SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME _____

CLASS _____

CHEMISTRY 9647/03

Preliminary Examination **22 August 2012**

Paper 3 Free Response Questions **2 hours**

Additional Materials: Data Booklet
Writing Papers

READ THESE INSTRUCTIONS FIRST

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

Answer any **four** questions.
A Data Booklet is provided.
You are reminded of the need for good English and clear presentation in your answers

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

This document consists of **13** printed pages and **1** blank page

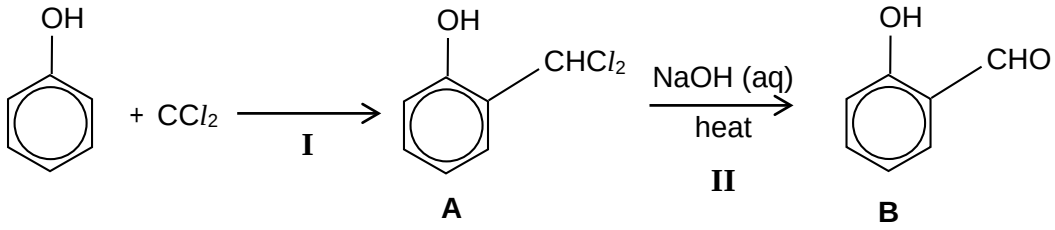
Answer any **four** questions

1 **(a)** Aqueous sodium hydroxide is an important reagent in many organic reactions where the hydroxide ion can act as both a base and a nucleophile.

In the Reimer-Tiemann reaction, phenol is heated with chloroform in the presence of aqueous sodium hydroxide to give 2-hydroxybenzaldehyde, compound **B**. The reaction involves the formation of a reactive intermediate, CCl_2, through an acid-base reaction.

$$CHCl_3 + OH^- \rightarrow CCl_2 + H_2O + Cl^-$$

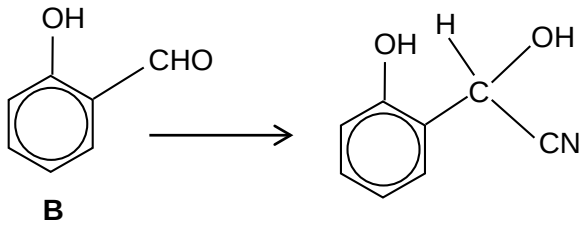
chloroform



(i) State the type of reaction that occurred in reaction **I**.

(ii) Suggest a chemical test to differentiate compounds **B** and **A** under room conditions.

(iii) Compound **B** can undergo further reaction to form the product below.



Name and describe the mechanism involved, using curly arrows to show the movement of electrons and indicating all charges.

(iv) Comment on the relative acidity of phenol and compound **B**.

[9]

(b) Besides its extensive use in organic chemistry, aqueous sodium hydroxide is also used in photographic development.

The black-and-white photography process involves four steps:

Step 1 Photo-taking: Interaction of light with silver halides (AgX) on film.

Step 2 Developing: Redox reactions to develop the actual image.

Step 3 Fixing: Changing the solubility of chemical compounds with different conditions to preserve the image on the film.

Step 4 Printing: Shining light through the film onto photosensitive paper, producing the final photograph using the same chemistry as step 1 to 3.

When light is shone on the film during the phototaking process, a very small number of X^- ions in AgX are oxidised.

(i) A small amount of silver is produced as a result of the oxidation reaction of X^-. The silver produced catalyses the reduction of the surrounding AgX to black silver metal in the presence of a reducing agent, **D**, during the developing process.

$$2AgX + \mathbf{D} + 2OH^- \rightarrow 2Ag + \mathbf{E} + 2H_2O + 2X^-$$

State and explain why the rate of reaction changes as the developing process proceeds.

(ii) Under appropriate conditions, chloride can be oxidised to chlorine gas. With the aid of an equation, suggest how Cl_2 will react with hydroxide ions under room conditions.

(iii) **E**, formed from the oxidation of **D**, has the molecular formula $C_6H_4O_2$.

E forms an orange precipitate when warmed with 2,4-dinitrophenylhydrazine. One mole of **E** decolourises two mole of bromine dissolved in tetrachloromethane. Heating **E** with acidified potassium manganate(VII) produces only one product.

D has the molecular formula $C_6H_6O_2$. It is insoluble in water but can dissolve in aqueous sodium hydroxide. Addition of sodium carbonate to **D** does not result in effervescence but addition of sodium metal to **D** gives mild effervescence.

