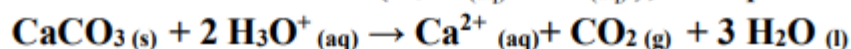# Question 1: Kinetic study

It is required to follow-up the progress of the reaction between solid calcium carbonate, $CaCO_3$, and hydrochloric acid solution HCl ($H_3O^+_{(aq)}$ + $Cl^-_{(aq)}$), the equation of the reaction is:

$$CaCO_{3\,(s)} + 2\,H_3O^+_{(aq)} \rightarrow Ca^{2+}_{(aq)} + CO_{2\,(g)} + 3\,H_2O_{(l)}$$

For this aim the following experiment is realized:

At time t = 0 sec, a mass m = 2.0 g of calcium carbonate is rapidly introduced into a flask containing a volume V = 50.0 ml of hydrochloric acid solution, of concentration C = 4.0×10^{-2} mol.L^{-1}, at temperature T= 25 °C. The volume of the heterogeneous reaction mixture is considered constant throughout the experiment.

> **Given:**
> - Molar volume of a gas at the conditions of this exercise is V_m = 24 L.mol^{-1}.
> - Molar mass of calcium carbonate ($CaCO_3$) is M = 100 g.mol^{-1}.

1. Preliminary study

1.1. Show that, at the end of the reaction, the reaction mixture remains heterogeneous.

1.2. Determine at t_∞ the volume of carbon dioxide V $(CO_2)_\infty$.

2. Kinetic study of the reaction

An appropriate method allows us to follow the evolution of the concentration of oxonium ions, H_3O^+, with time. The values obtained are shown in **document-1.**

Time (sec)	10	20	30	40	50	60	70	80	90	100
$[H_3O^+] \times 10^{-2}$ mol.L^{-1}	3.6	3.2	2.8	2.5	2.3	2.0	1.8	1.7	1.5	1.4

Document-1

2.1. Draw, on the graph paper, the curve $[H_3O^+] = f(t)$ within the time interval: [0 - 100 s].
Take the following scales:
1 cm for 10 s in abscissa   and 1 cm for 0.4 ×10^{-2} mol.L^{-1} in ordinate.

2.2. Determine graphically the half - life time of the reaction.

2.3. The rate of disappearance of H_3O^+ at t =20 s : r $(H_3O^+)_{20}$ = 2.75 × 10^{-4} mol.L^{-1}s^{-1}.
Deduce the rate of reaction at this instant.

2.4. During a chemical reaction, the rate changes versus time.

 2.4.1. One of the three curves in **document-2** represents the variation of the rate of disappearance of H_3O^+ versus time , r(H_3O^+) = g(t). Choose, by justifying, the correct curve.

Document-2
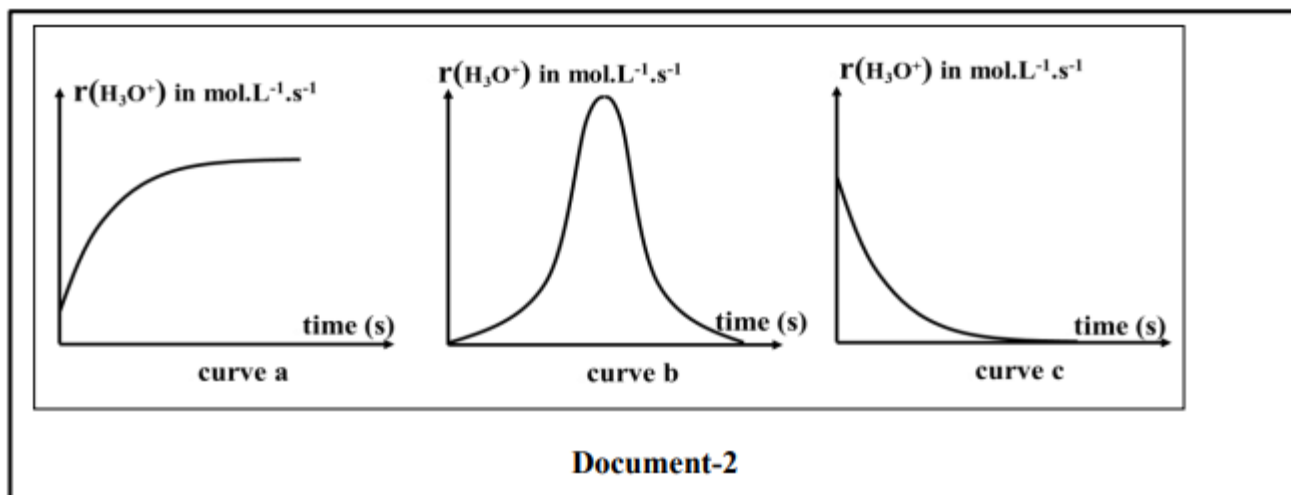
2.4.2. Sami, a student in grade 12, gave the following proposition:

"The amount of CO_2 produced during the experiment increases as time passes, and thus the rate of formation of CO_2 increases as function of time".

Specify whether the proposition given by Sami is true or false.

2.5. The same experiment realized above, is carried out again, but with one change: the flask is placed in a bath maintained at temperature T'< T.

On the same graph of part 2.1, plot the shape of the curve representing the new variation of the concentration of H_3O^+ ions as a function of time: $[H_3O^+] = h$ (t). Justify.

Part	Answer
1.1	• $n(CaCO_3)_{initial} = \dfrac{m}{M(CaCO_3)} = \dfrac{2}{100} = 0.02$ mol • $HCl + H_2O \rightarrow H_3O^+ + Cl^-$ $n(H_3O^+)_{initial} = n(HCl) = C_aV_a = 4 \times 10^{-2} \times 50 \times 10^{-3} = 2 \times 10^{-3}$ mol • $R(CaCO_3) = \dfrac{n(CaCO_3)initial}{1} = 0.02$ • $R(H_3O^+) = \dfrac{n(H_3O^+)initial}{1} = \dfrac{2 \times 10^{-3}}{2} = 1 \times 10^{-3}$ $R(H_3O^+) < R(CaCO_3)$ then H_3O^+ is the limiting reactant, and $CaCO_3$ is in excess. Then: At the end of the reaction, the mixture will contain solid $CaCO_3$ => **heterogeneous**
1.2	At the end of the reaction and according to stoichiometric ratio: $\dfrac{n(H_3O^+)_0}{2} = \dfrac{n(CO_2)_\infty}{1}$ $n(CO_2)_\infty = 1 \times 10^{-3}$ mol $V(CO_2)_\infty = n(CO_2)_\infty \times V_m = 1 \times 10^{-3} \times 24 = 24 \times 10^{-3}$ L
2.1	
2.2	Half-life : it is the time needed for half the amount of the limiting reactant (H_3O^+) to disappear. $n(H_3O^+)t_{\frac{1}{2}} = \dfrac{2x10^{-3}}{2} = 1 \times 10^{-3}$ mol Graphically it corresponds to $t_{1/2} = 60$ sec.
2.3	According to S.R : $r(reaction)_{t=20} = \dfrac{r(H3O^+)_{t=20}}{2}$ $r(reaction)_{t=20} = 1.375 \times 10^{-4}$ mol.L^{-1}.sec^{-1}

|	
2.4.1	The rate of disappearance of H_3O^+ begins high then it decreases with time (due to the decrease of concentration of reactant H_3O^+) till it reaches zero at the end of reaction. Then curve (C) is correct.
2.4.2	The rate of formation of CO_2 decreases with time since it depends on concentration of reactant H_3O^+ (which decreases with time) and not on the concentration of product formed (CO_2) which increases with time. Therefore, the proposition is false.
2.5	All conditions in the two experiments are the same except temperature. Temperature is a kinetic factor, when temperature decreases, rate of disappearance of H_3O^+ decreases ($r(H_3O^+)_t$ at temp $T > r(H_3O^+)_t$ at temp T') At any time t : $[H_3O^+]_{remaining\ at\ temp\ T'} > [H_3O^+]_{remaining\ at\ temp\ T}$ Then the curve $[H_3O^+]= h(t)$ is above $[H_3O^+]= f(t)$

