ANDERSON JUNIOR COLLEGE

2017 JC 2 PRELIMINARY EXAMINATIONS

CHEMISTRY **9729/01**

Paper 1 Multiple Choice **18 September 2017**

1 hour

Additional Materials:	Multiple Choice Answer Sheet Data Booklet

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READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, glue or correction fluid.

There are **thirty** questions on this paper. 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 choice in **soft pencil** on the Multiple Choice Answer Sheet.

Each correct answer will score one mark. A mark will not 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.

Multiple Choice Answer Sheet

Write your name, PDG and NRIC / FIN number, **including** the reference letter.

Shade the NRIC / FIN number.

Exam Title: JC2 PRELIM

Exam Details: H2 Chemistry / Paper 1

Date: 18/09/2017

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

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

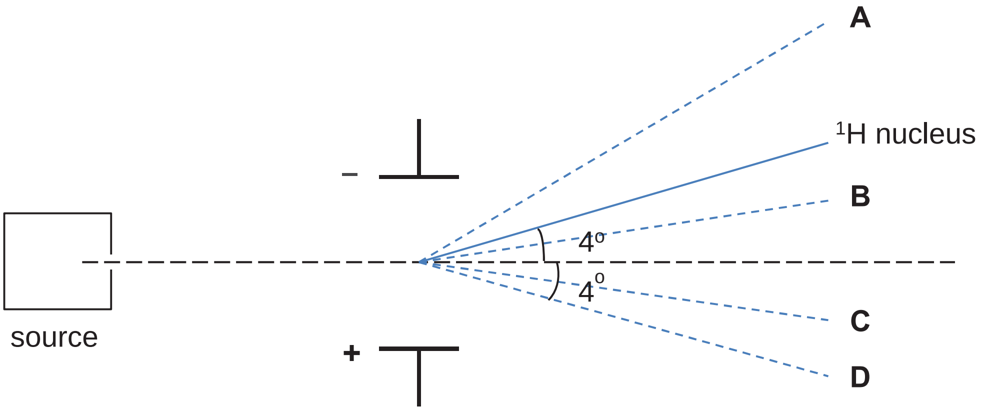
Tritium, $^{3}_{1}H$, a radioactive isotope of hydrogen, slowly turns into a helium isotope $^{3}_{2}He$.

Which statements about the two isotopes are **incorrect**?

1 Both isotopes have more neutrons than electrons.
2 Both isotopes have the same number of protons in their nuclei.
3 Both isotopes have the same number of charged sub–atomic particles.

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

2 When passed through an electric field, the ^{1}H nucleus is deflected as shown below.

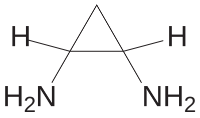


Which of the above beams represents the deflection for an ion $^{2}X^{2-}$?

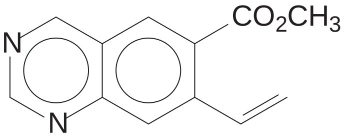
3 Which of the following molecules / ions has the smallest bond angle?

A SF_2 **B** XeF_2 **C** SO_3^{2-} **D** AlH_4^{-}

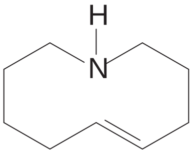
4 Compounds **F, G** and **H** are cyclic compounds.



F



G



H

Which bond is **not** present in the compounds above?

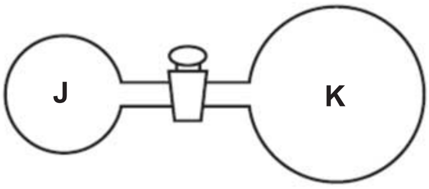
A a σ bond formed by sp^3–sp^3 overlap between two C atoms in **F**

B a σ bond formed by sp^2–sp^2 overlap between C and N atoms in **G**

C a σ bond formed by sp^3–sp^2 overlap between two C atoms in **H**

D a σ bond formed by sp^2–sp^2 overlap between C and N atoms in **H**

5 Two glass vessels **J** and **K** are connected by a closed valve.



J contains helium gas at 20 °C and a pressure of 1×10^5 Pa. **K** has been evacuated, and has three times the volume of **J**. In an experiment, the valve is opened and the temperature of the whole apparatus is raised to 100 °C.

What is the final pressure in the system?

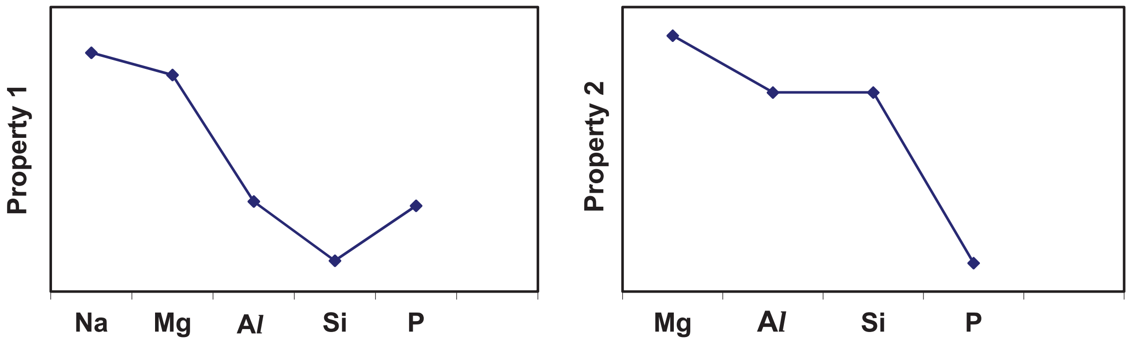
A 3.18×10^4 Pa

B 4.24×10^4 Pa

C 1.25×10^5 Pa

D 5.09×10^5 Pa

6 The graphs below show the variation of two properties of some period 3 elements and/or their compounds.



Which of the following correctly describes properties 1 and 2?

	Property 1	Property 2
A	atomic radius of the elements	electrical conductivity of the elements
B	melting point of the chlorides	pH of oxides when added to water
C	melting point of the elements	first ionisation energies of the elements
D	electrical conductivity of elements	pH of chlorides when added to water

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

If iron is heated separately with chlorine, bromine and iodine, what are the likely products?

	chlorine	bromine	iodine
A	$FeCl_2$	$FeBr_2$	FeI_2
B	$FeCl_3$	$FeBr_2$	FeI_2
C	$FeCl_3$	$FeBr_3$	FeI_2
D	$FeCl_3$	$FeBr_3$	FeI_3

8 When 10 cm^3 of a hydrocarbon was burnt in 100 cm^3 of excess oxygen, the volume of the residual gas mixture contracted by 20 cm^3 after passing through a solution of aqueous sodium hydroxide. The remaining volume of gas was just sufficient to completely burn exactly 30 cm^3 of the same hydrocarbon. All volumes were measured at room temperature and pressure conditions.

What is the formula of the hydrocarbon?

A C_2H_2 **B** C_2H_3 **C** C_2H_4 **D** C_2H_6

9 Sulfuric acid, one of the most important industrial chemicals, can carry out several functions in chemical reactions.

Three examples of industrial reactions in which sulfuric acid is used are shown below.

reaction 1 $Al_2O_3 + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2O$

reaction 2 $Cu + H_2SO_4 \longrightarrow CuO + SO_2 + H_2O$

reaction 3 $(CH_3)_3COH + H_2SO_4 \longrightarrow (CH_3)_2C{=}CH_2 + H_2SO_4 + H_2O$

What is the function of sulfuric acid in each reaction?

	reaction 1	reaction 2	reaction 3
A	acidic	oxidising	dehydrating
B	acidic	acidic	dehydrating
C	dehydrating	oxidising	catalytic
D	dehydrating	acidic	catalytic

10 *Some of these data are also relevant to question 14*.

Given the following enthalpy change

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) \qquad \Delta H^{\ominus} = -92\ \text{kJ mol}^{-1}$$
$$N_2(g) + 4H_2(g) + Cl_2(g) \longrightarrow 2NH_4Cl(s) \qquad \Delta H^{\ominus} = -629\ \text{kJ mol}^{-1}$$
$$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s) \qquad \Delta H^{\ominus} = -176\ \text{kJ mol}^{-1}$$

What is the standard enthalpy change of formation of gaseous hydrogen chloride?

A -361 kJ mol^{-1}

B -185 kJ mol^{-1}

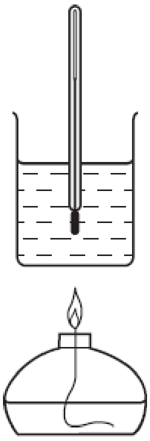
C -92.5 kJ mol^{-1}

D -46.3 kJ mol^{-1}

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

A student carried out an experiment to determine the enthalpy change of combustion of ethanol.

The following results were obtained by the student.



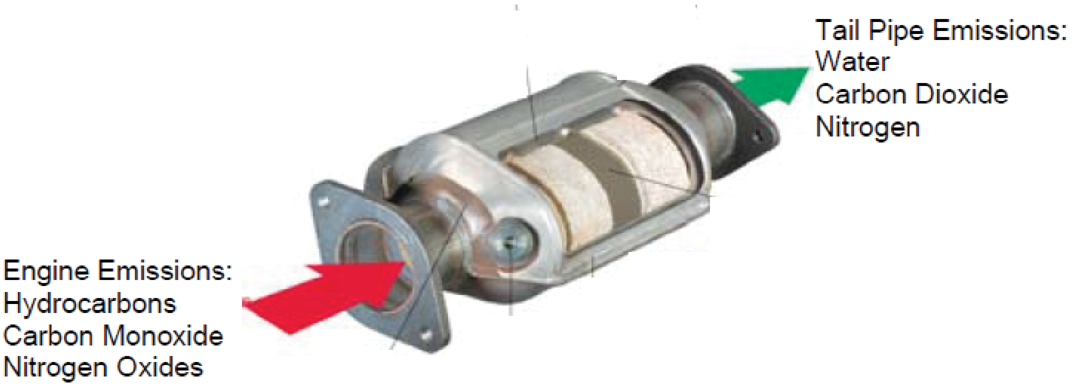
initial temperature of the water	25 °C
final temperature of the water	68 °C
mass of alcohol burner before burning	260.65 g
mass of alcohol burner after burning	259.65 g
mass of glass beaker plus water	160.00 g
mass of glass beaker	60.00 g

Given that the enthalpy change of combustion of ethanol is −1370 kJ mol^{-1}, what is the efficiency of heat transferred to the water?

A 46% **B** 60% **C** 81% **D** 97%

12 An example of a three–way honeycomb type catalytic converter is shown below.

The catalytic converter involves three simultaneous reactions. In the first, NO_x gases get reduced; in the second and third, unburnt hydrocarbon and carbon monoxide are completely oxidised.



Which of the following equations does **not** represent the reactions that took place in the catalytic converter?

A $C(g) + O_2(g) \longrightarrow CO_2(g)$

B $2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$

C $2NO(g) + 2CO(g) \longrightarrow N_2(g) + 2CO_2(g)$

D $2C_8H_{18}(g) + 25O_2(g) \longrightarrow 16CO_2(g) + 18H_2O(g)$

13 A radioactive element has two isotopes, **L** and **M**, with half–lives of 3 min and 9 min respectively.

An experiment starts with *n* times as many atoms of **L** as of **M**. After 9 min, the number of atoms of **L** and **M** are both equal.

Given that radioactive decay is a first order reaction, what is the value of *n*?

A 0.5 **B** 2 **C** 4 **D** 8

14 *Use of the data in question 10 is relevant to this question.*

Which of the following statement is true about the Haber process for the manufacture of ammonia?

A Adding a catalyst increases the equilibrium yield of ammonia but the rate of production of ammonia is faster.

B Adding neon gas at constant pressure increases the equilibrium yield of ammonia but the rate of production of ammonia is slower.

C Decreasing the temperature increases the equilibrium yield of ammonia but the rate of production of ammonia is slower.

D Removing nitrogen gas at constant volume increase the equilibrium yield of ammonia but the rate of production of ammonia is slower.

15 The Gibbs free energy change of reaction, $\Delta G^{\ominus}$, for the contact process is shown below.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta G^{\ominus} = -142 \text{ kJ mol}^{-1}$$

Which statement about the equilibrium constant, K_p at 25 °C is true?

A K_p is less than 1.

B K_p is greater than 1.

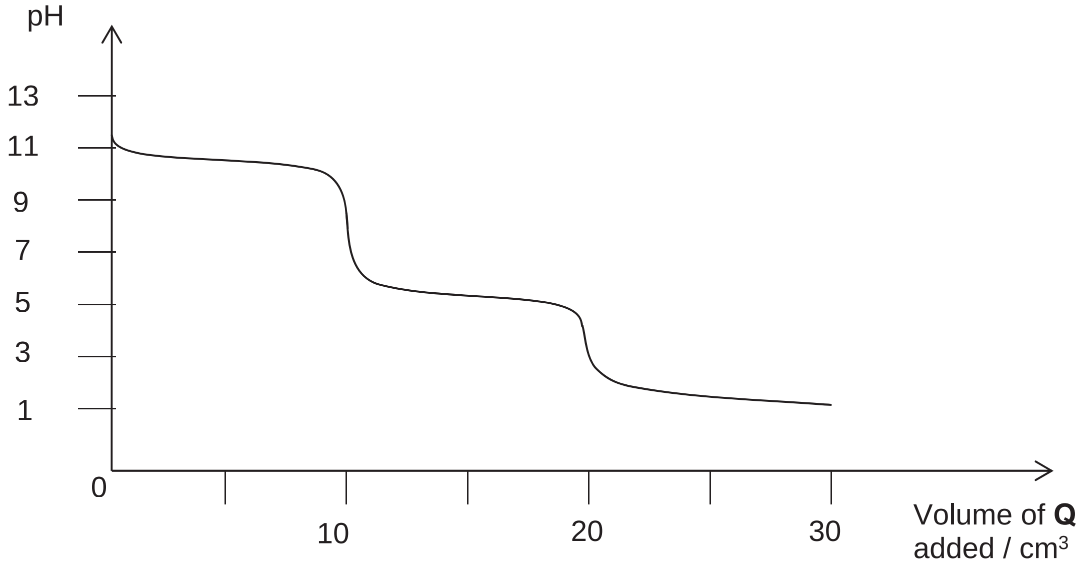
C K_p is equal to 1.

D No conclusion can be drawn about K_p.

16 What is the pH of the final solution formed when 30 cm^3 of 0.10 mol dm^{-3} HNO_3 is added to 20 cm^3 of 0.20 mol dm^{-3} ammonia?
[K_b of ammonia = 1.8 x 10^{-5} mol dm^{-3}]

A 4.3 **B** 5.2 **C** 8.8 **D** 10.8

17 The diagram below shows the change of pH produced by gradually adding aqueous **Q** to a certain volume of aqueous **P**. The concentration of each constituent of the aqueous solutions **P** and **Q** is 0.1 mol dm^{-3}.



What could **P** and **Q** be?

	P	**Q**
A	NaOH + KOH	HC*l*
B	$H_2NCH_2CH_2NH_2$	HC*l*
C	Na_2CO_3	$CH_2(COOH)_2$
D	KOH	CH_3COOH

18 When heated with chlorine, the hydrocarbon 2–methylbutane, $CH_3CH_2CH(CH_3)_2$, undergoes free radical substitution.

In a propagation step, which free radical will be formed most readily?

A $\overset{\bullet}{C}H_2CH_2CH(CH_3)_2$

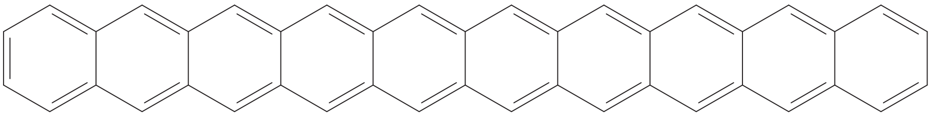
B $CH_3\overset{\bullet}{C}HCH(CH_3)_2$

C $CH_3CH_2\overset{\bullet}{C}(CH_3)_2$

D $CH_3CH_2CH(\overset{\bullet}{C}H_2)CH_3$

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

The longest acene, decacene, comprising of 10 linearly fused benzene ring, has been made for the first time in 2017.



Which statements about the molecule are correct?

1 Each of the C–C–C bond angle is 120°.

2 The π electrons are delocalised.

3 The bond energy of each carbon–carbon bond in the molecule is equal to 350 kJ mol^{-1}.

4 Each C atom has a valency of 3.

A 1, 3 and 4 only

B 2, 3 and 4 only

C 1 and 2 only

D 1 and 3 only

20 Ozone depletion potential (ODP) is a measure of the effectiveness of chlorofluoroalkanes in destroying stratospheric ozone.

In which sequence are compounds listed in increasing order of their ODPs?

A $CHClF_2 < CH_3CCl_2F < CCl_2FCClF_2$

B $CHClF_2 < CCl_2FCClF_2 < CH_3CCl_2F$

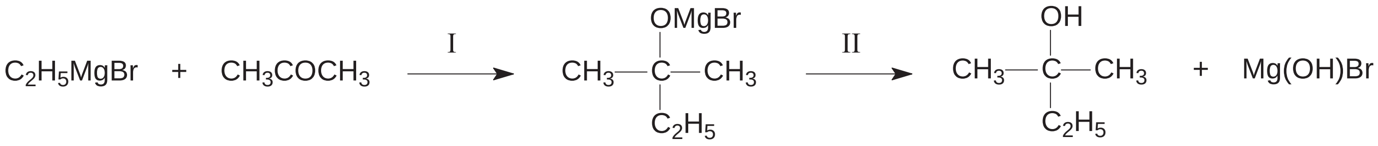
C $CCl_2FCClF_2 < CHClF_2 < CH_3CCl_2F$

D $CH_3CCl_2F < CCl_2FCClF_2 < CHClF_2$

The following information is relevant to questions **21** and **22**.

Most of the chemistry of magnesium relates to its ionic compounds. However, magnesium does form an important group of covalent compounds which are known as Grignard reagents. Many Grignard reagents, with different alkyl or aryl groups, are widely used in organic syntheses.

The following reaction scheme shows a typical example of the use of a Grignard reagent.

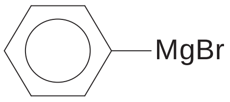
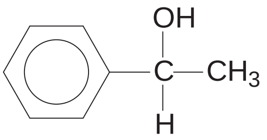
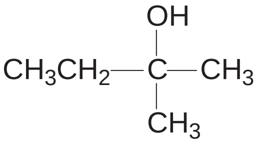
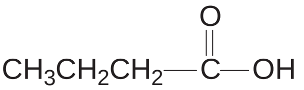


$$C_2H_5MgBr + CH_3COCH_3 \xrightarrow{I} CH_3C(OMgBr)(C_2H_5)CH_3 \xrightarrow{II} CH_3C(OH)(C_2H_5)CH_3 + Mg(OH)Br$$

21 What are the types of reaction shown in this reaction scheme?

	I	II
A	electrophilic addition	acid–base
B	nucleophilic substitution	elimination
C	nucleophilic addition	acid–base
D	nucleophilic addition	hydrolysis

22 Which of the following sets show the correct reactants and products obtained upon undergoing the same reaction scheme?

	reactants	products
1	 + CH_3CHO	 + Mg(OH)Br
2	$CH_3CH_2CH_2MgBr$ + CH_3COCH_3	 $CH_3CH_2C(OH)(CH_3)CH_3$ + Mg(OH)Br
3	$CH_3CH_2CH_2MgBr$ + CO_2	 $CH_3CH_2CH_2COOH$ + Mg(OH)Br

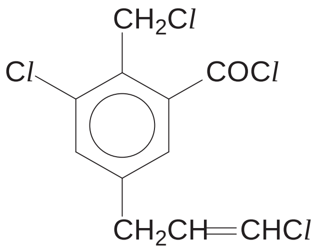
A 2 only

B 3 only

C 1 and 2 only

D 1 and 3 only

23 Compound **T** has the structure as shown below.

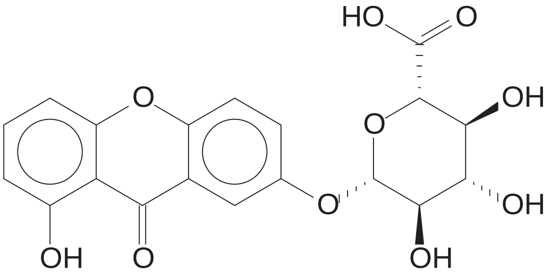


1 mol of compound **T** is warmed with aqueous sodium hydroxide. The resulting solution is cooled and acidified with dilute nitric acid. Excess aqueous silver nitrate is then added to it.

How many moles of silver chloride is precipitated out?

A 1 **B** 2 **C** 3 **D** 4

24 The pigment *Indian Yellow*, which first appeared in the 14th century and then vanished at the end of the Victorian era, was made famous by artist Joseph Mallord William Turner.



Indian Yellow

In the following reactions, R–O–R remains unaltered.

Which of the following observation is correct?

A It reacts with hot, alkaline aqueous iodine to give a yellow solid.

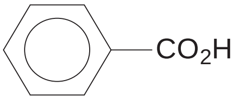
B It reacts with hot, acidified $K_2Cr_2O_7$ to give a compound with 3 carbonyl groups.

C It reacts with aqueous bromine to incorporate up to 6 atoms of bromine in each molecule.

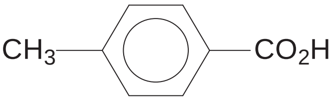
D It reacts with excess sodium metal to produce 2.5 mol of hydrogen gas for each mole of the molecule.

25 Consider the following four carboxylic acids.

1



2



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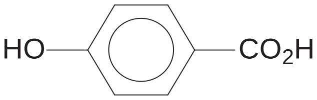
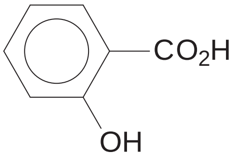


4

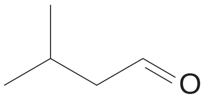


What is the relative order of **decreasing** pK_a?

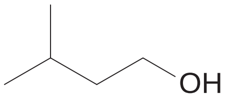
A	3	2	1	4
B	1	2	3	4
C	4	1	2	3
D	2	1	4	3

26 The following compounds are responsible for the smell of tequila.

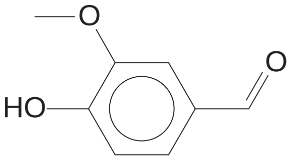
1



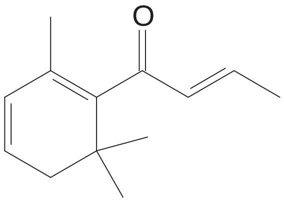
2



3



4



Which of the compounds can be oxidised by acidified potassium dichromate(VI) and can be reduced by sodium borohydride?

A 2 only

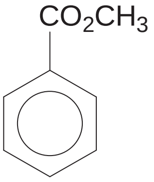
B 1 and 3 only

C 2 and 4 only

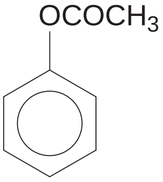
D 1, 3 and 4 only

27 Deuterium, D, is an isotope of hydrogen.

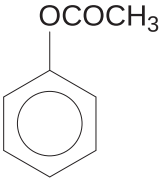
Which compounds will react to produce deuterophenol, C_6H_5OD, in good yield?

