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@wecantogther



https://linktr.ee/together_we_can



@wecantogther0



wecantogther70@gmail.com



+961-76 096391



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Join us in creating a better tomorrow,
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https://linktr.ee/together_we_can



@wecantogether0



wecantogether70@gmail.com



+961-76 096391

الاسم:	مسابقة في الكيمياء
الرقم:	المدة ساعتان

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 Three Following Exercises:

First Exercise (7 points) **Study of a Household Product “Windex”**

Ammonia, NH_3 , in aqueous solution is used often in cleaning. “Windex” is a household product used to clean glass. This exercise aims to titrate ammonia in “Windex” and to prepare a buffer solution.

This study is performed at 25°C .

Given:

Conjugate acid/base pair	$\text{H}_3\text{O}^+/\text{H}_2\text{O}$	$\text{NH}_4^+/\text{NH}_3$	$\text{H}_2\text{O}/\text{HO}^-$
pK_a	0	9.2	14

- Molar volume of a gas under the experimental conditions is $V_m = 24 \text{ L}\cdot\text{mol}^{-1}$.
- Ammonia gas is very soluble in water.

I- Dilution of a commercial hydrochloric acid solution

A bottle of a commercial hydrochloric acid solution is available. We have, among others, the following indications:

Density: $\rho = 1.12 \text{ g}\cdot\text{mL}^{-1}$; % by mass = 32.13%; $M_{\text{HCl}} = 36.5 \text{ g}\cdot\text{mol}^{-1}$.

- 1- Show that the molar concentration of this solution, noted (S_0) , is $C_0 = 9.86 \text{ mol}\cdot\text{L}^{-1}$.
- 2- A solution (S) is prepared by dilution of the solution (S_0) . The solution (S) is titrated with a sodium hydroxide solution. The obtained value of the concentration of (S) is $C_S = 0.07 \text{ mol}\cdot\text{L}^{-1}$.

The two following sets of glassware are available:

Set (a): 1000 mL volumetric flask, 10 mL graduated pipet (graduated 1/10), 50 mL beaker.

Set (b): 100 mL volumetric flask, 2 mL volumetric pipet, 50 mL beaker.

Explain, if each one of the two sets is convenient to perform the above dilution.

II- Titration of the “Windex” solution

A volume $V = 25 \text{ mL}$ of “Windex” solution is titrated with the hydrochloric acid solution (S) using a pH-meter.

Some of the experimental results are given in the following table:

$V_{(S)}$ in mL	0	22	30
pH	10.2	5.2	2.4

$V_{(S)}$ is the added volume of solution (S) during titration.

- 1- Write the equation of the titration reaction.
- 2- At the equivalence point we have: $V_{(S)Equivalence} = 22 \text{ mL}$ and $pH_{Equivalence} = 5.2$.
 - a) Justify the pH value which shows the acid nature of the obtained solution at equivalence.
 - b) Determine the volume of ammonia gas needed to prepare 1 L of « Windex » solution.
- 3- Draw the shape of the curve $pH = f(V_S)$ for: $0 \leq V_{(S)} \leq 30 \text{ mL}$, by locating four remarkable points on this curve.
Take the following scales: abscissa: 1cm for 2 mL and ordinate: 1 cm for 1 unit of pH.

III- Preparation of a buffer solution

The pH-meter, already used, was calibrated with a buffer solution of $\text{pH} = 7$ and another buffer solution of basic nature. The second solution was consumed; it is desired to prepare a buffer solution of $\text{pH} = 9.2$.

An ammonia solution of concentration $C_b = 0.06 \text{ mol.L}^{-1}$ and a hydrochloric acid solution of concentration $C_a = 0.07 \text{ mol.L}^{-1}$ are available.

Determine the volume of ammonia solution V_b added to $V_a = 60 \text{ mL}$ of hydrochloric acid solution in order to prepare this buffer solution.

Second Exercise (6 points) Kinetic of The Decomposition Reaction of Hydrogen Peroxide

It is suggested to study, at 25°C and in the presence of Fe^{3+} ions as catalyst, the kinetic of the decomposition reaction of hydrogen peroxide solution which is sold, in drugstores, in dark flasks. A volume $V = 50 \text{ mL}$ of a stabilized hydrogen peroxide solution, of molar concentration $C = 0.893 \text{ mol.L}^{-1}$, is poured into a 100 mL volumetric flask; this flask is then placed on a precision balance.

At time $t = 0$, a volume of 2 mL of iron III nitrate solution ($\text{Fe}^{3+} + 3\text{NO}_3^-$) is added into the volumetric flask. After a short time, a big amount of gas is observed. This gas is released from the decomposition of hydrogen peroxide according to the following equation:



With time, the balance indicates a decrease in mass. During the decomposition reaction, the variation of mass Δm represents practically the mass of oxygen gas released at each instant t .

Given:

- Molar mass: $M_{\text{O}_2} = 32 \text{ g.mol}^{-1}$.
- Oxygen gas is practically insoluble in water.

I- Preliminary study

- 1- Specify how the above decomposition reaction will be affected in each one of the two following cases:
 - a) Performing this study at 40°C .
 - b) Diluting the above hydrogen peroxide solution.
- 2- Show that, at instant t , the number of moles of hydrogen peroxide $n(\text{H}_2\text{O}_2)_t$ and the variation of mass Δm (expressed in grams) are related to each other by the following relation:

$$n(\text{H}_2\text{O}_2)_t = 4.46 \times 10^{-2} - \frac{\Delta m}{16}$$

II- Kinetic Study of the reaction

The table below shows the number of moles of H_2O_2 at different instants t:

t(min)	0	2	3	4	8	10	15	20	30	35	40
n(H_2O_2) (10^{-2} mol)	4.46	4.46	4.33	4.15	3.33	2.90	2.17	1.83	1.43	1.27	1.21

- Plot, on graph paper, the curve $n(\text{H}_2\text{O}_2) = f(t)$.
Take the following scales: abscissa: 1 cm for 2 min; ordinate: 5 cm for 1.00×10^{-2} mol.
- Determine the average rate of disappearance of H_2O_2 , in $\text{mol} \cdot \text{min}^{-1}$, between the two instants: $t_1 = 10$ min and $t_2 = 25$ min.
- Determine graphically the half-life of the reaction.
- After a certain time t, the value of Δm equals 713 mg.
Identify the chemical species that are present in the obtained solution at this time.

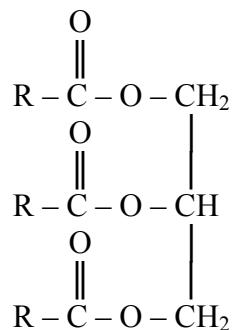
Third Exercise (7 points)

Synthesis of an Ester Starting With a Fatty Compound (A)

A fatty compound is a triglyceride formed from a fatty acid of formula $\text{R} - \text{COOH}$ and the glycerol of formula $\text{CH}_2\text{OH} - \text{CHOH} - \text{CH}_2\text{OH}$.

Given:

- Molar atomic mass in $\text{g} \cdot \text{mol}^{-1}$: $M_{\text{H}} = 1$; $M_{\text{O}} = 16$; $M_{\text{C}} = 12$.
- Formula of the fatty compound (A) :



- R is an alkyl radical.

N. B.

Use the condensed structural formulas of the organic compounds in the equations.

I- Formula of the Fatty Compound (A)

The fatty compound (A) has the following mass composition:

C: 59.6 %; O: 31.8 % ; H: 8.6 %.

- Show that, the molecular formula of (A) is $\text{C}_{15}\text{H}_{26}\text{O}_6$ and the formula of R is C_3H_7 .
- Write the condensed structural formula of (A).

II- Saponification reaction of (A)

The saponification reaction of the fatty compound (A) is carried out with a sodium hydroxide solution.

- 1- Write the equation of the saponification reaction and give the name of the obtained soap.
- 2- Give two characters of this reaction.
- 3- The following setup is suggested to carry out the saponification of (A). Pick out the mistake in this setup. Justify.

- 4- Specify the role of heating and that of reflux during the saponification reaction.
- 5- Indicate the two steps that will be followed to separate the soap from the other components of the obtained mixture.

III- Synthesis of an Ester Having Pineapple Smell

- 1- An aqueous solution of the obtained soap is treated by an aqueous solution of a strong acid. Write the equation of the reaction that takes place. Consider that the reaction is complete.
- 2- The carboxylic acid obtained in the above reaction is heated with ethanol, in presence of sulphuric acid as a catalyst. An organic compound (E), which is present in pineapple flavor, is obtained. Write the equation of the reaction and give the systematic name of (E).
- 3- Determine the number of moles of (E) obtained from 1 kg of (A) knowing that the yield of the all reactions is 60 %.

First Exercise (7 points)

Expected Answer	Mark	Comments
<p>I-</p> <p>1- The molar concentration of a solution is given by:</p> $C = \frac{n(\text{solute})_{\text{mol}}}{V(\text{solution})_L} = \frac{m(\text{solute})_{\text{g}}}{M(\text{solute})_{\text{g/mol}} \times V \times 10^{-3}}$ $m(\text{solute}) = m(\text{solution}) \times \frac{\%}{100} = \rho \times V \times \frac{\%}{100}$ <p>Then :</p> $C = \frac{\% \times \rho}{100 \times M \times 10^{-3}}$ <p>Using the given indications, we obtain: $C_0 = 9.86 \text{ mol.L}^{-1}$.</p> <p>2- By dilution, the number of moles of solute does not change, then : $C_0 \times V_0 = C_S \times V_S$;</p> <p>The factor of dilution:</p> $\delta = \frac{C_0}{C_S} = \frac{V_S}{V_0} = \frac{9.86}{0.07} \approx 141$ <p>The volume V_S must be 141 times that of V_0.</p> <p>Set (a) is convenient to perform the dilution. To use a 1000 mL volumetric flask, it is required a volume of commercial solution: $V_0 = \frac{1000}{141} = 7.1 \text{ mL}$, that could be removed with a graduated pipet of 10 mL.</p> <p>Set (b) is not convenient to perform this dilution. To use a 100 mL volumetric flask, it is required a volume of commercial solution: $V_0 = \frac{100}{141} = 0.71 \text{ mL}$. This volume cannot be removed with a 2mL volumetric pipet.</p>	1	-0.25 Lack of explanation. Any other correct method is acceptable.
<p>II-</p> <p>1- The equation of the titration reaction is:</p> $\text{NH}_3 + \text{H}_3\text{O}^+ \rightarrow \text{NH}_4^+ + \text{H}_2\text{O}$ <p>2-</p> <p>a) The main species at the equivalence point, other than water, are Cl^- and NH_4^+. Cl^- is a spectator ion while NH_4^+ is an acid that reacts with water to make acid solution at equivalence.</p> <p>b)</p> <p>*the concentration of ammonia in "Windex":</p> <p>At equivalence point, the number of moles of NH_3 in 25 mL of "Windex" is equal to the number of moles of H_3O^+ in 22 mL of solution (S):</p> $C(\text{NH}_3) \times V = C_{(S)} \times V_{(S)E}$ $C(\text{NH}_3) = \frac{0.07 \times 22 \times 10^{-3}}{25 \times 10^{-3}} = 0.06 \text{ mol.L}^{-1}$ <p>*The volume of ammonia required to prepare 1 L of "Windex":</p> $V(\text{NH}_3) = n(\text{NH}_3) \times V_m = C(\text{NH}_3) \times V \times V_m$	0.5 0.5 1.25	

$$V(\text{NH}_3) = 0.06 \times 1 \times 24 = 1.44 \text{ L.}$$

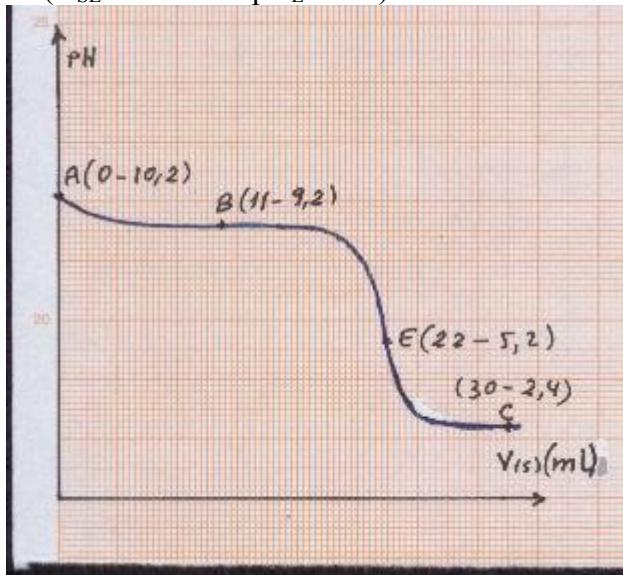
3- The 4 remarkable points are:

A: ($V_S = 0$ – pH = 10.2)

B: ($V_S = V_{SE}/2 = 11 \text{ mL}$ – pH = pK_a = 9.2)

C: ($V_S = 30 \text{ mL}$ – pH = 2.4)

E: ($V_{SE} = 22 \text{ mL}$ – pH_E = 5.2)



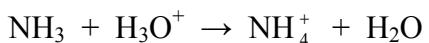
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-0.5 if the half equivalence point is not located.
Zero if the given three points are not located.

III-

When the pH of a buffer solution is equal to the pK_a of the conjugate acid/base, we have: [acid] = [base].

The equation of the reaction is:



Initial state	n_b	n_a	0
Final state	$(n_b - n_a)$	~0	n_a .

$$[\text{NH}_4^+] = \frac{n_a}{V} \text{ and } [\text{NH}_3] = \frac{(n_b - n_a)}{V}. \text{ But, in a solution:}$$

n_{solute} in mol = C in mol.L⁻¹ × V in L:

$$\frac{C_a x V_a}{V} = \frac{(C_b x V_b - C_a x V_a)}{V}$$

Since $V_a = 60 \text{ mL}$ so $V_b = 140 \text{ mL}$.

1.25

Second Exercise (6 points)

Expected Answer	Mark	Comments
I- 1- a) When the temperature increases, the rate of the reaction increases because the temperature is a kinetic factor. b) Dilution decreases the concentration of the reactant H ₂ O ₂ , then the rate of the decomposition reaction decreases. 2- According to the equation: 2 H ₂ O ₂ → 2 H ₂ O + O ₂ , we have, at each instant t: n(H ₂ O ₂) _{reacted} = 2n(O ₂) _{formed} . And, the remaining number of moles of H ₂ O ₂ at instant t is $n(\text{H}_2\text{O}_2)_t = n(\text{H}_2\text{O}_2)_{\text{initial}} - n(\text{H}_2\text{O}_2)_{\text{reacted}}$	0.5	
	1	

$= n(H_2O_2)_{\text{initial}} - 2 n(O_2)_{\text{formed}}$. Where:

$$n(O_2) = \frac{\Delta m}{M(O_2)},$$

$$\text{and } n(H_2O_2)_{\text{initial}} = Cx50 \times 10^{-3} \text{ mol} = 0,893 \times 0.05 \\ = 4.46 \times 10^{-2} \text{ mol.}$$

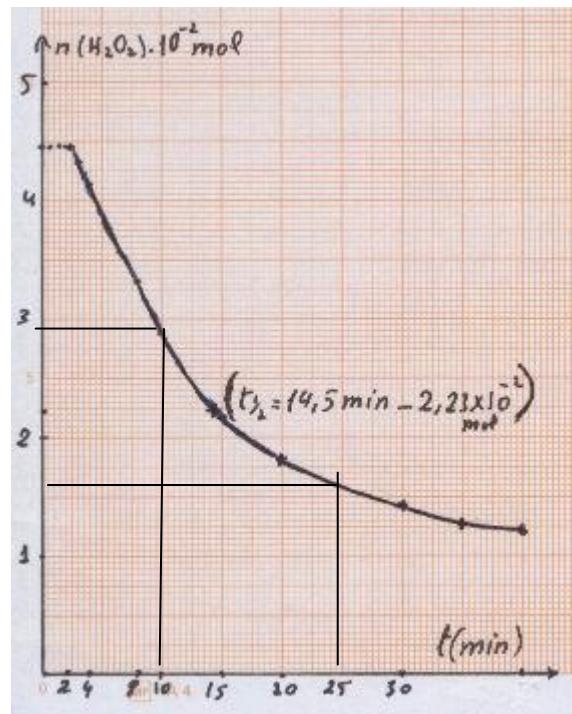
Then, we have:

$$n(H_2O_2)_t = 4.46 \times 10^{-2} - \frac{2\Delta m}{32} = 4.46 \times 10^{-2} - \frac{\Delta m}{16}, \text{ where}$$

Δm is expressed in grams.

II-

1-



1

2- The average rate of disappearance of H_2O_2 , between the two instants $t_1 = 10$ min and $t_2 = 25$ min, is given by:

1

$$\bar{r} = - \frac{n(H_2O_2)_{25} - n(H_2O_2)_{10}}{25 - 10} = - \frac{1.60 \times 10^{-2} - 2.9 \times 10^{-2}}{15} \\ = 8.67 \times 10^{-4} \text{ mol} \cdot \text{min}^{-1}.$$

3- The half-life of the reaction is the time needed for half the initial number of moles of H_2O_2 to be decomposed. The corresponding time for this value is $t_{1/2} = 14.5$ min.(refer to the graph).

1

4- Based on the question (1- 2-), we obtain:

1.5

$$n(H_2O_2)_t = 4.46 \times 10^{-2} - \frac{713 \times 10^{-3}}{16} \approx 0.$$

It is concluded that H_2O_2 is decomposed completely; and the chemical species present in the obtained solution are:

H_2O : which is a solvent and a product of the reaction;

Fe^{3+} : which is a catalyst;

NO_3^- : which is a spectator ion.

Third Exercise (7 points) L. S.

Expected Answer	Mark	Comments
I- Formula of (A) 1- The formula of (A) can be written as: $C_xH_yO_z$, with $z = 6$. The law of definite proportions permits to write: $\frac{12x}{\%C} = \frac{y}{\%H} = \frac{16z}{\%O}$. With the given percentages, we obtain: $x = 15$; $y = 26$. The molecular formula of (A) is then: $C_{15}H_{26}O_6$. According to the given formula, we conclude that the formula of R contains: $\frac{15-6}{3} = 3$ atoms of carbon and $\frac{26-5}{3} = 7$ atoms of hydrogen. The formula of R is then: C_3H_7 . 2- Since $RCOOH$ is a fatty acid so it has a non branched carbon chain. $CH_3 - CH_2 - CH_2$ and the condensed structural formula of (A) is:	1	
$ \begin{array}{ccccccc} & & O & & & & \\ & & & & & & \\ CH_3 & - & CH_2 & - & CH_2 & - & C - O - CH_2 \\ & & O & & & & \\ & & & & & & \\ CH_3 & - & CH_2 & - & CH_2 & - & C - O - CH \\ & & O & & & & \\ & & & & & & \\ CH_3 & - & CH_2 & - & CH_2 & - & C - O - CH_2 \end{array} $	0.5	Zero if R is branched.
II- Saponification of (A) 1- The equation of the saponification reaction is: $ \begin{array}{ccccccc} & & O & & & & \\ & & & & & & \\ CH_3 & - & CH_2 & - & CH_2 & - & C - O - CH_2 \\ & & O & & & & \\ & & & & & & \\ CH_3 & - & CH_2 & - & CH_2 & - & C - O - CH + 3 Na^+ + 3 HO^- \rightarrow \\ & & O & & & & \\ & & & & & & \\ CH_3 & - & CH_2 & - & CH_2 & - & C - O - CH_2 \end{array} $ $3CH_3 - CH_2 - CH_2 - COO^- + 3 Na^+$ $+ CH_2OH - CHOH - CH_2OH$ The name of the formed soap is sodium butanoate. 2- This reaction is slow and complete. 3- The mistake : the condenser is closed from the top with a stopper. Heating increases the pressure inside the flask that causes the setup to explode. 4- The role of heating is to increase the rate of the saponification reaction (kinetic role).	1	
	0.25 2×0.25 2×0.25 0.25	

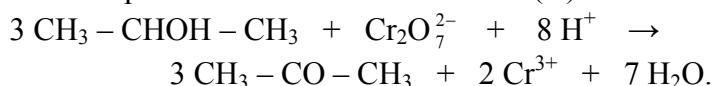
The role of the reflux is preventing to loose the components of the reaction by condensing their vapours.	0.25	
5- The two main steps which are followed to separate the soap from other components are successively: relargage (precipitation) and filtration.	0.5	
III- Synthesis of ester		
1- The equation of the reaction that is supposed to be complete is:	0.5	
$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{COO}^- + \text{H}_3\text{O}^+ \rightarrow \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{COOH} + \text{H}_2\text{O}$		
2- It is an esterification reaction of equation :	0.5	
$\begin{array}{l} \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \underset{\substack{\parallel \\ \text{O}}}{\text{C}} - \text{OH} + \text{HO} - \text{CH}_2 - \text{CH}_3 \rightleftharpoons \\ \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \underset{\substack{\parallel \\ \text{O}}}{\text{C}} - \text{O} - \text{CH}_2 - \text{CH}_3 + \text{H}_2\text{O} \end{array}$	0.25	
The systematic name of ester (E) is ethylbutanoate.		
3- The initial number of moles of (A) is:	1	
$n(\text{A})_{\text{initial}} = \frac{m_A}{M_a} = \frac{1000}{302} \text{ mol}$ $(M_A = 12 \times 15 + 26 + 16 \times 6 = 302 \text{ g.mol}^{-1})$.		
Based on the series of the the above equations, the number of moles of the ester that could be obtained if the yield is total is: $n(\text{ester})_{\text{formed}} = n(\text{acid}) = n(\text{soap}) = 3 n(\text{A})_{\text{initial}}$. Where the yield is 60 %, then the number of moles of ester obtained is: $n = 3 \times \frac{1000}{302} \times 0.60 \approx 6 \text{ mol}$.		

Third Exercise (7 points) G. S.

Expected Answer	Mark	Comments
I- 1- The general formula of a monoalcohol having a non branched open carbon chain is: $\text{C}_n\text{H}_{2n+2}\text{O}$ of molar mass: $M = 14n + 2 + 16$, where the percentage by mass of oxygen is: $26.67 = \frac{16 \times 100}{14n + 18}$. So $n = 3$, and the molecular formula of (A) is $\text{C}_3\text{H}_8\text{O}$. 2- The condensed structural formulas of the possible isomers of (A) are: $\text{CH}_3 - \text{CH}_2 - \text{CH}_2\text{OH}$ and $\text{CH}_3 - \text{CHOH} - \text{CH}_3$.	0.75 0.25×2	
II- 1- The positive test of (B), with 2,4 – DNPH, shows that (B) is an aldehyde or a ketone. The negative test of(B), with Fehling solution, shows that (B) is a ketone; which is derived from a secondary	1.5	

alcohol (A). (B) of formula $\text{CH}_3 - \text{CO} - \text{CH}_3$ is:
propanone. (A) is 2-propanol.

2- The equation of the mild oxidation of (A) is:

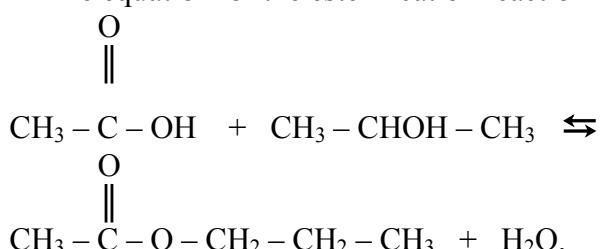


III-

Since menthone is a ketone having the same carbon chain of menthol which is a secondary alcohol, then it is possible to obtain the menthone by a mild oxidation of menthol.

IV-

1- The equation of the esterification reaction is:



2- The percentage of esterification is:

$$\% = \frac{n(\text{acid})_{\text{reacted}}}{n(\text{acid})_{\text{initial}}} \times 100$$

Since the initial mixture is equimolar :

$$n(\text{acid})_{\text{reacted}} = n(\text{ester})_{\text{formed}} = 0.12 \text{ mol.}$$

$$n(\text{ester})_{\text{theoretically}} = n(\text{acid})_{\text{initial}} = 0.2 \text{ mol.}$$

$$\text{We obtain } \% = \frac{0.12 \times 100}{0.2} = 60\%.$$

3-In the first experiment an equimolar initial mixture of the two reactants and zero mole of ester were used. The curve should begin at 0 and tends to 60 % as a limit.

So graph (c) represents this experiment.

In the second experiment: 2 mol of acid and 1 mol of alcohol were used, the limit of the reaction increases to exceed 60 %.

The curve (a) begins at 0 and tends to a limit >60 % .

Graph (a) corresponds to the second experiment.

In the third experiment, in the initial state, 0.5 mol of ester is added to 1 mol of alcohol and 1 mol of acid. So the curve will represent the amount of ester that should begin at 0.5 mol.

Graph (b) corresponds to the third experiment.

4- Increasing the temperature helps to reduce the time required to reach the equilibrium state, but does not change the yield of the reaction at equilibrium.

0.75

0.75

0.5

0.5

0.5

0.5

0.5

0.25

الاسم: مسابقة في الكيمياء
الرقم: المدة ساعتان

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 Three Following Exercises:

First Exercise (6.5 points) **Identification of an Organic Compound (B)**

A gaseous organic compound (B) has a rotten fish smell. The elementary analysis of (B) shows that it is composed of three elements: carbon, hydrogen and nitrogen.

Given

- Study is performed at 25 °C.
- Molar volume of a gas: $V_m = 24 \text{ L.mol}^{-1}$.
- Ion product of water: $K_w = 10^{-14}$.
- Molar atomic masses in g.mol⁻¹: $M_H = 1$; $M_C = 12$; $M_N = 14$.

I- Acid-base nature of (B)

One liter of solution (S) is prepared by dissolving 0.48 L of (B) in distilled water. The pH value of this solution is 11.1.

- 1- Determine the initial concentration C_B of solution (S).
- 2- Show that compound (B) is a weak base.
- 3- The compound (B) reacts with water according to the following equation:



Determine the value of pK_a of the pair BH^+/B .

II- Determination of the molar mass of (B)

A solution (S') is prepared by dissolving 150 mg of (B) in distilled water. The solution (S') is titrated by a hydrochloric acid solution of concentration $C_a = 0.10 \text{ mol.L}^{-1}$. The equivalence point is reached when 25.4 mL of the acid solution are added.

- 1- Write the equation of the titration reaction.
- 2- Show that the molar mass of (B) is $M = 59.05 \text{ g.mol}^{-1}$.

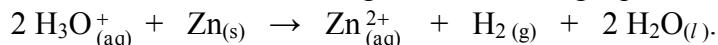
III- Identification of (B)

The study shows that compound (B) is a saturated monoamine.

- 1- Verify that the molecular formula of (B) is C_3H_9N .
- 2- Write the condensed structural formulas of the possible isomers of (B).
- 3- Identify (B) knowing that it does not react with acyl chlorides.

Second Exercise (7.5 points)
Kinetic of the Reaction Between Hydrochloric Acid and Zinc

Hydrochloric acid solution reacts with zinc according to the following equation:



This exercise aims to study the kinetic of this reaction.

Given

- Molar atomic mass: $M_{\text{Zn}} = 65.4 \text{ g.mol}^{-1}$.
- Molar volume of a gas at the experimental conditions: $V_m = 24 \text{ L.mol}^{-1}$.

I- Preliminary study

At time $t = 0$, a volume $V_a = 40 \text{ mL}$ of hydrochloric acid solution of concentration $C_a = 0.500 \text{ mol.L}^{-1}$ is poured into a flask containing a mass $m = 1 \text{ g}$ of powdered zinc. We admit that the volume of the mixture remains constant.

The volume of the collected hydrogen gas is measured with time.

- 1- Explain the advantage of the use of powdered zinc instead of a zinc strip in this study.
- 2- Determine at $t = \infty$ the concentration of Zn^{2+} ions: $[\text{Zn}^{2+}]_\infty$
- 3- Show that the concentration of H_3O^+ ions, $[\text{H}_3\text{O}^+]_0$ at $t = 0$, and that of $[\text{H}_3\text{O}^+]_t$ at each instant t , are related to the volume of hydrogen gas V_{H_2} , which is formed at each instant t , according to the following relation:

$$[\text{H}_3\text{O}^+]_t = [\text{H}_3\text{O}^+]_0 - \frac{V_{\text{H}_2}}{480}, \text{ where } V_{\text{H}_2} \text{ is expressed in mL.}$$

II- Kinetic of the reaction

Experimental results are given in the following table:

$t \text{ (s)}$	0	100	200	300	400	500	600	800	1000
$V_{\text{H}_2} \text{ (mL)}$	0	80	132	154	168	178	183	188	192
$[\text{H}_3\text{O}^+] \text{ (mol.L}^{-1}\text{)}$	x	0.333	0.225	0.179	0.150	0.129	0.119	y	0.100

- 1- Give the value of x , and calculate that of y in the above table.
- 2- Plot, on the graph paper, the curve $[\text{H}_3\text{O}^+] = f(t)$.
Consider the following scales: abscissa: 1 cm = 100 s; ordinate: 1 cm = 0.05 mol.L^{-1} .
- 3- Determine, graphically, the half-life of the reaction.
- 4- Give, at each instant t , the relation between the rate of formation of Zn^{2+} ions and that of the disappearance of H_3O^+ ions.
- 5- Trace, on the same graph, the shape of the curve which represents the variation of the concentration of Zn^{2+} ions in terms of time: $[\text{Zn}^{2+}] = g(t)$ and passing through the three points of abscissas: $t = 0$, $t = t_{1/2}$ and $t = 1000 \text{ s}$.

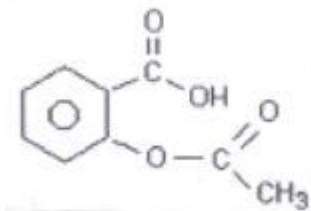
Third Exercise (6 points)

Titration of Aspirin

The aspirin is one of the most consumed drugs in the world. The aim of this exercise is to titrate the acetylsalicylic acid in a tablet of a simple aspirin “300” which is sold in the lebanese market. (“300” represents, in mg, the mass of pure acetylsalicylic acid in one tablet)

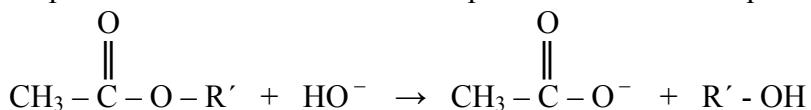
Given :

- Condensed structural formula of acetylsalicylic acid:



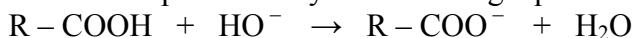
- $pK_a(\text{acetylsalicylic acid}/\text{acetylsalicylate ion}) = 3.5$
- $M(\text{acetylsalicylic acid}) = 180 \text{ g} \cdot \text{mol}^{-1}$.

- An ester, of formula $\text{CH}_3 - \overset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{O} - \text{R}'$, reacts with sodium hydroxide solution at high temperature. The reaction that takes place is total and is represented by the following equation:



I- Acid-base reaction

A weak acid, of formula $\text{R} - \text{COOH}$, reacts with sodium hydroxide solution at low temperature, according to a rapid reaction which is represented by the following equation:



Verify that this reaction is total, knowing that:

$$pK_a(\text{R} - \text{COOH}/\text{R} - \text{COO}^-) < 5 \text{ and } pK_a(\text{H}_2\text{O}/\text{HO}^-) = 14.$$

II- Preparation of acetylsalicylic acid solution

A tablet of a simple aspirin “300” is carefully grinded. The obtained powder is introduced into an appropriate volumetric flask which is partially filled with distilled water. The flask is shaken to dissolve completely the powder. Distilled water is then added to reach the line mark. The obtained solution is called (S).

Show that the appropriate volumetric flask to prepare (S) is of 200 mL capacity, knowing that:

- 50 mL and 200 mL volumetric flasks are only available in the laboratory,
- the solubility of acetylsalicylic acid, in water at 25 °C, is equal to $3.4 \text{ g} \cdot \text{L}^{-1}$.

III- Carrying out titration

The acid-base titration of a 200 mL solution (S) is carried out at low temperature, with sodium hydroxide solution of concentration $C_b = 0.10 \text{ mol.L}^{-1}$.

- 1- The volume added at the equivalence point is $V_{bE} = 17 \text{ mL}$. Verify that the mass of acetylsalicylic acid in the tablet of this aspirin is about 300 mg.
- 2- Rewrite, on the answer sheet, the formula of aspirin. Circle on it, the two functional groups containing oxygen and name them.
- 3- Name the two reactions that may take place, at high temperature, between hydroxide ions HO^- and aspirin.
- 4- Conclude why this acid-base titration should be carried out at low temperature.

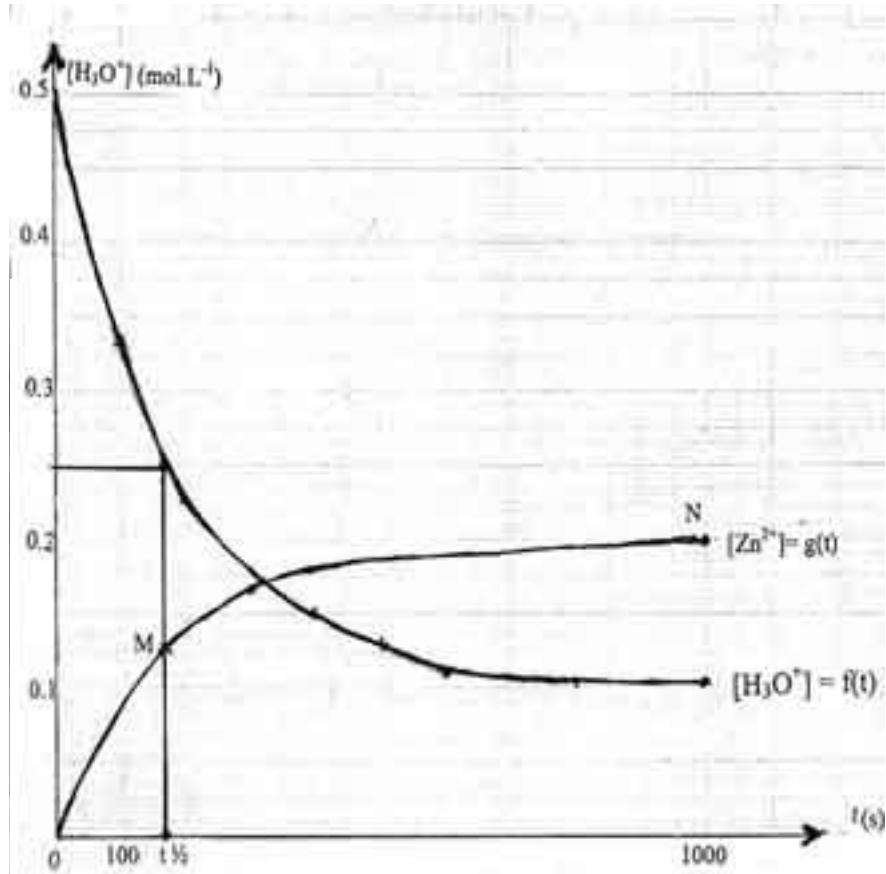
First exercise (6.5 points)

Expected answer	Comments									
<p>I-</p> <p>1- The concentration C_B, expressed in mol.L^{-1}, is given by:</p> $C_B = \frac{n_{\text{solute}} \text{in mol}}{V_{\text{solution}} \text{in L}} = \frac{\frac{V_{\text{solute}}}{V_m}}{V} \text{. With; } V_{\text{solute}} = 0.48 \text{ L; } V_m = 24 \text{ L -mol}^{-1}$ <p>and $V = 1 \text{ L}$, we have: $C_B = 0.02 \text{ mol.L}^{-1}$.</p> <p>2- The relation $\text{pH} = \text{pK}_w + \log [\text{HO}^-]$ permits to calculate $[\text{HO}^-]$. $\text{pH} = 11.1$; $\text{pK}_w = 14$ we get: $[\text{HO}^-] = 1.25 \times 10^{-3} \text{ mol.L}^{-1} < C_B = 0.02 \text{ mol.L}^{-1}$. The compound (B) is then a weak base.</p> <p>3- Determination of pK_a:</p> <table style="margin-left: auto; margin-right: auto;"> <tr> <td style="text-align: center;">B</td> <td style="text-align: center;">$+ \text{H}_2\text{O} \rightleftharpoons \text{BH}^+ + \text{HO}^-$</td> <td></td> </tr> <tr> <td style="text-align: center;">Initial state (mol L^{-1})</td> <td style="text-align: center;">0.02</td> <td style="text-align: center;">0</td> </tr> <tr> <td style="text-align: center;">At equilibrium</td> <td style="text-align: center;">$0.02 - x$</td> <td style="text-align: center;">x</td> </tr> </table> <p>The relation: $\text{pH} = \text{pK}_a + \log \frac{[B]}{[\text{BH}^+]}$ permits to calculate pK_a.</p> $\text{pK}_a = \text{pH} - \log \frac{[B]}{[\text{BH}^+]} = 11.1 - \log \frac{0.02 - x}{x}$ $\text{pK}_a = 11.1 - \log \frac{0.02 - 1.25 \times 10^{-3}}{1.25 \times 10^{-3}} = 9.92$	B	$+ \text{H}_2\text{O} \rightleftharpoons \text{BH}^+ + \text{HO}^-$		Initial state (mol L^{-1})	0.02	0	At equilibrium	$0.02 - x$	x	Each correct reasoning is acceptable.
B	$+ \text{H}_2\text{O} \rightleftharpoons \text{BH}^+ + \text{HO}^-$									
Initial state (mol L^{-1})	0.02	0								
At equilibrium	$0.02 - x$	x								
<p>II-</p> <p>1- The equation of the titration reaction is:</p> $B + \text{H}_3\text{O}^+ \rightarrow \text{BH}^+ + \text{H}_2\text{O}$ <p>2- Determination of the molar mass of (B):</p> <p>At the equivalence point, we have: $n_{(\text{acid})}$ added = $n_{(B)}$ contained in (S'). In a solution we have: $n_{(\text{solute})} = C \times V$.</p> $C_A \times V_A = n_{(B)} \text{. with: } 0.1 \times 25.4 \times 10^{-3} = n_B = \frac{m_B}{M_B} = \frac{150 \times 10^{-3}}{M_B} \text{. We have: } M_B = 59.05 \text{ g.mol}^{-1}$	//									
<p>III-</p> <p>1- The molecular formula of a saturated monoamine is: $C_nH_{2n+3}N$. $M = 12n + 2n + 3 + 14 = 59.05$. so $n = 3$ The molecular formula is then: C_3H_9N.</p> <p>2- The condensed structural formulas of possible isomers of (B) are: $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{NH}_2$; $\text{CH}_3 - \text{CH}_2 - \text{NH} - \text{CH}_3$;</p> <p>$\text{CH}_3 - \text{CH} - \text{CH}_3$ and $\text{CH}_3 - \underset{\text{NH}_2}{\text{N}} - \text{CH}_3$.</p> <p style="text-align: center;">$\begin{array}{c} \\ \text{NH}_2 \end{array}$ $\begin{array}{c} \\ \text{CH}_3 \end{array}$</p> <p>3- The compound (B) is an amine which does not react with the acyl chloride. (B) is then a tertiary amine of formula: $\text{CH}_3 - \underset{\text{CH}_3}{\text{N}} - \text{CH}_3$</p> <p>It is trimethylamine or N, N – dimethyl methanamine CH_3.</p>										

Second exercise (7.5 points)

Expected answer	Comments
<p>I-</p> <p>1- The contact surface between the reactants in the case (powder of zinc + hydrochloric acid solution) is bigger than the contact surface between the reactants in the case (strip of zinc + hydrochloric acid solution). Then the rate of the reaction, in the first case, is greater because the rate increases when the contact surface increases.</p> <p>2- Determination of the limiting reactant:</p> $R_{H_3O^+} = \frac{n(H_3O^+)_{\text{initial}}}{2} = \frac{C_a \cdot V_a}{2} = \frac{0.5 \times 40 \times 10^{-3}}{2} = 1 \times 10^{-2}$ $R_{Zn} = \frac{n(Zn) \text{ introduced}}{1} = \frac{m(Zn) \text{ introduced}}{M(Zn)} = \frac{1}{65.4} = 1.5 \times 10^{-2}$ <p>Since $R_{H_3O^+} < R_{Zn}$, then H_3O^+ is the limiting reactant.</p> <p>According to stoichiometric coefficients of the equation, we write:</p> $n(Zn) \text{ formed at } \infty = \frac{n(H_3O^+)_{\text{initial}}}{2} = 1 \times 10^{-2} \text{ mol.}$ <p>Concentration of Zn^{2+}:</p> $[Zn^{2+}]_\infty = \frac{n(Zn^{2+})}{V_a} = \frac{1 \times 10^{-2}}{40 \times 10^{-3}} = 0.25 \text{ mol.L}^{-1}$ <p>3- At instant t:</p> <p>$n(H_3O^+) \text{ remaining} = n(H_3O^+) \text{ initial} - n(H_3O^+) \text{ reacting.}$</p> <p>According to the stoichiometric coefficients of the equation, we could write: $n(H_3O^+) \text{ reacting} = 2 n(H_2) \text{ formed. So:}$</p> <p>$n(H_3O^+) \text{ remaining} = n(H_3O^+) \text{ initial} - 2 n(H_2) \text{ formed. Dividing by the constant volume of the solution, } 40 \times 10^{-3} \text{ L, we have then:}$</p> $[H_3O^+]_t = [H_3O^+]_0 - 2x \frac{n(H_2)}{V}$ $[H_3O^+]_t = [H_3O^+]_0 - 2x \frac{V(H_2) \times 10^{-3}}{V_m \times V \times 10^{-3}}$ $[H_3O^+]_t = [H_3O^+]_0 - 2x \frac{V(H_2)}{24 \times 40} = [H_3O^+]_0 - \frac{V(H_2)}{480}$ <p>II-</p> <p>1- <u>Value of x :</u> $x = [H_3O^+] = C_a = 0.500 \text{ mol.L}^{-1}$.</p> <p><u>Value of y :</u> $y = [H_3O^+]_{800} = 0.500 - \frac{188}{480} = 0.108 \text{ mol.L}^{-1}$.</p>	

2-



3- The half-life of the reaction is the time needed for half the amount of the limiting reactant to be consumed, according to the graph $t_{1/2} = 170\text{ s}$ when $[\text{H}_3\text{O}^+] = 0.25 \text{ mol L}^{-1}$

4- According to the stoichiometric coefficients of the equation, The two rates are related by: $R_{\text{disappearance}}(\text{H}_3\text{O}^+) = 2 \times R_{\text{formation}}(\text{Zn}^{2+})$.

5- The three points: O ($t = 0\text{ s}; [\text{Zn}^{2+}] = 0 \text{ mol L}^{-1}$); M ($t = t_{1/2} = 170 \text{ s}; [\text{Zn}^{2+}] = 0.125 \text{ mol L}^{-1}$) and N ($t = 1000 \text{ s}; [\text{Zn}^{2+}] = 0.2 \text{ mol L}^{-1}$).

Third exercise (6 points)

Expected answer	Comments
<p>I-</p> <p>1- The equation of the reaction is:</p> $\text{RCOOH} + \text{HO}^- \rightarrow \text{RCOO}^- + \text{H}_2\text{O}$ $K_R = \frac{[\text{RCOO}^-]}{[\text{RCOOH}][\text{HO}^-]} = \frac{[\text{RCOO}^-][\text{H}_3\text{O}^+]}{[\text{RCOOH}][\text{HO}^-][\text{H}_3\text{O}^+]}$ $K_R = \frac{K_a(\text{RCOOH}/\text{RCOO}^-)}{K_a(\text{H}_2\text{O}/\text{HO}^-)} = \frac{10^{-pK_a(\text{RCOOH}/\text{RCOO}^-)}}{10^{-pK_a(\text{H}_2\text{O}/\text{HO}^-)}} = 10^{pK_a(\text{H}_2\text{O}/\text{HO}^-) - pK_a(\text{RCOOH}/\text{RCOO}^-)}$	Direct application of the formula :1.

$K_R > 10^9 \gg 10^4$. The reaction is then total.

II-

1- The solubility of aspirin is 3.4 g, so the minimum volume of water needed to dissolve 300 mg = 0.3 g of aspirin is then: $V = \frac{0.3 \times 1}{3.4} = 0.088 \text{ L}$. which is $> 50 \text{ mL}$ and $< 200 \text{ mL}$.

Hence the capacity of the volumetric flask should be 200 mL.

Any reasonable answer is accepted.

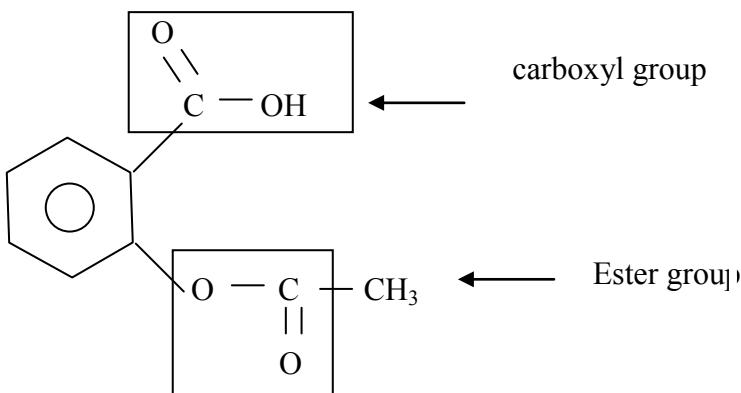
III-

1- At equivalence : n(aspirin) in the solution = n (HO^-) added

$$\frac{m}{180} = C_b \times V_{bE} = 0.1 \times 17 \times 10^{-3}$$

so $m = 0.306 \text{ g.} \cong 300 \text{ mg.}$

2-



3 – The reaction between the HO^- ions and the carboxyl group is an acid-base reaction.

The reaction between the HO^- ions and the ester group is a saponification reaction.

4- The acid-base titration is carried out at low temperature in order to avoid the saponification reaction that takes place at high temperature.

الاسم:
الرقم:

مسابقة في الكيمياء
المدة: ساعتان

This Exam Includes **Three Exercises**. It Is Inscribed On Three Pages Numbered From 1 to 3.
The Use of a Non-programmable Calculator Is Allowed.

Answer the Following Three Exercises:

First Exercise (7 points) **A Study of a Scale Removal, "W. C. NET"**

On the label of a scale removal " W. C. NET ", the following information is noted: contains hydrochloric acid of 13.5 % by mass.

The determination of the density of this liquid gives the following value: $d = 1.07 \text{ g.mL}^{-1}$.
The purpose of this exercise is to verify the indication 13.5 % by titration using pH - meter.

Given :

- $M_{\text{HCl}} = 36.5 \text{ g.mol}^{-1}$.
- $pK_a(\text{H}_3\text{O}^+/\text{H}_2\text{O}) = 0$; $pK_a(\text{H}_2\text{O}/\text{HO}^-) = 14$.

I- Dilution of the Scale Removal

- 1- Show, according to the above indication, that the concentration of hydrochloric acid in the scale removal is $C_0 = 3.92 \text{ mol.L}^{-1}$.
- 2- To perform the titration of the above scale removal, it is required to dilute this product 50 times. Choose, among the following list, the convenient glassware used to perform this dilution. Justify your choice.
 - 50, 100 and 200 mL beakers;
 - 5, 10 and 20 mL volumetric pipets;
 - 100, 200 and 500 mL volumetric flasks.

The obtained diluted solution is called (S_a).

II- Carrying Out Titration

A volume $V_a = 10 \text{ mL}$ of solution (S_a) is titrated with a sodium hydroxide solution of concentration $C_b = 7.8 \times 10^{-2} \text{ mol.L}^{-1}$.

- 1- Write the equation of the titration reaction and calculate its constant K_R .
- 2- The results of the pH-meter titration are given in the following table:

$V_b(\text{mL})$	0	2	4	6	8	9	9.5	10	10.5	11.5	12	12.5	14	16
pH	2.4	2.5	2.6	2.7	2.9	3.1	3.3	3.5	4.4	9.6	10.0	10.3	10.6	10.8

Plot, on the provided graph paper, the curve $\text{pH} = f(V_b)$.

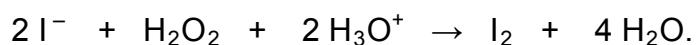
Take the following scale: abscissa (1 cm for 2 mL); ordinate (1 cm for 1 pH unit).

3- Determine:

- a) The coordinates of the equivalence point by the parallel tangents method.
- b) The concentration of solution (S_a).
- 4- Deduce, according to the titration results, the percentage by mass of HCl in the scale removal "W. C. NET." Specify if the information on the label is verified when the acceptable range of error is up to 5 %..

Third Exercise (6½ points)
Kinetic of the Oxidation of Iodide Ions by Hydrogen Peroxide

It is suggested to study the oxidation of iodide ions by hydrogen peroxide solution. This slow reaction takes place according to the following equation:



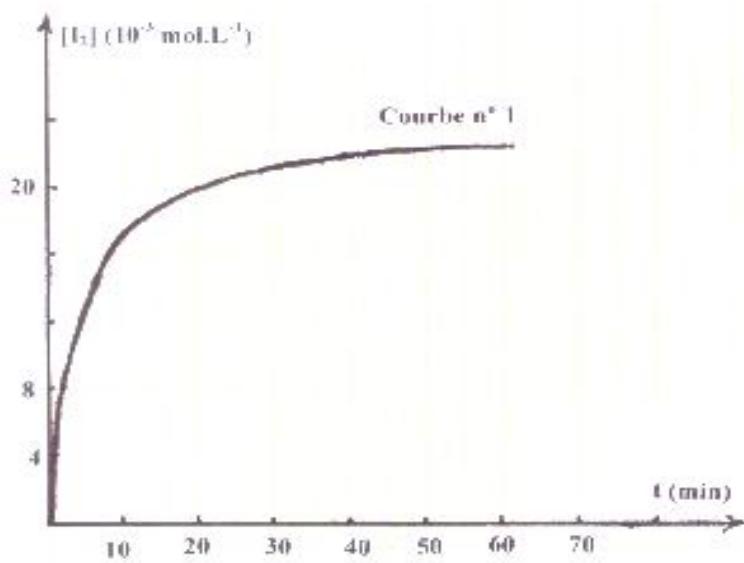
At time $t = 0$, a volume $V_1 = 60 \text{ mL}$ potassium iodide solution of concentration $C_1 = 0.1 \text{ mol.L}^{-1}$ is mixed, in a beaker, with a volume $V_2 = 40 \text{ mL}$ of an acidified hydrogen peroxide solution of concentration $C_2 = 0.06 \text{ mol.L}^{-1}$.

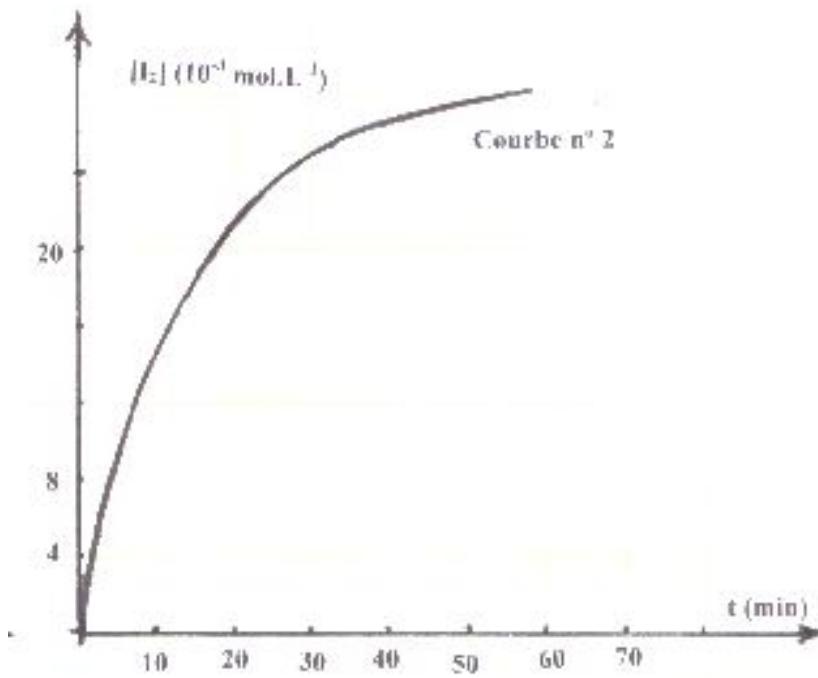
I- Preliminary Study

- 1- Calculate the concentration of iodide ions, $[\text{I}^-]_0$, and of hydrogen peroxide, $[\text{H}_2\text{O}_2]_0$, in the mixture at $t = 0$.
- 2- Determine the limiting reactant.

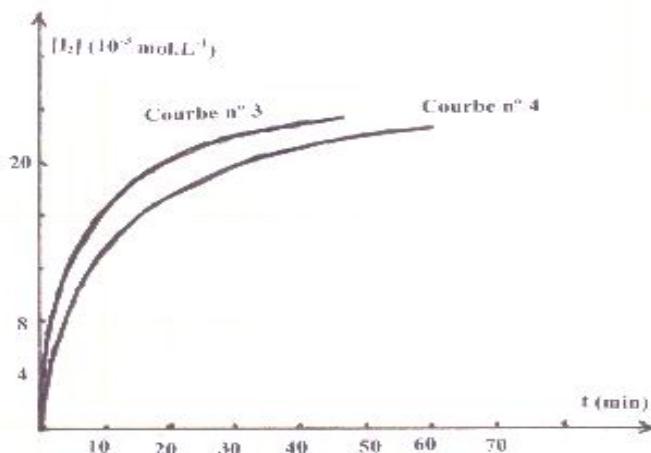
II- Kinetic Factors

- 1- Choose the curve that represents the variation of the concentration of I_2 as a function of time. Justify





- 2- The kinetic study of this reaction is performed with an appropriate setup. The curve that represents the variation of the concentration of iodine versus time is drawn. Two tangents are drawn on this curve at two different points and then their corresponding slopes are calculated. The obtained values are : $S_8 = 6.3 \times 10^{-4} \text{ mol.L}^{-1}.\text{min}^{-1}$ at $t = 8 \text{ min}$ and $S_{20} = 2 \times 10^{-4} \text{ mol.L}^{-1}.\text{min}^{-1}$ at $t = 20 \text{ min}$.
- Based on this information, deduce the rate of disappearance of I^- at $t = 8 \text{ min}$ and $t = 20 \text{ min}$.
 - By comparing the two rates, specify the involved kinetic factor.
- 3- Determine at $t_{1/2}$, the half-life of the reaction, the concentration of $[\text{I}^-]_{1/2}$.
- 4- We repeat, by using the same initial mixture, the kinetic study of the reaction at two different temperatures: $\theta_A = 25^\circ\text{C}$ and $\theta_B = 35^\circ\text{C}$. The two curves (n° 3 and n° 4) that represent the concentrations of I_2 versus time, at the two temperatures, are shown on the graph below.
- Attribute the curve that corresponds to each temperature and justify.



Second Exercise (6½ points)

A Chlorination Agent : PCl_5

The phosphorous pentachloride, PCl_5 is a white solid, at room temperature. It is a strong chlorination agent used in organic chemistry.

Given:

Molar atomic mass in $\text{g} \cdot \text{mol}^{-1}$: $M_{\text{H}} = 1$; $M_{\text{C}} = 12$; $M_{\text{O}} = 16$; $M_{\text{P}} = 31$; $M_{\text{Cl}} = 35.5$.

Molar mass of air is $29 \text{ g} \cdot \text{mol}^{-1}$.

I- PCl_5 Is an Unstable Compound

At 100°C and above, gaseous phosphorous pentachloride decomposes according to the following

equation:



1 mol of PCl_5 is introduced in a thermal reactor where the temperature could change from 100°C to 350°C . The decomposition of PCl_5 is followed by determining the density of the gaseous mixture relative to air (d), at different temperatures. The obtained results are given in the following table (1):

Temperature ($^\circ\text{C}$)	100	150	200	350
Relative density (d)	7.2	5.4	4.3	3.6

- 1- Rewrite the table (2) below, on the answer sheet, and complete it in terms of α , where α is the degree of dissociation of PCl_5 .

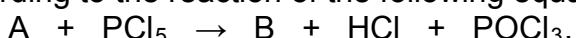
	PCl_5	PCl_3	Cl_2
Initial state (mol)	1	0	0
Equilibrium state (mol)			

- 2- Show that α and d are related to each other by the following relation: $d = \frac{208,5}{29(1+\alpha)}$.

- 3- Based on the contents of the table (1), deduce if the decomposition reaction of PCl_5 is endothermic or exothermic.

II- Chlorination Agent in Organic Chemistry

Phosphorous pentachloride reacts, at room temperature, with a carboxylic acid A, having a saturated carbon chain, according to the reaction of the following equation:



- 1- Determine the molecular formula of A. Write the condensed structural formula of A and of B and give the name of each. $M_{\text{A}} = 60 \text{ g} \cdot \text{mol}^{-1}$.

- 2 To prepare an ester having the banana odor, it is required to perform one of the two following reactions:

Reaction (1): the acid A is mixed with the alcohol 3-methyl-1-butanol ;

Reaction (2): the compound B is mixed with the alcohol 3-methyl-1-butanol.

a) Among the following terms, choose the convenient terms that characterize each one of the two reactions (1) and (2): athermic, complete, exothermic, reversible and endothermic.

b) Write the equation of the reaction between the acid A and the alcohol 3-methyl-1-butanol.

c) Deduce the advantage that results from the action of PCl_5 on acid A to give compound B in the preparation of esters.

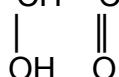
الاسم:
الرقم:مسابقة في مادة الكيمياء
المدة: ساعتان

This Exam Includes **Three Exercises**. It Is Inscribed on Three Pages Numbered From **1 to 3**.
The Use of A Non-programmable Calculator Is Allowed

Answer the Three Following Exercises:

First Exercise (6 points)
From Milk to Dipeptide

Lactose, main carbohydrate of milk, of molecular formula $C_{12}H_{22}O_{11}$, degrades to give lactic acid of condensed structural formula: $CH_3 - CH - C - OH$.



Given:

- Molar mass of lactic acid: $M = 90 \text{ g.mol}^{-1}$
- Milk is fresh when the concentration of lactic acid is lower than 1.8 g.L^{-1}
- Milk curdles when the concentration of lactic acid exceeds 5 g.L^{-1}

I- Study of the Condensed Structural Formula of Lactic Acid

Rewrite on the answer sheet the condensed structural formula of lactic acid.

- Circle the two functional groups in the molecule of lactic acid and give their corresponding names.
- Give the systematic name of lactic acid.
- Justify the existence of two enantiomers of lactic acid. Represent these two enantiomers according to Cram's representation.

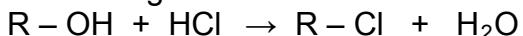
II- Titration of Lactic Acid in Milk

The lactic acid (weak acid noted as HA) in 20 mL of a milk is titrated with a sodium hydroxide solution of concentration $C_b = 5 \times 10^{-2} \text{ mol.L}^{-1}$. Equivalence point is reached when the added volume of sodium hydroxide solution is $V_{bE} = 11.9 \text{ mL}$.

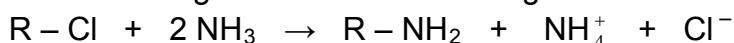
- Write the equation of the titration reaction.
- Calculate the concentration of lactic acid in the studied milk.
- Deduce if this milk can be considered as fresh or curdled milk.

III- From Lactic Acid to Dipeptide

An alcohol $R - OH$, when treated with hydrogen chloride, gives a chlorinated product $R - Cl$ according to the equation of the following reaction:



Compound $R - Cl$ reacts with ammonia to give an amine according to the following equation:



- Referring to the above reactions, write the equations of the reactions that permit to pass from lactic acid to 2-amino propanoic acid.
- Write the equation of the condensation reaction that permits to give the dipeptide from 2-amino propanoic acid.

Second Exercise (7 points)

An aldehyde: Ethanal

Ethanal is an organic compound highly used in chemical industry.

Ethanal is used in the preparation of ethanol, ethanoic acid, certain organic solvents, pharmaceutical products,

The melting and the boiling points of ethanal are respectively: $\theta_f = -123^\circ\text{C}$ and $\theta_b = 21^\circ\text{C}$.

I- Some Properties of Ethanal

- 1- Specify the physical state of ethanal at 18°C .
- 2- Indicate a chemical test to identify the reducing character of ethanal and give the expected corresponding observation.
- 3- Using condensed structural formulas, write the equations of the reactions that permit to prepare ethyl ethanoate from ethanal.

II- Kinetic of the Decomposition Reaction of Ethanal

In the gaseous phase, ethanal decomposes at high temperature $T = 780\text{ K}$, according to the equation of the following reaction:

$$\text{C}_2\text{H}_4\text{O}_{(g)} \rightarrow \text{CH}_4_{(g)} + \text{CO}_{(g)}$$

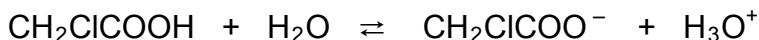
The kinetic study of this reaction is carried out by introducing n_0 mol of $\text{C}_2\text{H}_4\text{O}$ in a closed evacuated container of constant volume V . The total pressure P_t that predominates in the container is measured in terms of time (t). This study gives the following results at $T = 780\text{ K}$.

t (min)	0	5	10	15	20	30	40	50	60	80	100
$P_t(10^3\text{Pa})$	24.0	28.0	30.8	33.0	34.8	37.4	38.8	40.0	41.0	42.4	43.2

- 1- Give the expression of the total number of moles of the gaseous mixture, n_t , in terms of n_0 and x , where x represents the number of moles of CH_4 formed at instant t .
- 2- Interpret the increase of the pressure P_t with time.
- 3- Calculate the total pressure, P_t , in the container at the end of the reaction.
- 4- Trace, on the graph paper, the curve that represents the variation of the pressure P_t in terms of time (t): $P_t = f(t)$.
Take the following scale: abscissa (1 cm for 10 min); ordinate (1 cm for $4 \times 10^3\text{ Pa}$).
- 5- Determine, graphically, the half-life of the reaction.

Third Exercise (7 points)
Dilution of a Weak Acid Solution

Chloroacetic acid is a weak acid which reacts with water according to the following equation:



I- Study of a Solution of this Acid

100 mL of a solution (S) are prepared by dissolving 0.01 mol of chloroacetic acid in distilled water.

The pH of this solution is 1.93.

- 1- Calculate the concentration C of chloroacetic acid in solution (S).
- 2- Establish the following relation: $\alpha = \frac{10^{-pH}}{C}$ where α represents the degree of dissociation of chloroacetic acid in water. Calculate α .
- 3- Show that the pK_a of the pair chloroacetic acid/chloroacetate ion is close to 2.81.

II- Shape of the Curve of the Titration of (S) with a Strong Base

A volume $V = 20$ mL of solution (S) is titrated with a sodium hydroxide solution of concentration $C_1 = 0.1 \text{ mol.L}^{-1}$ by using a pH-meter.

- 1- Calculate the volume V_{bE} of sodium hydroxide solution added to reach the equivalence point.
- 2- Find the coordinates of the half-equivalence point.
- 3- The pH of the obtained mixture is equal to:
7.78 at equivalence and 12.50 upon the addition of 40 ml of the basic solution.
Draw the shape of the curve $\text{pH} = f(V_1)$, (V_1 is the volume of the basic solution added to carry out this titration and varies between 0 and 40 mL), using the coordinates of the four points previously found.
Take the following scale:
abscissa (1 cm for 2 mL); ordinate (1 cm for 1 unit of pH)

III- Effect of dilution on solution (S)

A sample of solution (S) is diluted 10 times to prepare a solution (S'). The measured pH of solution (S') is 2.53.

- 1- Calculate the concentration C' of chloroacetic acid in solution (S').
- 2- Deduce the effect of dilution of solution (S) on the degree of dissociation of chloroacetic acid in water.
- 3- A new titration is carried out, using a pH-meter, by adding progressively a sodium hydroxide solution of concentration 0.01 mol.L^{-1} into a beaker containing 20 mL of solution (S'). Justify that the obtained value of pH at the equivalence point, in this case, is between 7.00 and 7.78.

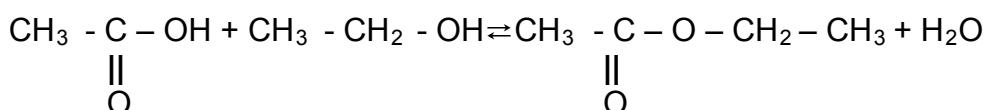
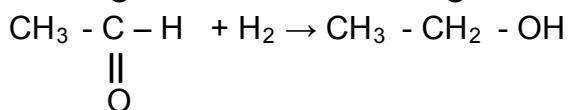
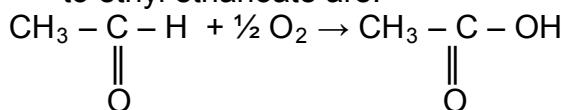
Expected Answer	Mark	Comments
<p>I-</p> <p>1- </p> <p>Carboxyl group</p> <p>Hydroxyl group</p> <p>2- The systematic name of lactic acid is 2-hydroxypropanoic acid.</p> <p>3- Carbon (2) in the carbon chain is attached to four different atoms or groups of atoms: H ; CH₃ ; OH ; and COOH. So carbon (2) is called asymmetric and there are two enantiomers for lactic acid shown as follows:</p> <p style="text-align: center;"> </p>	0.25x4	
	0.5	
	0.5	
	0.5	
<p>II-</p> <p>1- The equation of the titration reaction is: $HA + OH^- \rightarrow H_2O + A^-$</p> <p>2- At equivalence, number of moles of lactic acid in 20 ml of milk is equal to the number of moles of the hydroxide ions in V_{bE}. Or $n_{mol} = C \text{ in mol.L}^{-1} \times V \text{ in L of solution}$ so: $C_a V_a = C_b V_{bE}$ $C_a = \frac{5 \times 10^{-2} \times 11.9}{20} = 2.925 \times 10^{-2} \text{ mol.L}^{-1}$</p> <p>3- The concentration of lactic acid in milk in g.L⁻¹ is: $C = 2.925 \times 10^{-2} \times 90 = 2.63 \text{ g.L}^{-1}$. Since 1.8 < 2.63 < 5 so this milk is not fresh and does not curdle .</p>	0.5 0.25x2	Explanation 0.25
	0.25x2	
<p>III-</p> <p>1- The equations of the reactions are :</p> <p>$\begin{array}{ccc} CH_3 - CH - C(OH) - OH + HCl \rightarrow CH_3 - CH - C(Cl) - OH + H_2O \\ \quad \quad \quad \\ OH \quad O \quad Cl \quad O \end{array}$</p> <p>$CH_3 - CH - C(OH) - OH + 2 NH_3 \rightarrow CH_3 - CH - C(OH) - NH_4^+ + Cl^-$</p> <p>$\begin{array}{ccc} \quad \quad \quad \\ Cl \quad O \quad NH_2 \quad O \end{array}$</p> <p>2- The equation of the condensation reaction is : $CH_3 - CH - C(OH) - NH_2 + CH_3 - CO - OH \rightarrow CH_3 - CH - C(NH_2) - CH_3 + H_2O$</p> <p>$\begin{array}{ccc} \quad \quad \quad \quad \quad \\ NH_2 \quad O \quad CH_3 \quad O \quad NH_2 \quad O \quad H \quad CH_3 \quad O \end{array}$</p>	0.5 0.5 1	

Second exercice (7 points)
An Aldehyde, Ethanal

Expected Answer	Mark	Comments
<p>I-</p> <p>1- At 18° C, ethanal is in the liquid state since its temperature is between the melting point – 123°C and the boiling point 21° C.</p> <p>2- Ethanal is a reducing agent Fehling solution test gives a red-brick precipitate with ethanal This identifies the reducing character of</p>	0.5 0.25x2	0 without explanation Any other correct chemical test is

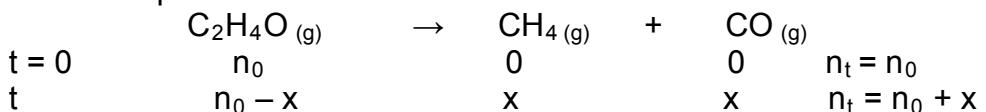
ethanal.

- 3- The equations of the reactions that permit to pass from ethanal to ethyl ethanoate are:



II-

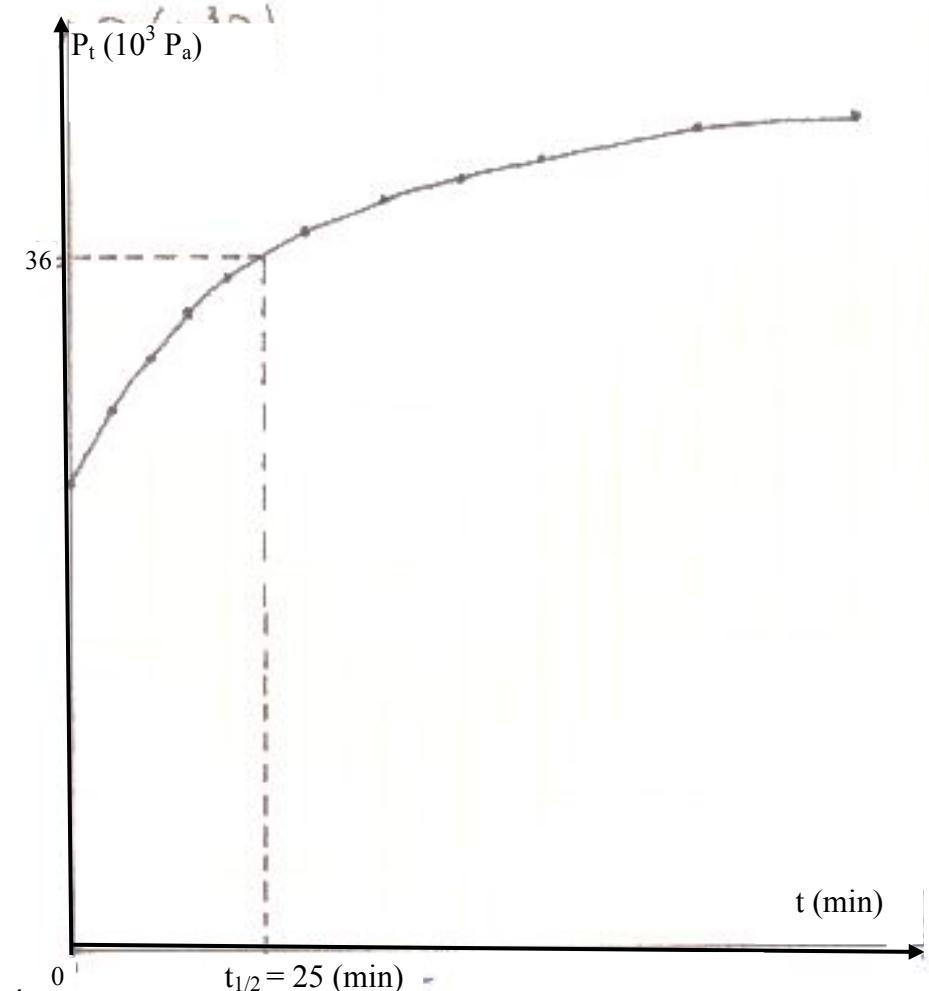
- 1- The equation of the reaction is :



- 2- According to the equation of state of an ideal gas $PV = nRT$, P_t is directly proportional to n_t since $T = \text{constant}$ and $V = \text{constant}$,

so P_t increases as n_t increases with time

- 3- At the end of the reaction, we have : $n_{t\infty} = 2n_0$
then $P_{t\infty} = 2P_0 = 2 \times 24 \times 10^3 \text{ Pa} = 48 \times 10^3 \text{ Pa}$



- 4- 5- the half-life of the reaction is the time needed for half the number of moles of ethanal to be decomposed.

acceptable

0.5

0.5

0.5

1

0.5

0.5

1

1.5

$$P_{t_{1/2}} = \frac{3}{2} P_0 = 36 \times 10^3 \text{ Pa. Graphically : } t_{1/2} = 25 \text{ min.}$$

Third exercice (7 points)
Dilution of a solution of a weak Acid

Expected Answer	Mark	Comments
I-		
1- The concentration of a solution is given by : $C = n_{\text{mol (soluté)}} / V_{\text{L (solution)}} = \frac{0.01}{0.1} = 0.1 \text{ mol.L}^{-1}$	0.5	
2- According to the equation of the reaction of the acid with water : $\text{CH}_2\text{ClCOOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_2\text{ClCOO}^- + \text{H}_3\text{O}^+$ $\begin{array}{lll} t=0 & C & 0 \\ t & C(1-\alpha) & C\alpha & C\alpha \end{array}$ We deduce : $[\text{H}_3\text{O}^+] = C\alpha$. so $\alpha = \frac{[\text{H}_3\text{O}^+]}{C} = \frac{10^{-pH}}{C} = 0.12$	1	
3- The constant K_a is shown by the expression : $K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_2\text{ClCOO}^-]}{[\text{CH}_2\text{ClCOOH}]} = \frac{(10^{-1.93})^2}{0.1 - 10^{-1.93}} = 10^{-2.81} \text{ and } pK_a = 2.81.$	0.75	
II-		
1- At equivalence: $n_{\text{chloroacetic acid in 20 mL}} = n_{\text{OH}^- \text{ added}}$ So: $V_{bE} = \frac{C_A V}{C_1} = \frac{0.1 \times 20}{0.1} = 20 \text{ mL.}$	0.5	
The coordinates of the half-equivalence point E' are : $pH = pK_a = 2.81$ and $V = \frac{V_{bE}}{2} = 10 \text{ mL.}$	0.5	
2- The curve admits two inflection points. E (20 – 7.78) and E' (10 – 2.81) and passes through the two points A (0 – 1.93) and B (40 – 12.5)		
	1.5	
III-		

<p>1- In dilution the number of moles of solute does not change $C' = C/10 = 0.01 \text{ mol.L}^{-1}$.</p> <p>2- $\alpha' = \frac{10^{-2,53}}{10^{-2}} = 0.295 > \alpha$. Dilution increases the degree of dissociation of chloroethanoic acid.</p> <p>3- At equivalence, the major species are the same as the preceding titration. Na^+ is a spectator ion and $\text{CH}_2\text{ClCOO}^-$ has basic character but with a lower concentration than before ; the pH remains greater than 7 but less than 7.78.</p>	0.5 0.75 1	
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الاسم:
الرقم:مسابقة في مادة الكيمياء
المدة: ساعتان

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.

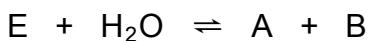
Answer The Following Three Exercises:

First Exercise (7 points) **Hydrolysis of an Ester**

The hydrolysis of an ester (E) gives an alcohol (A) and an acid (B). The aim of this exercise is to identify the compounds (A), (B), and (E).

I- Study of the Hydrolysis Reaction

A mixture of ester (E) and water is heated with few drops of concentrated sulphuric acid solution. After a certain time, the established homogenous equilibrium is represented by the following equation:



- 1- Let x be the number of moles of (B) formed at equilibrium. Rewrite and complete, on the answer sheet, the following table:

	E	H ₂ O	A	B
Initial state	1 mol	1 mol	0	0
Equilibrium state				

- 2- Indicate the role of heating and that of sulphuric acid in performing this hydrolysis reaction.
 3- Determine the equilibrium constant K_c knowing that $x = 0.4$ mol.
 4- Propose and justify a way to make the hydrolysis of (E) almost complete.

II- Identification of Compounds (A), (B) and (E)

After an almost complete hydrolysis of ester (E), the obtained alcohol (A) and acid (B) are separated.

- 1- A study shows that (A) is a saturated monoalcohol, with an open carbon chain, and the mass of carbon is 3 times that of oxygen.
 a) Determine the molecular formula of (A).
 b) In order to identify this alcohol, the following tests are carried out:

Test N°	Initial mixture	Observation and experimental results
Test 1	(A) + Acidified potassium permanganate solution (purple)	- Final solution is colorless. - Formation of an organic compound (C).
Test 2	(C) + 2,4- D.N.P.H.	- Yellow precipitate.
Test 3	(C) + Fehling's solution (blue)	- Blue solution.

Deduce the condensed structural formula of (A) and give its name.

- 2- A study shows that (B) is an α -amino acid.

