NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CHEMISTRY **9729/03**

Paper 3 Free Response **19 September 2019**

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Booklet
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 soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

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.

Section A

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

1 **(a)** When ethanoic acid reacts with ethanol to form ethyl ethanoate and water, the following equilibrium is established.

$$CH_3CO_2H(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3CO_2CH_2CH_3(l) + H_2O(l) \qquad \Delta H = -3.8 \text{ kJ mol}^{-1}$$

A student mixed 1.48 g of ethanoic acid in a conical flask with 0.92 g of ethanol and 1.80 g of water. He then carefully added 0.98 g of concentrated sulfuric acid to catalyse the reaction. The flask was sealed and placed in a thermostatic water bath set at 25 °C for 5 days.

After 5 days, the student added phenolphthalein indicator to the flask and titrated the entire contents of the conical flask with 0.800 mol dm^{-3} $Ba(OH)_2$. The indicator turned pink when 23.30 cm^3 of $Ba(OH)_2$ had been added.

(i) Calculate the amount of $Ba(OH)_2$ that has reacted with H_2SO_4. [1]

(ii) Write a balanced equation for the reaction of ethanoic acid with $Ba(OH)_2$. Using your answer in (a)(i), calculate the amount of ethanoic acid present at equilibrium. [2]

(iii) Write an expression for the equilibrium constant, K_c, for this reaction and calculate the value of K_c, stating its units. [3]

(iv) Suggest and explain what would happen to the position of this equilibrium and the value of K_c if the temperature is decreased. [2]

(b) **(i)** The addition of an acid to water generates heat and this process is termed as dilution. The dilution of ethanoic acid can be represented with the equation below.

$$CH_3COOH(l) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

Calculate the enthalpy change of dilution of ethanoic acid given the following:

	ΔH_f^θ / kJ mol^{-1}
$CH_3COO^-(aq)$	−486
$H^+(aq)$	0
$CH_3COOH(l)$	−485

[1]

(ii) In the presence of heat, ethyl ethanoate, $CH_3CO_2CH_2CH_3$ is able to react with $Ba(OH)_2$ as seen in the equation below:

$$2CH_3CO_2CH_2CH_3(l) + Ba(OH)_2(aq) \rightarrow (CH_3CO_2^-)_2Ba^{2+}(aq) + 2C_2H_5OH(l)$$

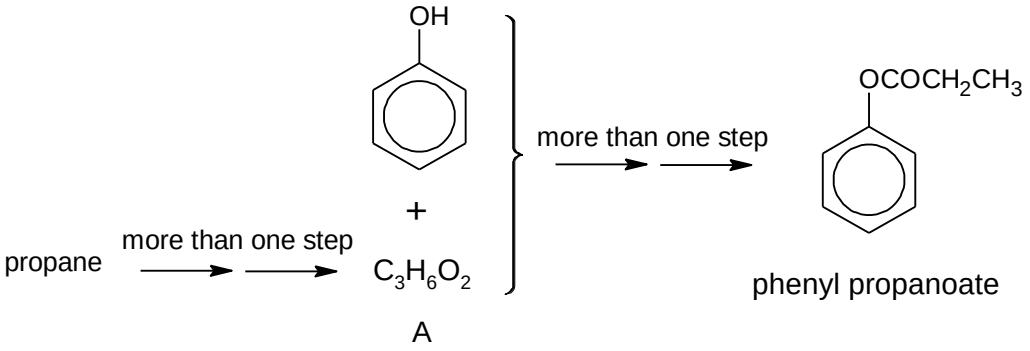
State the type of reaction occurring. [1]

(iii) Construct a fully labelled energy level diagram to calculate the enthalpy change of the reaction in (b)(ii).

Your diagram should include the data given in (a), (b)(i) and the following data.

Standard enthalpy change of neutralisation of $CH_3COOH(aq)$ and $Ba(OH)_2$ = –55 kJ mol^{-1} [3]

(c) Suggest a synthesis of phenyl propanoate starting from propane according to the scheme below. State the structure of compound A. Include reagents and conditions for all reactions, and the structures of all other intermediate compounds, in your answer.

