HWA CHONG INSTITUTION
C2 Preliminary Examinations
Higher 2

CANDIDATE NAME		**CT GROUP**	**16S**
CENTRE NUMBER		**INDEX NUMBER**	

CHEMISTRY

9729/02

Paper 2 Structured Questions

11 September 2017

2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your **name**, **CT group, centre number** and **index number** clearly in the spaces above.

Write in dark blue or black pen.

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

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

Answer all questions in the spaces provided in 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	
1	/ 12
2	/ 14
3	/ 16
4	/ 12
5	/ 13
6	/8
Deductions	
Total	/ 75

Calculator Model:

1 (a) Atmospheric hydrogen and iodine, each 0.10 mol, are placed in a 2 dm^3 evacuated flask at 400 °C. After 30 minutes, the following equilibrium was established and the amount of HI was found to be 0.12 mol.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

(i) Write the expression for K_c and calculate its value at 400 °C.

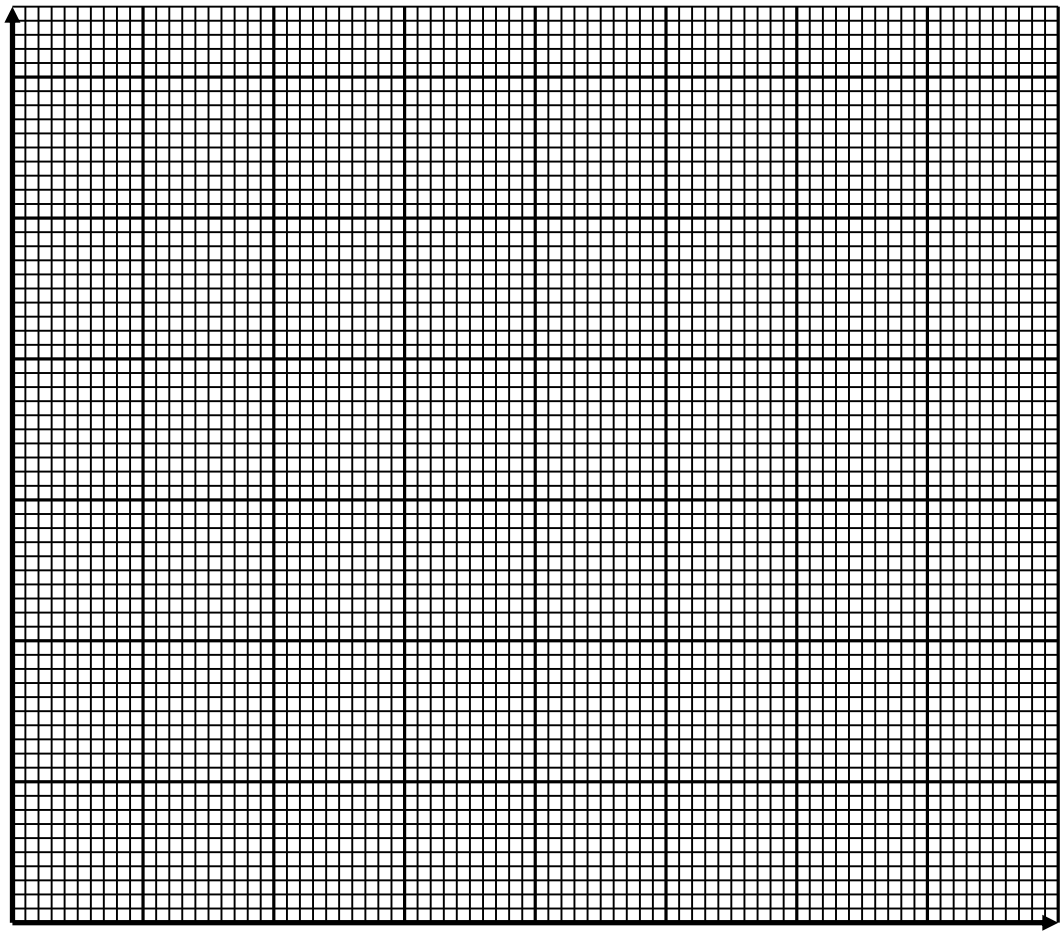
[2]

(ii) At 40 minutes, the temperature of the system was raised to 600 °C and equilibrium was re-established at 60 minutes.