- a) Write the general formula of an α -amino acid.
 b) Deduce the condensed structural formula of acid (B) knowing that its group R is composed of carbon and hydrogen atoms and its molar mass is $M_{(B)} = 89 \text{ g.mol}^{-1}$. Given, in g.mol^{-1} . $M_{(\text{C})} = 12$; $M_{(\text{H})} = 1$; $M_{(\text{O})} = 16$ and $M_{(\text{N})} = 14$.
 3-Write the condensed structural formula of ester (E) and give its name.

Second Exercise (6 points)
Kinetics for the Decomposition of $\text{C}_6\text{H}_5\text{N}_2\text{Cl}$

$\text{C}_6\text{H}_5 - \text{N}_2\text{Cl}$ is a non-oxygen explosive which is stored at a temperature less than 5°C . The decomposition of $\text{C}_6\text{H}_5 - \text{N}_2\text{Cl}$ in an aqueous medium at a temperature of 25°C is slow. This decomposition takes place according to the following equation:



Given:

- Molar volume of gas at the experimental conditions: $V_m = 25 \text{ L.mol}^{-1}$.

I- Preliminary Study

Consider 1 L of $\text{C}_6\text{H}_5 - \text{N}_2\text{Cl}$ aqueous solution of concentration $C = 2.0 \times 10^{-3} \text{ mol.L}^{-1}$.

- 1- Calculate, in mL, the volume of nitrogen gas formed as time tends to infinity.
- 2- Show, at each instant t , that the concentration of $\text{C}_6\text{H}_5 - \text{Cl}$, expressed in mol.L^{-1} is given by the following expression: $[\text{C}_6\text{H}_5 - \text{Cl}]_t = 4 \times 10^{-5} \times V$
 where V is the volume, in mL, of nitrogen gas formed at each instant t .

II- Kinetics of this Decomposition

The kinetics of this decomposition reaction in solution (S) is studied by measuring the volume V of the liberated nitrogen gas at different instants. The results are given in the following table:

t (min)	0	3	6	9	12	14	18	22
V (mL)	0	10.5	19	27	33	36	41	45
$[\text{C}_6\text{H}_5 - \text{Cl}]_t \times 10^4 (\text{mol.L}^{-1})$								

- 1- Rewrite and complete, on the answer sheet, the above table.
- 2- Plot, on a graph paper, the curve $[\text{C}_6\text{H}_5 - \text{Cl}] = f(t)$.
 Take the following scales: abscissa: 1 cm for 2 min; ordinate: 1 cm for $2 \times 10^{-4} \text{ mol.L}^{-1}$.
- 3- Determine the half-life of the reaction.
- 4- One liter of $\text{C}_6\text{H}_5 - \text{N}_2\text{Cl}$ solution, having a higher concentration than solution (S) is prepared. The kinetics of the decomposition of $\text{C}_6\text{H}_5 - \text{N}_2\text{Cl}$ is studied at the same temperature 25°C
 - The obtained volume of nitrogen gas at $t = 6$ min exceeds 19 mL. Justify.
 - Compare the volume of the liberated nitrogen gas at the end of the reaction ($t \rightarrow \infty$) to the volume of the nitrogen gas obtained in question (I- 1-).

Third Exercise (7 points) A Scale Product for Coffee-Pot

The main constituent of a scale product is sulfamic acid. It is sold commercially as white small crystals.

The aim of this exercise is to determine the percentage of sulfamic acid in the scale product by pH-metry.

Given:

- Sulfamic acid of formula $\text{NH}_2\text{SO}_3\text{H}$ will be represented as HA in this exercise.
- Molar mass of sulfamic acid in $\text{g}\cdot\text{mol}^{-1}$: $M = 97.1$.

Experimental Procedure:

first step: 2.05 g of this scale product are dissolved in distilled water to obtain a solution (S) of volume $V = 500 \text{ mL}$.

second step: A volume $V_a = 10 \text{ mL}$ of solution (S) is put into a beaker. A volume V' of distilled water is then added to immerse the electrode of the pH-meter.

third step: Titration is carried out by using sodium hydroxide solution of concentration $C_b = 4 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$.

I- Preliminary Study

- 1- Sulfamic acid is a strong acid. Write the equation of the reaction of this acid with water.
- 2- Indicate the appropriate material used to:
 - weigh the mass of 2.05 g ;
 - prepare the volume V ;
 - withdraw the volume V_a ;
 - add the sodium hydroxide solution.
- 3- Write the equation of the titration reaction.
- 4- Based on the chemical species which are present in the beaker, justify the value of $\text{pH} = 7$ at the equivalence point.

II- Make Use of the Titration Results

Part of the titration results is given in the following table:

$V_b (\text{mL})$	0	10.4	15
pH	2.4	7.0	11.0

- 1- Draw the shape of the curve $\text{pH} = f(V_b)$ for $0 \leq V_b \leq 15 \text{ mL}$. Take the following scales: abscissa : 1cm for 1mL, ordinate: 1 cm for 1 unit of pH.
- 2- Determine the concentration C_a of sulfamic acid in solution (S).
- 3- Deduce the mass percentage of sulfamic acid in this scale product.

III- Effect of Dilution on the pH Measurements

A solution (S') of the scale product is prepared by diluting solution (S) ten times.

- 1- Among the following kits, choose by justifying, the kit that should be used to carry out the most precise dilution of solution (S).

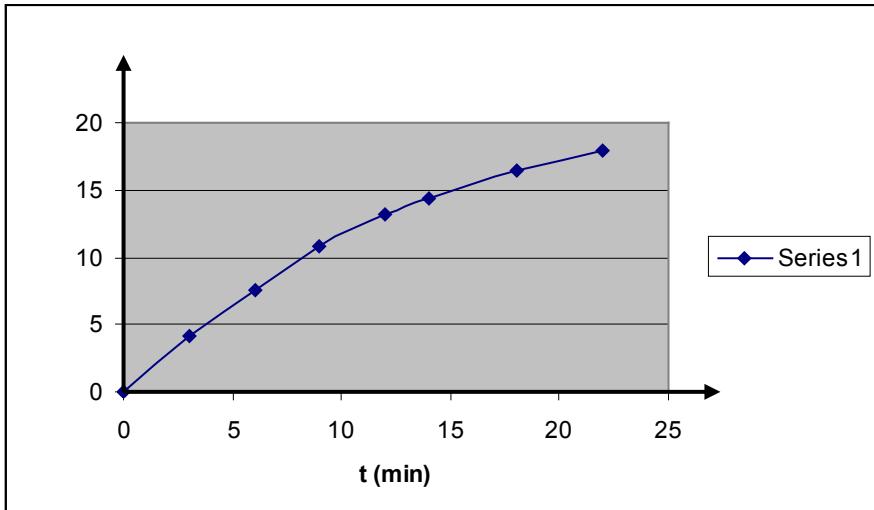
Kit – 1	Kit – 2	Kit - 3
<ul style="list-style-type: none"> • 10 mL volumetric pipet ; • 100 mL beaker. 	<ul style="list-style-type: none"> • 10 mL volumetric pipet ; • 100 mL volumetric flask. 	<ul style="list-style-type: none"> • 10 mL graduated cylinder; • 200 mL volumetric flask.

- 2- Another titration is carried out with (S') by repeating the second step of the above experimental procedure and using another sodium hydroxide solution of concentration $C_b' = 4 \times 10^{-3} \text{ mol.L}^{-1}$.

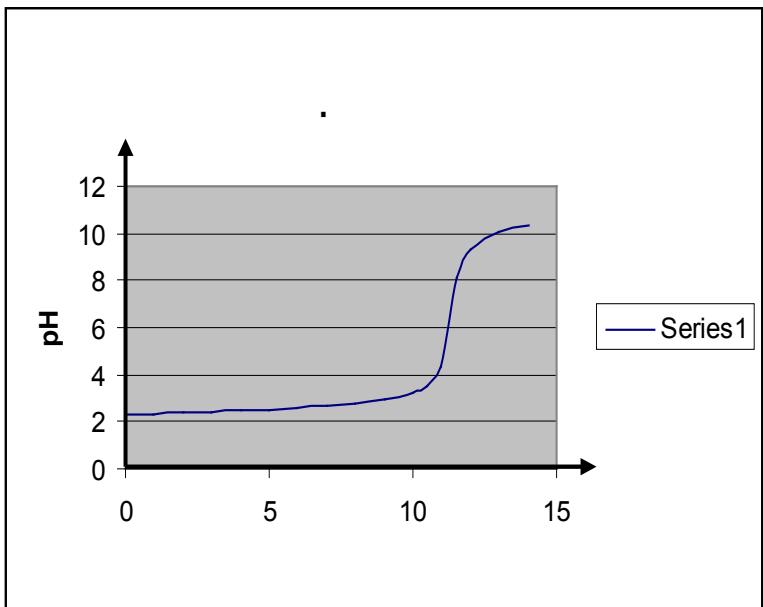
Give, by justifying, the value of pH that corresponds to the volume $V_b=10.4 \text{ mL}$.

Expected Answer	Mark	Comment															
I-																	
1- According to the stoichiometric coefficients, we have: $\frac{nE_{reacting}}{1} = \frac{nH_2O_{reacting}}{1} = \frac{nA_{formed}}{1} = \frac{nB_{formed}}{1} = x$ <table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td></td> <td style="text-align: center;">E</td> <td style="text-align: center;">H₂O</td> <td style="text-align: center;">A</td> <td style="text-align: center;">B</td> </tr> <tr> <td style="text-align: center;">Initial State</td> <td style="text-align: center;">1 mol</td> <td style="text-align: center;">1 mol</td> <td></td> <td></td> </tr> <tr> <td style="text-align: center;">Equilibrium State</td> <td style="text-align: center;">(1-x) mol</td> <td style="text-align: center;">(1-x) mol</td> <td style="text-align: center;">x mol</td> <td style="text-align: center;">x mol</td> </tr> </table>		E	H ₂ O	A	B	Initial State	1 mol	1 mol			Equilibrium State	(1-x) mol	(1-x) mol	x mol	x mol	1	
	E	H ₂ O	A	B													
Initial State	1 mol	1 mol															
Equilibrium State	(1-x) mol	(1-x) mol	x mol	x mol													
2- Heating increases the rate of the reaction (kinetic factor). Sulphuric acid, which is added in a small quantity, has the role of a catalyst.	0.25																
3- The equilibrium constant of the above reaction is given by the following relation: $K_c = \frac{[A][B]}{[E][H_2O]}$. We have then $K_c = \frac{\frac{0.4}{V} \cdot \frac{0.4}{V}}{\frac{0.6}{V} \cdot \frac{0.6}{V}} = \frac{4}{9} = 0.44.$	0.25																
4- In order to have a complete hydrolysis, we add a quantity of water. The reaction is then displaced in the forward direction (direction of hydrolysis), according to Le Chatelier's principle, when a stress is applied to a system at an equilibrium state, the system readjusts itself by reducing or opposing this stress.	0.5	Any other suitable proposition is acceptable															
II-																	
1- a) The general formula of a saturated monoalcohol of an open carbon chain is $C_nH_{2n+2}O$. Since $m_{(C)} = 3 m_{(O)}$, we have then: $12n = 3 \times 16$. $n = 4$. The molecular formula of (A) is then C_4H_9OH .	1	$C_nH_{2n+1}OH$															
b) According to test 1, we conclude that (A) is a primary or a secondary alcohol, because it undergoes mild oxidation. According to test 2, (C) is a carbonyl compound (aldehyde or ketone).	1																
According to test 3, we conclude that (C) is a ketone. Then (A) is a secondary alcohol of condensed structural formula: $CH_3 - CH_2 - CHO - CH_3$. Its name is 2-butanol.	2x0.25																
2- a) The general formula of an α -amino-acid is:																	
$R - CH - COOH$ $ $ $NH2$	0.5																
b) $M_R + 12 + 1 + 14 + 2 + 32 + 12 + 1 = 89$, then: $M_R = 15$. R formed of carbon and hydrogen should be in the form of CH_3 .	0.5																
c) The formula of ester (E) is then: $CH_3 - CH - C - O - CH - CH_2 - CH_3.$ $ \begin{array}{ccccc} & & & & \\ NH_2 & O & & CH_3 & \\ \parallel & & & & \end{array} $	0.25																
It is 2-butyl-2-amino propanoate .	0.25																

Second Exercise (6 points)
Kinetics Of the Decomposition of $C_6H_5N_2Cl$

Expected Answer	Mark	Comment																		
I-																				
1- According to the stoichiometric coefficients: $n(N_2)_{\text{formed at } t \rightarrow \infty} = n(C_6H_5N_2Cl) = CxV = 2 \times 10^{-3}$ mol. The volume of nitrogen is then: $V(N_2) = nxV_m = 2 \times 10^{-3} \times 25 = 50 \times 10^{-3}$ L=50 mL	1																			
2- $n(C_6H_5Cl)_{\text{formed}} = n(N_2)_{\text{formed}}$. $[C_6H_5Cl]_t = \frac{V(N_2)}{V_m \times V_{\text{solution}}} = \frac{V \times 10^{-3}}{V_m \times 1} = \frac{V \times 10^{-3}}{25} = 4 \times 10^{-5} V$	1																			
II-																				
1- We multiply by 0.4, we have then :																				
<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="padding: 2px;">t (min)</td> <td style="padding: 2px;">0</td> <td style="padding: 2px;">3</td> <td style="padding: 2px;">6</td> <td style="padding: 2px;">9</td> <td style="padding: 2px;">12</td> <td style="padding: 2px;">14</td> <td style="padding: 2px;">18</td> <td style="padding: 2px;">22</td> </tr> <tr> <td style="padding: 2px;">$[C_6H_5N_2Cl] \times 10^{-4} \text{ mol.L}^{-1}$</td> <td style="padding: 2px;">0</td> <td style="padding: 2px;">4.2</td> <td style="padding: 2px;">7.6</td> <td style="padding: 2px;">10.8</td> <td style="padding: 2px;">13.2</td> <td style="padding: 2px;">14.4</td> <td style="padding: 2px;">16.4</td> <td style="padding: 2px;">18.0</td> </tr> </table>	t (min)	0	3	6	9	12	14	18	22	$[C_6H_5N_2Cl] \times 10^{-4} \text{ mol.L}^{-1}$	0	4.2	7.6	10.8	13.2	14.4	16.4	18.0	0.5	
t (min)	0	3	6	9	12	14	18	22												
$[C_6H_5N_2Cl] \times 10^{-4} \text{ mol.L}^{-1}$	0	4.2	7.6	10.8	13.2	14.4	16.4	18.0												
2- The curve $[C_6H_5Cl] = f(t)$.	1																			
																				
3- The half-life of the reaction is the time needed for half the amount of $C_6H_5N_2Cl$ to disappear. So the time that corresponds to the concentration $[C_6H_5Cl]_{t1/2} = 10 \times 10^{-4} \text{ mol.L}^{-1}$ is $t_{1/2} = 8.2$ min.	1	or the time needed for half the maximum amount of C_6H_5Cl to appear .																		
4- a) Since the new solution has a higher concentration than solution (S), so the rate of the reaction is greater. Starting from the same volume 1 L, the obtained volume of nitrogen is greater than 19 mL at $t = 6$ min.	0.75																			
b) Because the solution has a higher concentration, starting from the same volume 1 L, the number of moles of the reactant is greater and consequently the volume of nitrogen gas at $t \rightarrow \infty$ is greater than the volume obtained in the first case.	0.75																			

Third Exercise (7 points)
Scale Product for Coffee-Pot

Expected Answer	Mark	Comment
<p>I-</p> <p>1- The equation of the reaction of sulfamic acid with water is: $\text{HA} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{A}^-$</p> <p>2- To weigh: sensitive balance (1/100). To prepare V = 500 mL: 500 mL volumetric flask. To take V_a: 10 mL volumetric pipet. To add NaOH: buret.</p> <p>3- Since, it is a reaction between a strong acid and a strong base, the equation is then: $\text{H}_3\text{O}^+ + \text{HO}^- \rightarrow 2 \text{H}_2\text{O}$.</p> <p>4- The species that are present at equivalence point, other than water, are Na^+ and A^-, which are spectator ions (neutral particles). The pH is then equal to 7.</p>	0.5 4x0.25 0.5 0.5	
<p>II-</p> <p>1-</p> 	1	
<p>2- At equivalence point, we have: $n_{\text{H}_3\text{O}^+}$ (in beaker) = n_{HO^-} (poured). Knowing that, in a solution: $n = CxV$, where: $C_aV_a = C_bV_{bE}$; we conclude: $C_a = \frac{4 \times 10^{-2} \times 10.4}{10} = 4.16 \times 10^{-2} \text{ mol.L}^{-1}$.</p> <p>3- $n(\text{HA}) = 4.16 \times 10^{-2} \times 0.5 = 2.08 \times 10^{-2} \text{ mol}$; $m(\text{HA}) = 2.08 \times 10^{-2} \times 97.1 = 2.02 \text{ g}$; and the percentage by mass is: $\% = \frac{2.02}{2.05} \times 100 = 98.53 \%$.</p>	0.25 0.75 1	
<p>III-</p> <p>1- When the solution is diluted ten times, the final volume becomes ten times greater than the initial volume. The suitable</p>		

<p>glass-ware that should be used are: 10 mL volumetric pipet and 100 mL volumetric flask, so kit-2- is convenient.</p> <p>2-</p> <p>Because the titration takes place between a strong acid and a strong base and both have been diluted 10 times, the pH at the equivalence point, where $V_{bE} = 10.4$ mL remains the same, is equal to 7.</p> <p>Or $C_b' V_b' = C_a' V_a' \Rightarrow V_b' = \frac{C_a}{C_b} \times 10 = \frac{4.16 \times 10^{-2}}{4 \times 10^{-2}} \times 10 = 10.4$ mL</p> <p>So the pH that corresponds to this volume is 7.</p>	1 0,5	
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الاسم:	مسابقة في الكيمياء
الرقم:	المدة ساعتان

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

Answer The Following Three Exercises:

First Exercise (6 points) **Propanoic Acid**

This exercise aims to prepare a solution of propanoic acid, which is a weak acid of formula ($C_2H_5 - COOH$), in order to determine the degree of purity of a sample of magnesium.

Given:

- Molar mass of magnesium: $M (Mg) = 24 \text{ g.mol}^{-1}$.
- pH range of bromothymol blue: yellow 6.0 – 7.6 blue.

I- Preparation of an Aqueous Solution of Propanoic Acid

Available material list:

- * 5 mL, 10 mL and 20 mL volumetric pipets;
- * 10 mL, 100 mL and 200 mL graduated cylinders;
- * 50 mL, 100 mL and 200 mL beakers;
- * 50 mL, 100 mL and 200 mL volumetric flasks;
- * A pipet filler.

A volume $V_S = 200 \text{ mL}$ of solution S of propanoic acid of concentration $C_S = 1 \text{ mol.L}^{-1}$ is required to be prepared from an aqueous solution of propanoic acid S_0 of concentration $C_0 = 10 \text{ mol. L}^{-1}$;

- 1- Find the expression that permits to calculate the volume V_0 of solution S_0 which could be taken for the preparation of solution S. Calculate V_0 .
- 2- Choose, from the above list, the appropriate material for this preparation.

II- Action of Propanoic Acid on Magnesium

A volume $V = 50 \text{ mL}$ of solution S, to which few drops of bromothymol blue has been added, is introduced into a beaker containing 0.45 g of a sample of magnesium. The propanoic acid attacks the magnesium by giving hydrogen gas and magnesium propanoate which is soluble in water. The remaining solution is still yellow at the end of the reaction.

- 1- Show that magnesium reacts completely.
- 2- Write the equation of the reaction that takes place in the beaker.

III- Determination of the Percentage of Magnesium In the Sample

The steps below are carried out in order to determine the degree of purity of magnesium in the sample:

- Filtration of the remaining solution at the end of the reaction in part II.
- Removal of impurities and magnesium ions Mg^{2+} from the filtrate.

- Titration of the acid in the filtrate with a sodium hydroxide solution of concentration $C_b = 0.5 \text{ mol. L}^{-1}$. The equivalence point is reached when the added volume of the basic solution is $V_{bE} = 32.5 \text{ mL}$.
- 1- Write the equation of the titration reaction.
 - 2- Determine the number of moles of the acid in the filtrate.
 - 3- Calculate the number of moles of the acid reacting with magnesium.
 - 4- Deduce the percentage by mass of magnesium in the used sample.

Second Exercise (7 points) Decomposition of Javel Water

Javel water is an aqueous solution containing the following ions: hypochlorite ClO^- , chloride Cl^- and sodium Na^+ . It is very often used as a disinfectant due to the oxidizing character of the hypochlorite ions.

Javel water decomposes very slowly according to the reaction of the following equation:



This reaction could be accelerated by light or by using a catalyst of a cobalt compound such as cobalt (II) chloride (CoCl_2).

Given:

- Take molar volume of gas: $V_m = 24 \text{ L.mol}^{-1}$.

I- Decomposition of Javel Water

In order to study the kinetic of the decomposition reaction of Javel water, at the instant when the cobalt ions Co^{2+} are introduced into a volume $V = 110 \text{ mL}$ of Javel water solution called (S), the volume of the obtained oxygen gas is measured.

The concentration of the remaining ions (ClO^-) in the solution (S) at each instant t is then deduced. The results are given in the following table:

$t \text{ (s)}$	0	30	60	90	120	150	180	210	240	300
$[\text{ClO}^-] \text{ mol.L}^{-1}$	0.24	0.20	0.17	0.14	0.12	0.10	0.080	0.060	0.046	0.026

- 1- Plot, on a graph paper, the curve representing the variation of $[\text{ClO}^-]$ versus time. Take the following scales:
abscissa: 1 cm for 30 s; ordinate: 1 cm for 0.02 mol.L^{-1} .
- 2- Determine the rate of disappearance of ClO^- at instant $t = 210 \text{ s}$
- 3- Knowing that the rate of disappearance of ClO^- , at instant $t = 0$, is $1.6 \times 10^{-3} \text{ mol.L}^{-1} \cdot \text{s}^{-1}$, identify the kinetic factor that is responsible for the variation of this rate with time.
- 4- Determine, graphically, the half-life of the reaction $t_{\frac{1}{2}}$.
- 5-
- a) Show that the concentration of hypochlorite ions $[\text{ClO}^-]_t$, in mol.L^{-1} , and the volume of oxygen gas $V(\text{O}_2)_t$, in mL, at instant t , are related by the following relation:

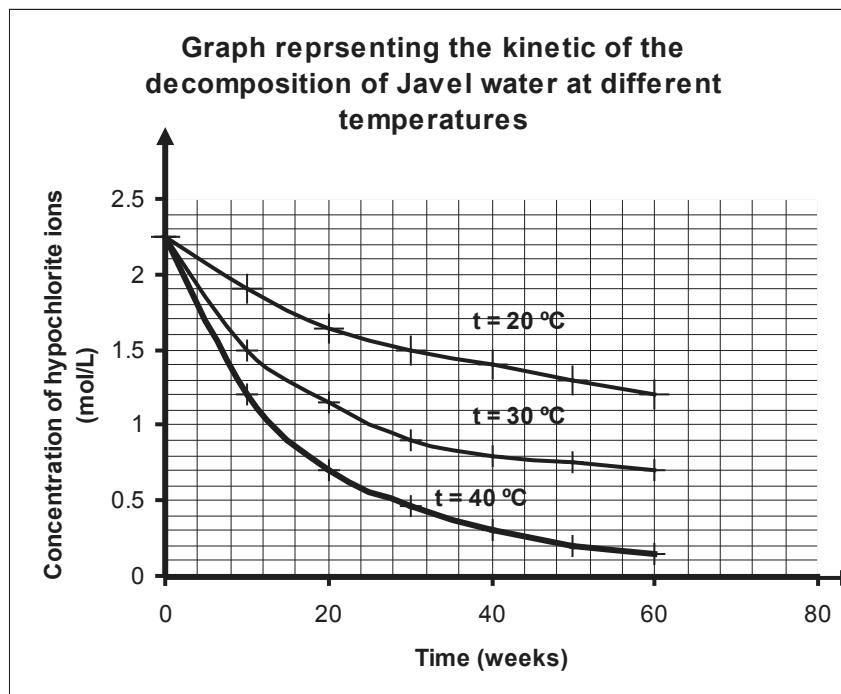
$$[\text{ClO}^-]_t = 0.24 - 7.57 \times 10^{-4} \times V(\text{O}_2)_t.$$
- b) Identify the chemical species which are present in the solution (S) when the volume $V(\text{O}_2) = 317 \text{ mL}$.

II- Stability and Precautions of Use

Among the recommendations on the label of a bottle of Javel water it is written: "store in cold place without exposure to sun and light".

The graph below shows the progress of the decomposition reaction of Javel water at different

temperatures.



Referring to the above graph, justify the recommendation " stored in cold place without exposure to sun ...".

Third Exercise (7 points) Saponification Reaction

This exercise aims to prepare soap by two processes and to study the principle of detergency of soap.

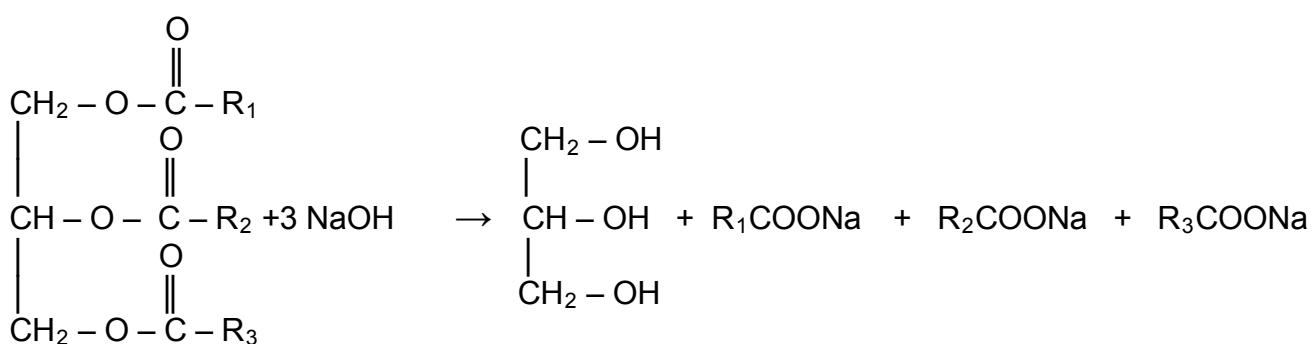
Given:

- Molar masses in g.mol⁻¹: palmitic acid: M₁ = 256; sodium palmitate: M₂ = 278.

I- Saponification of Glyceryl Palmitate

Glyceryl palmitate is the triester of palmitic acid ($C_{15}H_{31}-COOH$) and glycerol ($CH_2OH-CHOH-CH_2OH$).

Saponification is a reaction between fatty substances (fats and oils) with sodium hydroxide (or potassium hydroxide). It is represented by the following equation:



- 1- Write the equation of the saponification reaction between the glyceryl palmitate and

- sodium hydroxide.
- 2- Give the systematic name of the obtained alcohol (glycerol).
 - 3- Among the following terms: fast, slow, complete, reversible and impossible, choose those that characterize this saponification reaction.

II- Industrial Preparation of Soap

Soap could be prepared by the continuous process, designated as the hydrolysis process. By this process, fatty acids are prepared by the hydrolysis of the appropriate lipids and oils, under pressure and high temperature. These acids are separated from glycerol and purified, and then made to react with sodium hydroxide to obtain soap and water.

The above process is used to prepare the soap from 1 ton of beef fat.

- 1- Write the equation of the hydrolysis reaction of glyceryl palmitate.
- 2- Write the equation of the reaction between palmitic acid and sodium hydroxide.
- 3- Calculate the number of moles of the obtained palmitic acid, knowing that the mass of this acid issued from beef fat is equal to 25 % of the mass of the beef fat.
- 4- The obtained soap (sodium palmitate) has a mass of 250 kg. Determine the yield of this preparation of soap.

III- Structure of carboxylate ion

Carboxylate ion ($R - COO^-$) of soap is formed of two parts, the hydrocarbon chain ($R -$) and the carboxylate group ($- COO^-$).

- 1- Give the meaning of the two terms: hydrophilic and hydrophobic.
- 2- Indicate, in the carboxylate ion, the part that corresponds to the hydrophilic group and that part that corresponds to the hydrophobic group.
- 3- Specify the role of the structure of the carboxylate ion in the cleaning process by soap.

First Exercise (6 points)
Propanoic Acid

Expected Answer	Mark	Comment
I- Preparation of an aqueous solution of propanoic acid 1- By dilution the number of moles of solute does not change, that allows to write: $n = C_0 \times V_0 = C_S \times V_S$. where: $V_0 = \frac{C_S \times V_S}{C_0}$.	0.25	
$V_0 = \frac{1 \times 200}{10} = 20 \text{ mL.}$	0.25	
2- The material used to carry out this preparation includes: a 20 mL volumetric pipet, 200 mL volumetric flask, pipet filler and a beaker.	0.5	0 without pipet or volumetric flask
II-Action of propanoic acid on magnesium 1- Since the solution is still yellow at the end of the reaction this means that the medium is acidic because the BBT gives a yellow color when the pH is acid. Thus, we conclude that the magnesium reacted completely . 2-The equation of the reaction that takes place in the beaker is: $2 \text{CH}_3 - \text{CH}_2 - \text{COOH} + \text{Mg} \rightarrow 2 \text{CH}_3 - \text{CH}_2 - \text{COO}^- + \text{Mg}^{2+} + \text{H}_2 \text{(g)}$	0.75	
III-Determination of the percentage of magnesium in the sample 1- The equation of the titration reaction is: $\text{CH}_3 - \text{CH}_2 - \text{COOH} + \text{HO}^- \rightarrow \text{CH}_3 - \text{CH}_2 - \text{COO}^- + \text{H}_2\text{O}$	0.5	
2- At the equivalence point, the number of moles of acid in the beaker is equal to the number of moles of HO^- added. So the number of moles of the titrated acid is: $n_{\text{titrated}} = C_b (\text{mol.L}^{-1}) \times V_{bE} (\text{L}) = 0.5 \times 32.5 \times 10^{-3} = 16.25 \times 10^{-3} \text{ mol.}$	0.25	
3- The number of moles of acid reacting with magnesium is given by: $n = n_0 - n_{\text{titrated}} = C_S \times V_{(L)} - n_{\text{titrated}} = 1 \times 50 \times 10^{-3} - 16.25 \times 10^{-3}$. Where: $n = 33.75 \times 10^{-3} \text{ mol.}$	0.75	
4- The percentage by mass of magnesium in the sample is given by: $\frac{m_{(\text{Mg})} \times 100}{m_{(\text{min erai})}} = \frac{n_{(\text{Mg})} \times M_{(\text{Mg})} \times 100}{m_{(\text{min erai})}}$ According to the equation, we have: $n_{(\text{Mg}) \text{ reacting}} = \frac{n_{(\text{acid}) \text{ reacting}}}{2} = \frac{n}{2} = 16.875 \times 10^{-3} \text{ mol.}$ The percentage is then: $\frac{16.875 \times 10^{-3} \times 24 \times 100}{0.45} = 90\%.$	1.25	

Second Exercise (7 points)
Decomposition of Javel Water

Expected Answer	Mark	Comment												
I-Decomposition of Javel water 1- The curve representing the variation of $[ClO^-]$ versus time:	1.25													
<p>The graph shows a linear decrease in concentration over time, indicating a first-order reaction. The y-axis is labeled "Concentration of hypochlorite ions (mol/L)" and ranges from 0 to 0.3. The x-axis is labeled "Time (s)" and ranges from 0 to 400. A blue curve starts at (0, 0.24) and ends at (320, 0). A tangent line is drawn at t = 210 s, passing through points M(320, 0) and N(0, 0.19).</p> <table border="1"> <caption>Data points estimated from the graph</caption> <thead> <tr> <th>Time (s)</th> <th>Concentration (mol/L)</th> </tr> </thead> <tbody> <tr><td>0</td><td>0.24</td></tr> <tr><td>100</td><td>0.14</td></tr> <tr><td>200</td><td>0.06</td></tr> <tr><td>300</td><td>0.02</td></tr> <tr><td>320</td><td>0.00</td></tr> </tbody> </table>	Time (s)	Concentration (mol/L)	0	0.24	100	0.14	200	0.06	300	0.02	320	0.00		
Time (s)	Concentration (mol/L)													
0	0.24													
100	0.14													
200	0.06													
300	0.02													
320	0.00													
2- The rate of disappearance of ClO^- $r = -\frac{d[ClO^-]}{dt}$; is equal to the negative slope of the tangent to the curve at instant $t=210s$ Calculation of the rate : M & N are two points on the tangent of coordinates M(320-0) and N(0-0.19). So $r = -\frac{0 - 0.19}{320 - 0} = 5.9 \times 10^{-4} \text{ mol.L}^{-1}.\text{S}^{-1}$.	1.25													
3- Rate at $t=0$ > rate at $t=210$, the rate decreases with time. The factor that is responsible for this decrease is the concentration of hypochlorite ions that lead to reduce the rate.	0.5													
4- The half-life of the reaction is the time needed for half the concentration of $[ClO^-]_0$ to disappear. It becomes 0.12 mol.L^{-1} at time $t_{1/2} = 138 \text{ s}$.	1													
5-														
a) $[ClO^-]_t = \frac{n(ClO^-)_t}{V(solution)_L} = \frac{n_0 - n_{reacting}}{V} = [ClO^-]_0 - \frac{2n(O_2)_{formed}}{V}$ $[ClO^-]_t = 0.24 - \frac{2xV(O_2)_t}{24 \times 10^3 \times 110 \times 10^{-3}} = 0.24 - 7.57 \times 10^{-4} x V(O_2)_t$	1													
b) For a volume $V(O_2)_t = 317 \text{ mL}$ we have: $[ClO^-]_t = 0$. This means that the hypochlorite ions reacted completely and the species that are present in the solution other than water are the ions: chloride and cobalt.	1													
III- The graph shows that the increase in temperature accelerates the rate of the decomposition of hypochlorite ions. This leads to a decrease in the	1													

concentration of the hypochlorite ions that reduces its disinfecting power. Thus, Javel water should be stored away from heat sources like sun ...; that justifies this recommendation.

Third Exercise (7 points) Saponification Reaction

Expected Answer	Mark	Comment
I-		
1- $\begin{array}{c} \text{O} \\ \\ \text{CH}_2 - \text{O} - \text{C} - \text{C}_{15}\text{H}_{31} \\ \\ \text{O} \\ \\ \text{CH} - \text{O} - \text{C} - \text{C}_{15}\text{H}_{31} + 3(\text{NaOH}) \rightarrow \begin{array}{c} \text{CH}_2 - \text{OH} \\ \\ \text{CH} - \text{OH} + 3(\text{C}_{15}\text{H}_{31} - \text{COONa}) \\ \\ \text{CH}_2 - \text{OH} \\ \\ \text{CH}_2 - \text{O} - \text{C} - \text{C}_{15}\text{H}_{31} \end{array} \end{array}$	1	
2- It is the 1,2,3-tripropanol.	0.25	
3- The saponification reaction is slow and complete.	0.5	
II-		
1- The equation of the reaction is: $\begin{array}{c} \text{O} \\ \\ \text{CH}_2 - \text{O} - \text{C} - \text{C}_{15}\text{H}_{31} \\ \\ \text{O} \\ \\ \text{CH} - \text{O} - \text{C} - \text{C}_{15}\text{H}_{31} + 3\text{H}_2\text{O} \rightleftharpoons \begin{array}{c} \text{CH}_2 - \text{OH} \\ \\ \text{CH} - \text{OH} + 3\text{C}_{15}\text{H}_{31} - \text{COOH} \\ \\ \text{CH}_2 - \text{OH} \\ \\ \text{CH}_2 - \text{O} - \text{C} - \text{C}_{15}\text{H}_{31} \end{array} \end{array}$	1	
2 The equation of the reaction is: $\text{C}_{15}\text{H}_{31} - \text{COOH} + \text{NaOH} \rightarrow \text{C}_{15}\text{H}_{31} - \text{COONa} + \text{H}_2\text{O}$	0.5	
3- The number of moles palmitic acid is: $n = \frac{m(\text{acid})}{M(\text{acid})} = \frac{m(\text{tallow}) \times 25}{M(\text{acid}) \times 100} = \frac{10^6 \times 25}{256 \times 100} = 976.56 \text{ mol.}$	0.75	
4- The yield R = $\frac{n(\text{soap})_{\text{obtained}}}{n(\text{soap})_{\text{theoric}}} \times 100.$ $n_{\text{theoric}} = n_{\text{acid}}$ et $n_{\text{obtained}} = \frac{m(\text{soap})}{M(\text{soap})}$; where: $R = \frac{250 \times 10^3}{278 \times 976.56} \times 100 = 92 \text{ %}.$	1.5	
III-		
1- Hydrophilic means water loving; hydrophobic means water hating.	2x0.25	
2- The hydrocarbon group ($\text{R}-$) is hydrophobic and the group ($-\text{COO}^-$) is hydrophilic.	2x0.25	
3- This structure offers to carboxylate ions of soap the hydrophilic and hydrophobic characters which are at the base of the solubility of the soap in water and in lipids that facilitates its cleaning power.	0.5	

الاسم: الرقم:	مسابقة في مادة الكيمياء المدة: ساعتان
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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 to specify 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

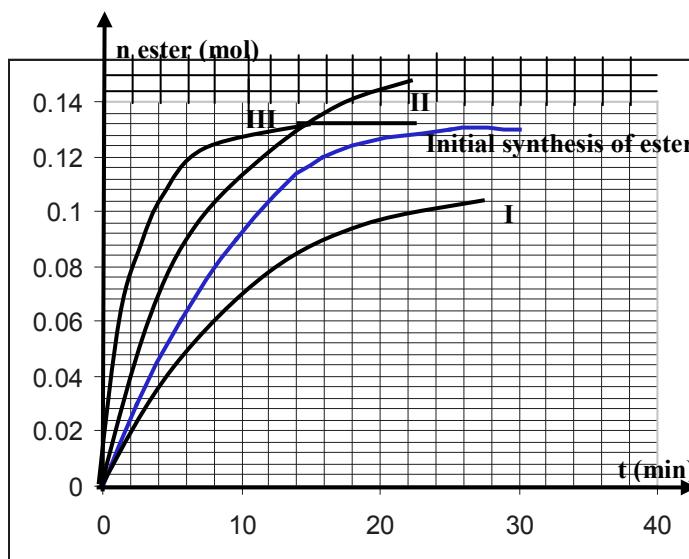
A volume $V_1 = 22$ mL of 1-pentanol and volume V_2 mL of ethanoic acid are introduced into a round bottom flask; 1 mL of concentrated sulfuric acid and boiling stones are then added into the flask. This mixture is heated for about 30 min. A mass of 17g of ester is obtained after cooling and separation.

- 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 ethanoic acid replaces this acid in order to increase the yield of esterification .
- Write the equation of this reaction.
 - 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:

$$2 \text{ H}_2\text{O}_2 \text{ (aq)} \rightarrow 2 \text{ H}_2\text{O} \text{ (l)} + \text{ O}_2 \text{ (g)}.$$

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 $C = 0.060 \text{ mol.L}^{-1}$ is required to be prepared starting from an initial solution of H_2O_2 of concentration $C_0 = 1.0 \text{ mol.L}^{-1}$.

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 $C = 0.060 \text{ mol.L}^{-1}$.

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:

$P (10^2 \text{ Pa})$	1015	1038	1055	1070	1081	1093	1100	1104	1106
$t (\text{min})$	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 $V = 300 \text{ mL}$ in the flask which is maintained at a constant temperature $T = 300 \text{ K}$.

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 $n_t = 1.2 \times 10^{-7}(P - P_0)$; Take $R = 8.3 \text{ m}^3 \cdot \text{Pa} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$.

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

$n_t (10^{-4} \text{ mol})$	-	2.8	4.8	6.6	7.9	9.4	-	10.7	10.9
$t (\text{min})$	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 $1.0 \times 10^{-4} \text{ mol}$.

4- Determine the rate of formation of O_2 at $t = 20 \text{ min}$.

5- Identify the species present in the solution when the pressure P is equal to $1140 \times 10^2 \text{ Pa}$.

Third Exercise (6.5 points) Formulation of Aspirin

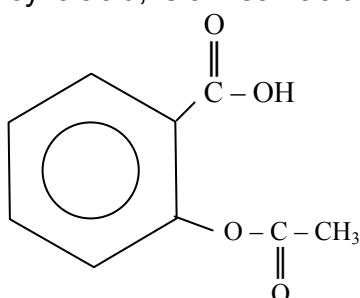
The aim of this exercise is to compare two formulations of aspirin represented as HA.

Given:

Acid/base pair	$\text{H}_3\text{O}^+/\text{H}_2\text{O}$	HA/A^-	$\text{CO}_2, \text{H}_2\text{O}/\text{HCO}_3^-$	$\text{H}_2\text{O}/\text{HO}^-$
pKa	0	3.5	6.4	14

Species	CO_2	HA	A^-	$(\text{Na}^+, \text{HCO}_3^-)$
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:



- 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.

$$2- \text{ Calculate the ratio: } \frac{[\text{A}^-]}{[\text{HA}]}$$

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 stomach

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First Exercise (7 points)
Synthesis of an Ester

Expected Answer	Mark	Comment
I- Esterification Reaction 1- The equation of this reaction is: $\text{CH}_3 - \underset{\substack{ \\ \text{O}}}{\text{C}} - \text{OH} + \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2\text{OH} = \text{CH}_3 - \underset{\substack{ \\ \text{O}}}{\text{C}} - \text{O} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 + \text{H}_2\text{O}$	0.75	
2- The ester formed is pentyl ethanoate. 3- This reaction is slow, athermic and reversible.	0.25 2x0.25	
II- Performing this Synthesis 1- a) Heating makes the reaction faster (kinetic factor). b) Concentrated sulfuric acid is a catalyst which speeds up the rate of the reaction.	0.25 0.25	
2- The number of moles is: $n = \frac{m}{M} = \frac{dxV}{M}$. Equimolecular mixture means that $n(\text{acid})_i = n(\text{alcohol})_i$. We have then: $\frac{d(\text{alcohol})xV_1}{M(\text{alcohol})} = \frac{d(\text{acid})xV_2}{M(\text{acid})} = \frac{0.81x22}{88} = \frac{1.05xV_2}{60} = 0.20 \text{ mol.}$ Hence: $V_2 = 11.57 \text{ mL}$.	1.25	1
3- The yield is $y = \frac{n(\text{ester}) \text{ experimental}}{n(\text{ester}) \text{ theoretical}} \times 100$. $n(\text{ester}) \text{ theoretical} = n(\text{alcohol})_i$ $y = \frac{\frac{m(\text{ester}) \text{ obtained}}{M(\text{ester})}}{\frac{d(\text{alcohol})xV_1}{M(\text{alcohol})}} \times 100 = \frac{\frac{17}{130}}{\frac{0.81x22}{88}} \times 100 = 64.57 \%$	0.5	
III- Changing the Experimental Conditions of this Synthesis 1- <ul style="list-style-type: none"> 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 ethanolic acid is in excess, the equilibrium is displaced to favor the forward reaction and the yield increases (curve II). 	0.5 0.5 0.5	
	0.75	
2- a) Ethanoyl chloride or ethanoic anhydride can be used:	2x0.25	

$\text{CH}_3 - \underset{\text{O}}{\overset{\parallel}{\text{C}}} - \text{Cl} + \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2\text{OH} \rightarrow$ $\text{CH}_3 - \underset{\text{O}}{\overset{\parallel}{\text{C}}} - \text{O} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 + \text{HCl}$ <p>b) This reaction is fast, complete and exothermic.</p>		
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Second Exercise (6,5 points)

Kinetic of the Decomposition of Hydrogen Peroxide (H_2O_2)

Expected Answer

Mark

Comment

I- Preparation of Solution (S) of H_2O_2

To prepare the solution (S) of concentration $C = 0.060 \text{ mol.L}^{-1}$ from the solution of concentration

1

$$C_0 = 1.0 \text{ mol.L}^{-1}, \text{ the dilution factor is equal to: } \frac{C_0}{C} = \frac{1.0}{0.06} = \frac{V}{V_0} = \frac{100}{6}$$

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

$$\text{volume } V_0 \approx \frac{100}{16.67} = 6.0 \text{ mL and dilute this volume in 100 mL volumetric flask.}$$

II- Kinetic of the Decomposition Reaction of H_2O_2

1- The pressure of O_2 at each instant is $P(\text{O}_2) = P - P_0$. The number of moles of O_2 at each

1

$$\text{instant is given by the equation of ideal gas: } n_t = \frac{P(\text{O}_2)xV}{R \times T} = \frac{(P - P_0)x300 \times 10^{-6}}{8.3 \times 300}$$

$$n_t = 1.20 \times 10^{-7}(P - P_0)$$

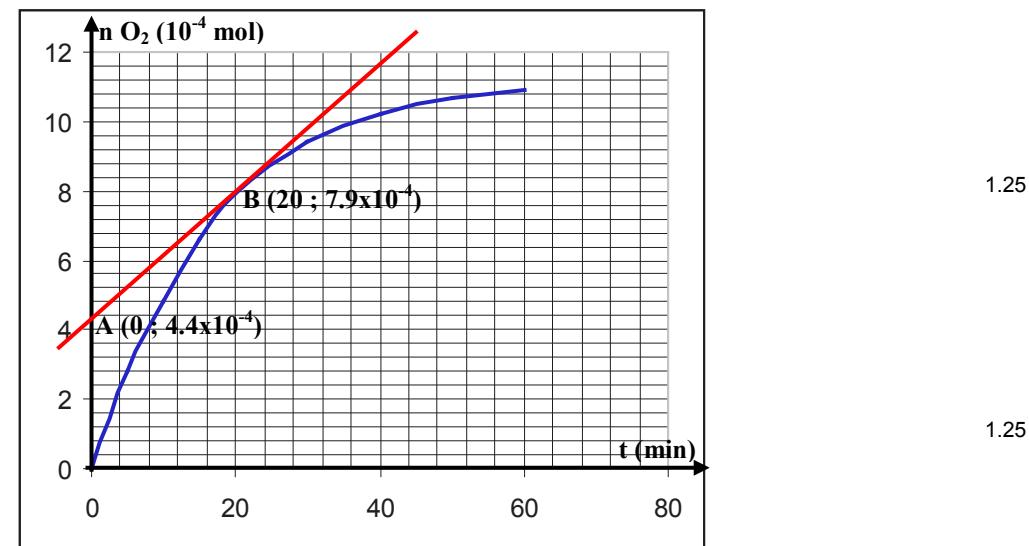
2- For $t = 0$, we have: $P = P_0$ and $n_0 = 0 \text{ mol}$.

$$n_t = 1.20 \times 10^{-7}(1100 - 1015) \times 10^{-7} = 10.2 \times 10^{-4} \text{ mol.}$$

For $t = 40 \text{ min}$, we have:

$$n_t = 1.20 \times 10^{-7}(1100 - 1015) \times 10^{-7} = 10.2 \times 10^{-4} \text{ mol.}$$

3- The curve :



4- The rate of formation of O_2 at $t = 20 \text{ min}$ is defined by: $r(t=20) = \frac{dn\text{O}_2}{dt}$. The

value of this rate is equal to the slope of the tangent to the curve $n(\text{O}_2) = f(t)$ at the point of abscissa $t = 20 \text{ min}$.

1.5

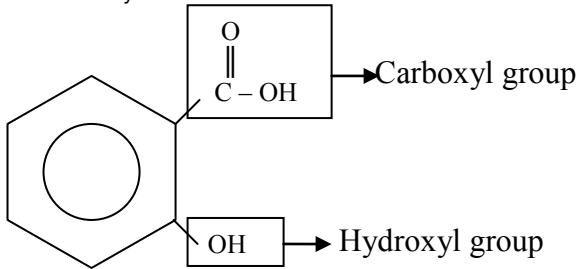
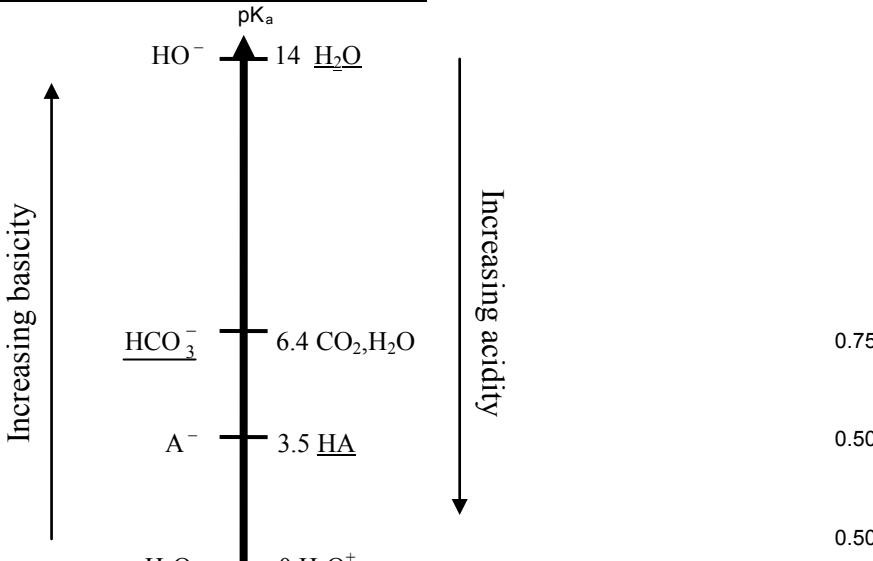
$$r(t=20) = \frac{n_B - n_A}{t_B - t_A} = \frac{(7.9 - 4.4) \times 10^{-4}}{20 - 0} = 17.5 \times 10^{-6} \text{ mol.min}^{-1}$$

5- When the pressure is $1140 \times 10^2 \text{ Pa}$, the number of moles of O_2 formed is $n\text{O}_2 = 1.2(1140 - 1015) \times 10^{-7} = 15.0 \times 10^{-4} \text{ mol}$ which is produced by $n\text{H}_2\text{O}_2 = 2 \times 15.0 \times 10^{-4} = 30.0 \times 10^{-4} \text{ mol}$. The initial number of moles of H_2O_2 is: $n_{\text{H}_2\text{O}_2 \text{ initial}} = C \times V_{(S)} = 0.06 \times 50 \times 10^{-3} = 30.0 \times 10^{-4} \text{ mol}$. We conclude that hydrogen peroxide decomposes completely.

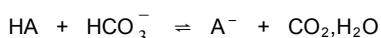
The species present in the obtained solution, (other than the dissolved O_2) are water (H_2O), iron (III) ions (Fe^{3+}) and chloride ions (Cl^-).

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: $\text{CH}_3 - \underset{\text{O}}{\overset{ }{\text{C}}} - \text{O} - \underset{\text{O}}{\overset{ }{\text{C}}} - \text{CH}_3$		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:			
$\text{HA} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{A}^-$			
2- The relation: $\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$ permits to calculate the ratio $\frac{[\text{A}^-]}{[\text{HA}]}$.			
$3 = 3.5 + \log \frac{[\text{A}^-]}{[\text{HA}]}$. $\log \frac{[\text{A}^-]}{[\text{HA}]} = -0.5$ so $\frac{[\text{A}^-]}{[\text{HA}]} = 0.316$.		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:

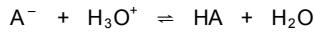


3- PH of the solution is $6.2 > \text{pK}_a(\text{HA}/\text{A}^-) + 1$

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

IV- Absorption of Aspirin by the Stomach

1- The equation of the reaction reproducing HA is:



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.

الاسم: الرقم:	مسابقة في مادة الكيمياء المدة ساعتان
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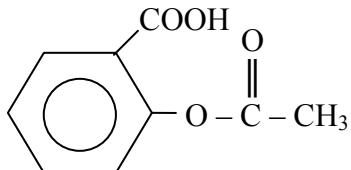
This Exam Includes **Three Exercises**. It Is Inscribed on Four Pages Numbered from **1** to **4**.
The Use of A Non-programmable Calculator Is Allowed

Answer the three following Exercises:

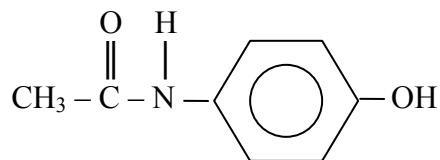
First Exercise (6 points)
Benorilate

“Benorilate” which is the ester of acetylsalicylic acid and paracetamol, is the active ingredient of a medicinal drug named SALIPRAN.

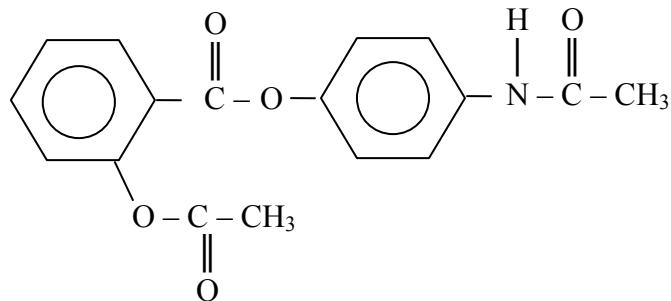
Given:



Acetylsalicylic acid (compound A)



Paracetamol (compound P)



Benorilate (compound B)

1- Paracetamol

Paracetamol is prepared by a reaction of ethanoic anhydride with para (aminophenol).

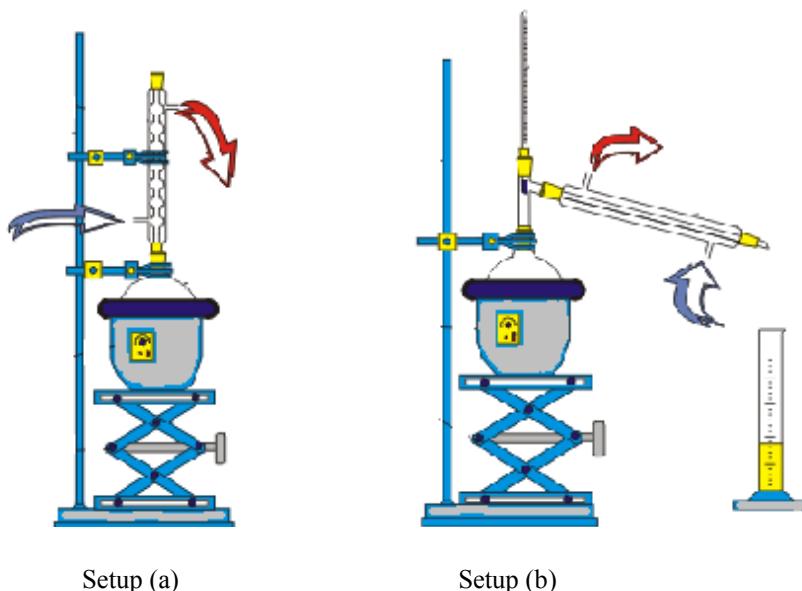
1.1- Write the equation of this reaction.

1.2- Copy, on the answer sheet, the formula of paracetamol, circle its two functional groups and give their names.

2- Acetylsalicylic Acid

To prepare acetylsalicylic acid or aspirin, a mixture of ethanoic anhydride and salicylic acid is subject to reflux heating, in the presence of few drops of concentrated sulfuric acid.

2.1- Choose, by justifying, among the two setups represented below, the convenient one to carry out this preparation.



2.2- Write the equation of the reaction of synthesis of aspirin.

2.3- Specify the reason for which ethanoic anhydride is used instead of ethanoic acid in this preparation.

2.4- Indicate the role of sulfuric acid in this reaction.

3- Benorilate

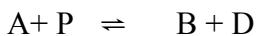
Given: Molar mass in g.mol⁻¹:

$$M(\text{aspirin}) = 180; M(\text{paracetamol}) = 151; M(\text{Benorilate}) = 313.$$

The leaflet of the medicinal drug SALIPRAN presents, among others, the following indications:

- Composition by bag: *Benorilate 2 g*
- Mode of administration: *the content of each bag should be diluted in a cup of water and swallowed immediately.*

3.1- Benorilate (B) is prepared from aspirin (A) and paracetamol (P) according to the reaction of the following equation:



3.1.1- Name this reaction.

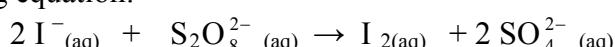
3.1.2- Identify compound D.

3.2- The content of a bag of Benorilate is prepared from 1150 mg of aspirin and 964 mg of paracetamol. Verify the indication on the leaflet concerning the composition of the bag, knowing that the reaction is made complete.

3.3- Specify the reason for which it is necessary "to swallow immediately the content of the bag after dilution in water".

Second Exercise (7 points) Oxidation of Iodide Ions

Iodide ions I^- are oxidized by peroxydisulfate ions $S_2O_8^{2-}$ in a slow and complete reaction according to the following equation:



At instant $t = 0$, a mixture S is prepared by mixing a volume $V_1 = 10 \text{ mL}$ of potassium iodide solution of concentration $C_1 = 0.50 \text{ mol.L}^{-1}$ with a volume $V_2 = 10 \text{ mL}$ of sodium peroxydisulfate solution of concentration $C_2 = 5.0 \times 10^{-3} \text{ mol.L}^{-1}$.

1- Study of the Reactional Mixture

- 1.1- Determine the limiting reactant in mixture S.
- 1.2- Draw a table representing the number of moles of the components of S in its initial and final state.

2- Kinetics of this Reaction

The kinetic of the formation of iodine in mixture (S), by an appropriate physical method, permits to measure the quantity of I_2 formed, $n(I_2)$, versus time t according to the following table:

$n(I_2)(10^{-6} \text{ mol})$	4.80	8.00	13.6	18.6	22.8	30.0	34.8	38.6	43.6	46.5
$t (\text{min})$	1	2	4	6	8	12	16	20	30	60

- 2.1- Plot the curve representing the variation of $n(I_2)$ versus time in the interval:

0 – 30 min.

Take the following scale:

abscissa: 1 cm for 2 min and ordinate: 1 cm for $4 \times 10^{-6} \text{ mol}$.

- 2.2- Determine:

2.2.1- The rate of this reaction at $t = 16 \text{ min}$.

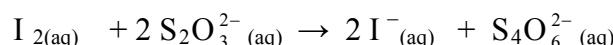
2.2.2- The half-life of this reaction $t_{1/2}$.

3- Titration of Iodine Formed After 60 Minutes

It is required to verify, by titration, the number of moles of I_2 given in the above table of part 2 at time $t = 60 \text{ min}$. For that, the following procedure is carried out:

- A volume $V = 5.0 \text{ mL}$ of the reactional mixture (S) is introduced into a beaker containing ice-water at time $t = 60 \text{ min}$.
- The iodine present in volume V is titrated with a sodium thiosulfate solution $(2\text{Na}^+ + \text{S}_2\text{O}_3^{2-})$ of concentration $C' = 2.0 \times 10^{-3} \text{ mol.L}^{-1}$, in the presence of few drops of starch solution.

The equation of this reaction is:



The volume of the thiosulfate solution added to reach equivalence is $V'_E = 11.6 \text{ mL}$.

- 3.1- Indicate the kinetic factors involved when volume V is introduced into the ice-water beaker. Deduce the purpose of this operation.

3.2- Note the variation of color observed in the beaker at equivalence.

3.3- Verify the value of $n(I_2)$ which is given in the table of part 2 at time $t = 60 \text{ min}$.

Third Exercise (7 points) Javelle water

Javelle water is an aqueous solution of sodium chloride and sodium hypochlorite.

Hypochlorite ion, ClO^- (aq), is the active constituent of Javelle water and the conjugate base of hypochlorous acid HClO (aq).

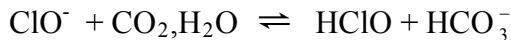
Given:

- This study is performed at 25°C .
- $\text{pK}_a(\text{CO}_2, \text{H}_2\text{O}/\text{HCO}_3^-) = 6.4$.
- $K_w = 1.0 \times 10^{-14}$.

- Molar mass: $M(Cl) = 35.5 \text{ g.mol}^{-1}$.
- Chlorine is a toxic gas.

1 - Acid-base Properties of Javelle Water

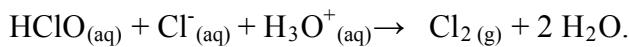
- 1.1- Write the equation of the acid-base reaction between hypochlorite ion and water.
- 1.2- Determine the value of pK_a of the conjugate acid/base pair (HClO/ClO^-), knowing that the degree of transformation of ClO^- is 0.50 when the pH of the solution is equal to 7.3.
- 1.3- Carbon dioxide of air reacts with hypochlorite ion according to the following equation:



- 1.3.1- Determine the equilibrium constant K of this reaction.
- 1.3.2- Explain why Javelle water is stored in well closed bottles.

2 – Javelle Water: Danger!

The pH of a sample of Javelle water is made 2.0. At this value of pH, the following reaction takes place:



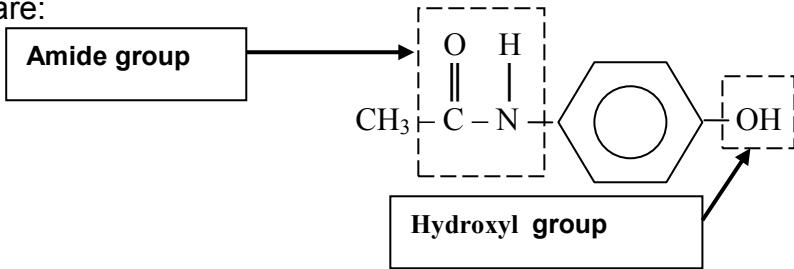
- 2.1- Identify the predominant specie of the pair HClO/ClO^- at $\text{pH} = 2$.
- 2.2- A detergent bottle containing hydrochloric acid is labeled: "do not mix with Javelle water". Justify this affirmation.

3 - Treatment of a Swimming Water Pool by Javelle Water

In most swimming pools, Javelle water is added to kill harmful bacteria by hypochlorite ions.

- 3.1- To make this process efficient, it is necessary to maintain the pH of water between 7.0 and 7.6.
Show that none of the two species ClO^- and HClO is predominant in the water of swimming pools at the above recommended pH range.
- 3.2- To avoid dangerous problems in swimming pools, the mass concentration of the element chlorine (in the two forms HClO and ClO^-) should be between 1 and 2 mg.L^{-1} .
In the water of a swimming pool, the concentration of hypochlorite ions ClO^- is $2 \times 10^{-5} \text{ mol.L}^{-1}$.
Verify that the water of this swimming pool has an acceptable concentration of the element chlorine knowing that the pH of this water is 7.3.

First Exercise(6 points)

Part	Answer	Mark
1	Paracetamol	
1.1	The equation of this reaction is: $\text{CH}_3 - \text{CO} - \text{O} - \text{CO} - \text{CH}_3 + \text{HO} - \text{C}_6\text{H}_4 - \text{NH}_2 \rightarrow \text{HO} - \text{C}_6\text{H}_4 - \text{NH} - \text{CO} - \text{CH}_3 + \text{CH}_3 - \text{COOH}$	0.75
1.2	The two groups are: : <div style="display: flex; align-items: center;"> <div style="border: 1px solid black; padding: 2px; margin-right: 10px;">Amide group</div>  <div style="border: 1px solid black; padding: 2px; margin-left: 10px;">Hydroxyl group</div> </div>	1
2	Acetylsalicylic Acid	
2.1	The setup (a) is convenient to perform the reflux heating. This setup makes it possible to heat the reactional system without losing any component of this system. While in the setup (b) there is separation of the components of the system by heating.	0.5
2.2	The equation of this reaction is: $\text{CH}_3 - \text{CO} - \text{O} - \text{CO} - \text{CH}_3 + \text{HO} - \text{C}_6\text{H}_4 - \text{COOH} \rightarrow \text{CH}_3 - \text{CO} - \text{O} - \text{C}_6\text{H}_4 - \text{COOH} + \text{CH}_3 - \text{COOH}$	0.75
2.3	The anhydride is used instead of the acid in order to make the reaction complete.	0.5
2.4	Sulfuric acid is a catalyst in this reaction.	0.25
3	Benorilate	
3.1.1	It is an esterification reaction.	0.25
3.1.2	(D) is obtained by reaction of the group – OH of paracetamol and the hydrogen of the carboxyl group of aspirin. Its formula is then H_2O , its name is water.	0.5
3.2	The number of moles is given by $n = \frac{m}{M}$, we have: $n(\text{aspirin})_{\text{initial}} = \frac{1.150}{180} = 6.38 \times 10^{-3} \text{ mol} ;$ $n(\text{paracetamol})_{\text{initial}} = \frac{0.964}{151} = 6.38 \times 10^{-3} \text{ mol.}$ Reaction being complete, $n(\text{Benorilate})_{\text{obtained}} = 6.38 \times 10^{-3} \text{ mol}$ whose mass is $6.38 \times 10^{-3} \times 313 = 1.99 \text{ g.}$ This value verifies the indication of the leaflet concerning the composition of the bag (2 g).	1
3.3	It is necessary "to swallow immediately the contents of the bag after dilution" in order to avoid the reaction of hydrolysis of Benorilate.	0.5

Second Exercise (7 points)

Part	Answer	Mark															
1	Study of the Reactional Mixture																
1.1	<p>Limiting reactant in mixture S:</p> $R_{(I^-)} = \frac{n(I^-)_{initial}}{2} = \frac{C_1 V_1}{2} = \frac{0.5 \times 10 \times 10^{-3}}{2} = 2.5 \times 10^{-3}$ $R_{(S_2O_8^{2-})} = \frac{n(S_2O_8^{2-})_{initial}}{1} = C_2 V_2 = 5 \times 10^{-3} \times 10 \times 10^{-3} = 5 \times 10^{-5} < R_{(I^-)}$ <p>∴ $S_2O_8^{2-}$ is the limiting reactant.</p>	0.75															
1.2	<p>The table is as follows:</p> $2I^-_{(aq)} + S_2O_8^{2-}_{(aq)} \rightarrow I_2_{(aq)} + 2SO_4^{2-}_{(aq)}$ <table style="margin-left: auto; margin-right: auto;"> <tr> <td>Initial state (mol)</td> <td>5.10^{-3}</td> <td>5.10^{-5}</td> <td>-</td> <td>-</td> </tr> <tr> <td>Final state (mol)</td> <td>$\sim 5.10^{-3}$</td> <td>0</td> <td>5.10^{-5}</td> <td>10.10^{-5}</td> </tr> </table>	Initial state (mol)	5.10^{-3}	5.10^{-5}	-	-	Final state (mol)	$\sim 5.10^{-3}$	0	5.10^{-5}	10.10^{-5}	0.75					
Initial state (mol)	5.10^{-3}	5.10^{-5}	-	-													
Final state (mol)	$\sim 5.10^{-3}$	0	5.10^{-5}	10.10^{-5}													
2	Kinetics of this Reaction																
2.1	<p>The curve</p> <table border="1"> <caption>Data points estimated from the graph</caption> <thead> <tr> <th>t (min)</th> <th>n(I₂) (10⁻⁶ mol) - Red Curve (A)</th> <th>n(I₂) (10⁻⁶ mol) - Blue Curve (B)</th> </tr> </thead> <tbody> <tr> <td>0</td> <td>0</td> <td>18</td> </tr> <tr> <td>10</td> <td>25</td> <td>34.8</td> </tr> <tr> <td>16</td> <td>34.8</td> <td>34.8</td> </tr> <tr> <td>30</td> <td>45</td> <td>45</td> </tr> </tbody> </table>	t (min)	n(I ₂) (10 ⁻⁶ mol) - Red Curve (A)	n(I ₂) (10 ⁻⁶ mol) - Blue Curve (B)	0	0	18	10	25	34.8	16	34.8	34.8	30	45	45	1.25
t (min)	n(I ₂) (10 ⁻⁶ mol) - Red Curve (A)	n(I ₂) (10 ⁻⁶ mol) - Blue Curve (B)															
0	0	18															
10	25	34.8															
16	34.8	34.8															
30	45	45															
2.2.1	<p>The rate of the reaction is equal at the rate of formation of I_2 at any instant t. This rate is equal to the slope of the tangent to the curve: $n(I_2) = f(t)$ at the point of abscissa t:</p> $v_{t=16 \text{ min}} = \frac{(34.8 - 18) \times 10^{-6}}{16 - 0} = 1.05 \times 10^{-6} \text{ mol} \cdot \text{min}^{-1}$	1															
2.2.2	<p>The half-life of the reaction is the time needed to reach the half for the maximum number of moles of I_2 formed :</p> $n(I_2)_{1/2} = \frac{50 \times 10^{-6}}{2} = 25 \times 10^{-6} \text{ mol}$ <p>which corresponds to: $t_{1/2} = 8.5 \text{ min.}$</p>	0.75															
3	Titration of Iodine Formed after 60 Minutes																
3.1	<p>The two kinetic factors are:</p> <ul style="list-style-type: none"> - The concentration of the reactant $S_2O_8^{2-}$ in solution S 	0.75															

	<p>- temperature.</p> <p>The purpose of this operation is to stop the reaction in volume V.</p>	
3.2	The contents of the beaker changes from intense blue coloring (starch solution + I ₂) to colorless, at equivalence point.	0.5
3.3	<p>At equivalence point, and according to stoichiometry proportion:</p> $n(I_2) \text{ in } V = \frac{n(S_2O_3^{2-}) \text{ added}}{2} = \frac{C' \cdot V'_E}{2}$ $n(I_2) \text{ in } V = \frac{C' \cdot V'_E}{2} = \frac{2 \times 10^{-3} \times 11.6 \times 10^{-3}}{2} = 11.6 \times 10^{-6} \text{ mol}$ <p>Where n(I₂) in the mixture S at 60 min = n(I₂) in</p> $V \times \frac{20}{5} = 46.4 \times 10^{-6} \text{ mol.}$ <p>It is almost the same value given in part 2.</p>	1.25

Third Exercise (7 points)

Part	Answer	Mark
1	Acid-base Properties of Javelle Water	
1.1	The equation of this reaction: ClO ⁻ + H ₂ O ⇌ HClO + HO ⁻	0.5
1.2	<p>pH = pK_a + log $\frac{[ClO^-]}{[HClO]}$</p> <p>for α = 0.5 half of the amount of ClO⁻ is transformed to HClO.</p> <p>So [ClO⁻] = [HClO] and log $\frac{[ClO^-]}{[HClO]}$ = 0</p> <p>then pH = pK_{a1} = 7.3.</p>	1.25
1.3.1	$K = \frac{[HClO][HCO_3^-]}{[ClO^-][CO_2, H_2O]} = 10^{(pK_{a1} - pK_{a2})}$ $; K = 10^{(7.3 - 6.4)} = 10^{0.9} = 7.9$	1
1.3.2	It is stored in well closed bottles to avoid the reaction between ClO ⁻ and CO ₂ of air. This diminishes the concentration of the active constituent of Javelle water.	0.75
2	Javelle Water: Danger!	
2.1	At pH = 2.0 ; the predominant specie is hypochlorous acid because the pH of the solution is less than pK _a – 1.	0.75
2.2	In the presence of an acidic medium, the reaction of hypochlorous acid with H ₃ O ⁺ ions produces chlorine gas which is very toxic.	0.75
3	Treatment of a Swimming Water Pool by Javelle Water	
3.1	Since the pH of the swimming water pool is between pK _a – 1 and pK _a + 1, none of the species is predominant.	0.75
3.2	<p>At pH = 7.3 ; pH = pK_a => [ClO⁻] = [HClO]</p> <p>then [HClO] = [ClO⁻] = $2 \times 10^{-5} \text{ mol.L}^{-1}$</p> <p>In 1L of solution:</p> <p>Concentration C of Chlorine = [HClO] + [ClO⁻] = $4 \times 10^{-5} \text{ mol.L}^{-1}$</p> <p>Cg.L⁻¹ = Cmol.L⁻¹ × M_{Cl} = $4 \times 10^{-5} \times 35.5 = 1.42 \times 10^{-3} \text{ g.L}^{-1} = 1.42 \text{ mg.L}^{-1}$.</p>	1.25

	C _{Cl} is between 1mg.L ⁻¹ and 2mg.L ⁻¹ . Then it is acceptable.	
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دورة سنة ٢٠٠٨ العادية	امتحانات الشهادة الثانوية العامة فرع علوم الحياة	وزارة التربية والتعليم العالي المديرية العامة للتربية دائرة الامتحانات
الاسم: الرقم:	مسابقة في مادة الكيمياء المدة ساعتان	

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

Answer the three following exercises:

First exercise (7 points)
Perfumed soap

During the 8th century, “hard” soap was discovered in north of Syria. “Soft” soap is obtained when caustic potash (potassium hydroxide) is used, while “hard” soap is obtained by using caustic soda (sodium hydroxide).

Aleppo’s soap is obtained by heating olive oil with sodium hydroxide. The chemical process used to produce soap could be represented by the following equation:



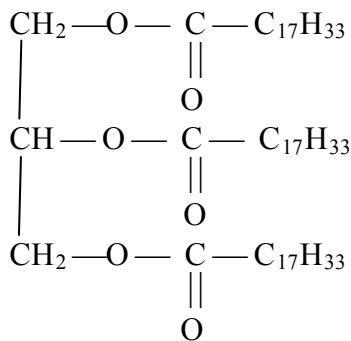
Extract from: "un article de la Compagnie Générale de Cosmétique"

Aleppo’s soap was perfumed by natural essences. Nowadays many samples of soap are perfumed by the use of synthetic esters as pentylbutanoate.

1- Saponification Reaction

1.1- Write the condensed structural formula of glycerol (1, 2, 3-propanetriol).

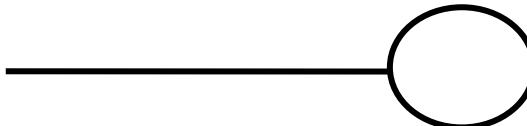
1.2- One of the fatty substances used in the manufacture of Aleppo’s soap is olein of formula :



Write the chemical equation of the reaction of formation of Aleppo’s soap.

1.3- Specify whether Aleppo’s soap is “hard” or “soft” soap.

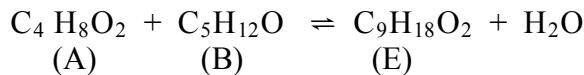
1.4- Carboxylate ion present in this soap is represented by the following schema, where the Straight part symbolizes the carbon chain and the circle symbolizes the carboxylate group.



Copy the above schema, on the answer sheet, and indicate the hydrophilic part and the lipophilic part of this ion. Give the meaning of each of these two terms.

2- Study of the Preparation Reaction of Perfume

Pentylbutanoate is obtained by an esterification reaction represented by the following equation :



2.1- Write the condensed structural formulas of carboxylic acid (A), alcohol (B) and ester (E). Give the systematic names of (A) and (B).

2.2- 16 mL of acid (A) and 0.17 mol of alcohol (B) are mixed in the presence of a few mL of concentrated sulfuric acid. This mixture is divided into identical parts which are placed into Erlenmeyer flasks that are then heated at constant temperature. The remaining acid, in each Erlenmeyer flask, is titrated at regular intervals of time.

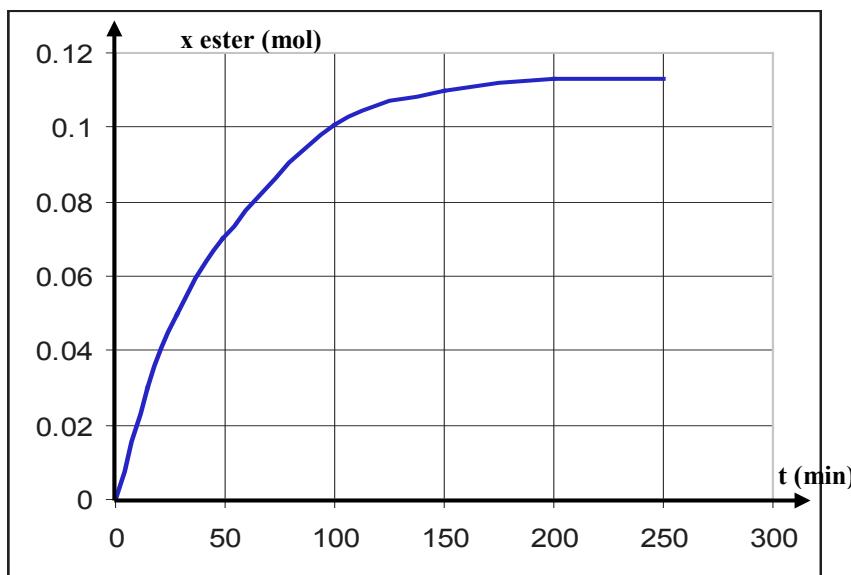
Given: For carboxylic acid (A):

- Density : $d_A = 0.96 \text{ g.mL}^{-1}$;
- Molar mass: $M(A) = 88 \text{ g.mol}^{-1}$.

