EXPERIMENT

The iodine clock

Goal

The goal of this laboratory is to use the **method of initial rates** to calculate the rate of a chemical reaction. On top of that, the student will also visualize experimentally the effect of **temperature** and of a **catalyst** on the rate of a chemical reaction.

Background

The rate law expresses the progress of a chemical reaction in function of the concentration of the reactant

$$\text{Rate} = k[\text{A}]^{a}[\text{B}]^{b},$$

where k is the proportionality constant called the **rate constant**, [A] and [B] are the respective concentrations for reactants A and B, and the exponents are the **orders of the reactants**, a way to establish their corresponding relevance in the reaction rate.

Initial rates method

The initial rates method is used to measure the rate for a chemical reaction and to find out the rate constant k and the order of the reactions. This method is based on the assumption that at the beginning of a chemical reaction, there is no reverse reaction, i.e. forming reactants from the products, can take place, and therefore the rate is solely affected by the reactants concentrations. The time for the reactant concentrations to change by the same amount is measured. Several experiments are carried out using all the same starting concentrations but for one reactant. The beauty of this experiment is the method used to make the reactant's concentration change by the same amount for all the experiments. This is probably the most often misunderstood part of this laboratory and it is key to understand it thoroughly.

The Iodine Clock

A watch system is a method used in the Navy to schedule regular periods aboard. A ship's bell is used to indicate the end of each period, allowing the crew to know when it is time to switch their task, take breaks, or have lunch.
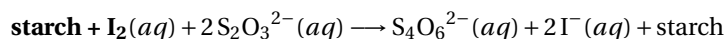
A **chemical clock** is a chemical reaction with a sudden change in one of its properties, the tempo of which can be adjusted by adjusting the concentrations. The **iodine clock** is a chemical clock marked by a sudden, almost magical, color change. For the present experiment, the iodine clock will be connected to the reaction being studied and will indicate the moment our reaction reaches the change in concentration desired. It is very important to understand the mechanism of the two competing reactions involved in this experiment to fully understand this activity.

The reaction setting the time is:

$$\text{I}_2(aq) + 2\,\text{S}_2\text{O}_3{}^{2-}(aq) \longrightarrow \text{S}_4\text{O}_6{}^{2-}(aq) + 2\,\text{I}^-(aq)$$
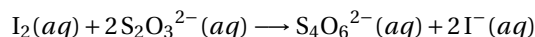
This reaction consumes iodine, I_2. Iodine reacts with starch turning the solution dark. The starch will be used in this experiment in a way similar to the indicator used in titration.

$$\text{starch with iodine} \qquad\qquad\qquad\qquad \text{starch , no I}_2$$
$$\textbf{starch + I}_\textbf{2}(aq) + 2\,\text{S}_2\text{O}_3{}^{2-}(aq) \longrightarrow \text{S}_4\text{O}_6{}^{2-}(aq) + 2\,\text{I}^-(aq) + \text{starch}$$
$$\text{black-dark blue} \qquad\qquad\qquad\qquad\qquad \text{transparent}$$
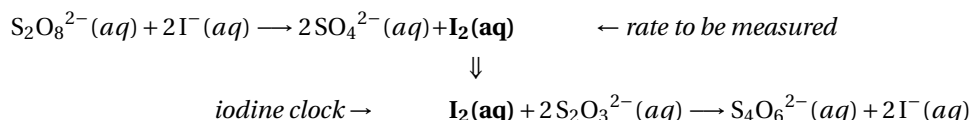
The iodine clock reaction will be running in parallel with another reaction that produces iodine. In the presence of starch, iodine becomes dark blue, almost black. Therefore, as long as there is thiosulfate ($S_2O_3^{2-}$) in the beaker the iodine will react with the latter and keep the solution transparent. We could say that the timer is adjusted by the concentration of thiosulfate ($S_2O_3^{2-}$).