Given that the K_c at 600 °C was 0.36, show that the equilibrium concentrations of H_2, I_2 and HI in the equilibrium mixture at 60 min are 0.0385 mol dm^{-3}, 0.0385 mol dm^{-3} and 0.0231 mol dm^{-3} respectively.

[2]

(iii) On the grid below, sketch the concentration versus time graphs for I_2 and HI respectively under the conditions as described in **(a)(i)** and **(a)(ii)** from 0 to 70 minutes. Label the graphs and indicate significant values on the axes.



[4]

(iv) To find the amount of HI present at equilibrium at 30 minutes, the flask can be rapidly cooled and the HI is dissolved in water. The solution obtained can be titrated against NaOH(aq). Explain why the flask has to be rapidly cooled.

……

……

[1]

(b) When I_2 combines with I^-, it forms the I_3^- ion which is responsible for the characteristic brown colour of aqueous I_2.

Draw a dot-and-cross diagram to show the bonding in I_3^-.

[1]

(c) Explain, in terms of structure and bonding, why I_2 has a higher boiling point than HI.

……

……

……

……

……

[2]

[Total: 12]

2 (a) Metal ions, especially transition metal ions, possess the ability to form complexes with both organic and inorganic *ligands*.

1,10-phenanthroline (also known as 'phen') and ferrozine are organic ligands that can form complexes with Fe^{2+} ions.

(i) Explain the term '*ligand*'.

……

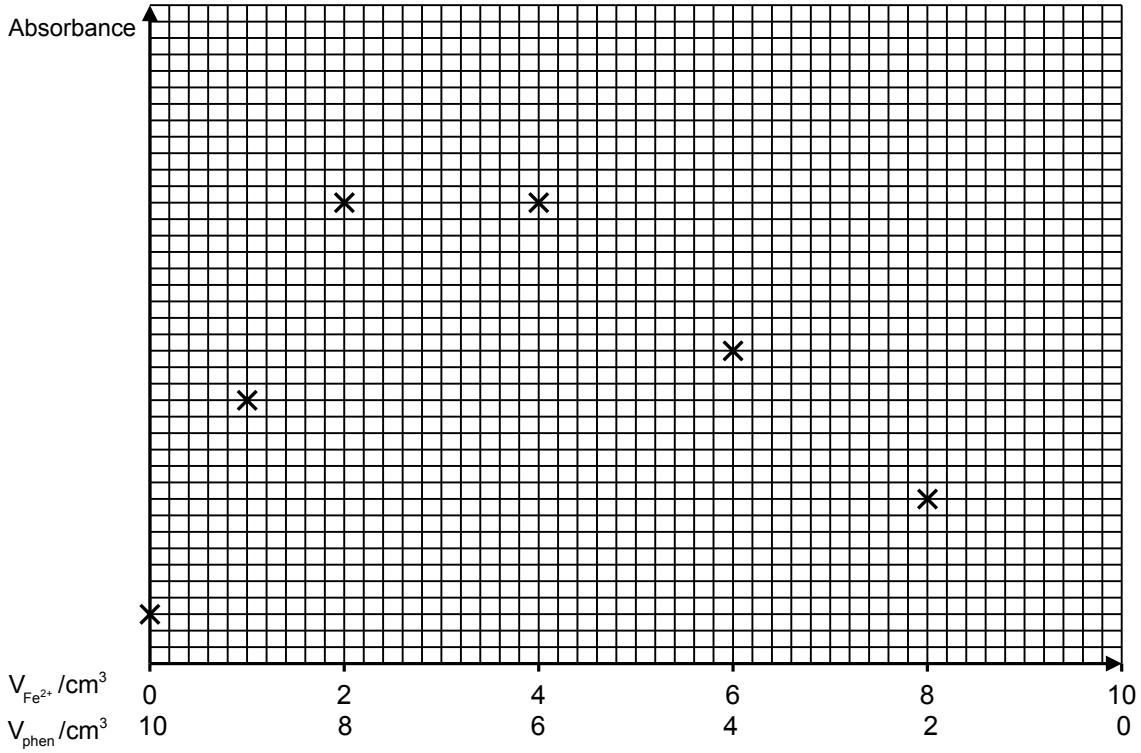
……

[1]

(ii) In the following experiment, varying volumes of solutions of 0.1 mol dm^{-3} Fe^{2+} and 0.1 mol dm^{-3} phen are mixed to produce a complex of orange-red colour.

$$x Fe^{2+} + y phen \rightarrow [Fe_x(phen)_y]^{2+}$$

The concentration of the orange-red complex formed is proportional to the absorbance of the solution which is measured using a colorimeter. The following graph is plotted using the results of the experiment.



