

This Exam Includes Three Exercises. It Is Inscribed on 8 Pages Numbered From 1 to 8 . The Use Of Non- Programmable Calculator Is Allowed.
Answer The Following Three Exercises:

## مسابقة في مـادة الكيمياء

المدة: ساعتان
(باللغة الإنكليزية)
$\qquad$
الرق:

## 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 $\mathrm{NaOH}: \mathrm{M}_{(\mathrm{NaOH})}=40 \mathrm{~g} \cdot \mathrm{~mol}^{-1}$.

## 1. Preparation of Sodium Hydroxide Solution (S)

A volume $\mathrm{V}=1 \mathrm{~L}$ of the solution $(\mathrm{S})$ is prepared by dissolving a mass $\mathrm{m}=$ 1.20 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 $V_{b}=20.0 \mathrm{~mL}$ of the solution $(\mathrm{S})$ of concentration $\mathrm{C}_{\mathrm{b}}$ 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 $\left(\mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{Cl}^{-}\right)$of concentration $\mathrm{C}_{\mathrm{a}}=0.05 \mathrm{~mol} . \mathrm{L}^{-1}$ into the beaker . The volume of the acid solution added to reach equivalence is $\mathrm{V}_{\mathrm{aE}}=11.2$ mL .
2.1.Write the equation of the titration reaction.
2.2. Show that the concentration of the sodium hydroxide solution $(S)$ is $\mathrm{C}_{\mathrm{b}}=0.028 \mathrm{~mol} . \mathrm{L}^{-1}$.
2.3. Knowing that the percentage by mass of NaOH is calculated as : Percentage by mass $=\frac{m_{\mathrm{NaOH}}}{m_{\text {pellets }}} \times 100$

- Find $\mathrm{m}(\mathrm{NaOH})$ in 1 L of solution.
- Calculate the percentage.
2.4. Each of the following propositions is correct. Justify :
2.4.1. The addition of distilled water into the beaker before titration does not affect $\mathrm{V}_{\mathrm{aE}}$.
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: $\mathrm{pK}_{\mathrm{a}}\left(\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COOH} / \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COO}^{-}\right)=4.2 \quad ; \mathrm{pK}_{\mathrm{a}}\left(\mathrm{H}_{2} \mathrm{O} / \mathrm{HO}^{-}\right)=14$
A volume $V_{1}=20 \mathrm{~mL}$ of the sodium hydroxide solution $(\mathrm{S})$ of concentration $\mathrm{C}_{\mathrm{b}}=0.028 \mathrm{~mol} . \mathrm{L}^{-1}$ is added to a beaker containing a volume $\mathrm{V}_{2}=30 \mathrm{~mL}$ of benzoic acid solution $\left(\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COOH}\right)$ of concentration $\mathrm{C}_{2}=0.04 \mathrm{~mol} . \mathrm{L}^{-1}$.
3.1. Complete the equation of the reaction taking place between benzoic acid and hydroxide ions $\mathrm{HO}^{-}$:

$$
\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COOH}+\mathrm{HO}^{-} \rightleftarrows
$$

3.2. - Give the expression of the constant $K_{\underline{R}}$ of this reaction.

- Calculate its value as a function of the given $\mathrm{pK}_{\mathrm{a}}\left(\mathrm{H}_{2} \mathrm{O} / \mathrm{HO}^{-}\right)$
- Deduce that it is complete.
3.3. - Calculate the number of moles of $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COOH}$ and of $\mathrm{HO}^{-}$
- Determine the limiting reactant.
3.4. Knowing that the pH of the obtained solution is calculated by: $\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}\left(\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COOH} / \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COO}^{-}\right)+\log \frac{\mathrm{n}_{\left(\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COO}^{-}\right) \text {formed }}}{\mathrm{n}_{\left(\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COOH}\right) \text { remained }}}$
- Calculate $\mathrm{n}_{\left(\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COO}^{-}\right) \text {formed }}$
- Deduce the value of the pH of the 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:
Ethanoic acid + isoamylic alcohol $\rightleftharpoons \quad$ Isoamyl acetate + water (A)
(B)
(E)

