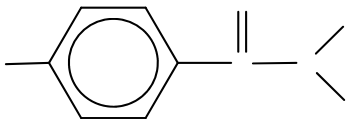
Answer any **four** questions

**1** **(a)** Acidified potassium manganate, $KMnO_4$, is a strong oxidising agent which can oxidise both $\mathbf{X}^{2+}$ and $C_2O_4^{2-}$ in $\mathbf{X}C_2O_4$. One of the products of this reaction is $CO_2$. 15.00 $cm^3$ of 0.1 mol $dm^{-3}$ acidified $KMnO_4$ was found to completely oxidise 25.0 $cm^3$ of 0.1 mol $dm^{-3}$ $\mathbf{X}C_2O_4$ solution.

**(i)** Write a balanced equation for the reaction between $MnO_4^-$ and $C_2O_4^{2-}$ only. Hence, determine the volume of $KMnO_4$ needed to oxidise $C_2O_4^{2-}$ only.

**(ii)** Using your answer in **(a)(i)**, find the oxidation state of **X** in the product. **[5]**

**(b)** The following table lists the boiling points of some organic compounds.

| Compound | Formula | $M_r$ | Boiling point / °C |
|---|---|---|---|
| **A** | $CH_3CH_2CH_2CH_2OH$ | 74 | 118 |
| **B** | $CH_3CH_2CH_2CH_2CH_3$ | 72 | 36 |
| **C** |  | 191 | 130 |

By reference to the type and extent of relevant intermolecular forces, explain the differences in boiling points between **A** and **B** and between **A** and **C**. **[4]**

**(c)** The elements **Y** and **Z** can be one of the following: Na, Mg, A*l*, Si and P.

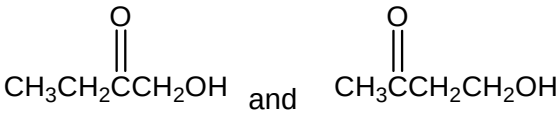
Both the chloride and oxide of **Y** can react with aqueous sodium hydroxide. The oxide of **Y** can also react with aqueous hydrochloric acid.

Element **Z** has a chloride and an oxide and both react vigorously with water to form a solution of pH = 2.

Identify the elements **Y** and **Z**.
Explain the above observations with the help of relevant balanced equations. **[5]**

**1** **(d)** Suggest a simple chemical test to distinguish between each pair of compounds. State the reagents and conditions needed and give the expected observations for each compound.

**(i)**




**P** **Q**

**(ii)**

and

**R** **S**

**[4]**

**(e)** Suggest a synthesis to convert $CH_2$=$CHCH_2Br$ into $CH_2$=CHCHO. Include all reagents and conditions and draw all intermediates formed. **[2]**

**[Total：20]**

O

**2** **(a)** In one compartment of a voltaic cell, a graphite rod dips into an acidic solution of $K_2Cr_2O_7$ and $Cr(NO_3)_3$. In the other compartment, a tin bar dips into a $Sn(NO_3)_2$ solution. A $KNO_3$ salt bridge joins the two compartments.

**(i)** Draw an apparatus diagram to show the set up of the cell. In your diagram, include the direction which electrons flow when the two compartments are connected by a wire.

**(ii)** Give one use of the $KNO_3$ salt bridge in the set up.

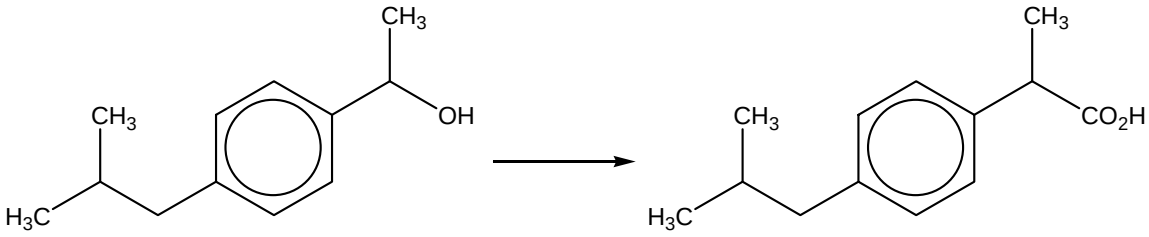
**(iii)** Write an equation for the overall cell reaction and calculate the overall cell potential under standard conditions.