Question 2: Sodium Thiosulfate

The reaction between sodium thiosulphate ($Na_2S_2O_3$) and hydrochloric acid (HCl) is usually the reaction chosen by many teachers and students to study the factors affecting rate of a chemical reaction.
The equation of reaction taking place is:

$$S_2O_3^{2-} \, _{(aq)} + 2H^+ \, _{(aq)} \rightarrow S \, _{(S)} + SO_2 \, _{(g)} + H_2O \, _{(l)}$$
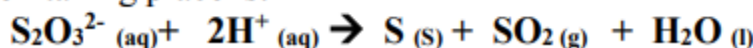
In this experiment, the reaction is carried out by mixing the reactants in a conical flask. As shown in **document-1**, before the reaction starts, the cross mark is clearly visible. However, as the reaction proceeds, Sulfur precipitates and makes the solution more opaque and eventually the cross mark gets completely masked. The time taken (t) for the mark to totally disappear indicates how fast the reaction has occurred.

Document-1
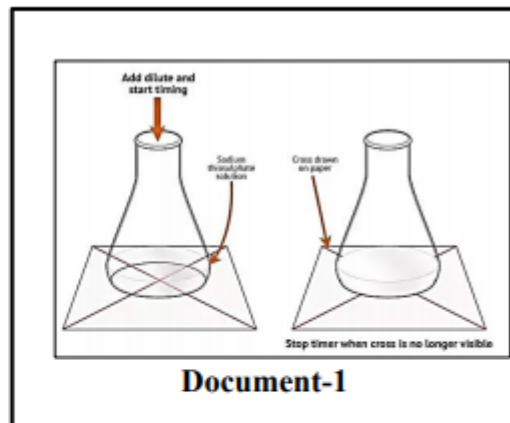
Available solutions:

- **Solution S_1:** an aqueous solution of sodium thiosulfate ($2Na^+_{(aq)} + S_2O_3^{2-}_{(aq)}$) of concentration $C_1 = 0.4$ mol.L^{-1}
- **Solution S_2:** an aqueous solution of hydrochloric acid ($H^+_{(aq)} + Cl^-_{(aq)}$) of concentration $C_1 = 2.0$ mol.L^{-1}

Given: Molar masses of sulfur : $M(S) = 32$ g.mol^{-1} .

1. Preparation of hydrochloric acid solution (S_2)

Solution (S_2) is prepared from a commercial solution carrying the following indications:

> percentage by mass of HCl in the solution : $p = 30\%$
> Density: $\rho = 1.216$ g.mL^{-1}
> $M(HCl) = 36.5$ g.mol^{-1}
> **Document-2-**

1.1. Referring to document-2-, show that the concentration of the commercial solution is $C_o = 10$ mol.L^{-1}.

1.2. Specify, among the following kits, the suitable one for the preparation of solution S_2.

Kit 1	Kit 2
❖ 20 mL volumetric pipet	❖ 20 mL volumetric pipet
❖ 250 mL volumetric flask	❖ 100 mL volumetric flask
❖ 50 mL beaker	❖ 50 mL beaker

2. Effect of kinetic factors on the rate of formation of sulfur.

The experiment that is summarized in **document-3** is performed at temperature T. The time needed in each of the two beakers for cross to become invisible is recorded.

Beaker	Volume taken from S_2 (in mL)	Volume taken from S_1 (in mL)	Volume of added water (in mL)	Time for the cross to become invisible (sec)
1	30	40	0	8
2	30	30	10	11

Document-3

2.1. Verify the following relation: $[S_2O_3^{2-}]_o = \frac{1}{175} V_1$. where $[S_2O_3^{2-}]_o$ in mol.L^{-1} is the initial concentration of $S_2O_3^{2-}$ in the reaction mixture; and V_1, in mL, is the volume of S_1 solution added to the reaction mixture.

2.2. Deduce how the initial concentration of $S_2O_3^{2-}$, $[S_2O_3^{2-}]_o$, changes from beaker 1 to beaker 2.

2.3. Explain the difference in the time needed for the cross to become invisible between the two beakers.

2.4. Determine the limiting reactant in beaker 1.

2.5. The graph of **document-4-** represents the variation of the mass of sulfur formed in beaker 1 as a function of time m(S) = f(t).
Copy the curve m(S) = f(t) on your answer sheet. Draw on the same graph the shape of the curve m(S) = g(t) for the reaction taking place in beaker 2.
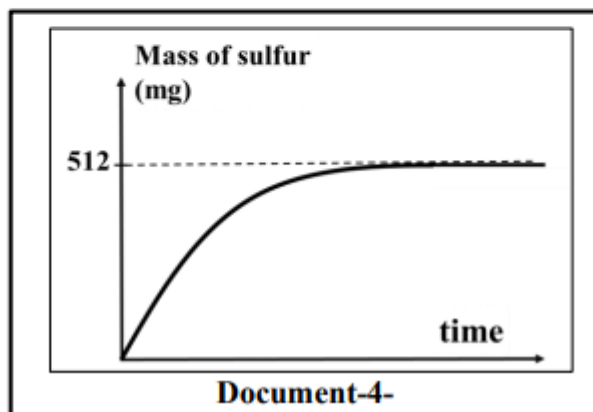
Take the following scale:On y-axis: 1cm = 100 mg

Document-4-

2.6. Choose, by justifying, the correct answer in each of the following cases.

2.6.1. The instantaneous rate of formation of S at an instant t, denoted as r (S)$_t$, and the instantaneous rate of disappearance of H^+ ions at the same instant t, denoted as r(H^+)$_t$, are related by the relation:

a) r(H^+)$_t$ = r (S)$_t$ b) r(H^+)$_t$ = 2 r (S)$_t$ c) r(H^+)$_t$ = ½ r (S)$_t$

2.6.2. at infinity, the rate of formation of sulfur in the beaker1 compared to that of beaker 2 is:

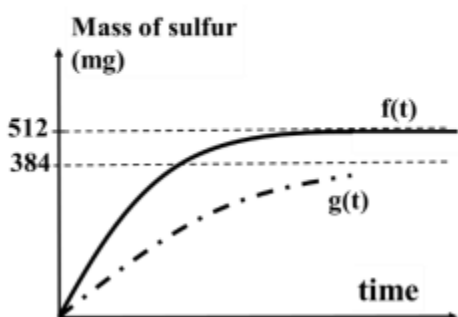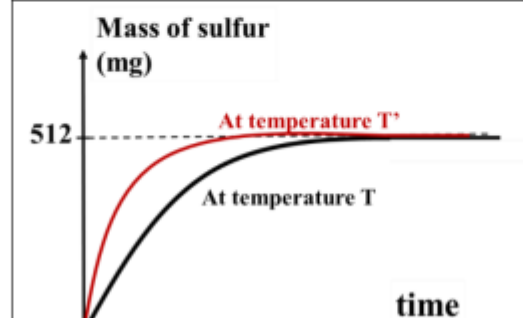a) r(S)$_\infty$ in beaker 1 > r(S)$_\infty$ in beaker 2
b) r(S)$_\infty$ in beaker 1 < r(S)$_\infty$ in beaker 2
c) r(S)$_\infty$ in beaker 1 = r(S)$_\infty$ in beaker 2

2.7. One more beaker is prepared , beaker 3, which has the same contents and conditions as beaker 1 except that it is placed at a temperature T' > T.
On the same graph of document-4-, draw the shape of the curve representing the variation of mass of sulfur as a function of time at temperature T'. Justify.

