NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CHEMISTRY

9647/03

Paper 3 Free Response

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.

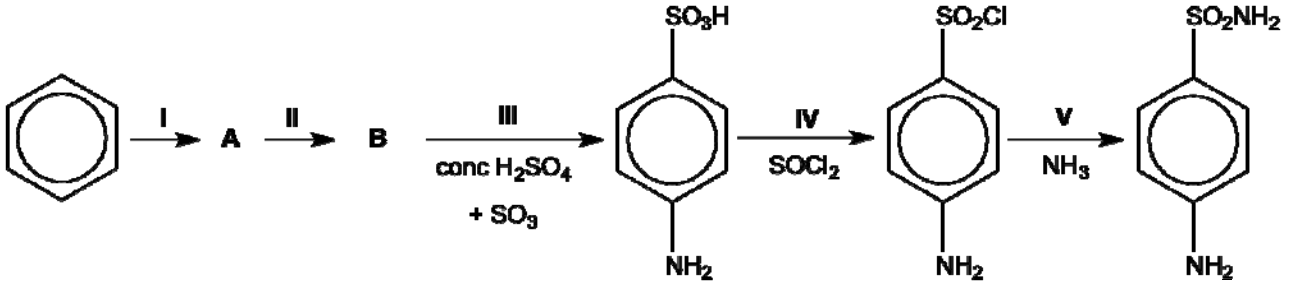
This document consists of **20** printed pages and **0** blank page.

[Turn over

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.

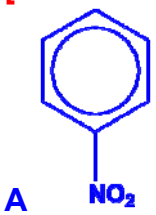


sulfanilamide

(i) Suggest reagents and conditions for steps **I** and **II**, and the structure of compounds **A** and **B**.

Step I:
Reagents: Concentrated HNO_3, Concentrated H_2SO_4
Condition: 55 – 60 °C
[1 mark for complete answer; no marks for partial answer]

Step II:
i) Reagents: Sn, HC*l*
Condition: Heat under reflux
ii) Reagent: NaOH(aq)
Condition: Room temperature
[1 mark for complete answer; no marks for partial answer]



[2 x 1 mark]

(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**.

$SO_3 + H_2SO_4 \rightarrow SO_3H^+ + HSO_4^-$ [1 mark]

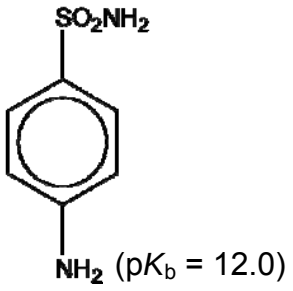
(iii) State the types of reaction in steps **II** and **V**.

Step II: Reduction
Step V: Nucleophilic substitution [1 mark each]

(iv) Explain why sulfanilamide is soluble in water.

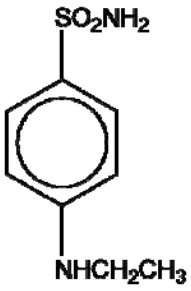
Sulfanilamide is soluble in water as they can form favourable hydrogen bonds with water. [1 mark]

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



(pK_b = 12.0)

sulfanilamide



C

(v) The amino group of sulfanilamide has a pK_b value of 12.0. Suggest a pK_b value for the amino group of compound **C**. Explain your answer.

$9 < pK_b < 12.0$ (pK_b of aniline = 9) [1 mark]

Compound C has an electron-donating ethyl substituent on the amine substituent of the benzene. Hence, the electron density on the N atom is increased, making its lone pair of electrons to be more readily available to accept a proton. [1 mark]

[10]

(b) Describe and explain the trend in thermal decomposition of Group II nitrates, writing an equation for any reaction that occurs. [3]

$2M(NO_3)_2(s) \rightarrow 2MO(s) + 4NO_2(g) + O_2(g)$ [1 mark]

Down the group from Mg to Ba, cationic radius increases but ionic charge remains the same. Therefore, charge density of Group II cations decreases, causing electron cloud of nitrate ion to be less easily polarised. [1 mark]
Hence, thermal stability of Group II nitrates increases from Mg to Ba. [1 mark]

(c) Ammonium nitrate is widely used as an explosive. It can easily decompose when ignited to give nitrogen gas, oxygen gas and steam.

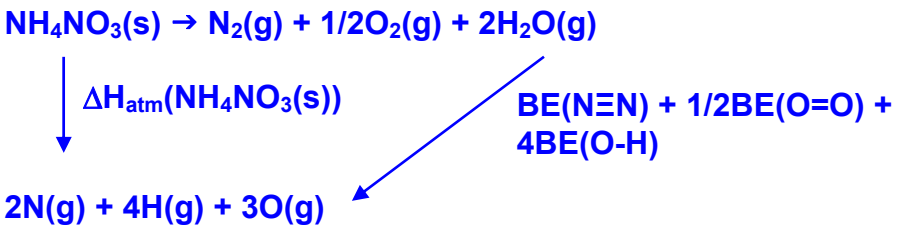
(i) Write a balanced equation, with state symbols, which represents the enthalpy change of decomposition of 1 mole of ammonium nitrate.

