VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CHEMISTRY 9729/01

Paper 1 Multiple Choice **19 September 2018**

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, highlighters, glue or correction fluid.
Write your Exam Number, name and CT group on the Multiple Choice Answer Sheet.

There are **thirty** questions. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the **one** you consider correct and record your choices in **soft pencil** on the separate Multiple Choice Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. No mark will be deducted for a wrong answer.
Any rough working should be done in this booklet.
The use of an approved scientific calculator is expected, where appropriate.

This document consists of **8** printed pages.

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, HCl 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 $\Delta S_{reaction}$ 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 NaCl 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–Cl and Cl–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 NaC*l*(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

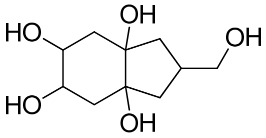
23 Organic compound **X** gives a precipitate when warmed with aqueous silver nitrate. This precipitate dissolves when concentrated aqueous ammonia is added.

What could **X** be?

1 1-bromopropane
2 1-chloropropane
3 chlorobenzene

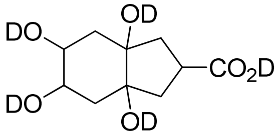
A	1, 2 and 3	**B**	1 and 2 only
C	2 and 3 only	**D**	1 only

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?

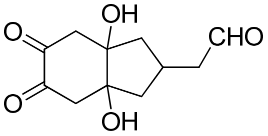


Compound **Y**

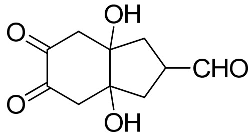
A



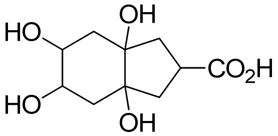
B



C



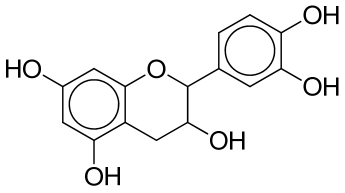
D



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?

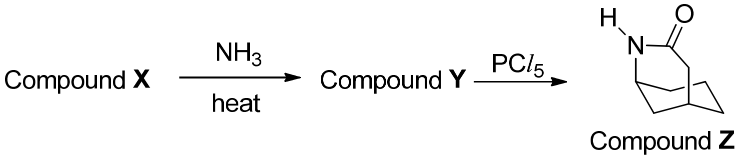
A 1 mol of catechin reacts with 5 mol of NaOH.

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

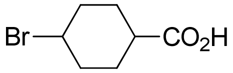
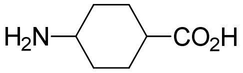
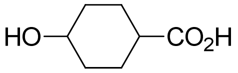
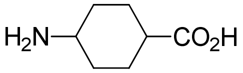
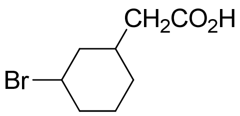
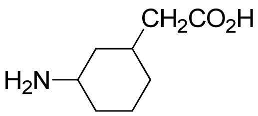
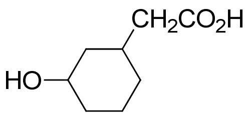
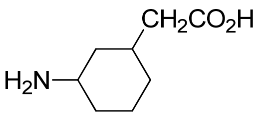
C It can undergo oxidation with hot alkaline $KMnO_4$(aq).

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**.



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

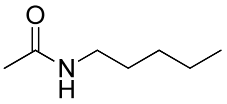
B 1 and 2 only

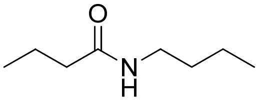
C 2 and 3 only

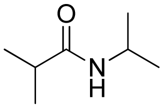
D 1 only

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

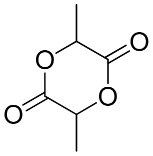
B 1 only

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**

Victoria Junior College
2018 JC2 H2 Chemistry Prelim Paper 1
Suggested Answers

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**

1 C

On average, each Cl atom has 35.5 – 17 = 18.5 neutrons.
Hence, for each Cl_2 molecule, there are 2 × 18.5 = 37 neutrons.
In 24 dm^3 of chlorine gas, there is 1 mol of Cl_2 molecules.
Thus, the total number of neutrons = $37L$.

2 C

Let the mass of ^{12}C isotope in the mixture be x g.
Hence, the mass of ^{14}C isotope is (1.000 – x) g.
When ^{12}C isotope is burnt completely, the mass of $^{12}CO_2$ formed = $\frac{44x}{12}$ g
When ^{14}C isotope is burnt completely, the mass of $^{14}CO_2$ formed = $\frac{46(1.000-x)}{14}$ g
Thus, $\frac{44x}{12} + \frac{46(1.000-x)}{14} = 3.629$
x = 0.900 g
Percentage by mass of ^{12}C isotope = = $\frac{0.900}{1.000}$ × 100% = 90.0 %

3 D

$$POCl_3 + 3H_2O \rightarrow H_3PO_4 + 3HCl$$

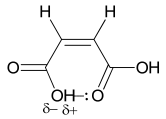
H_3PO_4 is a tribasic acid and 3 mol of NaOH is needed to neutralise 1 mol of H_3PO_4.
1 mol of NaOH is needed to neutralise 1 mol of HCl.
Hence, in total, 6 mol of NaOH is needed.

4 B (2 only)

1: Both $SiCl_4$ and PF_4^+ have 4 bond pairs and 0 lone pair of electrons. Thus, both of them are tetrahedral in shape and the bond angles should be 109.5°.
2: Both PH_3 and NH_3 have 3 bond pairs and 1 lone pair of electrons. Thus, they have the same shape, which is trigonal pyramidal.
N atom is more electronegative than P atom, so the bonding electrons are closer to the central atom in NH_3. This leads to greater inter-electronic repulsion between them. Hence, the bond angle in NH_3 is greater than PH_3.
3: SO_3^{2-} has 3 bond pairs and 1 lone pair of electrons, so the shape is trigonal pyramidal. CO_3^{2-} has 3 bond pairs and 0 lone pair of electrons, so the shape is trigonal planar. Hence, they have different shapes.

5 A (2 Only)

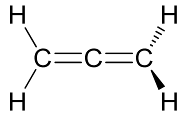
1: *cis* and *trans* isomers have different densities due to different packing structure in the solid state. This is a result of the difference in strengths of the inter-molecular forces.
2: The presence of the intramolecular hydrogen bonding in the *cis* isomer that is as shown, leads to a less extensive intermolecular hydrogen bonding between the *cis* isomers. Thus, less energy is needed to overcome the intermolecular forces of attraction and the melting point is lower for the *cis* isomer.



3: The *trans* isomer is less polar than the *cis* isomer due to the cancellation of dipole moments.

6 D

A: The central C atom in prop-1,2-diene is *sp* hybridised resulting in a greater *s* character. This leads to stronger attractions between the nuclei and the shared electrons. Whereas the C=C in ethene are formed by two *sp*^{2} hybridised carbon atoms. Thus, the C=C in prop-1,2-diene is stronger.
B: Since the two *p* orbitals of the central C atom are perpendicular to each other, the π-bonds formed are also perpendicular to each other.
C: The two terminal C atoms in prop-1,2-diene are *sp*^{2} hybridised and the central C atom is *sp* hybridised.
D: Since two π-bonds are perpendicular to each other, the two -CH_2 groups are on different planes as shown below. Thus, prop-1,2-diene is not a planar molecule.



7 D

A: Under very high pressure, particles are close to each other and the size of the particles becomes significanT as compared to the volume of the container. Thus, Cl_2 is less ideal as it is a larger molecule as compared to HCl.
B: Ideal gas molecules are assumed to have zero size.
C: Under low pressure, particles are far apart and the size of the particles are negligible as compared to the volume of the container. Under high temperature, the intermolecular forces of attractions can be overcome more readily. Thus, real gas approach ideal behaviour under low pressure and high temperature.
D: There are always collisions between gas molecules as they have kinetic energies and are thus in constant motion.

8 B

The magnitude of the lattice energy is directly proportional to the product of IONIC charges and inversely proportional to sum of the ionic radii (lattice energy $\propto \left|\frac{q^+q^-}{r^+ + r^-}\right|$).
MgO has the most exothermic lattice energy as both the cation and anion are doubly charged.
NaBr has the least exothermic lattice energy as both the cation and anion are singly charged.

Both MgBr_2 and Na_2O contain a singly charged and a doubly charged ions. But the sum of the ionic radii of MgBr_2 is larger than that of Na_2O, so it has a less exothermic lattice energy as compared to sodium oxide. The Br^- ion has one more electronic shell than O^{2-} ion.
Hence, in terms of magnitude, LE(MgO) > LE(Na_2O) > LE(MgBr_2) > LE(NaBr).

9 B

A: The number of moles of gaseous particles decreases in the reaction, thus ΔS is negative.
B: $\Delta H_{\text{reaction}} = \Delta H_f(\text{product}) - \Delta H_f(\text{reactant})$
$= (-85) - (+52)$
$= -137 \text{ kJ mol}^{-1}$
C: By Hess' Law, the enthalpy change of reaction is independent of the pathway taken.
D: Catalyst has no effect on the enthalpy change of a reaction

10 A (1, 2 and 3)

Since $\text{NH}_4\text{C}l$ dissolves readily at room temperature, $\Delta G < 0$ for the dissolution process at room temperature.
The process is endothermic since the temperature decreases. That is, ΔH is positive.
1: Given that $\Delta G < 0$ and $\Delta H > 0$, the $\Delta S > 0$ from $\Delta G = \Delta H - T\Delta S$. Hence, the reaction is favoured by the $\Delta S > 0$.
2: Since $\Delta H > 0$, at low temperature, the $\Delta G > 0$. Hence, dissolution is thermodynamically non-spontaneous.
3: Given $\Delta H > 0$, the hydration energy should be less exothermic than the LE from $\Delta H_{\text{solution}} = (-\text{LE}) + \Delta H_{\text{hydration}}$.

11 B

Compare experiments 1 and 2, the total volume is the constant and volume of H_2SO_4 used is doubled in experiment 2. Hence, [H_2SO_4] is doubled while the [$\text{Na}_2\text{S}_2\text{O}_3$] is constant. The rate is doubled because the time taken is halved. Thus, the reaction first order with respect to H_2SO_4.
For experiment 3, the total volume is not kept constant at 60 cm^3. The concentration of a solution after mixing has to be calculated as follow:
For example, if 10 cm^3 of stock H_2SO_4 solution is used.

$$[\text{H}_2\text{SO}_4]_{\text{mixed}} = \frac{10}{10+20}\,[\text{H}_2\text{SO}_4]_{\text{stock}} = \frac{1}{3}\,[\text{H}_2\text{SO}_4]_{\text{stock}}$$

Similarly, $[\text{Na}_2\text{S}_2\text{O}_3]_{\text{mixed}} = \frac{2}{3}[\text{Na}_2\text{S}_2\text{O}_3]_{\text{stock}}$
Hence, when experiments 1 and 3 are compared, [H_2SO_4] remains the same, while [$\text{Na}_2\text{S}_2\text{O}_3$] is doubled in experiment 3. Since the time is halved, the reaction is first order with respect to $\text{Na}_2\text{S}_2\text{O}_3$.

12 D

Proportion of uranium = $1/(1+7) = 1/8 = (1/2)^3$.
Hence, there 3 half-lives have passed.
The age = $4.5 \times 10^9 \times 3 = 1.35 \times 10^{10}$ years.

13 B (1 and 2 Only)

1: Catalyst provides an alternative pathway for the reaction. Hence, the mechanism has been altered.
2: Catalyst reduces the activation energy for both the forward and backward reaction by the same amount.
3: The catalyst has no impact on the equilibrium position and thus the composition of the equilibrium mixture will not change.

14 C

Let the initial partial pressure of $\text{NOC}l$ be x atm.
At equilibrium, the partial pressures of $\text{NOC}l$, NO and $\text{C}l_2$ are 0.7x, 0.3x and 0.15x atm, respectively.
Since the total pressure is p atm,
$0.7x + 0.3x + 0.15x = p$, therefore $x = \frac{1}{1.15}$ p atm
Partial pressure of $\text{NOC}l = \frac{0.7}{1.15}$ p atm
Partial pressure of $\text{NO} = \frac{0.3}{1.15}$ p atm
Partial pressure of $\text{C}l_2 = \frac{0.15}{1.15}$ p atm
$K_p = \{(\frac{0.3}{1.15}\text{p})^2(\frac{0.15}{1.15}\text{p})\} \div (\frac{0.7}{1.15}\text{p})^2$
$= 0.0240\text{p}$ atm

15 D

Amount of $\text{NH}_4\text{C}l$ = 0.100 × 0.10 = 0.010 mol
Amount of NaOH = 0.040 × 0.16 = 0.0060 mol
$\text{NH}_4\text{C}l + \text{NaOH} \rightarrow \text{NH}_3 + \text{NaC}l + \text{H}_2\text{O}$
Hence, NaOH is the limiting agent.
Amount of NH_3 formed = 0.0060 mol
$[\text{NH}_3] = 0.006 \div \frac{140}{1000} = 0.04286\text{mol dm}^{-3}$
Amount of NH_4^+ remaining = 0.0040 mol
$[\text{NH}_4^+] = 0.004 \div \frac{140}{1000} = 0.02857 \text{ mol dm}^{-3}$
Since $K_a = [\text{NH}_3][\text{H}^+] / [\text{NH}_4^+] = K_w / K_b$
$10^{-14}/10^{-4.75} = 0.006[\text{H}^+] / 0.004$
$[\text{H}^+] = 3.75 \times 10^{-10}$
pH = 9.43

16 C

$K_{sp} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}]$
A: Units are $\text{mol}^3 \text{ dm}^{-9}$
B: Addition of H^+ has no effect on K_{sp} values as K_{sp} is only affected by temperature.
C: $2\text{CrO}_4^{2-} + 2\text{H}^+ \rightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$. When H^+ is added, [CrO_4^{2-}] decreases. Hence, solubility increases.
D : Let the solubility be x mol dm^{-3}.
$K_{sp} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = (2x)^2.x = 4x^3 = 2.5 \times 10^{-22}$.
$x = 3.9 \times 10^{-8}$. mol dm^{-3}

17 D

A: Addition of water will cause the [$\text{C}l^-$] to decrease. Hence, position of equilibrium shifted right as reduction is more favoured. This leads to a more positive reduction potential.
B: Temperature will affect the equilibrium position and thus the reduction potential.
C: Ag^+ ions will react with $\text{C}l^-$ to form $\text{AgC}l$. Hence, [$\text{C}l^-$] decreases, position of equilibrium shifted right as reduction is more favoured. This leads to a more positive reduction potential.
D: When inert gas is added, it will not affect the partial pressure of $\text{C}l_2$ when the volume is kept

constant. Thus, there is no change in the equilibrium position and no change in the reduction potential.

18 A

Copper is formed at the cathode, while oxygen is formed at the anode. Thus, the amount of electrons transferred to form both substances is the same.
Amount of oxygen formed = y / 24 mol
For 1 mol of O_2 formed, 4 mol of electrons are needed.
Amount of electron transferred = 2x = y/6 mol
However, 2x or y/6 are not in the options.
Hence, amount of electron transferred = (2x+y/6)/2 = (x+y)/12 mol.

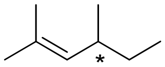
19 A

A: PCl_3 reacts with water to give H_3PO_3 and HC*l*. Cl_2O_7 will react with water to give $HClO_4$. Hence, the resultant solutions are acidic. [**Note: Non-metal oxides and chlorides are acidic in nature.**]
B: $AlCl_3$ is a non-conductor of electricity as it has a simple molecular structure in the molten state.
C: The low boiling points for simple molecular compounds are due to the weak intermolecular forces of attractions.
D: CCl_4 cannot react with water as there is no energetically accessible vacant orbitals to accommodate the lone pair of electrons from H_2O.

20 A

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
$Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s)$
Hence, the role of NH_3 is a Bronsted-Lowry base since it accepted a proton from water in the first step.

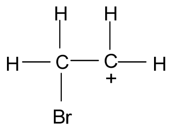
21 A



There are two methyl groups bonded to the same C atom of the C=C, so there is no *cis-trans* isomerism. The C atom labelled with * have 4 different groups attached. Thus, it can exhibit enantiomerism.