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. $\mathrm{mol}^{-1}: \mathrm{M}(\mathrm{H})=1 ; \mathrm{M}(\mathrm{C})=12 ; \mathrm{M}(\mathrm{O})=16$.
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 $130 \mathrm{~g} . \mathrm{mol}^{-1}$.
1.2.Verify that R is a methyl group of formula $\mathrm{CH}_{3}$.
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:

| $\mathrm{N}^{\mathrm{o}}$ of test | Reactants | Result |
| :--- | :--- | :---: |
| Test 1 | Compound (C) +2,4-D.N.P.H | Positve test |
| Test 2 | Compound (C) + Fehling reagent | Positve test |
|  | Document-2 |  |

1.4.1. Indicate what do you observe in the two tests (1) and (2).
1.4.2. What information can be drawn out :

- the positive result of test 1 .
- the positive result of test 2 .
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)
( formula of alcohol (B) : $\mathrm{CH}_{3}-\mathrm{CH}-\mathrm{CH}_{2}-\mathrm{CH}_{2}-\mathrm{OH}$ ).

$\mathrm{CH}_{3}$


## 2. Synthesis of Isoamyl Acetate

## Given:

- Density of ethanoic acid: $\mathrm{d}_{\text {(ethanoic acid) }}=1.05 \mathrm{~g} \cdot \mathrm{~mL}^{-1}$.
- Molar mass of ethanoic acid: $\mathrm{M}_{\text {(ethanoic acid) }}=60 \mathrm{~g} \cdot \mathrm{moL}^{-1}$.

A mixture of a volume $\mathrm{V}_{1}=30 \mathrm{~mL}$ 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 $\mathrm{n}_{\text {(ester) }}=0.14 \mathrm{~mol}$.
2.1. - Calculate the initial mass of ethanoic acid.

- Show that the initial number of moles of ethanoic acid is equal to 0.52 mol .
2.2. - Identify the limiting reactant.
- Calculate the maximum number of moles of ester obtained assuming that the reaction is complete.
- 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 $\mathrm{P}_{2} \mathrm{O}_{5}$.
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 $\mathrm{H}_{2} \mathrm{O}_{2}$ is a slow reaction and it is represented by the following equation:
$2 \mathrm{H}_{2} \mathrm{O}_{2(\mathrm{qq})} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}_{(\ell)}+\mathrm{O}_{2(\mathrm{~g})}$
The aim of this exercise is to determine the concentration of a hydrogen peroxide $\mathrm{H}_{2} \mathrm{O}_{2}$ solution ( S ) and to study the kinetic of its decomposition reaction.

Given : $\mathrm{V}_{\mathrm{m}}=24 \mathrm{~L}_{\mathrm{L}} . \mathrm{mol}^{-1}$.

## 1. Determination of The Concentration of The Solution (S) of $\mathbf{H}_{\mathbf{2}} \mathbf{O}_{\mathbf{2}}$

A volume $\mathrm{V}=10.0 \mathrm{~mL}$ of this solution $(\mathrm{S})$ is titrated by an acidified potassium permanganate solution $\left(\mathrm{K}^{+}+\mathrm{MnO}_{4}^{-}\right)$of concentration $\mathrm{C}_{1}=2.0 \times 10^{-2} \mathrm{~mol} . \mathrm{L}^{-1}$. The volume of potassium permanganate solution added to reach the equivalence is $V_{E}=14.6 \mathrm{~mL}$.

The equation of the titration reaction is the following:
$2 \mathrm{MnO}_{4}^{-}{ }_{(\mathrm{aq})}^{-}+5 \mathrm{H}_{2} \mathrm{O}_{2(\mathrm{aq})}+6 \mathrm{H}_{3} \mathrm{O}_{(\mathrm{aq})}^{+} \rightarrow 2 \mathrm{Mn}^{2+}{ }_{(\text {aq) }}+5 \mathrm{O}_{2(\mathrm{~g})}+14 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}$
1.1. Indicate the most precise glassware used to withdraw the volume V :
a. 20 mL volumetric pipet b. 10 mL volumetric pipet $\quad$ 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 : $100 \mathrm{~mL} \quad \mathrm{pH}$-meter

## Document-1

1.3. Knowing that the permanganate ion $\mathrm{MnO}_{4}^{-}$of violet color is the only colored species, indicate how the equivalence point is recognized.
1.4. Show that, the initial concentration of $\mathrm{H}_{2} \mathrm{O}_{2}$ is: $\left[\mathrm{H}_{2} \mathrm{O}_{2}\right]_{0}=7.3 \times 10^{-2} \mathrm{~mol} . \mathrm{L}^{-1}$.

