Smart College Shaping the future together	Chemistry	**Date: __ / __ / ___**
	Kinetics Extra Sheet	
Name: ____________________	Grade 12	

Exercise 1 Reaction Between Hydrochloric Acid and Zinc Metal

(2010 S_2 GS- Exercise 3)

Hydrochloric acid reacts with zinc according to the following equation:

$$Zn_{(s)} + 2\ H_3O^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2\ (g)} + 2\ H_2O_{(l)}$$

At time t = 0, a mass m of pure zinc granules is introduced into a beaker containing a volume V_1 = 50 mL of hydrochloric acid solution (S) of molar concentration C.

A release of gas starts.

To follow the evolution of this reaction, the volume of hydrogen gas released $V(H_2)$ is measured under conditions where the molar volume V_m is 25 $L.mol^{-1}$.

The results are given in the following table:

t (s)	50	100	200	300	400	500	700	900	1200	….	1500	2000
$V(H_2)$ mL	25	50	85	117	142	162	195	220	240	….	250	250

When the gas release ceases, a solid remains in the beaker.

1- <u>Preparation of the Solution (S)</u>

Solution (S) of volume V_S = 250 mL, is prepared by diluting 25 times a commercial solution of hydrochloric acid of concentration C_0.

Choose, by justifying, from the list given below, the most accurate glassware to carry out this preparation.

List of available material:

- 50, 100, 250 mL beakers
- 50, 100, 250 mL volumetric flasks
- 5, 10, 25 mL volumetric pipettes
- 5, 10, 25 mL graduated cylinders
- 50, 100, 250 mL Erlenmeyer flasks
- Funnel
- Watch glass and spatula
- Pipet filler

2- <u>Preliminary Study</u>

2.1- Extract, from the experimental study described before, the sentence which shows that H_3O^+ ion, is the limiting reactant of this reaction.

2.2- Show that the concentration C is equal to 0.4 $mol.L^{-1}$. Deduce the concentration C_0 of the commercial solution.

3- <u>Kinetic of this Reaction</u>

3.1- Show that, at any instant of time t, the concentration of H_3O^+ ions in mol.L^{-1}, $[H_3O^+]_t$, and the volume of H_2 gas in mL, $V(H_2)$, are related by the following relation:

$$[H_3O^+]_t = 0.4 - 1.6\times10^{-3}\times V(H_2).$$

3.2- The application of this relation allows to get the following results:

t (s)	0	50	100	200	300	400	500	700	900	1200
$[H_3O^+]_t$ (10^{-1} mol.L^{-1})		3.6	3.2	2.6	2.1	1.7	1.4	0.88	0.48	

Give the value of the concentration $[H_3O^+]$ at t = 0 and calculate its value at t = 1200 s.

3.3- Plot, on a graph paper, the curve representing the variation of $[H_3O^+]_t$ versus time, $[H_3O^+]_t = f(t)$, in the interval of time [0 – 1200 s]. Take the following scale: 1 cm for 100 s in abscissa and 1 cm for 4.0×10^{-2} mol.L^{-1} in ordinate.

3.4- The value of the rate of disappearance of H_3O^+ ions is 1.0×10^{-3} mol.L^{-1}.s^{-1} at t = 0 and is 2.4×10^{-4} mol.L^{-1}.s^{-1} at t = 700 s.
Specify the kinetic factor responsible for the variation of this rate.

3.5- The same experimental study is repeated again but at a higher temperature. Plot, by justifying, on the same graph of part 3.3, the shape of the curve $[H_3O^+]_t$ versus time.

Exercise 2 — Kinetics of H_2O_2 Decomposition

Available solutions:

Potassium permanganate solution ($K^+ + MnO_4^-$) of concentration C = 0.02 mol.L^{-1}.
Iron III chloride solution ($Fe^{3+} + 3Cl^-$).
Commercial H_2O_2 solution (S_0) of concentration C_0

1. Determination of the concentration of the commercial solution (S_0).

1.1. 100 ml solution (S) is prepared starting from the available commercial solution (S_0) of hydrogen peroxide, H_2O_2, by diluting a sample 10 times.

1.1.1. Suggest the glass ware to be used to prepare the diluted solution.
1.1.2. Describe the procedure.

1.2. 10 ml of the prepared solution (S) is titrated with the available potassium permanganate solution in acidic medium. Equivalence is reached when 17.8 ml of the permanganate solution is added.

