthalpy change for the Aldol Condensation reaction is different from that calculated in **(d)(i)**. [1]

Bond energies quoted from *Data Booklet* are average values derived from a full range of molecules that contain the particular bonds.
OR
The bond energies quoted are for gaseous molecules but the reactants and products are in liquid state. Hence, the enthalpy changes of vapourisation are not accounted for.

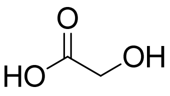
(iii) Suggest a simple chemical test to confirm the presence of but-2-enal in the product mixture. [1]

Test: Add $Br_2(aq)$ (at room temperature) to a small sample of the mixture.
Observation: If but-2-enal is formed, orange $Br_2(aq)$ decolourise.
OR
Test: Add Br_2 in CCl_4 (at room temperature) to a small sample of the mixture.
Observation: If but-2-enal is formed, orange-red Br_2 decolourise.

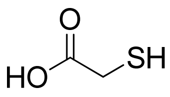
[Total: 20]

3 This question is about acids, bases and their derivatives.

(a) Glycolic acid and thioglycolic acid have very similar structures as shown below.



glycolic acid



thioglycolic acid

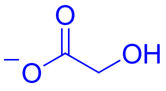
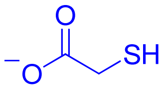
Glycolic acid has only one measurable pK_a value of 3.38. Thioglycolic acid has two measurable pK_a values of 3.67 and 10.31 respectively.

(i) Both oxygen and sulfur are Group 16 elements. Hence, suggest why the alcohol functional group of glycolic acid is a weaker acid than the –SH group of thioglycolic acid. [1]

The S–H bond is easier to break since S atom is bigger. Hence, less effective overlap of orbitals for the S–H bond.

(ii) Compare the first pK_a values of glycolic acid and thioglycolic acid. Explain its significance. [2]

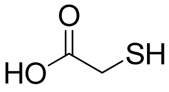
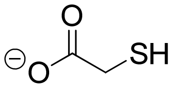
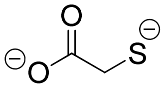
Glycolic acid is the stronger acid since it has a lower pK_a value.
O atom is more electronegative than S,

hence the anion formed,  is more stable than that of thioglycolic acid, . This is due to the stronger electron withdrawing effect of O atom, dispersing the negative charge.

(iii) Suggest the major species present in solutions of thioglycolic acid with the following pH values.

- pH 0
- pH 7
- pH 14

[2]

pH 0	pH 7	pH 14
		

(iv) Assuming thioglycolic acid to be H_2A, calculate the percentage of each of the ionic species of thioglycolic acid present at pH 9.0. [3]
Let the thioglycolic acid be H_2A. As pH 9 is after the 1st end-point, we shall use

pK_a = 10.31 for calculation.

$$pK_a = pH - \log_{10}\frac{[A^{2-}]}{[HA^-]}$$

$$10.31 = 9 - \log_{10}\frac{[A^{2-}]}{[HA^-]}$$

$$\log_{10}\frac{[A^{2-}]}{[HA^-]} = -1.31$$

$$\frac{[A^{2-}]}{[HA^-]} = 0.0490$$

Or $K_a = \frac{[A^{2-}][H^+]}{[HA^-]}$

$$\frac{[A^{2-}]}{[HA^-]} = \frac{K_a}{[H^+]} = \frac{10^{-10.31}}{10^{-9}} = 0.0490$$

$[A^{2-}] + [HA^-] = 100\%$

$0.049[HA^-] + [HA^-] = 100\%$

$\Rightarrow [A^{2-}] = 4.67\%$; $[HA^-] = 95.3\%$

(v) Hence, calculate the volume of 0.100 mol dm^{-3} aqueous sodium hydroxide needed to form the solution in **(iv)** when added to 25.0 cm^3 of 0.100 mol dm^{-3} thioglycolic acid. [2]

