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 equaction:

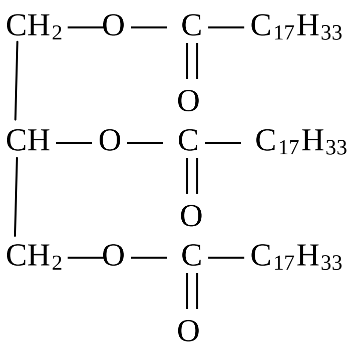
Olive oil + sodium hydroxide → soap + glycerol

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

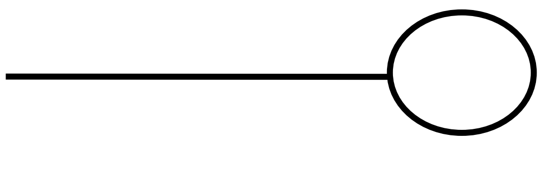
Aleppo's soap was perfumed by natural essences. Nowadays many samples of soap are perfumed by the use of synthetic esters as pentylbutanoate.

1- <u>Saponification Reaction</u>

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

$$\underset{(A)}{C_4H_8O_2} + \underset{(B)}{C_5H_{12}O} \rightleftharpoons \underset{(E)}{C_9H_{18}O_2} + H_2O$$

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.

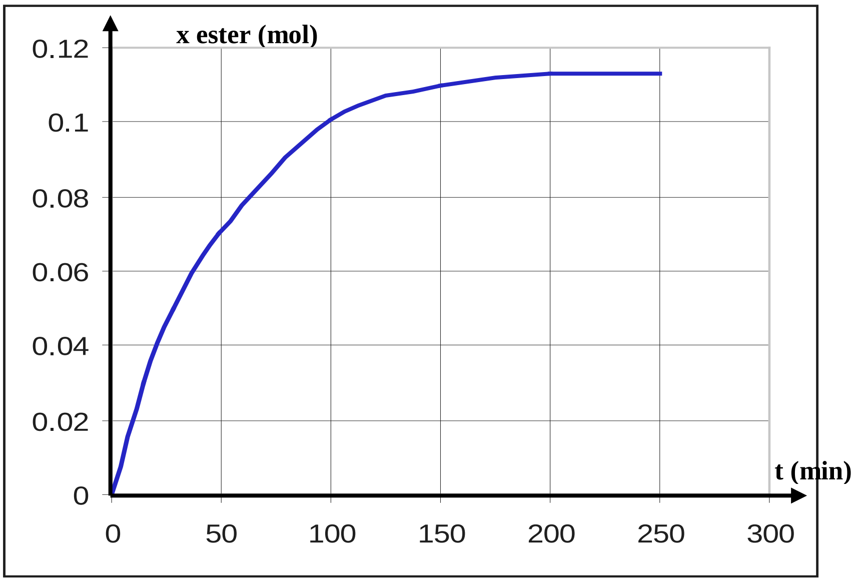
Given: For carboxylic acid **(A)**:

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

$$C_4H_8O_2 + Na^+ + HO^- \rightarrow C_2H_6O + Na^+ + CH_3\text{-}COO^-$$

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

1- <u>Structural Formulas</u>

1.1- Write the condensed structural formulas of ethylethanoate and ethanol.
1.2- Circle the functional group in each of the above formulas.

2- <u>Kinetic Study</u>.

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 $C = 5\times10^{-2}$ mol.L^{-1}.
The mixture is divided into equal parts, each part has a volume V = 10 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 $C_a = 10^{-2}$ mol.L^{-1}. The results are given in the table below:

t (min)	4	9	15	24	37	53	83	143
V_a (mL)	44.1	38.6	33.7	27.9	22.9	18.5	13.6	8.9
n (10^{-4} 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:
$n = 5\times10^{-4} - 10^{-2}\times V_a$, where V_a 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 min.
Take the following scales: 1cm for 10 min in abscissa and 1 cm for 0.2×10^{-4} mol in ordinate.
2.4- Determine the half-life of the reaction.

3- <u>Some Catalytic Reactions of Ethanol</u>

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:

$$Fe_{(s)} \ + \ 2\,H_3O^+_{(aq)} \ \rightarrow \ Fe^{2+}_{(aq)} \ + \ H_{2\,(g)} \ + \ 2\,H_2O_{\,(l)}$$

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 g.mol^{-1}.
- Molar volume of gas: V_m = 24 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 mL.

