Solution to N2017/P4/Q2c

Part (i)
Since the question stated that "The procedure you followed in **2(a)(i)** can be modified", the table below shows the modifications that are made from the procedures in **2(a)(i)** of the original exam question to study the effect of temperature on rate of decomposition.

You may take reference of the original procedure from Experiment 21 that you have done in JC2. You will only need to give the answer in the right-hand side column.

	Original procedure in Expt 2(a)	**Planning Procedure to answer 2(c)(i)**
1.	Fill the burette with **FA 3 (<u>$KMnO_4$</u>)**	Fill the burette with $KMnO_4$.
2.	Using a measuring cylinder, add 100.0 cm^3 of **FA 4** to the conical flask labelled **reaction mixture**.	Using a measuring cylinder, add 100.0 cm^3 of H_2O_2 to the conical flask labelled "reaction mixture". Place this conical flask labelled "reaction mixture" into a **<u>thermostatically controlled water bath maintained</u>** at 30°C. **<u>Insert a thermometer into the reaction mixture.</u>** Allow the **<u>temperature of the reaction mixture to equilibrate</u>** to within 1°C of the water bath. **<u>Record</u>** the **<u>temperature of the reaction mixture</u>**.
3.	Using a measuring cylinder, add 2.0 cm^3 of **FA 2 (**iron(III) nitrate, $Fe(NO_3)_3$, is an effective catalyst) to the same conical flask. Start the stopwatch and swirl the mixture thoroughly to mix its content. *Note: in 2022 JC2 experiment 21, the volume of FA2 used is 4.0 cm^3.*	Using a **<u>scalpel</u>**, cut a small piece of liver with **<u>dimension 1cm x 1cm x 1cm</u>**. Add the small piece of liver to the same conical flask. Start the stopwatch and swirl the mixture thoroughly to mix its content.
4.	Using a measuring cylinder, add 50.0 cm^3 of 0.2 mol dm^{-3} sulfuric acid to a second conical flask.	Using a measuring cylinder, add 50.0 cm^3 of 0.2 mol dm^{-3} sulfuric acid to a second conical flask.
5.	Transfer a 10.0 cm^3 aliquot (portion) of the reaction mixture to a 10 cm^3 measuring cylinder, using a dropping pipette.	Transfer a 10.0 cm^3 aliquot (portion) of the reaction mixture to a 10 cm^3 measuring cylinder, using a dropping pipette.
6.	**Immediately** transfer this aliquot into the second conical flask and vigorously swirl the mixture. Read and record the time of transfer in minutes and seconds, to the nearest second, when the aliquot is added.	Immediately transfer this aliquot into the second conical flask and vigorously swirl the mixture. Read and record the time of transfer in minutes and seconds, to the nearest second, when the aliquot is added.

	Original procedure in Expt 2(a)	**Planning Procedure to answer 2(c)(i)**
7.	**Immediately** titrate the H_2O_2 in the second conical flask with **FA 3**. The end-point is reached when a permanent **pale** pink colour is obtained. Record the titration results.	Immediately titrate the H_2O_2 in the second conical flask with $KMnO_4$. The end-point is reached when a permanent pale pink colour is obtained. Record the titration results.
8.	Wash out the second conical flask with water.	Wash out the second conical flask with water.
9.	Repeat steps **4** to **8** until a total of **five** aliquots have been titrated and their results recorded.	Repeat steps **4** to **8** until a total of **five** aliquots have been titrated and their results recorded.
10.		**Vary the temperature** of the thermostatically controlled water bath and **repeat steps 2 to 9, with 4 other temperatures** (25^oC, 35^oC, 40^oC, 45^oC)
11.		Plot all 5 graphs of **Vol_{KMnO4} against time.** **Draw a tangent to each graph at t= 0.** Find the initial rate of each reaction, which is the **gradient of tangent at t=0**

Mark Scheme

The following points are required by the question and the suggested marks distribution is as follows