Equation of titration: $\mathbf{5\,H_2O_2 + 2\,MnO_4^- + 6\,H^+ \rightarrow 2\,Mn^{2+} + O_2 + 8\,H_2O}$

1.2.1. Calculate the concentration of solution (S).
1.2.2. Deduce the concentration of the commercial solution S_0.

2. Kinetic study of the decomposition of H_2O_2.

Hydrogen peroxide, H_2O_2, decomposes slowly according to the reaction:

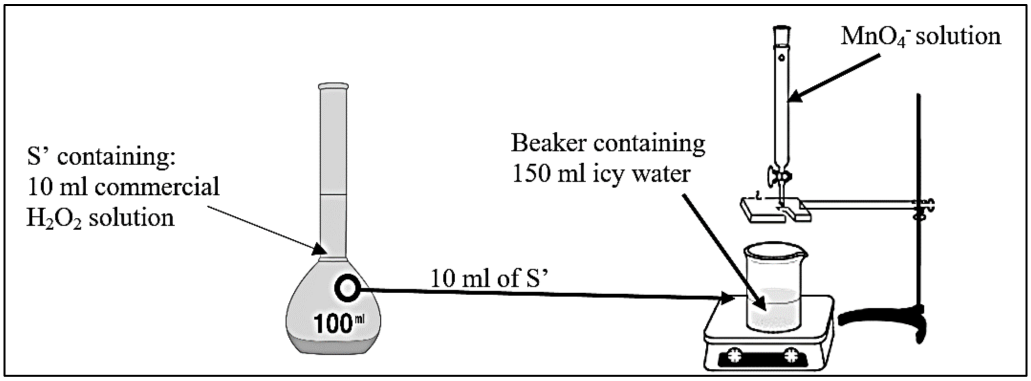
$$\mathbf{2\,H_2O_2 \rightarrow 2\,H_2O + O_2}$$

The decomposition is catalyzed by the presence of Fe^{3+} in the solution.

To study the kinetic of decomposition of H_2O_2, a 100 ml solution (S') is prepared by mixing:

- 10 ml of the commercial H_2O_2 solution (S_0)
- 5 ml of Iron III chloride solution ($Fe^{3+} + 3Cl^-$)
- The volume is completed by distilled water to 100 ml

To follow the change in concentration of H_2O_2 in solution S', a sample of the solution is taken at different instants of time, and is placed in a beaker containing 150 ml icy water and titrated with the potassium permanganate solution.



The volume V_E of potassium permanganate solution needed to reach equivalence each time is represented in the following table.

Time (min)	5	10	20	30	40
V_E (ml)	15.1	12.6	9.2	6.3	4.5
$[H_2O_2]$ ($mol.L^{-1}$)					

2.1. What is the aim of adding the sample into 150 ml icy water.
2.2. Is it necessary that the volume of icy water to be precise?
2.3. Explain how the equivalence point is detected during titration.
2.4. Prove the following relation: $[H_2O_2]_t = 5x\ 10^{-3}\ V_E$ (ml)
2.5. Complete the above table.
2.6. Plot $[H_2O_2]_t = f(t)$
2.7. The rate of disappearance of H_2O_2 at t=30 min is $r(H_2O_2)_{30} = 1.1x10^{-3}$ $mol.L^{-1}.min^{-1}$. choose among the following values the one that represents the rate of disappearance of H_2O_2 at t=0, $r(H_2O_2)_0$. Justify your answer.

- $r(H_2O_2)_0 = 1.1x10^{-3}$ $mol.L^{-1}.min^{-1}$
- $r(H_2O_2)_0 = 3.2x10^{-3}$ $mol.L^{-1}.min^{-1}$
- $r(H_2O_2)_0 = 0.1x10^{-3}$ $mol.L^{-1}.min^{-1}$

2.8. Specify the species present in solution S' when the reaction is over.

.

Kinetic Questions

Graphically

Example:
- Deduce graphically how the rate changes over time.
- Compare graphically the rate at t= 50 and at t =300.

Answer:
- Definition of rate: r = slope
- Draw tangents at different times
- Compare slopes: $S_{50} > S_{300}$
- Deduce: As time passes rate decreases.

Numerical: for the same substance but at different instants.