$NH_4NO_3(s) \rightarrow N_2(g) + 1/2O_2(g) + 2H_2O(g)$
[1 mark; NH_4NO_3 must be in 1 mole]

(ii) Define the term *enthalpy change of atomisation of ammonium nitrate*.

The enthalpy change of atomisation of ammonium nitrate is the energy required when 1 mole of ammonium nitrate is broken to form its constituent gaseous atoms. [1 mark]

(iii) The standard enthalpy change of atomisation of ammonium nitrate is +2928 kJ mol^{-1}. Using suitable data from the *Data Booklet*, construct an energy cycle to calculate the enthalpy change of decomposition of ammonium nitrate.



ΔH_r = +2928 – (+994) – ½(+496) –4(+460)
= –154 kJ mol^{-1}
[3 marks; 1 mark each for correct cycle with labelling, input of values and final answer]

(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)**.

$Q_{evolved}$ = mcΔT
= 100 x 4.18 x 4 = 1672 J

For 1 mole of ammonium nitrate,
$Q_{evolved}$ = 1672 ÷ (1.0/80) = 133.76 kJ [1 mark]

The value in (c)(iv) is lower than that in (c)(iii) as some of the heat evolved are lost to the surroundings. [1 mark]

[7]

[Total: 20]

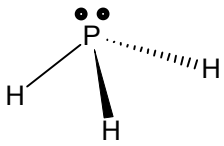
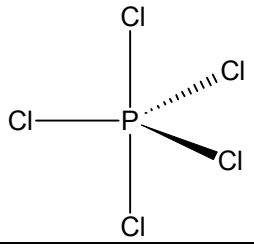
2 Phosphorus is the most abundant element of Group V, accounting for 0.10% of the mass of the Earth's crust. Phosphorus exists in two common allotropic forms: white phosphorus and red phosphorus. White phosphorus contains discrete tetrahedral P_4 molecules. Red phosphorus, by contrast, has a polymeric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

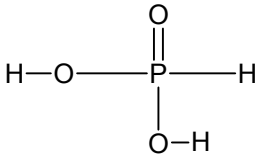
B is an off-white solid that melts at 167 ^{o}C and gives white fumes and phosphoric acid on contact with moist air.

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

A is PH_3	**B** is PCl_5
	
$PH_3 + 2O_2 \rightarrow H_3PO_4$	$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$

1 mark for suggesting both the identity of A and B correctly
1 mark for drawing both the shapes correctly
1 mark for writing each equation correctly; total 2 marks

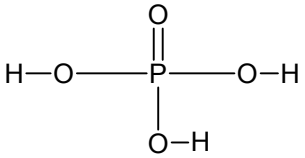
(b) When phosphorus burns in oxygen, it yields either P_4O_6 or P_4O_{10} depending on the amount of oxygen present. Both P_4O_6 and P_4O_{10} are acidic oxides, and they react with water to form aqueous solutions of phosphorous acid and phosphoric acid, respectively. Phosphorous acid is diprotic, while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



Phosphorous acid, H_3PO_3

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

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



Phosphoric acid, H_3PO_4

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

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

$K_{a3} = 4.8 \times 10^{-13}$ 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 $Ca(NO_3)_2$, 19.4 g of a white precipitate was obtained. The white precipitate could be either $CaHPO_3$ or $Ca_3(PO_4)_2$ 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.

$P_4 + 3O_2 \rightarrow P_4O_6$ $\quad\quad$ $P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$
$P_4 + 5O_2 \rightarrow P_4O_{10}$ $\quad\quad$ $P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$

(ii) Deduce the identity of the oxide and hence state the identity of the white precipitate obtained.

$H_3PO_3 + Ca(NO_3)_2 \rightarrow CaHPO_3 + 2HNO_3$
$2H_3PO_4 + 3Ca(NO_3)_2 \rightarrow Ca_3(PO_4)_2 + 6HNO_3$

If the oxide is P_4O_6, the mole ratio of P_4 : $CaHPO_3$ is as follows:

P_4 :	P_4O_6 :	H_3PO_3 :	$CaHPO_3$
1	1	4	4

1 mark for deducing the mole ratio of P_4 : $CaHPO_3$ correctly

If the oxide is P_4O_{10}, the mole ratio of P_4 : $Ca_3(PO_4)_2$

P_4 :	P_4O_6 :	H_3PO_3 :	$CaHPO_3$
1	1	4	2

1 mark for deducing the mole ratio of P_4 : $Ca_3(PO_4)_2$ correctly

$n(P_4) = 5.00/(4 \times 31.0) = 0.04032$ mol [1]

$Mr(CaHPO_3) = 120.1$
$Mr(Ca_3(PO_4)_2) = 310.3$ [1] for obtaining both Mr correct

$n(CaHPO_3) = 19.4/120.1 = 0.1615$ mol
$n(Ca_3(PO_4)_2) = 19.4/310.3 = 0.06252$ mol

$P_4 : CaHPO_3 = 0.04032 : 0.1615 \approx 1 : 4$
$P_4 : Ca_3(PO_4)_2 = 0.04032 : 0.06252 = 1 : 1.55$

[1]

The oxide is P_4O_6 [1] and the white precipitate is $CaHPO_3$ [1].

