ANDERSON SERANGOON JUNIOR COLLEGE

2023 JC 2 PRELIMINARY EXAMINATION

NAME:_____ ( ) **CLASS:** 23 / _____

CHEMISTRY **9729/03**

Paper 3 Free Response Questions **18 September 2023**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

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

Answer **all** questions in the spaces provided on the Question Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A
Answer **all** questions

Section B
Answer **one** question

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

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

For Examiner's Use				
Paper 3	A1	/ 15	Paper 1 (15%)	/ 30
	A2	/ 22	Paper 2 (30%)	/ 75
	A3	/ 23	Paper 3 (35%)	/ 80
	B4*	/ 20	Paper 4 (20%)	/ 55
	B5*	/ 20	Percentage	
	*Circle the question you have attempted		Grade	

This document consists of **32** printed pages.

Section A

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

1 **(a)** **(i)** Describe and explain the relative basicities of methylamine, dimethylamine and trimethylamine in the gas phase. [3]

(ii) Explain why amides are neutral. [1]

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(b) Deuterium (symbol D or $^{2}_{1}H$) was discovered in 1931. Deuterium accounts for 0.0156% of all the naturally occurring hydrogen in the oceans, while the most common isotope $^{1}_{1}H$ accounts for 99.98%. Tritium (symbol T or $^{3}_{1}H$), a rare and radioactive isotope of hydrogen account for only 0.0044%.

Chemically, deuterium behaves similarly to ordinary hydrogen.

(i) Calculate the average A_r of hydrogen. Give your answer to four decimal places. [1]

(ii) On the same diagram, sketch how a beam of singly positively charged deuterium ions and a beam of hydrogen ions will behave in an electric field.

In your diagram, indicate clearly the relative angle of deflection for each beam. (You may let the angle of deflection of hydrogen ions be $x°$) [2]

(iii) Explain the difference in the thermal stability of DC*l*, DBr and DI. [2]

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(c) Deuterium can replace the normal hydrogen in water molecules to form heavy water, D_2O.

Some data of light water and heavy water are given in Table 1.1.

Table 1.1

Property	D_2O (Heavy water)	H_2O (Light water)
Freezing point (^oC)	3.82	0.00
Boiling point (^oC)	101.4	100.0
Density at standard temperature and pressure (g cm^{-3})	1.106 (solid)	0.998 (solid)

(i) Suggest if distillation is effective in separating heavy water from light water. [1]

(ii) Using Table 1.1, suggest with reasoning, how a scientist can differentiate the two types of water without the use of a temperature measuring device.
(Density of liquid light water is 1.0 g cm^{-3}) [2]

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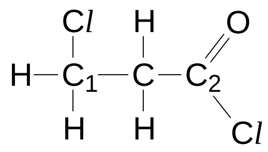
(d) Deuterated solvents (such as D_2O) are a group of compounds where one or more hydrogen atoms are substituted by deuterium atoms. It may be assumed that they have similar chemical reactivity as their hydrogen analogues.

(i) D_2O is added to 3-chloropropionyl chloride.



3-chloropropionyl chloride

Comment on the reactivity of C_1 and C_2 and write a balanced chemical equation for the reaction. [2]

(ii) Construct a balanced chemical equation to show how deuterated ethanol, C_2D_5OD, reacts with ethanoic acid, CH_3CO_2H in the presence of acid catalyst. [1]