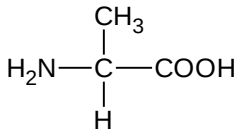


[5]

[Total: 18]

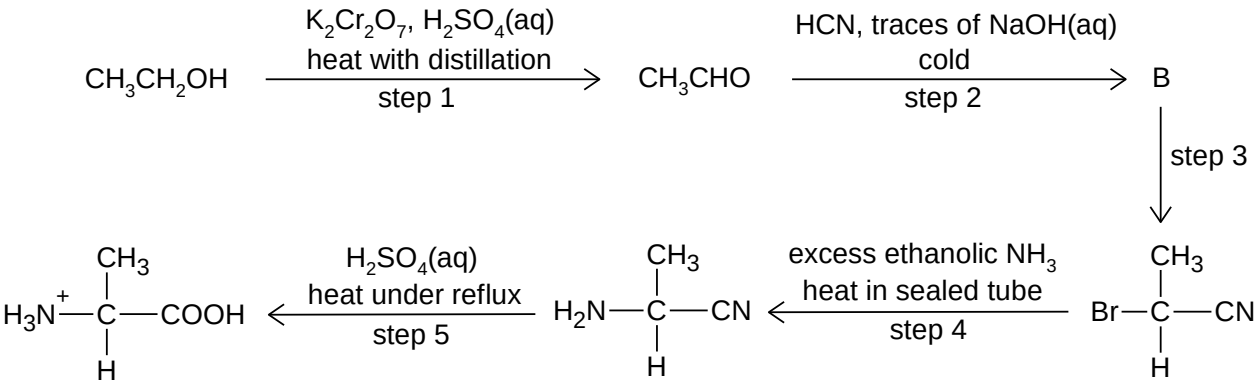
[Turn over

2 Alanine is a non-essential α-amino acid in humans and widely used for biosynthesis of proteins.



alanine

Protonated alanine can be synthesised in the laboratory from ethanol.



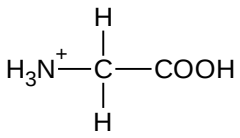
2-bromopropionitrile

(a) **(i)** Heating with distillation in step 1 is required for the synthesis of aldehyde to prevent the aldehyde from further oxidising to carboxylic acid. Explain why heating with distillation is suitable in isolating the aldehyde. [1]

(ii) Draw the displayed formula of compound B. [2]

(iii) Describe the mechanism in step 2. [3]

(iv) Protonated glycine can also be synthesised from methanol, CH_3OH, using the reaction scheme shown above.



protonated glycine

Suggest why the relative rate of step 2 will be higher in the synthesis of protonated glycine. [2]

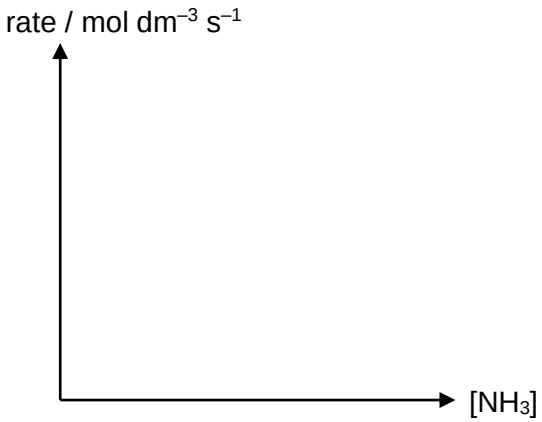
(v) Suggest the reagent and condition for step 3. [1]

(b) To prove that the mechanism in step 4 is S_N2, two separate experiments were performed and the rate equation was found to be

