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Exercise 1 (7 points) **Study of a Slow Reaction**

Hydrogen peroxide (H_2O_2) oxidizes iodide ions (I^-) in acidic medium in a slow reaction which takes place according to the following equation:

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

1. Preparation of a Hydrogen Peroxide (H_2O_2) Solution (S_1)

Available is a hydrogen peroxide solution (S_0) of concentration $C_0 = 2.7\ mol.L^{-1}$. It is required to prepare a hydrogen peroxide solution (S_1) of concentration $C_1 = 0.1\ mol.L^{-1}$.

Choose, from the **document-1**, the most suitable set of glassware to realize this dilution. Justify.

Set A	Set B	Set C
Volumetric flask of 100 mL Volumetric pipet of 10 mL Beaker of 50 mL	Volumetric flask of 100 mL Graduated pipet of 10 mL Beaker of 50 mL	Volumetric flask of 100 mL Graduated cylinder of 10 mL Beaker of 50 mL

Document-1

2. Preliminary Study

In a beaker, one mixes:

- A volume $V_1 = 18$ mL of potassium iodide solution ($K^+ + I^-$) of concentration $C_1 = 0.1\ mol.L^{-1}$
- A volume $V_2 = 9$ mL of sulfuric acid solution H_2SO_4 of concentration $C_2 = 1\ mol.L^{-1}$.

At instant t = 0 s, a volume $V_3 = 3$ mL of hydrogen peroxide solution H_2O_2 of concentration $C_3 = 0.1\ mol.L^{-1}$ is added to the beaker. *In this mixture, sulfuric acid is in excess.*

2.1. Calculate the initial concentrations of iodide ions $[I^-]_0$ and hydrogen peroxide $[H_2O_2]_0$ in the reaction mixture.

2.2. Show that hydrogen peroxide H_2O_2 is the limiting reactant.

3. Kinetic Study

By an appropriate method, the concentration of iodine $[I_2]$ at different instants is determined. The results are grouped in the table of **document-2**.

t (s)	100	200	300	400	500	600	650
$[I_2]$ (10^{-3} mol.L^{-1})	3.85	5.9	7.5	8.6	9.4	9.85	10

Document-2

3.1. Plot the curve representing the variation of the concentration of iodine as a function of time $[I_2] = f(t)$ in the interval of time [0 - 650 s].

Take the scales: *In abscissa: 1 cm for 50 s ;*
In ordinates: 1 cm for 1×10^{-3} mol.L^{-1}.

3.2. Show that t= 650s represents the end time of reaction.

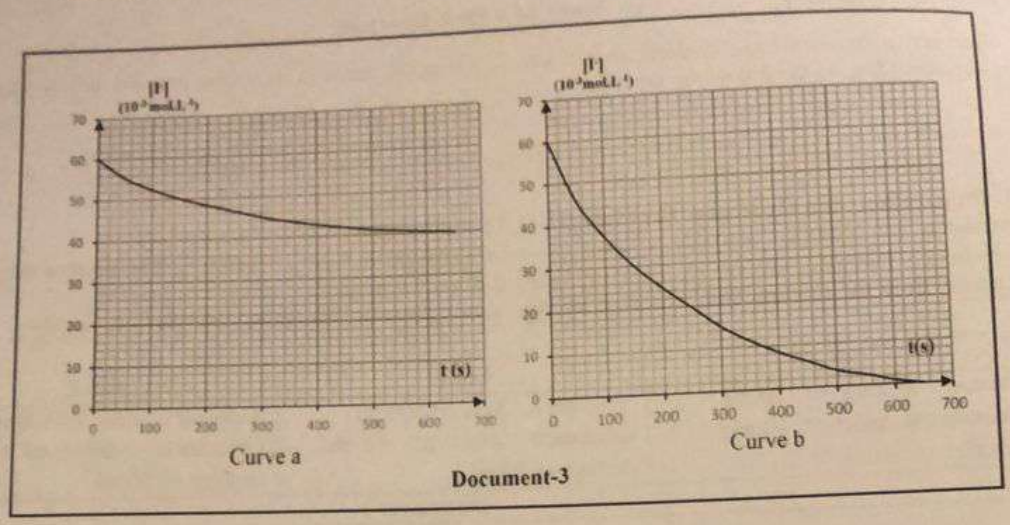
3.3. Determine graphically the half-life time of reaction $t_{1/2}$.

3.4. Justify the following statements:

3.4.1. The initial rate of formation of I_2 is greater than its rate of formation at t = 300 s.

3.4.2. The concentration of iodide ions at t ½ is $[I^-]_{1/2} = 50 \times 10^{-3}\ mol.L^{-1}$.

3.5. From the curves of **document-3**, specify the one that corresponds to the variation of the concentration of iodide ions as a function of time $[I^-] = g(t)$.



Document-3

Exercise 2 (7 points) **Kinetics Study at Constant Temperature**

Iodide ions (I^-) react with peroxydisulfate ions ($S_2O_8^{2-}$) according to the following equation:

$$S_2O_8^{2-} + 2\,I^- \rightarrow 2\,SO^{2-}_4 + I_2$$

The aim of this exercise is to study the kinetics of this reaction, in the absence and in the presence of iron II ions, at constant temperature.

Given: M (KI) = 166 g.mol^{-1}.

1. Preparation of Solutions (S_1) and (S_2)

Document -1 represents available materials and chemicals presented in the lab.

Materials	Chemicals
Sensitive balance. Spatula. 100 and 500 mL round bottom flask - Watch glass. 50 mL, 100 mL and 200 mL erlenmeyers. 50 mL, 100 mL and 200 mL volumetric flasks. 5 mL, 10 mL and 20 mL volumetric pipets. Pipette filler	Solid potassium iodide KI Solution (S_0) of sodium peroxydisulfate ($2Na^+$; $S_2O_8^{2-}$) of concentration $C_0 = 2$ mol.L^{-1}. Distilled water.

Document -1

Exercise 3(6 points) **Synthesis of Ammonia**

Ammonia is a colorless and irritating gas (pungent odor at low concentration, it burns eyes and lungs in its concentrated form)

1. **Study of the reaction:**

Into a flask of volume V=1L, we introduce 1 mol of N_2 and 3 mol of H_2, a chemical equilibrium is established according to the following equation: $N_{2(g)} + 3H_{2(g)} \leftrightarrow 2NH_{3(g)}$

Let α be the degree of conversion of N_2.

At different temperature, the total number of mol of reactional mixture at equilibrium is calculated. The results are collected in the table of document -1.

T(°C)	25	27	227	327	527	727
n_t (in mol)	2	2	2.32	2.7	3.46	3.8

Document-1

1.1. Copy and complete the table below in terms of α.

	$N_{2(g)}$	$3H_{2(g)}$	$2NH_{3(g)}$
Initial state (mol)			
Equilibrium state(mol)			

1.2. Express the total number of mol of mixture at equilibrium in terms of α.

1.3. Write the expression of Kc in terms of α.

1.4. The rate of the reaction at equilibrium is zero. Could we say that the reaction stops? Justify.

2. **Study of the reaction at temperature 227°C.**

2.1. Referring to document-1 and at temperature 227°C.

2.1.1. Calculate α at equilibrium. Deduce Kc.

2.1.2. Show that the % yield of the reaction is equal to 84%.

2.2. The experiment is repeated again by introducing 1 mol of N_2, 5 mol of H_2.

Choose with justification the correct answer:

The equilibrium constant Kc

i- Decreases ii- Increases iii- Remains constant

3. **Study of the reaction at temperature 27°C.**

Referring to document-1:

3.1. What is the value of α at temperature 27°C? Conclude.

3.2. Specify if equilibrium constant Kc could be determined below 27°C.

Refer to document-1, answer the following questions:

1.1. Choose, from the document-1, the material necessary to prepare a solution (S_1) of potassium iodide (K^+; I^-) of volume $V_1 = 200$ mL and concentration $C_1 = 0.8$ mol.L^{-1}. Justify.

1.2. Describe briefly, starting from solution (S_0), the experimental procedure necessary to prepare a solution (S_2) of sodium peroxydisulfate ($2Na^+$; $S_2O_8^{2-}$) of volume $V_2 = 200$ mL and concentration $C_2 = 0.2$ mol.L^{-1}.

2. Kinetic Study

Document -2 represents two experiments (1) and (2).

Experiment -1: Mix, at a constant temperature T, a volume $V_1 = 100$ mL of solution (S_1) and a volume $V_2 = 100$ mL of solution (S_2). Sample of the reacting mixture is taken at each time t, ice water is immediately added to each sample then titrated with an appropriate method in order to determine the concentration of the iodine formed (I_2).

Experiment -2: The same experiment -1 is repeated again, at the same temperature T, but in the presence of few drops of iron II sulfate solution (Fe^{2+}; SO_4^{2-}) at the beginning of the reaction.

Document -2

The results of the two experiments are given in the table of document -3.