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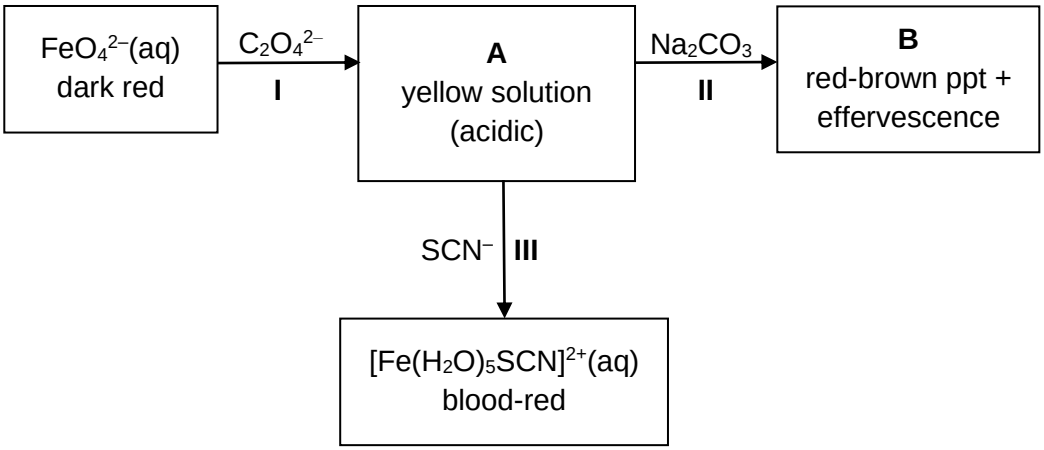
2 **(a)** Iron is a transition metal.

The following scheme illustrates a series of reactions involving various oxidation states of iron.



(i) Explain why $[Fe(H_2O)_5SCN]^{2+}(aq)$ is blood-red. [3]

(ii) State the formula of the cation present in **A** and identify **B**. [1]

(iii) State the type of reaction that occurred in **I, II** and **III**. [3]

(iv) With the aid of relevant equations, explain why
- solution **A** is acidic.
- effervescence was observed from reaction **II**. [3]

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(b) The electrolysis of an aqueous solution of potassium hydroxide was carried out using an iron anode and a platinum cathode. After a current was passed through the cell for some time, 360 cm^3 of gas was collected at the cathode (measured at r.t.p.) while there was a loss of mass of 0.279 g at the anode.

Determine the oxidation state of iron in the iron-containing product after electrolysis. [2]

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(c) Fig. 2.1 shows the octahedral geometry of a transition metal complex with six monodentate ligands, **L**.

(i) Explain what is meant by a *transition element*? [1]

(ii)

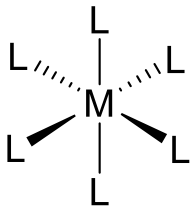

Fig. 2.1

With reference to an octahedral complex, the *cis-trans* isomers are defined as follows:

Cis isomer: Same groups of atoms are on the same side of the central metal atom, i.e. 90° from each other.

Trans isomer: Same groups of atoms are on directly opposite sides of the central metal atom i.e. 180° from each other.

$[Fe(H_2NCH_2CH_2NH_2)_2Cl_2]^+$ forms an octahedral cationic complex where each $H_2NCH_2CH_2NH_2$ ligand forms 2 bonds with the central Fe(III) ion. Similar to organic molecules, this complex can exist as a pair of *cis-trans* isomers.

Using the information above, draw the 3-dimensional structures of the *cis-trans* isomers of $[Fe(H_2NCH_2CH_2NH_2)_2Cl_2]^+$ and label the isomers. [2]

(iii) Identify the isomer in **(c)(ii)** that is optically inactive. Explain your answer. [1]

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A chemist used the set-up shown in Fig. 2.2 to investigate if a solution which consists of concentrated hydrochloric acid and iron(II) chloride, can be used to produce iron metal via electrolysis. An organic fuel cell, the direct ethanol fuel cell, is used to drive the electrolysis.