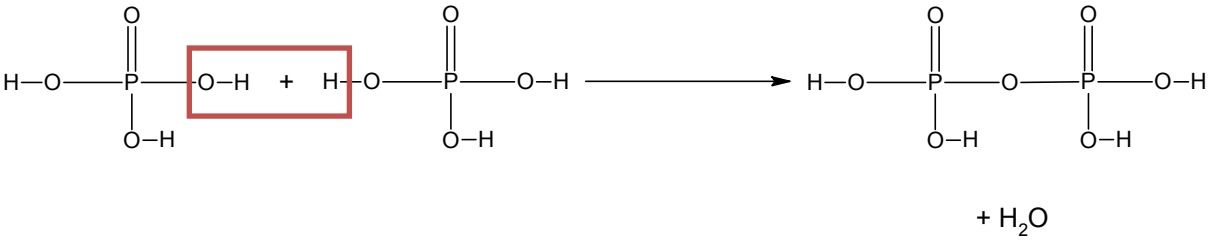
(iii) Calculate the pH of the 250 cm^3 solution.

$n(H_3PO_3) = 0.04032 \times 4 = 0.16128$ mol
$[H_3PO_3] = 0.016128 / (250/1000) = 0.64512$ mol dm^{-3} [1]
pH = $-\lg\sqrt{1.0\times10^{-2}\times0.64512} = 1.1$ [1]

[11]

(c) Phosphoric acid is sometimes called orthophosphoric acid to distinguish it from diphosphoric acid, $H_4P_2O_7$ that is obtained from the condensation of two phosphoric acid molecules.

Draw the full structural formula of $H_4P_2O_7$. [1]



+ H_2O

1 mark for drawing the full structural formula of product
The equation is not needed. It is included in the answer above to help student to understand how the product is formed.

(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:

$$N_2(g) \bullet 2N(g) \qquad \log K_p = -43.10$$
$$H_2(g) \bullet 2H(g) \qquad \log K_p = -17.30$$

(i) Suggest and explain whether the position of equilibrium of both the above catalytic dissociation lies more to the right or to the left.

The POE lies more to the left as the K_p values are large. [1]

(ii) Find the partial pressure of N at 1000 K and 200 atm.

Let the partial pressure of N be x
Partial pressure of N_2 = 200 – x ≈ 200 based on **(i)**

$$10^{-43.10} = \frac{x^2}{(200-x)}$$

x = 3.99 x 10^{-21} atm [1]

(iii) Calculate the number of N atoms present per dm^3.

PV=nRT

$$\text{N(N atoms)} = \frac{3.99\times10^{-21}\times101325\times1\times10^{-3}}{8.31\times1000}\times6.022\times10^{23} = 29 \text{ atoms}$$ [1]

(iv) Based on your answer in **(iii)**, explain which of the following is a more likely step after the catalytic dissociation.

Equation (1): $N(g) + H(g) \rightarrow NH(g)$
Equation (2): $N_2(g) + H(g) \rightarrow NH(g) + N(g)$

With only 29 atoms in 1 dm^3, the reaction described by equation (1) will produce virtually no NH(g) molecules. This equilibrium: $N_2(g) \bullet 2N(g)$ lies more to the left. There are much more N_2 molecules than N atoms, so the reaction described by equation (2) is the more likely step. [1]

[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.

$$CO_2(g) + 3H_2(g) \rightarrow CH_3OH(l) + H_2O(l)$$

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

The *standard enthalpy change of formation* of a compound is the energy change when one mole of compound is formed from its constituent elements in their standard states under standard conditions. [1]

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

$\Delta H_f(CH_3OH)$ = -238 kJ mol^{-1}

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

$\Delta H_c(H_2)$ = -286 kJ mol^{-1}

$\Delta H_{reaction} = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants})$

$= [(-238) + (-286)] - [(0) + 394]$

$= -130$ kJ mol^{-1}

Award [2] for correct answer with working :

- Correct application of formula (1 mk)
- Recognising

$\Delta H_f(CO_2)$ = -394 kJ mol^{-1}

$\Delta H_f(H_2O)$ = -286 kJ mol^{-1}

(iii) State the significance of the sign of $\Delta H_f(CH_3OH)$.

Methanol is energetically more stable than its constituent elements since $\Delta H_f(CH_3OH) < 0$ [1]

[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.

$$CH_3OH(l) + CO(g) \rightarrow CH_3COOH(l)$$

(i) Predict, with a reason, the sign of $\Delta S^{\bullet}$ for the reaction.

standard (molar) entropy change would be negative because of decrease in disorder / decrease in number of moles of gas particles [1]

(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.

Optimal conditions: moderate high temperature and pressure
By Le Chaterlier's principle, the production of ethanoic acid/forward reaction is favoured by low temperatures and high pressures. [1]
However, at low temperatures, the rate of reaction would be low, hence a moderately high temperature should be used. [1]
High pressure conditions would require very expensive factory equipment to build and maintain. Hence a moderately high pressure should be used. [1]

[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.

$$(CH_3COOH)_2(g) \bullet 2CH_3COOH(g)$$

(i) State and explain if the forward reaction is exothermic or endothermic.