Time in (min)	0	2.5	5	10	15	20	30
Experiment -1: $[I_2]$ x10^{-3}mol.L^{-1}	0	9.5	17.2	29.6	38.7	45.7	55.8
Experiment -2: $[I_2]$ x10^{-3}mol.L^{-1}	0	15.0	27.0	46.5	61.0	72.7	91.2

Document -3

2.1. Specify, by indicating the kinetic factor(s), the purpose of the addition of ice water before titration.

2.2. Determine, in each experiment, the concentration of I_2 at the end of the reaction.

2.3. Plot on the same graph the curve $[I_2] = f(t)$ for the experiment-1 and the curve $[I_2] = g(t)$ for the experiment-2. Take the following scale:

1 cm for 2 min in abscissa and 1 cm for 10.0x10^{-3} mol.L^{-1} in ordinate.

2.4. Determine the half-life in each of the two experiments ($t_{1/2}$ of experiment-1 and $t'_{1/2}$ in experiment-2).

2.5. Deduce the role of Fe^{2+} ions in the above reaction system.

2.6. The slope of the tangent, at time t=0 min, is X of the curve $[I_2] = f(t)$ (experiment-1) and Y of the curve $[I_2] = g(t)$ (experiment-2).

2.6.1. Compare X and Y.

2.6.2. Indicate the kinetic factor involved in this variation

Exercise 2(8 points) **Kinetics of the Decomposition of Hydrogen Peroxide H_2O_2**

In this exercise, the aim is to prepare H_2O_2 solution (S) then study the kinetic of the slow decomposition reaction of H_2O_2, in presence of Fe^{3+} as a catalyst. The equation of the reaction is:

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

Given: The experiment is performed at 25°C.

1. Preparation of H_2O_2 solution (S).

A solution (S) of concentration $C = 0.06\ mol.\ L^{-1}$ is required to be prepared starting from an initial solution (S_0) of H_2O_2 of concentration $C_0 = 4\ mol.\ L^{-1}$.

Choose, from document - 1, the needed glassware for the most precise preparation of solution (S). **Justify**.

- 100, 200 and 500 mL beakers.
- 5, 20 and 50 mL graduated cylinders.
- 500, 1000 and 2000 mL volumetric flasks.
- 50, 10 and 20 mL volumetric pipets.
- 1, 5 and 10 mL graduated pipets.

Document -1

2. Kinetic of the decomposition of H_2O_2.

A small quantity of powdered iron (III) chloride is added, without any change in the volume, into a round bottom flask containing V=35 mL of solution (S) of concentration $C = 0.06\ mol.\ L^{-1}$. Using appropriate method, the number of moles of O_2 gas produced is determined at different instants. The obtained values are given in document - 2:

Time(min)	5	10	15	20	30	40
$n_{O_2} \times 10^{-4} mol$	2.8	4.8	6.6	7.9	9.4	10.2

2.1. **Specify** if t = 40 min represents the end time of the reaction or not.

2.2. **Plot**, on a graph paper, the curve $n_{O_2} = (t)$ in the interval of time [0 , 40 min].
Take the following scale: Abscissa: 1 cm for 5 min ,; Ordinate 1 cm for 1 x 10^{-4} mol.

2.3. **Deduce**, graphically, how the rate of formation of O_2 changes with time.

2.4. **Specify** the kinetic factor responsible for this change.

2.5. **Determine** the half life time of the reaction.

2.6. **Draw** on the same graph of part 2.2 the shape of the curve $(H_2O_2) = g(t)$ passing through point abscissa t = 0, t = 30 min and t = 40 min.

2.7. The same experiment was repeated at a temperature T = 35° C. The number of moles of O_2 collected at t = 30 min is greater than 9.4 x 10^{-4}mol. **Justify**

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 o

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}	0.06	0.04	0.03	0.029	0.023	0.01

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 :

$[H_2O_2]_t = 0.06 - (8.3\times10^{-3}.V_{O_2})$ (V_{O_2} 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.

I. 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 ($HC\ell$) 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 :

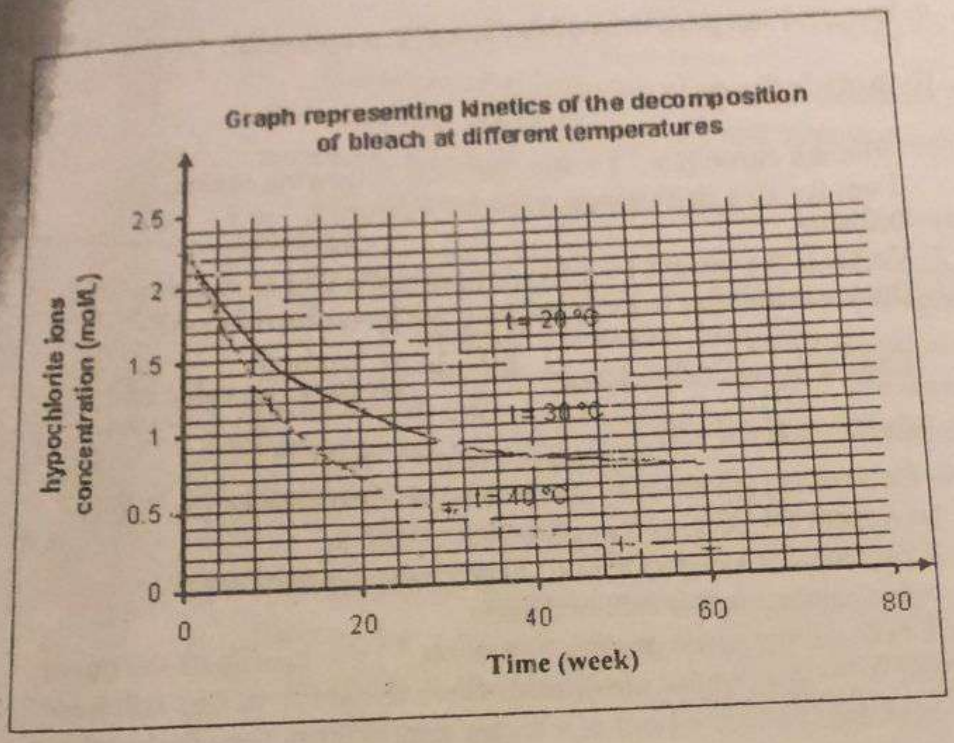
The same experiment is repeated by adding a suitable catalyst.

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



1- Determine, at 40 °C, the disappearance rate of hypochlorite ions at the instants: $t_1 = 0$ and $t_2 = 4$ weeks.
Explain the evolution of this rate.
2- Does the recommendation <preserve at freshness> seem justified to you?
3- It is misadvised to use bleach with another detergent based on acid (Flash...). Write down the equation of the reaction which interprets this recommendation.
4- The Javelle water is marketed in opaque containers. Why?

Exercise – 10

Kinetics of Oxidation Reaction of Oxalic Acid

We study, during time, the evolution of a mixture formed of 50 mL of an oxalic acid solution of concentration $C_1 = 6.0 \times 10^{-2}$ mol.L^{-1} and 50 mL of a potassium dichromate solution of concentration $C_2 = 0.02$ mol.L^{-1} in presence of an excess of sulfuric acid. We

follow the variation of concentration of Cr^{3+} ions formed during the reaction of the following equation.

$$Cr_2O_7^{2-} + 3\,H_2C_2O_4 + 8\,H_3O^+ \rightarrow 2\,Cr^{3+} + 6\,CO_2 + 15\,H_2O$$

We obtain the results grouped in the following table:

Time t (s)	0	10	20	30	50	70	100	140
$[Cr^{3+}]$ mmol.L^{-1}	0	3.5	6.0	7.6	10.5	12.3	14.2	16

I- Preparation of Oxalic Acid Solution

1- Calculate the mass of crystallized oxalic acid of formula ($H_2C_2O_4$, $2H_2O$) needed to prepare 100 mL of solution of concentration C_1.

2- Describe the procedure of this solution preparation.

II- Kinetic Study

1- Plot the curve $[Cr^{3+}] = f(t)$. Take the following scales: 1 cm for 10 s in abscissa; 1 cm for 1 mmol.L^{-1} in ordinate.

2- Verify if the instant t = 140 s indicates the end of reaction.

3- Demonstrate that at each instant t, we have the relation:

$$[Cr_2O_7^{2-}]_t = [Cr_2O_7^{2-}]_{initial} - \frac{[Cr^{3+}]_t}{2}$$

. Deduce the value of $[Cr_2O_7^{2-}]$ at t = 100 s.

4- Determine, graphically, the rate v_1 of formation of Cr^{3+} ions at instant t = 50 s, and v_2 at instant t =100 s.
Compare the rates v_2 and v_1. Specify the kinetic factor responsible for this rate evolution.

5- Draw, on the same graph of question 1-, the profile of the curve $[Cr^{3+}] = g(t)$ under conditions where the study of this reaction evolution is carried out at a higher temperature than that of the preceding study.

