المادة: الكيمياء – اللغة الإنكليزية الشهادة: الثانوية العامة الفرع: علوم الحياة نموذج رقم: 2 / 2019 المدّة: ساعتان	الهيئة الأكاديميّة المشتركة قسم: العلوم	المركز التربوي للبحوث والإنماء

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

Exercise 1 (7 points) Kinetics of the reaction of ethanoic acid with the bicarbonate ion

Ethanoic acid reacts with the bicarbonate ion in a slow reaction. This reaction is considered as complete and its equation is represented as follows:

$$CH_3COOH_{(aq)} + HCO_3^-{}_{(aq)} \rightarrow CO_{2(g)} + H_2O_{(\ell)} + CH_3COO^-{}_{(aq)}$$

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

Given: - Molar mass of sodium bicarbonate: $M_{NaHCO_3} = 84$ g.mol^{-1}

- Molar volume of gases under the conditions of the experiment: $V_m = 24$ L.mol^{-1}.

1. Preparation of the Solution (S) of Ethanoic Acid

A solution (S) of ethanoic acid of concentration C = 1 mol.L^{-1} is prepared from a commercial solution (S_0).

On the label of the commercial solution (S_0) of ethanoic acid one reads the indications given in **document-1.**

Percentage by mass: 90%	Density: $\rho = 1.05$ g.mL^{-1}
Molar mass in g.mol^{-1}: $M_{(CH_3COOH)} = 60$	

Document-1

1.1. Referring to **document-1**, show that the concentration of solution (S_0) of ethanoic acid is $C_0 = 15.75$ mol.L^{-1}.

1.2. To prepare a volume $V_S = 100$ mL of solution (S). Three sets of glassware are given in **document-2**. Choose, by performing the necessary calculation, the most suitable and precise set to achieve this preparation.

Set-1	Set-2	Set-3
Graduated cylinder 10 mL Volumetric flask 100 mL Beaker	Volumetric pipette 10 mL Volumetric flask 100 mL Beaker	Graduated pipette 10 mL Volumetric flask 100 mL Beaker

Document-2

2. Kinetic Study

A volume V = 60 mL of ethanoic acid solution (S) of concentration C = 1 mol.L^{-1} is introduced into a round bottom flask at constant temperature T.

At instant t = 0, a mass m = 1.25 g of sodium bicarbonate $NaHCO_{3\ (s)}$ is rapidly added to the flask, then the flask is closed and the volume of the released carbon dioxide gas CO_2 is measured by using a suitable method at different instants t. The obtained values are grouped in the table of **document-3**.

Time (s)	33	66	100	133	167	200	233	266	333	400
V_{CO_2} (mL)	79.2	144	180	199	216	228	240	247	257	262
$n_{CO_2} \times 10^{-3}$ (mol)	3.3	6	7.5	8.3	9	9.5	**a**	10.29	10.7	10.9

Document-3

2.1. Calculate the value of (**a**) that is missing in the table of **document-3**.

2.2. Plot the curve $n_{CO_2} = f(t)$ within the interval of time [0 - 400s]. Take the following scale: Abscissas: 1cm → 60 s and ordinates: 1cm → 1×10^{-3} mol.

2.3. Verify whether the bicarbonate ion HCO_3^- is the limiting reactant.

2.4. Three propositions are given. In case the proposition is correct justify it and in case it is false. correct it.

2.4.1. The rate of formation of CO_2 at t = 0 s is greater than that at t = 200s.

2.4.2. The time t = 400 s represents the end of the reaction.

2.4.3. If the same experiment is repeated with a single modification T'> T. The volume of released gas CO_2 at time t = 100 s is $V'(CO_2)$ < 180mL.

3. Determine the half-life time $t_{1/2}$.

Exercise 2 (7 points) The acidity of a butter

Butyric acid is an acid found in rancid butter, parmesan, where it releases a strong and unpleasant odor. The aim of this exercise is to study some properties of butyric acid and to verify its mass percentage in butter.