**(iv)** If a current of 0.2 A is drawn from the cell for 2.5 hours, what is the change in mass of the tin bar? **[8]**

**(b)** **(i)** When iodide ions ($I^-$) and peroxodisulfate ions ($S_2O_8^{2-}$) are mixed, the reaction proceeds at a very slow rate. However, when aqueous $CoCl_3$ is added, the reaction speeds up, producing $SO_4^{2-}$ and $I_2$.
By considering relevant $E^\theta$ values from the *data booklet*, show by means of balanced equations, how $CoCl_3$ carries out its role in this reaction.

**(ii)** Adding excess dilute ammonia to an aqueous solution of copper(II) sulfate, causes the formation of a deep blue solution. When a small amount of aqueous hexadentate edta ($edta^{4-}$) is added, the deep blue solution changes to a paler blue.
Explain the colour changes by means of balanced equations.
Hence, arrange the ligands involved in order of increasing strength. **[5]**

**2 (c)** Ibuprofen is an anti-inflammatory drug which is only available under doctor's prescription in Singapore. It can be synthesized in the following manner.




**A** **Ibuprofen**

**(i)** Suggest a synthesis to convert **A** into Ibuprofen.
Include all reagents and conditions and draw all intermediates formed.

**(ii)** Describe with the aid of a diagram, the type of isomerism present in Ibuprofen.

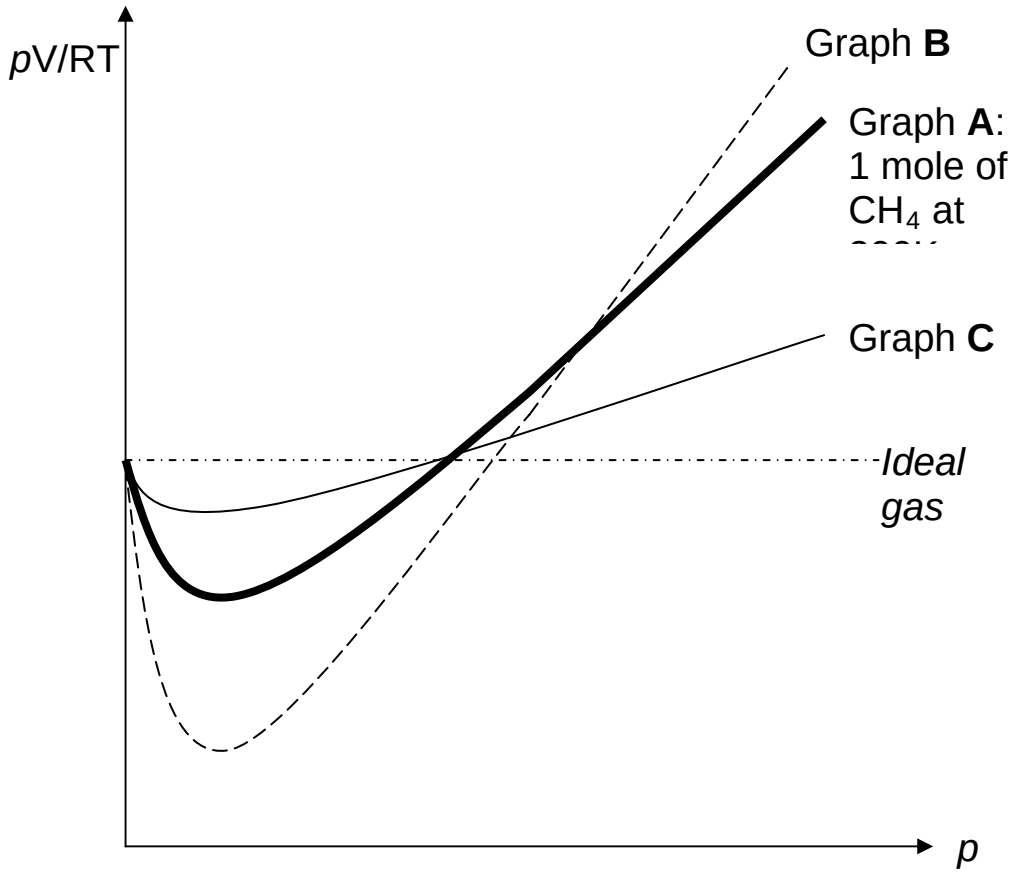
**(iii)** Explain if **A** or Ibuprofen has a higher p$K_a$ value. **[7]**

**[Total: 20]**

**3** **(a)** The values of pV/RT are plotted against p for one mole of the following gases at the specified temperature:

- One mole of $CH_4$ at 300K
- One mole of $CH_4$ at 500K
- One mole of $NH_3$ at 300K

Given that graph **A** is obtained for 1 mole of $CH_4$ at 300K, identify and explain what Graphs **B** and **C** represent.




