

الاسم: _____
الرقم: _____

مسابقة في مادة الكيمياء
المدة: ساعتان

**This Exam Includes Three Exercises. It Is Inscribed on 4 Pages Numbered From 1 to 4 .
The Use Of Non- Programmable Calculator Is Allowed.
Answer The Following Three Exercises:**

Exercise 1: (6 points)

Caustic Soda “ NaOH ”

In the laboratory, caustic soda is found as pellets. Sodium hydroxide NaOH or caustic soda is a strong base that is highly soluble in water. A flask contains pellets of NaOH without any indication about their purity.

The aim of this exercise is to determine the degree of purity of sodium hydroxide in the pellets of caustic soda and to study the reaction between this base and a weak acid.

Given: Molar mass of NaOH: $M_{(NaOH)} = 40 \text{ g.mol}^{-1}$.

1. Preparation of Sodium Hydroxide Solution (S)

A volume $V=1 \text{ L}$ of the solution (S) is prepared by dissolving a mass $m = 1.20 \text{ g}$ of sodium hydroxide pellets in distilled water.

List the essential material needed to prepare the solution (S).

2. pH-metric Titration of The Sodium Hydroxide Solution (S)

A volume $V_b = 20.0 \text{ mL}$ of the solution (S) of concentration C_b is poured into a beaker and distilled water is added to immerse properly the pH-meter electrode .

A pH-metric titration is carried out by adding gradually a hydrochloric acid solution ($\text{H}_3\text{O}^+ + \text{Cl}^-$) of concentration $C_a = 0.05 \text{ mol.L}^{-1}$ into the beaker . The volume of the acid solution added to reach equivalence is $V_{aE} = 11.2 \text{ mL}$.

2.1. Write the equation of the titration reaction.

2.2. Show that the concentration of the sodium hydroxide solution (S) is $C_b = 0.028 \text{ mol.L}^{-1}$.

2.3. Deduce the degree of purity (percentage by mass) of NaOH in these pellets.

2.4. Justify each of the following propositions:

2.4.1. The addition of distilled water into the beaker before titration does not affect V_{aE} .

2.4.2. The bromothymol blue (Yellow 6 – 7.6 Blue) is one of the appropriate colored indicators to carry out this titration.

3. Reaction of Sodium Hydroxide with Benzoic Acid

Given: $\text{pK}_a (\text{C}_6\text{H}_5\text{COOH} / \text{C}_6\text{H}_5\text{COO}^-) = 4.2$; $\text{pK}_a (\text{H}_2\text{O} / \text{HO}^-) = 14$

A volume $V_1 = 20$ mL of the sodium hydroxide solution (S) of concentration C_b is added to a beaker containing a volume $V_2 = 30$ mL of benzoic acid solution (C_6H_5COOH) of concentration $C_2 = 0.04 \text{ mol.L}^{-1}$

- 3.1. Write the equation of the reaction taking place between benzoic acid and hydroxide ions HO^- .
- 3.2. Calculate the constant K_R of this reaction .Deduce that it is complete.
- 3.3. Determine the limiting reactant.
- 3.4. Find the pH of the obtained solution.

Exercise 2: (7 points)

Isoamyl Acetate

Isoamyl acetate is an ester used in the chemical industry as food aroma.

In the laboratory, it can be prepared according to the reaction of the following word equation:

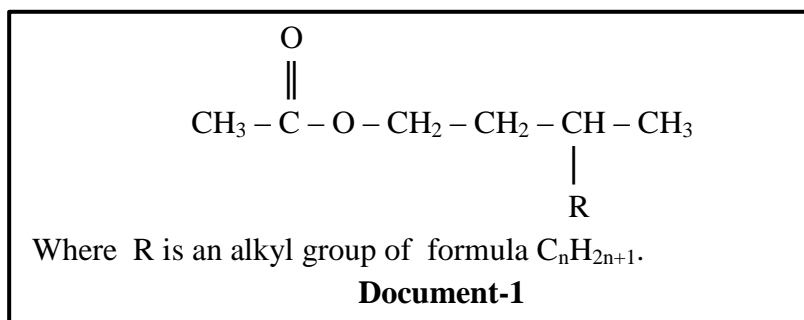


The aim of this exercise is to identify this ester and to realize its synthesis.

1. Determination of the Structural Formula of Isoamyl Acetate

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

The structural formula of isoamyl acetate, denoted (E) ,is given in **Document-1** :



The elemental analysis of isoamyl acetate shows that its percentage by mass of oxygen is 24.61 %

- 1.1. Show that the molar mass of the ester (E) is 130 g.mol^{-1} .
- 1.2. Verify that R is a methyl group of formula CH_3 .
- 1.3. Give the systematic name of the ester (E).
- 1.4. The isoamylic alcohol (B) can be prepared from the organic compound (C).

The chemical tests in **document-2** are carried out:

N° of test	Reactants	Result
Test 1	Compound (C) + 2,4-D.N.P.H	Positive test
Test 2	Compound (C) + Fehling reagent	Positive test

Document-2

- 1.4.1. Indicate what do you observe in the two tests (1) and (2) .
- 1.4.2. Deduce , from the result of each test ,the family of the compound (C) .
- 1.4.3. Write , using the condensed structural formulas, the equation of the reaction of preparation of the alcohol (B) starting from the compound (C) .

2. Synthesis of Isoamyl Acetate

Given:

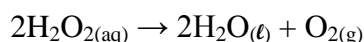
- Density of ethanoic acid: $d_{\text{(ethanoic acid)}} = 1.05 \text{ g.mL}^{-1}$.
- Molar mass of ethanoic acid: $M_{\text{(ethanoic acid)}} = 60 \text{ g.mol}^{-1}$.

