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:

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_3O^+/H_2O	CH_3COOH/CH_3COO^-	H_2O/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 - 500 mL Erlenmeyer flask - 10 mL volumetric pipet	- 50 mL beaker - 1000 mL volumetric flask - 20 mL volumetric pipet	- 50 mL beaker - 1000 mL graduated cylinder - 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- Writethe 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 yieldof 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^oC.
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 $C_b = 0.010$ mol.L^{-1}.
This procedure is repeated with the other tubes.
The equation of the titration reaction is:

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

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 Vb_E are related by the following relation:

$$n\,(ester)_t = 1.0\times10^{-4} - 1.0\times10^{-5}\times Vb_E$$

where Vb_E ,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(min)	0	10	20	30	40	50	60	90	t_∞
Vb_E (mL)		2.1	3.7	5.0	6.1	6.9	7.5	8.6	
n(ester) (10^{-5}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.

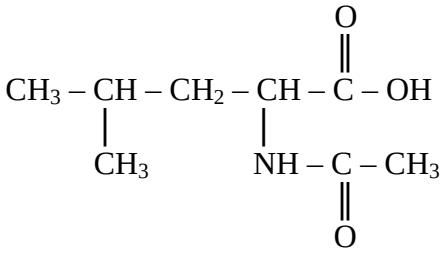
3.3- Determine the rate of disappearance of the ester at the instant t = 40 min.

3.4- Determine graphically the half-life time $t_{1/2}$ of the reaction.

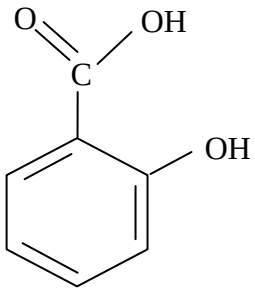
3.5- Suggest a way, other than heating, in order to reduce $t_{1/2}$ of this reaction.

Third Exercise (6 points)
Molecules of Some Medicinal Drugs

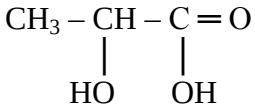
Acetyl-leucine is used as a medicinal drug to treat vertigo. Its condensed structural formula is:



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- <u>Molecular Structure</u>

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- <u>Hydrolysis of Acetyl-leucine</u>

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- <u>Salicylic Acid</u>

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:

Salicylic acid + ethanoicanhydride $\rightarrow$ (A) + (B)

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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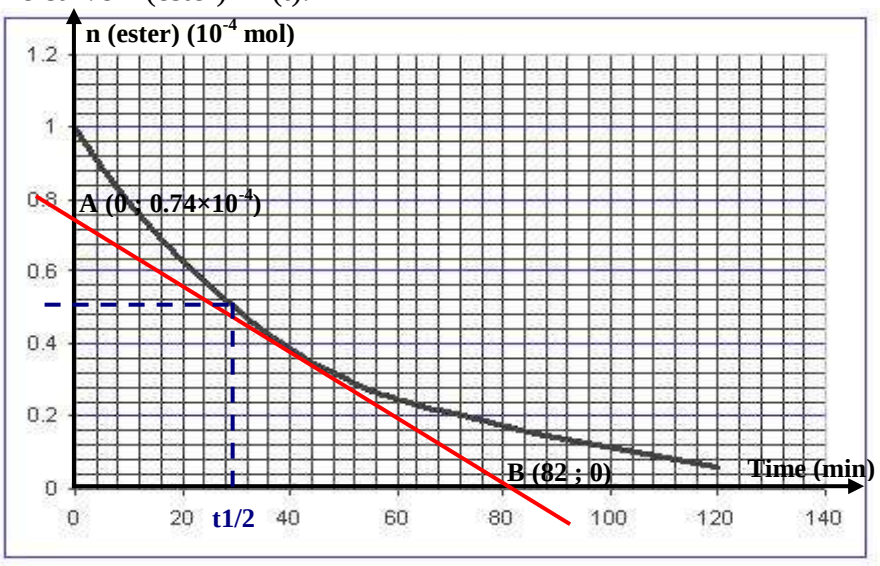
مشروع معيار التصحيح	مسابقة في مادة الكيمياء المدة ساعتان	