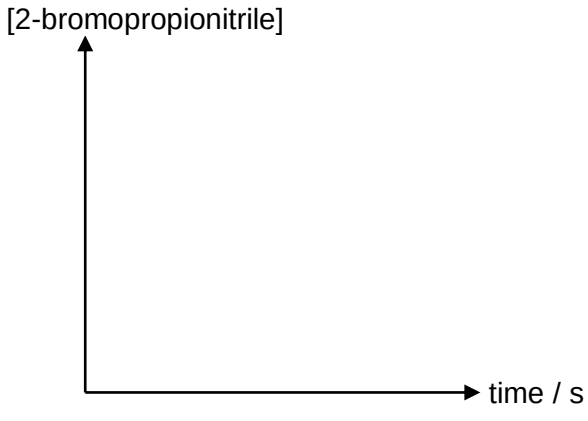
$$\text{rate} = k[NH_3][\text{2-bromopropionitrile}]$$

- In experiment 1, the rate of reaction was monitored with increasing concentration of NH_3.
- In experiment 2, concentration of 0.1 mol dm^{-3} of 2-bromopropionitrile was monitored over time.

(i) Copy the two graph axes below onto your answer booklet. Draw the graph for each experiment and explain the shape of your graphs.



Experiment 1



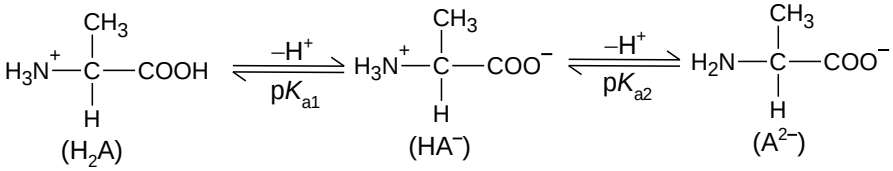
Experiment 2

[2]

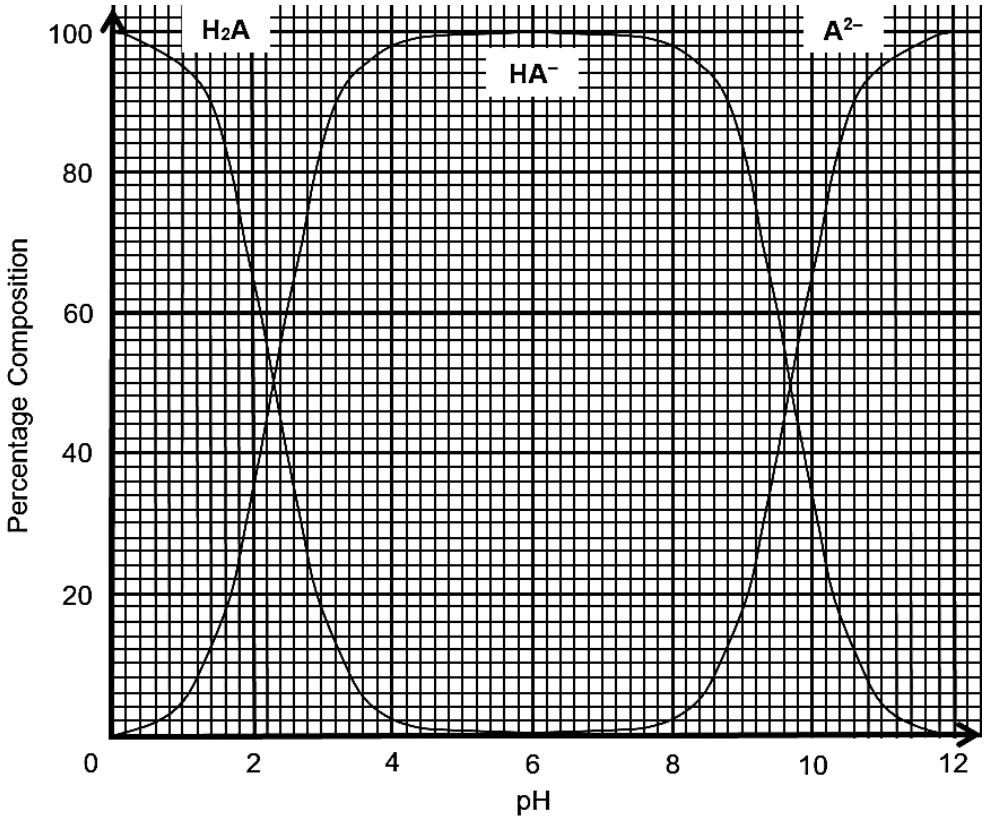
(ii) Suggest a suitable concentration of NH_3 in experiment 2. Explain your answer. [1]

(iii) Suggest why the mechanism in step 4 is unlikely to be S_N1. [1]

(c) Protonated alanine (H_2A) dissociates in two stages as shown below.



