This Exam Includes Three Exercises. It Is Inscribed On 10 Pages Numbered from 1 to 10.

The Use Of A Non-Programmable Calculator Is Allowed.

Answer The Three Following Exercises:

مسابقة في مادة الكيمياء

المدة: ساعتين

(باللغة الانكليزية)

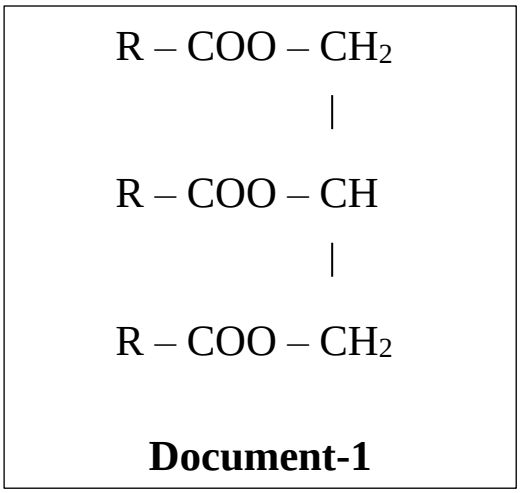
الاسم:.....

الرقم:.....

Exercice 1 (7 points) **From Butter to a Perfumed Compound**

Butyrin or glyceryl tributyrate is a triglyceride found in butter.

The general formula of triglyceride is represented in **document-1.**



Document-1

The aim of this exercise is to study the preparation of an organic compound used in perfumery from butter.

1. Structure of Butyrin

Referring to **document-1**:

1.1. **Show** that the formula of **R** is $\mathbf{C_3H_7}$**,** knowing that the molar mass of butyrin is $\mathbf{M = 302\ g.mol^{-1}}$ and **R** is an alkyl group of formula $\mathbf{C_nH_{2n+1}}$

Given:

Molar Masses in $g.mol^{-1}$: **M(C) = 12** ; **M(H) = 1** ; **M(O) = 16**

1.2. Write the condensed structural formula of butyrin.

2. Synthesis of an Ester (E)

Butyrin can be used to manufacture an ester (**E**), used in perfumery, according to the reactions given in **document-2.**

Reaction 1:

Butyrine + 3 ($Na^+ + HO^-$) ⟶ 3 ($C_3H_7 - COO^- + Na^+$) + **(G) (saponification reaction)**

Reaction 2 :

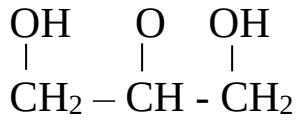
$C_3H_7 - COO^- + H_3O^+ \longrightarrow C_3H_7 - COOH + H_2O$

Reaction 3 :

$C_3H_7 - COOH$ + propan-2-ol ⇄ (E) + H_2O **(Esterification reaction)**

2.1. Referring to **document-2, specify** whether each of the following propositions is true or false.

2.1.1. Knowing that the condensed structural formula of compound (**G**) obtained by **reaction 1** is :



The systematic name of the compound (G) is glycerol.

2.1.2. The ion $C_3H_7 - COO^-$ is amphiphilic.

2.1.3. The sodium butanoate solution ($C_3H_7 - COO^- + Na^+$) is neutral.

2.1.4. The **reaction 2:** $C_3H_7 - COO^- + H_3O^+ \longrightarrow C_3H_7 - COOH + H_2O$ is an acid-base reaction.

2.2. – Write, using condensed structural formulas, the equation of the

reaction 3: C_3H_7 – COOH + 2-propanol ⇄ (E) + H_2O (Esterification)

- Give the systematic name of the ester **(E).**

2.3. Show that the molecule of compound (**E**) is achiral molecule.

3. Study of the Reaction 3

Starting from an equimolar mixture of **C_3H_7 – COOH** and **2-propanol**, the yield of the esterification reaction **(reaction 3)** is **60 %**.

