مسابقة في مادة الكيمياء
المدة: ساعتان

الاسم:
الرقم:

This Exam Includes **Three Exercises**. It Is Inscribed on 4 Pages Numbered From **1** to **4**.
The Use of A Non-programmable Calculator Is Allowed.

Answer The Following Three Exercises:

First Exercise (7 points)
Synthesis of an Ester

The aim of this exercise is to recall the experimental conditions of the synthesis reaction of an ester and tospecify the conditions that lead to a better yield.

Given:

	Ethanoic acid	1-pentanol	ester
Molar mass in $g.mol^{-1}$	60	88	130
Density in $g.mL^{-1}$	1.05	0.81	-

I- Synthesis Reaction

It is required to synthesize an ester by a reaction between 1-pentanol and ethanoic acid.

1- Using condensed structural formulas, Write the equation of this synthesis reaction.

2- Give the name of the ester formed.

3- State two characteristics of this reaction.

II- Performing this Synthesis

A volume V_1 = 22 mL of 1-pentanol and volume V_2 mL of ethanoic acid are introduced into a round bottom flask; 1 mL of concentrated sulfuric acid and boiling stones are then added into the flask. This mixture is heated for about 30 min. A mass of 17g of ester is obtained after cooling and separation.

1- Indicate:
   a) The purpose of heating;
   b) The role of the concentrated sulfuric acid.

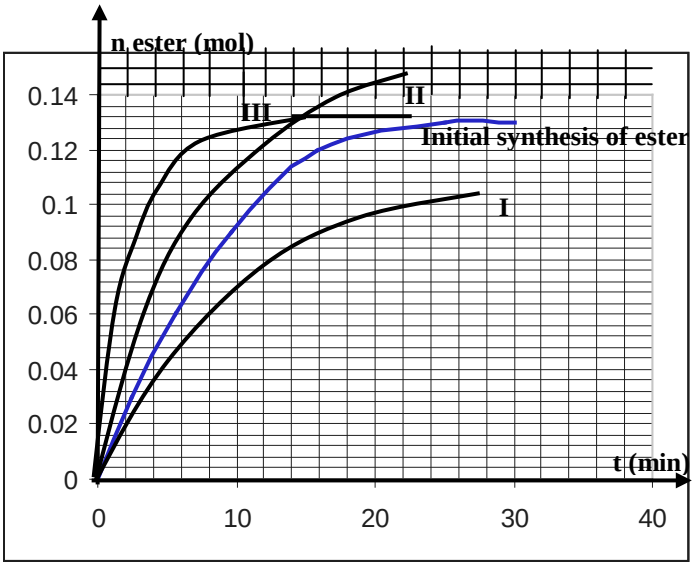
2- Determine the value of V_2 so that ethanoic acid and alcohol are in stoichiometric proportions.

3- Calculate the yield of this synthesis reaction.

III- Changing the Experimental Conditions of this Synthesis Reaction

1- Consider, below, the curves representing the variation of the number of moles of ester formed versus time, n = f(t), the synthesis is performed by changing, in each case, one of the experimental conditions:
   a. At a higher temperature;
   o Without the addition of 1 mL of concentrated sulfuric acid;

- Using an initial mixture of alcohol and excess ethanoic acid.



Associate, by justifying, each one of the curves I, II and III with the corresponding experimental condition.

2- A derivative of ethanioc acid replaces this acid in order to increase the yield of esterfication .
   a) Write the equation of this reaction.
   b) Give two of its characteristics.

Second Exercise (6.5 points)
Kinetic of the Decomposition of Hydrogen Peroxide H_2O_2

In this exercise, the aim is to study the kinetic of the decomposition reaction of H_2O_2 according the following equation: $2\ H_2O_{2\,(aq)} \rightarrow 2\ H_2O_{(l)} + O_{2\,(g)}$.

Given:
- The decomposition of H_2O_2 is spontaneous and complete.
- The gas O_2 is very slightly soluble in water at the temperature of this study.
- Iron (III) chloride $FeCl_3$, used as a catalyst in this reaction, is highly soluble in water.

