NAME ________________________ CLASS **20S**

JURONG PIONEER JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION 2021

CHEMISTRY
9729/03

Higher 2
20 September 2021

Paper 3 Free Response Questions
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

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 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 end of this booklet. The question number must be clearly shown.

Section A
Answer all questions.

Section B
Answer **one** question.

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	**20**
2	**20**
3	**20**
4 or 5	**20**
Penalty (delete accordingly)	
Lack **3sf** in final answer	**–1 / NA**
Missing/wrong **units** in final ans	**–1 / NA**
Bond linkages	**–1 / NA**
Total	**80**

This document consists of **27** printed pages and **1** blank page.

Answer **all** the questions.

1 Period 3 elements react with oxygen and nitrogen in various ways.

(a) Compounds **A**, **B** and **C** are the solid oxides of three Period 3 elements.

- When excess cold water is added separately to **A**, **B** and **C**, only **B** and **C** are able to dissolve readily.
- The resulting aqueous solution from **B** reacts with solid sodium carbonate in a mole ratio of 2:3. Effervescence is observed.
- The resulting aqueous solution from **C** reacts with solid ammonium nitrate to give a pungent gas upon heating.
- When **A** is added separately to the resulting aqueous solutions from **B** and **C**, it dissolves.

State and explain the identities of **A**, **B** and **C**. You are to include the equations for the reactions of the oxides, **B** and **C** with water. [6]

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(b) When heated, solid magnesium amide, $Mg(NH_2)_2$ decomposes to form magnesium nitride, Mg_3N_2, and ammonia gas as the only products.

(i) Construct a balanced equation for the thermal decomposition of $Mg(NH_2)_2$. [1]

(ii) The variation in the thermal stability of Group 2 amides is the same as that of Group 2 carbonates.

Explain whether magnesium amide is more or less thermally stable than barium amide. [2]

(iii) A sample of Mg was burnt in air to give 1.00 g of powder which was then added to hot water. The reaction is represented as follows.

$$Mg_3N_2(s) + 6H_2O(l) \rightarrow 3Mg(OH)_2(s) + 2NH_3(aq)$$

The ammonia evolved required 12.0 cm^3 of 0.50 mol dm^{-3} hydrochloric acid for complete neutralisation.

Calculate the percentage by mass of magnesium nitride in the 1.00 g of powder obtained from the burning of Mg in air. [2]

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(c) The presence of halide ions in natural water sources such as rivers and lakes are usually detected using aqueous ammonia and aqueous silver nitrate.

The following equation shows the precipitation of AgC*l*,

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

Thermodynamic quantity	**Value**
$K_{sp}(AgCl)$	1.8×10^{-10} mol^2 dm^{-6}
ΔS_{ppt} (AgC*l*)	–410 J mol^{-1} K^{-1}
ΔH_{hyd} (Ag^+)	–473 kJ mol^{-1}
ΔH_{hyd} (Cl^-)	–378 kJ mol^{-1}

Table 1.1

(i) 5 cm^3 of 0.0100 mol dm^{-3} of silver nitrate is added to a 30 cm^3 sample of river water containing chloride ions.

What is the minimum concentration, in mol dm^{-3}, of chloride ions present in the river water when the first trace of precipitate appears? [2]

(ii) To another sample of river water, aqueous silver nitrate is added, followed by excess aqueous ammonia. A cream precipitate is formed which is partially soluble in excess.

Suggest the identity of the precipitate and thus identify the halide present in this sample of river water. [1]

(iii) When a precipitate is formed, ΔG_{ppt} is given by the following expression.

$$\Delta G_{ppt} = RT \ln K_{sp}$$

Using appropriate data in **Table 1.1**, calculate ΔG_{ppt}, in kJ mol^{-1}, and hence ΔH_{ppt} for the precipitation of AgC*l* at room temperature.

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

[2]

(iv) Using your answer in **(c)(iii)** and data in **Table 1.1**, calculate the lattice energy for AgC*l*. [2]

(v) The theoretical lattice energy for AgC*l* is found to be –770 kJ mol^{-1}.