$H_2A + NaOH \rightarrow HA^- + H_2O$

$HA^- + NaOH \rightarrow A^{2-} + H_2O$

Amount of H_2A used = 25/1000 × 0.100 = 2.50×10^{-3} mol

Amount of NaOH required

= amount of NaOH to form HA^- from H_2A + amount of NaOH to form 4.67% A^{2-}

= $2.50 \times 10^{-3} + (4.67\% \times 2.50 \times 10^{-3})$

= 2.62×10^{-3} mol

Volume of NaOH

= amount of NaOH / [NaOH]

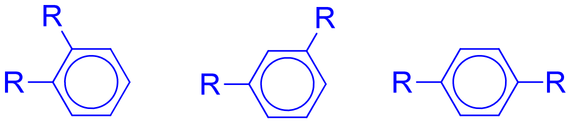
= $2.62 \times 10^{-3} \div 0.100$

= 0.0262 dm^3 = 26.2 cm^3

(b) The hydroxide ion is the strongest possible base in aqueous solution, but in organic solvents it is possible to have other stronger bases. In 2016, Australian researchers announced the formation of an organic gas-phase di-anion, DEB^{2-}. It is the strongest base known.

DEB^{2-} is produced from compound **A** which is a disubstituted benzene, $C_6H_4R_2$, where R− is the same substituent.

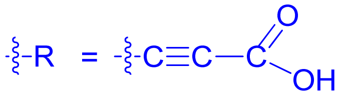
(i) Draw all the possible structures of $C_6H_4R_2$. [1]



(ii) Compound **A** has the molecular formula $C_{12}H_6O_4$ and effervesces on addition of sodium hydrogen carbonate.

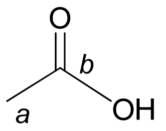
Suggest the functional group present in the substituent R− that is responsible for the effervescence. Hence, deduce a structure for R−. [1]

Carboxylic acid

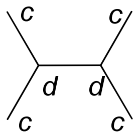


^{13}C nuclear magnetic resonance (NMR) spectroscopy is an analytical method. In simplistic use, it allows different types of carbon atoms to be deduced from the corresponding signals in the spectrum.

For example, the ^{13}C NMR spectra for the ethanoic acid and 2,3-dimethylbutane would both show two distinct signals since each molecule has only two different carbon environments. This is shown in the diagram below where equivalent carbon environments are labelled with the same letter.

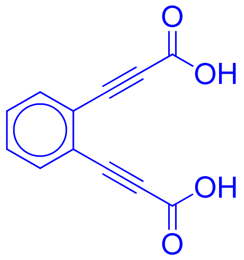


ethanoic acid



2,3-dimethylbutane

(iii) Compound **A** is found to have six signals in its ^{13}C NMR spectrum. Using your answers to **(b)(i)**, **(b)(ii)** and the information provided above, deduce the structure of compound **A**. [1]

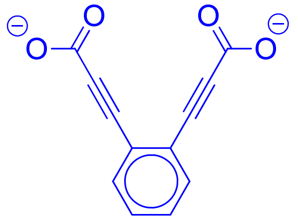


(iv) Compound **A** forms DEB^{2-} via intermediates **B**$^{2-}$ and **C**$^{2-}$ through the removal of positive ions or neutral molecule from the substituent R−.

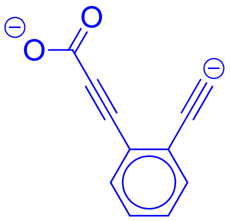
$$\text{Compound } \mathbf{A} \longrightarrow \mathbf{B}^{2-} \longrightarrow \mathbf{C}^{2-} \longrightarrow \text{DEB}^{2-}$$

$C_{12}H_6O_4$ $M_r = 212$ $M_r = 168$ $M_r = 124$

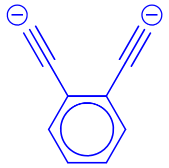
Determine the skeletal structures of **B**$^{2-}$, **C**$^{2-}$ and DEB^{2-}. [2]



B^{2-}



C^{2-}



DEB^{2-}

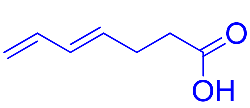
(c) An organic acid **D**, $C_7H_{10}O_2$, is refluxed with acidified $KMnO_4$ to produce only one organic compound **E**, $C_4H_6O_4$. Compound **D** decolourises bromine water. Gentle heating of the anhydrous crystals of compound **E** produces a neutral compound **F**, $C_4H_4O_3$, which does not react with sodium metal or give a precipitate with 2,4–dinitrophenylhydrazine.