By drawing suitable lines on the graph, deduce the formula of the complex formed between Fe^{2+} and phen.

Formula of the complex …….

[2]

(iii) Explain why the solution of the complex formed between Fe^{2+} and phen exhibits an orange-red colour.

……

……

……

……

[3]

(iv) Ferrozine reacts with Fe^{2+} in solutions to give a purple complex. Suggest why the colour of this complex is different from that formed with phen, by considering your answer to **(iii)**.

……

……

[1]

(b) Alkyl groups can be substituted into a benzene ring in the presence of a suitable catalyst. This is known as a Friedel-Crafts alkylation.

(i) Suggest a suitable reagent and condition to convert benzene to ethylbenzene.

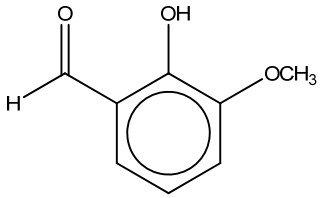
Reagent: ……. Condition: …….

[1]

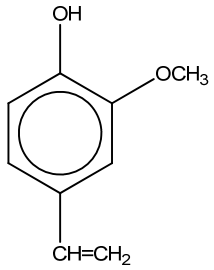
(ii) Name and outline the mechanism to convert benzene to ethylbenzene using the reagent and condition you proposed in **(b)(i)**. Show all charges and use curly arrows to show the movement of electron pairs.

[3]

(c) Fermentation produces phenolic compounds that give wheat beer its distinctive spicy, clove-like flavor. This flavor comes from phenolic molecules such as vanillin and 4-VG.

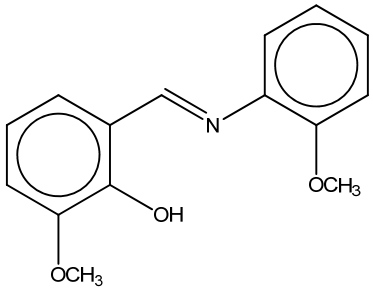


vanillin



4-vinylguaiacol
(4-VG)

(i) Schiff bases are an important class of ligands that form complexes which can be used as antimicrobial agents. They are derived when a condensation reaction takes place between an amine and a carbonyl group. Vanillin can be used to synthesise the Schiff base ligand below.



Give the structure of the molecule that reacted with vanillin to form this Schiff base ligand.

[1]

(ii) Suggest a simple chemical test to distinguish between vanillin and 4-VG. State the reagent and condition used and the expected observation for **each** compound.

……

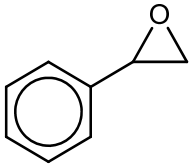
……

[2]

[Total: 14]

3 Epoxides are a class of organic compounds with a three-membered ring structure containing two carbon atoms and one oxygen atom. The three-membered ring in epoxides makes them highly reactive and susceptible to "ring-opening reactions" whereby one of the C–O bonds breaks. Hence, epoxides are important precursors for many industrial and commercial applications.

One such epoxide is styrene oxide.



styrene oxide

(a) **(i)** State the hybridisation of the carbon atoms in the three-membered ring in styrene oxide, and the typical bond angle around a carbon atom with the same hybridisation.

hybridisation: ……..

typical bond angle: …….

[2]

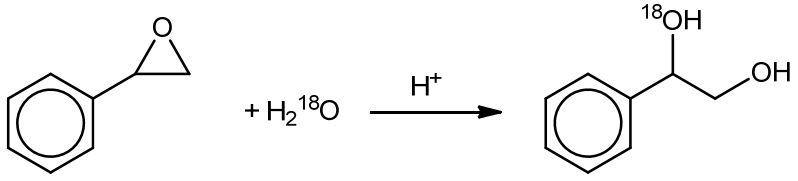
(ii) The actual bond angle in the three-membered ring in styrene oxide is 60°. By comparing this bond angle with your answer in **(a)(i)**, suggest why epoxides are susceptible to "ring-opening reactions".

