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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

The use of an approved scientific calculator is expected, where

question or part question.

This document consists of **30** printed pages and 2 blank pages.

Answer all questions in the spaces provided on the Question

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

Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

YISHUN INNOVA JUNIOR COLLEGE JC 2 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE

CHEMISTRY

Paper 3 Free Response

NAME

CG

Write your name, class and index number on all the work you hand in.

Write in dark blue or black pen on both sides of the paper. Do not use staples, paper clips, glue or correction fluid.

shown. Section A

Section B Answer one question.

Answer all the questions.

12 September 2024

For Examiner's Use

Section A

Section B

1

2

3

TEACHERS' COPY

INDEX NO

2 hours

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4 or 5		/ 20
Penalty	units	significant figures
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Section A

2

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

1 (a) The tripeptide A is made by reacting amino acids B, C and D together.



Table 1.1 shows the pK_a values of the different functional groups present on each amino acid.

amino acid	pK_a of α -carbonyl group	p <i>K</i> _a of α –amino group	pK_a of side chain
В	2.09	9.10	_
С	1.88	9.60	3.65
D	2.02	8.80	_

(i) Explain the term α -amino acid.

 α -amino acid is one with both the $-NH_2$ group and the $-CO_2H$ group bonded to the same carbon atom.

(ii) One of the amino acids, **B**, present in the tripeptide **A** contains more than one chiral carbon atom. Draw the displayed formula of **B**. [1]



(iii) Draw the predominant species of **C** at pH 4.0.



(iv) Suggest a pH at which the predominant species of C is a zwitterion using the information in Table 1.1.

pH 2.00 (accept any value between 1.88 and 3.65)

(v) Explain why the side-chain of **D** does not have a K_a value.

[1]

The amide side chain is neutral because the **lone pair of electrons on the N atom in –CONH**₂ group is **not available to accept H**⁺ **as it is delocalised into the** (electron-withdrawing) **C=O group**.

(b) 1,2-diaminopropane can be synthesised from propene by the following route.





^{1,2-}diaminopropane

 Outline the mechanism for step 1 to show the formation of 1-bromo-2-chloropropane. Show all charges, relevant lone pairs and show the movement of electron pairs using curly arrows.



(ii) Use your mechanism to explain the preferential production of 1-bromo-2-chloropropane over 2-bromo-1-chloropropane. [1]

The additional electron-donating alkyl group in the secondary carbocation disperse the positive charge on the C atom [$\sqrt{}$] more effectively. 1-bromo-2-chloropropane is preferentially formed as it came from a more stable [$\sqrt{}$] secondary carbocation as compared to the primary carbocation of 2-bromo-1-chloropropane.

(iii) State the reagents and conditions for step 2.

[1]

NH₃ (excess) in ethanol (or alcohol) or concentrated NH₃, heat in sealed tube.

(iv) 1,2-diaminopropane can react with bromoethane to form compound E, $C_7H_{18}N_2$. Suggest the structure for E.

[1]



- (c) Alkanes are very unreactive. However, alkanes such as butane, C₄H₁₀, do react with chlorine. There are two possible monochloroalkanes that can be formed from butane. One of the monochloroalkanes exhibits stereoisomerism.
 - (i) Suggest two reasons why alkanes are generally unreactive.

[2]

The C-H bond is non-polar.The C-H bond does not break heterolytically and only homolytically.The C-C and C-H bonds are strong.

(ii) Predict the relative proportions of 1-chlorobutane and 2-chlorobutane that are likely to be produced from C₄H₁₀. Explain your answer. [2]

Ratio of $CH_3CH_2CH_2CH_2Cl$ and $CH_3CHClCH_2CH_3 = 6 : 4 = 3 : 2$

Based on the different types of hydrogen, there are 6 possible H atoms which can be substituted to form 1-chlorobutane, while only 4 H atoms can be substituted to form 2-chlorobutane.

(iii) Draw three-dimensional structures for the two stereoisomers of the monochloroalkane formed from the chlorination of butane. [1]



(d) Use the data in Table 1.2, together with relevant data from the *Data Booklet*, to calculate the average bond energy of the Si-C*l* bond in SiC*l*₄. Show your working.