Compound **F** reacts with ethanol in the presence of a catalyst to form compound **G**, $C_6H_{10}O_4$.

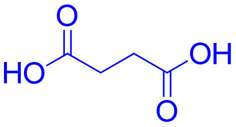
Compound **F** also reacts with methylamine, CH_3NH_2, to give a compound **H**, $C_5H_9NO_3$, which gives a salt on reaction with NaOH but not with HC*l*. Compound **H** does not display enantiomerism.

Both compounds, **G** and **H**, produce **E** on heating with dilute sulfuric acid.

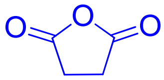
Suggest the structures of **D**, **E**, **F**, **G** and **H**. [5]



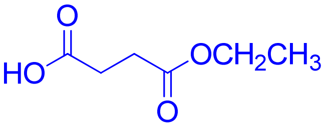
D



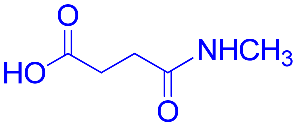
E



F



G



H

[Total: 20]

Section B

Answer **one** question from this section.

4 **(a)** Chlorine dioxide, ClO_2, is a reddish-yellow gas that does not occur naturally in the environment. When added to aqueous hydroxide, chlorine dioxide undergoes the following reaction producing chlorate(III) and chlorate(V) ions.

$$2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O$$

Unlike ClO_2, bromine dioxide is less stable and react with aqueous hydroxide to produce bromide and bromate(V) ions. Bromate(V) ion is formed more readily than chlorate(V) ion.

(i) Write a balanced equation for the reaction of bromine dioxide with sodium hydroxide. Hence, state the type of reaction. [2]

$6BrO_2 + 6NaOH \rightarrow NaBr + 5NaBrO_3 + 3H_2O$
Disproportionation.

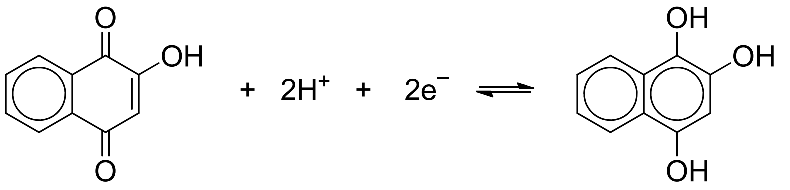
(ii) Explain why bromate(V) ion is formed more readily than the chlorate(V) ion in aqueous hydroxide. [1]

Bromine element is a stronger reducing agent than chlorine, hence, it is more likely to be oxidised to a higher oxidation state.
OR

Bromine atom is bigger / less electronegative, hence, easier to lose electrons to form the +5 oxidation state.

Lawsone is a dye that is extracted from the henna plant, *Lawsonia inermis*. Although its natural colour is yellow, lawsone reacts with the proteins in hair and skin to produce the characteristic brown henna colour.

Lawsone can be readily reduced to a colourless compound **A**, 1,2,4-trihydroxynaphthalene. However, the hair dye containing lawsone is relatively resistant to the decolourisation by chlorine water in swimming pools.



$E^\ominus = +0.36$ V

lawsone

compound **A**,
1,2,4-trihydroxynaphthalene

(iii) With reference to the *Data Booklet*, explain why chlorine water cannot spontaneously decolourise lawsone. [2]

$2HOCl + 2H^+ + 2e^- \rightleftharpoons Cl_2 + 2H_2O$ $\quad E^\ominus = +1.64$ V
If lawsone undergoes decolourisation, it is reduced while chlorine water is oxidised.
$E^\ominus_{cell} = E^\ominus_{Red} - E^\ominus_{Ox} \quad = +0.36 - (+1.64) = -1.28$ V
Since $E^\ominus_{cell} < 0$, the reaction is thermodynamically non-spontaneous.