I- Preparation of a Solution (S) of H_2O_2

A solution (S) of concentration C = 0.060 mol.L^{-1} is required to be prepared starting from an initial solution of H_2O_2 of concentration C_0 = 1.0 mol.L^{-1}.

Available Glassware :
- 100, 200 and 500 mL beakers.
- 5, 20 and 50 mL graduated cylinders.
- 100, 250 and 500 mL volumetric flasks.
- 5, 10 and 20 mL volumetric pipets.
- 5 and 10 mL graduated pipets.

Choose, from the above list, the needed glassware for the most precise preparation of solution (S). Taking into consideration that one take out of the initial solution is allowed.

II- Kinetic of the Decomposition Reaction of H_2O_2

A little amount of powdered iron (III) chloride is added, without any change in volume, into a round bottom flask containing 50 mL of solution (S) of concentration C = 0.060 mol.L^{-1}.
A convenient setup is connected to the flask in order to measure the pressure P of the gaseous phase in the flask.
The values of the pressure P, versus time t, are given in the following table:

P (10^2Pa)	1015	1038	1055	1070	1081	1093	1100	1104	1106
t (min)	0	5	10	15	20	30	40	50	60

In this study, O_2 produced by the decomposition of H_2O_2 occupies a volume V = 300 mL in the flask which is maintained at a constant temperature T = 300 K.

1- Consider :
n_t: quantity in moles of O_2 produced at each instant t;
P_0: initial pressure in the flask at t=0 before any decomposition of H_2O_2.
Show that $n_t = 1.2x10^{-7}(P - P_0)$; Take R = 8.3 m^3.Pa.mol^{-1}.K^{-1}.

2- Find the two missing numerical values in the following table:

n_t (10^{-4} mol)	-	2.8	4.8	6.6	7.9	9.4	-	10.7	10.9
t (min)	0	5	10	15	20	30	40	50	60

3- Plot, on a graph paper, the curve: $n_t = f(t)$.
Take the following scale: Abscissa: 1 cm for 5 min ; Ordinate: 1 cm for $1.0x10^{-4}$ mol.

4- Determine the rate of formation of O_2 at t = 20 min.

5- Identify the species present in the solution when the pressure P is equal to $1140x10^2$ Pa.

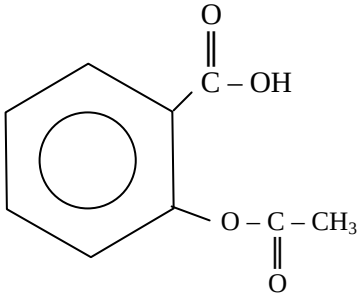
Third Exercise (6.5 points)
Formulation of Aspirin

The aim of this exercise is to compare two formulations of aspirin represented as HA.
Given:

Acid/base pair	H_3O^+/H_2O	HA/A^-	$CO_2,H_2O/HCO_3^-$	H_2O/HO^-
pKa	0	3.5	6.4	14

Species	CO_2	HA	A^-	(Na^+, HCO_3^-)
Solubility in water	slightly soluble	Very slightly soluble	Soluble	Highly soluble

Aspirin or acetylsalicylic acid, is a weak acid, of condensed structural formula:



It is sold in several formulations: simple aspirin, effervescent aspirin …
A tablet of simple aspirin is formed of binding big particles of acetylsalicylic acid. These big particles are absorbed very slowly by the blood system. HA is liposoluble. It is massively absorbed by the cells of the restricted area which is in direct contact with the tablet. This causes pain due to the irritation of the gastric mucous membrane.
On the other hand, a tablet of effervescent aspirin contains acetylsalicylic acid and sodium hydrogen carbonate (Na^+, HCO_3^-) in excess. These two ingredients are inert in a dry medium and reactive in an aqueous solution giving A^- ions. These A^- ions react in acidic medium to reproduce dispersed small crystals of HA.

I- Preparation of Aspirin

Aspirin is prepared from salicylic acid and compound (B) by an esterification reaction according to the following equation:
Salicylic acid + (B) → acetylsalicylic acid + acetic acid

1- Write the condensed structural formula of salicylic acid. Circle and name the two functional groups containing oxygen .
2- Write the condensed structural formula of compound (B) and name it.