22 C

In the first step of the electrophilic addition, one Br atom is added to the C=C generating the following carbocation.



$H-\underset{Br}{\overset{H}{C}}-\overset{H}{\underset{+}{C}}-H$

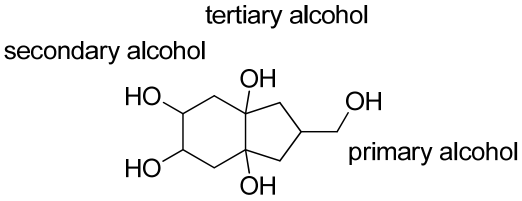
In the second step, the carbocation can react with Br^-, Cl^- or H_2O to get Br, C*l* or OH groups bonded to the electron-deficient C atom.

23 B (1 and 2 only)

Both 1-bromopropane and 1-chloropropane can react with aqueous silver nitrate to give AgBr and AgC*l* respectively. Both of them can dissolve in concentrated NH_3.

C*l* in chlorobenzene has a partial double bond character due to the delocalisation of the p electrons of the C*l* atom into the benzene ring. This is possible because of the overlap of the p-orbital of C*l* atom, which contains a lone pair of electrons, with the p-orbitals of the benzene ring. Thus, it will not undergo nucleophilic substitution reaction and no precipitate will be formed.

24 C



The primary alcohol will be oxidised into a carboxylic acid without a change in the number of C atoms.
The secondary alcohol will be oxidised into ketone.
The tertiary alcohol cannot be oxidised.

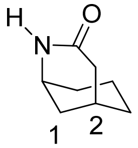
25 A

A: nucleophilic addition, followed by hydrolysis
B: condensation, followed by acid-base reaction
C: oxidative cleavage, followed by condensation
D: reduction, followed by condensation

26 C

A: There are 4 phenolic-OH groups, so 4 mol of NaOH are needed.
B: 5 mol of Br atoms can be substituted at the 2,4-positions relative to each of the phenolic-OH groups. Since 5 mol of HBr are formed as by-products, 5 mol of Br_2 are needed,
C: The secondary alcohol can be oxidised by the hot alkaline KMnO4.
D: Neither phenol nor secondary alcohol is acidic enough to react with Na_2CO_3.

27 C



There are two carbon atoms between the two substituents on the ring as labelled above. Hence, options **A** and **B** are incorrect.
Only the halogenoalkanes can react with NH_3 to give an amine. So option **D** is incorrect.

28 A (1, 2 and 3)

1: Carboxylic acid is strong enough to give an acidic solution while alcohol is neutral in water. Therefore, compound **Q** has a lower pH value.
2: $CH_3CH_2NH_2$ is a stronger base as the alkyl group exerts an electron donating inductive effect to make the lone pair of electrons on N more available for donation. While the lone pair of electrons on the N

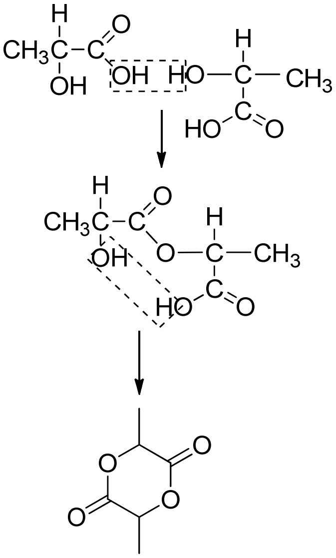
atom of $C_6H_5NH_2$ can delocalise into the benzene ring. Thus, $CH_3CH_2NH_2$ will give a higher pH value.
3: C_6H_5OH (phenol) is a weaker acid as compared to $C_6H_5CO_2H$ (carboxylic acid). Hence, the conjugate base of phenol, $C_6H_5O^-$, is a stronger base as compared to $C_6H_5CO_2^-$ (the conjugate base of $C_6H_5CO_2H$). Thus, C_6H_5ONa will give a higher pH value.

29 D (3 Only)

1: The empirical formula is $C_7H_{15}ON$. When the compound in option **1** is hydrolysed, it gives CH_3CO_2H, which has the empirical formula CH_2O.
2: The empirical formula is $C_8H_{17}ON$. When the compound in option **2** is hydrolysed, it gives $CH_3CH_2CH_2CO_2H$, which has the empirical formula C_2H_4O.
3: The empirical formula is $C_7H_{15}ON$. When the compound in option **3** is hydrolysed, it gives $(CH_3)_2CHCO_2H$, which has the empirical formula C_2H_4O.

30 B (1 and 2 Only)

Both compounds in options **1** and **2** can be formed as shown.



VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME ……………………………………………………..

CT GROUP ……………………………..

CHEMISTRY **9729/02**

Paper 2 Structured **11 September 2018**

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

Additional Materials: *Data Booklet*

READ THESE INSTRUCTIONS FIRST

Write your name and CT group on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions.

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

For Examiner's Use	
1	**/ 20**
2	**/ 20**
3	**/ 20**
4	**/ 15**
Total	**/ 75**

This document consists of **20** printed pages.

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 $Ag^+(BrF_4^-)$.

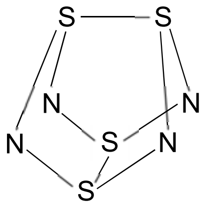
………………………..…………………………………………..…………………………… [1]

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

BrF_2^+	BrF_4^-

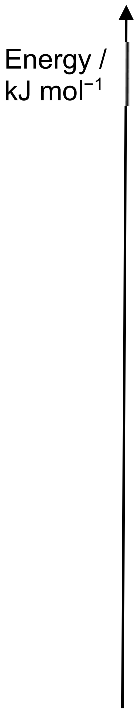
[2]

(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.



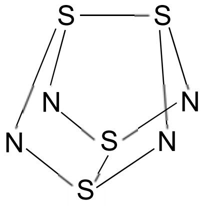
(i) Using the data given below, construct a suitable energy level diagram to calculate the S–N bond energy in S_4N_4.

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

…………………………………………………………………………………………….

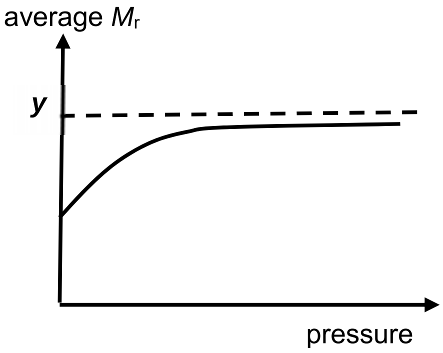
……………………….…………………….……………………………………………… .[1]

[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.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

…………………………………………………………………………………… [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.

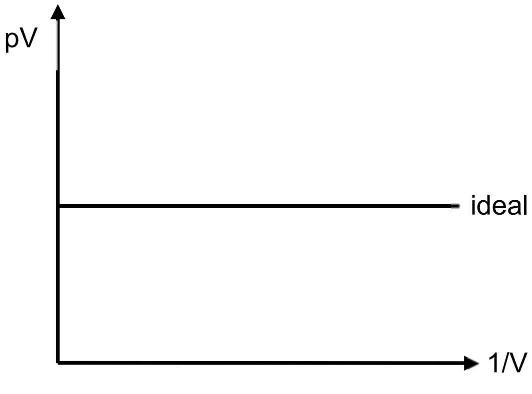
[1]

(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.

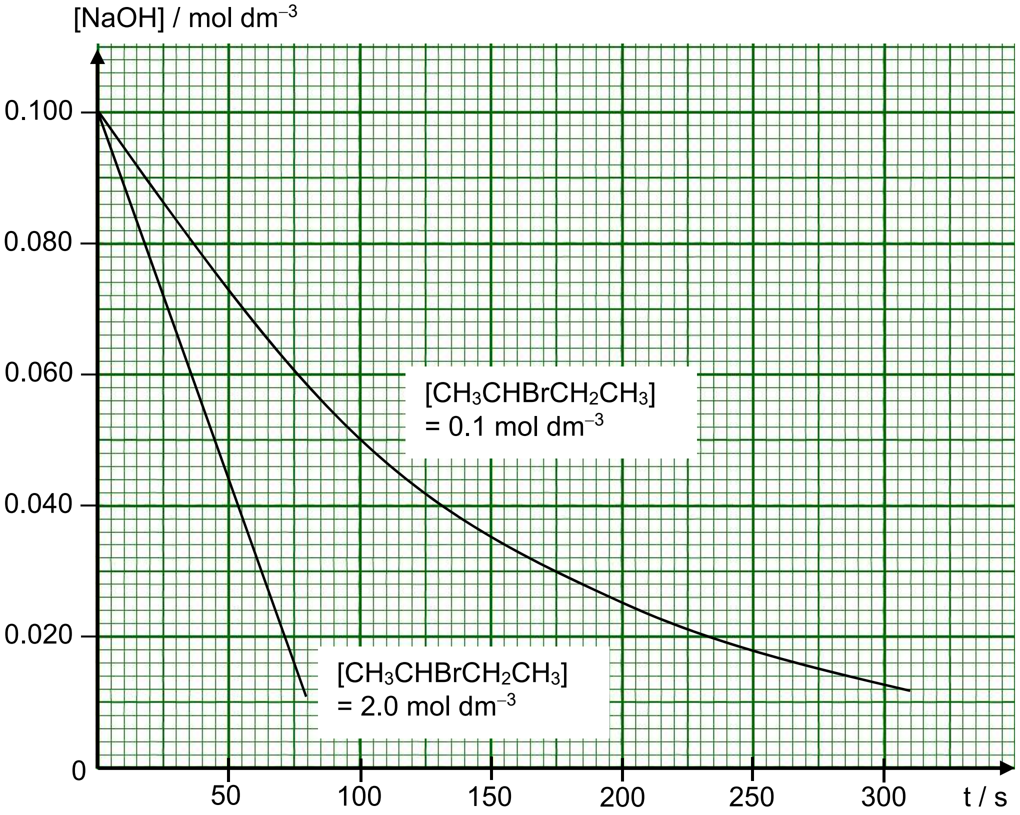


[1]

(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*.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

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

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

(I) NaOH, and

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

(II) $CH_3CHBrCH_2CH_3$

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………

[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.

……………………………………………………………………………………

…………………………………………………………………………………… [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.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

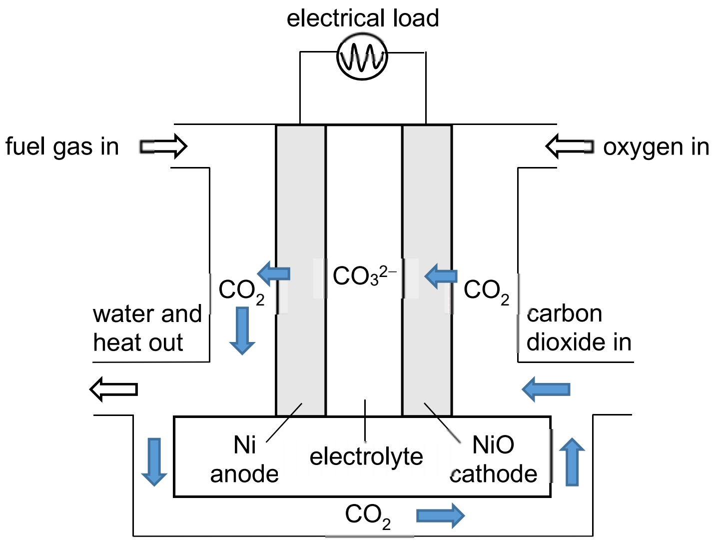
……………………………………………………………………………………………

…………………………………………………………………………………………… [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.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

………………………………………………………………………………………… [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.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

………………………………………………………………………………………… [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:

…………………………………………………………………………………………...

…………………………………………………………………………………………...

…………………………………………………………………………………………...

Barium carbonate:

…………………………………………………………………………………………...

…………………………………………………………………………………………...

…………………………………………………………………………………………...

[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.

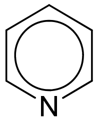
[2]

(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]

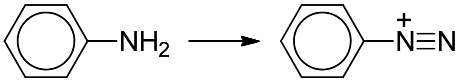
(iii) Write a balanced equation to show that pyridine is acting as

a Bronsted–Lowry base

a Lewis base but not a Bronsted–Lowry base

[2]

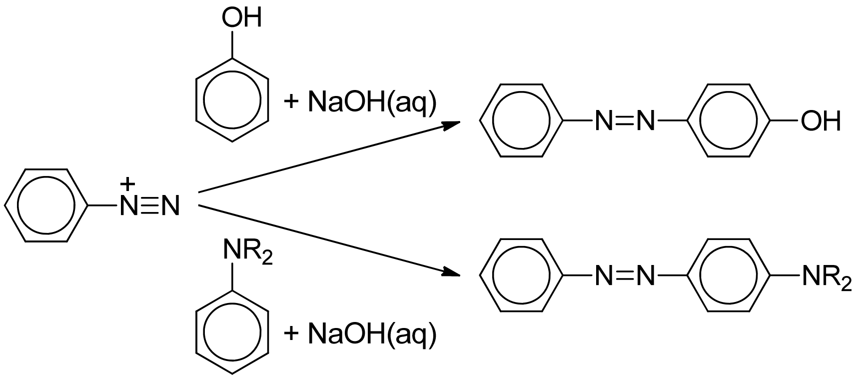
(b) Phenylamine and subsituted phenylamines are used to make dyes and food colourants. The first step in this process is the production of a diazonium ion as shown.



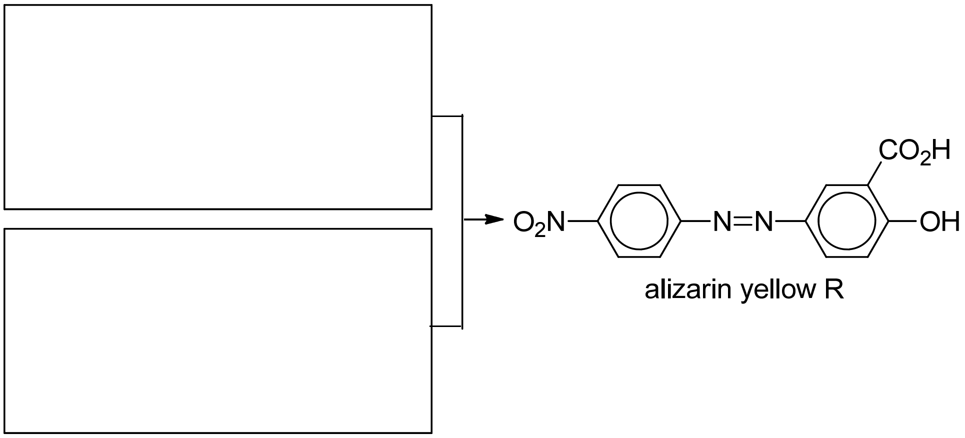
(i) State the type of reaction.

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

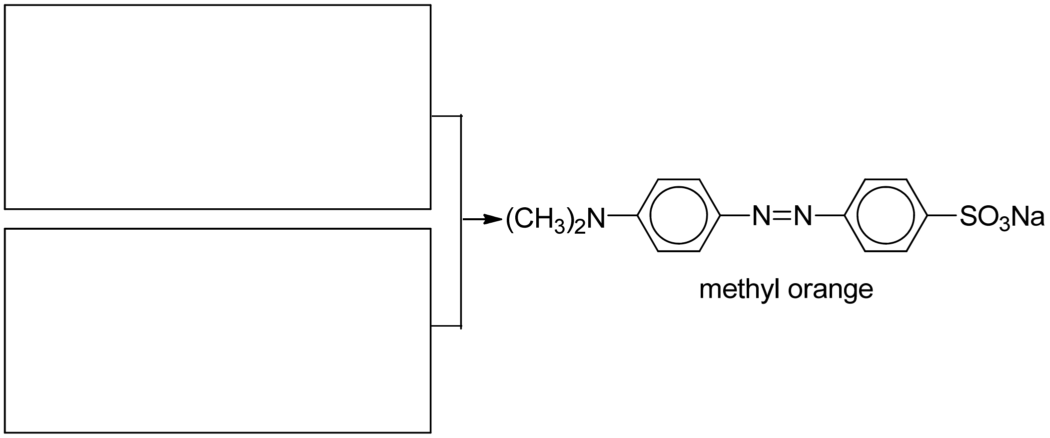
The diazonium ion is then reacted with a phenol or an arylamine in alkaline solution.