Question [7]	**Mark Scheme**
the **reactants and conditions** that you would use, [2]	1. Same quantity of H_2O_2, H_2SO_4 as used in 2(a)(i). 2. Fixed mass / volume of liver. 3. Vary temperature of the reaction mixture.
the **apparatus** that you would use **in addition** to that specified in **2(a)(i)**, [1]	1. Thermostatically water bath or water bath adjusted with ice/ hot water with thermometer. 2. Scalpel to cut the liver. 3. Thermometer to measure the temperature of reaction mixture.
the **procedure** that you would follow and the **measurements** that you would take, [3]	1. Record the temperature of the reaction mixture. 2. Ensure that the reaction mixture has been maintained at the required temperature BEFORE adding the liver and other reagents. 3. Prepare fixed mass of liver or piece of liver with fixed dimensions. 4. Start the stopwatch upon adding the liver. 5. Draw sample at appropriate time interval, quench and perform titration. Record volume of $KMnO_4$ used. 6. Repeat experiments by varying the temperature of the water bath to a suitable temperature below 50^oC. (Catalase will be denatured from temperatures above 50^oC) Any 2 points in correct order – 1 mark
how you would determine the **initial rate** of experiment. [1]	1. continuous method – plot 5 different graphs, 1 graph for each temperature. 2. draw a tangent at t=0 for each graph, gradient of tangent = initial rate. (Note that 5 graphs is necessary to obtain 5 rates and hence obtain 5 values of k' at the corresponding T to obtain minimum of 5 plotted points on lnk' vs T graph)

(ii) rate = $k'[H_2O_2]$

Expt	Temperature / ^oC	Temperature / K	$\frac{1}{T}$ / K^{-1}	Gradient of tangent at t=0, = initial rate	k' = rate/$[H_2O_2]$	ln k'
1	30.0					
2	25.0					
3	35.0					
4	40.0					
5	45.0					

Calculate k' = rate/$[H_2O_2]$ and ln k' -- [1]

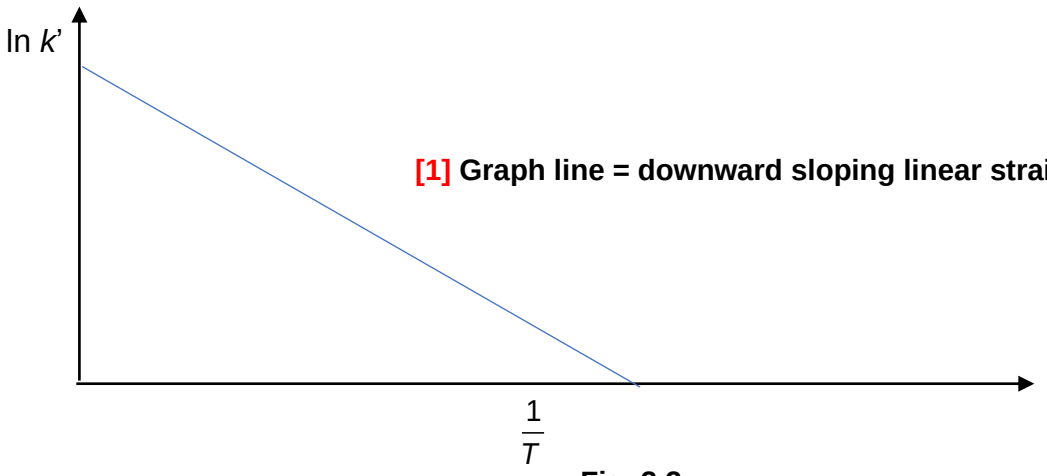
Calculate $\frac{1}{T}$ -- [1]

(iii) (Using information from the question: Plotting ln k' against $\frac{1}{T}$ gives a **straight line** of best fit.)

The gradient of this line is $\frac{-E_a}{R}$

[Note: Derivation of the gradient is shown in part (iv) answer below.]

