

NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CHEMISTRY

Paper 3 Free Response

9647/03

24 September 2014

2 hours

Additional Materials: Answer Paper
 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.

Answer any **four** questions.
A Data Booklet is provided.
You are reminded of the need for good English and clear presentation in your answers.

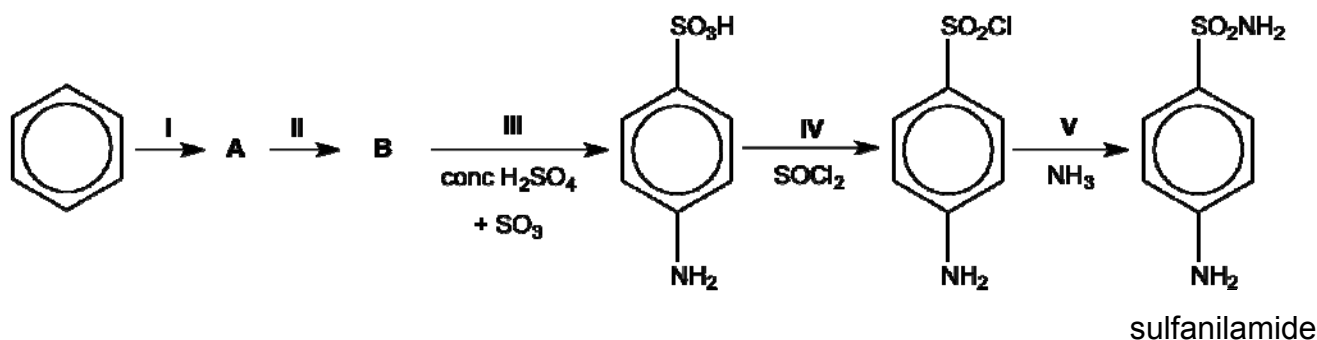
At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [] at the end of each question or part question.

This document consists of **12** printed pages and **0** blank page.

Answer any **four** questions.

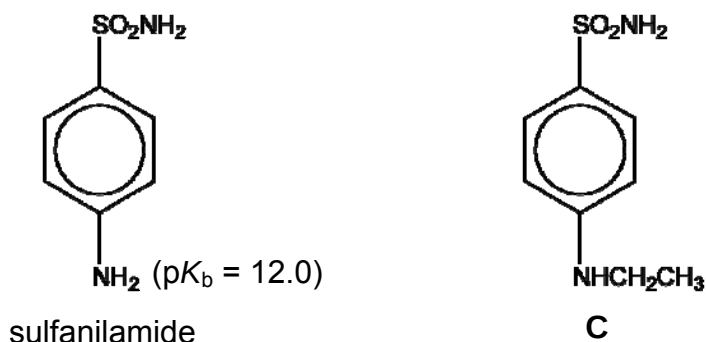
- 1** In 1939 the German chemist Gerhard Domagk was awarded the Nobel Prize in Physiology or Medicine for the discovery of the antibacterial effects of Prontosil. It was found that sulfanilamide was the active component of Prontosil.

- (a) Benzene can be used as the starting reagent for the synthesis of sulfanilamide by the following route.



- (i) Suggest reagents and conditions for steps I and II, and the structure of compounds A and B.
- (ii) Step III involves the reaction of concentrated H_2SO_4 together with SO_3 to generate the required electrophile. Write a balanced equation for the generation of the electrophile in Step III.
- (iii) State the types of reaction in steps II and V.
- (iv) Explain why sulfanilamide is soluble in water.

A derivative of sulfanilamide, compound C, is shown below.



- (v) The amino group of sulfanilamide has a $\text{p}K_{\text{b}}$ value of 12.0. Suggest a $\text{p}K_{\text{b}}$ value for the amino group of compound C. Explain your answer.

