**1 CJC 2016 Prelims (modified)**

One method of studying the kinetics of a chemical reaction, to find the order of reaction with respect to a particular reactant, is to measure the initial rates, by using the ‘clock experiment’.

To determine the initial rate, we can measure the time taken for a prominent visual change to occur in the course of a reaction.

When aqueous sodium thiosulfate, Na2S2O3, is added to a solution containing dilute hydrochloric acid, HCl, a fine, pale yellow precipitate of solid sulfur will be formed after a while. This is the prominent visual change that can be clearly identified.

The overall equation for the reaction is represented as follows:

S2O32- (aq) + 2H+ (aq) → S (s) + SO2 (g) + H2O (l)

The initial rate of this reaction is determined by measuring the time taken for sufficient precipitate of sulfur to be formed to just obscure a ‘cross’ marked on a piece of white paper below a reaction container.

A student carried out a series of preliminary experiments, using approximate volumes of the two reactants and each reaction mixture was made up to the same total volume with deionised water. The student found that the time taken for the pale yellow precipitate to appear doubled when the volume of hydrochloric acid added was halved.

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| **(a)** | **(i)** | State the relationship between the initial rate of reaction and the time taken for the pale yellow precipitate to appear.  [1]  Initial rate of reaction is **inversely proportional** to time taken for the pale yellow precipitate to appear. |
|  | **(ii)** | Explain why it is necessary to top up the reaction mixture with deionised water to the same total volume.  [1]  The volume of reactant used is the **only variable being changed.**  The **concentration** of each reactant is **proportional** to the **number of moles** of each reactant in the solution which is in turn **proportional** to the **volume** of each reactant added in the solution. |
| **(b)** | Hence, based on the results of the student’s preliminary experiments, predict the order of the reaction with respect to H+ ions.  [1]  **First** order. | |
| **(c)** | You are to design an experiment to study the kinetics of the reaction between S2O32- ions and H+ ions.  The following data in tabulated form is shown below.    30  10  10  20 | |
|  | **(i)** | Fill in the blanks in the table above, appropriate volumes of the reactants and deionised water to be used in experiments 2 and 3 such that the order of reaction with respect to S2O32-and H+ ions can be determined and verified.  [1]  Or any other appropriate volume + constant total volume at 50 cm3 |
|  | **(ii)** | Outline in a series of numbered steps, how experiment 1 could be carried out. Your plan should include:   * the apparatus used to measure the various volumes, * the order that the various solutions are mixed, * how the time to determine the rate of reaction is measured, and * other experimental details to ensure the consistency of the experiment.   (1 mark for hitting each question requirement)  [4]  **Suggested answer (refer to appendix for standard procedures)**   1. Using a **dry** **10 cm3 measuring cylinder**, measure and transfer 10 cm3 of sodium thiosulfate into a **dry** **100 cm3 beaker**. 2. Using a **dry** **25 cm3 measuring cylinder**, measure and transfer 20 cm3 of deionised water into the beaker. 3. Using a **dry** **25 cm3 measuring cylinder**, measure 20 cm3 of hydrochloric acid. 4. **Rapidly** pour / transfer the hydrochloric acid into the beaker AND **start the stopwatch at the same time**. 5. Place the beaker under a dry **white tile** marked with a ‘X’. **Use a glass rod to stir the solution a few times.** 6. Once the white precipitate formed completely obstructs the ‘X’ from view, **stop the stopwatch and record the time** taken for the ‘X’ to be obstructed (t1). |
|  | **(iii)** | Based on the table in (c)(i), explain how the results of any two of the three experiments can be used to determine the order of reaction with respect to S2O32- ions.  [3]   * Comparison between experiment 1 and 2 (1 mark) * Logical deduction made from comparison (2 marks) |
| **(d)** |  | Identify one potential safety hazard in this experiment and state how you would minimise this risk.  [1]  Any 1 of the following, or any other logical risks.   * HCl (aq) is **corrosive**, wear **hand gloves** to prevent direct contact with it. * SO2 gas liberated is **toxic**, wear **protective mask** or perform the experiment in a **well ventilated place** or using **a fume cupboard**.   [Total: 12] |

**2 DHS 2016 Prelims (part)**

The reaction between peroxodisulfate ions, S2O82- and ethanedioate ions, C2O42-, is slow and can be catalysed by Cu2+ ions.

S2O82- + C2O42- → 2SO42- + 2CO2

To determine the rate law of this reaction, it is necessary to selectively vary the concentrations of S2O82- and C2O42- ions and determine how the rate of reaction responds to these changes. The concentrations of the reactants are varied in such a way that one is in excess compared to the other in each experiment.