**[4]**

**3 (b)** Methane can react with steam to give carbon monoxide and hydrogen gas in the presence of a nickel catalyst.

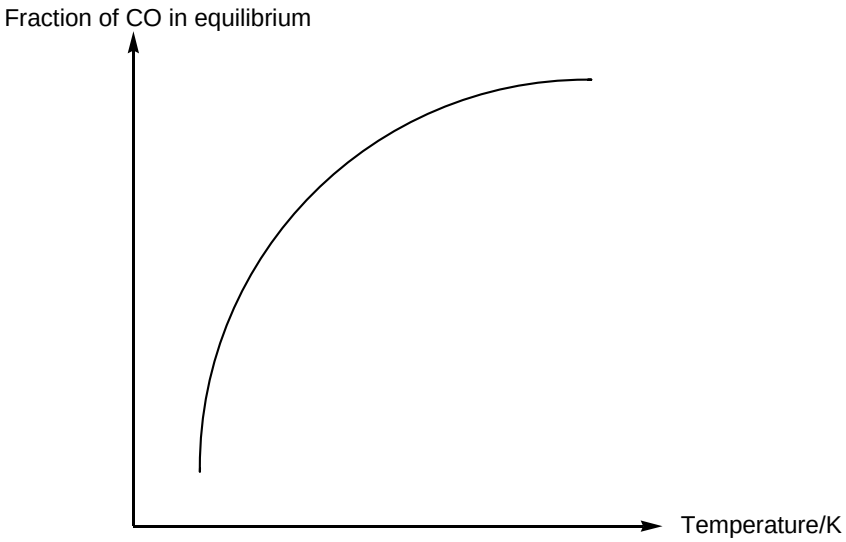
$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

When a 3:1 mole ratio of methane and steam at a total initial pressure of 4 atm is passed over nickel catalyst at 450 $^{o}$C, the partial pressure of carbon monoxide at equilibrium is found to be 0.66 atm.

**(i)** Write an expression for $K_p$ and calculate its value, giving its units.

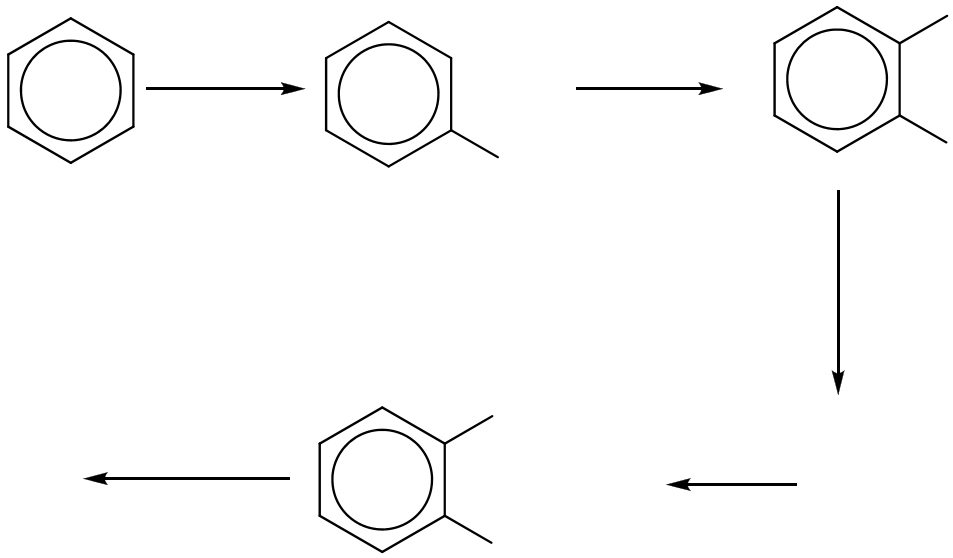
**(ii)** Predict and explain the effect of increasing pressure on the equilibrium position and the value of $K_p$.