2.2.1- Show that the initial reactional mixture is equimolar.

2.2.2- Indicate the reason for which the Erlenmeyer flasks are immersed in ice-water before carrying out the titration.

2.3- x represents the number of moles of ester formed at each instant in the initial mixture. The results of titration permit to plot the curve below: $x = f(t)$



Answer, by justifying, whether the proposals given below are true or false.

- Proposal 1: We can obtain "more ester" by eliminating the water formed during the transformation.
- Proposal 2: The instantaneous rate of the reaction increases with respect to time.
- Proposal 3: The percentage of the esterification of alcohol, at $t = 100 \text{ min}$, is 33 %.

Second exercise (6 points)
Ethanol

Ethanol is one of the most important organic compounds. It is widely used as an antiseptic and solvent for varnishes, and in perfumes and alcoholic beverages.

Ethanol can be obtained by the reaction between ethylethanoate solution and sodium hydroxide solution according to the following equation.



The aim of this exercise is to study the kinetics of this reaction.

1- Structural Formulas

1.1- Write the condensed structural formulas of ethylethanoate and ethanol.

1.2- Circle the functional group in each of the above formulas.

2- Kinetic Study

At time $t = 0$, an aqueous solution of ethylethanoate is mixed with a sodium hydroxide solution. The initial concentration of each reactant in the mixture is $C = 5 \times 10^{-2} \text{ mol.L}^{-1}$.

The mixture is divided into equal parts, each part has a volume $V = 10 \text{ mL}$. At different instants t , and in the presence of a colored indicator, the HO^- ions remained in each volume V , are titrated with an aqueous solution of hydrochloric acid of concentration $C_a = 10^{-2} \text{ mol.L}^{-1}$. The results are given in the table below:

$t \text{ (min)}$	4	9	15	24	37	53	83	143
$V_a \text{ (mL)}$	44.1	38.6	33.7	27.9	22.9	18.5	13.6	8.9
$n (10^{-4} \text{ mol})$	0.59		1.63	2.21	2.71	3.15		4.11

Let V_a be the volume of hydrochloric acid solution added to reach equivalence point in each volume V and n the number of moles of ethanol obtained in V at each instant t .

2.1- Write the equation of the titration reaction.

2.2- At any instant t , the number of moles of ethanol formed is given by the expression:

$$n = 5 \times 10^{-4} - 10^{-2} \times V_a, \text{ where } V_a \text{ is expressed in L.}$$

2.2.1- Calculate the missing values in the table above.

2.2.2- Deduce the value of n at the end of the reaction.

2.3- Plot, on a graph paper, the curve $n = f(t)$ in the interval of time $0 - 143 \text{ min}$.

Take the following scales: 1cm for 10 min in abscissa and 1 cm for $0.2 \times 10^{-4} \text{ mol}$ in ordinate.

2.4- Determine the half-life of the reaction.

3- Some Catalytic Reactions of Ethanol

3.1- Ethanol undergoes a dehydrogenation reaction when it is heated in the presence of copper.

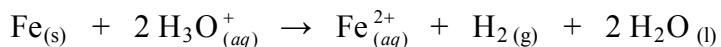
Write the equation of this reaction.

3.2- Ethanol undergoes intermolecular dehydration when it is heated in the presence of aluminum oxide. Write the equation of this reaction.

3.2- Conclude about the choice of the catalyst in these reactions.

Third exercise (7 points) Iron in acidic solutions

At room temperature, iron reacts with hydrochloric acid solution in a slow reaction according to the following equation:



A strip of a pure iron of mass $m = 0.28$ g is introduced into a flask containing a volume $V = 100$ mL of hydrochloric acid solution of concentration 0.2 mol.L^{-1} .

Given:

- $M(Fe) = 56 \text{ g.mol}^{-1}$.
 - Molar volume of gas: $V_m = 24 \text{ L.mol}^{-1}$.
 - $pK_a(CH_3COOH/CH_3COO^-) = 4.75$.

1- Preliminary Study

- 1.1- Show that the volume of hydrogen gas at the end of the reaction is: $V(H_2)_\infty = 120 \text{ mL}$.

1.2- Show at each instant t , the following relation: $[H_3O^+]_t = 0.2 - \frac{V(H_2)_t}{1200}$; where $V(H_2)_t$ is the volume of H_2 gas in mL at instant t and $[H_3O^+]_t$ is the concentration of H_3O^+ in mol.L^{-1} at the same instant t .

1.3- Deduce the concentration of H_3O^+ ions at the end of the reaction.

2- Kinetic Study of the Disappearance of H₃O⁺

3- Study of pH

- 3.1- To the solution obtained at the end of the reaction between iron and hydrochloric acid, distilled water is added up to 1 L. A solution S_1 is obtained.
Determine the pH of solution S_1 .

3.2- The same mass (0.28 g) of iron is now treated with 100 mL of ethanoic acid solution of concentration 0.2 mol.L^{-1} . At the end of the reaction, distilled water is added to obtain 1 L of solution called S_2 .

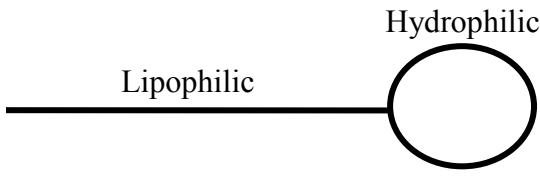
3.2.1- Write the equation of the reaction that takes place.

3.2.2- Determine the pH of solution S_2 . Give the characteristics of this solution.

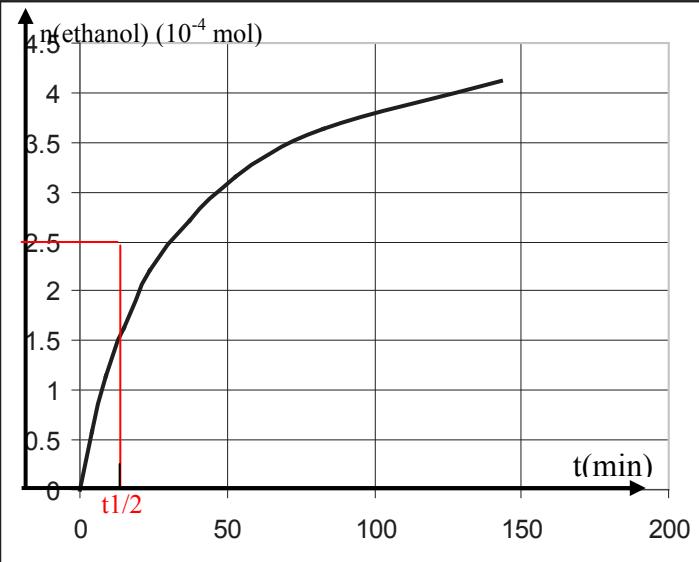
الاسم:
الرقم:مسابقة في مادة الكيمياء
المدة ساعتان

مشروع معيار التصحيح

**Marking Scheme
First exercise (7 points)**

Part of Q.	Answer	Mark
1.1	The condensed structural formula of glycerol is: $\begin{array}{c} \text{CH}_2 - \text{CH} - \text{CH}_2 \\ \quad \quad \\ \text{OH} \quad \text{OH} \quad \text{OH} \end{array}$	0.5
1.2	The equation of formation of Aleppo's soap is: $\text{C}_{17}\text{H}_{33}-\underset{\substack{ \\ \text{O}}}{\text{C}}-\text{O}-\text{CH}_2 + 3 \text{NaOH} \rightarrow 3 \text{C}_{17}\text{H}_{17}\text{COONa} + \text{CH}_2\text{OH}-\text{CHOH}-\text{CH}_2\text{OH}$	0.75
1.3	Aleppo's soap is hard because it is prepared from olive oil and sodium hydroxide.	0.5
1.4		1
	Lipophilic : likes lipids. Hydrophilic : likes water.	
2.1	The condensed structural formulas: (A) : $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{COOH}$; butanoic acid (B) : $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2\text{OH}$; 1-pentanol (E) : $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{COO} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$	1.25
2.2.1	$n(A)_{\text{initial}} = \frac{m(A)}{M(A)} = \frac{d(A)xV}{M(A)} = \frac{0.96 \times 16}{88} = 0.17 \text{ mol}$. We deduce that the initial mixture is equimolar.	0.75
2.2.2	To stop any expected reaction other than the titration reaction.	0.25
2.3	Proposition -1: True because, elimination of water displaces the equilibrium in the favor of the ester formation. Proposition - 2: false because the rate of reaction decreases with the decrease of the concentration of the reactants with respect to time. Proposition - 3 : false because the percentage of the esterification of alcohol is: $\% \text{ yield} = \frac{n(\text{B})_{\text{esterified}}}{n(\text{B})_{\text{initial}}} \times 100 = \frac{n(\text{E})_{\text{formed at 100 min}}}{n(\text{B})_{\text{initial}}} \times 100 = \frac{0.1}{0.17} \times 100 = 58.8 \% > 33 \text{ \%}.$	2

Second exercise (6 points)

Part of Q.	Answer	Mark
1.1	The condensed structural formula of ethylethanoate: $\text{CH}_3 - \underset{\substack{\parallel \\ \text{O}}}{\text{C}} - \text{O} - \text{CH}_2 - \text{CH}_3$ That of ethanol: $\text{CH}_3 - \text{CH}_2 - \text{OH}$	0.5
1.2	$\text{CH}_3 - \boxed{\text{C} - \text{O} -} \text{CH}_2 - \text{CH}_3$ $\text{CH}_3 - \text{CH}_2 - \boxed{\text{OH}}$	0.5
2.1	The equation of the titration reaction is: $\text{H}_3\text{O}^+ + \text{HO}^- \rightarrow 2\text{H}_2\text{O}$	0.5
2.2.1	$n(\text{ethanol})_{t=9} = 5 \times 10^{-4} - 10^{-2} \times 38.6 \times 10^{-3} = 1.14 \times 10^{-4} \text{ mol}$ and $n(\text{ethanol})_{t=83} = 5 \times 10^{-4} - 10^{-2} \times 13.6 \times 10^{-3} = 3.64 \times 10^{-4} \text{ mol.}$	0.5
2.2.2	The mixture is stoichiometric, At the end of the reaction value of V_a is zero since number of moles of HO^- has totally transformed so $n = 5.0 \times 10^{-4} \text{ mol.}$	0.5
2.3	The curve $n(\text{ethanol}) = f(t)$ is 	1
2.4	The half life of the reaction is the time needed for the number of moles of ethanol to increase to half of its final value. $n(\text{ethanol})_{t1/2} = \frac{5 \times 10^{-4}}{2} = 2.5 \times 10^{-4} \text{ mol}$; From the graph $t_{1/2} = 30 \text{ min}$	1
3.1	The equation of the dehydrogenation reaction of ethanol in the presence of copper is: $\text{CH}_3 - \text{CH}_2 - \text{OH} \rightarrow \text{CH}_3 - \text{CHO} + \text{H}_2$ (dehydrogenation)	0.5
3.2	The equation of the dehydration reaction of ethanol in the presence of Al_2O_3 is: $2 \text{CH}_3 - \text{CH}_2 - \text{OH} \rightarrow \text{CH}_3 - \text{CH}_2 - \text{O} - \text{CH}_2 - \text{CH}_3 + \text{H}_2\text{O}$	0.5
3.5	Ethanol undergoes, using different catalysts, different chemical reactions: dehydrogenation in the presence of copper and dehydration in the presence of aluminum oxide. Catalyst can direct a chemical reaction (selective).	0.5

Third exercise (7 points)

Part of the Q	Answer	Mark
1.1	<p>Calculation of the number of moles of each reactant.</p> $n_{Fe} = \frac{m_{Fe}}{M_{Fe}} = \frac{0.28}{56} = 5 \times 10^{-3} \text{ mol.}$ $n_{H_3O^+} = CxV = 0.2 \times 100 \times 10^{-3} = 2.0 \times 10^{-2} \text{ mol.}$ $R(Fe) = \frac{5 \times 10^{-3}}{1} < R(H_3O^+) \frac{2 \times 10^{-2}}{2} = 1 \times 10^{-2}$. Iron is the limiting reactant. The volume of hydrogen is: $V(H_2) = n(H_2) \times V_m = n(Fe) \times V(H_2) = 5 \times 10^{-3} \times 24 = 0.120 \text{ L} = 120 \text{ mL.}$	1
1.2	<p>$n(H_3O^+)$ left at instant $t = n(H_3O^+)_0 - n(H_3O^+)_{\text{reacting}}$ reacting at the same instant;</p> $n(H_3O^+)_{\text{reacting}} = 2 n(H_2)_{\text{formed}} = \frac{2 \times V(H_2)}{V_m} = \frac{V(H_2)_t}{12000};$ <p>$n(H_3O^+)$ left at instant $t = n_0 - 2 n(H_2)_{\text{formed}}$.</p> <p>Divide by V (volume of the solution), we have:</p> $[H_3O^+]_t = \frac{0.02}{0.1} - \frac{V(H_2)}{0.1 \times 12000} \text{ and } [H_3O^+]_t = 0.2 - \frac{V(H_2)}{1200}.$	1
1.3	<p>The concentration of H_3O^+ ions at the end of the reaction is given by:</p> $[H_3O^+]_\infty = 0.2 - \frac{V(H_2)_\infty}{1200} = 0.2 - \frac{120}{1200} = 0.1 \text{ mol.L}^{-1}.$	0.5
2.1	<p>According to the stoichiometry of the equation, we have:</p> $R(\text{reaction}) = \frac{R(H_3O^+) \text{ disappearance}}{2} = \frac{R(H_2) \text{ formation}}{1}$ <p>$R(H_3O^+) \text{ disappearance} = 2 R(H_2) \text{ formation}$.</p>	0.5
2.2	<p>Decreasing of the rate of appearance of H_2 with time is due to the decreasing of the rate of the reaction which decreases with the concentration of H_3O^+.</p>	0.5
2.3	<p>The half-life $t_{1/2}$ of the reaction will be less than 49 min since half the concentration of H_3O^+ will disappear faster than the second half because the concentration of this reactant decreases with time and hence the rate decreases.</p>	0.5
2.4	<p>The rate will increase because iron filings have a greater surface area and hence more contact with H_3O^+ ions. The end of the reaction will take place before 98 min.</p>	0.25
3.1	<p>The concentration of H_3O^+ ions in the solution S_1 is given by:</p> $[H_3O^+] = \frac{0.1 \times 100 \times 10^{-3}}{1} = 1 \times 10^{-2} \text{ mol.L}^{-1}.$ <p>Where $pH = -\log [H_3O^+] = -\log 1 \times 10^{-2} = 2$.</p>	0.75
3.2.1	<p>The equation of the reaction is:</p> $Fe_{(s)} + 2 CH_3COOH_{(aq)} \rightarrow Fe^{2+}_{(aq)} + 2 CH_3COO^-_{(aq)} + H_2(g)$	0.5
3.2.2	<p>Since the same amounts of reactants are used, hydrochloric acid is in excess and half the amount of this acid has reacted.</p> <p>The acid is in excess and half of the quantity of acid reacted:</p> <p>$n(CH_3COOH)_{\text{remaining}} = n(CH_3COO^-)_{\text{formed}}$ and these two species have consequently the same concentration.</p> <p>At the end of the reaction, we have:</p> $[CH_3COO^-] = [CH_3COOH] = \frac{0.01}{1} = 0.01 \text{ mol.L}^{-1}.$ $pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]} = pK_a + \log 1 = pK_a + 0$ <p>$pH = pK_a = 4.75$. The resulting solution is a buffer solution; its pH varies very slightly by adding a moderate amount of acid or of base or by dilution.</p>	1.5

الاسم: مسابقة في مادة الكيمياء
الرقم: المدة ساعتان

This Exam Includes Three Exercises. It Is Inscribed on four Pages Numbered from 1 to 4.

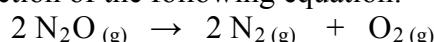
The Use of A Non-programmable Calculator Is Allowed.

Answer the three Following Exercises:

First Exercise (7 points)

Kinetic Study of the Decomposition Reaction of Dinitrogen Oxide

To ensure a suitable atmosphere in the space capsules, the decomposition of N_2O gas is carried out according to a complete reaction of the following equation:



1- Study of the Reacting System

Introduce into an evacuated flask, maintained at $\theta = 600^\circ C$, n_0 mol of N_2O .

1.1- x represents the number of moles of oxygen gas formed at instant t . Copy the following table, on the answer sheet, and complete it in terms of n_0 and x .

Time	N_2O (mol)	N_2 (mol)	O_2 (mol)
0	n_0	0	0
t			
End of reaction			

1.2- Determine the pressure P in the flask at the end of the reaction knowing that the initial pressure is $P_0 = 1.0 \times 10^5 \text{ Pa}$.

2- Kinetic Study of this Reaction

In order to study the kinetic of this slow reaction, the pressure P inside the flask is measured at different instants. The concentration of oxygen gas, $[O_2]$, is determined based on the measurement of P at each instant t . The results are given in the following table:

t (min)	0	12	25	45	70	100	130	160
$[O_2]_t$ (mol.m ⁻³)	0	0.88	1.68	2.68	3.72	4.56	5.12	5.40

2.1- Show that the concentration of O_2 at instant t , $[O_2]_t$, is given by the relation:

$$[O_2]_t = 1.38 \times 10^{-4} (P - P_0).$$

$$\text{Take: } R = 8.3 \text{ Pa.m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}.$$

2.2- Plot, on a graph paper, the curve $[O_2] = f(t)$. Take the following scale:
abscissa: 1 cm for 10 min and ordinate: 1 cm for 0.4 mol.m^{-3} .

2.3- Describe how to determine, graphically at instant t , the rate of this reaction.

2.4- Deduce the kinetic factor responsible for the change of this rate with time.

2.5- Determine graphically the half-life of this reaction.

2.6- The same study, in the same flask is done, at a temperature $\theta_1 > \theta$.

Specify the effect of the elevation of temperature on:

2.6.1- The rate of the reaction.

2.6.2- The concentration of O_2 gas, $[O_2]_\infty$, at the end of the reaction.

Second Exercise (7 points)
Aqueous Solution of Methylamine

The aim of this exercise is to study the acid-base behavior of methylamine in water.

Given: K_w is equal to 1.0×10^{-14} at $25^\circ C$.

1- Methylamine in Water

The pH of a solution S of methylamine, CH_3NH_2 , of concentration $C_b = 0.010 \text{ mol.L}^{-1}$ is measured and found to be equal to 11.3.

1.1- Write the equation of the reaction between methylamine and water.

1.2- Determine the transformation degree of methylamine in water.

1.3- Show that the pK_a of the conjugate acid/base pair ($\text{CH}_3\text{NH}_3^+/\text{CH}_3\text{NH}_2$) is equal to 10.7.

2- pH-metric Follow-up

A hydrochloric acid solution of concentration $C_a = 0.020 \text{ mol.L}^{-1}$ is gradually added into a beaker containing a volume $V_b = 40 \text{ mL}$ of solution S of methylamine.

The equation of the reaction which takes place is as follows:



2.1- Determine the volume of the acid solution, V_{aE} , added to reach equivalence.

2.2- The pH of the solution obtained at equivalence is close to 6.1.

Justify the acid character of the solution obtained at equivalence, based on the species present.

2.3- By specifying its remarkable points, trace the shape of the curve representing the variation of pH of the content of the beaker versus the added volume V_a of the acid.

Take the following scale: abscissa: 1 cm for 2 mL and ordinate: 1 cm for 1 unit of pH.

3- Buffer Solution

Consider a buffer solution S_1 where: $[\text{CH}_3\text{NH}_2] = [\text{CH}_3\text{NH}_3^+] = 2.0 \times 10^{-3} \text{ mol.L}^{-1}$.

3.1- Specify the pH of this solution.

3.2- Add to 1 L of solution S_1 , without variation in volume:

3.2.1- $1.0 \times 10^{-3} \text{ mol}$ of H_3O^+ ions. Determine the pH_1 of the obtained solution.

3.2.2- $4.0 \times 10^{-3} \text{ mol}$ of H_3O^+ ions. The new value of pH is $\text{pH}_2 = 2.7$.

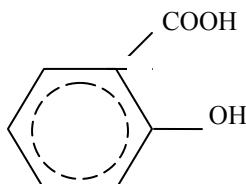
Indicate in which case the solution S_1 preserves its buffer properties.

Third Exercise (6 points) Salicylic Acid

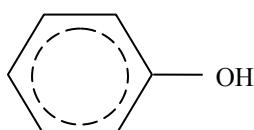
Salicylic acid is used in pharmaceutical and perfume industries.

Given:

- The structural formula of salicylic acid is:



- The primary raw material of the synthesis of salicylic acid is phenol of formula:



- $M(\text{phenol}) = 94 \text{ g.mol}^{-1}$ and $M(\text{salicylic acid } C_7H_6O_3) = 138 \text{ g.mol}^{-1}$.

1- Industrial Preparation of Salicylic Acid

This synthesis is carried out in three stages in which the third stage represents the reaction between sodium salicylate ($\text{HO} - \text{C}_6\text{H}_4 - \text{COO}^-$) solution and H_3O^+ ions (produced by sulfuric acid).

1.1- Write the equation representing the third stage (assume that this reaction is complete).

1.2- Determine the mass of salicylic acid obtained starting with the total transformation of 800 kg of phenol if the percentage yield of all operations covering the three stages is 85 %, knowing that one mole of phenol leads to the formation of one mole of salicylic acid.

2- Salicylic Acid in Cosmetic Industry

Salicylic acid can react with methanol to form an odorous ester called “essential oil of Wintergreen” which is used in perfume industry.

2.1- Write, using the structural formulas of the organic compounds, the equation of the reaction between salicylic acid and methanol.

2.2- Give two characteristics of this reaction.

2.3- A mixture of salicylic acid and an excess methanol is subject to reflux heating in the presence of few drops of concentrated sulfuric acid.

2.3.1- State the two kinetic factors involved in this experimental activity.

2.3.2- Specify the advantage of using an excess of methanol

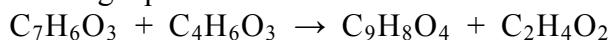
3- Salicylic Acid in Pharmaceutical Industry

Given:

- Sodium bicarbonate ($\text{Na}^+, \text{HCO}_3^-$) is highly soluble in water.
- $pK_a(\text{H}_2\text{O}/\text{OH}^-) = 14$; $pK_a(\text{H}_3\text{O}^+/\text{H}_2\text{O}) = 0$; $pK_a(\text{CO}_2, \text{H}_2\text{O}/\text{HCO}_3^-) = 6.4$.
- $pK_a(\text{HA}_1/\text{A}_1^-) = 3.5$ where HA_1 represents acetylsalicylic acid.
- $pK_a(\text{HA}_2/\text{A}_2^-) = 3.1$ where HA_2 represents citric acid considered as a monoacid.

- A gas is released from a solution only when this solution becomes saturated with it.

Salicylic acid is the essential chemical compound used in the synthesis of aspirin according to the chemical reaction of the following equation:



- 3.1- Write the structural formula of the two compounds: $\text{C}_4\text{H}_6\text{O}_3$ and $\text{C}_9\text{H}_8\text{O}_4$.
- 3.2- Circle and name the two functional groups in the structural formula of aspirin $\text{C}_9\text{H}_8\text{O}_4$
- 3.3- Pharmaceutical industry presents aspirin under several formulations. The information concerning the formulation of a buffered effervescent aspirin is given as:
acetylsalicylic acid; sodium bicarbonate; citric acid...
A tablet of this aspirin is introduced into a glass of water. A release of gas is observed as the tablet gradually disappears.
 - 3.3.1- Represent on a vertical pK_a axis the conjugate acid/base pairs given before.
 - 3.3.2- Write the equations of the two reactions responsible for the liberation of the gas when the bicarbonate is in an appropriate excess amount.
 - 3.3.3- Justify the two terms "buffered" and "effervescent".

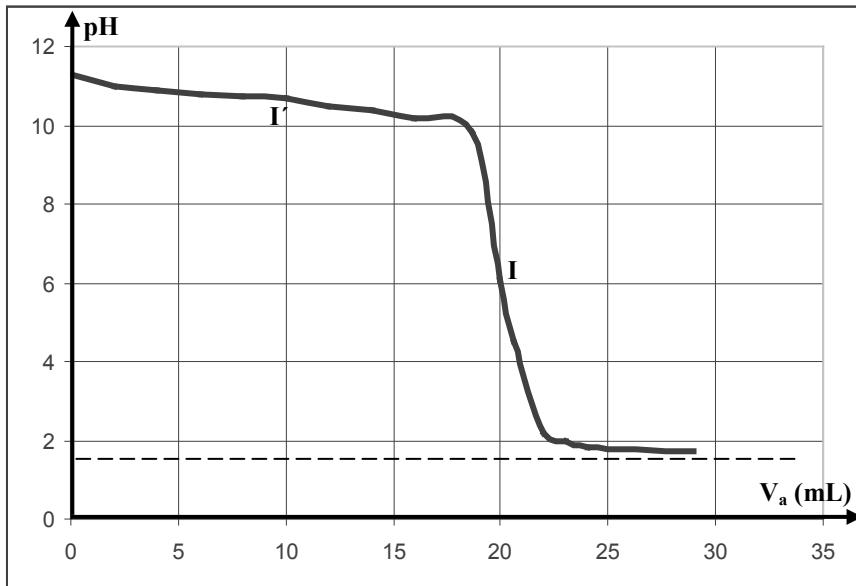
First Exercise (7 points)

Part of the Q	Answer	Mark																
1.1	<p>the table:</p> <table border="1"> <thead> <tr> <th>Time</th><th>$2 \text{ N}_2\text{O}$</th><th>2 N_2</th><th>O_2</th></tr> </thead> <tbody> <tr> <td>0</td><td>n_0</td><td>0</td><td>0</td></tr> <tr> <td>t</td><td>$n_0 - 2x$</td><td>$2x$</td><td>x</td></tr> <tr> <td>End of reaction</td><td>0</td><td>n_0</td><td>$\frac{n_0}{2}$</td></tr> </tbody> </table>	Time	$2 \text{ N}_2\text{O}$	2 N_2	O_2	0	n_0	0	0	t	$n_0 - 2x$	$2x$	x	End of reaction	0	n_0	$\frac{n_0}{2}$	1
Time	$2 \text{ N}_2\text{O}$	2 N_2	O_2															
0	n_0	0	0															
t	$n_0 - 2x$	$2x$	x															
End of reaction	0	n_0	$\frac{n_0}{2}$															
1.2	<p>At the end of the reaction, the number of moles is: $n = \frac{3n_0}{2}$. However: The ratio in moles is equal to the ratio of the pressures, because the volume and the temperature remain the same. We have:</p> $P = \frac{n}{n_0} P_0 = \frac{\frac{3n_0}{2}}{n_0} P_0 = \frac{3 \times 1.00 \times 10^5}{2} = 1.50 \times 10^5 \text{ Pa.}$	1																
2.1	<p>According to equation of state of ideal gases, we have: $P(\text{O}_2) \times V = n(\text{O}_2) \times R \times T$; $[O_2]_t = \frac{n(O_2)}{V} = \frac{P(O_2)}{R \times T}$. Or : at any moment, we have : $P(\text{N}_2) = 2 P(\text{O}_2)$; $P(\text{N}_2\text{O}) = P_0 - 2 P(\text{O}_2)$; $P = P(\text{N}_2\text{O}) + P(\text{N}_2) + P(\text{O}_2) = P_0 + P(\text{O}_2)$. Where : $P(\text{O}_2) = P - P_0$ and $[O_2]_t = \frac{P - P_0}{8.3(600 + 273)} = 1.38 \times 10^{-4}(P - P_0) \text{ mol.m}^{-3}$.</p>	1																
2.2	<p>- The curve: $[O_2] = f(t)$:</p>	1																
2.3	<p>The rate of this reaction at instant t is equal to the rate of formation of O_2, so: To determine the rate of the reaction at an instant t: - Trace the tangent to the curve $[O_2] = f(t)$, at the point of abscissa t. - Calculate the slope of this tangent.</p>	0.5																

	The rate of the reaction is equal to the value of this slope.	
2.4	The observation of the curve shows that this value decreases when the time passes. This decrease in the rate is due to the decrease in the concentration of the reactant (N_2O).	0.5
2.5	<p>The half-life of the reaction is the time when the concentration of O_2 will be equal to half of its concentration at the end of the reaction.</p> $[\text{O}_2]_{t=1/2} = \frac{[\text{O}_2]_{t=\infty}}{2} = \frac{1.38 \times 10^{-4} (1.50 \times 10^5 - 1.00 \times 10^5)}{2} = 3.45 \text{ mol.m}^{-3}$ <p>According to the graph, this concentration corresponds to : $t_{1/2} = 62 \text{ min.}$</p>	1
2.6.1	The increase in the temperature increases the reaction rate.	0.5
2.6.2	$[\text{O}_2] = \frac{n(\text{O}_2)}{V}$. Knowing that $n(\text{O}_2)_{t=\infty}$ and V are constants whatever is the temperature so the final concentration of O_2 does not vary with the temperature.	0.5

Second Exercise (7 points)

Part of the Q	Answer	Mark
1.1	<p>The equation of the reaction between methylamine and water is:</p> $\text{CH}_3\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{NH}_3^+ + \text{HO}^-.$	0.5
1.2	<p>By definition:</p> $\alpha = \frac{n(\text{CH}_3\text{NH}_2) \text{ transformed}}{n(\text{CH}_3\text{NH}_2) \text{ initial}} = \frac{n(\text{HO}^-) \text{ formed}}{n(\text{CH}_3\text{NH}_2) \text{ initial}} = \frac{[\text{HO}^-]}{C_b} = \frac{10^{\text{pH}-14}}{C_b} = \frac{10^{-2.7}}{0.01}; \text{ from where } \alpha = 10^{-0.7} = 0.2.$	075
1.3	<p>The acidity constant of this conjugate acid/base pair is:</p> $K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{NH}_2]}{[\text{CH}_3\text{NH}_3^+]} = \frac{10^{-\text{pH}} \times C_b (1-\alpha)}{[\text{HO}^-]} = 2 \times 10^{-11};$ <p>Where: $\text{pK}_a = -\log K_a = -\log 2 \times 10^{-11} = 10.7$.</p>	0.75
2.1	<p>At equivalence, $n(\text{H}_3\text{O}^+)$ added = $n(\text{CH}_3\text{NH}_2)$ introduced in the beaker</p> $C_a \times V_{aE} = C_b \times V_b$ <p>Where: $V_{aE} = \frac{C_b \times V_b}{C_a} = \frac{0.01 \times 40}{0.02} = 20 \text{ mL.}$</p>	0.75
2.2	<p>At equivalence, the species present are: CH_3NH_3^+, Cl^- and H_2O.</p> <p>Cl^- is a spectator species in water; CH_3NH_3^+ is a weak acid which reacts with water to make the medium acidic.</p>	0.5
2.3	<p>The remarkable points of this shape are:</p> <ul style="list-style-type: none"> - pH initial = 11.3 ; $V_{aE} = 20 \text{ mL}$ and $\text{pH}_E = 6.1$; - $V_{a(1/2 \text{ equivalence})} = 10 \text{ mL}$ and $\text{pH}_{(1/2 \text{ equivalence})} = \text{pK}_a(\text{CH}_3\text{NH}_3^+ / \text{CH}_3\text{NH}_2) = 10.7$ - The pH at which the curve tends is that of the added solution: $\text{pH} = -\log C_a = 1.7$ <p>The shape of the curve will be as follows:</p>	1.75



3.1	An equimolar mixture of the acid and its conjugate base has a pH equal to pK_a of this pair; thus the pH of the solution S ₁ is 10.7.	0.5
3.2.1	$\text{CH}_3\text{NH}_2 + \text{H}_3\text{O}^+ \rightarrow \text{CH}_3\text{NH}_3^+ + \text{H}_2\text{O}$ Initial state 2.0×10^{-3} mol 1.0×10^{-3} mol 2.0×10^{-3} mol solvant Obtained solution $\sim 1.0 \times 10^{-3}$ mol ~ 0 $\sim 3.0 \times 10^{-3}$ mol solvant $\text{pH}(\text{solution}) = \text{pK}_a(\text{CH}_3\text{NH}_3^+ / \text{CH}_3\text{NH}_2) + \log \frac{[\text{CH}_3\text{NH}_2]}{[\text{CH}_3\text{NH}_3^+]}$ $= 10.7 + \log 0.333 = 10.2.$	1
3.2.2	The solution S ₁ conserves its buffer properties in the case of question 3.2, because the variation of its pH is relatively little.	0.5

Third Exercise (6 points)

Part of the Q	Answer	Mark
1.1	The equation of this reaction is: Or $\text{HO} - \text{C}_6\text{H}_4 - \text{COO}^- + \text{H}_3\text{O}^+ \rightarrow \text{HO} - \text{C}_6\text{H}_4 - \text{COOH} + \text{H}_2\text{O}.$	0.5
1.2	$n(\text{salicylic acid}) \text{ formed} = n(\text{phenol}) \text{ initial} \times \frac{85}{100}$ $m(\text{salicylic acid}) \text{ formed} = 0.85 \times m(\text{phenol}) \times \frac{M(\text{salicylic acid})}{M(\text{phenol})}$ $= 0.85 \times 800 \times \frac{138}{94} = 998.3 \text{ kg.}$	0.5
2.1	The equation of this reaction is: $\text{HO} - \text{C}_6\text{H}_4 - \text{COOH} + \text{CH}_3\text{OH} \rightleftharpoons \text{HO} - \text{C}_6\text{H}_4 - \text{C}(=\text{O}) - \text{O} - \text{CH}_3 + \text{H}_2\text{O}$	0.5
2.2	This reaction is athermic, slow, reversible.	0.5

2.3.1	The two kinetic factors which are involved in this activity are: The temperature and the catalyst represented by concentrated sulfuric acid.	0.5																					
2.3.2	The excess of methanol favors the formation of the ester so the yield of the reaction increases.	0.5																					
3.1	<p>The condensed structural formula of compound $C_4H_6O_3$ is:</p> $CH_3 - C = O - O - C - CH_3$ <p>That of compound $C_9H_8O_4$ is:</p>	0.5																					
3.2		0.5																					
3.3.1	<p>$NaHCO_3$ completely ionized in water gives the ions: Na^+ and HCO_3^-.</p> <p>The conjugate acid/base pairs placed on the pK_a axis:</p> <table style="margin-left: auto; margin-right: auto;"> <tr> <td style="text-align: right;">HO^-</td> <td style="text-align: center;">↑</td> <td style="text-align: left;">14 H_2O</td> </tr> <tr> <td colspan="3" style="text-align: center;"> </td> </tr> <tr> <td style="text-align: right;">HCO_3^-</td> <td style="text-align: center;">6.4</td> <td style="text-align: left;">CO_2, H_2O</td> </tr> <tr> <td colspan="3" style="text-align: center;"> </td> </tr> <tr> <td style="text-align: right;">A_1^-</td> <td style="text-align: center;">3.5</td> <td style="text-align: left;">HA_1</td> </tr> <tr> <td style="text-align: right;">A_2^-</td> <td style="text-align: center;">3.1</td> <td style="text-align: left;">HA_2</td> </tr> <tr> <td style="text-align: right;">H_2O</td> <td style="text-align: center;">0</td> <td style="text-align: left;">H_3O^+</td> </tr> </table>	HO^-	↑	14 H_2O				HCO_3^-	6.4	CO_2, H_2O				A_1^-	3.5	HA_1	A_2^-	3.1	HA_2	H_2O	0	H_3O^+	0.5
HO^-	↑	14 H_2O																					
HCO_3^-	6.4	CO_2, H_2O																					
A_1^-	3.5	HA_1																					
A_2^-	3.1	HA_2																					
H_2O	0	H_3O^+																					
3.3.2	<p>The two equations of the two reactions responsible for the release of gas:</p> $HA_1 + HCO_3^- \rightleftharpoons A_1^- + CO_{2(g)} + H_2O$ $HA_2 + HCO_3^- \rightleftharpoons A_2^- + CO_{2(g)} + H_2O$	1																					
3.3.3	<p>The release of gas justify the term: "effervescent".</p> <p>Since HCO_3^- is in excess and the solution is saturated by CO_2 gas; the mixture formed by acid CO_2 dissolved an its conjugated base HCO_3^-, in the final solution, justify the term "buffered".</p>	0.5																					

الاسم:	مسابقة في مادة الكيمياء
الرقم:	المدة: ساعتان

Cette épreuve est constituée de trois exercices. Elle comporte trois pages numérotées de 1 à 3.

L'usage d'une calculatrice non programmable est autorisé.

Traiter les trois exercices suivants:

Premier exercice(6 points)

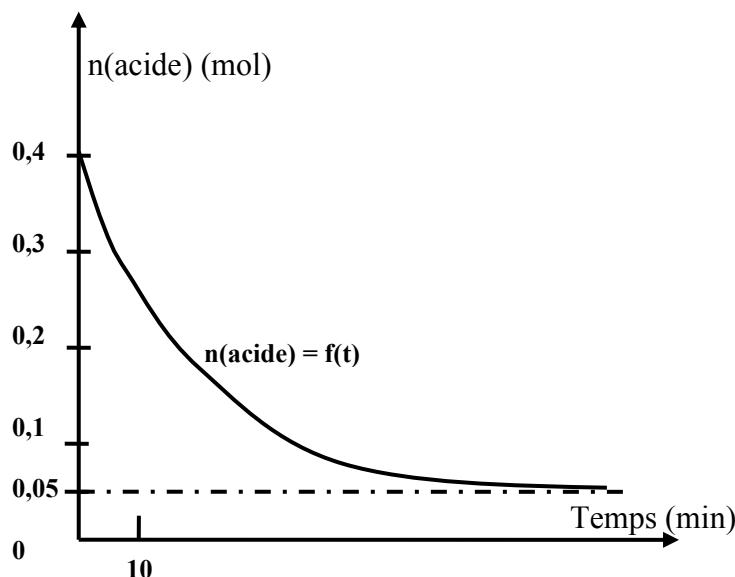
Synthèse d'un ester

L'odeur et la saveur des poires sont dues à l'ester synthétisé à partir de l'acide éthanoïque et du propan-1-ol. On désire synthétiser cet ester de poire et étudier l'effet de certains facteurs sur le progrès de la réaction de cette synthèse.

Donnée : Masse molaire en g.mol⁻¹ : M(acide éthanoïque) = 60 ; M(propan-1-ol) = 60.

1- Détermination de la constante K_c de la réaction de cette synthèse

À une température T₁, on mélange 24 g d'acide éthanoïque, 60 g de propan-1-ol et quelques mL d'acide sulfurique concentré. Une réaction a lieu et l'équilibre est atteint à cette température. La variation du nombre de moles de l'acide éthanoïque est déterminée par une méthode appropriée. La courbe n(acide) = f(t) est représentée par le graphique suivant :



- 1.1- Écrire, en utilisant les formules semi-développées, l'équation de la réaction de synthèse de l'ester de poire et donner le nom systématique de cet ester.
- 1.2- Préciser l'effet de l'acide sulfurique sur la vitesse de la réaction d'une part et sur son rendement d'autre part.
- 1.3- Déterminer la valeur de K_c à T₁ pour cette réaction d'estérification en se basant sur les informations fournies au début de l'exercice et sur le graphe ci-dessus.

2- Effet de quelques facteurs sur le progrès de cette réaction de synthèse

- 2.1- L'expérience ci-dessus est répétée à une température T₂ > T₁ jusqu'à ce que l'équilibre soit établi (**en utilisant les mêmes quantités initiales des réactifs**). Recopier le graphe ci-dessus sur la feuille de réponses. Sur le même graphe, tracer, en justifiant, l'allure de la nouvelle courbe n(acide) = g(t) à T₂.

2.2- La même expérience est répétée en remplaçant l'acide éthanoïque par son anhydride acide.

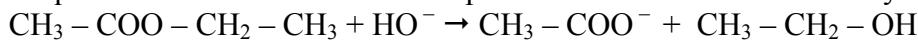
2.2.1-Écrire la formule semi-développée de l'anhydride acide.

2.2.2-Donner deux avantages de remplacer l'acide par son anhydride.

2.2.3-L'utilisation de l'anhydride acide exige l'utilisation d'une verrerie sèche. Pourquoi cette précaution devrait-elle être prise ?

Deuxième exercice (7 points) **Saponification de l'éthanoate d'éthyle**

On considère l'équation de la réaction lente de saponification de l'éthanoate d'éthyle :



À l'instant $t = 0$, on maintient à 25°C des bêchers identiques, contenant chacun un volume $V = 10 \text{ mL}$ d'un mélange équimolaire d'éthanoate d'éthyle et d'hydroxyde de sodium. À des différentes dates, on dose les ions HO^- restants dans chaque bêcher par une solution S d'acide chlorhydrique de concentration molaire $C_S = 1,0 \times 10^{-2} \text{ mol.L}^{-1}$ en présence d'un indicateur coloré convenable. On note x (en mL) le volume d'acide ajouté pour atteindre l'équivalence dans chaque bêcher.

Donnée :

- L'éthanoate d'éthyle et l'éthanol sont considérés neutres du point de vue acido-basique.
- $\text{pK}_a (\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-) = 4,8$

1- Étude du dosage

1.1- Écrire l'équation de la réaction de dosage.

1.2- Préciser le caractère acido-basique du milieu dans le bêcher à l'équivalence à $t > 0$.

1.3- Le dosage à $t = 0$ nécessite un volume $x = 50 \text{ mL}$.

Déterminer la concentration initiale en ions HO^- .

2- Suivi cinétique de la formation de l'éthanol

2.1- Montrer que la quantité de matière de l'éthanol (en mol), peut s'exprimer, à l'instant t , par la relation : $n(\text{C}_2\text{H}_5\text{OH}) = (50 - x)10^{-5}$. (x est exprimé en mL).

2.2- Donner la valeur de x à $t = 0$ et calculer la valeur qui manque dans le tableau ci-dessous :

$t \text{ (min)}$	0	4	9	14	24	37	53	83	143
$x \text{ (mL)}$		44,1	38,6	33,7	27,9	22,9	18,5	13,6	8,9
$n(\text{C}_2\text{H}_5\text{OH}) (10^{-2} \text{ mmol})$	0	5,9	11,4	16,3	22,1	27,1	31,5	36,4	

2.3- Tracer la courbe $n(\text{C}_2\text{H}_5\text{OH}) = f(t)$ dans l'intervalle de temps : [0 - 143 min]. Prendre les échelles suivantes : 1 cm pour 10 min en abscisses et 1 cm pour $4,0 \times 10^{-2} \text{ mmol}$ en ordonnées.

2.4- Déterminer le temps de demi- réaction.

3- Préparation d'une solution tampon

On considère le bêcher où la réaction de saponification est terminée.

3.1- Indiquer les espèces chimiques présentes dans ce bêcher.

3.2- On ajoute un volume $V_S \text{ mL}$ de la solution S d'acide chlorhydrique dans ce bêcher.

3.2.1- Écrire l'équation de la réaction qui a eu lieu. Calculer sa constante K_r .

3.2.2- Déterminer le volume V_S qu'il faut ajouter pour avoir une solution de $\text{pH} = 4,8$.

Troisième exercice (7 points)

L'eau de Javel

L'eau de Javel est une solution aqueuse de chlorure de sodium et d'hypochlorite de sodium. L'ion hypochlorite, $\text{ClO}^-_{(\text{aq})}$ est le constituant actif de l'eau de Javel et la base conjuguée de l'acide hypochloreux $\text{HClO}_{(\text{aq})}$.

Donnée :

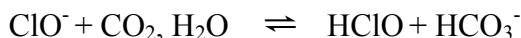
- Cette étude est effectuée à 25°C.
- $pK_a(\text{CO}_2, \text{H}_2\text{O}/\text{HCO}_3^-) = 6,4$.
- $pK_a(\text{HClO}/\text{ClO}^-) = 7,3$.
- $K_e = 1,0 \times 10^{-14}$.
- Masse molaire atomique du chlore : $M(\text{Cl}) = 35,5 \text{ g.mol}^{-1}$.
- Le dichlore est un gaz toxique peu soluble dans l'eau.

1- Propriétés acido-basiques de l'eau de Javel

1.1- Écrire l'équation de la réaction acido-basique entre l'ion hypochlorite et l'eau.

1.2- Déterminer le pH de la solution lorsque le degré de transformation de ClO^- dans cette réaction est 0,50.

1.3- Le dioxyde de carbone de l'air réagit avec l'ion hypochlorite selon l'équation suivante :



1.3.1- Déterminer la constante K_r de cette réaction.

1.3.2- Expliquer pourquoi l'eau de Javel est stockée dans des flacons bien bouchés.

2- Eau de Javel : danger !

Le pH d'un échantillon d'eau de Javel est amené à 2,0. Pour cette valeur de pH, une réaction a lieu selon l'équation suivante : $\text{HClO}_{(\text{aq})} + \text{Cl}^-_{(\text{aq})} + \text{H}_3\text{O}^+_{(\text{aq})} \rightarrow \text{Cl}_2^{(\text{g})} + 2 \text{H}_2\text{O}$.

2.1- Identifier l'espèce prédominante du couple HClO/ClO^- dans l'eau de Javel de pH = 2.

2.2- Sur l'étiquette d'un détergent contenant de l'acide chlorhydrique, il est indiqué :

"ne pas mélanger avec l'eau de Javel". Justifier cette indication.

3- Le traitement de l'eau de piscine par l'eau de Javel

Dans la plupart des piscines, l'eau de Javel est ajoutée pour détruire les bactéries nuisibles par les ions hypochlorite.

3.1- Pour que la désinfection soit efficace, il faut maintenir le pH de l'eau entre 7,0 et 7,6.

Montrer qu'aucune des deux espèces, ClO^- et HClO , n'est prédominante dans l'eau de piscine dans l'intervalle de pH recommandé.

3.2- Pour que l'eau de piscine ne présente pas de danger, il faut que la concentration en masse de l'élément chlore (sous ses deux formes HClO et ClO^-) soit comprise entre 1 et 2 mg.L^{-1} . La concentration des ions hypochlorite $\text{ClO}^-_{(\text{aq})}$ dans l'eau d'une piscine est $2 \times 10^{-5} \text{ mol.L}^{-1}$. Vérifier que l'eau de cette piscine a une concentration acceptable de l'élément chlore, sachant que le pH de cette eau est 7,3.

الاسم:
الرقم:مسابقة في مادة الكيمياء
المدة: ساعتان

مشروع معيار التصحيح

Premier exercice (6 points)
Synthèse d'un ester

Partie de la Q.	Corrigé	Note
1.1	<p>- L'équation est :</p> $\text{CH}_3\text{COOH} + \text{CH}_3 - \text{CH}_2 - \text{CH}_2\text{OH} \rightleftharpoons \text{CH}_3 - \underset{\substack{\parallel \\ \text{O}}}{\text{C}} - \text{O} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 + \text{H}_2\text{O}$ <p>Le nom de l'ester est l'éthanoate de propyle.</p>	1.25
1.2	L'acide sulfurique est un catalyseur, il fait accélérer la réaction (rôle cinétique). Il est sans effet sur le rendement de cette réaction.	0.5
1.3	<p>La constante d'équilibre est donnée par l'expression suivante :</p> $K_c = \frac{[\text{Ester}][\text{Eau}]}{[\text{Acide}][\text{Alcool}]}$ <p>À $t = 0$, $n(\text{acide}) = \frac{m}{M} = \frac{24}{60} = 0,4 \text{ mol}$ et $n(\text{alcool}) = \frac{60}{60} = 1 \text{ mol}$.</p> <p>À l'équilibre, $n(\text{acide})_{\text{restant}} = 0,05 \text{ mol}$ (valeur tirée de la courbe), $n(\text{ester})_{\text{formé}} = n(\text{eau})_{\text{formé}} = 0,4 - 0,05 = 0,35 \text{ mol}$ et $n(\text{alcool})_{\text{restant}} = 1 - 0,35 = 0,65 \text{ mol}$.</p> $K_c = \frac{\frac{0,35}{V} \times \frac{0,35}{V}}{\frac{0,05}{V} \times \frac{0,65}{V}} = 3,77$	1.5
2.1	<p>La courbe :</p> <p>L'élévation de la température fait augmenter la vitesse de la réaction, mais n'affecte pas son rendement puisque cette réaction est athermique. À tout instant t de l'évolution du système n de l'acide restant à T_2 est inférieur que n de l'acide restant à T_1.</p>	1.5
2.2.1	La formule de l'anhydride éthanoïque est :	0.25

	$\text{CH}_3 - \underset{\text{O}}{\overset{\parallel}{\text{C}}} - \text{O} - \underset{\text{O}}{\overset{\parallel}{\text{C}}} - \text{CH}_3$	
2.2.2	La réaction sera complète et plus rapide.	0.5
2.2.3	L'anhydride acide est un réactif qui réagit avec de l'eau selon une réaction exothermique et se transforme en acide éthanoïque.	0.5

Deuxième exercice (7 points)
Saponification

Partie de la Q.	Corrigé	Note																				
1.1	L'équation de la réaction de dosage est : $\text{HO}^- + \text{H}_3\text{O}^+ \rightarrow 2 \text{H}_2\text{O}$	0.5																				
1.2	Les espèces chimiques à l'équivalence sont : Na^+ , Cl^- , $\text{C}_2\text{H}_5\text{OH}$ et CH_3COO^- . Les trois premiers sont indifférents du point de vue acido-basique, l'ion CH_3COO^- est une base, elle rend le milieu basique.	1																				
1.3	À l'équivalence les réactifs réagissent totalement : $n_{(\text{acide versé})} = n_{(\text{base dosée})}$ $C_b V_b = C_s V_{sE}$, on tire $C_b = \frac{1,0 \times 10^{-2} \times 50}{10} = 0,05 \text{ mol.L}^{-1}$.	0.5																				
2.1	$n_{(\text{HO}^- \text{ réagissant})} = n_{(\text{éthanol formé})}$ $n_{(\text{HO}^- \text{ réagissant})} = n_{(\text{HO}^-) \text{ initial}} - n_{(\text{HO}^-)_t} = 10^{-2} \times 50 \times 10^{-3} - 10^{-2} \times x \times 10^{-3}$ $n(\text{C}_2\text{H}_5\text{OH}) = (50 - x)10^{-5}$.	0,5																				
2.2	La valeur de x à $t = 0$ est 50 mL et la valeur manquante est : $(50 - 8,9) \times 10^{-2} = 41,1 \times 10^{-2} \text{ mmol}$.	0.5																				
2.3	Tracé de la courbe $n(\text{C}_2\text{H}_5\text{OH}) = f(t)$:	1																				
	<table border="1"> <caption>Data points from the graph</caption> <thead> <tr> <th>Temps (min)</th> <th>n(C₂H₅OH) (10⁻² mmol)</th> </tr> </thead> <tbody> <tr><td>0</td><td>0</td></tr> <tr><td>10</td><td>12,5</td></tr> <tr><td>20</td><td>20</td></tr> <tr><td>30</td><td>25</td></tr> <tr><td>40</td><td>28</td></tr> <tr><td>50</td><td>30</td></tr> <tr><td>100</td><td>35</td></tr> <tr><td>150</td><td>38</td></tr> <tr><td>200</td><td>40</td></tr> </tbody> </table>	Temps (min)	n(C ₂ H ₅ OH) (10 ⁻² mmol)	0	0	10	12,5	20	20	30	25	40	28	50	30	100	35	150	38	200	40	
Temps (min)	n(C ₂ H ₅ OH) (10 ⁻² mmol)																					
0	0																					
10	12,5																					
20	20																					
30	25																					
40	28																					
50	30																					
100	35																					
150	38																					
200	40																					
2.4	Le temps de demi-réaction correspond à : $n(\text{C}_2\text{H}_5\text{OH}) = n(\text{C}_2\text{H}_5\text{OH})_{\text{final}} / 2 = 0,25 \text{ mmol}$. On détermine graphiquement : $t_{1/2} = 32 \text{ min}$.	0.5																				
3.1	Les espèces chimiques qui se trouvent dans ce bécher, en plus de l'eau, sont : Na^+ , CH_3COO^- et $\text{C}_2\text{H}_5\text{OH}$.	0.5																				
3.2.1	L'équation de la réaction est :	1																				

	$\text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+ \rightleftharpoons \text{CH}_3\text{COOH} + \text{H}_2\text{O}$ $K_r = -10^{4,8-0} = 10^{4,8}$.	
3.2.2	D'après la relation : $\text{pH} = \text{pK}_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$; on tire $\log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 0$; et $\frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1$ n_{base} dans le bécher avant l'ajout de l'acide = 5×10^{-4} mol. La réaction étant totale la moitié de la base CH_3COO^- se transforme en acide CH_3COOH . Le nombre de mol H_3O^+ qu'il faut ajouter est : $2,5 \times 10^{-4}$ mol ce qui correspond à un volume $V_s = 25 \text{ mL}$.	1

Troisième exercice (7 points)

Eau de Javel

Partie de la Q.	Corrigé	Note
1.1	L'équation de cette réaction est : $\text{ClO}^- + \text{H}_2\text{O} \rightleftharpoons \text{HClO} + \text{OH}^-$	0.5
1.2	On a $\text{pH} = \text{pK}_{\text{A}1} + \log \frac{[\text{ClO}^-]}{[\text{HClO}]}$ Pour $\alpha = 0,50$, la moitié de la quantité introduite de ClO^- est transformée en HClO ; on aura : $[\text{ClO}^-] = [\text{HClO}]$, d'où : $\log \frac{[\text{ClO}^-]}{[\text{HClO}]} = 0$ et $\text{pH} = \text{pK}_{\text{a}1} = 7,3$.	1.25
1.3.1	$K = \frac{[\text{HClO}] \times [\text{HCO}_3^-]}{[\text{ClO}^-] \times [\text{CO}_2, \text{H}_2\text{O}]} = 10^{(\text{pK}_{\text{A}1} - \text{pK}_{\text{A}2})}$ soit $K = 10^{(7,3 - 6,4)} = 10^{0,9} = 7,9$	1
1.3.2	L'eau de Javel est stockée dans des flacons bien bouchés pour éviter la réaction entre ClO^- et CO_2 de l'air, ce qui diminue la concentration de son constituant actif.	0.75
2.1	A un $\text{pH} = 2,0$ l'espèce prédominante est l'acide hypochloreux, d'après le diagramme car pH (solution) < $\text{pK}_a(\text{HClO}/\text{ClO}^-) - 1$	0.75
2.2	Car en milieu acide, la réaction de l'acide hypochloreux avec les ions H_3O^+ produit un dégagement de dichlore gazeux très toxique.	0.75
3.1	Comme le pH de l'eau de piscine est comprise entre $\text{pK}_a - 1$ et $\text{pK}_a + 1$; aucune espèce n'est prédominante.	0.75
3.2	On a $[\text{HClO}] = [\text{ClO}^-] = 2 \times 10^{-5} \text{ mol.L}^{-1}$, car $\text{pH} = 7,3 = \text{pK}_a$. Dans 1 L de la solution: La concentration C de l'élément chlore = $[\text{HClO}] + [\text{ClO}^-] = 4 \times 10^{-5} \text{ mol.L}^{-1}$ $\text{Cg.L}^{-1} = \text{Cmol.L}^{-1} \times M_{\text{Cl}} = 4 \times 10^{-5} \times 35,5 = 1,42 \times 10^{-3} \text{ g.L}^{-1} = 1,42 \text{ mg.L}^{-1}$. Donc C de l'élément chlore est compris entre 1 mg.L^{-1} et 2 mg.L^{-1} . Elle est acceptable.	1,25

الاسم: مسابقة في مادة الكيمياء
الرقم: المدة ساعتان

This Exam Includes **Three** exercises. It Is Inscribed on **Three** Pages Numbered from **1** to **3**.
The Use of A Non-programmable Calculator Is Allowed.

Answer the Three Following Exercises

First Exercise (6 points)

Identification of Some Organic Compounds

In the chemistry laboratory, are available an aqueous solution of a secondary saturated and noncyclic monoamine (B) and two liquid organic compounds, one of which is an alcohol (A) of molecular formula $C_4H_{10}O$ and the other is an ester (E) of molecular formula $C_3H_6O_2$.

1- Identification of Alcohol (A)

- 1.1- Write the condensed structural formulas of alcohols corresponding to the molecular formula of (A).
- 1.2- A sample of (A) is mixed with an acidified potassium permanganate solution. A compound (C) is obtained which reacts with 2,4-D.N.P.H. but does not reduce Fehling's solution.
Identify the alcohol (A) and write the condensed structural formula of (C).

2- Identification of Ester (E)

- 2.1- Write the condensed structural formulas of esters of formula $C_3H_6O_2$.
- 2.2- Hydrolysis of (E), in the presence of concentrated sulfuric acid, produces two compounds, one of which is the ethanoic acid.
 - 2.2.1- Give the name of (E).
 - 2.2.2- Write the equation of this hydrolysis reaction.

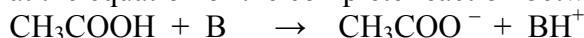
3- Identification of Amine (B)

Given:

- Molar mass of ethanoic acid: $M = 60 \text{ g.mol}^{-1}$
- Density of pure ethanoic acid: $d = 1.06 \text{ g.mL}^{-1}$.

To a volume $V_b = 100 \text{ mL}$ of amine (B) solution of concentration 27 g.L^{-1} , pure ethanoic acid is added drop by drop, in the presence of a convenient indicator. The added volume to reach the equivalence point is 3.4 mL .

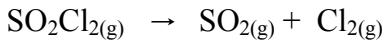
Knowing that the equation of the complete reaction between ethanoic acid and amine (B) is:



- 3.1- Determine, in mol.L^{-1} , the concentration of the solution of amine (B).
- 3.2- Show that the molecular formula of (B) is C_2H_7N .
- 3.3- Write the condensed structural formula of the secondary amine (B) and give its name.
- 3.4- The mixture obtained at equivalence is heated in order to get an amide.
Write the condensed structural formula of this amide and give its name.

Second Exercise (7 points) Decomposition of Sulfuryl Chloride

Sulfuryl chloride decomposes, in gaseous phase, according to a slow and complete reaction of the following equation:



To follow the kinetics of this decomposition, n_0 mol of sulfuryl chloride are introduced into a container evacuated of air and of constant volume V maintained at a temperature $T = 593$ K. A pressure gauge, associated to the container, permits to measure the pressure P_t of the reacting system with time. We deduce the concentration of SO_2 gas at different instants and the obtained results are given in the following table:

t (s)	100	200	300	400	550	700	900
$[\text{SO}_2]_t$ (10^{-3} mol.L $^{-1}$)	2.2	4.0	5.2	6.2	7.4	8.0	8.4

Given:

- Take constant of ideal gas: $R = 0.082$ L.bar.mol $^{-1}$.K $^{-1}$.

1- Preliminary Study

- 1.1- Determine the initial concentration C_0 of sulfuryl chloride, knowing that $P_0 = 0.52$ bar.
- 1.2- Having the initial pressure P_0 and P_t permits to calculate the concentration of SO_2 gas with time $[\text{SO}_2]_t$. Establish the relation among $[\text{SO}_2]_t$, P_0 and P_t .
- 1.3- Calculate the concentration of SO_2 at the end of the reaction.

2- Kinetic Follow-up

- 2.1- Plot the curve: $[\text{SO}_2] = f(t)$, in the interval of time $[0 - 900]$ s. Take the following scale: 1 cm for 100 s in abscissa and 1 cm for 1.0×10^{-3} mol.L $^{-1}$ in ordinate.
- 2.2- Show that the rate of formation of SO_2 at $t = 500$ s is about 7.4×10^{-6} mol.L $^{-1}$.s $^{-1}$. Deduce the reaction rate at this instant.
- 2.3- Choose, by justifying, which one of the two following values: 3.0×10^{-5} mol.L $^{-1}$.s $^{-1}$ or 3.0×10^{-6} mol.L $^{-1}$.s $^{-1}$, corresponds to the value of the initial rate ($t = 0$) of formation of SO_2 .
- 2.4- The concentration of sulfuryl chloride versus time is determined. The results are grouped in the following table:

t (s)	100	200	300	400	550	700	900
$[\text{SO}_2\text{Cl}_2]_t$ (10^{-3} mol.L $^{-1}$)	8.5	6.7	5.5	4.5	3.3	2.7	2.3

- 2.4.1- Find the relation between the concentration of sulfuryl chloride $[\text{SO}_2\text{Cl}_2]_t$ and that of sulfur dioxide $[\text{SO}_2]_t$ at each instant t during the change of the reacting system.
- 2.4.2- Plot, on the same graph of part 2.1, the curve: $[\text{SO}_2\text{Cl}_2] = g(t)$.
- 2.4.3- Specify what represents the abscissa of the intersection point of the two curves for the studied reaction.

Third Exercise (7 points) Buffer Effect

In biochemistry, several chemical reactions require the control of the pH of the reacting medium. The aim of this exercise is to study two solutions (S) and (S') in order to identify which is the appropriate solution for a reacting medium of controlled pH.

Given :

- This study is carried out at $25\text{ }^{\circ}\text{C}$.
- The ionic product of water $K_w = 1.0 \times 10^{-14}$.
- This study is performed with monoacids and monobases.

1- Study of the Solution (S)

Solution (S) is a solution of a strong base of concentration C_0 .

1.1- Calculate C_0 so that the pH of (S) is equal to 9.

1.2- The table below represents three experiments carried out with a volume $V_0 = 50\text{ mL}$ of the solution (S):

Experiment	Volume of S in mL	Added reactant	pH
I	50	1.0×10^{-5} mol of a strong base	10.3
II	50	1.0×10^{-5} mol of a strong acid	
III	50	50 mL distilled water	

1.2.1- Write the equation of the reaction that takes place in the experiment II.

1.2.2- Determine the missing values of pH in the above table.

2- Study of the Solution (S')

1 L of the solution (S') is prepared by dissolving, in water, 2.25×10^{-2} mol of a weak base (B) and 2.5×10^{-3} mol of hydrochloric acid. The pH of this solution is equal to 9.

2.1- Write the equation of the complete reaction between (B) and the hydrochloric acid solution.

2.2- Show that the value of pK_a of the conjugate acid/base pair (BH^+/B) is 8.1.

2.3- The table below represents three experiments carried out with a volume $V_0 = 50\text{ mL}$ of the solution (S'):

Experiment	Volume of S' in mL	Added reactant	pH
IV	50	1.0×10^{-5} mol of a strong base	
V	50	1.0×10^{-5} mol of a strong acid	8.96
VI	50	50 mL distilled water	9

2.3.1- Write the equation of the complete reaction that takes place in the experiment IV.

2.3.2- Determine the missing value of pH in the above table.

3- Choice of the Solution

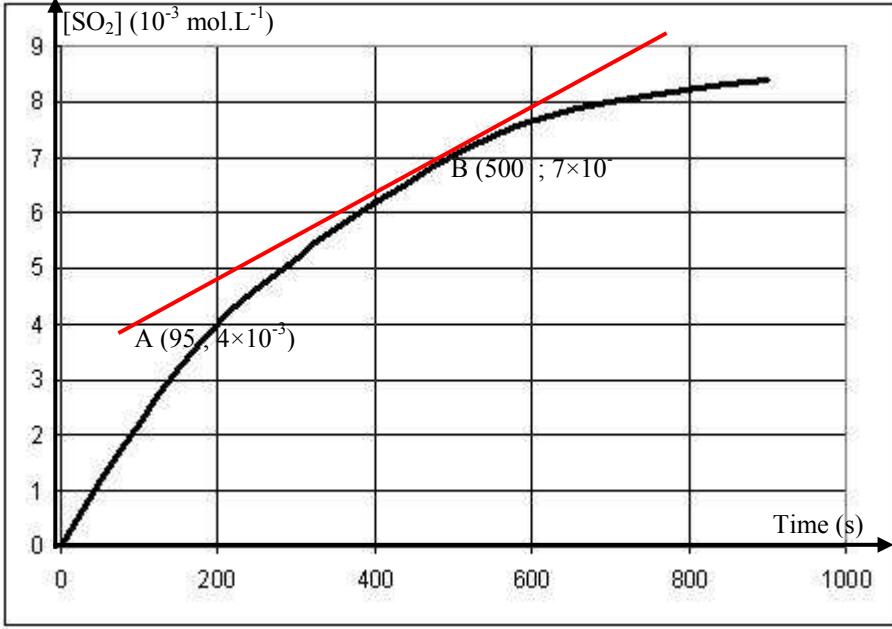
It is required to perform a reaction in a medium with a controlled $\text{pH} = 9$.

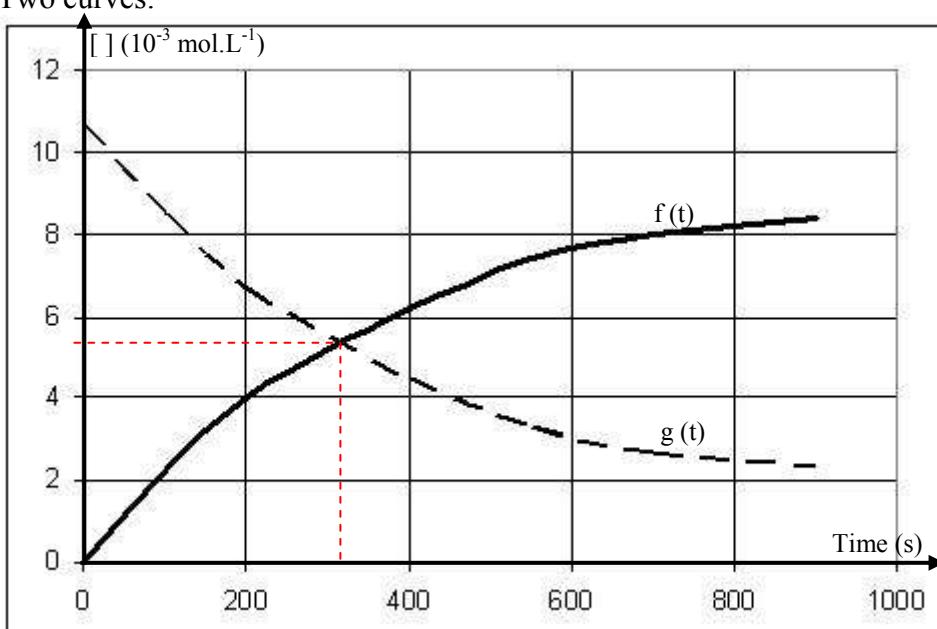
Choose, by justifying, which solution (S) or (S') permits to perform this task.

First Exercise (6 points)
Identification of Some Organic Compounds

Part of the Q	Answer	Mark
1.1	<p>The condensed structural formulas of alcohols are:</p> $\begin{array}{c} \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2\text{OH} ; \text{CH}_3 - \text{CH}_2 - \text{CHOH} - \text{CH}_3 ; \\ \text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_2\text{OH} \text{ and } \text{CH}_3 - \underset{\text{OH}}{\text{C}}(\text{CH}_3) - \text{CH}_3 \end{array}$	1
1.2	<p>The mild oxidation of (A) with an acidified potassium permanganate solution gives a compound (C) which reacts with 2,4-DNPH so it contains a carbonyl functional group and since it does not reduce Fehling's solution, this means that (C) is a ketone which comes from a secondary alcohol which is 2-butanol.</p> <p>The condensed formula of C is $\text{CH}_3 - \text{CH}_2 - \text{CO} - \text{CH}_3$.</p>	0.75
2.1	<p>The condensed structural formulas of esters having the molecular formula $\text{C}_3\text{H}_6\text{O}_2$ are: $\text{H} - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{O} - \text{CH}_2 - \text{CH}_3$ and $\text{CH}_3 - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{O} - \text{CH}_3$</p>	0.5
2.2.1	<p>Hydrolysis of ester gives an acid and an alcohol. The acid obtained is ethanoic acid means that the alcohol is methanol and (E) is methyl ethanoate.</p>	0.5
2.2.2	<p>The equation of the reaction is:</p> $\text{CH}_3 - \text{COOCH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3 - \text{COOH} + \text{CH}_3 - \text{OH}$	0.5
3.1	<p>At equivalence: $n(\text{ethanoic acid}) \text{ in } 3.4 \text{ mL} = n(\text{B}) \text{ in } 100 \text{ mL}$ of solution of B. $n(\text{ethanoic acid}) = C_b \times V_b$; $\frac{m(\text{acid})}{M(\text{acid})} = \frac{\mu \times V_a}{M} = \frac{1.06 \times 3.4}{60} = C_b \times 100 \times 10^{-3}$ and $C_b = 0.60 \text{ mol.L}^{-1}$.</p>	1
3.2	<p>The molar mass of B is given by: $C_b = \frac{m}{M \times V}$ and</p> $M = \frac{m}{C_b \times V} = \frac{27}{0.60 \times 1} = 45 \text{ g.mol}^{-1}$. <p>The formula of a noncyclic saturated amine is $\text{C}_n\text{H}_{2n+3}\text{N}$ of molar mass $14n + 17 = 45$ and $n = 2$. The formula of the amine is thus: $\text{C}_2\text{H}_7\text{N}$.</p>	0.75
3.3	<p>The condensed structural formula of (B) is $\text{CH}_3 - \text{NH} - \text{CH}_3$, it is N-methyl methanamine.</p>	0.5
3.4	<p>The formula of the amide obtained is: $\text{CH}_3 - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{N} - \text{CH}_3$</p> <p>It is N,N-dimethyl ethanamide.</p>	0.5

Second Exercise (7 points)
Decomposition of Sulfuryl Chloride

Part of the Q	Answer	Mark
1.1	According to the equation of the ideal gas: $C_0 = \frac{n_0}{V} = \frac{P_0}{R \times T} = \frac{0.52}{0.082 \times 593} = 10.7 \times 10^{-3} \text{ mol.L}^{-1}$	0.5
1.2	$\text{SO}_2\text{Cl}_{2(g)} \rightarrow \text{SO}_{2(g)} + \text{Cl}_{2(g)}$ At t=0 P_0 - - - At t $P_0 - P_1$ P_1 P_1 $P_t = P_0 + P_1$; where $P_1 = [\text{SO}_2] \times R \times T = P_t - P_0$. At the given temperature, knowing P_t and P_0 , we can deduce $[\text{SO}_2]_t$. $[\text{SO}_2]_t = \frac{P_t - P_0}{RT} = \frac{P_t - P_0}{48.63}$	1.25
1.3	At the end of the reaction, $P_t = 2 P_0$. $[\text{SO}_2]_\infty = \frac{2 \times 0.52 - 0.52}{48.63} = 10.7 \times 10^{-3} \text{ mol.L}^{-1}$	0.5
2.1	The curve is: 	1
2.2	The rate of formation of SO_2 , $r_f(\text{SO}_2) = \frac{d[\text{SO}_2]}{dt}$ at each instant t. $\frac{d[\text{SO}_2]}{dt}$ is the slope of the tangent to the curve $[\text{SO}_2] = f(t)$ at the point of abscissa 500 s. Two points of this tangent are chosen: A and B, such as: A (95 ; 4×10^{-3}) and B (500 ; 7×10^{-3}). Where, $r_f(\text{SO}_2) = \frac{(7 - 4) \times 10^{-3}}{500 - 95} = 7.40 \times 10^{-6} \text{ mol.L}^{-1} \cdot \text{s}^{-1}$. According to the equation of the reaction: $r(\text{reaction}) = r_f(\text{SO}_2) = 7.40 \times 10^{-6} \text{ mol.L}^{-1} \cdot \text{s}^{-1}$	1.25
2.3	The concentration of the reactant, SO_2Cl_2 , is a kinetic factor. When this concentration decreases, the rate of formation of SO_2 decreases. So, $r_f(\text{SO}_2)$ initial is equal to $3.0 \times 10^{-5} \text{ mol.L}^{-1} \cdot \text{s}^{-1}$ which is greater than $7.4 \times 10^{-6} \text{ mol.L}^{-1} \cdot \text{s}^{-1}$.	0.5

2.4.1	According to the equation, $n(\text{SO}_2\text{Cl}_2)_{\text{reacting}} = n(\text{SO}_2)_{\text{formed}}$; dividing by the volume of the solution, we have: $[\text{SO}_2\text{Cl}_2]_0 - [\text{SO}_2\text{Cl}_2]_t = [\text{SO}_2]_t$ $[\text{SO}_2\text{Cl}_2]_t = [\text{SO}_2\text{Cl}_2]_0 - [\text{SO}_2]_t = 10.7 \times 10^{-3} - [\text{SO}_2]_t$	0.5
2.4.2	Two curves: 	0.75
2.4.3	The point of intersection of the two curves has as abscissa the half-life of the reaction, because the ordinate of this point corresponds to: $[\text{SO}_2\text{Cl}_2] = [\text{SO}_2] = \frac{[\text{SO}_2\text{Cl}_2]_0}{2} = 5.35 \times 10^{-3} \text{ mol.L}^{-1}$. The half-life of the reaction is: $t_{1/2} = 310 \text{ s}$.	0.75

Third Exercise (7 points) Buffer Effect

Part of the Q	Answer	Mark
1.1	The pH of the solution (S) of a strong base is given by the relation: $\text{pH} = 14 + \log C_0$; $\log C_0 = 9 - 14 = -5$ hence $C_0 = 1.0 \times 10^{-5} \text{ mol.L}^{-1}$.	0.5
1.2.1	The equation of the reaction between hydrochloric acid and a strong base is: $\text{H}_3\text{O}^+ + \text{HO}^- \rightarrow 2 \text{H}_2\text{O}$	0.5
1.2.2	In the experiment II $n(\text{H}_3\text{O}^+)_0 = 10^{-5} \text{ mol}$. $n(\text{HO}^-)_0 = 10^{-5} \times 0.050 = 5 \times 10^{-7} \text{ mol}$. Since HO^- is the limiting reactant. $95 \times 10^{-7} \text{ mol H}_3\text{O}^+$ remain at the end of the reaction in 50 mL of solution we have: $[\text{H}_3\text{O}^+] = 19 \times 10^{-5} \text{ mol.L}^{-1}$ and $\text{pH} = 3.72$. In the experiment III the volume of the solution is doubled by dilution, the number of moles of the solute does not vary and the concentration of HO^- is divided by 2, it becomes: $[\text{HO}^-] = 0.5 \times 10^{-5} \text{ mol.L}^{-1}$ and $\text{pH} = 14 + \log 0.5 \times 10^{-5} = 8.7$.	2
2.1	The equation of the reaction is: $\text{B} + \text{H}_3\text{O}^+ \rightarrow \text{BH}^+ + \text{H}_2\text{O}$	0.5
2.2	The pKa is given according to the relation: $\text{pH} = \text{pKa} + \log \frac{[\text{B}]}{[\text{BH}^+]}$.	1

	<p>$R(H_3O^+) = 2.5 \times 10^{-3} < R(B) = 22.5 \times 10^{-3}$. $\Rightarrow H_3O^+$ is the limiting reactant.</p> <p>We have:</p> <p>$n(BH^+) = n(H_3O^+)$ and $n(B) = n(B)_{\text{initial}} - n(H_3O^+)$ and $V = 1 \text{ L}$. Where: $[BH^+] = 2.5 \times 10^{-3} \text{ mol.L}^{-1}$ and $[B] = 22.5 \times 10^{-3} - 2.5 \times 10^{-3} = 20 \times 10^{-3} \text{ mol.L}^{-1}$.</p> $9 = pK_a + \log \frac{20 \times 10^{-3}}{2.5 \times 10^{-3}}$ hence $pK_a = 8.1$.	
2.3.1	HO ⁻ reacts with BH ⁺ according to the following equation: $\text{HO}^- + \text{BH}^+ \rightarrow \text{B} + \text{H}_2\text{O}$	0.5
2.3.2	<p>At the end of the reaction:</p> <p>$n(B) = n(HO^-)_{\text{added}} + n(B)_{\text{initial}} = 1.0 \times 10^{-5} + 20 \times 10^{-3} \times 0.050 = 101 \times 10^{-5}$ mol.</p> <p>$n(BH^+) = n(BH^+)_{\text{initial}} - n(HO^-)_{\text{added}} = 2.5 \times 10^{-3} \times 0.050 - 1.0 \times 10^{-5} = 11.5 \times 10^{-5}$ mol.</p> $\text{pH} = 8.1 + \log \frac{\frac{101 \times 10^{-5}}{V}}{11.5 \times 10^{-5}}$ = 9.04.	1
3	<p>The same quantities (acid, base and water) are added to the same volume (50 mL) during the study of each solution (S) and (S'):</p> <ul style="list-style-type: none"> - the pH of solution (S) varies in a noticeable way in the first three experiments. - the pH of solution (S') varies very little and remains practically equal to 9 in the last three experiments. <p>So the solution (S') is the suitable solution to control the pH of the reacting medium.</p>	1

الاسم:	مسابقة في مادة الكيمياء
الرقم:	المدة ساعتان

This Exam Includes Three Exercises. It Is Inscribed on Four Pages Numbered from 1 to 4.