[10]

- (b) Describe and explain the trend in thermal decomposition of Group II nitrates, writing an equation for any reaction that occurs. [3]
- (c) Ammonium nitrate is widely used as an explosive. It can easily decompose when ignited to give nitrogen gas, oxygen gas and steam.
- (i) Write a balanced equation, with state symbols, which represents the enthalpy change of decomposition of 1 mole of ammonium nitrate.
- (ii) Define the term *enthalpy change of atomisation of ammonium nitrate*.
- (iii) The standard enthalpy change of atomisation of ammonium nitrate is $+2928 \text{ kJ mol}^{-1}$. Using suitable data from the *Data Booklet*, construct an energy cycle to calculate the enthalpy change of decomposition of ammonium nitrate.
- (iv) In a laboratory experiment, the decomposition of 1.0 g of ammonium nitrate is able to increase the temperature of 100 g of water by 4°C .

Calculate the heat evolved from the decomposition of one mole of ammonium nitrate from this experiment. Comment on the difference between the calculated values from (iii) and (iv).

[7]

[Total: 20]

- 2 Phosphorus is the most abundant element of Group V, accounting for 0.10% of the mass of the Earth's crust. Phosphorus exists in two common allotropic forms: white phosphorus and red phosphorus. White phosphorus contains discrete tetrahedral P_4 molecules. Red phosphorus, by contrast, has a polymeric structure.

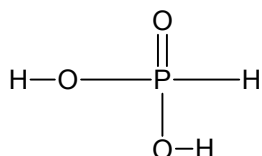
- (a) Compounds **A** and **B** contain phosphorus in oxidation states of -3 and $+5$ respectively. The relative molecular masses of **A** and **B** are 34.0 and 208.5 respectively.

The molecular shape of **A** is the same as that of ammonia and it burns easily in air to form phosphoric acid only.

B is an off-white solid that melts at $167\text{ }^{\circ}\text{C}$ and gives white fumes and phosphoric acid on contact with moist air.

Suggest the identities and draw the shapes of compounds **A** and **B**, writing equations to illustrate all the reactions mentioned. [4]

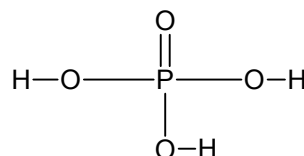
- (b) When phosphorus burns in oxygen, it yields either P_4O_6 or P_4O_{10} depending on the amount of oxygen present. Both P_4O_6 and P_4O_{10} are acidic oxides, and they react with water to form aqueous solutions of phosphorous acid and phosphoric acid, respectively. Phosphorous acid is diprotic, while phosphoric acid is triprotic and their successive dissociation constants are as follows:



Phosphorous acid, H_3PO_3

$$K_{a1} = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$$

$$K_{a2} = 2.6 \times 10^{-7} \text{ mol dm}^{-3}$$



Phosphoric acid, H_3PO_4

$$K_{a1} = 7.5 \times 10^{-3} \text{ mol dm}^{-3}$$

$$K_{a2} = 6.2 \times 10^{-8} \text{ mol dm}^{-3}$$

$$K_{a3} = 4.8 \times 10^{-13} \text{ mol dm}^{-3}$$

A 5.00 g sample of white phosphorus was burned in oxygen. The oxide produced was dissolved in enough water to make 250 cm^3 of solution.

When the solution was treated with an excess of aqueous $\text{Ca}(\text{NO}_3)_2$, 19.4 g of a white precipitate was obtained. The white precipitate could be either CaHPO_3 or $\text{Ca}_3(\text{PO}_4)_2$ depending on the oxide that was formed when white phosphorus burned in oxygen.

- (i) Write equations for the reactions of phosphorus with oxygen to yield either P_4O_6 or P_4O_{10} and for the subsequent reactions of both oxides with water.
- (ii) Deduce the identity of the oxide and hence state the identity of the white precipitate obtained.
- (iii) Calculate the pH of the 250 cm^3 solution.