A 

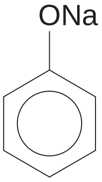
+ NaOD in D_2O, with heat

B 

+ NaOD in D_2O, with heat

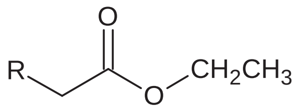
C 

+ DC*l* in D_2O, with heat

D 

+ D_2O

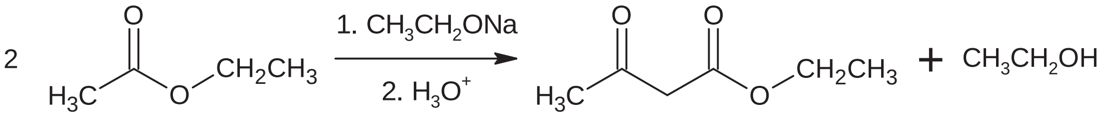
28 Members of an ethyl ester homologous series have the general formula



where R = C_nH_{2n+1}, and n = 0, 1, 2 …

Each member undergoes Claisen condensation with either itself or another member of the series to form a β–keto ester.

For example, the first member of the series, ethyl ethanoate, combines with itself in the presence of sodium ethanoate, followed by acidification, to form ethyl 3–oxobutanoate. Ethanol is eliminated in the process.

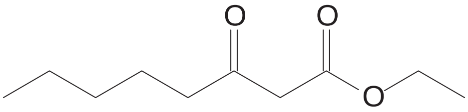


ethyl ethanoate

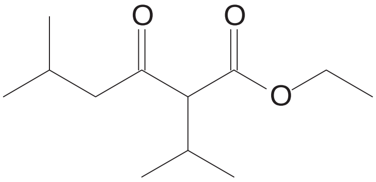
ethyl 3-oxobutanoate
(β-keto ester)

Which of the following is a possible product of the Claisen condensation between ethyl ethanoate and the **fourth** member of the series?

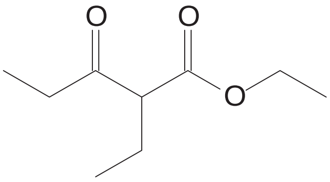
A



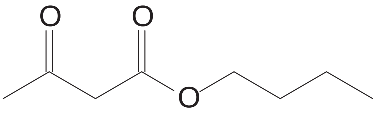
B



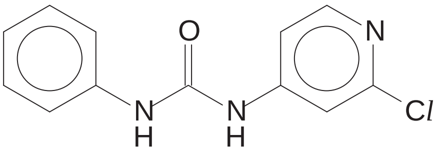
C



D

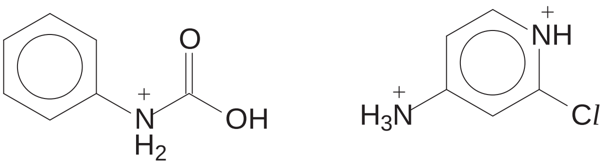


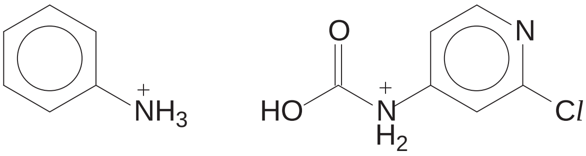
29 In 2011, farmers in Eastern China were hit by a spate of exploding watermelons. This was a result of the overuse of *forchlorfenuron*, a plant growth regulator.

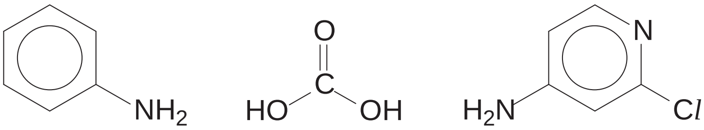


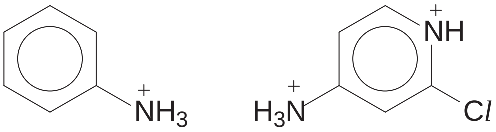
forchlorfenuron

What are the organic products formed when forchlorfenuron is heated with dilute acid?

A 

B 

C 

D 

30 When excess of NaOH(aq) are added to $Fe(NO_3)_2$(aq), a dirty green precipitate is formed. On standing in air, the precipitate turns reddish brown.

Which process does **not** occur in this sequence?

A Acid–base

B Ligand exchange

C Oxidation

D Precipitation

ANDERSON JUNIOR COLLEGE

2017 JC 2 PRELIMINARY EXAMINATIONS

NAME:___________________________ **PDG:**____ /16

CHEMISTRY **9729/02**

Paper 2 Structured Questions **13 September 2017**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, PDG and register number on all the work you hand in.
Write in dark blue or black pen.
You may use a pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, 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.
A Data Booklet is provided.

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.

For Examiner's Use		
Paper 2	1	/ 15
	2	/ 13
	3	/ 16
	4	/ 14
	5	/ 17
Total		/ 75

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

Answer **all** the questions.

1 **(a)** *Use of the Data Booklet will be relevant to this question.*

Iron ore from different mines will contain different percentages by mass of iron. The percentage of iron in a sample of ore can be estimated by converting all of the iron present into $Fe^{2+}(aq)$ ions and then using a redox titration.

The sample of ore is crushed, weighed and then dissolved in aqueous acid. The $Fe^{3+}(aq)$ ions are then reduced to $Fe^{2+}(aq)$ ions by reaction with an excess of aqueous tin(II) chloride, $SnCl_2$.

(i) Construct an ionic equation for the reduction of $Fe^{3+}(aq)$ ions with aqueous tin(II) chloride solution.

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

(ii) Calculate the standard cell potential, $E^{\ominus}_{cell}$, for this reaction.

[1]

(iii) Explain why tin(II) chloride will reduce $Fe^{3+}(aq)$ ions to $Fe^{2+}(aq)$ ions, but will **not** reduce $Fe^{2+}(aq)$ ions to metallic iron.

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

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

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

A sample of iron ore weighing 11.05 g was converted to $Fe^{2+}(aq)$ ions using the method described above. The resultant solution was then made up to a volume of 250 cm^3 in a volumetric flask.

25.0 cm^3 portions of this solution were then titrated with 0.100 mol dm^{-3} of aqueous potassium dichromate(VI) using a suitable indicator. The results are shown below.

titration number	1	2	3
initial burette reading / cm^3	0.00	19.95	2.10
final burette reading / cm^3	19.95	40.05	22.15
titre / cm^3	19.95		

(iv) Complete the table on page **2** and use the results to determine the number of moles of potassium dichromate(VI) required to react with the Fe^{2+} ions in 25.0 cm^3 of the solution.

[2]

(v) Write an ionic equation for the reaction of Fe^{2+} ions with acidified $Cr_2O_7^{2-}$ ions.

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

(vi) Calculate the total number of moles of Fe^{2+} in the original solution made up from the iron ore, and hence calculate the percentage by mass of iron in the sample of iron ore.

[2]

(b) Iron and magnesium form iodate(V) compounds as shown, Fe$(IO_3)_2$ and Mg$(IO_3)_2$. Upon heating, each of the iodates decomposes to give a solid residue. Purple fumes and a gas that relights a glowing splint are also observed.

(i) Draw a dot–and–cross diagram to show the bonding in iodate(V) ion, IO_3^-. In your diagram use the symbols '•' and 'x' to distinguish electrons from iodine and oxygen atoms, and the symbol '□' for any additional electrons responsible for the overall negative charge.

[1]

(ii) Write a balanced equation for the thermal decomposition of Mg$(IO_3)_2$.

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

(iii) Mg$(IO_3)_2$ is found to decompose at 900 K.

By quoting suitable data from the *Data Booklet*, suggest and explain if Fe$(IO_3)_2$ will decompose at a higher or lower temperature than Mg$(IO_3)_2$.

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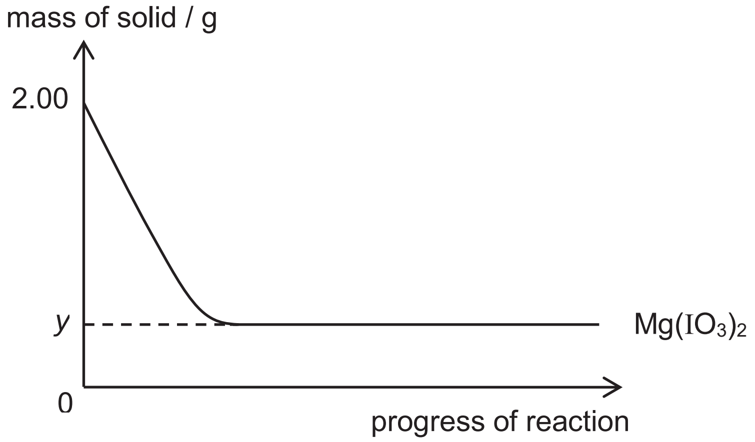
…………………………………………………………………………………………………......

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

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

The graph below shows the change in mass when 2.00 g of $Mg(IO_3)_2$ is heated at temperature, T °C.



(iv) Determine the value of *y*.

[1]

(v) On the same axes, show clearly the sketch for the decomposition of 2.00 g of $Fe(IO_3)_2$ at the same temperature. [1]

[Total: 15]

2 **(a)** Explain the meaning of the term *homogenous catalyst* and illustrate your answer by using one specific reaction involving a transition metal or its compound behaving as one.

……..

……..

……..

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

(b) *Use of the Data Booklet is relevant to this question.*

Aqueous hydrogen peroxide is fairly stable but when a mixture of cobalt(II) salt and tartaric acid $HO_2CCH(OH)CH(OH)CO_2H$ is added to aqueous hydrogen peroxide, the following changes take place.

The initial pink solution *slowly* turns into a green solution containing cobalt(III) species and then oxygen is *vigorously* evolved. Finally the solution turns pink again. Tartaric acid and the cobalt(II) salt can be recovered from the solution at the end.

(i) Write an equation for the overall reaction.

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

(ii) State the role of cobalt(II) salt in this reaction and give evidence to support your answer.

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

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

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

(iii) With the aid of relevant data in the *Data Booklet*, show that Co^{3+}(aq) is not stable in aqueous solution and hence comment on the role of tartaric acid in this reaction.

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

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

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

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

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

(c) The decomposition of hydrogen peroxide follows a first order kinetics.

A 100 cm^3 of hydrogen peroxide undergoes complete decomposition to liberate 96 cm^3 of oxygen gas. It is found that 48 cm^3 of oxygen gas was collected in 35 minutes. All gaseous volumes were measured at room temperature and pressure.

(i) Calculate the initial concentration of hydrogen peroxide.

[1]

(ii) Estimate the time taken for 88 cm^3 of oxygen gas to be collected.

[1]

(iii) Calculate the rate constant *k*, including the units for the reaction.

[2]

(iv) What percentage of the hydrogen peroxide in a solution of concentration 0.20 mol dm^{-3} would decompose in 35 minutes at the same temperature?

[1]

(v) Outline a suitable method, other than the gas collection method, to find the order of reaction for the decomposition of hydrogen peroxide.

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

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

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

[Total: 13]

3 The Pollutant Standards Index (PSI) is an air quality indicator. It is based on five pollutants: particulate matter (PM10), sulfur dioxide, carbon monoxide, ozone and nitrogen dioxide.

To calculate the overall PSI, the PSI value is first determined, using the following table, for **each** of the five pollutants.

i	**PSI value, P_i**	**Concentration, C_i**				
		PM10 ($\mu g\ m^{-3}$)	**SO_2 ($\mu g\ m^{-3}$)**	**CO ($mg\ m^{-3}$)**	**Ozone ($\mu g\ m^{-3}$)**	**NO_2 ($\mu g\ m^{-3}$)**
1	50	50	80	5.0	118	–
2	100	150	365	10.0	157	–
3	200	350	800	17.0	235	1130
4	300	420	1600	34.0	785	2260
5	400	500	2100	46.0	980	3000
6	500	600	2620	57.5	1180	3750

[1 $\mu g = 10^{-6}$ g; 1 mg = 10^{-3} g]

Given the concentration of a pollutant (with units as stated in the table above), where C_{i+1} > concentration of pollutant > C_i ,

$$\text{PSI of pollutant} = \left[\left(\frac{P_{i+1} - P_i}{C_{i+1} - C_i}\right)\left(\text{concentration of pollutant} - C_i\right)\right] + P_i$$

The overall PSI is then based on the maximum value out of the five calculated PSI pollutant values.

In Singapore, the 24–hr PSI is used by the National Environment Agency (NEA) to provide health advisory.

24–hr PSI	**Healthy Persons**	**Elderly, Pregnant women, Children**	**Persons with chronic lung disease, heart disease, stroke**
< 100	Normal activities		
101–200	Minimise prolonged or strenuous outdoor physical exertion.	Minimise prolonged outdoor activity.	Avoid all outdoor activities. If outdoor activity is unavoidable, wear N95 mask.
201–300	Avoid prolonged or strenuous outdoor physical exertion. If outdoor activity is unavoidable, wear N95 mask.	Avoid all outdoor activities. If outdoor activity is unavoidable, wear N95 mask (for adults).	
>300	Minimise all outdoor exposure. If outdoor activity is unavoidable, wear N95 mask.		

(a) **(i)** In a 1 m^3 sample of air, the mass of PM10 and carbon monoxide were found to be 320 μg and 20 mg respectively. Calculate the PSI values for each of the above pollutants, leaving your answers to **3 significant figures**.

[2]

(ii) Given that the PSI value of sulfur dioxide, ozone and nitrogen dioxide are 150, 112 and 133 respectively for the same sample of gas, use these values and your answers to **(a)(i)** to determine the overall PSI.

[1]

(iii) Assuming that the current overall PSI level is your answer in **(a)(ii)**, what advice would you give to a Physical Education (PE) teacher in Anderson Junior College who will be conducting a PE lesson soon?

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

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

(b) The amount of sulfur dioxide in a sample of air can be determined by first reacting it with sodium iodate, $NaIO_3$. Iodine is one of the products in this reaction.

(i) Write an ionic equation for the reaction between sulfur dioxide and sodium iodate.

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

(ii) When a 1 m^3 sample of air was bubbled through a solution of sodium iodate, the resulting solution was neutralised by 10.0 cm^3 of 0.005 mol dm^{-3} sodium hydroxide solution.

Calculate the concentration of sulfur dioxide, in $\mu g\ m^{-3}$, in the sample of air.

[2]

(c) Some countries have set limits for particulates in the air. For example, the European Union has a daily average (24–hour) limit of 180 μg m^{-3} for PM10. Cities that violate this daily limit face a hefty financial penalty that is calculated with consideration of many factors such as the severity the violation has on the ecosystem, duration of the non–compliance and country's GDP etc.

(i) A collected sample of air from the German city of Leipzig contains 2 x 10^{-5} % by mass of PM10. Given that the density of air is 1 kg m^{-3}, calculate the concentration of PM10 in the sample collected.

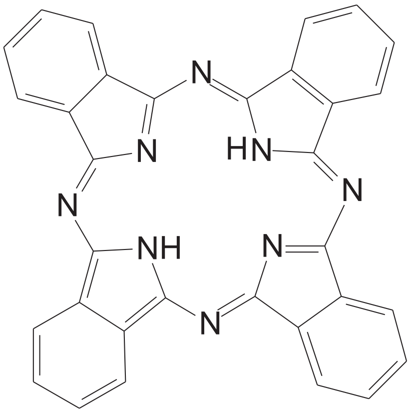
[1]

(ii) Hence, deduce whether the German city of Leipzig will be faced with any financial penalty.

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

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

(d) A team of researchers at the National University of Singapore has come up with an eco–friendly and cost–effective solution to keep out the harmful PM2.5 particles found in haze. They created a nanofibre liquid solution by modifying phthalocyanine, a blue–green coloured aromatic compound commonly used in dyes for clothes. The solution can be applied to non–woven mesh to become thin, see–through air filters that block out up to 90% of PM2.5 particles.



phthalocyanine

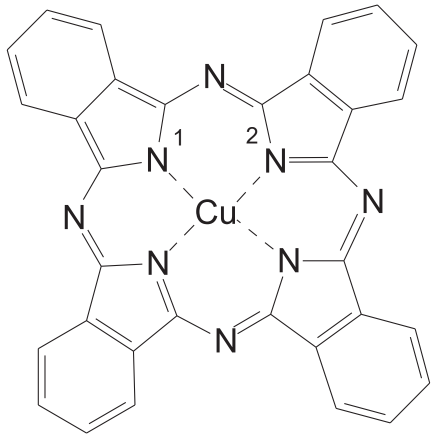
(i) Give the molecular formula of phthalocyanine.

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

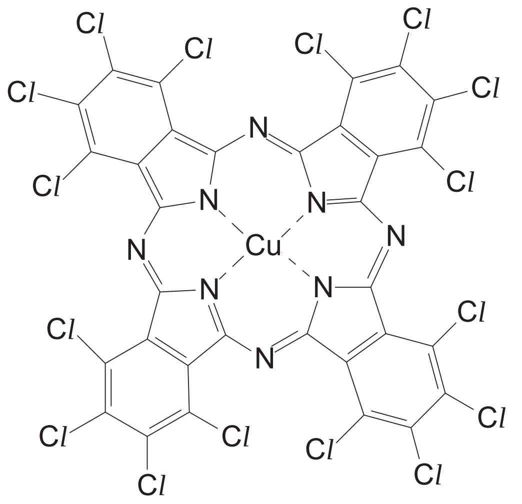
(ii) Suggest why phthalocyanine can be described as aromatic.

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

(e) Copper phthalocyanine dyes are artificial organic pigments derived from phthalocyanine. They are produced by introducing solubilising groups, such as methanesulfonic acid, CH_3SO_3H.



phthalocyanine blue



phthalocyanine green

(i) Name the type of bonds formed between copper and the nitrogen atoms numbered 1 and 2 in phthalocyanine blue.

N1 ……………………………………………

N2 …………………………………………… [2]

(ii) Give the electronic configuration of the copper in phthalocyanine blue.

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

(iii) Deduce the number of electrons around the N1 nitrogen atom.

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

(iv) Account for the difference in the colour of the two copper phthalocyanine dyes given above.

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

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

[Total: 16]

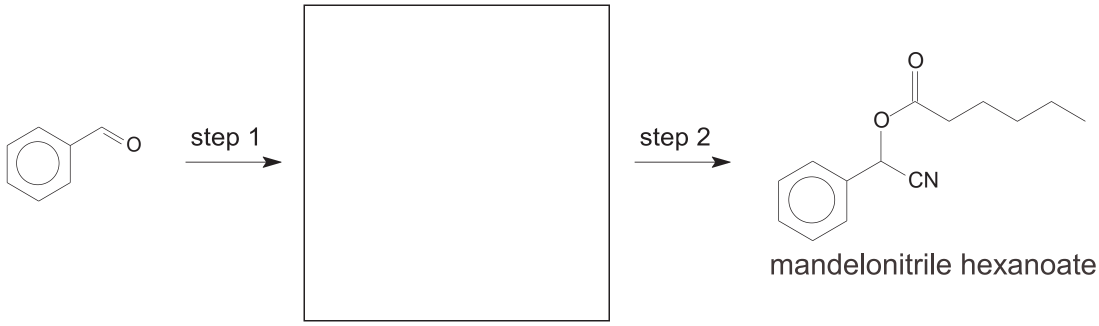
4 The *Oribatula tibialis* mite uses hydrogen cyanide, HCN, a highly volatile and toxic substance, to poison its predators.

The HCN is stored in the form of mandelonitrile hexanoate, $C_{14}H_{17}NO_2$, in the mite's oil glands, to avoid poisoning itself.

(a) In order to confirm the identity of mandelonitrile hexanoate in mite's oil glands, synthetic mandelonitrile hexanoate was made in the laboratory and dissolved in hexane.

Both synthetic mandelonitrile hexanoate and the extracted oil gland from *Oribatula tibialis* mite were then sent for analysis using various analytical techniques.

(i) Suggest the reagents that can be used to prepare mandelonitrile hexanoate from benzaldehyde at **low** temperature conditions. Show the structure of the intermediate organic compound in the box below.



step 1 ………………………………………………………………………………………………

step 2 ………………………………………………………………………………………………

[3]

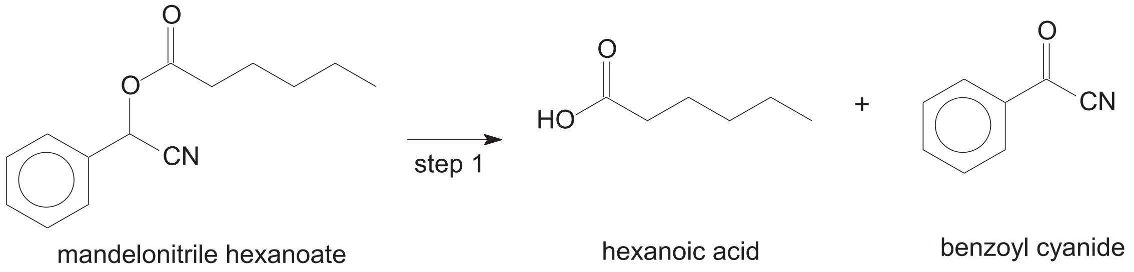
(ii) Suggest, in terms of the intermolecular forces involved, a reason why mandelonitrile hexanoate can dissolve in hexane.

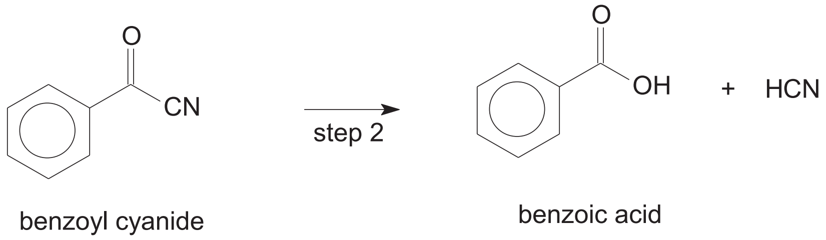
………………………………………………………………………………………………………

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

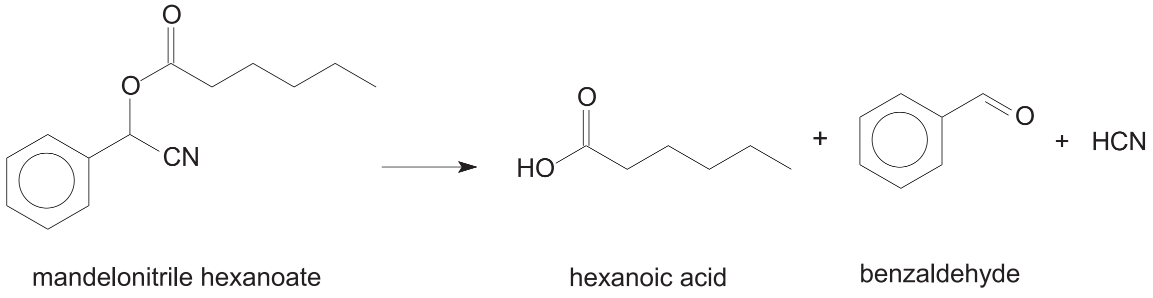
When attacked by predators, the *Oribatula tibialis* mite secretes mandelonitrile hexanoate, which then release HCN, when in contact with the moisture, for example, from the predators' saliva. The HCN can be released via two different chemical pathways.

Pathway **I** illustrates a two–step process.





In pathway **II**, benzaldehyde is produced instead of benzoic acid.



(b) **(i)** By considering the change in structural formula shown in pathway **I**, suggest **two** types of reaction that could have occurred in step 1.

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

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

(ii) In step 2 of pathway **I**, the intermediate benzoyl cyanide breaks down into benzoic acid and HCN.

It was reported that benzoyl cyanide is less reactive than benzoyl chloride when it is in contact with water. Suggest a possible reason for this.

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

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

(iii) Suggest a simple chemical test that could be carried out to confirm which chemical pathway has occurred.

You may assume that HCN has vapourised completely from the product mixture.

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

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

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

(c) Benzaldehyde can be oxidised by peroxybenzoic acid, without consumption of oxygen, to give benzoic acid.

The standard enthalpy change of the reaction below is –316 kJ mol^{-1}.

$$C_6H_5CHO(l) + C_6H_5CO_3H(s) \longrightarrow 2C_6H_5CO_2H(s)$$

The standard enthalpy change of formation of peroxybenzoic acid and benzaldehyde are given in the table below.