II- Introducing a Tablet of Simple Aspirin in Water

A grinded tablet of simple aspirin is introduced into 100 mL of distilled water. The mixture is agitated; some solid acid particles remain suspended. The pH of the obtained solution is pH = 3.

1- Write the equation of the reaction between aspirin (HA) and water.
2- Calculate the ratio: $\frac{[A^-]}{[HA]}$

III- Introducing a Tablet of Effervescent Aspirin in Water

A grinded tablet of effervescent aspirin is introduced into 100 mL of distilled water. A gas is released vigorously. The pH of the obtained solution is equal to 6.2.

1- Place on a pK_a axis, the acid/base pairs involved when this tablet of aspirin is dissolved in water.
2- Write the equation of the reaction between the strongest acid and the strongest base.
3- Specify the predominant species of the pair HA/A^-.

IV- Absorption of Aspirin by the Stomach

A person drinks a solution of an effervescent aspirin tablet. This solution reaches his stomach, where the medium is considered like a solution of hydrochloric acid of pH = 1.

1- Write the equation of the reaction that reproduces aspirin HA.
2- Explain how effervescent formulation of aspirin facilitates the absorption of aspirin by the stoma

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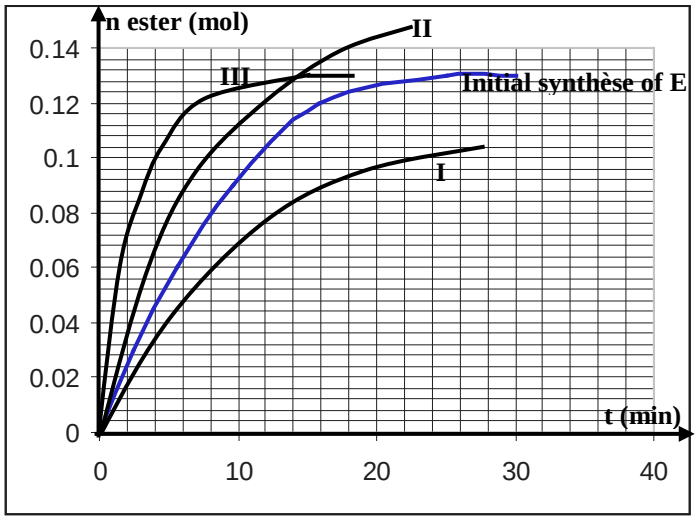
First Exercise (7 points)
Synthesis of an Ester

Expected Answer	Mark	Comment
I- <u>Esterification Reaction</u> 1- The equation of this reaction is: $CH_3 - C(=O) - OH + CH_3 - CH_2 - CH_2 - CH_2 - CH_2OH \rightleftharpoons CH_3 - C(=O) - O - CH_2 - CH_2 - CH_2 - CH_2 - CH_3 + H_2O$	0.75	
2- The ester formed is pentyl ethanoate.	0.25	
3- This reaction is slow, athermic and reversible.	2x0.25	
II- <u>Performing this Synthesis</u> 1- a) Heating makes the reaction faster (kinetic factor).	0.25	
b) Concentrated sulfuric acid is a catalyst which speeds up the rate of the reaction.	0.25	
2- The number of moles is: $n = \frac{m}{M} = \frac{dxV}{M}$. Equimolecular mixture means that n(acid)i = n(alcohol)i. We have then: $\frac{d(alcohol)xV_1}{M(alcohol)} = \frac{d(acid)xV_2}{M(acid)} = \frac{0.81x22}{88} = \frac{1.05xV_2}{60}$ = 0.20 mol. Hence: **V_2 = 11.57** mL.	1.25 1	
3- The yield is $y = \frac{n(ester)\,experimental}{n(ester)\,theoretical} x100$. n(ester) theoretical = n(alcohol)i $y = \frac{\frac{m(ester)obtained}{M(ester)}}{\frac{d(alcohol)xV_1}{M(alcool)}} x100 = \frac{\frac{17}{130}}{\frac{0.81x22}{88}} x100$ = **64.57** %	0.5	
III- <u>Changing the Experimental Conditions of this Synthesis</u> 1-	0.5	
o When the reaction is performed at higher temperature, it becomes faster and the equilibrium is reached with the same yield in a shorter time (curve III). o If the reaction is performed without the addition of sulfuric acid as a catalyst, the rate of the reaction decreases. Equilibrium will be reached in a longer time (curve I). o When ethanioc acid is in excess, the equilibrium is displaced to favor the forward reaction and the yield increases (curve II).	0.5	
	0.75	
2- a) Ethanoyl chloride or ethanoic anhydride can be used:	2x0.25	