State and explain the reason for the difference between the theoretical value and your answer in **(c)(iv)**. [2]

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For Examiner's Use

[Total: 20]

2 (a) Aqueous sodium carbonate reacts with H^+ in two stages.

$$CO_3^{2-} \xrightarrow{+H^+} HCO_3^- \xrightarrow{+H^+} CO_2 + H_2O$$

0.200 mol dm^{-3} nitric acid was added gradually to a 20.0 cm^3 solution containing both Na_2CO_3 and $NaHCO_3$. The changes in pH are monitored as shown in **Figure 2.1**.

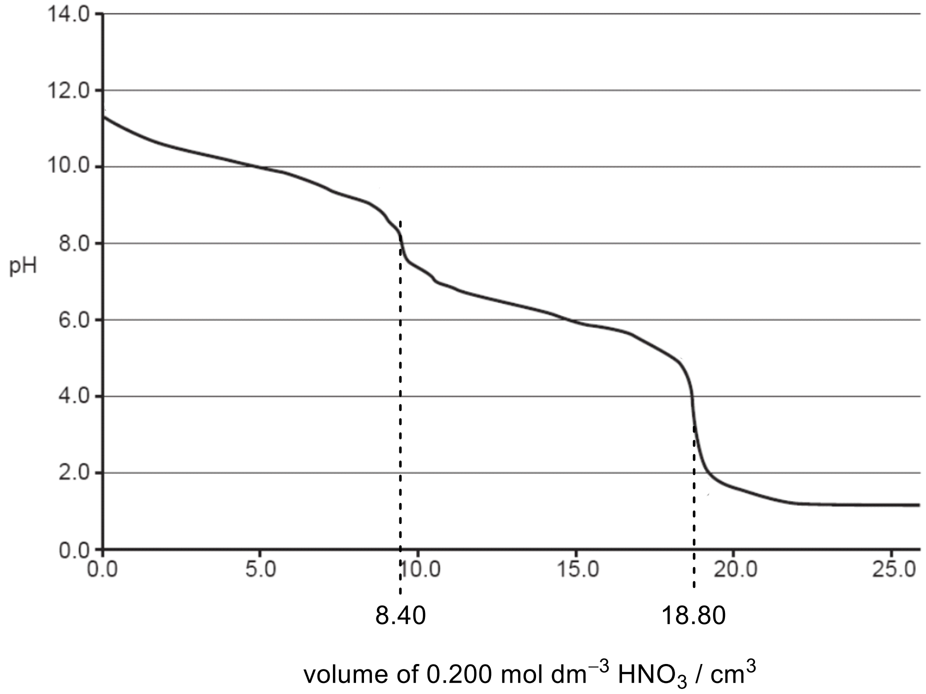


Figure 2.1

(i) A list of indicators and their pK_a values is given in **Table 2.1**.

indicator	thymol blue	methyl yellow	methyl red	cresol red	thymolphthalein
pK_a	1.7	3.1	5.1	8.3	9.2

Table 2.1

From **Table 2.1**, state and explain which two indicators are suitable to determine the two end-points in **Figure 2.1**. [2]

(ii) Calculate the concentration, in g dm^{-3}, of sodium carbonate and sodium hydrogencarbonate present in the original solution. [4]

For Examiner's Use

(b) Wines contain a mixture of organic acids, including dicarboxylic acids such as tartaric acid. These acids produce a prickling sensation on the tongue during wine-tasting.

Dicarboxylic acids ionise in stages.

$$HO_2C{-}(CH_2)_n{-}CO_2H \xrightarrow[pK_{a1}]{-H^+} HO_2C{-}(CH_2)_n{-}CO_2^- \xrightarrow[pK_{a2}]{-H^+} {}^-O_2C{-}(CH_2)_n{-}CO_2^-$$

Table 2.2 compares the pK_a values of two dicarboxylic acids, tartaric acid and succinic acid.