First Exercise (7 points)
Titration of a Household Product

Part of the Q	Answer	Mark
1.1	The density of the product: $d = \frac{m\,(solution)}{V(solution)} = \frac{120}{100} = 1.2 g.mL^{-1}$.	0.5
1.2	During dilution the number of moles of the solute is conserved. $C_0 \times V_0 = C_f \times V_f$ $\frac{V_f}{V_0} = \frac{C_0}{C_f} = 50$ with V_o is the volume of the pipet and V_f is the volume of the volumetric flask. 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.	1
2.1	The equation of the reaction: $H_3O^+ + HO^- \rightarrow 2\,H_2O$.	0.5
2.2	At equivalence, $n(HO^-)$ in 10 mL = $n(H_3O^+)$ added to reach equivalence ; $C_1 \times V_1 = C_2 \times V_{2E}$ and $C_1 = \frac{0.1 \times 11.2 \times 10^{-3}}{10 \times 10^{-3}} = 0.112\ mol.L^{-1}$.	0.75
2.3	The concentration of sodium hydroxide in the household product is: $C = 0.112 \times 50 = 5.56\ mol.L^{-1}$.	0.5
2.4	The mass of sodium hydroxide in 1 L of the household product is: $m = 5.56 \times 40 = 224$ g. The mass of 1 L of the household product is 1200 g. The percentage by mass of sodium hydroxide is then: $\frac{224 \times 100}{1200} = 18.66$ %.	1
2.5	The difference is: $\frac{20 - 18.66}{20} \times 100 = 6.7$ %. This difference exceeds the acceptable value 5 %. The indication is not verified.	0.5
3.1	The equation of the reaction is: $CH_3COOH + HO^- \rightarrow CH_3COO^- + H_2O$	0.5
3.2	$\Delta pK_a = pK_a(H_2O/HO^-) - pK_a(CH_3COOH/CH_3COO^-) = 14 - 4.8 = 9.2$ $K_R = 10^{9.2} > 10^4$. The reaction is complete, fast and unique; thus it can be used as a titration reaction.	0.75
3.3	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. 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.	1

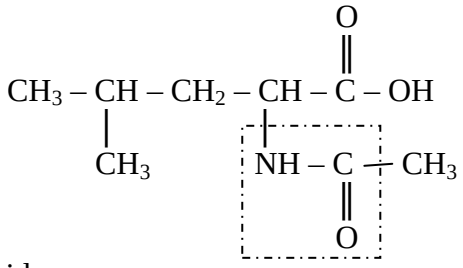
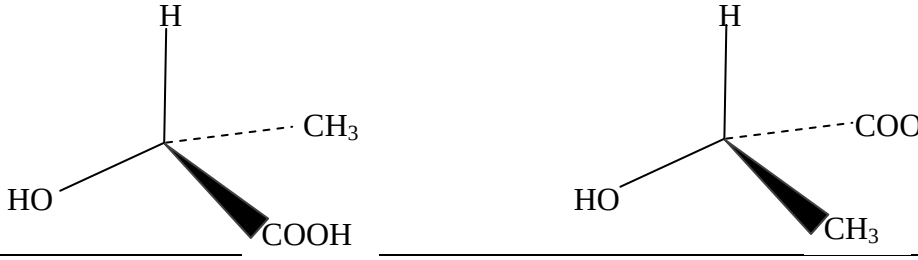
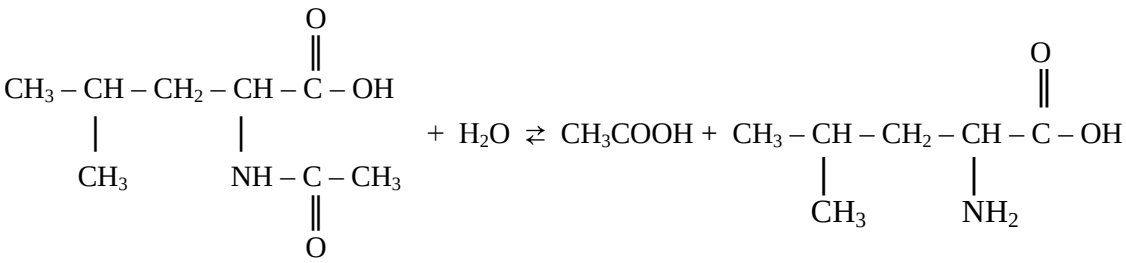
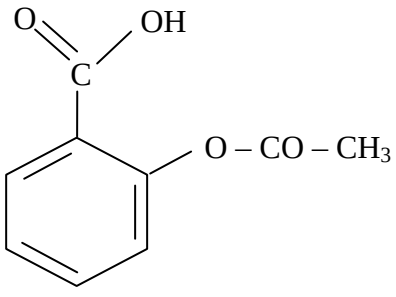
Second Exercise (7 points)
Hydolysis of an Ester