Table 1.2

enthalpy change of vapourisation of SiCl ₄ molecules,		120 k l mol-1
$SiCl_4(I) \rightarrow SiCl_4(g)$		723 KJ 1101
standard enthalpy change of atomisation of Si(s)	=	+338 kJ mol ⁻¹
standard enthalpy change of formation of $SiCl_4(I)$	=	–687 kJ mol ^{–1}



(e) Describe the reaction of SiCl₄ with water, stating the pH of the resulting mixture.

[1]

 $SiCl_4(I) + 2H_2O(I) \rightarrow SiO_2(s) + 4HCl(g) \qquad pH = 1 \text{ or } 2 [\sqrt{]}$

SiC l_4 which is covalent **undergoes complete hydrolysis** in water **vigorously** [$\sqrt{}$]to give strongly acidic solution.

(f) Elements in Group 17 are known as the halogens.
 State how the reactivity of the halogens as oxidising agents varies down the group, and relate this variation to relevant *E*^e values.

 $Cl_{2} + 2e^{-} \rightleftharpoons 2Cl^{-} \qquad E^{\oplus} = +1.36 \vee$ Br_{2} + 2e^{-} \rightleftharpoons 2Br^{-} \qquad E^{\oplus} = +1.07 \vee I_{2} + 2e^{-} \rightleftharpoons 2I^{-} \qquad E^{\oplus} = +0.54 \vee

Down the group, the reactivity of the halogens as oxidising agents decreases as indicated by the less positive E° values [$\sqrt{}$]. The halogens have a lower tendency to be reduced. [$\sqrt{}$]

[Total: 21]

2 (a) Alnico alloys are known for its strong magnetic properties and are commonly used in applications like permanent magnets and electronic devices.

Alnico alloys contain metals such as aluminum, magnesium, iron, and cobalt.

The densities of the four metals present in Alnico are given in Table 2.1.

Table 2.1

	metal 1	metal 2	metal 3	metal 4
density / g cm ⁻³	1.74	2.70	7.87	8.83

(i) Explain why iron and cobalt have a higher melting point than aluminium and magnesium.[1]

Iron and cobalt have **electrons in the 4s and 3d subshells** (or higher charge density) hence there is **stronger electrostatic attraction between the lattice of positive ions and the 'sea' of delocalised electrons** which requires a larger amount of energy to overcome.

(ii) State which two of the metals, Mg, A<u>l</u>, Fe and Co, which are present in Alnico, are metals 3 and 4. Explain why.

Iron and cobalt have higher relative atomic mass as compared to magnesium and aluminium. Cobalt have a smaller atomic radius than iron.

(b) The iron(II) complex, *ferrous bisglycinate hydrochloride* is sometimes prescribed, in capsule form, to treat iron deficiency or anaemia.

A capsule containing 500 mg of this iron(II) complex was dissolved in dilute H_2SO_4 and titrated with 0.0200 mol dm⁻³ KMnO₄. 18.10 cm³ of KMnO₄ solution were required to oxidise all the Fe²⁺ present in the capsule.

Calculate the molar mass of the iron(II) complex given that the ratio of Fe^{2+} to the complex is 1:1.

[2]

[3]

 $5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$ Amount of $MnO_4^- = 0.0200 \times 0.1810 = 3.62 \times 10^{-4}$ mol Amount of $Fe^{2+} = 5 \times (3.62 \times 10^{-4}) = 1.81 \times 10^{-3}$ mol

Molar mass of complex = $0.500 \div (1.81 \times 10^{-3}) = 276.2 \text{ g mol}^{-1}$

(c) $[Fe(H_2O)_6]^{3+}$ form a deep-red complex with thiocyanate ions, SCN⁻, as shown in reaction 1, and a vellow complex with EDTA⁴⁻ as shown in reaction 2.

reaction 1 $[Fe(H_2O)_6]^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons [Fe(SCN)(H_2O)_5]^{2+}(aq) + H_2O(I)$ $K_c = 1.00 \times 10^3$ deep-red

reaction 2 $[Fe(H_2O)_6]^{3+}(aq) + EDTA^{4-}(aq) \rightleftharpoons [Fe(EDTA)]^{-}(aq) + 6H_2O(I)$ $K_c = 1.26 \times 10^{26}$ yellow

(i) Explain why transition element complexes are usually coloured.