Since **activation energy is always positive** and **R is positive**,
Gradient of line will be negative and hence downwards sloping. [1]



[1] Graph line = downward sloping linear straight line

Fig. 2.2

(iv) In the graph of ln *k*' against $\frac{1}{T}$ gives a straight line of best fit, the gradient of this line is $\frac{-E_a}{R}$.

$k' = Ae^{\frac{-E_a}{RT}}$

$\ln k' = \ln(Ae^{\frac{-E_a}{RT}})$ *Note:* $\ln(AB) = \ln A + \ln B$

$\ln k' = \ln A + \ln e^{\frac{-E_a}{RT}}$

$\ln k' = \frac{-E_a}{RT} + \ln A$ -- [1] Note: ln e =1

$\ln k' = \frac{-E_a}{R}(\frac{1}{T}) + \ln A$

$\frac{-E_a}{R} = gradient$

$E_a = gradient \times (-1) \times R$ – –[1]

y intercept = ln A

A = $e^{\text{y-intercept}}$ [1]

Solution to N2019/P4/Q4

4(a)

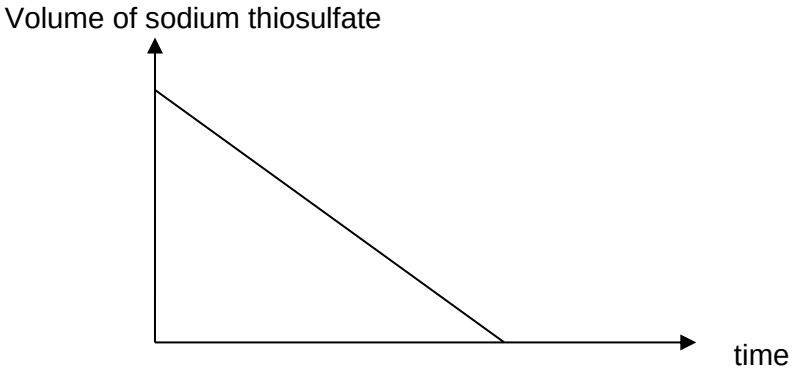
Suggested plan	1) Fill a burette with $Na_2S_2O_3$. 2) Using a **50 cm^3 measuring cylinder**, measure 30 cm^3 of propanone followed by 30 cm^3 of H_2SO_4 and transfer both solutions into a **250 cm^3 conical flask**. 3) Using **another 50 cm^3 measuring cylinder**, measure 30 cm^3 of iodine solution. 4) Transfer the iodine solution from step 3 into the conical flask from step 2. Start the **stopwatch** midway through pouring of iodine solution. **Swirl to mix well**. Label this as the "reaction mixture". 5) About 1 minute after starting the stopwatch, use a **10 cm^3 pipette** to draw out 10 cm^3 of the reaction mixture and **transfer it into another clean, dry 100 cm^3 conical flask**. 6) Using a **10 cm^3 measuring cylinder**, measure 10 cm^3 of $NaHCO_3$ solution. 7) At about 2 minutes after the start of the reaction, **pour** the 10 cm^3 of **$NaHCO_3$ solution (in excess)** into the **sample** from step 5 and **swirl to quench the reaction**. Record down the **exact time of quenching**. 8) **Titrate** the resulting solution against the standard $Na_2S_2O_3$ solution in the burette. When the solution turns from brown to pale yellow, add about 1 cm^3 of **starch** solution using a **dropper**. Continue to titrate until the solution turns from **blue-black to colourless**. 9) Record the **titration results**. 10) **Repeat** steps 5-8 at about 4 minutes intervals (2, 6, 10, 14, 18 min) to obtain **5 sets of results** in total to plot a graph.

Mark Scheme

The following points are required by the question and the suggested marks distribution is as follows.