(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.

…………………………………………………………………………………………….

…………………………………………………………………………………………….

…………………………………………………………………………………………….

…………………………………………………………………………………………….

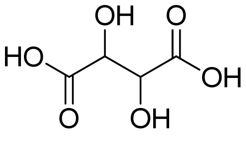
……………………………………………………………………………………… [2]

(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.

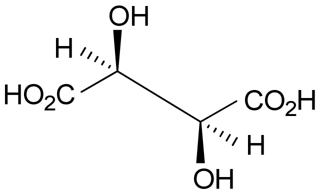


tartaric acid

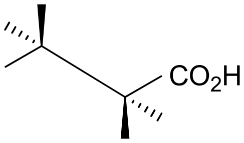
(i) Tartaric acid has two acid dissociation constants, K_{a1} and K_{a2}, for which the pK_a values are 2.99 and 4.40. Draw the species present at pH 4.40.

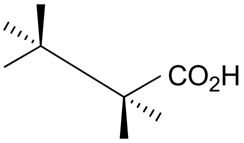
[1]

(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

VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME ……………………………………………………………..

CT GROUP ……………………………..

CHEMISTRY **9729/02**

Paper 2 Structured **11 September 2018**

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

Additional Materials: *Data Booklet*

READ THESE INSTRUCTIONS FIRST

Write your name and CT group on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions.

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

For Examiner's Use	
1	**/ 20**
2	**/ 20**
3	**/ 20**
4	**/ 15**
Total	**/ 75**

This document consists of **20** printed pages.

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 $Br_2(l)$, $S^{\ominus}(Br_2)$ / J mol^{-1} K^{-1}	152
Standard entropy of $BrF_3(l)$, $S^{\ominus}(BrF_3)$ / J mol^{-1} K^{-1}	178

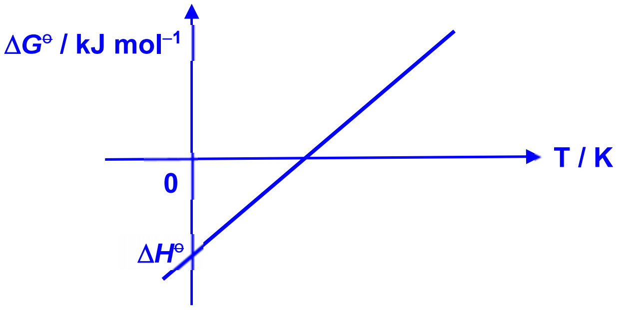
(i) The above reaction is spontaneous at 298 K even though $\Delta S^{\ominus}$ is negative. Explain qualitatively why $\Delta H^{\ominus}$ is the predominant factor that causes the reaction to be spontaneous.

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus} < 0$ at 298 K

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

[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.

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

$-403 = 2(178) - [152 + 3S^\ominus(F_2)]$
$S^\ominus(F_2) = 202$ J mol^{-1} 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 $Ag^+(BrF_4^-)$.

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

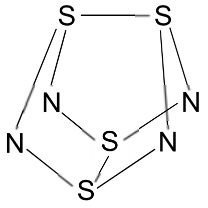
[1]

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

bent BrF_2^+	**square planar** BrF_4^-

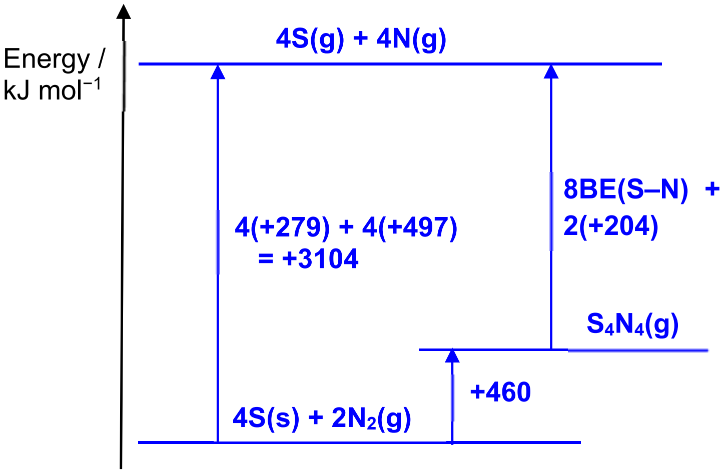
[2]

(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.

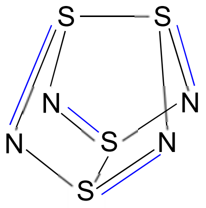
$\Delta H_f^\ominus [S_4N_4(g)] = +460$ kJ mol^{-1}
$\Delta H_{at}^\ominus [S(s)] = +279$ kJ mol^{-1}
$\Delta H_{at}^\ominus$ [nitrogen] = +497 kJ mol^{-1}
Bond energy of (S–S) in S_4N_4 = +204 kJ mol^{-1}



By Hess's Law,
8BE(S–N) + 2(+204) = –(+460) + 3104
BE(S–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.

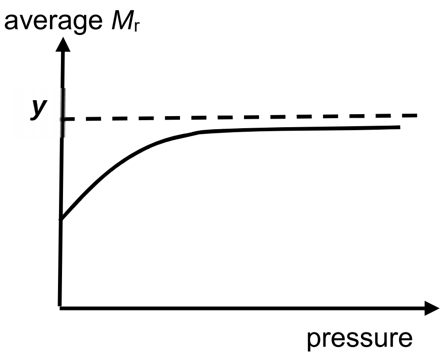
[1]

[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 × 0.0626
= 0.0252 mol

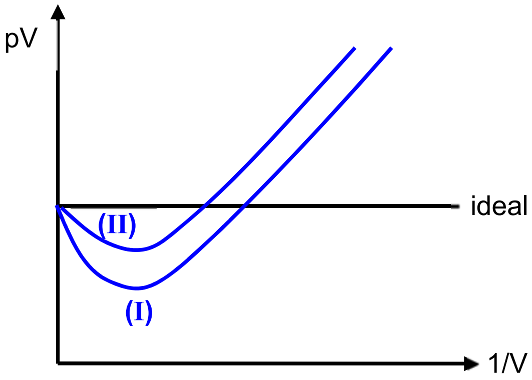
$n_{N_2O_4}$
= 0.0626 – 0.0252
= 0.0374 mol

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

[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.

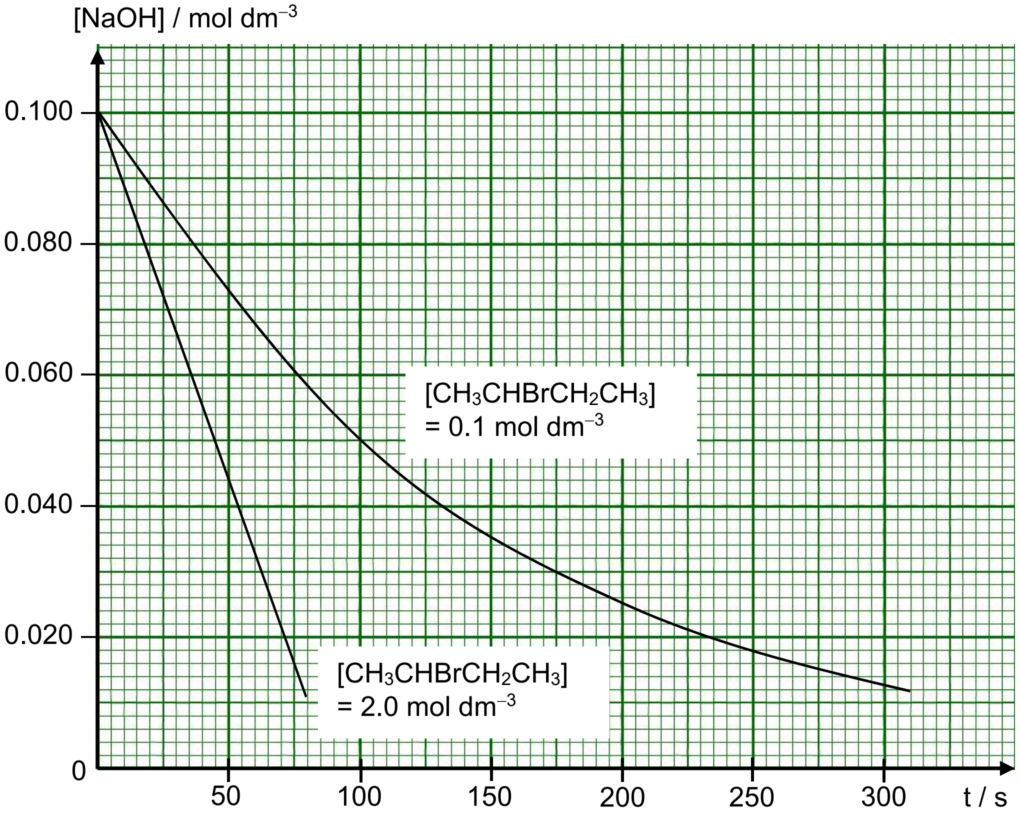


[1]

(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 ÷ 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.

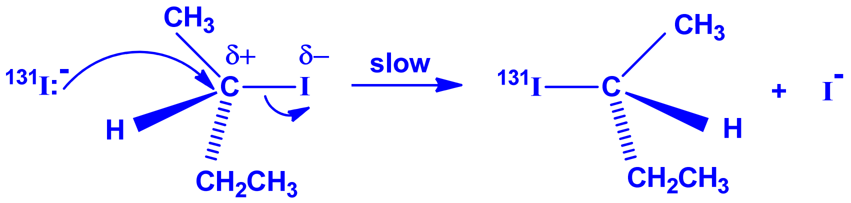
Let the percentage composition of B be z% and the percentage composition of A be $(100 - z)$%.

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

Since percenatge composition of B is less than 75 %, the predominant mechanism is $\underline{S_N1}$.

[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.

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

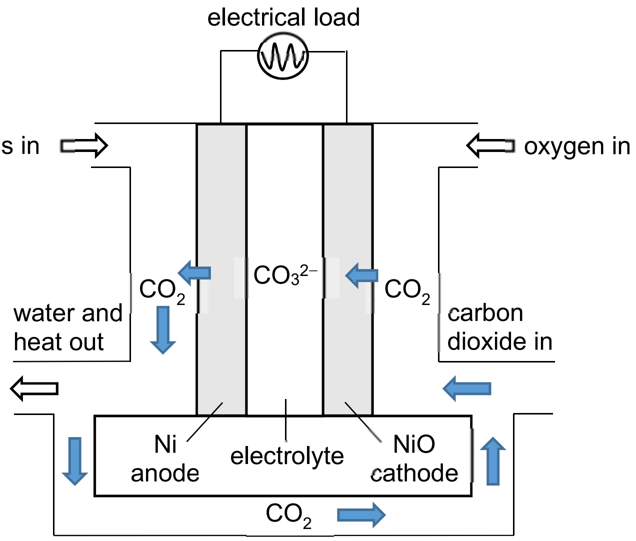
Standard reduction potential, $E^\ominus$, for nickel and iron are both much less negative than that of magnesium.

[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.

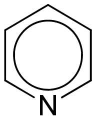
Percentage of Ba^{2+} ions remained
$= \frac{0.0146}{0.100} \times 100\%$ (ecf)
$= 14.6\% >> 1\%$

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]

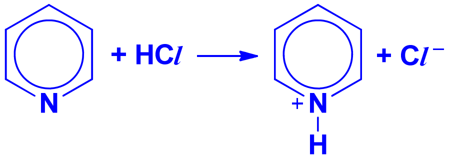
(ii) Hence, explain why pyridine has a higher pK_b than ethylamine, $CH_3CH_2NH_2$.

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.

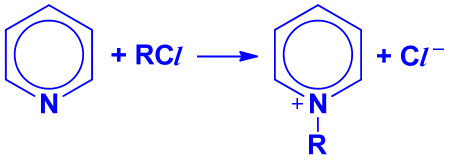
[1]

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

a Bronsted–Lowry base

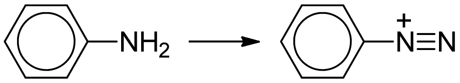


a Lewis base but not a Bronsted–Lowry base



[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.

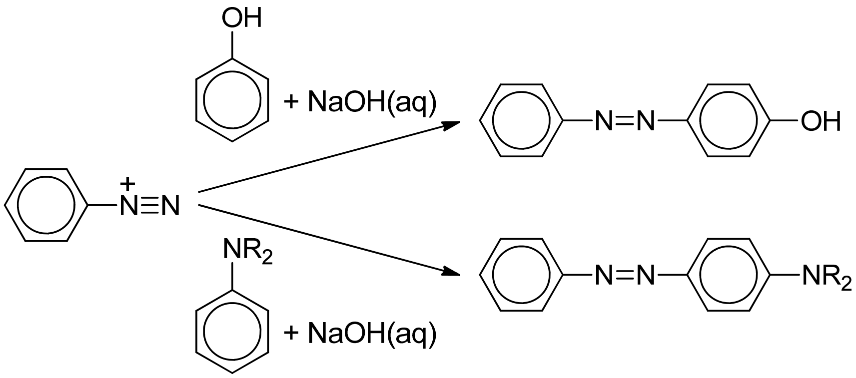


(i) State the type of reaction.

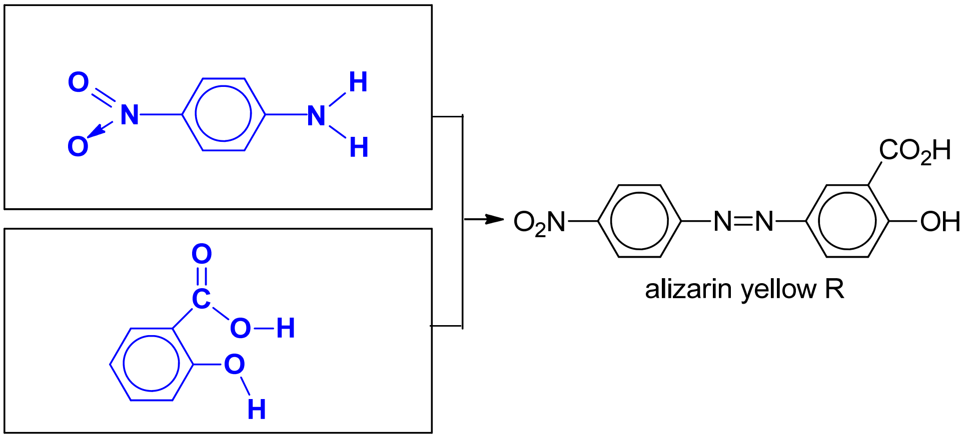
Oxidation

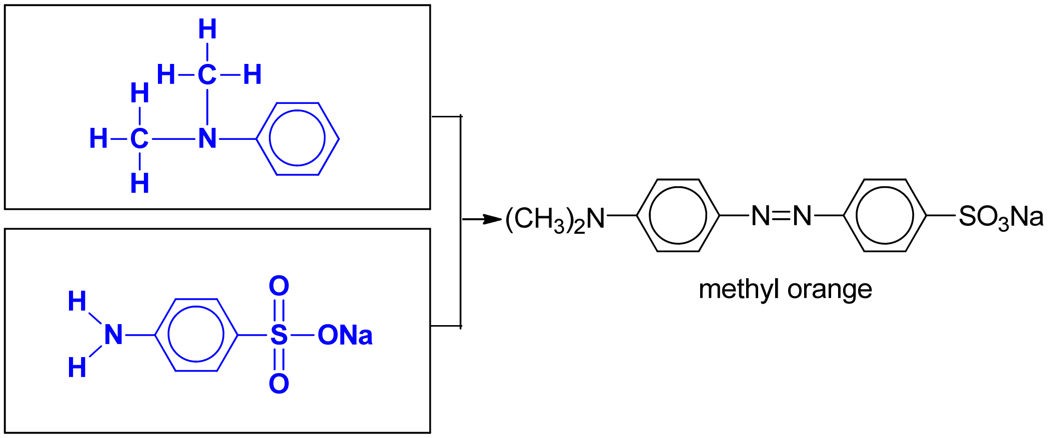
[1]

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 NaO₃S− group in methyl orange is less reactive towards bromine than the other benzene ring. Suggest **two** reasons.

