INNOVA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME

CLASS

INDEX NUMBER

CHEMISTRY

9647/02

Paper 2 Structured Questions

18 August 2016

2 hours

Candidates answer on the Question Paper

Additional Materials: *Data Booklet*

READ THESE INSTRUCTIONS FIRST

Write your index number, name and civics group.
Write in dark blue or black pen.
You may use pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions in the space provided.
A Data Booklet is provided.

You are advised to show all working in calculations.
You are reminded of the need for good English and clear presentation in your answers.
You are reminded of the need for good handwriting.
Your final answers should be in 3 significant figures.

You may use a calculator.

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

At the end of the examination, fasten all your work securely together.

For Examiner's Use	
Section A	
1	**12**
2	**17**
3	**10**
4	**18**
5	**15**
Significant figures	
Handwriting	
Total	**72**

This document consists of **17** printed pages and **1** blank page.

Answer ALL questions on the spaces provided.

1 Planning

Using the information below, you are to write a plan for determining number of molecules of water of crystalisation, *n*, in barium chloride crystals, $BaCl_2.nH_2O$ where *n* = 1,2 or 3. The basis of this investigation is a technique known as *precipitation titration* with the use of silver nitrate solution, $AgNO_3(aq)$.

$AgCl$, Ag_2CrO_4 and $BaCrO_4$ are sparing soluble salts and relevant information about these salts are given in the table below.

compound	**colour**	**Numerical value of K_{sp} at 25 °C**
$AgCl$	white	2.0×10^{-10}
Ag_2CrO_4	red	2.0×10^{-12}
$BaCrO_4$	yellow	1.0×10^{-10}

Some barium chloride crystals, $BaCl_2.nH_2O$, is dissolved to make up 250.0 cm^3 of standard solution. Approximately 10 cm^3 of 0.2 mol dm^{-3} of reagent ***X*** solution is added to a portion of this standard solution to precipitate the barium ions *before* a few drops of K_2CrO_4 indicator solution is added. A titration is then carried out on this portion of solution against silver nitrate solution, $AgNO_3(aq)$. Ag_2CrO_4 would just precipitate only when almost all of the Cl^- ions have been precipitated as $AgCl$. The titration is repeated until a more reliable average value, ***V*** cm^3, can be determined.

(a) **(i)** Identify reagent ***X***. [1]

$Na_2SO_4(aq)$ or $K_2SO_4(aq)$ [1]

(ii) A student suggested that $BaCrO_4$ is more soluble than Ag_2CrO_4 as $BaCrO_4$ has larger numerical value of K_{sp} than Ag_2CrO_4.

Suggest whether this student's claim is valid. [1]

This claim is **not true** as both **Ag_2CrO_4 and $BaCrO_4$ are of different unit formula or have different number of ions per formula unit**. [1]

Alternatively, students can prove from calculations of solubility of the two salts.

Solubility of $BaCrO_4 = \sqrt[2]{1.0 \times 10^{-10}}$ = **1.00×10^{-5} mol dm^{-3}**

Solubility of $Ag_2CrO_4 = \sqrt[3]{\frac{2.0\times10^{-12}}{4}}$ = **7.94×10^{-5} mol dm^{-3}**

From the calculations above, Ag_2CrO_4 has a higher solubility than $BaCrO_4$ despite Ag_2CrO_4 having a smaller numerical value of K_{sp} than $BaCrO_4$. [1]

(iii) Suggest why reagent ***X*** is added *before* a few drops of K_2CrO_4 indicator solution is added. [1]

This is to prevent the precipitation of $BaCrO_4$ that uses up the CrO_4^{2-} ions.

(b) You may assume that you are provided with

- 0.10 mol dm^{-3} silver nitrate
- 0.2 mol dm^{-3} of reagent ***X*** solution
- 10 g of barium chloride crystals, $BaCl_2.nH_2O$
- Potassium chromate solution, $K_2CrO_4(aq)$
- The equipment and materials normally found in a school or college laboratory.

Your plan should include the following

- brief, but specific details of the apparatus you would use, bearing in mind the levels of precision they offer
- details, including quantities, for preparation of 250.0 cm^3 of $BaCl_2$ solution from barium chloride crystals, $BaCl_2.nH_2O$
- essential details of the titration procedure
- an outline of how the results obtained, including ***V*** cm^3, would be used to determine n, in barium chloride crystals ($BaCl_2.nH_2O$)

Assuming titre volume of $AgNO_3(aq)$ used is 25.00 cm^3 and the volume of $BaCl_2$ solution pipetted is 25.0 cm^3,

$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$

$BaCl_2(aq) \longrightarrow Ba^{2+}(aq) + 2Cl^-(aq)$

Amt of $Ag^+(aq) = \frac{25.00}{1000} \times 0.10 = 0.00250$ mol = Amt of $Cl^-(aq)$ in 25 cm^3