Question [6]	**Marking points**
the **apparatus** that you would use [2]	Choice of apparatus and capacity • 50 cm^3 measuring cylinder to measure aq Iodine, propanone, H_2SO_4 • 250 cm^3 conical flask to hold 90 cm^3 reaction mixture. • 10.0 cm^3 pipette for 10 cm^3 aliquot samples. • 100 cm^3 dry conical flask for titration • 10 cm^3 measuring cylinder for $NaHCO_3$ • Burette for $Na_2S_2O_3$ • Dropper for starch
the **procedure** that you would follow [3]	Outline the steps in the procedure by reading the question. [1] • Mix aq iodine, H_2SO_4 and propanone together in a conical flask. • Start the stopwatch. • At regular time intervals, collect samples of the reaction mixture. • Add to another conical flask and add quenching reagent, $NaHCO_3$. • Titrate against $Na_2S_2O_3$. • Repeat sampling-quenching-titration at regular time interval. • Plot a graph of Vol of $Na_2S_2O_3$. against time. reliability [2] • Either mix acid + iodine first and add propanone last OR mix acid + propanone first and add iodine last. • Add the last reagent quickly and start the stopwatch. • 5-6 samples to be collected • Add starch indicator when reaction mixture turns from brown to pale yellow. (this is to make the end point colour change more visible)
the **measurements** that you would take [1]	Assume monitoring approximately 20 min reacting time. First sample to collect at 2 min, subsequent 4 min (regular time) interval. • Record the quenching time • Record the volume of thiosulfate used for each titration.

4(b) Graph: [1]



Explanation: [1]

In this experiment, <u>volume of $Na_2S_2O_3$ added in each titration is directly proportional to concentration of iodine reactant</u> remaining in the solution. As the reaction proceeds, there will be a <u>decrease in the concentration of the iodine, which will cause a decrease in the volume of $Na_2S_2O_3$ titre</u> required. Since <u>the reaction is zero order with respect to iodine</u>, the <u>gradient</u> of the line (which is the rate of the reaction) will <u>remain unchanged</u>.

Thinking process:
From the question, it was mentioned that the order of reaction with respect to iodine is zero. Since the volume of sodium thiosulfate used is directly proportional to the concentration of iodine, it can be concluded that the graph will follow a zero-order sketch of a straight line which corresponds to $[I_2]$ vs time.

Solution to N2020/P4/Q4

(a) No. of moles of nitrobenzene needed (70% yield) = $\frac{10.0}{123}$ = 0.0813 mol [1]

Theoretical no. of moles of nitrobenzene (if 100% yield)
= $\frac{100(0.0813)}{70} = 0.11614$ mol

Mass of benzene need = 0.116 x [6(12.0)+6(1.0)] = 0.11614 x 78.0 = 9.059 = 9.06 g [1]

(b) Quantities of reagents

Volume of benzene required = $\frac{9.06}{0.8765} = 10.3\ \text{cm}^3$

Since 8.0 cm^3 of benzene required 8.0 cm^3 of both conc HNO_3 and conc H_2SO_4, we can expect 10.3 cm^3 of benzene required 10.3 cm^3 of both conc HNO_3 and conc H_2SO_4 for reaction.[1]

8 cm^3 of conc HNO_3, 8 cm^3 of conc H_2SO_4 and 8 cm^3 of benzene required 75 cm^3 of deionised water.
Volume of deionised water used = 100 cm^3 (Minimum volume required = 75(10.3)/8 = 96.5 cm^3)

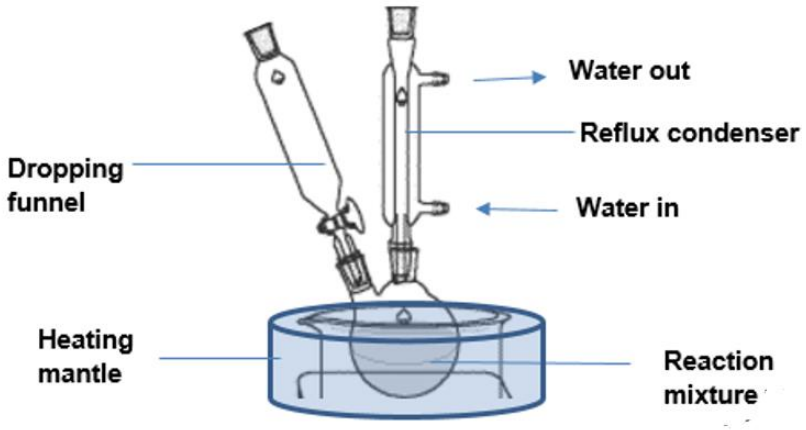
Volume of Na_2CO_3 used = 100 cm^3 (same vol as water)