$CH_3 - \underset{\underset{O}{\|}}{C} - Cl + CH_3 - CH_2 - CH_2 - CH_2 - CH_2OH \rightarrow$ $CH_3 - \underset{\underset{O}{\|}}{C} - O - CH_2 - CH_2 - CH_2 - CH_2 - CH_3 + HCl$ b) This reaction is fast, complete and exothermic.		

Second Exercise (6,5 points)
Kinetic of the Decomposition of Hydrogen Peroxide (H_2O_2)

Expected Answer **Mark** **Comment**

I- <u>Preparation of Solution (S) of H_2O_2</u>

To prepare the solution (S) of concentration C = 0.060 mol.L^{-1} from the solution of concentration C_0 = 1.0 mol.L^{-1}, the dilution factor is equal to: $\frac{C_0}{C} = \frac{1.0}{0.06} = \frac{V}{V_0} = \frac{100}{6}$ 1

To carry out the most precise preparation, a graduated pipet of 10 mL and a volumetric flask of 100 mL constitute the most convenient glassware because with this pipet we can take out a volume $V_0 \approx \frac{100}{16.67} = 6.0$ mL and dilute this volume in 100 mL volumetric flask.

II- <u>Kinetic of the Decomposition Reaction of H_2O_2</u>

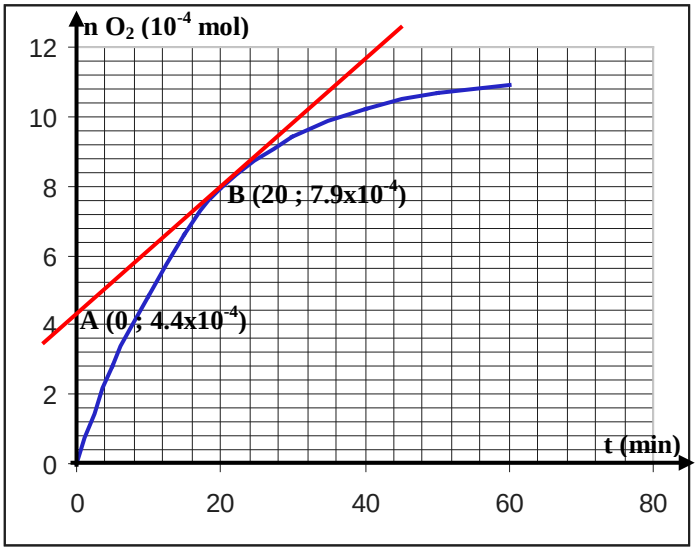
1- The pressure of O_2 at each instant is $P(O_2) = P - P_0$. The number of moles of O_2 at each instant is given by the equation of ideal gas: $n_t = \frac{P(O_2)xV}{RxT} = \frac{(P - P_0)x300x10^{-6}}{8.3x300}$ 1

$n_t = 1.20x10^{-7}(P - P_0)$

2- For t = 0, we have: P = P_0 and **$n_0 = 0$** mol. 2x0.25

For t = 40 min, we have: $n_t = 1.20x10^{-7}(1100 - 1015)x10^2$ = **$10.2x10^{-4}$ mol**.

3- The curve : 2



1.25

1.25

4- The rate of formation of O_2 at t = 20 min is defined by: $r_{(t=20)} = \frac{dnO_2}{dt}$. The value of this rate is equal to the slope of the tangent to the curve n (O_2) = f(t) at the point of abscissa t = 20 min. 1.5

$r_{(t=20)} = \frac{n_B - n_A}{t_B - t_A} = \frac{(7.9 - 4.4)x10^{-4}}{20 - 0}$ = **$17.5x10^{-6}$ mol.min^{-1}**.