……

……

[1]

(b) An example of an epoxide ring-opening reaction is the hydrolysis of styrene oxide in the presence of a strong acid catalyst to form styrene glycol. To determine the reaction mechanism, isotopic labelling was used. The hydrolysis was carried out using "heavy-oxygen water", $H_2{}^{18}O$.

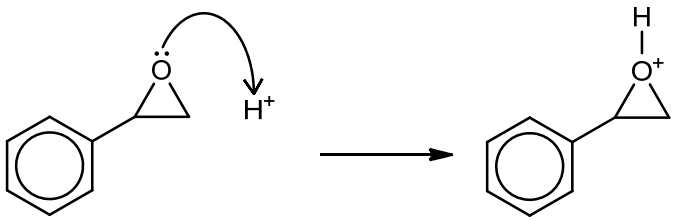


styrene glycol

It is found that the reaction follows a unimolecular nucleophilic substitution mechanism. Some details of the mechanism are as given.

1. Protonation of the oxygen atom by a strong acid catalyst
2. Heterolytic fission of the C–O bond to generate a carbocation intermediate
3. Attack of the carbocation by one molecule of $H_2{}^{18}O$ to form a new C–O bond
4. Loss of a proton to form styrene glycol and regenerate the acid catalyst

(i) Step 1 of the mechanism has been drawn for you:



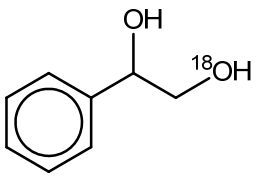
Describe steps 2 to 4 of the mechanism for this unimolecular nucleophilic substitution reaction. Show all relevant lone pairs and charges, and indicate the movement of electron pairs with curly arrows. You do not need to label the ^{18}O atom in any water molecules.

[3]

(ii) Draw the structure of a side product formed if the acid catalyst used is dilute hydrochloric acid.

[1]

(iii) Analysis of the styrene glycol product formed from the hydrolysis showed the presence of trace amounts of an isotopic isomer **A** (in which the oxygen-18 atom is bonded to a different carbon atom).



isotopic isomer **A**

Suggest how isotopic isomer **A** could have been formed during the reaction and why it was formed only in trace amounts.

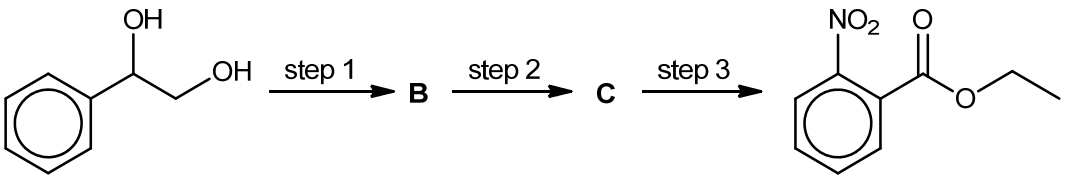
……

……

……

[2]

(c) Compound **D** can be synthesised from styrene glycol by the following route.



styrene glycol **D**

State the reagents and conditions for steps 1 to 3, and draw the structures of the intermediate compounds **B** and **C**.

step 1 ……

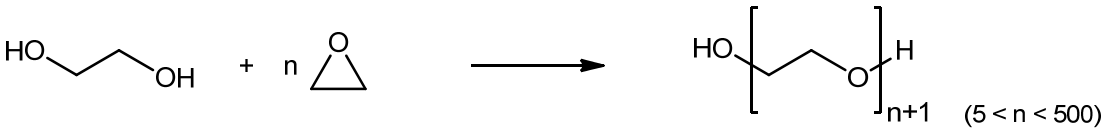
step 2 ……

step 3 ……

Compound **B**	Compound **C**

[5]

(d) Ethylene oxide is another epoxide, and can undergo polymerisation with a small amount of ethylene glycol to form polyethylene glycol (PEG).



ethylene glycol ethylene oxide polyethylene glycol (PEG)

PEG is highly soluble in water, in contrast to long-chain fatty acids such as lauric acid, $CH_3(CH_2)_{10}CO_2H$, which are only sparingly soluble.