The Use of A Non-programmable Calculator Is Allowed.

Answer The Three Following Exercises:

First Exercise (7 points)
Decomposition of Hydrogen Peroxide

The commercial hydrogen peroxide is an aqueous hydrogen peroxide solution. It is used for the maintenance of the contact lenses, as a disinfecting agent, ...

Hydrogen peroxide decomposes, at 25°C, in a very slow and complete reaction according to the following equation: $2 \text{ H}_2\text{O}_{2(\text{aq})} \rightarrow 2 \text{ H}_2\text{O}_{(\text{l})} + \text{ O}_{2(\text{g})}$

Suppose that, at the conditions of the experiment, oxygen gas is insoluble in water.

1- Catalysis of this Reaction

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

1.1- Name the type of the catalysis carried out in the presence of a platinum wire.

1.2- The mechanism of this catalysis occurs in three steps: adsorption, reaction and desorption.

1.2.1- Assign, to each step, one of the following propositions :

- The reactants are transformed into products.
- The products escape from the surface of the catalyst.
- The reactants are attached to the surface of the catalyst.

1.2.2- Deduce the importance of the contact surface between reactants and a catalyst.

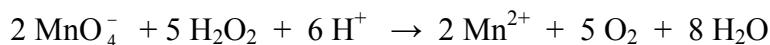
1.3- Consider a beaker containing an aqueous hydrogen peroxide solution in the presence of iron (III) chloride. Indicate the chemical species present in the solution obtained at the end of the decomposition reaction.

2- Kinetic of the Decomposition Reaction of H_2O_2

Nine beakers are available, each contains a volume $V_0 = 20.0 \text{ mL}$ of a hydrogen peroxide solution of concentration C_0 , in the presence of few drops of the iron (III) chloride solution.

The remaining hydrogen peroxide in each one of the beakers is titrated, at different instants, with an acidified potassium permanganate solution, of concentration $C = 2.0 \times 10^{-2} \text{ mol.L}^{-1}$.

The equation of the titration reaction is:



The volume of the permanganate solution, added to reach the equivalence point in each beaker is determined. The concentration of H_2O_2 , remained in V_0 , at the instant t , is deduced.

The results are grouped in the following table:

t (min)	0	3	6	9	15	21	27	33	39
$[\text{H}_2\text{O}_2] (10^{-2} \text{ mol.L}^{-1})$	-	4.2	3.5	2.9	2.0	1.4	1.0	0.70	0.50

- 2.1- Choose, from the following list, the material needed to carry out this titration:
 pH-meter and its electrode, stand, magnetic stirrer and its bar, 100 mL graduated cylinder, 100 mL volumetric flask and 50 mL graduated buret.
- 2.2- Before starting the titration, icy- water is poured into each beaker.
- 2.2.1- Indicate the two kinetic factors involved in this operation.
- 2.2.2- Specify the effect of each one of these two factors on the kinetic of the decomposition reaction of hydrogen peroxide.
- 2.3- Show that the initial concentration of the hydrogen peroxide solution is $C_0 = 5.0 \times 10^{-2} \text{ mol.L}^{-1}$, knowing that the volume of the potassium permanganate solution added to reach the equivalence point at $t = 0$ is $V_E = 20 \text{ mL}$.
- 2.4- Plot the curve representing the variation of the concentration of H_2O_2 versus time:
 $[\text{H}_2\text{O}_2] = f(t)$, in the time interval [0 – 39 min].
 Take the following scale: 1 cm for 3 min in abscissa,
 1 cm for $5.0 \times 10^{-3} \text{ mol.L}^{-1}$ in ordinate.
- 2.5- Determine the rate of disappearance of H_2O_2 at the instant $t = 18 \text{ min}$. Deduce the rate of the reaction at this instant.

Second Exercise (6 points) **α -Amino acids and Peptides**

Proteins and peptides enter in the constitution of the living organisms and take part in their operation while intervening in a large number of biochemical reactions. They are macromolecules obtained by the association of α -amino acids linked by peptide bond.

Given

- Molar Mass in g.mol^{-1} : M (H) = 1; M (C) = 12; M (N) = 14; M (O) = 16.

1- Identification of an α -Amino acid (A)

The analysis carried out on an α -amino acid (A) shows that:

- Its molecule contains only one nitrogen atom.
- The mass percentages of its elements are:
 $\% \text{ C} = 40.45$; $\% \text{ H} = 7.87$; $\% \text{ N} = 15.72$ and $\% \text{ O} = 35.96$

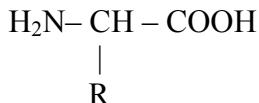
1.1- Show that the molecular formula of the acid (A) is $\text{C}_3\text{H}_7\text{NO}_2$.

1.2- Write its condensed structural formula and give its systematic name.

1.3- Represent, according to Cram, the two enantiomers of the acid (A).

2- Formation of the Dipeptide

A dipeptide (D) is prepared by the condensation reaction between one molecule of the acid (A) and one molecule of an α -amino acid (B) of formula:



where, R is an alkyl radical.

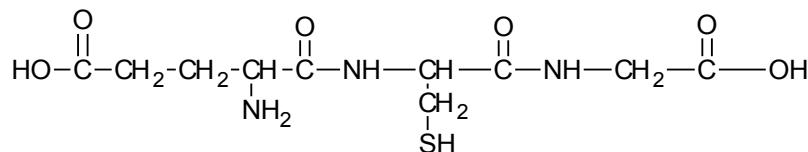
2.1- Show that the formula of R is C_4H_9 knowing that the molar mass of the dipeptide formed is equal to 202 g.mol^{-1} .

2.2- Write the condensed structural formula of the acid (B) knowing that its molecule contains two asymmetric carbon atoms. Give its systematic name.

2.3- Write the two possible condensed structural formulas of (D).

3- α -Amino acids Constituting Glutathione

Glutathione is a tripeptide which plays a regulatory role in the oxidation reduction reaction in animal cells. The condensed structural formula of glutathione is:



3.1- Give the number of the peptide bonds in the glutathione molecule.

3.2- Write the condensed structural formula of an acid produced from the hydrolysis of this tripeptide.

Third Exercise (7 points) Study of a Household Product

The indications on a label of the flask of a household product are not readable any more.

This product is one of the three following aqueous solutions: sodium hydroxide, ammonia or acetic acid.

In this exercise, it is required to identify the solute of this household product and to determine, using pH-metric follow-up, its concentration.

Given:

- The study is carried out at 25 °C.
- Ammonia is a weak base.
-

Acid/base pair	$\text{H}_3\text{O}^+/\text{H}_2\text{O}$	$\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$	$\text{NH}_4^+/\text{NH}_3$	$\text{H}_2\text{O}/\text{HO}^-$
pKa	0.0	4.8	9.2	14.0

1- Identification of the Solute of the Household Product

The measurement of the pH of this product gives a pH = 10.6

- 1.1- Draw, from this measurement, the conclusion concerning the identification of the solute of this household product.
- 1.2- A sample of this product is diluted 10 times, a solution of $\text{pH}' = 10.1$ is obtained. Deduce that this solute is ammonia.
- 1.3- Write the equation of the reaction between ammonia and water.

2- Titration of the Household Product

A volume $V_B = 10.0 \text{ mL}$ of the household product is poured into a 250 mL beaker, and distilled water is added to immerse properly the pH-meter electrode.

A pH-metric titration is then carried out, by adding gradually, a hydrochloric acid solution of concentration $C_a = 0.010 \text{ mol.L}^{-1}$ into the beaker.

The volume of the acid solution added to reach equivalence is $V_{aE} = 12.7 \text{ mL}$.

- 2.1- Write the equation of this titration reaction.
- 2.2- Justify the use of this fast reaction as a titration reaction.
- 2.3- Determine the concentration of ammonia in this household product.
- 2.4- For this pH-metric titration and its results, five statements are suggested.

When the statement is true, justify it.

When the statement is false, give the right answer.

- 2.4.1- The hydrochloric acid solution is added gradually using a 25 mL graduated cylinder.
- 2.4.2- The pH of the solution in the beaker, just before the addition of the acid solution, is equal to 10.6
- 2.4.3- The medium obtained at equivalence is acidic.
- 2.4.4- The pH of the mixture obtained for a large addition of the acid solution tends towards zero.
- 2.4.5- The pK_a of the conjugate pair $\text{NH}_4^+ / \text{NH}_3$ is given by the following relation:

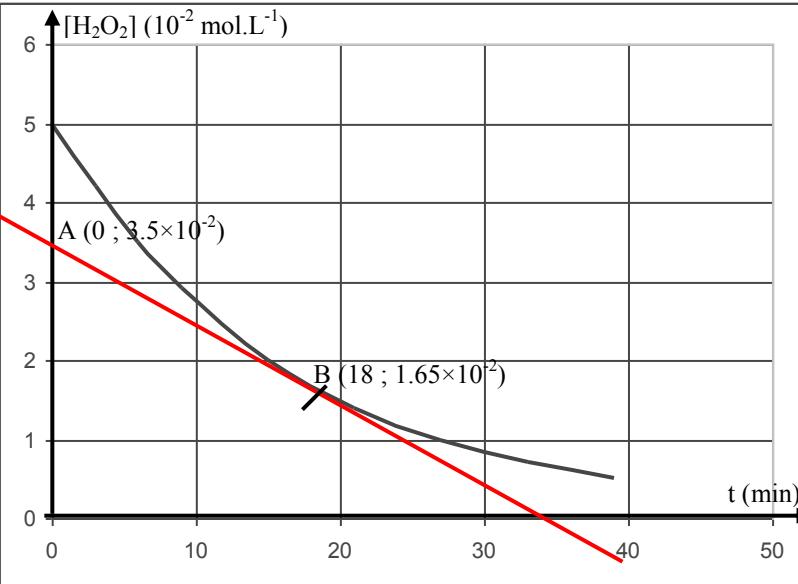
$$pK_a = \text{pH} - \log \frac{V_{aE} - V_a}{V_a};$$

where V_a is the volume of the acid solution added before the equivalence, and the pH is the pH of the mixture obtained at the time of this addition.

الاسم:
الرقم:مسابقة في مادة الكيمياء
المدة ساعتان

مشروع معيار التصحيح

Answer the three following exercises:**First exercise (7 points)**

Part of the Q	Answer	Mark								
1.1	The catalysis carried out with a platinum wire is a heterogeneous catalysis.	0.25								
1.2.1	Adsorption: The reactants are attached to the surface of the catalyst. Reaction: The reactants are transformed into products. Desorption: The products escape from the surface of the catalyst.	0.75								
1.2.2	As long as the contact surface: reactant-catalyst, increases, as long as the rate of the reaction is higher.	0.5								
1.3	The species present in the solution at the end of the decomposition reaction are: H_2O , Fe^{3+} and Cl^- .	0.75								
2.1	The material needed: 50 mL graduated buret, stand, magnetic stirrer and its bar.	0.75								
2.2.1	The two kinetic factors involved in this operation are: temperature of the reaction medium and the concentration of the reactant H_2O_2 .	0.5								
2.2.2	In this operation, the temperature decreases and $[\text{H}_2\text{O}_2]$ decreases. The rate of the reaction will decrease in such a way that the reaction will be practically blocked.	0.5								
2.3	At the equivalence point: $\frac{n(\text{MnO}_4^-) \text{ added}}{2} = \frac{n(\text{H}_2\text{O}_2) \text{ initial in the beaker}}{5},$ $\frac{C \times V_E}{2} = \frac{C_0 \times V_0}{5},$ $C_0 = \frac{5 \times C \times V_E}{2 \times V_0} = \frac{5 \times 0.02 \times 20}{2 \times 20} = 5.0 \times 10^{-2} \text{ mol.L}^{-1}.$	0.75								
2.4	The curve is:  <table border="1"> <caption>Data points from the graph</caption> <thead> <tr> <th>t (min)</th> <th>[H₂O₂] (10⁻² mol.L⁻¹)</th> </tr> </thead> <tbody> <tr> <td>0</td> <td>3.5 × 10⁻²</td> </tr> <tr> <td>18</td> <td>1.65 × 10⁻²</td> </tr> <tr> <td>40</td> <td>0</td> </tr> </tbody> </table>	t (min)	[H ₂ O ₂] (10 ⁻² mol.L ⁻¹)	0	3.5 × 10 ⁻²	18	1.65 × 10 ⁻²	40	0	1
t (min)	[H ₂ O ₂] (10 ⁻² mol.L ⁻¹)									
0	3.5 × 10 ⁻²									
18	1.65 × 10 ⁻²									
40	0									

<p>2.5</p> <p>By definition, $r(\text{H}_2\text{O}_2) = - \frac{d[\text{H}_2\text{O}_2]}{dt}$.</p> <p>Graphically, this rate is the negative slope of the tangent to the curve at the point of abscissa 18 min.</p> <p>Choose on this tangent the two points A and B such as: A (0; $3.5 \times 10^{-2} \text{ mol.L}^{-1}$) and B (18 min ; $1.65 \times 10^{-2} \text{ mol.L}^{-1}$). So $r(\text{H}_2\text{O}_2) = - \frac{0.035 - 0.0165}{0 - 18} = 1.03 \times 10^{-3} \text{ mol.L}^{-1}.\text{min}^{-1}$.</p> <p>The reaction rate at the same instant is:</p> $r_{\text{rxn}} = \frac{1}{2} r(\text{H}_2\text{O}_2) = \frac{1.03 \times 10^{-3}}{2} = 0.501 \times 10^{-3} \text{ mol.L}^{-1}.\text{min}^{-1}$	<p>1.25</p>
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Second exercise (6 points)

Part of the Q	Answer	Mark
1.1	<p>The sum of the percentages = 100 %, implies the molecular formula of A does not contain other elements than C, H, O, and N.</p> <p>The molecular formula of A is of the form $\text{C}_x\text{H}_y\text{O}_z\text{N}$. The law of the definite proportions makes it possible to write: $\frac{12x}{\% \text{C}} = \frac{y}{\% \text{H}} = \frac{16z}{\% \text{O}} = \frac{14}{\% \text{N}}$;</p> $\frac{12x}{40.45} = \frac{y}{7.87} = \frac{16z}{35.96} = \frac{14}{15.72}$. <p>$x = \frac{40.45 \times 14}{12 \times 15.72} = 3$; $y = 7$; $z = 2$. The molecular formula of A is $\text{C}_3\text{H}_7\text{O}_2\text{N}$</p>	1
1.2	<p>Since A is an α-amino acid its condensed structural formula is then: $\text{CH}_3 - \underset{\text{NH}_2}{\text{CH}} - \text{COOH}$; it is 2-aminopropanoic acid</p>	0.75
1.3	<p>The two enantiomers of A are:</p>	0.75
2.1	<p>$M(\text{B}) = M(\text{D}) + M(\text{H}_2\text{O}) - M(\text{A}) = 202 + 18 - 89 = 131 \text{ g.mol}^{-1}$.</p> <p>But $M(\text{B}) = M(\text{R}) + 74$ with R: $\text{C}_n\text{H}_{2n+1}$ $14n = 56$; $n = 4$. The formula of R is: C_4H_9.</p>	1
2.2	<p>The formula of B having two asymmetrical carbon atoms is: $\text{C}_2\text{H}_5 - \underset{\text{CH}_3}{\text{CH}} - \underset{\text{NH}_2}{\text{CH}} - \text{COOH}$; it is 2-amino-3-methylpentanoic acid.</p>	0.75
2.3	$\begin{array}{c} \text{H}_2\text{N} - \text{CH} - \overset{\text{O}}{\underset{ }{\text{C}}} - \text{NH} - \text{CH} - \overset{\text{O}}{\underset{ }{\text{C}}} - \text{OH} \\ \qquad \qquad \qquad \\ \text{H}_3\text{C} - \text{CH} - \text{C}_2\text{H}_5 \qquad \text{CH}_3 \end{array} \qquad \begin{array}{c} \text{H}_2\text{N} - \text{CH} - \overset{\text{O}}{\underset{ }{\text{C}}} - \text{NH} - \text{CH} - \overset{\text{O}}{\underset{ }{\text{C}}} - \text{OH} \\ \qquad \qquad \qquad \\ \text{CH}_3 \qquad \text{H}_3\text{C} - \text{CHC}_2\text{H}_5 \end{array}$	1
3.1	<p>There are two peptide bonds in this tripeptide.</p>	0.25

3.2	<p>One of the acids produced is:</p> $\text{HO}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_2-\text{CH}_2-\underset{\text{NH}_2}{\underset{ }{\text{CH}}}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{OH}$	0.5
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Third exercise (7 points)

Part of the Q	Answer	Mark
1.1	pH = 10.6 > 7 : basic medium, means that the solute is not acetic acid; it is either sodium hydroxide solution or ammonia solution.	0.5
1.2	Since the decrease in the pH is less than one unit; the solute is not a strong base, it is a weak base which is the ammonia.	0.5
1.3	The equation of the reaction between ammonia and water is : $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{HO}^-$	0.5
2.1	The equation of the titration reaction between ammonia and H_3O^+ ions is: $\text{NH}_3 + \text{H}_3\text{O}^+ \rightarrow \text{NH}_4^+ + \text{H}_2\text{O}.$	0.5
2.2	The reaction constant of this reaction: $K_r = \frac{[\text{NH}_4^+]}{[\text{NH}_3] \cdot [\text{H}_3\text{O}^+]} = \frac{1}{K_a(\text{NH}_4^+ / \text{NH}_3)} = 10^{9.2} > 10^4$; this fast reaction is complete, therefore we can use it as a titration reaction.	0.75
2.3	At the equivalence point: $n(\text{H}_3\text{O}^+)$ added to reach equivalence = $n(\text{NH}_3)$ in the volume V_b $C_a \cdot V_{aE} = C_b \cdot V_b$ The concentration of this ammonia product is: $C_b = \frac{C_a \times V_{aE}}{V_b} = \frac{0.01 \times 12.7}{10} = 1.27 \times 10^{-2} \text{ mol.L}^{-1}.$	1
2.4.1	This statement is false; the acid solution is added using a graduated buret.	0.5
2.4.2	This statement is false; the initial pH is <10.6 because the ammonia solution is diluted.	0.5
2.4.3	This statement is true; the medium at equivalence is acidic, because the species present are: Cl^- (spectator ion), H_2O and NH_4^+ which makes the medium acidic by its reaction with water.	0.5
2.4.4	This statement is false; for a large addition of acid solution the pH of the mixture tends towards the pH of the added solution. The pH tends towards: $-\log C_a = -\log 0.01 = 2.0$	0.75
2.4.5	This statement is true; before equivalence, <ul style="list-style-type: none"> - H_3O^+ is the limiting reactant. - there is a mixture of NH_3 and NH_4^+ - $[\text{NH}_3] = \frac{C_b \times V_b - C_a \times V_a}{V_a + V_b} = \frac{C_a \times V_{aE} - C_a \times V_a}{V_a + V_b}$ and $[\text{NH}_4^+] = \frac{C_a \times V_a}{V_a + V_b}$ $\text{pH} = \text{pK}_a + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]},$ $\text{pK}_a = \text{pH} - \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = \text{pH} - \log \frac{V_{aE} - V_a}{V_a}.$	1

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الاسم: الرقم:	مسابقة في مادة الكيمياء المدة ساعتان	

This Exam Includes Three Exercises. It Is Inscribed on 3 Pages Numbered From 1 to 3. The Use of A Non-programmable Calculator is Allowed.

Answer The Three Following Exercises:

First Exercise (6 points)
Carboxylic Acid Derivatives

Acid derivatives are more reactive than the corresponding carboxylic acids, especially in the preparation of esters.

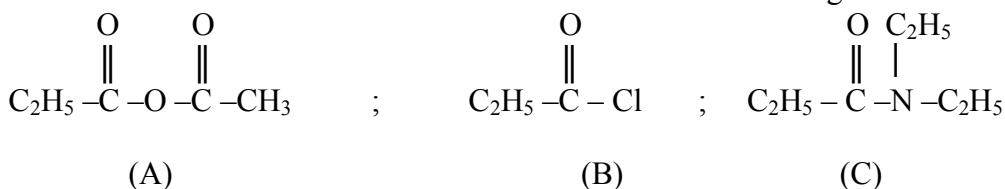
The aim of this exercise is to recognize some acid derivatives, their reactions and their preparations.

Given:

- Molar mass in g.mol⁻¹: M(H) = 1; M(C) = 12; M(O) = 16; M(Cl) = 35.5
- Density of the liquid compound (B): d = 1.065g.ml⁻¹.

1- Structural Formulas of Some Acid Derivatives

The condensed structural formulas of some acid derivatives are given below:



1.1- Give the systematic name of each (A), (B) and (C).

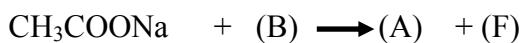
1.2- Write, using condensed structural formulas of the organic compounds, the equation of one preparation reaction of (C).

2- Preparation of the Compound (A)

The compound (A) is a mixed anhydride less important than acetic anhydride. It is used as an intermediate in the manufacture of many industrial chemicals: perfumes, plastics ...

The compound (A) is obtained, in the pure state, by proceeding as follows:

A volume V= 7 mL of liquid compound (B) is introduced into a dry beaker containing an excess of solid sodium ethanoate CH₃COONa. A fast reaction occurs according to the following equation:



A mass of 6.9 g of the compound (A) is obtained at the end of the reaction.

2.1- Write the formula of the compound (F).

2.2- Determine the percentage of the compound (B) which has reacted.

2.3- This reaction should be carried out in a dry beaker. Justify.

3- Preparation of an Ester (E) from the Compound (B)

A mixture of the compound (B) and of a saturated non cyclic monoalcohol (D) is heated in the presence of an appropriate catalyst. At the end of the reaction, an ester (E) having a molar mass $M = 130\text{ g.mol}^{-1}$ is obtained.

- 3.1- Determine the molecular formula of the ester (E).
- 3.2- Deduce that the molecular formula of the alcohol (D) is $\text{C}_4\text{H}_9\text{OH}$.
- 3.3- Write the possible condensed structural formulas of the alcohol (D).
- 3.4- Name this alcohol (D) knowing that its molecule contains one asymmetric carbon.
- 3.5- Identify the ester (E).

Second Exercise (7 points) Decomposition of Benzene Diazonium Chloride

Benzene diazonium chloride ($\text{C}_6\text{H}_5\text{N}_2\text{Cl}$) decomposes, in aqueous solution, as soon as the temperature is higher than 10°C according to the equation:



The kinetic of this reaction is followed by measuring the volume $V(\text{N}_2)$ of nitrogen gas released, under the pressure of 1 atm and at the temperature of 17°C , starting with a volume $V_0 = 35\text{ mL}$ of benzene diazonium chloride solution of initial concentration $C_0 = 8 \times 10^{-2}\text{ mol.L}^{-1}$

Given:

- Ideal gas constant: $R = 0.082\text{ L.atm.mol}^{-1}.K^{-1}$.
- Molar mass in g.mol^{-1} : $M(\text{H}) = 1$; $M(\text{C}) = 12$; $M(\text{N}) = 14$; $M(\text{Cl}) = 35.5$

1- Preliminary Study

- 1.1- Determine the volume of nitrogen gas formed when the time tends to infinity.
- 1.2- Show that, at each instant, the concentration of the benzene diazonium chloride solution $[\text{C}_6\text{H}_5\text{N}_2\text{Cl}]_t$, in terms of $V(\text{N}_2)$ is given by the relation:
$$[\text{C}_6\text{H}_5\text{N}_2\text{Cl}]_t = 8.0 \times 10^{-2} - 1.2 \times V(\text{N}_2) ;$$
 Where $V(\text{N}_2)$ is expressed in liters.

2- Kinetic Study of this Decomposition Reaction

The measurement of the volume of nitrogen gas, at different instants, permits to draw up the following table:

time t (s)	0	75	150	225	300	450	600	750	900	1200
$[\text{C}_6\text{H}_5\text{N}_2\text{Cl}]_t (10^{-2} \text{ mol.L}^{-1})$	8.0	7.0	6.2	5.6	5.1	4.2	3.3	2.6	2.0	1.5

- 2.1- Plot the curve $[\text{C}_6\text{H}_5\text{N}_2\text{Cl}]_t = f(t)$ in the interval of time $[0 - 1200\text{ s}]$.
Take the following scales: 1 cm for 100 s in abscissa
1 cm for $1.0 \times 10^{-2}\text{ mol.L}^{-1}$ in ordinate.
- 2.2- Determine graphically the half-life time $t_{1/2}$ of the reaction.
- 2.3- Calculate the volume of nitrogen gas released at the half-life time $t_{1/2}$
- 2.4- Determine the rate of disappearance of benzene diazonium chloride at the instant $t = 150\text{ s}$.
- 2.5- The rate of disappearance of benzene diazonium chloride at $t_{1/2}$ is equal to $6.0 \times 10^{-5}\text{ mol.L}^{-1}.s^{-1}$. Specify the kinetic factor responsible for its change between t and $t_{1/2}$

Third Exercise (7 points)

Commercial Solution to Decrease the pH of an Aquarium

"... .In fact, certain fishes can't grow except in an acid medium (...), others in a basic medium (...)" According to "Fishes and aquariums" - Larousse Edition.

The aim of this exercise is to study a commercial solution used to decrease the pH of the water in an aquarium.

Given:

- The study is carried out at $T = 25^\circ \text{C}$.
- $K_a(\text{CO}_2 \text{ (aq)}, \text{H}_2\text{O} / \text{HCO}_3^-) = 4 \times 10^{-7}$

1- Determination of the Concentration of the Commercial Solution

The commercial solution used to lower the pH of the water of an aquarium is a hydrochloric acid solution of concentration C_0 .

To determine C_0 , one proceeds as follows:

The commercial solution is diluted 50 times; The solution obtained is noted as S_a .

A volume $V_a = 20.0 \text{ mL}$ of S_a is titrated with sodium hydroxide solution of concentration $C_b = 4.0 \times 10^{-2} \text{ mol.L}^{-1}$. The volume of the base added to reach the equivalence point is $V_{bE} = 25 \text{ mL}$.

- 1.1- Describe, by specifying the material used, the procedure to be followed to prepare 1 L of solution S_a from the commercial solution.
- 1.2- Write the equation of the titration reaction.
- 1.3- Specify, based on the chemical species present, the pH of the medium obtained at the equivalence point.
- 1.4- Determine the concentration of the diluted solution S_a .
- 1.5- Deduce that the concentration of the commercial solution is 2.5 mol.L^{-1} .

2- Lowering the pH in an Aquarium

It is required to bring the pH of the water in an aquarium to a value close to 6

For that, one follows the instructions of the manufacturer that recommend that it is necessary to pour 20 mL of the commercial solution of concentration C_0 over 100 L of water of an aquarium. (The final volume will be considered 100 L).

- 2.1- Supposing that this is a simple dilution of H_3O^+ ions, show that the value of the pH of water in the aquarium will be 3.3
 - 2.2- In fact, the water used in the aquarium is very calcareous; it contains hydrogen carbonate ions (HCO_3^-). The H_3O^+ ions introduced in the aquarium will react with these ions according to the following equation: $\text{HCO}_3^- + \text{H}_3\text{O}^+ \rightleftharpoons \text{CO}_2 \text{ (aq)}, \text{H}_2\text{O} + \text{H}_2\text{O}_{(l)}$
- 2.2.1- Show that this reaction is complete.
 - 2.2.2- Interpret the difference between the value of $\text{pH} = 3.3$ and the required value of the pH of the water of the aquarium which is equal to 6

الدورة الإستثنائية للعام 2011	امتحانات الشهادة الثانوية العامة الفرع : علوم عامة وعلوم الحياة	وزارة التربية والتعليم العالي المديرية العامة للتربية دائرة الامتحانات
الاسم: الرقم:	مسابقة في مادة الكيمياء المدة ساعتان	مشروع معيار التصحيح

Answer the three following exercises:

First Exercise (6 points) (G.S)

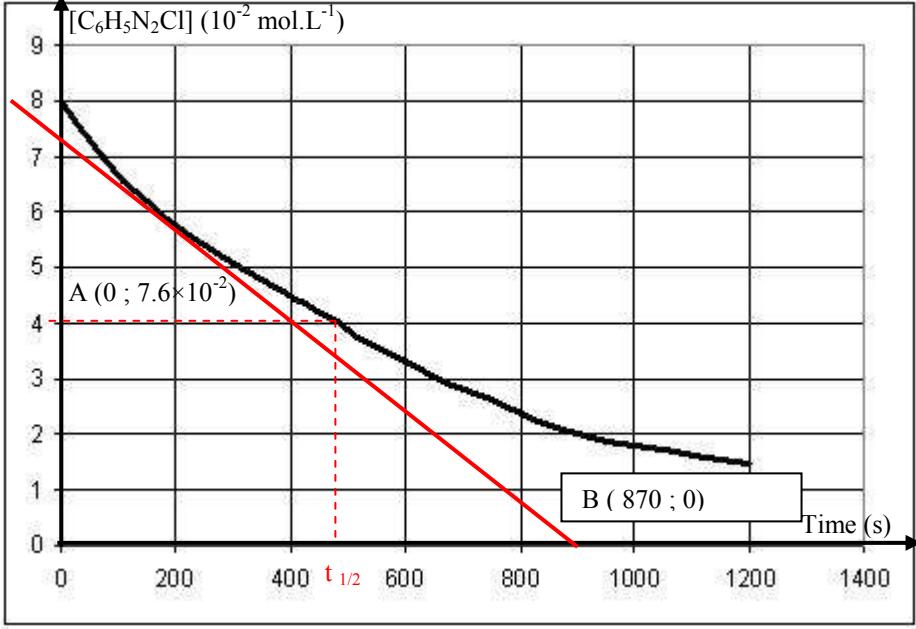
Part of the Q	Answer	Mark
1.1	Name of (A): ethanoic propanoic anhydride Name of (B): propanoyl chloride	0.5
1.2	$C_2H_5 - COOH + PCl_5 \longrightarrow C_2H_5 - COCl + POCl_3 + HCl$	0.5
2.1	The formula of C is NaCl.	0.25
2.2	$n(B)_{\text{reacted}} = n(A)_{\text{obtained}} = \frac{m(A)}{M(A)} = \frac{6.9}{116} = 0.06 \text{ mol} .$ $n(B)_{\text{initial}} = \frac{m(B)}{M} = \frac{\text{Volume}(B) \times \text{density}(B)}{M} =$ $\frac{7 \times 1.065}{92.5} = \frac{7.455}{92.5} = 0.08 \text{ mol}$ $\% (B) \text{ reacted} = \frac{n(B)_{\text{reacted}}}{n(B)_{\text{initial}}} \times 100 = \frac{0.06}{0.08} \times 100 = 75\%.$	1
2.3	The reaction should be carried out in a dry beaker in order to prevent the hydrolysis of the propanoyl chloride.	0.5
3.1	By stoichiometry: $n(\text{ester})_{\text{formed}} = n(B)_{\text{initial}} = 0.05 \text{ mol} .$ $M(E) = \frac{m(E)}{n(E)} = \frac{5.8}{0.05} = 116 \text{ g.mol}^{-1}$	0.5
3.2	By law of conservation of mass : $M(C_2H_5COCl) + M(D) = M(E) + M(HCl)$ $M(D) = (116 + 36.5) - 92.5 = 60 \text{ g.mol}^{-1}$. The general molecular formula of the alcohol (D) is $C_xH_{2x+1}OH$ $M(C_xH_{2x+1}OH) = 14x + 18 = 60 \Rightarrow x = 3$. So the molecular formula of alcohol (D) is C_3H_7OH .	0.75
3.3.1	Compound (M) is a carbonyl compound: an aldehyde or a ketone since it gives a yellow- orange precipitate with the reagent 2,4-DNPH. Since the compound (M) gives a brick red precipitate with Fehling's solution, so (M) is an aldehyde. Consequently the alcohol (D) is primary alcohol, since it produces an aldehyde by dehydrogenation.	0.5
3.3.2	Compound (D) : $CH_3 - CH_2 - CH_2OH$: 1-propanol. Compound (M) : $CH_3 - CH_2 - CHO$: propanal Compound (E) : $C_2H_5 - COO - CH_2 - CH_2 - CH_3$: propyl propanoate.	1.5

First Exercise (6 points) (L.S)

Part of the Q	Answer	Mark
1.1	- Name of (A): ethanoic propanoic anhydride Name of (B): propanoyl chloride Name of (C) : N,N-diethylpropanamide.	0.75
1.2	$C_2H_5 - COCl + (C_2H_5)_2 - NH \longrightarrow (C) + HCl$	0.5
2.1	The formula of (F) is NaCl.	0.25
2.2	$n(B)_{\text{reacted}} = n(A)_{\text{obtained}} = \frac{m(A)}{M(A)} = \frac{6.9}{116} = 0.06 \text{ mol}$. $n(B)_{\text{initial}} = \frac{m(B)}{M} = \frac{\text{Volume}(B) \times \text{density}(B)}{M} =$ $\frac{7 \times 1.065}{92.5} = \frac{7.455}{92.5} = 0.08 \text{ mol}$ $\% (B) \text{ reacted} = \frac{n(B)_{\text{reacted}}}{n(B)_{\text{initial}}} \times 100 = \frac{0.06}{0.08} \times 100 = 75\%$.	1
2.3	The reaction should be carried out in a dry beaker in order to prevent the hydrolysis of the propanoyl chloride.	0.25
3.1	The general formula of the ester (E) is $C_nH_{2n}O_2$, since it is obtained from a saturated acid derivative and a saturated monoalcohol. $M(E) = 14n + 32 = 130$; $n = 7$; the molecular formula of (E) is $C_7H_{14}O_2$.	0.5
3.2	By law of conservation of mass : $n(\text{carbon atoms}) \text{ in the alcohol (D)} = n(\text{carbon atoms}) \text{ in E} - n(\text{carbon atoms}) \text{ in B} = 7 - 3 = 4$ the molecular formula of alcohol (D) is C_4H_9OH .	0.75
3.3	The possible formulas of (D): $CH_3 - CH_2 - CH_2 - CH_2OH$; $CH_3 - CH_2 - CHO - CH_3$ $CH_3 - CH - CH_2OH$; $CH_3 - COH - CH_3$ <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> CH_3 $$ </div> <div style="text-align: center;"> CH_3 $$ </div> </div>	1
3.4	Alcohol (D) : 2-butanol.	0.25
3.5	Compound (E) : $CH_3 - CH_2 - COO - CH - CH_2 - CH_3$ <div style="text-align: center;"> $$ CH_3 1-methyl propyl propanoate </div>	0.75

Second Exercise (7 points)

Part of the Q	Answer	Mark
1.1	$\text{At } t_{\infty} n(\text{N}_2) \text{ formed} = n(\text{C}_6\text{H}_5\text{N}_2\text{Cl})_{\text{initial}} = C_0 \times V_0 = 8 \times 10^{-2} \times 35 \times 10^{-3}$ $= 2.8 \times 10^{-3} \text{ mol}$ $V(\text{N}_2)_{\infty} = \frac{n(\text{N}_2) \times R \times T}{P} = \frac{2.8 \times 10^{-3} \times 0.082 \times (273 + 17)}{1} = 66.6 \times 10^{-3} \text{ L}$	1.25
1.2	<p>n is the number of moles of $\text{C}_6\text{H}_5\text{N}_2\text{Cl}$ that reacts at instant t, so:</p> $n(\text{C}_6\text{H}_5\text{N}_2\text{Cl})_t = n(\text{initial}) - n(\text{reacted}) = n(\text{initial}) - n(\text{N}_2) \text{ formed.}$ $n(\text{N}_2) \text{ formed} = P \times V(\text{N}_2) / R \times T = 1 \times V(\text{N}_2) / (0.082 \times 290)$ $= 0.042 \text{ V}(\text{N}_2)$	1.5

	Divide by the volume of the solution: $[C_6H_5N_2Cl]_t = C_0 - 0.042 V(N_2) / 0.035 = 8.0 \times 10^{-2} - 1.2 \times V(N_2)$.	
2.1	the curve 	1
2.2	The half-life time of the reaction $t_{1/2}$ is the time needed for the decomposition of half the initial quantity of $C_6H_5N_2Cl$. $[C_6H_5N_2Cl]_{t_{1/2}} = 0.08 / 2 = 0.04 \text{ mol.L}^{-1}$. Graphically $t_{1/2} = 480 \text{ s}$.	1
2.3	At the time $t_{1/2}$: $V(N_2) = V(N_2)_{\infty}/2 = 6.66 \times 10^{-2} / 2 = 3.33 \times 10^{-2} \text{ L}$	0.5
2.4	The instantaneous rate of disappearance of benzene diazonium chloride is $r = -d[C_6H_5N_2Cl]/dt$. It is equal to the opposite of the slope of the tangent to the curve at the point of abscissa $t = 150 \text{ s}$. $r_{150} = -\frac{y_B - y_A}{x_B - x_A} = -\frac{(0 - 7.6) \times 10^{-2}}{870} = 8.7 \times 10^{-5} \text{ mol.L}^{-1}.s^{-1}$	1
2.5	The decrease in the rate between t and $t_{1/2}$ is explained by the decrease in the concentration of the reactant with time. This concentration is a kinetic factor.	0.75

Third Exercise (7 points)

Part of the Q	Answer	Mark
1.1	During dilution: n (solute) is conserved. $C_0 \times V_0 = C_a \times V$; implies $V/V_0 = C_0/C_a = 50$ $V_0 = 1000/50 = 20 \text{ mL}$. Take, using a 20 mL volumetric pipet and a pipet filler, 20 mL of the commercial solution. Introduce this volume into a volumetric flask of 1 L, filled partially with distilled water. Complete the volume with distilled water to reach the line mark. Shake several times to homogenize.	1.5
1.2	The equation of the reaction between a strong acid and a strong base is: $H_3O^+ + HO^- \rightarrow 2 H_2O$	0.5

1.3	the chemical species in the medium at the equivalence point are : Na^+ , Cl^- and H_2O . Na^+ and Cl^- are spectator ions. The pH at the equivalence point at $T = 25^\circ\text{C}$; The pH = 7	1
1.4	At the equivalence point: $n(\text{H}_3\text{O}^+)$ in 20 mL of S_a = $n(\text{HO}^-)$ added to reach equivalence. $C_a \times V_a = C_b \times V_{bE}$ and $C_a = \frac{4 \times 10^{-2} \times 25}{20} = 5.0 \times 10^{-2} \text{ mol.L}^{-1}$.	1
1.5	The solution S_a is obtained by diluting 50 times the commercial solution S , we draw that $C = 50 C_a = 2.5 \text{ mol.L}^{-1}$.	0.5
2.1	By neglecting the variation of volume we draw: $[\text{H}_3\text{O}^+] = \frac{n(\text{H}_3\text{O}^+)_{\text{initial}}}{V(\text{solution})} = \frac{20 \times 2.5 \times 10^{-3}}{100} = 5.0 \times 10^{-4} \text{ mol.L}^{-1}$. $\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log 5.0 \times 10^{-4} = 3.3$	0.75
2.2.1	the reaction constant is $K_r = \frac{[\text{CO}_{2(\text{aq})}]}{[\text{HCO}_{3(\text{aq})}^-][\text{H}_3\text{O}^+]} = \frac{1}{K_a} = \frac{1}{4 \times 10^{-7}} = 2.5 \times 10^6$. $K_r > 10^4$; the reaction is complete	1.25
2.2.2	In fact, $n(\text{H}_3\text{O}^+)$ introduced into the aquarium is not conserved. They react completely with $\text{HCO}_{3(\text{aq})}^-$ ions in a constant volume. $[\text{H}_3\text{O}^+]$ decreases. The pH of the medium is greater than 3.3; it will be equal to $pK_a + \log \frac{[\text{HCO}_{3(\text{aq})}^-]}{[\text{CO}_{2(\text{aq})}]}$; with $\frac{[\text{HCO}_{3(\text{aq})}^-]}{[\text{CO}_{2(\text{aq})}]} < 1$. The pH reaches a value close to 6 as the instructions of the manufacturer indicate.	0.5

الاسم:
الرقم:مسابقة في مادة الكيمياء
المدة: ساعتان

This Exam Includes Three Exercises. It Is Inscribed on four Pages Numbered from 1 to 4.

The Use of A Non-programmable Calculator Is Allowed.

Answer the three following exercises:

First Exercise (6 points)
Hydrochloric Acid and Calcium Carbonate

It is required to follow-up the progress of the reaction between solid calcium carbonate CaCO_3 and an excess of a hydrochloric acid solution ($\text{H}_3\text{O}^+ + \text{Cl}^-$). The equation of this reaction is:



At $T = 25^\circ\text{C}$, an excess of a hydrochloric acid solution is introduced into a flask containing a piece of calcium carbonate of mass $m = 40 \text{ g}$. The flask is immediately connected to a manometer that indicates an initial pressure P_0 representing the pressure of the air contained in the flask.

We read, then, the pressure P_t measured by the manometer at different times t .

The number of moles of the gas CO_2 released is determined and the results are grouped in the following table:

$t \text{ (s)}$	10	20	30	40	60	80	100	120
$n(\text{CO}_2) (10^{-2} \text{ mol})$	6.0	10	14	17.5	22.5	26.5	29.5	31.0

Given:

- Molar mass of calcium carbonate: $M = 100 \text{ g.mol}^{-1}$.
- Ideal gas constant: $R = 0.08 \text{ atm.L.mol}^{-1}.K^{-1}$.
- CO_2 gas is assumed to be an ideal gas.

1- Preliminary study

- 1.1- Choose, by justifying, among the following terms those which are convenient to describe the mixture at the end of the gas release: heterogeneous, homogeneous, acid, base and neutral.
- 1.2- Express, in terms of P_0 and P_t , the number of moles of the gas released $n(\text{CO}_2)$ where the gaseous mixture occupy a volume of 1 L.
- 1.3- Verify if the time $t= 120 \text{ s}$ represents the end-time of the reaction.

2- Kinetic Study

- 2.1- Plot the curve that represents the change in the number of moles of the gas released as a function of time: $n(\text{CO}_2) = f(t)$ in the interval of time: [0 -120 s].
Take the following scale:
1 cm for 10 s in abscissa and 1 cm for 2.5×10^{-2} mol in ordinate.
- 2.2- Deduce, graphically, the change in the rate of formation of CO_2 with time.
- 2.3- Determine the half-life time of this reaction.
- 2.4- The experiment realized at the beginning of the exercise is carried out again but with only one change: the flask is placed in an ice-water bath.
Plot on the same graph of the question 2.1, the shape of the curve representing the new change in the number of moles of the gas released as a function of time: $n(\text{CO}_2) = g(t)$. Justify.

Second Exercise (7 points) Sodium Hydroxide

Sodium hydroxide, an ionic solid of formula unit NaOH , is found generally as white pellets. Sodium hydroxide is highly soluble in water and in ethanol.

In the laboratory, aqueous standardized solutions of sodium hydroxide are used to titrate acidic solutions and the concentrated solutions are used to prepare soaps...

1- Titration of a Scale Removal

Given: The study is carried out at 25 °C.

List of available glassware in the laboratory

- Beakers: 100, 200 and 500 mL.
- Volumetric flasks: 100, 200 and 500 mL.
- Volumetric pipets: 5, 10 and 20 mL.
- Graduated cylinders: 5, 10 and 20 mL.
- Erlenmeyer flasks: 100, 200 and 500 mL.
- Graduated buret of 25 mL.

It is required to titrate a sanitary liquid scale removal containing hydrochloric acid (assumed to be the only chemical species present with an acid-base character). To do that, one proceeds as follows:

- A sample of this scale removal is diluted 50 times.
- A volume $V_A = 20.0$ mL of the dilute solution is taken and poured into an Erlenmeyer flask containing about 30 mL of distilled water and few drops of an appropriate colored indicator.
- A sodium hydroxide solution of concentration $C_B = 0.10 \text{ mol.L}^{-1}$ is added progressively to reach equivalence.

- 1.1- Choose, by justifying, from the above list, the essential glassware used for the dilution of the scale removal.
- 1.2- Write the equation of the titration reaction.
- 1.3- Determine the concentration of the hydrochloric acid in the dilute solution knowing that the volume of the basic solution added to reach equivalence is $V_{BE} = 9.2$ mL.
- 1.4- Deduce the concentration of the hydrochloric acid in the scale removal product.
- 1.5- Specify the effect of the presence of distilled water, in the Erlenmeyer flask, on the volume V_{BE} and on the pH at equivalence pH_E .

2- Preparation of a Soap

Given:

Molar mass of sodium oleate: $M = 304 \text{ g.mol}^{-1}$.

A mixture of 4.0×10^{-2} mol of olein (a triester of oleic acid) and an excess of a concentrated sodium hydroxide solution is heated in the presence of ethanol as a solvent.

Sodium oleate of formula $(\text{C}_{17}\text{H}_{33}\text{CO}_2^- + \text{Na}^+)$ and a compound (G) are obtained.

- 2.1- Deduce the formula of oleic acid and specify if it is a saturated acid or an unsaturated acid.
- 2.2- Write the equation of the saponification reaction of olein.
- 2.3- Give the systematic name of the compound (G).
- 2.4- Determine the mass of the soap obtained knowing that the yield of the reaction is 95 %.
- 2.5- Oleate ion possesses two parts: a hydrophilic part and a lipophilic part.
Indicate these two parts on the formula of this ion.

Third Exercise (7 points) Propanoic Acid

In the laboratory, available are three flasks of which the labels show the following indications:

Flask	1	2	3
Indication of the label	Pure propanoic acid	Aqueous solution of sodium propanoate $(\text{C}_2\text{H}_5\text{CO}_2^- + \text{Na}^+)$	2- Butanol

In this exercise, propanoic acid is used to prepare a buffer solution of $\text{pH} = 5.20$ and to synthesize a fruit odor ester.

Given:

- Ion product of water: $K_w = 1.0 \times 10^{-14}$
- $\text{pK}_a (\text{C}_2\text{H}_5\text{CO}_2\text{H} / \text{C}_2\text{H}_5\text{CO}_2^-) = 4.89$
- Density of pure propanoic acid: $d = 0.99 \text{ g.mL}^{-1}$.
- Molar mass of propanoic acid: $M = 74 \text{ g.mol}^{-1}$.

1- Preparation of the Buffer Solution

The pH of the solution contained in the flask 2 is found to be equal to 8.45

- 1.1- Write the equation of the reaction of the base $\text{C}_2\text{H}_5\text{CO}_2^-$ with water.
- 1.2- Show that the solution contained in the flask 2 has a concentration $C = 1.0 \times 10^{-2} \text{ mol.L}^{-1}$.
(in this solution $[\text{C}_2\text{H}_5\text{CO}_2\text{H}]$ is neglected compared to C).
- 1.3- Determine the volume V_1 of pure propanoic acid that should be added to a volume $V = 3 \text{ L}$ of the sodium propanoate solution in order to prepare a buffer solution of $\text{pH} = 5.20$

2- Synthesis of the Ester

An equimolar mixture of propanoic acid and 2-butanol is heated to reflux.

- 2.1- Write, using condensed structural formulas of the organic compounds, the equation of the reaction that takes place. Name the ester formed.
- 2.2- List two characteristics of this reaction.
- 2.3- The ester formed and the 2-butanol have the same type of configuration isomerism. Specify this type of isomerism.
- 2.4- Indicate the importance of the reflux heating in this synthesis.
- 2.5- Specify the effect of each of the three following proposals on the yield of this reaction:
 - The pure propanoic acid is replaced by an aqueous solution containing the same quantity of the acid.
 - A catalyst is added to the initial mixture.
 - An initial mixture in which the acid is used in excess with respect to the alcohol.

First Exercise (6 points)
Hydrochloric Acid and Calcium Carbonate

Part of the Q	Answer	Mark
1.1	Since the acid is in excess, the terms that describe this mixture are: homogeneous and acid.	0.75
1.2	According to the ideal gas law: $n(CO_2) = \frac{P(CO_2) \times V}{R \times T} = \frac{(P_t - P_o) \times V}{R \times T} = \frac{P_t - P_o}{0.08 \times 298} = \frac{P_t - P_o}{23.84}$ where the pressures are in atm.	0.75
1.3	$n(CO_2)$ formed at the end of the reaction = $n(CaCO_3)$ initial (since H_3O^+ is in excess) ; $= \frac{m(CaCO_3)initial}{M} = \frac{40}{100} = 0.4 \text{ mol}$ Since at $t = 120 \text{ s}$, $n(CO_2)$ formed = $0.31 \text{ mol} < 0.4 \text{ mol}$, so this time does not represent the end-time of the reaction.	1
2.1		1
2.2	The rate of formation of CO_2 is equal to the slope of the tangent at the curve at the point of abscissa t . This rate decreases with time since, graphically, the slope is maximal at $t = 0$ then it decreases with time as it shown in the graph 2.1	0.75
2.3	The half-life time is the time needed for $n(CO_2)$ to reach half its maximal value.	

	At $t_{1/2}$, $n(\text{CO}_2)$ formed = $0.4 / 2 = 0.2\text{mol}$. graphically $t_{1/2} = 50 \text{ s.}$	0.75
2.4	<p>The temperature, which is a kinetic factor, decreases in the ice-water bath and by consequence the rate of formation of CO_2 decreases.</p> <p>At each instant of time t, $n(\text{CO}_2)$ formed at $0^\circ\text{C} < n(\text{CO}_2)$ formed at 25°C; the shape of the curve is:</p>	1

Second Exercise (7 points) Sodium Hydroxide

Part of the Q	Answer	Mark
1.1	<p>During dilution, the number of moles of NaOH is conserved</p> $n_{\text{(before dilution)}} = n_{\text{(after dilution)}} ; C_o \times V_o = C_A \times V$; where C_o and C_A are the concentrations of the hydrochloric acid in the scale removal and in the dilute solution respectively.	1
	<p>Dilution factor $F = \frac{C_o}{C_A} = \frac{V}{V_o} = 50$ where V is the volume of the volumetric flask to be chosen and V_o is the volume of the pipet. From the list, we choose: a 10 mL volumetric pipet and a 500 mL volumetric flask and a beaker.</p>	
1.2	<p>The equation of the titration reaction</p> $\text{H}_3\text{O}^+ + \text{HO}^- \rightarrow 2 \text{H}_2\text{O}$.	0.5
1.3	<p>$n(\text{HO}^-)$ added to reach equivalence = $n(\text{H}_3\text{O}^+)$ introduced into the Erlenmeyer</p> $C_B \times V_{BE} = C_A \times V_A ; C_A = \frac{C_B \times V_{BE}}{V_A} = \frac{0.1 \times 9.2}{20} = 4.6 \times 10^{-2} \text{ mol.L}^{-1}$.	0.75
1.4	<p>The concentration of the hydrochloric acid in the scale removal is:</p> $C_o = 50 \times C_A = 50 \times 4.6 \times 10^{-2} = 2.3 \text{ mol.L}^{-1}$.	0.5
1.5	<p>The presence of water does not affect the initial quantity of H_3O^+ ions. So the volume added to reach equivalence V_{BE} is not affected.</p>	1

	At equivalence, the pH of the medium is that of the water formed ($pH_E = 7$). An additional quantity of water introduced before titration does not affect the pH_E .	
2.1	The formula of the oleic acid is: $C_{17}H_{33}CO_2H$. This formula does not satisfy the formula $C_xH_{2x}O_2$ or $C_nH_{2n+1}CO_2H$; so this acid is not a saturated acid. It is an unsaturated acid.	0.75
2.2	The equation of the saponification of olein : $\begin{array}{c} \text{CH}_2 - \text{O} - \underset{\text{O}}{\text{C}} - \text{C}_{17}\text{H}_{33} \\ \\ \text{CH} - \text{O} - \underset{\text{O}}{\text{C}} - \text{C}_{17}\text{H}_{33} + 3(\text{Na}^+ + \text{HO}^-) \rightarrow 3(\text{Na}^+ + \text{C}_{17}\text{H}_{33}\text{CO}_2^-) + \text{CH}_2 - \underset{\text{OH}}{\text{CH}} - \underset{\text{OH}}{\text{CH}} - \underset{\text{OH}}{\text{CH}_2} \\ \quad \quad \\ \text{CH}_2 - \text{O} - \underset{\text{O}}{\text{C}} - \text{C}_{17}\text{H}_{33} \end{array}$	0.75
2.3	The systematic name of the compound G is : 1,2,3-propanetriol.	0.25
2.4	n(soap) expected = $3 \times n(\text{olein})$ initial = $3 \times 0.04 = 0.12$ mol since NaOH is in excess. $m(\text{soap}) \text{ expected} = n(\text{ soap}) \times M = 0.12 \times 304 = 36.48 \text{ g}$. $m(\text{soap}) \text{ actual} = 36.48 \times 95 / 100 = 34.66 \text{ g}$.	1
2.5	$\text{C}_{17}\text{H}_{33}-\text{CO}_2^-$ lipophilic hydrophilic	0.5

Third Exercise (7 points)
Propanoic Acid

Part of the Q.	Answer	Mark
1.1	The equation of the reaction is: $\text{C}_2\text{H}_5\text{CO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{C}_2\text{H}_5\text{CO}_2\text{H} + \text{HO}^-$	0.5
1.2	[$\text{C}_2\text{H}_5\text{CO}_2^-$] initial is equal to C. $\text{C}_2\text{H}_5\text{CO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{C}_2\text{H}_5\text{CO}_2\text{H} + \text{HO}^-$ Initial state C solvent - - At equilibrium C - x solvent x x $K_r = \frac{[\text{HO}^-] \times [\text{C}_2\text{H}_5\text{CO}_2\text{H}]}{[\text{C}_2\text{H}_5\text{CO}_2^-]} = \frac{x^2}{C} = \frac{10^{-pK_w}}{10^{-pK_a}} = \frac{10^{-14}}{10^{-4.89}} = 10^{-9.11}$ Where: $[\text{HO}^-] = [\text{C}_2\text{H}_5\text{CO}_2\text{H}] = x = 10^{pH-14}$, [$\text{C}_2\text{H}_5\text{CO}_2^-$] = C So $C = 1.0 \times 10^{-2} \text{ mol.L}^{-1}$.	1.25
1.3	The initial number of moles of each one of the acid and its conjugate base is conserved in the obtained buffer solution.	

	<p>pH(solution) = pK_a (C₂H₅CO₂H / C₂H₅CO₂⁻) + log $\frac{[C_2H_5CO_2^-]}{[C_2H_5COOH]}$</p> <p>Where [C₂H₅CO₂⁻] = $\frac{C \cdot V}{V(mixture)}$ and [C₂H₅CO₂H] = $\frac{d \cdot V_1}{M \times V(mixture)}$;</p> <p>So $V_1 = \frac{C \times V \times M}{d \times 10^{pH - pK_a}} = \frac{0.01 \times 3 \times 74}{0.99 \times 10^{5.2 - 4.89}} = 1.1 \text{ mL}$.</p>	1.25
2.1	<p>The equation of this reaction:</p> $\text{CH}_3 - \text{CH}_2 - \text{COOH} + \text{CH}_3 - \text{CH}_2 - \underset{\substack{ \\ \text{OH}}}{\text{CH}} - \text{CH}_3 \rightleftharpoons \text{H}_2\text{O} + \text{CH}_3 - \underset{\substack{ \\ \text{O}}}{\text{CH}_2} - \text{C} - \underset{\substack{ \\ \text{CH}_3}}{\text{O}} - \text{CH} - \text{CH}_2 - \text{CH}_3$ <p>The name of the ester is 1-methylpropyl propanoate (2-butylpropanoate).</p>	1
2.2	Two characteristics are: slow and limited.	0.5
2.3	The isomerism is an enantiomerism, since the two molecules of both compounds have an asymmetric carbon.	0.5
2.4	Heating to reflux accelerate the reaction without losing any of the reaction mixture components.	0.5
2.5	<p>Water present at the start of the reaction favors the hydrolysis reaction of the ester (that is formed) and by consequence the yield of the synthesis reaction decreases.</p> <p>The catalyst accelerates both reactions (esterification and hydrolysis) in the same way and by consequence the yield of the synthesis reaction does not changes.</p> <p>The use of an initial mixture with an excess of acid favors the esterification reaction (% of the alcohol reacted increases) and the yield of the reaction increases.</p>	0.5 0.5 0.5

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الاسم: الرقم:	مسابقة في مادة الكيمياء المدة : ساعتان	

**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 three following exercises:**

First exercise (7 points) Ammonia Solution

Ammonia NH_3 is a gas which is highly soluble in water. It is widely used in chemical industry. The aim of this exercise is to study certain characters of a solution of ammonia NH_3 and to prepare a buffer solution.

Given:

- This study is carried at 25 °C.
- Molar volume of gas: $V_m = 24 \text{ L.mol}^{-1}$.
-

Acid/base Couple	$\text{H}_3\text{O}^+ / \text{H}_2\text{O}$	$\text{NH}_4^+ / \text{NH}_3$	$\text{H}_2\text{O} / \text{HO}^-$
pK_a	0	9.2	14

1- Determination of the degree of conversion of Ammonia in Water

The pH of an ammonia solution (S), of unknown concentration C_b , is equal to 10.6

- 1.1- Identify the acid-base nature of NH_3 in water.
- 1.2- Write the equation of the reaction of ammonia with water.
- 1.3- Give the expression of the equilibrium constant of the equation of this reaction.
Calculate its value.
- 1.4- Show that the molar concentration of ammonia solution (S) is $C_b = 1.0 \times 10^{-2} \text{ mol.L}^{-1}$.
(neglect $[\text{HO}^-]$ with respect to C_b)
- 1.5- Determine the degree of conversion of ammonia in water.
- 1.6- Calculate the volume of NH_3 gas needed to prepare 1 L of solution (S).

2- Preparation of a Buffer Solution

A volume V_1 of solution (S) and a volume V_2 of an ammonium chloride solution ($\text{NH}_4^+ + \text{Cl}^-$) of concentration $C_a = 6.0 \times 10^{-3} \text{ mol.L}^{-1}$ are mixed . 200 mL of a buffer solution of $\text{pH} = 9.0$ is obtained .

- 2.1-Write the equation of the predominant reaction (having the highest value of K_R).
- 2.2-Show that V_1 equals 55 mL.

2.3- To the obtained buffer solution, 5.0×10^{-4} mol of HCl (strong acid) is added ,without appreciable variation of volume.

2.3.1- Write the equation of the complete reaction that takes place.

2.3.2- Determine the pH of the resulting solution.

Second exercise (6 points)

Creation of an ester and amide functions

Available are organic compounds having the following condensed structural formulas:

Compound	A	B	C
Condensed structural formula	$\text{CH}_3 - \text{CO}_2\text{H}$	$\text{CH}_3 - \text{CH}_2 - \underset{\text{CH}_3}{\text{CH}} - \text{OH}$	$\text{NH}_2 - \text{CH}_2 - \text{CO}_2\text{H}$

In this exercise we study some chemical reactions where these compounds are involved .

- 1- Give the systematic name of the compounds A, B and C.
 - 2- Choose, among these compounds, the one which is chiral. Justify.
 - 3- A mixture of 0.2 mol of A and an excess of the compound B is heated. After a certain time, heating is stopped and the number of moles of the acid remaining is titrated; it is found to be 0.08 mol.
 - 3.1- Write the equation of the reaction between A and B. Name the organic product obtained.
 - 3.2- Determine the percentage of esterification of the compound A in this reaction.
 - 4- An equimolar mixture of the compound A and of ammonia, NH_3 , is introduced into a beaker. An ionic compound D is formed.
At high temperature, the compound D decomposes to form an amide.
 - 4.1- Write the equation of the formation of the compound D. Name this compound.
 - 4.2- Verify if this reaction is an acid-base reaction.
 - 4.3- Identify the amide formed during the decomposition of D.
 - 5- In appropriate conditions , we allow the reaction between any carboxyl group and any amine group in a mixture containing the compound C and the alpha amino acid of formula :
$$\text{CH}_3 - \underset{\text{NH}_2}{\text{CH}} - \text{CO}_2\text{H}$$
- 5.1- Give the number of dipeptides obtained in this reaction (without taking in consideration the enantiomers).
- 5.2- Write the condensed structural formula of one of these dipeptides and circle its peptide bond.

Third exercise (7 points) Oxidation of Oxalic Acid

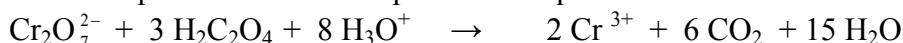
In order to carry out two kinetic follow-ups, the following solutions are available:

- Solution S₁ of oxalic acid H₂C₂O₄ of concentration C₁ = 0.10 mol.L⁻¹
- Solution S₂ of potassium dichromate (2K⁺ + Cr₂O₇²⁻)
- Solution S₃ of potassium permanganate (K⁺ + MnO₄⁻) of concentration C₃ = 2.0 × 10⁻² mol.L⁻¹
- Concentrated sulfuric acid.

1- Oxidation of Oxalic Acid by Dichromate Ions

At a constant temperature, a volume V₁ of solution S₁, a volume V₂ of solution S₂ and few drops of the concentrated sulfuric acid are mixed.

A slow and complete reaction takes place. The equation of this reaction is as follows:



The variation of the concentration of dichromate ions versus time is followed with an appropriate method. The variation of the concentration of Cr³⁺ ions formed are deduced.

The results are grouped in the following table :

t (s)	10	20	40	60	100	140	180	240	300
[Cr ³⁺] (10 ⁻³ mol.L ⁻¹)	1.2	2.2	4.0	5.5	7.5	9.1	10.3	11.5	12.2

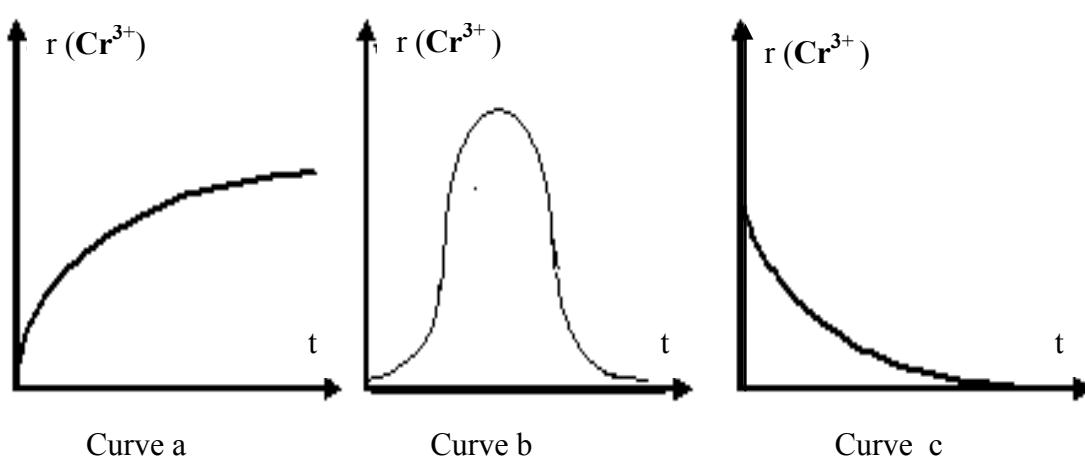
- 1.1- Plot the curve representing the variation of the concentration of Cr³⁺ ions versus time, [Cr³⁺] = f(t) in the interval of time: [0 – 300 s].

Take the following scale: 1 cm for 20s in abscissa and 1 cm for 1.0 × 10⁻³ mol.L⁻¹ in ordinate.

- 1.2- Determine the rate of formation of Cr³⁺ ions at t = 100 s. Deduce the rate of the reaction at this instant.

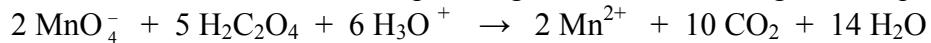
- 1.3- One of the three curves given below represents the variation of the rate of formation of Cr³⁺ ions versus time, r(Cr³⁺) = g(t).

Choose, by justifying, the correct curve.



2- Oxidation of Oxalic Acid by Permanganate Ions

Oxalic acid reduces, in acidic medium, permanganate ions according to the equation:



where MnO_4^- is the only colored species in this reacting medium.

A volume $V_1 = 10 \text{ mL}$ of solution S_1 , 200 mL of distilled water and 5 mL of concentrated sulfuric acid (in excess) are poured in a beaker.

Add 2 mL of solution S_3 to the beaker ; the reacting mixture is decolorized when the duration 210 s is attained . The addition of 2 mL of solution S_3 is repeated 6 times and the duration necessary for the decolorization of the reacting medium each time is noted .

The results are grouped in the following table:

Number of addition	1	2	3	4	5	6	7
Duration (s)	210	90	60	55	47	40	34

2.1- Interpret the decolorization of the reacting medium after each addition.

2.2- Determine the minimal volume of solution S_3 , needed to be added, so that the color due to permanganate ions persists definitively.

2.3- Based on the results of the above table :

2.3.1- Specify how the rate of disappearance of permanganate ions varies from one addition to another.

2.3.2- Interpret the change of this rate in this kinetic study. Give, then, the name of the involved chemical phenomenon.

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First exercise (7 points)

Part of the Q	Answer	Mark
1.1	Ammonia (NH_3) is a base because its dissolution in water leads to a medium of which $\text{pH} = 10.6 > 7$.	0.5
1.2	The equation of its reaction with water is: $\text{NH}_3 \text{(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{NH}_4^{\text{(aq)}} + \text{HO}^{-\text{(aq)}}$	0.5
1.3	The equilibrium constant of the equation of this reaction is: $K_R = \frac{[\text{NH}_4^+][\text{HO}^-]}{[\text{NH}_3]} \times \frac{[\text{H}_3\text{O}^+]}{[\text{H}_3\text{O}^+]}$ Its value is: $\frac{10^{-14}}{10^{-9.2}} = 10^{-4.8}$ $K_R = 1.58 \times 10^{-5}$.	0.75
1.4	Calculation of C_b : $10^{-4.8} = \frac{[\text{HO}^-]^2}{C_b - [\text{HO}^-]} = \frac{(10^{-3.4})^2}{C_b - 10^{-3.4}}$ $C_b = 0.01 \text{ mol L}^{-1}$.	0.5
1.5	The coefficient of the dissociation α is given by: $\alpha = \frac{n(\text{NH}_3) \text{dissociated}}{n(\text{NH}_3) \text{introduced}} = \frac{[\text{NH}_4^+]}{C_b} = \frac{[\text{HO}^-]}{C_b} = \frac{10^{pH-14}}{C} = \frac{1.0 \times 10^{-3.4}}{1.0 \times 10^{-2}}$. $\alpha = 10^{-1.4} = 0.04$	0.75
1.6	The volume of ammonia gas: $V = n \times V_m = C_b \times V_{(S)} \times V_m = 0.01 \times 1 \times 24 = 0.24 \text{ L}$.	0.5
2.1	The equation of the predominant reaction which takes place between the strongest acid and the strongest base introduced into the solution is: $\text{NH}_3\text{(aq)} + \text{NH}_4^{\text{(aq)}} \rightleftharpoons \text{NH}_4^{\text{(aq)}} + \text{NH}_3\text{(aq)}$	0.5
2.2	The initial quantities of NH_3 and NH_4^+ are conserved in the obtained solution : $pH = pK_a + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]}$ permits to calculate the values of the two volumes. $9 = 9.2 + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]}$; $\log \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = -0.2$ and $\frac{[\text{NH}_3]}{[\text{NH}_4^+]} = 0.63$. $\frac{n(\text{NH}_3)}{n(\text{NH}_4^+)} = \frac{V_1 \times 10^{-2}}{V_2 \times 6 \times 10^{-3}} = 0.63$ and $V_1 + V_2 = 200 \text{ mL}$. So $V_1 = 55 \text{ mL}$.	1
2.3.1	The equation of the reaction is: $\text{H}_3\text{O}^{\text{(aq)}} + \text{NH}_3\text{(aq)} \rightleftharpoons \text{NH}_4^{\text{(aq)}} + \text{H}_2\text{O(l)}$	0.5

2.3.2	$\text{H}_3\text{O}_{(aq)}^+ + \text{NH}_3_{(aq)} \rightleftharpoons \text{NH}_4^+_{(aq)} + \text{H}_2\text{O}_{(l)}$ <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 30%;">Initial state(n mol)</td><td style="width: 20%; text-align: center;">5.10^{-4}</td><td style="width: 20%; text-align: center;">5.5×10^{-4}</td><td style="width: 30%; text-align: center;">8.7×10^{-4} solvant</td></tr> <tr> <td>Resulting solution</td><td style="text-align: center;">--</td><td style="text-align: center;">5.10^{-5}</td><td style="text-align: center;">13.7×10^{-4} solvant</td></tr> </table> $\text{PH} = 9.20 + \log \frac{\frac{5 \times 10^{-5}}{V(\text{mixture})}}{\frac{13.7 \times 10^{-4}}{V(\text{mixture})}} = 7.76$	Initial state(n mol)	5.10^{-4}	5.5×10^{-4}	8.7×10^{-4} solvant	Resulting solution	--	5.10^{-5}	13.7×10^{-4} solvant	1.5
Initial state(n mol)	5.10^{-4}	5.5×10^{-4}	8.7×10^{-4} solvant							
Resulting solution	--	5.10^{-5}	13.7×10^{-4} solvant							

Second Exercice (6pts) (LS)

Part of the Q.	Answer	Mark
1	A : ethanoic acid ; B : 2-butanol et C : 2-aminoethanoic acid	0.75
2	B is the chiral compound since it contains an asymmetric carbon (the carbon number 2 of the hydrocarbon chain).	0.5
3.1	<p>The equation of the reaction between A and B is</p> $\text{CH}_3 - \text{CO}_2\text{H} + \text{CH}_3 - \text{CH}_2 - \text{CH} - \text{OH} \rightleftharpoons \text{CH}_3 - \underset{\text{CH}_3}{\underset{ }{\text{C}}} - \underset{\text{O}}{\underset{ }{\text{O}}} - \text{CH} - \text{CH}_2 - \text{CH}_3 + \text{H}_2\text{O}$ <p>The name of the ester is: 1-methylpropyl ethanoate.</p>	1
3.2	<p>% of A esterified =</p> $\frac{n(\text{A}) \text{ esterified}}{n(\text{A}) \text{ initial}} \times 100 = \frac{n(\text{A}) \text{ initial} - n(\text{A}) \text{ remaining}}{n(\text{A}) \text{ initial}} \times 100 = \frac{0.2 - 0.08}{0.2} \times 100 = 60\%.$	0.75
4.1	<p>The equation of this reaction:</p> $\text{CH}_3 - \text{CO}_2\text{H} + \text{NH}_3 \rightleftharpoons \text{CH}_3 - \text{CO}_2^- + \text{NH}_4^+$ <p>The name of the compound D is: ammonium ethanoate</p>	0.75
4.2	This reaction is an acid-base reaction since there is a proton exchange between the acid of the pair $\text{CH}_3 - \text{CO}_2\text{H} / \text{CH}_3 - \text{CO}_2^-$ and the base of the pair $\text{NH}_4^+ / \text{NH}_3$	0.5
4.3	<p>The amide formed is $\text{CH}_3 - \underset{\underset{\text{O}}{\parallel}{\text{C}}}{} - \text{NH}_2$; its name is ethanamide</p>	0.5
5.1	The number of dipeptides obtained in this reaction is four.	0.5
5.2	<p>The condensed structural formula is :</p> $\text{NH}_2 - \text{CH}_2 - \underset{\underset{\text{O}}{\parallel}{\text{C}}}{} - \text{NH} - \text{CH} - \text{CO}_2\text{H}$	0.75

Third exercise (7 points)

Part of the Q	[Cr ³⁺] (10 ⁻³ mol.L ⁻¹)	Answer	Mark
1.1			1
1.2	<p>By definition: $r(\text{Cr}^{3+}) = \frac{d[\text{Cr}^{3+}]}{dt}$ at $t = 100$ s.</p> <p>Graphically, this rate represents the slope of the tangent to the curve $[\text{Cr}^{3+}] = f(t)$ at the point of abscissa $t = 100$ s.</p> <p>Consider on this tangent two points A and B whose co-ordinates are as follows: A (0; 3.2×10^{-3}) and B (200; 12.0×10^{-3}).</p> <p>According to the equation of the reaction, we can write:</p> $r(\text{Cr}^{3+})_{t=100} = \frac{(12.0 - 3.2) \times 10^{-3}}{200} = 4.4 \times 10^{-5} \text{ mol.L}^{-1}.\text{s}^{-1}$ <p>The rate of the reaction = $r(\text{Cr}^{3+})/2 = 2.2 \times 10^{-5} \text{ mol.L}^{-1}.\text{s}^{-1}$.</p>	1.5	
1.3	<p>According to the curve, $r(\text{Cr}^{3+})$ is maximum at $t = 0$, and decreases with time. As the reaction is complete, this rate is cancelled at the end of the reaction. Therefore, the corresponding curve is the curve c.</p>		1
2.1	<p>The disappearance of coloring is due to the disappearance of permanganate ions added. MnO_4^- is the limiting reactant.</p>		0.5
2.2	<p>The minimal volume that must be added is equal to a volume V_3 such as:</p> $\frac{n(\text{MnO}_4^-) \text{ added}}{2} = \frac{n(\text{H}_2\text{C}_2\text{O}_4) \text{ initial}}{5} \quad \text{or} \quad \frac{C_3 \times V_3}{2} = \frac{C_1 \times V_1}{5};$ <p>Where $V_3 = \frac{2 \times C_1 \times V_1}{5 \times C_3} = \frac{2 \times 0.1 \times 10}{5 \times 0.02} = 20 \text{ mL}$.</p>		1.25
2.3.1	<p>With each addition, $n(\text{MnO}_4^-)$ is the same and the duration of disappearance of the color of these ions decreases each time, therefore the rate of disappearance of these ions increases.</p>		1

2.3.2	The increase in this rate is due to Mn ²⁺ ions formed that plays the role of a catalyst in this study and which is a product of the reaction (its concentration increases from one addition to another). The name of this phenomenon is the auto catalysis.	0.75
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Second exercise(6pts)(GS)

Part of the Q	Answer	Mark
1.1	<p>The result of the first experiment shows that the aqueous solution of A does not contain ions.</p> <p>The result of the second experiment shows that A can be an alcohol or an acid, because alcohols and acids react with sodium to give hydrogen gas and it is not an acid because it did not give ions in water.</p> <p>The result of the third experiment shows that A can be a primary or secondary alcohol because, by dehydrogenation, it gives a carbonyl compound which gives a yellow precipitate with 2,4-DNPH.</p>	1.5
1.2	<p>The carbon chain of A is saturated and does not contain a cycle, its molecular formula is thus of the form: C_nH_{2n+1}OH.</p>	0.5
2.1	<p>According to the equation:</p> $C_nH_{2n+1}OH + SOCl_2 \rightarrow C_nH_{2n+1}Cl + SO_2 + HCl$ <p>we have : n (A) = n (C_nH_{2n+1}Cl) ;</p> $\frac{d \times V}{M(A)} = \frac{m(RCl)}{M(RCl)} . \text{ With: } M(A) = (14n + 18) \text{ g.mol}^{-1} ;$ $M(RCl) = (14n + 36.5) \text{ g.mol}^{-1} ; d = 0.81 \text{ g.mL}^{-1} ; V = 9.1 \text{ mL and}$ $m(RCl) = 9.2 \text{ g.}$ <p>We obtain n = 4, the molecular formula of A is C₄H₉OH.</p>	1
2.2	<p>The possible condensed structural formulas of A are:</p> <p>CH₃ – CH₂ – CH₂ – CH₂ – OH ;</p> <p>CH₃ – CH₂ – CHO – CH₃ and CH₃ – CH – CH₂ - OH</p> <p style="text-align: center; margin-left: 100px;">$\begin{array}{c} \\ CH_3 \end{array}$</p>	0.75
3.1	<p>The compound B is an aldehyde because it reacts with Fehling's solution, it comes from the dehydrogenation of a primary alcohol. This test thus does not make it possible to identify A, because there are two primary alcohols.</p>	0.5
3.2	<p>The carbon chain of A is not branched, it is thus 1-butanol.</p>	0.25
3.3	<p>The equations are:</p> <p>Reaction with sodium:</p> $2 CH_3 – CH_2 – CH_2 – CH_2 – OH + 2 Na \rightarrow 2 CH_3 – CH_2 – CH_2 – CH_2 – ONa + H_2$ <p>Dehydrogenation:</p> $CH_3 – CH_2 – CH_2 – CH_2 – OH \rightarrow CH_3 – CH_2 – CH_2 – CHO + H_2$ <p>Intramolecular dehydration:</p> $CH_3 – CH_2 – CH_2 – CH_2 – OH \rightarrow CH_3 – CH_2 – CH = CH_2 + H_2O$	1.5

الاسم:
الرقم:مسابقة في الكيمياء
المدة ساعتان

السبت 29 حزيران 2013

This Exam Includes Three Exercises. It is Inscribed on Four Pages Numbered From 1 to 4.**The Use of a Non- Programmable Calculator Is Allowed.****Answer The Three Following Exercises.****First Exercise (7 points)****Identification of Organic Compounds**

The aim of this exercise is to identify two organic compounds: a liquid (A) of molecular formula C_2H_xO and a saturated non- cyclic chain primary monoamine (B) in order to study their action on ethanoic acid.