Transition element complexes are coloured because the transition metal ions have partially-filled 3d orbitals.

In the presence of **ligands**, the **3d orbitals** of the ions **split into two different energy levels with an energy gap**.

An electron in a lower energy 3d-orbital can absorb energy from the visible spectrum and be promoted to a higher energy 3d-orbital that is vacant.

The colour observed is the **complement of the colours absorbed**.

(ii) With reference to reaction 1 and 2, suggest and explain which reaction has a higher positive standard entropy change, ΔS° . [2]

Reaction 2 has a higher positive standard entropy change. Reaction 2 has more amount of products than reactants and more ways to distribute the particles resulting in greater disorder.

(iii) A few drops of KSCN was added to 5 cm³ of [Fe(EDTA)]⁻. Use the K_c values to predict and explain whether there is any colour change when a few drops of KSCN was added to 5 cm³ of [Fe(EDTA)]⁻.
[2]

Yellow colour of [Fe(EDTA)]⁻ remains unchanged.

Since K_c for the complex formed by EDTA⁴⁻ and Fe³⁺ ions (1.26 × 10²⁶) is **much larger** than that by SCN⁻ and Fe³⁺ ions (1.00 × 10³), the position of equilibrium for [Fe(EDTA)]⁻ lies more to the right. or [Fe(EDTA)]⁻ is more stable than [Fe(SCN)(H₂O)₅]²⁺, hence SCN⁻ cannot replace the EDTA⁴⁻ ligands and no ligand exchange reaction can occur.

(d) Compound **F** has the molecular formula $C_{11}H_{15}Cl$ and contains a chiral centre.

One mole of compound F is reacted separately with

- Iodine in aqueous NaOH with heating, followed by acidification to form compound **G** and a yellow precipitate.
- ethanolic NaOH with heating forming a mixture of isomeric alkenes.
- anhydrous FeCl₃ forming one mole of compound **H**.
- hot acidified KMnO₄ forming benzoic acid.



benzoic acid

Suggest possible structures for compounds **F**, **G** and **H**, explaining the reactions described. [6]

information	type of reaction	functional group present
Compound F reacts with aqueous	nucleophilic	Compound F is a halogenoalkane/
NaOH with heating	substitution	chloroalkane.
which further reacts with alkaline		Compound G contains one less
aqueous iodine, followed by	oxidation	carbon atom (vs compound F) and
		contains carboxyl group (-COOH)

acidification to give compound G and a yellow precipitate.		
Compound F reacts with ethanolic NaOH with heating forming a mixture of isomeric alkenes.	elimination	Compound F contains halogenoalkane/ chloroalkane.
Compound F reacts with anhydrous $FeCl_3$ forming one mole of compound H .	electrophilic substitution	Compound F undergoes intramolecular electrophilic substitution with its own side chain.
Compound F reacted with hot acidified KMnO ₄ forming benzoic acid.	(side chain) oxidation	Compound F has only 1 carbon side chain on its benzene ring.
	\sum	ОН

3 (a) The equation for the complete combustion of one mole of ethanol is shown.

 $CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$

Н

The standard enthalpy change of combustion of ethanol, ΔH_c^{e} is -1367 kJ mol⁻¹. The standard entropy change, ΔS^{e} , for the same reaction is -140 J mol⁻¹ K⁻¹.