Endothermic reaction as it involves bond breaking [1]

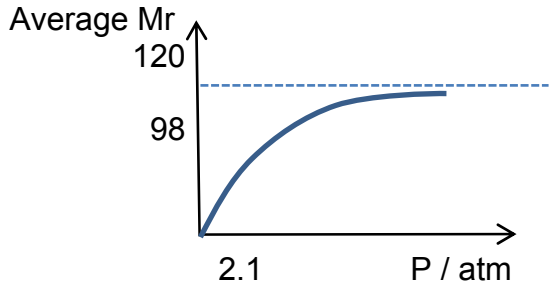
(ii) Calculate the partial pressures of $(CH_3COOH)_2$ and CH_3COOH in the mixture given that the average M_r is 98 and at a pressure of 2.1 atm.

Let the mole fraction of $(CH_3COOH)_2$ be x, and CH_3COOH be y.
x + y = 1 …(1)
98 = 120x + 60y …(2) [1] for forming 2 equations

(1)x120 : 120x+120y = 120 …(3)
(3) – (2) : 22 = 60y hence y = 0.3667
x = 1- 0.3667 = 0.6333 [1] for calculating mole fractions

$P_{(CH3COOH)2}$ = 0.6333 x 2.1 = 1.33 atm
$P_{(CH3COOH)}$ = 0.3667 x 2.1 = 0.770 atm [1] for correct partial pressures

(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.



[1] increase in ave Mr as P increase (due to POE shifting to the left as P increases)

[1] correct curve (and not straight line) as $Mr \alpha \frac{1}{P}$ from $PV=nRT$

[1] maximum ave Mr approaches 120 (an equilibrium mixture must always have both the ethanoic acid monomer and dimer)

[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.

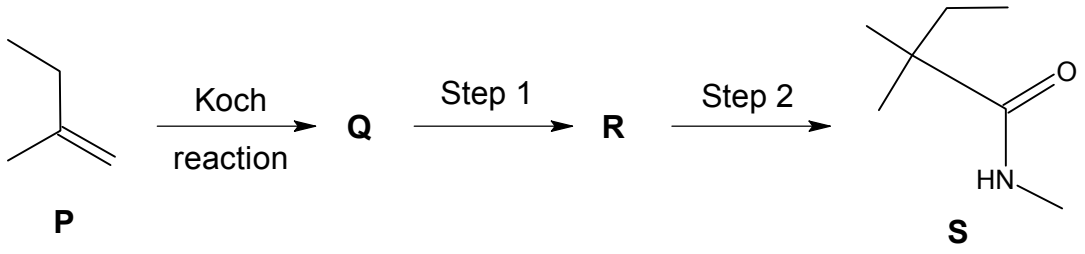
$$CH_3CH_2CHO + CO + H_2O \rightarrow CH_3CH_2CH(OH)CO_2H$$

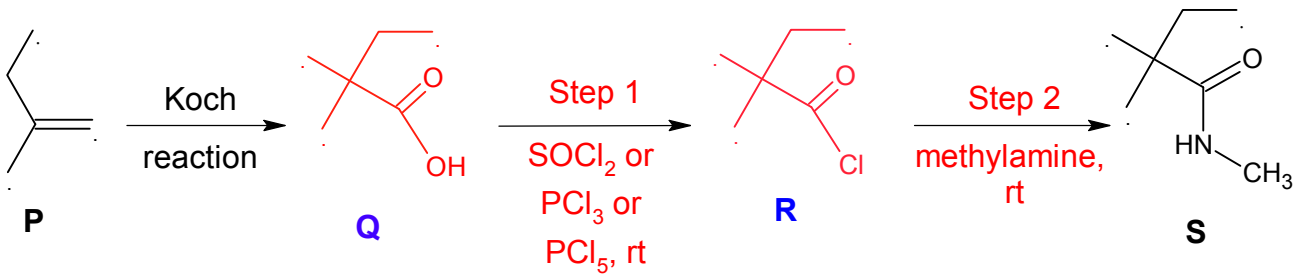
$$(CH_3)_2C{=}CH_2 + CO + H_2O \rightarrow (CH_3)_3CCO_2H$$

(i) Give the structural formula of the compound that would produce glycolic acid, $HOCH_2CO_2H$ upon undergoing the Koch reaction.

CH_2O [1]

(ii) Give the structural formula of **Q** and **R**, and reagents and conditions required for steps 1 and 2 in the following synthesis.



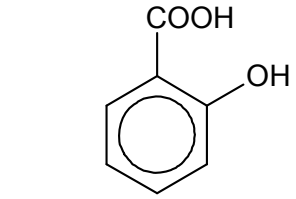


correct structural formula of Q & R [2 x 1]
correct reagents and conditions for step 1 & 2 [2 x 1]

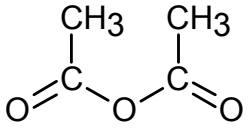
[5]

[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.