A mixture of a volume $V_1 = 30 \text{ mL}$ of ethanoic acid (A) and 0.18 mol of isoamylic alcohol is heated to reflux in the presence of few drops of concentrated sulfuric acid .At an instant t , the number of moles of ester (E) obtained is $n_{\text{(ester)}} = 0.14 \text{ mol}$.

- 2.1. Show that the initial number of moles of ethanoic acid is equal to 0.52 mol .
- 2.2. Determine the yield of this synthesis reaction at the instant of time t .
- 2.3. Isoamyl acetate can be obtained by replacing ethanoic acid by an acid derivative (D).
This compound (D) can be obtained by dehydration reaction of ethanoic acid in the presence of P_2O_5 .
 - 2.3.1. Give the condensed structural formula of the compound (D). Name it.
 - 2.3.2. Write , using the condensed structural formulas , the equation of the esterification reaction between the compound (D) and the alcohol (B) .
 - 2.3.3. List two characteristics of this reaction.

Exercise 3: (7 points) Kinetic Study of The Decomposition of Hydrogen Peroxide

The decomposition of hydrogen peroxide H_2O_2 is a slow reaction and it is represented by the following equation:



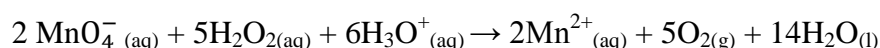
The aim of this exercise is to determine the concentration of a hydrogen peroxide H_2O_2 solution (S) and to study the kinetic of its decomposition reaction .

Given : $V_m = 24 \text{ L.mol}^{-1}$.

1. Determination of The Concentration of The Solution (S) of H_2O_2

A volume $V = 10.0 \text{ mL}$ of this solution (S) is titrated by an acidified potassium permanganate solution ($\text{K}^+ + \text{MnO}_4^-$) of concentration $C_1 = 2.0 \times 10^{-2} \text{ mol.L}^{-1}$. The volume of potassium permanganate solution added to reach the equivalence is $V_E = 14.6 \text{ mL}$.

The equation of the titration reaction is the following:



- 1.1. Indicate the most precise glassware used to withdraw the volume V :
 - a. 20 mL volumetric pipet
 - b. 10 mL volumetric pipet
 - c. 20 mL graduated pipet

1.2. Choose, from the list of **document-1**, the material needed to carry out the titration .

Graduated buret : 25 mL	magnetic stirrer and its bar
Volumetric flask : 100 mL	beaker : 100 mL pH-meter
Document-1	

1.3. Knowing that the permanganate ion MnO_4^- of violet color is the only colored species, indicate how the equivalence point is recognized.

1.4. Show that, the initial concentration of H_2O_2 is: $[\text{H}_2\text{O}_2]_0 = 7.3 \times 10^{-2} \text{ mol.L}^{-1}$.

2. Kinetic Study of The Decomposition Reaction of H_2O_2

The decomposition of hydrogen peroxide H_2O_2 is accelerated by using Fe^{3+} ions which are present in a solution of iron (III) chloride ($\text{Fe}^{3+} + 3 \text{Cl}^-$).

Into 250 mL beaker, 100.0 mL of the solution of the hydrogen peroxide solution (S) are introduced. At instant $t = 0$, few drops of a concentrated iron (III) chloride solution are added without a noticeable change in the volume. At different instants of time t , take 10.0 mL from the reacting mixture and introduce it into a beaker containing ice- water. The hydrogen peroxide is titrated by a solution of potassium permanganate .The results are grouped in the table of **document-2**:

t(min)	0	5	10	20	30	40
$[\text{H}_2\text{O}_2] (10^{-2} \text{ mol.L}^{-1})$	7.3	5.4	4.2	2.3	1.2	0.7
Document-2						

2.1. Plot, referring to **document-2**, the curve representing the variation of the concentration of H_2O_2 versus time ; $[\text{H}_2\text{O}_2] = f(t)$ within the interval of time $[0 - 40 \text{ min}]$.

Take the following scales: 1 cm for 5 min in abscissa.

1 cm for $1 \times 10^{-2} \text{ mol.L}^{-1}$ in ordinates.

2.2. The rate of disappearance of H_2O_2 is determined at two different instants of time. Match each rate to its convenient time.

a. $t = 0$ i. $r = 8 \times 10^{-5} \text{ mol.L}^{-1}.\text{min}^{-1}$

b. $t = 30 \text{ min}$ ii. $r = 6 \times 10^{-3} \text{ mol.L}^{-1}.\text{min}^{-1}$

2.3. Indicate the kinetic factor responsible for the evolution of the rate of disappearance of H_2O_2 with time.

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

2.5. The kinetic study of the decomposition reaction of H_2O_2 of the same solution (S) is carried out by measuring, using an appropriate method, the volume of the oxygen gas O_2 liberated with time.

2.5.1. Show that, at each instant of time t , the concentration of hydrogen peroxide, $[\text{H}_2\text{O}_2]_t$ expressed in mol.L^{-1} , and the volume of oxygen gas, $V(\text{O}_2)_t$ in mL, liberated, are related by the following relation:

$$[\text{H}_2\text{O}_2]_t = 7.3 \times 10^{-2} - \frac{V(\text{O}_2)_t}{1200}$$

2.5.2. At a given instant of time the volume of oxygen gas O_2 liberated is 87.6 mL. Specify whether this instant of time t represents the end of the reaction.