Part of the Q	Answer	Mark
1.1	The equation of the hydrolysis reaction of ethyl ethanoate is: $CH_3 - COO - CH_2 - CH_3 + H_2O \rightleftharpoons CH_3 - COOH + HO - CH_2 - CH_3$	**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, $n_{(HO^-)\text{ versed at equivalence}} = n_{(\text{acid}) \text{ formed}} = n_{(\text{ester}) \text{ reacting}} = Cb \times Vb_E = 0.01 \times Vb_E \times 10^{-3}$. $n_{(\text{ester})t} = n_{(\text{ester})\text{initial}} - n_{(\text{ester})\text{reacting}} = 1.0\times10^{-4} - 1.0\times10^{-5} VbE$	**1.25**
3.1	The missing value: $n(\text{ester})_{90} = (1.0\times 10^{-4} - 1.0\times10^{-5}\times8.6) = 1.4\times10^{-5}$ mol.	**0.5**
3.2	The curve n (ester) = f(t). 	**1**
3.3	The instantaneous rate of disappearance of ester is defined by: $r = -\frac{dn\,(ester)}{dt}$, it is equal to the opposite of the slope of the tangent of the curve: n (ester) = f (t) at the point of the curve of abscissa 40 min. So: $r_{t=40} = -\frac{y_B - y_A}{x_B - x_A} = -\frac{0 - 0.74\times10^{-4}}{82} = 9.0\times10^{-7}$ mol.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	The molar mass of A is: 12n + 2n + 2 + 16 = 14n + 18. The % of mass of oxygen: $\frac{16}{14n+18}\times 100 = 21.62$. The number of carbon atoms n = $\frac{1600-389.16}{302.68} = 4$. The molecular formula of A is $C_4H_{10}O$	**0.75**
1.2	The condensed structural formulas of alcohols isomers of A are : $CH_3 - CH_2 - CH_2 - CH_2OH$; $CH_3 - CH_2 - CHOH - CH_3$; $CH_3 - CH(CH_3) - CH_2OH$ and $CH_3 - COH(CH_3) - CH_3$	**1**
2.1	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.	**1**
2.2.1	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.	**0.75**
2.2.2	The condensed structural formula of the alkene which is the major one is: $CH_3 - CH = CH - CH_3$.	**0.25**
3.1	The equation is: $CH_3 - CH_2 - CHOH - CH_3 + PCl_5 \rightarrow CH_3 - CH_2 - CHCl - CH_3 + POCl_3 + HCl$	**0.5**
3.2	The equation of the inter molecular dehydration reaction is: $2\ CH_3 - CH_2 - CHOH - CH_3 \rightarrow CH_3 - CH_2 - CH(CH_3) - O - CH(CH_3) - CH_2 - CH_3 + H_2O$	**0.5**
3.3	$CH_3 - CH_2 - CHOH - CH_3 \rightarrow CH_3 - CH_2 - CO - CH_3 + H_2$	**0.5**
3.4	$CH_3 - CH_2 - CHOH - CH_3 + CH_3 - CH(CH_3) - COOH \rightleftharpoons CH_3 - CH(CH_3) - COO - CH(CH_3) - CH_2 - CH_3 + H_2O$	**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	 It is the amide group.	0.5
1.4	Lactic acid is a chiral moelcule since it contains an asymmetric carbon atom.	0.5
1.5	The two enantiomers are: 	0.75
2.1	The equation of the hydrolysis reaction is: 	0.75
2.2	CH_3COOH is ethanoic acid and the second compound is 2- amino- 4 – methylpentanoic acid.	0.75
3.1	Formula of (A) is:  formula of (B) is: CH_3COOH	0.75
3.2	The equation of this reaction is : $HO - C_6H_4 - COOH + CH_3OH \rightleftarrows HO - C_6H_4 - C(=O) - O - CH_3 + H_2O$	0.75
3.3	The functional group created is an ester group.	0.5