The graph below shows how the percentage composition of H_2A, HA^- and A^{2-} change with pH.



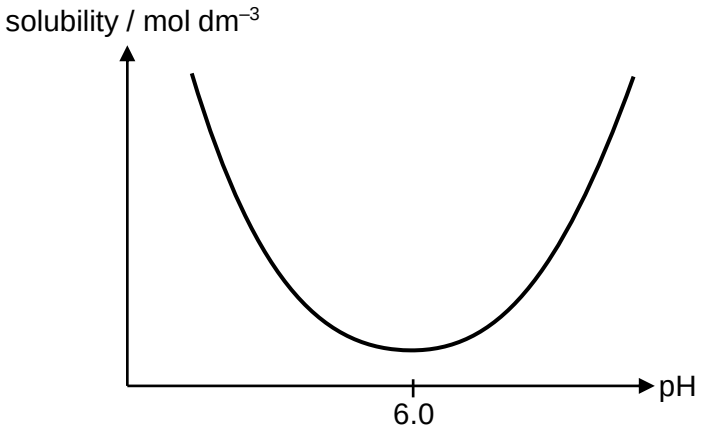
(i) State the values of pK_{a1} and pK_{a2} of alanine. [1]

(ii) A buffer of pH 10.3 is prepared by adding 0.100 mol of protonated alanine (H_2A) in 1 dm^3 of water and solid NaOH was subsequently added.

Using the graph above, determine the amount of HA^- and A^{2-} present in the buffer and hence, calculate the mass of solid NaOH added. [2]

(iii) Assuming 1 dm^3 of water is added to the buffer prepared in (c)(ii), explain qualitatively if the new buffer will result in a greater or smaller change in pH compared to the original buffer, when same amount of HC*l*(aq) is added. [2]

(iv) The solubility of alanine under different pH was investigated. The graph below shows the results of solubility against pH.



Isoelectric point is the pH at which the amino acid has a net zero charge.

With reference to the structures of H_2A, HA^- and A^{2-}, explain

- the low solubility of alanine at its isoelectric point of 6.0.
- the high solubility of alanine at low and high pH. [4]

[Total: 22]

3 This question looks at the chemistry of some compounds formed by transition metal ions and halides.

(a) When aqueous potassium iodide is mixed with aqueous copper(II) sulfate, a yellow brown precipitate is formed and the solution loses its blue colour. When the resulting mixture is shaken with hexane, a purple layer is formed which floats on top of the mixture. A white solid, D, remains which has a mass composition made up of one-third copper and two-third iodine.

(i) Deduce the empirical formula of white solid D. [1]

(ii) Write the electronic configuration of copper in white solid D. [1]

(iii) The filled orbitals of copper in white solid D have different shapes. Draw the shape of the orbital present in the largest quantity. [1]

(iv) Write an ionic equation, with state symbols, for the reaction of copper(II) sulfate with potassium iodide. Identify clearly the species responsible for the different colours observed during the reaction. [2]

(v) Standard redox potentials may be used to predict the feasibility of a reaction. Use E^{θ} values from the *Data Booklet* to show that the reaction between aqueous copper(II) sulfate and potassium iodide is unlikely to occur. [1]

(vi) By using your answer to (a)(iv), explain clearly in terms of changes in E^{θ} values, why this reaction does, in fact, occur. [1]

(b) When 1.00 g of a red solid, G, with formula K_xNiF_6, was reacted with water, 48 cm^3 of oxygen (measured at 293 K and 1 atm) was evolved and a green acidic solution, H, was formed. H consists of KF, NiF_2 and HF.

