IN DEPTH

17. Study of a commercial hydrogen peroxide solution

Oxygenated water is used as an antiseptic for wounds ; hydrogen peroxide (H_2O_2) is the essential component of a solution of oxygenated water. 10 mL of a commercial solution S_1 of hydrogen peroxide is diluted with water in a 200 mL volumetric flask to prepare a solution S_2.

10 mL of this solution S_2 are poured in an Erlenmeyer flask containing an excess of potassium iodide solution and 5 mL of sulfuric acid, a slow reaction will take place with the following equation :

$$H_2O_2 + 2H^+ + 2I^- \rightarrow I_2 + 2H_2O \quad (E_1)$$

At the end of this reaction, the contents of the Erlenmeyer flask are titrated by a solution of sodium thiosulfate of concentration 0.12 mol.L^{-1} in the presence of the starch according to the following equation :

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^- \quad (E_2)$$

1. About the titration

1.1. Indicate the glassware used to withdraw 10 mL of the solution S_1.

1.2. Discoloration of the iodine occurs at an average volume of 13.85 mL of the poured sodium thiosulfate solution. Determine the molar concentration of the S_2 solution.

1.3. Show that the molar concentration of the solution S_1 is 1.66 mol.L^{-1}.

1.4. Knowing that the title "by volume" of hydrogen peroxide is the volume expressed in liters of oxygen which would be released by a solution of hydrogen peroxide according to the equation :

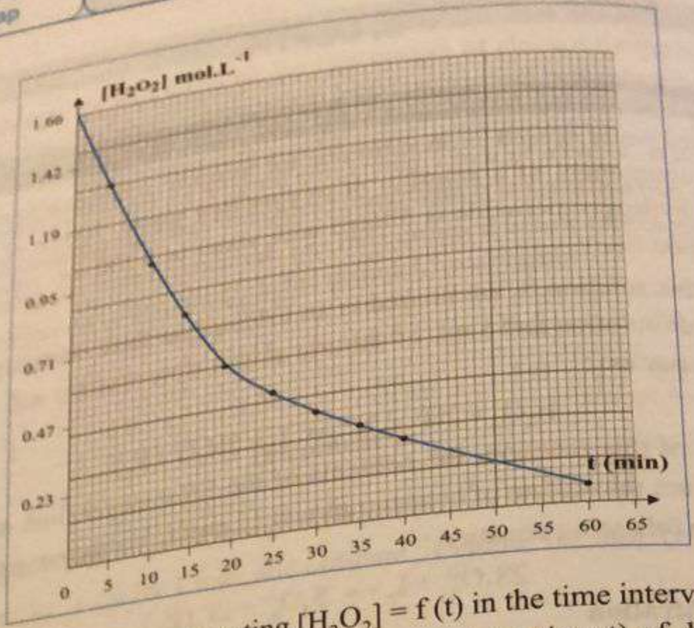
$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2}O_2 \quad (E_3)$$

Determine the title" by volume" of the commercial solution.

$V_m = 22.4$ L.mol^{-1} is given under the conditions of the problem.

2. Kinetic study of the decomposition reaction of the hydrogen peroxide in an aqueous solution of hydrogen peroxide

It is proposed to follow the disappearance of hydrogen peroxide during its decomposition according to the equation of the preceding reaction (E_3). This experiment is carried out at ambient temperature. The graph representing the evolution of the concentration of hydrogen peroxide as a function of time $[H_2O_2] = f(t)$, is as follows **(Document 1)** :