Amt of $Cl^-(aq)$ in 250 cm^3 = $0.00250 \times \frac{250}{25} = 0.0250$ mol

Amt of $BaCl_2(aq)$ in 250 cm^3 = 0.0250 mol ÷ 2 = 0.0125 mol

Conc of $BaCl_2(aq)$ = 0.0125 mol $\div \frac{250}{1000}$ = 0.0500 mol dm^{-3}
Assuming n = 1,
Min mass of $BaCl_2.nH_2O$ in 250 cm^3 = 0.0125 × 226.0 = 2.825 g
OR
Assuming n = 3,
Max mass of $BaCl_2.nH_2O$ in 250 cm^3 = 0.0125 × 262.0 = 3.725 g

Thus the suitable mass of $BaCl_2.nH_2O$ to be weighed ranges 2.825 g to 3.725 g.

Preparation of standard solution of $BaCl_2$

1. Weigh 2.825g – 3.275g g of $BaCl_2.nH_2O$ crystals in a clean and dry weighing bottle using a weighing balance.
2. Transfer the $BaCl_2.nH_2O$ crystals to a 100 cm^3 beaker.
3. Weigh the emptied weighing bottle and the residual $BaCl_2.nH_2O$ crystals to determine the mass of $BaCl_2.nH_2O$ crystals dissolved, ***m*** grams, by finding the

difference the weighings in (i) and (iii).

4. Add 100 cm^3 of de-ionised water to the $BaCl_2.nH_2O$ crystals in the 100 cm^3 beaker.
5. Use a glass stirrer to stir the solution in the 100 cm^3 beaker to ensure a homogeneous solution is obtained.
6. Transfer the homogeneous solution carefully to a 250 cm^3 volumetric flask.
7. Using 50 cm^3 of de-ionised water, rinse the beaker, the weighing bottle and the stirrer and transfer the washings carefully to the solution in the 250 cm^3 volumetric flask.
8. Top up to the mark with de-ionised water, stopper the bottle and shake this solution to obtain a homogeneous solution. Label this solution obtained as FA 2.

Titration Procedures

1. Fill up the burette with $AgNO_3(aq)$, noting the initial volume reading.
2. Pipette 25.0 cm^3 of FA 2 to a 250 cm^3 conical flask.
3. Using a 10cm^3 measuring cylinder, add 10 cm^3 of 0.2 mol dm^{-3} of Na_2SO_4 solution to the solution in the conical flask. Shake the mixture and let it equilibrate for about 15 minutes.
4. Add 5 drops of $K_2CrO_4(aq)$ indicator solution to the mixture in the conical flask.
5. Carry out the titration until permanent pink colour is obtained. (Colour change is from white ppt to pink due of 1 drop of $AgNO_3$*(aq) in excess to cause precipitation of red* Ag_2CrO_4)
6. Repeat titration until at least 2 consistent titre readings are obtained (titre volume differ not more than 0.10 cm^3). Use the average of these 2 consistent titres to obtain volume, ***V*** cm^3 for subsequent calculations.

Calculation Procedure

Amt of Cl^- ions in titration (25 cm^3) = $\frac{V}{1000} \times 0.10 = 0.000100\boldsymbol{V}$ mol

Amt of Cl^- ions in 250 cm^3 = $0.000100\boldsymbol{V} \times 10 = 0.00100\boldsymbol{V}$ mol

Amt of $BaCl_2 = 0.00100\boldsymbol{V} \div 2 = 0.000500\boldsymbol{V}$ mol

Mass of $BaCl_2 = 0.000500\boldsymbol{V} \times 208.0 = 0.104\,\boldsymbol{V}$ g

Mass of water of crystalisation = $(\boldsymbol{m} - 0.104\,\boldsymbol{V})$ g

Amt of water of crystalisation = $((\boldsymbol{m} - 0.104\,\boldsymbol{V}) \div 18)$ mol

No of molecules of water of crystalisation, n
= Amt of water of crystalisation ÷ Amt of $BaCl_2$
= $((\boldsymbol{m} - 0.104\,\boldsymbol{V}) \div 18) \div 0.0000500\boldsymbol{V}$

Marking points

1. **use of appropriate apparatus with correct capacities** i.e. weighing bottle for measuring mass of $BaCl_2.nH_2O$ crystals, 250 cm^3 volumetric flask to prepare $BaCl_2$ solution, 10 cm^3 measuring cylinder for measuring vol of reagent ***X*** solution, pipette+burette+ 250 cm^3 conical flask
2. **Appropriate volumes of solutions pipetted being 20.00 – 25.00 cm^3** based on appropriate choice of titre volume of 20.00 – 25.00 cm^3 **and max of 5 drops of indicator to be used.**
3. **appropriate mass of $BaCl_2.nH_2O$ crystals used = 2.825g – 3.275g**
4. **Quantitative transfer** of $BaCl_2$ solution to volumetric flask or **mass difference of weighing bottle+ crystals and mass of emptied weighing bottle to determine mass of $BaCl_2.nH_2O$ crystals**
5. **Repeat titration until two consistent readings (+ 0.10 cm^3) are obtained.**
6. Correct **colour change (white to pink or red)** at end point
7. Derivation of **mass of water of crystallisation**

