

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)
Benzoic Acid**

Benzoic acid is a white solid of formula C_6H_5COOH . It is used as a food preservative.

Given:

- $M(\text{benzoic acid}) = 122 \text{ g}\cdot\text{mol}^{-1}$
- $pK_a(H_3O^+/H_2O) = 0$; $pK_a(C_6H_5COOH/C_6H_5COO^-) = 4.2$; $pK_a(H_2O/HO^-) = 14$

1- Study of a Benzoic Acid Solution

A volume $V = 500.0 \text{ mL}$ of an aqueous benzoic acid solution (S) of concentration $C = 0.01 \text{ mol}\cdot\text{L}^{-1}$ 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 pKa 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 $C = 0.01 \text{ mol}\cdot\text{L}^{-1}$.

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.

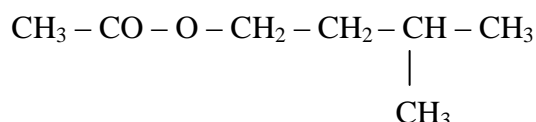
Second Exercise (6 points)

Hydrolysis of esters

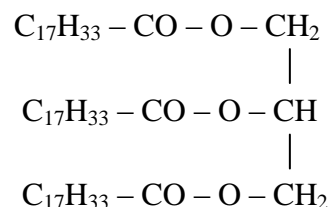
Esters are commonly prepared by the reaction of alcohols and carboxylic acids, where water is eliminated. Esters are often responsible for the natural aroma of fruits. They are widely used in synthetic flavors and in perfume industry.

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:



Isoamyl acetate



Olein

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:

<ul style="list-style-type: none">- Soap (sodium oleate) is practically insoluble in a saturated salty water solution.- M (sodium oleate) = 304 g.mol⁻¹.
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In order to produce soap, one proceeds as follows:

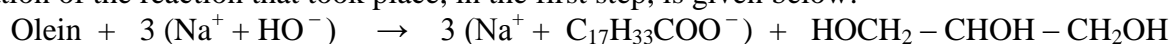
First step: A mixture of 2.0×10^{-2} mol of olein, an excess of a concentrated sodium hydroxide solution, a certain volume of ethanol and few boiling stones is heated to reflux for 30 minutes.

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.

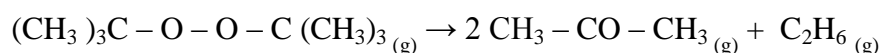
The equation of the reaction that took place, in the first step, is given below:



- 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
$[C_2H_6]$ ($10^{-4} \text{ mol.L}^{-1}$)	1.5	3.6	5.8	7.8	9.7	13.2	16.0	18.9

Given: Ideal gas constant: $R = 0.08 \text{ L.atm.K}^{-1} \cdot \text{mol}^{-1}$.

1- Preliminary Study

- 1.1- Show that the initial concentration of the compound (A) is equal to $71.4 \times 10^{-4} \text{ mol.L}^{-1}$, 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 $[0 - 46 \text{ min}]$. Take the following scales:

1 cm for 4 min in abscissa and 1 cm for $2.0 \times 10^{-4} \text{ mol.L}^{-1}$ in ordinate.

2.2- Determine the rate of formation of ethane at the instant of time $t = 30 \text{ min}$.

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: $[0 - 46 \text{ min}]$.

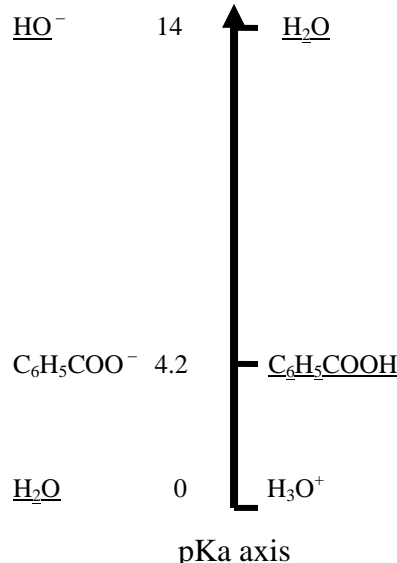
2.5- The kinetic study realized above is carried out again at a temperature $T_1 > T$.

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	$n(\text{acid}) \text{ needed} = C \times V = 0.01 \times 0.5 = 5 \times 10^{-3} \text{ mol}$. $m(\text{acid}) \text{ needed} = n(\text{acid}) \times M(\text{acid}) = 5 \times 10^{-3} \times 122 = 0.61 \text{ g}$.	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	$\text{pH} = 3.1 > -\log C = -\log 0.01 = 2$, 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 : $K_r = 10^{\text{pKa}(\text{H}_2\text{O}/\text{HO}^-) - \text{pKa}(\text{C}_6\text{H}_5 - \text{COOH}/\text{C}_6\text{H}_5 - \text{COO}^-)} = 10^{14 - 4.2} > 10^4$ 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