G

(i) Calculate the standard Gibbs free energy change, ΔG° , for the combustion of ethanol at 298K. [1]

 $\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} = (-1367) - (298)(-0.140) = -1.33 \times 10^{3} \text{ kJ mol}^{-1}$

(ii) Using the equation for the combustion of ethanol and your answer to (a)(i), calculate E^o_{cell} for the ethanol/oxygen fuel cell.
 [2]

oxidation half-equation: CH₃CH₂OH + 3H₂O \rightarrow 2CO₂ + 12H⁺ + 12e⁻ Amount of electrons = 12 Using $\Delta G^{\circ} = -nFE^{\circ}$ $E^{\circ} = -[(-1.33 \times 10^{3} \times 10^{3}) \div (12 \times 96500)] = +1.14 \text{ V}$

(b) Separate acidified samples of Cr²⁺(aq) and Mn²⁺(aq) are left to stand in the air.
 Use relevant E^a values from the Data Booklet to predict whether a reaction occurs in the samples after some time.

F

 $\begin{array}{ll} \mathsf{Mn}^{3+} + \mathrm{e}^- \rightleftharpoons \mathsf{Mn}^{2+} & E^{\mathrm{e}} = +1.54\mathsf{V} \\ \mathsf{Cr}^{3+} + \mathrm{e}^- \rightleftharpoons \mathsf{Cr}^{2+} & E^{\mathrm{e}} = -0.41\mathsf{V} \\ \mathsf{O}_2 + 4\mathsf{H}^+ + 4\mathrm{e}^- \rightleftharpoons 2\mathsf{H}_2\mathsf{O} & E^{\mathrm{e}} = +1.23\mathsf{V} \\ \end{array}$ For $\mathsf{Mn}^{2+}(\mathsf{aq})$ $E^{\mathrm{e}}_{\mathrm{cell}} = E^{\mathrm{e}}_{\mathrm{cathode}} - E^{\mathrm{e}}_{\mathrm{anode}} = +1.23 - (+1.54) = -0.31\mathsf{V} < 0$ Reaction is not spontaneous.
For $\mathsf{Cr}^{2+}(\mathsf{aq})$ $E^{\mathrm{e}}_{\mathrm{cell}} = E^{\mathrm{e}}_{\mathrm{cathode}} - E^{\mathrm{e}}_{\mathrm{anode}} = +1.23 - (-0.41) = +1.64\mathsf{V} > 0$ Reaction is spontaneous.

(c) At high temperatures, water and carbon monoxide undergoes the following reaction in the presence of nickel catalyst.

 $H_2O(g) + CO(g) \rightarrow H_2(g) + CO_2(g)$

Deduce the type of catalysis and explain how some transition elements, such as nickel, can act as catalyst.

Heterogenous catalysis.

Transition elements such as nickel have partially filled 3d orbitals (to form bonds with reactant molecules).

(ii) Outline the mode of action of nickel catalyst in this reaction.

[2]

The gaseous reactants, CO and H_2O are first **adsorbed** onto the active sites on the surface of the solid Ni catalyst.

This causes the **C-O and O-H bonds** in the reactants to be **weakened**, and thus **lowers** the **activation energy**. In addition, the **surface concentration** of the reactants in **increased**.

The **reaction** then occurs between the reactants which are close to each other and in the correct orientation. After the products, H₂ and CO₂, are formed, it will then **desorb** from the surface [$\sqrt{}$] of the catalyst.

(d) I and J are two elements in period 3.
 When oxides of I and J are added to water separately, the pH of the resultant solutions is 7. When NaOH(aq) is added to each oxide, only the oxide of I dissolves to form a colourless solution.
 Suggest the identity of I and J and write equations for any reactions that occurred. [3]

 ${\bf I}$ is aluminium and ${\bf J}$ is silicon.

(e) Aldehydes can react with hydroxy compounds to form hemiacetals as shown in Fig. 3.1.



Fig. 3.1

The reaction between propanal and phenol in aqueous sodium hydroxide is a nucleophilic addition reaction. Phenol dissolves in aqueous sodium hydroxide to form phenoxide ions.

(i) Draw the mechanism for this reaction, assuming phenoxide ion as the nucleophile.
 Show curly arrows, charges, dipoles and any relevant lone pairs. [3]



(ii) Explain why the product cannot rotate plane of polarised light.