Q	Expected Answers
1.1	$p \text{ (solute)} = \dfrac{m_{solute}}{m_{solution}} \times 100 = \dfrac{(n \times M)_{solute}}{(\rho \times V)_{solution}} \times 100 = \dfrac{(C_o \times M)_{solute}}{\rho_{solution}} \times 100$ $C_o = \dfrac{p_{solute} \times \rho_{solution}}{M_{solute} \times 100} = \dfrac{30 \times 1.216 \times 10^3}{36.5 \times 100} = 10 \text{ mol. L}^{-1}$
1.2	Upon dilution number of mol of initially dissolved solute (HCl) is conserved: n_{solute} (before dilution) $= n_{solute}$ (after dilution) then $C_o V_o = C_{S2} V_{S2}$ Dilution factor : $F = \dfrac{C_o}{C_{(S_2)}} = \dfrac{V_{(S_2)}}{V_o} \Rightarrow F = \dfrac{C_o}{C_{(S_2)}} = \dfrac{10}{2} = 5$ **Kit 1:** $F = \dfrac{V_{(S_2)}}{V_o} = \dfrac{250}{20} = 12.5$ while **Kit 2:** $F = \dfrac{V_{(S_2)}}{V_o} = \dfrac{100}{20} = 5$ Then kit 2 is suitable
2.1	When mixing solutions, number of moles of initially dissolved species is conserved. $n\,(S_2O_3^{2-})$ (before mixing) $= n\,(S_2O_3^{2-})$ (after mixing) $(C_1 \times V_1)\,S_2O_3^{2-}$ (before mixing) $= [S_2O_3^{2-}]_o \times V_{total}$ $[S_2O_3^{2-}]_o = \dfrac{0.40 \times V_1 \times 10^{-3}}{70 \times 10^{-3}} = \dfrac{V_1}{175}$
2.2	$[S_2O_3^{2-}]_o = V_1 \times \dfrac{1}{175}$ $[S_2O_3^{2-}]_o$ is directly proportional to V_1. V_1 decreases from beaker 1 to beaker 2, then $[S_2O_3^{2-}]_o$ in beaker 2 is less than $[S_2O_3^{2-}]_o$ in beaker 1.
2.3	All conditions are the same between beakers 1 and 2 except for the $[S_2O_3^{2-}]_o$ Initial concentration of reactant $(S_2O_3^{2-})$ is a kinetic factor . As $[S_2O_3^{2-}]_o$ decreases , the rate of reaction decreases. $[S_2O_3^{2-}]_o$ in beaker 1 $> [S_2O_3^{2-}]_o$ in beaker 2 ⇨ Rate of formation of sulfur is higher in beaker 1 than in beaker 2 ⇨ At each time t: $n\,(S)$ formed in beaker 1 $> n\,(S)$ formed in beaker 2 Then the cross needs less time to become invisible in beaker 1 than in beaker 2.

2.4	$R(S_2O_3^{2-}) = \dfrac{n(S_2O_3^{2-})_o}{1} = C_1 \times V_{1(in\ beaker\ 1)} = 0.4 \times 40 \times 10^{-3} = 16 \times 10^{-3}$ $R(H^+) = \dfrac{n(H^+)_o}{2} = \dfrac{C_2 \times 30 \times 10^{-3}}{2} = \dfrac{2 \times 30 \times 10^{-3}}{2} = 30 \times 10^{-3}$ $R(S_2O_3^{2-}) < R(H^+)$ Then $S_2O_3^{2-}$ is the limiting reactant.
2.5	At each time t: n (S) formed in beaker 1 > n (S) formed in beaker 2 (part 2.3) Then at each time t: m (S) formed in beaker 1 > m (S) formed in beaker 2 In beaker 2, $S_2O_3^{2-}$ is the limiting reactant, having same amount of H^+ but less amount of $S_2O_3^{2-}$ than beaker 1. At infinity, in beaker 2: $n(S)_\infty = n(S_2O_3^{2-})_o = C_1 \times V_{1(in\ beaker\ 2)} = 0.4 \times x\ 30\ x\ 10^{-3} = 12\ x\ 10^{-3}$ mol. $m(S)_\infty = n(S)_\infty \times M(S) = 12\ x\ 10^{-3}\ x\ 32 = 0.384\ g = 384$ mg
2.6.1	Correct answer: b) $r(H^+)_t = 2\ r(S)_t$ according to S.R : $\dfrac{r(H^+)_t}{2} = \dfrac{r(S)_t}{1}$ $\Rightarrow$ $r(H^+)_t = 2\ r(S)_t$
2.6.2	Correct answer: c) r (S)$_\infty$ in beaker 1 = r(S)$_\infty$ in beaker 2 At infinity, the reaction stops, no more formation of sulfur, hence the rate of formation of sulfur in both beakers will be zero .
2.7	All conditions are the same in the two experiments except for temperature. Temperature is a kinetic factor, As temperature increases ,the rate of the reaction increases. T' (in beaker 3) $> T$ (in beaker 1) So sulfur is formed faster at temperature T' (in beaker 3). **So at any time t : n (S)** at T' **> n (S)** at T

Question 3: Kinetic study of the reaction of hydrogen peroxide with iodide ions

We aim to study the kinetics of the slow reaction of hydrogen peroxide (H_2O_2) with iodide ions (I^-) in the presence of sulfuric acid.
The equation of the reaction taking place is:

$$H_2O_2 + 2\,I^- + 2\,H^+ \rightarrow 2\,H_2O + I_2$$
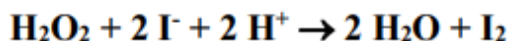
Available solutions:

- Solution S_1: potassium iodide solution KI ($K^+_{(aq)} + I^-_{(aq)}$) of concentration $C_1 = 0.10$ mol.L^{-1}.
- Solution S_2: hydrogen peroxide solution (H_2O_2) of concentration $C_2 = 0.10$ mol.L^{-1}.
- Concentrated sulfuric acid solution H_2SO_4.

At the time $t = 0$ min, a mixture (M_1) is prepared by mixing a volume $V_1 = 90.0$ mL of solution S_1, with a volume $V_2 = 10.0$ mL of solution S_2 and 50.0 mL of concentrated sulfuric acid solution such that sulfuric acid is in large excess.

10 mL samples of the reaction medium are taken at different intervals of time, the reaction in these samples is stopped immediately, and the concentration of I_2 formed at each time is determined by titration. The values obtained let us to draw the curve $[I_2] = f(t)$ shown in document-1.
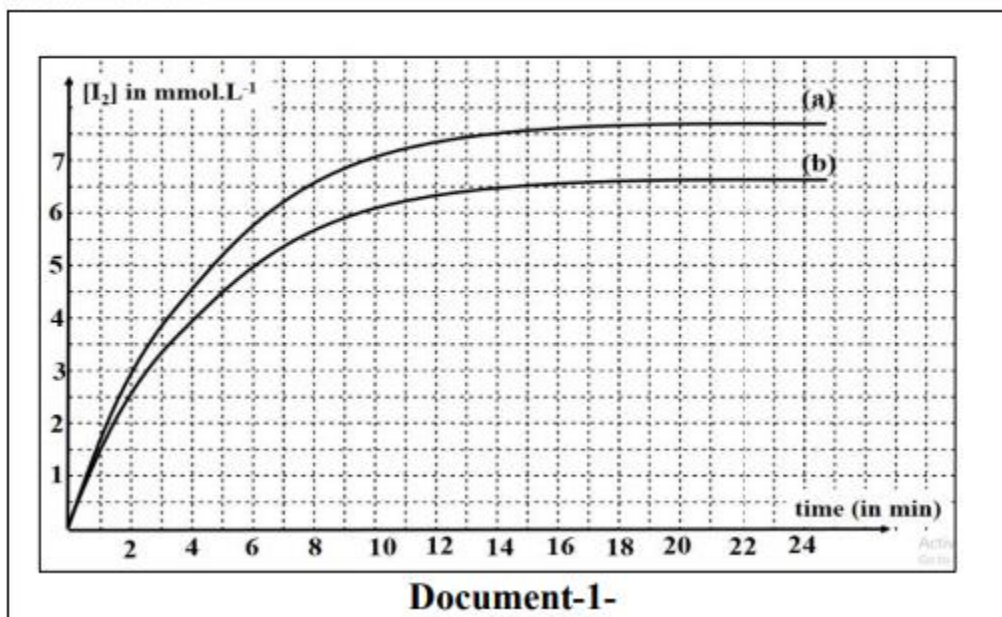
Document-1-

1. Preliminary study.

1.1. Show that the initial concentrations of I^- and H_2O_2 in the reaction mixture are $[I^-]_o = 0.06$ mol.L^{-1} and $[H_2O_2]_o = 6.66 \times 10^{-3}$ mol.L^{-1}.