## 2. Kinetic Study of The Decomposition Reaction of $\mathbf{H}_{\mathbf{2}} \mathrm{O}_{\mathbf{2}}$

100.0 mL of the solution of the hydrogen peroxide solution (S) are decomposed in the presence of few drops of $\mathrm{Fe}^{3+}$ ions (catalyst). The hydrogen peroxide is titrated by a solution of potassium permanganate .The appropriate kinetic study leads to the results grouped in the table of document-2:

| Document-2 |  |  |  |  |  |  |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{t}(\mathrm{min})$ | 0 | 5 | 10 | 20 | 30 | 40 |
| $\left[\mathrm{H}_{2} \mathrm{O}_{2}\right]\left(10^{-2} \mathrm{~mol} . \mathrm{L}^{-1}\right)$ | 7.3 | 5.4 | 4.2 | 2.3 | 1.2 | 0.7 |
|  |  |  |  |  |  |  |
|  |  |  |  |  |  |  |

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

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

Plot, referring to document-2, the curve representing the variation of the concentration of $\mathrm{H}_{2} \mathrm{O}_{2}$ versus time; $\left[\mathrm{H}_{2} \mathrm{O}_{2}\right]=\mathrm{f}(\mathrm{t})$ within the interval of time [0-40 min].
2.2. The rate of disappearance of $\mathrm{H}_{2} \mathrm{O}_{2}$ is determined at two different instants of time. Match each rate to its convenient time.
a. $\mathrm{t}=0$
i. $\mathrm{r}=8 \times 10^{-5} \mathrm{~mol} . \mathrm{L}^{-1} \cdot \mathrm{~min}^{-1}$
b. $\mathrm{t}=30 \mathrm{~min}$
ii. $\mathrm{r}=6 \times 10^{-3} \mathrm{~mol} . \mathrm{L}^{-1} \cdot \mathrm{~min}^{-1}$
2.3. Indicate the kinetic factor responsible for the evolution of the rate of disappearance of $\mathrm{H}_{2} \mathrm{O}_{2}$ with time.

## 2.4. - Define the half-life time of the reaction $t^{1 / 2}$.

- Determine graphically this time.
2.5. The kinetic study of the decomposition reaction of $\mathrm{H}_{2} \mathrm{O}_{2}$ of the same solution $(\mathrm{S})$ is carried out by measuring, using an appropriate method, the volume of the oxygen gas $\mathrm{O}_{2}$ liberated with time.
2.5.1. - Write the relation between $n\left(\mathrm{H}_{2} \mathrm{O}_{2}\right)_{\text {reacted }}$ and $\mathrm{n}\left(\mathrm{O}_{2}\right)_{\text {formed }}$.
- Knowing that $\mathrm{n}_{\left(\mathrm{O}_{2}\right) \text { formed }}=\frac{\mathrm{v}_{\left(\mathrm{O}_{2}\right) \mathrm{t}}}{\mathrm{v}_{\mathrm{m}}}$, show that, at each instant of time $t$, the concentration of hydrogen peroxide, $\left[\mathrm{H}_{2} \mathrm{O}_{2}\right]_{t}$ expressed in mol. $\mathrm{L}^{-1}$, and the volume of oxygen gas, $\mathrm{V}\left(\mathrm{O}_{2}\right)_{\mathrm{t}}$ in mL , liberated, are related by the following relation:

$$
\left[\mathrm{H}_{2} \mathrm{O}_{2}\right]_{\mathrm{t}}=7.3 \times 10^{-2}-\frac{\mathrm{V}_{\left(\mathrm{o}_{2}\right) \mathrm{t}}}{1200}
$$

2.5.2. At a given instant of time the volume of oxygen gas $\mathrm{O}_{2}$ liberated is 87.6 mL .

Specify whether this instant of time $t$ represents the end of the reaction.