Suggest the structures of **D** and **E**, explaining your reasoning.
(You are not required to explain the oxidation process of **E** from **D**)

[11]

Total 20 marks

2 Halogens are highly reactive and they are the only group in the Periodic Table which contains elements in all three familiar states of matter at 25 ^{o}C and 1 atm.

The halogens form hydrogen halides with hydrogen, all of which are strong acids with the exception of HF.

(a) Discuss the thermal stability trend of the hydrogen halides, HC*l*, HBr and HI and variation in volatility of the halogens from fluorine to iodine.

[5]

(b) Concentrated sulfuric acid will react with solid sodium halides NaX.
(X = C*l* $^{-}$, Br $^{-}$ or I^{-}).

Using relevant data from the *Data Booklet*, describe and explain why hydrogen chloride can be prepared by the reaction between sodium chloride and concentrated sulfuric acid while hydrogen iodide cannot be synthesised using a similar method with sodium iodide and concentrated sulfuric acid. You are to include relevant chemical equation(s) in your discussion.

[5]

(c) Halogens form many compounds with metals. These compounds range from ionic compounds such as lithium chloride, monomeric covalent compounds such as uranium hexafluoride, and polymeric covalent compounds like palladium chloride.

The Corey-Posner, Whitesides-House reaction is an organic reaction that involves the reaction of a lithium dialkyl cuprate with an alkyl halide to form a new alkane, an organocopper compound and a lithium halide.

The formation of propane from a halogeno compound using the Corey-Posner, Whitesides-House reaction is as shown.

$$(CH_3)_2CuLi + CH_3CH_2X \rightarrow CH_3CH_2CH_3 + CH_3Cu + LiX$$

(X = C*l* $^{-}$, Br $^{-}$ or I^{-})

(i) Draw the structural formulae of the three alkanes produced when $(C_3H_7)_2CuLi$ and C_3H_7Br undergo the Corey–Posner, Whitesides–House reaction.

(ii) Suggest with reasoning which of the alkanes in **(c)(i)** has the lowest boiling point.

[6]

(d) Chlorine and fluorine react exothermically to form an interhalogen compound, ClF_3.

(i) With the help of a Lewis structure, state the shape of the ClF_3 molecule.

(ii) The interhalogen compounds are very strong oxidising agents.

When gaseous ClF_3 is added to water, a vigorous reaction occurs, giving three gases as the only products. The gaseous product mixture appears as white fumes which forms a weak acid. The gaseous mixture not only turns moist blue litmus paper red but also bleaches it. In addition, it relights a glowing splint.

State the three gases in the gaseous mixture.
Hence, construct a balanced equation, including state symbols, for the reaction.

[4]

Total 20 marks

3 **(a)** Nitrous acid, HNO_2, is an unstable, weakly acidic compound. It can easily be prepared by acidifying a solution of a nitrite.

Barium nitrite, $Ba(NO_2)_2$ is often used since the insoluble barium sulfate can be easily filtered off.

$$Ba(NO_2)_2\,(aq) + H_2SO_4\,(aq) \rightarrow 2HNO_2\,(aq) + BaSO_4\,(s)$$

Nitrite ions can be oxidised by potassium manganate(VII) to form nitrate ions:

$$5NO_2^-\,(aq) + 2MnO_4^-\,(aq) + 6H^+\,(aq) \rightarrow 5NO_3^-\,(aq) + 2Mn^{2+}\,(aq) + 3H_2O\,(l)$$

The following are some thermochemistry data.

	ΔH^q / kJ mol^{-1}
enthalpy change of atomisation of barium	+175
enthalpy change of Ba (s) ® Ba^{2+} (aq) +2e	+286
enthalpy change of hydration of NO_3^-	-325
lattice energy of barium nitrate	-1395

(i) Using the data above, and relevant data from the *Data Booklet*, construct an energy cycle to calculate the enthalpy change of hydration of the barium ion.

(ii) The $\Delta S^q_{hydration}$ of barium ion is -188 J mol^{-1} K^{-1}. Explain why the sign of $\Delta S^q_{hydration}$ is negative.

(iii) Hence, calculate $\Delta G^q_{hydration}$ of barium ion at 298K.

(iv) Predict the effect of high temperature on the spontaneity of the above reaction.