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Exercise – 11

Kinetics of the Reaction between Hydrochloric Acid and Zinc

Hydrochloric acid reacts with zinc according to the reaction of equation:

$$Zn_{(s)} + 2\,H^{+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2\,(g)}$$

At instant t = 0, a mass m =1.0 g of zinc is introduced into a round flask containing a volume V = 40 mL of a hydrochloric acid solution (S) of molar concentration C = 0.50 mol.L^{-1}.

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

The results are grouped in the following table:

Time t (s)	0	50	100	150	200	250	300	400	500	750
$V(H_2)$ mL	0	36	64	86	104	120	132	154	170	200

I- Preparation of Solution (S)

The hydrochloric acid solution (S) was prepared from a commercial hydrochloric acid solution contained in a flask which label has the following indications:

Mass percentage: 32%; density: 1.14 g.mL^{-1}; M(HCl)=36.5 g.mol^{-1}.

1- Show that the commercial hydrochloric acid solution has a concentration C_0 close to 10 mol.L^{-1}.

2- Describe, with precision, the procedure followed to prepare 100 mL of solution (S).

II- Kinetic Follow-up of this Reaction :

1- Justify that instant t =750 s is the date which indicates the end of the reaction. M(Zn) = 65 g.mol^{-1}.

2- Calculate, at each instant t, the number of moles of H_2 : $n(H_2)$ in mol. (Give the results in the form of a table).

3- Plot, on graph paper, the curve representing the variation of $n(H_2)$ versus time : $n(H_2) = f(t)$.

Take the following sca ::

1cm for 50 s in abscissa and 1cm for 0.5.10^{-3}mol in ordinate.

passbac

4- Determine the reaction half-life.
5- Establish the following relation:

$$[H^+]_{at\ t} = [H^+]_{at\ t=0} - 2x10^{-3}\ xV(H_2)$$

6- Draw the profile of the curve: $[H^+] = g(t)$ by specifying the points that correspond to $t = 0$; $t = t_{1/2}$ and $t = 750s$.
7- We restart the same experiment with the same mass of Zinc, but we pour in the flask 40mL of hydrochloric acid of concentration $1 mol.L^{-1}$. On the same graph of question 3, draw the profile of the curve $n(H_2) = g(t)$ in the time interval: 0 – 750 s.

Exercise – 12
Decomposition of Pentacarbonyliron

The carbon monoxide forms with iron a compound of formula $Fe(CO)_5$, called pentacarbonyliron. At a temperature equal to 200°C, in the darkness, the gaseous pentacarbonyliron undergoes a slow decomposition according to the following equation:

$$Fe(CO)_{5\ (g)} \rightarrow Fe_{(s)} + 5\ CO_{(g)}$$

We lock up a quantity $n_0 = 2.06$ mmol of pentacarbonyliron in an enclosure of invariable volume V = 250 mL, emptied beforehand, and then we raise the temperature to 200° C.
Consider P_0 as the initial pressure at this temperature.
We follow-up the evolution of the total pressure P in the enclosure during time and we obtain the following results:

t (min)	0	5	10	15	20	25	30
P (10^4 Pa)	3.2	7.4	9.6	11.5	12.8	13.7	14.4

1- Explain the elevation of pressure during time.
2- Verify that the pressure P_0 is equal to $3.2x10^4$ Pa.
3- Justify if at t = 30 min the decomposition of pentacarbonyliron is complete.
4- Establish the following relation: $[CO] = \frac{P - P_0}{3140.72}$ where CO concentration is expressed in $mol.m^{-3}$.
5- Plot the curve representing the variation: [CO] = f (t). Scales to take:

Extra sheet.

55. Study of a drain opener

Unclogging your drain with soda bicarbonate is easy, efficient and natural. So why buy expensive and toxic chemicals?

A drain opener consists essentially of a base marked B and shows on its label the following indications **(Document 1)** :

> «... corrosive product... percentage by mass 29 % ; d = 1.23 ; M_B = 40 g.mol^{-1} ... »
> K_w = 1.0x10^{-14} at 25 °C
>
> **Document 1**

The objective of our study, which is carried out at 25 °C, is to determine the nature of this base, if it is strong or weak, and verify the indication of the label by carrying out the necessary experimental work.

1. **Nature of Base B**

1.1. Show that the molar concentration of this commercial solution noted (S_o) is C_o = 8.9 mol.L^{-1}.

1.2. A solution (S) of the drain opener is prepared by diluting 100 times the solution (S_o).

1.2.1. Among the proposed glassware sets **(Document 2)**, choose, by justification, which one should be used to achieve the most accurate dilution of the solution (S_o).

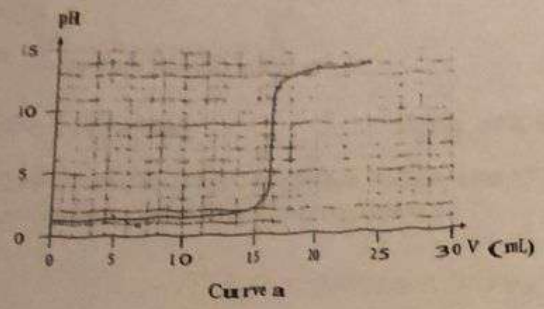
Set - a	Set - b	Set - c
5 mLvolumetric pipette	10 mLvolumetric pipette	10 mLGraduated pipette of
100 mLbeaker	1000 mLvolumetricflask.	1000 mLvolumetricflask.

Document 2

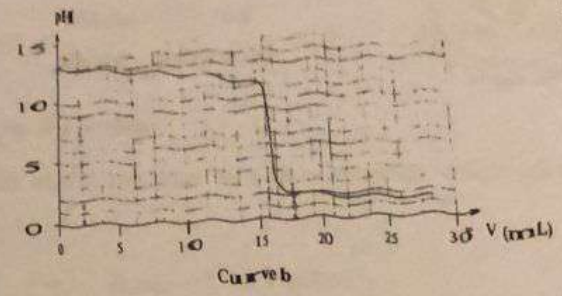
1.2.2. The pH of the solution (S) is measured and a value of 12.95 is obtained. Show that B is a strong base.

2. **Determination of the base B contained in the drain opener**

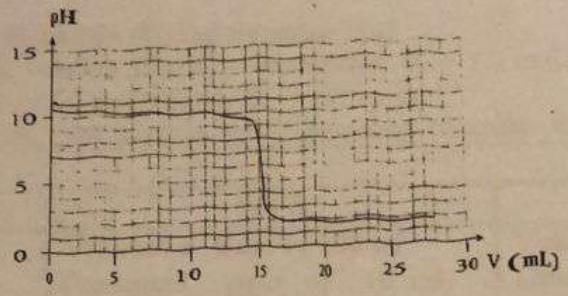
To ensure the indication of the label, titrate 10 mL of the solution (S) thus prepared by using a solution of hydrochloric acid of concentration C_a = 0.05 mol.L^{-1}, in the presence of a suitable color indicator. The equivalence is reached for a volume of the added acid V_{aE} = 16.6 mL.



Curve a



Curve b



Curve c

Document 5

This exam includes three exercises inscribed on four pages numbered from 1 to 4.
The use of a non-programmable calculator is allowed.
Answer the following three exercises:

Exercise 1 (6 points) **Perchloric acid**

Perchloric acid is used to separate potassium from sodium, and in many laboratory tests and industrial processes.
On the label of a bottle of commercial solution (S_0) of perchloric acid $HC\ell O_4$, we read the following information:

percentage by mass of $HC\ell O_4$ in the solution: p %
molar mass of $HC\ell O_4$: $M(HC\ell O_4) = 100.5\ g.mol^{-1}$
density of solution : $\rho = 1.67\ g.mL^{-1}$
Document-1-

The aim of this exercise is to determine the percentage by mass of perchloric acid in the commercial solution (S_0).

Given: - The study is carried out at 25°C .
- The ion product of water $K_w = 1\times10^{-14}$ at 25°C.

1- Preparation of a solution (S) of perchloric acid

A solution (S) of perchloric acid ($H_3O^+ + C\ell O_4^-$) is prepared by diluting 290 times a commercial solution (S_0) of perchloric acid.

Choose, from document-2-, the convenient set used in the preparation of solution (S).

Set (1)	Set (2)	Set (3)
50 mL beaker 250 mL volumetric flask 5 mL graduated cylinder	50 mL beaker 250 mL volumetric flask 2 mL volumetric pipet	50 mL beaker 250 mL volumetric flask 2 mL graduated pipet
Document-2-		

2- Behavior of sodium hydroxide in water

Available in laboratory, a bottle of sodium hydroxide solution NaOH ($Na^+ + HO^-$) noted (S) of molar concentration $C_b = 6.31\times10^{-2}\ mol.L^{-1}$.
We measure the pH of solution (S), we find $pH_{(S)} = 12.8$

2.1. Calculate the molar concentration of hydroxide ions $[HO^-]$ in the solution (S).
2.2. Deduce that sodium hydroxide is a strong base.