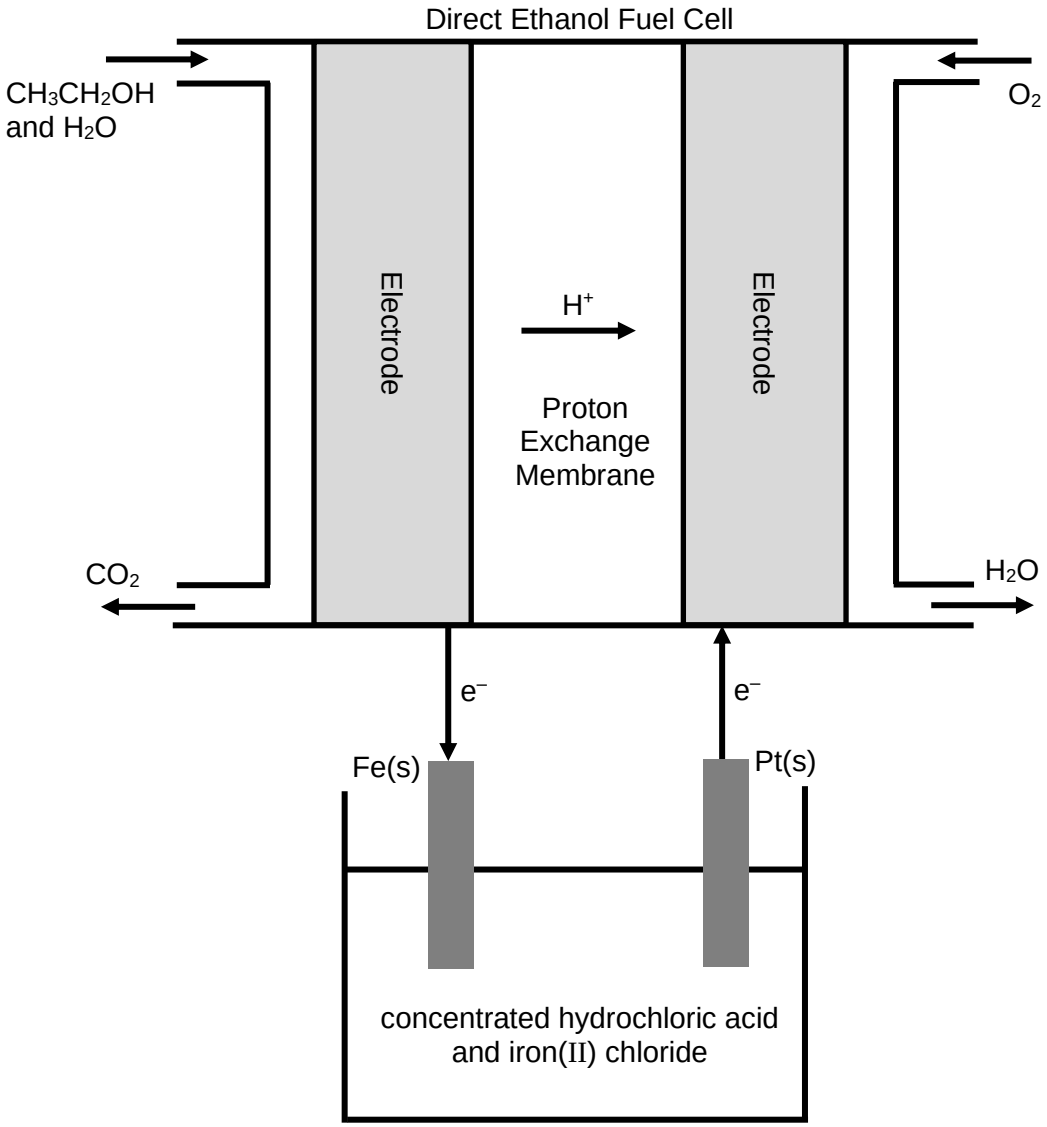

Fig. 2.2

(d) The reaction that takes place at one of the electrodes of the direct ethanol fuel cell involves the reduction of oxygen gas as follows.

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

(i) Construct the half equation at the anode of the direct ethanol fuel cell, given that carbon dioxide is produced at the anode. Hence, write the overall equation for the reaction that occur in the fuel cell. [2]

(ii) The direct ethanol fuel cell generates an e.m.f. of 1.56 V.