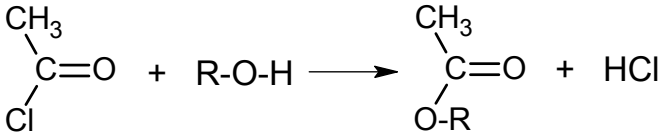


2-hydroxybenzoic acid

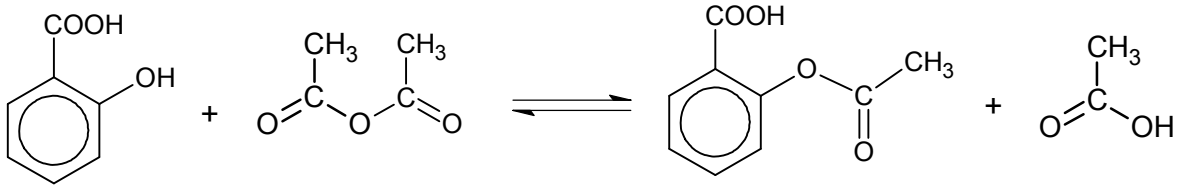


ethanoic anhydride

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

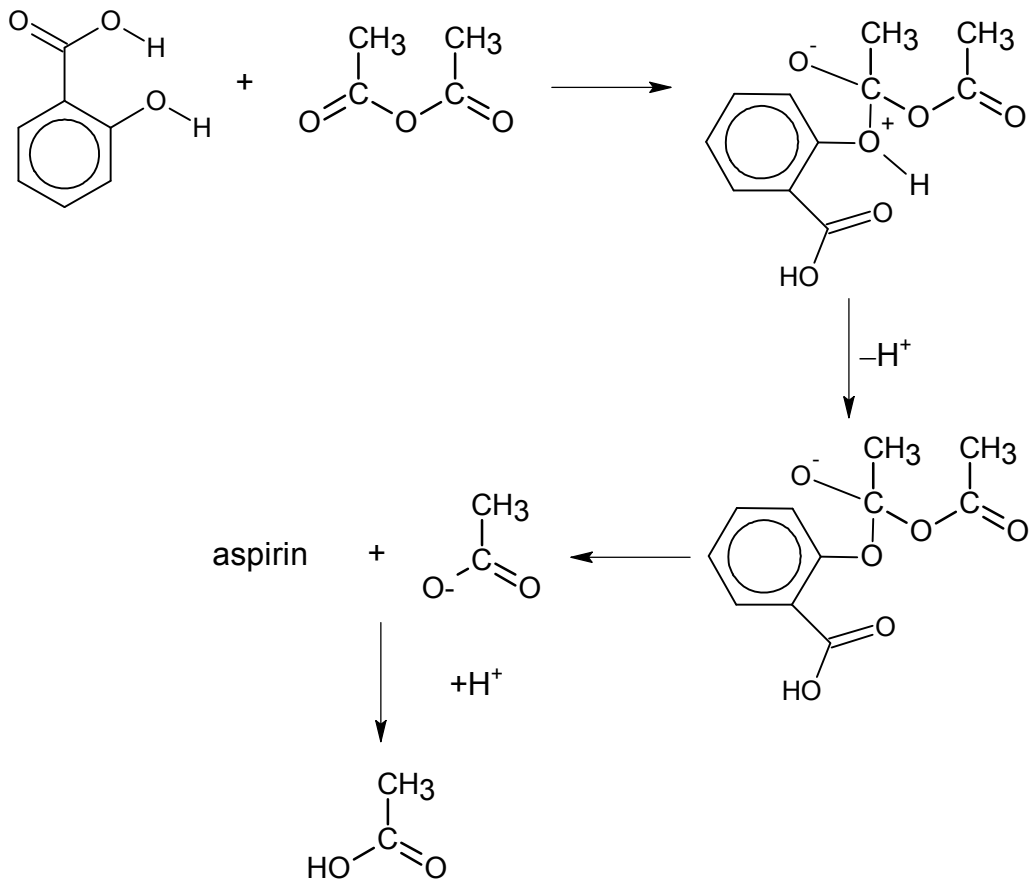


(i) Draw the structure of aspirin, and write a balanced equation for the synthesis of aspirin using 2-hydroxybenzoic acid and ethanoic anhydride.



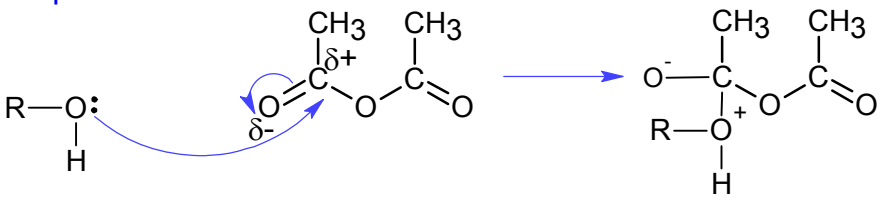
Aspirin structure [1]; eqn [1]

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



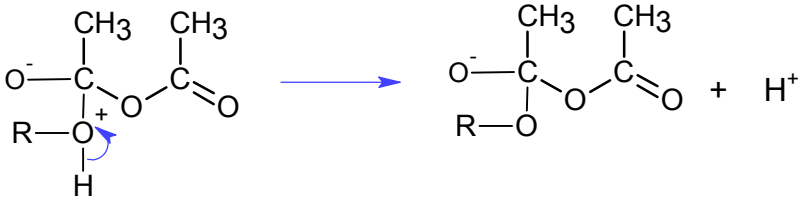
(ii) Using the information given above, state the type of mechanism in the first step and draw out the full mechanism for the reaction between 2-hydroxybenzoic acid and ethanoic anhydride. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons.