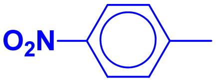
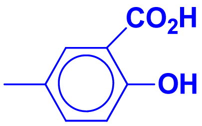
NaO₃S− group is an electron withdrawing group, making the benzene ring less electron–rich and less susceptible to electrophilic attack.

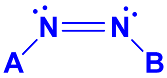
Lone pair of electrons on –N(CH₃)₂ can delocalise into the benzene ring, making the benzene ring more electron–rich and more susceptible to electrophilic attack.

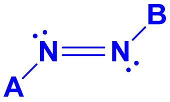
[2]

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

Draw the stereoisomers of alizarin yellow R.

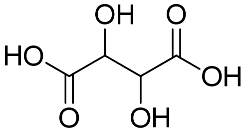
Let A be  **. Let B be**  .





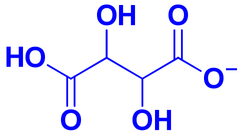
[1]

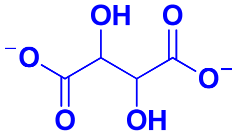
(c) Tartaric acid is present in many plants.



tartaric acid

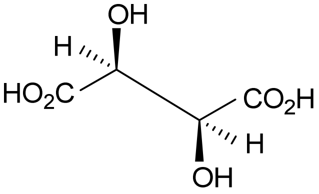
(i) Tartaric acid has two acid dissociation constants, K_{a1} and K_{a2}, for which the pK_a values are 2.99 and 4.40. Draw the species present at pH 4.40.



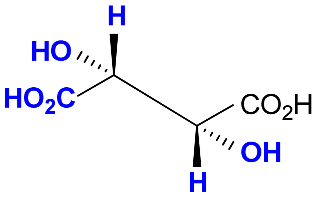


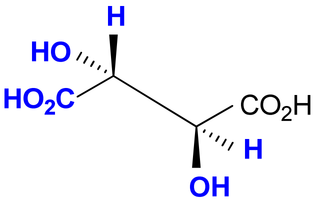
[1]

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



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





[2]

[Total: 15]

VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME ……………………………………………..…………..

CT GROUP ……………………………..

CHEMISTRY 9729/03

Paper 3 Free Response **17 September 2018**

Candidates answer on separate paper. **2 hours**

Additional Materials: Cover Page
Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and CT group on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.
You must start the answer to each question on a fresh piece of writing paper.

Section A
Answer **all** questions.

Section B
Answer **one** question.

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

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **11** printed pages and **1** blank page.

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.

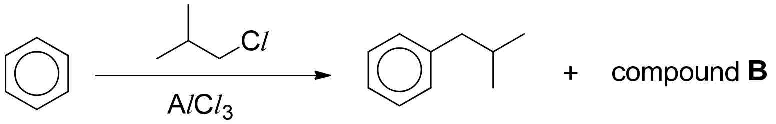
(II) When excess water was added, a solution of pH 3 was obtained. [2]

(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 **A**

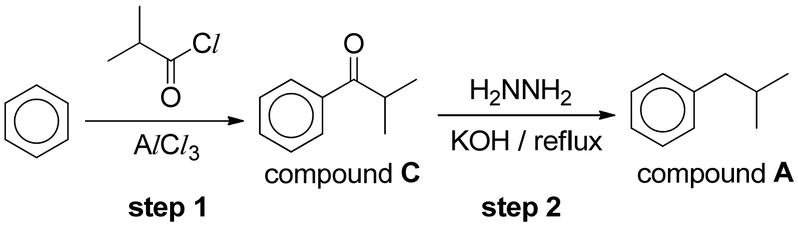
(i) Compound **B** rotates plane-polarised light. It is formed after the carbocation intermediate undergoes rearrangement through the movement of an alkyl group to an adjacent carbon atom bearing the positive charge.

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]

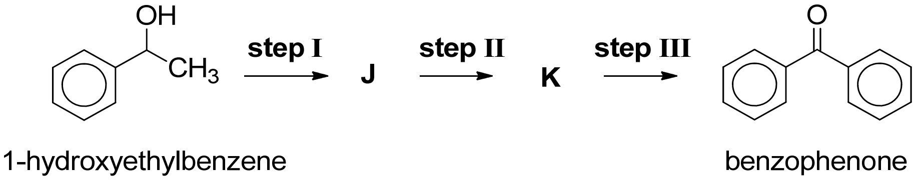
(c) Compound **A** can be formed via compound **C** as shown in **Reaction 2** below. **Step 1** involves Friedel–Crafts acylation, which have similar reaction conditions and mechanism as Friedel-Crafts alkylation.

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

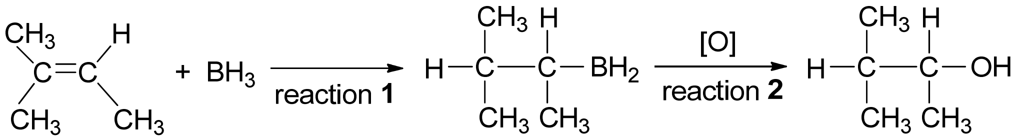
- ethanol, hexane, HC*l*(aq), NaOH(aq),
- separating funnel, and
- apparatus commonly found in a college laboratory.

[3]

[Total: 20]

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

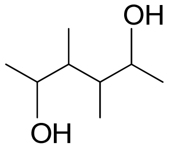
In reaction **1**, the BH_2 group from BH_3 is bonded to the **less** substituted carbon atom of the double bond. The remaining H atom from BH_3 is bonded to the other carbon atom.



(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.

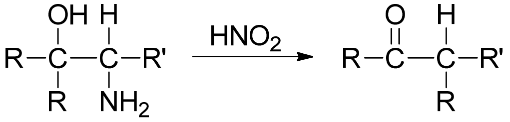


W

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.



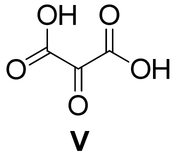
$$R-\underset{R}{\overset{OH}{C}}-\underset{NH_2}{\overset{H}{C}}-R' \xrightarrow{HNO_2} R-\overset{O}{\overset{\|}{C}}-\underset{R}{\overset{H}{C}}-R'$$

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]

(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]

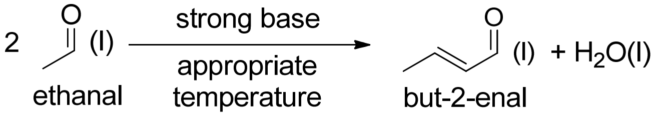
(c) Devise a three–step synthesis to obtain compound **V** from the carbonyl compound, $ClCH_2CHO$.



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]

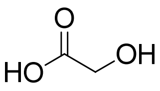
(ii) Explain why the actual enthalpy change for the Aldol Condensation reaction is different from that calculated in **(d)(i)**. [1]

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

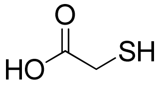
[Total: 20]

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.

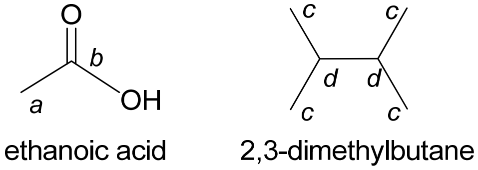
(i) Draw all the possible structures of $C_6H_4R_2$. [1]

(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−.

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

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.

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

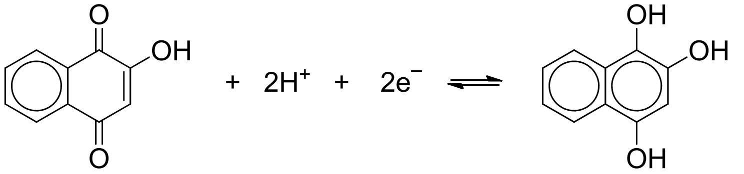
Unlike ClO_2, bromine dioxide is less stable and react with aqueous hydroxide to produce bromide and bromate(V) ions. Bromate(V) ion is formed more readily than chlorate(V) ion.

(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.



$E^\ominus = +0.36$ V

lawsone

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

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

(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}.

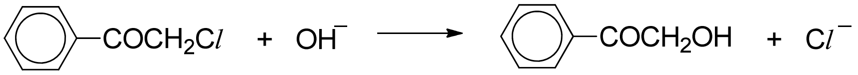
Using the answer from **(a)(iii)** and the *Data Booklet*, calculate K_c. Hence, deduce whether the position of equilibrium lies more on the left or right hand side of the equilibrium under standard conditions. [2]

(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 HC*l* and ZnC*l*$_2$ 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**.

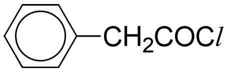
Suggest the skeletal formulae of compounds **B**, **C**, **D**, **E** and **F**. [5]

(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.

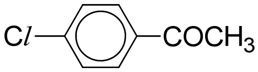


chloroacetophenone

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

VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME ………………………………………………..…………..

CT GROUP ……………………………..

CHEMISTRY **9729/03**

Paper 3 Free Response **17 September 2018**

Candidates answer on separate paper. **2 hours**

Additional Materials: Cover Page
Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and CT group on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.
You must start the answer to each question on a fresh piece of writing paper.

Section A
Answer **all** questions.

Section B
Answer **one** question.

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

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **11** printed pages and **1** blank page.

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.

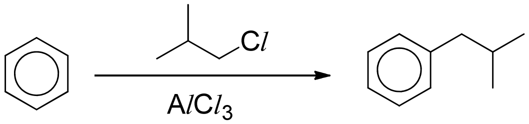
The oxygen released at the anode reacts with the aluminium surface to build up a thicker layer of aluminium oxide.

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:



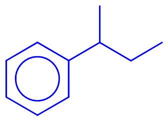
\+ compound **B**

compound **A**

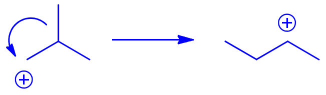
(i) Compound **B** rotates plane-polarised light. It is formed after the carbocation intermediate undergoes rearrangement through the movement of an alkyl group to an adjacent carbon atom bearing the positive charge.

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

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:

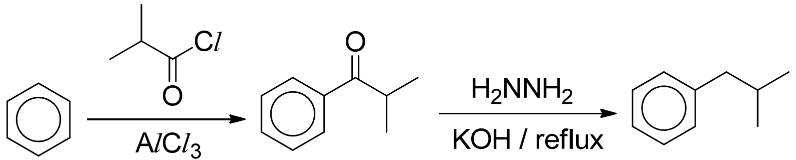


(ii) Explain why multi-substituted product is more favoured over mono-substituted product in **Reaction 1**. [1]

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:



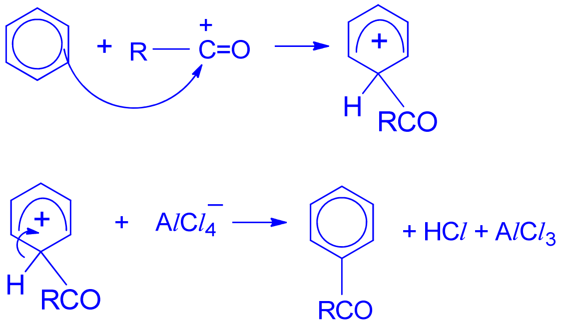
compound **C**

compound **A**

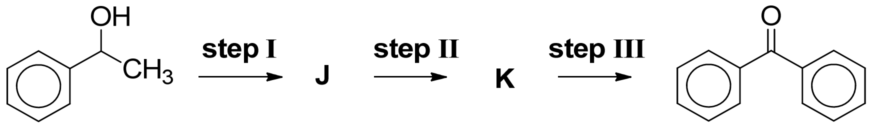
step 1

step 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**.

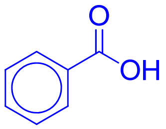


1-hydroxyethylbenzene

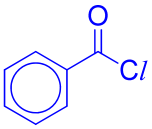
benzophenone

[4]

J:



K:



step I: $KMnO_4$, H_2SO_4, reflux
step II: PCl_5, room temperature OR PCl_3, reflux OR $SOCl_2$, reflux
step III: C_6H_6, anhydrous $AlCl_3$, 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, HCl(aq), NaOH(aq),
- separating funnel and
- apparatus commonly found in a college laboratory.

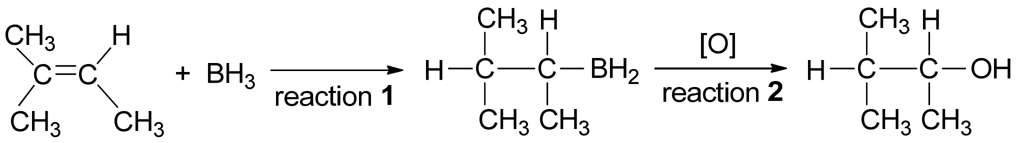
[3]

(i) Dissolve the solid sample in hexane.
(ii) Transfer the mixture to a separating funnel.
(iii) Add HCl(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, BH_3, is used to synthesise alcohols from alkenes as shown in the reaction sequence below.

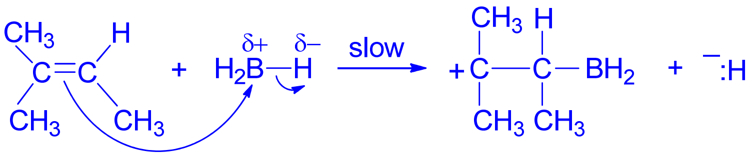
In reaction **1**, the BH_2 group from BH_3 is bonded to the **less** substituted carbon atom of the double bond. The remaining H atom from BH_3 is bonded to the other carbon atom.



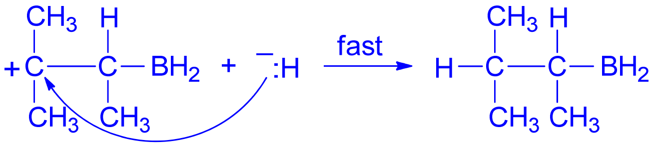
(i) Name and show the mechanism of reaction **1**. In your answer, show relevant charges, lone pairs of electrons and movement of electrons. [3]

Mechanism: Electrophilic addition

Step 1:



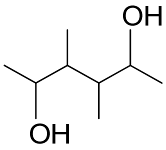
Step 2:



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

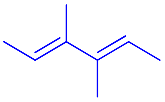
The product does not rotate plane-polarised light.
The alkene carbon atom is sp^2 hybridised (or trigonal planar).
Electrophile can attack from either the top or bottom plane of the C=C with equal probability. Hence, a racemic mixture is formed.

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



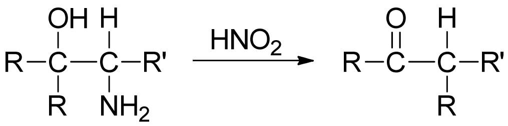
W

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.

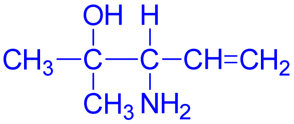


$R-C(OH)(R)-CH(NH_2)-R' \xrightarrow{HNO_2} R-CO-CH(R)-R'$

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.

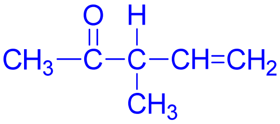
(i) Explain the chemistry of the reactions described and deduce the structural formulae of **X**, **Y** and **Z**. [5]

X is



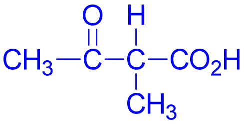
$CH_3-C(OH)(CH_3)-CH(NH_2)-CH=CH_2$

Y is



$CH_3-CO-CH(CH_3)-CH=CH_2$

Z is



$CH_3-CO-CH(CH_3)-CO_2H$

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

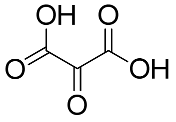
Y undergoes oxidative cleavage with hot acidified $KMnO_4(aq)$ to produce $CO_2(g)$ which forms white ppt. in limewater. Y is a terminal alkene (OR has $=CH_2$ group).