Solution H was divided into 2 equal portions.

Titration of one portion with 0.20 mol dm^{-3} NaOH required 19.90 cm^3 for neutralisation.

The other portion was electrolysed using a current of 0.40 A and it took 16 minutes to completely deposit the nickel metal at the cathode.

(i) Using the formula of the complex ion present in red solid G, explain what is meant by the term complex ion. You may assume the oxidation state of the metal in the complex ion is +n. [1]

(ii) Suggest a reason why the metal is able to form a complex ion identified in (b)(i). [1]

(iii) Calculate the amount of oxygen evolved. [1]

(iv) Calculate the amount of hydrogen ions and nickel ions in solution H. [2]

(v) Using your answers to (b)(iii) and (b)(iv), deduce the value of *x* with the aid of an equation. [2]

(vi) Write an equation to suggest the product formed at the other electrode during electrolysis of solution H. Use E^{θ} values from the *Data Booklet* to explain why it is formed.

[2]

(c) A spectrochemical series is a list of ligands based on the strength of their interaction with metal ions. It was first proposed in 1938 based on the results of absorption spectra of cobalt complexes. The ligands are ranked based on the energy gap, ΔE, formed between the split d-orbitals when the ligand is bonded to the cobalt metal centre. A partial spectrochemical series listing of ligands is given below.

small ΔE ⟶ large ΔE

$I^- < Br^- < Cl^- < F^- < NCS^-$ (N–bonded)* < $CH_3CN < NH_3 < H_2NCH_2CH_2NH_2$

**N-bonded means the ligand binds to the metal centre at the nitrogen atom*

Ligands on the left of this series are generally regarded as weaker ligands. On the other hand, ligands on the right are stronger ligands.

Propose suitable explanations for the following trends observed in the spectrochemical series.

(i) Halide ligands decrease in strength down the Group. [1]

(ii) CH_3CN is a stronger ligand than NCS^- (N-bonded). [1]

(iii) $H_2NCH_2CH_2NH_2$, a bidentate ligand, is a stronger ligand than NH_3, a monodentate ligand. Consider the standard Gibbs free energy change for the following ligand exchange reaction in your answer.

$[Co(NH_3)_6]^{3+}(aq) + 3H_2NCH_2CH_2NH_2(aq) \rightleftharpoons [Co(H_2NCH_2CH_2NH_2)_3]^{3+}(aq) + 6NH_3(aq)$

[2]

[Total: 20]

Section B

Answer **one** question from this section.

4 **(a)** Samples of anhydrous magnesium ethanoate, $Mg(CH_3COO)_2$ and barium ethanoate, $Ba(CH_3COO)_2$, were heated to a temperature of 600 ^oC causing them to decompose.

White residues were formed in both cases and a common gaseous product, X, with molecular formula of C_3H_6O was also given off. X gives a yellow precipitate upon warming with alkaline aqueous iodine. In addition, the decomposition of magnesium ethanoate also produced a second gaseous product, which forms a white precipitate with calcium hydroxide solution.

(i) Identify the gaseous product, X. [1]

(ii) Write a balanced equation with state symbols for each decomposition reaction. [2]

(iii) Account for the difference in the decomposition products. [2]

(b) During an earthquake, the heat generated by the friction of the fault in the Earth's crust may be large enough to decompose the mineral rocks present in the fault, releasing chemicals like sulfur dioxide, SO_2, and aluminium oxide, Al_2O_3.

One method for the removal of sulfur dioxide is to absorb it in a slurry of magnesium oxide, to produce magnesium sulfite, $MgSO_3$.

(i) Based on your knowledge of chemical periodicity, suggest whether Al_2O_3 can also be used to remove SO_2. [1]

(ii) State and explain the pH of the solutions formed when MgO, Al_2O_3 and SO_3 are separately added to water. [3]

(c) Phenol, phenylmethanol and benzoic acid are three compounds containing benzene rings. None of these compounds is particularly soluble in water. Both phenol and benzoic acid dissolve in NaOH(aq), but only benzoic acid dissolves in Na_2CO_3(aq).