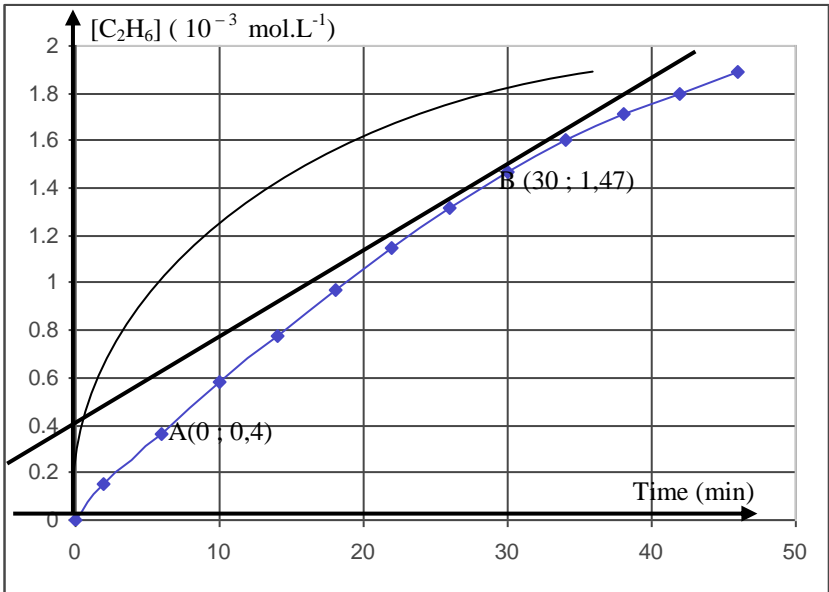
	with $\frac{[\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]} = \frac{C.V_2 / V(\text{mixture})}{C.V_1 / V(\text{mixture})} = \frac{V_2}{V_1}$ where $V_1 = 317.4 \text{ mL}$.	
3.2	It is a buffer solution, the pH of which varies slightly upon: <ul style="list-style-type: none"> - 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 $\text{C}_x\text{H}_y\text{O}_z$ be the molecular formula of the compound (A). According to the law of definite proportions : $\frac{M(\text{A})}{100} = \frac{12x}{\%(\text{C})} = \frac{1y}{\%(\text{H})} = \frac{16z}{\%(\text{O})}$ with $\%(\text{O}) = 100 - (\% \text{C} + \% \text{H}) = 100 - (48.65 + 8,11) = 43,24$ and $M(\text{A}) = 74$. then : $x = 3 ; y = 6 ; z = 2$ and the molecular formula of (A) is : $\text{C}_3\text{H}_6\text{O}_2$.	0.75
1.2	The condensed structural formulas of the possible isomers are: $\text{CH}_3 - \text{CH}_2 - \underset{\text{O}}{\parallel}{\text{C}} - \text{OH} ; \text{H} - \underset{\text{O}}{\parallel}{\text{C}} - \text{O} - \text{CH}_2 - \text{CH}_3 \text{ and } \text{CH}_3 - \underset{\text{O}}{\parallel}{\text{C}} - \text{O} - \text{CH}_3$	0.75
1.3	$\text{pH} = 3.1 < 7$, 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: $\text{CH}_3 - \text{CH}_2 - \underset{\text{O}}{\parallel}{\text{C}} - \text{OH} + \text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_2\text{OH} \rightleftharpoons \text{CH}_3 - \text{CH}_2 - \underset{\text{O}}{\parallel}{\text{C}} - \text{O} - \text{CH}_2 - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_3 + \text{H}_2\text{O}$	0.75
2.2	Its systematic name is : 2-methylpropylpropanoate	0.25
2.3	The yield of the reaction is: 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> <p>Initial state 0.2 mol 0.2 mol 0 0</p> <p>final state 0.1 mol 0.1 mol 0.1 mol 0.1 mol</p> <p>The quotient of this reaction :</p> $Q_t = \frac{[\text{ester}][\text{water}]}{[\text{acid}][\text{alcohol}]} = \frac{n(\text{ester})/V \times n(\text{water})/V}{n(\text{acid})/V \times n(\text{alcohol})/V} = \frac{0.1 \times 0.1}{0.1 \times 0.1} = 1$ <p>Since $Q_t < K$, therefore the equilibrium is not reached.</p>	1
2.5.1	The possible formulas are: $\text{CH}_3 - \text{CH}_2 - \text{CO} - \text{Cl}$ and $\text{CH}_3 - \text{CH}_2 - \text{CO} - \text{O} - \text{CO} - \text{CH}_2 - \text{CH}_3$	0.5
2.5.2	The two advantages are : The esterification reaction becomes complete and fast.	0.5

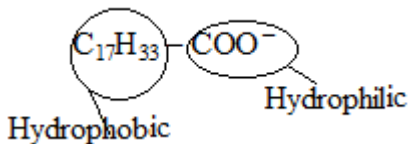
Third exercise (7 points)
Kinetic Study

Part of the Q	Answer	Mark
1.1	According to the equation of ideal gases , $[A] \text{ initial} = \frac{P_o}{RT} = \frac{0.24}{0.08 \times 420} = 71.4 \times 10^{-4} \text{ mol.L}^{-1}.$	0.75
1.2	At each instant t, we have: $P(A) = P_0 - x$; $P(\text{propanone}) = 2x$ and $P(\text{ethane}) = x$. The total pressure is therefore : $P = P_0 - x + 2x + x = P_0 + 2x$.	1
1.3	At the end of reaction , $P(\text{gaseous mixture}) = 3 \times P_0 = 3 \times 0.24 = 0.72 \text{ atm}$.	0.75
2.1	<p>The curve is :</p> 	1
2.2	<p>The rate of formation of ethane is defined by: $r = \frac{d[\text{C}_2\text{H}_6]}{dt}$. Its value is equal to the slope of the tangent drawn on the curve $[\text{C}_2\text{H}_6] = f(t)$ at a point of abscissa $t = 30 \text{ min}$.</p> $r(\text{C}_2\text{H}_6)_t = \frac{y_B - y_A}{t_B - t_A} = \frac{(1.47 - 0.4) \times 10^{-3}}{30} = 3.57 \times 10^{-5} \text{ mol.L}^{-1} \cdot \text{min}^{-1}.$	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 : $\text{CH}_3 - \text{CO} - \text{O} - \text{CH}_2 - \text{CH}_2 - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3 - \text{COOH} + \text{HOCH}_2 - \text{CH}_2 - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_3$	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