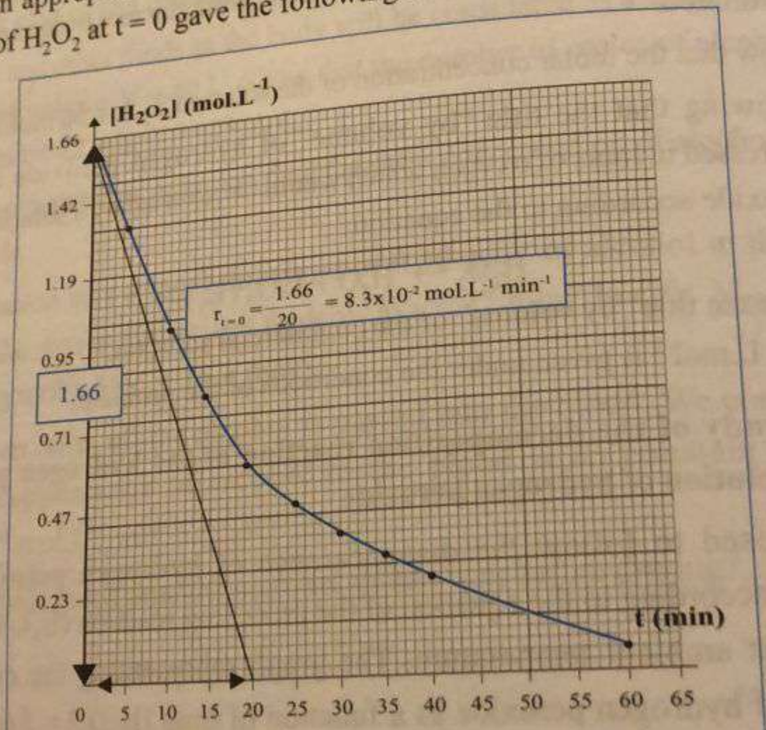


Document 1

2.1. Describe the curve representing $[H_2O_2] = f(t)$ in the time interval [0 - 60 min].

2.2. Write the formula of the instantaneous rate (at a time t) of disappearance of H_2O_2. Give its geometric signification.

2.3. By an appropriate method, the graphical determination of the disappearance rate of H_2O_2 at $t = 0$ gave the following result **(Document 2)**:



Document 2

Deduce the rate of formation of the oxygen at $t = 0$.

2.4. How does this rate evolve over time? Explain.

18. Javel water Bleach - Precautionary use - Stability

Given: Javel water is a common product used for its disinfectant power. It can be obtained by dissolving chlorine gas in an aqueous solution of sodium hydroxide according to the equation :

$$C\ell_2 + 2Na^+ + 2HO^- \rightarrow C\ell O^- + C\ell^- + 2Na^+ + H_2O \quad (1)$$

1. Concentration of Javel water

It is often defined by the chlorometric degree (° chl). It corresponds to the volume (expressed in liters) of chlorine gas, measured under normal conditions of temperature and pressure, which would have to be used to manufacture 1 L of this bleach according to the equation (1). Under these conditions the molar volume is $V_m = 22.4\ L.mol^{-1}$. The table below gives the chlorometric degrees (° chl) of two solutions of Javel water sold in flasks and cartons **(Document 1)** :

Packaging	in flasks (1 or 2 L)	in cartons (concentrated)
°chl	12°	48°

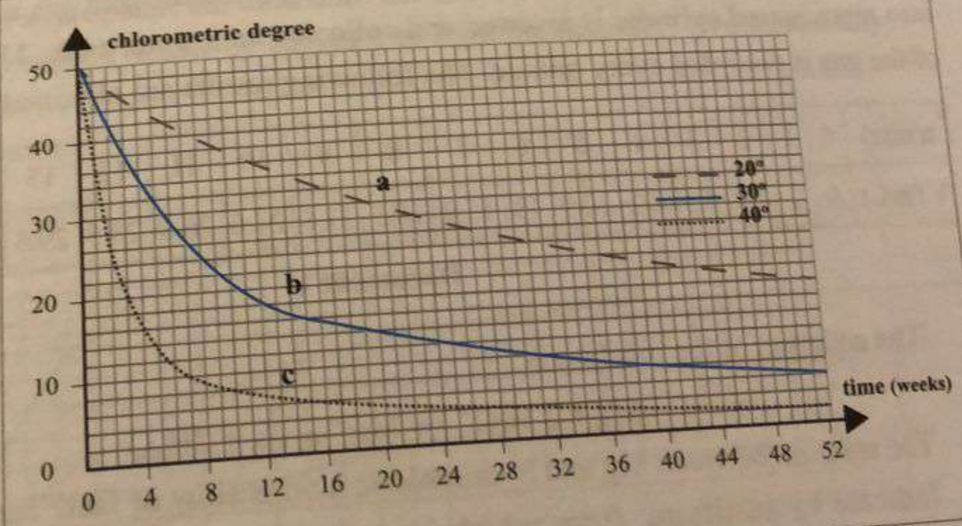
Document 1

Deduce, from the definition of the chlorometric degree,the concentration of hypochlorite ions[$C\ell O^-$] in a Javel water of 48 °chl.

