مسابقة في مادة الكيمياء المدة: ساعتان	الاسم: الرقم:

This Exam Includes Three Exercises. It Is Inscribed On 4 Pages Numbered from 1 to 4.
The Use Of A Non-Programmable Calculator Is Allowed.

Answer The Three Following Exercises.

Exercise 1 (6 points) Kinetic of an Esterification Reaction

The synthesis reaction of pentyl methanoate is a slow and reversible reaction represented by the following equation:

$$HCOOH + HO - CH_2 - (CH_2)_3 - CH_3 \rightleftarrows HCOO - CH_2 - (CH_2)_3 - CH_3 + H_2O$$

The aim of this exercise is to study the kinetic of this reaction and to titrate the remained methanoic acid at different instants of time t.

Given: - This study is realized at 25°C**.**

Acid / base pair	H_2O / HO^-	CH_3COOH / CH_3COO^-	$HCOOH / HCOO^-$
pK_a	14	4.75	3.75

1. Study of the Titration Reaction

In order to titrate methanoic acid with a convenient base, available are the two following basic aqueous solutions:
Sodium hydroxide solution ($Na^+ + HO^-$) and sodium ethanoate solution ($CH_3COO^- + Na^+$).
The study of the reaction of methanoic acid with each of these two bases is represented in the **document-1:**

Reaction	**Characteristics**		**Reaction constant**
HO^- ions with HCOOH	Fast	Unique	$K_{R_1} = 1.78\times10^{10}$
CH_3COO^- ions with HCOOH	Fast	Unique	K_{R_2}

Document-1

1.1. Calculate the reaction constant K_{R_2}.
1.2. By referring to **document-1**, choose which of the two reactions the convenient reaction to realize the titration. Justify.
1.3. Write the equation of this titration reaction.

2. Kinetic Study of the Esterification Reaction

Ten sealed tubes are prepared, each containing 40 mmol of methanoic acid and 40 mmol of 1- pentanol.
At instant of time t = 0, these tubes are placed in a hot water bath maintained at a constant temperature.
The remained acid is titrated at different instants of time t. The obtained results are given in the table of **document-2**, where n_a is the remaining number of moles of the acid at each instant of time t.

t (min)	2	4	6	10	14	18	24	…..	t (equilibrium)
n_a (mmol)	32	27.2	24.8	21.2	19.0	17.0	16.0	……	13.3

Document-2

2.1. Plot the curve representing the variation of the remaining number of moles of the acid as a function of time: $n_a = f(t)$, within the interval of time [0 – 24 min].
Take the following scales: 1 cm for 4 min in abscissa; 1 cm for 4 mmol in ordinate.

2.2. Specify graphically, the variation of the rate of disappearance of the acid with respect to time.

2.3. The above study is carried out again but with only one modification: few drops of concentrated sulfuric acid are added to the content of each tube.
Trace, on the same graph of **question 2.1**, the shape of the curve representing the variation of the number of moles of the remaining acid as a function of time: $n_a = g(t)$. Justify.

2.4. The number of moles of ester formed experimentally at the end of the evolution of the reaction system is represented by n_{exp} .

2.4.1. Determine the theoretical number of moles n_{theo} of the ester formed.

2.4.2. Choose the value that corresponds to n_{exp}. Justify.

a. n_{exp} = 40 mmol   **b.** n_{exp} = 13.3 mmol   **c.** n_{exp} = 26.7 mmol

Exercise 2 (7 points) Lactic Acid

Lactic acid can be used as a scale removal for washing machines and coffee pots …In addition it possesses anti-bacterial properties.
The aim of this exercise is to study the structure of lactic acid and then to determine its percentage by mass in the commercial scale removal.