8. Derivation n being **mole ratio of water of crystallisation to $BaCl_2$**

[8]

(c) Explain why this titration cannot be conducted under acidic *or* alkaline medium. [1]

Under **acidic medium, CrO_4^{2-} ions will undergo condensation or acid-base reaction to form $Cr_2O_7^{2-}$ ions**, thus the indicator ions of CrO_4^{2-} will be absent and the end-point of the titration cannot be detected. **[1]**

OR

Under **alkaline medium, Ag^+ ions will be precipitated** as Ag_2O resulting in a much higher than accurate titre reading. **[1]**

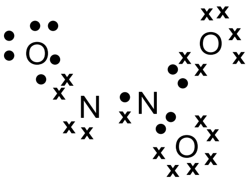
[Total: 12]

2 This question is about the oxides of nitrogen and its reactions. Oxides of nitrogen constitute air pollutants originating from emission of car exhaust that cause acid rain and photochemical smog.

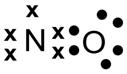
The two gases of NO and N_2O_4 slowly react to form the blue compound, N_2O_3 according to the following equation.

$$2NO(g) + N_2O_4(g) \rightleftharpoons 2N_2O_3(g)$$

(a) **(i)** Draw the dot and cross diagrams of the two molecules, NO and N_2O_3. The N_2O_3 molecule contains a N−N bond.
[2]



N_2O_3



NO

(ii) From your answer in **(a)(i)**, suggest why the forward reaction is likely to occur.

[1]

The NO molecule contains an **unpaired electron/lone electron**[√] or The NO molecule is a **free radical**.
Thus, it is **highly reactive/unstable**[√], and reacts to form N_2O_3 molecule (that has all atoms attaining noble gas configuration).

(b) In an experiment, a mixture containing NO and N_2O_4 was introduced into a 1.48 dm^3 evacuated vessel was allowed to reach equilibrium at 280 K. The equilibrium pressure is 98.9 kPa.

Calculate the total number of moles of gases at equilibrium, assuming the gases behave ideally.
[2]

$$PV = nRT \rightarrow n = \frac{PV}{RT} = \frac{(98900Pa)(1.48\times10^{-3})}{(8.31)(280)} = \textbf{0.0629 mol}$$ **[1]**

[1] for working (correct unit conversion)

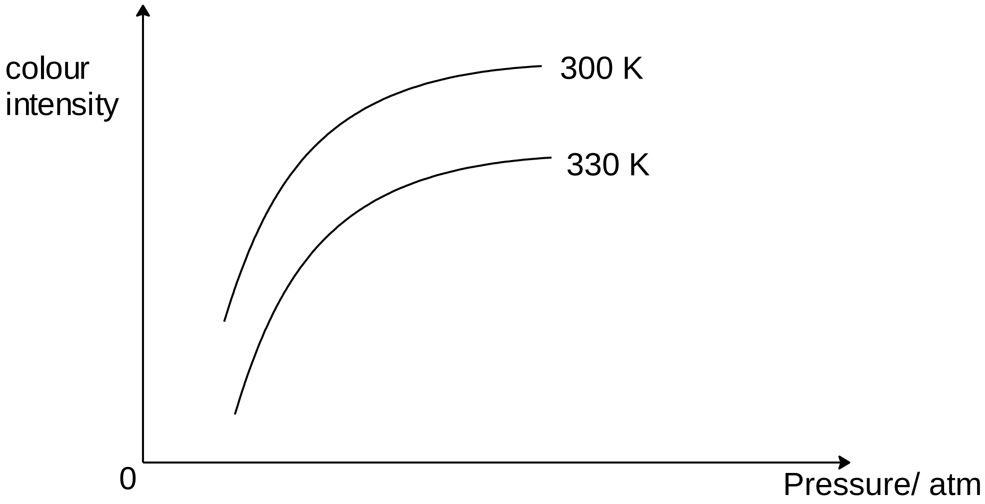
(c) Two colourless gases NO and N_2O_4 slowly react to form the blue compound, N_2O_3

according to the following equation.

$$2NO(g) + N_2O_4(g) \rightleftharpoons 2N_2O_3(g)$$

Equimolar mixtures of NO and N_2O_4 are mixed at varying pressure P but at two different temperatures of 300 K and 330 K, and the variation in colour intensity was monitored over a period of time.

The graphs below show the variation of the colour intensity with pressure at temperatures of 300 K and 330 K.



(i) What is the significance of the colour intensity in this reaction? [1]

The colour intensity changes with changes in partial pressure/ concentration/ amount of N_2O_3 produced. **[1]**

Accept any answers of similar meaning.