(v) Using your answer in **(a)(i)**, and relevant data from the table, calculate the enthalpy change of solution of barium nitrate.

(b) **(i)** When barium nitrate is heated, it decomposes. Write an equation to represent the thermal decomposition of barium nitrate.

(ii) Group II iodates decomposed according to the following equation.

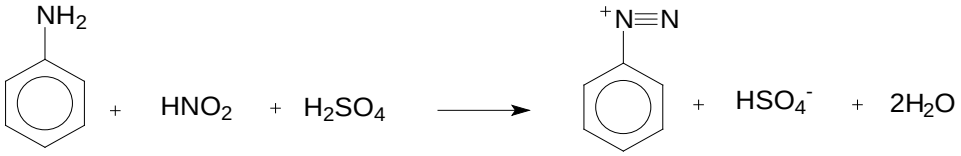
$$2Mg(IO_3)_2\,(s) \rightarrow 2MgO\,(s) + 2I_2\,(g) + 5O_2\,(g)$$

Describe and explain how the thermal stabilities of Group II iodates vary down the group.

[10]

(c) Nitrous acid is useful in converting amines into diazonium compounds:

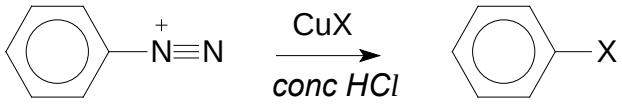
Reaction 1



diazonium salt

In a process named the Sandmeyer reaction, the $-\overset{+}{N}\equiv N$ is replaced by –C*l* or –Br using the corresponding cuprous halide, CuX, together with concentrated HC*l*.

Reaction 2

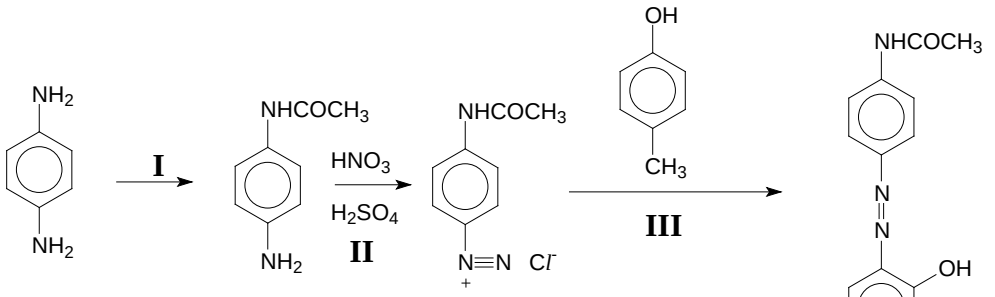


Outline how you could convert nitrobenzene into 1,3-dichlorobenzene in a **four steps synthesis**, using both reactions 1 and 2 in your synthesis. In your answer, you are to clearly state the reagents and conditions used and the intermediates formed.

[5]

(d) The diazonium salt can undergo a coupling reaction with activated aromatic rings to obtain brightly coloured azo compounds which can be used as dyes.

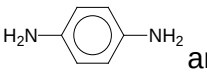
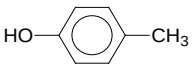
The dye, Disperse Yellow, is formed as follows:



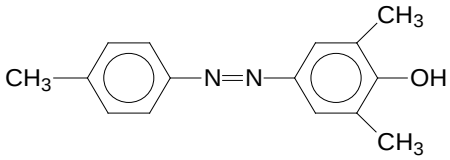
diazonium salt

Disperse Yellow

(i) Identify a reagent which might be used for step **I**.

(ii) Propose a chemical test to differentiate  and  .
In your answer, state clearly the reagents and conditions required and any observations made.

(iii) Another azo dye, **H**, can be obtained from an amine and a phenol under suitable conditions.