1- Identification of Compound (A)

- 1.1- Write the possible condensed structural formulas of the organic compounds of molecular formula C_2H_xO .
 1.2- In order to identify (A), the two experimental activities below are carried out:

Number of the activity	Experimental activity	Result
1	An excess of a potassium permanganate solution is added to the compound (A) in acidic medium.	A compound (C) is obtained which, dissolved in water, gives a solution with a pH clearly less than 7
2	A mixture of (A) and thionyl chloride is heated gently.	A gaseous mixture evolves and a chlorinated organic compound is formed.

Consider each one of these two results and specify if it allows identifying the organic compound (A).

2- Identification of the Compound (B)**Given:**

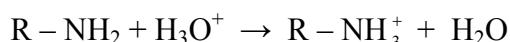
Molar mass in $g \cdot mol^{-1}$: $M(H) = 1$; $M(C) = 12$ and $M(N) = 14$

A mass $m = 3.70$ g of the amine (B) is dissolved in distilled water in such a way to obtain 500 mL of a solution (S).

A volume $V_1 = 20.0$ mL of this solution is titrated with a hydrochloric acid solution of concentration $C_2 = 0.20 \text{ mol} \cdot L^{-1}$ in the presence of an appropriate colored indicator.

The color change of this colored indicator is observed when a volume $V_E = 10.2$ mL of the acid solution is added.

The equation of the titration reaction is:



- 2.1- Determine the molar concentration C_1 of the solution (S).
 2.2- Deduce the molar mass of the amine (B).
 2.3- Show that its molecular formula is $C_4H_{11}N$.
 2.4- Write the possible condensed structural formulas of (B).
 2.5- Identify (B) knowing that its carbon chain is straight (non branched) and does not possess any asymmetric carbon.

3- Action of the Ethanoic Acid on (A) and (B)

The following two experiments are carried out:

Experiment 1: A mixture of ethanoic acid and the compound (A) is heated; a fruity odor ester is formed.

Experiment 2: A mixture of ethanoic acid and compound (B) is heated; an amide is formed.

3.1- Give two characteristics of the reaction carried out in the experiment 1.

3.2- Identify the amide obtained in the experiment 2.

3.3- Write the condensed structural formula of an organic compound that could replace the ethanoic acid in each of the two experiments 1 and 2. Name it.

Second Exercise (7 points) Acid-Base Reactions

Four flasks are numbered and an aqueous solution of one of the species below is introduced into each one of these flasks.

Number of the flask	Chemical species	
	Name	Formula
1	Hydrogen fluoride	HF
2	Sodium methanoate	HCOONa
3	Ammonia	NH ₃
4	Ammonium chloride	NH ₄ Cl

These solutions have the same molar concentration C.

Given :

-

Acid / base pair	NH ₄ ⁺ / NH ₃	HF / F ⁻	HCOOH / HCOO ⁻
pK _a	9.2	3.2	3.8

• Sodium methanoate and ammonium chloride are both ionic compounds highly soluble in water.

1- Classify the above four solutions as acidic and basic solutions.

2- Preparation of the Solution of the Flask 3

The solution in the flask 3 of molar concentration C, has been prepared starting from a commercial ammonia solution of which the label shows the following indications:

Percentage by mass = 25% density: d = 0.91 g.mL⁻¹ M(NH₃) = 17 g.mol⁻¹

A volume V_o = 1.5 mL of this commercial solution is taken and distilled water is added to this volume in such a way to obtain a solution of volume V = 2.0 L.

2.1- Determine the molar concentration C_o of the commercial solution.

2.2- Show that the molar concentration C = 1.0×10⁻² mol.L⁻¹.

- 2.3- Choose, from the following glassware, those that are essential for the preparation of the solution in the flask 3:
 2 mL volumetric pipet, 2 mL graduated cylinder, 2 mL graduated pipet, 2 L graduated cylinder and 2 L volumetric flask.

3- Study of the Solution of the Flask 1

- 3.1- Write the equation of the reaction between HF and water.
 3.2- Determine the degree of ionization of HF in the solution of the flask 1.
 ([F⁻] is neglected compared to the concentration C)

4- Mixture of Two Solutions

A volume $V_1 = 40$ mL of the solution of the flask 1 (HF solution) is mixed with a volume $V_2 = 30$ mL of the solution of the flask 3 (NH₃ solution). The equation of the reaction that takes place is the following:



- 4.1- Justify that this reaction is complete.
 4.2- Specify the limiting reactant.
 4.3- Deduce the pH of the obtained mixture.

Third Exercise (6 points) Kinetic of the Oxidation of 2-propanol

The oxidation of 2-propanol with permanganate ions in acidic medium is slow and complete.
 The equation of this reaction is the following:

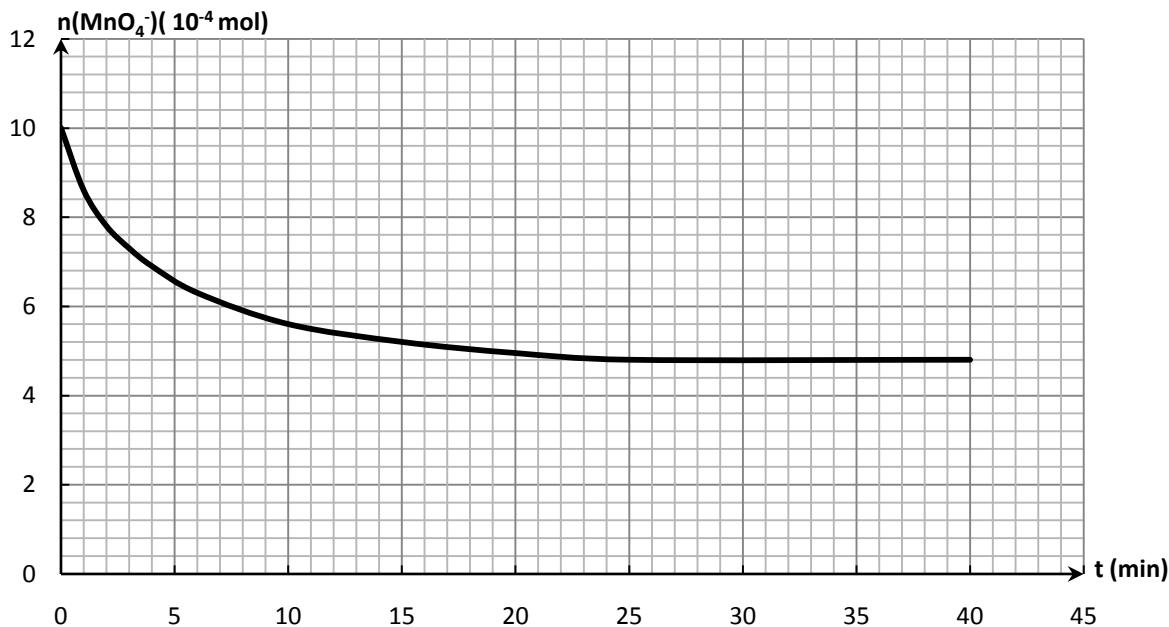


The kinetic study of this transformation is carried out by titrating the permanganate ions remaining, at each instant of time t, with an iron (II) sulfate solution.

Procedure

- Available are eight beakers, each containing a volume $V_0 = 10$ mL of an acidified potassium permanganate solution of concentration $C_0 = 0.10 \text{ mol.L}^{-1}$ (excess of sulfuric acid solution)
- At the instant of time $t = 0$, two drops of 2-propanol are added to the content of each beaker which is stirred using magnetic stirrer.
- At an instant of time $t_1 = 1$ min, one of these beakers is immersed rapidly in an icy-water bath and the remaining permanganate ions are titrated with an iron (II) sulfate solution.
- The preceding step is repeated with the other beakers at the different instants of time indicated in the following graph below.

The different titrations carried out allow to plot the curve below representing the variation in the number of moles of permanganate ions remaining as a function of time.



1- Identification of The Compound C₃H₆O

- 1.1- Specify the chemical family of the organic compound obtained in the reaction 1.
- 1.2- Identify this organic compound.

2- Preliminary Study

- 2.1- Based on the curve given above, deduce that the 2-propanol is the limiting reactant in the reaction 1.
- 2.2- Establish the following relation: $n(C_3H_6O)_t = \frac{5}{2} [1.0 \times 10^{-3} - n(MnO_4^-)_t]$.
Where $n(C_3H_6O)_t$ is the number of moles of C₃H₆O at t and $n(MnO_4^-)_t$ is the number of moles of MnO₄⁻ remaining at the same instant of time t, in each one of the eight beakers.
- 2.3- Indicate the aim of placing each beaker in an icy-water bath before carrying out the titration.

3- Kinetic Study

- 3.1- Calculate the average rate of disappearance of MnO₄⁻ within the time interval: [0-10 min].
- 3.2- One of the following values represents the half life time of the oxidation reaction of 2-propanol:
 $t = 25$ min, $t = 12.5$ min and $t = 2.5$ min.
Choose the appropriate value. Justify.
- 3.3- The procedure realized above is carried out again but with one single change: four drops of 2-propanol are added to the content of each beaker (without noticeable change in the volume V₀)
Verify whether the number of moles of permanganate ions remaining at t = 6 min is less, equal or greater than 6.3×10^{-4} mol.

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First Exercise (7 points)
Identification of Organic Compounds

Part of the Q	Answer	Mark
1.1	The possible condensed structural formulas are: $\text{CH}_3 - \text{CH}_2\text{OH}$; $\text{CH}_3 - \text{CHO}$ and $\text{CH}_3 - \text{O} - \text{CH}_3$	0.75
1.2	1st result The pH of the aqueous solution of (C) is less than 7 ; (C) is an acid. (C) is obtained by the mild oxidation of (A) ; (A) could be ethanol or ethanal. 2 nd result : The organic product is chlorinated; a chlorine atom substitutes a hydroxyl group. So (A) is ethanol of formula $\text{CH}_3 - \text{CH}_2\text{OH}$.	1
2.1	At the equivalence point : $n(\text{H}_3\text{O}^+)$ added = $n(R - \text{NH}_2)$ titrated $\text{C}_2 \times V_E = C_1 \times V_1 ; C_1 = \frac{C_2 \times V_E}{V_1} = \frac{0.20 \times 10.2}{20} = 0.10 \text{ mol.L}^{-1}$	0.75
2.2	$M(B) = \frac{m(B) \text{ in } 500 \text{ mL}}{n(B) \text{ in } 500 \text{ mL}} = \frac{3.7}{0.10 \times 0.5} = 74 \text{ g.mol}^{-1}$	0.75
2.3	(B) is a saturated non cyclic chain monoamime; its general formula is of the form $C_nH_{2n+3}N$. $M(B) = 14n + 17 = 74$, so $n = 4$. So its molecular formula is $C_4H_{11}N$	0.5
2.4	The possible condensed formulas of (B) : $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{NH}_2$; $\text{CH}_3 - \text{CH}_2 - \underset{\substack{ \\ \text{NH}_2}}{\text{CH}} - \text{CH}_2 - \text{NH}_2$ $\text{CH}_3 - \underset{\substack{ \\ \text{CH}_3}}{\text{C}} - \text{CH}_3$	1
2.5	The straight chain of (B) is non branched and does not contain an asymmetric carbon; (B) is 1- butanamine (of formula $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{NH}_2$).	0.5
3.1	The two characteristics of the reaction carried out in the experiment 1 are: slow and reversible	0.5
3.2	The formula of the amide obtained is : $\text{CH}_3 - \text{CO} - \text{NH} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$ Its name: N-butylethanamide.	0.75
3.3	The compound may have the formula: $\text{CH}_3 - \underset{\substack{ \\ \text{O}}}{\text{C}} - \text{O} - \underset{\substack{ \\ \text{O}}}{\text{C}} - \text{CH}_3$ Its name is ethanoic anhydride	0.5

Second Exercise (7 points)
Acid-Base Reactions

Part of the Q	Answer	Mark															
1	The acidic solutions are: HF solution and ammonium chloride solution. The basic solutions are: sodium methanoate solution and ammonia solution.	1															
2.1	<p>The concentration C_o of the commercial solution is :</p> $C_o = \frac{n(NH_3)}{V(solution)} ;$ $\% \text{ by mass} = \frac{m(NH_3)}{m(solution)} \times 100 = 25 \text{ and } d(\text{solution}) = \frac{m(\text{solution})}{V(solution)} = 0.91 \text{ g.mL}^{-1}$ $\text{and } M(NH_3) = \frac{m(NH_3)}{n(NH_3)} = 17 \text{ g.mol}^{-1} ;$ <p>The relation below can be deduced:</p> $C_o = \frac{\% \text{ by mass} \times d(\text{solution}) \times 10}{M(NH_3)} = 13.4 \text{ mol.L}^{-1}.$	1.25															
2.2	<p>During dilution the number of moles of the solute is conserved.</p> $C_o \times V_o = C \times V ; C = \frac{C_o \times V_o}{V} = \frac{13.4 \times 1.5}{2000} = 1.0 \times 10^{-2} \text{ mol.L}^{-1}.$	0.75															
2.3	We must choose 2 mL graduated pipet to take the volume V_o and 2 L volumetric flask to prepare the volume V .	0.5															
3.1	The equation of the reaction between HF and water: $\text{HF} + \text{H}_2\text{O} \rightleftharpoons \text{F}^- + \text{H}_3\text{O}^+$	0.5															
3.2	$\alpha = \frac{n(\text{HF})_{\text{dissociated}}}{n(\text{HF})_{\text{initial}}} = \dots = \frac{[\text{F}^-]}{C}$ $\text{HF} + \text{H}_2\text{O} \rightleftharpoons \text{F}^- + \text{H}_3\text{O}^+$ <table style="margin-left: 100px;"> <tr> <td>Initial state</td> <td>C</td> <td>solvent</td> <td>-</td> <td>-</td> </tr> <tr> <td>At equilibrium</td> <td>C - Cα</td> <td>solvent</td> <td>Cα</td> <td>Cα</td> </tr> <tr> <td>(obtained solution)</td> <td colspan="4"></td> </tr> </table> $K_a = K_{(\text{reaction})} = \frac{[\text{F}^-] \times [\text{H}_3\text{O}^+]}{[\text{HF}]} = \frac{C\alpha \times C\alpha}{C - C\alpha} = C \cdot \alpha^2 ; \text{ So } \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{10^{-3.8}}{10^{-2}}} = 0.12$	Initial state	C	solvent	-	-	At equilibrium	C - C α	solvent	C α	C α	(obtained solution)					1
Initial state	C	solvent	-	-													
At equilibrium	C - C α	solvent	C α	C α													
(obtained solution)																	
4.1	<p>The reaction constant K_r is :</p> $K_r = 10^{pK_a(\text{NH}_4^+/\text{NH}_3) - pK_a(\text{HF}/\text{F}^-)} = 10^{9.2 - 3.2} = 10^6 > 10^4 ; \text{ so the reaction is complete.}$	0.5															
4.2	$R(\text{HF}) = \frac{n(\text{HF})}{1} = \frac{C \times V_1}{1} = 10^{-2} \times 40 \times 10^{-3} = 4 \times 10^{-4}$ $R(\text{NH}_3) = \frac{n(\text{NH}_3)}{1} = \frac{C \times V_2}{1} = 10^{-2} \times 30 \times 10^{-3} = 3 \times 10^{-4}$ <p>$R(\text{NH}_3) < R(\text{HF})$ implies NH_3 is the limiting reactant.</p>	0.5															

4.3	$\text{HF} + \text{NH}_3 \rightarrow \text{F}^- + \text{NH}_4^+$ <table style="margin-left: 20px; border-collapse: collapse;"> <tr> <td style="padding-right: 20px;">initial state</td><td>4×10^{-4}</td><td>3×10^{-4}</td><td>-</td><td>-</td></tr> <tr> <td>final state</td><td>4×10^{-4}</td><td>3×10^{-4}</td><td>0</td><td>3×10^{-4}</td></tr> </table> <p style="text-align: right; margin-top: -20px;">1</p> $\text{pH(solution)} = \text{pK}_a(\text{HF} / \text{F}^-) + \log \frac{[\text{F}^-]}{[\text{HF}]}$ $\text{with } \log \frac{[\text{F}^-]}{[\text{HF}]} = \log \frac{\frac{3 \times 10^{-4}}{70 \times 10^{-3}}}{\frac{1 \times 10^{-4}}{70 \times 10^{-3}}} = \log 3$ <p style="margin-top: 10px;">and $\text{pH} = 3.2 + \log 3 = 3.7$</p>	initial state	4×10^{-4}	3×10^{-4}	-	-	final state	4×10^{-4}	3×10^{-4}	0	3×10^{-4}					
initial state	4×10^{-4}	3×10^{-4}	-	-												
final state	4×10^{-4}	3×10^{-4}	0	3×10^{-4}												

Third Exercise (6 points)
Kinetic of The Oxidation of 2-propanol

Part of the Q	Answer	Mark
1.1	C ₃ H ₆ O is produced by the mild oxidation of a secondary alcohol (2-propanol), so this compound belongs to the ketone family.	0.75
1.2	The condensed structural formula of C ₃ H ₆ O is : CH ₃ – CO – CH ₃ , it is the propanone	0.75
2.1	The oxidation reaction of 2- propanol is complete and the H ⁺ ions are in excess. According to the graph, the end of the reaction is reached (t = 25 min) and MnO ₄ ⁻ ions are not consumed completely. So 2-propanol is the limiting reactant.	0.75
2.2	$n(C_3H_6O)_t = \frac{5}{2} n(MnO_4^-) \text{ disappeared at } t = \frac{5}{2} [n(MnO_4^-) \text{ initial} - n(MnO_4^-)_t]$ $= \frac{5}{2} [(1.0 \times 10^{-3} - n(MnO_4^-)_t)]$	0.75
2.3	The immersing of the beaker in an icy-water bath blocks the oxidation reaction of 2- propanol.	0.5
3.1	The average rate of disappearance of MnO ₄ ⁻ ions is: $r(MnO_4^-) = -\frac{\Delta(MnO_4^-)}{\Delta t} = -\frac{n(MnO_4^-)_{10 \text{ min}} - n(MnO_4^-)_0}{10} = \frac{(10 - 5.6) \times 10^{-4}}{10}$ $= 4.4 \times 10^{-5} \text{ mol} \cdot \text{min}^{-1}$	1
3.2	t = 25 min and t = 12.5 min could not be the half life time of the reaction since the first one represents the end time of the reaction and the 2 nd one is t _∞ /2. thus, t _{1/2} = 2.5 min.	0.75
3.3	The number of moles of 2-propanol increases in the same volume, implies the concentration of 2-propanol has increased. The concentration of 2-propanol is a kinetic factor, as the concentration increases the rate of the reaction increases. In the first case n (MnO ₄ ⁻) remaining at 6 min is equal to 6.3×10^{-4} mol In the second case n (MnO ₄ ⁻) remaining at 6 min is less than 6.3×10^{-4} mol.	0.75

الاسم: الرقم:	مسابقة في مادة الكيمياء المدة ساعتان
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**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 Three Following Exercises:

**First Exercise (7 points)
Titration of a Household Product**

The label of a bottle containing a liquid household product used to open drains shows, among others, the following information: 20 % by mass of sodium hydroxide.

The aim of this exercise is to verify the value of the percentage by mass indicated above.

Given:

- Molar mass in g.mol⁻¹: M(NaOH) = 40

Acid/base pair	H ₃ O ⁺ /H ₂ O	CH ₃ COOH/CH ₃ COO ⁻	H ₂ O/HO ⁻
pK _a	0	4.8	14

1- Preliminary Study

In order to determine the percentage by mass of sodium hydroxide in this household product, the two following preliminary steps are carried out:

- First step: A volume of 100 mL of this household product is weighed; the mass is found to be 120 g.
- Second step: A solution S is prepared by diluting 50 times a certain volume of this product.

- 1.1- Calculate the density of the household product.
- 1.2- Choose, by justifying, among the three following sets, the appropriate one to carry out, precisely, the dilution required in the second step.

Set (a)	Set (b)	Set (c)
- 50 mL beaker	- 50 mL beaker	- 50 mL beaker
- 500 mL Erlenmeyer flask	- 1000 mL volumetric flask	- 1000 mL graduated cylinder
- 10 mL volumetric pipet	- 20 mL volumetric pipet	- 20 mL volumetric pipet

2- Titration of the Solution S with a Hydrochloric Acid Solution

A volume $V_1 = 10.0$ mL of solution S is titrated with a hydrochloric acid solution of concentration $C_2 = 0.10$ mol.L⁻¹.

- 2.1- Write the equation of the titration reaction.
- 2.2- Determine the molar concentration of the sodium hydroxide in the solution S, knowing that the volume of the acid solution added to reach equivalence is $V_{2E} = 11.2$ mL.

- 2.3- Calculate the concentration of sodium hydroxide in the above household product.
- 2.4- Deduce the percentage by mass of sodium hydroxide in this household product.
- 2.5- Specify whether the labeled percentage by mass is verified, knowing that the difference between the indicated value and obtained one in the experiment should not exceed 5 %.

3- Titration of the Solution S by an Ethanoic Acid Solution

The solution S can be titrated with an ethanoic acid solution, CH_3COOH , instead of the hydrochloric acid solution.

- 3.1- Write the equation of the reaction that took place between CH_3COOH and HO^- ions.
- 3.2- This reaction is unique and fast. Show that it can be used as a titration reaction.
- 3.3- Compare, based on the chemical species present, the pH at equivalence in this titration with that of the titration carried out in the part 2 of this exercise.

Second Exercise (7 points) Hydrolysis of an Ester

The reaction between an ester and water is a slow and reversible. It is represented by the following equation: Ester + Water \rightleftharpoons Acid + Alcohol.

The aim of this exercise is to study the kinetic of the hydrolysis reaction of the ethyl ethanoate.

1- Hydrolysis Reaction of Ethyl ethanoate

- 1.1- Write, using condensed structural formulas of the organic compounds, the equation of the hydrolysis reaction of ethyl ethanoate.
- 1.2- Specify the effect of the presence of large excess of water on the yield of the hydrolysis reaction.

2- Kinetic Follow-up of the Hydrolysis Reaction

At the instant $t = 0$, ten tubes, each contains 1.0×10^{-4} mol of ethyl ethanoate and a large excess of water, are placed in a water bath maintained at 40°C .

At the instant of time t , one of the tubes is taken and it is immersed in the ice, and the formed acid (noted as HA) is then titrated, using a sodium hydroxide solution of molar concentration $C_b = 0.010 \text{ mol.L}^{-1}$.

This procedure is repeated with the other tubes.

The equation of the titration reaction is:



- 2.1- Justify the cooling of the reacting system before carrying out the titration.
- 2.2- Show that the number of moles of the ester remaining in each tube, at each instant of time t and the volume V_{bE} are related by the following relation:

$$n(\text{ester})_t = 1.0 \times 10^{-4} - 1.0 \times 10^{-5} \times V_{\text{bE}}$$

where V_{bE} , expressed in mL, is the volume of the sodium hydroxide solution added to reach equivalence at the time t .

3- Make-use of the Results

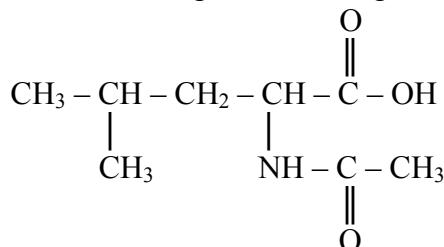
- 3.1- Calculate the missing number of moles of the ester in the table below:

$t(\text{min})$	0	10	20	30	40	50	60	90	t_∞
$V_{\text{bE}} (\text{mL})$		2.1	3.7	5.0	6.1	6.9	7.5	8.6	
$n(\text{ester}) (10^{-5} \text{ mol})$	10	7.9	6.3	5.0	3.9	3.1	2.5		0.0

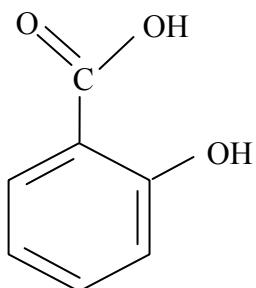
- 3.2- Plot, on a graph paper, the curve: n (ester) = $f(t)$ in the interval of time [0 – 90 min]. Take the following scales: 1 cm for 10 min in abscissa and 1 cm for 1.0×10^{-5} mol in ordinate.
- 3.3- Determine the rate of disappearance of the ester at the instant $t = 40$ min.
- 3.4- Determine graphically the half-life time $t_{1/2}$ of the reaction.
- 3.5- Suggest a way, other than heating, in order to reduce $t_{1/2}$ of this reaction.

Third Exercise (6 points)
Molecules of Some Medicinal Drugs

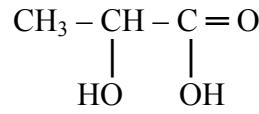
Acetyl-leucine is used as a medicinal drug to treat vertigo. Its condensed structural formula is:



Keratosis pilaris is a skin disorder that could be treated with a moisturizing cream containing atleast 2% of salicylic acid and/or lactic acid.



Salicylicacid



Lactic acid

The aim of this exercise is to study some of the properties of the molecules of the above compounds.

1- Molecular Structure

- 1.1- Name the common functional group among the three molecules: acetyl-leucine, salicylic acid and lactic acid.
- 1.2- Write the molecular formula of salicylic acid.
- 1.3- Recopy the formula of acetyl-leucine molecule, circle and name the functional group which is not present in the two other molecules.
- 1.4- Justify the chirality of lactic acid molecule.
- 1.5- Represent, according to Cram, the two enantiomers of lactic acid molecule.

2- Hydrolysis of Acetyl-leucine

It is advised to keep this medicinal drug away from humidity.

- 2.1- Write the equation of the hydrolysis reaction of acetyl-leucine.
- 2.2- Give the systematic name of each one of the products of this reaction.

3- Salicylic Acid

Salicylic acid is used in the hemisynthesis of aspirin. It is also used in the preparation of a fragrant compound (E) named methyl salicylate.

- 3.1- Write the condensed structural formulas of the compounds (A) and (B) shown in the equation below:



- 3.2- Write the equation of the preparation of (E) starting from salicylic acid.

- 3.3- Give the name of the functional group created in the two above reactions.

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	مسابقة في مادة الكيمياء المدة ساعتان	مشروع معيار التصحيح

First Exercise (7 points)
Titration of a Household Product

Part of the Q	Answer	Mark
1.1	The density of the product: $d = \frac{m \text{ (solution)}}{V(\text{solution})} = \frac{120}{100} = 1.2 \text{ g.mL}^{-1}$.	0.5
1.2	<p>During dilution the number of moles of the solute is conserved. $C_0 \times V_0 = C_f \times V_f$</p> $\frac{V_f}{V_0} = \frac{C_0}{C_f} = 50$ <p>with V_0 is the volume of the pipet and V_f is the volume of the volumetric flask.</p> <p>Set (b) is appropriate, since we have a 1000 ml volumetric flask and 20 ml volumetric pipet which are the appropriate glassware to carry out this dilution with precision.</p>	1
2.1	The equation of the reaction: $\text{H}_3\text{O}^+ + \text{HO}^- \rightarrow 2 \text{H}_2\text{O}$.	0.5
2.2	<p>At equivalence, $n(\text{HO}^-)$ in 10 mL = $n(\text{H}_3\text{O}^+)$ added to reach equivalence ;</p> $C_1 \times V_1 = C_2 \times V_{2E} \text{ and } C_1 = \frac{0.1 \times 11.2 \times 10^{-3}}{10 \times 10^{-3}} = 0.112 \text{ mol.L}^{-1}$.	0.75
2.3	The concentration of sodium hydroxide in the household product is: $C = 0.112 \times 50 = 5.56 \text{ mol.L}^{-1}$.	0.5
2.4	<p>The mass of sodium hydroxide in 1 L of the household product is: $m = 5.56 \times 40 = 224 \text{ g}$.</p> <p>The mass of 1 L of the household product is 1200 g.</p> <p>The percentage by mass of sodium hydroxide is then:</p> $\frac{224 \times 100}{1200} = 18.66 \text{ %}$.	1
2.5	<p>The difference is: $\frac{20 - 18.66}{20} \times 100 = 6.7 \text{ %}$.</p> <p>This difference exceeds the acceptable value 5 %. The indication is not verified.</p>	0.5
3.1	The equation of the reaction is: $\text{CH}_3\text{COOH} + \text{HO}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O}$	0.5
3.2	$\Delta pK_a = pK_a(\text{H}_2\text{O}/\text{HO}^-) - pK_a(\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-) = 14 - 4.8 = 9.2$ $K_R = 10^{9.2} > 10^4$. The reaction is complete, fast and unique; thus it can be used as a titration reaction.	0.75
3.3	<p>In the titration of the part 2 : the chemical species present at the equivalence (other than water) are : Na^+ and Cl^- which are spectator ions, so the pH is that of pure water which is equal to 7.</p> <p>The chemical species present in the solution at equivalence in this titration, others than water, are Na^+ ions which are spectator ions and CH_3COO^- which is the conjugate base of the weak acid. Thus, the pH at equivalence is greater than 7.</p>	1

Second Exercise (7 points)

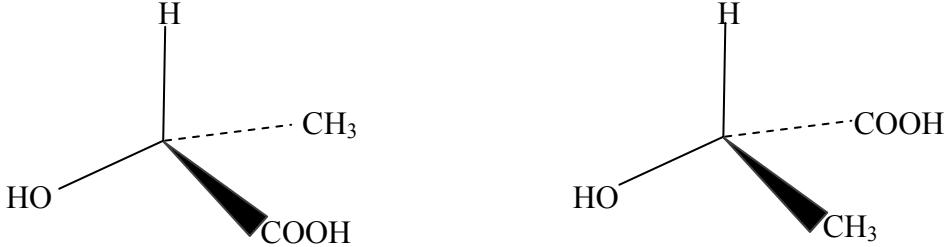
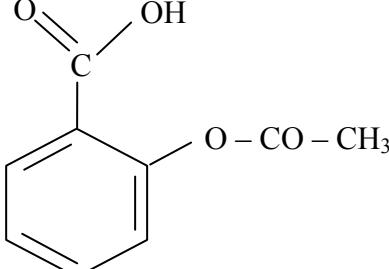
Hydrolysis of an Ester

Part of the Q	Answer	Mark								
1.1	The equation of the hydrolysis reaction of ethyl ethanoate is: $\text{CH}_3 - \text{COO} - \text{CH}_2 - \text{CH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3 - \text{COOH} + \text{HO} - \text{CH}_2 - \text{CH}_3$	0.75								
1.2	The presence of water in large excess favors the hydrolysis reaction, so it increases the yield of this reaction.	0.5								
2.1	The cooling of the reacting system before carrying out the titration blocks any reaction other than the titration reaction.	0.5								
2.2	At equivalence, $n(\text{HO}^-)$ versed at equivalence = $n(\text{acid})$ formed = $n(\text{ester})$ reacting $= C_b \times V_{bE} = 0.01 \times V_{bE} \times 10^{-3}$. $n(\text{ester})_t = n(\text{ester})_{\text{initial}} - n(\text{ester})_{\text{reacting}} = 1.0 \times 10^{-4} - 1.0 \times 10^{-5} V_{bE}$	1.25								
3.1	The missing value: $n(\text{ester})_{90} = (1.0 \times 10^{-4} - 1.0 \times 10^{-5} \times 8.6) = 1.4 \times 10^{-5} \text{ mol.}$	0.5								
3.2	<p>The curve $n(\text{ester}) = f(t)$.</p> <table border="1"> <caption>Data points estimated from the graph</caption> <thead> <tr> <th>Time (min)</th> <th>n (ester) (10⁻⁴ mol)</th> </tr> </thead> <tbody> <tr> <td>0</td> <td>0.74 × 10⁻⁴</td> </tr> <tr> <td>40</td> <td>0</td> </tr> <tr> <td>82</td> <td>0</td> </tr> </tbody> </table>	Time (min)	n (ester) (10 ⁻⁴ mol)	0	0.74 × 10 ⁻⁴	40	0	82	0	1
Time (min)	n (ester) (10 ⁻⁴ mol)									
0	0.74 × 10 ⁻⁴									
40	0									
82	0									
3.3	<p>The instantaneous rate of disappearance of ester is defined by:</p> $r = -\frac{dn(\text{ester})}{dt}$, it is equal to the opposite of the slope of the tangent of the curve: $n(\text{ester}) = f(t)$ at the point of the curve of abscissa 40 min. $\text{So: } r_{t=40} = -\frac{y_B - y_A}{x_B - x_A} = -\frac{0 - 0.74 \times 10^{-4}}{82} = 9.0 \times 10^{-7} \text{ mol} \cdot \text{min}^{-1}$.	1								
3.4	The half-life of the reaction corresponds to time needed for half of the initial quantity of ester disappears, which corresponds to 0.5×10^{-4} mol. Graphically the half-life of the reaction is $t_{1/2} = 30$ min.	1								
3.5	We can add an appropriate catalyst in order to accelerate the reaction and by consequence reduce the half-life time of this reaction.	0.5								

Third Exercise (6 points)
Identification of an Alcohol

Part of the Q	Answer	Mark
1.1	<p>The molar mass of A is: $12n + 2n + 2 + 16 = 14n + 18$.</p> <p>The % of mass of oxygen: $\frac{16}{14n + 18} \times 100 = 21.62$.</p> <p>The number of carbon atoms n = $\frac{1600 - 389.16}{302.68} = 4$.</p> <p>The molecular formula of A is $C_4H_{10}O$</p>	0.75
1.2	<p>The condensed structural formulas of alcohols isomers of A are :</p> <p>$CH_3 - CH_2 - CH_2 - CH_2OH$; $CH_3 - CH_2 - CHOH - CH_3$;</p> <p>$CH_3 - CH - CH_2OH$ and $CH_3 - COH - CH_3$</p> <p style="text-align: center;"> $\begin{array}{c} \\ CH_3 \end{array} \qquad \qquad \qquad \begin{array}{c} \\ CH_3 \end{array}$ </p>	1
2.1	<p>The compound which gives a yellow-orange precipitate with 2,4-DNPH could be an aldehyde, which is obtained from a mild oxidation of a primary alcohol, or a ketone, which is obtained from mild oxidation of a secondary alcohol. The names of the alcohols are: 1-butanol; 2-methyl-1-propanol and 2-butanol.</p>	1
2.2.1	<p>Among these three alcohols, 2-butanol, which is a secondary alcohol, is the only one which gives, by intramolecular dehydration, according to Zaitsev's rule, two alkenes: in majority, and in minority.</p>	0.75
2.2.2	<p>The condensed structural formula of the alkene which is the major one is:</p> <p>$CH_3 - CH = CH - CH_3$.</p>	0.25
3.1	<p>The equation is:</p> <p>$CH_3 - CH_2 - CHOH - CH_3 + PCl_5 \rightarrow CH_3 - CH_2 - CHCl - CH_3 + POCl_3 + HCl$</p>	0.5
3.2	<p>The equation of the inter molecular dehydration reaction is:</p> <p>$2 CH_3 - CH_2 - CHOH - CH_3 \rightarrow CH_3 - CH_2 - CH - O - CH - CH_2 - CH_3 + H_2O$</p> <p style="text-align: center;"> $\begin{array}{c} \\ CH_3 \end{array} \qquad \qquad \qquad \begin{array}{c} \\ CH_3 \end{array}$ </p>	0.5
3.3	<p>$CH_3 - CH_2 - CHOH - CH_3 \rightarrow CH_3 - CH_2 - CO - CH_3 + H_2$</p>	0.5
3.4	<p>$CH_3 - CH_2 - CHOH - CH_3 + CH_3 - CH(CH_3) - COOH \rightleftharpoons$</p> <p style="text-align: center;">$CH_3 - CH(CH_3) - COO - CH - CH_2 - CH_3 + H_2O$</p> <p style="text-align: center;"> $\begin{array}{c} \\ CH_3 \end{array}$ </p>	0.75

Third Exercise (6 points) life Sciences
Molecules of some Medicinal Drugs

Part of the Q	Answer	Mark
1.1	The common functional group among the three molecules is the carboxyl group.	0.25
1.2	The molecular formula of salicylic acid is $C_7H_6O_3$.	0.5
1.3	$ \begin{array}{ccccccc} & & & & \text{O} & & \\ & & & & \parallel & & \\ \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH} - \text{C} - \text{OH} & & & & & & \\ & & & & & & \\ \text{CH}_3 & & & \text{NH} - \text{C} - \text{CH}_3 & & & \\ & & & & & & \\ & & & \text{O} & & & \end{array} $ <p>It is the amide group.</p>	0.5
1.4	Lactic acid is a chiral molecule since it contains an asymmetric carbon atom.	0.5
1.5	<p>The two enantiomers are:</p> 	0.75
2.1	<p>The equation of the hydrolysis reaction is:</p> $ \begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH} - \text{C} - \text{OH} \\ \qquad \\ \text{CH}_3 \qquad \text{NH} - \text{C} - \text{CH}_3 \\ + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH} - \text{C} - \text{OH} \\ \qquad \qquad \qquad \qquad \\ \qquad \qquad \qquad \text{CH}_3 \qquad \text{NH}_2 \end{array} $	0.75
2.2	CH_3COOH is ethanoic acid and the second compound is 2- amino- 4 – methylpentanoic acid.	0.75
3.1	<p>Formula of (A) is:</p>  <p>formula of (B) is:</p> CH_3COOH	0.75
3.2	<p>The equation of this reaction is :</p> $\text{HO} - \text{C}_6\text{H}_4 - \text{COOH} + \text{CH}_3\text{OH} \rightleftharpoons \text{HO} - \text{C}_6\text{H}_4 - \text{C}(\text{O}) - \text{O} - \text{CH}_3 + \text{H}_2\text{O}$	0.75
3.3	The functional group created is an ester group.	0.5

الاسم:	مسابقة في مادة الكيمياء
الرقم:	المدة: ساعتان

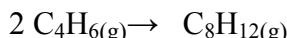
**This Exam Includes Three Exercises. It Is Inscribed on Four Pages Numbered from 1 to 4.
The Use of A Non-programmable Calculator Is Allowed.**

Answer The Three Following Exercises:

First Exercise (6 points)

Kinetic of Dimerization of Butadiene

At high temperature, butadiene dimerizes in gaseous phase in a complete reaction of which the equation is:



In an evacuated container of constant volume V , maintained at a temperature $T = 609\text{K}$, $n_0\text{mol}$ of butadiene gas introduced. A manometer, attached to this container, measures the total pressure P at different instants of time of the evolution of the reacting system.

The concentration of C_8H_{12} gas is determined at those instants. The results are listed in the table below:

t (min)	8	15	30	60	90	120	150	180
$[\text{C}_8\text{H}_{12}] 10^{-3} \text{ mol.L}^{-1}$	1.9	3.0	4.6	6.3	7.2	7.8	8.1	8.4

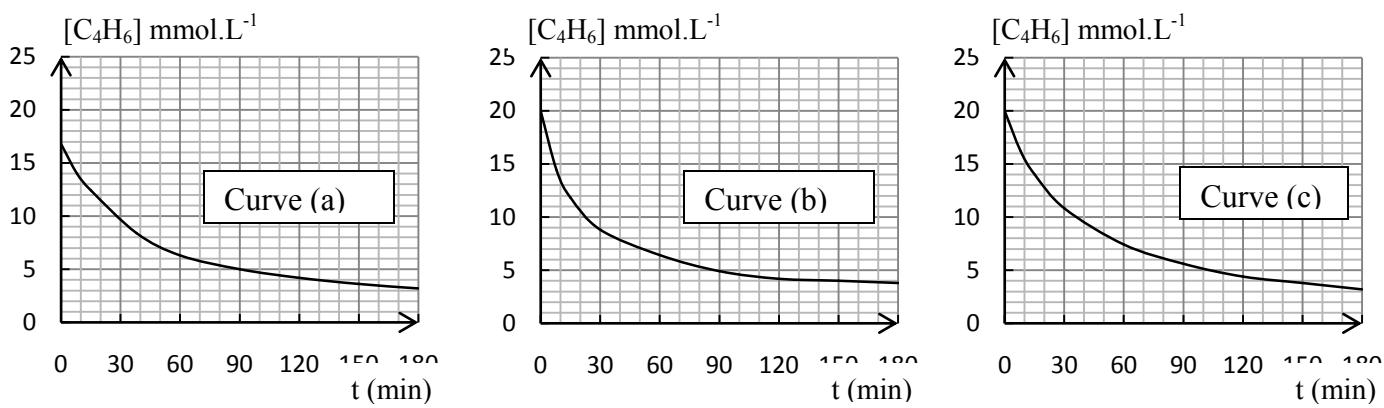
Given: - Gases of the reacting mixture are supposed to be ideal.
- Ideal gas constant: $R = 0.082 \text{ atm.L.mol}^{-1}\text{.K}^{-1}$.

1- Preliminary Study

- 1.1- Draw up a table representing the composition of the reacting mixture at the initial state and at the instant of time t of its evolution as a function of n_0 and x . (x is the number of moles of C_8H_{12} formed at t).
- 1.2- Establish the relation among: the concentration of C_8H_{12} gas at the instant of time t , the total pressure P at this instant, and the initial pressure P_0 in the container.
- 1.3- Show that the concentration of C_8H_{12} at the end of the chemical transformation is equal to $1.0 \times 10^{-2} \text{ mol.L}^{-1}$ knowing that the initial pressure inside the container is $P_0 = 1.0 \text{ atm}$.

2- Kinetic Study

- 2.1- Plot the curve representing the change in the concentration of C_8H_{12} as a function of time: $[\text{C}_8\text{H}_{12}] = f(t)$, in the interval of time: $[0 - 180 \text{ min}]$. Take the following scales :
1 cm for 15 min in abscissa and $1.0 \times 10^{-3} \text{ mol.L}^{-1}$ in ordinate.
- 2.2- Deduce, graphically, the change in the rate of formation of C_8H_{12} with time.
- 2.3- Determine the half-life time of the reaction.
- 2.4- Consider each one of the three following curves and specify whether it represents the change in the concentration of C_4H_6 as a function of time.



Second Exercise(7 points) Hydrolysis Reactions

Water is a universal solvent which plays different roles in chemistry. It can react with carboxylic acid derivatives ($R - CO - Z$) according to hydrolysis reactions of which the general equation is:



Given:

- Starting from equimolar mixture of ester and water, theyield of the hydrolysis reaction of the ester at equilibrium is 33% when a primary alcohol is formed.
- Ethanol and glycerol are miscible with water in all proportions.

1- Hydrolysis of a Dipeptide

The hydrolysis of the dipeptide (Gly-Val), of formula: $H_2N - CH_2 - \overset{||}{C} - NH - \underset{|}{CH} - \overset{||}{C} - OH$

produces two products (A) and (B)

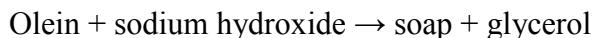
- 1.1- Name the functional groupsthat characterizethe molecule (Gly-Val).
- 1.2- Write the condensed structural formulas of the products (A) and (B).
- 1.3- Represent, according to Cram, the two enantiomers of the chiral product of this hydrolysis.

2- Hydrolysis of Esters

- 2.1- A mixture of 1 mol of ethyl propanoate and of 3mol of water is heated to reflux in the presence of an acid catalyst.
 - 2.1.1- Write, using condensed structural formulas of the organic compounds, the equation of this hydrolysis reaction.
 - 2.1.2- One of the following values represents the number of moles of the acid formed at equilibrium:
0.33 mol ; 0.53 mol and 1 mol. Choose, by justifying, the appropriate value.

2.2- A mixture of olive oil and an excess of concentrated aqueous solution of sodium hydroxide in the presence of ethanol as solvent is heated to reflux.

The word equation of this reaction is:



2.2.1- Write the condensed structural formula of glycerol and the formula of olein knowing that it is a triester of oleic acid of formula $\text{C}_{17}\text{H}_{33}-\text{COOH}$.

2.2.2- After the relargage of soap in a saturated aqueous sodium chloride solution, two phases are obtained: the soap and the aqueous phase.

List four chemical species, other than water, that exist in the aqueous phase.

2.3- The two statements below are suggested for the above two realized reflux heating and their results :

2.3.1- At the end of the reflux heating, the volume of the reacting medium does not change.

2.3.2- The end of the transformation is reached faster than that when the reacting mixture is kept at room temperature.

When the statement is true, justify it; when it is false, specify the correct answer.

Third Exercise(7 points) **Sodium Bicarbonate**

Sodium bicarbonate or sodium hydrogen carbonate, of formula NaHCO_3 , is used in the production of beverages and carbonated water. Also it is used to reduce the excess stomach acid.

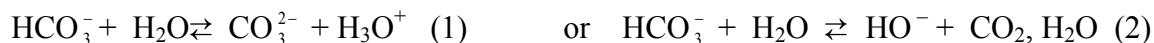
This exercise aims to study the behavior of hydrogen carbonate ions HCO_3^- in water, as well as to determine the percentage by mass(degree of purity) of NaHCO_3 in a sample of medicinal sodium bicarbonate.

Given:

- Ionic compounds NaHCO_3 and Na_2CO_3 are solids highly soluble in water.
- $$\frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = \frac{\%(\text{by mol})\text{CO}_3^{2-}}{\%(\text{by mol})\text{HCO}_3^-}$$
- $M(\text{NaHCO}_3) = 84 \text{ g.mol}^{-1}$.

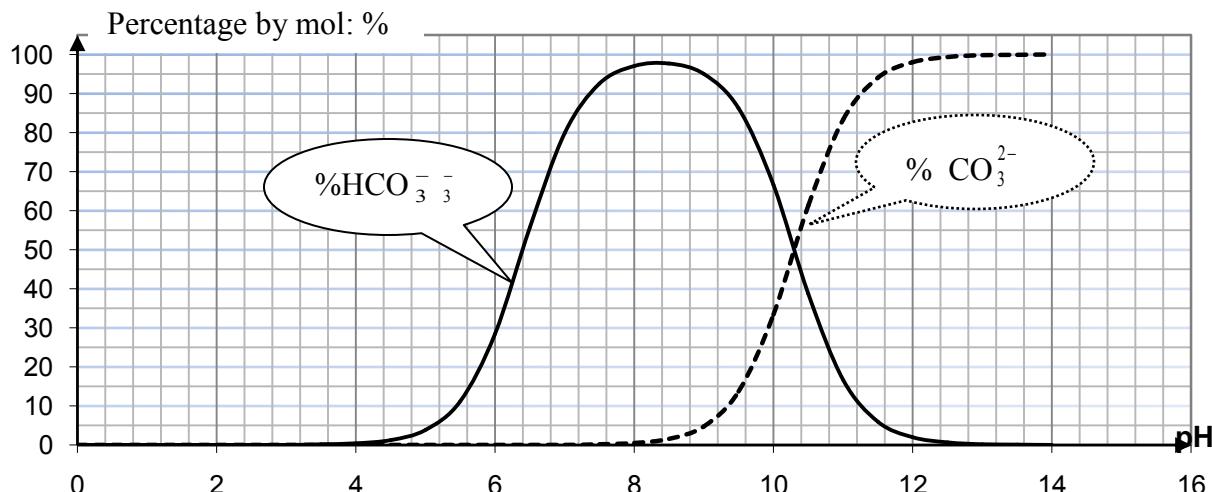
1- Study of Hydrogen Carbonate Ion

Hydrogencarbonate ion, HCO_3^- , can react with water according to two chemical reactions of equations:



1.1- Show that hydrogencarbonate ion has an amphoteric character (ampholyte).

1.2- The following graph represents the change in the percentages by moles of the chemical species HCO_3^- and CO_3^{2-} in an aqueous solution (A) as a function of pH:



1.2.1- Calculate, based on the above graph, the ratio $\frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$ when the pH of solution (A) is equal 10

1.2.2- It is required to prepare a buffer solution of pH = 10 using 3.0×10^{-2} mol of Na_2CO_3 and a mass m of NaHCO_3 . Determine the mass m needed for this preparation.

2- Degree of Purity of a Sample of Sodium Bicarbonate

In order to determine the degree of purity of a sample of powder medicinal sodium bicarbonate one proceeds as follows:

- A mass m = 1.50 g, of the powder of this sodium bicarbonate, is weighed and dissolved in distilled water in such a way to obtain a volume $V_0 = 200.0$ mL of a solution noted (S).
- A volume $V_1 = 10.0$ mL of the solution (S) is removed and introduced into a beaker then few drops of an appropriate colored indicator are added.
- A hydrochloric acid solution of concentration $C = 5.0 \times 10^{-2}$ mol.L⁻¹ is added progressively to reach equivalence.

The equation of this titration reaction is: $\text{H}_3\text{O}^+ + \text{HCO}_3^- \rightarrow \text{CO}_2 + \text{H}_2\text{O}$

2.1- Choose, from the list below, the materials needed for the preparation of the solution (S) :

Precision balance, 25 mL graduated buret, 10 mL volumetric pipet, 200 mL volumetric flask, magnetic stirrer, funnel, watch glass and stand.

2.2- Determine the molar concentration of HCO_3^- ions in the solution (S), knowing that the volume of the acid added to reach equivalence is $V_E = 16.8$ mL.

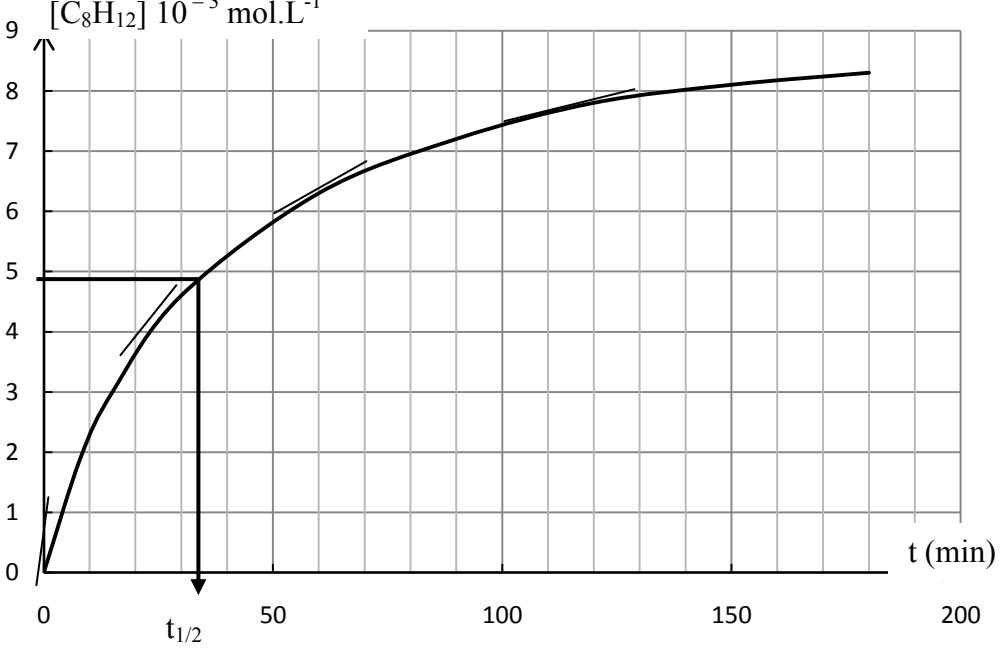
2.3- Deduce the percentage by mass of NaHCO_3 in the sample of the medicinal powder.

2.4- The above titration is carried out again but with one change: the volume V_1 is introduced into a beaker containing 20 mL distilled water and the appropriate colored indicator.

By consulting the table below, compare V'_E and V_E on one hand and pH'_E and pH_E on the other hand. Justify.

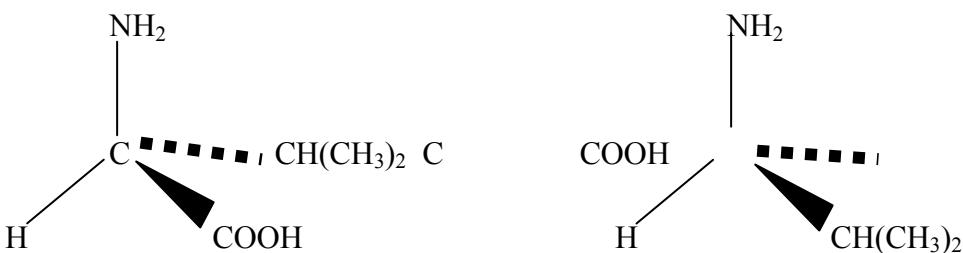
	Volume of the acid added at equivalence	pH of the mixture at equivalence
Titration without addition of distilled water	V_E	pH_E
Titration with addition of distilled water	V'_E	pH'_E

First Exercise (6 points)
Kinetic of Dimerization of Butadiene

Question	Answer	mark
1.1	$2 \text{ C}_4\text{H}_{6(g)} \rightarrow \text{C}_8\text{H}_{12(g)}$ Initial state $n_0 -$ At t $n_0 - 2x$	0.5
1.2	Ideal gas law: $P \times V = (n_0 - x) \times R \times T = n_0 \times R \times T - x \times R \times T$ but $[\text{C}_8\text{H}_{12}] = \frac{x}{V} = \frac{P_0 - P}{RT} = \frac{P_0 - P}{49.998}$ where P is in atm and $[\text{C}_8\text{H}_{12}]$ in mol.L ⁻¹ .	1
1.3	At the end of the transformation, $P = P_0 / 2$. $[\text{C}_8\text{H}_{12}] = \frac{P_0}{2 \times 49.938} = 0.010 \text{ mol.L}^{-1}$	0.5
2.1	The curve is : 	1
2.2	Graphically, the rate of formation of C_8H_{12} is equal to the slope of the tangent at the curve at the point of abscissa t. At $t = 0$, this slope is maximal and decreases with time.	0.75
2.3	The half-life time of a reaction is the time required for C_8H_{12} to reach half its maximum concentration. At $t_{1/2}$, $[\text{C}_8\text{H}_{12}] = \frac{[\text{C}_8\text{H}_{12}]_{\max}}{2} = \frac{0.01}{2} = 5.0 \times 10^{-3} \text{ mol.L}^{-1}$.	0.75

	Graphically : $t_{1/2} = 36 \text{ min.}$	
2.4	<p>The curve that represents the change in the $[C_4H_6]$ as a function of time should pass through two specific points: (At $t = 0$) $[C_4H_6] \text{ initial} = 2 \times [C_8H_{12}]$ at the end of transformation = 0.020 mol.L^{-1}. At $t_{1/2}$, $[C_4H_6]$ should have the value of $0.020 / 2 = 0.010 \text{ mol.L}^{-1}$. The curve (a) is not the convenient one since its initial concentration $[C_8H_{12}]_0 = 16.8 \text{ mmol.L}^{-1}$ The curve (b) is not the convenient one since $t_2^1 = 20 \text{ min}$ Therefore, the graph (c) represents this change since $[C_4H_6]_0 = 0.020 \text{ mol.L}^{-1}$ and $t_2^1 = 36 \text{ min}$</p>	1.5

Second Exercise (7 points) Hydrolysis Reactions

Question	Answer	mark
1.1	The functional groups are: carboxyl group, amide group and amino group.	0.75
1.2	the formulas are: $H_2N - CH_2 - COOH$ and $NH_2 - \begin{array}{c} \\ CH - CH(CH_3)_2 \\ \\ COOH \end{array}$	0.5
1.3	<p>The two enantiomers are:</p> 	0.75
2.1.1	<p>The equation of this reaction is:</p> $CH_3 - CH_2 - COO - CH_2 - CH_3 + H_2O \rightleftharpoons CH_3 - CH_2 - COOH + CH_3 - CH_2OH$	0.75
2.1.2	<p>This reaction is a limited reaction, n (acid) formed at equilibrium could not be 1 mol. The initial mixture is not equimolar, n (acid) formed at equilibrium could not be 0.33 mol. Therefore n (acid formed) is 0.53 mol.</p>	1
2.2.1	<p>The condensed structural formula of glycerol is: $CH_2OH - CHOH - CH_2OH$. That of olein is:</p>	0.25

	$\begin{array}{c} \text{CH}_2 - \text{O} - \text{CO} - \text{C}_{17}\text{H}_{33} \\ \\ \text{CH} - \text{O} - \text{CO} - \text{C}_{17}\text{H}_{33} \\ \\ \text{CH}_2 - \text{O} - \text{CO} - \text{C}_{17}\text{H}_{33} \end{array}$	0.5
2.2.2	The chemical species that exist in the aqueous phase are: Na^+ , OH^- , Cl^- , ethanol and glycerol.	1
2.3.1	During the reflux heating the volume of the reacting mixture does not change since the vapors released from the flask are condensed and returned back to the flask.	0.75
2.3.2	Temperature is a kinetic factor, when it increases, the rate of the reaction increases. Therefore the end time of reaction is reached faster when the reacting medium is heated.	0.75

Third Exercise(7 points)
Sodium Bicarbonate

Question	Answer	mark
1.1	Hydrogen carbonate ion has an amphoteric character since it belongs to two acid/base pairs: HCO_3^- / CO_3^{2-} and CO_2 , H_2O / HCO_3^- .	0.5
1.2.1	From the graph, the % by mol of HCO_3^- is 67 ; that of CO_3^{2-} is 33 $\frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = \frac{\% \text{ by mol CO}_3^{2-}}{\% \text{ by mol HCO}_3^-} = 33 / 67 = 0.5$	0.75
1.2.2	The introduced quantity of HCO_3^- ions (produced by NaHCO_3) and that of CO_3^{2-} ions (produced by Na_2CO_3) are conserved in the obtained solution. $\frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = \frac{\frac{n_1}{V(\text{solution})}}{\frac{n_2}{V(\text{solution})}} = \frac{n_1}{n_2}$ With $n_1 = n(\text{CO}_3^{2-})$ formed in the solution = $n(\text{Na}_2\text{CO}_3)$ initial = 3.0×10^{-2} mol and $n_2 = n(\text{HCO}_3^-)$ formed in the solution = $n(\text{NaHCO}_3)$ initial = $\frac{m(\text{NaHCO}_3) \text{ initial}}{M(\text{NaHCO}_3)} = \frac{m}{84}$ mol. By calculation $m = 5.04$ g.	1.25
2.1	The materials needed for the preparation of the solution (S) is : Precision balance, watch glass, funnel and 200 mL volumetric flask.	1
2.2	$n(\text{NaHCO}_3)$ dissolved in $V_1 = n(\text{HCO}_3^-)$ initial in $V_1 = n(\text{H}_3\text{O}^+)$ added to reach	1

	<p>equivalence.</p> <p>Therefore $[\text{HCO}_3^-] \times V_1 = C \times V_E$; $[\text{HCO}_3^-] = \frac{C \times V_E}{V_1} = \frac{0.05 \times 16.8}{10} = 8.4 \times 10^{-2} \text{ mol.L}^{-1}$</p>	
2.3	<p>$n(\text{NaHCO}_3)$ in the sample = $n(\text{HCO}_3^-)$ dissolved in $V_0 = 8.4 \times 10^{-2} \times 0.2 = 1.68 \times 10^{-2} \text{ mol}$.</p> <p>$m(\text{NaHCO}_3)$ in the sample = $n(\text{NaHCO}_3) \times M(\text{NaHCO}_3) = 1.68 \times 10^{-2} \times 84 = 1.41 \text{ g}$.</p> <p>Degree of purity = $\frac{m(\text{NaHCO}_3) \text{ pure}}{m(\text{sample})} \times 100 = \frac{1.41}{1.50} \times 100 = 94 \%$.</p>	1.5
2.4	<p>$V'_E = \frac{n(\text{HCO}_3^-) \text{ initial in } V_1}{C}$. the dilution of solution does not change the initial quantity of HCO_3^- and C is the concentration of the acid solution in the buret, therefore $V'_E = V_E$</p> <p>The solution obtained at equivalence is acidic, the dilution of an acidic solution increases its pH, therefore $\text{pH}'_E > \text{pH}_E$.</p>	0.5 0.5

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 Three Following Exercises:

First Exercise (7 points)
Acid-Base Reaction

The label of a bottle containing a commercial hydrobromic acid solution shows, among others, the following indications:

46 % by mass of HBr; density: 1.47 g.mL^{-1} .

The aim of this exercise is to perform an acid-base study of a dilute aqueous hydrobromic acid solution.

Given:

- $M(\text{HBr}) = 81 \text{ g.mol}^{-1}$
- $pK_a(\text{NH}_4^+/\text{NH}_3) = 9.2$

1- Dilution of the Commercial Solution

- 1.1- Show that the molar concentration of the commercial solution is $C_0 = 8.35 \text{ mol.L}^{-1}$.
- 1.2- Describe the experimental procedure to be followed in order to prepare 1 L of a solution (S) by diluting the commercial solution 200 times .
- 1.3- The pH of the solution (S) is equal to 1.38
 - 1.3.1- Show that HBr is a strong acid.
 - 1.3.2- Write the equation of its reaction with water.

2- Titration of an Aqueous Ammonia Solution.

The solution (S) is added, progressively, into a beaker containing a volume $V_b = 10.0 \text{ mL}$ of an ammonia solution (NH_3) of concentration C_b , in the presence of an appropriate colored indicator. The volume of the acid added to reach equivalence is $V_{ae} = 12 \text{ ml}$

- 2.1- Write the equation of the titration reaction.
- 2.2- Justify, based on the chemical species present at equivalence, the acid character of this medium.
- 2.3- Show that the concentration of the ammonia solution is $C_b = 5.0 \times 10^{-2} \text{ mol.L}^{-1}$.
- 2.4- Calculate the volume of ammonia gas needed to prepare 1 L of the ammonia solution of concentration C_b , knowing that the molar volume of a gas is $V_m = 24 \text{ L.mol}^{-1}$.

3- Preparation of a Buffer Solution

Determine the volume V_1 of the solution (S) that should be added to a volume $V_2 = 50 \text{ mL}$ of the ammonia solution of concentration C_b in order to prepare a buffer solution of $\text{pH} = 9.0$

Second Exercise (6 points) Synthesis of an Ester

Available are two flasks: one containing glacial (pure) ethanoic acid and the other contains a liquid of a pure saturated noncyclic chain organic compound (A).

The aim of this exercise is to identify the organic compound (A) then to study its reaction with ethanoic acid.

1- Identification of the Family of (A)

In order to identify the chemical family of the compound (A), the experiments listed below are carried out:

Number of the experiment	Experiment	Result of the experiment
1	(A) + sodium metal	Hydrogen gas release.
2	Heating a mixture of : (A)+ thionyl chloride (SOCl_2)	Formation of an organic compound (B) accompanied with the release of two gases.

Moreover, a study of the compound (B) shows that the molecule of the compound (B) contains only carbon, hydrogen and chlorine.

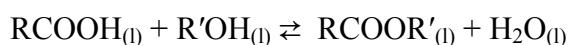
- 1.1- Interpret the result of experiment 1.
- 1.2- Deduce from the experiment 2, the possible chemical families of the compound (B).
- 1.3- Show that the compound (A) is an alcohol of general formula $\text{C}_x\text{H}_{2x+2}\text{O}$.

2- Esterification Reaction

A mixture of 0.5 mol of ethanoic acid and of 0.5 mol of the compound A is heated. At equilibrium, a quantity of 0.3 mol of an ester E of molecular formula $\text{C}_6\text{H}_{12}\text{O}_2$ is obtained.

Given:

The equilibrium constant K, associated with the equation:



is equal to 4.12 if the alcohol is primary and to 2.25 if the alcohol is secondary.

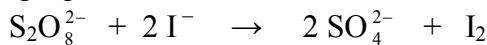
- 2.1- Determine the molecular formula of the alcohol (A).
- 2.2- Write the possible condensed structural formulas of the ester (E).
- 2.3- Show that the equilibrium constant of the equilibrium realized above is equal to 2.25
- 2.4- Identify the alcohol (A) and name the ester (E).

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

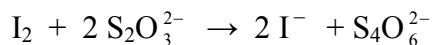
Third Exercise (7 points) Oxidation of Iodide Ions

A solution (S) is prepared by mixing a volume 100 mL of a potassium iodide solution($K^+ + I^-$) of concentration $C_1 = 0.80 \text{ mol.L}^{-1}$ with a volume 100 mL of sodium peroxydisulfate solution ($2 \text{ Na}^+ + \text{S}_2\text{O}_8^{2-}$) of concentration $C_2 = 0.20 \text{ mol.L}^{-1}$.

A brown color is observed which intensifies with time representing a complete reaction that takes place according to the following equation:



At different time intervals, a precise volume of the solution (S) is taken and the iodine formed is titrated, in the presence of starch solution, using a sodium thiosulfate solution($2 \text{Na}^+ + \text{S}_2\text{O}_3^{2-}$) according to the equation:



Given:

- Fe^{2+} is a catalyst for the reaction of formation of iodine.
- $M(\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}) = 248 \text{ g.mol}^{-1}$

1- Preparation of Sodium Thiosulfate Solution

The sodium thiosulfate solution, used to titrate iodine, is prepared by dissolving a mass $m = 25.0 \text{ g}$ of the hydrated powder ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$) in distilled water in order to have a solution of volume $V = 500.0 \text{ mL}$.

1.1- List the essential materials needed to carry out this preparation.

1.2- Calculate the molar concentration C of this solution.

2- Titration of Iodine

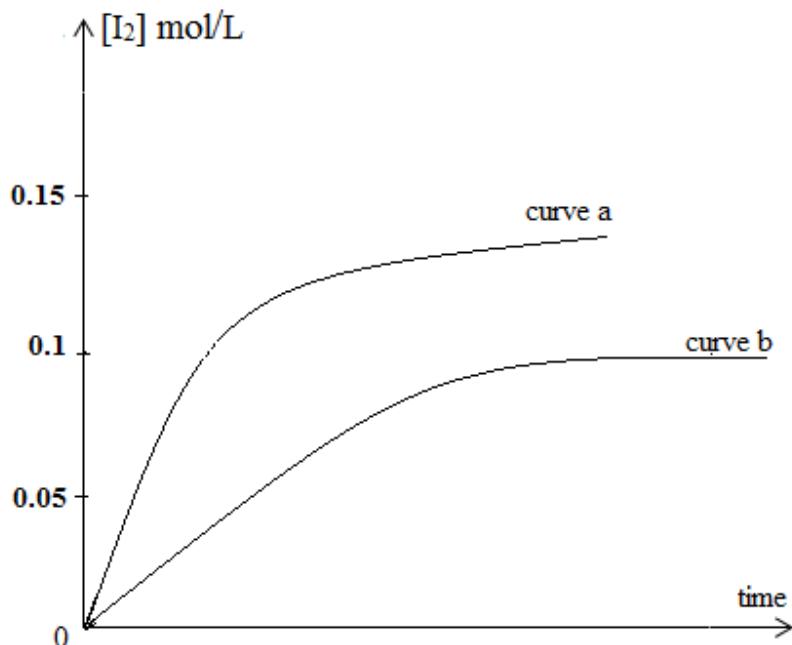
2.1- Propose, by justifying, an experimental way to stop the formation of iodine in each volume taken before carrying out titration.

2.2- Specify the color change at equivalence.

3- Kinetic Study

3.1- Given the shapes of the two curves a and b.

Choose the one that corresponds to the change of the iodine concentration, in the solution S, versus time: $[\text{I}_2] = f(t)$. Justify



3.2- The experimental study shows that this reaction ends at $t = 70$ min.

3.2.1- Define the half-life time of the reaction

3.2.2- Choose, by justifying, among the three following proposals, the appropriate one for the half-life time :

$$t_{1/2} = 35 \text{ min} ; \quad t_{1/2} > 35 \text{ min} ; \quad t_{1/2} < 35 \text{ min}.$$

3.3- The interval of time Δt denotes the end time of reaction for each of the reacting mixtures considered in the table below:

Reacting mixture	Temperature of the mixture	Δt
Mixture (1) : a volume V of solution (S)	40°C	Δt_1
Mixture (2) : a volume V of solution (S) + few mL of a solution of Fe^{2+} ions (without a noticeable change in volume).	20°C	Δt_2

Verify whether Δt_1 and Δt_2 could be compared.

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This Exam Includes Three Exercises. It is Inscribed on 4 Pages Numbered From 1 to 4.
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Answer The Three Following Exercises:

First Exercise (7 points)
Chemical Kinetic

In a laboratory session, one decides to identify two organic compounds before carrying out a kinetic study of the reaction taking place in a mixture of these two organic compounds.

These two compounds are liquids and each one of these two compounds is found in a flask of which the label shows the following indications:

Saturated non cyclic chain carboxylic acid: HA

Saturated non-cyclic chain Monoalcohol; $M = 74 \text{ g.mol}^{-1}$

Flask (1)

Flask (2)

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

1- Identification of The Acid HA

A mass $m = 5.0 \text{ g}$ of the acid HA is taken from the flask (1) and it is dissolved in distilled water in such a way to obtain a volume of 500.0 mL of a solution noted (S_1).

A volume $V_a = 20.0 \text{ mL}$ of the solution (S_1) is titrated with a sodium hydroxide solution ($\text{Na}^+ + \text{HO}^-$) of molar concentration $C_b = 0.20 \text{ mol.L}^{-1}$.

The equation of the titration reaction is: $\text{HA} + \text{HO}^- \rightarrow \text{A}^- + \text{H}_2\text{O}$

- 1.1- Determine the molar concentration of the solution (S_1), knowing that the volume of the basic solution added to reach equivalence is $V_{bE} = 16.6 \text{ mL}$.
- 1.2- Deduce the molar mass of the acid HA.
- 1.3- Identify the acid HA.

2- Identification of The Content of The Flask (2)

A mild oxidation of the alcohol contained in the flask (2) is carried out in the presence of an excess of oxidizing agent. An organic compound is obtained, which gives a yellow-orange precipitate with 2.4-DNPH, but does not react with Fehling's reagent.

- 2.1- Show that the molecular formula of this alcohol is $\text{C}_4\text{H}_{10}\text{O}$.
- 2.2- Identify this alcohol.

3- Evolution with Time

Eight Erlenmeyer flasks numbered 1 through 8, each containing a mixture of 0.20 mol of the acid HA and 0.20 mol of the alcohol of the flask (2), are maintained at constant temperature T. All these Erlenmeyer flasks are prepared at the instant of time $t = 0$ and the remaining acid in the mixture is titrated hourly.

The number of moles of the ester formed after each titration is determined. The results are grouped in the table below:

t (hour)	1	2	3	4	5	6	7	15
n (ester) (10^{-2} mol)	4.5	7.8	10	11.2	11.7	12	12	12

3.1- Write the condensed structural formula of the organic compound obtained in this reaction and name it.

3.2- Plot the curve representing the change in the number of moles of the ester formed with time:

$$n(\text{ester}) = f(t) \text{ in the interval of time } [0 - 7 \text{ hours}].$$

Take the following scales: 2 cm for 1 hour in abscissa and 1 cm for 1.0×10^{-2} mol in ordinate.

3.3- Determine the rate of formation of the ester at $t = 3$ hours.

3.4- The kinetic study realized above is carried out again but with one change: each Erlenmeyer flask is prepared by mixing 0.20 mol of the acid HA, 0.20 mol of the alcohol of the flask (2), and few drops of a catalyst (source of H^+ ions).

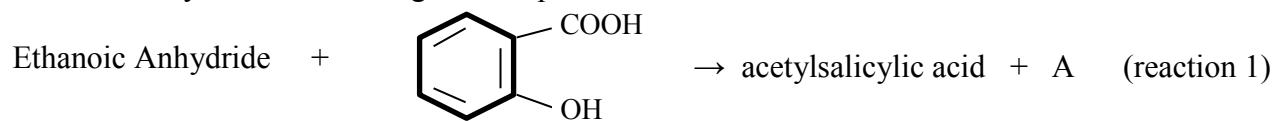
Plot, on the same graph of the question 3.2-, the shape of the curve $n(\text{ester}) = g(t)$. Justify.

Second Exercise (6 points)

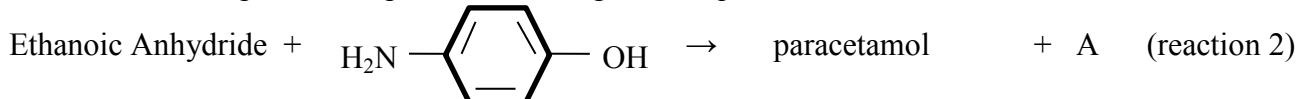
Ethanoic Anhydride

Ethanoic anhydride ($\text{CH}_3 - \text{CO} - \text{O} - \text{CO} - \text{CH}_3$) is an organic compound that participates in the creation of new functions in the organic chemistry.

It reacts with salicylic acid according to the equation:



and it can react with para-aminophenol according to the equation :



1- Preparation of Ethanoic Anhydride

Ethanoic anhydride can be prepared starting from ethanoic acid in the presence of a strong dehydrating agent P_2O_5 .

- 1.1- Write the equation of this reaction.
- 1.2- Specify the importance of using P_2O_5 in this chemical transformation.

2- About The Reactions 1 and 2

- 2.1- Name the functional group created in the acetylsalicylic acid molecule.
- 2.2- Write the condensed structural formula of the compound (A).
- 2.3- Indicate the effect on the yield of the reaction 1 if the ethanoic anhydride is replaced with ethanoic acid. Justify.

3- Preparation of Paracetamol

A mass m containing 3.3×10^{-2} mol of para-aminophenol is dissolved in acidic medium and an excess of ethanoic anhydride is added drop by drop to this mass.

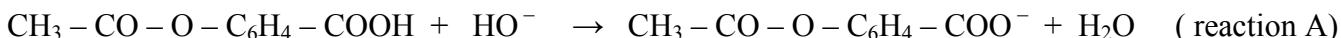
At the end of the preparation, a quantity of 2.5×10^{-2} mol of pure paracetamol is obtained.

3.1- Write the structural formula of paracetamol.

3.2- Determine the yield of this reaction.

4- Acetylsalicylic Acid and Sodium Hydroxide

The action of an aqueous sodium hydroxide solution on acetylsalicylic acid leads to two types of chemical reactions:



4.1- Assign to each one of the reactions A and B the corresponding qualifying terms among the following: acid-base, oxidation-reduction, hydrolysis in basic medium (saponification), slow or fast.

4.2- Name the ions produced in the reaction B.

Third Exercise (7 points)

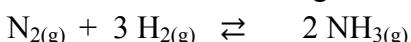
Ammonia NH_3

Ammonia, NH_3 , is a colorless irritating gas. In addition to its usual cooling properties, it is used in the synthesis of many other compounds as fertilizers...

The aim of this exercise is to approach its industrial synthesis as well as its presence in a household product.

1- Industrial Synthesis of Ammonia

Industrially, the synthesis of ammonia is carried out in gaseous phase according to the following equilibrium:



Into a reactor, one introduces a mixture of n moles N_2 gas and $3n$ moles of H_2 gas in the presence of solid iron catalyst.