(ii) Explain why colour intensity of the reaction mixture increases with increasing pressure. [1]

When **the pressure is increased, the equilibrium position shifts right**[√], to **decreasing the number of moles of gaseous molecules**[√] present.

Or

An increase in pressure **favours the forward reaction**, causing **more N_2O_3 to be formed**. Hence, the colour intensity increases.

(iii) Using information from the graphs, state and explain whether the formation of N_2O_3 from NO and N_2O_4 is an exothermic reaction. [2]

At the higher temperature of 330 K, the colour intensity is lower. This implies **less N_2O_3 is produced** [√] and hence indicates that the **backward reaction is favoured at higher temperatures.** [√]

By Le Chatelier's principle, **when temperature of a system is increased, the system favours endothermic reaction in order to remove the excess heat** [√]
Since the backward reaction is favoured/ less products are formed, the **forward reaction is exothermic**. [√]

Or

At the lower temperature of 300 K, the colour intensity is higher. This implies **more N_2O_3 is produced** [√] and hence indicates that the **forward reaction is favoured at lower temperatures.** [√]

By Le Chatelier's principle, **when temperature of a system is decreased, the system favours exothermic reaction in order to produce heat** [√].

Since the forward reaction is favoured/ more products are formed, the **forward reaction is exothermic**. [√]

(d) Nitrogen monoxide reacts with chlorine to form nitrosyl chloride, according to the equation:

$$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g).$$

In an experiment, the amount of Cl_2(g) was kept in *large excess* while the initial partial pressure of NO(g) was varied at constant temperature of 500K.
The table below shows the experimental results obtained.

time / s	P_{NO} / atm	($Rate / P_{NO}$) / s^{-1}	($Rate / (P_{NO})^2$) / ($atm^{-1}\ s^{-1}$)
0	0.917	1.033×10^{-4}	1.126×10^{-4}
1000	0.827	9.312×10^{-5}	1.126×10^{-4}
2000	0.753	8.486×10^{-5}	1.127×10^{-4}
3000	0.691	7.788×10^{-5}	1.127×10^{-4}
4000	0.638	7.190×10^{-5}	1.127×10^{-4}

(i) Suggest why the amount of Cl_2(g) was kept in *large excess.*
[1]

Since the amount of Cl_2(g) was kept in *large excess*, **the partial pressure of Cl_2(g) remains relatively constant** [1] so that any change in rate is due to the changes in the partial pressure of NO(g) only.

(ii) Using the data from the table above, deduce the order of reaction with respect to NO(g).
[1]

Since **Rate / $(P_{NO})^2$ is constant throughout the reaction** [√] (and thus rate of reaction is directly proportional to $(P_{NO})^2$), the reaction is **second order with respect to NO**. [√]

(iii) In another experiment, the initial partial pressure of NO(g) was 4.2 atm and it was reacted with Cl_2(g) at a constant temperature of 500 K. The partial pressure of Cl_2(g) was recorded at time intervals of 30 s. The data obtained are tabulated below.

Time / s	**Partial pressure of Cl_2(g) / atm**
0	0.78
30	0.76
60	0.72
90	0.70
120	0.66
150	0.63
180	0.59
210	0.57
240	0.54
270	0.52
300	0.49
330	0.46
360	0.44
390	0.42
420	0.39
450	0.38
480	0.36
510	0.34
540	0.33
570	0.32

Using the data but without the plotting of any graph, deduce the order of reaction with respect to Cl_2(g). [1]

1st $t_{1/2}$
= time taken for P_{Cl2} to decrease from 0.78 atm to 0.39 atm
= 420 s

2nd $t_{1/2}$
= time taken for P_{Cl2} to decrease from 0.72 atm to 0.36 atm (or 0.66 → 0.33)
= 480 – 60
= 420 s

Since **$t_{1/2}$ is constant at 420s** **[√]**, the reaction first order with respect to Cl_2.
Hence order of reaction with respect to Cl_2 = 1 **[√]**

(iv) Write the rate equation for this reaction.
Hence, calculate the rate constant, including its units [3]

Rate = k $(P_{NO})^2(P_{Cl2})$ [1] , allow ecf based on answers in (ii) and (iii)
Rate = k' (P_{Cl2}) where k' = k $(P_{NO})^2$

$t_{1/2}$ = 420 s = $\frac{\ln 2}{k(P_{NO})2} = \frac{\ln 2}{k(4.2)2}$

k = 9.36×10^{-5} [1] atm^{-2} s^{-1} [1]

(v) One possible mechanism of the reaction is given below.

Step I $NO(g) + Cl_2(g) \rightleftharpoons NOCl_2(g)$ fast

Step II $NOCl_2(g) + NO(g) \longrightarrow 2NOCl(g)$ slow

Explain whether it is consistent with the observed kinetics data in **(d)(iv)**.