A suitable end point (the point at which the final time reading is made) for the experiments will be when the reaction produced the same volume of CO2 gas. With the measured reaction time, relative rate of the reaction can be determined.

**You are required to write a plan to determine the rate law of the reaction between S2O82- and C2O42- ions.**

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| **(a)** | Suggest an explanation why this reaction is slow when performed in the absence of a catalyst.  [1]  **High Ea** due to the **repulsion** of **2 negatively charged ions**. |
| **(b)** | You may assume that you are provided with   * **FA1**: 1.00 mol dm-3 Na2S2O8 * **FA2**: 1.00 mol dm-3 Na2C2O4 * 10 cm3 of **FA3**: aqueous copper (II) ions * the equipment and materials normally found in a school laboratory.   It can be assumed that a reactant is in excess if its volume is at least **five** times the volume of the other reactant used.  Your plan should include the following:   * **quantities** of reactants and condition you would use in four different reaction mixtures * the **measurements** you would take * an outline of how one of the reaction mixtures is **prepared**   [5]  **Suggested answer (refer to appendix for standard procedure)**  Question analysis:   * In this question, you have to determine the order of reaction with respect to the 2 ions. * So you need to have a pair of experiments to determine the order of reaction with respect to 1 of the 2 ions. * When S2O82- is used in excess, the rate law for the C2O42- ion can be determined. * Similarly, when C2O42- is used in excess, the rate law for the S2O82- ion can be determined. * As stated in the question, Cu2+ **catalyses the reaction**. This means that **the volume of Cu2+ should be constant for each pair of experiment**. * As there are **4** different experiments, it is advisable that you **use a table** to state the volume of **reactants** needed. However, you need to specify that the other experiments needs to be conducted with the volume of reactants shown in the table.   **Table**   |  |  |  |  |  | | --- | --- | --- | --- | --- | | Experiment | Volume of FA1 / cm3 | Volume of FA2 / cm3 | Volume of FA3 / cm3 | Volume of deionised water / cm3 | | 1 | 50 | 10 | 2 | 0 | | 2 | 50 | 5 | 2 | 5 | | 3 | 10 | 50 | 2 | 0 | | 4 | 5 | 50 | 2 | 5 |  * Note: Total volume of each reaction mixture is **constant** at 62 cm3.   To prepare experiment 1…   1. Using a **dry** **50 cm3 measuring cylinder**, measure and transfer 50 cm3 of FA1 into a **dry** **125 cm3 conical flask**. 2. Using a **dry** **10 cm3 measuring cylinder**, measure and transfer 2 cm3 of FA3 into the conical flask. **Swirl the conical flask lightly to mix its contents.** 3. Using a **dry** **10 cm3 measuring cylinder**, measure 10 cm3 of FA2. 4. Set up the apparatus as shown in the diagram. 5. **Reset the gas syringe**. 6. **Rapidly** pour / transfer FA2 into the conical flask, AND **stopper** the conical flask **at the same time** by inserting the rubber stopper at the mouth of the conical flask. **Immediately start the stopwatch**. 7. **Swirl the contents of the conical flask a few times**. 8. **When the reading on the gas reaches 40 cm3, stop the stopwatch.** **Record the time taken.** 9. **Repeat experiments 2 to 4 with the volume of reactants stated in the table.** For measuring out the volume of deionised water, a **dry** **10 cm3 measuring cylinder** should be used. This is to keep the volume of the reaction mixture **constant**. 10. For experiments with excess FA2 used, the **order of pouring** FA2 and FA1 into the conical flask should be **exchanged**, as well as the **apparatus** used.  * **quantities** of reactants and condition you would use in four different reaction mixtures (1 mark)   + Appropriate volumes used   + One of the reactants must be in excess   + Volume of Cu2+ is constant   + Volume of reaction mixture is the same   + Pair of experiments is corresponding to one another   + Correct table, with headers + units * the **measurements** you would take (1 mark)   + Correct apparatus with stated appropriate capacity used to measure volume of reactant / gas.   + Correct starting and stopping command for the stopwatch.   + Volume to trigger endpoint * an outline of how one of the reaction mixtures is **prepared** (2 marks)   + Correct order of mixing reactants (1 mark)   + Appropriate diagram OR elaborate description of setup (1 mark) * **Additionally**, stating that experiments 2 to 4 (or otherwise) should be conducted with the volume of reactants as stated in the table. (1 mark)   [Total: 6] |

**3 JJC 2016 Prelims (part)**



When iodine is mixed with propanone in the presence of dilute sulfuric acid, one of the hydrogen atoms in propanone is replaced by an iodine atom and hydroiodic acid, HI, is produced.