The reaction to be studied

In this experiment, the student will determine the reaction rate of the reduction of potassium persulfate ($K_2S_2O_8$) with sodium iodide (NaI).

$$K_2S_2O_8(aq) + 2\,NaI(aq) \longrightarrow 2\,Na_2SO_4(aq) + I_2(aq)$$
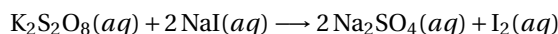
As ionic compounds dissociate in aqueous solutions it is more accurate to write the **net ionic equation**. These are the ionic net equations for the two reactions, the reduction of potassium persulfate with sodium iodide and the iodine clock:

$$S_2O_8^{2-}(aq) + 2\,I^-(aq) \longrightarrow 2\,SO_4^{2-}(aq) + \mathbf{I_2(aq)} \qquad \leftarrow \textit{rate to be measured}$$
$$\Downarrow$$
$$\textit{iodine clock} \rightarrow \qquad \mathbf{I_2(aq)} + 2\,S_2O_3^{2-}(aq) \longrightarrow S_4O_6^{2-}(aq) + 2\,I^-(aq)$$

To summarize: The first reaction will be running producing I_2, which would turn dark blue in the presence of starch. However, the second reaction will avoid the color change by reducing the iodine into iodide. The solution will remain transparent as long as there is thiosulfate ($S_2O_3^{2-}$) available. Once the thiosulfate is finished, iodine will finally remain in the solution turning it dark blue. Since the amount of thiosulfate will be constant for all the experiments to be performed, the amount of iodine produced in the first reaction, and therefore the reactant's concentration change, will be the same each time the solution turns dark. The iodine clock is being used to schedule a constant change in the reactant's concentrations.

The experiment

The experiment today is divided into the following parts: obtaining the reaction rate constant, evaluating the influence of the temperature on the reaction rate, and evaluating the influence of a catalyst on the reaction rate.

Part A. Obtaining the reaction rate constant.

The reaction to be studied and its rate law are:
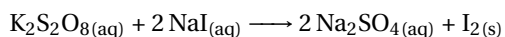
$K_2S_2O_8{}_{(aq)} + 2\,NaI_{(aq)} \longrightarrow 2\,Na_2SO_4{}_{(aq)} + I_2{}_{(s)}$ $\qquad\qquad\qquad\qquad$ $r = k\,[S_2O_8^{2-}]^a\,[I^-]^b$

Using the **initial rates method** the reactants orders, a and b, can be solved. Find the suitable combinations of experiments where only one initial concentration of $S_2O_8^{2-}$ or I^- changes and compare the rates using a fraction. The initial concentrations must be recalculated using the volumes and their original concentrations. Once the reactant orders are known and the initial concentrations of $S_2O_8^{2-}$ and I^- for each reaction have been recalculated, the reaction constant, k, can be solved. See the example for more details:

	Volume					⏱
	NaI	NaCl	$Na_2S_2O_3$	Starch	K_2SO_4	$K_2S_2O_8$
	0.2M	0.2M	0.01M	2%	0.2M	0.2M
Exp. 1	2.0	2.0	2.0	1.0	2.0	2.0
Exp. 2	2.0	2.0	2.0	1.0	0	4.0
Exp. 3	4.0	0	2.0	1.0	2.0	2.0

Example

The reaction starts from a solution containing A (1 M) and B (0.5) M and D (1 M). There are two reactions occurring in the solution. A slow reaction were C is produced and a fast reaction where C is reduced to E ions by D:

$$A + B \longrightarrow 2\,C$$
$$C + D \longrightarrow E$$
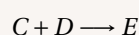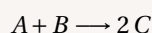
An indicator is added, such that the solution will turn dark in the presence of substance C.
Three experiments are performed using different initial volumes and the following times for the solution to turn dark are measured;

	Volumes (mL)				time
	A	*B*	*D*	*Water*	*(s)*
Exp. 1	*4.0*	*2.0*	*2.0*	*2.0*	*20*
Exp. 2	*4.0*	*1.0*	*2.0*	*2.0*	*40*
Exp. 3	*2.0*	*1.0*	*2.0*	*4.0*	*160*

Calculate the reactant orders and the reaction rate constant.

Answer: First write the reaction rate expression: Rate = $k[A]^a[B]^b$

Recalculate the concentrations for each reactant. Use the formula for dilutions $M_1V_1 = M_2V_2$, where V_2 is the total volume $V_A + V_B + V_D + V_{water}$.