3- pH-metric titration of perchloric acid

A volume $V_a = 10$ ml of solution (S) of perchloric acid, is placed in a beaker then distilled water is added to immerse the electrode of pH-meter. A pH-metric titration is realized by adding progressively into the beaker the solution (S') of sodium hydroxide NaOH of molar concentration $C_b = 6.31 \times 10^{-2}$ mol.L^{-1}. The volume of NaOH added to reach equivalence is $V_{b,E} = 6.4$ mL.

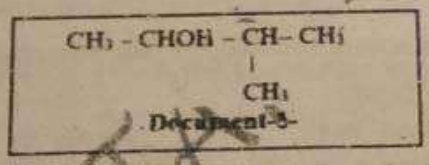
3.1. Write the net-equation of titration reaction.
3.2. Specify the value of pH at equivalence.
3.3. Show that the molar concentration (C_a) of perchloric acid in the solution (S) is equal to 4×10^{-2} mol.L^{-1}.
3.4. Deduce the percentage by mass of perchloric acid in the commercial solution (S0).
3.5. Determine the pH of the obtained solution after addition of 10 ml of basic solution NaOH.

Exercise 2 (7 points) — Esterification Reaction

Esters of general formula RCOOR' are very abundant in nature. Many of them have agreeable characteristic odor and contribute to natural or artificial tastes and flavors of certain fruits, plants, and candies.
The aim of this exercise is to study the preparation reaction of an ester (E).

1. Study of compound (A)

The condensed structural formula of monoalcohol (A) is given in **document-1-**.



Document-1-

1.1. Give the systematic name of (A). Indicate the class of this alcohol.

FOR LS

1.2. Show that (A) is a chiral molecule.
1.3. Represent, according to Cram, the two enantiomers of this alcohol.

FOR GS

1.2. Identify a positional isomer of (A).
1.3. Identify a skeletal isomer of (A).

2. Identification of compound (B)

Document-2- gives information about compound (B).

- (B) is a saturated, noncyclic and monofunctional organic compound of molecular formula $C_xH_yO_2$.
- The analysis of (B) gives the following percentages by mol:
  % C = 25% and % H = 50%

Document-2-

2.1. Show that the molecular formula of (B) is $C_4H_8O_2$. Deduce the possible families of (B).
2.2. When the compound (B) is dissolved in water, a solution of a pH clearly less than 7 is obtained. Identify (B).

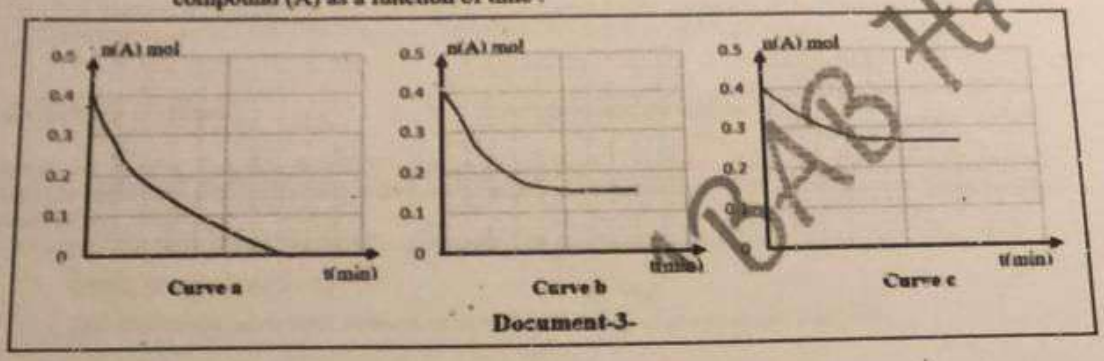
3. Synthesis of ester (E)

In order to synthesize (E), a mixture formed of $n_1 = 0.5$ mol of (B) and $n_2 = 0.4$ mol of (A) is heated to reflux.

3.1. Write ,using condensed structural formula , the equation of esterification reaction . List two of its charateristics.

3.2. Give the systematic name of ester (E).

3.3. Assuming that the esterification yield is 66.75 % .Choose , by justifying, from **document-3-** the curve that corresponds to the evolution of the number of moles of compound (A) as a function of time .



Document-3-

3.4. Determine the equilibrium constant of the reaction.

Exercise 3 (7 points) **Kinetic Study of a Slow Reaction**

A hydrochloric acid solution $HC\ell$ ($H_3O^+ + C\ell^-$) reacts with calcium carbonate $CaCO_3$ according to a slow and complete reaction as shown by the equation below:

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

In order to study the kinetic of this reaction, one introduces a mass m g of calcium carbonate in an Erlenmeyer flask.

At instant $t = 0$, a volume $V = 1L$ of a hydrochloric acid solution (S) HCl ($H_3O^+ + Cl^-$) of molar concentration $C = 1$ mol.L^{-1} is poured into the Erlenmeyer flask.

Using an appropriate method, the number of moles of carbon dioxide gas $n(CO_2)$ is determined at different instants t.

The results are grouped in the table of **Document-1**:

t (min)	10	20	30	40	60	80	100	120
n (CO_2) 10^{-2} mol	6.0	10	14	17.5	22.5	26.5	29.5	31.0

Document-1

Given:

- Molar mass of calcium carbonate is: $M(CaCO_3) = 100$ g.mol^{-1}
- The study is realized at a temperature $T = 25°C$.
- H_3O^+ is the only chemical species with acid character in the reacting system.

1- **Preliminary study**

At the end of the reaction, the pH of the obtained solution is: pH = 0.7

1.1. Deduce that $CaCO_3$ is the limiting reactant.

1.2. Show that at each instant t, the number of moles of CO_2 in mol $n(CO_2)_t$ and the pH of solution are related according to the following relation: $n(CO_2)_t = 0.5 - \frac{10^{-pH}}{2}$

1.3. Deduce whether t = 120 min represents the end of reaction time.

2- **Kinetic study**

2.1. Plot the curve that represents the change in the number of moles of carbon dioxide gas (CO_2) as afunction of time: $n(CO_2) = f(t)$ in the interval of time: [0 -120 min].

Take the following scale:

1 cm for 10 min in abscissa and 1 cm for 2.5×10^{-2} mol in ordinate.

2.2. Determine the average rate of formation of CO_2 between the times t_1=10 min and the time t_2 = 80 min. Deduce the average rate of disappearance of H_3O^+ between t_1 and t_2.

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

2.4. The experiment realized at the beginning of the exercise is carried out again but with only modification: the flask is placed in a water bath at temperature T = 5°C.

Choose, with justification, the correct answer:

2.4.1. The number of moles of CO_2 at instant t = 40 min is:

a) $n(CO_2) > 17.5\times10^{-2}$ mol ; b) $n(CO_2) < 17.5\times 10^{-2}$mol ; c) $n(CO_2) = 17.5\times 10^{-2}$ mol

2.4.2. the half-life time ($t_{1/2}$) of this reaction:

a) decreases b) increases c) remains the same

Revision

Trial- 1

Exercise 1

Study of a disproportionation reaction

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

$$2H_2O_{2(aq)} \rightarrow 2H_2O_{(l)} + O_{2(g)} \quad (1)$$

Commercially, hydrogen peroxide is available in an opaque bottle to prevent light from favoring the previous chemical transformation. The flask used in this study is marked as follows :

"10-Volume Hydrogen Peroxide". This indication is called the titer of hydrogen peroxide.

By definition, the titer is the volume of oxygen (expressed in liters) released by one liter of aqueous hydrogen peroxide solution according to reaction (1) under standard conditions of temperature and pressure (V_m = 24 L.mol^{-1}). It will be considered as a first approximation that the conditions of the experiment can be identical to normal conditions.

Document 1

Calculation of the expected value of the concentration of hydrogen peroxide

Before carrying the kinetic follow-up of the disproportionation reaction, we want to check the given indication in the flask concerning the titer of the commercial hydrogen peroxide solution used.

1.1. According to the definition of titer given in **document-1**, what volume of oxygen $V_{(O_2)}$ is liberated by a volume V = 1.00 L of the commercial solution during the disproportionation of hydrogen peroxide?

1.2. Deduce the amount of matter (in mol) of oxygen formed during this transformation.

1.3. The preceding transformation is considered complete, verify that the concentration of Hydrogen peroxide noted $[H_2O_2]_{theo}$ is 8.4×10^{-1} mol.L^{-1}.

2. **Determination of the real value of the concentration of hydrogen peroxide**

To verify the value of the preceding concentration, we carry the titration of a volume V_0 = 10.0 mL of this solution by an acidified potassium permanganate solution of concentration $C_1 = 2.0 \times 10^{-1}$ mol.L^{-1}. The volume of potassium permanganate solution added to reach the equivalence is V_{eq} = 14.6 mL.