Given: Molar mass of butyric acid: M = 88 $g.mol^{-1}$.

pKa (H_2O / HO^-) = 14

1. Some Properties of Butyric Acid

- Butyric acid is a saturated, non-cyclic and linear-chain carboxylic acid of molecular formula $C_4H_8O_2$.
- Butyric acid is soluble in water.
- At 25° C, an aqueous solution (S) of butyric acid of concentration C = 3×10^{-2} $mol.L^{-1}$ has a pH = 3.18.

Document-1

1.1. Identify, by referring to **document-1**, the butyric acid.

1.2. Write by using the condensed structural formulas, the equation of the reaction between butyric acid and water.

1.3. Referring to **document-1**, justify the following propositions:

1.3.1. Butyric acid is a weak acid.

1.3.2. The degree of dissociation of this acid in water is α = 0.022.

1.3.3. The pKa of the acid / base pair of this acid is 4.82 at 25°C.

1.3.4. Butyric acid predominates its conjugate base in the solution (S).

2. Analysis of Butter

> Butter is rancid if the percentage by mass of butyric acid that it contains is greater than or equal to 4%, which means there is 4g or more of butyric acid in 100 g of butter.
>
> **Document-2**

To titrate the butyric acid contained in a butter, a mass m = 8 g of melted butter is introduced into an erlenmeyer flask, to which a volume of distilled water is added. The content is stirred in order to dissolve completely in water all the butyric acid present in the butter. A solution of sodium hydroxide ($Na^+_{(aq)}$ + $HO^-_{(aq)}$) of concentration C_b = 0.4 mol.L^{-1} is then added. The equivalence is reached after adding a volume V_{bE} = 7.5 mL of the base.

The equation of the titration reaction is:

$$C_4H_8O_{2\,(aq)} + HO^-_{(aq)} \rightarrow H_2O_{(\ell)} + C_4H_7O_2^-{}_{(aq)}$$

2.1. Name the ion $C_4H_7O_2^-$.

2.2. Determine the constant K_R of the titration reaction. Deduce that this reaction is complete.

2.3. Two other properties must characterize the titration reaction. Choose from the propositions given below which is most suitable for the titration reaction:

a. slow and unique.

b. fast and unique.

c. fast and limited.

2.4. The same titration is carried out by using a pH-meter shows that the value of pH at equivalence pH_E = 8.7.

Choose the most convenient indicator in **document-3** to be used to achieve this titration. Justify.

> Methyl red (4.2 - 6.2)
> Bromophenol blue (3.0 - 4.6)
> Cresol Red (7.2 - 9.0)
> **Document-3**

2.5. Determine the number of moles of butyric acid contained in the mass m = 8 g of the titrated butter.

2.6. Deduce the mass of butyric acid contained in this sample of butter.

2.7. Referring to **document-2**, verify whether the analyzed butter is rancid.

Exercise 3 (6 points) Fruity Odor Esters

Esters usually have an agreeable odor. They are found naturally in the fruits of which they are often responsible for the aroma. These esters are obtained by extraction or synthesis.

The aim of this exercise is to identify some fruity odor esters and study their synthesis.

Ester	Molecular formula	Odor
(E_1)	$C_5H_{10}O_2$	Melon
(E_2)	$C_6H_{12}O_2$	Strawberry

Document-1

Given: M_C = 12 g.mol^{-1} ; M_H = 1 g.mol^{-1} ; M_O = 16 g.mol^{-1}

1. Study of the Alcohol Used in the Synthesis of the Ester (E_1)

The alcohol used in the synthesis of the melon-odor ester (E_1) is noted (A). To identify the alcohol (A), the tests are carried out in **document-2.**

Chemical test	Result
(A) + Acidified potassium permanganate solution	Organic compound (B)
(B) + 2,4-DNPH	yellow-orange precipitate
(B) + Schiff's Reagent	No change is observed