2. Influence of kinetic factors

The examination of Figure 1 below **(Document 2)** reveals two kinetic factors :

Evolution of reaction (2) at different temperatures.



Document 2

2.1. What are these two kinetic factors?

2.2. Explain the effect of each factor on the rate of disappearance of $C\ell O^-$ ions.

3. **Mode of action of Javel water and label reading**

During the preparation of the Javel water, the hydroxide ions are introduced in excess. The pH of the Javel water is between 11 and 12. The properties of the Javel water are due to the oxidizing character of the hypochlorite ions $C\ell O^-$. These ions can give rise to various reactions, involving various factors : pH, concentrations, temperature, catalysts (metal ions), radiation (UV). In particular, the hypochlorite ions react in the presence of water according to :

- In basic medium : $C\ell O^- \rightarrow C\ell^- + \frac{1}{2}O_2$ (2)
- In acidic medium : $C\ell O^- + C\ell^- + 2H_3O^+ \rightarrow C\ell_2 + 3H_2O$ (3)

A few recommendations read on the packaging of Javel water :

Keep cool, away from Sun and light.

Do not use in combination with other products : in contact with an acid, produces a toxic gas.

3.1. What is the toxic gas which it produces in the recommendations? Justify.

3.2. Is the "keep cool" recommendation justified?

3.3. Why the Javel water is sold in opaque containers?

3.4. No deadline time of use is shown on the Javel water bottles unlike the cartons. Justify this difference

19. Reaction between magnesium and hydrochloric acid :

In a 250 mL flask pour 10 mL of concentrated hydrochloric acid solution of concentration 1 mol. L^{-1} and 20 mL of water. Quickly add 0.03 g of a well coated magnesium Ribbon, while triggering a stopwatch. The hydrogen gas which is discharged into a graduated cylinder is inverted and collected on a water tank. The volume V (mL) of the gas is recorded every minute. The following results are obtained **(Document 1) :**

t(min)	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
V (mL)	0	0	2.9	5.5	8.2	10.9	13	15.9	18.5	21.5	24.6	26.8	28.5	29.5	30.1	31	31.6	31.6

Document 1

The equation of the reaction is :

$$Mg + 2\,H_3O^+ \rightarrow Mg^{2+} + H_2 + 2H_2O$$

1. The reaction between Mg and hydrochloric acid is slow or fast? Justify
2. Indicate by justifying from which instant we can consider that the reaction is completed.
3. From the table, determine the quantity of matter (in mol) of hydrogen gas produced at the end of the experiment, knowing that the molar volume under the conditions of the experiment is 24 $L.mol^{-1}$.

4. Draw a table allowing to follow the evolution of the transformation in terms of the number of mol (x) of Mg which has reacted, showing 2 times : t = 0 and t = 16 min.
5. Determine by calculation the final state of the system and compare it with the experimental results.

Given : Atomic molar mass ($g.mol^{-1}$) : Mg = 24.

20. Decomposition of hydrogen peroxide by iodide ions

Mixtures A, B and C, containing the same reactants in different proportions, are given. The experimental values are given in the table below of **document 1** :

Given : Atomic molar mass ($g.mol^{-1}$) : Mg = 24.