Given: - pKa (lactic acid / lactate ion) = 3.9
- $M_{\text{(Lactic acid)}} = 90\ g.mol^{-1}$

1. Study of Lactic Acid

The condensed structural formula of lactic acid is:

$CH_3 – CH – COOH$ (with OH on the central CH)

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CH3 – CH – COOH
        |
       OH
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For the following propositions, justify the correct one (s) and correct the false one (s)

1.1. The systematic name of lactic acid is: 2-hydroxy-2-methylethanoic acid.

1.2. Lactic acid possesses two enantiomers.

1.3. The catalytic mild oxidation of lactic acid with oxygen gas gives an organic compound that reacts with 2,4-D.N.P.H.

2. Preparation of a Dilute Solution (S) of Lactic Acid

Available a flask containing a commercial solution (S_0) of lactic acid.
A volume V_o = 2.2 mL of the commercial solution (S_0) is withdrawn in order to prepare a lactic acid solution (S) of volume V_S = 1.0 L.

Choose, from the list of **document-1**, the most precise glassware used to prepare (S):

- Beakers: 100 mL, 250 mL and 500 mL	- volumetric flasks: 100 mL, 500 mL and 1000 mL
- Graduated cylinders: 5 mL, 10 mL and 25 mL	- volumetric pipets: 5 mL, 10 mL and 25 mL
- Graduated pipets: 1 mL and 5 mL	

Document-1

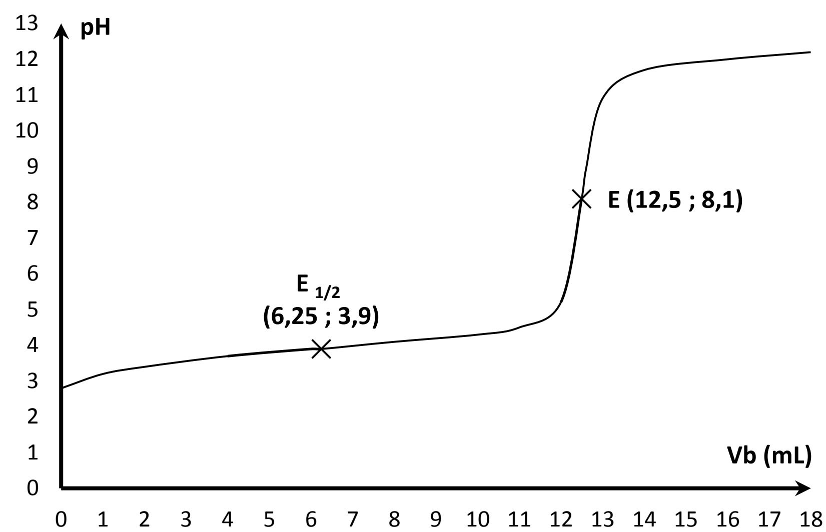
3. Titration of the Solution (S)

At $25^{o}C$, a pH-metric titration of volume V_a = 25.0 mL of solution (S) by sodium hydroxide solution ($Na^+ + HO^-$) of concentration $C_b = 5.0\times10^{-2}$ mol.L^{-1} is carried out. Distilled water is added in order to immerse properly the pH-meter electrode.

The titration reaction of lactic acid denoted as HA is given by the following equation:

$$HA + HO^- \rightarrow A^- + H_2O$$

The titration follow-up permits us to obtain the curve pH = f (V_b) of **document-2**:



Document-2

3.1. By referring to the curve of **document-2**:

3.1.1. Pick out two reasons that show that lactic acid is a weak acid.

3.1.2. Verify that the titrated acid is lactic acid.

3.2. Show that the concentration of the lactic acid solution (S) is $C_a = 2.5\times10^{-2}$ mol.L^{-1}.

3.3. Determine the percentage by mass of lactic acid in solution (S_0) knowing that density $d_{(S_0)}$ = 1.2 g.mL^{-1}.

4. Action of Lactic Acid on Lime Scale

Given: - The chemical formula of lime scale is (Ca^{2+}, CO_3^{2-})

- pKa (CO_2,H_2O / HCO_3^-)= 6.4
- pKa (HCO_3^-/CO_3^{2-}) = 10.3
- pKa (H_2O /HO^-) = 14
- pKa (H_3O^+ /H_2O) = 0

The action of excess lactic acid on lime scale produces an effervescence.