Name	Formula	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
peroxybenzoic acid	$C_6H_5CO_3H(s)$	–367
benzaldehyde	$C_6H_5CHO(l)$	–87

(i) Define the term *standard enthalpy change of formation*, $\Delta H_f^{\ominus}$ of a compound.

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

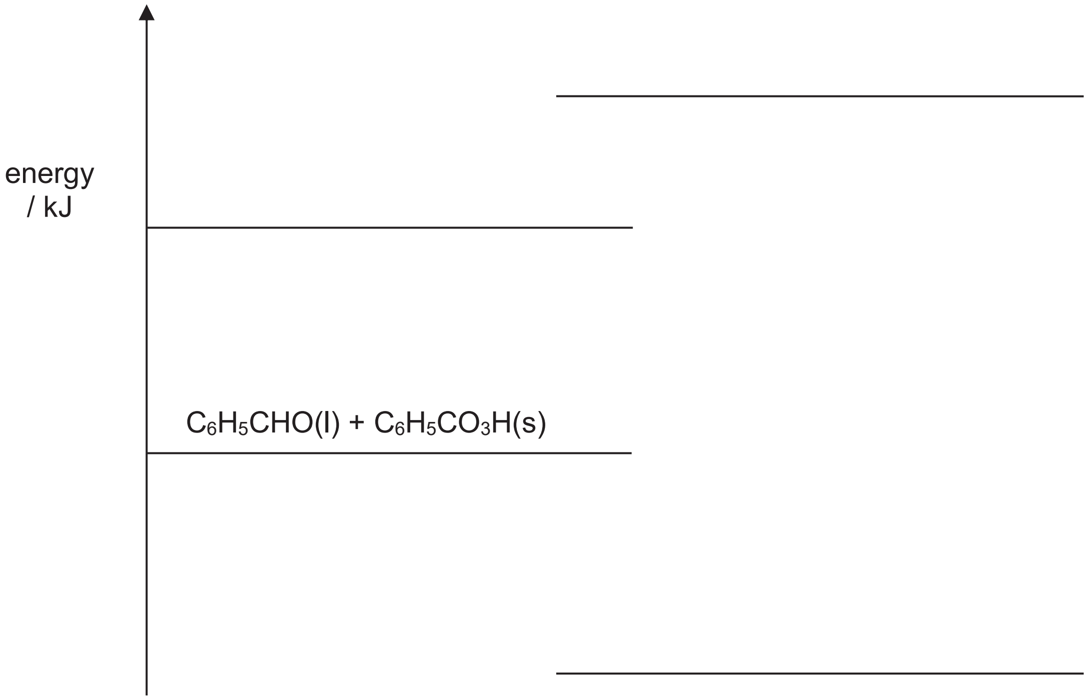
……………………………………………………………………………………………………[1]

(ii) Use the data given above to calculate the enthalpy change of formation of benzoic acid.

[1]

(iii) Draw arrows on the energy diagram below to show each of the energy terms involved in the steps you have used in your calculation in **(c)(ii)**.

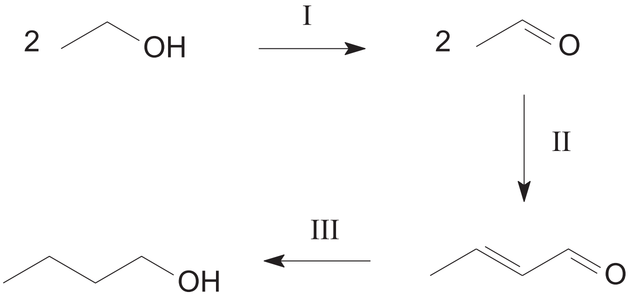
Label each level with the appropriate formulae.



[3]

[Total: 14]

5 Scientists in the United States of America have come up with a simple 3–stage process to convert ethanol into butan–1–ol, in what could be an important step forward for renewable energy.



G

(a) **(i)** State the reagents and conditions required for stages I and III.

stage I ……………………………………………………………………………………......

stage III ……………………………………………………………………………………....
[2]

(ii) Write an equation for the incomplete combustion of butan–1–ol, giving CO_2 and CO in a 3 : 1 ratio.

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

(iii) Describe the type(s) of stereoisomerism shown by compound **G**.
Draw the displayed formula of the stereoisomers of **G**.

Type of isomerism ………………………………………………..

[2]

(iv) **G** reacts with a suitable reducing agent to give compound **H**.

H effervesces with sodium metal but does not react with 2,4–dinitrophenylhydrazine. **H** also decolourises aqueous bromine.

Suggest the structure of **H** and explain these observations.

……………………………………………………………………………………………

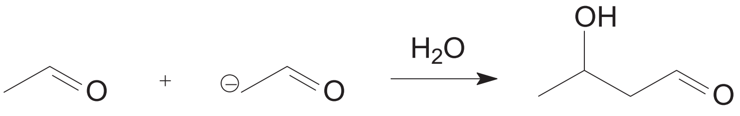
……………………………………………………………………………………………

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

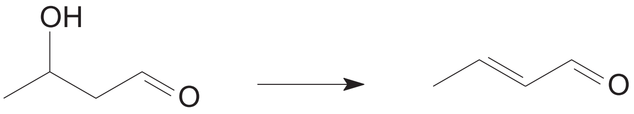
(b) The mechanism for stage II of the process in forming the α,β–unsaturated aldehyde **G** is thought to involve three steps.

Step 1 The first step involves an acid–base reaction.

Step 2 This is followed by a nucleophilic addition reaction to form the intermediate 3–hydroxybutanal.

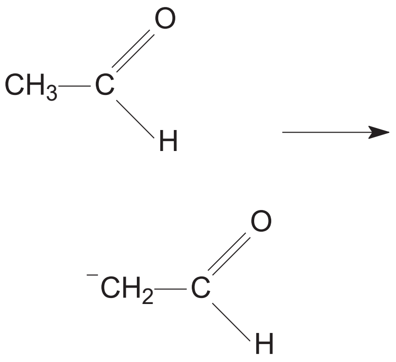


Step 3 Elimination of water is involved in the last step.



G

(i) Complete the diagram to suggest a mechanism to show how 3–hydroxybutanal intermediate is formed. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows.



[2]

(ii) A different product can be formed together with **G**, in step 3, albeit in lower yield. Suggest a reason for this.

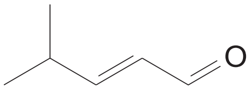
……………………………………………………………………………………………………

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

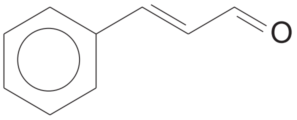
……………………………………………………………………………………………………[1]

(iii) Deduce the structures of suitable carbonyl compounds to synthesise each of the following α,β–unsaturated aldehyde.

(I)



(II)



[3]

(c) Butan–1–ol has a number of constitutional isomers.

(i) Draw the structural formula of the other three alcohols with the same molecular formula as butan–1–ol. Label your structures **J**, **K** and **L**. Classify these alcohols as primary, secondary or tertiary.

[2]

(ii) Identify which alcohol reacts with alkaline aqueous iodine and write a balanced equation for the reaction, showing the structural formula of the products.

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

[2]

[Total: 17]

ANDERSON JUNIOR COLLEGE

2017 JC 2 PRELIMINARY EXAMINATIONS

CHEMISTRY **9729/03**

Paper 3 Free Response **15 September 2017**

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, PDG and register number on all the work you hand in.
Write in dark blue or black pen.
You may use a pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

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.

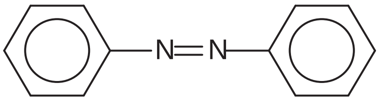
This document consists of **13** printed pages.

Section A

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

1 **(a)** Scientists in Germany have developed a liquid crystal elastomers (LCE)–based adhesive that uses UV light to switch and control its level of stickiness within seconds.

To control adhesion, the team used azobenzene, $C_{12}H_{10}N_2$ in the LCE as the light responsive molecule, which isomerises quickly from one state to another and changes size under UV light. This effect flexes the material enough to cause the microstructures to peel away from a surface and unstick, akin to how a gecko loses adhesion by moving its feet. When the light is removed, the material quickly recovers to its flat, sticky state.



azobenzene

(i) State the type of hybridisation that is present on the nitrogen atom and draw the shape of the hybrid orbitals around one of the nitrogen atom in azobenzene. Suggest the bond angle around this nitrogen atom. [3]

(ii) State the type of isomerism that is present in azobenzene and draw the two structures that illustrate the isomerism. [2]

(iii) Suggest, with a reason, the isomer that is responsible for the peeling of microstructures away from a surface. [1]

(b) *Use of the Data Booklet is relevant to this question.*

Compound **U,** $C_{17}H_{17}N_3O_3$ is not soluble in NaOH(aq) and HC*l*(aq). It gives 2 products when heated under reflux with acidified potassium dichromate. Orange potassium dichromate turns green during the process. Upon careful neutralisation of the resultant mixture, compounds **V** and **W** are formed.

V, $C_{13}H_{10}N_2O_2$ is a derivative of azobenzene, and has a proton (^1H) chemical shift value of 13.0 ppm.

W gives an orange precipitate when treated with 2,4–dinitrophenylhydrazine but it has no reaction with Tollens' reagent. It gives a yellow precipitate and compound **X** when warmed with aqueous mixture of sodium hydroxide and iodine. Effervescence was observed when **W** was treated with aqueous sodium hydrogencarbonate.

When **W** is heated with excess CH_3Cl, it gives compound **Y,** $C_7H_{14}NO_3Cl$, as the major product.

Suggest structures for **U** – **Y** and explain the reactions described above.
(The –N=N– structure remains unaltered in this question) [9]

[Total: 15]

2 Silver forms a series of halides of general formula Ag*X*. The chloride, bromide and iodide of silver are sparingly soluble in water at room temperature.

Data about the solubilities in water and the solubility products of the chloride, bromide and iodide of silver at 298 K are given below.

Salt	Solubility / mol dm^{-3}	Solubility product / mol^2 dm^{-6}
$AgCl$	1.4×10^{-5}	2.0×10^{-10}
$AgBr$	7.1×10^{-7}	5.0×10^{-13}
AgI	8.9×10^{-9}	to be calculated

In this question, give **each** of your numerical answers to **one** decimal place.

(a) **(i)** Write an expression for the solubility product, K_{sp} of silver iodide. [1]

(ii) From the data above, calculate a value for K_{sp} of silver iodide. [1]

(iii) To a 2.0 dm^3 of saturated solution of AgI, 0.025 g of $AgNO_3(s)$ was added. Calculate the mass of precipitate formed. [2]

(b) When a precipitate is formed, $\Delta G^{\ominus}_{ppt}$ is given by the following expression.

$$\Delta G^{\ominus}_{ppt} = 2.303\ RT \log_{10} K_{sp}$$

(i) Use the data above to calculate $\Delta G^{\ominus}_{ppt}$, for silver chloride. [1]

(ii) When silver nitrate is added to solution containing chloride ions, a white precipitate is observed. The white precipitate dissolves when aqueous ammonia was added. Upon adding of aqueous sodium bromide to the resultant mixture, a cream precipitate is obtained.

With the aid of suitable equations, explain the chemistry that is occurring during these reactions. [3]

(c) For silver fluoride, AgF, K_{sp} = 1.006 mol^2 dm^{-6} at 298 K.
Use the expression given in **(b)** to determine whether silver fluoride is soluble in water at 298 K.

Explain your answer. [2]

[Total: 10]

3 **(a)** Great research efforts have been put into the production of sustainable fuels, such as hydrogen and synthetic hydrocarbons. One of particular interest is a solar–driven thermochemical process which utilises a metal oxide catalyst to produce carbon monoxide from carbon dioxide.

In the first stage, the metal oxide (MO_2) is reduced to release oxygen gas. In the second stage, carbon dioxide then oxidises the reduced metal oxide to generate carbon monoxide.

The 2–stage process is as shown below.

Stage 1: $MO_2(s) \rightleftharpoons MO_{2-x}(s) + \frac{x}{2}O_2(g)$ $\Delta H_1 > 0$

Stage 2: $MO_{2-x}(s) + xCO_2(g) \rightleftharpoons MO_2(s) + xCO(g)$

(i) Stage 1 is carried out at a high temperature of 1500 ^{o}C.

State *Le Chatelier's Principle* and use it to explain why such a high temperature is necessary. [2]

(ii) Give the equation, with state symbols, for the overall equilibrium reaction. [1]

(iii) The $\Delta H^{\ominus}$ of the reaction in **(a)(ii)** is +283 kJ mol^{-1} when $x = 1$.

Using relevant data from the *Data Booklet*, calculate the carbon–oxygen bond energy in carbon monoxide. [2]

(iv) Given that the standard Gibbs free energy change, $\Delta G^{\ominus}$, of the reaction in **(a)(ii)** is +237 kJ mol^{-1} at 298 K, calculate the $\Delta S^{\ominus}$ for this reaction and comment on its sign with respect to the reaction. [2]

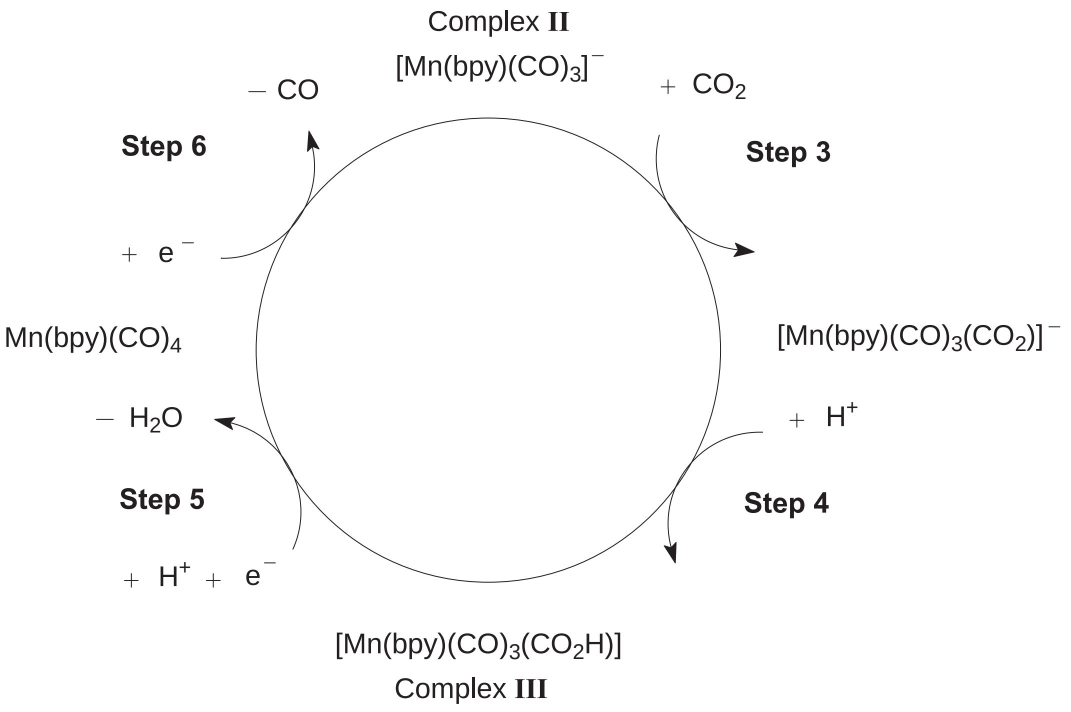
(b) The conversion of carbon dioxide to carbon monoxide is also important in helping to slow down global warming. Another method that was developed by scientists involves the use of metal complexes as catalysts to capture carbon dioxide and reduce it to carbon monoxide using visible light.

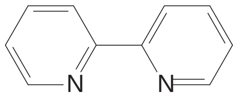
The starting reagent for the method involves the conversion of Complex **I**, $Mn(bpy)(CO)_3(Br)$ to the catalyst for the process, Complex **II**, $[Mn(bpy)(CO)_3]^-$.

Step 1: $Mn(bpy)(CO)_3(Br) + e^- \longrightarrow [Mn(bpy)(CO)_3(Br)]^-$

Step 2: $[Mn(bpy)(CO)_3(Br)]^- + e^- \longrightarrow [Mn(bpy)(CO)_3]^- + Br^-$

Complex **II** then undergoes a catalytic reduction process with carbon dioxide as seen below.



where bpy = 

(i) Using  to represent the bpy ligand, draw the structure of Complex **I** and state its shape. [2]

(ii) State which of the six steps involve a **decrease** in the number of ligands bonded to the manganese ion. [1]

(iii) Suggest the type of reaction which takes place in steps 1 and 4. [1]

(iv) A solution containing Complex **III** is orange in colour.

Explain how such a colour could arise. [3]

(c) The CarbFix project in Iceland is also targeted at alleviating the global problem of increasing industrial carbon dioxide (CO_2) emissions and climate change. All waters in contact with the atmosphere absorb CO_2, but this method speeds up the process by injecting waters containing CO_2 into basaltic rocks which are rich in divalent cations such as calcium and magnesium. The method is called "stoning" as the CO_2 is captured and stored in the rocks as insoluble carbonates.

Water containing CO_2 reacts with the divalent cations present in basaltic rocks according to the following equilibrium.

$$M^{2+} + CO_2 + H_2O \rightleftharpoons MCO_3 + 2H^+ \quad \text{———— (1)}$$

(i) Explain why the precipitation of the metal carbonate takes place at high pH. [1]

(ii) Water containing CO_2 also reacts with Group 2 carbonates to form the corresponding soluble hydrogencarbonates in the following equilibrium.

$$CO_2(g) + H_2O(l) + MCO_3(s) \rightleftharpoons M(HCO_3)_2(aq) \quad \text{———— (2)}$$

These soluble compounds are then washed away by rainwater that percolates through rocks on hills and mountains and emerges as springs in the hillside. These are known as mineral waters and they often contain chlorides and hydrogencarbonates of Group 2 metals.

One such mineral water has the following composition.

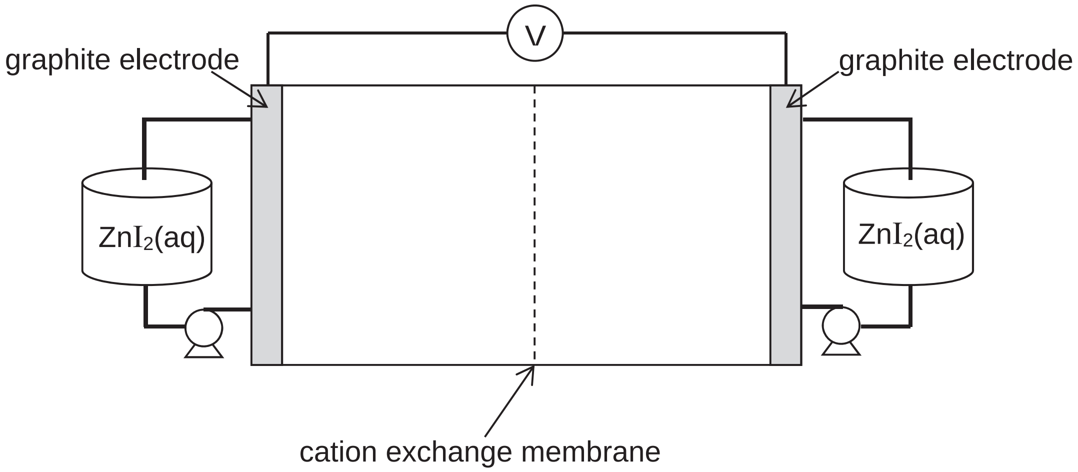
ion	**concentration / g dm^{-3}**
Ca^{2+}	0.0120
Mg^{2+}	0.0073
Cl^-	0.0284
HCO_3^-	0.0244

Calculate the concentrations of these ions in mol dm^{-3} and hence suggest the formulae of the salts that could exist in the solution, and their relative amounts. [3]

(iii) Suggest the composition of the rock through which the rainwater had percolated and use equation (2) to explain how the mineral water had been formed. [2]

[Total: 20]

4 Redox flow batteries are rechargeable batteries that have received growing attention as a cost–effective energy storage solution. Compounds with iodine can be used to generate electrical energy in redox flow batteries. One such battery is the zinc–iodide battery shown below.



In the zinc–iodide flow cell, graphite is used as the electrodes and the two half–cells are separated by a cation exchange membrane which allows cations to flow through. The electrolyte, $ZnI_2(aq)$, is stored in two external tanks. When required, the electrolyte is pumped into both half–cells.

During charging, metallic zinc is deposited on the negative electrode and iodine is formed at the positive electrode. When a light bulb is connected across the two electrodes, the bulb lights up as the battery discharges.

(a) **(i)** By reference to the *Data Booklet*, choose two half–equations to construct the balanced equation for the reaction that occurs during the discharging process. [2]

(ii) Calculate the value for $E^{\ominus}_{cell}$ for this zinc–iodide battery. [1]

(iii) Hence calculate the $\Delta G^{\ominus}$ for this cell. [1]

(iv) Suggest why there is a need for a cation exchange membrane in the battery. [1]

(b) The iodine formed during charging can complex with the iodide ions in the electrolyte to form triiodide ions, I_3^-. This reduces the efficiency of the battery, as formation of triiodide ions reduces the amount of I^- available for redox reaction.

Recent research has shown that addition of bromide, Br^-, to the zinc–iodide battery frees up the iodide ions, as bromide can form a similar complex with iodine.

Draw a dot and cross diagram of the complex formed between iodine and bromide ion and state its shape. [2]

(c) Compounds with a halogen and an alcohol group are known as halohydrins. Halohydrins are useful intermediates in organic synthesis as they contain two reactive functional groups.

(i) Halohydrins can be synthesised from the reaction of alkenes with aqueous bromine.

Describe the mechanism of the reaction between 1–methylcyclohexene and aqueous bromine to form bromohydrin. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons. [4]

(ii) The bromohydrin formed in **(c)(i)** exists as a mixture of stereoisomers. Draw the structure of each stereoisomers of the bromohydrin formed. [2]

(iii) Suggest one simple test–tube reaction, other than aqueous bromine, to distinguish 1–methylcyclohexene and the bromohydrin formed in **(c)(i)**, stating clearly the reagents and conditions required and the observations you would see. [2]

[Total: 15]

Section B

Answer **one** question from this section.

5 The oxygen family, also called the chalcogens, consists of the elements found in Group 16 of the Periodic Table and is considered among the main group elements. It consists of the elements oxygen, sulfur, selenium, tellurium and polonium.

(a) State and explain the trend in the first ionisation energy of the Group 16 elements down the group. [2]

(b) **(i)** State two assumptions of the kinetic theory of gases. [2]

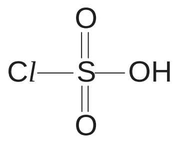
(ii) Sketch the expected variations of pV with p for a given amount of an ideal gas at constant temperature. [1]

In an experiment conducted at constant temperature, the volumes of separate samples containing equal amounts of gases **D** and **E** were measured at different pressures and the results are tabulated below. The two unknown gases **D** and **E** could be hydrogen or oxygen.