The equation of the titration reaction is the following :

$$2MnO^-_{4(aq)} + 5H_2O_{2(aq)} + 6H_3O^+_{(aq)} \rightarrow 2Mn^{2+}_{(aq)} + 5O_{2(g)} + 14H_2O \quad (2)$$

2.1. Knowing that, the permanganate ion $MnO_{4\,(aq)}^-$ is purple in aqueous solution. How the equivalence is detected?

2.2. Show that at initial instant we have : $[H_2O_2]_0 = 7.3 \times 10^{-1}$ mol.L^{-1}.

2.3. Compare the obtained value to the theoretical value. How can we explain the discard in concentration, apart from handling errors?

3. **Kinetic study of the disproportionation reaction**

The disproportionation of hydrogen peroxide is a slow reaction, but it can be accelerated by using for example iron (III) $Fe^{3+}_{(aq)}$ ions present in a solution of iron (III) chloride or a platinum wire.

The studied transformation is catalyzed by iron (III) ions. We mix 10.0 mL of the commercial solution with 85 mL of distilled water. At the instant t = 0, 5 mL of an iron (III) chloride solution are introduced into the system. After a specified time, 10.0 mL of the reaction mixture is taken and poured into an ice-water beaker. The contents of the beaker are then titrated with a solution of potassium permanganate in order to determine the concentration of hydrogen peroxide present in the reaction medium. The results are grouped in the table of **document 2 :**

t (min)	0	5	10	20	30	35
$[H_2O_2] \times 10^{-2}$ mol.L^{-1}	7.3	5.25	4.2	2.35	1.21	0.90

Document 2

3.1. Establish at each instant t of the reaction the relation between the concentration of hydrogen peroxide in the beaker $[H_2O_2]_t$ and the volume of oxygen liberated $V_{(O_2)}$ in mL.

3.2. Plot by referring to **document 2** the curve $[H_2O_2] = f(t)$.

3.3. Define the instantaneous rate of disappearance of H_2O_2 at a given instant t.

3.4. By a physical appropriate method, we determine the rate of disappearance of H_2O_2 at 3 different instants. Match each rate to its time.

time:	rate:
a. t = 0	i. $r = 1.2 \times 10^{-3}$ mol.L^{-1}.min^{-1}
b. t = 15 min	ii. $r = 8.6 \times 10^{-3}$ mol.L^{-1}.min^{-1}
c. t = 30 min	iii. $r = 2.9 \times 10^{-3}$ mol.L^{-1} min^{-1}

3.5. Specify the kinetic factor responsible for the evolution of the rate of disappearance of H_2O_2 during time.

3.6. Determine $t_{1/2}$.

3.7. If we repeat the same experiment without catalyst. Plot by justifying the curve $[H_2O_2] = g(t)$.

3.8. We repeat the same experiment at higher temperature T' > T. Explain graphically how the rate of disappearance of H_2O_2 varies with time.

4) Choose the correct statement that explains the effect of dilution on the dissociate molecules of a weak acid.
   a) Dilution increases the percent of dissociated molecules of a weak acid.
   b) Dilution decreases the percent of dissociated molecules of a weak acid.

C) Reaction between different couples

Consider the two conjugate acid – base pairs

pK_a (C_6H_5COOH / $C_6H_5COO^-$) = 4.16 and pK_a (NH_4^+/NH_3) = 9.2

1) Arrange the two couples on a pK_a axis
2) Between which species of these two pairs is there a possibility for a reaction? Write the equation of this reaction.
3) Determine the reaction constant K_R. Draw a conclusion.

Exercise 16

Ammonia

A) Acid-base properties of ammonia

5×10^{-3} mol of ammonia gas NH_3 is dissolved in 100mL of distilled water. A solution (S) of pH = 10.9 is obtained.

1) Calculate the concentration of ammonia solution.
2) Show that ammonia is a weak base.
3) Write the equation of the reaction of ammonia with water.
4) Determine the degree of transformation of ammonia.
5) Show that pK_a NH_4^+/NH_3 = 9.1.

B) Effect of dilution on the pH of ammonia

10mL of the above solution is diluted 10 times, the % of transformation of ammonia after dilution is 5.63 %.

1) Determine the pH' of the diluted solution.
2) Describe the effect of dilution on the pH of ammonia.

C) Reaction between different couples

50mL of the diluted ammonia solution is mixed with 100mL of hydrochloric acid solution of concentration 10^{-3} mol/L.

1) Place on a pK_a axis the different couples.
2) Write the equation of the predominant reaction.
3) Determine the constant K_R of the reaction. Deduce that the reaction is complete.
4) Determine the pH of the resulting solution.

Exercise: 17 **Benzoic acid and Sodium benzoate (food preservatives)**

Benzoic acid and Sodium benzoate are food preservatives used particularly in refreshing drinks of type soda. Benzoic acid is of formula C_6H_5COOH while Sodium benzoate of formula C_6H_5COONa. The solubility of benzoic acid at 25°C is 2.5 g/L.

Given: pK_a ($C_6H_5COOH/C_6H_5COO^-$) = 4.2 pK_a $H_3O^+/H_2O = 0$ $pK_a = H_2O/OH^- = 14$

$M(C_6H_5COOH) = 122$ g/mol

A) Benzoic acid (a weak acid)

Consider a saturated solution of benzoic acid noted as (S).

1) Show that the concentration of (S) is 2×10^{-2} mol / L.
2) Write the equation of the reaction of benzoic acid and water.
3) Determine the pH of the benzoic acid solution (S).
4) Calculate the % of transformation for the solution (S).
5) Determine for solution (S) the value of the ratio $\frac{[C_6H_5COO^-]}{[C_6H_5COOH]}$.

B) Reaction between benzoic acid and sodium hydroxide

Into a beaker we introduce 50mL of the above solution of benzoic acid and 50mL of sodium hydroxide of C = 0.01 mol / L.

1) Place on a pK_a scale the acid-base couples needed in the above mixture.
2) Write the equation of the predominant reaction.
3) Determine the constant Kr of the reaction.
4) Show that the reaction is complete.
5) Calculate the pH of the resulting mixture.

Exercise: 18 **Strength of weak acids and weak bases**

Given the following conjugate acid-base pairs and the pK_a of each pair.

pK_a $H_3O^+/H_2O = 0$ pK_a $CH_3COOH/CH_3COO^- = 4.8$

$pK_a HClO/ClO^- = 8.3$ pK_a $NH_4^+/NH_3 = 9.2$ pK_a $H_2O/OH^- = 14$

Five beakers named from (A) to (E) each contains an aqueous solution of the chemical compounds given in the table below.

The solutions have the same concentration.

Beakers	(A)	(B)	(C)
Compound present in the beaker	CH_3COOH Acetic Acid	HClO Hypochlorous Acid	KOH Potassium Hydroxide
Beakers	(D)	(E)	
Compound	NH_3 Ammonia	HBr Hydrobromic Acid	

A) <u>Strength of acids and bases</u>

1) Arrange the pH of the five solutions in an ascending order.
2) **The pH of solution (B) has a value of 5.**
   a) Write the equation of the reaction of (B) with water.
   b) Show that the molar concentration C_0 is 2×10^{-2} mol/L.

B) <u>Effect of dilution on pH and α of a weak base</u>

Now 10mL of (D) is taken, distilled water is added until we obtain a solution (D') of volume V = 100mL.

1) Write the equation of the reaction between (D) and water.
2) Complete the values missing in the table below

Solution	(D)	(D')
pH	10.75	?
α	0.028	?

3) Deduce the effect of dilution on the pH and α of a weak base.

C) <u>Acid-base reaction</u>

150mL of (A) is mixed with 50mL of potassium hydroxide (solution C)

1) Place the couples of the involved available species on a pK_a axis.
2) Write the equation of the reaction.
3) Show that the above reaction is complete.
4) Determine the pH of the resulting solution.

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Bekaa Youth Education Center
Cycle: IV
Grade: L1-G1
Name: Mohammed S.

Subject: Chemistry
Duration: 90 minutes
Mark: /16
Date: 8/1/2024

Exercise 1 (8 points) **Properties of an Alcohol**

Alcohols are products with a great industrial and commercial importance. They undergo many and diverse chemical reactions and are used in the synthesis of many compounds such as esters. The aim of this exercise is to study the chemical properties of the alcohol (A) and its reaction with methanoic acid.

Given: Molar mass in $g.mol^{-1}$: $M_{(H)} = 1$; $M_{(C)} = 12$; $M_{(O)} = 16$.

1. Chemical properties of the Alcohol (A)

Available is a saturated and non-cyclic mono-alcohol denoted (A). The quantitative analysis of alcohol (A) shows that the percentage by mass of oxygen is %O = 21.62% .

1.1. Show that the molecular formula of the alcohol (A) is $C_4H_{10}O$.

1.2. The condensed structural formula of the alcohol (A) is:

$$CH_3 - CH_2 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_3$$

1.2.1. Indicate the class of alcohol (A).

1.2.2. Give its systematic name.

1.2.3. Write the condensed structural formulas of the other three alcohol isomers of alcohol (A).

1.2.4. Justify that the molecule of the alcohol (A) is chiral.

1.2.5. Represent, according to Cram, the two enantiomers of alcohol (A).

1.3. The mild oxidation of the alcohol (A) by a solution of acidified potassium permanganate leads to the formation of an organic compound (B).