This synthesis is carried out at a pressure $P = 250$ bar and at a temperature of 450°C .

1.1- Indicate the type of this catalysis. Justify.

1.2- Give the molar composition of the mixture obtained at equilibrium in terms of n and α , where α is the degree of transformation of N_2 at equilibrium.

1.3- Specify how one should act on the pressure in order to increase the degree of transformation (α) of the nitrogen gas N_2 .

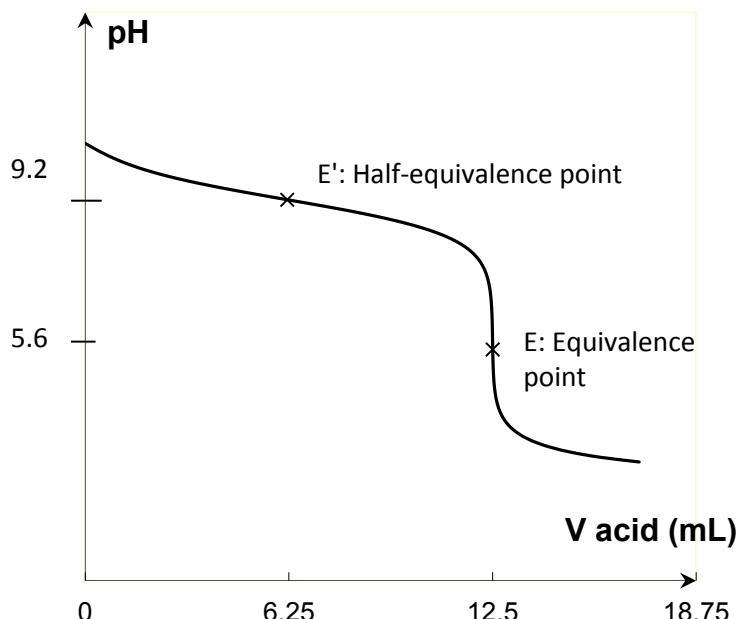
2- Ammonical Household Product

“ *Ammoniaque Alcali* ” is a commercial ammonia solution used for cleaning carpets, removing fat stains; brighten colors of some fabrics...

In order to determine the percentage by mass of ammonia in this commercial solution, one proceeds as follows:

- The commercial solution is diluted 650 times; the obtained solution is noted (S).
- A pH-metric titration is carried out, at 25 °C, of a volume $V_S = 10.0 \text{ mL}$ of the solution (S) with a hydrochloric acid solution ($\text{H}_3\text{O}^+ + \text{Cl}^-$) of concentration $C = 8.0 \times 10^{-3} \text{ mol.L}^{-1}$.

This titration allows us to plot the curve, given below, representing the change of pH as a function of the volume of the acid added.



- 2.1- Draw out, from the graph, two criteria which show that NH_3 is a weak base.
- 2.2- Write the equation of the titration reaction.
- 2.3- Determine the molar concentration C_S of the solution (S) in ammonia.
- 2.4- Deduce the molar concentration of the commercial solution "Ammoniaque Alcali" in ammonia.
- 2.5- Calculate the percentage by mass of ammonia in this commercial solution, knowing that the density of this solution is equal to 0.92 g.mL^{-1} .
Given: $M(\text{NH}_3) = 17 \text{ g.mol}^{-1}$.
- 2.6- Extract, from the graph, the pK_a of the pair $\text{NH}_4^+ / \text{NH}_3$.
- 2.7- In order to prepare a buffer solution of $\text{pH} = 9.2$, one suggests to realize the two following mixtures:

25 mL of the hydrochloric acid solution of concentration C + 40 mL of the solution (S) of concentration C_S .

Mixture (a)

25 mL of the hydrochloric acid solution of concentration C + 60 mL of the solution (S) of concentration C_S .

Mixture (b)

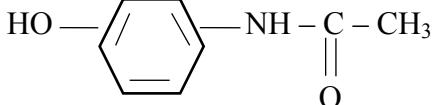
Choose, from these two mixtures, the one that leads to this buffer solution. Justify.

First Exercise

Question	Answer	mark																														
1.1	<p>At the equivalence point : $n(OH^-)$ added to reach equivalence = $n(HA)$ introduced into the beaker</p> $C_b \times V_{bE} = C_a \times V_a$ <p>The Concentration of the solution (S) is: $C_a = \frac{C_b \times V_{bE}}{V_a} = \frac{0.2 \times 16.6}{20} = 16.6 \times 10^{-2} \text{ mol.L}^{-1}$</p>	0.75																														
1.2	<p>$n(HA)$ in 500 mL of solution = $\frac{16.6}{2} \times 10^{-2} = 8.3 \times 10^{-2} \text{ mol.}$</p> <p>Molar mass of the acid: $M(HA) = \frac{m(HA)}{n(HA)} = \frac{5}{8.3 \times 10^{-2}} = 60.2 \text{ g.mol}^{-1}$.</p>	0.75																														
1.3	<p>HA is an alcanoic acid, its general formula is $C_nH_{2n}O_2$. $M(HA) = 14n + 32 = 60.2$; therefore $n = 2$. The acid HA is the ethanoic acid of formula CH_3COOH.</p>	0.75																														
2.1	<p>The general formula of a saturated non-cyclic chain monoalcohol is $C_xH_{2x+1}OH$. $M(alcohol) = 14x + 18 = 74$; therefore $x = 4$ and the molecular formula of this alcohol is $C_4H_{10}O$.</p>	0.5																														
2.2	<p>The product of the mild oxidation of the alcohol is a ketone since it gives a yellow-orange precipitate with 2,4-DNPH but it does not react with Fehling solution. so the alcohol is a secondary alcohol. Its formula is :$CH_3 - CH_2 - \overset{\underset{OH}{\mid}}{CH} - CH_3$ Its name is 2-butanol.</p>	1																														
3.1	<p>The condensed structural formula of the organic compound obtained is: $CH_3 - \overset{\underset{CH_3}{\parallel}}{C} - O - CH - CH_2 - CH_3$; its name is 1-méthylpropyl ethanoate</p>	0.5																														
3.2	<p>The curve is:</p> <table border="1"> <caption>Data points estimated from the graph</caption> <thead> <tr> <th>t(h)</th> <th>n(ester) 10⁻² mol (Grey Curve - B)</th> <th>n(ester) 10⁻² mol (Black Curve)</th> </tr> </thead> <tbody> <tr><td>0</td><td>0</td><td>0</td></tr> <tr><td>1</td><td>8</td><td>4</td></tr> <tr><td>2</td><td>11</td><td>7</td></tr> <tr><td>3</td><td>12</td><td>9</td></tr> <tr><td>4</td><td>12</td><td>10</td></tr> <tr><td>5</td><td>12</td><td>11</td></tr> <tr><td>6</td><td>12</td><td>11.5</td></tr> <tr><td>7</td><td>12</td><td>11.8</td></tr> <tr><td>8</td><td>12</td><td>12</td></tr> </tbody> </table>	t(h)	n(ester) 10 ⁻² mol (Grey Curve - B)	n(ester) 10 ⁻² mol (Black Curve)	0	0	0	1	8	4	2	11	7	3	12	9	4	12	10	5	12	11	6	12	11.5	7	12	11.8	8	12	12	1
t(h)	n(ester) 10 ⁻² mol (Grey Curve - B)	n(ester) 10 ⁻² mol (Black Curve)																														
0	0	0																														
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5	12	11																														
6	12	11.5																														
7	12	11.8																														
8	12	12																														

3.3	<p>The rate of formation of the ester is: $r = \frac{d n(\text{ester})}{dt}$ at $t = 3$ hours.</p> <p>Graphically, it is equal to the slope of the tangent at the curve at the point of abscissa 3 hours.</p> <p>A(0 ; 5.10^{-2} mol) and B(3 heures; 10.10^{-2} mol)</p> $r = \frac{Y_B - Y_A}{X_B - X_A} = \frac{(10 - 5) \times 10^{-2}}{3} = 1.6 \times 10^{-2} \text{ mol.h}^{-1}$	1
3.4	<p>The presence of the catalyst increases the rate of this reaction.</p> <p>At each instant of time t, n (ester) formed (in the presence of H^+) is greater than n (ester) formed (in the absence of H^+).</p>	0.75

Second Exercise

Question	Answer	mark
1.1	The equation of the reaction: $2 \text{CH}_3\text{COOH} \rightarrow (\text{CH}_3\text{CO})_2\text{O} + \text{H}_2\text{O}$	0.75
1.2	P_2O_5 is a strong dehydrating agent that absorbs the water formed in this reaction therefore shifting the equilibrium in the direction of formation of the anhydride.	0.5
2.1	Chemical function created in the reaction 1: ester function	0.5
2.2	When ethanoic acid replaces ethanoic anhydride, the yield of the reaction decreases since the reaction becomes limited.	0.75
2.3	The formula of A is CH_3COOH	0.5
3.1	The structural formula of paracetamol is:	0.5
		
3.2	<p>The yield of this reaction: yield = $\frac{n(\text{paracetamol}) \text{ experimental}}{n(\text{paracetamol}) \text{ theoretical}} = \frac{n_1}{n_2}$</p> <p>$n_2 = n(\text{para-aminphenol}) \text{ initial} = 0.033 \text{ mol}$.</p> <p>with $n_1 = 0.025 \text{ mol}$, the yield is equal to 0.757, or 75.7 %.</p>	1
4.1	Reaction A : acid-base and fast. Reaction B : hydrolysis in basic medium.	1
4.2	the produced ions: ethanoate ion and salicylate ion.	0.5

Third Exercise

Question	Answer	mark
1.1	This is a heterogeneous catalysis since the reactants and the catalyst are in different phases.	0.5
1.2	$N_2 : n(1 - \alpha) \text{ mol}$; $H_2 : 3n(1 - \alpha) \text{ mol}$ and $NH_3 : 2n\alpha \text{ mol}$	1
1.3	In order to increase the degree of transformation α , one should increase the total pressure under which the synthesis is carried out (Le Chatelier's principle).	1
2.1	The two criteria are: - The curve shows two inflection points. - The pH at equivalence is less than 7.0	0.5
2.2	The equation of the titration reaction is: $H_3O^+ + NH_3 \rightarrow NH_4^+ + H_2O$	0.5
2.3	At the equivalence : $n(H_3O^+)$ added to reach equivalence = $n(NH_3)$ introduced into the beaker $C \times V_E = C_S \times V$ $C_S = \frac{C \times V_E}{V_S} = \frac{8 \times 10^{-3} \times 12.5}{10} = 0.01 \text{ mol.L}^{-1}$	1
2.4	The Concentration of the commercial solution is: $C_0 = 0.01 \times 650 = 6.5 \text{ mol.L}^{-1}$	0.5
2.5	% by mass of the commercial solution in NH_3 = $\frac{C_0 \times M(NH_3)}{d(solution) \times 10}$ with $d(solution) = 0.92 \text{ g/mL}$; therefore % by mass in $NH_3 = 12.0 \%$	1
2.6	$pK_a(NH_4^+ / NH_3) = pH(\text{mixture})$ at half-equivalence = 9.2	0.25
2.7	in order to obtain a buffer solution of $pH = 9.2$, the ratio of the volume of the base over that of the acid should be equal to $6.25/10$ the mixture (a) is the appropriate one since the ratio in this mixture is equal to $25/40 = 6.25/10$	0.75

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Answer the three following Exercises:

First Exercise (7 points)
Benzoic Acid

Benzoic acid is a white solid of formula C_6H_5COOH . It is used as a food preservative.

Given:

- $M(\text{benzoic acid}) = 122 \text{ g.mol}^{-1}$
- $pK_a(H_3O^+/H_2O) = 0$; $pK_a(C_6H_5COOH/C_6H_5COO^-) = 4.2$; $pK_a(H_2O/HO^-) = 14$

1- Study of a Benzoic Acid Solution

A volume $V = 500.0 \text{ mL}$ of an aqueous benzoic acid solution (S) of concentration $C = 0.01 \text{ mol.L}^{-1}$ is prepared.

- 1.1- Calculate the mass m of benzoic acid needed for the preparation of the solution (S).
- 1.2- Choose, from the following list, the materials needed for this preparation :
volumetric flask: 250 and 500 mL ; Erlenmeyer flask 500 mL ; precision balance ; spatula ; watch glass and pH-meter.
- 1.3- Write the equation of the reaction of benzoic acid with water.
- 1.4- Justify that benzoic acid is a weak acid knowing that the pH of the solution (S) is equal to 3.1

2- Reaction of Benzoic Acid with a Strong Base

A volume of a sodium hydroxide solution ($Na^+ + HO^-$) is added to a sample of the solution (S).

- 2.1- Place, on a pK_a axis, the different conjugate acid/base pairs involved.
- 2.2- Write the equation of the reaction that took place between the strongest acid and the strongest base.
- 2.3- Show that this reaction is complete.

3 - Reaction of Benzoic Acid with a Weak Base

A volume V_1 of the solution (S) is added to a volume $V_2 = 200 \text{ mL}$ of a sodium benzoate solution ($C_6H_5COO^- + Na^+$) of concentration $C = 0.01 \text{ mol.L}^{-1}$.

The pH of the obtained buffer solution is equal to 4.0

- 3.1- Determine the volume V_1 .
- 3.2- List the characteristics of the obtained solution.

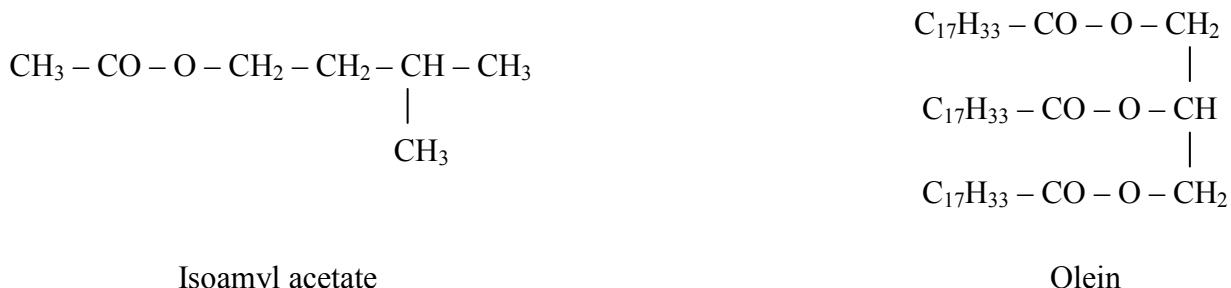
Second Exercise (6 points)

Hydrolysis of esters

Esters are commonly prepared by the reaction of alcohols and carboxylic acids, where water is eliminated. Esters are often responsible for the natural aroma of fruits. They are widely used in synthetic flavors and in perfume industry.

Esters functions are found in many biological molecules, especially triglycerides.

The aim of this exercise is to approach the hydrolysis of the two following chemical compounds:



1- Hydrolysis in acidic medium

Isoamyl acetate is used as a food aroma having the odor and flavor of banana.

- 1.1- Give the systematic name of isoamyl acetate.
- 1.2- Specify whether the isoamyl acetate molecule is a chiral molecule.
- 1.3- Write the equation of the hydrolysis of isoamyl acetate, in the presence of sulfuric acid as a catalyst.
- 1.4- Name the two products of this reaction.

2- Hydrolysis in basic medium.

Olein is a triglyceride naturally occurring in oils and solid vegetable fatty substances. It is used in the production of soap.

Given:

- Soap (sodium oleate) is practically insoluble in a saturated salty water solution.
- M (sodium oleate) = 304 g.mol⁻¹.

In order to produce soap, one proceeds as follows:

First step: A mixture of 2.0×10^{-2} mol of olein, an excess of a concentrated sodium hydroxide solution, a certain volume of ethanol and few boiling stones is heated to reflux for 30 minutes.

Second step: The mixture is left to cool then it is poured into a beaker containing a saturated aqueous sodium chloride solution.

Third step: The obtained mixture is filtered. The obtained solid is washed, dried and weighed.

The actual mass obtained is $m_{\text{act}} = 11.2$ g.

The equation of the reaction that took place, in the first step, is given below:

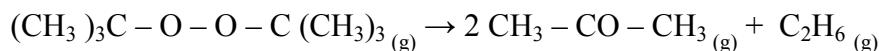


- 2.1- Choose, from the following list, the most appropriate materials needed to carry out the reflux heating :
- Heating mantle, round bottom flask, graduated buret, 100 mL beaker, 100 mL volumetric flask, condenser.
- 2.2- Specify the importance of using a saturated sodium chloride solution in the second step.
- 2.3- Oleate ion $C_{17}H_{33}COO^-$ consists of two parts qualified as hydrophilic and hydrophobic.
- 2.3.1- Give the meaning of the two terms; hydrophilic and hydrophobic.
 - 2.3.2- Indicate, in the oleate ion, the hydrophilic part and the hydrophobic part.
- 2.4- Determine the yield of this preparation.
- 2.5- It is suggested to realize separately the two following changes to the above carried out experiment:
- Use an initial quantity of olein less than 2.0×10^{-2} mol.
 - Extend the heating time.

Indicate the effect of each one of these two changes on the yield of this reaction. Justify.

Third Exercise (7 points) Kinetic Study

Ditertbutyl peroxide (A) dissociates in gaseous phase according to a slow and complete reaction, the equation of which is:



At constant temperature $T = 420$ K, n_0 mol of the compound (A) is introduced in an evacuated reactor of constant volume V . At different instants of time t of the evolution of reacting system, the pressure P of the gaseous mixture is measured.

The concentration of ethane C_2H_6 is deduced at these instants of time t .

The results are listed in the table below:

t (min)	2	6	10	14	18	26	34	46
$[C_2H_6]$ (10^{-4} mol.L $^{-1}$)	1.5	3.6	5.8	7.8	9.7	13.2	16.0	18.9

Given: Ideal gas constant: $R = 0.08$ L.atm.K $^{-1}$. mol $^{-1}$.

1- Preliminary Study

- 1.1- Show that the initial concentration of the compound (A) is equal to 71.4×10^{-4} mol .L $^{-1}$, knowing that the pressure P_0 , prevailing in the reactor at $t = 0$, is equal to 0.24 atm.
- 1.2- Establish the relation among the pressure P of the gaseous mixture at an instant of time t , the pressure x of C_2H_6 at this instant of time t and the initial pressure P_0 .
- 1.3- Calculate the pressure of the gaseous mixture at the end of the reaction.

2- Kinetic Study

2.1- Plot the curve representing the change of the concentration of C_2H_6 as a function of time:

$[C_2H_6] = f(t)$ in the interval of time [0 - 46 min]. Take the following scales:

1 cm for 4 min in abscissa and 1 cm for 2.0×10^{-4} mol.L⁻¹ in ordinate.

2.2- Determine the rate of formation of ethane at the instant of time $t = 30$ min.

2.3- Deduce the rate of formation of propanone at this instant of time.

2.4- Verify whether the half-life time of the reaction is reached in the interval of time: [0 – 46 min].

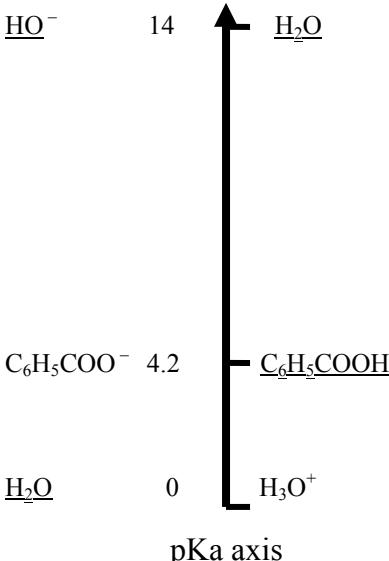
2.5- The kinetic study realized above is carried out again at a temperature $T_1 > T$.

Plot, on the same graph of the part 2.1, the shape of the curve representing the change of the concentration of C_2H_6 as a function of time $[C_2H_6] = g(t)$. Justify.

	امتحانات الشهادة الثانوية العامة الفرع : علوم عامة وعلوم حياة	وزارة التربية والتعليم العالي المديرية العامة للتربية دائرة الامتحانات
		مشروع معيار التصحيح

Answer the three following exercises:

**First Exercise (7 points)
Benzoic Acid**

Part of the Q	Answer	Mark
1.1	n(acid) needed = $C \times V = 0.01 \times 0.5 = 5 \times 10^{-3}$ mol . m(acid) needed = $n(\text{acid}) \times M(\text{acid}) = 5 \times 10^{-3} \times 122 = 0.61\text{g}$.	1
1.2	The materials required for this preparation : Volumetric flask 500 mL ; precision balance ; spatula and watch glass .	1
1.3	The equation of the reaction is: $\text{C}_6\text{H}_5 - \text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5 - \text{COO}^- + \text{H}_3\text{O}^+$	0.5
1.4	pH = 3.1 > - log C = - log 0.01 = 2, that characterizes a weak acid. The benzoic acid is a weak acid.	0.75
2.1	The pairs involved on pKa axis are : 	0.75
2.2	The equation of the reaction is: $\text{C}_6\text{H}_5 - \text{COOH} + \text{HO}^- \rightleftharpoons \text{C}_6\text{H}_5 - \text{COO}^- + \text{H}_2\text{O}$	0.5
2.3	The constant of this reaction is : $K_r = 10^{pK_a(\text{H}_2\text{O}/\text{HO}^-) - pK_a(\text{C}_6\text{H}_5 - \text{COO}^-/\text{C}_6\text{H}_5 - \text{COO}^-)} = 10^{14 - 4.2} > 10^4$ Therefore , this reaction is complete	0.75
3.1	The initial quantities of the acid $\text{C}_6\text{H}_5 - \text{COOH}$ and its conjugate base $\text{C}_6\text{H}_5 - \text{COO}^-$ are conserved in the solution obtained. According to the relation: $\text{pH} = \text{pKa} + \log \frac{[\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]}$, then $\frac{[\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]} = 10^{4 - 4.2} = 0.63$	1

	with $\frac{[C_6H_5COO^-]}{[C_6H_5COOH]} = \frac{C.V_2 / V(\text{mixture})}{C.V_1 / V(\text{mixture})} = \frac{V_2}{V_1}$ where $V_1 = 317.4 \text{ mL}$.	
3.2	It is a buffer solution , the pH of which varies slightly upon: - addition of a moderate quantity of a strong acid; - addition of a moderate quantity of a strong base; - or by dilution.	0.75

**Second Exercise (6 points) G.S
Preparation of an Ester**

Part of the Q	Answer	Mark
1.1	let $C_xH_yO_z$ be the molecular formula of the compound (A). According to the law of definite proportions : $\frac{M(A)}{100} = \frac{12x}{\%(\text{C})} = \frac{1y}{\%(\text{H})} = \frac{16z}{\%(\text{O})}$ with $\%(\text{O}) = 100 - (\% \text{ C} + \% \text{ H}) = 100 - (48.65 + 8.11) = 43.24$ and $M(A) = 74$. then : $x = 3 ; y = 6 ; z = 2$ and the molecular formula of (A) is : $C_3H_6O_2$.	0.75
1.2	The condensed structural formulas of the possible isomers are: $\begin{array}{c} \text{CH}_3-\text{CH}_2-\underset{\underset{\text{O}}{\parallel}}{\text{C}}-\text{OH} \\ \\ \text{H}-\text{C}-\underset{\underset{\text{O}}{\parallel}}{\text{O}}-\text{CH}_2-\text{CH}_3 \end{array} \text{ and } \begin{array}{c} \text{CH}_3-\underset{\underset{\text{O}}{\parallel}}{\text{C}}-\text{O}-\text{CH}_3 \\ \\ \text{O} \end{array}$	0.75
1.3	pH = 3.1 < 7, this means that compound (A) has an acid character. So (A) is propanoic acid of formula $\text{CH}_3-\text{CH}_2-\text{COOH}$.	0.5
2.1	The equation of the reaction is: $\begin{array}{c} \text{CH}_3-\text{CH}_2-\underset{\underset{\text{O}}{\parallel}}{\text{C}}-\text{OH} + \text{CH}_3-\underset{\underset{\text{CH}_3}{ }}{\text{CH}}-\text{CH}_2\text{OH} \rightleftharpoons \text{CH}_3-\text{CH}_2-\underset{\underset{\text{O}}{\parallel}}{\text{C}}-\text{O}-\text{CH}_2-\underset{\underset{\text{CH}_3}{ }}{\text{CH}}-\text{CH}_3 + \text{H}_2\text{O} \end{array}$	0.75
2.2	Its systematic name is : 2-methylpropylpropanoate	0.25
2.3	The yield of the reaction is: $\text{Yield} = \frac{n(\text{ester}) \text{ actual}}{n(\text{ester}) \text{ theoretical}} = \frac{n_1}{n_2}$ With $n_1 = \frac{m(\text{ester}) \text{ actual}}{M(\text{ester})} = \frac{13}{130} = 0.1 \text{ mol}$ and $n_2 = n(\text{acid}) \text{ initial} = 0.2 \text{ mol}$. Where Yield = 0.5 , the % yield is 50%.	1

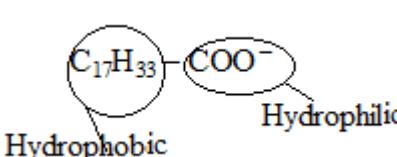
2.4	<p style="text-align: center;">Alcohol + acid \rightleftharpoons ester + water</p> <table border="0" style="width: 100%;"> <tr> <td>Initial state</td><td>0.2 mol</td><td>0.2 mol</td><td>0</td><td>0</td></tr> <tr> <td>final state</td><td>0.1 mol</td><td>0.1 mol</td><td>0.1 mol</td><td>0.1 mol</td></tr> </table> <p>The quotient of this reaction :</p> $Q_r = \frac{[\text{ester}][\text{water}]}{[\text{acid}][\text{alcohol}]} = \frac{n(\text{ester}) / V \times n(\text{water}) / V}{n(\text{acid}) / V \times n(\text{alcohol}) / V} = \frac{0.1 \times 0.1}{0.1 \times 0.1} = 1$ <p>Since $Q_r < K$, therefore the equilibrium is not reached.</p>	Initial state	0.2 mol	0.2 mol	0	0	final state	0.1 mol	0.1 mol	0.1 mol	0.1 mol	1
Initial state	0.2 mol	0.2 mol	0	0								
final state	0.1 mol	0.1 mol	0.1 mol	0.1 mol								
2.5.1	<p>The possible formulas are:</p> $\text{CH}_3 - \text{CH}_2 - \text{CO} - \text{Cl}$ and $\text{CH}_3 - \text{CH}_2 - \text{CO} - \text{O} - \text{CO} - \text{CH}_2 - \text{CH}_3$	0.5										
2.5.2	<p>The two advantages are :</p> <p>The esterification reaction becomes complete and fast.</p>	0.5										

Third exercise (7 points) Kinetic Study

Part of the Q	Answer	Mark
1.1	<p>According to the equation of ideal gases ,</p> $[\text{A}]_{\text{initial}} = \frac{P_0}{RT} = \frac{0.24}{0.08 \times 420} = 71.4 \times 10^{-4} \text{ mol.L}^{-1}$	0.75
1.2	<p>At each instant t, we have:</p> $P(\text{A}) = P_0 - x$; $P(\text{propanone}) = 2x$ and $P(\text{ethane}) = x$. <p>The total pressure is therefore : $P = P_0 - x + 2x + x = P_0 + 2x$.</p>	1
1.3	<p>At the end of reaction , $P(\text{gaseous mixture}) = 3 \times P_0 = 3 \times 0.24 = 0.72 \text{ atm}$.</p>	0.75
2.1	<p>The curve is :</p> <p>A graph showing the concentration of ethane, $[C_2H_6]$, in $10^{-3} \text{ mol.L}^{-1}$ on the y-axis versus Time in minutes on the x-axis. The y-axis ranges from 0 to 2 with increments of 0.2. The x-axis ranges from 0 to 50 with increments of 10. A smooth curve starts at the origin (0,0) and increases parabolically. A straight tangent line is drawn at the point where $x=0$ and $y=0.4$, labeled as point A(0, 0.4). Another point on the curve is labeled as B(30, 1.47).</p>	1
2.2	<p>The rate of formation of ethane is defined by: $r = \frac{d[C_2H_6]}{dt}$. Its value is equal to the slope of the tangent drawn on the curve $[C_2H_6] = f(t)$ at a point of abscissa $t = 30 \text{ min}$.</p> $r(C_2H_6)_t = \frac{y_B - y_A}{t_B - t_A} = \frac{(1.47 - 0.4) \times 10^{-3}}{30} = 3.57 \times 10^{-5} \text{ mol.L}^{-1} \cdot \text{min}^{-1}$	1

2.3	From the equation, the coefficient of propanone is twice that of ethane; consequently, $r(\text{propanone}) = 2 r(\text{C}_2\text{H}_6) = 7.14 \times 10^{-5} \text{ mol.L}^{-1}.\text{min}^{-1}$.	0.5
2.4	Half-life time of the reaction is the time at which the concentration of C_2H_6 attains half its maximal value. $[\text{C}_2\text{H}_6] \text{ at } t_{1/2} = [\text{C}_2\text{H}_6] \text{ max} / 2 = [\text{A}] \text{ initial} / 2 = 35.7 \times 10^{-4} \text{ mol.L}^{-1} > [\text{C}_2\text{H}_6] \text{ at } t = 46 \text{ min.}$ So the half-life time is not reached.	1
2.5	When the temperature increases, the rate of formation of ethane increases. At each instant, $[\text{C}_2\text{H}_6] \text{ at } T_1 > [\text{C}_2\text{H}_6] \text{ at } T$.	1

Second Exercise (6 points) L.S Hydrolysis of esters

Part of the Q	Answer	Mark
1.1	The systematic name of isoamyl acetate is: 3- methylbutylethanoate.	0.25
1.2	The molecule of isoamyl acetate is not chiral since it does not contain an asymmetric carbon.	0.5
1.3	The equation of this hydrolysis reaction is : $\text{CH}_3 - \text{CO} - \text{O} - \text{CH}_2 - \text{CH}_2 - \underset{\substack{ \\ \text{CH}_3}}{\text{CH}} - \text{CH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3 - \text{COOH} + \text{HOCH}_2 - \underset{\substack{ \\ \text{CH}_3}}{\text{CH}_2} - \underset{\substack{ \\ \text{CH}_3}}{\text{CH}} - \text{CH}_3$	0.5
1.4	the two products are : ethanoic acid and 3-methyl-1-butanol.	0.5
2.1	the convenient materials needed to realize reflux heating are: Heating mantle, round bottom flask and condenser.	0.75
2.2	The saturated solution of sodium chloride helps the precipitation almost complete of soap since soap is insoluble in this solution.	0.5
2.3.1	Hydrophilic: loves water. Hydrophobic: hates water.	0.5
2.3.2	The formula is : 	0.5
2.4	$\text{yield} = \frac{n(\text{soap})_{\text{actual}}}{n(\text{soap})_{\text{theoretical}}} = \frac{n_1}{n_2}$ With $n_1 = \frac{m_{\text{act}}}{M(\text{soap})} = \frac{11.2}{304} = 3.7 \times 10^{-2} \text{ mol.}$ and $n_2 = 3 \times n(\text{olein initial}) = 3 \times 2.0 \times 10^{-2} = 6.0 \times 10^{-2} \text{ mol.}$ then $\text{yield} = 0.616$	1
2.5	- Using an initial quantity of oleine less than $2.0 \times 10^{-2} \text{ mol}$: n_1 decreases and n_2 decreases but the ratio of these two quantities does not change (at the same experimental conditions); then the yield of reaction does not change . - Extend the heating time: n_1 increases but the quantity n_2 does not change (at the same experimental conditions); then the yield of the reaction increases.	0.5 0.5

الاسم:
الرقم:

مسابقة في مادة الكيمياء
المدة: ساعتان

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

Answer the Three Following Exercises:

Exercise 1: (6 points) Kinetic of the Reaction of Magnesium with Hydrochloric Acid

Magnesium metal is attacked by a hydrochloric acid solution ($\text{H}_3\text{O}^+ + \text{Cl}^-$) according to a slow and complete reaction as shown by the equation below:



In order to study the kinetic of this reaction the following experiment is carried out at constant temperature.

A volume $V_1=100$ mL of a hydrochloric acid solution (S_1) of molar concentration $C_1 = 0.20 \text{ mol.L}^{-1}$ is introduced into an Erlenmeyer flask.

At instant $t = 0$, a mass $m = 0.15$ g of powdered magnesium is added to the Erlenmeyer flask and the chronometer is set to function.

The volume V , of the released hydrogen gas H_2 , is measured at different instants t , and then the numbers of moles of hydrogen gas are deduced at these instants. The obtained values are given in document-1.

t (s)	20	40	60	80	100	120
n(H_2) (10^{-5} mol)	50	90	123	152	176	195

Document-1

Given: $M_{(\text{Mg})} = 24 \text{ g.mol}^{-1}$

1. Preparation of The Acid Solution

Available is a bottle of an aqueous hydrochloric acid solution (S_0) labelled with the following indications: 32.3% by mass of the acid, density $d = 1.13 \text{ g.mL}^{-1}$, $M_{(\text{HCl})} = 36.5 \text{ g.mol}^{-1}$.

1.1. Show that the molar concentration C_0 of the solution (S_0) is close to 10 mol.L^{-1} .

1.2. The solution (S_1) is prepared starting from the solution (S_0).

1.2.1. Calculate the volume V_0 withdrawn from (S_0) to prepare 200 ml of solution (S_1).

1.2.2. Choose, from document-2, the most precise glassware for the preparation of (S_1)

- Volumetric pipets: 5mL and 10mL
- Graduated pipets: 2mL and 5 mL

- Volumetric flasks: 200mL, 250 mL and 500 mL
- Graduated cylinders: 5mL and 10 mL

Document -2

2. Kinetic Study

- 2.1. Determine the limiting reactant.
- 2.2. Specify whether the time $t = 120\text{s}$ represents the end of the reaction.
- 2.3. Plot the curve that represents the variation of the number of moles of H_2 gas as a function of time, $n(\text{H}_2)=f(t)$ within the time interval $[0 ; 120\text{s}]$.
Take the following scale: abscissa: 1cm for 10s ; ordinate: 1cm for $20 \times 10^{-5} \text{ mol}$.
- 2.4. Deduce, graphically, the variation of the rate of formation of H_2 as a function of time.
- 2.5. The preceding experiment is repeated with one modification, the solution (S_1) is replaced by hydrochloric acid solution (S_2) of concentration C_2 , where $C_2 > C_1$.
Given the following propositions:
 - 2.5.1. The end of the reaction is reached faster.
 - 2.5.2. The number of moles of hydrogen gas produced at the end of the reaction increases.In the case the proposition is correct. Justify. In the case, the proposition is false. Correct it.

Exercise 2 (7 points)

Titration of a Basic Solution

Two flasks are available in the laboratory:

The first contains a white solid of benzoic acid $\text{C}_6\text{H}_5\text{COOH}$ and the second contains sodium hydroxide solution ($\text{Na}^+ + \text{HO}^-$) of molar concentration $C_b \text{ mol.L}^{-1}$.

The aim of this exercise is to determine the concentration C_b of the basic solution.

Given:

- This study is realized at 25°C .
- Molar mass of benzoic acid: $M = 122 \text{ g.mol}^{-1}$.

1. Behavior of Benzoic Acid in Water

One prepares a solution (S) of benzoic acid of molar concentration $C_a = 6.5 \times 10^{-3} \text{ mol.L}^{-1}$. The pH measurement of this solution gives a value of 3.2

- 1.1. Write the equation of the reaction between benzoic acid and water.
- 1.2. Determine the dissociation coefficient α of benzoic acid. Deduce that benzoic acid is a weak acid.

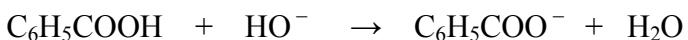
2. pH-metric Titration of The Sodium Hydroxide Solution

A volume $V_a=10.0 \text{ mL}$ of benzoic acid solution of concentration $C_a=6.5 \times 10^{-3} \text{ mol.L}^{-1}$, is taken and introduced into a beaker, then a certain volume of distilled water is added to immerse properly the pH - meter electrode. The sodium hydroxide solution of concentration C_b is added progressively.
Some of the experimental results are shown in document-1.

$V_b \text{ (mL)}$	0	10	16.2
pH	3.5	4.4	7.6

Document-1

The equation of the titration reaction is:



2.1. Indicate the appropriate glassware to:

2.1.1. Withdraw the volume V_a of the benzoic acid solution.

2.1.2. Add progressively the sodium hydroxide solution.

2.2. Determine the concentration C_b of the basic solution, knowing that the volume added at equivalence is $V_{bE} = 16.2\text{mL}$.

2.3. Justify, based on the chemical species present, the basic character of the solution obtained at equivalence.

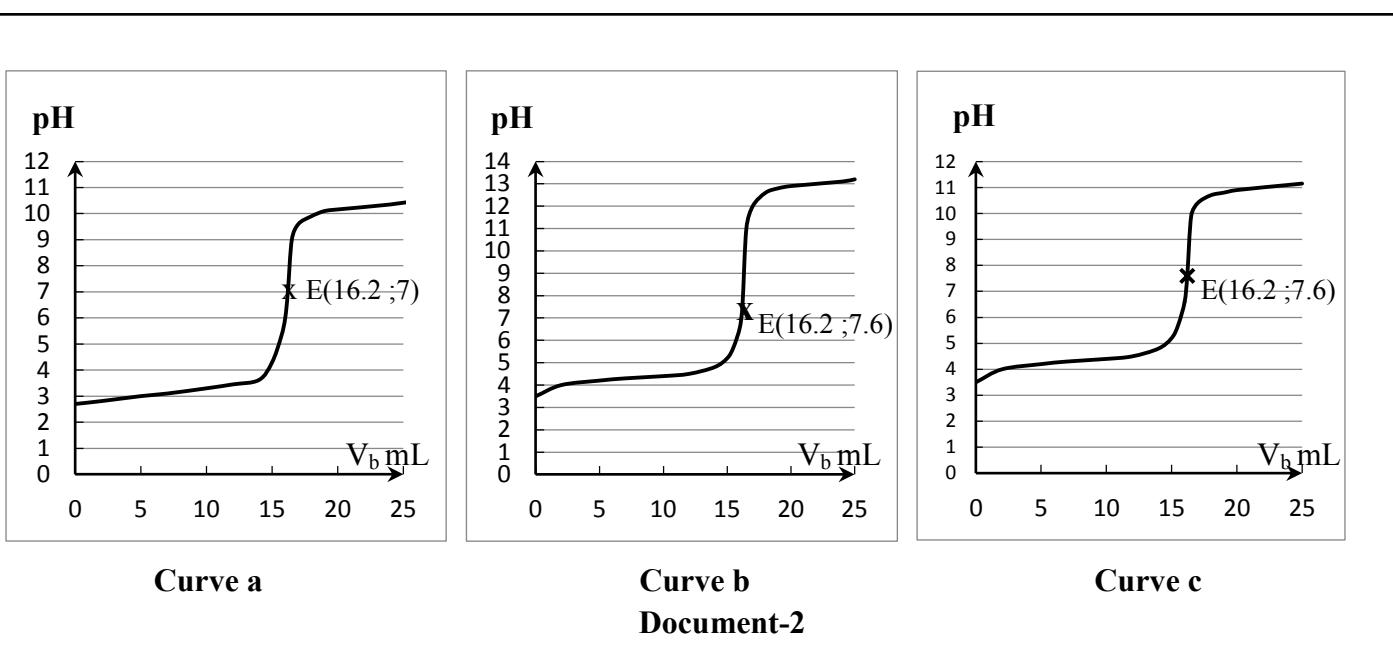
2.4. For a volume V_b of the base added, where $V_b < V_{bE}$.

2.4.1. Show that the pH of the obtained solution is given by the following relation:

$$\text{pH} = \text{pK}_a + \log \frac{V_b}{V_{bE} - V_b}.$$

2.4.2. Referring to document-1, deduce that the pK_a value of the $\text{C}_6\text{H}_5\text{COOH} / \text{C}_6\text{H}_5\text{COO}^-$ pair is equal to 4.2

2.5. Given the three curves a, b, and c in document-2 which represent the variation of the pH as a function of the volume of the base added. Specify whether each curve corresponds to the above realized titration.



Exercise 3 (7 points)

Study of an Esterification Reaction

Four flasks are available each contains, one of the following organic compounds:
Propanoic acid, 1-propanol, 3-pentanol and 2-butanol.

The available flasks are numbered and their contents are noted as follows:

Number of flask	1	2	3	4
Organic compound	A	B	C	D

Document-1

The aim of this exercise is to identify the content of each flask in order to carry out an esterification reaction.

1. Identification of The Content of Each Flask

The following tests are carried out:

Chemical test	Experimental result
Mild oxidation of compound (A) by an acidified potassium permanganate solution.	An organic compound (F) is obtained which reacts with DNPH and Fehling solution.
The pH of an aqueous solution of compound (B) is measured.	The pH is clearly less than 7.0

Document-2

1.1. Referring to document-2, identify the organic compounds (A) and (B).

1.2. Knowing that the molecule of compound (C) is chiral:

1.2.1. Write its condensed structural formula. Justify its chirality.

1.2.2. Represent according to Cram its two enantiomers.

1.3. Give the condensed structural formula of the compound (D).

2. Esterification Reaction

- For an initial equimolar mixture of a carboxylic acid and a secondary alcohol, the yield of the reaction at equilibrium is 60%.
- Density of the propanoic acid is $d = 0.99 \text{ g.mL}^{-1}$.
- Molar masses in g.mol^{-1} : M (propanoic acid) = 74 ; M (E) = 130.

Document-3

A mixture of 0.25 mol of 2-butanol and a volume $V = 30 \text{ mL}$ of propanoic acid is heated to reflux. At instant t, heating is stopped. The mass of the ester (E) obtained at instant t is 19.5 g.

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

Name the obtained ester (E).

2.2. Calculate the initial number of moles of propanoic acid.

2.3. Determine the yield of this reaction at instant t.

2.4. Referring to document-3, verify whether the equilibrium is reached at this instant t.

2.5. It is suggested to realize the following modifications during this study:

- Modification 1: Extend the duration of heating.
- Modification 2: Add a catalyst to the initial mixture of the reactants.

Specify the effect of each modification on the yield of this reaction.

Exercice 1 (6 points)

Kinetic of the Reaction of Magnesium with Hydrochloric Acid

Part of the Q.	Answer	Mark
1.1	$C_0 = \frac{n_{HCl}}{V_s} = \frac{m_{HCl}}{M \times V_s} = \frac{dxV_s \times P}{M \times V_s \times 100} = \frac{1130 \times 32.3}{36.5 \times 100} = 10 \text{ mol.L}^{-1}$	0.75
1.2.1	upon dilution the number of moles of solute is conserved $n_0 = n_1 ; C_0 V_0 = C_1 V_1 ; V_0 = \frac{C_1 V_1}{C_0} = \frac{0.2 \times 0.2}{10} = 0.004 \text{ L ou } 4 \text{ mL}$	0.5
1.2.2	Graduated pipet of 5mL, and volumetric flask 200mL	0.5
2.1	$n_{Mg} = \frac{m_{Mg}}{M} = \frac{0.15}{24} = 6.25 \times 10^{-3} \text{ mol}$ $n_{H_3O^+} = C_1 V_1 = 0.2 \times 0.1 = 0.02 \text{ mol}$ $R_{Mg} = \frac{n_{Mg}}{1} = 6.25 \times 10^{-3} < R_{H_3O^+} = \frac{n_{H_3O^+}}{2} = 10 \times 10^{-3}$; Mg is the limiting reactant	0.75
2.2	At the end of the reaction: $\frac{n_{H_2(\infty)}}{1} = \frac{n_{Mg(0)}}{1} = 6.25 \times 10^{-3} = 6.25 \times 10^{-5} \text{ mol}$ From the table $n(H_2)_{120} = 195 \times 10^{-5} \text{ mol} < 625 \times 10^{-5} \text{ mol}$. Then the time $t = 120 \text{ s}$ doesn't represent the end of the reaction.	0.75
2.3	<p style="text-align: center;">$n_{H_2} \cdot 10^{-5} \text{ mol}$</p> <p style="text-align: right;">1</p>	
2.4.	The rate of formation of hydrogen gas is equal to the positive slope of the tangent drawn on the curve $n(H_2) = f(t)$ at point of abscissa t . From the curve the slope of the tangent 1 is greater than the slope of tangent 2 therefore the rate of formation of H_2 decreases with time.	0.75
2.5.1	True. Concentration is a kinetic factor. When concentration of H_3O^+ increases the rate of the reaction increases and hence the end of the reaction is attained rapidly (faster).	0.5

2.5.2	False. The number of mole of hydrogen H ₂ at the end of the reaction depends only on the limiting reactant, since the limiting reactant Mg doesn't change, then the number of mole of H ₂ final remains the same.	0.5
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Exercise 2 (7 points)

Titration of a Basic Solution

Part of the Q	Answer	Mark
1.1.	The equation of the reaction: $C_6H_5COOH + H_2O \rightleftharpoons C_6H_5COO^- + H_3O^+$	0.5
1.2	$\alpha = \frac{n_{C_6H_5COOH(\text{reacted})}}{n_{C_6H_5COOH(\text{initial})}} = \frac{n_{H_3O^+(\text{formed})}}{n_{C_6H_5COOH(\text{initial})}} = \frac{[H_3O^+]xV(s)}{[C_6H_5COOH]xV(s)}$ $\alpha = \frac{[H_3O^+]_{(\text{formed})}}{[C_6H_5COOH]_0} = \frac{10^{-\text{pH}}}{C_a} = \frac{10^{-3.2}}{6.5 \times 10^{-3}} = 0.097 \text{ or } 9.7\%$ $\alpha < 1$ then benzoic acid is a weak acid	1 0.25
2.1.1.	Pipet of 10 mL	0.25
2.1.2.	Graduated buret	0.25
2.2	At equivalence : n (HO ⁻) added from the burette = n (C ₆ H ₅ COOH) Introduced into the beaker $C_b \times V_{bE} = C_a \times V_a$; then $C_b = \frac{C_a \times V_a}{V_{bE}} = \frac{6.5 \times 10^{-3} \times 10}{16.2} = 4.0 \times 10^{-3} \text{ mol.L}^{-1}$	1
2.3	At equivalence, the chemical species present are: Na ⁺ , C ₆ H ₅ COO ⁻ and water. Na ⁺ is spectator ion, H ₂ O neutral and C ₆ H ₅ COO ⁻ is the conjugate base which renders the nature of the solution basic.	0,75
2.4.1	$\begin{array}{ccccccc} C_6H_5COOH & + & HO^- & \rightarrow & C_6H_5COO^- & + & H_2O \\ \text{Initial state} & & C_a V_a & & C_b V_b & - & \text{solvent} \\ \text{Obtained solution} & & (C_a V_a - C_b V_b) & & 0 & C_b V_b & \text{solvent} \\ \text{HO}^- \text{ is the limiting reactant since } V_b < V_{bE}. \end{array}$ $\text{pH (solution)} = \text{pK}_a(C_6H_5COOH / C_6H_5COO^-) + \log \frac{[C_6H_5COO^-]}{[C_6H_5COOH]}$ $\text{pH} = \text{pK}_a + \log \frac{\frac{C_b V_b}{V(S)}}{\frac{C_a V_a - C_b V_b}{C_a V_a}} = \text{pK}_a + \log \frac{V_b}{V_{bE} - V_b} \quad \text{with } C_a V_a = C_b V_{bE}$	1
2.4.2	$\text{pK}_a = \text{pH} - \log \frac{V_b}{V_{bE} - V_b} = 4.4 - \log \frac{10}{16.2 - 10} = 4.2$	0,5
2.5.	<ul style="list-style-type: none"> - The curve (a) doesn't correspond to the realized titration, since it shows one inflection point, then it corresponds to the titration of a strong acid with a strong base. - The curve (b) doesn't correspond to the realized titration, although it represents two inflection points, but the pH exceeds the limited value $pH = 14 + \log C_b = 14 + \log 4.10^{-3} = 11.6$ - The curve (c) corresponds to the realized titration, since it shows two inflection points and the pH doesn't exceed the value 11.6 	0,5 0,5 0,5

Exercise 3 (7 points)

Study of the esterification reaction

Part of the Q.	Answer	Mark
1.1.	<p>- The mild oxidation of compound (A) produces a compound (F), since (F) reacts with DNPH and with Fehling's reagent, then (F) is an aldehyde and the compound (A) is a primary alcohol.</p> <p>- (A) is 1-propanol of condensed structural formula: $\text{CH}_3 - \text{CH}_2 - \text{CH}_2\text{OH}$</p> <p>The solution of compound (B) gives a value of $\text{pH} < 7$. Then (B) is a carboxylic acid.</p> <p>(B) is propanoic acid of condensed structural formula: $\text{CH}_3 - \text{CH}_2 - \text{COOH}$</p>	1.5
1.2.1.	<p>The compound (C) is 2-butanol of a condensed structural formula:</p> $\text{CH}_3 - \text{CH}_2 - \overset{*}{\text{CH}} - \text{CH}_3$ <p style="text-align: center;"> </p> <p style="text-align: center;">OH</p> <p>It is chiral molecule since it contains an asymmetric carbon (carbon number 2) which is attached to 4 different atoms or groups of atoms.</p>	0.75
1.2.2		0.75
1.3	<p>(D): $\text{CH}_3 - \text{CH}_2 - \underset{\underset{\text{OH}}{ }}{\text{CH}} - \text{CH}_2 - \text{CH}_3$</p>	0.25
2.1	<p>The equation of this reaction is:</p> $\text{CH}_3 - \text{CH}_2 - \text{COOH} + \text{CH}_3 - \text{CHOH} - \text{CH}_2 - \text{CH}_3 \rightleftharpoons \text{CH}_3 - \text{CH}_2 - \text{COO} - \underset{\underset{\text{CH}_3}{ }}{\text{CH}} - \text{CH}_2 - \text{CH}_3 + \text{H}_2\text{O}$ <p>The name of (E) is : 1-methylpropyl propanoate or 2-butyl propanoate</p>	0.75
2.2	$n_{\text{acid(initial)}} = \frac{m(\text{acid})}{M(\text{acid})} = \frac{d(\text{acid}) \times V(\text{acid})}{M(\text{acid})} = \frac{0.99 \times 30}{74} = 0.40 \text{ mol.}$	0.5
2.3	<p>The yield of this reaction:</p> $Y = \frac{n(\text{ester}) \text{ experimental}}{n(\text{ester}) \text{ theoretical}} = \frac{n_1}{n_2}; \text{ and } n_1 = \frac{m(\text{ester}) \text{ experimental}}{M(\text{ester})} = \frac{19.5}{130} = 0.15 \text{ mol}$ <p>and $n_2 = n(\text{alcohol})_{\text{initial}} = 0.25 \text{ mol.}$ then $Y = 0.60 \text{ or } 60\%.$</p>	0.75
2.4	<p>The initial mixture of reactants isn't equimolar; the yield of this reaction at equilibrium should be greater than 60% therefore the equilibrium isn't reached yet.</p>	0.5
2.5	<p>- Extended duration of heating increases the $n(\text{ester})_{\text{formed}}$ and as a result the yield increases.</p> <p>- Adding a catalyst to the initial mixture of reactants: increases the rate of the reaction without affecting the yield.</p>	0.5

الاسم: الرقم:	مسابقة في الكيمياء المدة: ساعتان
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This Exam Includes Three Exercises. It Is Inscribed on Four pages, Numbered from 1 to 4.
The use of A Non-programmable Calculator Is Allowed.

Answer the Three Following Exercises:

Exercise 1 (7 points)

Lactic Acid

The quantity of free lactic acid contained in commercial yogurt should not be less than 0.7 gram per 100 grams of yogurt when sold to the consumer. It is important to verify regularly that the sold yogurt respects the given standards.

It is assumed that the acidity of the yogurt is only due to lactic acid.

Document-1

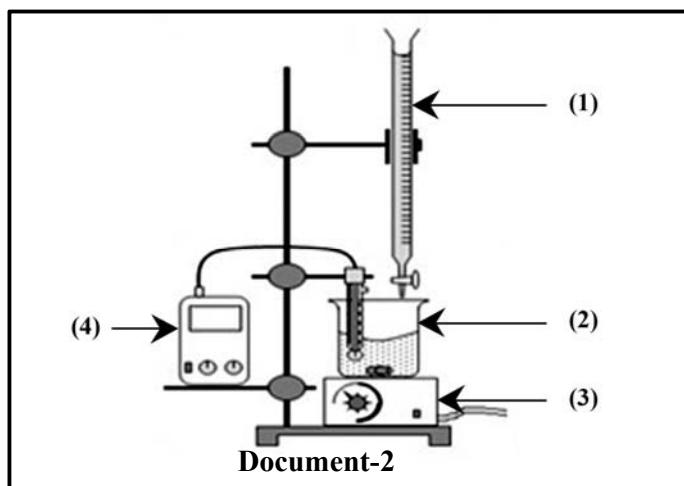
The aim of this exercise is to titrate the lactic acid noted HA contained in the commercial yogurt and to study some of its characteristics.

Given: - Molar mass of lactic acid: $M = 90 \text{ g.mol}^{-1}$
- Lactic acid is a weak acid.

1. pH-metric Titration of Lactic Acid Contained in Commercial Yogurt

Lactic acid contained in a sample of mass $m = 10.0\text{g}$ of commercial yogurt is titrated with a sodium hydroxide solution ($\text{Na}^+ + \text{HO}^-$) of concentration $C_b = 0.10 \text{ mol.L}^{-1}$. Before starting titration, a sufficient quantity of distilled water is added while stirring to the sample of yogurt to homogenize the solution.

The schema of the titration setup used is shown in **document-2**



1.1. Name the parts 1, 2, 3 and 4 of the titration setup of **document-2**.

1.2. Write the equation of the titration reaction.

1.3. Choose which one of the values given below corresponds to the pH of the solution at equivalence. Justify.

a- 5.6

b- 7.0

c- 8.3

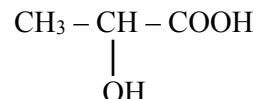
1.4. The equivalence point is reached when the volume of the basic solution added is $V_{BE} = 12\text{mL}$. Determine the number of moles of lactic acid contained in the titrated sample.

1.5. Deduce the mass percentage of lactic acid in the commercial yogurt.

1.6. Referring to **document-1**, specify whether the yogurt respects the above given standards.

2. Characteristics of Lactic Acid

The condensed structural formula of lactic acid is:



2.1. Name the two functional groups present in the above formula.

2.2. Give the systematic name of lactic acid.

2.3. Why lactic acid molecule is chiral?

2.4. Represent according to Cram the two enantiomers of lactic acid.

2.5. Lactic acid undergoes a mild oxidation with an acidified potassium permanganate solution ($\text{K}^+ + \text{MnO}_4^-$) to produce pyruvic acid.

2.5.1. Indicate in lactic acid molecule the functional group which is involved in this mild oxidation.

2.5.2. Write the condensed structural formula of pyruvic acid.

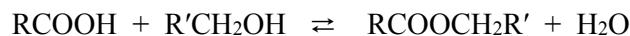
Exercise 2 (6 points)

Chemical Kinetic

In order to follow-up the kinetic of esterification reaction, one proceeds as follows:

- Nine Erlenmeyer flasks each containing 50 mmol of 1-butanol are immersed in a water bath maintained at constant temperature of 60°C.
- At instant $t = 0$, a quantity of 50 mmol of ethanoic acid is added simultaneously into each flask.
- At instant t , one of the Erlenmeyer flasks is removed and ice-water is added into this flask then the remained acid is titrated with sodium hydroxide solution ($\text{Na}^+ + \text{HO}^-$) and the number of moles of the ester formed is deduced. This step is repeated at different instants with the other Erlenmeyer flasks.

- The equation of the reaction between a carboxylic acid and a primary alcohol is:



- The equilibrium constant associated with this reaction is $K_C = 4.12$
- The transformation, in each Erlenmeyer flask, takes place without loss of any quantity of constituents of the reactional mixture due to evaporation.

Document-1

1. Theoretical Study

1.1. Write, using condensed structural formulas, the equation of the reaction between ethanoic acid and 1-butanol.

1.2. Give the name of the ester formed.

2. Kinetic Study

The results of the realized kinetic study are grouped in the table of **document-2**.

t (min)	2	5	8	12	16	20	25	35	50
n (ester) mmol	9	19	24	29	31.5	32.4	32.8	33.3	33.5

Document-1

- 2.1. Indicate the effect of adding ice-water to each Erlenmeyer flask. List the two kinetic factors involved.
- 2.2. Plot the curve that represents the variation of the quantity of the ester formed as a function of time: $n(\text{ester}) = f(t)$ within the interval of time [0 – 50 min].
Take the following scale: 1 cm for 5 min in abscissa and 1 cm for 3 mmol in ordinate.
- 2.3. Deduce graphically the variation of the rate of formation of ester with time.
- 2.4. Determine the number of moles of each constituent of the reactional mixture at $t = 50\text{ min}$.
- 2.5. Show that at time $t = 50\text{ min}$, a chemical equilibrium is reached.
- 2.6. Specify whether each of the following statements is true or false.
 - 2.6.1. The addition of a quantity of alcohol to the reactional mixture at equilibrium increases the yield of the reaction
 - 2.6.2. Realizing the same above experiment by modifying only the temperature from 60°C to 70°C produces a number of moles of the ester at equilibrium greater than 33.5 mmol.

Exercise 3 (7 points)

Sodium Hydroxide

An aqueous solution of sodium hydroxide ($\text{Na}^+ + \text{HO}^-$), also referred as "soda" reacts easily with carboxylic acids.

At high concentrations and temperature, the "soda" can undergo, a saponification reaction with an ester.

1. Sodium Hydroxide in Acid-Base Reaction

Available are two solutions:

- A solution (S_1) of sodium hydroxide ($\text{Na}^+ + \text{HO}^-$)
- A solution (S_2) of benzoic acid $\text{C}_6\text{H}_5\text{-COOH}$
Both solutions have the same molar concentration $C = 0.01\text{ mol.L}^{-1}$.

Given: Molar mass of $\text{NaOH} = 40\text{ g.mol}^{-1}$;

acid/base pair	$\text{H}_3\text{O}^+ / \text{H}_2\text{O}$	$\text{C}_6\text{H}_5\text{-COOH} / \text{C}_6\text{H}_5\text{-COO}^-$	$\text{H}_2\text{O}/\text{HO}^-$
pKa	0	4.2	14

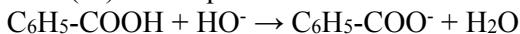
- 1.1. The solution (S_1) is prepared by dissolving a mass m of NaOH in distilled water to obtain 100 mL of an aqueous solution. Calculate the mass m .

1.2. Choose, from **document-1**, the appropriate materials for the preparation of the solution (S_1).

- | | | |
|--|-------------------|---------------------|
| - Volumetric flasks: 50, 100, and 1000 mL; | - watch glass; | - spatula; |
| - Volumetric pipets: 5, 10, and 20 mL; | - buret of 25mL ; | - Precision balance |

Document-1

1.3. A solution (S) of pH= 5 is prepared by mixing a volume V_1 of the solution (S_1) and a volume V_2 of the solution (S_2). The equation of the reaction that takes place is:



- 1.3.1.** Justify that this reaction is complete.
- 1.3.2.** Place on the pH axis the predominance domains of the species of the pair $C_6H_5\text{-COOH} / C_6H_5\text{-COO}^-$.
- 1.3.3.** Deduce that, at pH=5, HO^- ion is the limiting reactant.
- 1.3.4.** Determine the volume V_2 knowing that $V_1 = 54$ mL.

2. Sodium Hydroxide in the Saponification Reaction

An excess of a concentrated aqueous solution of sodium hydroxide is introduced into a flask. A certain volume of ethyl benzoate $C_6H_5COOC_2H_5$ is added. A condenser was adjusted to the flask and the mixture was heated to reflux for 20 minutes. Sodium benzoate and ethanol are obtained.

2.1. Ethyl benzoate is prepared by the action of benzoic anhydride on ethanol.

2.1.1. Give the condensed structural formula of benzoic anhydride.

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

2.1.3. Choose the correct answer. This esterification reaction is:

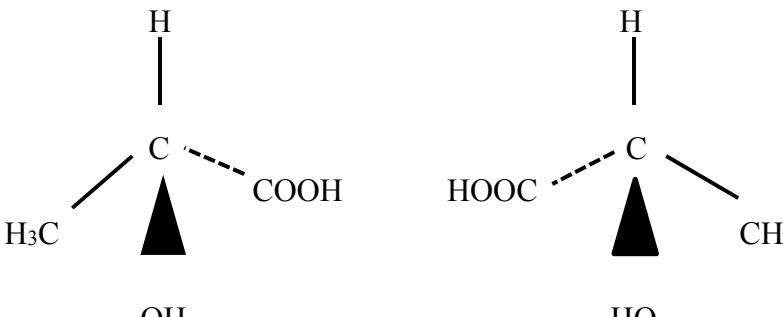
a- limited and athermic **b-** complete and endothermic **c-** complete and exothermic

2.2. Write the equation of the saponification reaction occurring between ethyl benzoate and the hydroxide ions.

2.3. Indicate the importance of the reflux heating.

Exercice 1 (7 points)

Lactic acid

Part of the Q.	Expected Answer	Mark
1.1	(1) : Graduated Buret (2) : Beaker (3) : magnetic stirrer (4) : pH meter	1
1.2	$\text{HA} + \text{HO}^- \rightarrow \text{A}^- + \text{H}_2\text{O}$	0.5
1.3	The chemical species present at equivalence in the mixture are: Na^+ (spectator ion), H_2O (neutral) and A^- (weak base) which renders the medium basic with $p_{\text{HE}} > 7$. $c - p_{\text{HE}} = 8.3$.	0.75
1.4	At equivalence: $n_{\text{HA(present)}} = n_{\text{HO-(added to reach equivalence)}} = C_b \times V_{\text{bE}} = 0.1 \times 12 \times 10^{-3} = 1.2 \times 10^{-3} \text{ mol.}$	0.75
1.5	The mass of lactic acid contained in the sample = $n \times M = 1.2 \times 10^{-3} \times 90 = 0.108 \text{ g}$ in 100g yogurt : % lactic acid = $0.108/10 \times 100 = 1.08\%$	0.5
1.6	$1.08\% > 0.7\%$ so the yogurt respects the given standards	0.5
2.1	$\text{CH}_3 - \text{CH} - \text{COOH}$ ← carboxyl group OH ← hydroxyl group	0.5
2.2	2-hydroxypropanoic acid.	0.5
2.3	The molecule of lactic acid is chiral since the carbon number 2 is an asymmetric carbon (it is bonded to 4 different atoms or group of atoms)	0.5
2.4		0.75
2.5.1	The hydroxyl group undergoes mild oxidation.	0.5
2.5.2	$\text{CH}_3 - \underset{\parallel}{\text{C}} - \text{COOH}$	0.5

Exercice 2 (6 points)
Chemical Kinetic

Part of the Q	Expected Answer	Mark										
1.1	The equation of the reaction is : $\text{CH}_3 - \text{COOH} + \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2\text{OH} \rightleftharpoons \text{CH}_3 - \text{COO} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 + \text{H}_2\text{O}$	0.75										
1.2	The ester obtained is butyl ethanoate.	0.25										
2.1	To block the slow esterification reaction. Temperature and the initial concentration of the reactants.	0.75										
2.2	<p style="text-align: center;">n(ester) mmol</p>	1										
2.3	The instantaneous rate of the formation of the ester, is equal to the slope of the tangent drawn on the curve at a point of abscissa t. Graphically, the slope of the tangent at each point on the curve decreases with time then the rate decreases.	0.75										
2.4	<p style="text-align: center;">Acid + Alcohol \rightleftharpoons Ester + water</p> <table style="margin-left: auto; margin-right: auto;"> <tr> <td>A t = 0</td> <td>0.05 mol</td> <td>0.05 mol</td> <td>-</td> <td>-</td> </tr> <tr> <td>A t = 50</td> <td>0.05-x</td> <td>0.05-x</td> <td>x</td> <td>x</td> </tr> </table> With $x = 0.0335 \text{ mol} = n(\text{ester}) = n(\text{water})$ $n(\text{acid}) = n(\text{alcohol}) = 0.05 - 0.0335 = 0.0165 \text{ mol}$	A t = 0	0.05 mol	0.05 mol	-	-	A t = 50	0.05-x	0.05-x	x	x	0.75
A t = 0	0.05 mol	0.05 mol	-	-								
A t = 50	0.05-x	0.05-x	x	x								
2.5	Quotient of the reaction at $t = 50 \text{ min}$: $Q_r = \frac{[\text{ester}] \times [\text{water}]}{[\text{alcohol}] \times [\text{acid}]} = \frac{\frac{n(\text{ester})}{V} \times \frac{n(\text{water})}{V}}{\frac{n(\text{acid})}{V} \times \frac{n(\text{alcohol})}{V}} = \frac{(0.0335)^2}{(0.05 - 0.0335)^2} = 4.12$ The quotient Q_r is equal to the equilibrium constant K_c , thus the reactional medium reaches chemical equilibrium	0.75										
2.6.1	True. The addition of alcohol at equilibrium displaces the equilibrium in the forward direction according to Le Chatelier's principle which results in increasing the experimental quantity of ester formed whereas theoretical quantity of ester remains the same. Then the yield of esterification increases.	0.5										
2.6.2	False. The increase in temperature doesn't affect the yield at equilibrium since the reaction is athermic.	0.5										

Exercice 3 (7 points)

Sodium Hydroxide

Part of the Q.	Expected Answer	Mark
1.1	$m = n \times M = C \times V \times M = 0.01 \times 0.1 \times 40 = 0.04\text{g}$	0.5
1.2	- volumetric flask 100mL - watch glass - spatule - precision balance.	1
1.3.1	$K_R = 10^{\Delta pK_a} = 10^{9.8} > 10^4$ the reaction is complete.	0.5
1.3.2		0.75
1.3.3	For pH = 5 the two species C ₆ H ₅ -COOH and C ₆ H ₅ -COO ⁻ exist with close concentration. Since the reaction is complete, C ₆ H ₅ -COOH doesn't disappear so it is in excess while HO ⁻ is the limiting reactant.	0.5
1.3.4	$\text{C}_6\text{H}_5\text{-COOH} + \text{HO}^- \rightarrow \text{C}_6\text{H}_5\text{-COO}^- + \text{H}_2\text{O}$ at t=0 CV ₂ CV ₁ - excess at t _f CV ₂ -CV ₁ 0 CV ₁ excess $pH = pK_a + \log \frac{[\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]} = pK_a + \log \frac{CV_2 / V_t}{(CV_1 - CV_2) / V_t} = pK_a + \log \frac{V_2}{V_1 - V_2}$ $\log \frac{V_2}{V_1 - V_2} = pH - pK_a = 5 - 4.2 = 0.8; \frac{V_2}{V_1 - V_2} = 10^{0.8} = 6.3$ $V_2 = 6.3 \times (V_1 - V_2); 7.3V_2 = 6.3V_1; V_2 = 1.16V_1 = 1.16 \times 54 = 62.6 \text{ mL}$	1
2.1.1	C ₆ H ₅ -C-O-C- C ₆ H ₅ O O	0.5
2.1.2	C ₆ H ₅ -C-O-C- C ₆ H ₅ + CH ₃ -CH ₂ -OH → C ₆ H ₅ -COO-C ₂ H ₅ + C ₆ H ₅ -COOH O O	0.75
2.1.3	c- total and exothermic.	0.5
2.2	C ₆ H ₅ COOC ₂ H ₅ + HO → C ₆ H ₅ COO ⁻ + C ₂ H ₅ OH	0.5
2.3	Heating under reflux increases the rate of the reaction without losing any quantity of reactants or products by condensing the vapors escaping and returning them to the reactional mixture.	0.5

الاسم:
الرقم:

مسابقة في مادة الكيمياء
المدة: ساعتان

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

Answer the Three Following Exercises:

Exercise 1 (7 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.

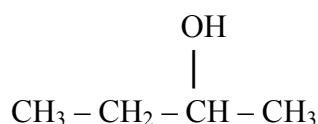
Given: Molar mass in g.mol⁻¹: M_(H) = 1; M_(C) = 12; M_(O) = 16.

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 C₄H₁₀O.

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



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:

1.3.1. The systematic name of (B) is butanal.

1.3.2. The compound (B) gives white crystals with 2,4- DNPH.

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:



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

- 2.1. Write, using the condensed structural formulas, the equation of this esterification reaction.
- 2.2. Determine the number of moles of each constituent of the reacting mixture, at equilibrium.
- 2.3. Deduce the value of the equilibrium constant K_c .
- 2.4. 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. $t < t'$

Exercise 2 (6 points)

Kinetic of the Oxidation of Javel Water with Ammonia

In an aqueous solution, ammonia (NH_3) reacts with hypochlorite ions (ClO^-) in a slow and complete reaction that takes place according to the equation below:



The aim of this exercise is to study the kinetic of this reaction.

- Javel water is a sodium hypochlorite aqueous solution ($\text{Na}^+ + \text{ClO}^-$).

- Nitrogen gas (N_2) is slightly soluble in water.

Document- 1

1. Preparation of a Javel Water Solution (S_1)

A volume $V_1 = 250 \text{ mL}$ of the solution (S_1) of molar concentration $C_1 = 0.25 \text{ mol.L}^{-1}$ is prepared by diluting 25 times a commercial Javel water solution (S_0).

- 1.1. Determine the volume V_0 withdrawn from solution (S_0) to prepare the solution (S_1).
- 1.2. Choose, from document- 2, the essential glassware needed to carry out the preparation of solution (S_1).

- Beakers : 100ml, 250 ml and 500ml

- Volumetric flasks: 100ml, 250 ml and 500ml

- Graduated cylinders: 5 ml, 10ml and 25ml

- Volumetric pipets: 5 ml, 10ml and 25ml

Document- 2

2. Kinetic Study

A volume $V_1=200$ mL of a solution (S_1) of Javel water solution of molar concentration $C_1 = 0.25\text{ mol.L}^{-1}$ is mixed with an excess of ammonia solution at constant temperature $T = 27^\circ\text{C}$. Using an appropriate method, the number of moles of nitrogen gas N_2 formed is determined at different instant t , the results obtained are grouped in the table of **document- 3**

t (min)	2	4	6	8	10	12	16
$n(\text{N}_2) (10^{-3} \text{ mol})$	4.3	8.0	10.3	12.0	13.3	14.3	15.5

Document-3

2.1. Calculate the initial number of moles of hypochlorite ions ClO^- .

2.2. Verify whether the instant of time $t = 16$ min represents the end of the reaction.

2.3. Plot the curve representing the variation in the number of moles of (N_2) as a function of time:

$n(\text{N}_2) = f(t)$ within the interval of time $[0 - 16 \text{ min}]$.

Take the following scales: In abscissas: 1cm for 1 min;

In ordinates: 1cm for $1 \times 10^{-3} \text{ mol}$.

2.4. Deduce, graphically, the variation of the rate of formation of (N_2) as a function of time.

2.5. Choose the correct answer:

The instantaneous rate of formation of N_2 at an instant of time t is denoted as $r_{(\text{N}_2)t}$ and the instantaneous rate of disappearance of ClO^- at the same instant t is denoted as $r_{(\text{ClO}^-)t}$ are related by the relation:

$$\text{a. } r_{(\text{ClO}^-)t} = 3 r_{(\text{N}_2)t} \quad \text{b. } r_{(\text{ClO}^-)t} = \frac{r(\text{N}_2)t}{3} \quad \text{c. } r_{(\text{ClO}^-)t} = r_{(\text{N}_2)t}$$

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

2.7. The same kinetic study is carried out again but with one change: the temperature of the reacting medium is higher than 27°C .

Specify, in this study, whether the following statement is true or false:

The number of moles of nitrogen gas (N_2) formed at $t = 4$ min becomes less than $8.0 \times 10^{-3} \text{ mol}$.

Exercise 3 (7 points)

Titration of an Ethanoic Acid Solution

Ethanoic acid is a weak acid of formula CH_3COOH . At room temperature, it is a colorless liquid with a pungent odor and it is highly miscible in water.

The aim of this exercise is to study the behavior of ethanoic acid in water and to determine its molar concentration by pH-metric titration.

Given: - This study is carried out at 25°C .

- pKa of the pair $(\text{CH}_3\text{COOH} / \text{CH}_3\text{COO}^-) = 4.8$

1. Study of the Behavior of Ethanoic Acid in Water

In the laboratory, available is a flask containing an ethanoic acid solution (S) of unknown molar concentration C_a .

1.1. Write the equation of the reaction of ethanoic acid with water.

1.2. Knowing that α is the degree of dissociation of ethanoic acid in water , verify the following relation :

$$\frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{\alpha}{1-\alpha}$$

1.3. Show that the value of α is close to 0.04, knowing that pH of the solution (S) is equal to 3.4

1.4. Based on the value of α , justify that ethanoic acid is a weak acid.

2- Titration of the Ethanoic Acid Solution (S)

Into a beaker, introduce a volume $V_a = 20.0$ mL of the ethanoic acid solution (S) and a certain volume of distilled water to immerse properly the pH-meter electrode. A sodium hydroxide solution ($\text{Na}^+ + \text{HO}^-$) of molar concentration $C_b = 2.0 \times 10^{-2}$ mol.L⁻¹ is added progressively. A sample of the experimental results is given in **document-1** :

V_b (mL)	0	5	10	15
pH	3.5	4.8	pH_E	11.2

Document-1

2.1. From the given material of **document-2**, choose the most suitable ones needed to carry out the titration .

- Volumetric flasks: 50 and 100 mL
- Graduated cylinders: 10, 20 and 50 mL
- Graduated buret : 25 mL
- Precision balance

- Beaker : 100 mL
- Magnetic stirrer and its bar
- pH – meter and its electrode

Document-2

2.2. Write the equation of the titration reaction.

2.3. Based on the chemical species present in the beaker at equivalence. Specify the point that represents the equivalence point:

A ($V_{bE} = 10$ mL ; $\text{pH}_E = 8.3$) ; B ($V_{bE} = 10$ mL ; $\text{pH}_E = 7$) ; C ($V_{bE} = 10$ mL ; $\text{pH}_E = 5.8$).

2.4. Determine the molar concentration of ethanoic acid in the solution (S).

2.5. Plot the shape of the curve representing the change in the pH as a function of the volume of the base added $\text{pH} = f(V_b)$ passing by the four remarkable points extracted from the table of **document-1**.

Take the following scales: In abscissa 1 cm = 1 mL;

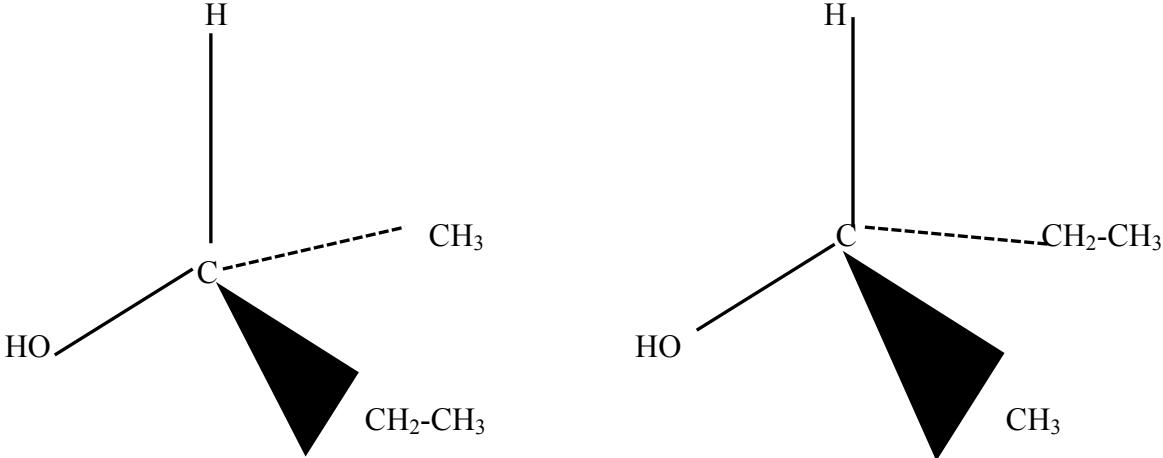
In ordinates; 1cm = 1 unit of pH.