The rate equation for the reaction is determined to be

rate = *k*[CH3COCH3][H+]

Initially the reaction mixture is brown due to the iodine that is present. The reaction is complete when all the iodine has reacted and the solution becomes colourless.

A teacher demonstrates this experiment as follows.

She prepares two separate solutions, **X** and **Y**.

Solution **X** contains 5.00 g dm-3 iodine solution.

Solution **Y** is a mixture of 50 cm3 of 1.0 mol dm-3 propanone and 50 cm3 of   
1.0 mol dm-3 dilute sulfuric acid.

She mixes 10 cm3 of solution **X** with 10 cm3 of solution **Y** at room temperature of 25°C and, after about 40 seconds, the mixture decolourises.

**Data: Boiling point of propanone is 56°C.**

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| **(a)** | Consider the description of the experiment given above.  Write a plan to determine how the rate of this reaction changes with temperature.  In your plan, you should use the same volumes of solution **X** and solution **Y** described above.  Your plan should include five experiments. Ensure that at least one of your experiments would be expected to take more than 40 seconds.  You may assume that you are provided with the following:   * solution **X** containing 5.00 g of iodine in 1.0 dm3 of water * 1.0 mol dm-3 dilute sulfuric acid * 5.0 mol dm-3 propanone solution * deionised water, hot water and crushed ice * boiling tubes and other apparatus normally found in a school or college laboratory   Your plan should contain the following:   * details for the preparation of 1.0 mol dm-3 propanone solution provided * details for the preparation of solution **Y** * the temperatures at which the five experiments would be carried out * all measurements you would make * all essential experimental details to ensure accurate results   **Suggested answer (refer to appendix for standard procedure)**  **(Marking point 1) Preparation of 1.0 mol dm-3 propanone solution**   1. Fill a **dry** **50.00 cm3 burette** with 5.0 mol dm-3 propanone solution. Transfer 50.00 cm of the solution into a **dry** **250 cm3 volumetric flask**. 2. **Top up to the mark** with **deionised water**. **Stopper** the flask and **shake** to ensure a **homogeneous solution**.   **(Marking point 2) Preparation of solution Y**   1. Using a **dry** **50 cm3 measuring cylinder**, measure and transfer 50 cm3 of the diluted propanone solution into a **dry** **150 cm3 beaker**. 2. Using a **dry** **50 cm3 measuring cylinder**, measure and transfer 50 cm3 of 1.00 mol dm-3 H2SO4 into the beaker. 3. **Stir** the solution with a **dry** glass rod a few times. This solution is solution Y.   **(Marking point 3 and 4) Preparation of X and Y (at least one of them must be in a boiling tube) with incubation of solutions**   1. Using a **dry** **10 cm3 measuring cylinder**, measure and transfer 50 cm3 of solution Y into a **dry** **boiling tube**. 2. Using a **dry** **10 cm3 measuring cylinder**, measure 10 cm3 of solution X. 3. Place a (0.2°C) **thermometer** inside the boiling tube. 4. **Leave** the measuring cylinder and the boiling tube **in a cold water bath** containing **crushed ice and tap water**. Allow the temperature of the solution in the boiling tube to **equilibrate** at 15°C.   **(Marking point 5) Mixing and recording of time taken and final temperature**   1. **Rapidly** pour solution X into the boiling tube. **Start the stopwatch at the same time**. **Stir well with the thermometer.** 2. When the solution in the boiling tube **turns completely colourless, stop the stopwatch and record the time taken** for the solution to turn colourless. 3. Record the **final temperature of the mixture**. Calculate the **average temperature** by taking the average of the initial and final temperature of the reaction mixture.   **(Marking point 6) Mixing and recording of time taken and final temperature**   1. **Repeat steps 1 to 12** with temperatures of 20°C, 25°C, 30°C, 35°C.      1. For temperatures **below room temperature**, prepare the water bath by mixing tap water and **ice water**. 2. For temperatures **above room temperature**, prepare the water bath by mixing tap water and **hot water**.   [6] |
| **(b)** | Identify one potential safety hazard in this experiment and state how you would minimise this risk.  [1]  **Any 1 of the following, or any other acceptable risk**   * Propanone is highly **flammable**, so a **hot water bath** is used **instead of a Bunsen flame**. * Sulfuric acid is corrosive, wear **hand gloves** to prevent direct contact with it. |
| **(c)** | The activation energy, Ea, for the reaction can be determined from the following Arrhenius equation:      Outline how the data collected in your experiment would be used to determine the activation energy, Ea, for the reaction.   * The rate is **inversely proportional** to time taken. Consequently, the rate constant (*k*) is **inversely proportional** to time taken. * Hence, plot a graph of ln against , and find the gradient of the graph. The activation energy Ea = - gradient R.   [2] |
| **(d)** | What is the effect on ***t***, the time taken for the reaction mixture to decolourise, if the concentration of iodine solution used is halved? Explain your answer.  [2]   * As **rate** is **independent** of [I2], * The time taken will be **halved**.   [Total: 11] |

