

# Anglo-Chinese Junior College

JC2 Preliminary Examination

Higher 2



A Methodist Institution  
(Founded 1868)

CANDIDATE  
NAME

**SUGGESTED SOLUTIONS**

FORM  
CLASS

TUTORIAL  
CLASS

INDEX  
NUMBER

## CHEMISTRY

Paper 4 Practical

**9729/04**

**1 August 2023**

**2 hours 30 minutes**

Candidates answer on the Question Paper.

### READ THESE INSTRUCTIONS FIRST

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

Give details of the practical shift and laboratory, where appropriate, in the boxes provided.

Write in dark blue or black pen.

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

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.

You may lose marks if you do not show your working or if you do not use appropriate units.

Qualitative Analysis Notes are printed on pages 21 and 22.

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.

**Shift**

**Laboratory**

### For Examiner's Use

<b>1</b>	<b>/ 16</b>
<b>2</b>	<b>/ 19</b>
<b>3</b>	<b>/ 20</b>
<b>Total</b>	<b>/ 55</b>

This document consists of **20** printed pages and **2** blank pages.

# 1 Determination of the change in the oxidation number of a transition metal ion, $X^{2+}$

**FA 1** is  $0.0125 \text{ mol dm}^{-3}$  potassium manganate(VII),  $\text{KMnO}_4$

**FA 2** is  $0.0720 \text{ mol dm}^{-3}$  transition metal salt,  $\text{XSO}_4$

**FA 3** is  $1.00 \text{ mol dm}^{-3}$  sulfuric acid,  $\text{H}_2\text{SO}_4$

You are to determine, by titration, the change in the oxidation number of a transition metal ion,  $X^{2+}$ , upon oxidation by acidified potassium manganate(VII).

## (a) Procedure

1. Fill the burette with **FA 1**.
2. Using the pipette, transfer  $25.0 \text{ cm}^3$  of **FA 2** into the conical flask.
3. Using a measuring cylinder, transfer  $10.0 \text{ cm}^3$  of **FA 3** to the same conical flask.
4. Titrate the mixture in the conical flask with **FA 1**. The end-point is reached when the first permanent pale pink colour is seen.
5. Record your titration results, to an appropriate level of precision, in the space provided.
6. Repeat steps 2 to 5 to obtain consistent results.

## (i) Titration results

Final burette reading / $\text{cm}^3$	27.90	27.90
Initial burette reading / $\text{cm}^3$	0.00	0.00
Volume of <b>FA1</b> used / $\text{cm}^3$	27.90	27.90

[2]

- (ii) From your titration results in (a)(i), obtain a suitable volume of **FA 1**,  $V_{\text{FA 1}}$ , to be used in your calculations. Show clearly how you obtained this volume.

$$\text{Average titre volume} = (27.90 + 27.90) / 2 = \underline{27.90 \text{ cm}^3}$$

$$V_{\text{FA 1}} = \dots\dots\dots [4]$$

- (b) (i) Calculate the amount of  $\text{MnO}_4^-$  present in  $V_{\text{FA 1}}$  obtained in (a)(ii).

$$\begin{aligned}\text{Amount of } \text{MnO}_4^- &= 27.90/1000 \times 0.0125 \\ &= 3.488 \times 10^{-4} = \underline{3.49 \times 10^{-4} \text{ mol}} \text{ (3 s.f.)}\end{aligned}$$

amount of  $\text{MnO}_4^-$  = ..... [1]

- (ii) Calculate the amount of  $\text{X}^{2+}$  in  $25.0 \text{ cm}^3$  of FA 2.

$$\text{Amount of } \text{X}^{2+} = 25.0/1000 \times 0.0720 = \underline{0.00180 \text{ mol}}$$

amount of  $\text{X}^{2+}$  = ..... [1]

- (iii) The half-equation for the reduction of  $\text{MnO}_4^-$  is shown.



It is known that  $\text{X}^{2+}$  is oxidised to either  $\text{X}^{3+}$  or  $\text{X}^{4+}$ , but not both.

Determine the stoichiometric ratio of:

- $\text{MnO}_4^-$  to  $\text{X}^{2+}$  if  $\text{X}^{3+}$  is formed,
- $\text{MnO}_4^-$  to  $\text{X}^{2+}$  if  $\text{X}^{4+}$  is formed.