**(iii)** The graph below shows how the fraction of CO produced varies with temperature.




Deduce whether the reaction of methane with steam is an exothermic or an endothermic process. **[7]**

**3 (c)** Benzene can be used as a starting reagent for many chemical compounds.

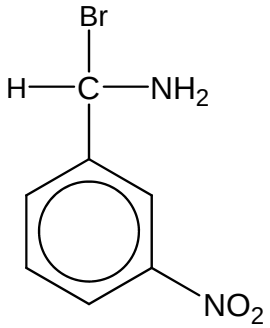


**(i)** Name the type of reaction in Step **I** and outline the mechanism.

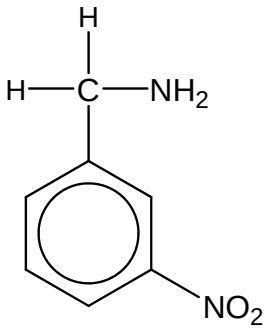
**(ii)** List the reagents and conditions required for Steps **II** to **III**.

**(iii)** Draw the structures of **P** and **Q**.

**(iv)** State and explain which of the following compounds, **R** or **S**, will have a higher p$K_b$ value.




**R**




**S**

**[9]**

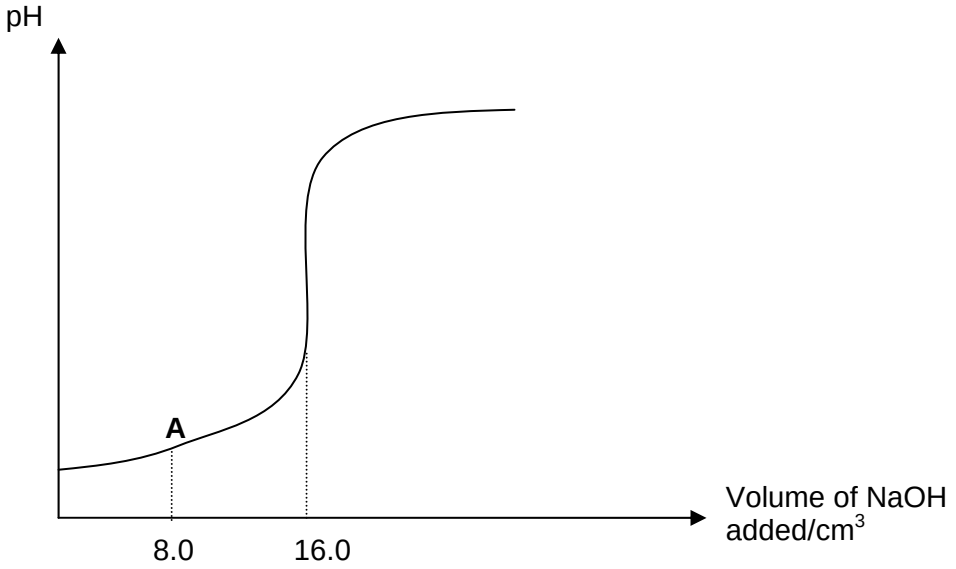
**[Total: 20]**



ethanoyl

**4** **(a)** The major acidic component of soured milk is lactic acid, $CH_3CH(OH)COOH$.

When 10.0 $cm^3$ of a solution of 0.08 mol $dm^{-3}$ of the lactic acid was titrated against sodium hydroxide solution, the following titration curve was obtained.




**(i)** The pH of lactic solution before adding any NaOH(aq) is 2.5.

Deduce the acid dissociation constant, $K_a$, of lactic acid.

**(ii)** Calculate the pH of the solution at point **A**.

**(iii)** Explain, with the aid of an equation, what happens when a small amount of acid is added at point **A**.

**(iv)** Calculate the pH at the equivalence point and state a suitable type of indicator for this titration. **[7]**

**4 (b)** Barium is a group II element that is commonly used in glassmaking and fireworks to give a green colouration.

Common compounds of barium include barium nitrate and barium chloride.

**(i)** Write a balanced equation for the thermal decomposition of barium nitrate.

**(ii)** How does the temperature required to decompose the nitrates of Group II elements vary down the group?
Explain this trend.

**(iii)** How would you expect the lattice energy of barium nitrate to differ from barium chloride? Explain.

**[5]**

**(c)** Stereoisomer **A**, with molecular formula $C_6H_{11}Cl$, reacts with hot acidified potassium manganate(VII) solution to form a mixture of **B** and **D**.