2.6. Referring to **document-1** and using the predominance axis of the chemical species of the pair $\text{CH}_3\text{COOH} / \text{CH}_3\text{COO}^-$, specify the chemical species which predominates at the end of the titration for $V_b = 15$ mL.

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Exercise 1 (7 points)

Properties of an alcohol

Part	Answer	Pts
1.1	(A) is a saturated and non-cyclic mono-alcohol , Its general formula is $C_nH_{2n+2}O$ So $z = 1$ $\frac{16x1}{\% O} = \frac{12n + 2n + 2 + 16}{100}$; $\frac{16}{21,62} = \frac{14n + 18}{100}$; $n = 4$ So the molecular formula of (A) is $C_4H_{10}O$	0,75
1.2.1	(A) is a secondary alcohol	0,25
1.2.2	2- butanol	0,25
1.2.3	$CH_3 - CH_2 - CH_2 - CH_2OH$ $\begin{array}{c} CH_3 \\ \\ CH_3 - C - CH_3 \\ \\ OH \end{array}$ $CH_3 - CH - CH_2OH$	0,75
1.2.4	The molecule of (A) chiral since it posseses an assymetric carbon (the carbon 2 which is connected to four different atoms or groups of atoms)	0,5
1.2.5		0,75
1.3.1	Butanone	0,5
1.3.2	(B) with 2,4-DNPH gives a yellow orange precipitate (B) with $NaHSO_3$ gives white crystals	0,5
2.1	$HCOOH + HO - CH - CH_2 - CH_3 \rightleftharpoons HCOO - CH - CH_2 - CH_3 + H_2O$ $\begin{array}{c} \\ CH_3 \end{array} \qquad \qquad \qquad \begin{array}{c} \\ CH_3 \end{array}$	0,75
2.2	$Methanoic\ acid + (A) \rightleftharpoons (E) + H_2O$ At $t = 0$ 0.2 mol 0.2 mol - - At t_{eq} 0.08 mol 0.08 mol 0.12 mol 0.12 mol	1
2.3	$K_c = \frac{[E][H_2O]}{[Acide][A]} = \frac{(0.12/V)^2}{(0.08/V)^2} = \frac{(0.12)^2}{(0.08)^2} = 2.25$	0,5
2.5	c. $t < t'$ the catalyst is a kinetic factor , in absence of a catalyst the rate decreases and the time required to reach the equilibrium state is greater .	0,5

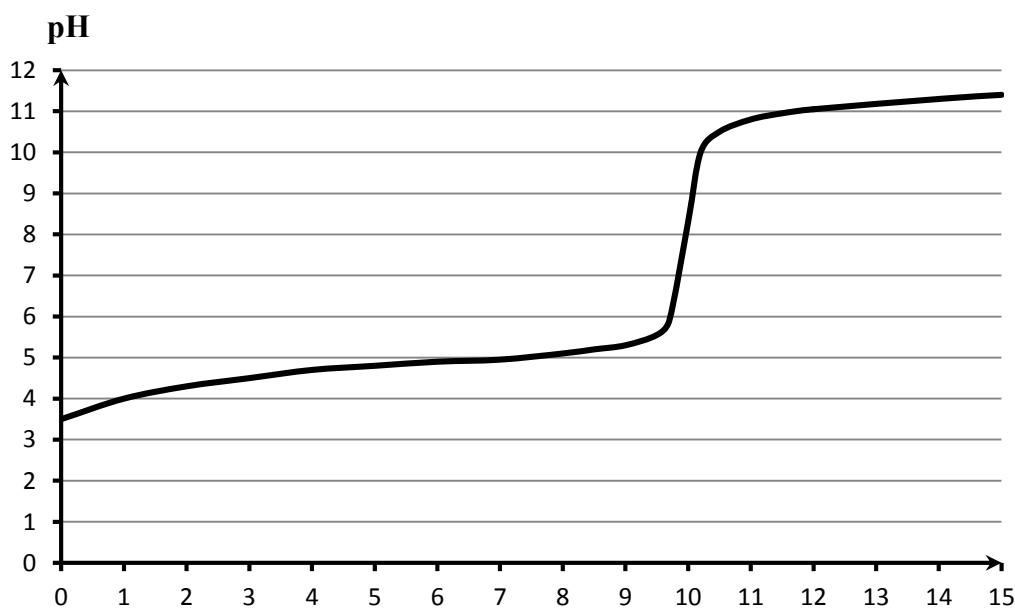
Exercise 2

Kinetics of the oxidation of Javel water with ammonia

Part	Answers	Note
1.1	By dilution , the number of moles of solute is consvred : $n_0 = n_1 ; C_0 \times V_0 = C_1 \times V_1 ; F = \frac{C_0}{C_1} = \frac{V_1}{V_0} ; V_0 = \frac{V_1}{F} = \frac{250}{25} = 10 \text{ mL}.$	0,5
1.2	The glassware needed to prepare te solution (S_1) : Volumetric flask :250 mL, volumetric pipet : 10 mL and (beaker 100 mL).	0,5
2.1	$n(\text{ClO}^-) \text{ initial} = C_1 \times V_1 = 0.25 \times 0.2 = 5 \times 10^{-2} \text{ mol.}$	0,5
2.2	According to ST. R. : $n(\text{ClO}^-)_0 / 3 = n(\text{N}_2)_{\infty} ; n(\text{N}_2)_{\infty} = 5 \times 10^{-2} / 3 = 16.6 \times 10^{-3} \text{ mol}$ Or at $t = 16 \text{ min}$, we have $n(\text{N}_2) = 15.5 \times 10^{-3} \text{ mol} < 16.6 \times 10^{-3} \text{ mol}$. So $t = 16 \text{ min}$ does not correspond to the end of the reaction .	0,75
2.3	<p style="text-align: right;">1</p>	
2.4	The instantaneous rate of formation de N_2 is equal to the slope of the tangent drawn to the on the curve at a point of abscissa t . The slope of the tangent decreases at each point So the intantaneous rate of formation de N_2 deacreases with time.	0,75
2.5	a. $r_{(\text{ClO}^-)_t} = 3 r_{(\text{N}_2)_t}$.	0,5
2.6	The half life time is the time needed to for the la quantity of N_2 to become the half of its maximal value At $t_{1/2}$: $n(\text{N}_2)_{t_{1/2}} = n(\text{N}_2)_{\infty} / 2 = 16.6 \times 10^{-3} / 2 = 8.3 \times 10^{-3} \text{ mol.}$ Graphically $t_{1/2} = 4.3 \text{ min.}$	1
2.7	False . The temperature is a kinetic factor , when it increases the rate of the reaction increases so the number of moles of N_2 at instant $t = 4 \text{ min}$ becomes greater than to $8.0 \times 10^{-3} \text{ mol.}$	0,5

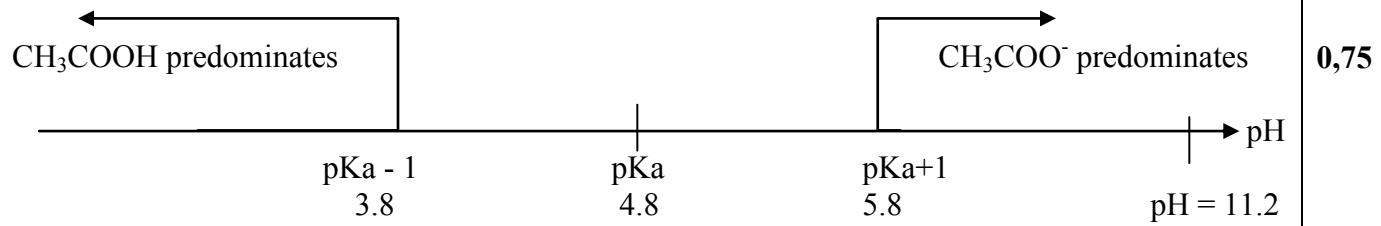
Exercise 3 (7 points) Titration of an Ethanoic Acid Solution

Part	Answer	pts
1.1	$\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$	0,5
1.2	$\begin{array}{lllll} \text{at } t = 0 & C_a & \text{solvent} & 0 & 0 \\ \text{at } t \rightleftharpoons & C_a - C_a \alpha & \text{solvent} & C_a \alpha & C_a \alpha \end{array}$ <p>According to the table :</p> $\frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{C_a \alpha}{C_a(1-\alpha)} = \frac{\alpha}{1-\alpha} \quad \text{Verified}$	0,75
1.3	$\text{pH} = \text{pK}_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$ $3.4 - 4.8 = \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$ $-1.4 = \log \frac{\alpha}{1-\alpha}$ $\frac{\alpha}{1-\alpha} = 10^{-1.4}; \alpha = 0.038, \text{ it is close to } 0.04$ <p>Verified</p>	0,5
1.4	Since $\alpha = 0.04 < 1$ So the ethanoic acid CH_3COOH is a weak acid .	0,25
2.1	The most suitable material needed to carry out the titration are : <ul style="list-style-type: none"> - Beaker : 100 mL - Graduated buret : 25 mL - pH – meter and its electrode . - Magnetic stirrer and its bar 	1
2.2	$\text{CH}_3\text{COOH} + \text{HO}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O}$	0,5
2.3	The chemical species presents in the beaker at the equivalence are : Na^+ (spectator ion) ; H_2O (neutral) and CH_3COO^- (ion of basic character so $\text{pH}_E > 7$) , we deduce that the point that corresponds to the equivalence point is : A ($V_{bE} = 10 \text{ mL}$; $\text{pH}_E = 8.3$).	0,75
2.4	At equivalence : $n(\text{CH}_3\text{COOH}) \text{ introduced in the beaker} = n(\text{HO}^-) \text{ added to reach equivalence point}$ $C_a V_a = C_b V_{bE}$ $C_a = (C_b \cdot V_{bE}) / V_a = (2 \cdot 10^{-2} \times 10 \cdot 10^{-3}) / 20 \times 10^{-3} = 10^{-2} \text{ mol.L}^{-1}$.	1
2.5		



1

2.6



0,75

For $V_b = 15$ mL; $pH = 11.2 > pK_a + 1 = 5.8$ so CH_3COO^- is the predominant species .

الاسم:
الرقم:

مسابقة في مادة الكيمياء
المدة: ساعتان

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

Answer the Three Following Exercises:

Exercise 1 (7 points)

Study of an Alcohol (A)

Alcohols have a long history of several uses worldwide. They have many medical and industrial uses. The aim of this exercise is to identify a saturated non cyclic chain monoalcohol (A), and to study some of its chemical properties.

Given:

- Molar masses in g.mol⁻¹: M (H) = 1; M (C) = 12; M (O) = 16
- Density of ethanoic acid: d = 1.06 g.mL⁻¹.

1. Identification of The Alcohol (A)

The elemental analysis of a sample of the alcohol (A) shows that the percentage by mass of oxygen is 21.62 %.

1.1. Show that the molecular formula of the alcohol (A) is C₄H₁₀O.

1.2. In order to identify the alcohol (A), the experiments in **document-1** are carried out.

Experiment 1: The alcohol (A) is treated with an acidified potassium dichromate solution (2K⁺ + Cr₂O₇²⁻). The color of the medium is changed from orange to green and an organic compound (B) is formed.

Experiment 2: A solution of 2,4-DNPH is added to a sample of compound (B). A yellow orange precipitate is formed.

Experiment 3: A mixture of a sample of compound (B) and a blue Fehling's solution is heated gently. The mixture remains blue and no precipitate is observed.

Document- 1

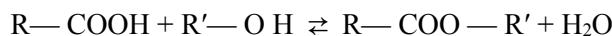
Based on the results of each of the three experiments of **document-1**, justify that the alcohol (A) is 2-butanol.

1.3. Verify that the molecule of 2- butanol is chiral.

1.4. Represent, according to Cram, the two enantiomers of 2-butanol.

2. Reaction of the Alcohol (A) with Ethanoic Acid

Alcohols react with carboxylic acids according to the following general equation:



A mixture containing 0.10 mol of 2-butanol, a volume V= 5.7 mL of pure ethanoic acid and few drops of concentrated sulfuric acid is heated to reflux.

2.1. Write, using condensed structural formulas, the equation of the reaction that takes place. Give the systematic name of the ester formed.

2.2. Choose, from the following list, the appropriate materials needed to construct the reflux heating set-up: Heating mantle, round bottom flask, graduated burette, 100 mL beaker, and condenser.

2.3. Indicate the importance of the reflux heating for this synthesis.

2.4. After a certain time t , heating is stopped, the reaction medium is cooled and the remained ethanoic acid is titrated; the number of moles of ethanoic acid is found to be 0.06 mol.

2.4.1. Show that the initial number of moles of ethanoic acid is 0.10 mol.

2.4.2. Copy and complete the following table:

	$R-COOH$	$+ R'-OH \rightleftharpoons$	$R-COO-R' + H_2O$
At instant t_0	0.10 mol	0.10 mol	0
At instant t	0.06 mol		

2.4.3. Specify whether equilibrium is reached at instant t , knowing that the equilibrium constant of this reaction is $K_C = 2.3$

Exercise 2 (7 points)

Kinetic of a Reaction

Aspirin is one of the most used medicinal drugs worldwide.

The aim of this exercise is to study the preparation of aspirin and to realize the kinetic of its reaction with bicarbonate ion.

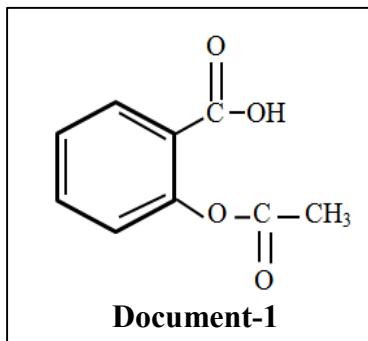
Given: Molar mass of aspirin: $M_{(Asp)} = 180 \text{ g.mol}^{-1}$

1. Preparation of Aspirin

Aspirin can be prepared starting from salicylic acid and ethanoic anhydride. The condensed structural formula of aspirin is given in **document-1**.

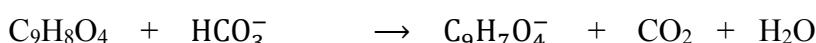
1.1. Copy the formula of aspirin, circle and name its functional groups.

1.2. Write, using condensed structural formulas, the equation of the preparation reaction of Aspirin.



2. Kinetic Study

Aspirin ($C_9H_8O_4$) reacts slowly with bicarbonate ion (HCO_3^-) according to a reaction which is considered complete, and is represented by the following equation:



A volume $V_1 = 10 \text{ mL}$ of a sodium bicarbonate solution ($Na^+ + HCO_3^-$) of concentration $C_1 = 0.50 \text{ mol.L}^{-1}$ is poured into a closed flask containing a mass $m = 460 \text{ mg}$ of aspirin. Using an appropriate method, the number of moles of carbon dioxide gas released in the flask at constant temperature T can be determined at each instant t .

The results are listed in the table of **document-2**.

Time (s)	50	100	150	200	250	300	350	400	500	600
$n(CO_2) (10^{-4} \text{ mol})$	11.50	17.75	21.00	22.75	23.75	24.50	25.00	25.25	25.55	25.55

Document-2

2.1. Show that aspirin is the limiting reactant.

2.2. Plot the curve representing the variation in the number of moles of carbon dioxide as a function of time: $n(CO_2) = f(t)$ in the time interval [0 – 500 s]. Take the following scales:

Abscissa: 1cm for 50 s ; Ordinate : 1 cm for $2.5 \times 10^{-4} \text{ mol}$.

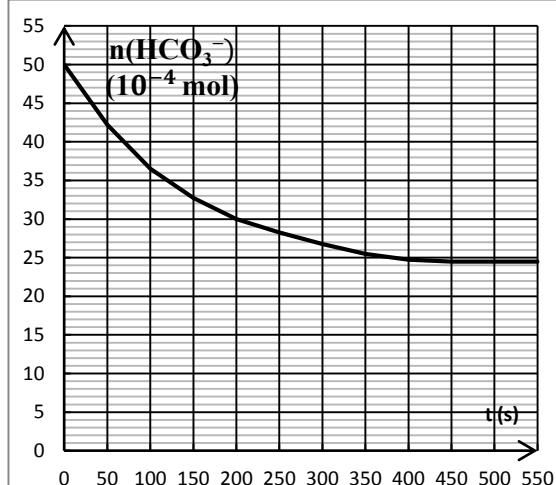
2.3. Deduce, graphically, the variation in the rate of formation of CO_2 as a function of time.

2.4. Determine the half-life time, $t_{1/2}$.

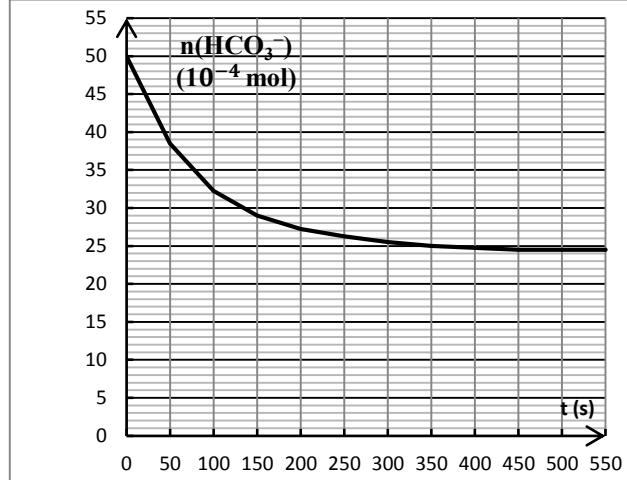
2.5. Show that at the half-life time ($t_{1/2}$) : $n(\text{HCO}_3^-)_{t_{1/2}} = n_0(\text{HCO}_3^-) - \frac{n_0(\text{Asp})}{2}$,

where $n_0(\text{HCO}_3^-)$ is the initial number of moles of HCO_3^- and $n_0(\text{Asp})$ is the initial number of moles of aspirin.

2.6. Consider the two curves given in **document-3**, deduce the one that corresponds to $n(\text{HCO}_3^-) = f(t)$.



Curve a



Curve b

Document-3

Exercise 3 (6 points)

Acidic and Basic Solutions

Available are three flasks containing two weak acid solutions denoted solution (1), solution (2) and a sodium hydroxide solution ($\text{Na}^+ + \text{HO}^-$) denoted solution (3). The labels on these three flasks show the indications given in the **document -1**.

Solution (1)	Solution (2)	Solution (3)
Monoacid HA_1 $C_1 = ?$ $\text{pH}_1 = 2.6$	Monoacid HA_2 $C_2 = ?$ $\text{pH}_2 = 2.7$	$(\text{Na}^+ + \text{HO}^-)$ $C_3 = 4 \times 10^{-2} \text{ mol.L}^{-1}$ $\text{pH}_3 = 12.6$

Document -1

The aim of this exercise is to study the strength of the two acids.

Given: - This study is carried out at $T = 25^\circ\text{C}$.

$$- K_w = 10^{-14}$$

1. Study of The Behavior of Acids and Base

1.1. Verify that sodium hydroxide is a strong base.

1.2. Each of the two solutions (1) and (2) is diluted **ten times**; the solutions (A) and (B) are obtained respectively. The measurements of pH of the obtained solutions are shown in **document-2**.

Solution (A)	Solution (B)
Monoacid HA_1 $\text{pH}_A = 3.1$	Monoacid HA_2 $\text{pH}_B = 3.2$

Document-2

Choose, from the sets of **document-3**, the most convenient one in order to prepare solution (A) from solution (1). Justify.

Set 1	Set 2	Set 3
Volumetric pipet 10.0 mL Volumetric flask 1000.0 mL Beaker 50 mL	Volumetric pipet 5.0 mL Volumetric flask 50.0 mL Beaker 50 mL	Graduated cylinder 10.0 mL Volumetric flask 50.0 mL Beaker 50 mL

- 1.3.** Verify, based on the **documents 1 and 2**, that the two acids HA_1 and HA_2 are weak acids.
1.4. Write the equation of the reaction of HA_1 with water.

2. Titration of Solution (1)

A volume $V_1 = 20.0$ mL of the solution (1) is taken and introduced into a beaker, and then a certain volume of distilled water is added to immerse properly the pH-meter electrode. The sodium hydroxide solution (3) of concentration $C_3 = 4 \times 10^{-2}$ mol.L⁻¹ is added progressively.

The volume of the basic solution added to reach equivalence is $V_{bE} = 25.0 \text{ mL}$.

- The volume of the basic solution added to reach equivalence is $V_{\text{eq}} = 20.0 \text{ mL}$.

 - 2.1. Write the equation of the titration reaction.
 - 2.2. Determine the concentration C_1 of the solution (1).
 - 2.3. At equivalence, A_1^- ions predominates HA_1 in the solution. Deduce which of the following values corresponds to the pK_a of the $\text{HA}_1 / \text{A}_1^-$ pair, knowing that the pH at equivalence is equal to 8.0

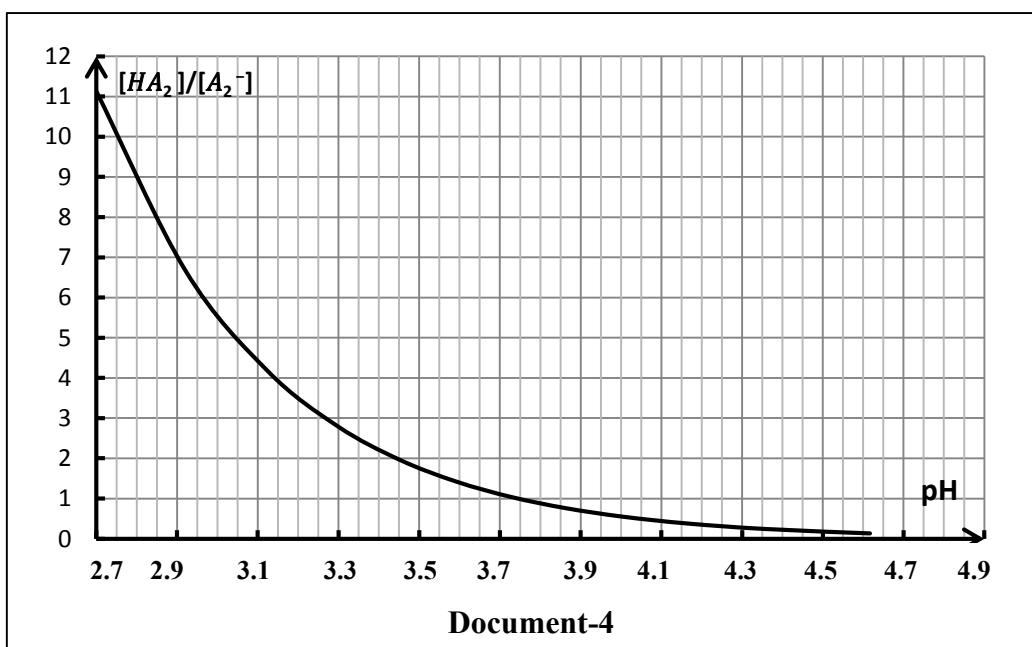
a. 3.9

b. 8.0

c, 10.0

3. Determination of The pKa of the Pair $\text{HA}_2^- / \text{A}_2^-$

Document-4 shows the variation of the ratio $\frac{[\text{HA}_2]}{[\text{A}_2^-]}$ as a function of pH during the addition of the solution (3) to a volume V_2 of the solution (2).



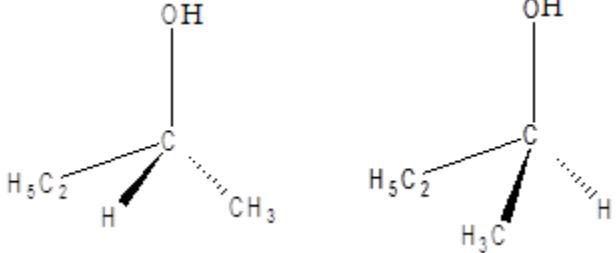
- 3.1.** Based on document 4, show that the value of the pKa of the pair $\text{HA}_2^- / \text{A}_2^-$ is 3.75
3.2. Specify, among the three following propositions, the one that corresponds to C_2 .

a. $C_2 > C_1$ **b.** $C_2 = C_1$ **c.** $C_2 < C_1$

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Exercise 1 (7 points)

Study of an Alcohol (A)

Part of the Q	Answer	Mark																		
1.1	<p>The general formula of a saturated non cyclic chain alcohol is $C_nH_{2n+2}O$. $\%O = 21.62 \%$. $\frac{M(A)}{100} = \frac{16}{\%O}$, with $M(A) = 14n+18$ $n = 4$ and the molecular formula of (A) is $C_4H_{10}O$</p>	0.5																		
1.2.	<p>From experience 1: (A) is oxidized so we deduce that it is not a tertiary alcohol, it is a primary or a secondary alcohol. From experience 2: since a yellow orange precipitate is formed so (B) is a carbonyl compound (aldehyde or ketone). From experience 3: we deduce that (B) is a ketone since it does not react with Fehling's solution ; So (A) is a secondary alcohol that 2-butanol</p>	1																		
1.3	Since the molecule of the 2-butanol contains an asymmetric carbon atom (a tetrahedral carbon atom linked to 4 atoms or group of atoms all different)	0.5																		
1.4.		0.75																		
2.1.	<p>The equation of the reaction is: $CH_3 - CHO - CH_2 - CH_3 + CH_3 - COOH \rightleftharpoons CH_3 - C(=O) - O - CH_2 - CH_3 + H_2O$ The systematic name of the ester is: 1-methylpropylethanoate</p>	1																		
2.2.	The most appropriate materials needed to carry out the reflux heating: Heating mantle, round bottom flask, and condenser.	0.75																		
2.3.	The importance of reflux heating is to accelerate the reaction without any loss in the constituents of the reacting mixture.	0.5																		
2.4.1.	$n(alcohol)_{initial} = \frac{m(alcohol)_{initial}}{M(alcohol)} = \frac{V(alcohol).d(alcohol)}{M(alcohol)} = \frac{5.7 \times 1.06}{60} = 0.10mol$	0.5																		
2.4.2	<table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 10%;">Initial state</td> <td style="width: 15%;">Acid</td> <td style="width: 15%;">+ alcohol</td> <td style="width: 15%;">\rightleftharpoons</td> <td style="width: 15%;">ester</td> <td style="width: 15%;">+ water</td> </tr> <tr> <td>At t</td> <td>0.1 mol</td> <td>0.1 mol</td> <td></td> <td>-</td> <td>-</td> </tr> <tr> <td></td> <td>0.06</td> <td>0.06</td> <td></td> <td>0.04</td> <td>0.04</td> </tr> </table>	Initial state	Acid	+ alcohol	\rightleftharpoons	ester	+ water	At t	0.1 mol	0.1 mol		-	-		0.06	0.06		0.04	0.04	0.75
Initial state	Acid	+ alcohol	\rightleftharpoons	ester	+ water															
At t	0.1 mol	0.1 mol		-	-															
	0.06	0.06		0.04	0.04															
2.4.3	$Q_r = \frac{[ester] \times [water]}{[alcohol] \times [acid]} = \frac{\frac{0.04^2}{V^2}}{\frac{(0.06)^2}{V^2}} = 0.44 < K_c$; system does not reach equilibrium yet.	0.75																		

Exercise 2 (7 points)
Kinetic of a Reaction

Part of the Q	Answer	Mark
1.1.	<p>carboxyl group ester group</p>	1
1.2.	$\text{C}_6\text{H}_5\text{COOH} + (\text{CH}_3)_2\text{C}(=\text{O})\text{OC}(=\text{O})\text{CH}_3 \rightarrow \text{C}_6\text{H}_5\text{COOC}(=\text{O})\text{CH}_3 + \text{CH}_3\text{COOH}$	1
2.1.	$n(\text{HCO}_3^-) = C \times V = 0.5 \times 0.01 = 5 \times 10^{-3} \text{ mol}$; $R(\text{HCO}_3^-) = 5 \times 10^{-3}$ $n(\text{asp}) = \frac{m(\text{asp})}{M(\text{asp})} = \frac{0.460}{180} = 25.5 \times 10^{-4} \text{ mol}$; $R(\text{asp}) = 25.5 \times 10^{-4}$ $R(\text{HCO}_3^-) > R(\text{asp})$ implies aspirin is the limiting reactant.	0.75
2.2.	<p>The curve:</p>	1
2.3.	<p>The rate of formation of CO_2 is equal to the slope of the tangent to the curve at the point of abscissa t.</p> <p>Slope of tangent $T_0 >$ slope of tangent T</p> <p>Therefore the rate of formation of CO_2 decreases with time.</p>	0.75
2.4.	<p>The half-life time of a reaction is the time needed for the formation of half the maximum number of moles of CO_2.</p> $n(\text{CO}_2)_{\text{max}} = n_0(\text{asp}) = 25.5 \times 10^{-4} \text{ mol}$ $n(\text{CO}_2)_{t1/2} = 25.5 \times 10^{-4}/2 = 12.75 \times 10^{-4} \text{ mol}$ <p>Graphically $t^{1/2} = 55 \text{ s}$</p>	1

2.5.	$\text{C}_9\text{H}_8\text{O}_4 + \text{HCO}_3^- \rightarrow \text{C}_9\text{H}_7\text{O}_4^- + \text{CO}_2 + \text{H}_2\text{O}$ At $t = 0$ $n_0(\text{Asp}) n_0(\text{HCO}_3^-)$ At $t_{1/2}$ $\frac{n_0(\text{Asp})}{2} n_0(\text{HCO}_3^-) - \frac{n_0(\text{Asp})}{2}$ $n(\text{HCO}_3^-)_{t=1/2} = n_0(\text{HCO}_3^-) - \frac{n_0(\text{Asp})}{2}$	0.75
2.6	The curve that represents $n(\text{HCO}_3^-) = f(t)$ starts from $n_0 = 50 \times 10^{-4}$ mol, $n(\text{HCO}_3^-)_{t=1/2} = n_0(\text{HCO}_3^-) - \frac{n_0(\text{Asp})}{2} = 50 \times 10^{-4} - \frac{25.5 \times 10^{-4}}{2} = 37.25 \times 10^{-4}$ mol with $t_{1/2} = 55$ s Therefore curve b.	0.75

Exercise 3 (6 points)

Acidic and Basic Solutions

Part of the Q	Answer	Mark
1.1	$14 + \log C_3 = 14 + \log 4 \times 10^{-2} = 12.6$ $\Rightarrow \text{pH} = 14 + \log C_3$; therefore sodium hydroxide is a strong base.	0.75
1.2	During dilution, the number of moles of solute is conserved $\frac{C_1}{C_A} = \frac{V_A}{V_1} = 10$ $\Rightarrow V_A = 10 \times V_1$; with V_A = volume of volumetric flask and V_1 = volume of the pipet; so set 2 must be used (pipet of 5 mL and volumetric flask of 50 mL)	1
1.3	For the solution (1); when the solution is diluted 10 times, pH has increased by less than 1 unit ($3.1 - 2.6 = 0.5$), so HA_1 is a weak acid. The increase of pH in the solution (2) is also less than 1, therefore HA_2 is a weak acid.	0.75
1.4	$\text{HA}_1 + \text{H}_2\text{O} \rightleftharpoons \text{A}_1^- + \text{H}_3\text{O}^+$	0.5
2.1	The equation of the titration reaction is: $\text{HA}_1 + \text{HO}^- \rightarrow \text{A}_1^- + \text{H}_2\text{O}$	0.5
2.2	At the equivalence point: $n(\text{HA}_1)$ introduced into the beaker = $n(\text{HO}^-)$ added to reach equivalence $C_1 \times V_1 = C_3 \times V_E$; so the concentration of the solution (1) is : $C_1 = \frac{C_3 \times V_E}{V_1} = \frac{4 \times 10^{-2} \times 25}{20} = 5 \times 10^{-2} \text{ mol.L}^{-1}$.	1
2.3	Since the species A_1^- predominates so $\text{pH} > \text{pKa} + 1$ For $\text{pH} = 8.0$, pKa should be less than 8 $\Rightarrow \text{pka} = 3.9$ answer (a)	0.5
3.1	pKa of the pair $\text{HA}_2 / \text{A}_2^- = \text{pH}$ when $\frac{[\text{HA}_2]}{[\text{A}_2^-]} = 1$ graphically $\frac{[\text{HA}_2]}{[\text{A}_2^-]} = 1$ for a $\text{pH} = 3.75$; pKa of the pair $\text{HA}_2 / \text{A}_2^- = 3.75$	0.5
3.2	HA_2 is a stronger acid than HA_1 (since $\text{pKa}(\text{HA}_2 / \text{A}_2^-) < \text{pKa}(\text{HA}_1 / \text{A}_1^-)$) $\text{pH}_1 < \text{pH}_2$, The $[\text{H}_3\text{O}^+]$ in the solution (1) is greater than that in solution (2) even though HA_2 is a stronger acid than HA_1 : this can be explained only by the fact that the concentration C_1 is greater than the concentration C_2 The answer is c	0.5

الاسم: مسابقة في مادة الكيمياء
الرقم: المدة: ساعتان

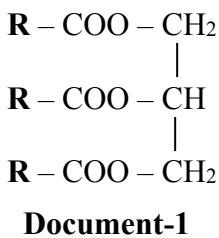
This Exam Includes Three Exercises. It Is Inscribed On 4 Pages Numbered from 1 to 4.
The Use Of A Non-Programmable Calculator Is Allowed.

Answer The Three Following Exercises:

Exercise 1 (7 points)

From Butter to a Perfumed Compound

Butyrin or glyceryl tributyrate is a triglyceride found in butter.
The general formula of triglyceride is represented in **document-1**.



The aim of this exercise is to study the preparation of an organic compound used in perfumery from butter.

Given: - Molar Masses in g.mol⁻¹: M(C) = 12; M(H) = 1; M(O) = 16
- R is an alkyl group of formula C_nH_{2n+1}

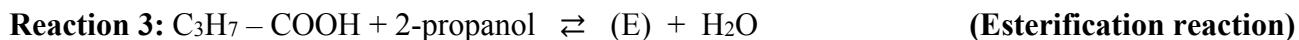
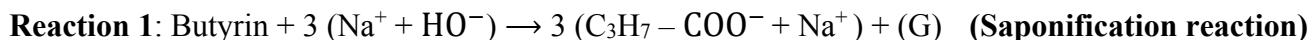
1. Structure of Butyrin

Referring to **document-1**:

- 1.1. Show that the formula of R is C₃H₇, knowing that the molar mass of butyrin is M = 302 g.mol⁻¹.
1.2. Write the condensed structural formula of butyrin.

2. Synthesis of an Ester (E)

Butyrin can be used to manufacture an ester (E), used in perfumery, according to the reactions given in **document-2**.



Document-2

- 2.1.** Referring to **document-2**, specify whether each of the the following propositions is true or false.

- 2.1.1. The systematic name of the compound (G) is glycerol.
2.1.2. The ion C₃H₇ – COO⁻is amphiphilic.
2.1.3. The sodium butanoate solution (C₃H₇ – COO⁻ + Na⁺) is neutral.
2.1.4. The **reaction 2** is an acid-base reaction.

- 2.2.** Write, using condensed structural formulas, the equation of the **reaction 3**. Give the systematic name of the ester (E).

- 2.3.** Specify whether the molecule of compound (E) is chiral.

3. Study of the Reaction 3

Starting from an equimolar mixture of $\text{C}_3\text{H}_7 - \text{COOH}$ and 2-propanol, the yield of the esterification reaction (**reaction 3**) is 60 %.

3.1. Propose a way to increase the yield of this reaction starting from the same reactants.

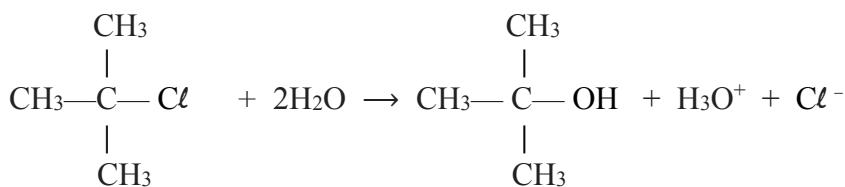
3.2. This reaction becomes complete when one of the reactants is replaced by its chlorinated derivative.

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

Exercise 2 (6 points)

Kinetics of the Hydrolysis of t-Butyl Chloride

2-chloro-2-methylpropane, commonly known as t-butyl chloride, is a colorless organic compound belonging to the series of halogenoalkanes. When tert-butyl chloride is dissolved in water-acetone mixture, it reacts with water to form tert- butyl alcohol and hydrochloric acid in a slow and complete reaction that took place according to the equation shown below.



The aim of this exercise is to study the kinetic of this reaction.

Given: - Molar mass of tert-butyl chloride: $M = 92.5 \text{ g.mol}^{-1}$
- Density of tert-butyl chloride: $d = 0.85 \text{ g.mL}^{-1}$

1. Preliminary Study

1.1. Give the systematic name of tert-butyl alcohol.

1.2. Specify its class.

1.3. What is observed when an excess of an orange acidified potassium dichromate solution is poured into a test tube containing tert-butyl alcohol? Justify.

2. Kinetic Study

At the instant of time $t = 0$, a volume $V = 1.0 \text{ mL}$ of t-butyl chloride is introduced into a flask containing water-acetone mixture, maintained at constant temperature T . The final volume of the reacting mixture is $V_1 = 100.0 \text{ mL}$. (Water is in large excess)

Using an appropriate method, the concentrations of hydronium ions are determined at different instants and the concentrations of tert-butyl chloride (noted $[\text{RCl}]$) are deduced at these instants. The results are grouped in the table of **document-1**.

t (min)	0	15	30	45	60	75	90
$[\text{RCl}] (10^{-2}\text{mol.L}^{-1})$	9.2	6.6	5.2	4.1	3.2	2.5	2.1

Document-1

2.1. Verify that the initial concentration of tert-butyl chloride $[\text{RCl}]_0 = 9.2 \times 10^{-2} \text{ mol.L}^{-1}$.

2.2. Establish the relation between the concentration of hydronium ions, $[\text{H}_3\text{O}^+]_t$, formed at the instant of time t and the concentration of tert-butyl chloride, $[\text{RCl}]_t$, at the same instant t .

2.3. Plot the curve representing the change of the concentration of tert-butyl chloride as a function of time: $[\text{RCl}] = f(t)$, in the interval of time: $[0 - 90 \text{ min}]$.

Take the following scales:

In abscissa: 1 cm for 15 min ;

In ordinate: 1 cm for $1.0 \times 10^{-2} \text{ mol.L}^{-1}$.

2.4. For each of the two following propositions, justify the correct one and correct the false one

2.4.1. The half-life time of this reaction is $t_{1/2} = 38 \text{ min}$.

2.4.2. As the concentration of the tert-butyl alcohol increases with time, the rate of its formation increases.

2.5. The same experiment is repeated but with only one modification: the reacting mixture is maintained at a temperature T' greater than T . Trace on the same graph of the part **2.3**, the shape of the curve $[RCl] = g(t)$ in the interval of time: [0 – 90 min].

Exercise 3 (7 points)

Acid-Base Reactions

The labels of three available flasks show the indications given in **document -1**.

Flask (1)	Flask (2)	Flask (3)
Benzoic acid crystals $M(C_6H_5COOH) = 122 \text{ g.mol}^{-1}$	Ethylamine aqueous solution percentage by mass = 33% Density = 0.914 g.mL^{-1} $M(C_2H_5NH_2) = 45 \text{ g.mol}^{-1}$	Hydrochloric acid solution $(H_3O^+ + Cl^-)$ $C_a = 5 \times 10^{-2} \text{ mol.L}^{-1}$

Document -1

Given: - The study is carried out at 25°C .

- Ethylamine is a weak base.

- pKa of Acid/Base pairs:

$pKa(C_6H_5COOH/C_6H_5COO^-) = 4.2$; $pKa(C_2H_5NH_3^+/C_2H_5NH_2) = 10.8$; $pKa(H_2O/HO^-) = 14$

The aim of this exercise is to prepare acidic and basic solutions of same concentration C and to study some acid – base reactions.

1. Preparation of Benzoic Acid Solution (S_1)

A mass m of benzoic acid crystals is introduced into a volumetric flask of 250 mL. Enough distilled water is added to dissolve the solid then distilled water is added to reach the line mark. A solution (S_1) of benzoic acid of concentration $C = 2 \times 10^{-2} \text{ mol.L}^{-1}$ is obtained.

1.1. Calculate the mass m .

1.2. Write the equation of the reaction of benzoic acid with water.

2. Preparation of an Aqueous Ethylamine Solution (S_2)

It is required to prepare 1.0 L of an ethylamine solution (S_2) of concentration $C = 2 \times 10^{-2} \text{ mol.L}^{-1}$ starting from the solution of the flask (2).

2.1. Show that the volume that should be withdrawn from the flask (2) to realize this preparation is $V = 3 \text{ mL}$.

2.2. Choose, from the sets of **document-2**, the most convenient one to realize the above preparation.

Set 1	Set 2	Set 3
Volumetric pipet 5 mL	Graduated pipet 5 mL	Graduated cylinder 5mL
Volumetric flask 1000mL	Volumetric flask 1000mL	Erlenmeyer flask 1000 mL
Beaker 50 mL	Beaker 50 mL	Beaker 50 mL

Document-2

2.3. Specify, from the following propositions, the one that corresponds to the pH of the solution (S_2).

a. $pH = 12.3$

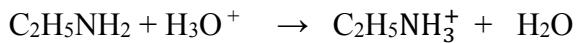
b. $1.7 < pH < 7$

c. $7 < pH < 12.3$

3. pH-metric Study

A hydrochloric acid solution of concentration $C_a = 5 \times 10^{-2} \text{ mol.L}^{-1}$ is added progressively into a beaker containing a volume $V_b = 20.0 \text{ mL}$ of the ethylamine solution (S_2) of concentration C .

The equation of the complete reaction that took place is:



3.1. Justify the following statements:

- 3.1.1.** The volume of the acid solution added to reach the equivalence point is 8 mL.
- 3.1.2.** The pH at equivalence, based on the chemical species present at equivalence, is $\text{pH}_E < 7$
- 3.1.3.** The coordinates of the half equivalence point are ($V_a = 4 \text{ mL}$; $\text{pH} = 10.8$).

4. Acid-Base Mixture

A volume $V_1 = 72 \text{ mL}$ of the benzoic acid solution (S_1) is mixed with a volume $V_2 = 28 \text{ mL}$ of the above ethylamine solution (S_2).

4.1. Write the equation of the complete reaction that took place in this mixture.

4.2. Determine the ratio $\frac{[\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]}$ in the obtained solution, knowing that ethylamine is the limiting reactant.

4.3. Given the three following values of pH :

- a.** $\text{pH} < 3.2$; **b.** $\text{pH} = 4$; **c.** $\text{pH} > 5.2$

Choose the one that corresponds to the pH of the obtained solution. Justify without calculation.

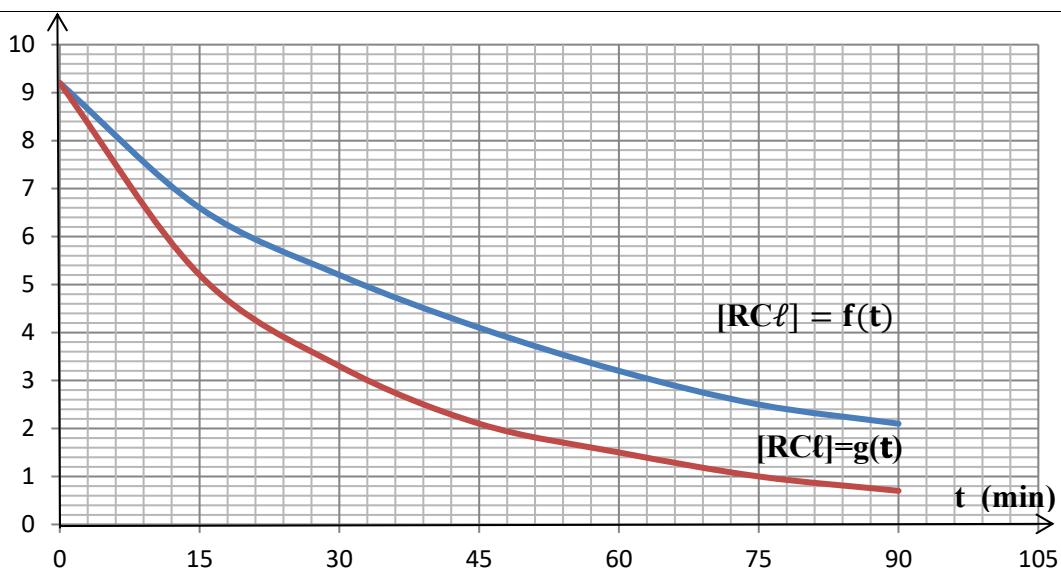
مشروع معيار التصحيح
المادة: كيمياء

	Exercise 1 (7 points) From Butter to a Perfumed Compound	
Part of the Q	Answer	Mark
1.1	The molar mass of butyrin is: $M = 3R + 6(12) + 6(16) + 5 = 302 \text{ g.mol}^{-1}$, $M(R) = (302 - 173) \div 3 = 43 \text{ g.mol}^{-1}$, R is an alkyl group of formula $C_nH_{2n+1} = 43$, $12n + 2n+1 = 43$, $n = 3$, then formula of alkyl group R is C_3H_7	0.75
1.2	$\begin{array}{c} CH_3 - CH_2 - CH_2 - COO - CH_2 \\ \\ CH_3 - CH_2 - CH_2 - COO - CH \\ \\ CH_3 - CH_2 - CH_2 - COO - CH_2 \end{array}$	0.5
2.1.1	False. The systematic name of the compound (G) is 1,2,3 – propanetriol	0.75
2.1.2	True. The ion $C_3H_7 - COO^-$ has two ends: ($C_3H_7 -$) is the tail which is lipophilic (or hydrophobic), and COO^- is the head which is hydrophilic (or lipophobic), thus $C_3H_7 - COO^-$ is amphiphilic.	0.75
2.1.3	False. The sodium butanoate solution ($C_3H_7 - COO^- + Na^+$) is basic, due to the presence of the ion $C_3H_7 - COO^-$ which is a basic species and Na^+ is a spectator ion.	0.75
2.1.4	True. Reaction 2 is an acid base reaction since there is a proton (H^+) transfer from H_3O^+ to $C_3H_7 - COO^-$	0.75
2.2	$CH_3 - CH_2 - CH_2 - COOH + CH_3 - CH(OH) - CH_3 \rightleftharpoons CH_3 - CH_2 - CH_2 - COO - CH(CH_3) - CH_3 + H_2O$ <p>The systematic name of (E) 1-methylethylbutanoate.</p>	1
2.3	The molecule of compound (E) is not chiral since it doesn't contain an asymmetric carbon atom.	0.5
3.1	One can increase the yield of this reaction starting from the same reactants by using a non equimolar reacting mixture	0.5
3.2	The equation of the reaction using a chlorinated derivative is: $CH_3 - CH_2 - CH_2 - COCl + CH_3 - CH(OH) - CH_3 \rightarrow CH_3 - CH_2 - CH_2 - COO - CH(CH_3) - CH_3 + HCl$	0.75
	Exercise 2 (6 points) Kinetics of the Hydrolysis of t-Butyl Chloride	
Part of	Answer	Mark

the Q																		
1.1	The systematic name of this alcohol is 2-methyl-2-propanol	0.5																
1.2	This alcohol is a tertiary alcohol since the carbon bearing the hydroxyl group is linked to three alkyl groups.	0.5																
1.3	Since the alcohol is a tertiary alcohol, then it doesn't undergo mild oxidation reaction with strong oxidizing agent such as potassium dichromate. The orange color of the potassium dichromate solution persists.	0.5																
2.1	The initial concentration of tert-butyl chloride $[RCl]_0 = \frac{n(RCl)}{V_t} = \frac{m(RCl)}{M(RCl) \times V_t} = \frac{d \times v}{M(RCl) \times V_t} = \frac{0.85 \times 1}{92.5 \times 0.1} = 9.2 \times 10^{-2} \text{ mol.L}^{-1}$.	0.5																
2.2	$n_o(RCl) = n(RCl)_t + n(RCl)_{\text{disap}}$ $n(RCl)_{\text{disap}} = n(H_3O^+)_{\text{formed}}$ $n_o(RCl) = n(RCl)_t + n(H_3O^+)_{\text{formed}}$ $n(RCl)_t = n_o(RCl) - n(H_3O^+)_t$ divided by V_t $[RCl]_t = [RCl]_0 - [H_3O^+]_t$, $[RCl]_t = 9.2 \times 10^{-2} - [H_3O^+]_t$	0.75																
2.3	<p>The curve is :</p> <table border="1"> <caption>Data points estimated from the graph</caption> <thead> <tr> <th>t (min)</th> <th>[RCl] (10⁻² mol.L⁻¹)</th> </tr> </thead> <tbody> <tr><td>0</td><td>9.2</td></tr> <tr><td>15</td><td>6.8</td></tr> <tr><td>30</td><td>4.4</td></tr> <tr><td>45</td><td>2.2</td></tr> <tr><td>60</td><td>1.8</td></tr> <tr><td>75</td><td>1.4</td></tr> <tr><td>90</td><td>1.0</td></tr> </tbody> </table>	t (min)	[RCl] (10 ⁻² mol.L ⁻¹)	0	9.2	15	6.8	30	4.4	45	2.2	60	1.8	75	1.4	90	1.0	1
t (min)	[RCl] (10 ⁻² mol.L ⁻¹)																	
0	9.2																	
15	6.8																	
30	4.4																	
45	2.2																	
60	1.8																	
75	1.4																	
90	1.0																	
2.4.1	<p>True. The half-life time of a reaction is the time needed for the disappearance of half the initial quantity of RCl.</p> $[RCl]_{t1/2} = (9.2 \times 10^{-2}) \div 2 = 4.6 \times 10^{-2} \text{ mol.l}^{-1}$ <p>Graphically $t \frac{1}{2} = 38 \text{ min}$</p>	1																
2.4.2	<p>False. As the concentration of the tert-butyl alcohol increases with time, the concentration of the reactants decreases and since the concentration of reactants is a kinetic factor, so the rate of the formation of the alcohol decreases with time.</p>	0.75																
	$[RCl] (10^{-2}\text{mol.L}^{-1})$																	

2.5

0.5

**Exercise 3 (7 points)****Acid-Base Reactions**

Part of the Q	Answer	Mark
1.1	$m = C \times V \times M = 0.02 \times 0.25 \times 122 = 0.005 \times 122 = 0.61\text{g}$	0.5
1.2	Benzoic acid is a weak acid $\text{C}_6\text{H}_5\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{COO}^- + \text{H}_3\text{O}^+$	0.5
2.1	During dilution, the number of moles of solute is conserved: $n = C \times V = 0.02 \times 1 = 0.02 \text{ mol}$ mass of $\text{C}_2\text{H}_5\text{NH}_2$ present in 1 L of solution (S_2) = $0.02 \times 45 = 0.9 \text{ g}$ mass of solution of the flask (2) : $m = \frac{0.9 \times 100}{33} = 2.72 \text{ g}$ volume of solution of the flask (2): $V = \frac{2.72}{0.914} = 3 \text{ mL}$	1
2.2	The most convenient set is the set (2)	0.5
2.3	Since $\text{C}_2\text{H}_5\text{NH}_2$ is a weak base so its pH is greater than 7 but less than $14 + \log C$, $14 + \log C = 12.3$ The answer is c	0.5
3.1.1	At the equivalence point: $n(\text{H}_3\text{O}^+)_\text{added to reach equivalence} = n(\text{C}_2\text{H}_5\text{NH}_2)_\text{introduced into the beaker}$ $C_3 \times V_E = C \times V_b \Rightarrow V_E = \frac{C \times V_b}{C_3} = \frac{0.02 \times 20}{0.05} = 8 \text{ mL.}$	0.75
3.1.2	The chemical species present in solution at equivalence (other than H_2O) are: Cl^- which is a spectator ion. $\text{C}_2\text{H}_5\text{NH}_3^+$: the conjugate weak acid of the weak base $\text{C}_2\text{H}_5\text{NH}_2$. therefore the solution at equivalence is acidic and its pH is less than 7	0.5

3.1.3	<p>The equivalence point: $V_E = 8\text{mL}$ At half equivalence $V = \frac{V_E}{2} = 4\text{ mL}$, $\text{pH} = \text{pK}_a = 10.8$ then the coordinates of the half equivalence point are: $(V_a = 4\text{ mL}, \text{pH} = 10.8)$.</p>	0.5										
4.1	<p>The equation of the reaction:</p> $\text{C}_6\text{H}_5\text{COOH} + \text{C}_2\text{H}_5\text{NH}_2 \rightarrow \text{C}_2\text{H}_5\text{NH}_3^+ + \text{C}_6\text{H}_5\text{COO}^-$	0.5										
4.2	<p>since ethylamine is the limiting reactant then:</p> $\text{C}_6\text{H}_5\text{COOH} + \text{C}_2\text{H}_5\text{NH}_2 \rightarrow \text{C}_2\text{H}_5\text{NH}_3^+ + \text{C}_6\text{H}_5\text{COO}^-$ <table style="margin-left: auto; margin-right: auto;"> <tr> <td>Initial state</td> <td>$C \times V_1$</td> <td>$C \times V_2$</td> <td>0</td> <td>0</td> </tr> <tr> <td>Final state</td> <td>$C \times V_1 - C \times V_2$</td> <td>0</td> <td>$C \times V_2$</td> <td>$C \times V_2$</td> </tr> </table> $\frac{[\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]} = \frac{n_{\text{C}_6\text{H}_5\text{COO}^-} \div V_t}{n_{\text{C}_6\text{H}_5\text{COOH}} \div V_t} = \frac{(C \times V_2)}{(C \times V_1) - (C \times V_2)}$ $\frac{[\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]} = \frac{V_2}{V_1 - V_2} = \frac{28}{72 - 28} = 0.636$	Initial state	$C \times V_1$	$C \times V_2$	0	0	Final state	$C \times V_1 - C \times V_2$	0	$C \times V_2$	$C \times V_2$	1
Initial state	$C \times V_1$	$C \times V_2$	0	0								
Final state	$C \times V_1 - C \times V_2$	0	$C \times V_2$	$C \times V_2$								
4.3	$\frac{[\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]} = 0.636$ <p>Since $[\text{C}_6\text{H}_5\text{COO}^-] < 10 [\text{C}_6\text{H}_5\text{COOH}]$, $\text{C}_6\text{H}_5\text{COO}^-$ doesn't predominate $\text{C}_6\text{H}_5\text{COOH}$ in the solution. So $\text{pH} < \text{pK}_a + 1 = 5.2$</p> <p>Similarly, $\frac{[\text{C}_6\text{H}_5\text{COOH}]}{[\text{C}_6\text{H}_5\text{COO}^-]} = \frac{1}{0.636} = 1.572$, $[\text{C}_6\text{H}_5\text{COOH}] < 10 [\text{C}_6\text{H}_5\text{COO}^-]$, $\text{C}_6\text{H}_5\text{COOH}$ doesn't predominate $\text{C}_6\text{H}_5\text{COO}^-$ in the solution. So $\text{pH} > \text{pK}_a - 1 = 3.2$</p> <p>The answer is b.</p>	0.75										

الاسم:	مسابقة في مادة الكيمياء
الرقم:	المدة: ساعة ونصف

This Exam Includes Three Exercises. It Is Inscribed on Four Pages, Numbered from 1 to 4.

The Use of A Non-programmable Calculator Is Allowed.

Answer the Three Following Exercises:

Exercise 1 (7 points)

Kinetic Study of a Slow Reaction

A hydrochloric acid solution ($\text{H}_3\text{O}^+ + \text{Cl}^-$) reacts with magnesium metal according to a slow and complete reaction as shown by the equation below:



In order to study the kinetic of this reaction, one introduces a mass $m = 0.12 \text{ g}$ of magnesium in an Erlenmeyer flask.

At instant $t = 0$, a volume $V = 100.0 \text{ mL}$ of a hydrochloric acid solution (S) of molar concentration C is poured into the Erlenmeyer flask.

Using an appropriate method, the number of moles of hydrogen gas $n(\text{H}_2)$ is determined at different instants t .

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

$t \text{ (min)}$	2	4	6	8	10	12	14	16
$n(\text{H}_2) 10^{-4} \text{ mol}$	8	14	18.8	22.2	25	26.8	28.2	29

Document-1

Given:

- Molar mass of magnesium (Mg) is: $M = 24 \text{ g.mol}^{-1}$
- The study is realized at a temperature $T = 25^\circ\text{C}$.
- H_3O^+ is the only chemical species with acid character in the reacting system.

1- Preparation of Hydrochloric Acid Solution (S)

The solution (S) is prepared by diluting 50 times a hydrochloric acid solution (S_0).

Choose, from **Document-2**, the most precise set for the preparation of solution (S). Justify.

Set 1	Set 2	Set 3
Beaker of 100 mL Graduated cylinder of 10 mL Volumetric flask of 500 mL	Beaker of 100 mL Volumetric pipet of 10 mL Volumetric flask of 500 mL	Beaker of 100 mL Volumetric pipet of 10 mL Volumetric flask of 250 mL

Document-2

2- Preliminary Study

At the end of the reaction, the pH of the obtained solution is: $\text{pH} = 0.77$

2.1. Deduce that magnesium is the limiting reactant.

2.2. Specify whether the instant $t = 16 \text{ min}$ represents the end time of this reaction.

3- Kinetic Study

3.1. Plot the curve that represents the variation of the number of moles of hydrogen gas (H_2) as a function of time: $n(H_2) = f(t)$ within the interval of time [0 – 16 min]

Take the following scale: Abscissa: 1cm for 1 min

Ordinate: 1cm for 2×10^{-4} mol.

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

3.3. Choose the correct answer. Justify.

3.3.1. The rate of the reaction at a given instant t denoted by r_{rxn} and the rate of disappearance of H_3O^+ ions at same instant t denoted by $r_{(H_3O^+)_t}$ are related by the following relation:

a) $r_{rxn} = \frac{r_{(H_3O^+)_t}}{2}$

b) $r_{rxn} = 2r_{(H_3O^+)_t}$

c) $r_{rxn} = r_{(H_3O^+)_t}$

3.3.2. The rate of the disappearance of H_3O^+ at instant $t_1 = 6$ min is $r_1 = 2.05 \times 10^{-4}$ mol.min $^{-1}$. The rate of disappearance of H_3O^+ at instant $t_2 = 12$ min is:

a) $r_2 = 4.1 \times 10^{-4}$ mol.min $^{-1}$ b) $r_2 = 2.05 \times 10^{-4}$ mol.min $^{-1}$ c) $r_2 = 0.86 \times 10^{-4}$ mol.min $^{-1}$

3.3.3. When the above experiment is carried out at a temperature $T' > T$ (as the only modification), the number of moles of H_2 at instant $t = 12$ min is:

a) $n(H_2) > 26.8 \times 10^{-4}$ mol b) $n(H_2) < 26.8 \times 10^{-4}$ mol c) $n(H_2) = 26.8 \times 10^{-4}$ mol

Exercise 2 (6 points)

Sulfamic Acid

Sulfamic acid is a white crystalline solid which is an efficient agent for descaling. It is used for cleaning a number of domestic appliances and industrial equipment.

The aim of this exercise is to study the behavior of sulfamic acid in water and to determine the mass composition of sulfamic acid in a sulfamic acid based powder descaling agent.

Given:

- Molar mass of sulfamic acid is: $M = 97.0 \text{ g.mol}^{-1}$
- This study is carried out at 25°C

1. Behavior of Sulfamic Acid in Water

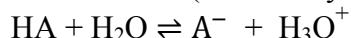
Available is, in the laboratory, a sulfamic acid solution (S) of molar concentration $C = 1.0 \times 10^{-2}$ mol.L $^{-1}$. The pH of the solution (S) is measured and found to be $\text{pH}_{(S)} = 2.0$

1.1. Calculate the molar concentration of hydronium ions, $[H_3O^+]$, in the solution (S).

1.2. Justify that sulfamic acid is a strong acid.

1.3. For each of the two following statements, justify when the statement is true and correct when it is false:

1.3.1. The equation of the reaction of sulfamic acid (denoted by HA) with water is:



1.3.2. The dilution 100 times of the solution (S), increases its pH by 2 units.

2. Determination of the Mass Composition of a Descaling Agent

A sample of sulfamic acid based powder descaling agent of mass $m = 1.00 \text{ g}$ is used to prepare a solution (S') of volume $V = 1.0 \text{ L}$.

A volume $V_a = 20.0$ mL of the solution (S') is introduced into a beaker then distilled water is added in order to immerse properly the pH-meter electrode. A pH-metric titration is realized by adding progressively into the beaker a sodium hydroxide solution ($\text{Na}^+ + \text{HO}^-$) of molar concentration $C_b = 2.0 \times 10^{-2}$ mol.L $^{-1}$. The volume of the basic solution needed to reach equivalence is $V_{bE} = 9.8$ mL.

- 2.1. Name the glassware needed to add the basic solution.
- 2.2. Write the equation of the titration reaction.
- 2.3. Determine the molar concentration of sulfamic acid in the solution (S').
- 2.4. Calculate the mass of sulfamic acid in 1L of the solution (S').
- 2.5. Deduce the percentage by mass of sulfamic acid in the descaling agent.

Exercise 3 (7 points)

Isobutyl Propanoate

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 isobutyl propanoate which characterizes the rum odor.

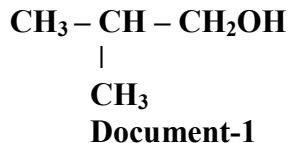
1. Study of the Structure of Propanoic Acid

The molecular formula of propanoic acid is $\text{C}_3\text{H}_6\text{O}_2$

- 1.1. Write the condensed structural formula of propanoic acid.
- 1.2. Circle and name the functional group of this acid.

2. Isobutyl Alcohol

The condensed structural formula of isobutyl alcohol is given in **Document-1**.



- 2.1. Give the systematic name of isobutyl alcohol.
- 2.2. Identify the class of this alcohol.

3. Synthesis of Isobutyl Propanoate

Isobutyl propanoate can be prepared starting from isobutyl alcohol and propanoic acid.

- 3.1. Write, using condensed structural formulas, the equation of the preparation reaction of isobutyl propanoate.
- 3.2. Give the systematic name of the ester formed.
- 3.3. An equimolar mixture (M) containing 0.1 mol of isobutyl alcohol and 0.1 mol of propanoic acid is heated to reflux for 40 min in the presence of few drops of concentrated sulfuric acid as a catalyst. The mass of the ester obtained is 8.71g.

- For an initial equimolar mixture of a carboxylic acid and a primary alcohol, the yield of the reaction at equilibrium is 67%.
- Molar mass of isobutyl propanoate is: $M = 130 \text{ g.mol}^{-1}$.

Document-2

3.3.1. Indicate the importance of the reflux heating.

3.3.2. Determine the yield of this esterification reaction at $t = 40 \text{ min}$.

3.3.3. Verify that the reacting system is at equilibrium at this instant.

3.3.4. Another reacting mixture containing 0.1 mol of isobutyl alcohol and 0.1 mol of propanoyl chloride is prepared.

3.3.4.1. Write, using condensed structural formulas, the equation of the preparation of propanoyl chloride starting from propanoic acid.

3.3.4.2. Choose, with justifying, the correct answer.

The mass m of the ester obtained at the end of the reaction is:

a) $m = 8.71 \text{ g}$

b) $m < 8.71 \text{ g}$

c) $m > 8.71 \text{ g}$

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

Part of the Q.	Answer	Mark																								
1	<p>During dilution, the number of moles of solute is conserved</p> <p>Dilution factor = $\frac{C_o}{C} = \frac{V}{V_0}$</p> <p>For $V = 500 \text{ mL}$; $V_o = \frac{V}{F} = \frac{500}{50} = 10 \text{ mL}$</p> <p>We must use a volumetric pipet of 10 mL and a volumetric flask of 500 mL</p> <p>Then set 2</p>	1																								
2.1	Since the pH of the obtained solution is $0.77 < 7$ so, the final medium is acidic, therefore the hydrochloric acid is in excess and magnesium is the limiting reactant.	0.75																								
2.2	$n(\text{Mg}) = \frac{m(\text{Mg})}{M(\text{Mg})} = \frac{0,12}{24} = 50 \times 10^{-4} \text{ mol}$ $\frac{n(\text{Mg})_o}{1} = \frac{n(\text{H}_2)_\infty}{1}$ <p>Then $n(\text{H}_2)_\infty = 50 \times 10^{-4} \text{ mol} > n(\text{H}_2)_{\text{at } t=16 \text{ min}} = 29 \times 10^{-4} \text{ mol}$</p> <p>So $t = 16 \text{ min}$ does not represent the end time of the reaction.</p>	1																								
3.1	<table border="1"> <caption>Data points estimated from the graph</caption> <thead> <tr> <th>t (min)</th> <th>n(H₂) 10⁻⁴ mol</th> </tr> </thead> <tbody> <tr><td>0</td><td>0</td></tr> <tr><td>2</td><td>4</td></tr> <tr><td>4</td><td>7</td></tr> <tr><td>6</td><td>10</td></tr> <tr><td>8</td><td>13</td></tr> <tr><td>10</td><td>15</td></tr> <tr><td>12</td><td>17</td></tr> <tr><td>14</td><td>19</td></tr> <tr><td>16</td><td>21</td></tr> <tr><td>18</td><td>23</td></tr> <tr><td>20</td><td>25</td></tr> </tbody> </table>	t (min)	n(H ₂) 10 ⁻⁴ mol	0	0	2	4	4	7	6	10	8	13	10	15	12	17	14	19	16	21	18	23	20	25	1
t (min)	n(H ₂) 10 ⁻⁴ mol																									
0	0																									
2	4																									
4	7																									
6	10																									
8	13																									
10	15																									
12	17																									
14	19																									
16	21																									
18	23																									
20	25																									
3.2	<p>The half-life time of the reaction is the time needed for the formation of half the maximum quantity of the product.</p> $n(\text{H}_2)_{t1/2} = \frac{n(\text{H}_2)_\infty}{2} = \frac{50 \times 10^{-4}}{2} = 25 \times 10^{-4} \text{ mol}$ <p>Graphically $t_{1/2} = 10 \text{ min}$</p>	1																								
3.3.1	a since from the stoichiometric ratios:	0.75																								

	$r(\text{reaction}) = \frac{r(\text{disappearance of } \text{H}_3\text{O}^+ \text{ ions})}{2}$	
3.3.2	c [H ₃ O ⁺] decreases with time (kinetic factor) so the rate of disappearance of H ₃ O ⁺ ions deceases with time.	0.75
3.3.3.	a Since the temperature increases, the rate of formation of hydrogen increases. Therefore at t = 12 min: n(H ₂)formed at temperature T' > n(H ₂)formed at temperature T	0.75

Exercice 2 (6points)

Sulfamic Acid

Part of the Q.	Answer	Mark
1.1	[H ₃ O ⁺] = 10 ^{-pH} = 10 ⁻² mol.L ⁻¹	0.5
1.2	Since [H ₃ O ⁺] = C then sulfamic acid is a strong acid.	0.5
1.3. 1	HA + H ₂ O → A ⁻ + H ₃ O ⁺	0.5
1.3. 2	When the solution is diluted 100 times, its concentration becomes $C = \frac{C_o}{100} = \frac{10^{-2}}{100} = 10^{-4}$ mol.L ⁻¹ $pH = -\log C = -\log 10^{-4} = 4$ $pH - pH_o = 4 - 2 = 2$ So the pH increases by 2 units.	0.75
2.1	Graduated buret	0.5
2.2	H ₃ O ⁺ + HO ⁻ → 2H ₂ O	0.75
2.3	At the equivalence point : n(H ₃ O ⁺) introduced into the beaker = n(HO ⁻) added to reach equivalence $C_a \times V_a = C_b \times V_{bE}$ $C_a = \frac{C_b \times V_{bE}}{V_a} = \frac{2 \times 10^{-2} \times 9.8 \times 10^{-3}}{20 \times 10^{-3}} = 0.0098$ mol.L ⁻¹	1.25
2.4	n (sulfamic acid) = C × V = 0.0098 × 1 = 0.0098 mol m(sulfamic acid) = n . M = 0.0098 × 97 = 0.9506 g	0.5
2.5	% = $\frac{m(\text{sulfamic acid})}{m(\text{descaling})} \times 100 = \frac{0.9506}{1} \times 100 = 95.06\%$	0.75

Exercise 3 (7 points)

Isobutyl Propanoate

Part of the Q.	Answer	Mark
1.1	The condensed structural formula of propanoic acid is CH ₃ – CH ₂ – COOH	0.5
1.2	CH ₃ – CH ₂ – COOH The functional group of this acid is carboxyl group.	0.5
2.1	The systematic name of isobutyl alcohol is : 2-methyl-1-propanol	0.5
2.2	This alcohol is a primary alcohol since the functional carbon is connected to one alkyl	0.5

	group.	
3.1	$\text{CH}_3 - \text{CH}_2 - \text{COOH} + \text{CH}_3 - \text{CH} - \text{CH}_2\text{OH} \rightleftharpoons \text{CH}_3 - \underset{\text{H}_2\text{O}}{\underset{ }{\text{CH}_3}} - \text{CH}_2 - \text{COO} - \text{CH}_2 - \text{CH} - \text{CH}_3 +$	1
3.2	the systematic name of the ester formed is 2-methylpropylpropanoate	0.5
3.3.1	The reflux heating accelerates the rate of the esterification reaction without any loss of reactants or products due to evaporation.	0.5
3.3.2	$\% \text{Yield} = \frac{n(\text{ester})_{\text{actual}}}{n(\text{ester})_{\text{theoretical}}} \times 100$ $n(\text{ester})_{\text{actual}} = \frac{m(\text{ester})_{\text{actual}}}{M} = \frac{8.71}{130} = 0.067 \text{ mol}$ <p>assuming that the reaction is complete:</p> $R(\text{alcohol}) = \frac{n(\text{alcohol})}{1} = 0.1$ $R(\text{acid}) = \frac{n(\text{acid})}{1} = 0.1$ <p>Then the mixture is stoichiometric</p> $n(\text{ester})_{\text{theoretical}} = n(\text{alcohol}) = 0.1 \text{ mol}$ $\% \text{Yield} = \frac{n(\text{ester})_{\text{actual}}}{n(\text{ester})_{\text{theoretical}}} \times 100 = \frac{0.067}{0.1} \times 100 = 67 \%$	1
3.3.3	Since the initial mixture of a carboxylic acid and a primary alcohol is equimolar and the yield of the reaction at equilibrium is 67% then the reacting system is at equilibrium at this instant.	0.5
3.3.4.1	True Since this mixture is an equimolar mixture.	0.75
3.3.4.2	<p>False</p> $\% \text{Yield} = \frac{n(\text{ester})_{\text{actual}}}{n(\text{ester})_{\text{theoretical}}} \times 100$ $n(\text{ester})_{\text{actual}} = \frac{\% \text{Yield} \times n(\text{ester})_{\text{theoretical}}}{100} = \frac{67 \times 0.2}{100} = 0.134 \text{ mol}$ $m(\text{ester})_{\text{actual}} = n \times M = 0.12 \times 130 = 17.42 \text{ g}$	0.75

Special part LS

3.3.4.1	$\text{CH}_3 - \text{CH}_2 - \text{COOH} + \text{PCl}_5 \rightarrow \text{CH}_3 - \text{CH}_2 - \text{COCl} + \text{HCl} + \text{POCl}_3$	0.75
3.3.4.2	c since the esterification reaction using propanoyl chloride instead of propanoic acid becomes complete.	0.75

الاسم:
الرقم:

مسابقة في مادة الكيمياء
المدة: ساعة ونصف

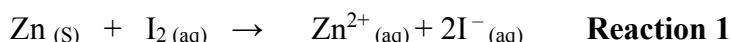
**This Exam Includes Three Exercises. It Is Inscribed On 4 Pages Numbered from 1 to 4.
The Use Of A Non-Programmable Calculator Is Allowed.**

Answer The Following Three Exercises:

Exercise 1 (7 points)

Kinetic of The Reduction of Iodine by Zinc

Zinc metal (Zn) reacts with an aqueous solution of iodine (I_2 (aq)) in a slow and complete reaction that takes place according to the equation given below:



The aim of this exercise is to study the kinetic of this reaction.

Given: Molar mass of Zinc is: $M(Zn) = 65.4 \text{ g.mol}^{-1}$

1. Preliminary Study

At instant $t = 0$, a volume $V = 280.0 \text{ mL}$ of iodine solution (I_2) of concentration $C_0 = 2.0 \times 10^{-2} \text{ mol.L}^{-1}$ is poured into a beaker containing a mass $m = 346 \text{ mg}$ of pure zinc metal.

Reaction 1 is realized at a temperature T maintained constant.

- 1.1. Determine the limiting reactant.
- 1.2. Establish the relation between the concentration of iodine at instant t , $[I_2]_t$, and the concentration of zinc ions at same instant t , $[Zn^{2+}]_t$.
- 1.3. Show that the concentration of zinc ions at the end of the reaction is $[Zn^{2+}]_\infty = 18.9 \times 10^{-3} \text{ mol.L}^{-1}$.

2. Kinetic Study

Document-1 shows the concentration of Zn^{2+} ions, $[Zn^{2+}]$, obtained at different instants.

$t \text{ (s)}$	30	100	200	400	600	800	1000	1200
$[Zn^{2+}] \text{ (}10^{-3} \text{ mol.L}^{-1}\text{)}$	2.4	7.9	10.5	13.8	15.8	17.4	17.9	18.4

Document-1

- 2.1. Plot the curve representing the variation of the concentration of Zn^{2+} ions as a function of time: $[Zn^{2+}] = f(t)$ in the interval of time: $[0 - 1200 \text{ s}]$.
Take the following scales: 1 cm for 100 s in abscissa
1 cm for $2.0 \times 10^{-3} \text{ mol.L}^{-1}$ in ordinate.
- 2.2. Specify, graphically, the variation in the rate of formation of Zn^{2+} ions over time.
- 2.3. Determine, graphically, the half-life time of the reaction $t_{1/2}$.
- 2.4. The above kinetic study is carried out but with only one modification: $T' > T$. Trace, on the same graph of question 2.1, the shape of the curve representing the variation of the concentration Zn^{2+} ions as a function of time at T' : $[Zn^{2+}] = g(t)$. Justify.

Exercise 2 (6 points)

Sodium Hydroxide

Sodium hydroxide solution ($\text{Na}^+ + \text{HO}^-$) is colorless and odorless that can react violently with strong acids and water. Sodium Hydroxide is commonly used as a drain cleaner.

The aim of this exercise is to study the behavior of sodium hydroxide in water then to determine its concentration in a commercial drain cleaner.

Given:

- Molar mass of sodium hydroxide: $M_{(\text{NaOH})} = 40 \text{ g.mol}^{-1}$
- Density of commercial drain cleaner solution: $d = 2.13 \text{ g.mL}^{-1}$
- The study is carried out at $T = 25^\circ\text{C}$
- Ion product of water at 25°C : $K_w = 1.0 \times 10^{-14}$

1. Behavior of Sodium Hydroxide in Water

A mass $m = 0.40 \text{ g}$ of solid sodium hydroxide are dissolved in distilled water in order to prepare a volume $V = 1.0 \text{ L}$ of a sodium hydroxide solution (S).

The pH of the obtained solution (S) is: $\text{pH} = 12$

- 1.1. Verify that the molar concentration of the solution (S) is $C = 1.0 \times 10^{-2} \text{ mol.L}^{-1}$
- 1.2. Calculate the concentration of hydronium ions, $[\text{H}_3\text{O}^+]$, in the solution (S).
- 1.3. Deduce the concentration of hydroxide ions, $[\text{HO}^-]$, in this solution.
- 1.4. Justify the statement: "Sodium hydroxide is a strong base."

2. Dilution of the Commercial Drain Cleaner Solution

The commercial drain cleaner solution noted (S_o) is too concentrated. A sodium hydroxide ($\text{Na}^+ + \text{HO}^-$) solution (S') is prepared by diluting 500 times the commercial solution (S_o).

Choose, from **Document-1**, the most precise set for the preparation of solution (S').