Example:
Given $r(H_3O^+)_{300}$ = 4.5x 10^{-4} $mol.L^{-1}.s^{-1}$. choose the value that represents $r(H_3O^+)_{800}$:
- $r(H_3O^+)_{800}$ = 4.5x 10^{-4} $mol.L^{-1}.s^{-1}$
- $r(H_3O^+)_{800}$ = 2.5x 10^{-4} $mol.L^{-1}.s^{-1}$
- $r(H_3O^+)_{800}$ = 7.5x 10^{-4} $mol.L^{-1}.s^{-1}$

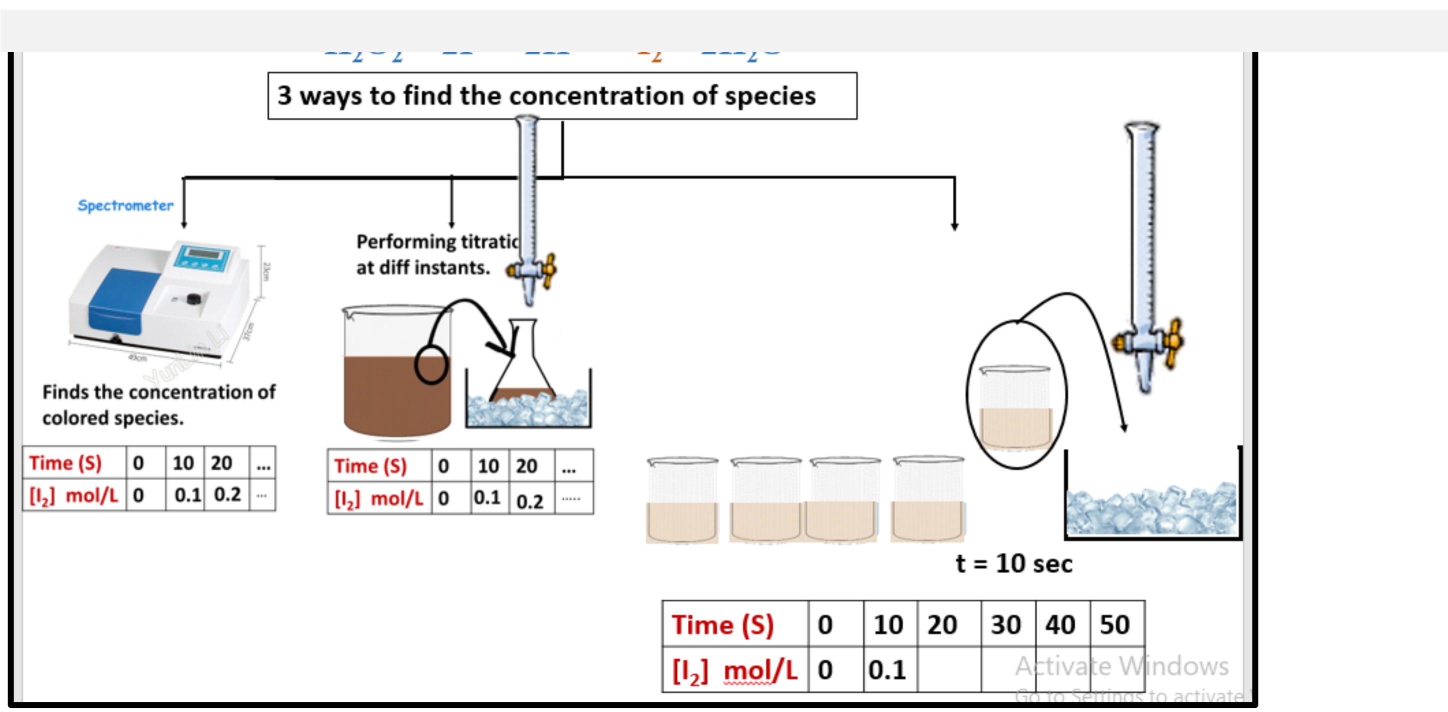
Answer:
- As time passes rate decreases due to the consumption of reactant(s).
- Deduce the correct answer.

Numerical: for two different substances but at the same instant.

Example:
For the reaction:
$2H_2O_2 \rightarrow 2H_2O + O_2$
Given: $r(O_2)_{t=300}$ = 3.2 x 10^{-2} $mol.s^{-1}$.
Deduce $r(H_2O_2)_{t=300}$/

Answer:
- Use stoichiometric Ratios.