Document-2

1.1. Referring to **document-2**, identify the family of compound (B).

1.2. Deduce the class of alcohol (A).

1.3. The quantitative analysis of alcohol (A) shows that the percentage by mass of carbon is 60%.

1.3.1. Show that the molecular formula of alcohol (A) is C_3H_8O.

1.3.2. Write the condensed structural formula of compounds (A) and (B).

2. Identification of Esters E_1 and E_2

2.1. Referring to **document-1** and to the molecular formula of alcohol (A). Choose the carboxylic acid used in the synthesis of the ester (E_1). Justify.

a. HCOOH

b. $CH_3 – COOH$

c. $CH_3 – CH_2 – COOH$

2.2. Identify the ester (E_1).

2.3. The systematic name of the ester (E_2) is ethyl –2 – methylpropanoate. Write the condensed structural formula of (E_2).

3. Synthesis of Esters

At equilibrium, the percent yield of esterification reaction of equimolar mixture between acid and alcohol is 66% for primary alcohol and 60% for secondary alcohol.

Document-3

The synthesis of ester is generally carried out between a carboxylic acid and an alcohol. The mixture is heated to reflux for a certain time. The equation of the esterification reaction is given by:

$$R – COOH + HO – R' \rightleftharpoons R – COO – R' + H_2O$$

3.1. Explain the importance of reflux heating.

3.2. Correct the following propositions. Justify.

3.2.1. In order to synthesize the esters (E_1) and (E_2) by mixing the same number of mole of alcohol and carboxylic acid such that $n_{alcohol} = n_{acid} = 0.1$ mol, the number of mole of each ester obtained at equilibrium is $n_{(E_1)} = 0.066$ mol and $n_{(E_2)} = 0.06$ mol.

3.2.2. The use of the derivative acid anhydride instead of the carboxylic acid in the synthesis of an ester does not change the yield at the end of the reaction but increases the rate of the reaction.

3.2.3. The addition of a small amount of concentrated sulfuric acid increases the yield of esterification at equilibrium.

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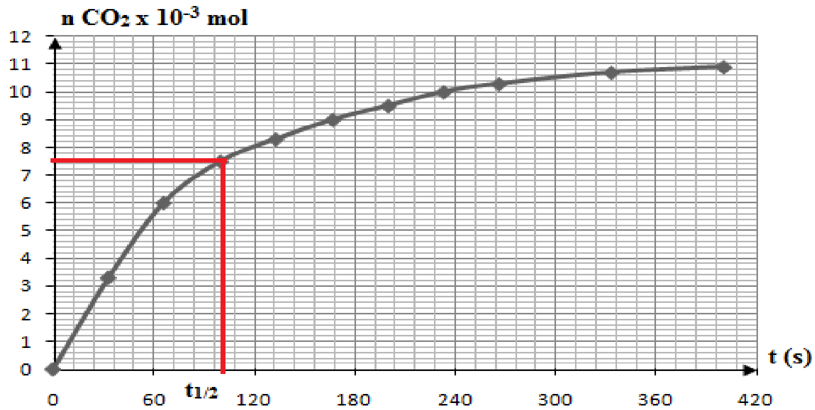
أسس التصحيح:

Part of question	Exercise 1 : (7 points) **Kinetics of the reaction of ethanoic acid with the bicarbonate ion** **Expected Answer**	Mark
1.1	Mass of 1L solution (S_0) : $m_{S_0} = \rho \times V_{S_0} = 1.05 \times 1000 = 1050$ g. Mass of CH_3COOH in 1L solution (S_0) : $m_{CH_3COOH} = 0.9 \times 1050 = 945$g. $n_{CH_3COOH} = \frac{m_{CH_3COOH}}{M_{CH_3COOH}} = \frac{945}{60} = 15.75$ mol and $C_0 = \frac{n_{CH_3COOH}}{Vs} = 15.75$ mol.L^{-1}.	**0.75**
1.2	Upon dilution the number of moles of solute is conserved: $n_0 = n_f$; $C_0 \times V_0 = C_f \times V_f$; The volume Vo withdrawn from solution (S_0) to prepare the solution (S): $V_0 = \frac{C_f V_f}{C_0} = \frac{1x0.1}{15.75} = 0.0063 L$ or $6.3 mL$. **Set-3** is the most precise one since we need: - a 10 mL graduated pipette is required to withdraw V_0. - a 100 mL volumetric flask to prepare V_f.	**0.75**
2.1	At t = 233s we have: $n_{CO_{2(t=233)}} = \frac{V_{CO_{2(t=233)}}}{V_m} = \frac{240x10^{-3}}{24} = 10x10^{-3}\ mol$	**0.5**
2.2		**1**
2.3	n $(CH_3COOH)_0$= C x V = 1 x 0.06 = 0.06 mol. $n(NaHCO_3)_{initial} = \frac{m}{M} = \frac{1.25}{84} = 0.015 mol = n_{HCO_3^-}$ Ratio: $R_{CH_3COOH} = \frac{0.06}{1} = 0.06 > R_{HCO_3^-} = \frac{0.015}{1} = 0.015$ HCO_3^- is the limiting reactant.	**1**
2.4.1	True. The rate of formation of CO_2 starts maximum initially and then decreases with time. At t=0s, the rate of formation of CO_2 is greater than that at t = 200 s.	**0.75**
2.4.2	False. According to stoichiometric ratios:	**0.75**

	$\frac{n(HCO_3^-)_{reacted}}{1} = \frac{n_{CO_2\,(produced\,at\,t=\infty)}}{1} = 0.015 mol$; $n_{CO_2\,(\infty)} = 15x10^{-3}\ mol > n_{CO_2\,(at\,t=400s)} = 10.9x10^{-3} mol$ Then t = 400 s does not represent the end of the reaction.	
2.4.3	False. If the temperature which is a kinetic factor increases, the slope of the tangent at each point of the curve increases (increasing rate) and the volume of CO_2 at t = 100s is $V'(CO_2) > 180$ mL.	**0.75**
3	The half life time $t_{1/2}$ of the reaction is the time needed to for the la quantity of product CO_2 to become the half of its maximal value. $\frac{n_{CO_2\,(\infty)}}{2} = 7.5x10^{-3} mol$ Graphically $t_{1/2}$ = 100s.	**0.75**

Part of question	**Exercise 2 (7 points)** **The acidity of a butter** **Expected Answer**	**Mark**
1.1	$CH_3 - CH_2 - CH_2 - COOH$ butanoic acid.	**0.5**
1.2	$CH_3 - CH_2 - CH_2 - COOH + H_2O \rightleftharpoons CH_3 - CH_2 - CH_2 - COO^- + H_3O^+$.	**0.5**
1.3.1	$[H_3O^+] = 10^{-pH} = 10^{-3.18} = 6.6\times10^{-4}\ mol.L^{-1} < C = 3\times10^{-2}\ mol.L^{-1}$ The butyric acid is a weak acid.	**0.5**
1.3.2	$\alpha = \frac{n_{(butyric\,acid)\,reacted}}{n_{(butyric\,acid)\,initial}}$ At constant volume: $\alpha = \frac{[Butyric\,acid]_{reacted}}{[Butyric\,acid]_{initial}} = \frac{[H_3O^+]}{C} = \frac{6.6x10^{-4}}{3x10^{-2}} = 0.022.$	**0,5**
1.3.3	$CH_3 - CH_2 - CH_2 - COOH + H_2O \rightleftharpoons CH_3 - CH_2 - CH_2 - COO^- + H_3O^+$ at t = 0: C; excess; -; - at t_{eq}: C – Cα; excess; Cα; Cα $pH = pKa + \log\frac{[C_4H_7O_2^-]}{[C_4H_8O_2]} = pKa + \log\frac{C\alpha}{C(1-\alpha)}$; $pKa = pH - \log\frac{\alpha}{1-\alpha} = 3.18 - \log\frac{0.022}{1-0.022} = 4.82$	**1**
1.3.4	pH = 3.18 < pKa – 1 = 3.82 Thus butyric acid predominates in the solution (S).	**0.5**
2.1	The butanoate ion.	**0.25**
2.2	$K_R = \frac{[C_4H_7O_2^-]}{[C_4H_8O_2][HO^-]} x \frac{[H_3O^+]}{[H_3O^+]} = \frac{Ka}{Kw} = \frac{10^{-4.82}}{10^{-14}} = 1.51x10^9$ $K_R > 10^4$. The reaction is complete.	**0.75**
2.3	**b.** Fast and unique.	**0.25**
2.4	Cresol red (7.2 – 9.0) since pH_E = 8.7 is included in its pH range.	**0.5**
2.5	At equivalence:	**0.75**