As the phenoxide ion (nucleophile) can attack the **trigonal planar carbonyl carbon** from **either side of the plane with equal probability**. This will result in the **formation of an equal amount of the two enantiomers**. The **rotation of the plane polarised light by each of the enantiomers is cancelled off by one another**. Hence, gives an optically inactive racemic mixture which does not rotate plane-polarised light.

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



- This result in an increase in the frequency of effective collisions.
- A higher temperature results in a larger rate constant, k, and hence an increase in reaction rate.

(g) Describe and explain the relative basicities of N,N-diethylamine and N-ethylphenylamine. [2]



N,N-diethylamine is more basic (or is a stronger base) than N-ethylphenylamine.

 $(CH_3CH_2)_2NH$ contains one additional electron-donating ethyl groups bonded to the N atom. This increases electron density on N atom and makes the lone pair on N more available for donation to H⁺. Hence, $(CH_3CH_2)_2NH$ is more basic.

N-ethylphenylamine is less basic than $(CH_3CH_2)_2NH$ due to the **delocalisation of lone pair on N into the benzene ring** [$\sqrt{}$]. This decreases electron density on N atom and makes the lone pair on N less available for donation to H⁺.

[Total: 21]

Section B

Answer **one** question in this section.

4 (a) Sulfuryl chloride, SO_2Cl_2 , is often used as a source of Cl_2 for various organic reactions. When heated, it decomposes as shown.

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$

13.51 g of $SO_2Cl_2(g)$ and 3.55 g of $Cl_2(g)$ was introduced in a container at 550 K and left to equilibrate. The total amount of gases at equilibrium was found to be 0.225 mol, and the total pressure of gases was 5.00 atm.

(i) Write an expression for the equilibrium constant for the decomposition reaction, K_{p} , stating its units. [1]

 $K_p = pSO_2 \times p(Cl_2) / p(SO_2Cl_2)$ Units = atm (or kPa or Pa)

(ii) Use your expression to calculate the value of K_{p} for this reaction.

[4]

Initial amount of $SO_2Cl_2(g) = 13.51 \div 135.1 = 0.100$ mo	
Initial amount of $Cl_2(g) = 3.55 \div 71.0 = 0.0500$ mol	

	SO_2Cl_2	SO ₂	Cl_2
Initial amount / mol	0.100	0	0.0500
Change in amount / mol	- <i>x</i>	+ <i>x</i>	+ <i>x</i>
Equilibrium amount / mol	0.100 <i>- x</i>	x	0.0500 + <i>x</i>

Total amount of gases = (0.100 - x) + x + (0.0500 + x) = 0.225 and x = 0.0750 mol

	SO_2Cl_2	SO ₂	Cl_2
Equilibrium amount / mol	0.0250	0.0750	0.125
Equilibrium partial pressure / atm	0.55555	1.6667	2.777

 $K_{\rm p} = (1.6667 \times 2.777) \div 0.5555 = 8.33$ atm

(b) Under industrial conditions, gases do not behave ideally. Fig. 4.1 shows how one mole of an ideal gas, one mole of SO₂Cl₂, and one mole of SO₂ behave at a temperature of 550 K.





(i) Explain the differences in the behaviour of SO_2 and SO_2Cl_2 at 550 K. [1]

 SO_2 deviates less from ideality. SO_2 has a smaller electron cloud size than SO_2Cl_2 . Hence, it is less polarisable resulting in weaker instantaneous dipole – induced dipole interactions between the SO_2 molecules.

(ii) Sketch how SO₂ will behave at 700 K in Fig. 4.1. Explain your answer.

[2]



At a higher temperature of 700 K, the SO₂ molecules possess **more kinetic energy**, hence the **intermolecular forces of attraction between SO₂ molecules become less significant** and there is smaller deviation from ideality.

(c) SO₃ dissolves in rainwater to form sulfate ions, which are absorbed into the soil. The sulfate ions formed can react with calcium ions found in the soil. Calcium sulfate, CaSO₄, is sparingly soluble in water.

 $CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$

The numerical value of K_{sp} is 4.93 × 10⁻⁵.