1.2. The curves (a) and (b) of **document-1** represent the change of concentration of I_2 versus time.

Specify the one that corresponds to the reaction taking place in mixture (M_1).

2. Study of titration of the samples.

The titration of I_2 in the 10 mL samples is done using sodium thiosulfate solution ($2Na^+_{(aq)} + S_2O_3^{2-}_{(aq)}$) of concentration (C), placed in 50 mL buret. The volume of thiosulfate solution needed to reach equivalence is V_E. The equation of titration is :

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

2.1. Propose, with justification, an experimental way to stop the reaction in each sample before titration.

2.2. Name the glassware used to take the samples from the reaction medium.

2.3. Before filling the buret for titration, it is rinsed with distilled water and then with the thiosulfate solution.

Explain the importance of rinsing the buret with the thiosulfate solution on the accuracy of V_E value.

3. Kinetic study.

The rate of formation of I_2 at $t = 2$ min is equal to 0.86 mmol.L^{-1}.min^{-1}

3.1. Define the rate of formation of iodine at an instant (t).

3.2. The rate of formation of iodine , $r(I_2)$, is determined at two other instants.

Match each rate to its convenient time. Justify your answer.

    a. $t = 0$ **i.** $r = 3$ mmol.L^{-1}.min^{-1}

    b. $t = 11$ min   **ii.** $r' = 0.15$ mmol.L^{-1}.min^{-1}

3.3. Choose, with justification, the value that represents the rate of disappearance of I^- at $t = 2$ min.

    a) $r(I^-) = 1.72$ mmol.L^{-1}.min^{-1} b) $r(I^-) = -1.72$ mmol.L^{-1}.min^{-1}

    b) c) $r(I^-) = 0.43$ mmol.L^{-1}.min^{-1}

3.4. Determine the half - life time($t_{1/2}$) of the reaction .

3.5. Another mixture (M_2) is prepared by mixing the following volumes:

A volume $V_1' = 50.0$ mL of solution S_1, a volume $V_2 = 10.0$ mL of solution S_2, 50.0 mL of concentrated sulfuric acid solution, and 40 mL of distilled water.

Verify whether the following statement is true.

The maximum value of $[I_2]$ in (M_2) is less than 6.66 mmol.L^{-1}.

Q	Expected Answers
1.1	Upon mixing, number of moles of initially dissolved species is conserved: **For H_2O_2:** $n(H_2O_2)_{before\ mixing} = n(H_2O_2)_{after\ mixing}$ $n_2 = [H_2O_2]_o \times V_{total}$ $[H_2O_2]_o = \dfrac{n_2}{V_{total}} = \dfrac{C_2V_2}{V_{total}} = \dfrac{0.1\times10\times10^{-3}}{150\times10^{-3}}$ $= 6.66 \times10^{-3}$ mol.L^{-1} **For I^-:** $n(I^-)_{before\ mixing} = n(I^-)_{after\ mixing} = n(KI)_o$ $n_1 = [I^-]_o \times V_{total}$ $[I^-]_o = \dfrac{n_1}{V_{total}} = \dfrac{C_1V_1}{V_{total}} = \dfrac{0.1\times90\times10^{-3}}{150\times10^{-3}}$ $= 0.06$ mol.L^{-1}
1.2	$R(H_2O_2) = \dfrac{n_2}{1} = \dfrac{C_2V_2}{1} = \dfrac{0.1\times10\times10^{-3}}{1} = 1\times10^{-3}$ $R(I^-) = \dfrac{n_1}{2} = \dfrac{C_1V_1}{2} = \dfrac{0.1\times90\times10^{-3}}{2} = 4.5\times10^{-3}$ $R(H_2O_2) < R(I^-)$ then H_2O_2 is the limiting reactant. At the end of the reaction and according to S.R: $\dfrac{n(I_2)_\infty}{1} = \dfrac{n(H_2O_2)_0}{1}$ Divide by constant volume of solution : $[I_2]_\infty = [H_2O_2]_o = 6.66\times10^{-3}$ mol.L^{-1} = 6.66 mmol.L^{-1} Then Curve b is the correct curve
2.1	Pour the 10 mL sample in a flask containing ice water (sudden cooling with dilution) . By diluting the sample ,the concentration of reactants decreases which decreases the rate of reaction (concentration of reactants H_2O_2 and I^- is a kinetic factor) . And by decreasing the temperature ,the rate of the reaction decreases more leading to stop the reaction between H_2O_2 and I^- (temperature is a kinetic factor).
2.2	10 mL volumetric pipet
2.3	At equivalence and according to S.R : $\dfrac{n(I_2)_{present\ in\ beaker}}{1} = \dfrac{n(S_2O_3^{2-})_{added\ from\ buret}}{2}$; If the buret is rinsed only with distilled water, some drops of water will remain in the buret, this will cause a slight dilution of the thiosulfate solution (C decreases). $n(I_2)_{present\ in\ beaker}$ is constant then $n(S_2O_3^{2-})_{added} = \dfrac{C \times V_E}{2}$ is constant too . If C decreases, V_E will increase, and we will not obtain accurate V_E value.

3.1	The rate of formation of iodine (I_2) is the positive slope of the tangent to the curve at point of abscissa (t): $r(I_2)_t = \dfrac{d[I_2]}{dt}$
3.2	As time passes $r(I_2)$ decreases due to the decrease of concentration of reactants H_2O_2 and I^- (concentration of reactants is a kinetic factor). Then $r(I_2)_{t=0} > r(I_2)_{t=11}$ At t= 0 → r = 3 mmol.L^{-1}.min^{-1} At t= 11 → r' = 0.15 mmol.L^{-1}.min^{-1}
3.3	According to S.R : $\dfrac{r(I^-)_t}{2} = \dfrac{r(I_2)_t}{1}$ $\Rightarrow r(I^-)_{2\ min} = 2\ r(I_2)_{2\ min} = 2 \times 0.86 = 1.72$ mmol.L^{-1}.min^{-1}
3.4	Half life time is the time needed for the product to reach half of its maximum amount. $[I_2]_{t\frac{1}{2}} = \dfrac{[I_2]_\infty}{2} = \dfrac{6.66}{2} = 3.33$ mmol.L^{-1} graphically it corresponds to $t_{\frac{1}{2}} = 3$ min
3.5	$R(H_2O_2) = \dfrac{n_2}{1} = \dfrac{C_2 V_2}{1} = \dfrac{0.1 \times 10 \times 10^{-3}}{1} = 1 \times 10^{-3}$ $R(I^-) = \dfrac{n'_1}{2} = \dfrac{C_1 V'_1}{2} = \dfrac{0.1 \times 50 \times 10^{-3}}{2} = 2.5 \times 10^{-3}$ $R(H_2O_2) < R(I^-)$ then H_2O_2 is the limiting reactant. At the end of the reaction and according to S.R: $\dfrac{n(I_2)_\infty}{1} = \dfrac{n(H_2O_2)_0}{1}$ $n(I_2)_\infty = 1 \times 10^{-3}$ mol.L^{-1} $[I_2]_\infty = \dfrac{n(I_2)_\infty}{V_{total}} = \dfrac{1 \times 10^{-3}}{150 \times 10^{-3}} = 6.66 \times 10^{-3}$ mol.L^{-1} = 6.66 mmol.L^{-1} Then the statement is false.