	$\frac{n_{acid\,(present\,in\,the\,sample)}}{1} = \frac{n_{HO^-\,(added\,in\,V_{bE})}}{1}$; $n_{acid} = C_b \, x V_{bE} = 0.4\,x\,7.5x10^{-3} = 0.003\,mol$	
2.6	m $_{acid}$ = n x M = 0.003 x 88 = 0.264 g	**0.5**
2.7	$\%\ by\ mass\ of\ butyric\ acid = \frac{0.264}{8}x100 = 3.3\% < 4\%$ Thus the analyzed butter is not rancid.	**0.5**

Part of question	**Exercise 3 (6 points) Fruity Odor Esters** **Expected Answer**	**Mark**
1.1	(B) gives a positive test with 2,4-DNPH then the compound (B) is a carbonyl compound (aldehyde or ketone) and a negative test with Schiff's reagent then (B) is a ketone.	**0.5**
1.2	Since (B) is ketone; (A) is a secondary alcohol.	
1.3.1	According to the law of proportions: $\frac{12n}{\%C} = \frac{M_A}{100}\ then\ \frac{12n}{60} = \frac{14n+18}{100}$ n = 3 hence the molecular formula of (A) is C_3H_8O.	**0.75**
1.3.2	(A): $CH_3 - CHOH - CH_3$ (B) : $CH_3 - CO - CH_3$.	**0.5**
2.1	**b.** $CH_3 - COOH$. The molecular formula ($C_5H_{10}O_2$) of the ester (E_1) satisfies the general formula of an open chain saturated ester. The ester (E_1) is formed of 5 carbon atoms ($C_5H_{10}O_2$) and the alcohol (A) is formed of 3 carbon atoms (C_3H_8O). It remains for the carboxylic acid 5 - 3 = 2 carbons.	**0.75**
2.2	(E_1) : $CH_3 - COO - CH - CH_3$ | 1-methylethyl ethanoate. CH_3	**0.5**
2.3	(E_2) : $CH_3 - CH - COO - CH_2 - CH_3$ | CH_3	**0.5**
3.1	- Reflux heating under reflux increases the rate of the reaction. - The reflux is preventing to lose the components of the reaction by condensing their vapors escaping and returning them to the reactional mixture. To conserve the mass of reactants and products during heating.	**0.5**
3.2.1	In order to synthesize E_1 and $E_{2,}$ The initial mixture of reactants is equimolar then no excess reactant. - For the ester (E_1), the alcohol used is a secondary then the yield of this synthesis must be 60%. Thus $n_{acid} = n_{ester(theoretical)}$ = 0.1 mol. $n_{ester(experimental)}$ = yield x $n_{ester(theoretical)}$ = 0.6 x 0.1 = 0.06 mol. - For the ester (E_2), the alcohol used is a primary then the yield of this synthesis must be 66%. Thus $n_{acid} = n_{ester(theoretical)}$ = 0.1 mol and $n_{ester(experimental)}$ = yield x $n_{ester(theoretical)}$ = 0.66 x 0.1 = 0.066 mol.	**1**
3.2.2	If the carboxylic acid used in the preparation of ester is replaced by its acid anhydride derivative, the esterification reaction will be complete and faster, and then the yield increases.	**0.5**
3.2.3	Concentrated sulfuric acid in small amounts acts as a catalyst that accelerates the rate of the reaction without affecting the yield.	**0.5**