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]

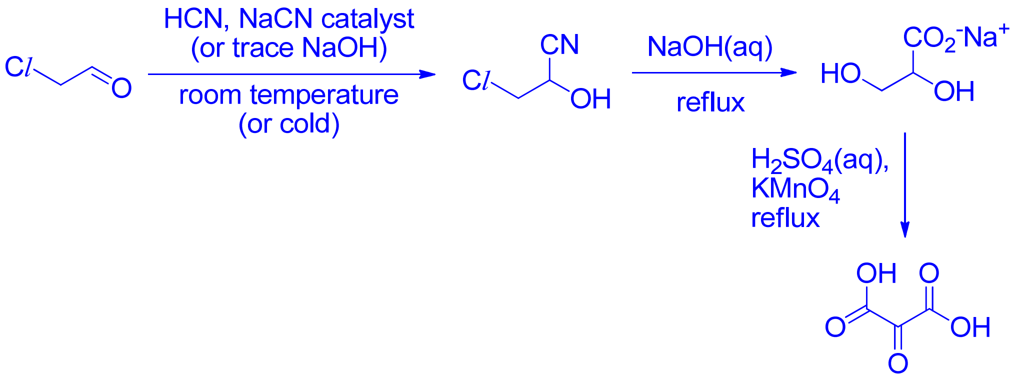
1670 – 1740 cm^{-1} due to ketone functional group.

(c) Devise a three–step synthesis to obtain compound **V** from the carbonyl compound, C*l*CH$_2$CHO.

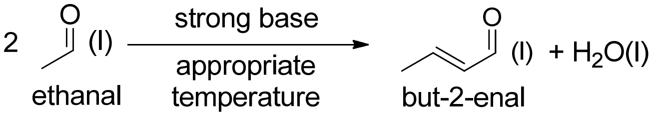


V

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

ΔH = +1560 – (+1530) = +30 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.

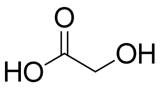
(iii) Suggest a simple chemical test to confirm the presence of but-2-enal in the product mixture. [1]

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.

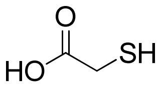
[Total: 20]

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

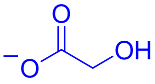
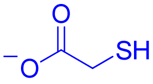
Glycolic acid has only one measurable pK_a value of 3.38. Thioglycolic acid has two measurable pK_a values of 3.67 and 10.31 respectively.

(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]

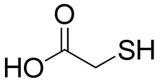
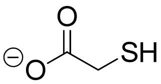
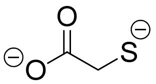
Glycolic acid is the stronger acid since it has a lower pK_a value.
O atom is more electronegative than S,

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]

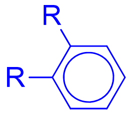
= $2.62 \times 10^{-3} \div 0.100$

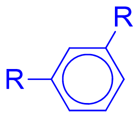
= 0.0262 dm^3 = 26.2 cm^3

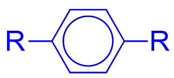
(b) The hydroxide ion is the strongest possible base in aqueous solution, but in organic solvents it is possible to have other stronger bases. In 2016, Australian researchers announced the formation of an organic gas-phase di-anion, DEB^{2-}. It is the strongest base known.

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]



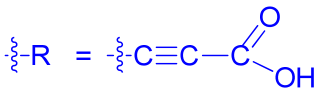




(ii) Compound **A** has the molecular formula $C_{12}H_6O_4$ and effervesces on addition of sodium hydrogen carbonate.

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

Carboxylic acid

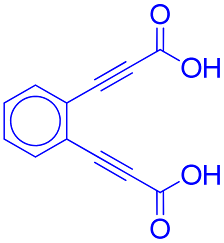


^{13}C nuclear magnetic resonance (NMR) spectroscopy is an analytical method. In simplistic use, it allows different types of carbon atoms to be deduced from the corresponding signals in the spectrum.

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

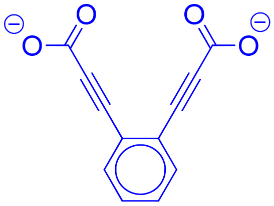
(iii) Compound **A** is found to have six signals in its ^{13}C NMR spectrum. Using your answers to **(b)(i)**, **(b)(ii)** and the information provided above, deduce the structure of compound **A**. [1]



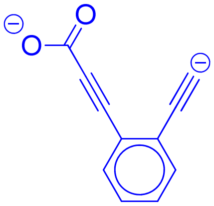
(iv) Compound **A** forms DEB^{2-} via intermediates **B**$^{2-}$ and **C**$^{2-}$ through the removal of positive ions or neutral molecule from the substituent R−.

$$\underset{C_{12}H_6O_4}{\text{Compound } \mathbf{A}} \longrightarrow \underset{M_r = 212}{\mathbf{B}^{2-}} \longrightarrow \underset{M_r = 168}{\mathbf{C}^{2-}} \longrightarrow \underset{M_r = 124}{\text{DEB}^{2-}}$$

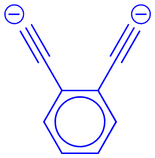
Determine the skeletal structures of **B**$^{2-}$, **C**$^{2-}$ and DEB^{2-}. [2]



B^{2-}



C^{2-}



DEB^{2-}

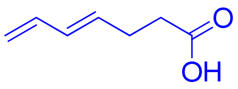
(c) An organic acid **D**, $C_7H_{10}O_2$, is refluxed with acidified $KMnO_4$ to produce only one organic compound **E**, $C_4H_6O_4$. Compound **D** decolourises bromine water. Gentle heating of the anhydrous crystals of compound **E** produces a neutral compound **F**, $C_4H_4O_3$, which does not 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**, $C_6H_{10}O_4$.

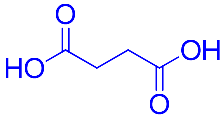
Compound **F** also reacts with methylamine, CH_3NH_2, to give a compound **H**, $C_5H_9NO_3$, which gives a salt on reaction with NaOH but not with HC*l*. Compound **H** does not display enantiomerism.

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

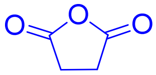
Suggest the structures of **D**, **E**, **F**, **G** and **H**. [5]



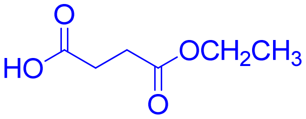
D



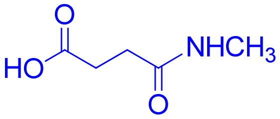
E



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.

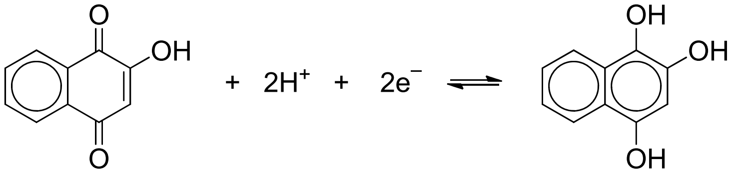
(ii) Explain why bromate(V) ion is formed more readily than the chlorate(V) ion in aqueous hydroxide. [1]

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:

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

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]

$\Delta G^\ominus = -nFE^\ominus_{cell} = -2 \times 96500 \times (-1.28) = 2.47 \times 10^5$ J mol^{-1}

$\Delta G^\ominus = -RT \ln K_c = -8.31 \times 298 \times \ln K_c = 2.47 \times 10^5$

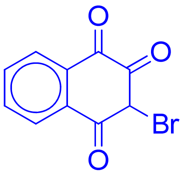
$\Rightarrow K_c = 4.73 \times 10^{-44} << 1$ means position of equilibrium lies more to the left.

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

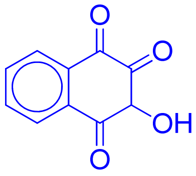
$NaBH_4$ (in ethanol) or $LiAlH_4$ (in dry ether)

(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**.

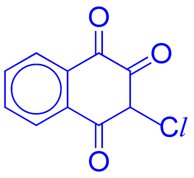
Suggest the skeletal formulae of compounds **B**, **C**, **D**, **E** and **F**. [5]



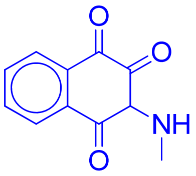
B



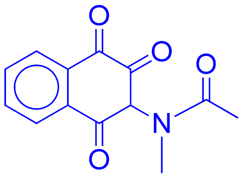
C



D

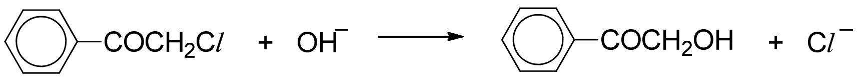


E



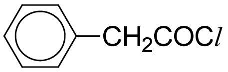
F

(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.

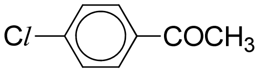


chloroacetophenone

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.

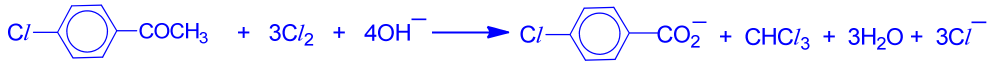
(ii) Iodoacetophenone is even more reactive than chloroacetophenone towards alkaline hydrolysis. Briefly explain why it is so. [1]

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]

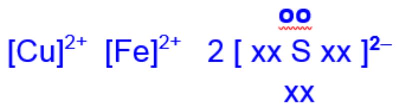


Pale greenish-yellow solution decolourised.

[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]



$$[Cu]^{2+} \quad [Fe]^{2+} \quad 2\,[\,xx\,\overset{oo}{\underset{xx}{S}}\,xx\,]^{2-}$$

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

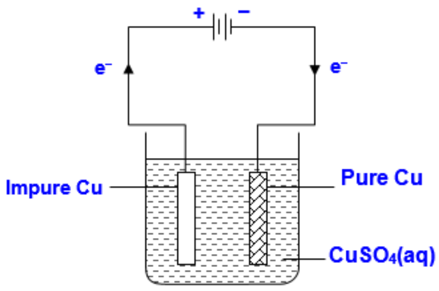
$CuFeS_2 + \frac{7}{2}O_2 + SiO_2 \rightarrow Cu + FeSiO_3 + 2SO_3$

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.
$Ni^{2+} + 2e^- \rightleftharpoons Ni \quad -0.25\ V$
$Cu^{2+} + 2e^- \rightleftharpoons Cu \quad +0.34\ V$
$Ag^+ + e^- \rightleftharpoons Ag \quad +0.80\ V$

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.

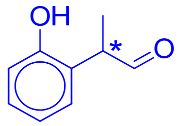
(b) Compounds **W**, **X**, **Y** and **Z** are constitutional isomers with molecular formula $C_9H_{10}O_2$ and none of them shows *cis-trans* isomerism. All four isomers can form intra-molecular hydrogen bonding. The results of seven tests carried out on the four isomers are shown below.

	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

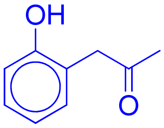
3	Heat with acidified $K_2Cr_2O_7$	Orange solution turned green	Orange solution did not turn green	Orange solution turned green	Orange solution turned green
4	Add 2,4-DNPH	Orange precipitate	Orange precipitate	No orange precipitate	Orange precipitate
5	Warm with Fehling's solution	Brick-red precipitate	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]

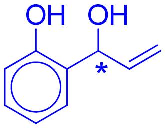
W



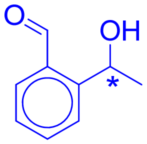
X



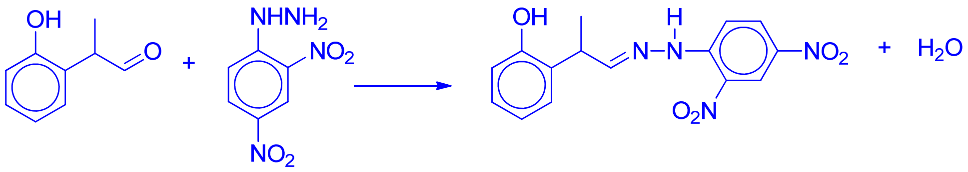
Y



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

VICTORIA JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME ………………………………………………….…………..

CT GROUP ……………………………..

CHEMISTRY

9729/04

Practical

30 August 2018

2 hours 30 minutes

Additional Materials: As listed in the instructions below

READ THESE INSTRUCTIONS FIRST

Write your name and CT group on all the work you hand in.
Give details of the practical shift and laboratory where appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use a HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 14 and 15.
Periodic Table is printed on page 16.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

Shift
Laboratory

For Examiner's Use	
1	
2	
3	
4	
Total	

This document consists of **16** printed pages.

1 You are to determine the concentration, in g dm^{-3}, of sodium ethanedioate in a mixture of sodium ethanedioate and ethanedioic acid.

This experiment involves two titrations.
In titration one, you will carry out a titration to find the total amount of ethanedioate ion, $C_2O_4^{2-}$.
In titration two, you will use the information provided to find the amount of ethanedioic acid, $H_2C_2O_4$.
Finally, you will use the values found in the two titrations to calculate the concentration, in g dm^{-3}, of sodium ethanedioate in **FA 1**.

FA 1 is a mixture of aqueous sodium ethanedioate, $Na_2C_2O_4$, and ethanedioic acid, $H_2C_2O_4$.
FA 2 is approximately 2 mol dm^{-3} sulfuric acid, H_2SO_4.
FA 3 is 0.0200 mol dm^{-3} potassium manganate(VII), $KMnO_4$.

Titration One

(a) 1. By using a burette, measure 42.50 cm^3 of **FA 1** into the 250 cm^3 graduated (volumetric) flask.
2. Record your burette readings and the volume of **FA 1** added to the flask in the space below.

[1]

3. Make up the contents of the flask to the 250 cm^3 mark with deionised water. Place the stopper in the flask and mix the contents thoroughly by slowly inverting the flask a number of times. Label this solution **FA 4**.
4. Fill a second burette with **FA 3**.
5. Pipette 25.0 cm^3 of **FA 4** from the graduated flask into a conical flask.
6. Use a measuring cylinder to add 25 cm^3 of **FA 2** to the conical flask.
7. Place the conical flask on a tripod and gauze and heat to about 65 °C.
8. If the neck of the flask is too hot to hold safely, use a folded paper towel to hold the flask.
9. Titrate the mixture in the conical flask with **FA 3** until a permanent pale pink colour is obtained. This is the end-point.
10. **If a brown colour appears during the titration**, reheat the flask to 65 °C. The brown colour should disappear and the titration can be completed as above. **If the brown colour does not disappear on reheating**, discard the solution and start the titration again.
11. Carry out as many titrations as you think necessary to obtain consistent results.
12. Record in an appropriate form below all of your burette readings and the volume of **FA 3** added in each titration.

[5]

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

25.0 cm^3 of **FA 4** required ………………… cm^3 of **FA 3**. [1]

Titration Two

(c) When 25.0 cm^3 of **FA 4** used in **(a)** is titrated with 0.100 mol dm^{-3} sodium hydroxide using phenolphthalein as the indicator, 15.50 cm^3 of sodium hydroxide is needed for complete reaction.

(i) Write an equation for the reaction between sodium hydroxide and ethanedioic acid.

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

(ii) Calculate the number of moles of sodium hydroxide required to react with 25.0 cm^3 of **FA 4**.

moles of NaOH = ………………… mol [1]

(iii) Hence, calculate the number of moles of ethanedioic acid in 25.0 cm^3 of **FA 4**.

moles of $H_2C_2O_4$ in 25.0 cm^3 of **FA 4** = ………………… mol [1]

(d) **(i)** Use your answer from **(b)** to calculate the number of moles of potassium manganate(VII), **FA 3**, required to react with 25.0 cm^3 of **FA 4** in **Titration One**.

moles of $KMnO_4$ = ………………… mol [1]

(ii) The equation for the reaction between acidified manganate(VII) ions and ethanedioate ions is shown below.

$2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$

Use your answer from **(d)(i)** to calculate the total number of moles of ethanedioate ions in 25.0 cm^3 of **FA 4**.

total moles of $C_2O_4^{2-}$ in 25.0 cm^3 of **FA 4** = ………………… mol [1]

(iii) Use your answers from **(c)(iii)** and **(d)(ii)** to calculate the number of moles of ethanedioate ions which came from the sodium ethanedioate in 25.0 cm^3 of **FA 4**.

moles of $C_2O_4^{2-}$ from $Na_2C_2O_4$ in 25.0 cm^3 of **FA 4** = ………………… mol [1]

(iv) Hence, calculate the concentration, in g dm^{-3}, of sodium ethanedioate in **FA 1**.