State what these observations indicate about the relative acidities of the three compounds, and explain this trend in acidity. [3]

(d) Compound P, $C_6H_{11}O_2Cl$, reacts with 2,4-dinitrophenylhydrazine to form an orange precipitate and decolourises hot, acidified potassium manganate(VII). When compound P is heated with excess aqueous sodium hydroxide, compound Q, $C_6H_{12}O_3$, is formed. Aqueous iodine is subsequently added to the hot mixture of this reaction and compound R, $C_4H_4O_5Na_2$, is formed. P reacts with excess concentrated sulfuric acid at 170 °C to give three possible isomeric products S, T and U.

S, but not T and U, reacts with excess ammonia to form an amine.

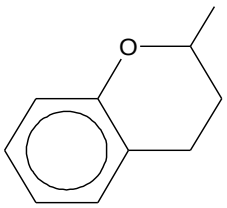
(i) Suggest the structures of P, Q and R, explaining your reasoning. [6]

(ii) Describe and explain how the ease of hydrolysis of S differs from that of T and U. [2]

[Total: 20]

5 **(a)** A is an aromatic compound. It undergoes various reactions as stated below:

- 1 mol of A, $C_{10}H_{13}OCl$, reacts with 2 mol of aqueous Br_2 to give P.
- 3 mol of A reacts with 1 mol of methylamine to give R.
  R reacts immediately with cold silver nitrate to give a white precipitate.
- 1 mol of A reacts with 1 mol of sodium hydroxide at room temperature to form a homogeneous solution.
- 1 mol of A reacts with 1 mol of sodium and gives the following compound,



Suggest structures for A and P. Explain all the reactions, taking into account the molar ratios of the reactants when applicable. [7]

(b) B, a constitutional isomer of A, is also an aromatic compound and reacts very differently with the above mentioned reagents.

- B does not react with aqueous Br_2, methylamine or sodium hydroxide.
- B does not react with hot acidified potassium dichromate(VI) but with hot acidified potassium manganate(VII), B gives $C_8H_5O_4Cl$.
- B does not react with alkaline aqueous iodine.
- 1 mol of B reacts with 1 mol of sodium.
- B does not exhibit enantiomerism.

(i) Based on the above information, state all the possible functional groups in B. [1]

(ii) Hence suggest a structure of B, giving the skeletal formula for the structure. [2]

(c) Anhydrous aluminium chloride, $AlCl_3$ is a powerful Lewis acid, and is used as a catalyst in Friedel-Crafts alkylation of aromatic compounds.

Anhydrous $AlCl_3$ adopts three different structures, depending on the temperature and the state (solid, liquid, gas). Solid $AlCl_3$ exists as cubic close packed layers. In the liquid state, aluminium trichloride exists as the dimer Al_2Cl_6. Al_2Cl_6 dimers are also found in the vapour phase.

(i) Draw a dot-and-cross diagram for the dimer of aluminium chloride, and state the bond angle about the Al atom. [2]

(ii) A 0.52 g sample contains a mixture of $AlCl_3$ and its dimer. It takes up a volume of 70 cm^3 at a temperature of 150 ^{O}C and a pressure of 1 atm.
By determining the average M_r of the mixture, deduce the percentage composition of the aluminium chloride dimer under these conditions. [3]

(iii) How would you predict the average M_r of the mixture to change as the temperature is increased? Explain your answer. [1]

(iv) With the aid of an equation, explain why the hydrated form of aluminium chloride cannot act as a Lewis acid. [2]

(d) Beryllium dichloride has properties similar to those of aluminium chloride.

Beryllium dichloride and ammonia reacts in the molar ratio 1:2. By considering the number of bonding and non-bonding electron pairs, explain the molar ratio and draw a diagram to show the bonding in the product. [2]

[Total: 20]