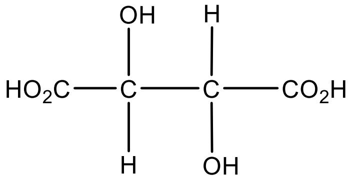
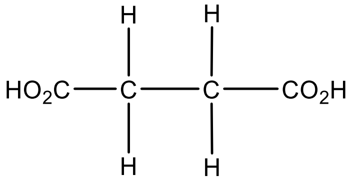
Acid	Formula	pK_{a1}	pK_{a2}
Tartaric	 $HO_2C{-}CH(OH){-}CH(OH){-}CO_2H$	2.95	4.25
Succinic	 $HO_2C{-}CH_2{-}CH_2{-}CO_2H$	4.20	5.60

Table 2.2

(i) Explain why the pK_{a2} values are higher than pK_{a1} values for both acids. [1]

(ii) By considering the structure of the respective monoanions, explain why succinic acid has a higher pK_{a1} value than tartaric acid. [2]

(iii) An amphiprotic species is one that reacts with both an acid and a base. The monoanion of a dicarboxylic acid, $HO_2C{-}(CH_2)_n{-}CO_2^-$, is an amphiprotic species.

The pH of an amphiprotic species is given by the following expression.

$$pH = \tfrac{1}{2}(pK_{a1} + pK_{a2})$$

Using tartaric acid as an example, write two equations to show that its monocarboxylate ion is an amphiprotic species. [2]

(iv) The pH–volume added curve when 55 cm^3 of 0.20 mol dm^{-3} aqueous NaOH is added to 25.0 cm^3 of 0.20 mol dm^{-3} tartaric acid is shown in **Figure 2.2**.

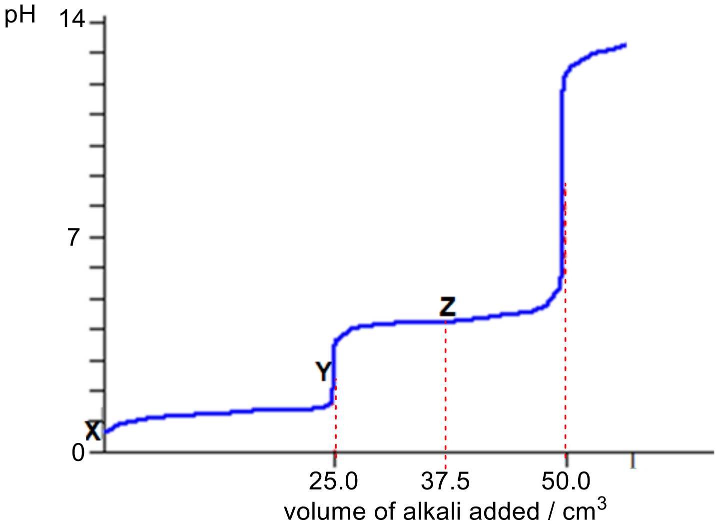


Figure 2.2

Using **Figure 2.2** and the data from **Table 2.2**, determine the pH at points **X**, **Y** and **Z**. [3]