$\text{MnO}_4^- : \text{X}^{2+}$  if  $\text{X}^{3+}$  is formed = 1 : 5

$\text{MnO}_4^- : \text{X}^{2+}$  if  $\text{X}^{4+}$  is formed = 2 : 5

[1]

- (iv) Using your answers from (b)(i) to (iii), determine the change in the oxidation number of  $\text{X}^{2+}$  upon oxidation by acidified  $\text{MnO}_4^-$ .

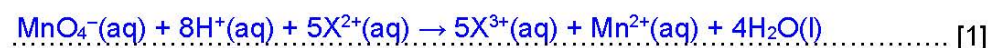
$$\text{MnO}_4^- : \text{X}^{2+} = 3.49 \times 10^{-4} : 0.00180 = 1 : 5.16 = \underline{1 : 5}$$

Hence,  $\text{X}^{3+}$  is formed.

$$\text{Change in oxidation number} = +3 - (+2) = \underline{+1}$$

change in oxidation number = ..... [2]

- (v) Hence, write a balanced equation, with state symbols, for the oxidation of  $\text{X}^{2+}$  by acidified  $\text{MnO}_4^-$ .



- (c) A student claimed that using a burette to measure 25.0 cm<sup>3</sup> of FA 2 in Step 2 would give a more accurate result than using a pipette.

The maximum error in each volume reading on a burette is  $\pm 0.05$  cm<sup>3</sup>.

The percentage error incurred using a 25.0 cm<sup>3</sup> pipette is 0.24%.

By calculating the percentage error incurred using a burette, deduce if the claim by the student is correct.

.....  
 % error incurred using a burette =  $[2(0.05) / 25.0] \times 100\% = 0.40\%$

.....  
 As the % error incurred using a burette is higher than that of a pipette, the claim by the student is incorrect. .... [1]

- (d) Explain whether using a burette instead of a measuring cylinder to measure 10.0 cm<sup>3</sup> of FA 3 in Step 3 would affect the accuracy of the experimental results.

.....  
 As sulfuric acid is used in excess to provide the acidic medium for the oxidation, using a burette would not affect the accuracy of the experimental results. .... [1]

- (e) Table 1.1 shows electrode reactions with their standard electrode potential values.

Table 1.1

electrode reaction	$E^\circ / \text{V}$
$\text{X}^{3+} + \text{e}^- \rightleftharpoons \text{X}^{2+}$	+0.77
$\text{X}^{4+} + 2\text{e}^- \rightleftharpoons \text{X}^{2+}$	+0.86
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+1.52
$\text{NO}_3^- + 3\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{HNO}_2 + \text{H}_2\text{O}$	+0.94

Use the relevant data to explain, with reference to the expected titre readings, whether nitric acid can be used in place of sulfuric acid in the oxidation of X<sup>2+</sup> by MnO<sub>4</sub><sup>-</sup>.

.....  
 Since  $E^\circ$  of NO<sub>3</sub><sup>-</sup>/HNO<sub>2</sub> is more positive than  $E^\circ$  of X<sup>3+</sup>/X<sup>2+</sup>,

.....  
 (OR  $E^\circ_{\text{cell}} = +0.94 - (+0.77) = +0.17 \text{ V} > 0$ )

.....  
 X<sup>2+</sup> can also be oxidised by nitric acid on top of MnO<sub>4</sub><sup>-</sup>.

.....  
 As such, nitric acid cannot be used in place of sulfuric acid as the titre readings obtained would be lower than expected. .... [2]

[Total: 16]

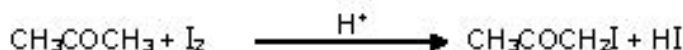




## 2 Determination of the kinetics of the iodination of propanone

The rate of a chemical reaction is affected by the concentration of reactants according to the rate equation which has to be determined experimentally.

In this experiment, propanone is reacted with iodine in the presence of an acid catalyst.



The order of reaction with respect to iodine can be found by titrating the concentration of iodine remaining at regular time intervals with sodium thiosulfate solution.