Concentration of sodium ethanedioate in **FA 1** = ………………… g dm^{-3} [2]

(e) Explain why the decolourisation of **FA 3** in **Titration One** is initially slow but becomes faster as the reaction proceeds.

…………………………………………………………………………………………………

…………………………………………………………………………………………………

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

[Total: 16]

2 This question concerns the solubility of **FA 5**, potassium bromate(V), $KBrO_3$, in water.

The **solubility** of a substance in water is defined as:
the mass of substance that will dissolve in and just saturate 100 g of water at a particular temperature.
When a solution is saturated, the dissolved solid is in equilibrium with undissolved solid.
When a solution of potassium bromate(V) is cooled, it becomes saturated when crystals form in the solution.

You are to investigate how the solubility of **FA 5** in water varies with temperature.

You are provided with the following materials

- weighing bottle labelled **FA 5**, containing potassium bromate(V), $KBrO_3$, and
- deionised water.

Read through the instructions before starting any practical work.

(a)

1. Prepare a hot water bath by filling a 250 cm^3 beaker half full of water and heat it over the Bunsen burner until almost boiling. Turn off the Bunsen burner.
2. Weigh an empty boiling tube.
3. Add the contents of the weighing bottle labelled **FA 5** to the boiling tube.
4. Reweigh the boiling tube and its contents.
5. Record, in an appropriate form below, your weighings and the mass of **FA 5** used.

6. Use the 10 cm^3 measuring cylinder to transfer 8.0 cm^3 of deionised water to the weighed boiling tube containing **FA 5**.
7. Use the clamp as a holder for the boiling-tube. Take care not to break the tube by clamping it too tightly.
8. Warm the tube carefully in the water bath, while stirring the contents with a thermometer, until all the solid has dissolved. (Take care that you do not break the thermometer bulb or the tube while stirring.)
9. Remove the tube from the water bath and attach the clamp to a retort stand.
10. Let the tube cool and continue to stir gently with the thermometer.
11. Watch the solution carefully. Note and record (**on the next page**) the temperature at which you **first** notice crystals forming in the solution.
12. If you are uncertain about the temperature when crystals first form, warm the tube again for a few moments and repeat the cooling.
13. As soon as you have recorded the temperature, add a further 2.0 cm^3 of deionised water to the tube using the 10 cm^3 measuring cylinder.
14. Warm the tube in the water bath to re-dissolve the solid and cool as before.
15. Note and record (**on the next page**) the temperature at which crystals now form in the solution. This will be lower than the temperature obtained with 8.0 cm^3 of water.
16. Repeat the addition of 2.0 cm^3 of deionised water, the heating and the cooling, until you have **four** readings in total.

17. In an appropriate form in the space below, record the following.
    - the total volume of deionised water in the boiling-tube,
    - the temperature at which crystals first appeared for each solution,
    - the solubility (in grams of solid per 100 g of water) which can be calculated using the following formula

$$\text{solubility} = \frac{100}{\text{volume of water}} \times \text{mass of } \mathbf{FA\ 5} \text{ dissolved}$$

[6]

(b) On the grid, plot a graph of solubility against temperature and draw an appropriate line through the points. Do **not** start at zero on either axis. You will need to be able to find the solubility of **FA 5** at 55 °C.

[3]

(c) Use your solubility curve in **(b)** to answer the following.

(i) Explain if dissolving potassium bromate(V), $KBrO_3$, is an exothermic or endothermic process.

$$KBrO_3(s) \rightleftharpoons K^+(aq) + BrO_3^-(aq)$$

……………………………………………………………………………………………………

……………………………………………………………………………………………………

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

(ii) Calculate the solubility of potassium bromate(V), $KBrO_3$, at 55 °C in mol dm^{-3}.
[Given that the M_r of $KBrO_3$ is 167.0.]

[1]

(iii) Hence, calculate the K_{sp} of potassium bromate(V) at this temperature, giving the units.

[2]

(d) Student **A** claims that both the solubility and solubility product of potassium bromate(V) will decrease with the addition of some solid potassium nitrate at a particular temperature. Comment on this student's claim.

……………………………………………………………………………………………………

……………………………………………………………………………………………………

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

(e) A literature value for the solubility of potassium bromate(V) is 13.1 g per 100 g of water at 40 °C. Student **A** followed the instructions in part **(a)** and obtained a solubility value for $KBrO_3$ to be 15.0 g per 100 g of water at the same temperature. Calculate the magnitude of the percentage experimental error for student **A**'s measurement.

[1]

[Total:15]

3 Planning

FA 6 is a powdered mixture of mica and iron(III) oxide, Fe_2O_3, which is used as ingredients in mineral makeup such as eye shadow or blusher. Iron(III) oxide adds a red colour to makeup while mica gives makeup a light reflecting quality.

The reaction between Fe_2O_3, and ethanedioic acid, $H_2C_2O_4$, is exothermic as shown.

$$Fe_2O_3(s) + 3H_2C_2O_4(aq) \rightarrow Fe_2(C_2O_4)_3(aq) + 3H_2O(l) \quad \Delta H < 0$$

In a thermometric titration, the end–point is reached when the maximum temperature change occurs. A thermometric titration between Fe_2O_3 and $H_2C_2O_4$ can be carried out to find out the percentage by mass of iron(III) oxide in **FA 6**. The temperature of the reaction mixture is monitored when a certain mass of **FA 6** is added into a fixed volume of aqueous $H_2C_2O_4$ solution. The experiment is then repeated using different masses of **FA 6**. You may assume mica remains unchanged in this experiment.

The data obtained is plotted and two best–fit graph lines are drawn. One line is drawn using data before the end–point and the second line using the remaining data. These lines are then extrapolated until they intersect.

(a) Using the information given above, you are required to write a plan for a thermometric titration between **FA 6** and aqueous $H_2C_2O_4$ solution.

You are provided with

- 500 cm^3 of 1.00 mol dm^{-3} $H_2C_2O_4$,
- 30 g of solid **FA 6** containing approximately 90% by mass of Fe_2O_3,
- styrofoam cup,
- thermometer, and
- apparatus commonly found in a college laboratory.

In your plan you should include details of

- justification of specific quantities of reactants that you would use,
- the apparatus you would use and the procedure you would follow,
- a sketch of the graph you would expect to obtain, with the end–point clearly labelled, and
- how the data obtained from the graph would be used to calculate the actual percentage by mass of Fe_2O_3 in **FA 6**.

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....

....[10]

(b) A student suggested that using a burette to measure the 25.0 cm^3 of acid would give a more accurate result than using a pipette. The percentage error of a 25.0 cm^3 pipette is 0.24%. Is the student correct? Explain your answer.

....

....

....

....[2]

[Total: 12]

4 You are given samples of eight aqueous solutions.

FB 1	containing bromide ions, Br^-
FB 2	containing bromate(I) ions, BrO^-
FB 3	containing iron(III) ions, Fe^{3+}
FB 4	containing hydrogen peroxide, H_2O_2
FB 5	containing aqueous iodine, I_2
FB 6	containing iodide ions, I^-
FB 7	containing potassium manganate(VII), $KMnO_4$

You are also given hexane, sulfuric acid and starch solution.

You will perform a series of tests to investigate if any redox reaction has occurred.

You will make deductions about the relative oxidising powers of different substances.

For example, under appropriate conditions, chlorine water will oxidise iodide ions to iodine.

$$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$$

Deduction would be that chlorine is a stronger oxidising agent than iodine. This is represented by $Cl_2 > I_2$.

In another example, iodine will **not** oxidise bromide ions to bromine. So, the deduction would be that bromine is a stronger oxidising agent than iodine. This is represented by $Br_2 > I_2$.

(a) Perform the tests described in **Table 1**. Record your observations in the spaces provided. If there is no observable reaction, write **'no reaction'** in the observations column.

Your observations should allow you to deduce the relative oxidising powers of the substances involved.

State the relative oxidising power of the substances involved under the deductions column of **Table 1**. They should be written in the form e.g. $Cl_2 > I_2$.

[10]

Table 1

Tests		Observations	Deductions
1	Add 1 cm^3 of **FB 6** to a test–tube. Then add 8 drops of **FB 3**, followed by 5 drops of starch solution.		
2	Add 1 cm^3 of **FB 3** to a test–tube. Then, add 1 cm^3 of **FB 1** followed by 1 cm^3 of hexane. Shake the mixture.		
3	Add 1 cm^3 of **FB 4** to a test–tube. Then add 8 drops of **FB 5**.		
4	Add 1 cm^3 of **FB 4** to a test–tube. Now add 1 cm^3 of dilute sulfuric acid. Then add 1 cm^3 of **FB 1** followed by 1 cm^3 of hexane. Shake the mixture.		
5	Add 1 cm^3 of **FB 1** to a test–tube. Now add 4 drops of dilute sulfuric acid. Then add 1 cm^3 of **FB 2**.		
6	Add 1 cm^3 of **FB 4** to a test–tube. Then add 1 cm^3 of **FB 3**. Make observations for about 2 minutes before recording your results.		

Tests		Observations	Deductions
7	Add 1 cm^3 of **FB 1** in a test–tube followed by 1 cm^3 of dilute sulfuric acid. Then add 8 drops of **FB 7** and 1 cm^3 of hexane. Shake the mixture.		

(b) Using your answers in **Table 1**, arrange the following substances below in descending order of their oxidising power.

Br_2, BrO^-, Fe^{3+}, I_2, O_2

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

(c) What are the roles of **FB 3** in tests **1** and **6** respectively?

……………………………………………………………………………………………………

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

[Total: 12]

End of paper

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white. ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

anion	*reaction*
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, $Cl^-(aq)$	gives white ppt. with $Ag^+(aq)$ (soluble in $NH_3(aq)$)
bromide, $Br^-(aq)$	gives pale cream ppt. with $Ag^+(aq)$ (partially soluble in $NH_3(aq)$)
iodide, $I^-(aq)$	gives yellow ppt. with $Ag^+(aq)$ (insoluble in $NH_3(aq)$)
nitrate, $NO_3^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and Al foil
nitrite, $NO_2^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, $SO_4^{2-}(aq)$	gives white ppt. with $Ba^{2+}(aq)$ (insoluble in excess dilute strong acids)
sulfite, $SO_3^{2-}(aq)$	SO_2 liberated with dilute acids; gives white ppt. with $Ba^{2+}(aq)$ (soluble in dilute strong acids)

(c) Tests for gases

gas	*test and test result*
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	*colour of element*	*colour in aqueous solution*	*colour in hexane*
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

The Periodic Table of Elements

Group

1	2											13	14	15	16	17	18
							1 H hydrogen 1.0										2 He helium 4.0
3 Li lithium 6.9	4 Be beryllium 9.0			**Key** atomic number atomic symbol name relative atomic mass								5 B boron 10.8	6 C carbon 12.0	7 N nitrogen 14.0	8 O oxygen 16.0	9 F fluorine 19.0	10 Ne neon 20.2
11 Na sodium 23.0	12 Mg magnesium 24.3	3	4	5	6	7	8	9	10	11	12	13 Al aluminium 27.0	14 Si silicon 28.1	15 P phosphorus 31.0	16 S sulfur 32.1	17 Cl chlorine 35.5	18 Ar argon 39.9
19 K potassium 39.1	20 Ca calcium 40.1	21 Sc scandium 45.0	22 Ti titanium 47.9	23 V vanadium 50.9	24 Cr chromium 52.0	25 Mn manganese 54.9	26 Fe iron 55.8	27 Co cobalt 58.9	28 Ni nickel 58.7	29 Cu copper 63.5	30 Zn zinc 65.4	31 Ga gallium 69.7	32 Ge germanium 72.6	33 As arsenic 74.9	34 Se selenium 79.0	35 Br bromine 79.9	36 Kr krypton 83.8
37 Rb rubidium 85.5	38 Sr strontium 87.6	39 Y yttrium 88.9	40 Zr zirconium 91.2	41 Nb niobium 92.9	42 Mo molybdenum 95.9	43 Tc technetium –	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
55 Cs caesium 132.9	56 Ba barium 137.3	57–71 lanthanoids	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.6	81 Tl thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium –	85 At astatine –	86 Rn radon –
87 Fr francium –	88 Ra radium –	89–103 actinoids	104 Rf rutherfordium –	105 Db dubnium –	106 Sg seaborgium –	107 Bh bohrium –	108 Hs hassium –	109 Mt meitnerium –	110 Ds darmstadtium –	111 Rg roentgenium –	112 Cn copernicium –		114 Fl flerovium –		116 Lv livermorium –		

lanthanoids	57 La lanthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.2	61 Pm promethium –	62 Sm samarium 150.4	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.1	71 Lu lutetium 175.0
actinoids	89 Ac actinium –	90 Th thorium 232.0	91 Pa protactinium 231.0	92 U uranium 238.0	93 Np neptunium –	94 Pu plutonium –	95 Am americium –	96 Cm curium –	97 Bk berkelium –	98 Cf californium –	99 Es einsteinium –	100 Fm fermium –	101 Md mendelevium –	102 No nobelium –	103 Lr lawrencium –

Apparatus and Chemicals for each candidate

Apparatus list

1. 2 × 50.00 cm^3 burette (to invert burette and put on retort stand)
2. 1 × 25.0 cm^3 pipette
3. 2 × 250 cm^3 conical flask
4. 2 x 150 cm^3 beaker
5. 1 × 250 cm^3 beaker
6. 1 × 250 cm^3 graduated flask
7. 1 × 10 cm^3 measuring cylinder
8. 1 × 50 cm^3 measuring cylinder
9. 1 × glass rod
10. Plastic bag: 6 × dropper, 1 × long wooden splint, 2 × paper towel, blue & red litmus papers, filter paper strips
11. Plastic bag: 5 test tubes
12. 1 × dry boiling tube (pack with 5 test tubes)
13. 1 × pipette filler
14. 1 × retort stand and burette clamp
15. 1 × clamp – to hold a boiling tube (to mount on retort stand)
16. 1 × white tile
17. 2 × filter funnel
18. 1 × Bunsen burner
19. 1 × wire gauge (heat proof mat)
20. 1 × tripod stand
21. 1 × lighter
22. 1 × alcohol thermometer (–10 °C to 110 °C at 1 °C)
23. 1 × wash bottle containing distilled water
24. 1 × test tube rack
25. 1 × test tube holder
26. 1 × visualiser per lab
27. electronic weighing balance (5 per lab)
28. synchronise all the clocks in the 8 labs

Chemical List

29. **FA 1** is 0.250 mol dm^{-3} sodium ethanedioate, $Na_2C_2O_4$ (100 cm^3 in a vial labelled **FA 1**)
30. **FA 2** is approximately 2 mol dm^{-3} sulfuric acid, H_2SO_4 (100 cm^3 in a vial labelled **FA 2**)
31. **FA 3** is 0.0200 mol dm^{-3} potassium manganate(VII), $KMnO_4$ (120 cm^3 in a vial labelled **FA 3**)
32. **FA 5** is solid potassium bromate(V), $KBrO_3$ (1.90–2.10 g in a weighing bottle labelled **FA 5**)
33. One rack of bench reagents (only for show, no need to prepare fresh solutions)
34. 1 red tub per student for 3 shifts containing **FB 1** to **FB 8**, sulfuric acid, hexane and starch

Label	Capacity per student in capped reagent bottle
FB 1	10 cm^3 of 0.1 mol dm^{-3} potassium bromide, KBr, made by dissolving about 11.9 g of KBr in 1 dm^3 of deionised water
FB 2	10 cm^3 of 10% aqueous potassium bromate(I), KBrO
FB 3	5 cm^3 of 0.2 mol dm^{-3} ammonium iron(III) sulfate, $NH_4Fe(SO_4)_2{\cdot}12H_2O$, made by dissolving about 96.4 g of $NH_4Fe(SO_4)_2{\cdot}12H_2O$ in 1 dm^3 of deionised water
FB 4	10 cm^3 of 20 volume hydrogen peroxide, H_2O_2 (containing 200 cm^3 of freshly opened 100 volume hydrogen peroxide, made up to 1 dm^3 with deionised water)
FB 5	5 cm^3 of 0.01 mol dm^{-3} aqueous iodine, I_2, made by dissolving about 2.5 g of iodine and about 8 g of potassium, KI, in 1 dm^3 of deionised water
FB 6	5 cm^3 of 0.1 mol dm^{-3} potassium iodide, KI, made by dissolving about 16.6 g of KI in 1 dm^3 of deionised water
FB 7	5 cm^3 of 0.0200 mol dm^{-3} potassium manganate(VII) (same solution as **FA 3**)
sulfuric acid	one labelled reagent bottle containing 2 mol dm^{-3} H_2SO_4 (same solution as **FA 2**, one full reagent bottle)
hexane	hexane (one full reagent bottle)
starch	starch (one full reagent bottle)

VICTORIA JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME ……………………………………………….…………..