With the aid of a labelled diagram, explain why PEG is highly soluble in water despite its large M_r.

……..

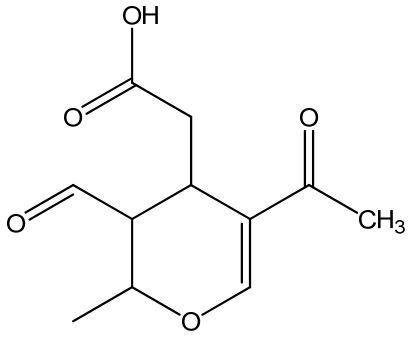
……..

……..

[2]

[Total: 16]

4 The olive tree has been used for centuries in the Mediterranean region for culinary and medicinal practices. The leaves and the fruit contain a number of organic compounds which are responsible for these benefits. One of these compounds is elenolic acid. The structure of elenolic acid is shown below.



elenolic acid

(a) Name **four** functional groups, other than the ether functional group (–C–O–C–), that are present in the elenolic acid molecule.

……

……

[4]

(b) Draw the structural formula of all the organic products formed when elenolic acid is treated with the following reagents. Assume the ether functional group is inert.

(i) $LiAlH_4$ in dry ether

[1]

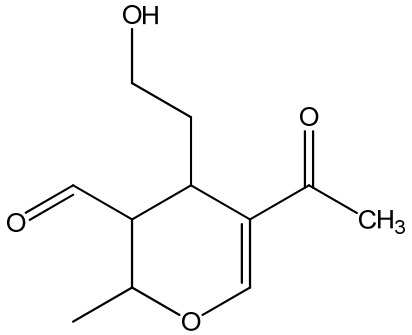
(ii) hot aqueous iodine in an excess of sodium hydroxide

[2]

(iii) hot aqueous $KMnO_4$ in an excess of dilute sulfuric acid

[2]

(c) Explain how the acidity of elenolic acid compares with that of compound **M**.



M

……

……

……

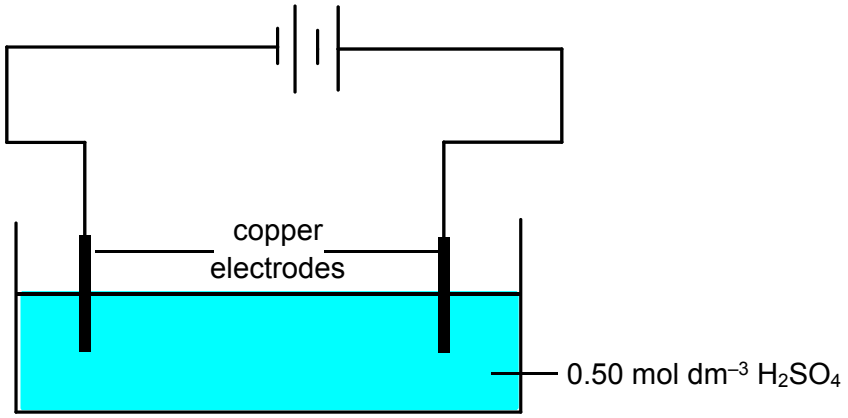
……

……

[3]

[Total: 12]

5 (a) The Avogadro constant may be determined via an electrolytic method in a school laboratory. In a typical experiment, copper electrodes are connected to a battery and dipped into an electrolyte of dilute sulfuric acid.



The experimental results are tabulated as follows.

Initial mass of anode/ g	0.968
Final mass of anode/ g	0.254
Time of electrolysis/ s	3100
Average current/ A	0.700

(i) Write an equation for the reaction that occurs at the anode. Include state symbols in your answer.

……

[1]

(ii) Using the above experimental results, calculate a value for the Avogadro constant.

[3]

(b) A 10-cent coin is typically made up of cupronickel, an alloy consisting of both copper and nickel. In another electrolytic experiment, a 10-cent coin is made the anode and dipped in an electrolyte of 6.0 mol dm^{-3} HC*l*. Graphite is used as the cathode.

The 10-cent coin is gradually but completely dissolved, resulting in an intensely green-coloured electrolyte. Copper is deposited at the cathode.