By using suitable data from the *Data Booklet*, suggest a value for the $E^{\ominus}$ of the CO_2/CH_3CH_2OH electrode reaction. [1]

(iii) Use data from the *Data Booklet* to predict the reaction that will occur at the iron electrode of the electrolytic cell. Write equation for the reaction.

Hence, deduce if iron can be produced using the set up in Fig. 2.2. [2]

(iv) Suggest why chlorine gas is preferentially produced at the platinum electrode. [1]

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3 (a) The position of substitution in the electrophilic substitution of mono-substituted arenes can be explained based on the stability of the intermediate carbocation formed.

Fig. 3.1 shows three possible first steps in the nitration of methylbenzene.

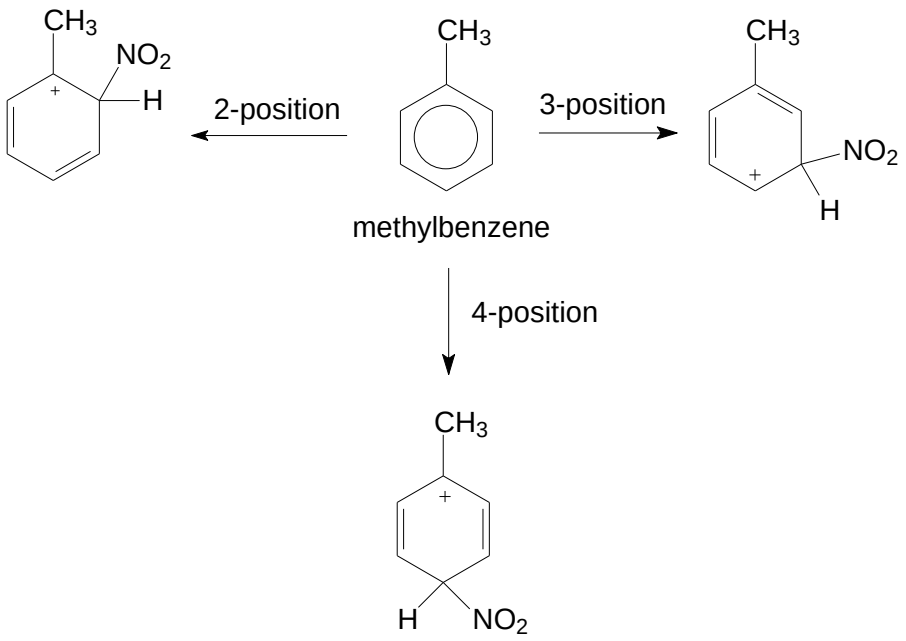

Fig. 3.1

(i) Use the information in Fig. 3.1 to suggest why the $-CH_3$ group directs incoming electrophiles to the 2– and 4–positions in preference to the 3–position. [2]

(ii) When nitration of methylbenzene is carried out and the isomers are analysed, it was found that the mole ratio between 2-nitromethylbenzene and 4-nitromethylbenzene is about 2 : 1.

Suggest an explanation for this. [1]

(iii) 3–aminobenzoic acid can be synthesised from methylbenzene as shown in Fig. 3.2.

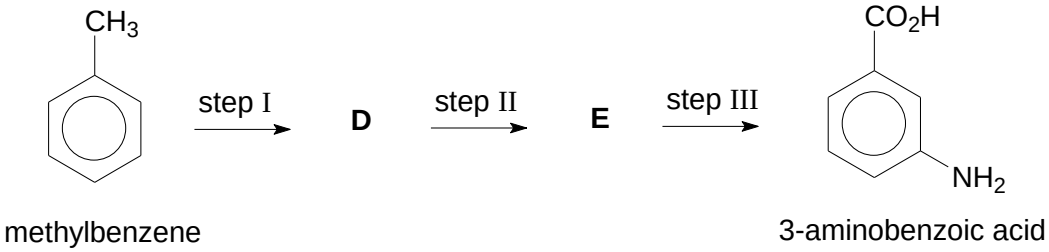

Fig. 3.2

Suggest structures for the intermediates **D** and **E** and the reagents and conditions for steps I, II and III. [5]

(b) Friedel–Crafts alkylation, using $AlCl_3$ as a catalyst, is usually carried out in anhydrous conditions.