[11]

- (c) Phosphoric acid is sometimes called orthophosphoric acid to distinguish it from diphosphoric acid, $\text{H}_4\text{P}_2\text{O}_7$ that is obtained from the condensation of two phosphoric acid molecules.

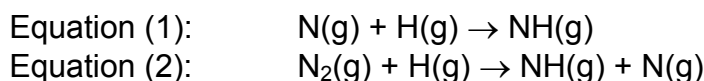
Draw the full structural formula of $\text{H}_4\text{P}_2\text{O}_7$. [1]

- (d) Nitrogen is another element of Group V. It is a colourless, odourless and tasteless gas that makes up 78% of the Earth's atmosphere by volume. The most important use of nitrogen is in the Haber process for the manufacture of ammonia, used in nitrogen fertilisers.

Apart from the Haber process, another possible process for the synthesis of ammonia proposes that N_2 and H_2 molecules are catalytically dissociated into atoms in separate reaction vessels as shown by the equations below:



- (i) Suggest and explain whether the position of equilibrium of both the above catalytic dissociation lies more to the right or to the left.
- (ii) Find the partial pressure of N at 1000 K and 200 atm.
- (iii) Calculate the number of N atoms present per dm^3 .
- (iv) Based on your answer in (iii), explain which of the following is a more likely step after the catalytic dissociation.

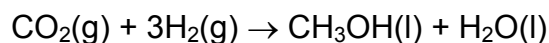


[4]

[Total: 20]

- 3** Methanol is an important intermediate used to produce chemicals like methanal and ethanoic acid in industry and can also be used as a fuel. Worldwide, about 65 million tonnes of methanol are produced each year.

- (a)** In 2012, German scientists came up with a new method for producing methanol using carbon dioxide and hydrogen as shown below. Carbon dioxide is a greenhouse gas and causes global warming.



- (i)** What is meant by the *standard enthalpy change of formation* of a compound?

- (ii)** Calculate the enthalpy change for this reaction, by using the following data :

$$\Delta H_f(\text{CH}_3\text{OH}) = -238 \text{ kJ mol}^{-1}$$

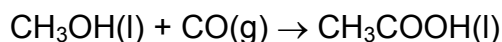
$$\Delta H_c(\text{C}) = -394 \text{ kJ mol}^{-1}$$

$$\Delta H_c(\text{H}_2) = -286 \text{ kJ mol}^{-1}$$

- (iii)** State the significance of the sign of $\Delta H_f(\text{CH}_3\text{OH})$.

[4]

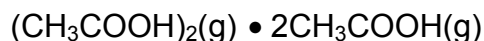
- (b)** Carbonylations are reactions that produce organic carbonyls, i.e. compounds that contain the C=O functional group such as aldehydes, carboxylic acids, and esters. One industrial method of manufacturing ethanoic acid uses methanol as a feedstock in the following exothermic reaction.



- (i)** Predict, with a reason, the sign of $\Delta S^\bullet$ for the reaction.
- (ii)** State the optimal conditions for temperature and pressure to be used in the industry for the above reaction. Explain your answer in terms of kinetic and equilibrium factors.

[4]

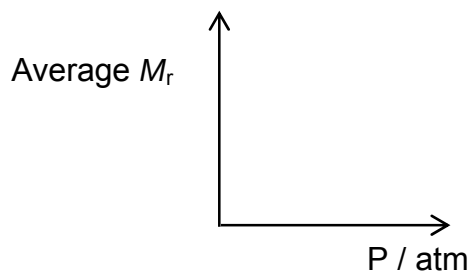
- (c)** In the solid state and in the gaseous phase, ethanoic acid exists as dimers. The following equilibrium exists in a sample of ethanoic acid vapour.



- (i)** State and explain if the forward reaction is exothermic or endothermic.
- (ii)** Calculate the partial pressures of $(\text{CH}_3\text{COOH})_2$ and CH_3COOH in the mixture given that the average M_r is 98 and at a pressure of 2.1 atm.