(i) Explain, by quoting relevant $E^{\ominus}$ values, why copper instead of nickel is deposited at the cathode.

……

……

……

[2]

(ii) The complex responsible for the colour of the electrolyte is $NiCl_4^{2-}$. State the electronic configuration of Ni in $NiCl_4^{2-}$.

……

[1]

(iii) $NiCl_4^{2-}$ is an example of a tetrahedral complex. Similar to an octahedral complex, the d subshell of a transition metal ion in a tetrahedral complex is split into two energy levels. However, the d orbitals found in the upper energy level in the octahedral complex are now found in the lower energy level of the tetrahedral complex and vice versa.

Using the Cartesian axes given below, draw **fully-labelled** diagrams of the following.

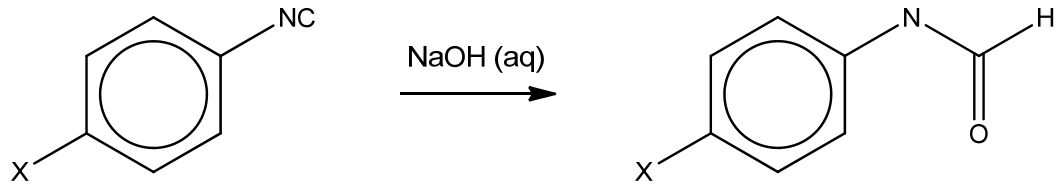
- One of the d orbitals at the upper energy level in a tetrahedral complex.
- One of the d orbitals at the lower energy level in a tetrahedral complex.

<u>upper</u> <u>lower</u>

[2]

(c) An isocyanide is an organic compound with the functional group –NC. When the –NC group is attached to a benzene ring, the compound is called an aromatic isocyanide.

Aromatic isocyanides have been found to react in NaOH (aq) yielding the corresponding formamides.

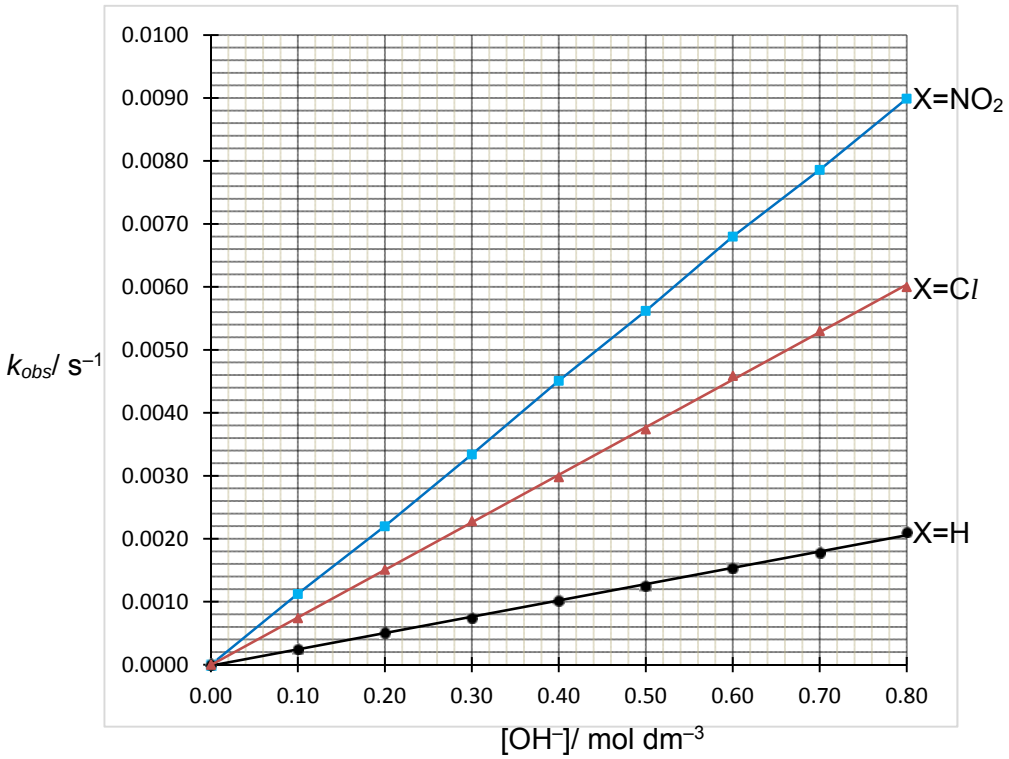


aromatic isocyanide, with a possible substituent at the 4-position

formamide

The order of reaction with respect to the aromatic isocyanide was found to be one in an earlier series of experiments.