1.2- Show at each instant t, the following relation: $[H_3O^+]_t = 0.2 - \dfrac{V(H_2)_t}{1200}$; 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 H_3O^+

2.1- Compare the rate of disappearance of H_3O^+ ions to that of appearance of H_2 gas, at the same instant t.

2.2- The rate of appearance of gas bubbles of H_2 decreases with time. Specify the kinetic factor that explains this variation.

2.3- The above reaction is complete and is ended after 98 minutes. Choose, by justifying, among the following, the half-life of this reaction:
a) 49 min. b) More than 49 min. c) Less than 49 min.

2.4- The above reaction is repeated without changing the amounts of reactants but using iron filings instead of the strip. Justify if the end of the reaction takes place:
a) Before 98 min; b) At 98 min; c) After 98 min.

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.

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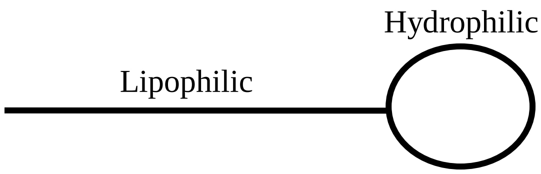
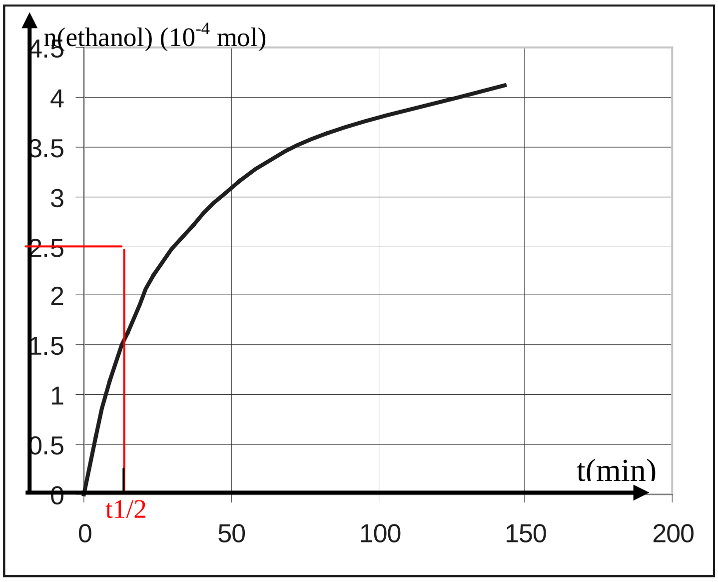
مشروع معيار التصحيح	مسابقة في مادة الكيمياء المدة ساعتان	الاسم: الرقم:

Marking Scheme
First exercise (7 points)

Part of Q.	Answer	Mark
1.1	The condensed structural formula of glycerol is: $CH_2 - CH - CH_2$ (each carbon bearing an OH) $\quad | \quad\ \ | \quad\ \ |$ $\ OH \quad OH \quad OH$	**0.5**
1.2	The equation of formation of Aleppo's soap is: $C_{17}H_{33} - C(=O) - O - CH_2$ $C_{17}H_{33} - C(=O) - O - CH$ + 3 NaOH → 3 $C_{17}H_{17}COONa$ + $CH_2OH—CHOH—CH_2OH$ $C_{17}H_{33} - C(=O) - O - CH_2$	**0.75**
1.3	Aleppo's soap is hard because it is prepared from olive oil and sodium hydroxide.	**0.5**
1.4	 Lipophilic : likes lipids. Hydrophilic : likes water.	**1**
2.1	The condensed structural formulas: (A) : $CH_3 - CH_2 - CH_2 - COOH$; butanoic acid (B) : $CH_3 - CH_2 - CH_2 - CH_2 - CH_2OH$; 1-pentanol (E) : $CH_3 - CH_2 - CH_2 - COO - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$	**1.25**
2.2.1	$n(A)_{initial} = \frac{m(A)}{M(A)} = \frac{d(A)xV}{M(A)} = \frac{0.96x16}{88} = 0.17$ 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: $\% \text{ yield} = \frac{n(B)esterified}{n(B)_{initial}} \times 100 = \frac{n(E)_{formed} at100min}{n(B)_{initial}} \times 100 = \frac{0.1}{0.17} \times 100 = 58.8\ \% > 33\ \%.$	**2**

Second exercise (6 points)