(iv) The Gibb's free energy change, $\Delta G^\ominus$, is related to the equilibrium constant, K_c, through the following equation:

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

where $\Delta G^\ominus$ is in J mol^{-1}.

Using the answer from **(a)(iii)** and the *Data Booklet*, calculate K_c. Hence, deduce whether the position of equilibrium lies more on the left or right hand side of the equilibrium under standard conditions. [2]

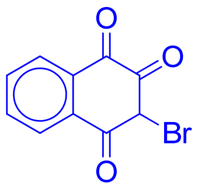
$\Delta G^\ominus = -\text{nF}E^\ominus_{cell} = -2 \times 96500 \times (-1.28) = 2.47 \times 10^5$ J mol^{-1}
$\Delta G^\ominus = -\text{RT} \ln K_c = -8.31 \times 298 \times \ln K_c = 2.47 \times 10^5$
$\Rightarrow K_c = 4.73 \times 10^{-44} << 1$ means position of equilibrium lies more to the left.

(v) Suggest a reagent that could be used to convert lawsone into compound **A** in the laboratory. [1]

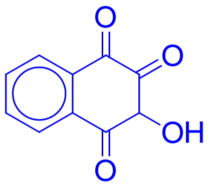
$NaBH_4$ (in ethanol) or $LiAlH_4$ (in dry ether)

(vi) When lawsone is reacted with Br_2(aq), compound **B** with molecular formula, $C_{10}H_5O_3Br$, is formed. **B** reacts with 3 mol of 2,4-DNPH. Reaction of **B** with NaOH(aq) gives **C**. Compound **C** reacts with HCl and $ZnCl_2$ to produce **D**. The reaction of **D** with methylamine gives **E** with molecular formula, $C_{11}H_9O_3N$, which further reacts with CH_3COCl to give a neutral compound **F**.

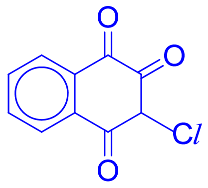
Suggest the skeletal formulae of compounds **B**, **C**, **D**, **E** and **F**. [5]



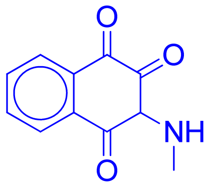
B



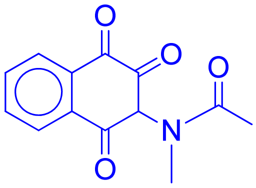
C



D

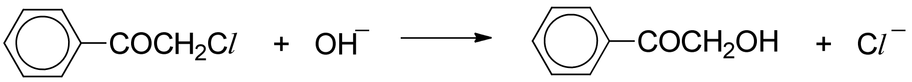


E



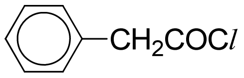
F

(b) Chloroacetophenone was formerly the most widely used tear gas, under the codename *CN*. It was used in warfare and in riot control. Residues of *CN* can be destroyed by the hydrolysis of alkali.

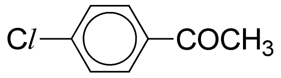


chloroacetophenone

G and **H** are isomers of chloroacetophenone.



G



H

(i) Arrange the isomers, chloroacetophenone, **G** and **H**, in increasing ease of hydrolysis. Explain your choice. [3]

Increasing ease of hydrolysis: H < chloroacetophenone < G
H: The partial double bond character due to the overlapping of the p-orbitals between the C*l* and C atoms of benzene makes the C−C*l* bond difficult to break.
G: The carbonyl carbon is highly electron-deficient due to the presence of electronegative O atom. Hence, more susceptible to nucleophilic attack by water molecule.