<u>Remark: Determination of concentration of a substance during kinetic study.</u>



Time (S)	0	10	20	...
$[I_2]$ mol/L	0	0.1	0.2	...

Time (S)	0	10	20	...
$[I_2]$ mol/L	0	0.1	0.2	.....

Time (S)	0	10	20	30	40	50
$[I_2]$ mol/L	0	0.1				

Exercise 3 Reaction of Hydrochloric Acid with Zinc

Hydrochloric acid reacts with zinc according to the following reaction: $\mathbf{2H^+ + Zn \rightarrow H_2 + Zn^{2+}}$

At instant t = 0, we introduce a mass m = 1.3 g of Zn powder in a beaker containing 50 ml of 0.5 $mol.L^{-1}$ hydrochloric acid solution. We measure the volume of H_2 gas formed at different intervals of time, where the following data is obtained:

Time (s)	0	100	200	300	400	500	600	700	800	900
$V(H_2)$ ml	0	73	123	157	179	195	207	218	225	235
$[Zn^{2+}]$ $mol.L^{-1}$										

Given: molar mass of Zn in $g.mol^{-1}$ is 65.4
Molar volume of a gas is Vm = 22.4 $L.mol^{-1}$

1. **Preliminary Study:**

1.1. Prove the following relation: $[Zn^{2+}]_t = \frac{V(H_2)_t}{1120}$ where $V(H_2)$ is in ml.
1.2. Complete the above table.
1.3. Show that t =900s does not represent the end time of the reaction.

2. **Kinetic study of the reaction.**

2.1. Plot the curve $[Zn^{2+}]_t = f(t)$ using the following scale:
x-axis: 1cm = 100 s and Y –axis: 1cm = 0.02 $mol.L^{-1}$.
2.2. Determine the average rate of formation of Zn^{2+}betrween instants t = 0 and t = 500s.
2.3. Given that the slope of the tangent on the curve at point of abscissa t =600 s is $S_{600} = 2.87 * 10^{-4}$.
2.3.1. Determine the rate of formation of Zn^{2+} at t= 600s.
2.3.2. Deduce the following rates: $r(H_2)_{600}$, $r(H_3O^+)_{600}$, and $r(\text{reaction})_{600}$.
2.4. Determine the half-life of the reaction.
2.5. Explain graphically how the rate of reaction varies over time.

Exercise 4 Kinetic of Oxidation of Oxalic Acid

We prepare the following aqueous acidified solution containing initially 0.01 $mol.L^{-1}$ $Cr_2O_7^{2-}$ ions and 0.2 $mol.L^{-1}$ $H_2C_2O_4$ molecules.

Given : E^0 ($Cr_2O_7^{2-}/Cr^{3+}$) >E^0 ($CO_2/H_2C_2O_4$)

1. Show that the balanced equation of the reaction taking place is :
$$\mathbf{Cr_2O_7^{2-} + 3\ H_2C_2O_4 + 8\ H^+ \rightarrow 2\ Cr^{3+} + 6CO_2 + 7\ H_2O}$$
2. Which of the above reactants is the limiting reactant?
3. What is the limit of $[Cr^{3+}]$ when t tends to infinity?

The values of concentration of Cr^{3+} at different instants of time are given in the following table:

Time (min)	**5**	**10**	**15**	**20**	**25**	**35**	**45**
$[Cr^{3+}]$ in $mmol.L^{-1}$	3.25	7.02	9.7	11.80	13.6	16.0	17.0
$[Cr_2O_7^{2-}]$ in $mmol.L^{-1}$							

4. Plot the curve $[Cr^{3+}]$ = f(t) in the interval [0 -45] . scale: 1 cm = 5 min; 1cm = 2$mmol.L^{-1}$
5. Compare, graphically, the rate at t= 5 and at t=20 min. Conclude.
6. Determine the half-life time of the reaction.

7. Prove the following relation:
   $[Cr_2O_7^{2-}]_t = [Cr_2O_7^{2-}]_0 - [Cr^{3+}]_t/2$
8. Complete the table above.
9. Plot on the same graph, the shape of the curve $[Cr_2O_7^{2-}] = g(t)$
10. Compare the shapes of the 2 curves.