(i) Write an expression for the solubility product, K_{sp} , of CaSO₄, stating its units. [1]

 $K_{sp} = [Ca^{2+}][SO_4^{2-}]$ Units: mol² dm⁻⁶

(ii) A 20 cm³ water sample from soil contains 0.0100 mol dm⁻³ of calcium ions.
 Calculate the minimum amount of sulfate ions that must be present in the soil for the precipitation of calcium sulfate to occur. [2]

At the point where the first trace of precipitate is seen, ionic product = K_{sp} lonic product = $[Ca^{2+}][SO_4^{2-}] = 0.010 \times [SO_4^{2-}] = 4.93 \times 10^{-5}$ $[SO_4^{2-}] = 4.93 \times 10^{-3} \text{ mol dm}^{-3}$ Minimum amount of $SO_4^{2-} = (4.93 \times 10^{-3}) \times 0.020 = 9.86 \times 10^{-5} \text{ mol}$

(iii) Describe and explain, how the solubility of $CaSO_4$ is affected by adding $Na_2SO_4(aq)$. [1]

The solubility of CaSO₄ will decrease. The addition of Na₂SO₄ increases the concentration of SO₄²⁻. This cause the position of the equilibrium to shift to the left to decrease the concentration of SO₄²⁻.



Fig. 4.2

(i) State the *types of reaction* that occur during each of the steps 1 and 2.

Step 1: reduction Step 2: acid-base		

(ii) In step 3, the phenoxide ion readily undergoes a nucleophilic substitution reaction with CH₃CH₂CH₂Cl as shown in Fig 4.3.



Fig 4.3

On Fig 4.3, draw curly arrows to show the mechanism for this reaction. Show all relevant dipoles in your answer. [1]



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[2]

18

(e) (i) *Metoprolol* and N-methylbenzamide are white solids and insoluble in water. A student accidentally added N-methylbenzamide to a sample of metoprolol.



Outline how metoprolol can be obtained as a solid from the mixture.

[2]

Method 1

Add excess $H_2SO_4(aq)$ (or any strong acids) to the mixture. (Only metoprolol will dissolve as it undergoes acid-base reaction)

Filter the mixture.

Add excess NaOH(aq) to the filtrate to obtain metoprolol as a solid.

Method 2

Add excess NaOH(aq) (or any strong bases) to the mixture and heat. (N-methylbenzamide will dissolve as it will undergo hydrolysis)

Filter the mixture. The residue is metoprolol.

(ii) N-methylbenzamide can be synthesised from benzoic acid. Suggest reagents and conditions for each step. Draw the structure of the intermediate compound. [3]



5 (a) Methanoic acid can be oxidised by bromine to form carbon dioxide gas.

 $HCO_2H(aq) + Br_2(aq) \rightarrow CO_2(g) + 2H^+ + 2Br(aq)$

The rate of the oxidation reaction can be followed by measuring the concentration of aqueous bromine remaining after various times at a constant temperature.

The following reaction mixture was prepared for this experiment.

initial $[Br_2] = 0.0500 \text{ mol } dm^{-3}$ initial $[HCO_2H] = 0.500 \text{ mol } dm^{-3}$

Fig 5.1 shows the graph obtained from the experiment.



Fig. 5.1

(i) Using the graph in Fig 5.2, show that the order of reaction with respect to [Br₂] is 1. Show all working and draw clearly any construction lines on Fig 5.1.



(ii) The rate of the reaction is directly proportional to the [HCO₂H].Use the information given to write the overall rate equation for the oxidation reaction. [1]

rate = $k[HCO_2H][Br_2]$

(iii) The experiment was repeated using 0.0400 mol dm⁻³ of Br₂ and 0.500 mol dm⁻³ of HCO₂H. The initial rate is found to be 1.54 × 10⁻³ mol dm⁻³ s⁻¹. Use this information, and your answer in (c)(ii) to calculate the value for rate constant. State its unit.

rate = k[HCO₂H][Br₂] 1.54 × 10⁻³ = k (0.500 × 0.0400) k = 0.0770 mol⁻¹ dm³ s⁻¹

[2]

(b) Methanoic acid and sodium methanoate forms a buffer.