Correct the following propositions: "The family of (B) is aldehyde".

2. Reaction of the Alcohol (A) With Methanoic Acid

A mixture of 0.2 mol of alcohol (A) and 0.2 mol of methanoic acid is heated to reflux, in the presence of few drops of concentrated sulfuric acid as a catalyst.

The esterification reaction is represented by the following equation:

Methanoic acid + alcohol (A) ⇌ ester (E) + water

At an instant of time t, the equilibrium is reached. The number of moles of methanoic acid remained at equilibrium is $n_{(acid)} = 0.08$ mol.

2.1. Write, using the condensed structural formulas, the equation of this esterification reaction.

2.2. Give the characteristics of the above reaction.

2.3. Determine the number of moles of each constituent of the reacting mixture at equilibrium.

2.4. Deduce the value of the equilibrium constant Kc.

2.5. The same experiment is carried out again with only one change: "without the addition of concentrated sulfuric acid". The equilibrium state is reached at an instant of time t'. **Choose** the correct answer. Justify.

a. $t > t'$ **b.** $t = t'$ **c.** $t < t'$

II. Esterification reaction

The pure ethanoic acid CH_3-COOH reacts with pure methanol CH_3-OH to form the ester methyl ethanoate CH_3-COO-CH_3 and water according to a slow and limited esterification reaction represented by the following equation :

$$CH_3 - COOH + CH_3 - OH \rightleftarrows CH_3 - COO - CH_3 + H_2O$$

	Formula	M ($g.mol^{-1}$)
Ethanoic acid	$CH_3 - COOH$	60
Methanol	$CH_3 - OH$	32

Document 1

- Concentrated sulfuric acid is a dehydrating substance if used in large mount in the esterification reaction.
- Concentrated sulfuric acid is a catalyst if used in a small amount in the esterification reaction.
- At 100 °C, $K_c = 4$.

Document 2

1. **Study of the reaction mixture**

30 g of ethanoic acid are mixed in a flask with 16 g of methanol and then the reaction mixture is heated for a time t at a temperature to 100 °C. A quantity x of the ester is formed.

1.1. Express the number of mole of each constituent at time t in terms of x.

1.2. An appropriate titration of the remaining acid shows that 0.25 mol of acid remains at time t. Verify if a chemical equilibrium state is attained at this instant of time.

1.3. Specify the effect of heating on the yield of the reaction.

2. **Experimental study**

A mixture of ethanoic acid and methanol when heated to 100 °C in the presence of a few drops of concentrated sulfuric acid, leads to the formation of 0.33 mol of ester after a few hours.

2.1. Show in this case that the chemical equilibrium is reached.

2.2. Deduce the coefficient of conversion of the acid at equilibrium.

2.3. Determine the yield Y of this esterification.

2.4. In the case where a large quantity of sulfuric acid is used. Indicate by justifying which of the following three proposals is correct :

a. $Y' < Y$ **b.** $Y' = Y$ **c.** $Y' > Y$

2.5. In the case where twice of the initial quantity of reactants is used, how will the yield of the esterification reaction be affected? Justify.

3. **Influence of concentration and catalyst at a constant temperature** 27 °C :

3.1. The same experiment as in part 1 is repeated with only one change, we introduce an amount of 1 mol of NO_2 with 1.2 mol of N_2O_4. Choose by justifying the correct answer :

a. $\alpha' < \alpha$ b. $\alpha' = \alpha$ c. $\alpha' > \alpha$.

3.2. To increase the yield of the reaction, a student suggests the following :

a. Eliminate NO_2 by an appropriate method.

b. Use an appropriate catalyst.

For each suggestion, indicate if it is correct or wrong. Justify.

43. Synthesis of Nitrosyl Bromide NOBr

The synthesis of nitrosyl bromide NOBr is schematized by the equation :

$$2\,NO_{(g)} + Br_{2(g)} \rightleftarrows 2\,NOBr_{(g)}$$

1. **Equilibrium study :**

In a bulb of volume 15 L, we introduce 0.6 mol of nitrogen monoxide **NO** and 0.3 mol of bromine gas Br_2 at a temperature $\Theta_1 = 700°C$.

At equilibrium the total number of moles of gaseous mixture is 0.85 mol.

1.1. Complete the following table :

	2 NO(g)	+	Br_2(g)	⇄	2 NOBr(g)
Initial state	0.6		0.3		0
Equilibrium state	0.6 - 2x		0.3 - x		2x

x represents the number of moles of NOBr obtained at equilibrium

1.2. Calculate the number of moles of each gas at equilibrium.

1.3. Deduce the equilibrium constant K_{c_1} at Θ_1.

2. **Effect of temperature :**

At a temperature $\Theta_2 = 800°C$, a new equilibrium state is established where the new molar composition of gaseous mixture is the following : 0.32 mol of nitrogen monoxide, 0.16 mol of bromine and 0.28 mol of nitrosyl bromide. (V and P are constant).

2.1. Explain in which direction the equilibrium is shifted

2.2. Specify whether the synthesis of NOBr is exothermic or endothermic.

2.3. Calculate the value of the equilibrium constant K_{c_2} at the temperature Θ_2.

3. **Shifting Equilibria :**

Under the same conditions of V and P, we consider a new mixture formed of 0.4 mol of NO ; 0.2 mol of Br_2 and 0.4 mol of NOBr at the temperature $\Theta_2 = 800$ °C.

3.1. Choose from the following values the one corresponds to the quotient Q :

a. 71.7 b. 75 c. 57

Justify your answer.

3.2. Does the new mixture reach equilibrium? If not, Specify in which direction must be shifted to reach equilibrium?

Exercise 7 **Catalytic reactions of Alcohols**

A saturated mono alcohol (A): C_xH_yO has the following mass percent composition:

% H = 13.51 % **% O = 21.62 %**

A) Molecular formula and Isomerism

1) Show that the molecular formula of (A) is $C_4H_{10}O$.
2) Write the condensed structural formula of all possible isomers of compound (A). Name each one.

B) Dehydrogenation Reaction:

The two unbranched isomers undergo dehydrogenation reaction at a temperature of 300°C and in absence of oxygen using Cu as a catalyst.

1) Write using condensed structural formulas the equations of the reactions that took place.
2) Indicate the family and the name of the organic compounds obtained.
3) The above reactions show the mild oxidation of an alcohol. Define mild oxidation.

C) Esterfication reaction

A mixture of 0.2 mol of ethanoic acid and a volume V = 20 mL of the unbranched primary isomer of alcohol (A) is heated in presence of few drops of concentrated sulfuric acid until having a constant quantity of ester. This quantity is 0.13mol.

1) Write the equation of this reaction. Name the obtained organic compound.
2) Verify that the initial reactants are in equimolar amounts.
3) Calculate the equilibrium constant K_c of the esterfication reaction.
4) Determine the % yield of the esterfication reaction.

Given: $\rho_{(alcohol)}$: 0.74 g/mL C = 12 H = 1 O = 16 g/mol

Exercise: 8 **From an Alcohol to Carbonyl compounds**

The complete combustion of 2.2g of an alcohol (A) of formula C_xH_yO gives 5.5g of carbon dioxide gas and 2.7g of water vapor.

A) Molecular formula and Isomerism

1) Show that the molecular formula of (A) is $C_5H_{12}O$.
2) Write all possible isomers of (A).

B) Yield of a reaction

0.2 mol of an isomer (B) of the above alcohol is treated with excess phosphorus penta chloride to give 20g of 1 – chloro – 2 – methyl butane as one of the products.

1) Deduce the condensed structural formula and the class of (B).
2) Write the equation of the reaction.
3) Determine the % yield of the reaction.

2) Indicate the family and the name of the organic compound (C) obtained.
3) Draw a conclusion about the choice of catalysis in the dehydrogenation reaction and in the dehydration reaction of alcohol (A).

C) Esterfication reaction

An equimolar mixture of 1 mol of the two compounds (A) and (B) react in presence of few drops of sulfuric acid until equilibrium is attained.

1) Write the equation of the esterfication reaction. Give its characteristics.
2) Name the ester (E) formed.
3) Indicate the role of sulfuric acid used in the above reaction.
4) Calculate the % yield of the esterification reaction if the equilibrium constant of the above reaction is $K_c = 4.12$.
5) Suggest two methods to increase the yield of the above reaction.