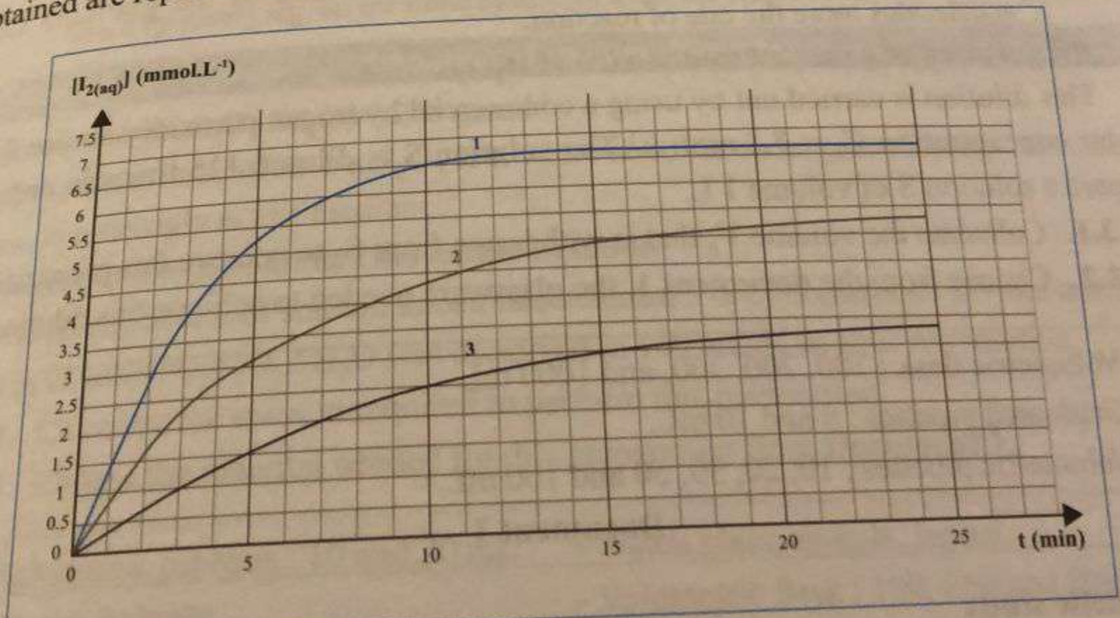
	Sulfuric acid $C_0 = 1.0\ mol.L^{-1}$	**Potassium iodide** $C_1 = 0.10\ mol.L^{-1}$	**Hydrogen peroxide** $C_2 = 0.10\ mol.L^{-1}$	**Total volume of the solution after dilution**
A	10 mL	15 mL	2.0 mL	30 mL
B		10 mL	2.0 mL	
C		10 mL	1.0 mL	

Document 1

The reaction between hydrogen peroxide and iodide ions is considered to be complete and its balance equation is :

$$H_2O_{2(aq)} + 2H^+_{(aq)} + 2I^-_{(aq)} \rightarrow 2H_2O_{(l)} + I_{2(aq)}$$

For each of the three mixtures, the $[I_2]$ formed at different time intervals are determined by an appropriate method until the end of the reaction ; the kinetic curves obtained are represented below by curves 1 to 3 (in the disorder) **(Document 2)** :



Document 2

Referring to documents 1 and 2, answer the following questions :

1. Determine graphically the half-life time $t_{1/2}$ for the mixture represented by the curve (3).
2. Answer this questionnaire by true or false. Justify the answer.
   - 2.1. In mixture C, the limiting reactant is not the iodide ion.
   - 2.2. From the value of $[I_2]$ final, it is deduced that curve 3 corresponds to mixture C.
   - 2.3. At t = 5 min, the value of r_3 is greater than that of r_1. (r_1 and r_3 denote respectively the reaction rates for curves 1 and 3 at t = 5 min).
   - 2.4. Knowing that the curve 1 corresponds to the mixture A and that the curve 2 corresponds to the mixture B, it can be affirmed that the curve 2 will reach the same limit as the curve 1.

21. Kinetics of the decomposition of hydrogen peroxide H_2O_2

The decomposition of hydrogen peroxide H_2O_2 is a slow reaction given by the following equation :

$$2\,H_2O_{2(aq)} \rightarrow 2\,H_2O_{(l)} + O_{2(g)}$$

1. **Study of the reaction medium**

Catalysis is said to be homogeneous if the reactants and the catalyst form a single phase, whereas it is said to be heterogeneous if the reactants and the catalyst constitute several phases.

This reaction is very slow ; it can be accelerated by adding a platinum strip or a solution containing the Fe^{2+} ions.

- 1.1. Indicate in which case the catalysis is homogeneous and in which case it is heterogeneous. Justify
- 1.2. Explain why the use of platinum powder instead of the platinum strip accelerates more the rate of reaction.