Question 4: Factors affecting kinetics of a chemical reaction

The aim of this exercise is to study the kinetic of reaction of peroxydisulfate ions($S_2O_8^{2-}$) with iodide ions (I^-).

Available solutions:
- Solution 1 (S_1): potassium iodide solution KI ($K^+_{(aq)} + I^-_{(aq)}$) of concentration $C_1 = 5.0$ mol.L^{-1}.
- Solution 2 (S_2): potassium peroxydisulfate solution ($2 K^+_{(aq)} + S_2O_8^{2-}{}_{(aq)}$) of concentration $C_2 = 1.0$ mol.L^{-1}

Given: molar mass in g.mol^{-1} : $M(K) = 39$; $M(I) = 127$

1. Preparation of solution (S_1).

50 mL of solution (S_1) is initially prepared from potassium iodide crystals (KI) present in the laboratory.

  1.1. Calculate the mass (m) of potassium iodide crystals required to prepare solution (S_1).

  1.2. Choose, from **document-1-**, the most suitable materials to carry out this preparation.
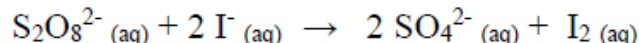

- Volumetric flask : 50 , 500 and 1000 mL   - graduated buret : 25 and 50 mL
- Graduated cylinder : 20, 50 and 250 mL   - precision balance
- Volumetric pipet : 5,10 and 20 mL   - funnel
- Watch glass and spatula   - distilled water bottle

Document -1-

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2. Kinetic study.

Experiment 1: At 25°C , a solution is prepared by mixing 10 mL of solution(S_1) and 10 mL of solution (S_2), distilled water is then added to obtain a total constant volume (V).
  A slow and complete reaction takes place according to the following equation:
$$S_2O_8^{2-}{}_{(aq)} + 2 I^-{}_{(aq)} \rightarrow 2 SO_4^{2-}{}_{(aq)} + I_2{}_{(aq)}$$
The amount of I_2 is determined at different intervals of time. The results are represented in **document-2-**.

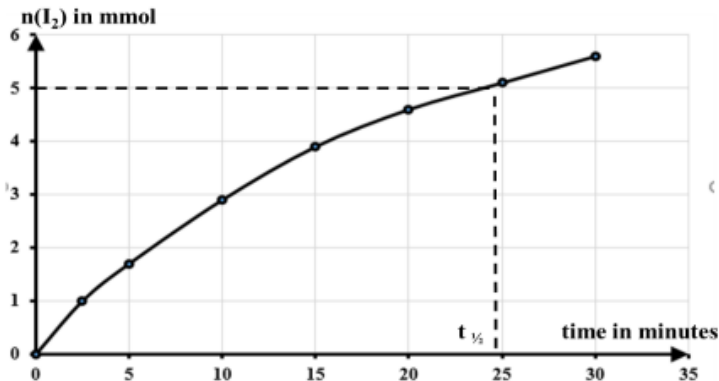| t (min)	2.5	5	10	15	20	25	30
n (I_2) in mmol	1.0	1.7	2.9	3.9	4.6	5.1	5.6

Document-2

2.1. Specify whether the time t=30 min represents the end time of the reaction.

2.2. Plot the curve representing the variation of $n(I_2)$ as function of time $n(I_2) = f(t)$ in the interval of time [0-30 min].

Take the following scale: 1cm → 5 min in abscissa and 1cm → 1 mmol in ordinates.

2.3. Verify whether the following statement is true or false:

The rate of formation of I_2 is equal to zero at t = 0, and its value is maximum at the end of reaction (t_∞).

2.4. The rate of formation of (I_2) at t=10 min is $r(I_2)_{t= 10\ min} = 2.3 \times 10^{-4}$ mol. min^{-1} .

Calculate the rate of disappearance of (I⁻) ions at t =10 minutes.

2.5. Determine, graphically, the half-life time ($t_{1/2}$) of the reaction of experiment 1.

2.6. Three other experiments are performed to study the effect of some factors on the progress of the reaction. The 3 experiments are summarized in **document-3-** .

Experiment	Composition of reaction medium	Total volume of the solution	Temperature at which the experiment is performed
1	10 mL of S_1, 10 mL of S_2 and distilled water	V	25°C
2	10 mL of S_1, 10 mL of S_2 and distilled water	V	40°C
3	10 mL of S_1, 10 mL of S_2 and distilled water	V'	25°C
4	10 mL of S_1, 10 mL of S_2, 2 mmol of I_2 and distilled water	V	25°C

Document-3-

2.6.1. The rate of formation of I_2 at t=10 min in experiment 3 is less than that in experiment 1($r(I_2)_{10}$ in exp 3 < $r(I_2)_{10}$ in exp 1).

Choose ,with justification, the correct answer.

a) V' = V   b) V' > V   c) V' < V

2.6.2. Indicate, in each of experiments 2 and 4, whether the initial rate of formation of I_2 will be equal to, less than or greater than that of experiment 1. Justify your answer in each case.

Q	Expected Answer
1.1	The necessary mass of KI to prepare solution (S_1) : $m(KI) = n(KI) \times M(KI) = C_1 \times V_1 \times M(KI)$ with $M(KI) = 39 + 127 = 166$ g.mol^{-1} Then $m(KI) = 5 \times 50 \times 10^{-3} \times 166 = 41.5$ g
1.2	50 mL volumetric flask – precision balance – funnel – watch glass and spatula – distilled water bottle
2.1	$n(I^-)_{initial} = C_1 \times V_1 = 5 \times 10 \times 10^{-3} = 0.05$ mol $\Rightarrow R(I^-) = \frac{0.05}{2} = 0.025$ $n(S_2O_8^{2-})_{initial} = C_2 \times V_2 = 1 \times 10 \times 10^{-3} = 0.01$ mol $\Rightarrow R(S_2O_8^{2-}) = \frac{0.01}{1} = 0.01$ $R(S_2O_8^{2-}) < R(I^-)$ then $S_2O_8^{2-}$ is the limiting reactant. At end of reaction and according to S.R : $\frac{n(S_2O_8^{2-})_{initial}}{1} = \frac{n(I_2)_\infty}{1}$ then $n(I_2)_\infty = 0.01$ mol $= 10$ mmol $> n(I_2)_{t=30\ min} = 5.6$ mmol Therefore $t = 30$ min is not the end time of the reaction.
2.2	
2.3	False : The concentration of reactants (I^- and $S_2O_8^{2-}$) is a kinetic factor, it is maximum initially at t= 0, then rate of formation of (I_2) is maximum initially. At infinity, limiting reactant ends and the reaction stops, then the rate of formation of I_2 becomes null.
2.4	According to S.R : $\frac{r(I^-)_{t=10\ min}}{2} = \frac{r(I_2)_{t=10\ min}}{1}$ $r(I^-)_{t=10min} = 2\, r(I_2)_{t=10\ min} = 2 \times 2.3 \times 10^{-4} = 4.6 \times 10^{-4}$ mol.min^{-1}