Experiment No.	**Gas D**		**Gas E**	
	p / Pa	**V / m^3**	**p / Pa**	**V / m^3**
1	3.5×10^5	6.50×10^{-3}	4.0×10^5	5.80×10^{-3}
2	7.0×10^5	3.14×10^{-3}	8.0×10^5	2.85×10^{-3}
3	14.0×10^5	1.50×10^{-3}	15.0×10^5	1.46×10^{-3}
4	21.0×10^5	9.30×10^{-4}	20.0×10^5	1.07×10^{-3}

(iii) Compute the pV values for each of the above experiments and use them to identify gases **D** and **E**. Explain your reasoning. [3]

(c) The diagram below shows the structure of chlorosulfuric acid, HSO_3Cl, which is a Lewis base.



$$Cl-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$$

chlorosulfuric acid

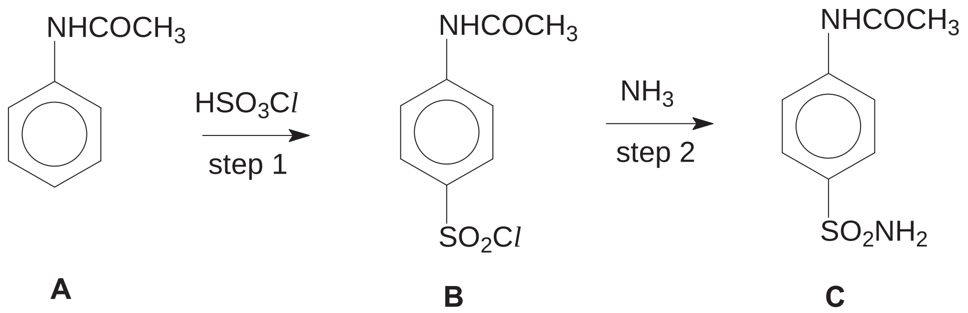
(i) What do you understand by the term *Lewis base*? [1]

(ii) Chlorosulfuric acid is made by reacting sulfuric acid with phosphorus pentachloride, PCl_5. Acidic white fumes are evolved during the reaction.

Write a balanced equation for the reaction between sulfuric acid and phosphorus pentachloride. [1]

(iii) By comparing the structure of chlorosulfuric acid with that of sulfuric acid, explain why sulfuric acid is expected to be a stronger acid than chlorosulfuric acid. [1]

(d) The following reaction scheme shows the synthesis of **C**, a precursor to the sulfonamide antibacterial drugs.



(i) Explain why compound **A** is neutral. [1]

(ii) $C_6H_5CONHCH_3$ is an isomer of **A**. Describe a simple chemical test to distinguish between the two isomers, stating clearly how each compound behaves in the test. [2]

Step 1 is catalysed by concentrated sulfuric acid.

(iii) Write an equation to illustrate the reaction between concentrated sulfuric acid and chlorosulfuric acid, HSO_3Cl. [1]

(iv) Hence, name and describe the mechanism for the reaction involved in the preparation of **B**, including curly arrows to show the movement of electrons, and all charges. [3]

Step 2 is carried out under anhydrous condition.

(v) What type of reaction is step 2? [1]

(vi) Suggest why step 2 has to be carried out under anhydrous condition. [1]

[Total: 20]

6 **(a)** In acidic solution, bromate(V) ions, BrO_3^-, slowly oxidise bromide ions to bromine. The progress of the reaction may be followed by adding a fixed amount of phenol together with some methyl red indicator.

The bromine produced during the reaction reacts very rapidly with phenol. When all the phenol is consumed, any further bromine bleaches the indicator immediately. The initial rate of formation of Br_2 is indicated by the time for the bromine to bleach the indicator.

The total volume of the reaction mixture is the same in all four experiments and the following kinetic data are obtained at 25 °C.

Experiment	**$[BrO_3^-]$ / mol dm^{-3}**	**$[Br^-]$ / mol dm^{-3}**	**pH**	**Initial rate of formation of Br_2 / mol dm^{-3} s^{-1}**
1	0.10	0.10	1.00	8×10^{-2}
2	0.10	0.05	1.00	4×10^{-2}
3	0.05	0.05	1.00	2×10^{-2}
4	0.05	0.10	1.30	1×10^{-2}

(i) Write a balanced equation for the reaction between bromide ion and bromate(V) ion. [1]

(ii) Determine the order of the reaction with respect to each of the following reactants

- BrO_3^-
- Br^-
- H^+. [2]

(iii) Write the rate equation for this reaction. [1]

(iv) Calculate the rate constant of the reaction at this temperature, stating its units. [1]

(b) Describe, and explain in molecular terms, how the rate of reaction is affected by an increase in temperature. You should include a reference to the Boltzmann distribution in your answer. [3]

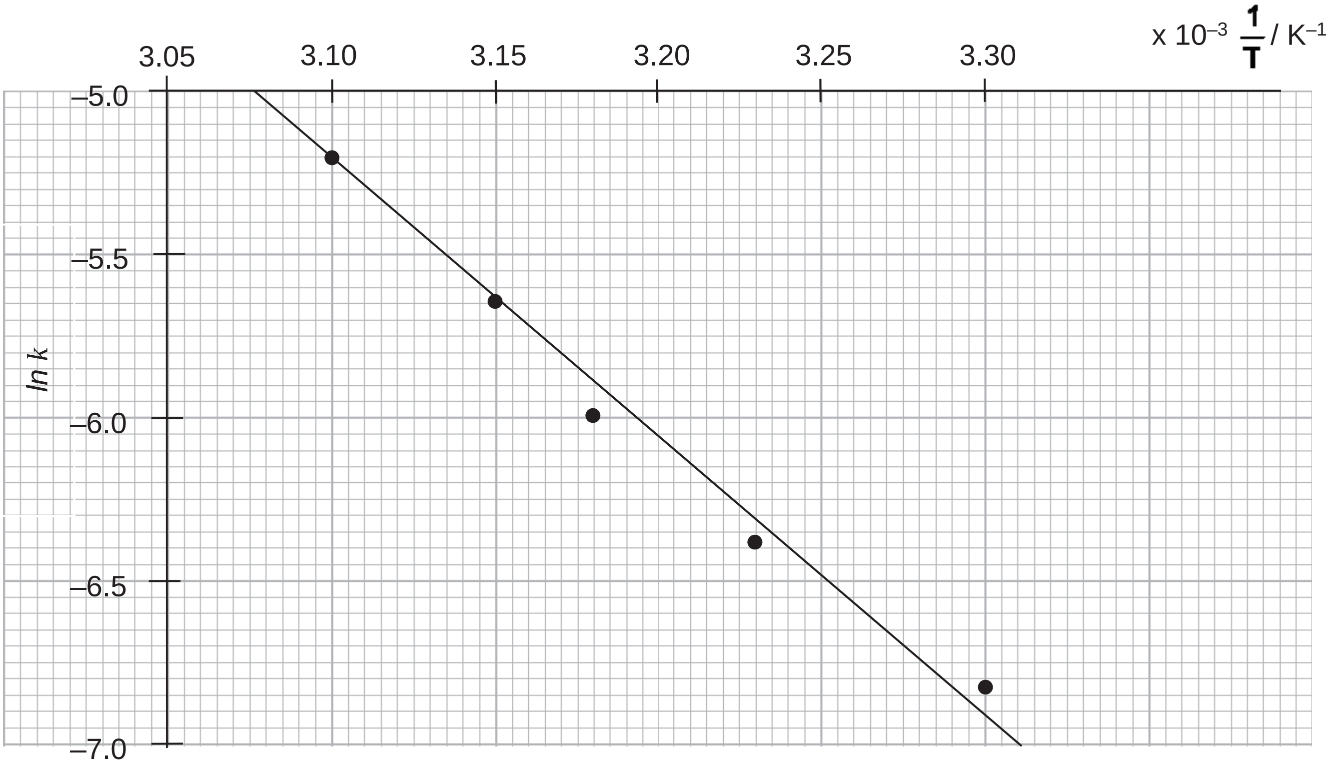
(c) The effect of temperature on the rate constant, *k*, can be expressed by the following equation.

$$ln\ k = ln\ A - \frac{E_a}{R}\left(\frac{1}{T}\right)$$

A is a constant;
E_a is the activation energy;
R is the molar gas constant (8.31 J K^{-1} mol^{-1}) and
T is the absolute temperature.

In a separate experiment to investigate the effect of temperature on the rate constant of the reaction between bromide ion and bromate(V) ion, the graph below was obtained.

Graph of *ln k* against $\frac{1}{T}$



(i) Calculate the activation energy, E_a, of the reaction. [1]

(ii) Suggest why the activation energy of the reaction is high. [1]

(iii) Make a sketch of the graph shown above onto your writing paper. On the same axes, sketch the graph of *ln k* versus $\frac{1}{T}$ when the reaction proceeds in the presence of a catalyst. Label your graphs clearly. Explain your answer. [1]

(d) This question is about compound **K**, C_6H_7ON, which is formed when phenylhydroxylamine, C_6H_5NHOH, is warmed with dilute sulphuric acid.

- Compound **K** is not very soluble in water, but dissolves in HC*l*(aq).
- It also dissolves in NaOH(aq), but not in Na_2CO_3(aq).
- On reaction with 1 mol of ethanoyl chloride, CH_3COCl, **K** forms compound **L**, $C_8H_9O_2N$.

On reaction with Br_2 (aq), **L** produces compound **M**, $C_8H_7O_2NBr_2$. When **K** is reacted with 2 mol of ethanoyl chloride, it produces compound **N**, $C_{10}H_{11}O_3N$, which is not soluble in either HC*l*(aq) or NaOH(aq).

Compound **K** can be synthesised by treating phenol with dilute nitric acid, followed by reaction with tin metal and hydrochloric acid.

(i) Deduce the structures of compounds **K**, **L**, **M** and **N**. Explain the chemistry of the reactions described, writing equations where appropriate. [There is no need to comment on the chemistry of the formation of **K** from phenylhydroxylamine.] [7]

(ii) The reaction of **K** to form **L** produces a minor product **P**, which is a constitutional isomer of **L**. Suggest the structure of **P** and explain this observation. [2]

[Total: 20]

H2 Chemistry 9729 **AJC 2017 JC2 PRELIM** **Paper 1 – 30 marks**

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

A	**7**
B	**8**
C	**8**
D	**7**

Anderson Junior College
H2 Chemistry 9729 **2017 JC2 PRELIM Paper 1 Suggested Solutions**

1 $^{3}_{1}H$ contains 1 proton, 1 electron and 2 (3 – 1) neutrons. **D**

$^{3}_{2}He$ contains 2 protons, 2 electrons and 1 (3 – 2) neutron.

1 ^{3}He has less neutrons than electrons.
2 ^{3}H has one proton while ^{3}He has two protons.
3 ^{3}H has two charged sub–atomic particles while ^{3}He has four charged sub–atomic particles.

2 **D**

angle of deflection $\alpha \ \dfrac{\text{charge size}}{\text{mass}}$

for $^{1}H^{+}$, $\dfrac{z}{m} = +\dfrac{1}{1}$

for $^{2}X^{2-}$, $\dfrac{z}{m} = -\dfrac{2}{2}$

Hence, angle of deflection for $^{2}X^{2-}$ = –4°

3 **A**

		shape / angle
A	SF_2	bent / ~104.5°
B	XeF_2	linear / 180°
C	SO_3^{2-}	trigonal pyramidal / ~107°
D	AlH_4^-	tetrahedral / 109.5°

4 The hybridisation state of N atom can be determined using similar approach as that for C atoms, except the *lone pair of electrons on N* can sometimes be occupying a *sp^2 (norm)* or *sp^3 hybrid orbital*. The question will likely provide information on the shape of the molecule with respect to N atom to link it to the hybridisation state – planar (sp^2) and tetrahedral (sp^3). **D**

A is correct. All C atoms in **F** are sp^3 hybridised. Hence, each C–C bond is a σ bond formed by a sp^3–sp^3 overlap between two C atoms.

B is correct. The N atoms in **G** has the same hybridisation state as carbon in benzene (i.e. sp^2) except that in place of a C–H bond pair, a lone pair now occupies the sp^2 hybrid orbital. The unhybridised p orbital of each N atom overlap with the adjacent p orbitals of C atoms to form a delocalised ring of π electron cloud.

C is correct. There are two sp^2 hybridised C atoms and both are bonded to sp^3 hybridised C atoms.

D **is incorrect**. From option **C**, the two sp^2 hybridised C atoms are not bonded to any N atom. And the N atom in **H** is likely to be sp^3 hybridised.

5 $pV = nRT$ **A**

for the same amount of He gas, n and R remain constant throughout. He gas will diffuse to occupy both vessels **J** and **K** when the valve is opened, i.e. volume of space occupied by gas = (v + 3v)

$p_i = 1 \times 10^5$ Pa	p_f = ? Pa
T_i = (20 + 273) K	T_f = (100 + 273) K
V_i = v	V_f = 4v (sum of vessels **J** and **K**)

$$\left(\frac{pV}{T}\right)_i = \left(\frac{pV}{T}\right)_f$$

$$p_f = \frac{(1\text{x}10^5)(\text{v})}{(20+273)} \text{x} \frac{(100+273)}{4\text{v}}$$

$= \underline{3.18 \times 105 \text{ Pa}}$

6 Property 1: melting point of chlorides **B**

Chlorides of Mg form giant ionic lattice structures, have much higher melting point than simple molecular chlorides of A*l*, Si and P

Property 2: pH of oxides

oxides	MgO	Al_2O_3	SiO_2	P_4O_{10}
Structure	giant ionic lattice		giant molecular	simple molecular
Reaction with water	weakly alkaline solution (pH ≈ 9)	insoluble (pH = 7)		acidic solution (pH = 1)

The most obvious clue to identifying the property would be the plateau from A*l* to Si, which is due to the insoluble oxides of the two elements.

7 On heating with Cl_2, Br_2 and I_2, the respective iron(II) halides will be formed, since their reduction potential are more positive than that of Fe^{2+}/Fe. **C**

$Fe^{2+} + e^- \rightleftharpoons Fe$ –0.44 V

$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ +1.36 V

$Br_2 + 2e^- \rightleftharpoons 2Br^-$ +1.07 V

$I_2 + 2e^- \rightleftharpoons 2I^-$ +0.54 V

Due to the oxidising nature of the halogens, Cl_2 and Br_2 can further oxidise the iron(II) to iron(III) since their reduction potential are more positive than that of Fe^{3+}/Fe^{2+}.

$Fe^{3+} + e \rightleftharpoons Fe^{2+}$ +0.77 V

(Note: Fe is not oxidised to Fe^{3+} in a single reaction because the reduction potential of Fe^{3+}/Fe (–0.04 V) is less negative than that of Fe^{2+}/Fe (–0.44 V). Fe will more likely be oxidised to Fe^{2+}.)

8 Given that molar ratio of carbon dioxide : hydrocarbon is 2 : 1, there are two carbon atoms. ∴ let formula of hydrocarbon be C_2H_x **A**

$$\Rightarrow C_2H_x(g) + (2 + \frac{x}{4})O_2(g) \longrightarrow 2CO_2(g) + \frac{x}{2}H_2O(l)$$

Since the remaining O_2 can burn up exactly 30 cm^3 of the same hydrocarbon, this means that 100 cm^3 of O_2 can burn 40 cm^3 of the hydrocarbon.

$\Rightarrow$ Molar ratio of hydrocarbon : O_2 = 40 : 100 = 1 : $\frac{5}{2}$

$\Rightarrow 2 + \frac{x}{4} = 2.5$

$\Rightarrow x = 2$

Formula of hydrocarbon is C_2H_2.

9 **A**

reaction 1 $Al_2O_3 + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2O$

reaction 2 $Cu + H_2SO_4 \longrightarrow CuO + SO_2 + H_2O$

reaction 3 $(CH_3)_3COH + H_2SO_4 \longrightarrow (CH_3)_2C{=}CH_2 + H_2SO_4 + H_2O$

Reaction 1 is an acid–base reaction (clue: O.N. of the elements remain).
Reaction 2 is a redox reaction (most obvious clue: O.N. of Cu increases; S decreases).
Reaction 3 is an elimination reaction; H_2SO_4 is a catalyst here (clue: H_2SO_4 remains unchanged after the reaction).

10 **C**

$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ $\Delta H^\ominus = -92$ kJ mol^{-1}

$N_2(g) + 4H_2(g) + Cl_2(g) \longrightarrow 2NH_4Cl(s)$ $\Delta H^\ominus = -629$ kJ mol^{-1}

$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$ $\Delta H^\ominus = -176$ kJ mol^{-1}

$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl(g)$ $\Delta H_f^\ominus(HCl)$

$$\begin{tikzcd} N_2(g) + 4H_2(g) + Cl_2(g) \arrow[r, "-629"] \arrow[d, "-92"'] & 2NH_4Cl(s) \\ 2NH_3(g) + H_2(g) + Cl_2(g) \arrow[r, "2\Delta H_f^\ominus(HCl)"'] & 2NH_3(g) + 2HCl(g) \arrow[u, "2(-176)"'] \end{tikzcd}$$

$2\Delta H_f^\ominus(HCl) = -(-92) + (-629) - 2(-176)$

$\Delta H_f^\ominus(HCl) = \underline{-92.5 \text{ kJ mol}^{-1}}$

11 Info from *Data Booklet*, c = 4.18 J g^{-1} K^{-1} **B**

Heat absorbed by water = (160 – 60) x 4.18 x (68 – 25)
= 17974 J

Heat released by ethanol = $1370 \times 1000 \times \dfrac{1.0}{2(12.0)+6(1.0)+16.0}$
= 29783 J

The <u>difference</u> in the heat transferred is due to <u>heat loss</u>. Hence in this case, efficiency can be calculated by taking the ratio $\dfrac{\text{heat absorbed}}{\text{heat released}}$.

% efficiency = $\dfrac{17974}{29783} \times 100\%$
= <u>60 %</u>

12 The reactions taking place in the catalytic converter include <u>simultaneous reduction of NO_x and oxidation of CO</u> (option **C**), <u>oxidation of unburnt hydrocarbons</u> (option **D**) and <u>oxidation of CO</u> (option **B**). **A**

Hydrocarbons contain C and H atoms. Carbon is not a hydrocarbon.

13 The easiest approach to answering this question is to start from the *equimolar quantities of **L** and **M** after 9 min* and work backwards. Let the amount be. **C**

Since **L** has undergone 3 half–lives, its initial concentrations will be 8**L**.
Initial concentration of **M** will be 2**M** as it has undergone 1 half–lives.

$$\begin{tikzcd}
8x\,\mathbf{L} \arrow[r] & 4x\,\mathbf{L} \arrow[r] & 2x\,\mathbf{L} \arrow[r] & x\,\mathbf{L} \\
2x\,\mathbf{M} \arrow[rrr] & & & x\,\mathbf{M}
\end{tikzcd}$$

∴ value of $n = \dfrac{8x}{2x}$
= <u>4</u>

14 $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ $\Delta H^\ominus = -92\ \text{kJ mol}^{-1}$ **C**

A is incorrect. Adding a catalyst does not affect the equilibrium yield; it only increases the rate of achieving equilibrium because the rates of both forward and backward reaction increase by the same extent.

B is incorrect. Adding neon at constant pressure will decrease the partial pressures of the particles present (both reactants and products)*. Since the reaction results in a decrease in no. of moles of gaseous particles, position of equilibrium (P.O.E.) shifts to the left to increase the pressure, resulting in a decrease in equilibrium yield.

*[$p_a = \dfrac{n_a}{n_{total}} p_{total}$, n_{total} increases while n_a and and p_{total} remain]

Addition of an inert gas at constant volume will have no impact on the P.O.E. because the partial pressure of the reactants and products are not affected.

[$p_a = \dfrac{n_a}{n_{total}} p_{total}$, n_{total} and p_{total} increase to the same extent while n_a remains]

C **is correct**. Decreasing the temperature favours the forward exothermic reaction and P.O.E. shifts to the right (equilibrium yield increase) and the rate of production of ammonia is slower as the average kinetic energy of the particles decrease.

D is incorrect. Removing N_2 at constant volume ($\Rightarrow$ partial pressure of N_2 decreases) will cause the P.O.E. to shift to the left (decrease in yield) and rate of production of ammonia is slower due to a decrease in concentration of reactants.

15 Since $\Delta G^\ominus < 0$ **B**

$\Rightarrow$ the forward reaction is spontaneous and
$\Rightarrow$ position of equilibrium lies to the right.
$\Rightarrow$ the amount of products at equilibrium is more than that of the reactants.
i.e. K_p is greater than 1

Alternatively, using $\Delta G^\ominus = -RT \ln K$
$\Rightarrow K > 1$

16 By inspection, ammonia is in excess. An alkaline buffer (excess unreacted NH_3 and NH_4^+) is obtained. **C**

$[NH_4^+]$ = nHC*l* ÷ total volume
= (30 x 0.1) ÷ 50
= 0.06 mol dm $^{-3}$

$[NH_3]$ = (20 x 0.2 – 30 x 0.1) ÷ 50
= 0.02 mol dm^{-3}

$K_b = \dfrac{[NH_4^+][OH^-]}{[NH_3]}$

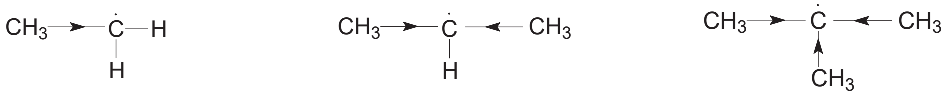
$[OH^-] = 6 \times 10^{-6}$
pOH =5.2
pH = 8.8

or use

$pOH = pK_b + \lg \dfrac{[NH_4^+]}{[NH_3]}$

17 By inspection, the base is diprotic (2 equivalence points) and likely to be a weak one (low initial pH). And since the final pH is approximately 1, the acid added is likely a strong acid. **C**

18 Due to the inductive electron-donating effect of alkyl groups, the stability of the radicals are in increasing order of: **C**



a primary radical < a secondary radical < a tertiary radical

Thus, the tertiary radical being the most stable will be formed most readily.

19 The following hint "… *comprising of 10 linearly fused benzene ring* …" is useful in solving the question. **C**

1 **is correct**. Each C atom is sp^2 hybridised. The sp^2 hybridised orbitals are arranged in a trigonal planar manner about each C atom, giving a bond angle of 120°.

2 **is correct**. The delocalised ring of π electrons is formed by the overlapping of p orbitals on adjacent C atoms.

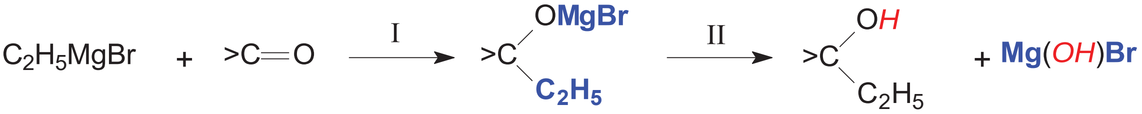
3 is incorrect. The carbon–carbon bond energies should be intermediate between that of the bond energy of a C–C bond in alkane and the C=C bond in alkene.

[refer to the *Data Booklet* – bond energy of C=C (benzene) is 520 kJ mol^{-1}, between 350 kJ mol^{-1} (C–C) and 610 kJ mol^{-1} (C=C)]

4 is incorrect. The valency of each C is still 4. In each C, 3 valence electrons are used in the formation of three σ bonds, and 1 electron is delocalised into the 42 π–electron system.

20 Chlorofluoroalkanes generate C*l*• radicals which destroy stratospheric ozone. The more C*l* atoms that is present in the molecule, the more C*l*• radicals can be generated, and the higher the ODP. **A**

21 **D**



Step I involves the addition of –$\mathbf{C_2H_5}$ and –**MgBr** across the carbonyl group (in bold). As the reactive carbon is electron deficient, it is susceptible to nucleophilic attack.

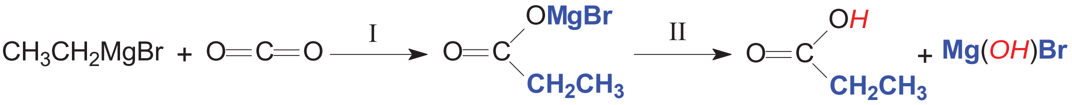
Step II involves the hydrolysis of O–Mg bond (observe the *H* and *OH* added – in italics). This reaction is dependent on the polarity across the O(δ–) – Mg(δ+) bond.