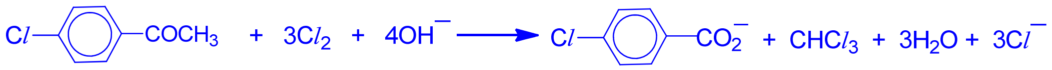
(ii) Iodoacetophenone is even more reactive than chloroacetophenone towards alkaline hydrolysis. Briefly explain why it is so. [1]

The C−I bond is weaker than the C−C*l* bond because less effective overlap of orbitals due to bigger I atom.

(iii) Suggest a suitable experimental technique for studying the rate of hydrolysis. [1]

Monitor the concentration of OH^- by titration with acid at regular time intervals.
OR Monitor the change in pH using a pH probe at regular time intervals.

(iv) Compound **H** reacts with alkaline aqueous iodine to give a yellow solid, CHI_3. Similar reaction occurs between compound **H** and alkaline aqueous chlorine. Write a balanced equation for the reaction of compound **H** with alkaline aqueous chlorine. State the observation. [2]



Pale greenish-yellow solution decolourised.

[Total: 20]

5 **(a)** Copper can be extracted from a double salt, $CuFeS_2$, by reacting it with oxygen and silicon dioxide. In this reaction, copper, iron(II) silicate, $FeSiO_3$, and an oxide of sulfur are produced. The oxide of sulfur does not decolourise acidified potassium manganate(VII).

(i) Draw a dot-and-cross diagram for $CuFeS_2$. [1]

oo
$[Cu]^{2+}$ $[Fe]^{2+}$ 2 [xx S xx $]^{2-}$
xx

(ii) Write a balanced equation for the overall reaction. Deduce the reducing agent in the reaction. [2]

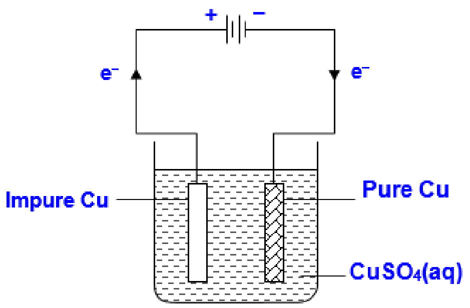
$CuFeS_2 + \frac{7}{2}O_2 + SiO_2 \rightarrow Cu + FeSiO_3 + 2SO_3$

S^{2-} or sulfide is the reducing agent as the oxidation number of S increases from –2 to +6

(iii) Copper(I) sulfide is one of the reaction intermediate. Write the full electronic configuration of copper(I). [1]

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

(iv) The crude copper obtained contains trace amount of silver and nickel. With relevant data from the *Data Booklet* and a labelled diagram, describe how the crude copper can be purified through electrolysis. [4]



Set up an electrolytic cell with pure Cu connected to the negative terminal of the power source whereas the crude Cu to the positive end. Aqueous copper(II) sulfate is the electrolyte used.
At the anode, both Ni and Cu are oxidised due to their more negative/less positive $E^\ominus$ value than Ag.
Cu is oxidized to form Cu^{2+}.

Ag will not be oxidised because of a more positive $E^\ominus$ value. It will fall off.
$Ni^{2+} + 2e^- \rightleftharpoons Ni$ -0.25 V
$Cu^{2+} + 2e^- \rightleftharpoons Cu$ $+0.34$ V
$Ag^+ + e^- \rightleftharpoons Ag$ $+0.80$ V

At the cathode, Cu^{2+} is reduced to Cu because the $E^\ominus$ value is more positive than that of Ni^{2+}.

(v) 5.0 g of crude copper containing 0.1 g of silver and 0.1 g of nickel is purified through electrolysis as in **(a)(iv)**. During electrolysis, 80% of the current is used to oxidise the metals. With reference to the *Data* Booklet, determine the time needed to purify the copper completely using a current of 2 A. [2]

Amount of Cu = 4.8/63.5 = 0.0756 mol
Amount of Ni = 0.1/58.7 = 0.00170 mol
Total amount of electrons needed = (0.0756 + 0.00170) x 2 = 0.1546 mol
Charge needed = 0.1546 x 96500 = 14918.9 C
Time = Q/I

$= \frac{14918.9}{2} \times \frac{100}{80}$ s

$= \frac{7459.45}{60} \times \frac{100}{80}$ min

= 155.3 min or 155 min

(vi) A student accidentally added some iron(III) nitrate into a solution of copper(II) nitrate. You are provided with

- NH_3(aq), NaOH(aq), HNO_3(aq) and
- apparatus commonly found in a college laboratory.