(i) Suggest why the reaction has to be carried out under anhydrous condition. [1]

In the presence of $AlCl_3$ and under suitable conditions, benzene reacts with CCl_4 via electrophilic substitution to form a mixture of trichlorophenylmethane, $C_6H_5CCl_3$ and dichlorodiphenylmethane, $(C_6H_5)_2CCl_2$.

The reaction occurs in several steps.

- The first step is an acid–base reaction between $AlCl_3$ and CCl_4.

$$AlCl_3 + CCl_4 \rightarrow AlCl_4^- + CCl_3^+$$

- The benzene ring is then attacked by the CCl_3^+ electrophile in the second step.

(ii) $AlCl_3$ behaves as a Lewis acid in the first step. Explain what is meant by the term *Lewis acid*. [1]

(iii) Suggest a mechanism for the reaction between benzene and CCl_3^+ electrophile to form $C_6H_5CCl_3$. [2]

(iv) Suggest a reason why further alkylation of $(C_6H_5)_2CCl_2$ does not take place. [1]

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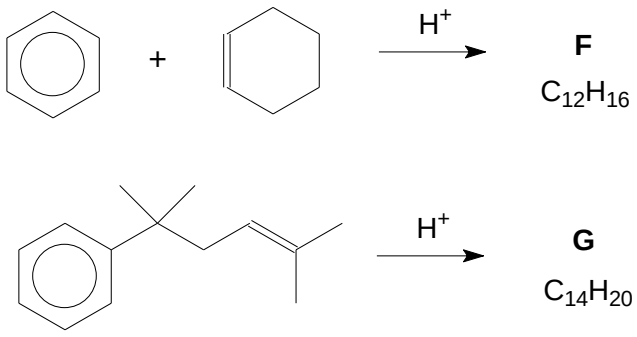
An example of Friedel–Crafts alkylation which can be done in non–anhydrous conditions is shown in Fig. 3.3.

Reaction I

Fig. 3.3

(c) **(i)** Using the information given about **Reaction I**, suggest the structure of the product for each of the following reactions.

Both compounds **F** and **G** do not react with aqueous bromine. Only compound **F** decolourises hot, acidified potassium manganate(VII).



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Electrophilic substitution in phenol occurs much faster, and under milder conditions, than in benzene. Fig. 3.4 shows another Friedel–Crafts alkylation carried out in acidic condition.

Reaction II

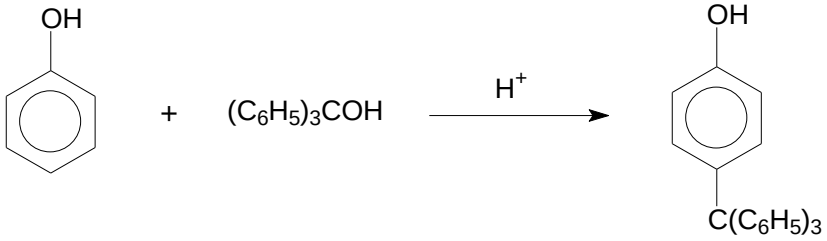
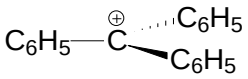


Fig. 3.4

Reaction II cannot take place if benzene is used instead of phenol.

(ii) The electrophile formed in **Reaction II** is shown below.