Given: C = 12 H = 1 O = 16 g/mol

Exercise: 10 **Organic compounds**

Given the following set of compounds:

(A): $CH_3 - CH_2 - CH_2 - CH_2 - OH$ (B): $CH_3CH_2 - CH_2 - CHO$ Carbonyl group

(C): $CH_3 - CH_2 - \overset{\overset{O}{\|}}{C} - CH_3$ (D): $CH_3 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} - OH$ Hydroxyl group

(E): $CH_3 - CH_2 - \underset{\underset{OH}{|}}{CH} - CH_3$ (F): $CH_3 - CH_2 - CH_2 - COOH$

A) Isomers and functional groups

1) Give the systematic name of each of the above compounds and circle the corresponding functional groups.
2) Specify the isomerism type of each set of the two compounds (A, E), (B, C) and (E, D).

B) Organic reactions on different compounds

1) Write the equation of the reaction to prepare (B) starting from (A).
2) Write the equation of the reaction to prepare (C) starting from (E).
3) Write the equation of the reaction to prepare (F) starting from (A).

C) **Oxidation of alcohols by potassium permanganate.**

10 mL of each of the alcohols (A), (D) and (E) are poured in three tubes then treated with excess potassium permanganate solution $KMnO_4$. The obtained results are given in the table below:

Tubes	Results of the reaction with $KMnO_4$
1	Formation of compound (F)
2	Formation of compound (C)
3	Negative result

1) Analyze the results in the above table.
2) Identify the content of each tube.

D) **Synthesis reaction**

A volume V_1 = 20 mL of (A) and volume V_2 of (F) are introduced into a round bottom flask, 2 mL of sulfuric acid is added into the flask. The mixture is heated for about 20 min. An ester of mass 25g is obtained.

1) Write the equation of the esterification reaction.
2) Indicate the purpose of heating.
3) Determine the volume V_2 of (F) so that the reactants are in stochiometric proportion.
4) Calculate the yield of the esterification reaction.

Given: $\rho(A) = 0.81$ g/ml $\quad \rho(F) = 0.95$ g/ml

$C = 12 \quad H = 1 \quad O = 16$ g/mol

Exercise: 11

Esterification Reaction

For an equimolar amount of a mono alcohol and a mono carboxylic acid the % yield of the reaction at equilibrium is as follows:

Class of alcohol	Primary alcohol	Secondary alcohol	Tertiary alcohol
% yield	67 %	60 %	5 %

2.85 ml of an alcohol (A) is introduced into a round bottom flask with propanoic acid) to give an ester (E): $C_nH_{2n}O_2$ of molar mass 116 g/mol as shown in the reaction:

$$(A) + (B) \rightleftarrows (E) + H_2O$$

ven: The initial mixture in equimolar amounts.

Molecular formula of (E) and (A):

1) Determine the molecular formula of ester (E).
2) Show that the molecular formula of (A) is C_3H_8O.

B) Results of the esterification reaction:

1) Determine the number of moles of each of alcohol (A) and the acid (B) initially introduced if $f_{(A)} = 0.84$ g/ml .

The acid left in the flask is titrated and the results are recorded in the following table:

t (sec)	0	10	20	30	40	80	130	150
n acid (mol)	0.6	0.48	0.39	0.33	0.28	0.22	0.2	0.2

2) Plot the curve n (acid) = f (t)
Take the scale: 1 cm → 0.1 mol 1 cm → 20 sec

3) Determine the composition of the mixture at equilibrium.

4) Determine the % yield of the reaction.

5) Identify the alcohol (A).

6) Write the equation of the esterification reaction. Name the ester obtained.

C) Catalytic reactions of alcohol (A):

The primary isomer of alcohol (A) undergoes catalytic oxidation in presence of oxygen and Cu as a catalyst to give two organic compounds:

$$A + \frac{1}{2}O_2 \rightarrow (B) \qquad A + O_2 \rightarrow (C)$$

1) Copy and complete the above reactions using condensed structural formula.

2) Name the organic compounds (B) and (C) obtained.

Exercise: 12

Oxidation of an Alcohol

6 g of a saturated mono alcohol (A) reacts with sodium to give hydrogen gas of volum 1.12 L at S.T.P. according to the following reaction:

$$R\text{-}OH + Na \rightarrow R\text{-}ONa + \tfrac{1}{2} H_2$$

A) Molecular formula and isomerism

1) Determine the molecular formula of (A).

2) Write all the possible isomers of (A).

B) Identification of Alcohol (A)

3 g of the given alcohol is treated with excess thionyl chloride to 1-chloro propane as one of the products.

1) Write the condensed structural formula of the product obtained. Deduce th alcohol (A).

2) Write the equation of the reaction using condensed structural formulas.

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Cycle: IV
Grade: LS-GS
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77.5/80

Subject: Chemistry
Duration: 80 minutes
Mark: / 20
Date: 8/1/2024

Exercise 1(10 points) **Identification Of Organic Compounds**

In an organic chemistry laboratory, we find four bottles numbered A, B, C and D. Each bottle contains one organic compound represented in document-1-.
The objective of this exercise is to identify the four organic compounds.

Given: $M(C) = 12\ g.mol^{-1}$; $M(H) = 1\ g.mol^{-1}$; $M(O) = 16\ g.mol^{-1}$

A	B	C	D
Saturated noncyclic monoalcohol % by mass of O=26.67%	2-methyl-2-propanol	Propanal	Propanone

Document-1

1- Identification Of Organic Compound (A) :

1.1. Referring to document-1-, determine the molecular formula of (A).

1.2. Identify (A) Knowing that it is a secondary alcohol.

2- Distinctive Properties of Organic Compounds.

2.1. Write the condensed structural formulas of compounds (B), (C) and (D).

2.2. Indicate the family to which belongs each of the compounds (B), (C) and (D).

2.3. Circle and name the functional groups of the compound (B) and (C).

2.4. Choose the correct answer: (C) and (D) are:

a- Positional isomers **b-** Functional isomers **c-** Skeletal isomers

3- Identification test of Organic Compounds

The four compounds of document -1- are represented in a random order from 1 to 4. **Document 2** represents chemical test realized in order to identify each compound

Compound	Test 1 with DNPH	Test 2 with Schiff s reagent	Test 3: Mild oxidation with $KMnO_4$ solution
C 1	Yellow-orange precipitate	Pink color	Decolorization of purple color
A 2	Negative	Negative	Decolorization of purple color
D 3	Yellow-orange precipitate	Negative	Persistence of purpl color
B 4	Negative	Negative	Negative

Document 2

Referring to chemical tests obtained in document 2, match with justification the compounds A,B. and D to 1,2,3 and 4.

Exercise 2(10points) **Study of An Esterification Reaction**

Esters are very abundant in nature. The simplest form is commonly called fruit esters. The objective of this exercise is to study the characteristics and the yield of esterification reaction.

1. **Study of Equilibrium State:**

At the instant of time t = 0, a quantity of 0.5 mol of carboxylic acid (A) is mixed with 0.5 mol of alcohol (B) and the mixture is heated to reflux at constant temperature **T1**. The equation of the esterification reaction is:

Carboxylic acid (A) + alcohol (B) ⇌ ester + water

- Let α be the degree of conversion of carboxylic acid (A) in the round bottom flask at equilibrium.
- Starting from initial equimolar mixture of carboxylic acid and alcohol, the yield of esterification reaction at equilibrium is equal to 67%
- After a certain time (t_1), the number of acid remaining in the solution is equal to 0.22 mol.

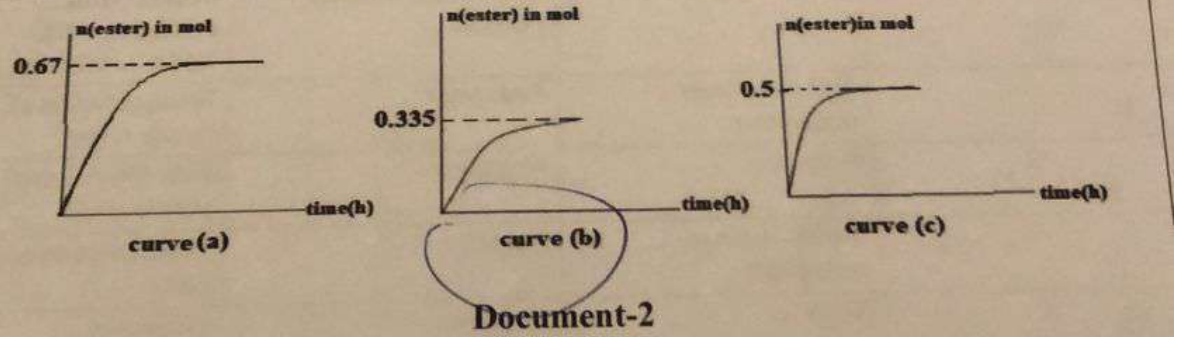
Document -1

1.1. Complete the following table of progress in terms of α.

	Carboxylic acid	alcohol	ester	water
Initial state				
Equilibrium state				

1.2. Show that the equilibrium constant Kc is expressed as: $K_c=\frac{\alpha^2}{(1-\alpha)^2}$

1.3. During the reaction, we study the variation in the number of moles of the ester formed as a function of time. The variation is represented by one of the three graphs given in document-2:



Document-2

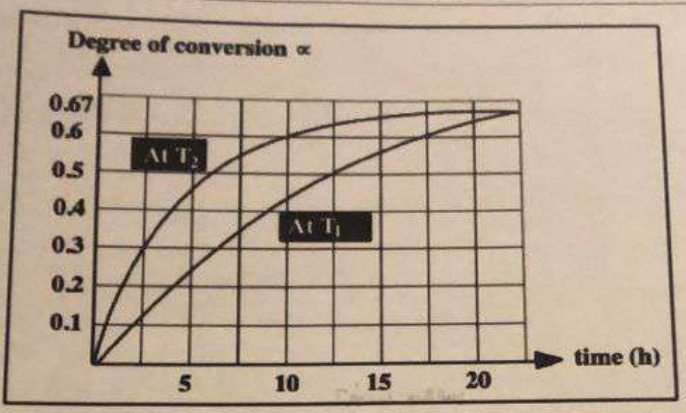
1.3.1. Indicate among the three graphs, the one that corresponds to the study carried out. Justify yo answer.