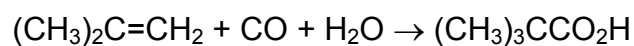
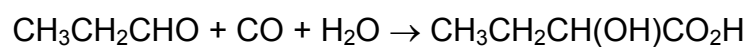
- (iii)** Sketch a graph to show how the average M_r of the mixture would vary with pressure starting with pressure = 2.1 atm. Copy the diagram below and

indicate the average M_r values on your sketch.

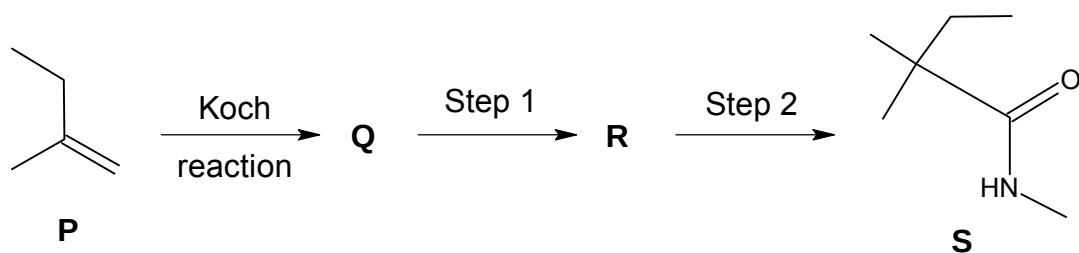


[7]

- (d) The Koch reaction is another example of carbonylation. It involves the addition of carbon monoxide to unsaturated compounds in the presence of strong acids such as sulfuric acid.



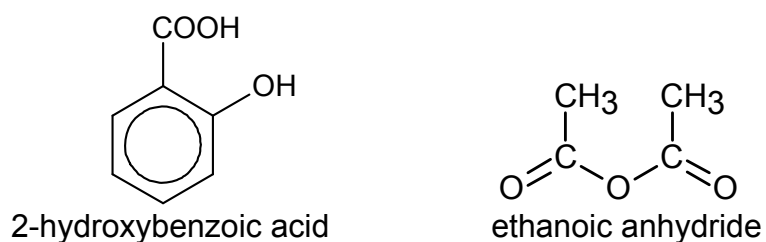
- (i) Give the structural formula of the compound that would produce glycolic acid, $\text{HOCH}_2\text{CO}_2\text{H}$ upon undergoing the Koch reaction.
- (ii) Give the structural formula of **Q** and **R**, and reagents and conditions required for steps 1 and 2 in the following synthesis.



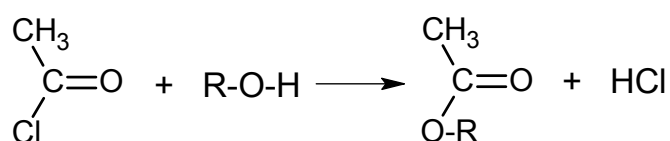
[5]

[Total: 20]

- 4(a)** Aspirin is one of the most widely used drug in the world. Its properties make it a powerful analgesic (pain reliever), antipyretic (fever reducer) and anti-inflammatory drug. It is synthesised using 2-hydroxybenzoic acid and ethanoic anhydride. The other product of this reaction is ethanoic acid.