[2]

If Step II is the rds: rate = k' $(P_{NOCl2})(P_{Cl2})$

Since rate equation should not contain $NOCl_2$ intermediate, from step 1:

$$K_p = \frac{P_{NOCl_2}}{P_{NO}P_{Cl_2}}$$

$$\text{Hence, } P_{NOCl_2} = K_p P_{NO} P_{Cl_2}$$

Substitute into the rate equation:

rate = $k'(P_{NOCl2})(P_{Cl2}) = k' K_p (P_{NO})(P_{Cl2})(P_{NO}) = k (P_{NO})^2(P_{Cl2})$ **[1]**

Step II is the rate-determining step since its rate equation is consistent with the experimentally determined rate law, rate = $k (P_{NO})^2(P_{Cl2})$. [1]

[Total: 17]

3 Organic compounds can undergo combustion. Chemical companies produce containers filled with butane for use by campers.

The enthalpy change of combustion of butane is – 3000 kJ mol^{-1}.

(a) **(i)** Define the term *standard enthalpy of combustion of butane*.[1]

It is enthalpy change when 1 mole of butane is burnt in excess oxygen under standard conditions of 298K and 1 atm. [1]

(ii) Calculate the mass of water at 25 °C that could be brought to the boiling point by the combustion of 1.2 dm^3 of butane gas. Assume 75% of the heat from the butane is absorbed by the water. [2]

Heat = $mc\Delta T$
Moles of butane = (1.2) / 24 = 0.05 moles
Heat released = 3000 x 0.05 = 150 kJ
Heat absorbed = 0.75 x 150 = 112.5 kJ [1]
$112.5 \times 10^3 = m \times 4.18 \times (100 – 25)$
m = 358 g [1]

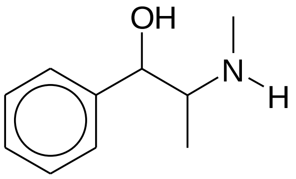
(b) **(i)** Explain in terms of structure and bonding, why butanone has a higher boiling point than pentane. [2]

Both butanone and pentane have **simple molecular structures**[√] with similar Mr

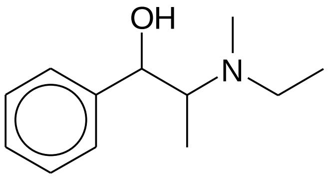
Butanone has a higher boilng point as it **requires more energy**[√] to **overcome its stronger p.d-pd interactions between its molecules** [√]compared to **id-id interactions between butane molecules.** [√]

4[√] – 2m (accept answers along this line – SBE, comparing strength)

(c) Organic compounds are also widely used for pharmaceutical purposes such as ephedrine which is an anti-asthmatic and stimulant. Ephedrine can be converted into ethylephedrine via a S_N2 reaction.



Ephedrine



Ethylephedrine

(i) Suggest the reagent that can be used to perform this conversion.[1]

CH_3CH_2I [1]

(ii) Explain why an S_N2 mechanism is favoured for this reaction. [1]

There is only **1 bulky alkyl group bonded to the α–carbon of the CH_3CH_2I that could possibly block the backside approach of the nucleophile**. Thus there is **less steric hindrance in the halogenoalkane and** hence S_N2 mechanism is favoured. [1]

(d) Complete hydrolysis of proteins produces individual units of amino acids, but partial hydrolysis can break the protein down into dipeptide or tripeptide fragments.

Partial hydrolysis of a tetrapeptide (containing four amino acid residues) produces the following three dipeptides, as well as the individual amino acids.

$NH_2CH_2CONHCH(CH_3)CO_2H$

$NH_2CH_2CONHCH_2CO_2H$

$NH_2CH(CH_3)CONHCH(CH_3)CO_2H$

(i) Define the primary structure of a protein [1]

Primary structure is the sequence of amino acids in a polypeptide chain[1]

(ii) Deduce the order in which the amino acids are bonded together in the tetrapeptide. [1]
$NH_2\mathbf{CH_2}CONH\mathbf{CH_2}CONH\mathbf{CH(CH_3)}CONH\mathbf{CH(CH_3)}CO_2H$ [1]

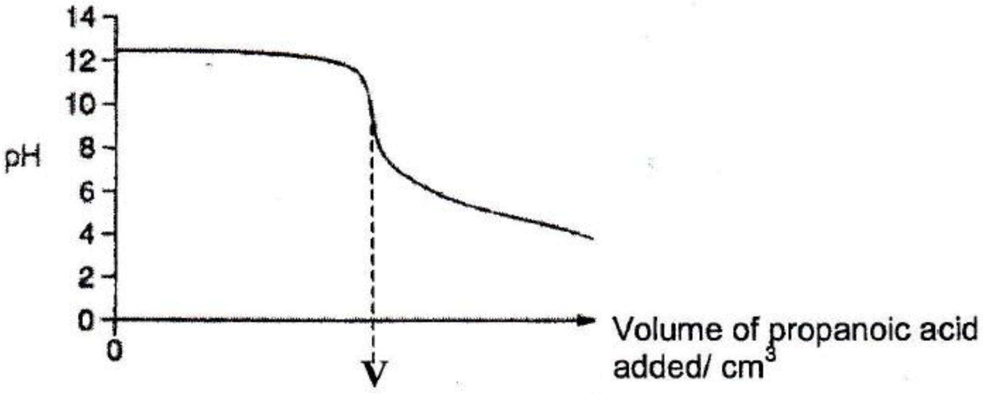
(iii) Suggest suitable reagents and conditions to hydrolyse the tetrapeptide into its individual amino acids. [1]
Reagents : dilute H_2SO_4 / HCl [√]
Condition: prolonged heating (many hours) [√]