Part of Q.	Answer	Mark
1.1	The condensed structural formula of ethylethanoate: $CH_3 - C(=O) - O - CH_2 - CH_3$ That of ethanol: $CH_3 - CH_2 - OH$	**0.5**
1.2	CH_3 [$- C(=O) - O -$] $CH_2 - CH_3$ $CH_3 - CH_2 -$ [OH]	**0.5**
2.1	The equation of the titration reaction is: $H_3O^+ + HO^- \rightarrow 2H_2O$	**0.5**
2.2.1	$n(\text{ethanol})_{t=9} = 5\times10^{-4} - 10^{-2}\times38.6\times10^{-3} = 1.14\times10^{-4}$ mol and $n(\text{ethanol})_{t=83} = 5\times10^{-4} - 10^{-2}\times13.6\times10^{-3} = 3.64\times10^{-4}$ 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 $n = 5.0\times10^{-4}$ mol.	**0.5**
2.3	The curve n(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. $n(\text{ethanol})_{t1/2} = \frac{5\times10^{-4}}{2} = 2.5\times10^{-4}$mol ; From the graph $t_{1/2} = 30$ min	**1**
3.1	The equation of the dehydrogenation reaction of ethanol in the presence of copper is: $CH_3 - CH_2 - OH \rightarrow CH_3 - CHO + H_2$ (dehydrogenation)	**0.5**
3.2	The equation of the dehydration reaction of ethanol in the presence of Al_2O_3 is: $2\ CH_3 - CH_2 - OH \rightarrow CH_3 - CH_2 - O - CH_2 - CH_3 + H_2O$	**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	Calculation of the number of moles of each reactant. $nFe = \frac{mFe}{MFe} = \frac{0.28}{56} = 5x10^{-3}$ mol. $nH_3O^+ = CxV = 0.2x100x10^{-3} = 2.0x10^{-2}$ mol. $R(Fe) = \frac{5x10^{-3}}{1} < R(H_3O^+)\ \frac{2x10^{-2}}{2} = 1x10^{-2}$. Iron is the limiting reactant. The volume of hydrogen is: $V(H_2) = n(H_2)xV_m = n(Fe)xV(H_2) = 5x10^{-3}x24 = 0.120$ L =120 mL.	**1**
1.2	$n(H_3O^+)$ left at instant t = $n(H_3O^+)_0 - n(H_3O^+)$reacting at the same instant; $n(H_3O^+)$reacting = 2 $n(H_2)$formed = $\frac{2\times V(H_2)}{V_m} = \frac{V(H_2)_t}{12000}$; $n(H_3O^+)$left at instant t = $n_0 - 2\ n(H_2)$formed. Divide by V(volume of the solution), we have: $[H_3O^+]_t = \frac{0.02}{0.1} - \frac{V(H_2)}{0.1\times 12000}$ and $[H_3O^+]_t = 0.2 - \frac{V(H_2)}{1200}$.	**1**
1.3	The concentration of H_3O^+ ions at the end of the reaction is given by: $[H_3O^+]_\infty = 0.2 - \frac{V(H_2)_\infty}{1200} = 0.2 - \frac{120}{1200} = 0.1\ mol.L^{-1}$.	**0.5**
2.1	According to the stoichiometry of the equation, we have: $R(reaction) = \frac{R(H_3O^+)disappearance}{2} = \frac{R(H_2)formation}{1}$ $R(H_3O^+)$disappearance = 2 $R(H_2)$formation.	**0.5**
2.2	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^+.	**0.5**
2.3	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.	**0.5**
2.4	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.	**0.25**
3.1	The concentration of H_3O^+ ions in the solution S_1 is given by: $[H_3O^+] = \frac{0.1x100x10^{-3}}{1} = 1x10^{-2}\ mol.L^{-1}$. Where $pH = -\log [H_3O^+] = -\log 1x10^{-2} = 2$.	**0.75**
3.2.1	The equation of the reaction is: $Fe_{(s)} + 2\ CH_3COOH_{(aq)} \rightarrow Fe^{2+}_{(aq} + 2\ CH_3COO^-_{(aq)} + H_{2\,(g)}$	**0.5**
3.2.2	Since the same amounts of reactants are used, hydrochloric acid is in excess and half the amount of this acid has reacted. The acid is in excess and half of the quantity of acid reacted: $n(CH_3COOH)_{remaining} = n(CH_3COO^-)_{formed}$ and these two species have consequently the same concentration. At the end of the reaction, we have: $[CH_3COO^-] = [CH_3COOH] = \frac{0.01}{1} = 0.01\ mol.L^{-1}$. $pH = pK_a + \log\frac{[CH_3COO^-]}{[CH_3COOH]} = pK_a + \log 1 = pK_a + 0$ $pH = pK_a = 4.75$. 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.	**1.5**