**B** is an unsymmetrical molecule which forms a yellow precipitate with hot alkaline iodine solution. Cold alkaline hydrogen cyanide is added to **B** and the product formed is reduced to form compound **C**.

Compound **D** forms a white precipitate when refluxed with ethanolic silver nitrate and also reacts with phosphorous pentachloride to form compound **E**.

Compounds **C** and **E** are then reacted to form compounds **F** and **G**. Compound **F** is neutral and both compounds **F** and **G** have an identical molecular formula, $C_7H_{14}O_2NCl$.

Suggest the identities of **A**, **B, C, D**, **E**, **F**, and **G**, explaining your reasoning. **[8]**

**[Total：20]**

**5** **(a)** **(i)** Define the term enthalpy change of hydration, with reference to the chloride ion.

**(ii)** By using the following data, calculate the enthalpy change of hydration of the chloride ion.

| | |
|---|---|
| Enthalpy change of solution of sodium chloride | - 2 kJ $mol^{-1}$ |
| Enthalpy change of hydration of sodium ion | - 390 kJ $mol^{-1}$ |
| Lattice energy of sodium chloride | -722 kJ $mol^{-1}$ |

**(iii)** Explain how you would expect the numerical value of enthalpy change of hydration of the iodide ion to compare with that of the chloride ion. **[4]**

**(b)** Carbon dioxide gas is produced when aqueous bromine reacts with methanoic acid, as shown in the equation below.

$$Br_2(aq) + HCOOH(aq) \rightarrow 2Br^-(aq) + 2H^+(aq) + CO_2(g)$$

An experiment was conducted to determine the order of reaction with respect to bromine. 20 $cm^3$ of 0.50 mol $dm^{-3}$ of aqueous bromine was reacted with 20 $cm^3$ of 5 mol $dm^{-3}$ methanoic acid. The volumes of carbon dioxide gas produced at various times in the reaction is shown in **Table 1**.

| ***Time / s*** | ***Volume of $CO_2$ / $cm^3$*** |
|---|---|
| 0 | 0 |
| 30 | 24.00 |
| 60 | 45.60 |
| 90 | 64.80 |
| 120 | 81.60 |
| 180 | 112.80 |
| 240 | 134.40 |
| 360 | 170.40 |
| 480 | 194.40 |
| 600 | 208.80 |

**Table 1**

All volumes are measured at room temperature and pressure.

**5 (b) (i)** Determine the maximum volume of $CO_2$ which can be produced from the experiment.

**(ii)** Plot a graph of volume of $CO_2$ produced against time.

A second set of experiment was conducted with the concentration of $Br_2$(aq) kept constant at 0.50 mol $dm^{-3}$ and the concentration of HCOOH(aq) varied. The following results were obtained.

| ***Experiment no.*** | ***initial [HCOOH] / mol $dm^{-3}$*** | ***initial rate of production of $CO_2$ / $cm^3$ $s^{-1}$*** |
|---|---|---|
| 1 | 5.0 | 0.825 |
| 2 | 1.25 | 0.206 |

**Table 2**

**(iii)** Using your graph, together with the results in **Table 2**, deduce the order of reaction with respect to:

1. $Br_2$
2. HCOOH

**(iv)** Experiment 1 was repeated using 0.40 mol $dm^{-3}$ $Br_2$(aq) instead of 0.50 mol $dm^{-3}$. The concentration of HCOOH was kept constant at 5 mol $dm^{-3}$. Sketch, on the same axes as **(b)(ii)**, the graph of the volume of carbon dioxide gas produced against time for this experiment.

**(v)** The above reaction is catalysed by acid. With the aid of a well-labelled diagram of a Boltzmann Distribution curve, explain how the rate of reaction will be affected by the catalyst. **[10]**

**5 (c)** *The Use of the Data Booklet is relevant in this part question.*

Two structural isomers, **A** and **B**, have the molecular formula $C_3H_6O_2$.

Both **A** and **B** do not give any effervescence with solid sodium carbonate.
**A** and **B** also do not give any precipitates with hot alkaline aqueous $I_2$.

0.370 g of **A** reacts with sodium metal to form a flammable gas that takes up 125.8 $cm^3$ of space at 32.5 $^oC$ and 101 kPa while **B** does not produce any gas with sodium.

Draw the displayed formulae of **A** and **B**, explain the reactions as fully as you can. **[6]**

**[Total：20]**

**~ END OF PAPER ~**