In further experiments, to determine the order of reaction with respect to OH^-, the concentration of aromatic isocyanide used was kept at 5.0×10^{-4} mol dm^{-3} while the concentration of OH^- used was varied between 0.10 and 0.80 mol dm^{-3}. To determine the effect of different substituents X, the reaction was carried out using different aromatic isocyanides. The graph of the observed rate constant, k_{obs} against $[OH^-]$ is plotted as follows.



(i) Given that $k_{obs} = k[OH^-]^m$, deduce the order of reaction with respect to OH^-.

.....

[1]

(ii) Hence or otherwise, write a rate equation for the reaction between aromatic isocyanides and OH^- and use it to determine the rate of the reaction for X = C*l* when $[OH^-] = 0.74$ mol dm^{-3}.

[2]

(iii) In the reaction, OH^- acts as a nucleophile to attack the carbon atom of the isocyanide group. Explain why the gradients of the graph for X = NO_2 and X = C*l* were steeper than that for X = H.

……

……

[1]

[Total: 13]

6 A common magic demonstration where containers of "water" are mixed to obtain "milk" makes use of the following reaction between methanal and sulfite:

$$HCHO + SO_3^{2-} + H_2O \rightarrow CH_2(OH)(SO_3^-) + OH^-$$

As the reaction produces hydroxide ions, the pH of the solution rises. If a buffer solution is present, this rise is gradual at first. Eventually, when the buffer is exhausted, the pH rises quickly. If the cation Mg^{2+} is also present, the solution soon becomes saturated in magnesium hydroxide and a white precipitate appears.

The procedure of the demonstration is given below.

Procedure (steps 1 to 3 are prepared ahead of the demonstration whereas step 4 is performed in front of the audience)

To the same beaker, the following solutions are added:

1. Add 100 cm^3 of 0.100 mol dm^{-3} Na_2SO_3 (solution A).
2. Add 100 cm^3 of 0.400 mol dm^{-3} $NaHSO_3$ (solution B).
3. Add 5 cm^3 of 2.00 mol dm^{-3} $MgCl_2$ (solution C).
4. Add 200 cm^3 of 0.300 mol dm^{-3} HCHO (solution D) and swirl.

20 s after step 4 is carried out, a white cloudy solution ("milk") suddenly appears in the beaker owing to the precipitation of magnesium hydroxide.

The following information are relevant.

K_a of HSO_3^-	1.02×10^{-7} mol dm^{-3}
K_{sp} of $Mg(OH)_2$	5.66×10^{-12} mol^3 dm^{-9}

(a) What do you understand by the term *buffer solution*?

……

……

[1]

(b) Calculate the pH of the buffer solution in the beaker after Step 2.

[1]

(c) Write **one** equation to show how this buffer performs its function in **(a)**, in the process delaying the appearance of the white precipitate.

……

[1]

(d) Show that the white precipitate first appears when the pH in the beaker is 9.18.

[2]

(e) State a solution (A, B, C or D) whose concentration you would **decrease** in order for the white precipitate to appear earlier.

……

[1]

(f) The procedure can be slightly amended as follows to produce "tea" instead of "milk".

- Steps 1, 2 and 4 are unchanged.
- In step 3, instead of solution C, add 5 cm^3 of 3-nitrophenol indicator.

Indicator	colour in acidic solution	colour in alkaline solution	working pH range
3-nitrophenol	colourless	yellow	6.7 – 8.7

In this way, a yellow solution suddenly appears at the end of the demonstration.

Previously, "milk" appeared 20 s after step 4 was carried out. Explain whether "tea" appears earlier, later or also at 20 s after step 4 was carried out.

……

……

[1]

(g) Suggest another indicator you could use in place of 3-nitrophenol so that "red wine" may be obtained instead of "tea".

……

[1]

[Total: 8]