4.1. Place on a pKa axis all the acid/base pairs involved in this reaction.

4.2. By referring to the pKa axis, interpret the observed effervescence.

Exercise 3 (7 points) Preparation of Soap

Soap, known for long time ago, is used more for medicine and for purification than as washing detergents.
Fatty acids and sodium hydroxide are the primary raw materials for manufacturing of soaps.
The aim of this exercise is to prepare a sodium hydroxide solution in order to prepare soap.

Given: Molar mass in $g.mol^{-1}$: $M_{(NaOH)} = 40$; $M_{(sodium\ oleate)} = 304$

1.Preparation of sodium hydroxide solution (S)

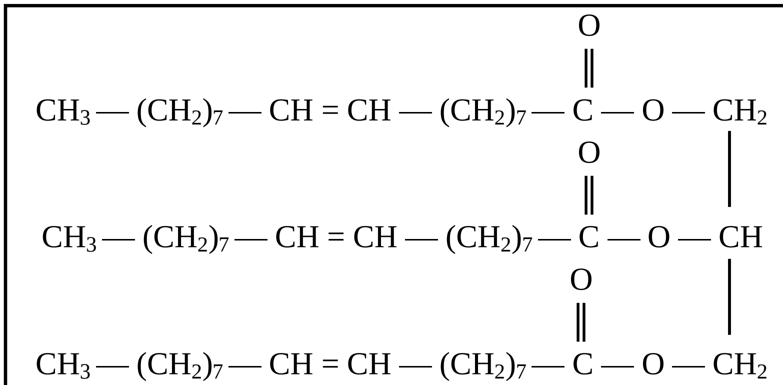
Available is a flask containing sodium hydroxide NaOH pellets. A mass m of sodium hydroxide is dissolved in distilled water in order to obtain a solution (S) of volume V_S =100.0 mL and of concentration C_b = 5.0 $mol.L^{-1}$.

1.1. Calculate the mass m of NaOH needed to prepare the solution (S).

1.2. Name the essential material needed to prepare this solution.

2.Olein

Olein is a triester prepared from oleic acid and glycerol.
The condensed structural formula of olein is:



Document-1

2.1. By referring to **document-1**, write the condensed structural formula of:

- **2.1.1.** Oleic acid.
- **2.1.2.** Glycerol.

2.2. Give the systematic name of glycerol.

3. Preparation of Soap

Introduce, in a round bottom flask a volume of olive oil containing 0.10 mol of olein and an excess of solution (S) already prepared, then add few ml of ethanol.
This mixture is heated to reflux for 45 min.After cooling the flask, the soap formed is recovered, purified and weighed; the obtained mass is equal to 82.6 g.