[Total: 10]

4 **(a)** A 0.031 mol dm^{-3} solution of a base, MOH, has a pH of 12.5. (M is a metal.)

25 cm^3 of the solution of MOH was titrated with 0.025 mol dm^{-3} propanoic acid, CH_3CH_2COOH, at 25 °C. The pH of the solution was followed using a pH meter and the following titration curve was obtained.

Ka of propanoic acid = 1.29×10^{-5} mol dm^{-3}



(i) Calculate the concentration of hydroxide ions present in the sample of MOH and use it to explain whether it is a strong or weak base. [1]
pH = 12.5
pOH = 14 – 12.5 = 1.5
$[OH^-] = 10^{-1.5} = 0.0316$ mol dm^{-3} [√]

MOH has dissociated completely, thus it is a strong base [√].

(ii) Calculate the value of **V**. [1]
$CH_3CH_2COOH + MOH \rightarrow CH_3CH_2COO^-M^+ + H_2O$

Amt of MOH = 0.031 x 25/1000
= 7.75×10^{-4} mol

Amt of CH_3CH_2COOH required = 7.75×10^{-4} mol [√]

Volume of CH_3CH_2COOH required = $(7.75 \times 10^{-4}) / 0.025$
= $0.031\ dm^3$
= $31.0\ cm^3$

V = 31.0 [√]

(iii) Explain, with the aid of an equation, why the pH when **V** cm^3 of propanoic acid was added, is greater than 7. [2]

When V cm^3 of acid is added, the acid and base react completely to produce a **basic salt**, which undergoes **hydrolysis** in water to **produce hydroxide ions / an alkaline solution**. [1]

$CH_3CH_2COO^-\ (aq) + H_2O\ (l) \rightleftharpoons CH_3CH_2COOH\ (aq) + OH^-\ (aq)$ [1]

(b) The colour of blackberries is due to a compound known as cyanidin. Cyanidin is a weak organic acid which may be represented by CyH. In aqueous solution, CyH dissociates slightly:

$$\underset{\text{red}}{CyH\ (aq)} \rightleftharpoons \underset{\text{purple}}{Cy^-\ (aq)} + H^+\ (aq)$$

The colours of CyH and Cy^- are indicated in the above equation.
Acid dissociation constant, K_a, of CyH is 5.0×10^{-5} mol dm^{-3} at 25 °C.

A glass of blackberry juice has a pH of 3.00 at 25 °C. Calculate the ratio of the red to purple form in the juice, and hence predict its colour. [3]

When a mix of CyH and Cy- is present, system is an acidic buffer.

$$\mathbf{pH = pK_a + \log_{10} \frac{[salt]}{[acid]}}$$

$$3.00 = -\log_{10}(5.0 \times 10^{-5}) + \log_{10}\frac{[Cy^-]}{[CyH]} \quad [1]$$

$$\frac{[Cy^-]}{[CyH]} = 0.05$$

$$\frac{[CyH]}{[Cy^-]} = 20 : 1 \quad [1]$$

Colour of juice: red [1]

(c) When chlorine is bubbled through cold sodium hydroxide solution and acidified silver nitrate solution, only half of the chlorine that has dissolved is precipitated as silver chloride. When the sodium hydroxide is hot, up to five–sixth of the chlorine can be precipitated. Explain the observations, giving balanced equations where appropriate. [3]

cold NaOH: $\mathbf{2OH^-\ (aq) + Cl_2\ (aq) \rightarrow Cl^-\ (aq) + ClO^-\ (aq) + H_2O\ (l)}$ [1]

hot NaOH: **$6\ OH^-\ (aq) + 3\ Cl_2\ (aq) \rightarrow 5\ Cl^-\ (aq) + ClO_3^-\ (aq) + 3\ H_2O\ (l)$** **[1]**

The free chloride ions will be precipitated out as silver chloride with silver nitrate.