Nucleophilic addition [1]
2-hydroxybenzoic acid represented by R–O–H
Step 1



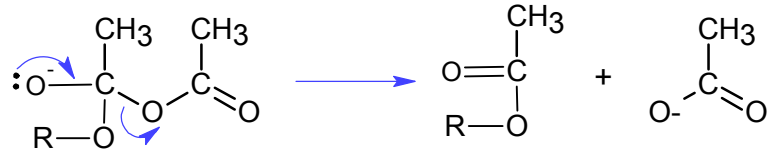
[1]

Step 2



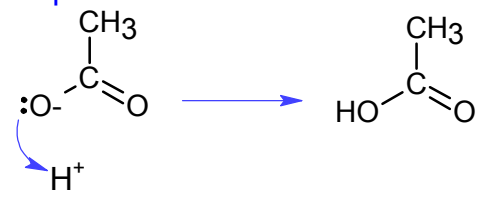
[1]

Step 3



[1]

Step 4



[1]

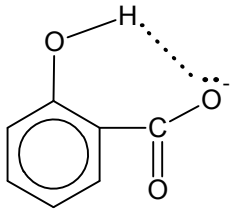
(iii) State a reason why ethanoic anhydride is used rather than ethanoyl chloride for the synthesis of aspirin.

Safer because it is less corrosive and less readily hydrolysed. [1]
(Do not produce corrosive and poisoning fumes of HCl)

(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 3.0 and 4.4, whereas in the other isomer, they are 1.9 and 6.2.
Use the pK_a values to suggest which isomer produces the more stable monoanion on treatment with 1 mol of NaOH. Explain your answer.

2-hydroxybenzoic acid as it has a lower pK_a. [1]

(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.



[1] stabilised by intramolecular hydrogen bonding. [1]

[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**.

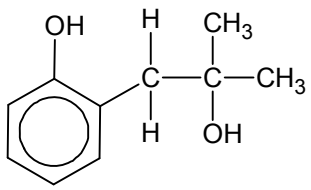
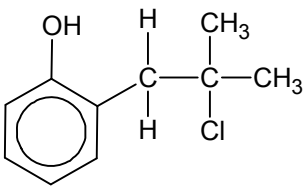
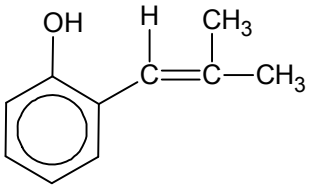
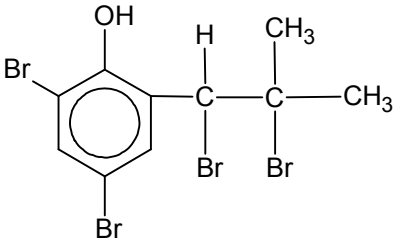
Compound **A** undergoes dehydration to produce **C**. Compound **C** does not show any stereoisomerism. 1 mol of **C** reacts with 3 mol of Br_2(aq) to produce **D**. Upon heating **C** with acidified potassium manganate(VII), 2-hydroxybenzoic acid and compound **E** are formed. Compound **E** reacts 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**.

Excess conc H_2SO_4, 170 °C [1]

(ii) Explain why compound **C** does not show any stereoisomerism.
There are 2 $-CH_3$ groups attached to the same C involved in C=C bond. [1]

(iii) Draw all the structure formulae of compounds **A** to **G**.

A 	**B** 
C 	**D** 

E	**F**	**G**
CH_3COCH_3	CHI_3	CH_3COO^-

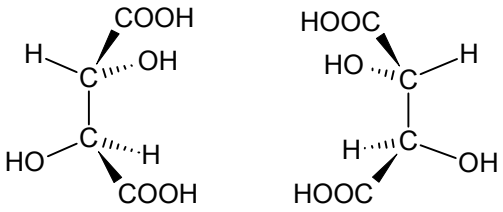
[7 x 1]

[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:

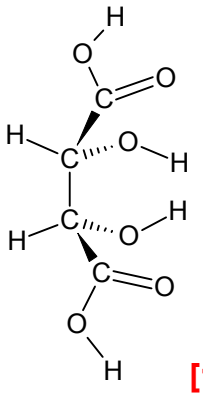


A **B**

(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.



[1]

Sample 2 contains Isomer **B** which is the **mirror image** of Isomer **A**, hence rotates plane-polarised light in opposite direction. **[1]**
Sample 3 contains **equal amounts of Isomer A and B** which is a **racemic mixture**. Hence optical rotation is zero. **[1]**

(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.