22 **D**

1 **is correct**. Similar to the above steps, –$\mathbf{C_6H_5}$ and –**MgBr** are added to the carbonyl group of CH_3CHO, followed by hydrolysis of the O–Mg bond to form $\mathbf{C_6H_5}$CH(O*H*)CH_3 and **Mg**(*OH*)**Br**.

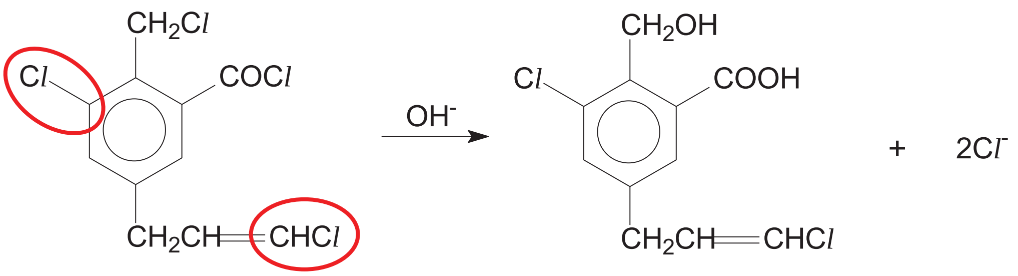
2 is incorrect. The reactant has a longer carbon chain (additional –CH_2–).

3 **is correct**. By observation, a carboxylic acid will be formed when CO_2 reacts with a Grignard reagent.



(To visualize, replace the 2 R group substituents on the reactive carbon (>C) with an oxygen doubly bonded (=O) to the carbon in CO_2.)

23 **B**



Nucleophilic substitution does not occur due to the delocalisation of the lone pair of electrons on the C*l* atom into the benzene ring (or adjacent C=C double bond), creating a partial double bond character in the C–C*l* bond (circled). The polarity of the C–C*l* bond is also decreased due to the delocalisation and hence the C atom of the C–C*l* bond is less electron deficient and less susceptible to attack by the OH^- nucleophile.
Steric hindrance due to repulsion of the nucleophile by the π electron cloud could also be used as a reason.

24 **D**

1 is incorrect. Absence of CH_3COR or $CH_3CH(OH)R$. Hence, it does not react with I_2/OH^-(aq).

2 is incorrect. All three 2° alcohol present in *Indian Yellow* will be oxidised by $Cr_2O_7^{2-}/H^+$ to give a compound with four carbonyl groups.

3 is incorrect. Only 2 atoms of Br will be substituted on the benzene ring at the 2nd and 4th position with respect to phenol group. Even if you had use the concept that ether (R–O–R group) has similar reactivity as phenol, still the number of Br atom incorporated will be less than 6 Br atoms. However, do note that reactivity of ether is not in the syllabus. Hence, you have to follow the clue given in the question to decide when it is reactive and when it is assumed to be inert. (refer to N2008/III/5d, N2013/II/3aiv, N2009/I/24 etc)

4 **is correct.** Each mole of –OH group reacts with Na metal to form ½mol of H_2(g). Since there are 5 mol of –OH group per mol of *Indian Yellow*, 2.5 mol of H_2(g) is formed.

25 **A**

decreasing pK_a ⇒ increasing K_a and increasing strength of acid
Observe that all four compounds are carboxylic acids, hence the order of strength is dependent on the substituent present and its position relative to –COOH group.

Recall: Strength of an acid depends on the stability of its conjugate base.
(Why? $pK_a + pK_b = 14$ at 298 K, so the bigger the pK_b is, the smaller the pK_a will be. A stable base will mean it is unreactive/weak base ⇒ greater K_a for its conjugate acid.)

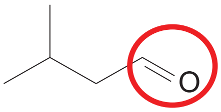
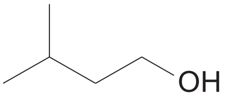
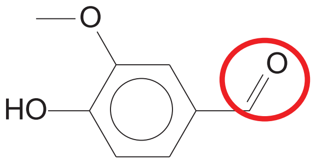
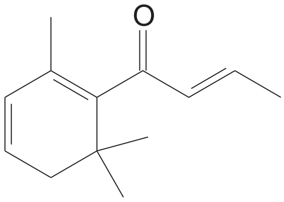
Compare carboxylate ions: **H**–$C_6H_4COO^-$ and **CH_3**–$C_6H_4COO^-$

- Presence of electron donating alkyl group in $CH_3C_6H_4CO_2H$ reduces the dispersal of the –ve charge to a smaller extent and thus stabilises the conjugate base to a smaller extent.
- Hence $CH_3C_6H_4CO_2H$ has a larger pK_a than $C_6H_5CO_2H$. (narrow down to options **A** and **D**)

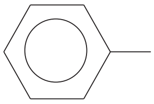
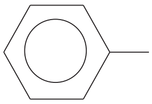
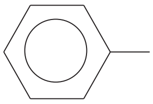
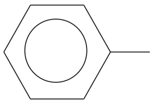
Compare: 4–hydroxybenzoic acid and 2–hydroxybenzoic acid**.**

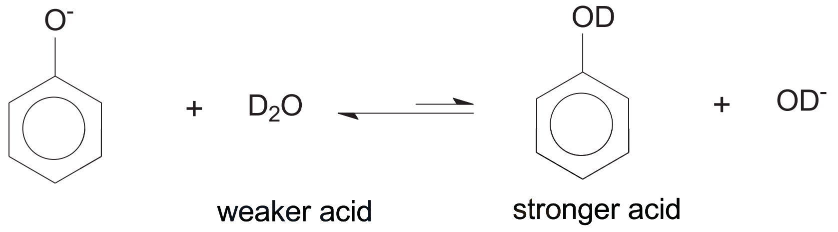
- Close proximity of the phenol group to carboxylic acid group in 2–hydroxybenzoic acid enables it to form intramolecular hydrogen bonding which helps to stabilise the conjugate base to a greater extent.
- Hence 2–hydroxybenzoic acid has a lower pK_a than 4–hydroxybenzoic acid. (option **A**)

26 $Cr_2O_7^{2-}/H^+$ is able to oxidise 1°, 2° alcohols and <u>aldehyde</u>. **B**
NaBH$_4$ is able to reduce <u>aldehyde</u> and ketones.

		$Cr_2O_7^{2-}/H^+$	$NaBH_4$
1		√	√
2		√	X
3		√	√
4		√	X

27 **C**

	Type of reaction	**Products**
A	base–catalysed hydrolysis	 $CO_2^-Na^+$ + CH_3OD
B	base–catalysed hydrolysis	 O^-Na^+ + $CH_3CO_2^-Na^+$
C	acid–catalysed hydrolysis	 OD + CH_3CO_2D
D	no reaction	 O^-Na^+

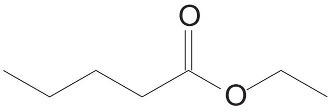


Since C_6H_5OD is a stronger acid than D_2O, the position of equilibrium lies to the left as C_6H_5OD is a better proton donor. $C_6H_5O^-$ will not react with D_2O to give a good yield of C_6H_5OD.

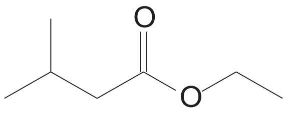
28 Given that the first member of the series is ethyl ethanoate **B**

⇒ n = 0

∴ the fourth member of the series (n = 3) will be either

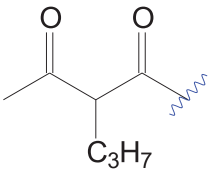


or



(branched isomer)

By observation, a possible product must have one of the following structures.



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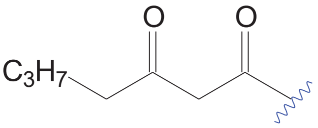
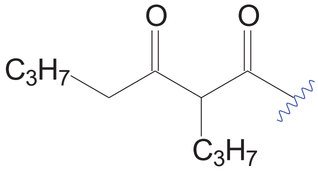


or



Hence,

A is incorrect. One of its reactants is the fifth member of the series (i.e. n = 4).

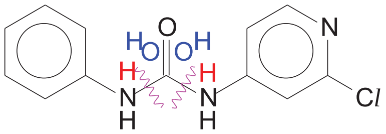
B **is correct**. It is formed between two fourth members of the series.

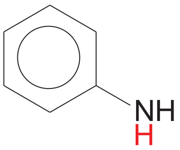
C is incorrect. It is formed between a second and a third member of the series.

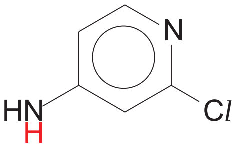
D is incorrect. It is not part of the ethyl ester series. It is a butyl ester.

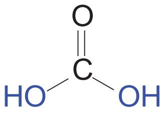
29 **D**

When forchlorfenuron undergoes hydrolysis







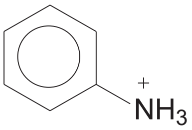


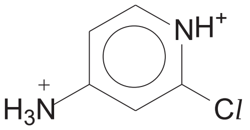
non organic product

are formed.

However as the reaction was carried out in acidic medium,

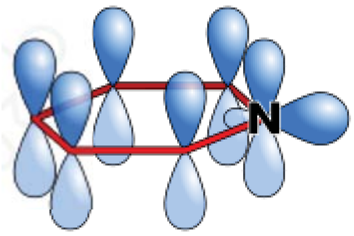
the basic groups will be protonated (e.g. $-NH_2$)





FYI

The N atom in the pyridine is basic as its lone pair is not delocalised in the ring but occupies the sp^2 hybrid orbital. Instead, it is the unhybridised p orbital (with an electron) overlap with the p orbitals of the adjacent C atoms to form an aromatic ring as illustrated in the diagram on the right.



30 When excess of NaOH (aq) are added to $Fe(NO_3)_2$(aq), a dirty green precipitate of $Fe(OH)_2$(s) is formed. **B**

$$[Fe(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \longrightarrow [Fe(OH)_2(H_2O)_4](s) + 2HOH(l)$$

OH^- accepts a proton from the hydrated iron(II) complex (acid–base reaction), resulting in the precipitation of $Fe(OH)_2$(s).
On standing in air, $Fe(OH)_2$(s) is oxidised to $Fe(OH)_3$(s), reddish brown precipitate.

Anderson Junior College
H2 Chemistry 9729 **2017 JC2 Prelim Paper 2 Suggested Solutions**

1 (a) (i) $2Fe^{3+}(aq) + Sn^{2+}(aq) \longrightarrow 2Fe^{2+}(aq) + Sn^{4+}(aq)$ [1]

ignore state symbols

(ii) $E^\ominus (Fe^{3+}/Fe^{2+}) = +0.77$ V [1]
$E^\ominus (Sn^{4+}/Sn^{2+}) = +0.15$ V

$$E^\ominus_{cell} = E^\ominus_{reduction} - E^\ominus_{oxidation}$$
$$= +0.77 - (+0.15)$$
$$= \underline{+0.62\text{ V}}$$

(iii) Reduction of Fe^{3+} to Fe^{2+} by $SnCl_2$ is spontaneous since the $E^\ominus_{cell}$ calculated in **(ii)** is positive. [2]

$E^\ominus (Fe^{2+}/Fe) = -0.44$ V
$E^\ominus (Sn^{4+}/Sn^{2+}) = +0.15$ V

$$E^\ominus_{cell} = -0.44 - (+0.15)$$
$$= \underline{-0.59\text{ V}} < 0 \text{ (not spontaneous)}$$

However, the reduction of Fe^{2+} to Fe by $SnCl_2$ is not spontaneous since the $E^\ominus_{cell}$ is negative.

[1]: determine $E^\ominus_{cell}$ for reduction of Fe^{2+}
[1]: conclusion based on both $E^\ominus_{cell}$

(iv) [2]

titration number	1	2	3
initial burette reading / cm^3	0.00	19.95	2.10
final burette reading / cm^3	19.95	40.05	22.15
titre / cm^3	19.95	20.10	20.05

average volume of KI used = ½(20.10 + 20.05)
= $\underline{20.08\text{ cm}^3}$

$$n(K_2Cr_2O_7)\text{ required} = \frac{20.08}{1000} \times 0.100$$
$$= 0.002008\text{ mol}$$
$$= \underline{0.00201\text{ mol}}$$

[1]: correctly determine the titre for run 2 and 3 and used it to find the average titre based on hierarchy rule (i.e. within 0.05 cm^3 in this case)
[1]: $n(K_2Cr_2O_7)$

(v) $6Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \longrightarrow 6Fe^{3+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$ [1]

ignore state symbols

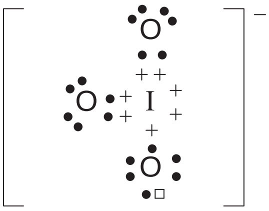
(vi) n(Fe^{2+}) in 25.0 cm^3 of solution = 6 x 0.00201 [2]
= 0.01206 mol
n(Fe^{2+}) in 250 cm^3 of solution = 0.01206 x 10
= <u>0.1206 mol</u>

mass of Fe present = 0.1206 x 55.8
= 6.729 g

$$\text{\% by mass of iron in the sample of iron ore} = \frac{6.729}{11.05} \times 100\%$$
$$= \underline{60.9\ \%}$$

[1]: n(Fe^{2+}) originally present in 250 cm^3 (scaling)
[1]: % by mass of iron in iron ore (ecf)

(b) **(i)** [1]



□ e from metal
\+ e from I
• e from O

[1]: correct dot–and–cross

(ii) [1]

$$\mathbf{Mg(IO_3)_2 \longrightarrow MgO + I_2 + \frac{5}{2}\,O_2}$$

(iii) [2]

- size of cations : <u>Mg^{2+}(0.065nm) > Fe^{2+}(0.061nm)</u>
- charge of the cations is the same
- <u>charge density</u> of M^{2+}: $Mg^{2+} < Fe^{2+}$
- <u>polarising power</u> of M^{2+}: $Mg^{2+} < Fe^{2+}$
- Fe^{2+} ion is able to <u>distort</u> electron cloud of IO_3^- anion to a <u>greater extent</u>. Hence, I–O covalent bond within the IO_3^- anion is <u>more weakened</u> in $Fe(IO_3)_2$.
- $Fe(IO_3)_2$ will need to be heated to a <u>lower temperature</u> for decomposition.

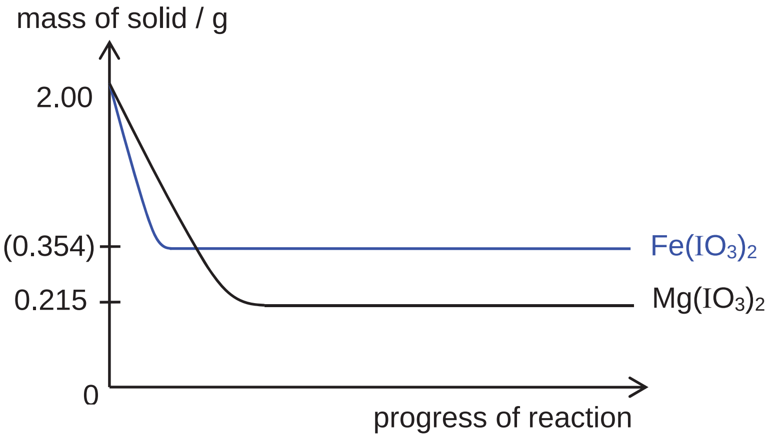
[1]: charge density / polarsising power (based on ionic radius quoted)
[1]: extent of distortion / weakening of I–O bond and lower temperature required

(accept comparable / similar temperature)

(iv) [1]

$$n(Mg(IO_3)_2) \text{ reacted} = \frac{2.00}{24.3 + 2[126.9 + 3(16.0)]} \quad \left(\text{or } \frac{2.00}{374.1}\right)$$
$$= 5.35 \times 10^{-3} \text{ mol}$$
mass of MgO left, $y = 5.35 \times 10^{-3} \times (24.3 + 16.0)$
$= \underline{0.215\ g}$

(v) [1]



[1]: steeper gradient and larger mass of residue

$$n(Fe(IO_3)_2) \text{ reacted} = \frac{2.00}{55.8 + 2[126.9 + 3(16.0)]} \quad \left(\text{or } \frac{2.00}{405.6}\right)$$

$= 4.93 \times 10^{-3}$ mol

mass of FeO left, y = $4.93 \times 10^{-3} \times (55.8 + 16.0)$

= $\underline{0.354 \text{ g}}$

2 **(a)** Homogenous catalyst increases the rate of a reaction where the reactant(s) and the catalyst exist in the same phase. For example, Fe^{2+}(aq) catalyses the reaction between I^-(aq) and $S_2O_8^{2-}$(aq). [2]

[1]: definition
[1]: example (accept other homogeneous system e.g. H_2O_2/Mn^{2+})

(b) **(i)** $H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$ [1]

(ii) (homogeneous) catalyst [2]

Rate of reaction is slow without cobalt(II) but becomes vigorous in its presence. Cobalt(II) forms an intermediate (cobalt(III)) and is regenerated at the end of the reaction.

[1]: role
[1]: evidence (either one)

(iii) $E^\ominus$ $(Co^{3+}/Co^{2+}) = +1.89$ V [2]
$E^\ominus$ $(O_2/H_2O) = +1.23$ V

$E^\ominus_{cell} = +1.89 - (+1.23)$
$= \underline{+0.66\ V} > 0$ (spontaneous)

Co^{3+}(aq) readily reduces to Co^{2+}(aq) in aqueous solution but yet Co(III) is formed in this reaction (green solution).

Tartaric acid acts as a ligand which stabilises Co(III).

[1]: shows unstability of Co^{3+}(aq)
[1]: role of tartaric acid

(c) **(i)** [1]

$$n(O_2) = \frac{96}{24000}$$
$$= 4.00 \times 10^{-3} \text{ mol}$$
$$n(H_2O_2) = 2 \times 4.00 \times 10^{-3}$$
$$= 8.00 \times 10^{-3} \text{ mol}$$
$$[H_2O_2] = \frac{8.00\text{x}10^{-3}}{0.100}$$
$$= \underline{0.0800 \text{ mol dm}^{-3}}$$

(ii) When volume of O_2(g) collected reaches 88 cm^3, 8 cm^3 of O_2 is left to be collected $(\frac{8}{96} = \frac{1}{12})$. [1]

$$1 \longrightarrow \frac{1}{2} \longrightarrow \frac{1}{4} \longrightarrow \frac{1}{8} \longrightarrow \longrightarrow \frac{1}{12}\ [(\frac{1}{2})^n]$$

$$\frac{C}{C_o} = (\frac{1}{2})^n$$, where n = no. of half–life undergone

$$\frac{1}{12} = (\frac{1}{2})^n$$

$$n = \ln(\frac{1}{12}) \div \ln(\frac{1}{2})$$
$$= 3.58$$

estimated time taken for 88 cm^3 of O_2 collected = 3.58 x 35
= <u>125 min</u>

(accept 4 x 35 = 140 min because $\frac{8}{96} \approx (\frac{1}{2})^4$ / 3.5 x 35 = 122.5 min because $\frac{1}{12}$ is between $\frac{1}{8}$ and $\frac{1}{16}$, i.e. 3rd and 4th half–life)

(iii) $k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{35}$ [2]

$= \underline{0.0198 \text{ min}^{-1}}$

(iv) <u>time taken</u> for H_2O_2 to <u>decrease to the same extent</u> (i.e. <u>50%</u> in this case) will be the <u>same</u> regardless $[H_2O_2]$ is 0.08 mol dm^{-3} or 0.2 mol dm^{-3} because "*half–life is independent of the initial concentration*". [1]

<u>Alternatively</u>,
rate = $k\,[H_2O_2]$ (1st order reaction)
If $[H_2O_2]$ x 2.5 times, <u>rate x 2.5 times</u>.

Hence,

for 0.08 M H_2O_2	0.04 mol dm^{-3} decomposed in 35 min
for 0.2M H_2O_2	0.1 mol dm^{-3} decomposed in 35 min (as rate x 2.5) i.e. $\frac{0.1}{0.2}$ x 100% = <u>50% decomposed</u>

(v) Titrate the $[H_2O_2]$ remaining at regular time intervals against a standard solution of $KMnO_4$. [1]
Monitor the decrease in mass of the H_2O_2 solution at regular time intervals.

[1] either one

3 **(a)** **(i)** [2]

$$\text{PSI of PM10} = \frac{200-100}{350-150}(320-150)+100 = \underline{185}$$

$$\text{PSI of CO} = \frac{300-200}{34-17}(20-17)+200 = \underline{218}$$

[1] each

(ii) overall PSI is the maximum value out of 185, 218, 112, 133 and 150. Hence overall PSI is <u>218</u>. [1] ecf

(iii) I would advise the PE teacher to <u>avoid strenuous physical exertion</u> / <u>conduct the lesson indoor</u> (words to the effect based on valid reasoning). [1] ecf

(b) **(i)** [1]

$SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 4H^+ + 2e^-$ (x 5)

$2IO_3^- + 12H^+ + 10e^- \longrightarrow I_2 + 6H_2O$

overall: $\mathbf{5SO_2 + 4H_2O + 2IO_3^- \longrightarrow 5SO_4^{2-} + 8H^+ + I_2}$

(ii) $H^+ + OH^- \longrightarrow H_2O$ [2]

n(NaOH) reacted = 0.01 x 0.005
= 5 x 10^{-5} mol
n(H^+) reacted with NaOH = 5 x 10^{-5}

n(SO_2) in 1 m^3 sample of air = 5 x 10^{-5} x $\frac{5}{8}$
= <u>3.125 x 10^{-5} mol</u>
mass of SO_2 in 1 m^3 sample of air = 3.125 x 10^{-5} x [32.1 + 2(16.0)] (or 64.1)
= 0.00200 g
= 2000 μg
concentration of SO_2 = <u>2000</u> μg m^{-3}

[1]: [SO_2] in mol m^{-3}
[1]: [SO_2] in μg m^{-3}

(c) **(i)** In 1 m^3, [1]

mass of air is 1 kg

mass of PM10 is $\frac{2\text{x}10^{-5}}{100}$ x 1 = 2 x 10^{-7} kg = 0.0002 g = 200 μg

Hence concentration of PM10 is <u>200</u> μg m^{-3}

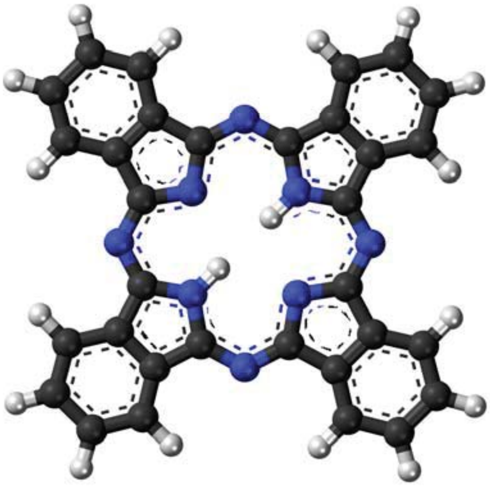
(ii) Since concentration calculated in **(c)(i)** is <u>more than 180</u>, the sample of air has exceeded the limit. [1] ecf

The German city of Leipzig <u>will be fined</u>.