Exercise 5 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:

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

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 $C = 4.0\times10^{-2}$ mol.L $^{-1}$, at temperature T= 25 ^{0}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 $V(CO_2)_\infty$.

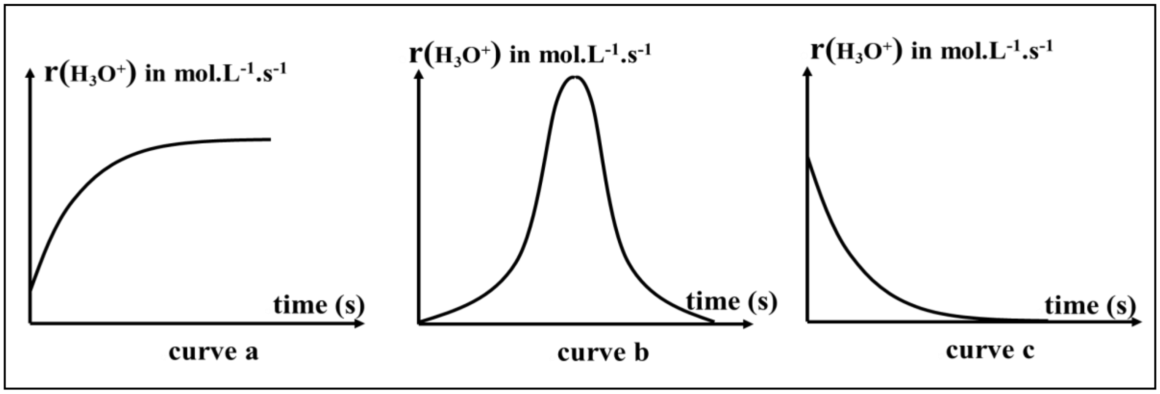
2. Kinetic study of the reaction

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 : $r(H_3O^+)_{20} = 2.75\times10^{-4}$ 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 a 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.

Exercise 6 Kinetic Study of the Reaction of Formic Acid with Bromine

Formic (methanoic) acid (HCOOH) is a colorless corrosive liquid secreted by ants and other insects. It is commonly used in paper and textile industries and in the manufacture of insecticides ….

The aim of this exercise is to know some of the uses of formic acid in organic synthesis and to study the kinetic of its reaction with bromine liquid.

Given: Molar volume of gas: V_m = 24 L.mol^{-1}.

I- Preliminary study

In aqueous solution, formic acid reacts slowly with molecular Bromine according to the following equation:

$$\mathbf{HCOOH_{(aq)} + Br_{2\,(aq)} \rightarrow 2Br^-_{(aq)} + 2H^+_{(aq)} + CO_{2\,(g)}}$$

Aqueous bromine solution (Br_2) has a red brown color, while hydrobromic acid ($H^+ + Br^-$) solution is colorless.

At t = 0, a volume V_1 = 50 mL of aqueous solution of bromine of molar concentration C_1 = 0.024 mol.L^{-1}is mixed with a volume V_2 = 50 mL of formic acid solution of molar concentration C_2 = 0.030 mol.L^{-1}.

1.1. Show that bromine is the limiting reagent.

1.2. Show the following relation: $\mathbf{[Br_2]_t = 0.012 - 4.16\times10^{-4} \times V(CO_2)_t}$
Where $[Br_2]_t$ is the molar concentration of Bromine remained at instant t and $V(CO_2)_t$ is the volume of CO_2 formed at the same instant t in mL.

II- Kinetic Study

The volume of CO_2 gas released, at different instants, is measured using an appropriate method and the values obtained are given in the table of Document – 1:

t (sec)	0	50	100	150	200	250	300	350	400
$V(CO_2)$ (mL)	0	4.56	8.50	11.76	14.50	16.80	18.72	20.40	21.70
$[Br_2]$ (10^{-3} mol.L^{-1})	x	10.1	8.46	7.11	y	5.01	4.21	3.51	z

Document – 1

2.1. Give the value of x, and then calculate y and z.

2.2. Plot, on a graph paper, the curve showing the variation of the concentration of Br_2 as function of time $[Br_2]$ = f(t).
Use the following scale: Abscissa: 1cm for 50 s and ordinate 1cm for 1.0×10^{-3} mol.L^{-1}

2.3. Explain graphically how does the instantaneous rate of disappearance of bromine change as a function of time.

2.4. Determine graphically the half-life of the reaction.

2.5. At t = 550 s, the volume of carbon dioxide released becomes 28.8 mL; Show that the solution becomes colorless.

3. The previous experiment is carried out again but with only one modification: a volume V_2= 50 mL of a bromine solution is used of molar concentration $C_2 > C_1$ is used. For each proposition answer by true or false. Justify your answer.