3.1. Propose a way to increase the yield of this reaction starting from the same reactants.

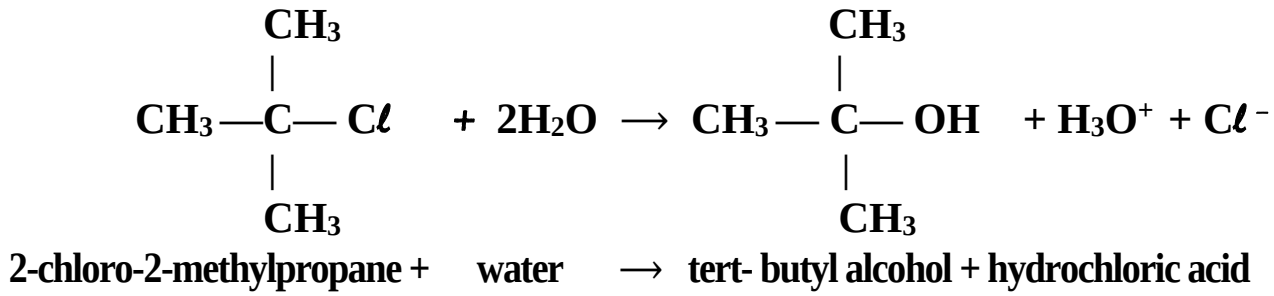
3.2. This reaction becomes complete when the reactant **C_3H_7 – COOH** is replaced by its chlorinated derivative:

- **Give** the systematic name of this chlorinated derivative.
- **Write**, using condensed structural formulas, the equation of the reaction of the preparation of the ester (**E**).

Exercice 2 (6 points) Kinetics of the Hydrolysis of t-Butyl Chloride

2-chloro-2-methylpropane, commonly known as t-butyl chloride, is a colorless organic compound belonging to the series of halogenoalkanes.

When **tert-butyl chloride is dissolved** in water-acetone mixture, it **reacts with water <u>to form tert- butyl alcohol and hydrochloric acid</u>** in a slow and complete reaction that took place according to the equation shown below:



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

1. Preliminary Study

1.1. Give <u>the systematic name of tert-butyl alcohol</u>.

1.2. Show that its class is <u>tertiary</u>.

1.3. What is observed when an excess of an orange acidified potassium dichromate solution is poured into a test tube containing tert-butyl alcohol? **Justify**.

2. Kinetic Study

At the instant of time **t = 0**, a volume **V= 1.0 mL** of t-butyl chloride is introduced into a flask containing water-acetone mixture, maintained at constant temperature **T**. The final volume of the reacting mixture is $\mathbf{V_1 = 100.0\ mL}$. (Water is in large excess).

Using an appropriate method, the concentrations of hydronium ions are determined at different instants and the concentrations of tert-butyl chloride (noted **[RCℓ]**) are deduced at these instants.

The results are grouped in the table of **document-1**.

t (min)	0	15	30	45	60	75	90
[RCℓ](10^{-2}mol.L^{-1})	9.2	6.6	5.2	4.1	3.2	2.5	2.1

Document-1

Given:

- Molar mass of tert-butyl chloride: $\mathbf{M = 92.5\ g.mol^{-1}}$
- Density of tert-butyl chloride: $\mathbf{d= 0.85\ g.mL^{-1}}$

2.1. Verify that the initial concentration of tert-butyl chloride is:

$\mathbf{[RC\ell\ ]_o = 9.2\times10^{-2}\ mol.L^{-1}.}$

2.2. Show that the concentration of hydronium ions, $\mathbf{[H_3O^+]_t}$, formed at the instant of time **t** and the concentration of tert-butyl chloride, $\mathbf{[RC\ell\ ]_t}$, at the same instant **t** are related according to the following relation:

$$\mathbf{[H_3O^+]_t = 9.2\times10^{-2} - [RC\ell\ ]_t}$$

2.3. Plot the curve representing the change of the concentration of tert-butyl chloride as a function of time: **[RCℓ]= f (t)**, in the interval of time:

[0 – 90 min].

Take the following scales:

In abscissa: 1 cm for 15 min

In ordinate: 1 cm for 1.0×10^{-2} mol.L^{-1}

2.4. For each of the two following propositions, **indicate** the correct and the false one. **Correct** the false proposition:

2.4.1. The half-life time of this reaction is **t ½ = 38 min.**

2.4.2. As the concentration of the tert-butyl alcohol increases with time, the rate of its formation increases.

2.5. The same experiment is repeated but with only one modification: the reacting mixture is maintained at a temperature **T ′ > T**.