**Appendix:**

**Common standard procedures in kinetics**

1. Diluting a solution

* Using a burette: Fill a **dry** burette with FA1. Transfer X cm3 of FA1 into a **dry** 250 cm3 volumetric flask.

**OR**

Using a pipette: Pipette 25.0 cm3 of FA1 into a **dry** 250 cm3 volumetric flask.

* **Top up to the mark** with deionised water.
* **Stopper** the flask and **shake/mix well** until a homogeneous solution is obtained.

1. Transferring a solution

* Example: Using a **dry** 50 cm3 measuring cylinder, **measure** and **transfer** 30 cm3 of FA1 into a **dry** 100 cm3 beaker.
* State the **capacity** of the apparatus, **volume** of reactant.
* Everything is **dry**!

1. Transferring the last solution to kickstart the reaction

* **Rapidly** **transfer** FA2 into the beaker. Start the stop watch immediately.
* **Stir** the solution a few times using a **dry** **glass rod**.

1. Endpoint of reaction

* Example: When the solution in the beaker turns from **brown** to (completely) **colourless**, **stop** the stopwatch and **record** the time taken for the solution to turn **colourless**.
* Above: State the **colour change**. **Stop** the stopwatch. **Record** the time.
* When the **white precipitate** in the beaker **completely obstructs** the ‘X’ marked on the while tile, **stop** the stopwatch and **record** the time taken for the time taken for the ‘X’ to be obstructed.
* In general: State the **criteria** for the **endpoint** to be reached.

1. Repeat the experiment with varying concentrations

* Repeat (steps A to B) according to the **table** below. Using a measuring cylinder, add **deionised water** to keep the **total volume** of the final reaction mixture **constant**.
* Remember to **draw your table**.
* Even if the volume of reactants used throughout the sets are the **same**, there still needs to be a column for that.
* Correct headers with **units**.
* Have a column for separate **volumes of all reactants**.

1. Varying the temperature of solutions

* **Example**

Place the measuring cylinders in the water bath which is prepared by **mixing tap water and ice water**.

Place a (0.2°C interval) **thermometer** inside A and leave to allow both tubes inside the water bath for some time solutions in the boiling tubes to **equilibrate** **at 15°C**.

(Adding process, start stopwatch)

**Stir well** with the **thermometer**.

(Endpoint reached, stop stopwatch)

Record the **final temperature** of the **solution**. (If required show the working to calculate the average of the final and initial temperature)

**Repeat** the experiment for X other temperatures of T1, T2, T3, T4…

For temperature **above room temperature**, prepare the water bath by mixing tap water and **hot water**.

For temperature **below room temperature**, prepare the water bath by mixing tap water and **ice water**.

* State how the water bath is prepared.
* Record the **initial** and **final** temperature of the solution.

1. Withdrawing aliquots and quenching process

* (Reaction is prepared and has started, start stopwatch)
* **Before X mins** from the start time, **pipette** 10.0 cm3 of the reaction mixture into a dry 250 cm3 conical flask.
* **At X mins**, quench the withdrawn sample by adding 100 cm3 of cold water/any other quenching reagent. **Record** the **exact time of quenching**.
* Carry out the **titration** of the quenched sample **immediately**.
* **Before X mins**, repeat steps A to B. Carry out the **titration** of each quenched sample.

1. Gas collection

* (Adding of reactants into conical flask except the reactant that kickstarts the reaction)
* Set up the experiment as shown in the diagram (Note: the stopper should be open)
* (Add the reactant that kickstarts the reaction)
* **Stopper** the conical flask **immediately** (Note: **only** use a **conical flask** to contain the reactant mixture) by inserting the rubber stopper at the mouth of the conical flask. **Start** the stopwatch **at the same time**.
* Swirl the conical flask a few times gently and regularly. **Record** the reading on the gas syringe **every 0.5 minutes** until the reaction is complete. (That is when 3 consecutive readings recorded are the same/show no increase.)