(d) **(i)** $\mathbf{C_{32}H_{18}N_8}$ [1]

(ii) It contains a <u>ring of delocalised pi electron clouds</u> / the p orbitals of the N and C atoms can overlap sideways to form <u>conjugated ring system of pi bonds</u>. [1]

FYI



ball and stick diagram

(e) **(i)** copper and N1: ionic [2]
copper and N2: dative

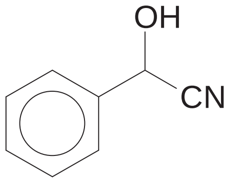
[1] each

(ii) electronic configuration of Cu is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$ [1]
electronic configuration of Cu^{2+} is $\mathbf{1s^2 2s^2 2p^6 3s^2 3p^6 3d^9}$

(iii) **8** [1]

(iv) presence of C*l* atoms alters the extent of d–orbital splitting by the ligands and hence energy absorbed by electron (d–d transition) and colour observed will be different [1]

4 **(a)** **(i)** [3]



step 1: HCN in the presence of NaCN (or trace of NaOH)

step 2: $CH_3CH_2CH_2CH_2CH_2COCl$ (do not accept its carboxylic acid)

[1]: structure
[1] each reagent

(ii) The instananeous dipole–induced dipole attractions between the non–polar benzene ring / pentyl (–$(CH_2)_4CH_3$) group in mandelonitrile hexanoate molecule and the non–polar hexane molecule are comparable in strength to that between mandelonitrile hexanoate molecules and between hexane molecules. [1]

(b) **(i)** Hydrolysis (or nucleophilic acyl substitution) of ester and oxidation of 2° alcohol [2]

[1] each

(ii) the C–C bond in COCN is stronger than the C–C*l* bond in COC*l* [1]
or CN^- in COCN is poorer leaving group than Cl^- in COC*l*
or the carbonyl C in COCN is less electron deficient than in COC*l*

[1] either one

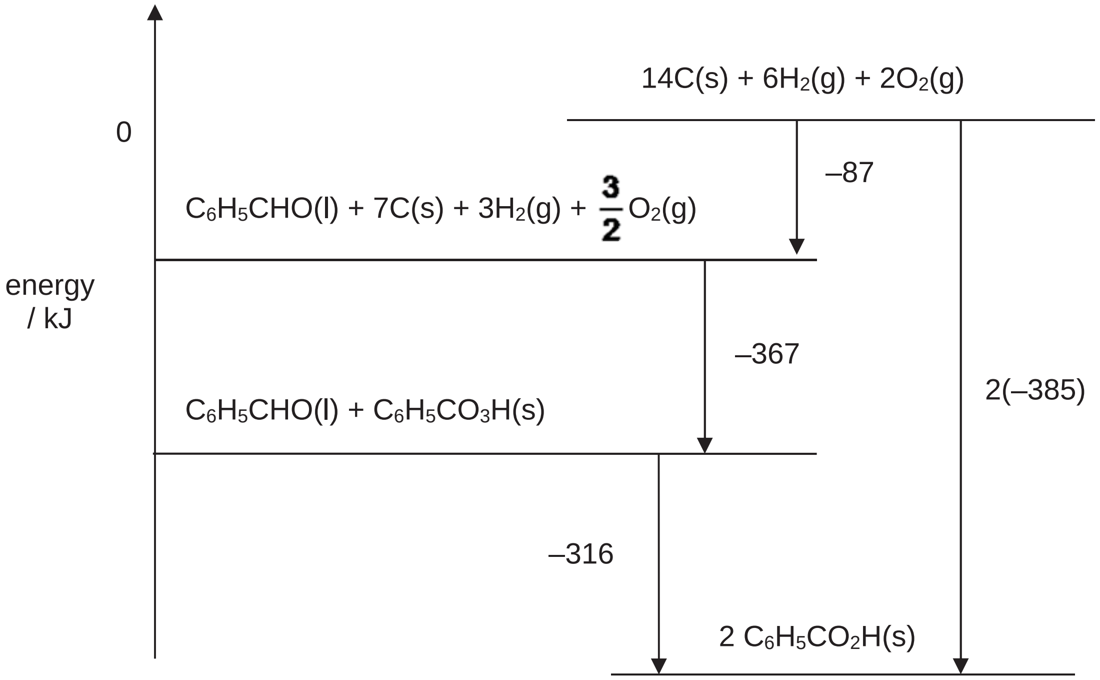
(iii) Add Tollens' reagent and warm, if a silver mirror (or grey ppt) is formed, benzaldehyde is present. Hence, pathway II has occurred. Otherwise, pathway I has occurred. [2]

(accept 2,4–dinitrophenylhydrazine, $Cr_2O_7^{2-}/H^+$, MnO_4^-/H^+ / yellow (orange) ppt, orange solution turned green, purple solution decolourised due to benzaldehyde)

(c) **(i)** The amount of heat absorbed or evolved when one mole of substance is formed from its constituent elements in their standard states *at* 298 K and 1 bar. [1]

(ii) $-316 = 2\Delta H_f^\ominus(C_6H_5CO_2H) - [(-367) + (-87)]$ [1]
$\Delta H_f^\ominus(C_6H_5CO_2H) = \underline{-385 \text{ kJ mol}^{-1}}$

(iii) [3]



[1]: constituent elements at the highest energy level (assigned 0)
[1]: corresponding compounds at the 3 other energy levels
[1]: correct stoichiometry, state symbols and arrow directions

5 **(a)** **(i)** stage I: $K_2Cr_2O_7$, dilute H_2SO_4, warm with immediate distillation [2]

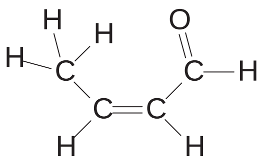
stage III: H_2, Pt / Pd, room temperature (accept Ni, with or w/o warm/heat)

[1] each

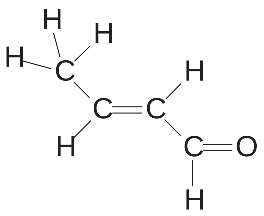
(ii) [1]

$$\mathbf{C_4H_{10}O + \frac{11}{2}O_2 \longrightarrow 3CO_2 + CO + 5H_2O}$$

(iii) cis–trans isomerism [2]



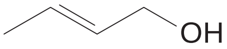
cis



trans

[1]: type of isomerism with correct label
[1]: displayed structure

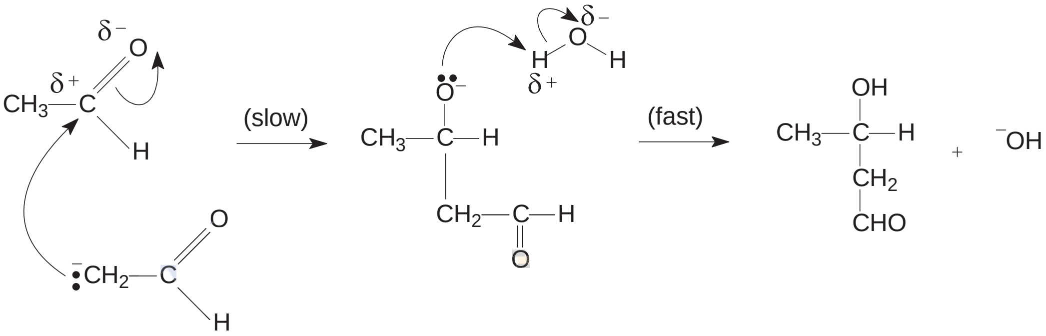
(iv) [2]



G is reduced to **H** (an alcohol) which reacts with sodium metal to give effervescence of H_2. **H** does not react with 2,4–DNPH due to absence of aldehyde/ketone. It reacts with aqueous Br_2 because of the C=C bond present.

[1]: structure of **H**
[1]: explanation (alcohol and C=C essential; do not accept hydroxyl or –OH group in place of alcohol)

(b) **(i)** [2]



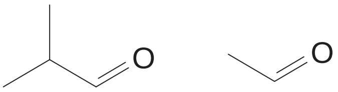
[1]: dipoles (BOD if missing on H_2O), charges and lone pairs
[1]: curly arrows and intermediate

(ii) Able to lose H and OH on adjacent C atoms in 2 different ways, giving rise a different product formed. [1]
Absence of resonance stabilised / delocalised structure / less substituted alkene compared to **G**, resulting in lower yield.

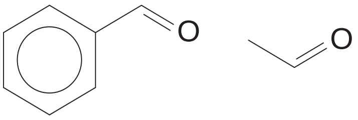
The other product is $CH_2{=}CHCH_2CHO$.

(iii) [3]

I

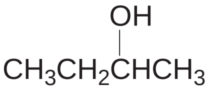


II



[1]: ethanal (CH_3CHO) for both
[1] each for the other 2

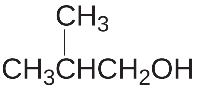
(c) **(i)** [2]



$$CH_3CH_2\overset{OH}{C}HCH_3$$

J

2^o



$$CH_3\overset{CH_3}{C}HCH_2OH$$

K

1^o

$(CH_3)_3COH$

L

3^o

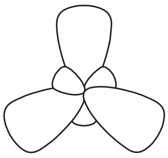
[1]: all 3 structural isomers correctly identified and labelled (in any order)
[1]: corresponding classification of 3 alcohols

(ii) **J** reacts with alkaline aqueous iodine [2]

$$CH_3CH_2CH(OH)CH_3 + 4I_2 + 6OH^- \longrightarrow CH_3CH_2CO_2^- + CHI_3 + 5I^- + 5H_2O$$

[1]: correctly identified the alcohol with positive reaction with I_2/OH^-
[1]: balanced equation

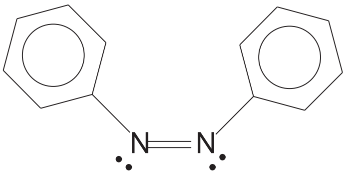
1 **(a)** **(i)** Hybridisation: sp^2 [3]



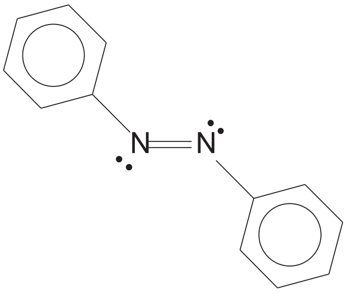
bond angle = 117° (accept 110° < angle < 120°)

[1]: hybridisation
[1]: hybrid orbitals (allow ecf if hybridisation was wrongly determined)
[1]: bond angle (ecf)

(ii) cis–trans isomerism [1]



cis



trans

[1]: type of isomerism
[1]: structure with correct label (ignore if lp are missing)

(iii) cis–isomer [2]

For the cis–isomer, bending / flexing occurred which allows the microstructure to peel away from the surface.

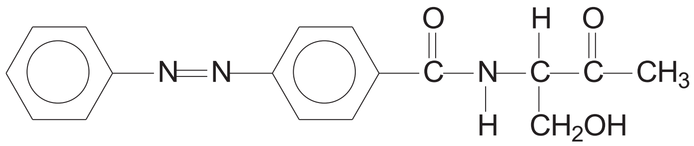
(b) [2]

Observation	Type of reaction	Deduction
Compound **U,** $C_{17}H_{19}N_3O_3$ is not soluble in NaOH(aq) and HC*l*(aq).	(absence of acid–base reaction)	**U** likely to contain amide.
U gives 2 products when heated under reflux with $Cr_2O_7^{2-}/H^+$.	hydrolysis	**U** contains amide or ester group.
Orange $Cr_2O_7^{2-}/H^+$ changes from orange to green during the process.	oxidation	**U** or its hydrolysed products contain 1° / 2° alcohol or aldehyde group.
V, $C_{13}H_{10}N_2O_2$ has a proton chemical shift of 13.0 ppm.		**V** contains –COOH. **W** contains 4 C atoms and 1 N atom.

W gives an orange precipitate when treated with 2,4–DNPH but it has no reaction with Tollens' reagent.	condensation / addition–elimination	**W** contains ketone group.
W gives a yellow precipitate and **X** when warmed with I_2/NaOH.	oxidation	**W** contains $RCOCH_3$. **X** is a sodium salt
Effervescence was observed when **W** was treated with $NaHCO_3(aq)$.	acid–base	**W** contains –COOH
When **W** is heated with excess CH_3Cl, it gives **Y,** $C_7H_{14}NO_3Cl$, as the major product.	nucleophilic substitution	**W** contains 1° amine **Y** is a quaternary salt.

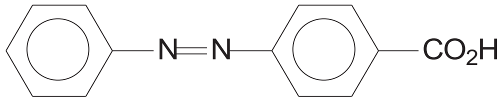
[4]: 14–18 points
[3]: 10–13 points
[2]: 7–9 points
[1]: 3–6 points

U



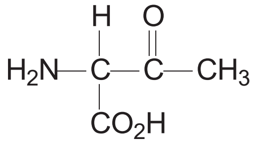
(ecf from **V** and **W**)

V



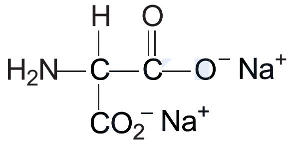
(allow –COOH group to be in other positions)

W



$$H_2N-\underset{CO_2H}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$$

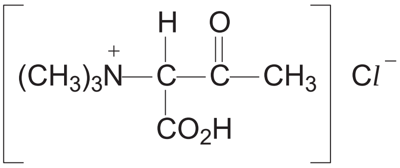
X



$$H_2N-\underset{CO_2^-\,Na^+}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-O^-\,Na^+$$

(ecf from **W**)

Y



$$\left[(CH_3)_3\overset{+}{N}-\underset{CO_2H}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-CH_3\right]\ Cl^-$$

(ecf from **W**)

[1] each correct structure

(overall only penalised once if final answers are not given to 1 dp for this question)

2 **(a)** **(i)** $K_{sp} = [Ag^+][I^-]$ [1]

(ii) $[Ag^+] = [I^-] = [AgI(aq)]$ [1]

$K_{sp} = (8.9 \times 10^{-9})^2$
$= \underline{7.9 \times 10^{-17}}$ $mol^2\ dm^{-6}$

[1]: answer given to 1 dp

(iii) $[Ag^+] = \frac{1}{2}\left(\frac{0.025}{[107.9 + 14.0 + 3(16.0)]}\right)$ [2]

$= \underline{7.4 \times 10^{-5}}$ mol dm^{-3}

Let the solubility of AgI, after addition of $AgNO_3$, be s.
$K_{sp} = [Ag^+][I^-]$
$7.92 \times 10^{-17} = (7.36 \times 10^{-5} + s)(s)$
Since solubility of AgI in water is << 10^{-5}, $(7.36 \times 10^{-5} + s) \approx 7.36 \times 10^{-5}$

$s = 1.08 \times 10^{-12}$ mol dm^{-3}

Mass of AgI ppted = $(8.9 \times 10^{-9} - 1.08 \times 10^{-12}) \times 2 \times (107.9 + 126.9)$
$= \underline{4.2 \times 10^{-6}\ g}$

[1]: $[Ag^+]$ added to 2 dm^3 saturated solution
[1]: mass of AgC*l* ppted

(b) **(i)** $\Delta G^{\ominus}_{ppt} = 2.303\ RT \log_{10} K_{sp}$ [1]
$= 2.303(8.31)(298)(\log 2.0 \times 10^{-10})$ J mol^{-1}
$= \underline{-5.5 \times 10^4\ J\ mol^{-1}}$

(ii) $Ag^+ + Cl^- \longrightarrow AgCl(s)$ [3]
White ppt is formed due to the <u>formation of insoluble AgC*l*</u>.

$AgCl + 2NH_3 \longrightarrow [Ag(NH_3)_2]^+ + Cl^-$
White ppt <u>dissolves</u> due to the <u>formation of a complex ion</u>.

$Ag+ + Br^- \longrightarrow AgBr(s)$
Cream ppt is obtained when NaBr is added to the resultant mixture because <u>K_{sp} of AgBr < K_{sp} of AgC*l*</u>

[1] each equation and explanation

(c) $\Delta G^{\ominus}_{ppt} = 2.303\ RT \log_{10} K_{sp}$ [2]
$= 2.303(8.31)(298)(\log_{10} 1.006)$
$= \underline{+14.8\ J\ mol^{-1}}$

Since $\Delta G^{\ominus}_{ppt}$ is +ve, precipitation will <u>not occur</u>
i.e. AgF is soluble

[1]: $\Delta G^{\ominus}_{ppt}$ calculated
[1]: conclusion (ecf)

3 (a) (i) *Le Chatelier's Principle* states that if a change is made to a reversible reaction in dynamic equilibrium, the position of equilibrium shifts so as to minimise that change and to re–establish equilibrium. [2]

A high temperature favours the forward endothermic reaction which helps to absorb the excess heat. Position of equilibrium lies to the right for stage 1.

[1]: stating Le Chatelier's Principle
[1]: explanation

(ii) $x\text{CO}_2\text{(g)} \rightleftharpoons x\text{CO(g)} + \frac{x}{2}\text{O}_2\text{(g)}$ [1]

(iii) $\Delta H_f^{\ominus}$ = ΣBE(bonds broken) – ΣBE(bonds formed) [2]

283 = 2BE(C=O) – [BE(C≡O) + ½BE(O=O)]

BE(C≡O) = 2(805) – 283 – ½(496)

= +1079 kJ mol^{-1}

[1]: correct identification of bonds broken and bonds formed
[1]: BE(C≡O) (ecf if 740 is used as BE(C=O); i.e. +949 kJ mol^{-1})

(iv) $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ [2]

$237 = 283 - (298)(\Delta S^{\ominus})$

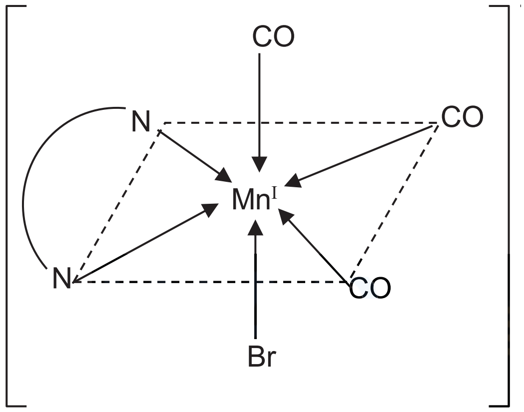
$\Delta S^{\ominus}$ = +0.154 kJ $\text{K}^{-1}\text{mol}^{-1}$

= +154 J $\text{K}^{-1}\text{mol}^{-1}$

Entropy change for the reaction is positive, indicating an increase in disorder of system / ways of distributing energy as seen from the equation in **(ii)** where there is an increase in number of moles of gaseous particles.

[1]: $\Delta S^{\ominus}$, include units
[1]: explaining link between entropy change and disorder of reaction

(b) (i) [2]



shape: octahedral

[1]: structure (dative bonds of bidentate ligand cannot be both on axial position)
[1]: shape

(ii) steps 2 and 6 [1]

(iii) step 1: reduction [1]
step 4: acid base reaction

(iv) In the presence of ligands, the partially filled 3d orbitals of Mn are split into two levels (non–degenerate) with a small energy gap (d orbital splitting). [3]
When light passes through, energy corresponding to the blue light is absorbed and an electron in a lower energy d–orbital is promoted to a higher energy d–orbital. (d–d transition).
The orange colour of the solution is the complementary colour of the blue light absorbed.

[1]: partially filled 3d–orbital; small energy gap
[1]: d–d transition
[1]: absorption of blue (complementary to orange)

(c) **(i)** When pH is high, $[H^+]$ is low, position of equilibrium shifts to the right and hence more metal carbonate will be precipitated. [1]

(ii) [3]

$$[Ca^{2+}] = \frac{0.0120}{40.1} = \underline{2.99 \times 10^{-4}\ \text{mol dm}^{-3}}$$

$$[Mg^{2+}] = \frac{0.0073}{24.3} = \underline{3.00 \times 10^{-4}\ \text{mol dm}^{-3}}$$

$$[Cl^-] = \frac{0.0284}{35.5} = \underline{8.00 \times 10^{-4}\ \text{mol dm}^{-3}}$$

$$[HCO_3^-] = \frac{0.0244}{[1.0+12.0+3(16.0)]} = \underline{4.00 \times 10^{-4}\ \text{mol dm}^{-3}}$$

$CaCl_2 : MgCl_2 : Ca(HCO_3)_2 : Mg(HCO_3)_2 = \underline{2 : 2 : 1 : 1}$

[2]: all concentrations; [1]: any two correct
[1]: correct ratio

(iii) The rock is made up of calcium carbonate, magnesium carbonate, (calcium chloride and magnesium chloride). [2]

Rainwater containing dissolved atmospheric carbon dioxide shifts the equilibrium position of (2) to the right.

$$CO_2(g) + H_2O(l) + MCO_3(s) \rightleftharpoons M(HCO_3)_2(aq)$$

Group 2 bicarbonates are soluble, hence it accounts for the presence of HCO_3^- in mineral water.

Calcium chloride and magnesium chloride present in the rock also can dissolve in the rainwater, causing Ca^{2+}, Mg^{2+} and Cl^- to be present in mineral water.

[1]: composition of rock
[1]: explanation using equation (2) to account for presence of bicarbonate

4 **(a)** **(i)** anode: $Zn \longrightarrow Zn^{2+} + 2e^-$ [2]

cathode: $I_2 + 2e^- \longrightarrow 2I^-$

$\mathbf{Zn + I_2 \longrightarrow 2I^- + Zn^{2+}}$

[1]: 2 correct half–equations
[1]: balanced equation

(ii) $E^\ominus_{cell} = 0.54 - (-0.76)$ [1]

$= \underline{+1.30\ V}$

(iii) $\Delta G^\ominus = -nFE^\ominus_{cell}$ [1]

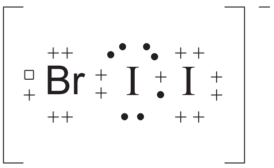
$= -2 \times 96500 \times 1.30$

$= \underline{-2.50 \times 10^5\ J\ mol^{-1}}$

(value of n depends on balanced equation in (i))

(iv) To allow Zn^{2+} ions to move from the anode to the cathode during discharging to prevent built up of charges / to maintain electrical neutrality. [1]

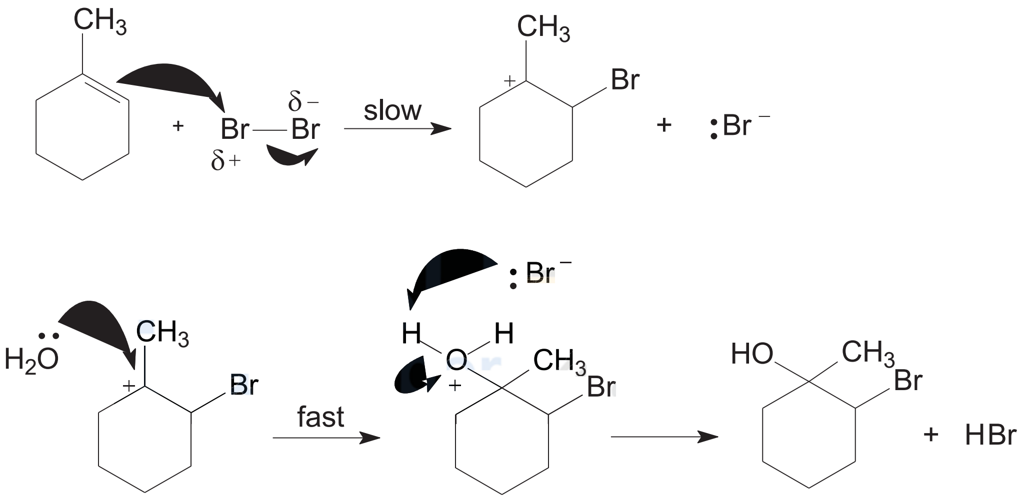
(b) [2]



shape: linear

[1]: dot–and–cross
[1]: shape

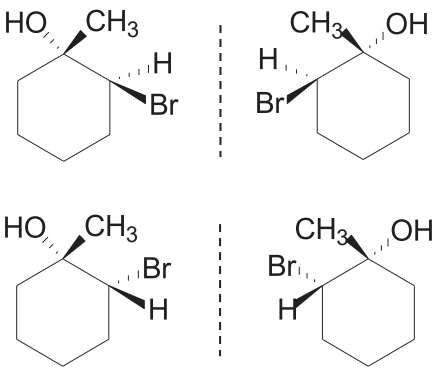
(c) **(i)** electrophilic addition [4]



(accept if deprotonation by Br^- is shown over 2 steps)

[1]: name of mechanism
[1]: dipoles and charges
[1]: lone pairs and curly arrows
[1]: intermediates and product

(ii) [2]



[2]: all 4
[1]: any 2

(iii) Reagents and condition: Na metal, room temperature [2]
Observation: effervescence observed with bromohydrin but no effervescence observed with cyclohexene.