**FA 3** is 1.00 mol dm<sup>-3</sup> sulfuric acid, H<sub>2</sub>SO<sub>4</sub>.

**FA 4** is 1.00 mol dm<sup>-3</sup> propanone, CH<sub>3</sub>COCH<sub>3</sub>.

**FA 5** is a solution of iodine dissolved in potassium iodide solution.

**FA 6** is 0.010 mol dm<sup>-3</sup> sodium thiosulfate, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.

**FA 7** is 0.05 mol dm<sup>-3</sup> sodium hydrogencarbonate, NaHCO<sub>3</sub>.

starch indicator

### (a) Procedure:

**Notes:** You will perform each titration **once** only. Great care must be taken that you do not overshoot the end-point.

Once you have started the stopwatch, it must continue running for the duration of the experiment. You must **not** stop it until you have finished this experiment.

1. Fill the burette labelled **FA 6**, with **FA 6**.
2. Using a measuring cylinder, add 25.0 cm<sup>3</sup> of **FA 3** to the conical flask labelled **reaction mixture**. Using the same measuring cylinder, add 25.0 cm<sup>3</sup> of **FA 4** into the same conical flask.
3. Using a measuring cylinder, add 50.0 cm<sup>3</sup> of **FA 5** to the same conical flask. Insert the stopper, start the stopwatch, and swirl the mixture to mix its contents.
4. Using a measuring cylinder, add 10.0 cm<sup>3</sup> of **FA 7** to a second conical flask.
5. At approximately 5 minutes, pipette 10.0 cm<sup>3</sup> of the reaction mixture into the second conical flask and vigorously swirl the mixture. Read and record the actual time of transfer in minutes and seconds, to the nearest second, when the aliquot is completely transferred to the second conical flask.
6. **Immediately** titrate the I<sub>2</sub> in the second conical flask with **FA 6** until the solution turns yellow. Using a dropping pipette, add 1 cm<sup>3</sup> of starch indicator and continue titrating until the solution becomes colourless. Record your titration results.
7. Repeat steps 4 to 6 at approximately 10, 15, 20 and 25 minutes.
8. Record your results in Table 2.1 provided. In addition, you should convert all values of actual time to a decimal time, *t*, in minutes, recorded to 1 decimal place. For example, an actual time of 5 min 11 s becomes 5 min + 11/60 min = 5.2 min.

## Results

Table 2.1

time / min	actual time / min and s	decimal time, $t$ / min	initial burette reading / cm <sup>3</sup>	final burette reading / cm <sup>3</sup>	volume of FA 6 used / cm <sup>3</sup>
5	5 ' 0 "	5.0	0.00	12.90	12.90
10	10 ' 0 "	10.0	12.90	22.90	10.00
15	15 ' 0 "	15.0	22.90	29.90	7.00
20	20 ' 0 "	20.0	29.90	34.60	4.70
25	25 ' 0 "	25.0	34.60	36.90	2.30

[3]

- (b) Plot a graph of volume of FA 6 used against decimal time,  $t$ , on the grid in Fig. 2.2. Your scale on the  $y$ -axis should allow for extrapolation. Start the  $x$ -axis at time = 0.