Preparation of nitrating mixture

- Using a 25 cm^3 measuring cylinder, transfer 11 cm^3 of conc HNO_3 and 11 cm^3 of conc H_2SO_4 into a 100 cm^3 round bottomed flask.
- Place the round-bottomed flask in a thermostatically controlled water bath maintained at 50°C.

Nitration

- Using a syringe/measuring cylinder, transfer 10.3 cm^3 of benzene to the round-bottomed flask in four separate equal portions (about $\frac{10.3}{4} = 2.6\ \text{cm}^3$) with stirring using a magnetic stirrer.
- Ensure that the thermostatically controlled water bath is maintained at 50°C during the addition of benzene.
- Place a condenser at the opening of the flask and increase temperature of the thermostatically controlled water bath to 60°C.
- Allow the reaction mixture to be heated under reflux for 30 min.



(Diagram not required)

Purification

- Using a 100 cm^3 measuring cylinder, transfer 100 cm^3 of deionised water into a 250 cm^3 beaker.
- Pour the reaction mixture into the 250 cm^3 beaker and stir the contents thoroughly (with a glass rod).
- Decant the upper water layer.
- Using another 100 cm^3 measuring cylinder, transfer 100 cm^3 of aq Na_2CO_3 solution into the remaining oily layer in the 250 cm^3 beaker with constant stirring. Pour away the aqueous layer.
- Add another 100 cm^3 of deionised water into the oily layer in the 250 cm^3 beaker with constant stirring. Pour away the aqueous layer.
- Add about 20 g (or excess) anhydrous $CaCl_2$ to the oily layer and leave the mixture to stand for 20 minutes.
- Filter the reaction mixture and collect the organic filtrate in a dry round-bottomed flask.
- Set up the distillation apparatus with a (water-cooled) condenser and a thermometer in the neck of a round-bottomed distillation flask and gently heat the mixture in the flask using an electrical heater/oil bath/sand bath/isomantle.
- When the thermometer shows 211 ^oC, pure nitrobenzene is distilled over, cooled and is collected.

Mark Scheme

The following points are required by the question and the suggested marks distribution is as follows.

Question [7]	**Marking points**
an estimate of the **quantities of acids** to be used to ensure a yield of 10.0 g of nitrobenzene [2]	• Benzene, conc HNO_3 and conc H_2SO_4 [1] • deionised water and Na_2CO_3 [1] • $CaCl_2$
the **apparatus** that you would use [2]	• Measuring cylinders/syringe for measurements • Round-bottomed flasks for reaction and distillation • Thermostatically controlled water bath • Reflux condenser • Magnetic stirrer • Beaker for purification • Distillation setup with condenser All 7 points correct: 2 marks Any 4 - 6 points correct: 1 mark)
the **procedure** that you would follow to obtain **pure** and **dry** nitrobenzene[3]	General Procedure [1] • Mix conc HNO_3 and conc H_2SO_4 with benzene • Add water and pour the upper water layer away. • Add Na_2CO_3 solution and pour the upper aqueous layer away. • Add water again and pour the upper water layer away. • Add $CaCl_2$ to dry the organic layer • Purify nitrobenzene using distillation Reliability/ Safety [2] • Add benzene in four separate equal portions • reflux for 30 min. • Maintaining of temperature at 50 ^oC and 60 ^oC • Distillation and collect distillate at 211 ^oC. (Any 3: 2 marks, Any 2: 1 mark)

(c) It is to neutralise the unreacted acids in the mixture. [1]

(d) Safety issue 1: Both benzene and nitrobenzene are highly flammable.
Precaution: No naked flame is used to heat the reaction mixture. Instead, water bath is used for heating.