For example, to calculate the concentration of A in Experiment 1:

$$M_1V_1 = M_2V_2 \qquad M_2 = \frac{M_1V_1}{V_2} \qquad M_2 = \frac{1M4mL}{10mL} = 0.4M$$

	[A]	[B]	[D]	rate (Ms^{-1})
Exp. 1	0.4 M	0.2 M	0.2 M	$5 \cdot 10^{-3}$
Exp. 2	0.4 M	0.1 M	0.2 M	$2.5 \cdot 10^{-3}$
Exp. 3	0.2 M	0.1 M	0.2 M	$6.25 \cdot 10^{-4}$

The reaction rate is the change in concentration per unit time. The change in concentration is determined by the second reaction (the clock). For the first experiment it takes 20 seconds to turn black. In those 20 seconds all of D has reacted, i.e. 0.2 M in 20 seconds.

Following the stoichiometry of the reaction, if 1 mole of D reacts with 1 mole of C and every 2 moles of C are produced when 1 mole of A reacts. The relation between D and A is 2:1.

$$1 \text{ mole of A} = 1 \text{ mole A} \frac{2 \text{ moles C}}{1 \text{ moles A}} \frac{1 \text{ mole D}}{1 \text{ mole C}} = 2 \text{ moles of D}$$

Therefore, 0.2 M of D corresponds to 0.1 M of A reacting in 20 s. The rate for experiment 1 is $5 \cdot 10^{-3}$ M/s.

The order of the reactants are calculated by comparing the rate laws. Each time, choose two experiments were only one parameter is different.

$$\frac{\text{Rate 2}}{\text{Rate 3}} = \frac{k \, [A]^a [B]^b}{k [A]^a [B]^b} = \frac{k \, 0.4^a 0.1^b}{k \, 0.2^a 0.1^b} = \frac{2.5 \cdot 10^{-3}}{6.25 \cdot 10^{-4}}$$

$$2^a = 4 \qquad a = 2$$

Similarly, using rate 2 over rate 1, b=1 is obtained.

The reactant order can be used to obtain the reaction rate.

$$Rate = k[A]^a [B]^b \qquad k = \frac{Rate}{[A]^a [B]^b} = \frac{5 \cdot 10^{-3} M s^{-1}}{(0.4M)^2 (0.1M)^1} = 0.15625 M^{-2} s^{-1}$$

Since experimentally it is more likely to obtain one slightly different k for each experiment, an average should be calculated.

Parts B. Evaluating the influence of the temperature on the reaction rate.

According to **Arrhenius equation**, the rate constant is affected by the temperature following the equation:

$$k = A e^{-E_a / RT}$$

where A is a constant, E_a is the activation energy, R is the universal gas constant, and T is the temperature. A higher temperature would make the negative exponent smaller, and therefore the k would be greater. In other words, an increase in the temperature should accelerate the reaction. It is possible to calculate the activation energy by measuring the reaction rates at two different temperatures. After calculating the respective rate constants these are compared in their logarithmic forms:

$$\ln(k) = -\frac{E_a}{RT} + \ln(A)$$

After subtracting the expression above for both temperatures, T_1 and T_2, the following equation is generated:

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

The values of k_1 and k_2 obtained respectively at T_1 and T_2 are used to calculate E_a. The temperatures should be given in Kelvins since $R = 8.3145$ J/K mol.

Part C. Evaluating the influence of a catalyst on the reaction rate.

A catalyst is a substance that without being consumed, accelerates the reaction. The catalyst generates a new reaction path with a lower activation energy. Looking at the Arrhenius equation, the effect of lowering the activation energy works in the same way as an increase in temperature. The catalyst used in this experiment will be copper sulfate ($CuSO_4$). The Cu(II) cations are responsible for the catalytic effect.

Procedure

Part A. Obtaining the rate law. Preparing the mixtures

☐ *Step 1:* – Obtain three large test tubes with their corresponding stoppers, a suitable grid or rack, a Mohr pipet, and a thermometer.

☐ *Step 2:* – Label the test tubes with numbers 1, 2 and 3.