With reference to the structure of the electrophile formed, suggest why the activation energy of **Reaction II** is high. [1]

(iii) Hence, suggest why phenol is required for **Reaction II** to occur. [1]

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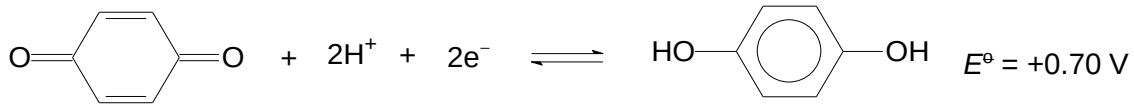
(d) Quinone, $C_6H_4O_2$, can be formed by oxidising quinol, $C_6H_6O_2$ with acidified $KMnO_4$.



quinone quinol

(i) Calculate $E^{\ominus}_{cell}$ for the overall reaction between quinol and acidified $KMnO_4$. [1]

(ii) Construct a balanced equation for this reaction and hence determine its $\Delta G^{\ominus}$, in kJ mol^{-1}. [3]

(iii) Using the list of standard electrode potentials in the *Data Booklet*, identify a gas that would reduce quinone to quinol. Explain your answer. [2]

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Section B

Answer **one** question from this section.

4 (a) In aqueous solution, chlorine dioxide, ClO_2, reacts with hydroxide ions as shown.

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

A series of experiments is carried out using different concentrations of ClO_2 and OH^-. Table 4.1 shows the results obtained.

Table 4.1

Experiment	$[ClO_2]$ / mol dm^{-3}	$[OH^-]$ / mol dm^{-3}	Initial rate / mol dm^{-3} min^{-1}
1	0.02	0.030	7.20×10^{-4}
2	0.02	0.120	2.88×10^{-3}
3	0.05	0.015	2.25×10^{-3}

(i) Define the term order of reaction. [1]

(ii) Use the data in the Table 4.1 to determine the order of reaction with respect to each reactant, ClO_2 and OH^-.

Explain your reasoning. [2]

(iii) Use your answer to **(a)(ii)** to construct the rate equation for this reaction. Hence, calculate the value of the rate constant *k*. [2]

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(b) Explain, with the aid of a labelled Boltzmann distribution diagram, the effect on a rate constant on increasing temperature from T_1 to T_2. [3]

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(c) A three-step synthesis of benzaldehyde from methylbenzene is shown in Fig. 4.1.

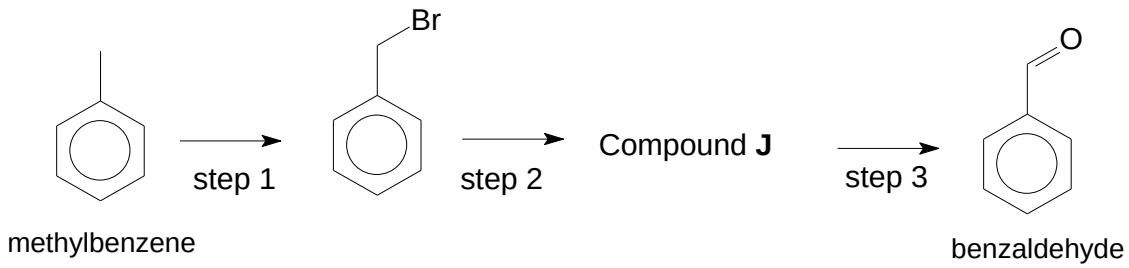

Fig. 4.1

Compound **J** does not dissolve in aqueous NaOH.

(i) Suggest the structure of compound **J**. [1]

(ii) State the reagents and conditions for steps 2 and 3. [2]

(iii) A hydrocarbon by-product $C_{14}H_{14}$ was formed from step 1. Draw the structure of this hydrocarbon and suggest how it was formed. [1]

(iv) $LiAlH_4$ reacts with benzaldehyde but not with alkenes. Explain why. [2]

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(d) Solid samples of **K**, **L** and **M** are added separately into hydrochloric acid and sodium hydroxide. The observations are recorded in Table 4.2.
Each sample is known to be pure and can only be Na_2O, Al_2O_3, SiO_2 or P_4O_{10}.