1.3.2. Determine the value of α .Deduce Kc.

1.3.3. Specify whether the reactional system is at equilibrium at t_1 .

2. Characteristics of esterification reaction:

An experiment 2 is performed with only one modification from experiment 1: the temperature is changed from T1 to T2. Document-3 shows the variation of the degree of conversion of carboxylic acid (A) as a function of time in the two experiments.



Document-3

2.1. Verify, using **document-3**, that the esterification reaction is incomplete and athermic.

2.2. Compare T1 and T2. Justify your answer.

2.3. Choose, with justification, the equilibrium constant Kc2 at temperature T2 is:

a- Equal to Kc1 **b-** More than Kc1 **c-** Less than Kc1

2.4. A student of class G12 suggest to increase the temperature of reacting mixture to increase the yield of esterification reaction. Specify whether the proposition of the student is true.

3. Yield of Esterification reaction

In order to increase the yield of the reaction, the two experiments of document 4 are suggested:

	Carboxylic acid	Alcohol	Sulfuric acid
Experiment 3	1 mol	1 mol	Few drops
Experiment 4	1 mol	2.5 mol	----------

Specify whether the yield increases in each experiment of **document-4**.

Exercise: 1 **Javelle water**

The aim of this exercise is to study the acid-base properties of Javelle water.

The acid base couple relative to water is $HClO/ClO^-$

A) Acid-base properties of Javelle water

The pH of a 10^{-2} mol/L of Javelle water is 10.15

1) Write the equation of the acid-base reaction between hypochlorite ion and water.
2) Based on bronsted definition, specify if water is an acid or a base in this reaction.
3) Show that Javelle water is a weak base.
4) Determine the degree of transformation of hypochlorite in water.
5) Using Handerson relation, prove that the pK_a of the couple $HClO/ClO^-$ is 8.3.

B) Reaction between javelle water and hydrochloric acid

A hydrochloric acid solution of concentration $C_2 = 10^{-2}$ mol/L is poured into a beaker containing a certain volume of the above basic solution.

1) Place on a pK_a axis the conjugate acid-base pairs.
2) Write the equation of the predominant reaction.
3) Verify that the reaction is total.

C) Dangers of mixing Javelle water with hydrochloric acid

The pH of a sample of Javelle water is made equal to 2 for this value of pH a reaction takes place according to the following equation:

$$HClO + Cl^- + H_3O^+ \rightleftarrows Cl_2 + 2H_2O$$

1) Identify the predominant species of the couple in Javel water of pH = 2.
2) On the label of a detergent containing hydrochloric acid "Don't mix with Javelle water". Justify this recommendation.

Exercise: 2 **Carboxylic acid and its derivatives**

1.32 g of a carboxylic acid (A) is dissolved in water, a solution (S) is obtained of V = 100 mL. 20 mL of solution (S) is titrated by a solution of sodium hydroxide of concentration C = 0.3 mol/L. Equivalence is detected when 10 mL of the basic solution is added.

A) Identification of (A)

1) Write the equation of the titration reaction.
2) Show that the molecular formula of (A) is $C_4H_8O_2$.

3) Knowing that the carbon chain of (A) is non branched, identify (A).

B) Formation of derivatives of acid (A)

1) Acid (A) reacts with thionyl chloride to give an acid derivative (C)
Write the equation of the reaction. Give the systematic name of (C).

2) Acid (A) is heated in presence of a dehydrating agent P_2O_5 to give an acid derivative (D). Write the equation of the reaction. Give the systematic name of (D).

C) Synthesis of Ethyl butanoate

Ethyl butanoate is an ester which has the odor of pine apple. We carry out a mixture of 13.2 g of (A) and 8.75 mL of ethanol and few drops of sulfuric acid. The mixture is heated, after few hours equilibrium is attained where $\frac{2}{3}$ of (A) has reacted.

1) Write the equation of the formation of ethyl butanoate.
2) Show that the initial reactants are in equimolar amounts.
3) Calculate the equilibrium constant K_C of the reaction.
4) Determine the % yield of the above reaction.
5) Give the name and write the condensed structural formula of two derivatives of acid (A) that could react with ethanol in order to synthesize (E).
6) Write the equation of the reaction of ethanol with a convenient derivative to obtain (E). What can be said about the yield of the above reaction?

Given: $\rho_{(alcohol)} = 0.79$ g/ml C = 12 H = 1 O = 16 g/mol

Exercise: 3 — **Coconut Oil** — Only 1/3

Coconut oil is mainly formed of a triglyceride of Lauric acid. This triglyceride is obtained by the reaction between the saturated fatty acid (Lauric acid) and the alcohol glycerol.

A) Molecular formula of Lauric acid

The analysis of Lauric acid $C_xH_yO_2$ gave the following mass composition:

% C = 72 % % H = 12 % % O = 16 %

1) Show that the molecular formula of Lauric acid is $C_{12}H_{24}O_2$.
2) Write the condensed structural formula of Lauric acid.
3) Referring to the text, write the equation of formation of coconut oil.

5) Deduce how does the concentration of ethanoate ion [CH_3COO^-] varies with pH at constant temperature.

B) Making use of results.

1) Establish the relation between the rate of disappearance of OH^- ions and rate of formation of CH_3COO^- ions at given time.
2) The rate of disappearance of OH^- ions was measured at t = 10min and t = 20 min using an appropriate method. The following values are obtained 1.4×10^{-4}mol.L^{-1} min^{-1} and 1×10^{-3}mol.L^{-1} min^{-1}.
   a) Assign to each instant the corresponding value of this rate.
   b) Indicate the kinetic factor involved in this variation.
3) Determine graphically the half-life of the reaction.

Exercise: 3 **Organic Chemistry**

A) Molecular formula and Isomerism.

The analysis of an organic substance (A) containing the elements carbon, hydrogen and oxygen gives the following mass composition:

C = 64.864% **H = 13.513%** **O = 21.621%**

1) Show that the molecular formula of (A) is $C_4H_{10}O$, if its molar mass is 74g.mol^{-1}.
2) Knowing that (A) is an alcohol; give the condensed structural formula and the name of the isomers of (A).
3) **0.2mol of the tertiary isomer of (A) is treated with an excess phosphorus pentachloride (PCl_5) solution to give 0.15 mol of an organic compound.**
   a) Write the equation of the reaction.
   b) Calculate the % yield of the reaction.

B) Esterification reaction:

A mixture of 0.5mol of the branched primary isomer of the alcohol (A) and a volume 28.571mL of ethanoic acid (CH_3COOH) is heated, in the presence of some drops of concentrated H_2SO_4. After a certain time (t), the titration of the reaction mixture shows that it contains 0.165 mol of ethanoic acid.

1) Write the equation of the reaction between (A) and CH_3COOH.
2) Give the name and the characteristics of this reaction.
3) Show that the initial mixture is in equimolar amounts.
4) Determine the % yield of the above reaction.
5) Explain the influence of the following on the yield of ester:
   a) Using an excess acid b) Removing H_2SO_4

Results of the esterification reaction:

... moles of each of alcohol (A) and the acid (B) initially

Given: * Density of ethanoic acid = 1.05 g/ml

*** M (CH_3COOH) = 60g/mol**

*** M ($C_4H_{10}O$) = 74g/mol**

C) Other Esterification Reaction:

The experiment described above is realized again by mixing 0.5 mol of alcohol (A) and 0.75 mol of ethanoic acid. The yield of esterification reaction is 67 %.

1) Verify if a state of equilibrium is attained at instant (t).
2) Specify if the % yield of the reaction will change upon mixing 0.75 mol of (A) and 0.75 mol of ethanoic acid under same experimental conditions.
3) **A compound (D) contains chlorine atom can replace ethanoic acid to prepare the same ester.**
   a) Give the condensed structural formula and the name of (D).
   b) List the advantages of using compound (D).
   c) Write the equation of the reaction between (D) and (A).

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