☐ *Step 3:* – Read the Good Lab Practice box

> ### Good Lab Practice
>
> ✍ Pipettes are always used together with a suction bulb or a syringe. **Never** such a chemical using the mouth!
>
> ✍ **Never** leave a pipette laying on the table **while connected to the syringe**. Remaining liquid can leak into the syringe. The syringe will be damage and the liquid will return contaminated to the pipette.
>
> ✍ Always wash pipettes with distilled water and rinse them using the same product to be measured. Such a small volume, disconnect the syringe and move the liquid about displacing the distilled water. Discard the rinsing liquid as waste. Rinse twice.

☐ *Step 4:* – Obtain about 25 mL **0.20 M NaI** in a small beaker.

☐ *Step 5:* – Clean and rinse the pipette with NaI. Pipette 2.0 mL in test tube 1, 2.0 mL in test tube 2 and 4.0 mL in test tube 3. Refer to the table below (Table of quantities) for the reagent quantities to add.

☐ *Step 6:* – Obtain no more than 20 mL **0.20 M NaCl** in a small beaker.

☐ *Step 7:* – Clean and rinse the pipette with NaCl. Pipette 2.0 mL in test tube 1 and 2.0 mL in test tube 2. Nothing in test tube 3. Refer to the table below (Table of quantities) for the reagent quantities to add.

☐ *Step 8:* – Obtain no more than 20 mL **0.010 M $Na_2S_2O_3$** in a small beaker.

☐ *Step 9:* – Clean and rinse the pipette with $Na_2S_2O_3$. Pipette 2.0 mL in each test tube. Refer to the table below (Table of quantities) for the reagent quantities to add.

☐ *Step 10:* – Obtain aproximately 10 mL **2% starch solution** in a small beaker.

☐ *Step 11:* – Clean and rinse the pipette with starch. Pipette 1.0 mL in each test tube. Refer to the table below (Table of quantities) for the reagent quantities to add.

☐ *Step 12:* – Obtain no more than 20 mL **0.20 M K_2SO_4** in a small beaker.

☐ *Step 13:* – Clean and rinse the pipette with K_2SO_4. Pipette 2.0 mL in test tube 1, nothing in test tube 2 and 2.0 mL in test tube 3. Refer to the table below (Table of quantities) for the reagent quantities to add.

☐ *Step 14:* – Check that the volumes in the 3 test tubes make sense with the following table. Test tubes 1 and 3 should have the same volume. Test tube 2 should have slightly less volume.

☐ *Step 15:* – Using the thermometer, record the room temperature.

Table of quantities						
	Volume (mL)					⏱
	NaI 0.2M	NaCl 0.2M	$Na_2S_2O_3$ 0.01M	Starch 2%	K_2SO_4 0.2M	$K_2S_2O_8$ 0.2M
Exp. 1	2.0	2.0	2.0	1.0	2.0	2.0
Exp. 2	2.0	2.0	2.0	1.0	0	4.0
Exp. 3	4.0	0	2.0	1.0	2.0	2.0

Part A. Obtaining the rate law. Mixing the test tubes

☐ *Step 1:* – Now you are about to start up the reaction. It is critical to follow the steps below.

☐ *Step 2:* – Every reaction should be done in **the same way** to be comparable. The same steps, in the same order and at the same pace should be followed.

☐ *Step 3:* – You will be adding $K_2S_2O_8$. After adding the $K_2S_2O_8$, the test tube should be closed with the stopper, and the content should be mixed by inverting the test tube 16 times. Do not rush, turn the test tube *Mississippily*. Do the same for the following reactions.

> ⚠CAUTION!
>
> ⚠ The stopper should always be placed before inverting the test tube.
>
> ⚠ Failure to place the stopper will cause the spill of the reaction.
>
> ⚠ There is a story behind every Caution Box.

Part A. Obtaining the rate law. Starting the reaction

☐ *Step 1:* – Obtain about 25 mL **0.20 M $K_2S_2O_8$** in a small beaker. Clean and rinse the pipette with $K_2S_2O_8$.

☐ *Step 2:* – Get test tube 1 and a stopper. Set the time to zero.

☐ *Step 3:* – Start the stopwatch as you pipette 2.0 mL of $K_2S_2O_8$ in test tube 1. Time should start to be measured as soon as you add the first drop of $K_2S_2O_8$ in a test tube. Mix the reaction as explained above.

☐ *Step 4:* – Stop the stopwatch when the solution turns dark. The color will appear suddenly. If more than 5 minutes elapse without the solution turning dark, start doubting about what have you mixed.