3.1. The volume of CO_2 at t = 100 s remains equal to 8.5 ml.

3.2. The volume of CO_2 at the end of the reaction is equal to that found in the question (2.5).

3.3. Draw on the same graph paper the shape of the curve showing the variation of the concentration of Br_2, $[Br_2]$ = g(t) in the new experiment.

Exercise 7 Study of the Decomposition of Hydrogen Peroxide Solution

Commercial hydrogen peroxide, H_2O_2 solution is an aqueous solution that has many uses.

At 25ºC, hydrogen peroxide decomposes according to a slow reaction represented by the following equation:

$$2H_2O_{2\ (aq)} \rightarrow 2\ H_2O_{(L)} + O_{2\ (g)} \text{..... } \textbf{reaction 1}$$

Given: MnO_4^- is the only colored species in this study, it has a purple color.

1. **Preparation of Hydrogen Peroxide Solution (S):**
   A volume V_S = 500 mL of hydrogen peroxide solution (S) of concentration $C_S = 5 \times 10^{-2}$ mol.L^{-1} is prepared from a commercial solution S_o of concentration C_o = 1mol.L^{-1}.

   1.1. Choose, among the three sets of document-1, the most precise one to perform the above preparation. Justify.

Set (A)	Set (B)	Set (C)
500 mL volumetric flask 25 mL volumetric pipet 50 mL beaker	500 mL volumetric flask 25 mL graduated pipet 50 mL beaker	500 mL volumetric flask 25 mL graduated cylinder 50 mL beaker

Document-1

   1.2. Describe the preparation procedure.

2. **Kinetic of the Decomposition of Hydrogen Peroxide**

In order to study the kinetics of the slow decomposition reaction of H_2O_2 , a beaker containing 200 mL of solution (S) is prepared and few drops of a solution containing Fe^{3+} ions are added without affecting the total volume.

At different instants, a volume V=20 mL is taken from the beaker and is poured into icy water, then the remaining H_2O_2 , at different instants, is titrated by potassium permanganate solution ($K^+ + MnO_4^-$) of concentration $C = 2 \times 10^{-2} mol.L^{-1}$. The equation of titration reaction is

$$2\,MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2\,Mn^{2+} + 5\,O_2 + 8\,H_2O \text{.... } \textbf{Reaction 2}$$

The volume of the permanganate solution, added to reach the equivalence point, V_E, is determined. The number of moles of O_2, produced at each instant from reaction-, is deduced. The results are grouped in curve -A of **document-2**.

2.1. What is the aim of placing the sample in icy water before titration.

2.2. Indicate the kinetic factor(s) involved in this case.

2.3. Explain how to detect the equivalence point.

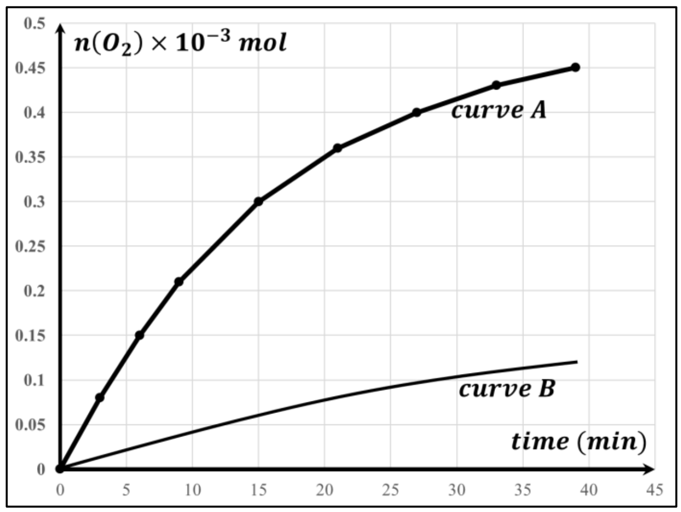
2.4. Determine the maximum number of moles of O_2 that is produced from reaction-1 at ∞.