2.5	Half-life time of a reaction is the time needed for half of the maximum quantity of I_2 to be formed $n(I_2)_{t\frac{1}{2}} = \frac{n(I_2)_{t\infty}}{2} = \frac{10}{2} = 5$ mmol. Graphically it corresponds to $t_{\frac{1}{2}} = 24$ min
2.6.1	The concentration of reactants is a kinetic factor. As concentration of reactants decreases the rate of formation of I_2 decreases. $r(I_2)_{10\ in\ exp\ 3} < r(I_2)_{10\ in\ exp\ 1} \Rightarrow [reactants]_{in\ exp\ 3} < [reactants]_{in\ exp\ 1}$ $C = \frac{n(solute)_{initial}}{V(solution)_{total}}$ (C and V are inversely proportional) The initial number of moles of the two reactants (I^- and $S_2O_8^{2-}$) in both experiments is the same. Then $V_{total\ in\ exp\ 3} > V_{total\ in\ exp\ 3} \Rightarrow V' > V$ Therefore, the correct answer is (b)
2.6.2	**<u>Comparing $r_o(I_2)$ of experiments 1 and 2:</u>** Temperature is a kinetic factor. As temperature increases, the rate of formation of I_2 increases. Both experiments 1 and 2 have same conditions except for temperature: Temperature in exp 1 (25°C) < Temperature in exp 2 (40°C) $\Rightarrow r_{o\ of\ exp\ 1} < r_{o\ of\ exp\ 2}$ Then the initial rate of formation of (I_2) in exp 2 is more than that of exp 1. **<u>Comparing $r_o(I_2)$ of experiments 1 and 4:</u>** Both experiments 1 and 4 have same conditions of temperature and initial concentration of reactants. Except that in experiment 4 there is presence of some amount of product (I_2) initially. The initial amount of product in the reaction medium does not affect the rate of a chemical reaction (it is not a kinetic factor) and thus the rate is the same in both experiments. Then the initial rate of formation of (I_2) in exp 4 is equal to that of exp 1.

Question 5: Kinetics of the decomposition reaction of hydrogen peroxide

Commercial hydrogen peroxide is an aqueous solution of hydrogen peroxide. It is used for the maintenance of contact lenses, as a disinfectant, ...

Hydrogen peroxide decomposes at $25°$ C, according to a very slow and total reaction whose equation is: $\quad\quad 2\ H_2O_2\ _{(aq)} \rightarrow 2\ H_2O\ _{(l)} + O_2\ _{(g)}$
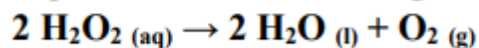
It is assumed that the oxygen gas is insoluble in water under these conditions.

1. Catalysis of this reaction

This decomposition reaction can be accelerated by using, as a catalyst, a platinum wire or iron(III) chloride, $(Fe^{3+} + 3\ Cl^-)$.

    1.1. Identify the type of catalysis (homogeneous or heterogeneous) carried out in the presence of a platinum wire.

    1.2. Consider a beaker containing an aqueous solution of hydrogen peroxide in the presence of iron (III) chloride.

    Indicate the chemical species present in the solution obtained at the end of the decomposition reaction.

2. Influence of the amount of catalyst .

The following objective is given to 4 different groups of students (A, B, C, and D):
Carry out the reaction with various amounts of catalyst to determine the proper amount for the slow decomposition reaction of hydrogen peroxide which will end in one hour.
For each of the 4 groups, the hydrogen peroxide solution of concentration C_1, called stock solution is the same; the catalyst solution is also the same.

The method is as follows:
- withdraw 10 ml of hydrogen peroxide, and introduce them into a beaker which will be called the reactor
- add a volume V_1 of water
- at time $t = 0$, add a volume V_2 of catalyst and start the stopwatch simultaneously

	A	B	C	D
$V(H_2O_2)$ mL	10	10	10	10
V_1 (mL)	89	88	87	85
V_2 (mL)	1	2	3	5

Document-1-

2.1. Define a catalyst.

2.2. From the first moments, students notice that the evolution of gas is higher in the reactor of group D than in the reactor of group A.
Indicate the experimental origin of this difference.

2.3. What can be deduced from this observation about the influence of the volume of catalyst on the rate of the reaction?

3. Kinetic study

At different times t , using 10.0 mL volumetric pipet, students take a sample from the reaction mixture, and introduce it into an Erlenmeyer flask containing 50 mL of ice-water.
The remaining amount of hydrogen peroxide is determined by titrating the samples with acidified potassium permanganate solution (S) $KMnO_4$ ($K^+_{(aq)}$+$MnO_4^-{}_{(aq)}$).
The equation of the titration reaction is:

$2\ MnO_4^-\ + 5\ H_2O_2\ +\ 6\ H^+\ \rightarrow\ 2\ Mn^{2+}\ +\ 5\ O_2\ +\ 8\ H_2O$

At equivalence, the added volume of solution (S) is denoted V_3.
The values of V_3 , expressed in ml, are grouped in **Document-2-.**
Document-3 - shows the curves of variation of concentration of H_2O_2 with time for groups A, B and D

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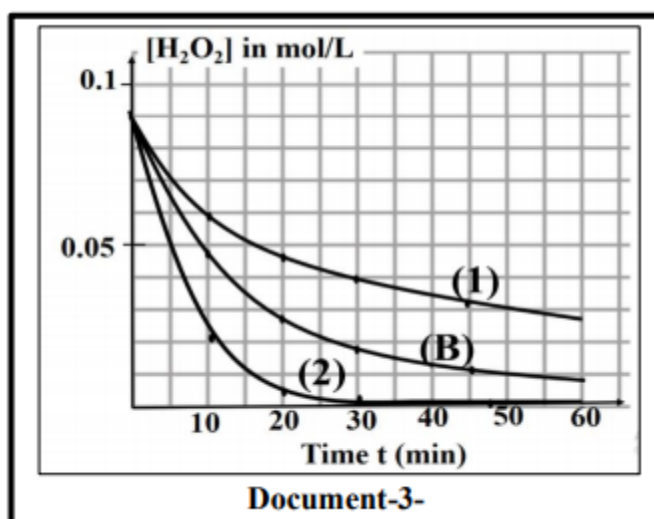
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Document-3 - shows the curves of variation of concentration of H_2O_2 with time for groups A, B and D

Group / t (min)	A	B	C	D
0	18.0	18.0	18.0	18.0
10	12.1	9.0	6.5	4.1
20	9.4	5.2	3.0	0.5
30	7.8	3.1	1.4	0.1
45	5.9	1.6	0.5	0.05
60	5.0	1.0	0.3	0

Document-2-

Document-3-

3.1. Choose, from the list below, the material needed to carry out the titration:
pH meter and its electrode, stand, magnetic stirrer and bar, graduated cylinder of 100 mL, 100 mL volumetric flask and 50 mL buret.

3.2. Before starting the titration, ice - water is poured into each beaker.

3.2.1. Indicate the two kinetic factors involved in this operation.

3.2.2. Specify the effect of each of these two factors on the kinetic of the decomposition reaction of hydrogen peroxide.

3.3. Referring to **Document-3-**:

3.3.1. Assign the curves (1) and (2) to the groups (A) and (D). Justify your answer.

3.3.2. Verify that the decomposition reaction of H_2O_2 is complete.

3.3.3. Indicate the initial concentration of H_2O_2 in the reaction mixture.

3.3.4. By studying the composition of mixtures A, B, C and D (**Document-1-**), show that hydrogen peroxide solution of concentration C_1 was diluted 10 times. Deduce the value of C_1.