 $\text{HCO}_2\text{H} \rightleftharpoons \text{HCO}_2^- + \text{H}^+$ $K_a = 1.77 \times 10^{-4} \text{ at } 298\text{K}$

Sodium methanoate is formed when methanoic acid reacts with NaOH(aq) as shown.

$$HCO_2H + NaOH \rightarrow HCO_2Na + H_2O$$

The above buffer of pH 3.85 is prepared using 45 cm³ of 0.0200mol dm⁻³ HCO₂H and x mol of solid NaOH.

Assume that all the NaOH reacts with HCO₂H to form HCO₂Na.

(i) Explain what is meant by a buffer solution.

[1]

A buffer is a solution in which the **pH remains relatively constant** (or does not change significantly) on addition of **small amount of acid or base**.

(ii) Calculate the amount, *x*, of NaOH required to make a buffer solution of pH 3.85. [3]

Amount of NaOH used = x mol Amount of HCO₂H used = 0.0200 × 0.045 = 0.000900 mol [$\sqrt{}$] Amount of HCO₂Na formed = x mol [$\sqrt{}$] Amount of HCO₂H left = (0.000900 - x) mol [$\sqrt{}$] pH = pK_a + log $\frac{[salt]}{[acid]}$ 3.85 = -log(1.77 × 10⁻⁴) + log $(\frac{x/0.045}{0.0009 - x/0.045})$ 3.85 = -log(1.77 × 10⁻⁴) + log $(\frac{x}{0.0009 - x})$ [$\sqrt{}$] $(\frac{x}{0.0009 - x}) = 1.2531$ $x = 5.01 \times 10^{-4}$ mol

(c) (i) In terms of structure and bonding, explain why HCO₂H is a liquid while HCO₂Na is a solid at room temperature. [2]

 HCO_2Na has a giant ionic structure, with strong electrostatic forces between HCO_2^- and Na^+ ions which can attract the oppositely charge ions into a regular lattice. HCO_2H has a simple molecular structure, with weaker hydrogen bonds between the molecules which is unable to attract the molecules into a regular lattice. (ii) HCO₂H is soluble in water.

Draw a diagram to illustrate the type of interaction between HCO₂H and a water molecule. Show any relevant dipoles. [2]



(d) Magnesium forms an important group of covalent compounds known as Grignard reagents. An example of a Grignard reagent is CH₃CH₂MgBr, which is a source of the carbanion, CH₃CH₂⁻.

Grignard reagents can be used in the synthesis of butanone from nitrile compounds as shown in Fig. 5.1.

$$H_{3}C \longrightarrow C \equiv N \xrightarrow{CH_{3}CH_{2}MgBr} \xrightarrow{N^{-}} \xrightarrow{H_{3}O^{+}} \xrightarrow{O}$$



(i) The reaction between CH₃CH₂MgBr and CH₃CN in step 1 is a nucleophilic addition reaction. Suggest why CH₃CH₂MgBr reacts with CH₃CN but does not react with propyne, CH₃C≡CH.
[2]

The C atom in C=N is electron-deficient as it is bonded to the highly electronegative N atom, hence, it can attract $CH_3CH_2^-$ carbanion.

The C=C / pi electrons in CH₃C=CH is electron rich. Hence, it will repel the negatively charged CH₃CH₂⁻ carbanion (or the C=C in CH₃C=CH is non-polar / lacks electron deficient carbon. Hence, it does not attract the negatively charged CH₃CH₂⁻ carbanion)

(ii) The presence of butanone can be confirmed using alkaline aqueous iodine.
 State the expected observation and draw the structure of the organic products formed. [2]

Yellow precipitate. $CH_3CH_2CO_2^-$ and CHI_3 (e) Hot, concentrated potassium manganate(VII) oxidises organic compounds to ketones, carboxylic acids or carbon dioxide. By this means, the structures of compounds can be determined.

The following scheme shows the reactions of compounds L and its oxidation products.



(i) Compound **M** effervesces with sodium metal but does **not** react with warm acidified potassium dichromate(VI). Explain these observations. [1]