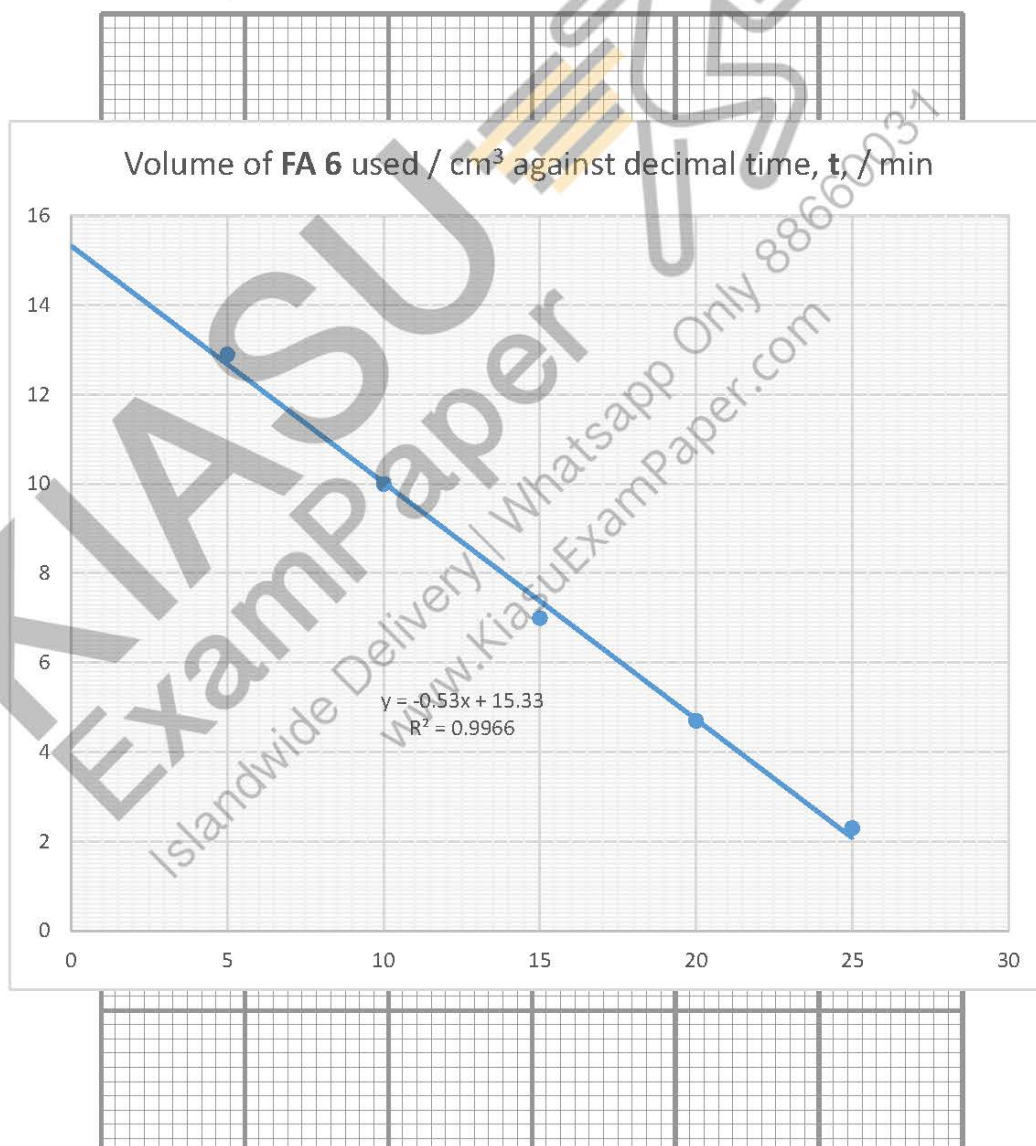


Fig. 2.2

[3]

- (c) (i) Write an equation for the reaction between iodine and thiosulfate ions.



- (ii) State the relationship between concentration of iodine remaining in the reaction mixture at regular time intervals and the volume of FA 6 used.

Concentration of iodine remaining is directly proportional to volume of FA 6 used. [1]

- (iii) A student stated that the determination of actual time in step 5 is of low accuracy.

Suggest a modification to the procedure in steps 4 and 5 to improve the accuracy of actual time determined.

Record the time when 10.0 cm<sup>3</sup> of FA 7 is added to 10.0 cm<sup>3</sup> of the reaction mixture which has already been pipetted out. [1]

- (d) Using the graph plotted, answer the following questions about the reaction between iodine and propanone.

- (i) Deduce the order of reaction with respect to the concentration of iodine.

Zero order with respect to the concentration of iodine as the graph obtained has a constant negative gradient, indicating rate is independent of concentration. [1]

- (ii) Explain the significance of the intercept of the graph with the y-axis.

The y-intercept gives the volume of thiosulfate which will react with iodine in 10.0 cm<sup>3</sup> of reaction mixture at time = 0 min. [1]

- (iii) Calculate the initial concentration of iodine in FA 5.

From the graph, y-intercept = 15.35 cm<sup>3</sup>

$$n(\text{S}_2\text{O}_3^{2-}) \text{ in } 15.35 \text{ cm}^3 = (15.35/1000) \times 0.010 = 1.535 \times 10^{-4} \text{ mol}$$

$$n(\text{I}_2) \text{ in } 10.0 \text{ cm}^3 \text{ diluted solution} = 1.535 \times 10^{-4} \div 2 = 7.675 \times 10^{-5} \text{ mol}$$

$$n(\text{I}_2) \text{ in } 100 \text{ cm}^3 \text{ diluted solution} = 7.675 \times 10^{-4} \text{ mol}$$

$$n(\text{I}_2) \text{ in } 50 \text{ cm}^3 \text{ original solution} = 7.675 \times 10^{-4} \text{ mol}$$

$$[\text{I}_2] = 7.675 \times 10^{-4} \div 0.050 = 0.01535 = \underline{0.0154 \text{ mol dm}^{-3}} \text{ (3 s.f.)}$$

[2]



**(e) Planning**

In determination of the kinetics of the iodination of propanone, we have only deduced the order of reaction with respect to iodine thus far.