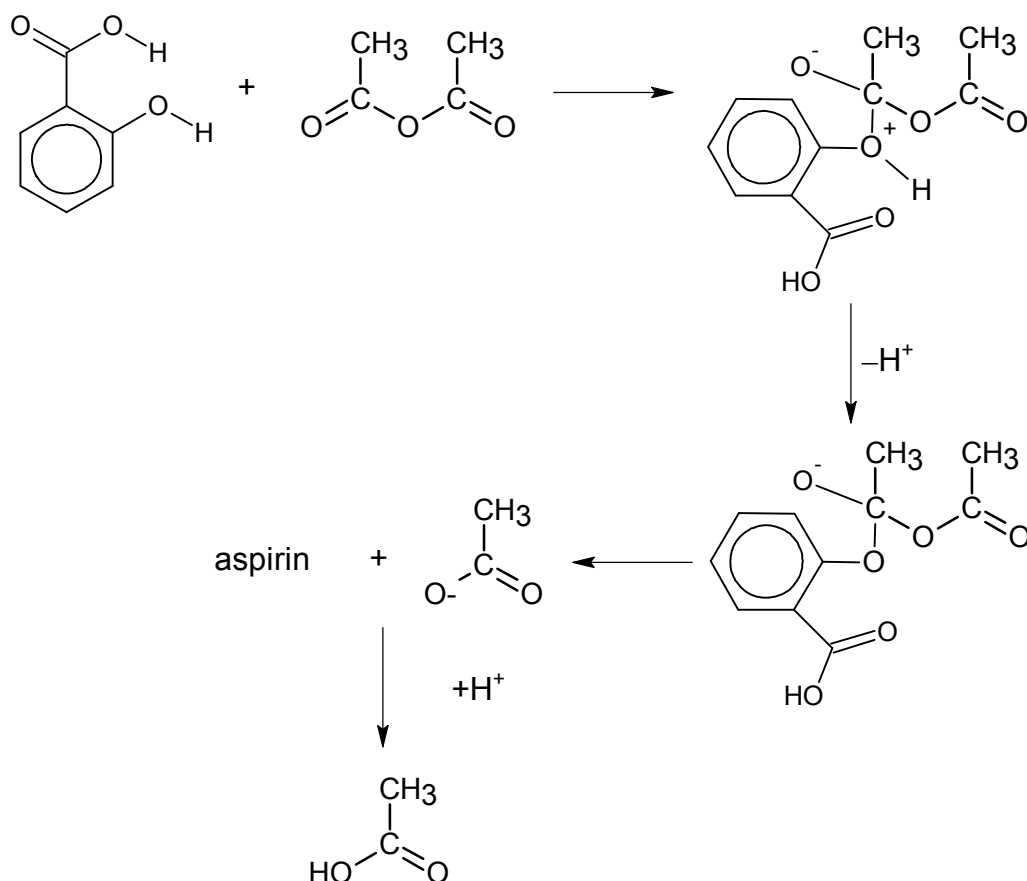


Ethanoic anhydride undergoes a similar reaction as ethanoyl chloride with 2-hydroxybenzoic acid. A general equation is shown below.



- (i)** Draw the structure of aspirin, and write a balanced equation for the synthesis of aspirin using 2-hydroxybenzoic acid and ethanoic anhydride.

The mechanism for the reaction between 2-hydroxybenzoic acid and ethanoic anhydride involves four steps. It is proposed as below:



- (ii) Using the information given above, state the type of mechanism in the first step and draw out the full mechanism for the reaction between 2-hydroxybenzoic acid and ethanoic anhydride. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons.
- (iii) State a reason why ethanoic anhydride is used rather than ethanoyl chloride for the synthesis of aspirin.
- (iv) One of the isomers of 2-hydroxybenzoic acid is 4-hydroxybenzoic acid. The pK_a values of the two acidic groups in one isomer are 4.5 and 9.3, whereas in the other isomer, they are 2.9 and 13.4.
Use the pK_a values to suggest which isomer, 2-hydroxybenzoic acid or 4-hydroxybenzoic acid, produces the more stable monoanion on treatment with 1 mol of NaOH. Explain your answer.
- (v) Draw the displayed formula of the mono-anion produced in (iv), and use your formula to suggest an explanation for why it is more stable than the mono-anion of the other isomer.

[11]

- (b) Compound **A** ($C_{10}H_{14}O_2$) does not react with sodium carbonate and hot acidified potassium dichromate. 1 mol of **A** produces 1 mol of hydrogen gas with sodium metal. Compound **A** is soluble in aqueous sodium hydroxide. Compound **A** reacts with PCl_5 to give **B**.