When chlorine reacts with cold NaOH, mole ratio of Cl^- : ClO^- = 1 : 1 **[√]**

When chlorine reacts with hot NaOH, Cl^- : ClO_3^- = 5 : 1 **[√]**

(d) The table below gives data about some physical properties of the elements calcium, nickel and copper.

	calcium	nickel	copper
atomic radius / nm	0.197	0.124	0.128
electronic configuration	$[Ar]4s^2$	$[Ar]3d^8 4s^2$	$[Ar]3d^{10} 4s^1$

(i) What do you understand by the term *transition element*? [1]

A transition element is a d-block element that forms **at least one stable ion** with a **partially filled d-subshell**. [**1**]

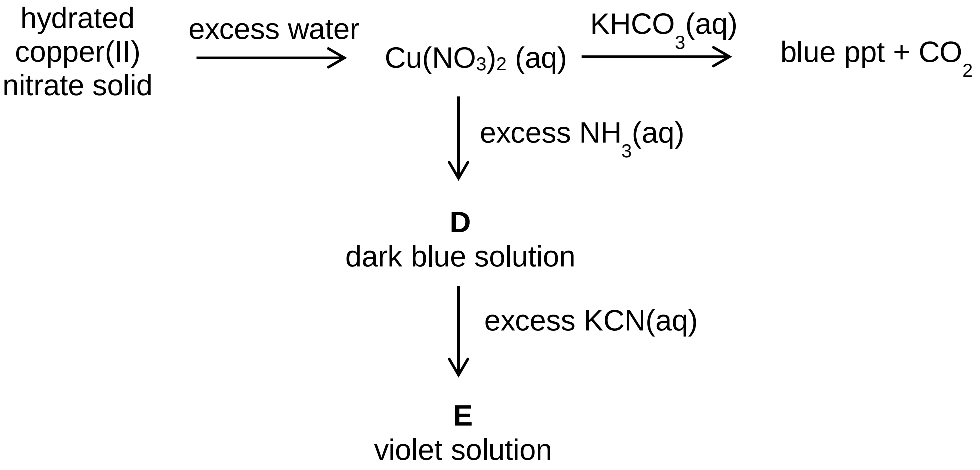
(ii) Although the nickel and copper atoms have more electrons than the calcium atom, the atomic radii of nickel and copper are smaller than that of calcium. Suggest an explanation for this. [3]

Nuclear charge of Ni and Cu are larger. **[√]** However, **shielding effect of 3d electrons of Ni and Cu is poorer** **[1]** than that of 3s and 3p electrons of Ca because 3d orbitals are more diffused. Hence, **Ni and Cu have larger effective nuclear charge**. **[1]** **Valence electrons of Ni and Cu are attracted more strongly to nucleus** **[√]**, so have smaller atomic radii.

OR

- Ni and Cu has **higher nuclear charge** than Ca. **[√]**
- For Ni and Cu, electrons are added to the inner 3d subshell. These inner **3d electrons shield the outer 4s electrons more effectively**. **[√]**
- For Ni and Cu, the effect of increasing nuclear charge is reduced by the increasing shielding effect. / **the increase of nuclear charge outweighs the increase of shielding effect [1]**
- Thus **effective nuclear charge of Ni and Cu is slightly higher than Ca** **[√]**
- **Valence electrons of Ni and Cu are attracted more strongly to nucleus** **[√]**, so have smaller atomic radii

(e) The following are some reactions involving copper(II) nitrate.



(i) Explain why carbon dioxide is evolved when $KHCO_3$(aq) is added to aqueous copper(II) nitrate. Include any relevant equations with state symbols in your answer. [2]

A solution of Cu^{2+} is **acidic** [✓] in nature due to the **high charge density** [✓] of the cation and is able to polarise the electron cloud of water molecule.

$[Cu(H_2O)_6]^{2+}(aq) + H_2O(l) \rightleftharpoons [Cu(H_2O)_5(OH)]^{+}(aq) + H_3O^{+}(aq)$ (good to have but not necessary)

$2H^{+} + CO_3^{2-} \rightarrow CO_2 + H_2O$ **[1]**

(ii) Suggest a formula for the complex ion present in **D**. [1]

$[Cu(H_2O)_2(NH_3)_4]^{2+}$ OR $[Cu(NH_3)_4]^{2+}$

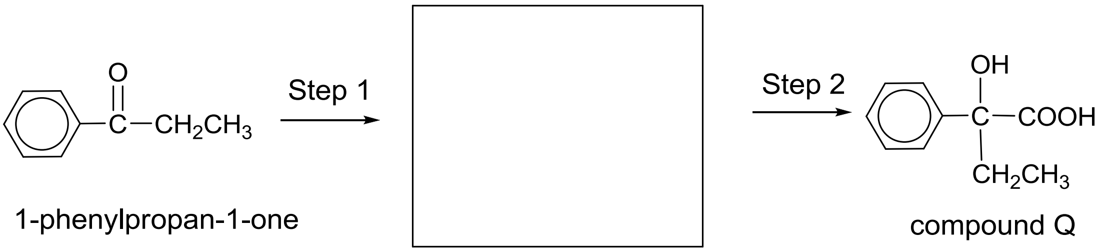
(iii) The metal ion in complex **E** is known to have a coordination number of four. Suggest a formula for complex ion **E**. [1]

$[Cu(CN)_4]^{2-}$

[Total: 19]

5 Benzene reacts with propanoyl chloride and 1-phenylpropan-1-one is formed in the reaction.

(a) State the reagents and conditions needed to convert 1-phenylpropan-1-one into compound **Q**. Show the structure of the intermediate in the box provided.