☐ *Step 5:* – Repeat the previous steps now for test tube 2 and pipetting this time 4.0 mL of $K_2S_2O_8$ into the test tube. .

☐ *Step 6:* – Repeat one more time the previous steps now for test tube 3 and pipetting this time 2.0 mL of $K_2S_2O_8$ into the test tube.

☐ *Step 7:* – Now you need to repeat all steps above (mixture preparation and reaction) to do a second trial for the three test tubes.

☐ *Step 8:* – Discard the solutions in the indicated waste container and clean the test tubes.

Part B. Evaluating the influence of the temperature on the reaction rate.

☐ *Step 1:* – Label three large test tubes with the letters "**T**", "**C**"' and "**K**"'. "T" stands for "Temperature", "C" for "Catalyst" and "K" for "$K_2S_2O_8$".

☐ *Step 2:* – Add to test tubes "T" and "C" the same volumes of NaI, NaCl, $Na_2S_2O_3$, Starch and K_2SO_4 as for test tube 1. Do not add the $K_2S_2O_8$ yet. Reserve test tube "C" in the rack for Part C.

☐ *Step 3:* – Add about 5 mL of $K_2S_2O_8$ to test tube "K".

☐ *Step 4:* – Obtain a 600 mL beaker and, with the help of the thermometer, add hot and cold water until you have about 400 mL of water between 40 and 45 degrees Celsius.

☐ *Step 5:* – Place the test tubes "T" and "K" in the hot water bath and allow them to temper for at least 5 minutes. Part C can be done during those 5 minutes. .

☐ *Step 6:* – Measure the temperature of the water after the tempering time. Write down this temperature in the results table. Start the reaction by pipetting 2 mL of $K_2S_2O_8$ from test tube "K" into test tube "T". After the 16-Mississippi mixing, return the test tube to the bath and wait to record the time it takes for the solution to turn dark.

Part C. Evaluating the influence of a catalyst on the reaction rate.

☐ *Step 1:* – Add **one drop** of **0.2 M CuSO$_4$** to test tube "C". Shake the test tube to mix the solution.

☐ *Step 2:* – Start the stopwatch as you pipette 2.0 mL of $K_2S_2O_8$ in the test tube. Mix the reaction as explained above.

Calculations

⓪ This is lab temperature. You will use this value for Part B as well.

① This is the volume of iodine added in each experiment.

② This is the volume of thiosulfate added in each experiment.

③ This is the volume of peroxydisulfate added in each experiment.

④ This is the total volume v_{total} of the reacting mixture.

⑤ This is the peroxy disulfate concentration in the mixture:

$$[S_2O_8{}^{-2}] = \frac{v_{S_2O_8{}^{-2}} \cdot c_{S_2O_8{}^{-2}}}{v_{total}} = \frac{③ \cdot 0.2}{④}$$

⑥ This is the iodine concentration in the mixture:

$$[I^-] = \frac{v_{I^-} \cdot c_{I^-}}{v_{total}} = \frac{① \cdot 0.2}{④}$$

⑦ This is the change in thiosulfate concentration during the reaction:

$$\Delta[S_2O_3{}^{-2}] = \frac{v_{S_2O_3{}^{-2}} \cdot c_{S_2O_3{}^{-2}}}{v_{total}} = \frac{② \cdot 0.01}{④}$$

⑧ This is the average time Δt for each experiment.

⑨ This is the reaction rate:

$$r = \frac{\Delta[S_2O_3{}^{-2}]}{2 \cdot \Delta t} = \frac{⑦}{2 \cdot ⑧}$$

⑩ This is the peroxy disulfate order in the rate law:

$$a = \frac{\ln\left(\frac{r_{Exp1}}{r_{Exp2}}\right)}{\ln\left(\frac{[S_2O_8{}^{-2}]_{Exp1}}{[S_2O_8{}^{-2}]_{Exp2}}\right)} = \frac{\ln\left(⑨_{Exp1} \div ⑨_{Exp2}\right)}{\ln\left(⑤_{Exp1} \div ⑤_{Exp2}\right)}$$

(11) This is the iodide order in the rate law:

$$b = \frac{\ln\left(\frac{r_{Exp1}}{r_{Exp3}}\right)}{\ln\left(\frac{[I^-]_{Exp1}}{[I^-]_{Exp3}}\right)} = \frac{\ln\left(\boxed{9}_{Exp1} \div \boxed{9}_{Exp3}\right)}{\ln\left(\boxed{6}_{Exp1} \div \boxed{6}_{Exp3}\right)}$$

(12) The are the rate constant calculated for each experiment:

$$k = \frac{r}{[S_2O_8{}^{-2}] \cdot [I^-]} = \frac{\boxed{9}}{\boxed{5} \cdot \boxed{6}}$$

(13) This is the average rate constant.