Compound **A** undergoes dehydration to produce **C**. Compound **C** does not show any stereoisomerism. 1 mol of **C** reacts with 3 mol of $Br_2(aq)$ to produce **D**. Upon heating **C** with acidified potassium manganate(VII), 2-hydroxybenzoic acid and compound **E** are formed. Compound **E** reacts with aqueous sodium hydroxide and aqueous iodine to give a yellow solid **F** and compound **G**.

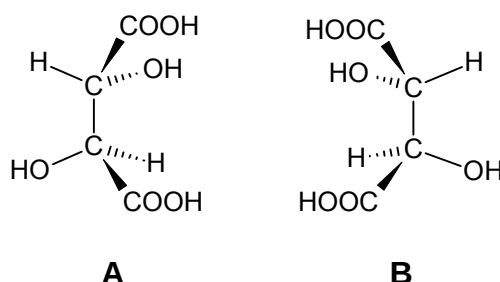
- (i) Suggest the reagents and conditions for the dehydration of compound **A** to **C**.
- (ii) Explain why compound **C** does not show any stereoisomerism.
- (iii) Draw all the structure formulae of compounds **A** to **G**.

[9]

[Total: 20]

- 5 Tartaric acid occurs naturally in many plants, particularly grapes, bananas and tamarinds and is one of the main acids found in wine.

- (a) Tartaric acid exists in two possible isomeric forms:



- (i) Naturally occurring tartaric acid is heated with aqueous potassium hydroxide under different conditions. Three different samples of tartaric acid were isolated:

Sample	Optical rotation
1	+12°
2	-12°
3	0°

Sample 1 was found to contain only isomer **A**. Identify the isomer(s) present in the other 2 samples, explaining your answer.

- (ii) Tartaric acid exists as a third isomeric form which shows zero optical rotation. Suggest and draw the displayed structure of this isomer, explaining why it does not rotate plane-polarised light.

[4]

- (b) Tartaric acid (pK_a : 3.03 and 4.54) is a white crystalline diprotic organic acid. Salts of tartaric acid are known as tartrates or hydrogen tartrates. For example, potassium hydrogen tartrate, $KC_4H_5O_6$, also commonly known as 'cream of tartar', is a slightly soluble salt. To find the K_{sp} of the salt, a titration can be carried out.

About 1.0 g of finely powdered potassium hydrogen tartrate was weighed and transferred to a beaker containing 100 cm³ of water and stirred for 20 minutes, producing a saturated solution. The temperature of the solution was noted. 25.0 cm³ of the filtered solution was titrated against 0.0710 mol dm⁻³ NaOH, using phenolphthalein as an indicator. The volume of NaOH needed for the indicator to change colour is 7.10 cm³.

- (i) Assuming that the hydrogen tartrate ion is a monobasic acid, calculate the pH of the solution after addition of 7.10 cm³ of NaOH.
- (ii) Sketch the pH-volume added curve you would expect to obtain for the above titration, labelling the various key points of the curve.
- (iii) Calculate the K_{sp} value of potassium hydrogen tartrate.