3.1. Write the equation of the preparation reaction of soap**.**

3.2. Choose the correct answer:

3.2.1. The oleate ion has:

a. acid character **b.** base character **c.** neutral character

3.2.2. The two characteristics of the saponification reaction are:

a. Slow and reversible **b.** Slow and complete **c.** Fast and reversible

3.3. Determine the yield of this reaction.

3.4. Oleate ion is an amphiphilic species .Justify.

3.5. Sea water (containing among others the ions Na^+ and $C\ell^-$) reduces the detergency effect of soap. Explain.

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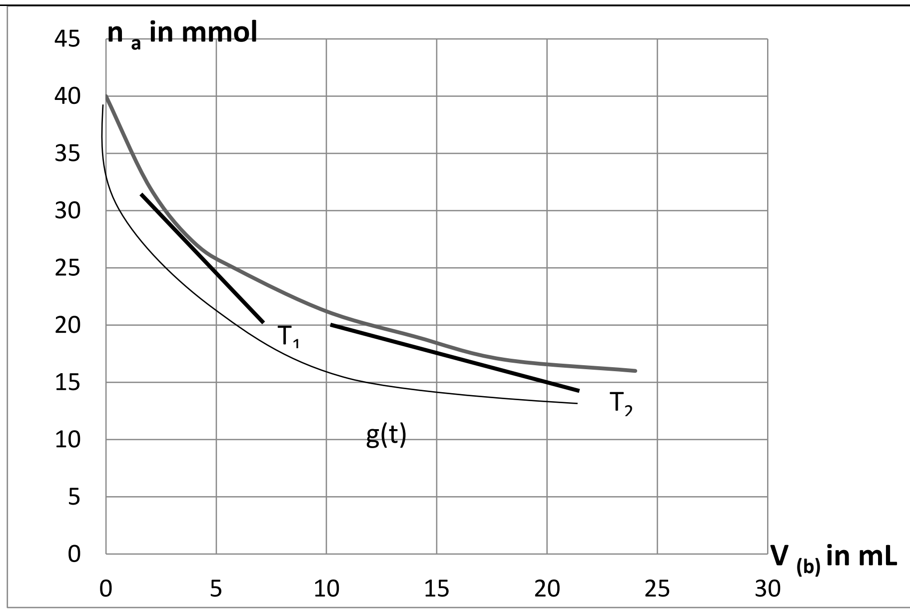
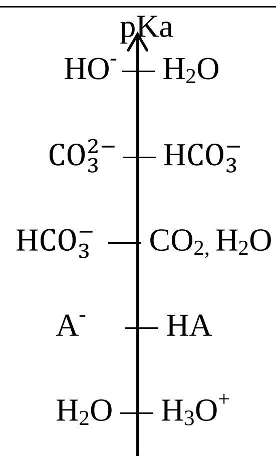
الثلاثاء ٧ آب ٢٠١٨

مشروع معيار التصحيح

Exercise 1 (6 points) **Kinetic of an Esterification Reaction**

Part of the Q	**Answer**	**mark**
1.1	$K_{R_2} = 10^{pKa(CH_3COOH/CH_3COOH)\ -\ pKa(HCOOH/HCOO^-)} = 10^{4.75-3.75} = 10^1 = 10$	0.5
1.2	Both reactions are fast and unique but $K_{R_2} < 10^4$ then the reaction 2 is reversible while $K_{R_1} > 10^4$ then the reaction 1 is complete, which shows that the reaction between HO^- ions and HCOOH is the convenient one.	0.75
1.3.	The equation of the reaction is: $HCOOH + HO^- \longrightarrow HCOO^- + H_2O$	0.5
2.1		1
2.2	The rate of disappearance of HCOOH is represented by the negative slope of the tangent drawn on the curve na = f(t) at point of abscissa t . The negative slope of the tangent (T_1)at t_1 is greater than the negative slope of the tangent (T_2)at t_2 (graph) , thus as time increases the rate of the reaction decreases.	0.75
2.3	Curve. Sulfuric acid acts as a catalyst that increases the rate of the reaction At each instant of time t: $n_{a(t)\text{ with catalyst}} < n_{a(t)\text{ without catalyst}}$	1
2.4.1.	Assuming that the reaction is complete: R(alcohol) = R(acid) = 40 according to the stoichiometry of the esterification reaction: $n\text{ (ester)}_{theo} = n\text{ (HCOOH)}_o = 40$ mmol.	0.5
2.4.2	At equilibrium: $n\text{(acid)}_{consumed} = n\text{(ester)}_{formed} = 40 - n\text{(acid)}_{remaining}$ $= 40 - 13.3 = 26.7$ mmol. The answer is c	1