2. **Preparation of a diluted solution (S) of H_2O_2**

This dilution is carried out by using a commercial hydrogen peroxide solution S_0 of molar concentration C_0 = 7.5 mol. L^{-1}.The solution $S_0$is diluted 125 times in order to prepare a solution S of volume 1 L.

- 2.1. Calculate the volume V_0 that is withdrawn from S_0 to achieve this preparation.
- 2.2. Choose from the **document 1**, the glassware needed to achieve this dilution.

-Volumetric flask : 100, 200, 300, and 1000 mL
-Graduated pipettes : 5 and 10 mL.
-Volumetric pipettes : 10, 20, 30, 50 and 100 mL.

Document 1

3. **Kinetic study**

In order to study the kinetics of the decomposition of hydrogen peroxide, 10 mL of the solution S are withdrawn and poured into a large beaker, and then a few drops of iron (II) sulfate solution are added at a constant temperature of 25°C. We measure using a suitable device the volume of oxygen gas released at different time instants.

Considered that the volume of the aqueous solution of hydrogen peroxide remains constant and the molar volume of a gas is $V_m = 24\ L.mol^{-1}$. The results are grouped in the table below (**Document 2**) :

$t(min)$	0	5	10	15	20	30
$V_{O_2}(mL)$	0	1.56	2.74	3.65	4.42	5.26
$[H_2O_2]_t\ mol.L^{-1}$						

Document 2

3.1. Show that the molar concentration of the remaining H_2O_2 in the solution at any instant t during the reaction is given by the relation :

$$[H_2O_2]_t = 0.06 - (8.3x10^{-3}.\ V_{O_2})\ (V_{O_2} \text{ is expressed in mL}).$$

3.2. Complete the table of **document 2** and draw the curve $[H_2O_2]_t = f(t)$

Take for scales : 1 cm → 5 min and 1 cm → 10^{-2} mol. L^{-1}.

3.3. At the beginning of the reaction the release of oxygen starts very active, and overtime it becomes less active. Explain this phenomenon.

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

3.5. The same experiment is repeated in the following two cases :

3.5.1. The operation is carried out at a temperature of 45 °C.

3.5.2. The operation is carried out at a temperature of 25 °C but without the Fe^{2+} ions.

Trace by justifying, on the same system of axes, the shape of the curve in each case.

22. Kinetic study of disproportionation of sodium thiosulfate

Given : $M(Na_2S_2O_3.5H_2O) = 248\ g.mol^{-1}$

The sodium thiosulfate $Na_2S_2O_3$ is a white solid. It undergoes disproportionation reaction in a strongly acidic medium.

1. **Preparation of a Sodium Thiosulfate Solution**

To prepare 100 mL of sodium thiosulfate solution S of concentration $C = 0.5\ mol.L^{-1}$, a mass m of solid $Na_2S_2O_3.5H_2O$ was dissolved in 100 mL of an aqueous solution.

1.1. Calculate the mass m required to perform this preparation.

1.2. Choose the material needed for this preparation from **Document 1.**

- Volumetric pipettes : 10 and 20 mL	- Watch glass, spatula, funnel.
- Precise balance.	- Volumetric flask : 100, 250 and 500 mL.

Document 1

2. The sodium thiosulfate Disproportionation

Experiment1 :

At 25 °C pour V' = 10 mL of a solution of hydrochloric acid (HCℓ) of concentration C' = 5 mol.L^{-1} in V = 40 mL of a solution of sodium thiosulfate ($Na_2S_2O_3$) of concentration C = 0.5 mol. L^{-1}. The mixture gradually whitens by formation of solid sulfur. The balance equation of the reaction is written :

$$S_2O_3^{2-} + 2H_3O^+ \rightarrow S + SO_2 + H_2O$$

2.1. Determine the maximum number of moles that sulfur can reach when $T \rightarrow \infty$.

2.2. An appropriate titration of the remaining $S_2O_3^{2-}$ ions, gave the following values of the **document 2** :

t(min)	0	1	2	3	4	5
$n_{(t)}S_2O_3^{2-}$ mol	0.02	0.008	0.004	0.002	0.001	0.0005
$n_{(t)}S$ mol						