4. Study of the mixture (C)

The remaining concentration of H_2O_2 of groupe (C) is calculated. The results are grouped in the table in document-4-:
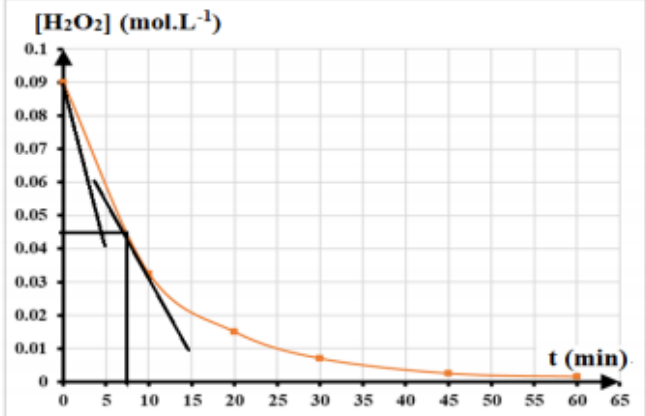
t (min)	0	10	20	30	45	60
$[H_2O_2]$ $(10^{-2}$ mol $L^{-1})$	-	3.25	1.5	0.7	0.25	0.15

Document -4-

4.1. Draw the curve representing the variation of the concentration of H_2O_2 as function of time: $[H_2O_2] = f(t)$, in the interval of time [0 - 60 min].
Take the following scales: 1cm for 5 min on the abscissa,
1 cm for 1.0×10^{-2} mol.L^{-1} on the ordinate.

4.2. Deduce, graphically, the evolution of the rate of disappearance of H_2O_2 with time.

**4.3.** Determine the half-time of the reaction.

Q.	Expected answer
1.1	The catalysis performed by a platinum wire is a heterogeneous catalysis.
1.2	The species present at the end of the decomposition are: H_2O, Fe^{3+} and Cl^-
2.1	a catalyst is a substance that increases the rate of a chemical reaction; it participates in the reaction but it does not appear in the equation of this reaction.
2.2	For groups A, B, C and D, we have: - same temperature T - same amount of H_2O_2 dissolved in the same final volume, so the initial concentration of H_2O_2 is the same. -the only difference is the quantity (concentration) of catalyst used per each group. The amount (concentration) of catalyst in Experiment D is five times greater than that in Experiment A. - The evolution of gas is higher in the reactor of group D than in the reactor of group A. This is due to the fact that the amount (concentration) of catalyst is larger in D than in A.
2.3	-The reaction system is moving faster because the amount (concentration) of the catalyst used is greater. -The more the amount (concentration) of the catalyst used, the greater the system evolves quickly and H_2O_2 decomposes rapidly.

3.1	The materiel needed is graduated buret 50 mL , stand , magnetic stirrer and bar.
3.2.1	The two kinetic factors involved in this operation are: temperature of reaction medium and concentration of reactant H_2O_2.
3.2.2	In this operation, the temperature decreases sharply and $[H_2O_2]$ decreases. The reaction rate decreases so that the reaction will be practically blocked
3.3.1	At an instant t : the higher the quantity (concentration) of the catalyst ,the higher the rate of the reaction, then the quantity of H_2O_2 reacted increases ; therefore the concentration of H_2O_2 remaining decreases. • V_2 of catalyst in (D) = 5 mL > V_2 of catalyst in (A) = 1 mL $\Rightarrow$ rate of disappearance of H_2O_2 in (D) > rate of disappearance of H_2O_2 in (A). • Referring to document-2- : $[H_2O_2]$ t remaining of curve 2 < $[H_2O_2]$ t remaining of curve 1 $\Rightarrow$ rate of disappearance of H_2O_2 in (2) > rate of disappearance of H_2O_2 in (1). Therefore , the curve (1) corresponds to the experiment of group (A) and the curve (2) corresponds to the experiment of group (D).
3.3.2	From the curve (2), the concentration of H_2O_2 becomes zero at t = 30 min, so H_2O_2 reacts completely and consequently the reaction is complete.
3.3.3	The initial concentration of H_2O_2 in the reaction mixture is 0.09 mol L^{-1}

3.3.4	According to the table given in **Document -1-**, each reactional mixture has a volume of 100 mL. Each reactional mixture contains 10 mL of hydrogen peroxide. Initially it was therefore diluted by a factor of 10 the solution of hydrogen peroxide ($\frac{V_{total}}{V_{H_2O_2}} = \frac{100}{10} = 10$). The dilution factor is 10, then $C_1 = 10 \times 0.09 = 0.9$ mol.L^{-1}.
4.1	
4.2	The rate of disappearance H_2O_2 is equal to the negative slope of the tangent to the curve at point of abscissa t. the negative slope of the tangent to the curve at point of abscissa t decreases. Then the rate of disappearance of H_2O_2 decreases.
4.3	$t_{1/2}$ is the time required for half of the amount of limiting reactant H_2O_2 to be consumed. $[H_2O_2]_{t_{1/2}} = \frac{[H_2O_2]_0}{2} = \frac{0.09}{2} = 0.045$ mol.L^{-1}. From graph , this value corresponds to t = 7.5 minutes . Then $t_{1/2}$ = 7.5 minutes.

Question 6: Iodine Clock reaction

The balanced equation of the reduction of hydrogen peroxide (H_2O_2) by the iodide ions I^- is:

$$H_2O_2 + 2I^- + 2H^+ \rightarrow I_2 + 2H_2O \quad \text{(reaction 1)}$$
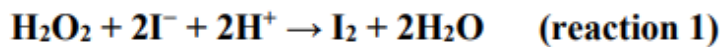
This reaction is slow.

To study the kinetics of reaction 1, we will measure the time required to produce a certain amount of iodine (I_2).

To determine this duration, the very fast oxidation-reduction reaction is used between the iodine (I_2) produced from reaction 1 and the thiosulphate ions ($S_2O_3^{2-}$) according to reaction (2).

$$I_2 + 2\,S_2O_3^{2-} \rightarrow 2\,I^- + S_4O_6^{2-} \quad \text{(reaction2)}$$
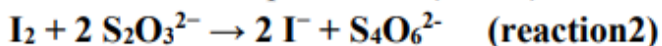
Reactions (1) and (2) take place successively in the reaction medium.

Document-1- summarizes the steps of the experiment.

- At a time $t = 0$ s, a solution is prepared by mixing 10 ml of hydrogen peroxide solution of concentration $C = 0.040$ mol.L^{-1} with an excess amount of acidified potassium iodide solution KI ($K^+_{(aq)} + I^-_{(aq)}$), 1 ml of sodium thiosulphate solution ($2Na^+_{(aq)} + S_2O_3^{2-}{}_{(aq)}$) of concentration $C' = 0.10$ mol. L^{-1} and a few drops of starch paste. The total volume of the reaction mixture is kept constant throughout the experiment ($V_{total} = 125$ mL).
- Since the I_2 formed by the reaction (1) is consumed instantaneously by the reaction (2), the solution remains colorless until the time $t_1 = 48$ s, at which the solution is colored blue.
- At the time t_1, another 1 mL of sodium thiosulfate solution is added, which makes the blue color disappear. The blue color reappears at time $t_2 = 103$ s.
- A third milliliter of sodium thiosulfate solution is added, and the blue color disappears to reappear again at time t_3 where another milliliter of thiosulfate solution is added, and so on.

Document-1

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1. Preliminary Study.

1.1. Show that the number of moles of iodine reduced by the addition of 1 ml of sodium thiosulfate solution is $n(I_2) = 0.05$ mmol.

1.2. Specify whether the acid is considered as catalyst in reaction (1).

1.3. Justify the disappearance of dark blue color every time 1 mL of thiosulfate solution is added.

1.4. Show, without calculation, that the number of moles of I^- ions remains unchanged during the progress of the reaction. **Deduce** the limiting reactant in reaction(1).