(14) The data on this row should be the same as in the first row in the Results table of Part B.

(15) This is the activation energy. You need to use the two different reaction constants at different temperatures. R is 3.184 J/K·mol:

$$E_a = \frac{T_1 \cdot T_2}{T_2 - T_1} \cdot R \cdot \ln\left(\frac{k_2}{k_1}\right)$$

Pre-lab Questions

The iodine clock

1. Using collision theory, explain how the concentration of the reactants affect the rate of the reaction.

2. For the reaction $2A + 3B \rightarrow C$ what is the mathematical expression that relates the rate of A (r_a) and the rate of B (r_b)?

3. Explain the Iodine clock reaction used in this experiment.

4. What is starch and where can you find it in nature?

5. Low-quality boiled ham often contains potatoes to make it cheaper. How could you test if one piece of ham is pure meat or it contains potatoes?

6. Find out the difference between a **Mohr pipette** and a **transfer pipette**.

Results
EXPERIMENT
The iodine clock

Ⓞ Laboratory Temperature ——— K

Trial	Exp.	c_{NaI}	c_{NaCl}	$c_{Na_2S_2O_3}$	c_{Starch}	$c_{K_2SO_4}$	$c_{K_2S_2O_8}$	V_{Total}	time	$[S_2O_8^{-2}]$	$[I^-]$	$\Delta[S_2O_3^{-2}]$
		0.2M	0.2M	0.01M	2%	0.2M	0.2M	(mL)	(s)	(M)	(M)	(M)
		①	②			③	④		⑤	⑥	⑦	
1	1	2mL	2mL	2mL	1mL	2mL	2mL	11mL	——	——	——	——
1	2	2mL	2mL	2mL	1mL	0mL	4mL	11mL	——	——	——	——
1	3	4mL	0mL	2mL	1mL	2mL	2mL	11mL	——	——	——	——
2	1	2mL	2mL	2mL	1mL	2mL	2mL	11mL	——	——	——	——
2	2	2mL	2mL	2mL	1mL	0mL	4mL	11mL	——	——	——	——
2	3	4mL	0mL	2mL	1mL	2mL	2mL	11mL	——	——	——	——

⑧ Average time Δt(s)

1	——
2	——
3	——

Part A. Obtaining the rate law.

	Exp.	$\Delta[S_2O_3^{-2}]$ (M) ⑦	Δt (s) ⑧	r (M/s) ⑨	$[S_2O_8^{-2}]$ (M) ⑤	$[I^-]$ (M) ⑥	k ⑫
⑭	1	_____	_____	_____	_____	_____	_____
	2	_____	_____	_____	_____	_____	_____
	3	_____	_____	_____	_____	_____	_____

$$r = k\,[S_2O_8^{2-}]^a\,[I^-]^b$$

⑩ a= _____   ⑪ b= _____   ⑬ Average k (write down units)= _____

Parts B and C. Evaluating the influence of the temperature on the reaction rate and a catalyst

	Exp.	Temperature (K)	$\Delta[S_2O_3^{-2}]$ (M) ⑦	Δt (s) ⑧	r (M/s) ⑨	$[S_2O_8^{-2}]$ (M) ⑤	$[I^-]$ (M) ⑥	k ⑫
⑭	1	_____	_____	_____	_____	_____	_____	_____
	1	_____	_____	_____	_____	_____	_____	_____
		(Results on the first row of Table A and Table B should be the same)						
Catalyst	1	_____		_____				

⑮ E_a= _____   J/K·mol

Post-lab Questions

The iodine clock

1. Explain the effect of adding a catalyst to the reaction rate.