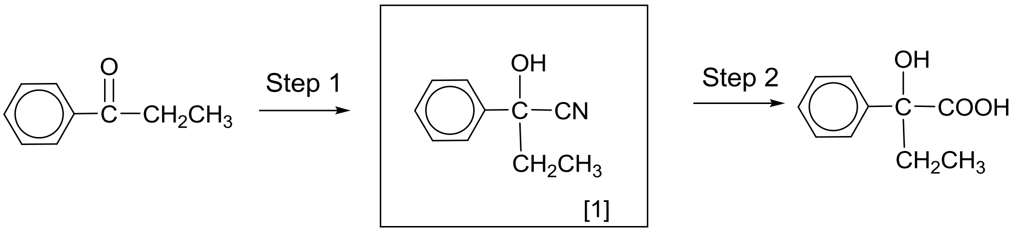
1-phenylpropan-1-one

compound Q

Reagents and conditions

Step 1 ………………………………………………………………………………

Step 2 ....
[3]



Step 1 HCN, trace amt of NaOH/NaCN, 10-20°C (can they use cold?) [1]

Step 2 Dilute or (aq) HCl/H_2SO_4, heat [1]

(b) Describe the mechanism in step 1 in part(a). In your answer, you should show all charges and lone pairs and show the movement of electrons by curly arrows.
[3]

Mechanism: Nucleophilic Addition[1]

Step 1:
HCN $\rightleftharpoons$ H+ CN-
NaCN → $Na^+ + CN^-$

Step 2: Nu attack on butanone to form intermediate

Step 3: Protonation

Step 4: Regeneration of catalyst

Correct mechanism (include all important aspect)
-correct arrows
-partial charges
-correct intermediate [2]

(c) The 2,4-D weed killer, $C_8H_6Cl_2O_2$, is widely used on cereal crops, pastures and orchards. Compound **R** is an isomer of the weed killer under development to improve its properties. It is an aromatic compound which contains **three** functional groups.

The following tests are carried out in the order given. In **each** case, state **all** deductions about the compound **R** you can make at **that** stage. When identifying the functional groups, your answers should be unambiguous.

(i) When Compound **R** is treated with Na, $C_8H_5Cl_2O_2Na$ is formed.

deduction(s)..

....[1]
Acid metal reaction.[√]
Possible functional groups present: alcohol or phenol or carboxylic acid[√]
2[√] [1]
~~Must give **both** functional possible functional gps based on 2 O atoms.~~

(ii) When Fehling's solution is added to Compound **R**, red brick precipitate is obtained.

deduction(s)..

....[1]

Mild oxidation occurs. [√]
Aliphatic aldehyde is present [√]
2[√] - [1] [aldehyde alone is not accepted]

(iii) When 1 mole of Compound **R** is boiled with ethanolic silver nitrate, 287 g of white precipitate is formed.

deduction(s)..

....

....

....[2]

2 moles of AgCl is formed with 1 mole of compound R. This suggests the presence of 2 aliphatic chloro substituted atoms undergone nucleophilic substitution.
Alphatic halogeno compound is present or chlorine atoms are on the aliphatic side chain and not bonded to the ring.

[1]: identify aliphatic halogeno compound
[1] : identify **two** Cl aliphatic atoms

(iv) When Compound **R** is treated with concentrated nitric acid, $C_8H_3Cl_2N_3O_8$ is formed.

1. What type of reaction takes place?

   ....

   Electrophilic substitution[1]

2. Name the functional group present in Compound **R** that is confirmed by this reaction.

   ....

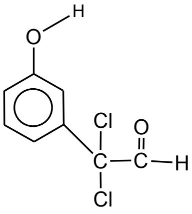
   [2]

   Phenol- [1]

   aromatic compound not accepted as catalyst will be required

(v) You now have enough information to determine the structural formula of **R**.

1. Draw the fully displayed structure of **R**.

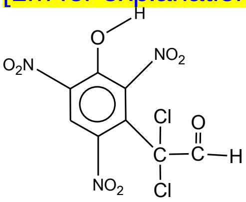


side chain must be at position 3

2. Explain clearly why you have placed each of the ~~aromatic~~ substituent groups in their particular positions.

[3]

As phenol is 2- and 4- directing, and trisubstitution took place, as seen by $3NO_2$ substituent groups added in the electrophilic substitution reaction. Thus, the side chain is not on the 2-, 4- or 6- position but on position 3.
[1m for explanation along the lines]



$C_8H_3Cl_2N_3O_8$

[1m] tri-substitution takes position 2,4,6
[1m] side chain on 3rd position

[Total:15]