2. Kinetic study.

The follow up of the experiment allows to draw the table of **document-2-**:

Time (sec)	$t_0= 0$	$t_1= 48$	$t_2= 103$	$t_3= 170$	$t_4= 254$	$t_5= 366$	$t_6= 536$	$t_7= 900$
[I$_2$] (mmol.L^{-1})	0	0.4	0.8	1.2	1.6	2	2.4	2.8
[H$_2$O$_2$] (mmol.L^{-1})	x	2.8	2.4	2.0	y	1.2	0.8	0.4

Document-2

2.1. **Verify** the following relation at each instant t : $[H_2O_2]_t = [H_2O_2]_0 - [I_2]_t$

Where $[H_2O_2]_t$ represents the concentration of H_2O_2 in the reaction mixture, and $[I_2]_t$ represents the concentration of I_2 produced from reaction (1) at any time, both expressed in mmol.L^{-1}.

2.2. **Find** the values of x and y in **document-2-**. (consider that the total volume of the reaction mixture is constant throughout the experiment)

2.3. **Plot** the curve $[H_2O_2] = f(t)$ on graph paper in the interval of time $[0 ; 900]$.

Take the following scale: x-axis: 1 cm for 50 s ; ordinate axis: 5 cm for 1 mmol.L^{-1} .

2.4. **Compare**, graphically, the rate of disappearance of H_2O_2 at t= 0 and t = 170 sec.
Indicate the kinetic factor responsible for this change.

2.5. **Determine** the half life time of the reaction ($t_{1/2}$).

2.6. **Another** experimental study is performed again, with the same conditions as in the previous one, but under temperature T', where T' > T.
Plot, on the same graph of part 2.3, the shape of the curve $[H_2O_2] = g(t)$ for the experiment taking place at temperature T', in the same interval of time $[0 ; 900]$.
Justify.

Q	Expected Answer
1.1	According to S.R (reaction 2): $\dfrac{n(I_2)_{reacted}}{1} = \dfrac{n(S_2O_3{}^{2-})_{reacted}}{2}$ $\Rightarrow n(I_2)_{reduced} = \dfrac{[S_2O_3{}^{2-}] \times V_{added}}{2} = \dfrac{0.1 \times 1 \times 10^{-3}}{2} = 0.05 \times 10^{-3}$ mol $= 0.05$ mmol
1.2	The acid is not considered as a catalyst since a catalyst must be regenerated at the end of reaction. In reaction 1 H^+ ions are converted into H_2O.
1.3	Throughout the experiment, iodine produced by reaction (1) is consumed by $S_2O_3{}^{2-}$ by the fast reaction (2) when 1 mL of sodium thiosulfate is added. Until the number of moles of $S_2O_3{}^{2-}$ added in the 1ml are totally consumed, at this instant, I_2 produced will directly complex with starch to give dark blue color
1.4	According to S.R (reaction 1): $\dfrac{n(I^-)_{reacted}}{1} = \dfrac{n(I_2)\ produced}{2}$ $\Rightarrow n(I^-)_{reacted\ in\ (1)} = 2\ n\ (I_2)_{produced\ in\ (1)}$ According to S.R (reaction 2): $\dfrac{n(I_2)\ reacted}{1} = \dfrac{n(I^-)\ produced}{2}$ $\Rightarrow 2\ n\ (I_2)_{reacted\ in\ (2)} = n(I^-)_{produced\ in\ (2)}$ But: $n\ (I_2)_{produced\ in\ (1)} = n\ (I_2)_{reacted\ in\ (2)}$ Thus: $n(I^-)_{reacted\ in\ (1)} = n(I^-)_{produced\ in\ (2)}$ Then the concentration of I^- ions remains the same. Therefore, H_2O_2 is the limiting reactant.
2.1	$n(H_2O_2)_{remaining} = n(H_2O_2)_0 - n(H_2O_2)_{reacted}$ According to S.R : $\dfrac{n(H_2O_2)\ reacted}{1} = \dfrac{n(I_2)\ produced}{1}$ $\Rightarrow n(H_2O_2)_{remaining} = n(H_2O_2)_0 - n(I_2)_{produced}$ At each instant t : $n(H_2O_2)_t = n(H_2O_2)_0 - n(I_2)_{(t)}$ Divide by constant volume of solution : $[H_2O_2]_t = [H_2O_2]_0 - [I_2]_{(t)}$
2.2	• $x = ?$ Upon mixing number of moles of species (H_2O_2) is conserved: $n(H_2O_2)_0 = C \times V = 0.04 \times 10 \times 10^{-3} = 0.4 \times 10^{-3}$ mol $= 0.4$ mmol. $[H_2O_2]_0 = \dfrac{n(H_2O_2)_0}{V_{total}} = \dfrac{0.4 \times 10^{-3}}{125 \times 10^{-3}} = 3.2 \times 10^{-3}$ mol.$L^{-1} = 3.2$ mmol.$L^{-1} \Rightarrow x = 3.2$ • $y = ?$ $\quad y$ is at t= 254 s ; $\quad$ from table : $[I_2]_{(t=254)} = 8$ mmol.L^{-1} Substitute in relation of part 2.2 then $y = 18-8 = 10$ mmol.$L^{-1} \Rightarrow y = 1.6$

2.3	
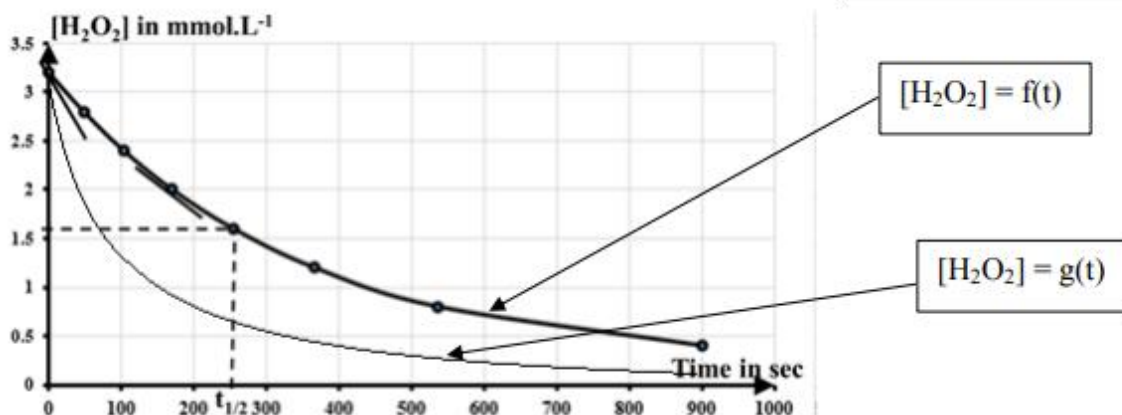
2.4	Draw a tangent on the curve at point of abscissa t= 0 and at point of abscissa t = 170 s. The negative slope of tangent to the curve at t=0 is greater than that at t = 170 min. The rate of disappearance of H_2O_2 equals negative slope of the tangent to the curve at point of abscissa t. Therefore $r(H_2O_2)_0 > r(H_2O_2)_{170}$ The kinetic factor responsible for this change is the concentration of reactants H_2O_2 and I^-.

2.5	Half life: it the time needed for half amount of the limiting reactant to be consumed. $[H_2O_2]_{t½} = \frac{[H_2O_2]_0}{2} = \frac{3.2}{2} = 1.6$ mmol.L^{-1} Graphically it corresponds to $t_{1/2} \approx 254$ sec

2.6	Temperature is a kinetic factor, as temperature increases, rate of disappearance of H_2O_2 increases. Then H_2O_2 disappears faster at T'. At each instant t: $[H_2O_2]_{t\ left\ at\ T'} < [H_2O_2]_{t\ left\ at\ T}$ The curve $[H_2O_2]_t = g(t)$ will be below $[H_2O_2]_t = f(t)$ (The two curves tend to the same limit value at the end of reaction(same initial amounts of reactants).