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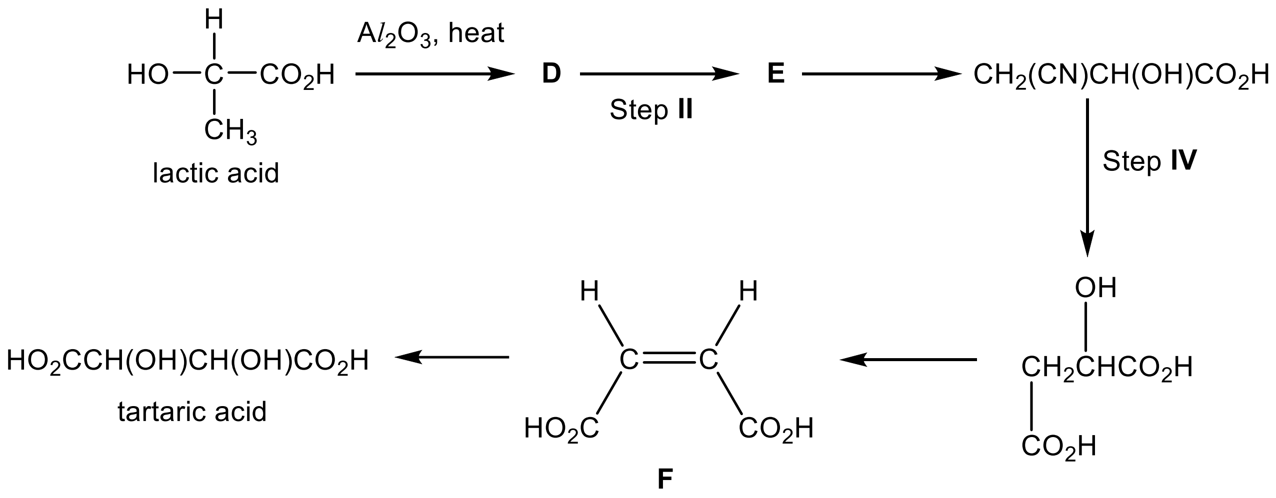
(c) Tartaric acid can be synthesised from lactic acid in the laboratory via the following reaction sequence.



(i) Suggest the structural formulae of **D** and **E**. [2]

(ii) Give the reagents and conditions for steps **II** and **IV**. [2]

(iii) Suggest a simple chemical test to confirm that all of compound **F** has been converted to tartaric acid. [2]

[Total: 20]

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3 **(a)** Nitrogen can be introduced into organic compounds by reacting a carbonyl group with a weak acid such as HCN in the presence of a base to form a cyanohydrin.

An example of such reaction is shown using ethanol as an example.

$$CH_3CHO + HCN \xrightarrow{NaOH} \underset{\text{cyanohydrin}}{CH_3C(OH)CN}$$

The kinetics of this reaction was studied by monitoring the initial rate when the concentration of ethanal and NaOH are varied while using excess HCN.

HCN is used in excess for all experiments.

experiment	initial concentration of / mol dm^{-3}		initial rate of cyanohydrin formation / mol dm^{-3} s^{-1}
	CH_3CHO	NaOH	
1	1.25×10^{-2}	1.25×10^{-4}	1.15×10^{-14}
2	2.50×10^{-2}	1.25×10^{-4}	2.30×10^{-14}
3	3.75×10^{-2}	2.50×10^{-4}	6.90×10^{-14}

Table 3.1

(i) State and explain why NaOH is needed in the reaction of CH_3CHO and HCN. [2]

(ii) Use the data in **Table 3.1** to determine the order of reaction with respect to CH_3CHO and NaOH. [2]

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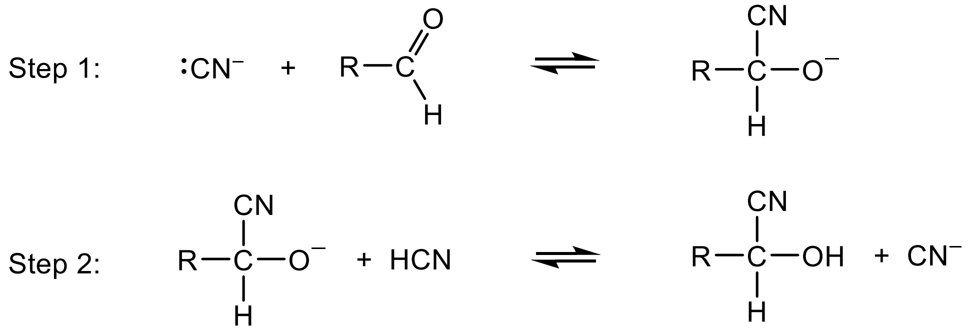
(b) The uncatalysed addition of HCN to a carbonyl group to give a cyanohydrin proceeds by two steps.