Exercise 2 (7 points) **Lactic Acid**

Part of the Q	Answer	mark
1.1	False, it is 2-hydroxypropanoic acid	0.5
1.2	True, since this molecule is chiral with an asymmetric carbon at carbon n^0 2.	0.5
1.3	True, since mild oxidation of lactic acid containing a secondary alcohol function leads to the formation of carbonyl group compounds (ketone).	0.5
2	Graduated pipet of 5 mL, volumetric flask of 1000 mL, (beaker of 100mL)	0.5
3.1.1	Lactic acid is weak acid since the curve pH = f (V) presents two inflection points and the pH at equivalence point is greater than 7.	1
3.1.2	Graphically at half-equivalence pH = 3.9 = pKa (lactic acid / lactate ion) so the titrated acid is lactic acid.	0.75
3.2	At equivalence : $n(HO^-)$ added to reach equivalence = n(HA)introduced into the beaker $C_b \times V_{bE} = C_a \times V_a$ Then: $C_a = \dfrac{C_b \times V_{bE}}{V_a} = \dfrac{5.0\times10^{-2} \times 12.5}{25}$ = 2.5×10^{-2} mol.L^{-1}.	1
3.3	By dilution, n(solute) introduced is conserved: $C_o \times V_o = C_a \times V_S$ Then $C_o = \dfrac{C_a \times V}{V_o} = \dfrac{2.5\times10^{-2}\times1000}{2.2} = 11.36$ mol.L^{-1} The percentage by mass is : % by mass = $\dfrac{masso\ of\ solute}{mass\ of\ solution} \times 100 = \dfrac{C_0\ x\ M\ (lactic\ acid) x\ V_O \times 100}{d_{(s0)\ in\ g/L} \times V_O} =$ $\dfrac{C_0\ x\ M\ (lactic\ acid) \times 100}{d_{(s0)\ in\ g/L}} = \dfrac{11.36 \times 90 \times 100}{1200} = 85.2\ \%$	1
4.1	 	0.5
4.2	The reaction that takes place between lactic acid (HA) and carbonate ions (CO_3^{2-}) leads to the formation of bicarbonate ions HCO_3^-.these ions react with the excess of HA producing CO_2 gas responsible for the effervescence observed.	0.75

Exercise 3 (7 points) **Preparation of Soap**

Part of Q	Answer	Mark
1.1	m = n (NaOH) x M (NaOH) = $C_b \times V_s \times M = 5\times0,1\times40 = 20$ g	0.75
1.2	The essential material: precision balance; volumetric flask 100 mL.	0.5
2.1.1	The condensed structural formula of oleic acid is ; $CH_3 — (CH_2)_7 — CH = CH — (CH_2)_7 — COOH$	0.5
2.1.2	The condensed structural formula of glycerol is: $CH_2OH – CHOH – CH_2OH$	0.5
2.1	The systematic name of glycerol is 1,2,3-propantriol	0.5
3.1	The equation of the reaction is: $C_{17}H_{33} – COO – CH_2$ $C_{17}H_{33} – COO – CH + 3 (Na^+ + HO^-) \rightarrow 3 (C_{17}H_{33}COO^- + Na^+) + CH_2OH – CHOH – CH_2OH$ $C_{17}H_{33} – COO – CH_2$	1
3.2.1	b	0.5
3.2.2	b	0.5
3.3	The yield of the reaction : R = $\frac{n(soap)\,experimental}{n(soap)\,theoratical} = \frac{n_1}{n_2}$ With $n_1 = \frac{m(soap)experimental}{M(\text{sodium oleate})} = \frac{82.6}{304}$ = 0.27 mol and $n_2 = 3 \times n(A)$ initial = 3×0.10 = 0.30 mol. Then R = 0.90, the percentage yield is 90%.	1
3.4	The soap formed has a lipophilic end and hydrophilic end.	0.5
3.5	The equation of the dissolution of soap in water : $C_{17}H_{33}COONa_{(s)} \rightleftarrows C_{17}H_{33}COO^- + Na^+$ The presence of Na^+ ions in sea water shifts the equilibrium in direction 2 in the direction of the formation of solid soap (common ion effect). The concentration of oleate ions decreases and consequently the detergency effect of soap decreases.	0.75