CT GROUP ……………………………..

CHEMISTRY 9729/04

Practical

30 August 2018

2 hours 30 minutes

Additional Materials: As listed in the instructions below

READ THESE INSTRUCTIONS FIRST

Write your name and CT group on all the work you hand in.
Give details of the practical shift and laboratory where appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use a HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 14 and 15.
Periodic Table is printed on page 16.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

Shift
Laboratory

For Examiner's Use	
1	
2	
3	
4	
Total	

This document consists of **16** printed pages.

1 You are to determine the concentration, in g dm^{-3}, of sodium ethanedioate in a mixture of sodium ethanedioate and ethanedioic acid.

This experiment involves two titrations.
In titration one, you will carry out a titration to find the total amount of ethanedioate ion, $C_2O_4^{2-}$.
In titration two, you will use the information provided to find the amount of ethanedioic acid, $H_2C_2O_4$.
Finally, you will use the values found in the two titrations to calculate the concentration, in g dm^{-3}, of sodium ethanedioate in **FA 1**.

FA 1 is a mixture of aqueous sodium ethanedioate, $Na_2C_2O_4$, and ethanedioic acid, $H_2C_2O_4$.
FA 2 is approximately 2 mol dm^{-3} sulfuric acid, H_2SO_4.
FA 3 is 0.0200 mol dm^{-3} potassium manganate(VII), $KMnO_4$.

Titration One

(a) 1. By using a burette, measure between 42.50 cm^3 of **FA 1** into the 250 cm^3 graduated (volumetric) flask.
2. Record your burette readings and the volume of **FA 1** added to the flask in the space below.

Final burette reading / cm^3	42.50
Initial burette reading / cm^3	0.00
Volume of **FA 1** used / cm^3	42.50

[1]

3. Make up the contents of the flask to the 250 cm^3 mark with deionised water. Place the stopper in the flask and mix the contents thoroughly by slowly inverting the flask a number of times. Label this solution **FA 4**.
4. Fill a second burette with **FA 3**.
5. Pipette 25.0 cm^3 of **FA 4** from the graduated flask into a conical flask.
6. Use a measuring cylinder to add 25 cm^3 of **FA 2** to the conical flask.
7. Place the conical flask on a tripod and gauze and heat to about 65 °C.
8. If the neck of the flask is too hot to hold safely, use a folded paper towel to hold the flask.
9. Titrate the mixture in the conical flask with **FA 3** until a permanent pale pink colour is obtained. This is the end-point.
10. **If a brown colour appears during the titration**, reheat the flask to 65 °C. The brown colour should disappear and the titration can be completed as above. **If the brown colour does not disappear on reheating**, discard the solution and start the titration again.
11. Carry out as many titrations as you think necessary to obtain consistent results.
12. Record in an appropriate form all of your burette readings and the volume of **FA 3** added in each titration.

Final burette reading / cm^3	19.50	39.50
Initial burette reading / cm^3	0.00	20.00
Volume of **FA 3** used / cm^3	19.50	19.50

[5]

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

Average volume of **FA 3** used
= (19.50 + 19.50) ÷ 2
= 19.50 cm^3

25.0 cm^3 of **FA 4** required …19.50……… cm^3 of **FA 3**. [1]

Titration Two

(c) When 25.0 cm^3 of **FA 4** used in **(a)** is titrated with 0.100 mol dm^{-3} sodium hydroxide using phenolphthalein as the indicator, 15.50 cm^3 of sodium hydroxide is needed for complete reaction.

(i) Write an equation for the reaction between sodium hydroxide and ethanedioic acid.

$H_2C_2O_4 + 2NaOH \rightarrow Na_2C_2O_4 + 2H_2O$ [1]

(ii) Calculate the number of moles of sodium hydroxide required to react with 25.0 cm^3 of **FA 4**.

No. of moles of NaOH required
= $0.100 \times 15.50 \times 10^{-3}$
= 1.55×10^{-3} mol

moles of NaOH = 1.55×10^{-3} …… mol [1]

(iii) Hence, calculate the number of moles of ethanedioic acid in 25.0 cm^3 of **FA 4**.

No. of moles of $H_2C_2O_4$ present in 25.0 cm^3
= ½ × no. of moles of NaOH required
= $\frac{1}{2} \times 1.55 \times 10^{-3}$
= 7.75×10^{-4} mol

moles of $H_2C_2O_4$ in 25.0 cm^3 of **FA 4** = 7.75×10^{-4} …… mol [1]

(d) **(i)** Use your answer from **(b)** to calculate the number of moles of potassium manganate(VII), **FA 3**, required to react with 25.0 cm^3 of **FA 4** in **Titration One**.

No. of moles of $KMnO_4$ required
= $0.0200 \times 19.50 \times 10^{-3}$
= 3.90×10^{-4} mol

moles of $KMnO_4$ = 3.90×10^{-4} …… mol [1]

(ii) The equation for the reaction between acidified manganate(VII) ions and ethanedioate ions is shown below.

$$2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$$

Use your answer from **(d)(i)** to calculate the total number of moles of ethanedioate ions in 25.0 cm^3 of **FA 4**.

Total no. of moles of $C_2O_4^{2-}$ present in 25.0 cm^3
= 5/2 × no. of moles of MnO_4^- required
= $5/2 \times 3.90 \times 10^{-4}$
= 9.75×10^{-4} mol

total moles of $C_2O_4^{2-}$ in 25.0 cm^3 of **FA 4** = 9.75×10^{-4} …… mol [1]

(iii) Use your answers from **(c)(iii)** and **(d)(ii)** to calculate the number of moles of ethanedioate ions which came from the sodium ethanedioate in 25.0 cm^3 of **FA 4**.

No. of moles of $C_2O_4^{2-}$ from $Na_2C_2O_4$ in 25.0 cm^3
$= (9.75 \times 10^{-4}) - (7.75 \times 10^{-4})$
$= 2.00 \times 10^{-4}$ mol

moles of $C_2O_4^{2-}$ from $Na_2C_2O_4$ in 25.0 cm^3 of **FA 4** = 2.00×10^{-4} mol [1]

(iv) Hence, calculate the concentration, in g dm^{-3}, of sodium ethanedioate in **FA 1**.

No. of moles of $Na_2C_2O_4$ in 250 cm^3 of solution of **FA 4**
$= 2.00 \times 10^{-4} \times \frac{250}{25.0}$
$= 2.00 \times 10^{-3}$ mol

Mass of $Na_2C_2O_4$ in 42.70 cm^3 of **FA 1**
$= 2.00 \times 10^{-3} \times (2\times23.0 + 2\times12.0 + 4\times16.0)$
= 0.268 g

Concentration, in g dm^{-3}, of $Na_2C_2O_4$ in **FA 1**
$= 0.268 \div \frac{42.50}{1000}$
$= 6.31$ g dm^{-3}

Concentration of sodium ethanedioate is 6.31 g dm^{-3} [2]

(e) Explain why the decolourisation of **FA 3** in **Titration One** is initially slow but becomes faster as the reaction proceeds.

Sufficient auto-catalyst, $Mn^{2+}(aq)$ ions, will be formed to catalyse the reaction to occur faster.

[1]

[Total: 16]

2 This question concerns the solubility of **FA 5**, potassium bromate(V), $KBrO_3$, in water.

> The **solubility** of a substance in water is defined as:
> the mass of substance that will dissolve in and just saturate 100 g of water at a particular temperature.
> When a solution is saturated, the dissolved solid is in equilibrium with undissolved solid.
> When a solution of potassium bromate(V) is cooled, it becomes saturated when crystals form in the solution.

You are to investigate how the solubility of **FA 5** in water varies with temperature.

You are provided with the following materials
- weighing bottle labelled **FA 5**, containing potassium bromate(V), $KBrO_3$, and
- deionised water.

Read through the instructions before starting any practical work.

(a) 1. Prepare a hot water bath by filling a 250 cm^3 beaker half full of water and heat it over the Bunsen burner until almost boiling. Turn off the Bunsen burner.
2. Weigh an empty boiling tube.
3. Add the contents of the weighing bottle labelled **FA 5** to the boiling tube.
4. Reweigh the boiling tube and its contents.
5. Record, in an appropriate form below, your weighings and the mass of **FA 5** used.

Mass of boiling tube + **FA 5** / g	32.360
Mass of boiling tube / g	30.299
Mass of **FA 5** used / g	2.061

6. Use the 10 cm^3 measuring cylinder to transfer 8.0 cm^3 of deionised water to the weighed boiling tube containing **FA 5**.
7. Use the clamp as a holder for the boiling-tube. Take care not to break the tube by clamping it too tightly.
8. Warm the tube carefully in the water bath, while stirring the contents with a thermometer, until all the solid has dissolved. (Take care that you do not break the thermometer bulb or the tube while stirring.)
9. Remove the tube from the water bath and attach the clamp to a retort stand.
10. Let the tube cool and continue to stir gently with the thermometer.
11. Watch the solution carefully. Note and record (**on the next page**) the temperature at which you **first** notice crystals forming in the solution.
12. If you are uncertain about the temperature when crystals first form, warm the tube again for a few moments and repeat the cooling.
13. As soon as you have recorded the temperature, add a further 2.0 cm^3 of deionised water to the tube using the 10 cm^3 measuring cylinder.
14. Warm the tube in the water bath to re-dissolve the solid and cool as before.
15. Note and record (**on the next page**) the temperature at which crystals now form in the solution. This will be lower than the temperature obtained with 8.0 cm^3 of water.
16. Repeat the addition of 2.0 cm^3 of deionised water, the heating and the cooling, until you have **four** readings in total.
17. In an appropriate form in the space below, record the following.
    - the total volume of deionised water in the boiling-tube
    - the temperature at which crystals first appeared for each solution

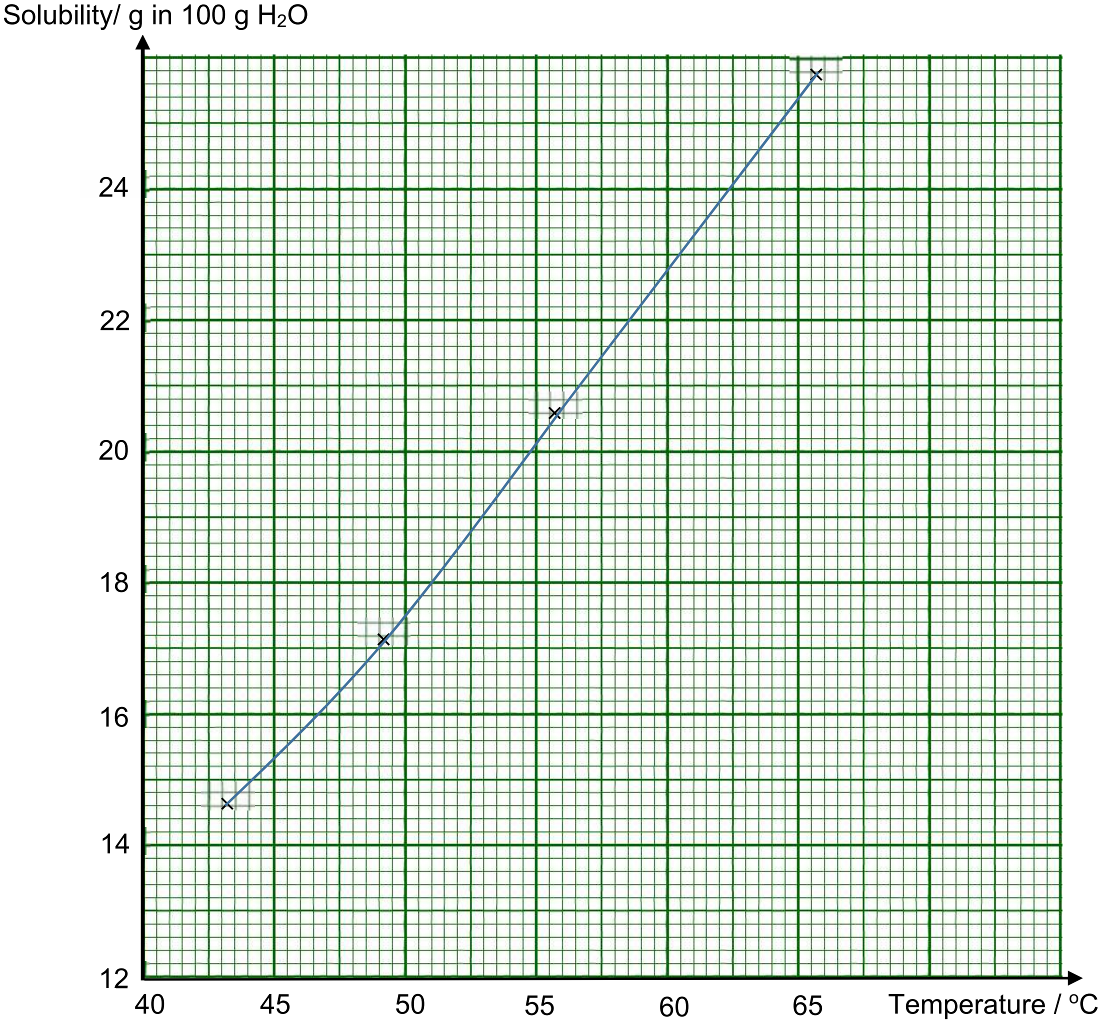
- the **solubility** (in grams of solid per 100 g of water) which can be calculated using the following formula

$$\text{solubility} = \frac{100}{\text{volume of water}} \times \text{mass of } \textbf{FA 5} \text{ dissolved}$$

Volume of water/ cm^3	Temperature at first appearance of crystals/ °C	Solubility/ g per 100 g H_2O
8.0	65.5	25.8
10.0	55.5	20.6
12.0	49.0	17.2
14.0	43.0	14.7

[6]

(b) On the grid, plot a graph of solubility against temperature and draw an appropriate line through the points. Do **not** start at zero on either axis. You will need to be able to find the solubility of **FA 5** at 55 °C.



[3]

(c) Use your solubility curve in **(b)** to answer the following.

(i) Explain if dissolving potassium bromate(V), $KBrO_3$, is an exothermic or endothermic process.

$$KBrO_3(s) \rightleftharpoons K^+(aq) + BrO_3^-(aq)$$

The graph has a positive gradient. Hence, solubility of $KBrO_3$ increases with temperature. Dissolving $KBrO_3$ is an endothermic process.

[1]

(ii) Calculate the solubility of potassium bromate(V), $KBrO_3$, at 55 °C in mol dm^{-3}.
[Given that the M_r of $KBrO_3$ is 167.0.]

From the graph, solubility of $KBrO_3$ is 20.2 g per 100 g of H_2O.

Solubiity in mol dm^{-3} = $\frac{20.2}{167.0} \times \frac{1000}{100}$ = 1.21 mol dm^{-3}

[1]

(iii) Hence, calculate the K_{sp} of potassium bromate(V) at this temperature, giving the units.

$K_{sp} = [K^+][BrO_3^-] = (1.21)^2 = 1.46 \text{ mol}^2 \text{ dm}^{-6}$ (ecf)

[2]

(d) Student **A** claims that both the solubility and solubility product of potassium bromate(V) will decrease with the addition of some solid potassium nitrate at a particular temperature. Comment on the student's claim.

On addition of potassium nitrate, concentration of K^+ increases and the position of equilibrium shift left. Solubility of $KBrO_3$ decreases.

However, solubility product is only dependent on temperature/independent of temperature and hence remains unchanged.

[1]

(e) A literature value for the solubility of potassium bromate(V) is 13.1 g per 100 g of water at 40 °C. Student **A** followed the instructions in **(a)** and obtained a solubility value for $KBrO_3$ to be 15.0 g per 100 g of water at the same temperature. Calculate the magnitude of the percentage experimental error for student **A**'s measurement.