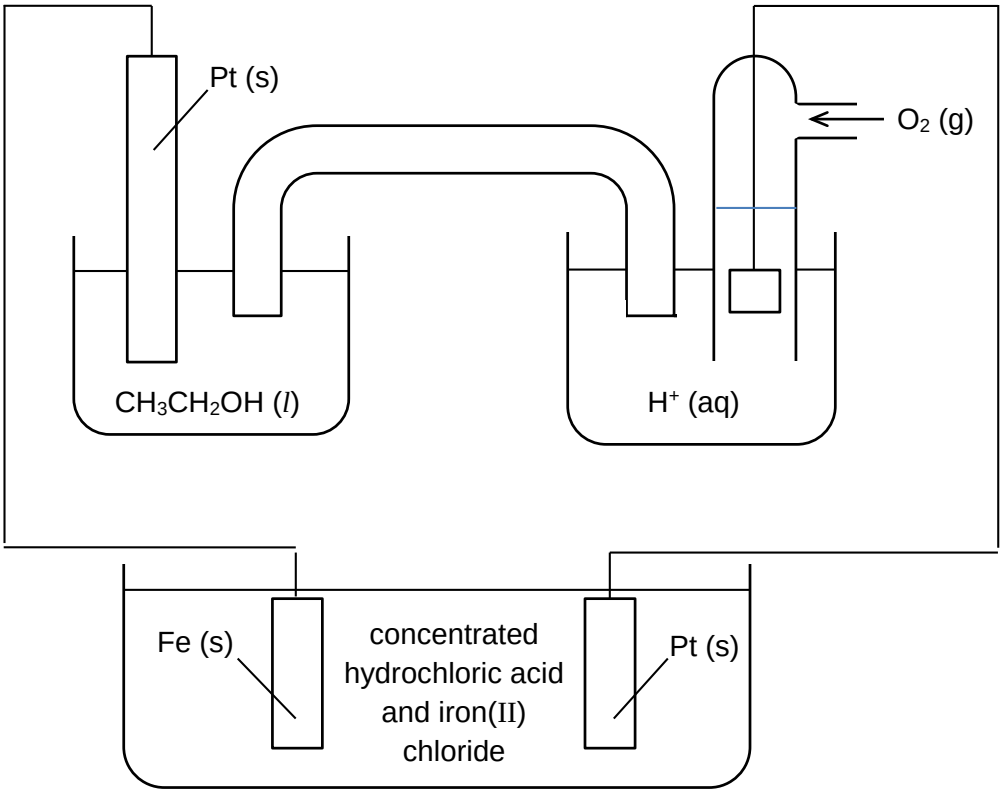
azo dye, **H**

Draw the structural formulae of the amine and of the phenol used to make **H**.
[5]

Total 20 marks

4 The pickling of steel is the process of removing rust, or iron(III) oxide, from steel by using excess concentrated hydrochloric acid to react with layers of the oxide and iron metal. The reaction produces a solution of iron(II) chloride.

A chemist used the set-up shown below to investigate if the resulting solution which consists of concentrated hydrochloric acid and iron(II) chloride, from the pickling of steel, can be used to produce iron metal via electrolysis.



(a) An organic fuel cell, the direct ethanol fuel cell, is used to drive the electrolysis. The reaction that takes place at one of the electrodes involves the reduction of oxygen gas as follows:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

(i) Construct the overall equation for the fuel cell reaction, given that carbon dioxide is produced at the anode.

(ii) Write the cell diagram for the direct ethanol fuel cell, stating the polarity of the respective electrodes.

[3]

(b) **(i)** Construct a balanced equation for the reaction that takes place during the pickling of steel, indicating the state symbols clearly.

(ii) Write half-equations for the reactions taking place at the cathode and anode of the electrolytic cell and state all observations made within the cell.

(iii) Suggest the observation made at the anode when nitric acid is used in the pickling of steel instead of hydrochloric acid.

[6]

(c) Upon addition of cyanide ions, the colour of the electrolyte changes from pale green to “Prussian blue”.

Explain why iron complexes are coloured.

[3]

(d) Another chloride of iron, $FeCl_3$, has similar characteristics as aluminium chloride. Both form dimers at low temperatures, produce acidic solutions when dissolved in water and are used in the electrophilic substitution reactions of benzene rings.

(i) Using suitable data from the *Data Booklet*, explain the acidic nature of $FeCl_3$ in water.

(ii) State what role does iron(III) chloride play in the electrophilic substitution reaction of benzene ring with chlorine.

[4]

(e) **(i)** Haemoglobin, which contains iron(II) ions is a protein found in the red blood cells that carries oxygen. Describe the protein components of haemoglobin.

(ii) In World War II, the use of cyanide pills were frequently recorded. Pilots of B-29 Superfortress bombers sent to drop atomic bombs on Japan were issued with the lethal pills. Fortunately, all aircraft returned safely and none of the pills were used. These pills contain a concentrated solution of potassium cyanide and the release of the fast-acting poison causes brain death within minutes.