Document 2

2.2.1. Show that the number of mole of sulfur formed over time is related to the number of mole of remained $S_2O_3^{2-}$ ions by the relation : $n_{(t)}S = 0.02 - n_{(t)}S_2O_3^{2-}$

2.2.2. Complete the table of **document 2** and draw the curve $n_S = f(t)$.

Scales : 1 cm = 1 min ; 1 cm = 0.005 mol

2.3. Define the instantaneous rate of formation of sulfur S at a given instant of time t.

2.4. Deduce the relation between the instantaneous rate of disappearance of H_3O^+ ions and the instantaneous rate of formation of sulfur S at a given instant of time t.

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

3. Study of some kinetic factors

Experiment2 :

The same experiment is repeated by adding a suitable catalyst.

3.1. Trace by justifying, the shape of the new curve $n_S = g(t)$ on the same system of axes.

3.2. A change in half-life time $t'_{1/2}$ is noted. Choose by justifying from **document 3**, which of the 2 results is correct :

Experiment	2	2
Half-life time $t_{1/2}$	$t'_{1/2} > t_{1/2}$	$t'_{1/2} < t_{1/2}$

Document 3

23. Reaction between Hydrogen peroxide and Iodide Ions

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

$$H_2O_2 + 2H_3O^+ + 2I^- \rightarrow I_2 + 4H_2O$$

In order to study the kinetic of the above complete and slow reaction, two reacting mixtures A and B are prepared at the same temperature Θ, where the composition of each is given in the table of **document 1** below :

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

Document 1

1. **Preliminary study :**

In the two mixtures H_2O_2 is introduced at the same time $t = 0$.

1.1. Determine the number of moles of each reactant in the two mixtures A and B.

1.2. In the two mixtures A and B choose by justifying which of the following statement is correct?

a. The reaction is not stoichiometric and I^- is the limiting reactant.

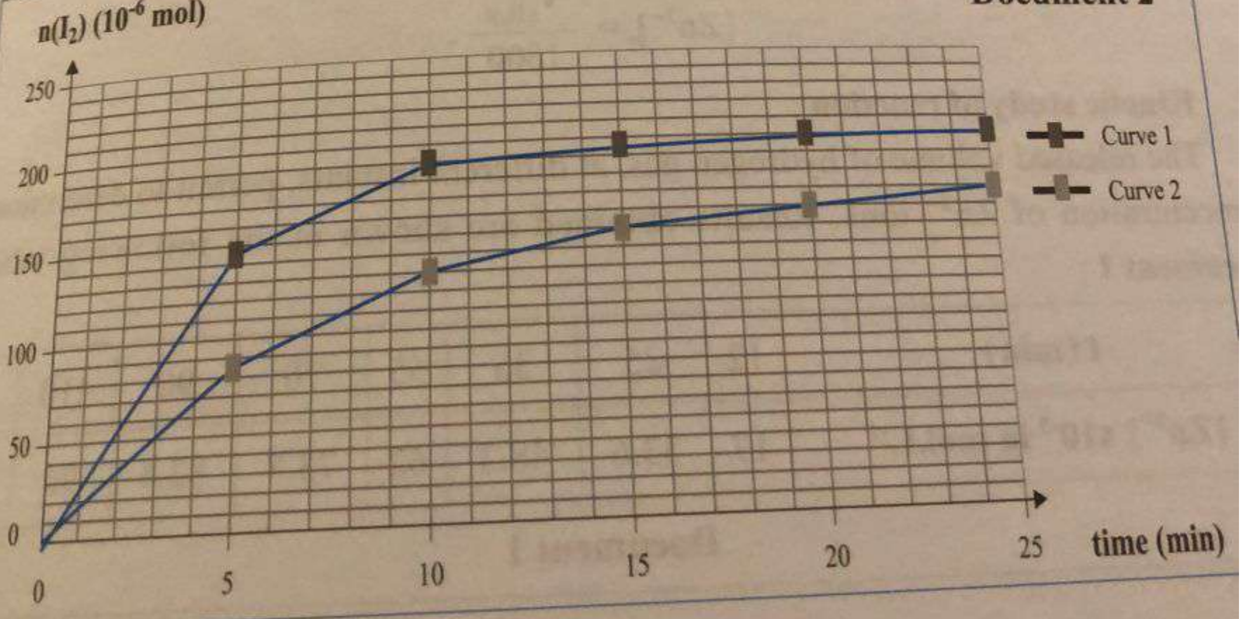
b. The reaction is stoichiometric.

c. The reaction is not stoichiometric and H_2O_2 is the limiting reactant.