Safety issue 2: Benzene which has a boiling point 80.1 ^oC is volatile. Inhalation of the vapour can be toxic.
Precaution: Hence, the synthesis should be done in a fume cupboard.

[1] each

Solution to N2021/P4/Q2d

(i) Suggested Procedure

1. Weigh accurately a **dry boiling tube** using an **electronic balance**.
2. Weigh accurately about **5 g of sodium carbonate crystals**, $Na_2CO_3.xH_2O$ in the boiling tube. Record the mass.
3. **Heat the mixture gently** first (to prevent spattering) followed by **strongly and evenly for 5 min**.
   Ensure that heat is applied evenly to the solid in the boiling tube.
   Ensure that water that has condensed on the sides of the boiling tube is driven off completely.
4. Allow the boiling tube and contents to **cool on a heat–proof mat**.
5. **Reweigh the boiling tube and its content**.
6. **Repeat the heating–cooling–weighing process** until **2 consistent readings with a difference of less than 0.05 g** is obtained.
7. **Record the mass readings**.
8. **Repeat Steps 1 to 7** with another 5 g of sodium carbonate crystals.

Before heating

Mass of boiling tube + solid / g	M_2
Mass of boiling tube / g	M_1
Mass of solid used / g	$M_2 - M_1$

After heating

Mass of boiling tube + residue / g 1st reading 2nd reading 3rd reading	 M' M'' M_f
Mass of residue / g	$M_f - M_1$
Mass loss / g	$M_2 - M_f$

Comments

The challenge of this question lies in identifying the correct mass to use for residue and mass lost from heating.

By presenting the masses in the form of a table, it clearly shows the masses involved and you can easily identify the ones to use for subtraction.

This will also help you later in (d)(ii) when you show how the data collected is being used to determine value of x.

Question [6]	**Marking points**
the **apparatus** you would use [1]	electronic balance, boiling tube, heat-proof mat
the **quantities** you would use [1]	use 10 g of $Na_2CO_3.xH_2O$ in 2 batches
the **procedure** you would follow [2]	Procedure: • weigh $Na_2CO_3.xH_2O$ in boiling tube • heat gently first, then strongly • Cool boiling tube, then reweigh • Repeat heating–cooling–weighing process
the **measurements** you would make (you may find it useful to label measurements in your plan as M1, M2 etc.) [1]	• mass of empty boiling tube • mass of boiling tube with sample • mass of sample used • mass of boiling tube with residue after heating • mass of residue
how you would ensure that an **accurate** and **reliable** value of x is obtained [1]	Repeat the heating–cooling–weighing process until 2 consistent readings with a difference of less than 0.05 g. Repeat the experiment on a second sample of sodium carbonate crystals to obtain an average mass of heat loss to help ensure accuracy of results. *Note: A common error is to use all 10 g of sample provided in one go, without setting aside some to repeat the experiment.*

(d)(ii)	Mass loss is due to the loss of water. $Na_2CO_3.xH_2O \rightarrow Na_2CO_3 + xH_2O$ amt of water = $\frac{M2-Mf}{18.0}$ **[1]** amt of Na_2CO_3 formed = $\frac{Mf-M1}{2(23)+12+3(16)}$ **[1]** amt of water/amt of Na_2CO_3 = x $(\frac{M2-Mf}{18.0}) = \frac{Mf-M1}{2(23)+12+3(16)} \times x$ $(\frac{M2-Mf}{18.0}) = \frac{(Mf-M1)x}{106}$ $x = \frac{106(M2-Mf)}{18(Mf-M1)}$ **[1]**	[3]