Trace on the same graph of the **part 2.3**, the shape of the curve **[RCℓ] = g(t)** in the interval of time: **[0 – 90 min].**

Exercice 3 (7 points) **Acid-Base Reactions**

The labels of three available flasks show the indications given in **document -1.**

Flask (1)	Flask (2)	Flask (3)
Benzoic acid crystals $M(C_6H_5COOH) = 122\ g.mol^{-1}$	- Ethylamine aqueous solution - percentage by mass = 33% - Density = $0.914\ g.mL^{-1}$ - $M(C_2H_5NH_2) = 45 g.mol^{-1}$	Hydrochloric acid solution $(H_3O^+ + C\ell^-)$ $C_a = 5\times10^{-2}\ mol.L^{-1}$

Document -1

Given:

The study is carried out at 25°C.

Ethylamine is a weak base.

pKa of Acid/Base pairs:

pKa ($C_6H_5COOH/C_6H_5COO^-$) = 4.2

pKa ($C_2H_5NH_3^+/C_2H_5NH_2$)= 10.8

pKa(H_2O/HO^-) = 14

The aim of this exercise is to prepare acidic and basic solutions of same concentration **C** and to study some acid – base reactions.

1. Preparation of Benzoic Acid Solution (S_1)

- A mass **m** of benzoic acid crystals is introduced into a volumetric flask of **250 mL**.
- Enough distilled water is added to dissolve the solid
- Distilled water is added to reach the line mark.
- A solution (**S_1**) of benzoic acid of concentration **$C = 2\times10^{-2}\ mol.L^{-1}$** is obtained.

1.1. Calculate the mass **m**.

1.2. Write the equation of the reaction of benzoic acid **C_6H_5COOH** with water.

2. Preparation of an Aqueous Ethylamine Solution (S_2)

It is required to prepare **1.0 L** of an ethylamine solution (**S2**) of concentration **C = 2×10^{-2} mol.L^{-1}** starting from the solution of the flask (2).

2.1. – Calculate the molar concentration of the ethylamine solution contained in flask (2)

- **Show that** the volume that should be withdrawn from the flask (2) to realize this preparation is **V= 3 mL.**

2.2. Choose, from the sets of **document-2**, the most convenient one to realize the above preparation.

Set 1	Set 2	Set 3
Volumetric pipet 5 mL	Graduated pipet 5 mL	Graduated cylinder 5mL
Volumetric flask 1000mL	Volumetric flask 1000mL	Erlenmeyer flask 1000 mL
Beaker 50 mL	Beaker 50 mL	Beaker 50 mL

Document-2

2.3. Verify that the pH of the solution (S_2) is between **7** and **12.3**:

7 < pH < 12.3

3. pH-metric Study

A hydrochloric acid solution $H_3O^+ + C\ell^-$ of concentration $C_a = 5\times10^{-2}\ mol.L^{-1}$ is added progressively into a beaker containing a volume **Vb = 20.0 mL** of the ethylamine solution (**S_2**) $C_2H_5NH_2$ of concentration **C**.

The equation of the complete reaction that took place is:

$$C_2H_5NH_2 + H_3O^+ \rightarrow C_2H_5NH_3^+ + H_2O$$

3.1. Justify the following statements:

3.1.1. The volume of the acid solution added to reach the equivalence point is **8 mL**.

3.1.2. The pH at equivalence, based on the chemical species present at equivalence, is $pH_E < 7$

3.1.3. The coordinates of the half equivalence point are **(Va = 4 mL; pH = 10.8).**

4. Acid-Base Mixture

A volume a volume $V_1 = 72$ **mL** of the benzoic acid solution C_6H_5COOH (S_1) is mixed with a volume $V_2 = 28$ **mL** of the above ethylamine solution $C_2H_5NH_2$ **(S_2)**

4.1. Complete the equation of the reaction that occurs:

$$C_6H_5COOH + C_2H_5NH_2 \rightarrow \text{----------} + \text{----------}$$

4.2. Verify that the value of the ratio $\frac{[C_6H_5COO^-]}{[C_6H_5COOH]}$ in the obtained solution is **0.63** knowing that the ethylamine is the limiting reacting.

4.3. Given the three following values of pH :

a. pH < 3.2 ; **b.** pH = 4 ; **c.** pH > 5.2

Referring to the answer in part 4.2, **deduce** the **pH** that corresponds to the obtained solution. **Justify** without calculation.