The procedure in **2(a)** can be modified to investigate the order with respect to propanone and the acid catalyst, and then obtain the experimentally determined rate equation.

Plan an investigation, based on the experiment described in **2(a)**, to determine the order of reaction with respect to propanone.

You may assume that you are provided with

- the same chemicals and their respective quantities in **2(a)**,
- a 50 cm<sup>3</sup> volumetric flask, and
- the equipment normally found in a school or college laboratory.

In your plan you should include brief details of

- the reactants that you would use,
- the apparatus that you would use in addition to that specified in **2(a)**,
- the procedure that you would follow and the measurements that you would take,
- how you would determine the order of reaction with respect to propanone.

**Note:**

For similar procedural steps in **2(a)**, you may quote "Repeat steps ... to ... in **2(a)**."

1. Fill a burette with **FA 6**.
2. Using a pipette, add 25.0 cm<sup>3</sup> of **FA 4** to the 50 cm<sup>3</sup> volumetric flask. Top up to the mark with deionised water. Stopper and shake to obtain homogeneous solution. Label this **FB 4**.
3. Using a measuring cylinder, add 25.0 cm<sup>3</sup> of **FA 3** to the conical flask labelled **reaction mixture**. Using the same measuring cylinder, add 25.0 cm<sup>3</sup> of **FB 4** into the same conical flask.
4. Repeat steps 3 to 8 in **2(a)**.
5. Plot a graph of volume of **FA 6** used against decimal time.
6. Compare the rate of reaction (or gradient) in **2(a)** and **2(e)**.
7. If the rate is the same, then order of reaction w.r.t. propanone is 0<sup>th</sup> order. If the rate in **2(e)** is halved, then order of reaction w.r.t. propanone is 1<sup>st</sup> order. If the rate in **2(e)** is quartered, then order of reaction w.r.t. propanone is 2<sup>nd</sup> order.



[6]

[Total: 19]

### 3 Organic Analysis

**Before starting this analysis, please ensure that your Bunsen burner is turned off.**

In this question you will deduce the identities of four organic compounds, **FA 8**, **FA 9**, **FA 10**, and **FA 11**. You will perform a series of test-tube reactions and use your observations to help you distinguish between the compounds.

In addition to having access to the usual bench reagents, you are also provided with the following:

- iodine solution; and
- aqueous bromine located in the fume cupboard.

- (a) You are provided with the liquid samples of **FA 8**, **FA 9** and **FA 11**, each of which, together with **FA 10**, is one of the following compounds.

propanone    cyclohexene    ethanal    2-methylpropan-2-ol

**FA 10** is not provided; observations for **FA 10** have already been recorded in Table 3.1. Use these provided observations for **FA 10** and your own observations to deduce the identities of **FA 8**, **FA 9**, **FA 10** and **FA 11**.

- (i) Perform the tests described in Table 3.1. Record your observations in the table. Test and identify any gases evolved.

**Use a fresh sample of each liquid in each test. Samples of FA 8, FA 9 and FA 11 are provided in sample tubes. It is essential that you replace the lid as soon as you have removed the sample for each test.**

**Table 3.1**

	Observations with FA 8	Observations with FA 9	Observations with FA 10	Observations with FA 11
<p>Add 5 drops of FA 8 into a clean test-tube.</p> <p>To this test-tube, add about 1 cm depth of bromine water. Shake the contents vigorously.</p> <p>Repeat using FA 9 and FA 11, in place of FA 8.</p>	<p>Solution remains orange.</p>	<p>Solutions remains orange.</p>	<p>Solution remains orange.</p>	<p>Orange solution decolourises.</p>
<p>Add about 1 cm depth of sulfuric acid into a clean test-tube. To this test-tube, add 5 drops of FA 8, followed by 5 drops of <math>\text{KMnO}_4</math>.</p> <p>Repeat using FA 9 and FA 11, in place of FA 8.</p>	<p>Purple solution decolorises.</p> <p>Brown ppt.</p>	<p>Solution remains purple.</p>	<p>Solution remains purple.</p>	<p>Purple solution decolourises.</p>