Describe how the student could separate these two metal ions in the mixture. Give relevant equations and state the types of reactions that have occurred. [3]

Add aqueous NH_3 to the mixture. Cu^{2+} undergoes precipitation to form $Cu(OH)_2$ when ionic product > K_{sp}. Then in excess NH_3(aq), ligand exchange reaction takes place with NH_3.
$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
$Cu^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Cu(OH)_2(s)$
$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(H_2O)_2(NH_3)_4]^{2+} + 4H_2O$
Fe^{3+} will form insoluble $Fe(OH)_3$ through precipitation when ionic product > K_{sp}.
$Fe^{3+}(aq) + 3OH^-(aq) \rightleftharpoons Fe(OH)_3(s)$
Filter the mixture.

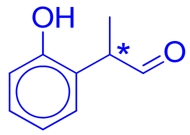
(b) Compounds **W**, **X**, **Y** and **Z** are constitutional isomers with molecular formula $C_9H_{10}O_2$ and none of them shows *cis-trans* isomerism. All four isomers can form intra-molecular hydrogen bonding. The results of seven tests carried out on the four isomers are shown below.

	Test	W	X	Y	Z
1	Rotate plane-polarised light	Yes	No	Yes	Yes
2	Add dilute NaOH at room temperature	Soluble	Soluble	Soluble	Insoluble

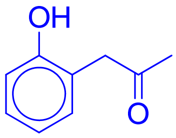
3	Heat with acidified $K_2Cr_2O_7$	Orange solution turned green	Orange solution did not turn green	Orange solution turned green	Orange solution turned green
4	Add 2,4-DNPH	Orange precipitate	Orange precipitate	No orange precipitate	Orange precipitate
5	Warm with Fehling's solution	Brick-red precipitate	No brick-red precipitate	No brick-red precipitate	No brick-red precipitate
6	Warm with Tollens' reagent	Grey ppt	No grey ppt	No grey ppt	Grey ppt
7	Warm with I_2(aq) and NaOH(aq)	No pale yellow precipitate	Pale yellow precipitate	No pale yellow precipitate	Pale yellow precipitate

(i) Use the information in the table above to suggest a skeletal formula for each of these four isomers. [4]

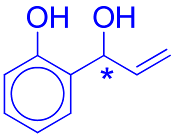
W



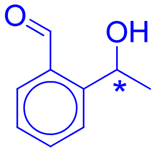
X



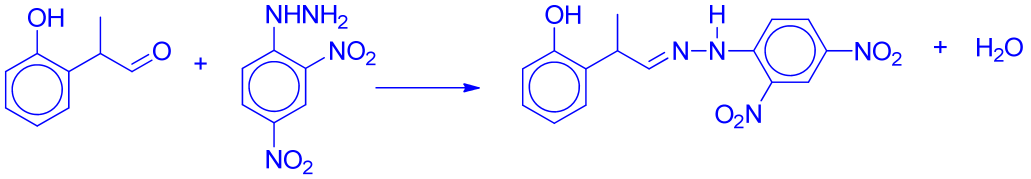
Y



Z



(ii) Write a balanced equation for the reaction between **W** and 2,4-DNPH. [1]



(iii) Explain why **W** is soluble in NaOH(aq) at room temperature. [2]

W contains phenol which undergo neutralization with NaOH to form ionic sodium phenoxide.

The ion-dipole interactions formed between the ions and water release sufficient energy to overcome the hydrogen bondings between water molecules and ionic bonds in sodium phenoxide.

[Total: 20]

End of Paper