The rate equation for the formation of cyanohydrin is as follows:

$$\text{rate} = k\,[\text{carbonyl compound}]\,[\text{CN}^-]$$

The overall reaction is an equilibrium, and the value of the equilibrium constant, K_c, has been measured under identical experimental conditions for a number of carbonyl compounds.

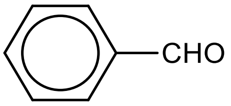
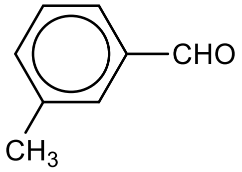
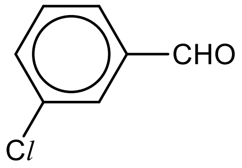
	carbonyl compound	$K_c = \dfrac{[\text{cyanohydrin}]}{[\text{carbonyl compound}][\text{HCN}]}$ / $\text{mol}^{-1}\,\text{dm}^3$
I		210
II		175
III		500

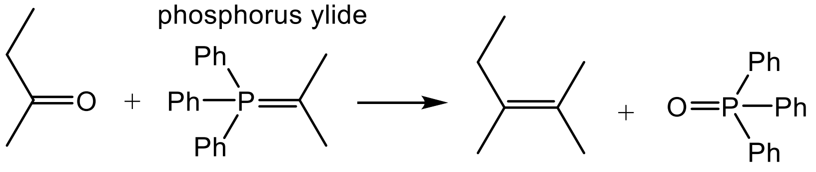
Table 3.2

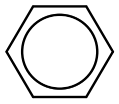
(i) Which is the rate-determining step of the reaction? [1]

(ii) By considering the mechanism for the reaction of the carbonyl compound with HCN, account for the different values of K_c shown in **Table 3.2**. [3]

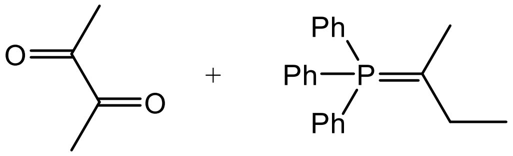
For Examiner's Use

(c) A phosphorous ylide is used in the Wittig reaction which converts a carbonyl compound to an alkene. An example of a Wittig reaction is shown below.



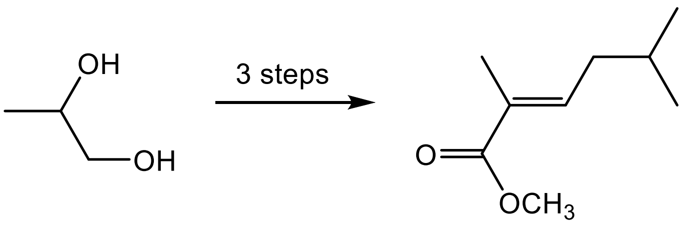
where Ph = 

(i) Suggest the structure formed when 1 mole of the following carbonyl compound reacts with 2 moles of the phosphorous ylide via the Wittig reaction.



Hence, suggest the number of stereoisomers that can be formed. [2]

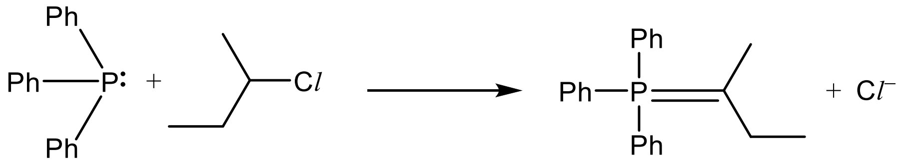
(ii) Using the Wittig reaction as one of the steps in a three-step synthesis route, suggest suitable reagents and conditions to synthesise compound **G** from propane-1,2-diol.



propane-1,2-diol compound **G**

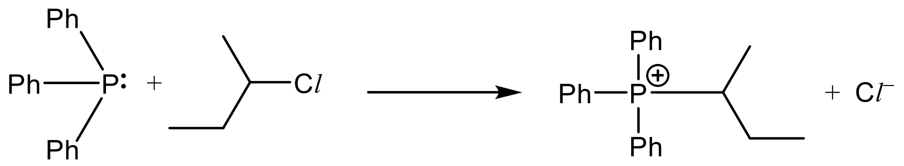
In your answer, include the structure of the intermediates formed. [5]

A phosphorus ylide is formed by reacting a suitable phosphine and an alkyl halide. An example of a phosphorus ylide is given below.



phosphorus ylide

(iii) The initial structure of the ylide formed carries a positive charge as shown.