Table 4.2

Unknown	Observations
K	Reacts with both hydrochloric acid and sodium hydroxide
L	Reacts with hot concentrated sodium hydroxide
M	Reacts with hydrochloric acid

(i) Use Table 4.2 to identify unknown **K**, **L** and **M**. [1]

(ii) Write equations to show how **K** reacts with hydrochloric acid and sodium hydroxide. [2]

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(e) Salts are often used as a de-icing agent to melt ice on roads in winter. When the salt dissolves in water present on the roads, it causes the melting point of ice to drop to below 0 ^{o}C, promoting the melting of the remaining ice.

Table 4.3

Lattice energy of $CaCl_2$(s)	–2240 kJ mol^{-1}
enthalpy change of hydration of Cl^-(g)	–378 kJ mol^{-1}
enthalpy change of hydration Ca^{2+}(g)	–1579 kJ mol^{-1}

(i) Using information from Table 4.3, calculate ΔH_{sol} of $CaCl_2$(s). [1]

(ii) By considering ΔG of the dissolution of $CaCl_2$, your answer from **(e)(i)** and assuming that ΔS_{sol} of $CaCl_2$(s) is close to zero , state and explain if $CaCl_2$ can also be used to de-ice roads. [2]

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5 **(a)** Diazomethane, CH_2N_2, reacts with water to give methanol and nitrogen gas.

$$CH_2N_2 + H_2O \rightarrow CH_3OH + N_2$$

When 2.50×10^{-3} mol of CH_2N_2 was added into water, the volume of nitrogen gas evolved at various time intervals after the start of the reaction were measured. The experiment results are plotted in Fig. 5.1.