2. **Kinetic Factors**

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 time interval [0-25 minutes].

Document 2



2.1. Verify, based on the above table and graph, whether the reaction in each of the mixtures A and B has finished at the instant t = 25 minutes.

2.2. Specify the kinetic factor responsible for the difference in the shapes between the curves 1 and 2.

2.3. Starting with the reaction mixtures A and B, propose a way that can lessen the difference in shape, between the two curves 1 and 2.

2.4. The instantaneous rate of formation of iodine in the mixture B is determined by an appropriate method at instants of time t = 5 min and t = 15 min and the obtained values are : 2.77×10^{-6} mol.min^{-1} and 12.30×10^{-6} mol.min^{-1}.

Relate, by justifying, each rate to its corresponding time.

24. Kinetic study of oxidation of zinc metal

Zinc is a metal that reacts with an aqueous solution of hydrochloric acid ($H_3O^+_{(aq)}$, $Cl^-_{(aq)}$) according to the following equation :

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

This exercise aims to study the kinetic of the above reaction.

Given :

- Molar mass of zinc : $M(Zn) = 65.4$ g.mol^{-1}.
- Under the conditions of experiment the molar volume of gases : $V_m = 24$ L.mol^{-1}

1. **Preliminary study of the reaction ;**

At a temperature of 25 °C, add 0.5 g of zinc powder metal into a closed flask containing a volume V = 75 mL of hydrochloric acid solution of concentration $C_a = 0.4$ mol.L^{-1} (the volume of the solution doesn't change).

1.1. Determine the limiting reactant.

1.2. Deduce the concentration of Zn^{2+} ions at the end of the reaction.

1.3. Show that, at each instant of time t during the reaction, the relation between $[Zn^{2+}]_t$ in mol.L^{-1} and $V(H_2)_t$ in mL is :

$$[Zn^{2+}]_t = \frac{V_{(H_2)t}}{1800}.$$

2. **Kinetic study of reaction** :

The released volume of hydrogen gas, at different instants, permit to determine the concentration of Zn^{2+} ions. Results obtained are shown in the following table of

document 1 :

t (min)	12	25	35	55	70	90	110	135
$[Zn^{2+}] \times 10^{-3}$ in mol.L^{-1}	17	33.6	48.3	62	73.8	82.8	90	94

Document 1

2.1. Plot the curve representing : $[Zn^{2+}] = f(t)$. Take the following scale :
Abscissa : 1 cm for 20 min and Ordinate : 1 cm for 10×10^{-3} $mol.L^{-1}$.

2.2. Determine the half-life time $t_{1/2}$ of this reaction.

2.3. At instant t = 190 min, the volume of released hydrogen gas is 183.6 mL. Verify if 190 min represents the end of the reaction.

3. **Effect of some kinetic factors :**

Two studies (experiments a and b) are followed for the same previous experiment with one modification in each study :

Experiment a : the initial concentration of H_3O^+ ions is 0.5 $mol.L^{-1}$.

Experiment b : it takes place at a temperature different than 25 °C.

3.1. The results of the previous experiment and that of experiment (a) are represented in the following table of **document 2 :**

	$[H_3O^+]$ $mol.L^{-1}$	Rate of formation of Zn^{2+}	The molar concentration of Zn^{2+} at final time
Previous Experiment	0.4	r	$[Zn^{2+}]$
Experiment (a)	0.5	r'	$[Zn^{2+}]'$

Document 2

Answer by true or false. Justify

a. $r = r'$.

b. $[Zn^{2+}] < [Zn^{2+}]'$.

3.2. The concentration of $[Zn^{2+}]$ in experiment (b) at the instant 35 min is $[Zn^{2+}]'' > [Zn^{2+}]$.

Specify whether the temperature in experiment (b) is greater or smaller than 25 °C.