5- When the pressure is $1140x10^2$ Pa, the number of moles of O_2 formed is $n\ O_2 = 1.2(1140 - 1015)x10^{-7} = 15.0x10^{-4}$ mol which is produced by $n\ H_2O_2 = 2x15.0x10^{-4} = 30.0x10^{-4}$ mol. The initial number of moles of H_2O_2 is: $n\ H_2O_2$ initial $= CxV_{(S)} = 0.06x50x10^{-3} = 30.0x10^{-4}$ mol. We conclude that hydrogen peroxide decomposes completely.

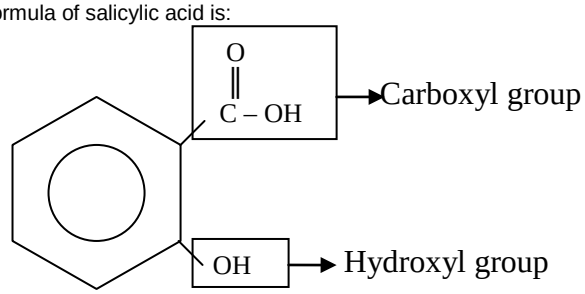
The species present in the obtained solution, (other than the dissolved O_2) are water (H_2O), iron (III) ions (Fe^{3+}) and chloride ions (Cl^-).

Third Exercise (6 points)
Formulation of Aspirin

Expected Answer	Mark	Comment

I- Preparation of Aspirin

1- Formula of salicylic acid is: 1.25



0.5

0.25

2- Formula of (B) is: $CH_3 - \underset{\underset{O}{\|}}{C} - O - \underset{\underset{O}{\|}}{C} - CH_3$ 0.5

This is ethanoic (acetic) anhydride. 0.5

II- Introducing a Tablet of Simple Aspirin in water

1- The equation of this reaction is:

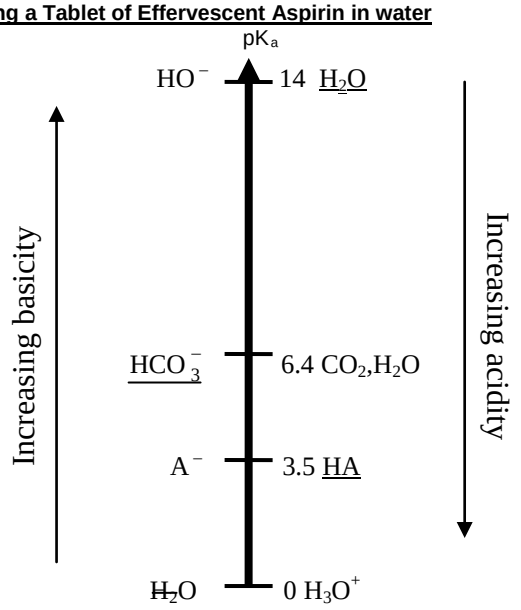
$HA + H_2O \rightleftharpoons H_3O^+ + A^-$

2- The relation: $pH = pK_a + \log \frac{[A^-]}{[HA]}$ permits to calculate the ratio $\frac{[A^-]}{[HA]}$.

$3 = 3.5 + \log \frac{[A^-]}{[HA]}$. $\log \frac{[A^-]}{[HA]} = -0.5$ so $\frac{[A^-]}{[HA]}$ **= 0.316**. 0.75

III- Introducing a Tablet of Effervescent Aspirin in water

1-



0.75

0.50

0.50

1

2- This reaction takes place between the acid HA and hydrogen carbonate ion having the following equation:

$HA + HCO_3^- \rightleftharpoons A^- + CO_2,H_2O$

3- PH of the solution is $6.2 > pK_a (HA/A^-) + 1$

$6.2 > 3.5 + 1 \Rightarrow 6.2 > 4.5$ so A^- is the species that predominates

IV- Absorption of Aspirin by the Stomach

1- The equation of the reaction reproducing HA is:

$A^- + H_3O^+ \rightleftharpoons HA + H_2O$

2- Formulation of effervescent aspirin has the advantage of the dispersion of aspirin in the ionic form (A^-) in aqueous solution. In the stomach, this ion reacts with H_3O^+ (gastric juice) to reproduce HA in the form of small crystals which are dispersed in all over the stomach to be rapidly absorbed and hence reducing the risk.