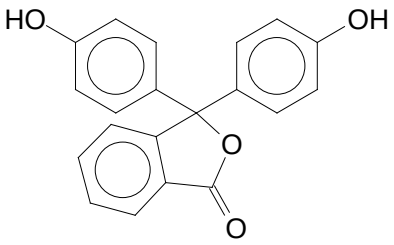
Suggest why brain death occurs within minutes after the poison is administered.

[4]

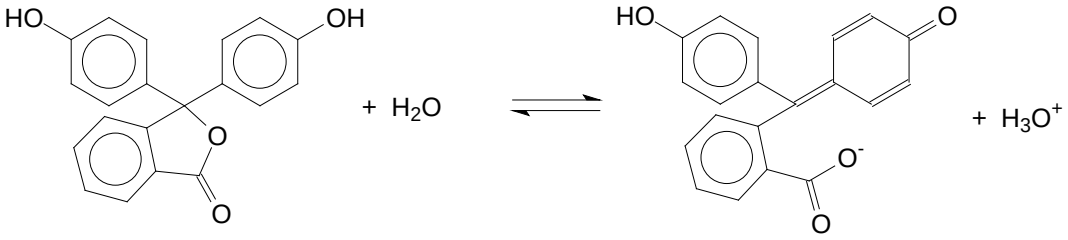
Total 20 marks

5 **(a)** The Kastle-Meyer test is often used to test for the presence of blood at a crime scene. It relies on the peroxidase-like activity of haemoglobin in blood to catalyse the oxidation of colourless phenolphthalein into its bright pink conjugate base.

Phenolphthalein has the following structure:



Phenolphthalein is a *weak acid* which dissociates in water according to the following equation:



colourless (acid) pink (conjugate base)

The pK_a of phenolphthalein is 9.7.

(i) Draw the structure of the compound formed when phenolphthalein is heated with aqueous sodium hydroxide.

(ii) Using Le Chatelier's principle, explain why phenolphthalein appears colourless in an acidic solution.

(iii) Calculate the ratio of the concentration of the conjugate base to the concentration of the acid at pH 10.
Using this ratio, predict and explain the colour of phenolphthalein at pH 10.

[6]

(b) Cinnamic acid, commonly found in cinnamon, has a molecular formula of $C_9H_8O_2$.

It is known that cinnamic acid can react with liquid bromine in the dark. It also undergoes oxidation to form benzoic acid and in the process, carbon dioxide gas was released.