<p>Add about 1 cm depth of deionised water into a clean test-tube. To this test-tube, add 5 drops of FA 8 and 6 drops of sodium hydroxide. Now add iodine solution, dropwise, till a yellow colour is present permanently.</p> <p>Prepare a hot water bath.</p> <p>Warm the mixture for about 2 minutes.</p> <p>Repeat using FA9 and FA 11, in place of FA 8.</p>	<p>Observations with FA 8</p> <p>Yellow ppt.</p>	<p>Observations with FA 9</p> <p>Yellow ppt.</p>	<p>Observations with FA 10</p> <p>No yellow precipitate.</p>	<p>Observations with FA 11</p> <p>No yellow ppt.</p>
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[4]

- (ii) Complete Table 3.2, using the observations in Table 3.1, to identify the compounds FA 8, FA 9, FA 10 and FA 11.

Table 3.2

	compound
FA 8	Ethanal
FA 9	Propanone
FA 10	2-methylpropan-2-ol
FA 11	Cyclohexene

[2]

## (b) Investigation of some reactions of D-glucose

D-glucose is a sugar with molecular formula  $C_6H_{12}O_6$ . In aqueous solution, D-glucose exists in a number of isomeric forms.

In aqueous solution, an equilibrium mixture of these isomers is formed. It is thought that at any one time less than 1% of the D-glucose molecules are present in the non-cyclic form, as shown in Fig. 3.3.

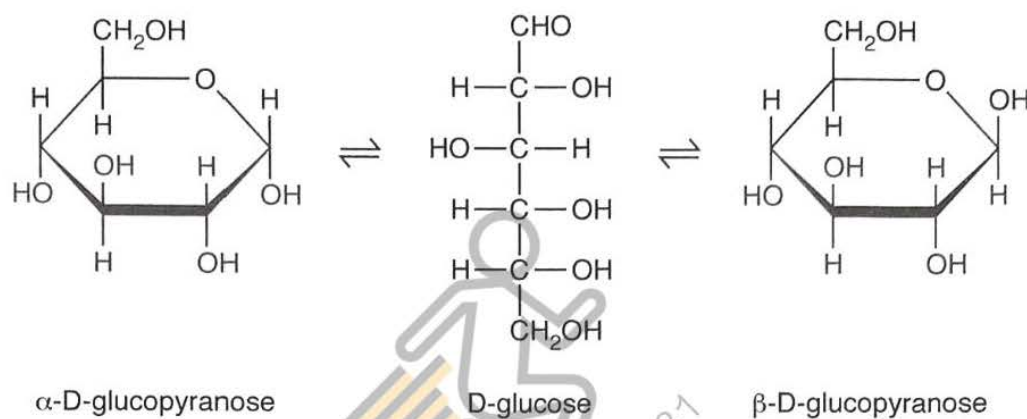


Fig. 3.3

FA 12 is  $0.5 \text{ mol dm}^{-3}$  D-glucose,  $C_6H_{12}O_6$ .

- (i) Carry out the following test. Carefully record your observations in Table 3.4.

Unless otherwise stated, the volumes given below are approximate and should be estimated rather than measured.

Table 3.4

test	observations
1. Add 2 cm depth of aqueous silver nitrate to a clean dry boiling tube. Add 1 cm depth of aqueous sodium hydroxide slowly to the same tube.	Grey/brown precipitate
2. Add aqueous ammonia slowly, with shaking, until the precipitate just dissolves. You may use a clean glass rod to help dissolve the precipitate.	Ppt dissolves to form a colourless solution

<p>3. Add 2 cm depth of FA 12 to this mixture and shake the tube.</p> <p>Place the boiling tube in the test-tube rack and leave it for 3 minutes.</p>	<p>Silver mirror / black ppt observed</p>
<p><b>Important: After about 3 minutes, pour the mixture down the sink and wash out the boiling tube several times with tap water.</b></p>	

[3]

- (ii) By using two chemical equations, explain the observations in tests 1 and 2.