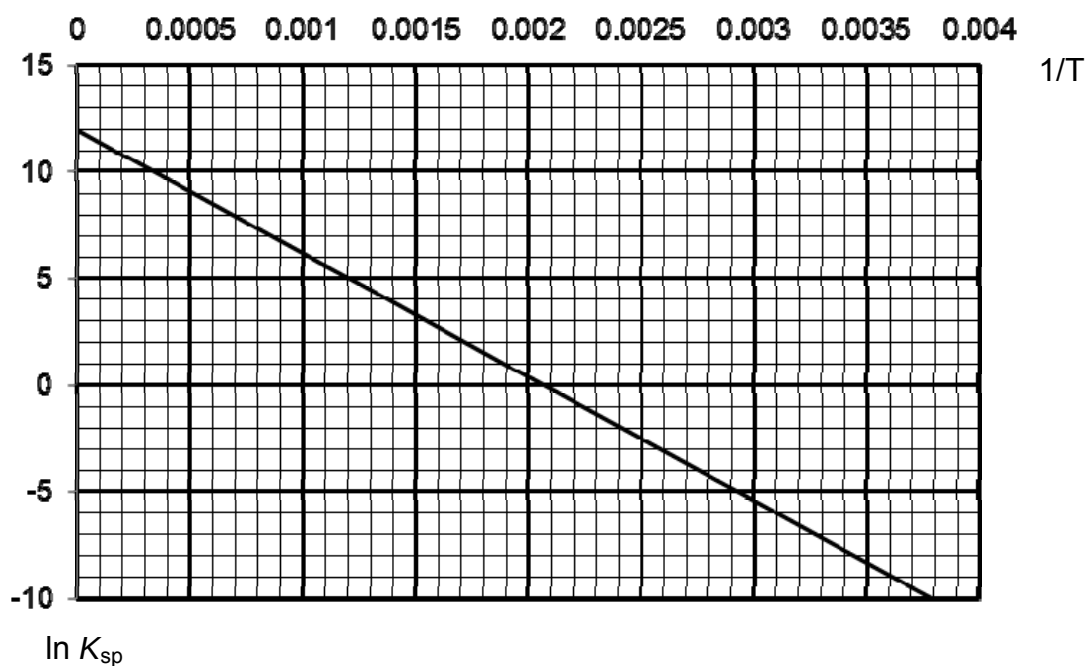
[7]

- (c) The Van't Hoff equation relates equilibrium constants to energy and entropy changes as follows:

$$\ln K = -\frac{\Delta H^\theta}{RT} + \frac{\Delta S^\theta}{R}$$

where R is the molar gas constant

The titration in (b) was repeated at different temperatures and the following results were obtained:



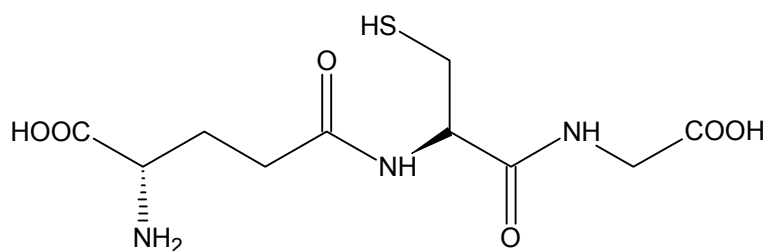
- (i) Using the graph, calculate ΔH and ΔS for the dissolution of potassium hydrogen tartrate in water. In your answer, include appropriate units.
- (ii) Hence, predict the temperature at which potassium hydrogen tartrate becomes soluble.

[3]

- (d) The Biuret test is used to test for the presence of peptide bonds. The Biuret reagent is a blue solution made from copper(II) sulfate, potassium hydroxide and sodium potassium tartrate.

During the test, each copper ion forms a square planar complex with the nitrogen atoms of the peptide bonds in the protein. The solution turns pink as a result. Dipeptides and free amino acids cannot be detected using the Biuret test. Only tripeptides and larger polypeptides can be detected,

- (i) Draw the structure of the copper complex formed when the Biuret reagent is added to a solution of glutathione.



Glutathione

- (ii) Hence, suggest why dipeptides cannot be detected using the Biuret test. [3]
- (e) Adding KI(aq) to a solution containing $\text{Cu}^{2+}(\text{aq})$ causes a reaction to take place, which produces a brown solution and white precipitate.
- (i) Construct a balanced equation for this reaction.
- (ii) With appropriate data from the *Data Booklet*, explain why it would be expected that this redox reaction would **not** occur.
- (iii) Suggest a possible reason for why it does in fact occur. [3]

[Total: 20]