OR
Reagents and condition: anhydrous PCl_5 / $SOCl_2$, room temperature
Observation: white fumes observed with bromohydrin but no white fumes observed with cyclohexene.
OR
Reagents and condition: $KMnO_4$, dilute H_2SO_4, cold/heat
Observation: purple $KMnO_4$ decolourises for cyclohexene but purple $KMnO_4$ remains for bromohydrin.

Alternative (less preferred)
Reagents and condition: NaOH(aq) and heat, cool and add HNO_3 then $AgNO_3$.
Observation: cream ppt observed with bromohydrin but no ppt observed with cyclohexene.

[1]: reagents and condition (do not accept aq. Br_2)
[1]: corresponding observations

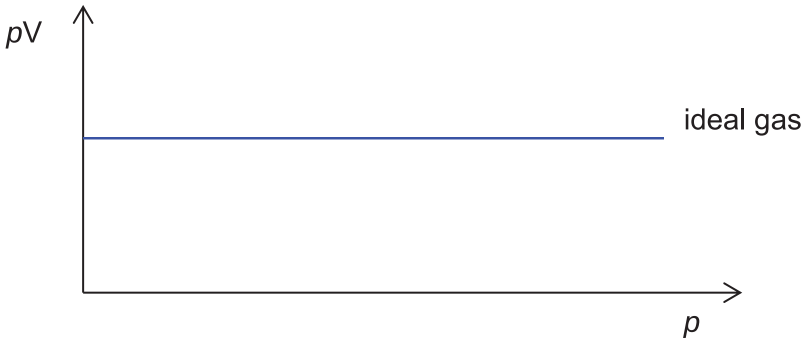
5 **(a)** First I.E. decreases down the group [2]
nuclear charge increase
but electrons are added to next electron/quantum shell
attraction between the nucleus and the valence electron decreases
less energy required to remove the valence electron.

[1]: trend
[1]: explanation in terms of increased nuclear charge but weaker attraction due to valence electron being further from nucleus / at a higher energy level

(b) **(i)** Gas particles occupies negligible space [2]
Negligible forces of attraction between gas particles

[1] each

(ii)



[1]: sketch complete with ideal gas line and axes labelled

(iii) [3]

Experiment No.	pV for gas **D**	pV for gas **E**
1	2275	2320
2	2198	2280
3	2100	2190
4	1953	2140

The pV values of Gas **D** deviates more from a constant value than Gas **E**. Hence, Gas **D** behaves less like an ideal gas than Gas **E**.

Gas **E** is H_2, which is smaller in size and also has weaker instantaneous dipole–induced dipole interactions between molecules and deviate less from ideality while gas **D** is O_2 which is a larger molecule with relatively stronger instantaneous dipole–induced dipole interactions.

[1]: all pV values
[1]: identify gases **D** and **E**
[1]: explanation

(c) **(i)** *Lewis base* is defined as an electron pair donor. [1]

(ii) $PCl_5 + SO_2(OH)_2 \longrightarrow ClSO_3H + POCl_3 + HCl$ [1]

(iii) [1]

$$H_2SO_4 + H_2O \rightleftharpoons HSO_4^- + H_3O^+$$
$$ClSO_3H + H_2O \rightleftharpoons ClSO_3^- + H_3O^+$$

The HSO_4^- conjugate base is more stable because there will be greater charge dispersal as it has an additional and more electronegative O. Thus the P.O.E. of H_2SO_4 acid ionisation lie more to the right.

(d) **(i)** The lone pair of electrons on N is delocalised to the carbonyl carbon and hence it is not available in accepting a proton, making **A** a neutral compound. [1]

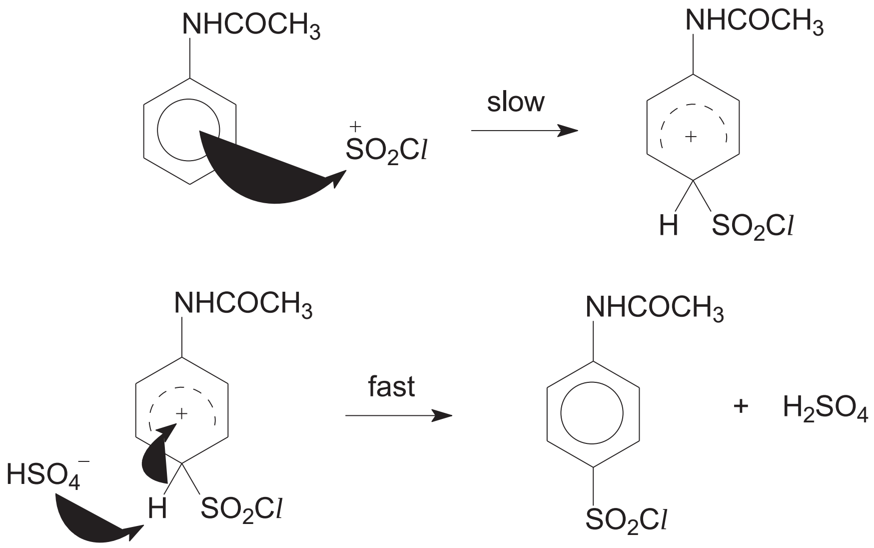
(ii) Boil/heat with NaOH(aq), followed by adding Br_2(aq) to the resultant hydrolysed products. [2]
The product of **A** (phenylamine) will decolorise the orange Br_2(aq) together with a white ppt but not the other isomer.

[1]: reagents and condition (accept HC*l*, if followed by excess NaOH)
[1]: corresponding observations

(iii) $ClSO_3H + 2H_2SO_4 \longrightarrow ClSO_2^+ + 2HSO_4^- + H_3O^+$ [1]

(accept $ClSO_3H + H_2SO_4 \longrightarrow ClSO_2^+ + HSO_4^- + H_2O$)

(iv) electrophilic substitution [3]



[1]: name of mechanism
[1]: dipoles, charges and lone pairs
[1]: curly arrows, intermediate and regeneration of catalyst

(v) nucleophilic substitution [1]

(vi) H_2O nucleophile competes with NH_3 nucleophile for the electron deficient S to displace Cl^-, affecting the yield of **C**. [1]

6 **(a)** **(i)** [R] $BrO_3^- + 6H^+ + 5e^- \longrightarrow \frac{1}{2}Br_2 + 3H_2O$ [1]
[O] $Br^- \longrightarrow \frac{1}{2}Br_2 + e^-$

$\mathbf{5Br^- + BrO_3^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O}$

(ii) Comparing Expt 1 & 2, [2]

when $[Br^-]$ increases by 2 times, rate increases by 2 times $(\frac{8\text{x}10^{-2}}{4\text{x}10^{-2}})$.

$\Rightarrow$ rate is directly proportional to $[Br^-]$
$\Rightarrow$ reaction is <u>1st order with respect to Br^-</u>

Comparing Expt 2 & 3,

when $[BrO_3^-]$ increases by 2 times, rate increases by 2 times $(\frac{4\text{x}10^{-2}}{2\text{x}10^{-2}})$.

$\Rightarrow$ rate is directly proportional to $[BrO_3^-]$
$\Rightarrow$ reaction is <u>1st order with respect to BrO_3^-</u>

$[H^+]$ at pH 1.00 = 0.100 mol dm^{-3}
$[H^+]$ at pH 1.30 = 0.0501 mol dm^{-3}

Comparing Expt 1 & 4 and let order of reaction with respect to H^+ be x

$$\frac{8 \text{ x } 10^{-2}}{1 \text{ x } 10^{-2}} = \frac{(0.10)(0.10)(0.1)^x}{(0.05)(0.10)(0.05)^x}$$

x = 2
$\Rightarrow$ reaction is <u>2nd order with respect to H^+</u>

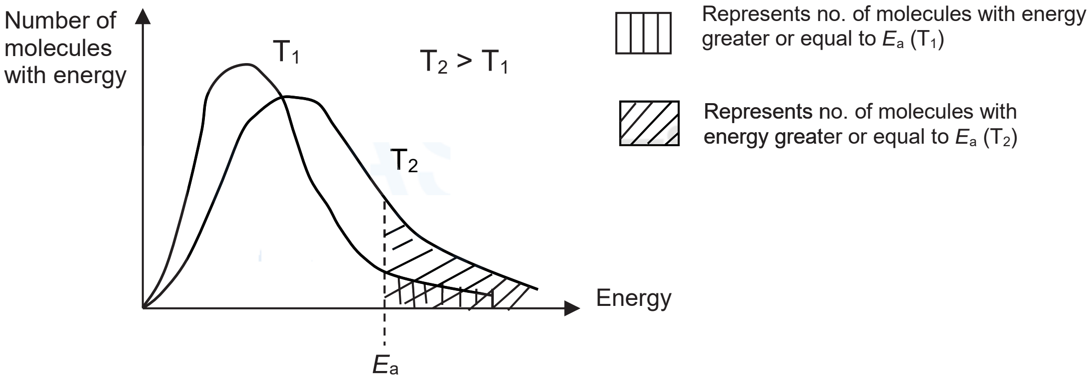
[1] each

(iii) $\mathbf{rate = \mathit{k}\,[BrO_3^-]\,[Br^-]\,[H^+]^2}$ [1]

(iv) Using values from Expt 1, [1]

$8 \text{ x } 10^{-2} = k\,(0.10)\,(0.10)\,(0.10)^2$
k = <u>800 mol^{-3} dm^9 s^{-1}</u>

(b) [2]



When temperature increases, the <u>(average) kinetic energies of the reactant molecules increase</u>.
As shown on the diagram, the <u>number of reactant molecules with energy greater or equal to the activation energy</u> will <u>increase</u>.
This results in an increase in the <u>frequency of effective collisions</u>. Hence, the <u>rate of reaction increases</u>.

[1]: correct axes, shape of graph (including beginning from origin) and correct shift of graph and shading when T increase
[1]: correct explanation (in terms of ave KE increase and frequency of effective collision increase)
[1]: correct conclusion

(c) **(i)** As seen in the equation, $\ln k = \ln A - \frac{E_a}{R}(\frac{1}{T})$ [1]

gradient = $-\frac{E_a}{R}$

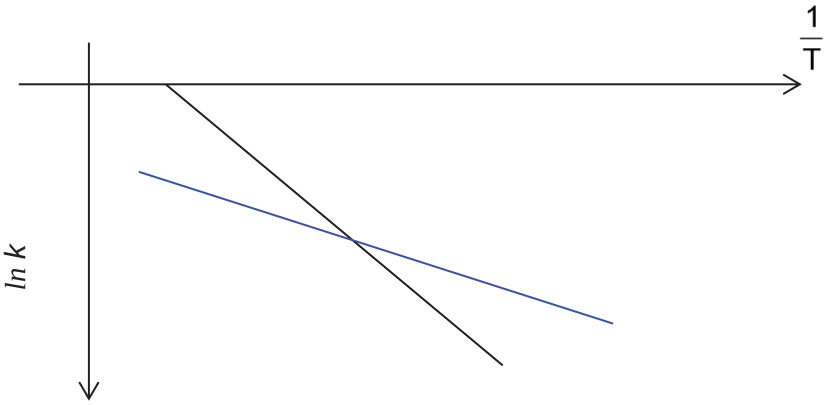
Taking points from the graph, gradient = $\frac{-5.20 - (-6.90)}{(3.10 - 3.30) \times 10^{-3}} = -8500$

$-8500 = -\frac{E_a}{R}$

E_a = <u>+70600 J mol^{-1}</u>

(ii) Both BrO_3^- and Br^- are <u>negatively charged</u> and they experience <u>inter–electronic repulsion</u> and hence E_a of the reaction is high. [1]

(iii) [1]



Since the reaction will have a <u>lower activation energy</u> in the presence of a catalyst, the slope will be <u>less steep.</u>

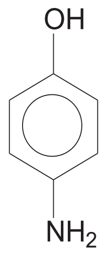
(d) **(i)** [7]

Observation	**Type of reaction**	**Deduction**
K, C_6H_7ON, is not very soluble in water, but dissolves in HC*l*(aq).	acid–base	**K** contains basic <u>amine</u> group.
K also dissolves in NaOH(aq), but not in Na_2CO_3(aq).	acid–base	**K** contains acidic <u>phenol</u> group Absence of $-CO_2H$.
On reaction with 1 mol of CH_3COCl, **K** forms compound **L**, $C_8H_9O_2N$.	nucleophilic (acyl) substitution / condensation	**L** contains an <u>amide</u> group or <u>ester</u> group.
On reaction with Br_2(aq), **L** produces compound **M**, $C_8H_7O_2NBr_2$.	electrophilic substitution	2 x Br substituted suggests that <u>one of the 2, 4 or 6 position</u> of L is occupied.

When **K** is reacted with 2 mol of ethanoyl chloride, it produces compound **N**, $C_{10}H_{11}O_3N$.	nucleophilic (acyl) substitution / condensation	**N** contains an amide group and an ester group.
N is not soluble in either HCl(aq) or NaOH(aq).	–	absence of basic amine and acidic phenol group
K can be synthesised by treating phenol with dil. HNO_3.	electrophilic substitution	4–nitrophenol (or 2–nitrophenol) is formed.
Followed by reaction with Sn metal and HCl.	reduction	4–nitrophenol is reduced to form **K** which contains an amine group.

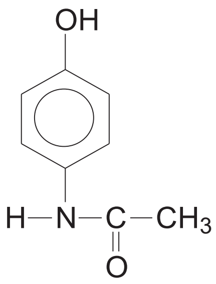
[3]: 14–18 points
[2]: 9–13 points
[1]: 4–8 points

K

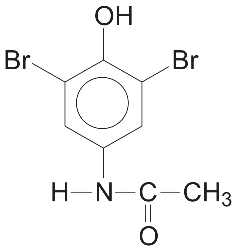


Accepts 2–aminophenol.
Likewise for **L**, **M**, **N**.

L

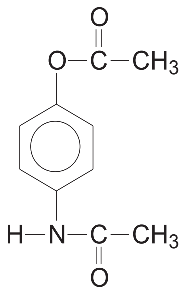


M



(ecf from **L**, i.e. give **P** instead)

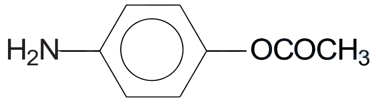
N



[1] each correct structure

(ii) [2]

P is



Presence of nucleophilic $-NH_2$ and–OH groups in **K** allows the 1 mol of CH_3COCl to react with the more nucleophilic $-NH_2$ group to form **L** or to react with the less nucleophilic –OH group to form minor product **P**.

[1]: structure of **P**
[1]: explanation why there 2 possible products and which is major/minor

AJC 2017 JC2 Preliminary Examinations

H2 Chemistry (9729/04) Science Practical Preparation List

Apparatus List

No.	Apparatus	Quantity per student
1	10 cm^3 measuring cylinder	2
2	50 cm^3 measuring cylinder	1
3	250 cm^3 conical flask	2
4	250 cm^3 volumetric flask	1
5	250 cm^3 beaker	1
6	burette with clip – one labelled as **FA 1**	2
7	25.0 cm^3 pipette with pipette filler	1
8	filter funnel	2
9	weighing bottle	2
10	styrofoam cup with lids	2
11	thermometer (-5 °C to +50 °C at 0.2 °C)	1
12	test tube rack	1
13	test tube (big)	6
14	test tube (small)	6
15	test tube holder	1
16	plastic bag of – litmus papers, plastic teat droppers x 3, tissue, splinter, filter paper strip	1
17	white tile	1
18	retort stand	1
19	safety goggles	1
20	deionised water bottle	1
21	access to weighing balance	communal
22	lighter	1 per bench

Chemicals Required

No.	Label	Identity and concentration	Quantity per student
1	**FA 1**	20 g dm^{-3} $KMnO_4$	80 cm^3
2	**FA 2**	0.100 mol dm^{-3} $Na_2S_2O_3(aq)$	150 cm^3
3	**FA 3**	100 g dm^{-3} KI(aq)	50 cm^3
4	**FA 4**	1 mol dm^{-3} H_2SO_4	50 cm^3
5	**FA 6**	1 mol dm^{-3} of HC*l*	200 cm^3
6	**FA 7**	$Na_2CO_3(s)$	~ 6g
7	**FA 8**	$NaHCO_3(s)$	~ 5g
8	**FA 9**	50 g dm^{-3} hydrated $Cu(NO_3)_2(aq)$	20 cm^3
9	**FA 10**	50 g dm^{-3} $FeSO_4$ (aq)	20 cm^3

Bench Reagents (shared by 2 students)

No.	Label	Concentration
1	aqueous NaOH	2.0 mol dm^{-3}
2	dilute H_2SO_4	1.0 mol dm^{-3}
3	aqueous NH_3	2.0 mol dm^{-3}
4	KI(aq)	0.1 mol dm^{-3}
5	aluminum powder	-
6	$K_2CrO_4(aq)$	50 g dm^{-3}
7	starch solution	1%
8	$Na_2S_2O_3$	200 g dm^{-3}
9	concentrated HC*l*	36%
10	limewater	-

<table>
<tr><th>Qn</th><th>Suggested Mark Scheme</th><th>Mark</th></tr>
<tr><td>1(a)(i), (ii)</td><td>Correctly calculates the volume of FA 1 used and volume of FA 1 used is within 40.00 to 45.00 cm^3, both inclusive.</td><td>1</td></tr>
<tr><td></td><td>Tabulates initial and final burette readings for table and volume of FA 2 used in (a)(ii).

Table has appropriate headers and units.
Tabulation may be vertical or horizontal; lines are not essential but there should be no absences of headers.
Where units have not been included in the header, there should be the appropriate unit for each entry in the table.

Do NOT award this mark if any final and initial burette readings in either table are inverted or 50 is used as the initial burette reading in either table.</td><td>1</td></tr>
<tr><td></td><td>All the final/initial burette readings for all accurate titres in BOTH tables are recorded to the nearest 0.05 cm^3.

<i>Treat all titres as “accurate” unless labelled rough or 1st titre is of lower precision than subsequent titres</i></td><td>1</td></tr>
<tr><td></td><td>Has at least TWO uncorrected titires for end–point within 0.10 cm^3

* refers to uncorrected titres i.e. ignore arithmetical errors made when calculating the titre values</td><td>1</td></tr>
<tr><td></td><td>Check and correct, if necessary, subtractions in the titre table.

Examiner then selects the “best” titre using the hierarchy:
two identical; titres within 0.05 cm^3; titres within 0.1 cm^3, etc

Calculate student titre x $\frac{\text{student volume of FA 1 added}}{\text{teacher volume of FA 1 added}}$

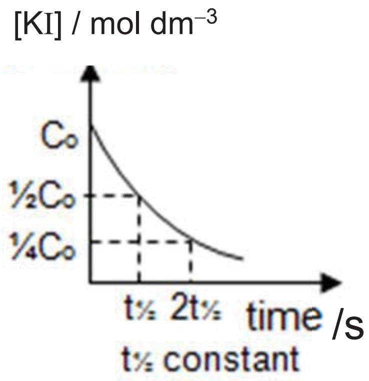
<i>Teacher’s results</i>
<table>
<tr><th>Shift</th><th>volume of FA 1 added / cm^3</th><th>average titre volume / cm^3</th></tr>
<tr><td>1</td><td>40.90</td><td>25.78</td></tr>
<tr><td>3</td><td></td><td>25.85</td></tr>
</table>

Calculate difference in teacher and student scaled values (Δ <i>titre</i>) and award “quality” marks as below.

Give 3 marks if this difference is within 0.20 cm^3
Give 2 marks if this difference is > 0.20 cm^3 but $\leq$ 0.40 cm^3
Give 1 mark if this difference is > 0.40 cm^3 but $\leq$ 0.60 cm^3
Give 0 marks for a difference that is > 0.60 cm^3.</td><td>3</td></tr>
<tr><td></td><td></td><td></td></tr>
</table>

(a)(iii)	Obtains appropriate ‘average’, to 2 d.p., from any experiments with uncorrected end–point values within 0.10 cm^3. *Do not award this mark if the titres used are not identified either in the table (by, for examples, a tick) or in a calculation.* *Do **not** award this mark if there are arithmetic errors in the table.*	1
(b)(i)	Let the volume of **FA 1** used for dilution be V_{FA1} cm^3. n(MnO_4^-) in **FA 1** used = $\frac{V_{FA1}}{1000} \times 0.100 = V_{FA1} \times 10^{-4}$ mol n(MnO_4^-) in 25.0 cm^3 of **FA 5** = $\frac{V_{FA1} \times 10^{-4}}{10} = V_{FA1} \times 10^{-5}$ mol	 1 1
(b)(ii)	n($S_2O_3^{2-}$) = 5 x n(MnO_4^-) in 25.0 cm^3 of **FA 5** = $V_{FA1} \times 10^{-5} \times 5$ mol	1
(b)(iii)	Let the average volume of **FA 2** used = V_m cm^3. [$S_2O_3^{2-}$] in **FA 2** = $V_{FA1} \times 10^{-5} \times 5 \times \frac{1000}{V_m}$ mol dm^{-3}	1
(c)	No, using burettes to measure the volume of **FA 3** and **FA 4** will not improve the accuracy of the titration data as <u>both **FA 3** and **FA 4** are used in excess</u> OR the <u>amount of I_2 formed</u> only <u>depends on the amount of $KMnO_4$ used</u>, which was already accurately measured.	1
(d)	% error in volumetric flask $= \frac{0.15 \times 100}{250} = 0.06\%$ % error in pipette = $\frac{0.1 \times 100}{25.0} = 0.4\%$ % error in burette = $\frac{2(0.05) \times 100}{25.65} = 0.390\%$ Total error = <u>0.850%</u> Also accept if the error for measuring 40.00 cm^3 and 45.00 cm^3 of **FA 1** with burette is included, then the total error = 1.07 – 1.1%	1
(e)(i)	Order of reaction = 1	1
(e)(ii)	Since total volume of reaction mixture is kept constant, • [KI] $\propto V_{KI}$ used Also since rate $\alpha \frac{1}{t}$ (as the volume of $Na_2S_2O_3$ is kept constant) AND • when the volume of KI is doubled, the time taken for the iodine to appear is halved. Rate of reaction is directly proportional to [KI]. OR • $V_{KI} \times t$ = constant	1 1

(e)(iii)



1

(e)(iv)

1. Using a 50 cm^3 measuring cylinder, measure 40 cm^3 of KI and pour the solution into a 250 cm^3 conical flask.
2. Using a 10 cm^3 measuring cylinder, measure 10 cm^3 of $Na_2S_2O_3$ and add this into the same conical flask.
3. Using a 25 cm^3 measuring cylinder, measure 25 cm^3 of H_2O and pour into the conical flask.
4. Measure 25 cm^3 of X using another 25 cm^3 measuring cylinder.
5. Rapidly pour X into the conical flask and start the stop–watch at the same time.
6. Swirl the reaction mixture.
7. Note the time taken for brown colour of iodine to first appear.