The 3rd form is the meso isomer. There is zero optical rotation as there is an **internal plane of symmetry**. **[1]**

[4]

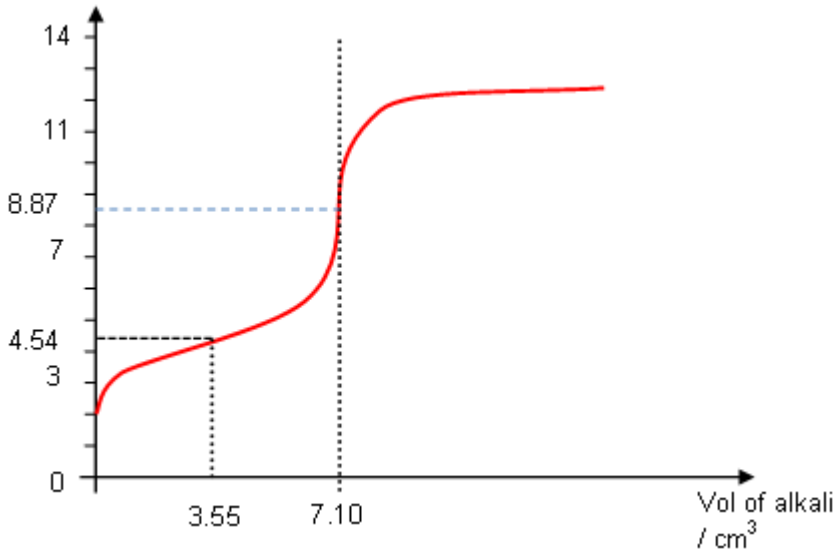
(b) Tartaric acid (pK_a: 3.03 and 4.54) is a white crystalline diprotic organic acid. Salts of tartaric acid are known as tartrates or hydrogen tartrates. For example, potassium hydrogen tartrate, $KC_4H_5O_6$, also commonly known as 'cream of tartar', is a slightly soluble salt. To find the K_{sp} of 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 cm^3 of water and stirred for 20 minutes, producing a saturated solution. The temperature of the solution was noted. 25.0 cm^3 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 cm^3.

(i) Assuming that the hydrogen tartrate ion is a monobasic acid, calculate the pH of the solution after addition of 7.10 cm^3 of NaOH.

At 7.10 cm^3, only $C_4H_4O_6^{2-}$, which is a weak conjugate base, is present.
$[C_4H_4O_6^{2-}] = (0.0710 \times 7.10) / (25+7.10) = 0.0157$ mol dm^{-3} **[1]**
$K_b = 10^{-14} / 10^{-4.54} = 3.47 \times 10^{-10}$ mol dm^{-3} **[1]**
$[OH^-] = \sqrt{[(3.47 \times 10^{-10})(0/0157)]} = 2.33 \times 10^{-6}$
pOH = 5.63
pH = 8.37 **[1]**

(ii) Sketch the pH-volume added curve you would expect to obtain for the above titration, labelling the various key points of the curve.



[1] Correct shape (vertical region>pH7)
[1] Endpoint volume & pH correct, max buffering point correctly labelled

(iii) Calculate the K_{sp} value of potassium hydrogen tartrate.

$[C_4H_5O_6^-] = (0.0710 \times 7.10) / 25 = 0.0202$ mol dm^{-3}
$K_{sp} = [K^+][C_4H_5O_6^-] = (0.0202)^2 = 4.07 \times 10^{-4}$ mol^2dm^{-6} **[1]**

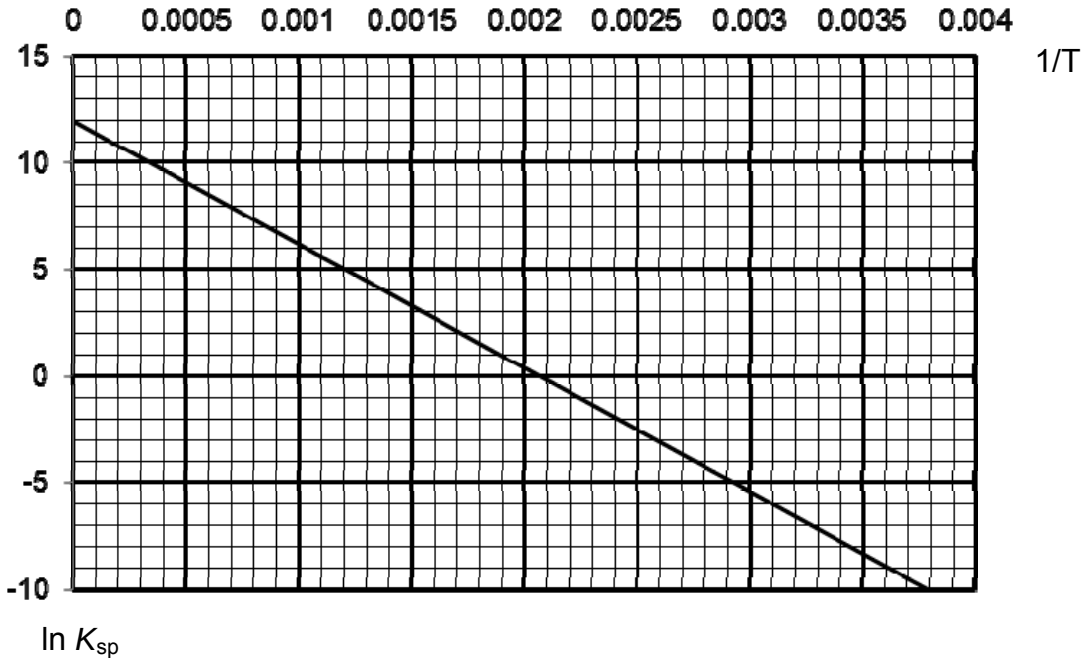
[7]

(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.