Experimental error = $\left| \frac{13.1 - 15.0}{13.1} \right|$ x 100% = 14.5%

[1]

[Total:15]

3 Planning

FA 6 is a powdered mixture of mica and iron(III) oxide, Fe_2O_3, which is used as ingredients in mineral makeup such as eye shadow or blusher. Iron(III) oxide adds a red colour to makeup while mica gives makeup a light reflecting quality.

The reaction between Fe_2O_3, and ethanedioic acid, $H_2C_2O_4$, is exothermic as shown.

$$Fe_2O_3(s) + 3H_2C_2O_4(aq) \rightarrow Fe_2(C_2O_4)_3(aq) + 3H_2O(l) \qquad \Delta H < 0$$

In a thermometric titration, the end–point is reached when the maximum temperature change occurs. A thermometric titration between Fe_2O_3 and $H_2C_2O_4$ can be carried out to find out the percentage by mass of iron(III) oxide in **FA 6**. The temperature of the reaction mixture is monitored when a certain mass of **FA 6** is added into a fixed volume of aqueous $H_2C_2O_4$ solution. The experiment is then repeated using different masses of **FA 6**. You may assume mica remains unchanged in this experiment.

The data obtained is plotted and two best–fit graph lines are drawn. One line is drawn using data before the end–point and the second line using the remaining data. These lines are then extrapolated until they intersect.

(a) Using the information given above, you are required to write a plan for a thermometric titration between **FA 6** and aqueous $H_2C_2O_4$ solution.

You are provided with

- 500 cm^3 of 1.00 mol dm^{-3} of $H_2C_2O_4$,
- 30 g of solid **FA 6** containing approximately 90% by mass of Fe_2O_3,
- styrofoam cup,
- thermometer, and
- apparatus commonly found in a college laboratory

In your plan you should include details of

- justification of specific quantities of reactants that you would use,
- the apparatus you would use and the procedure you would follow,
- a sketch of the graph you would expect to obtain, with the end–point clearly labelled, and
- how the data obtained from the graph would be used to calculate the actual percentage by mass of Fe_2O_3 in **FA 6**

(i) **Justification of quantities of reactants used for the experiments**

Assume 50 cm^3 of 1.00 mol dm^{-3} $H_2C_2O_4$ is used.
Amount of $H_2C_2O_4$ used in 50 cm^3 of $H_2C_2O_4$ = (50/1000) x 1.00
= 0.0500 mol

Mass of Fe_2O_3 required to react completely with 50 cm^3 of $H_2C_2O_4$
= (0.05/3) x (55.8x2 + 16.0x3)
= 2.66 g

Approximate mass of FA 6 required to react with 50 cm^3 of $H_2C_2O_4$
= (2.66/90) x 100
= 2.96 g

Experiment	Volume of $H_2C_2O_4$/cm^3	Mass of FA 6 /g	ΔT / °C
1	50.0	1.000	
2	50.0	1.500	
3	50.0	2.000	
4	50.0	2.500	
5	50.0	3.000	
6	50.0	3.500	
7	50.0	4.000	
8	50.0	4.500	
9	50.0	5.000	

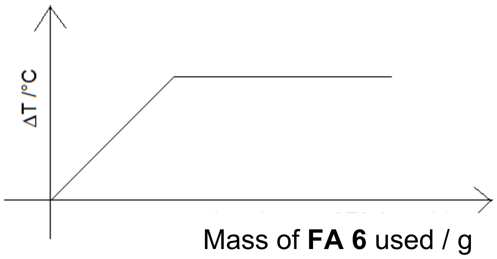
(ii) **Procedure**

1. Use a 50 cm^3 burette to introduce 50.00 cm^3 of 1 mol dm^{-3} of $H_2C_2O_4^-$ into a dry styrofoam cup.

2. Place the thermometer into the solution and record initial temperature of the solution.
3. Weigh accurately 1.000 g of FA 6 and put it into the Styrofoam cup.
4. Stir gently with the thermometer. Record the highest temperature rise.
5. Reweigh the emptied weighing bottle to get the actual mass of FA 6 that has been used.
6. Repeat steps 1 to 5 for experiment 2 to experiment 9.

(iii) Sketch of graph

1. Plot a graph of ∆T versus actual mass of FA 6 added.
2. Correct shape and indicate the intersection point will give us the mass of FA 6 needed to completely react with $H_2C_2O_4$. This is when end–point has been reached.



(iv) Calculations

Percentage mass of Fe_2O_3 in FA 6
= (2.66/Mass of FA 6 obtained from the graph) x 100%

[10]

(b) A student suggested that using a burette to measure the 25.0 cm^3 of acid would give a more accurate result than using a pipette. The percentage error of a 25.0 cm^3 pipette is 0.24%. Is the student correct? Explain your answer.

Percentage error for burette = $\frac{2 \text{ x } 0.05}{25.0}$ x 100 = 0.40 %
No, the pipette is more accurate. This is because the percentage error of using the burette to measure the 25.0 cm^3 of acid is greater than the pipette.

[2]

[Total: 12]

4 You are given samples of eight aqueous solutions.

FB 1	containing bromide ions, Br^-
FB 2	containing bromate(I) ions, BrO^-
FB 3	containing iron(III) ions, Fe^{3+}
FB 4	containing hydrogen peroxide, H_2O_2
FB 5	containing aqueous iodine, I_2
FB 6	containing iodide ions, I^-
FB 7	containing potassium manganate(VII), $KMnO_4$

You are also given hexane, sulfuric acid and starch solution.

You will perform a series of tests to investigate if any redox reaction has occurred.

You will make deductions about the relative oxidising powers of different substances.

For example, under appropriate conditions, chlorine water will oxidise iodide ions to iodine.

$$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$$

Deduction would be that chlorine is a stronger oxidising agent than iodine. This is represented by $Cl_2 > I_2$.

In another example, iodine will **not** oxidise bromide ions to bromine. So, the deduction would be that bromine is a stronger oxidising agent than iodine. This is represented by $Br_2 > I_2$.

(a) Perform the tests described in **Table 1**. Record your observations in the spaces provided. If there is no observable reaction, write **'no reaction'** in the observations column.

Your observations should allow you to deduce the relative oxidising powers of the substances involved.

State the relative oxidising power of the substances involved under the deductions column of **Table 1**. They should be written in the form e.g. $Cl_2 > I_2$.

[10]

Table 1

Tests		Observations	Deductions
1	Add 1 cm^3 of **FB 6** to a test–tube. Then add 8 drops of **FB 3**, followed by 5 drops of starch solution.	• Solution turned brown. • Solution turned blue–black with starch.	• $Fe^{3+} > I_2$
2	Add 1 cm^3 of **FB 3** to a test–tube. Then, add 1 cm^3 of **FB 1** followed by 1 cm^3 of hexane. Shake the mixture.	• No reaction.	• $Br_2 > Fe^{3+}$
3	Add 1 cm^3 of **FB 4** to a test–tube. Then add 8 drops of **FB 5**.	• No reaction.	• $O_2 > I_2$
4	Add 1 cm^3 of **FB 4** to a test–tube. Now add 1 cm^3 of dilute sulfuric acid. Then add 1 cm^3 of **FB 1** followed by 1 cm^3 of hexane. Shake the mixture.	• Aqueous layer turned yellow/orange. • Organic layer turned orange/red/brown	• $H_2O_2 > Br_2$
5	Add 1 cm^3 of **FB 1** to a test–tube. Now add 4 drops of dilute sulfuric acid. Then add 1 cm^3 of **FB 2**.	• Solution turned orange/red/yellow.	• $BrO^- > Br_2$
6	Add 1 cm^3 of **FB 4** to a test–tube. Then add 1 cm^3 of **FB 3**. Make observations for about 2 minutes before recording your results.	• Solution turned brown. • Effervescence (or bubbles) observed. • O_2 gas • relighted a glowing splint. • Solution remained yellow/brown.	• $Fe^{3+} > O_2$

7	Add 1 cm^3 of **FB 1** in a test–tube followed by 1 cm^3 of dilute sulfuric acid. Then add 8 drops of **FB 7** and 1 cm^3 of hexane. Shake the mixture.	• Aqueous layer turned yellow/orange/red. • Organic layer turned orange/brown/red.	• $MnO_4^- > Br_2$

(b) Using your answers in **Table 1**, arrange the following substances below in descending order of their oxidising power.

Br_2, BrO^-, Fe^{3+}, I_2, O_2

$BrO^- > Br_2 > Fe^{3+} > O_2 > I_2$

[1]

(c) What are the roles of **FB 3** in tests **1** and **6** respectively?

In test 1, it is acting as an oxidising agent (as it is reduced) while in test 6, it is a catalyst.

[1]

[Total: 12]

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

cation	***reaction with***	
	NaOH(aq)	NH_3(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH_4^+(aq)	ammonia produced on heating	–
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white. ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

anion	***reaction***
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, $Cl^-(aq)$	gives white ppt. with $Ag^+(aq)$ (soluble in $NH_3(aq)$)
bromide, $Br^-(aq)$	gives pale cream ppt. with $Ag^+(aq)$ (partially soluble in $NH_3(aq)$)
iodide, $I^-(aq)$	gives yellow ppt. with $Ag^+(aq)$ (insoluble in $NH_3(aq)$)
nitrate, $NO_3^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and Al foil
nitrite, $NO_2^-(aq)$	NH_3 liberated on heating with $OH^-(aq)$ and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, $SO_4^{2-}(aq)$	gives white ppt. with $Ba^{2+}(aq)$ (insoluble in excess dilute strong acids)
sulfite, $SO_3^{2-}(aq)$	SO_2 liberated with dilute acids; gives white ppt. with $Ba^{2+}(aq)$ (soluble in dilute strong acids)

(c) Tests for gases

gas	***test and test result***
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	***colour of element***	***colour in aqueous solution***	***colour in hexane***
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

The Periodic Table of Elements

Group																	
1	2											13	14	15	16	17	18
				Key			1 H hydrogen 1.0										2 He helium 4.0
3 Li lithium 6.9	4 Be beryllium 9.0			atomic number atomic symbol name relative atomic mass								5 B boron 10.8	6 C carbon 12.0	7 N nitrogen 14.0	8 O oxygen 16.0	9 F fluorine 19.0	10 Ne neon 20.2
11 Na sodium 23.0	12 Mg magnesium 24.3	3	4	5	6	7	8	9	10	11	12	13 Al aluminium 27.0	14 Si silicon 28.1	15 P phosphorus 31.0	16 S sulfur 32.1	17 Cl chlorine 35.5	18 Ar argon 39.9
19 K potassium 39.1	20 Ca calcium 40.1	21 Sc scandium 45.0	22 Ti titanium 47.9	23 V vanadium 50.9	24 Cr chromium 52.0	25 Mn manganese 54.9	26 Fe iron 55.8	27 Co cobalt 58.9	28 Ni nickel 58.7	29 Cu copper 63.5	30 Zn zinc 65.4	31 Ga gallium 69.7	32 Ge germanium 72.6	33 As arsenic 74.9	34 Se selenium 79.0	35 Br bromine 79.9	36 Kr krypton 83.8
37 Rb rubidium 85.5	38 Sr strontium 87.6	39 Y yttrium 88.9	40 Zr zirconium 91.2	41 Nb niobium 92.9	42 Mo molybdenum 95.9	43 Tc technetium –	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
55 Cs caesium 132.9	56 Ba barium 137.3	57–71 lanthanoids	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.6	81 Tl thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium –	85 At astatine –	86 Rn radon –
87 Fr francium –	88 Ra radium –	89–103 actinoids	104 Rf rutherfordium –	105 Db dubnium –	106 Sg seaborgium –	107 Bh bohrium –	108 Hs hassium –	109 Mt meitnerium –	110 Ds darmstadtium –	111 Rg roentgenium –	112 Cn copernicium –		114 Fl flerovium –		116 Lv livermorium –		

lanthanoids	57 La lanthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.2	61 Pm promethium –	62 Sm samarium 150.4	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.1	71 Lu lutetium 175.0
actinoids	89 Ac actinium –	90 Th thorium 232.0	91 Pa protactinium 231.0	92 U uranium 238.0	93 Np neptunium –	94 Pu plutonium –	95 Am americium –	96 Cm curium –	97 Bk berkelium –	98 Cf californium –	99 Es einsteinium –	100 Fm fermium –	101 Md mendelevium –	102 No nobelium –	103 Lr lawrencium –

Apparatus and Chemicals for each candidate

Apparatus list

1. 2 × 50.00 cm^3 burette (to invert burette and put on retort stand)
2. 1 × 25.0 cm^3 pipette
3. 2 × 250 cm^3 conical flask
4. 2 x 150 cm^3 beaker
5. 1 × 250 cm^3 beaker
6. 1 × 250 cm^3 graduated flask
7. 1 × 10 cm^3 measuring cylinder
8. 1 × 50 cm^3 measuring cylinder
9. 1 × glass rod
10. Plastic bag: 6 × dropper, 1 × long wooden splint, 2 × paper towel, blue & red litmus papers, filter paper strips
11. Plastic bag: 5 test tubes
12. 1 × dry boiling tube (pack with 5 test tubes)
13. 1 × pipette filler
14. 1 × retort stand and burette clamp
15. 1 × clamp – to hold a boiling tube (to mount on retort stand)
16. 1 × white tile
17. 2 × filter funnel
18. 1 × Bunsen burner
19. 1 × wire gauge (heat proof mat)
20. 1 × tripod stand
21. 1 × lighter
22. 1 × alcohol thermometer (–10 °C to 110 °C at 1 °C)
23. 1 × wash bottle containing distilled water
24. 1 × test tube rack
25. 1 × test tube holder
26. 1 × visualiser per lab
27. electronic weighing balance (5 per lab)
28. synchronise all the clocks in the 8 labs

Chemical List

29. **FA 1** is 0.250 mol dm^{-3} sodium ethanedioate, $Na_2C_2O_4$ (100 cm^3 in a vial labelled **FA 1**)
30. **FA 2** is approximately 2 mol dm^{-3} sulfuric acid, H_2SO_4 (100 cm^3 in a vial labelled **FA 2**)
31. **FA 3** is 0.0200 mol dm^{-3} potassium manganate(VII), $KMnO_4$ (120 cm^3 in a vial labelled **FA 3**)
32. **FA 5** is solid potassium bromate(V), $KBrO_3$ (1.90–2.10 g in a weighing bottle labelled **FA 5**)
33. One rack of bench reagents (only for show, no need to prepare fresh solutions)
34. 1 red tub per student for 3 shifts containing **FB 1** to **FB 8**, sulfuric acid, hexane and starch

Label	Capacity per student in capped reagent bottle
FB 1	10 cm^3 of 0.1 mol dm^{-3} potassium bromide, KBr, made by dissolving about 11.9 g of KBr in 1 dm^3 of deionised water
FB 2	10 cm^3 of 10% aqueous potassium bromate(I), KBrO
FB 3	5 cm^3 of 0.2 mol dm^{-3} ammonium iron(III) sulfate, $NH_4Fe(SO_4)_2 \cdot 12H_2O$, made by dissolving about 96.4 g of $NH_4Fe(SO_4)_2 \cdot 12H_2O$ in 1 dm^3 of deionised water
FB 4	10 cm^3 of 20 volume hydrogen peroxide, H_2O_2 (containing 200 cm^3 of freshly opened 100 volume hydrogen peroxide, made up to 1 dm^3 with deionised water)
FB 5	5 cm^3 of 0.01 mol dm^{-3} aqueous iodine, I_2, made by dissolving about 2.5 g of iodine and about 8 g of potassium, KI, in 1 dm^3 of deionised water
FB 6	5 cm^3 of 0.1 mol dm^{-3} potassium iodide, KI, made by dissolving about 16.6 g of KI in 1 dm^3 of deionised water
FB 7	5 cm^3 of 0.0200 mol dm^{-3} potassium manganate(VII) (same solution as **FA 3**)
sulfuric acid	one labelled reagent bottle containing 2 mol dm^{-3} H_2SO_4 (same solution as **FA 2**, one full reagent bottle)
hexane	hexane (one full reagent bottle)
starch	starch (one full reagent bottle)