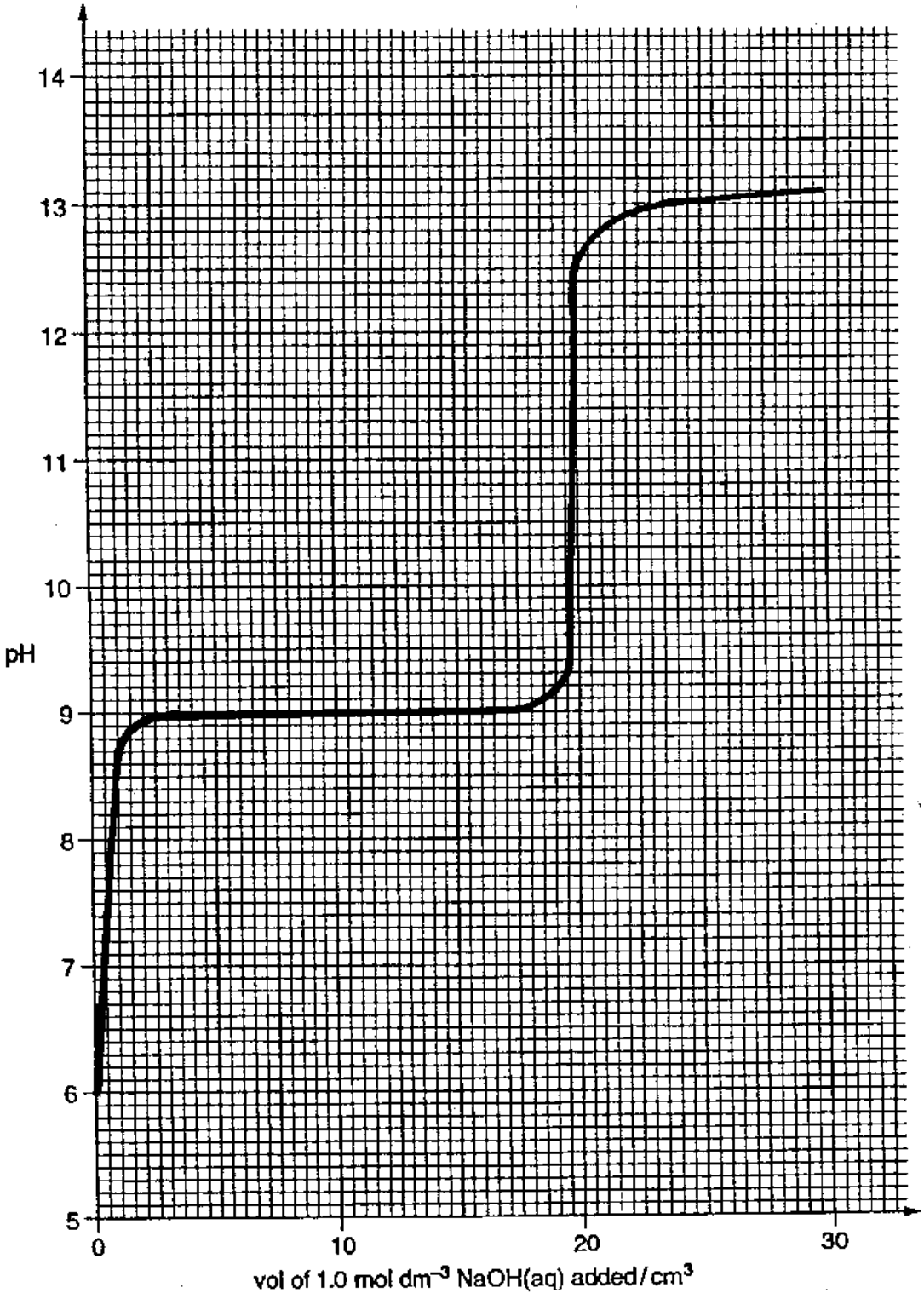
An isomer of cinnamic acid also reacts with liquid bromine in the dark. Upon oxidation with potassium manganate(VII),1 mole of this isomer reacts with 1 mole of sodium carbonate.

Suggest the displayed formulae of cinnamic acid and its isomer and state the type of isomerism exhibited by cinnamic acid.

[3]

(c) Phenolphthalein is usually used as an indicator in a strong base and weak acid titration.

Aqueous magnesium chloride can act as a weak monobasic acid. In an experiment, 50.0 cm^3 of aqueous magnesium chloride was titrated with 1.00 mol dm^{-3} sodium hydroxide. The variation of pH of the solution is as shown in the diagram.



(i) Explain what is meant by the term *weak acid.*

(ii) Write an equation showing hydrated magnesium ion acting as an acid.

(iii) Using the graph above, calculate the initial concentration of magnesium ions.

(iv) Calculate the K_a value for aqueous magnesium chloride.

(v) At the point where 10.0 cm^3 of sodium hydroxide has been added to the solution, a saturated solution of a sparingly soluble salt, magnesium hydroxide, $Mg(OH)_2$, is formed.

Calculate the solubility product, K_{sp} of $Mg(OH)_2$.

[7]

(d) Iodine reacts with propanone in acid solution as follows.

$$I_2 + CH_3COCH_3 \xrightarrow{H^+} CH_3COCH_2I + HI$$

Kinetics studies have shown that the reaction is second order overall, and it has been suggested that the mechanism involves the following three steps.

$$CH_3COCH_3 + H^+ \rightleftharpoons CH_3\overset{+}{C}(OH)CH_3 \quad \text{(fast)}$$

$$CH_3\overset{+}{C}(OH)CH_3 \rightleftharpoons H_2C{=}C(OH)CH_3 + H^+ \quad \text{(slow)}$$

$$H_2C{=}C(OH)CH_3 + I_2 \longrightarrow CH_3COCH_2I + HI \quad \text{(fast)}$$

(i) Explain the meaning of *order of reaction.*

(ii) Construct the rate equation for this reaction.

(iii) An experiment was carried out at 60 °C using reagents of the following concentrations.

Initial concentration / mol dm^{-3}		
$[I_2]$	$[CH_3COCH_3]$	$[H^+]$
0.002	0.050	0.050

The initial rate of reaction was found to be 1.25×10^{-6} mol dm^{-3} s^{-1} under these conditions. Calculate the rate constant for this reaction, stating its units.

[4]

Total 20 marks

END