Set 1	Set 2	Set 3
Beaker of 100 mL	Beaker of 100 mL	Beaker of 100 mL
Graduated cylinder of 10 mL	Volumetric pipet of 2 mL	Volumetric pipet of 2 mL
Volumetric flask of 500 mL	Volumetric flask of 1 L	Volumetric flask of 500 mL

Document-1

3. pH-metric Titration of Solution (S')

A volume $V_b = 10.0 \text{ mL}$ of the solution (S') is introduced into a beaker then distilled water is added in order to immerse properly the pH-meter electrode. A pH-metric titration is realized by adding progressively into the beaker a hydrochloric acid solution ($\text{H}_3\text{O}^+ + \text{Cl}^-$) of molar concentration $C_a = 2.50 \times 10^{-2} \text{ mol.L}^{-1}$. The volume of the acid solution needed to reach equivalence is $V_{aE} = 21.3 \text{ mL}$.

- 3.1. Write the equation of the titration reaction.
- 3.2. Specify, based on the chemical species present in the solution, whether the addition of water to immerse properly the pH-meter electrode affects the pH at equivalence, pH_E .
- 3.3. Determine the molar concentration of the solution (S').
- 3.4. Deduce the molar concentration of sodium hydroxide in the commercial drain cleaner (S_o).
- 3.5. Choose the value that corresponds to the percentage by mass of the sodium hydroxide in the drain cleaner solution (S_o). Justify.
a) 20% **b) 50%** **c) 35 %**

Exercise 3 (7 points)

Isobutyric Acid Ethyl Ester

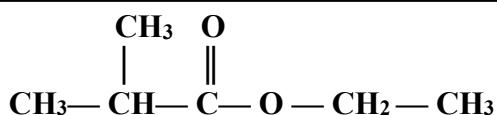
Isobutyric acid ethyl ester is a sweet tasting compound. It is prepared by an esterification reaction between an acid (A) and an alcohol (B).

Outside of the human body, it has been detected in several different foods, such as apples, figs ...

The aim of this exercise is to identify the acid (A) and the alcohol (B) and to study the effect of some factors on the esterification reaction yield.

1. Study the Structure of Isobutyric Acid Ethyl Ester

The condensed structural formula of isobutyric acid ethyl ester is given in **Document-1**:

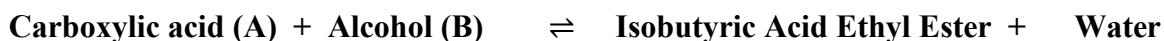


Document-1

- 1.1. Recopy the condensed structural formula of isobutyric acid ethyl ester and circle its functional group.
- 1.2. Give the systematic name of isobutyric acid ethyl ester.
- 1.3. Isobutyric acid ethyl ester is obtained from the reaction between a carboxylic acid (A) and an alcohol (B). Identify the acid (A) and the alcohol (B).

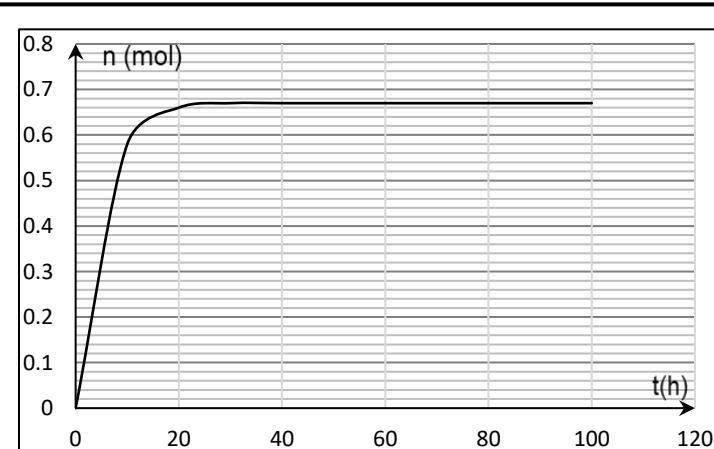
2. Synthesis of Isobutyric Acid Ethyl Ester

Isobutyric acid ethyl ester can be prepared starting from carboxylic acid (A) and alcohol (B) according to the following equation:



An equimolar mixture (M) containing 1.0 mol of carboxylic acid (A) and 1.0 mol of the alcohol (B) is heated to reflux for several hours in the presence of few drops of sulfuric acid as a catalyst.

Document-2 represents the change in the number of moles of the ester formed with time.



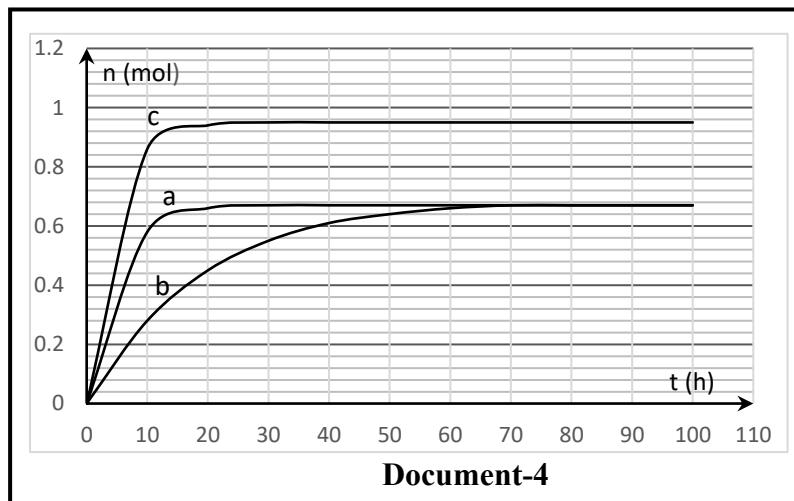
Document-2

- 2.1. Give the importance of heating this reacting mixture.
- 2.2. Justify, based on **Document-2**, that the system has reached equilibrium state.
- 2.3. Determine the yield of this synthesis reaction.
- 2.4. We realize other reacting mixtures given in the table of **Document-3**.

Reacting mixture	Number of moles of (A)	Number of moles of (B)	Catalyst	Corresponding curve
M	1.0 mol	1.0 mol	H ₂ SO ₄	a
M'	1.0 mol	1.0 mol		b
M''	1.0 mol	5.0 mol	H ₂ SO ₄	c

Document-3

Document-4 shows the curves that represent the variation of n(ester) with time in each mixture.

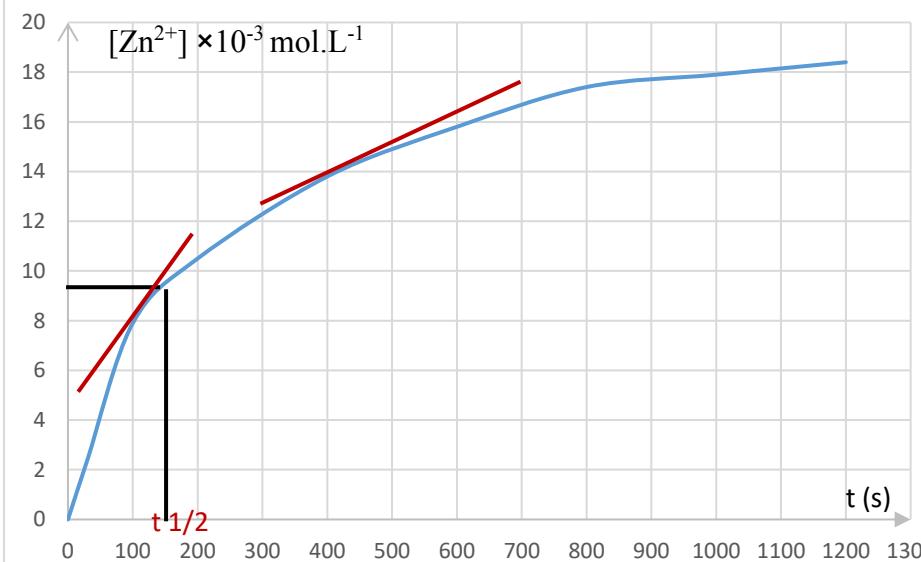


Referring to **Document-3** and **Document-4**:

- 2.4.1. Deduce the effect of the use of a catalyst on the equilibrium state.
- 2.4.2. Suggest a way to increase the yield of the esterification reaction. Justify.

Exercise 1 (7 points)

Kinetic of The Reduction of Iodine by Zinc

Part of the Q	Answer	Mark
1.1	$R(I_2) = \frac{n(I_2)_{initial}}{1} = \frac{C \times V}{1} = \frac{2 \times 10^{-2} \times 280 \times 10^{-3}}{1} = 5.6 \times 10^{-3}$. $R(Zn) = \frac{n(Zn)_{initial}}{1} = \frac{m}{M} = \frac{346 \times 10^{-3}}{65.4} = 5.29 \times 10^{-3}$. $R(I_2) > R(Zn)$ therefore Zn is the limiting reactant.	1
1.2	$n(I_2)$ remained at $t = n(I_2)_{initial} - n(I_2)$ reacted at t , at each instant, $n(I_2)$ reacted = $n(Zn^{2+})$ formed; $n(I_2)$ remained at $t = n(I_2)_{initial} - n(Zn^{2+})$ formed at t ; Divide by $V_{solution}$: $[I_2]_t = [I_2]_0 - [Zn^{2+}]_t$	1
1.3	$n(Zn)_0 = n(Zn^{2+})_{\infty} = 5.29 \times 10^{-3} \text{ mol}$; $[Zn^{2+}] = \frac{n(Zn^{2+})_{\infty}}{V_{solution}} = \frac{5.29 \times 10^{-3}}{280 \times 10^{-3}} = 18.9 \times 10^{-3} \text{ mol.L}^{-1}$	0.75
2.1		1
2.2	<p>The rate is equal to the positive slope of the tangent drawn on the curve $[Zn^{2+}] = f(t)$. The slope of the tangent at instant $t_1 >$ the slope of the tangent at instant t_2. (Shown on curve). Then the rate at $t_1 >$ the rate at t_2 and thus the rate decreases with time.</p>	1
2.3	<p>Half life time ($t_{1/2}$) is the time needed for half the maximum amount of the product to be formed.</p>	1

	At $t_{1/2}$: $[Zn^{2+}] = \frac{[Zn^{2+}]_\infty}{2} = \frac{18.9 \times 10^{-3}}{2} = 9.45 \times 10^{-3} \text{ mol.L}^{-1}$. Graphically $t_{1/2} = 150\text{s}$	
2.4	Temperature is a kinetic factor. As temperature increases, the rate of the reaction increases. At each instant the rate at $T' >$ the rate at T . and then at each instant $[Zn^{2+}]$ at $T' > [Zn^{2+}]$ at T . The curve $[Zn^{2+}] = g(t)$ is above $[Zn^{2+}] = f(t)$	1.25

Exercise 2 (6 points)

Sodium Hydroxide

Part of the Q	Answer	Mark
1.1	$C = \frac{n(naOH)}{V_{solution}} = \frac{m}{M \times V} = \frac{0.4}{40 \times 1} = 1 \times 10^{-2} \text{ mol.L}^{-1}$	0.5
1.2	$\text{pH} = -\log[H_3O^+]$; $[H_3O^+] = 10^{-\text{pH}} = 10^{-12} \text{ mol.L}^{-1}$	0.5
1.3	$K_w = [HO^-][H_3O^+]$; $[HO^-] = \frac{10^{-14}}{[H_3O^+]} = \frac{10^{-14}}{10^{-12}} = 1 \times 10^{-2} \text{ mol.L}^{-1}$	0.5
1.4	Since $[HO^-] = 1 \times 10^{-2} \text{ mol.L}^{-1} = C$, then NaOH is a strong base	0.5
2.	Upon dilution: n(solute) is conserved Then $\frac{V}{V_0}$ = dilution factor = 500. For a volumetric flask of volume $V = 1 \text{ L}$, $\frac{1}{500} = 2 \text{ mL}$ to be taken by a volumetric pipet. Set 2 is the most precise set.	0.75
3.1	$H_3O^{(aq)} + HO^{(aq)} \rightarrow 2H_2O_{(\ell)}$	0.5
3.2	At equivalence, the chemical species present in the solution are: Na^+ , H_2O and Cl^- . Na^+ and Cl^- are spectator ions. H_2O is a neutral species, then pH_E remains 7 after the addition of distilled water.	0.75
3.3	At equivalence: $n(H_3O^+)$ added to reach equivalence = $n(HO^-)$ introduced into the beaker $C_a \times V_{aE} = C_b \times V_b$;	0.75
Part Q	$C_b = \frac{2.5 \times 10^{-2} \times 21.3}{10} = 0.053 \text{ mol.L}^{-1}$	
3.4 the Q	$C_o = 500 \times C_b = 500 \times 0.053 = 26.625 \text{ mol.L}^{-1}$	0.75
3.5	$\% m = \frac{m_{solute}}{m_{solution}} \times 100 = \frac{n \times M}{d \times V} \times 100 = \frac{C_o \times M}{d} \times 100 = \frac{26.625 \times 40}{2.13 \times 10^3} \times 100 = 50 \%$ Answer b	0.75

Exercise 3 (7 points)

Isobutyric Acid Ethyl Ester

1.1		0.5
1.2	Ethyl 2-methylpropanoate	0.75
1.3	(A) : 2-methylpropanoic acid (B): Ethanol	1.5
2.1	Heating increases the rate of the slow esterification reaction.	0.5
2.2	Esterification reaction is a reversible reaction, referring to Document-2 and starting from $t = 20\text{hrs}$ $n(\text{ester})$ remains constant and doesn't change, then it reaches the equilibrium state.	0.5
2.3	From Document-2 $n(\text{ester}) = 0.66 \text{ mol}$, this is an equimolar mixture and $R_A = R_B$, $n(\text{ester}) \text{ theoretical} = 1.0 \text{ mol} = n(A)_0 = n(B)_0$ $\% \text{ yield} = \frac{n_{\text{actual}}}{n_{\text{theoretical}}} \times 100 = \frac{0.66}{1} \times 100 = 66 \%$	1
2.4.1	Comparing mixtures M and M': Starting with the same equimolar mixture. A catalyst is added to Mixture M, from Document-4 the rate of the reaction in mixture M (represented by curve a) is greater than the rate of the reaction in mixture M' (represented by curve b) where mixture M reaches the same equilibrium state as in mixture M' but in less time, so the catalyst increases the rate of esterification reaction to reach equilibrium faster.	1.25
2.4.2	Using Documents 3 and 4 curve c reaches equilibrium state at a value: $n(\text{ester}) = 0.96 \text{ mol}$ which is greater than 0.66 mol and thus yield increases, therefore using a non-equimolar mixture as (M'') increases the yield of an esterification reaction.	1

الاسم: الرقم:	مسابقة في مادة الكيمياء المدة: ساعة ونصف
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**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:**

Exercise 1 (6 points)

Household Product

A commercial household product containing hydrochloric acid is available in a one-liter bottle. This household product instantly dissolves rust, hard water deposits, and uric acids while destroying odor-causing bacteria.

The aim of this exercise is to determine the percentage by mass of HCl in this household product.

Given:

- Molar mass of HCl : $M(\text{HCl}) = 36.5 \text{ g.mol}^{-1}$.
- Density of the commercial household product: $d = 1.11 \text{ g.mL}^{-1}$.
- This study is carried out at 25°C .
- Ion product of water at 25°C : $K_w = 1.0 \times 10^{-14}$

1. Behavior of Hydrochloric Acid in Water

Available is, in the laboratory, a bottle of hydrochloric acid solution ($\text{H}_3\text{O}^+ + \text{Cl}^-$) noted (S) of molar concentration $C = 2.5 \times 10^{-2} \text{ mol.L}^{-1}$.

We measure the pH of the solution (S), we find $\text{pH}_{(S)} = 1.6$

- 1.1. Calculate the molar concentration of hydronium ions, $[\text{H}_3\text{O}^+]$, in the solution (S).
- 1.2. Justify that hydrochloric acid is a strong acid.

2. Dilution of the Commercial Household Product

The commercial household product solution noted (S_0) is highly concentrated. A hydrochloric acid solution ($\text{H}_3\text{O}^+ + \text{Cl}^-$) noted (S') is prepared by diluting 250 times the solution (S_0). Choose, from Document-1, the most precise set for the preparation of solution (S'). Justify.

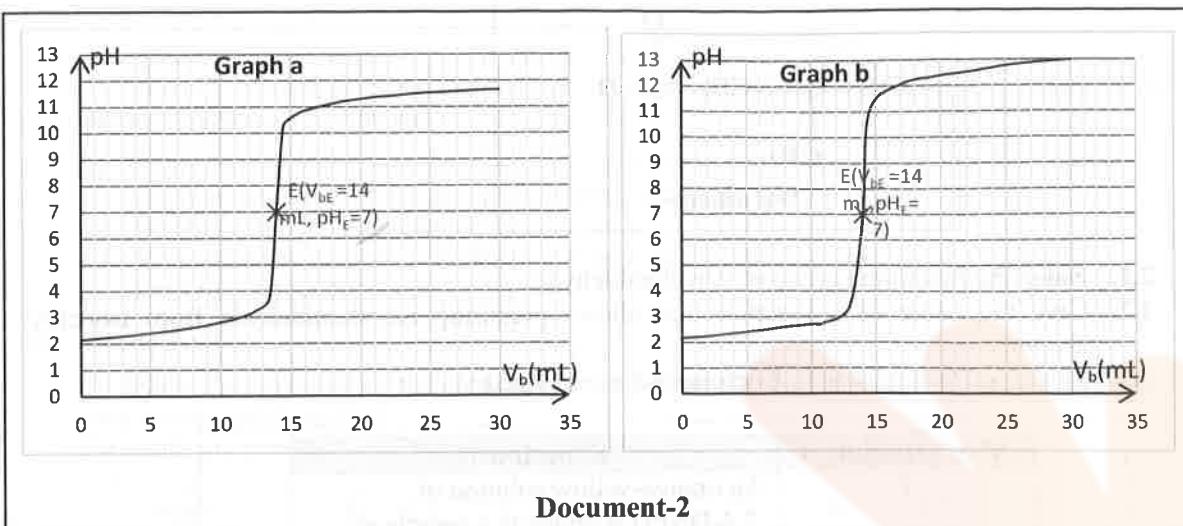
Set 1	Set 2	Set 3
Beaker of 100 mL Volumetric pipet of 5 mL Volumetric flask 1000 mL	Beaker of 100 mL Graduated cylinder of 10 mL Erlenmeyer Flask 500 mL	Beaker of 100 mL Volumetric pipet of 2mL Volumetric flask of 500 mL

Document-1

3. pH-metric Titration of Solution (S')

A volume $V(s') = 10.0 \text{ mL}$ of the solution (S') is introduced into a beaker then distilled water is added in order to immerse properly the pH-meter electrode. A pH-metric titration is realized by adding progressively into the beaker a sodium hydroxide solution ($\text{Na}^+ + \text{HO}^-$) of molar concentration $C_b = 2.0 \times 10^{-2} \text{ mol.L}^{-1}$.

- 3.1. Write the equation of the titration reaction.
- 3.2. Specify, between the two graphs of Document-2, the one that represents the variation of pH of the solution (S') as a function of the volume of the base added.



Document-2

- 3.3. Determine the molar concentration of hydrochloric acid solution (S').
- 3.4. Deduce the molar concentration of hydrochloric acid solution (S_0).
- 3.5. Choose, by justifying, the value that corresponds to the percentage by mass of the HCl in the commercial household product.

a- 0.092%

b- 23 %

c- 35%

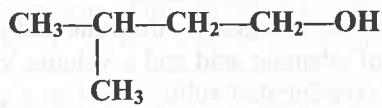
Exercise 2 (7 points)

Isopentyl Alcohol

Isopentyl alcohol, acts as an antifoaming agent and as an intermediate in the production of other compounds such as isovaleraldehyde and isopentyl ethanoate.

1. Study of the Structure of Isopentyl Alcohol

The condensed structural formula of isopentyl alcohol is given in Document-1

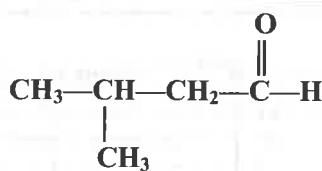


Document-1

- 1.1. Copy the structure of isopentyl alcohol on your answer sheet, circle and name its functional group.
- 1.2. Justify that isopentyl alcohol is a primary alcohol.
- 1.3. Give the systematic name of isopentyl alcohol.

2. Preparation of Isovaleraldehyde from Isopentyl Alcohol

Isovaleraldehyde is a pungent liquid that occurs in natural oils. The structure of isovaleraldehyde is given in **Document-2**



Document-2

- 2.1. Name the functional group of isovaleraldehyde.
- 2.2. Give the name of a reaction that allows preparing isovaleraldehyde from isopentyl alcohol.
- 2.3. The experiments listed in **Document-3** are realized.

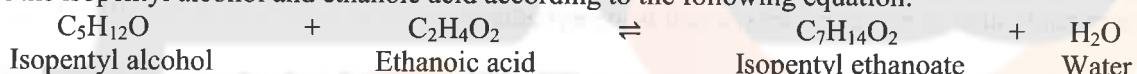
Nº of experiment	Experiment
1	An orange-yellow solution of 2,4-DNPH is added to a sample of isovaleraldehyde
2	A mixture of isovaleraldehyde and Fehling's blue solution is heated

Document-3

- 2.3.1. What is observed in each of the experiments 1 and 2?

3. Synthesis of Isopentyl Ethanoate

Isopentyl ethanoate has a fruity banana or pear odor widely used to flavor foods. It can be prepared from the isopentyl alcohol and ethanoic acid according to the following equation:



Given: Molar mass of isopentyl alcohol is: $M(\text{C}_5\text{H}_{12}\text{O}) = 88 \text{ g.mol}^{-1}$

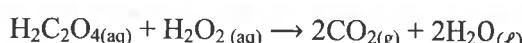
Density of isopentyl alcohol: $d = 0.82 \text{ g.mL}^{-1}$

- 3.1. Write the condensed structural formula of ethanoic acid.
- 3.2. Write the condensed structural formula of isopentyl ethanoate and give its systematic name.
- 3.3. An equimolar mixture of 0.1mol of ethanoic acid and a volume V of isopentyl alcohol is heated to reflux in the presence of concentrated sulfuric acid as a catalyst. The number of moles of isopentyl ethanoate obtained at equilibrium is 0.067 mol.
 - 3.3.1. Give the importance of reflux heating.
 - 3.3.2. Calculate the volume V of isopentyl alcohol.
 - 3.3.3. Determine the yield of the esterification reaction at equilibrium.

Exercise 3 (7 points)

Oxalic Acid

Oxalic acid reacts with hydrogen peroxide according to a slow and complete reaction as shown by the equation below:



The aim of this exercise is to study the kinetic of this reaction at constant temperature T.

1. Preliminary Study

One introduces, in an Erlenmeyer flask:

- A volume $V_1 = 12.0 \text{ mL}$ of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) of molar concentration $C_1 = 0.5 \text{ mol.L}^{-1}$.
- A volume $V_2 = 2 \text{ mL}$ of concentrated nitric acid HNO_3 (catalyst).
- A volume $V_3 = 13 \text{ mL}$ of distilled water.

At instant $t = 0$, a volume $V = 3.0 \text{ mL}$ of hydrogen peroxide (H_2O_2) solution of concentration $C = 10 \text{ mol.L}^{-1}$ is added to the reactional mixture in the Erlenmeyer flask. **The total volume of the reactional mixture is $V_t = 30 \text{ mL}$.**

- 1.1. Show that the initial concentration of oxalic acid and that of hydrogen peroxide in the reaction mixture are: $[\text{H}_2\text{C}_2\text{O}_4]_0 = 0.2 \text{ mol.L}^{-1}$ and $[\text{H}_2\text{O}_2]_0 = 1 \text{ mol.L}^{-1}$.
- 1.2. Determine the limiting reactant.
- 1.3. Verify that the number of moles of carbon dioxide formed at the end of reaction is $n(\text{CO}_2)_\infty = 12 \times 10^{-3} \text{ mol}$.

2. Kinetic Study

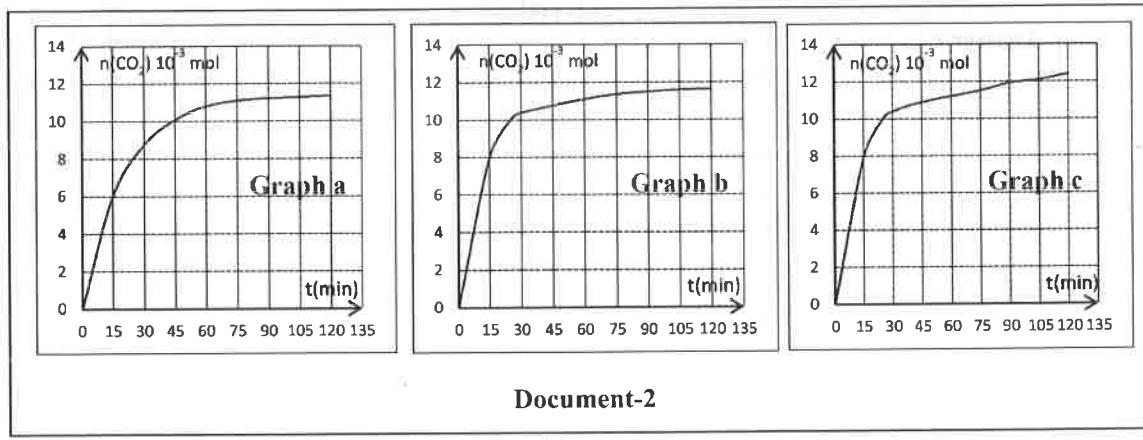
We follow the evolution of the concentration of oxalic acid remained at different instants t using an appropriate method.

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

$t \text{ (min)}$	0	15	30	45	60	75	90	105	120
$[\text{H}_2\text{C}_2\text{O}_4] (10^{-2} \text{ mol.L}^{-1})$	20	10	5.4	3.2	2.0	1.5	1.3	1.1	1.0

Document-1

- 2.1. Plot the curve representing the variation of the concentration of oxalic acid as a function of time $[\text{H}_2\text{C}_2\text{O}_4] = f(t)$ within the interval of time $[0 - 120 \text{ min}]$.
Take the following scales: abscissa: 1 cm for 15 min; ordinate: 1 cm for $2 \times 10^{-2} \text{ mol.L}^{-1}$.
- 2.2. Deduce, graphically, the variation in the rate of disappearance of $\text{H}_2\text{C}_2\text{O}_4$ as a function of time.
- 2.3. Determine, graphically, the half-life time of the reaction $t_{1/2}$.
- 2.4. Specify whether each of the following propositions is true or false.
 - 2.4.1. The time $t = 120 \text{ min}$ represents the end of the reaction.
 - 2.4.2. The relation between the rate of the reaction $r_{(t)}$ at a given instant t , and the rate of disappearance of $\text{H}_2\text{C}_2\text{O}_4$, $r(\text{H}_2\text{C}_2\text{O}_4)_t$, at same instant t is: $r_{(t)} = \frac{r(\text{H}_2\text{C}_2\text{O}_4)_t}{2}$.
- 2.5. In order to study the effect of some kinetic factors on the kinetics of this reaction, the previous study is carried out again but with only one modification: the hydrogen peroxide solution of concentration C is replaced by another hydrogen peroxide solution of concentration C' , such that $C' > C$.
Choose, from the graphs of **Document-2**, the one that corresponds to the variation of the number of moles of CO_2 as a function of time in this study. Justify.



الاسم: _____
الرقم: _____
محللة لماء الكلوراء
المدة: ساعه ونصف

Exercise 1: (6 points)

Household product

Part of the Q	Answer	Mark
1.1.	$\text{pH} = -\log[\text{H}_3\text{O}^+]$, $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-16} \text{ mol L}^{-1}$ $= 2.5 \times 10^{-2} \text{ mol L}^{-1}$	0.5
1.2.	Since $[\text{H}_3\text{O}^+] = 2.5 \times 10^{-2} \text{ mol L}^{-1} = C$, then hydrochloric acid is a strong acid	0.5
2.	Upon dilution, n(solute) is conserved Then $\frac{C}{C'} = \frac{V}{V_0}$ dilution factor = 250. For a volumetric flask of volume $V = 500 \text{ mL}$, $\frac{500}{250} = 2 \text{ mL}$, to be taken by a volumetric pipet (2 mL). Set 3 is the most precise set.	1
3.1.	$\text{H}_3\text{O}^{(aq)} + \text{H}_2\text{O}^{(aq)} \rightarrow 2\text{H}_2\text{O}_{(l)}$	0.75
3.2.	Since it is a strong acid-strong base titration, then pH at equivalence is $\text{pH}_e = 7$, but the pH_e must not exceed a value determined by the concentration of the base solution added from the burette and becomes asymptotic to a value: $\text{pH} = 14 + \log C_b = 14 + \log (2.0 \times 10^{-2}) = 12.3$ and this corresponds to Curve a	0.75
3.3.	At equivalence: $n(\text{H}_3\text{O}^+)$ added to reach equivalence = $n(\text{H}_3\text{O}^+)$ introduced into the beaker $C_b \times V_{\text{H}_3\text{O}^+} = C_b \times V_a$: $C_{\text{H}_3\text{O}^+} = \frac{2.0 \times 10^{-2} \times 14}{10} = 2.8 \times 10^{-2} \text{ mol L}^{-1}$	1
3.4.	$C_{\text{base}} = 250 \times C = 250 \times 2.8 \times 10^{-2} = 7 \text{ mol L}^{-1}$	0.5
3.5.	$\% \text{ m} = \frac{\text{m solute}}{\text{m solution}} \times 100 = \frac{n \times M}{d \times V} \times 100 = \frac{C \times M}{d} \times 100 = \frac{7 \times 36.5}{1.11 \times 10^3} \times 100 = 23\%$	1
Answer c		

Exercise 2 (7 points)

Isopentyl Alcohol

Part of the Q	Answer	Mark
1.1.	$\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_2-\text{OH} \\ \\ \text{CH}_3 \end{array}$ hydroxyl group	0.75
1.2.	Since the hydroxyl group is bonded to a carbon atom holding two hydrogen atoms then it is a primary alcohol.	0.5
1.3.	3-methyl-1-butanol	0.5
2.1.	The functional group is the carbonyl group	0.25
2.2.	Mild oxidation	0.5
2.3.1	Experiment 1: a yellow orange precipitate is formed Experiment 2 : a red brick precipitate is formed	1
3.1.	$\begin{array}{c} \text{O} \\ \\ \text{CH}_3-\text{C}-\text{OH} \qquad \text{CH}_3-\text{COOH} \end{array}$	0.25
3.2.	$\begin{array}{c} \text{O} \\ \\ \text{CH}_3-\text{C}-\text{O} \quad \text{CH}_2-\text{CH}_2-\text{CH}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$ 3-methylbutyl ethanoate	1
3.3.1.	Reflux heating increases the rate of the esterification reaction but without losing any of the components of the reaction (reactants or products).	0.5
3.3.2.	Since the reaction is an equimolar mixture : $n(\text{isopentyl alcohol})_0 = n(\text{ethanoic acid})_0 = 0.1 \text{ mol}$ $0.1 \text{ mol} = \frac{m(\text{alcohol})}{M(\text{alcohol})} = \frac{d \times V}{M} = \frac{0.82 \times V}{88}, V = 10.73 \text{ mL}$	0.75
3.3.3.	$\% \text{Yield} = \frac{n(\text{ester})_{\text{actual}}}{n(\text{ester})_{\text{theoretical}}} \times 100$ $n(\text{ester})_{\text{actual}} = 0.067 \text{ mol}$. Assuming that the reaction is complete: $R(\text{alcohol}) = R(\text{carboxylic acid}) = 0.1$, then $n(\text{ester})_{\text{theoretical}} = n(\text{alcohol})_0 = 0.1 \text{ mol}$. $\% \text{Yield} = \frac{0.067}{0.1} \times 100 = 67 \%$	1

Exercise 3 (7 points)

Oxalic acid

Part of the Q	Answer	Mark																				
1.1.	$[\text{H}_2\text{C}_2\text{O}_4]_0 = \frac{n(\text{H}_2\text{C}_2\text{O}_4)\text{initial}}{V_t} = \frac{C_1 V_1}{V_t} = \frac{0.5 \times 12}{30} = 0.2 \text{ mol.L}^{-1}$ $[\text{H}_2\text{O}_2]_0 = \frac{n(\text{H}_2\text{O}_2)\text{initial}}{V_t} = \frac{C \times V}{V_t} = \frac{10 \times 3}{30} = 1 \text{ mol.L}^{-1}$	1																				
1.2.	$R(\text{H}_2\text{C}_2\text{O}_4) = \frac{n(\text{H}_2\text{C}_2\text{O}_4)\text{initial}}{1} = \frac{C_1 \times V_1}{1} = \frac{0.5 \times 12 \times 10^{-3}}{1} = 6 \times 10^{-3}$ $R(\text{H}_2\text{O}_2) = \frac{n(\text{H}_2\text{O}_2)\text{initial}}{1} = \frac{C \times V}{1} = \frac{10 \times 3 \times 10^{-3}}{1} = 30 \times 10^{-3}$ <p>$R(\text{H}_2\text{O}_2) > R(\text{H}_2\text{C}_2\text{O}_4)$ then $\text{H}_2\text{C}_2\text{O}_4$ is the limiting reactant.</p>	0.75																				
1.3.	<p>According to stoichiometric ratios</p> $n(\text{H}_2\text{C}_2\text{O}_4)_0 = \frac{n(\text{CO}_2)_{\infty}}{2}; n(\text{CO}_2)_{\infty} = 2 \times C_1 \times V_1 =$ $2 \times 0.5 \times 12 \times 10^{-3} = 1.2 \times 10^{-2} \text{ mol}$	0.75																				
2.1.	$[\text{H}_2\text{C}_2\text{O}_4](10^{-2} \text{ mol.L}^{-1})$ <table border="1"> <caption>Data points estimated from the graph</caption> <thead> <tr> <th>t (min)</th> <th>[H₂C₂O₄] (10⁻² mol.L⁻¹)</th> </tr> </thead> <tbody> <tr><td>0</td><td>20</td></tr> <tr><td>15</td><td>10</td></tr> <tr><td>30</td><td>5</td></tr> <tr><td>45</td><td>3</td></tr> <tr><td>60</td><td>2</td></tr> <tr><td>75</td><td>1.5</td></tr> <tr><td>90</td><td>1</td></tr> <tr><td>105</td><td>0.5</td></tr> <tr><td>120</td><td>0.2</td></tr> </tbody> </table>	t (min)	[H ₂ C ₂ O ₄] (10 ⁻² mol.L ⁻¹)	0	20	15	10	30	5	45	3	60	2	75	1.5	90	1	105	0.5	120	0.2	1
t (min)	[H ₂ C ₂ O ₄] (10 ⁻² mol.L ⁻¹)																					
0	20																					
15	10																					
30	5																					
45	3																					
60	2																					
75	1.5																					
90	1																					
105	0.5																					
120	0.2																					

2.2	<p>The rate of disappearance is represented by the negative slope of the tangent drawn on the curve $H_2C_2O_4 = r(t)$.</p> <p>The negative slope of the tangent at instant $t_1 >$ the negative slope of the tangent at instant t_2. (Shown on curve).</p> <p>Then the rate of disappearance at $t_1 >$ the rate of disappearance at t_2 and therefore the rate of disappearance of $H_2C_2O_4$ decreases with time.</p>	0.75
2.3	<p>Half life time ($t_{1/2}$) is the time needed for half the initial amount of the limiting reactant to be consumed.</p> <p>At $t=0$: $H_2C_2O_4 _{t=0} = \frac{ H_2C_2O_4 _0}{2} = \frac{0.2}{2} = 10 \times 10^{-2} \text{ mol.L}^{-1}$.</p> <p>Graphically $t_{1/2} = 15 \text{ min}$</p>	1
2.4.1	False. At $t=120 \text{ min}$, $ H_2C_2O_4 = 1 \times 10^{-2} \text{ mol.L}^{-1}$ but it is a limiting reactant so at the end of reaction it should be consumed completely	0.5
2.4.2	False. The rate of the reaction and the rate of disappearance are related stoichiometric ally, then $r_t = r(H_2C_2O_4)_t$	0.5
2.5	<p>Initial concentration of one of the reactants is a kinetic factor.</p> <p>using $C' > C$ (the volume of the mixture is not changed), then the initial concentration of H_2O_2 increases and the rate of the reaction increases so at each instant t</p> <p>$n(CO_2)$ in new experiment $>$ $n(CO_2)$ in the previous experiment, but the limit of $n(CO_2)$ at infinity ($n(CO_2)_{\infty}$) remains $12 \times 10^{-3} \text{ mol}$ since it is determined by the limiting reactant ($H_2C_2O_4$). So not curve 3.</p> <p>As concentration increases the rate of the reaction increases ; therefore the time needed to produce the half quantity of carbon dioxide decreases so $t_{1/2}$ in the new experiment $< t_{1/2} = 15 \text{ min}$ in the previous experiment.</p> <p>Then curve 2 is the correct graph.</p>	0.75

الاسم:
الرقم:

مسابقة في مادة الكيمياء
العدة: ساعة ونصف

This Exam Includes Three Exercises. It is Inscribed on Four Pages Numbered From 1 to 4.
The Use of a Non-Programmable Calculator is Allowed.

Answer the Three Following Exercises:

Exercise 1: (7 points) Kinetics of the Decomposition Reaction of Hydrogen Peroxide

Commercial hydrogen peroxide is an aqueous solution of H_2O_2 , sold in opaque bottles to prevent its decomposition under the action of light.

The decomposition reaction of H_2O_2 is slow and complete. The reaction is represented by the following equation:



The aim of this exercise is to study the kinetics of this reaction at constant temperature T.

Given:

- The gas O_2 is slightly soluble in water at the temperature of this study.
- The decomposition reaction of H_2O_2 may be catalyzed by Fe^{3+} ions.

1. Preparation of Solution (S) of Hydrogen Peroxide

In order to prepare a solution (S) of hydrogen peroxide of a molar concentration $C = 0.06 \text{ mol.L}^{-1}$, a commercial solution of hydrogen peroxide of concentration $C_0 = 1.78 \text{ mol.L}^{-1}$ is diluted.

Choose, from **Document-1**, the most convenient set to prepare the solution (S). Justify.

	Set A	Set B	Set C
2. Kinetic	5 mL volumetric pipet 250 mL Erlenmeyer flask 50 mL beaker	10 mL volumetric pipet 250 mL volumetric flask 50 mL beaker	10 mL graduated pipet 250 mL volumetric flask 50 mL beaker

Document-1

c Study of the Decomposition Reaction of H_2O_2

At instant $t = 0$, few drops of iron (III) chloride solution ($\text{Fe}^{3+} + 3\text{Cl}^-$) are added into an Erlenmeyer flask containing a volume $V = 50.0 \text{ mL}$ of the solution (S) of hydrogen peroxide of concentration

$$C = 0.06 \text{ mol.L}^{-1}.$$

By an appropriate method, the number of moles of H_2O_2 remained at each instant t is determined and the results are grouped in the table of **Document-2**:

t (min)	0	5	10	15	20	30	40	50	60
n (H_2O_2) 10^{-4} mol	30	24.4	19.4	16.8	14.2	11.2	9.6	8.6	8.2

Document-2

ify that the initial number of moles of H_2O_2 ; $n_0(\text{H}_2\text{O}_2) = 30 \times 10^{-4}$ mol.

- 2.2. Plot the curve that represents the variation of the number of moles of H_2O_2 as a function of time, $n(\text{H}_2\text{O}_2) = f(t)$ within the time interval [0 - 60 min].

Take the following scale: abscissa: 1cm for 5 min; ordinate: 1cm for 5×10^{-4} mol.

- 2.3. The rate of disappearance of H_2O_2 decreases as a function of time.

2.3.1. Justify this statement by referring to the curve $n(\text{H}_2\text{O}_2) = f(t)$.

2.3.2. What is the kinetic factor responsible for this variation?

- 2.4. The rate of disappearance of H_2O_2 at $t = 20$ min is 3.5×10^{-5} mol.min $^{-1}$. Deduce the rate of the reaction at this instant.

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

- 2.6. Identify the chemical species present in the solution at the end of the reaction.

Exercise 2: (6points)

Study of a Household Product

Available is, a commercial household product containing hydrochloric acid.

The aim of this exercise is to determine the percentage by mass of HCl in this household product.

Given:

- $M(\text{HCl}) = 36.5 \text{ g.mol}^{-1}$.
- Density of the household product solution: $d = 1.07 \text{ g.mL}^{-1}$.
- This study is carried out at 25°C .
- Ion product of water: $K_w = 1.0 \times 10^{-14}$.

1. Behavior of Sodium Hydroxide in Water

Available are, in the laboratory, two solutions of sodium hydroxide ($\text{Na}^+ + \text{HO}^-$) with the indications given in the table of **Document-1**:

Solution	$C(\text{mol.L}^{-1})$	pH
(S)	7.8×10^{-2}	12.9
(S ₁)	C_1	pH ₁

Document-1

- 1.1. Show that the solution (S) corresponds to a strong base solution.

- 1.2. The solution (S₁) is prepared by diluting 10 times the solution (S). Choose, by justifying, the pH value of the solution (S₁).

a. 13.9

b. 12.9

c. 11.9

2. pH-metric Titration of the Household Product

In order to determine the percentage by mass of HCl in this commercial solution, one proceeds as follows:

- The commercial solution is diluted 50 times; the obtained solution is noted as (S_A).
- A pH-metric titration is carried out, at 25°C , of a volume $V_A = 10.0 \text{ mL}$ of the solution (S_A) with a solution (S) of sodium hydroxide of concentration $C_b = 7.8 \times 10^{-2} \text{ mol.L}^{-1}$.

The volume of the basic solution added to reach equivalence is $V_{bE} = 11.2 \text{ mL}$.

- 2.1. Write the equation of the titration reaction.
- 2.2. Justify, based on the chemical species present, that the solution at equivalence is neutral.
- 2.3. Determine the molar concentration of hydrochloric acid in the solution (S_A).
- 2.4. Deduce the percentage by mass of HCl in this household product.

Exercise 3: (7 points) Identification of Organic Compounds

(A) and (B) are two organic compounds with saturated non-cyclic chains.

The aim of this exercise is to identify the two organic compounds (A) and (B) and to synthesize an ester (E) using one of these compounds.

1. Identification of Compounds (A) and (B)

In order to identify the compound (B), one realizes two chemical tests where the results are grouped in the table of Document-1:

	Reagents	Observation
Test 1	Compound (B) + 2,4-DNPH	Yellow-orange precipitate
Test 2	Compound (B)+Blue Fehling's Reagent	Brick-red precipitate

Document-1

- 1.1. Based on the results of the above two tests, deduce the family of compound (B).
- 1.2. Knowing that compound (B) is obtained by catalytic dehydrogenation of compound (A), indicate the family and the class of the compound (A).
- 1.3. Attribute to each of the compounds (A) and (B) the corresponding general molecular formula:
a. $\text{C}_n\text{H}_{2n}\text{O}_2$ b. $\text{C}_n\text{H}_{2n}\text{O}$ c. $\text{C}_n\text{H}_{2n+2}\text{O}$

- 1.4. The elemental analysis of the compound (**B**) shows that the percentage by mass of oxygen is 22.22%.

- 1.4.1. Show that the molecular formula of compound (**B**) is C_4H_8O .

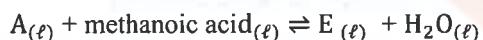
Given: Molar masses in g.mol⁻¹: H = 1 ; C = 12 ; O = 16

- 1.4.2. Write the two possible condensed structural formulas of compound (**B**).

- 1.4.3. Knowing that the carbon chain of the compound (**B**) is branched, identify the compounds (**B**) and (**A**).

2. Synthesis of an Ester (**E**)

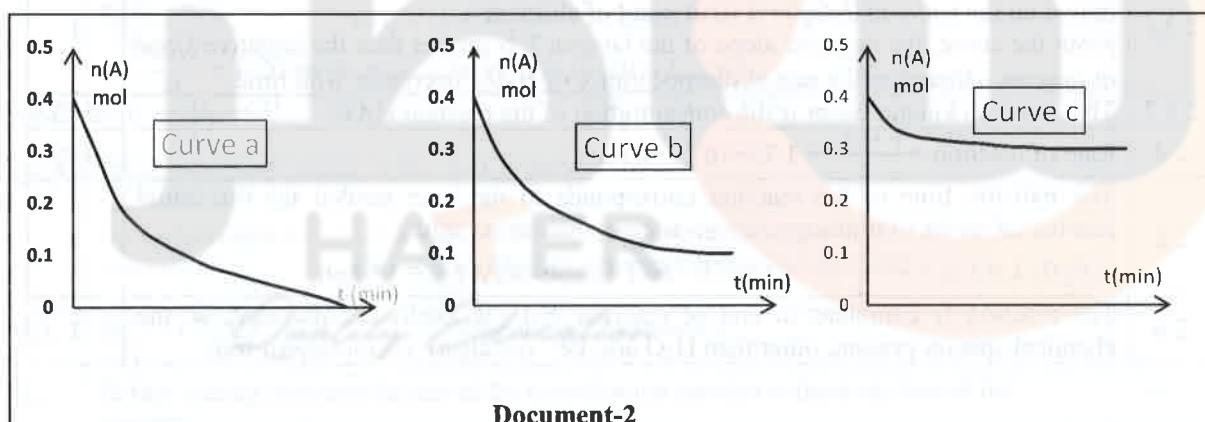
An ester (**E**) is used in food industry. Its smell resembles that of raspberry. In order to synthesize (**E**), a mixture formed of $n_1 = 0.5$ mol of methanoic acid and $n_2 = 0.4$ mol of compound (**A**) is heated to reflux. The reaction is represented by the given equation:



- 2.1. Write the condensed structural formula of the ester (**E**). Give its systematic name.

- 2.2. Indicate the importance of reflux heating.

- 2.3. Assuming that the esterification yield is 75%. Choose, by justifying, from **Document-2** the curve that corresponds to the evolution of the number of moles of compound (**A**) as a function of time.



Exercise 1: (7 points) Kinetics of the Decomposition Reaction of Hydrogen Peroxide

Part	Expected answer	Mark																											
1	<p>Upon dilution, the number of moles of the solute dissolved is conserved Then $n_{(\text{solute withdrawn})} = n_{(\text{solute in the prepared solution})}$ then $C_0 \cdot V_0 = C \cdot V$ Dilution factor; $f = \frac{C_0}{C} = \frac{V}{V_0} = \frac{1.78}{0.06} = 29.67$ $\frac{V}{V_0} = \frac{250 \text{ mL}}{V_0} = 29.67$, then $V_0 = 8.42 \text{ mL}$, this volume can be measured by a 10 mL graduated pipet, so set C is the convenient set.</p>	1																											
2.1	$n_0 (\text{H}_2\text{O}_2) = C \cdot V = 30 \times 10^{-4} \text{ mol}$	0.5																											
2.2	<p>$n(\text{H}_2\text{O}_2) 10^{-4} \text{ mol}$</p> <table border="1"> <caption>Data points estimated from the graph</caption> <thead> <tr> <th>t (min)</th> <th>n(H₂O₂) 10⁻⁴ mol (Steeper)</th> <th>n(H₂O₂) 10⁻⁴ mol (Flatter)</th> </tr> </thead> <tbody> <tr><td>0</td><td>30</td><td>30</td></tr> <tr><td>5</td><td>20</td><td>25</td></tr> <tr><td>10</td><td>15</td><td>20</td></tr> <tr><td>20</td><td>10</td><td>15</td></tr> <tr><td>30</td><td>8</td><td>12</td></tr> <tr><td>40</td><td>7</td><td>10</td></tr> <tr><td>50</td><td>6</td><td>8</td></tr> <tr><td>60</td><td>5</td><td>7</td></tr> </tbody> </table>	t (min)	n(H ₂ O ₂) 10 ⁻⁴ mol (Steeper)	n(H ₂ O ₂) 10 ⁻⁴ mol (Flatter)	0	30	30	5	20	25	10	15	20	20	10	15	30	8	12	40	7	10	50	6	8	60	5	7	1
t (min)	n(H ₂ O ₂) 10 ⁻⁴ mol (Steeper)	n(H ₂ O ₂) 10 ⁻⁴ mol (Flatter)																											
0	30	30																											
5	20	25																											
10	15	20																											
20	10	15																											
30	8	12																											
40	7	10																											
50	6	8																											
60	5	7																											
2.3.1	<p>The rate of disappearance of H_2O_2 is equal to the negative of the slope of the tangent drawn on the curve $n(\text{H}_2\text{O}_2) = f(t)$ at point of abscissa t. From the curve, the negative slope of the tangent 1 is greater than the negative slope of tangent 2 therefore the rate of disappearance of H_2O_2 decreases with time.</p>	1																											
2.3.2	The involved kinetic factor is the concentration of the reactant H_2O_2 .	0.75																											
2.4	Rate of reaction = $\frac{r_{\text{H}_2\text{O}_2}}{2} = 1.75 \times 10^{-5} \text{ mol} \cdot \text{min}^{-1}$	0.75																											
2.5	<p>The half-life time of the reaction corresponds to the time needed for the initial number of moles of limiting reactant to reach half of its value. $n(\text{H}_2\text{O}_2)$ at $t \frac{1}{2} = \frac{n_0(\text{H}_2\text{O}_2)}{2} = 1.5 \times 10^{-3} \text{ mol}$. Graphically, $t \frac{1}{2} = 18 \text{ min}$.</p>	1																											
2.6	The reaction is complete, at end of reaction H_2O_2 is totally decomposed, so the chemical species present, other than H_2O are: Fe^{3+} (catalyst), Cl^- (spectator ion).	1																											

Exercise 2: (6 points)

Study of a sanitary household product

Part	Expected answer	Mark
1.1	<p>A base is said to be strong if $[\text{HO}^-] = C_b$ $[\text{HO}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{10^{-14}}{10^{-12.9}} = 007.9 \text{ mol.L}^{-1}$ and $C = 7.9 \times 10^{-2} \text{ mol.L}^{-1}$ then $[\text{HO}^-] = C_b$, hence this base is completely dissociated in water, it is a strong base.</p>	0.75
1.2	For a strong base solution, the pH of the solution decreases by one unit upon diluting	0.75

	this solution 10 times. Thus the new value of pH is 11.9	
2.1	$\text{H}_3\text{O}^+ + \text{HO}^- \rightarrow 2 \text{H}_2\text{O}$	0.75
2.2	The reaction is between a strong acid and a strong base, the chemical species that are present at equivalence point, other than water, are Na^+ and Cl^- , which are spectator ions (neutral particles). The pH is then equal to 7.	1
2.3	At equivalence point: according to the stoichiometric ratios: $n \text{ H}_3\text{O}^+ \text{ (present in beaker in 10 mL)} = n \text{ HO}^- \text{ (added from burette in 11.2 mL)}$ Knowing that, in a solution: $n = C \cdot V$ then: $C_a \cdot V_a = C_b \cdot V_b$ $C_a = \frac{C_b \cdot V_b}{V_a} = \frac{7.8 \times 10^{-2} \text{ mol/L} \times 11.2 \text{ mL}}{10 \text{ mL}} = 0.0873 \text{ mol L}^{-1}$	1.25
2.4	$C_o = C_a \times 50 = 4.37 \text{ mol L}^{-1}$ $\% \text{ by mass} = \frac{m \text{ HCl}}{m \text{ solution}} \times 100 = \frac{\frac{n \times M}{d \times V} \times 100}{\frac{C_o \times V \times M}{d \times V} \times 100} = \frac{4.37 \times 36.5}{1070} = 14.9\%$	1.5

Exercise 3: (7 points)

Identification of Organic Compounds

Part	Expected answer	Mark
1.1.	Test 1: compound B reacts with 2,4-DNPH, so (B) is a carbonyl compound (aldehyde or ketone). Test 2: Compound (B) reacts with Fehling's reagent, so (B) is an aldehyde	0.5
1.2.	Compound (A) is a primary alcohol	0.5
1.3.	The general formula of (A) is $\text{C}_n\text{H}_{2n+2}\text{O}$; (B) is $\text{C}_n\text{H}_{2n}\text{O}$	1
1.4.1.	According to the law of definite proportions $\frac{M(B)}{100} = \frac{M(O)}{\% O} ; 14n + 16 = \frac{16 \times 100}{22.22} = 72 \text{ g.mol}^{-1}$ $n = \frac{72 - 16}{14} = 4. \text{ Then the molecular formula of (B) is } \text{C}_4\text{H}_8\text{O.}$	1
1.4.2.	$\text{CH}_3 - \underset{\text{CH}_3}{\text{CH}_2} - \text{CH}_2 - \text{CHO}$ $\text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \text{CHO}$	0.5
1.4.3.	(B) is 2-methylpropanal: $\text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \text{CHO}$ the carbon chain is conserved upon catalytic dehydrogenation of alcohols then (A) is: $\text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_2\text{OH}$ 2-methyl-1-propanol	1
2.1.	$\text{HC}(\text{O}) - \text{O} - \text{CH}_2 - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_3$ 2-methylpropyl methanoate	1
2.2.	Reflux heating increases the rate of the esterification reaction without any loss of the reagents	0.5
2.3.	If esterification reaction is complete $R(A) = \frac{0.4}{1} < R(\text{HCOOH}) = \frac{0.5}{1}$ then compound (A) is the limiting reactant The percentage yield of the reaction is 75% $n(A)_{\text{consumed}} = \frac{75}{100} n(A)_{\text{initial}} = 0.75 \times 0.4 = 0.3 \text{ mol}$ $n(A)_{\text{equilibrium}} = n(A)_{\text{initial}} - n(A)_{\text{consumed}} = 0.4 - 0.3 = 0.1 \text{ mol}$ then the correct curve is curve b.	1

الاسم:	مسابقة في مادة الكيمياء
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This Exam Includes Three Exercises. It Is Inscribed on Four Pages, Numbered from 1 to 4.

The Use of A Non-programmable Calculator Is Allowed.

Answer the Three Following Exercises

Exercise 1 (7 points)

Kinetic Study

Hydrogen peroxide (H_2O_2) reacts, in acidic medium, with iodide ions (I^-) in a slow and complete reaction that takes place according to the following equation:



The aim of this exercise is to study, at constant temperature T, the kinetic of this reaction.

1. Preliminary Study

In order to study the kinetic of this reaction, one introduces into an Erlenmeyer flask, at a constant temperature T:

- A volume $V_1 = 10.0 \text{ mL}$ of potassium iodide solution ($\text{K}^+ + \text{I}^-$) of molar concentration $C_1 = 0.1 \text{ mol.L}^{-1}$.
- A volume $V_2 = 18.0 \text{ mL}$ of sulfuric acid solution considered **in excess**.

At instant $t = 0$, a volume $V = 2.0 \text{ mL}$ of hydrogen peroxide solution (H_2O_2) of molar concentration $C = 0.1 \text{ mol.L}^{-1}$ is added into the Erlenmeyer flask. The number of moles of iodine formed at different instants is determined by an appropriate method. The results are grouped in the table of **Document-1**.

t (min)	0	4	8	12	16	20	24
n (I_2) $\times 10^{-5}$ mol	0	8	12	14	15.2	16	16.6

Document -1

1.1. Show that hydrogen peroxide (H_2O_2) is the limiting reactant.

1.2. Specify whether the instant $t = 24 \text{ min}$ represents the end time of the reaction.

2. Kinetic Study

2.1. Plot the curve that represents the variation of the number of moles of iodine I_2 as a function of time, $n(\text{I}_2) = f(t)$ within the time interval $[0 - 24 \text{ min}]$.

Take the following scales: abscissa: 1 cm for 2 min;

ordinate: 1 cm for $2 \times 10^{-5} \text{ mol}$.

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

2.3. The rate of formation of iodine decreases with time.

2.3.1. Justify this statement by referring to the curve $n(\text{I}_2) = f(t)$.

2.3.2. Indicate the kinetic factor responsible for this variation.

2.4. The instantaneous rate of formation of iodine at an instant t is denoted $r(\text{I}_2)_t$. Choose the relation that corresponds to the rate of disappearance of iodide ions (I^-), $r(\text{I}^-)_t$, at the same instant t .

$$\text{a- } r(\text{I}^-)_t = r(\text{I}_2)_t \quad \text{b- } r(\text{I}^-)_t = \frac{r(\text{I}_2)_t}{2} \quad \text{c- } r(\text{I}^-)_t = 2 r(\text{I}_2)_t$$

2.5. The above study is carried out again but with only one modification, the potassium iodide solution is replaced by another solution of concentration $C' > C_1$. Draw, on the same graph of question **2.1**, the shape of the curve $n(\text{I}_2) = g(t)$. Justify.

Exercise 2 (6 points)

Caustic Soda

Caustic soda 30% is a commercial sodium hydroxide solution. Caustic soda is a detergent, active, deep-action and strongly alkaline character used for the removal of organic pollution.

The aim of this exercise is to determine the percentage by mass of NaOH in this commercial solution.

Given:

- Molar mass: $M(\text{NaOH}) = 40 \text{ g.mol}^{-1}$
- Density of the commercial solution: $d = 1.34 \text{ g.mL}^{-1}$
- The study is carried out at 25°C .
- Ion product of water at 25°C : $K_w = 1.0 \times 10^{-14}$

1. Preliminary Study

Sodium hydroxide NaOH is a **strong base**.

The pH of a sodium hydroxide solution ($\text{Na}^+ + \text{HO}^-$) of molar concentration C is equal to 10.4

Choose, by justifying, the value of the concentration of hydroxide ions $[\text{HO}^-]$ in this solution.

a- $[\text{HO}^-] = 3.98 \times 10^{-11} \text{ mol.L}^{-1}$ b- $[\text{HO}^-] = 2.51 \times 10^{-4} \text{ mol.L}^{-1}$ c- $[\text{HO}^-] = 3.98 \times 10^3 \text{ mol.L}^{-1}$

2. Dilution of the Commercial Solution

The commercial solution noted as (S_0) is highly concentrated. A sodium hydroxide solution noted (S_1) of molar concentration C_1 is prepared by diluting 125 times the commercial solution (S_0) .

Choose, from **Document-1**, the convenient set for the preparation of solution (S_1) . Justify.

Set 1	Set 2	Set 3
Beaker of 100 mL Volumetric pipet of 5 mL Volumetric flask of 1000 mL	Beaker of 100 mL Graduated pipet of 5 mL Volumetric flask of 500 mL	Beaker of 100 mL Volumetric pipet of 5 mL Volumetric flask of 500 mL

Document-1**3. pH-metric Titration of Solution (S_1)**

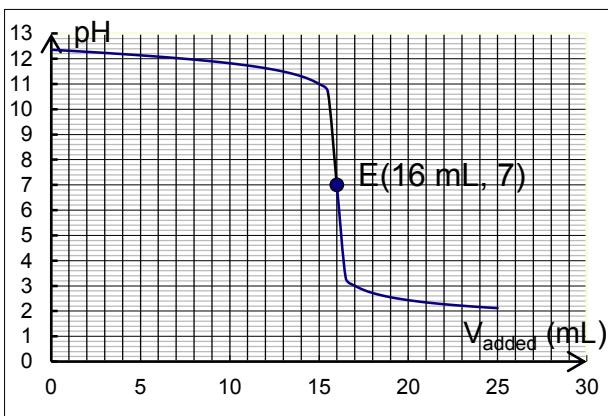
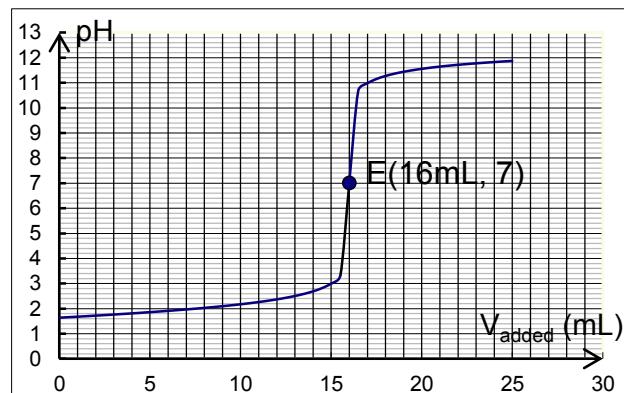
A volume $V_{(S_1)} = 10.0 \text{ mL}$ of the solution (S_1) is introduced into a beaker then distilled water is added in order to immerse properly the pH-meter electrode. A pH-metric titration is realized by adding progressively into the beaker a hydrochloric acid solution ($\text{H}_3\text{O}^+ + \text{Cl}^-$) of molar concentration $C_a = 5.0 \times 10^{-2} \text{ mol.L}^{-1}$.

3.1. Write the equation of the titration reaction.

3.2. Choose, from the following, two characteristics of the titration reaction:

Reversible	Complete	Fast	Slow	Unique
------------	----------	------	------	--------

3.3. Specify which of the two curves of **Document-2** represents the variation of pH of the solution in the beaker as a function of the volume of the acid added in the above pH-metric titration.

**Curve a****Curve b****Document-2**

3.4. Justify, based on the chemical species present in solution, that the pH at equivalence is $\text{pH}_E = 7$

3.5. Determine the molar concentration C_1 of the sodium hydroxide solution (S_1) .

3.6. Show that the molar concentration of sodium hydroxide in the commercial solution is $C_0 = 10.0 \text{ mol.L}^{-1}$.

3.7. Determine the percentage by mass of NaOH in the commercial solution.

Exercise 3 (7 points)

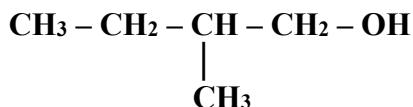
Esterification Reaction

Esters often have a pleasant odor. They are found naturally in fruits and are often responsible for the aroma. Esters are obtained by extraction or by synthesis.

The aim of this exercise is to identify an ester (E) with fruity odor and to study its synthesis reaction.

1. Study of the Structure of an Alcohol (A)

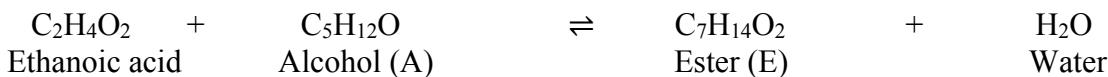
The condensed structural formula of an alcohol (A) is given as follows:



- 1.1. Copy the structure of the alcohol (A) on your answer sheet then circle and name its functional group.
- 1.2. Give the systematic name of the alcohol (A).
- 1.3. Justify the following two statements:
 - 1.3.1. Alcohol (A) is a primary alcohol.
 - 1.3.2. The molecule of the alcohol (A) is chiral.
- 1.4. Represent, according to Cram, the two enantiomers of the alcohol (A) molecule.

2. Synthesis of the Ester (E)

The ester (E) is a sweet and fruity tasting compound. It can be prepared, in the laboratory, starting from ethanoic acid and the alcohol (A) according to the following equation:



- 2.1. Give the condensed structural formula of ethanoic acid.
- 2.2. Choose, from the two condensed structural formulas A and B of **Document-1**, the one that corresponds to the condensed structural formula of the ester (E).

Condensed structural formula A	Condensed structural formula B
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3 - \text{O} - \text{C} - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3 - \text{C} - \text{O} - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$

Document-1

- 2.3. Give the systematic name of the ester (E).

- 2.4. A mixture containing 0.1 mol of ethanoic acid and 0.2 mol of the alcohol (A) is heated to reflux for a certain time in the presence of few drops of sulfuric acid as a catalyst.

The mass of the ester obtained at equilibrium is 11.05g.

- For an initial equimolar mixture of a carboxylic acid and a primary alcohol, the yield of the reaction at equilibrium is 67%.
- The molar mass of ester (E) is $M = 130 \text{ g.mol}^{-1}$.

Document-2

- 2.4.1. Determine the yield, at equilibrium, of this synthesis reaction.

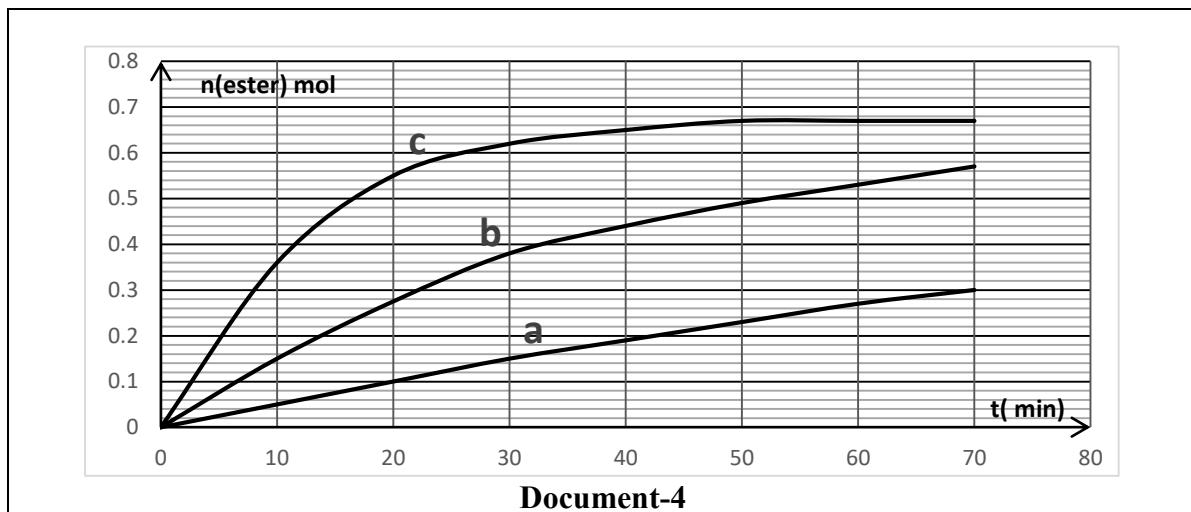
- 2.4.2. Deduce the importance of using a non-equimolar initial mixture of reactants on the synthesis reaction of an ester.

3. Factors Affecting the Rate of the Esterification Reaction

In order to study the effect of temperature and that of the presence of a catalyst on the esterification reaction, we realize the three reacting mixtures as given in the table of **Document-3**.

Reacting mixture	Number of moles of ethanoic acid	Number of moles of alcohol (A)	Temperature	Catalyst	Corresponding curve in Document-4
M	1.0 mol	1.0 mol	20°C		a
M ₁	1.0 mol	1.0 mol	70°C		b
M ₂	1.0 mol	1.0 mol	20°C	H ₂ SO ₄	c

Document-3

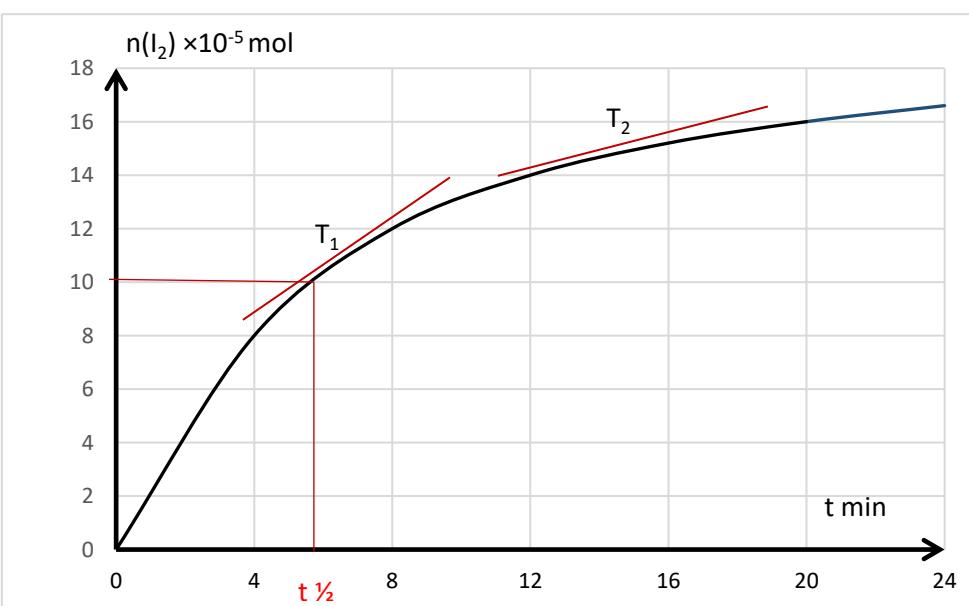


Referring to the table of **Document-3** and graph of **Document-4**, deduce the effect on the rate of the esterification reaction of:

3.1. Increasing the temperature of the reacting medium.

3.2. Using a catalyst.

الكيمياء
معيار اسس التصحيح**Exercise 1: (7 points) Kinetic Study**

Part	Answer	Mark
1.1	$n_o(I^-) = C_1 \times V_1 = 0.1 \times 10 \times 10^{-3} = 1 \times 10^{-3} \text{ mol}$ (0.25 pts) $n_o(H_2O_2) = C \times V = 0.1 \times 2 \times 10^{-3} = 2 \times 10^{-4} \text{ mol}$ (0.25 pts) $\text{Ratio } (I^-) = \frac{n_o(I^-)}{2} = 5 \times 10^{-4}$ $\text{Ratio } (H_2O_2) = \frac{n_o(H_2O_2)}{1} = 2 \times 10^{-4}$, (0.25 pts) $\text{Ratio } (H_2O_2) < \text{Ratio } (I^-)$ then the limiting reactant is H_2O_2 (0.25 pts)	1
1.2	Apply stoichiometric ratio: $\frac{n_{\infty}(I_2)}{1} = \frac{n_0(H_2O_2)}{1}$, then $n(I_2)_{\infty} = 2 \times 10^{-4} \text{ mol}$ $= 20 \times 10^{-5} \text{ mol}$ (0.5 pts) And $n(I_2)_{24} = 17 < n(I_2)_{\infty} = 20 \times 10^{-5} \text{ mol}$ (0.25 pts) thus $t = 24 \text{ min}$ is not the end time of the reaction. (0.25 pts)	1
2.1		1
2.2	Half-life is the time needed for the number of mole of I_2 to reach half its maximum value. (0.5 pts) At $t_{1/2}$: $n(I_2) = \frac{n_{\infty}(I_2)}{2} = 10 \times 10^{-5} \text{ mol}$, (0.25 pts) Graphically (0.25 pts) $t_{1/2} = 5.6 \text{ min}$ (0.25 pts)	1
2.3.1	The rate of formation of a product (I_2) at an instant t is the slope of the tangent to the curve $n(I_2) = f(t)$ at a point of instant (t) . (0.5pts) Plot the tangents T_1 and T_2 (0.25 pts) Graphically: Slope of $T_1 >$ Slope of T_2 (0.25 pts) Then, rate of formation of iodine decreases with time. (0.25 pts)	1.25

2.3.2	The kinetic factor that is responsible for this variation is the concentration of the reactants (H_2O_2 , I^- et H_3O^+).	0.25
2.4	Apply stoichiometric ratios: $r(\text{I}^-)_t = 2 r(\text{I}_2)_t$	0.5
2.5	<p>Concentration of I^- is a kinetic factor, as this concentration increases the rate of formation of I_2 increases. At any instant t, $n(\text{I}_2)$ second study > $n(\text{I}_2)$ first study. Therefore, the curve $n(\text{I}_2) = g(t)$ is above that $n(\text{I}_2) = f(t)$. However, the curve tends to the same maximum as the first study since I^- is in excess (number of mole of the product formed at the end of reaction depends on the limiting reactant).</p>	1

Exercise 2 (6 points) Caustic soda

Part	Answer	Mark
1	The answer is b: $[\text{HO}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{10^{-14}}{10^{-pH}} = 2.51 \times 10^{-4} \text{ mol.L}^{-1}$.	0.5
2	Upon dilution, the number of moles of solute is conserved (0.25 pts) $C_0 \times V_0 = C_1 \times V_1$ $\frac{C_0}{C_1} = \frac{V_1}{V_0} = 125$. So, if 500 mL volumetric flask is used, then: $V_0 = \frac{500}{125} = 4 \text{ mL}$ which can be taken by means of a 5 mL graduated pipet. (0.25 pts) Thus set 2 is convenient. (0.5 pts)	1
3.1	$\text{H}_3\text{O}^{+(\text{aq})} + \text{HO}^{-(\text{aq})} \rightarrow 2\text{H}_2\text{O}^{(\text{l})}$	0.5
3.2	Titration reaction is complete and fast (unique)	0.5
3.3	Curve a. In this case the basic solution is in the beaker; thus, pH initially is basic, and it decreases with the addition of H_3O^+ and the titration curve is descending.	0.5
3.4	At equivalence, the chemical species present in solution other than H_2O are Na^+ and Cl^- . These ions are spectator ions and have no effect on pH. Thus $\text{pH}_E = 7$	0.5
3.5	At equivalence: $n(\text{HO}^-)$ present in 10 mL of (S1) = $n(\text{H}_3\text{O}^+)$ added to reach equivalence (0.25 pts) $: C_{S1} \times V_{S1} = C_{ae} \times V_{ae}$ Then, $C_{S1} = \frac{0.05 \times 16}{10} = 0.08 \text{ mol.L}^{-1}$	1
3.6	$\frac{C_0}{C_{S1}} = 125$, then $C_0 = 125 \times 0.08 = 10.0 \text{ mol.L}^{-1}$	0.5
3.7	$\% \text{ NaOH} = \frac{m \text{ solute}}{m \text{ solution}} \times 100$. (0.25 pts)	1

$$= \frac{n \times M}{d \times V_{solution}} \times 100$$

Then: $\% = \frac{C_0 \times M}{d} \times 100$.

$\% \text{ of NaOH} = \frac{10 \times 40}{1340} \times 100 = 29.85\%$. (0.75 pts)

Exercise 3 (7 points) Esterification Reaction

Part	Answer	Mark
1.1	$\begin{array}{c} \text{CH}_3 - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{OH} \\ \\ \text{CH}_3 \end{array}$ hydroxyl group	0.75
1.2	2-methyl-1-butanol	0.25
1.3.1	This alcohol is primary because the functional C is bonded to 2 H atoms and 1 alkyl group	0.5
1.3.2	This molecule is chiral because it has an asymmetric carbon (carbon number 2), a carbon atom bonded to 4 different groups of atoms (H, $\text{CH}_3 - \text{CH}_2 -$, $\text{CH}_3 -$ and $- \text{CH}_2 - \text{OH}$)	0.5
1.4		0.75
2.1	Condensed structural formula of ethanoic acid: $\text{CH}_3 - \text{COOH}$	0.25
2.2	Structure B	0.5
2.3	2-methylbutyl ethanoate	0.25
2.4.1	<p>Assuming that the reaction is complete, $\text{Ratio ethanoic acid} = 0.1 < \text{Ratio alcohol} = 0.2$ Ethanoic acid is the limiting reactant. (0.5 pts) then:</p> <p>$n(\text{ester})_{\text{(theoretical)}} = n(\text{ethanoic acid}) = 0.1 \text{ mol}$ (0.25 pts)</p> <p>$m(\text{ester})_{\text{theoretical}} = 0.1 \times 130 = 13 \text{ g}$.</p> <p>$\% \text{ Yield} = \frac{m(\text{ester})_{\text{actual}}}{m(\text{ester})_{\text{theoretical}}} = \frac{11.05}{13} \times 100 = 85\%$ (0.5 pts)</p>	1.25
2.4.2	<p>In this case the mixture is non-equimolar, and yield of the reaction is 85%. Which is greater than the yield of 67 % obtained for an initial equimolar mixture of a carboxylic acid and a primary alcohol.</p> <p>Thus, using a non-equimolar mixture of reactants leads to an increase in the yield of esterification reaction.</p>	0.5
3.1	<ul style="list-style-type: none"> - The mixtures M and M_1 have the same initial number of moles. - temperature of $M_1 >$ temperature of M. <p>at each instant t of the evolution of the system, curve b has a higher slope than curve a, therefore at each instant t, the rate of formation of the ester in mixture M_1 is greater than that in mixture M. (0.5 pts)</p> <p>Thus, as temperature increases rate of formation of ester increases.(0.25 pts)</p>	0.75
3.2	<ul style="list-style-type: none"> - The mixtures M and M_2 have the same initial number of moles. - temperature of $M =$ temperature of M_2. - Catalyst is present in mixture M_2 <p>at each instant t of the evolution of the system, curve c has a higher slope than curve a, therefore at each instant t, the rate of formation of the ester in mixture M_2 is greater than that in mixture M. (0.5 pts)</p> <p>Thus, the presence of a catalyst increases the rate of formation of ester. (0.25 pts)</p>	0.75



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@wecantogether0



wecantogether70@gmail.com



+961-76 096391