The formation of the silver(I) diammine complex causes the position of equilibrium in (1) to shift left, hence causing the precipitate to dissolve.

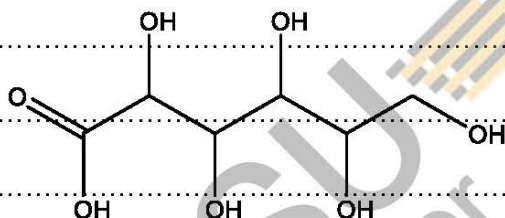
[3]



- (iii) In (b)(i), the organic product Z can be obtained from D-glucose. Product Z has a non-cyclic structure with molecular formula  $C_6H_{12}O_7$ .

Name the type of reaction that D-glucose undergoes in (b)(i).  
Draw the structure of Z.

Oxidation



[2]

- (iv) Consider the observations recorded in Table 3.5.

You should not do the following tests. Observations have been recorded for you.

Table 3.5

test	observations
Add 1 cm depth of FA 12 to a test-tube. Add 5 cm depth of 2,4-dinitrophenylhydrazine solution to the test-tube. Observe the mixture for a short time.	no observable change
Repeat this test but replace FA 12 with propanone.	yellow precipitate formed

Name the functional group in FA 12 that can be identified using 2,4-dinitrophenylhydrazine.

Aldehyde

[1]

- (v) Suggest why FA 12 does not give a positive result with 2,4-dinitrophenylhydrazine, whereas propanone does.

Only 1 percent of the D-glucose exists in the non-cyclic aldehyde form.

[1]

Optical activity is the ability of a chiral molecule to rotate the plane of plane-polarised light. It is measured by a polarimeter.

The specific rotation of a chiral molecule is defined as the angle of rotation (in terms of degrees) of the plane of polarisation of a ray of monochromatic light that passes through a 1 decimeter long tube containing the substance at a concentration of 1 gram per  $\text{dm}^3$ . For comparison's sake, the path length is usually fixed.

The specific rotation of  $\alpha$ -D-glycopyranose is  $+112.2^\circ$ .

The specific rotation of  $\beta$ -D-glycopyranose is  $+18.7^\circ$ .

- (vi) By examining the signs and the magnitudes of their specific rotations, explain the relationship between the  $\alpha$ - and  $\beta$ -D-glycopyranose.

As the magnitudes of their specific rotations are not the same, and their signs

are the same, the two glycopyranoses are stereoisomers but not enantiomers.

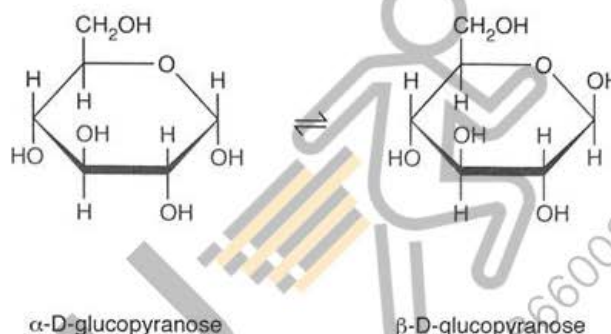
[2]

- (vii) The sum of the optical activities of each chiral component in a solution is the net optical activity of a solution.

Consider Fig. 3.3 on page 15 and information on page 18. The interconversion between the three forms of D-glucose is an example of mutarotation, which was discovered in 1846. Mutarotation is a change in the optical rotation of a solution due to a change in the equilibrium between the  $\alpha$  and  $\beta$  forms of a carbohydrate, upon dissolution in the aqueous solution.

When a pure sample of either  $\alpha$ - or  $\beta$ -D-glucopyranose is dissolved in water, the value of the specific rotation changes over time, eventually reaching the same value of  $+52.5^\circ$ .

Calculate the  $K_c$  of the following equilibrium.



Let  $x$  be the fraction of the  $\beta$  stereoisomer  
(hence the fraction of the other stereoisomer is  $1-x$ ).

$$18.7x + 112.2(1-x) = 52.5$$

$$\text{Solving, } x = 0.6385$$

$$K_c = 0.6385 / (1 - 0.6385) = 1.766 = \underline{1.77} \text{ (3 s.f.)}$$

[2]

[Total: 20]