5

Marks	Requirements	Key Marking Points
[2]	Appropriate quantities of substances used	1. vol of $Na_2S_2O_3$ = 10 cm^3 2. vol of KI = 40 cm^3 or 20 cm^3 3. vol of X = 25 cm^3 (or other volume except 50 cm^3) 4. vol of water added to maintain total volume at 100 cm^3 (1 mark for any 2 points, 2 marks for all 4 points)
[1]	Appropriate apparatus and their capacities	1. $Na_2S_2O_3$: 10 cm^3 measuring cylinder or 50 cm^3 burette or 10 cm^3 pipette 2. KI / X /H_2O : 50 cm^3 / 25 cm^3 measuring cylinder or 50 cm^3 burette or 25 cm^3 pipette 3. 250 cm^3 conical flask
[2]	Essential experimental details to ensure reliable results	1. Start reaction by adding X last and rapidly 2. Simultaneously start reaction with starting stopwatch 3. Swirl the reaction mixture 4. Stop stopwatch when brown colour of iodine appears (1 mark for any 2 points, 2 marks for all 4 points)

<table>
<tr><th>Qn</th><th>Suggested Mark Scheme</th><th>Mark</th></tr>
<tr><td>2</td><td>
<table>
<tr><td>Mass of empty weighing bottle / g</td><td></td></tr>
<tr><td>Mass of weighing bottle and FA 7/8 / g</td><td></td></tr>
<tr><td>Mass of weighing bottle and <u>residual</u> FA 7/8 / g</td><td></td></tr>
<tr><td>Mass of FA 7/8 used / g</td><td></td></tr>
</table>
<table>
<tr><td>Highest / Lowest temperature reached / °C</td><td></td></tr>
<tr><td>Initial temperature of FA 6 / °C</td><td></td></tr>
<tr><td>Temperature rise / drop / °C
Or Change in temperature / °C</td><td></td></tr>
</table>

Tabulates weighings / temperature in appropriate manner. Tabulation may be vertical or horizontal; lines are not essential but there should be no absence of headers.
Correct use of highest and lowest temperature.
Correct use of rise/ drop.
Tables have correct headers and units. Where units have not been included in the header, there should be the appropriate unit for each entry in the tables.
For students who record “Change” in temperature, the corresponding sign must be included.
<i>Ignore the absence of a calculated mass for FA 7/8.</i>

</td><td>1</td></tr>
<tr><td></td><td>Complete set of masses (refer to table above)
<i>Do not award mark if Tare function is used.</i>

The mass of FA 7/8 weighed is within specified limits.
4.45 g ≤ FA 7 ≤ 5.05 g
3.45 g ≤ FA 8 ≤ 4.05 g

Correctly calculate the mass of FA 7/8.</td><td>1</td></tr>
<tr><td></td><td>All the mass readings are recorded to 3 d.p.
All temperatures are recorded to 0.1 °C</td><td>1</td></tr>
<tr><td></td><td><u>Accuracy mark.</u>

If $\frac{\Delta T}{\text{mass of FA 7/8}}$ for both experiments +/– 0.05 from Teacher’s result

If $\frac{\Delta T}{\text{mass of FA 7/8}}$ for both experiments +/– 0.2 from Teacher’s result

<i>Teacher’s results</i>
<table>
<tr><th>Shift</th><th>ΔT / m for FA 7</th><th>ΔT / m for FA 8</th></tr>
<tr><td>1</td><td>6.2 / 4.523 = 1.371</td><td>5.4 / 3.620 = 1.492</td></tr>
<tr><td>3</td><td>6.4 / 4.831 = 1.325</td><td>5.6 / 3.674 = 1.524</td></tr>
</table>
</td><td>2
(max)

1</td></tr>
<tr><td></td><td></td><td></td></tr>
<tr><td>(a)</td><td>Correctly calculates $q = V_{\textbf{FA 6}} c \Delta T = 50 \times 4.2 \times \Delta T$
Ignore if q has sign or has a wrong unit.
Ignore if ΔT was calculated wrongly.</td><td>1</td></tr>
</table>

(b)	Correctly calculates no of moles of HC*l* = $1 \times \frac{50}{1000}$ = 0.0500 mol	1
(c)	Correctly calculates number of moles of Na_2CO_3 used = $\frac{\text{mass of FA 7 used}}{106.0}$	1
(d)	Since 0.0500 moles of HC*l* requires only 0.0250 moles of Na_2CO_3 for complete reaction, Na_2CO_3 is in excess.	1
(e)	Correctly calculates $\Delta H_1 = -\frac{q}{nHCl} = -\frac{q}{0.0500} \times 2 = -a$ kJ mol^{-1} Correct sign for ΔH_1 = –ve	1
(f)	Correctly calculates $q = V_{FA\,6}c\Delta T = 50 \times 4.2 \times \Delta T$ Ignore if q has sign or has a wrong unit. Ignore if ΔT was calculated wrongly.	1
(g)	Correctly calculates number of moles of $NaHCO_3$ used = $\frac{\text{mass of FA 8 used}}{84.0}$	1
(h)	Recognises that the limiting reagent is $NaHCO_3$ and uses the number of moles of $NaHCO_3$ to determine ΔH. Correctly calculates $\Delta H_2 = +\frac{q}{nNaHCO_3} = +b$ kJ mol^{-1} Correct sign for ΔH_2 = +ve	1
(i)	Correctly calculates $\Delta H_3 = 2\Delta H_2 - \Delta H_1 = 2b - (-a)$ kJ mol^{-1}	1
	Shows working in all calculations in **1(a)(iii)**, **1(b)**, **2(a) – (c) and 2(e) – (i)**. All calculations must be relevant although they may not be complete or correct. *Any calculations not attempted loses this mark.*	1
	Shows appropriate significant figures (3 s.f.) in all final answers in **1(b)**, **2(a) – (c) and 2(e) – (i)**. Shows appropriate units in **1(a)(iii)**, **1(b)**, **2(a) – (c) and 2(e) – (i)**. *Any calculations not attempted loses this mark.*	1
(j)	No effect. This is because HC*l* was already used in excess, hence ΔH_2 calculated is independent of the number of moles of HC*l*. Therefore, ΔH_3 will not be affected.	1

Qn	Suggested Mark Scheme
3(a)	

	observations for FA 9	observations for FA 10
Add NaOH(aq), followed by a spatula load of aluminium powder.	blue ppt (1), insoluble in excess NaOH (1). pungent gas evolved turned moist red litmus blue (1) – NH_3 (1)	
Add concentrated HC*l* dropwise.	blue solution turns (green) then yellowish green/yellow (1) no effervescence observed (1). no NO_2 gas evolved (1).	
To the **FA 9** and concentrated HC*l* mixture, add deionised water.	yellowish–green/yellow solution turns (green) then blue (1)	
Add KI(aq). To the resulting solution, add $Na_2S_2O_3$(aq).	(white/cream) ppt in brown solution (1) brown colour discharged (1) white/cream ppt observed (1)	
Add 1 cm^3 dilute H_2SO_4 followed by 1 cm^3 of K_2CrO_4(aq). Divide into 2 portions.		pale blue green solution turns (green) then yellowish–brown (1)
To one portion, add KI(aq) followed by 1 cm^3 of starch solution.		brown solution formed (1) turns dark blue / blue–black on addition of starch. (1)
To the other portion, add NaOH(aq).		brown ppt (1) insoluble in excess NaOH.

Scoring for **QA** of **FA 9** and **FA 10**:	
Number of correct observations	Award (max 4)
11 and more	4
7 – 10	3
4 – 6	2
at least 3	1

<table>
<tr><th>Qn</th><th>Suggested Mark Scheme</th><th>Mark</th></tr>
<tr><td></td><td>SUMMARY

FA 9: Cu^{2+}, NO_3^- (do not accept NH_4^+, NO_2^-)
FA 10: Fe^{2+}
Correctly identifies both cations

Correctly identifies anion and supports answer with evidence that NH_3 evolved with NaOH and Al powder (either NO_3^- or NO_2^-) but no NO_2 gas evolved on addition of acid (so can only be NO_3^-).</td><td>1

1</td></tr>
<tr><td></td><td></td><td></td></tr>
<tr><td>(b)(i)

(ii)</td><td>ligand exchange

redox</td><td>1

1</td></tr>
<tr><td></td><td></td><td></td></tr>
<tr><td>(c)(i)</td><td>
<table>
<tr><th></th><th>dilute HCl</th><th>NaOH(aq)</th></tr>
<tr><td>MgO</td><td>soluble</td><td>insoluble</td></tr>
<tr><td>Al_2O_3</td><td>soluble</td><td>soluble</td></tr>
<tr><td>SiO_2</td><td>insoluble</td><td>insoluble</td></tr>
<tr><td>ZnO</td><td>soluble</td><td>soluble</td></tr>
</table>

All correct
At least 2 correct</td><td>2(max)
1</td></tr>
<tr><td></td><td></td><td></td></tr>
<tr><td>(ii)</td><td>Outline a logical sequence of testing that
• successfully identifies FA 11
• reduces the possibility to 2
• reduces the possibility to 3

(Broad workable outline, not on details)

Deduction with:
• correct formula of species present (or balanced equations)
• correct observations
• explanations

8 out of 10 given ($\geq 80\%$)

5 – 7 ($\geq 50\%$)

At least 3 (30%)</td><td>2(max)
1
0

3(max)

2

1</td></tr>
</table>

Suggested Plan

Test	Observation	Deduction	Explanation
1. Add excess aq NaOH to a portion of **FA 11**.	Dissolves (1)	Al_2O_3 or ZnO	Both are amphoteric oxides, react with aq NaOH forming soluble salts: (1) $Al_2O_3(s) + 2OH^-(aq) + H_2O(l) \longrightarrow \underline{2Al(OH)_4^-(aq)}$ $ZnO(s) + 2OH^-(aq) + H_2O(l) \longrightarrow \underline{Zn(OH)_4^{2-}(aq)}$
	Does not dissolve (1)	SiO_2 or MgO.	MgO is a basic oxide and has no reaction with a base/an alkali. (1) SiO_2 an acidic oxide with giant molecular structure, no reaction with aqueous alkali nor soluble in aqueous solution. (1) (SiO_2 would only react with hot conc. NaOH)
2. If oxide not soluble in step 1, add aq HC*l* to a portion of **FA 11**	Oxide insoluble (1)	SiO_2	An acidic oxide which does not react nor dissolve in aq acid.
	Dissolves (1)	MgO	MgO is a basic oxide that reacts and dissolve in dil. HC*l*. $MgO(s) + 2H^+(aq) \longrightarrow \underline{Mg^{2+}(aq)} + H_2O(l)$
3. If oxide soluble in step 1, dissolve a portion of **FA 11** in dil. HC*l*.			The amphoteric oxides react and dissolve in dil. HC*l*. $ZnO(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2O(l)$ $Al_2O_3(s) + 6H^+(aq) \longrightarrow 2Al^{3+}(aq) + 3H_2O$
To the solution, add aq NH_3 till excess	white ppt, soluble in excess aq NH_3 (1)	ZnO	$Zn^{2+}(aq) + 2OH^-(aq) \longrightarrow Zn(OH)_2(s)$ $Zn(OH)_2(s) + 4NH_3(aq) \longrightarrow \underline{Zn(NH_3)_4^{2+}(aq)} + 2OH^-(aq)$ (1)
	white ppt, insoluble in excess aq NH_3 (1)	Al_2O_3	$\underline{Al(OH)_3(s)}$

ANDERSON JUNIOR COLLEGE

2017 JC 2 PRELIMINARY EXAMINATIONS

NAME:___________________________ **PDG:**____ /16

CHEMISTRY **9729/04**

Paper 4 Practical **23 August 2017**

2 hours 30 minutes

Candidates answer on the Question Paper.

Additional Materials: As listed in the Confidential Instructions

---

READ THESE INSTRUCTIONS FIRST

Write your name, PDG and register number 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 pencil for any diagrams, graphs or rough working.
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.
Quantitative Analysis Notes are printed on pages 17 and 18.

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	
Total	

This document consists of **18** printed pages.

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

1 Determination of the concentration of thiosulfate ions

Potassium manganate(VII), $KMnO_4$, is an oxidising agent that can be used to determine the concentration of a solution of sodium thiosulfate.

To do this, aqueous potassium manganate(VII) is used to react with excess aqueous potassium iodide, KI to produce iodine solution. In this reaction, iodide ions are oxidised to iodine by manganate(VII) ions in acidic solution.

$$2MnO_4^-(aq) + 10I^-(aq) + 16H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 5I_2(aq) + 8H_2O(l)$$

The iodine produced is then titrated with aqueous thiosulfate ions.

$$2S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

You are provided with the following.
FA 1 is 0.100 mol dm^{-3} of potassium manganate(VII), $KMnO_4$.
FA 2 is an aqueous solution of sodium thiosulfate, $Na_2S_2O_3$.
FA 3 is an aqueous solution of potassium iodide, KI.
FA 4 is dilute sulfuric acid, H_2SO_4.

In this question, you are to perform a dilution of the $KMnO_4$ provided before carrying out a titration. The data from this titration will be used to determine the concentration of $S_2O_3^{2-}$ in **FA 2**.

(a) (i) Dilution of FA 1

1. Fill a burette with **FA 1**.
2. Run between 40.00 cm^3 and 45.00 cm^3 of **FA 1** into 250 cm^3 volumetric flask.
3. Make up to the mark with deionised water.
4. Shake the volumetric flask to obtain a homogeneous solution and label this solution **FA 5**.
5. Record all burette readings and the volume of **FA 1** that you used for dilution in the space provided in Table 1.1 below.

Table 1.1

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

[1]

(ii) Titration of iodine liberated by FA 5 with FA 2

1. Fill a second burette with **FA 2**.
2. Using a pipette, transfer 25.0 cm^3 of **FA 5** into the conical flask.
3. Using appropriate measuring cylinders, add about 10 cm^3 of **FA 3** and about 10 cm^3 of **FA 4** to the conical flask.
4. Run **FA 2** from the burette into this flask until the colour of the solution just turns colourless.
5. Record your titration results in the space provided below. Make certain that your recorded results show the precision of your working.
6. Repeat points **1** to **5** as necessary until consistent results are obtained.

Results

[6]

(iii) From your titrations, obtain a suitable volume of **FA 2** to be used in your calculations. Show clearly how you obtained this volume.

volume of **FA 2** = ………………………………………….. [1]

(b) **(i)** Calculate the amount of manganate(VII) ions, MnO_4^-, in 25.0 cm^3 of **FA 5**.

amount of MnO_4^- in 25.0 cm^3 of **FA 5** = ……………………………………….. [2]

(ii) Given that one mole of manganate(VII) ions liberates sufficient iodine from potassium iodide to react with five moles of thiosulfate ions, $S_2O_3^{2-}$, calculate the number of moles of thiosulfate ions present in the volume of **FA 5** that you found necessary in the titration.

amount of $S_2O_3^{2-}$ ions needed = ……………………………………….. [1]

(iii) Determine the concentration, in mol dm^{-3}, of $S_2O_3^{2-}$ in **FA 2**.

concentration of $S_2O_3^{2-}$ in **FA 2** = ……………………………………….. [1]

(c) A student suggests that the volumes of **FA 3** and **FA 4** should be measured using a burette instead of measuring cylinders, so as to improve the accuracy of the titration data.

Do you agree with the student? Explain your answer.

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

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

(d) A teacher performs this same experiment, using the quantities described earlier, and obtains a mean titre volume of 25.65 cm^3.

The errors (uncertainties) associated with each reading using a volumetric flask, pipette and burette are ±0.15 cm^3, ±0.1 cm^3 and ±0.05 cm^3 respectively.

Calculate the maximum total percentage error (uncertainty) of this mean titre value.

[1]

(e) **Planning**

X is another oxidising agent that can react with potassium iodide, KI, to give iodine, I_2.

The rate equation for this reaction is rate = $k\,[KI]^a\,[X]^b$, where a and b are the orders of reaction with respect to KI and X respectively.

An investigation was carried out to determine the order of reaction with respect to KI. This is done by mixing different volumes of the X and KI, together with a fixed volume of sodium thiosulfate, $Na_2S_2O_3$. The I_2 produced from the reaction between X and KI will react with the $Na_2S_2O_3$ added and be reduced back to iodide, I^-. When all the $Na_2S_2O_3$ is used up, the colour of I_2 will appear.

The kinetics of this reaction can be determined by measuring the time taken for the colour of I_2 to first appear.

The following experiments were carried out to determine the order of reaction with respect to KI.

Experiment	volume of X / cm^3	volume of KI / cm^3	volume of H_2O / cm^3	volume of $Na_2S_2O_3$ / cm^3	time / s
1	50	40	0	10	40
2	50	20	20	10	82

(i) From the data given above, state the order of reaction with respect to KI.

.... [1]

(ii) Explain clearly how the above results support your answer in **(e)(i)**.

....

....

....

....

.... [2]

(iii) Sketch the graph of concentration of KI against time based on the order you have determined in **(e)(i).**

[1]

(iv) You are to plan an investigation for **one further experiment**, which together with those above, will allow you to determine the order of reaction with respect to X.

In your plan, you should include details of

- the volumes of the solutions you would use
- the apparatus and their capacities that you would use
- the procedure that you would follow, including details on how you would obtain reliable results.

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…………………………………………………………………………………………………… [5]

[Total: 23]

2 **Determination of the enthalpy change of a reaction, ΔH_r**

You are required to obtain values of ΔH for two chemical reactions and use them to calculate ΔH for a third reaction.

FA 6 is 1 mol dm^{-3} hydrochloric acid, HCl.
FA 7 is solid sodium carbonate, Na_2CO_3.
FA 8 is solid sodium hydrogencarbonate, $NaHCO_3$.

Experiment 1

1. Weigh an empty weighing bottle.
2. Place between 4.50 g and 5.00 g of **FA 7** in the weighing bottle.
3. Place a dry Styrofoam cup inside a 250 cm^3 beaker.
4. Using a measuring cylinder, place 50 cm^3 of **FA 6** into the Styrofoam cup.
5. Place the lid onto the cup through the thermometer from the top. Stir the liquid in the cup with the thermometer and measure its temperature when it reaches a steady temperature. Read and record this temperature in your table.
6. Tip **cautiously** the contents of the weighing bottle into the acid in the Styrofoam cup, stir gently with the thermometer and record the **highest** temperature obtained in your table.
7. Calculate the change in temperature.
8. Reweigh the empty weighing bottle.

In an appropriate format in the space provided below, record all measurements of mass and temperature. Calculate the mass of **FA 7** used.

Results

(a) If 4.2 J are required to raise the temperature of 1 cm^3 of solution by 1 ^oC, calculate the amount of heat absorbed in **Experiment 1**.

[1]

(b) Calculate the number of moles of HC*l* added to the cup.

[1]

(c) Calculate the number of moles of Na_2CO_3 added to the cup.
[M_r (Na_2CO_3) = 106.0]

[1]

(d) Explain which reagent was added in excess.

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

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

(e) Calculate the enthalpy change ΔH_1 for the following reaction.

$$Na_2CO_3(s) + 2HCl(aq) \longrightarrow 2NaCl(aq) + H_2O(l) + CO_2(g) \qquad \text{---}\ \Delta H_1$$

[1]

Experiment 2

1. Weigh an empty weighing bottle.
2. Place between 3.50 g and 4.00 g of **FA 8** in the weighing bottle.
3. Place a dry Styrofoam cup inside a 250 cm^3 beaker.
4. Using a measuring cylinder, place 50 cm^3 of **FA 6** into the Styrofoam cup.
5. Place the lid onto the cup through the thermometer from the top. Stir the liquid in the cup with the thermometer and measure its temperature when it reaches a steady temperature. Read and record this temperature in your table.
6. Tip **cautiously** the contents of the weighing bottle into the acid in the Styrofoam cup, stir gently with the thermometer and record the **lowest** temperature obtained in your table.
7. Calculate the change in temperature.
8. Reweigh the empty weighing bottle.

In an appropriate format in the space provided below, record all measurements of mass and temperature. Calculate the mass of **FA 8** used.

Results

[5]

(f) If 4.2 J are required to raise the temperature of 1 cm^3 of solution by 1 °C, calculate the amount of heat absorbed in **Experiment 2**.

[1]

(g) Calculate the number of moles of $NaHCO_3$ added to the cup.
[M_r ($NaHCO_3$) = 84.0]

[1]

(h) Calculate the enthalpy change ΔH_2 for the following reaction.

$$NaHCO_3(s) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l) + CO_2(g) \quad \text{---} \ \Delta H_2$$

[1]

(i) Use your answers in **(e)** and **(h)** to calculate ΔH_3 for the following reaction.

$$2NaHCO_3(s) \longrightarrow Na_2CO_3(s) + H_2O(l) + CO_2(g) \quad \text{---} \ \Delta H_3$$

[3]

(j) A student decides to repeat the experiment with 2.0 mol dm^{-3} HCl in **Experiment 2** instead of the given concentration of 1.0 mol dm^{-3} as specified in the instructions.

This mistake may lead to differences in heat exchange and reaction rate.

Is there any other effect this mistake would have on the value of ΔH_3 that she has calculated?

effect on ΔH_3 ....

explanation ....

....

.... [1]

[Total: 17]

3 Inorganic Qualitative Analysis

(a) Carry out the following tests on **FA 9** and **FA 10** which contain cations and anions from the following list:
NH_4^+, Mg^{2+}, Al^{3+}, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, CO_3^{2-}, NO_3^-, NO_2^-, SO_3^{2-}, SO_4^{2-}, Cl^-, Br^-, I^-.

Record your observations in the space provided in Table 3.1.

Your answers should include

- details of colour changes and precipitates formed.
- the names of gases evolved and details of the test used to identify each one.

Use a fresh 1 cm^3 sample of each solution for each test.

In all tests, the reagent should be added gradually until no further change is observed, with shaking after each addition.

Table 3.1

test	observations with **FA 9**	observations with **FA 10**
Add NaOH(aq), followed by a spatula load of aluminium powder.		
Add concentrated HC*l* dropwise. To the **FA 9** and concentrated HC*l* mixture, add deionised water.		

test	observations with **FA 9**	observations with **FA 10**
Add KI(aq). To the resulting solution, add $Na_2S_2O_3$(aq).		
Add 1 cm^3 dilute H_2SO_4 followed by 1 cm^3 of K_2CrO_4(aq). Divide into 2 portions. To one portion, add KI(aq) followed by 1 cm^3 of starch solution. To the other portion, add NaOH(aq).		

[4]

Summary

Use your observations to identify the following ions

FA 9 contains the cation …………………………… and anion ……………………………

FA 10 contains the cation ……………………………

State and explain all the evidence for your identification of the anion in **FA 9**.

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

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

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

(b) State the type of reaction that occurs when

(i) concentrated HC*l* is added to **FA 9**.

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

(ii) K_2CrO_4(aq) is added to **FA 10**.

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

(c) **Planning**

FA 11 is a sample of white powder which contains **one** of the four oxides:

magnesium oxide (MgO), aluminium oxide (Al_2O_3), zinc oxide (ZnO), silicon dioxide (SiO_2)

(i) Fill in the spaces in Table 3.2 the expected solubility for each of the oxides, when mixed separately, in dilute HC*l* and aqueous NaOH.

Table 3.2

	dilute HC*l*	NaOH(aq)
MgO		
Al_2O_3		
SiO_2		
ZnO		

[2]

(ii) Using your expected observation in **(c)(i)**, suggest a plan using test tube reactions to identify the oxide present in **FA 11**.

In planning your tests you may use **only** the following reagents and no others.
Dilute hydrochloric acid, HCl
Aqueous sodium hydroxide, $NaOH(aq)$
Aqueous ammonia, $NH_3(aq)$

You may use a flow scheme or a table to chart the sequence of reactions to establish the identity of **FA 11**.

Your completed plan should include expected observations, deductions with explanation and/or formula of species present at **each** stage. Definite deductions may be made from tests where there appears to be no reaction.

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……………………………………………………………………………………… [5]

[Total: 15]

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

ion	*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 A*l* foil
nitrite, NO_2^-(aq)	NH_3 liberated on heating with OH^-(aq) and A*l* 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 on warming 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