Gradient value = ΔH/ R = (12 + 10) / (0.0038 –0)
= 5789

ΔH = 5789 x 8.31 = 48110 = 48.1 kJ mol^{-1} **[1]**

y-intercept value = ΔS/ R = 12

ΔS = 12 x 8.31 = 99.7 J K^{-1} mol^{-1} **[1]**

(ii) Hence, predict the temperature at which potassium hydrogen tartrate becomes soluble.

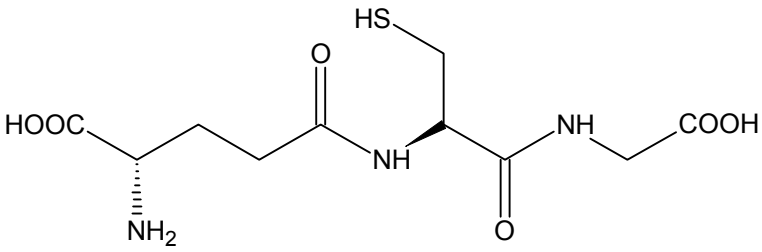
ΔG = ΔH – T ΔS = 0
T = ΔH / ΔS = 48110 / 99.7 = 483 K **[1]**

[3]

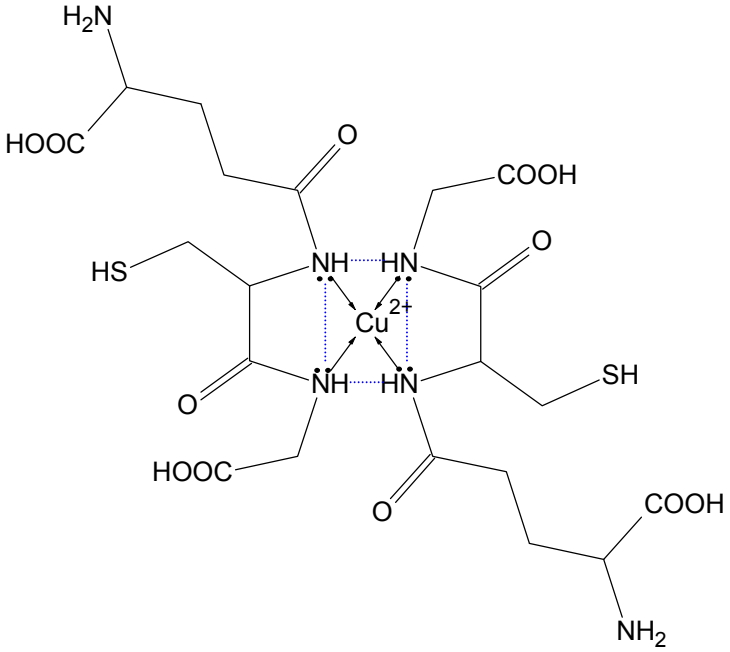
(d) The Biuret test is used to test for the presence of peptide bonds. The Biuret reagent is a blue solution made from copper(II) sulfate, potassium hydroxide and sodium potassium tartrate.

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 gluthathione.



Gluthathione



[1] Draw square planar shape i.e. Cu^{2+} bonded to 4 N atoms. Must show dative bonds and lone pair on N atom.
[1] Connect Cu^{2+} to N atoms of 2 peptide bonds of 2 gluthathione molecules

(ii) Hence, suggest why dipeptides cannot be detected using the Biuret test.

Dipeptides only have 1 peptide bond, hence Cu^{2+} forms bonds with 4 dipeptides, resulting in steric hindrance, thus causing the complex formed to be unstable. **[1]**

[3]

(e) Adding KI(aq) to a solution containing $Cu^{2+}(aq)$ causes a reaction to take place, which produces a brown solution and white precipitate.

(i) Construct a balanced equation for this reaction.

$2Cu^{2+}(aq) + 4I^{-}(aq) \rightarrow 2CuI(s) + I_2(aq)$ **[1]**

(ii) With appropriate data from the *Data Booklet*, explain why it would be expected that this redox reaction would **not** occur.

$E_{cell} = +0.15 - 0.54 = -0.39$ V
Since $E_{cell} < 0$, Reaction is energetically not feasible **[1]**

(iii) Suggest a possible reason for why it does in fact occur.

The formation of **insoluble CuI lowers [Cu^{+}]** in solution, hence driving **position of equilibrium to the right**. **[1]**

[3]

[Total: 20]