By considering the type of reaction that occurred, give one reason why the reaction occurs more readily with $CH_3(CH_2)_2CH_2Cl$ than with $CH_3CH_2CHClCH_3$. [1]

(iv) By considering the structure of the phosphorous ylide given, explain why Ph_3N cannot be used for the formation of the ylide. [1]

For Examiner's Use

(d) Arenes undergo electrophilic substitution reactions.

The position of substitution during the electrophilic substitution of arenes can be explained based on the stability of the carbocationic arenium ion.

An example involving the bromination of methlybenzene is shown in **Figure 3.1**.

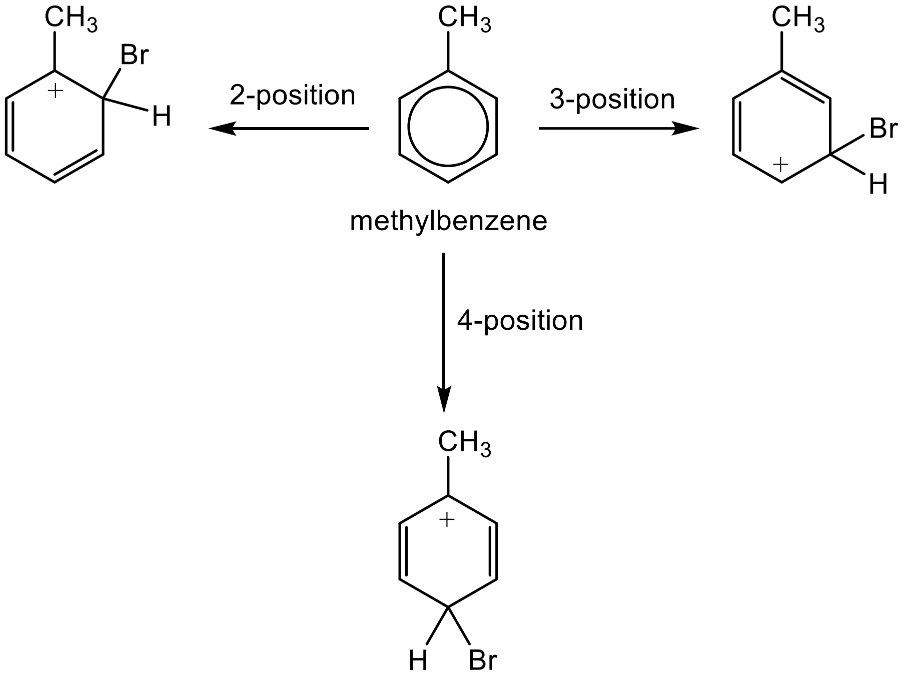


Figure 3.1

(i) Based on the stability of the carbocationic arenium ions, suggest why the methyl group directs incoming electrophiles to the 2- and 4-positions in preference to the 3-position. [2]

(ii) Draw the structure of the product formed when benzaldehyde undergoes bromination. [1]

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Section B

Answer **one** question from this section.

For Examiner's Use

4 Carbon, "the building block of life", combines with hydrogen and oxygen to form compounds that make up living things.

(a) Dinitrogen oxide, N_2O, has a molecular shape similar to that of carbon dioxide, CO_2.

(i) Draw the dot-and-cross diagram for N_2O. [1]

(ii) Predict, with reasons, which of the two compounds, N_2O or CO_2, has a lower boiling point. [2]

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(b) Either carbon or carbon monoxide can bring about the reduction of iron(III) oxide in a blast furnace.