2.5. Prove the following relation for the reaction taking place in the beaker containing 200 mL solution (S):

$$n(O_2)_t = 5 \times 10^{-3} - \frac{V_E \times 10^{-3}}{4}$$

Where is the number of moles of O_2 gas produced at a given instant during reaction-1, and V_E is the volume of MnO_4^- added to reach equivalence at the same instant (t).

2.6. Determine the rate of the formation of O_2 between t = 6 min, and t=21 min. in experiment-1.



Document-2

2.7. Explain graphically, how the rate of formation of O_2 changes over time in experiment-1. Specify the kinetic factor involved in this case.

2.8. The same experiment performed above is repeated with only one change, the reaction is allowed to take place without adding few drops of Fe^{3+} solution. The corresponding curve of this experiment (experiment-2) is curve (B) of document-2.

Deduce the role of Fe^{3+} ions.

Exercise 8 Reaction of Hydrogen Peroxide and Iodide Ions

(2010 S_2 LS- Exercise 1)

Hydrogen peroxide (H_2O_2) reacts with iodide ions in acidic medium according to the equation:

$$\boldsymbol{H_2O_2 + 2H_3O^+ + 2I^- \rightarrow I_2 + 4\,H_2O}$$

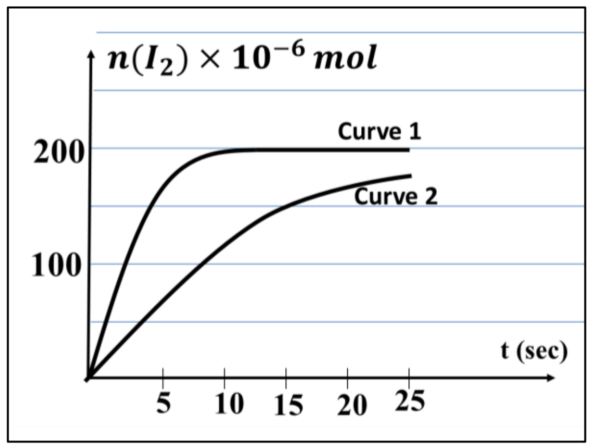
In order to study the kinetic of the above complete and slow reaction, three reacting mixtures A,B, and C are prepared at the same temperature (T), where the composition of each is given in the table of **document-1**:

	Mixture A	Mixture B	Mixture C
Sulfuric acid solution (1mol.L^{-1})	V_1 = 10 ml	V_1 = 10 ml	V_1 = 10 ml
KI solution (0.1 mol.L^{-1})	V_2 = 18 mL	V_2 = 10 mL	V_2 = 10 mL
H_2O_2 solution (0.1 mol/L)	V_3 = 2 mL	V_3 = 2 mL	V_3 = 1 mL
Distilled water	-	V_4 = 8 ml	V_4 = 9 ml

Document -1

In the three mixtures, sulfuric acid is in excess, and H_2O_2 is introduced at the same time t =0 .

The curves 1 and 2 of **document- 2** represent respectively, the variation of the number of moles of iodine I_2 in the mixtures (A) and (B), within the interval [0-25 minutes]



Document-2

1. **Kinetic Factors**
   1.1. Explain whether H_3O^+ is considered as catalyst in this reaction.
   1.2. Justify based on the graph of **document-2,** whether the reaction in each of the mixtures A and B has finished at the instant t = 25 min.
   1.3. Specify the kinetic factor responsible for the difference in shape between curves 1 and 2.
   1.4. Starting with the reacting mixtures A and B, propose a way that can lessen the difference between the two curves 1 and 2.
   1.5. The rate of formation of I_2 in the mixture B is determined at t=5 min and t = 15 min. The obtained values are:
   $r = 2.77 \times 10^{-6} mol.min^{-1}$ and
   $r' = 12.30 \times 10^{-6} mol.min^{-1}$.
   Relate, by justifying, each rate to its corresponding time.

2. **Study of mixture C**
   2.1. Determine the number of moles of iodine formed at the end of the reaction in mixture C.
   2.2. Draw on the graph of document-2 the shape of the curve 3, $n(I_2)$= f(t) corresponding to mixture C. Justify your answer.