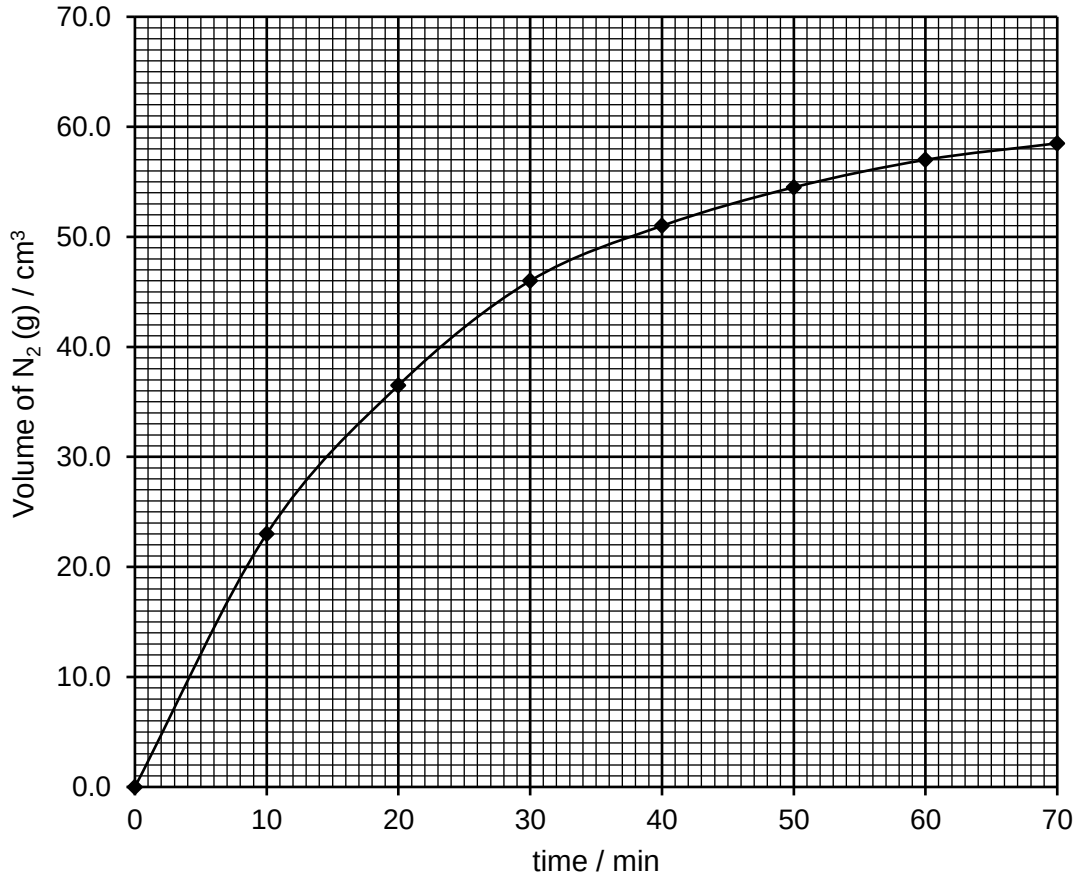

Fig. 5.1

(i) Using the information provided, show that the maximum volume of nitrogen gas, collected at room temperature and pressure is 60 cm^3. [1]

(ii) Hence, use Fig. 5.1 to show that the reaction is first order with respect to $[CH_2N_2]$. [1]

The reaction of CH_2N_2 with water takes place in the presence of an acid.
Two experiments were conducted at different pH values to investigate the kinetics of this reaction. The results are shown in Table 5.1.

Table 5.1

Experiment	initial $[CH_2N_2]$ / mol dm^{-3}	pH	Relative initial rate
1	1.00×10^{-3}	1.00	1
2	6.00×10^{-3}	1.30	1.5

(iii) Calculate the concentration of $H^+(aq)$ in experiment 1 and 2. [1]

(iv) Use the data provided to determine the order of reaction with respect to $[H^+]$, and hence write the rate equation for the reaction. [2]

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(b) Tartrate ions, $(CHOHCO_2^-)_2$ are oxidised by hydrogen peroxide to carbon dioxide and water. The reaction can be catalysed by adding $Fe^{2+}(aq)$ catalyst.

(i) State the property, typical of transition metals, which allows $Fe^{2+}(aq)$ to behave as a catalyst in this reaction. [1]

(ii) Using the half equation,

$$4CO_2(g) + 8H^+(aq) + 10e^- \rightleftharpoons (CHOHCO_2^-)_2(aq) + 2H_2O(l)$$

and relevant half equations from the *Data Booklet,* suggest a two-step mechanism to show how $Fe^{2+}(aq)$ functions as a catalyst in this reaction. [2]

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(c) The synthesis of HCN was developed in the early 1900s.

$$CH_4(g) + NH_3(g) + \frac{3}{2} O_2(g) \rightarrow HCN(g) + 3\ H_2O(l) \qquad \Delta H = -506\ kJ\ mol^{-1}$$

(i) Explain why the entropy change of the above reaction is negative. [2]

(ii) Hence, comment on the effect of temperature on the spontaneity of this reaction. [2]

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(d) **P** and **Q** are oxides of Period 3 elements.

P is a solid with a high melting point. It conducts electricity when molten. **P** is sparingly soluble in water to form a solution of pH 9.0.

Q is a solid at room temperature. It dissolves in water to form a solution of pH 2.

Identify **P** and **Q** and write equations for all reactions. [4]

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(e) Compound **X**, $C_3H_4O_3$, liberates a gas when treated with aqueous sodium carbonate.

Compound **X** is formed as the only organic product when a neutral organic compound **Y**, $C_4H_8O_3$, is heated with acidified $KMnO_4$.

Both **X** and **Y** give yellow precipitate with alkaline aqueous iodine.

Deduce the structures of **X** and **Y.** Suggest explanations for your answer that are consistent with information provided. [4]

[Total: 20]

Additional answer space

If you use the following page to complete the answer to any question, the question number must be clearly shown.