Reaction **1**: $Fe_2O_3(s) + \frac{3}{2}C(s) \longrightarrow 2Fe(s) + \frac{3}{2}CO_2(g) \quad \Delta H_1 = +234 \text{ kJ mol}^{-1}$

Reaction **2**: $Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g) \quad \Delta H_2 = -24.8 \text{ kJ mol}^{-1}$

(i) By considering the thermodynamic spontaneity of the two reactions, state and explain which reaction is more favoured at low temperatures. [3]

(ii) The carbon monoxide is formed by the following reaction:

$$C(s) + CO_2(g) \rightarrow 2CO(g) \quad \Delta H_r$$

Calculate ΔH_r for this reaction. [2]

For Examiner's Use

(c) A commercial production of methanol involves the reaction of carbon monoxide with hydrogen gas at 7500 kPa.

One of the steps in the production as shown below is carried out at 7500 kPa.

$$CO(g) + 2H_2(g) \ll CH_3OH(g)$$

(i) The reaction was carried out in the laboratory. After the reaction reached equilibrium, the mixture of gases contained 38.0 g of hydrogen, 462 g of carbon monoxide and 7200 g of methanol.

Calculate the mole fraction of each gas in the mixture. [2]

(ii) Write an expression for the equilibrium constant, K_p, for the reaction.

Using your answer in **(c)(i)**, calculate a value for K_p, stating its units. [2]

(iii) Compound **J** has molecular formula C_8H_9N and is soluble in dilute HC*l* solution. When compound **J** is reacted with steam in the presence of catalyst at high temperature and pressure, two possible isomeric organic products, **L** and **M** are formed. One mole of **J** requires 4 moles of aqueous bromine for reaction.

Compound **L** is optically active but not **M**. Compound **L** reacts with alkaline aqueous iodine to form yellow precipitate.

Separate samples of **J**, **L** and **M** reacts with hot concentrated $KMnO_4$ to form the same product **Q**, $C_7H_7O_2N$, which is a crystalline solid upon evaporation.

Deduce the structures of **J**, **L**, **M** and **Q**. Explain your reasoning. [8]

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For Examiner's Use

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For Examiner's Use

5 **(a)** During the corrosion of iron in the presence of oxygen and water, Fe is oxidised to Fe^{2+} while O_2 is reduced to OH^{-}.

(i) Using appropriate data from the *Data Booklet*, draw a fully labelled diagram of a cell set-up to measure the cell potential of the reaction between iron and oxygen gas.

On your diagram, state the direction of electron flow. [4]

(ii) Calculate the cell potential of the overall reaction. [1]

(iii) Write an equation, including state symbols, for the overall cell reaction. [1]

(iv) Calculate the standard Gibbs free energy change ΔG , in kJ mol^{-1}, for the overall reaction.

Comment on the significance of your answer in terms of the feasibility of the overall reaction. [2]

(v) Predict and explain how feasibility of the overall cell reaction will change when NaOH(aq) is added to the iron half-cell. [2]

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(b) When an organic compound, **G**, with molecular formula $C_{10}H_9O_3Br$, is boiled with aqueous sodium hydroxide followed by acidification, it gives two compounds, **H** and **J**.

Compound **H**, $C_7H_8O_2$, forms a violet colouration with neutral ferric chloride. One mole of **H** decolourises 2 moles of aqueous bromine to form a symmetrical product.

When sodium hydrogen carbonate is added to compound **J**, effervescence is observed. In addition, **J** forms a yellow precipitate on warming with alkaline aqueous iodine. When **J** is heated with hydrogen gas and nickel, it gives **L**. Heating **L** in the presence of an acid catalyst gives a sweet-smelling liquid **M**, $C_6H_8O_4$.

Deduce the structures of **G**, **H**, **J**, **L** and **M**, giving an account of the chemistry involved. Chemical equations are not required. [10]

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Additional answer space

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