This Exam Includes Three Exercises. It Is Inscribed On Ten Pages Numbered From 1 to 10. The Use of a Non-programmable Calculator Is Allowed.

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الرقم:

## Exercise 1 (7 points)

## Synthesis of an Organic Compound

The organic compound (E) of raspberry odor is used in food industry. The condensed structural formula of this compound is represented in document-1.


## 1. Study of the Structure of The Compound (E)

1.1. Name the functional group of this compound.
1.2. Give the systematic name of (E).

## 2. Preparation of the compound (E)

The compound (E) can be obtained from the reaction of a carboxylic acid (A) and an alcohol (B).
2.1.Identify the carboxylic acid (A) and the alcohol (B).
2.2.Indicate the class of the alcohol (B).
2.3. Write, using condensed structural formulas, the equation of the preparation reaction of the compound (E) starting from the compounds (A) and (B).
2.4.At the instant of time $t=0$, a quantity of 0.5 mol of $(\mathrm{A})$ is mixed with 0.5 mol (B), then few drops of concentrated sulfuric acid are added and the mixture is heated to reflux at constant temperature $\mathbf{T}$.

The curve of the document- 2 represents the evolution of the number of moles of the compound (E) formed as a function of time.

2.4.1. Determine the theoretical number of moles of the organic compound (E) formed at the end of the reaction.
2.4.2. Referring to the document-2, justify each of the following propositions:

Proposition 1: The reaction of preparation of the compound (E) is slow.
Proposition 2: The reaction of preparation of the compound (E) is limited.
2.4.3. Calculate the yield of this reaction at equilibrium.
$r=\frac{n(E) \text { experimental }}{n(E) \text { theoretical }} \times 100$

In order to increase the yield of this reaction, the two experiments of doc. $\mathbf{3}$ are suggested:

|  | Carboxylic acid <br> $(\mathbf{A})$ | Alcohol <br> $(\mathbf{B})$ | Sulfuric <br> acid | Temperature |
| :---: | :---: | :---: | :---: | :---: |
| Experiment <br> $\mathbf{1}$ | 0.5 mol | 0.5 mol | Few drops | $\mathbf{T}_{\mathbf{1}}>\mathbf{T}$ |
| Experiment <br> $\mathbf{2}$ | 0.5 mol | $\mathbf{2 . 5} \mathbf{~ m o l}$ | Few drops | T |
| Document-3 |  |  |  |  |

2.5. Specify whether the yield increases in each experiment of document-3.
2.6. The yield can be increased by using a chlorinated acid derivative (D) instead of the carboxylic acid (A).
2.6.1. Write the condensed structural formula of the compound (D).
2.6.2. Name the compound (D).

Vinegar is an aqueous ethanoic acid solution.
The aim of this exercise is to determine the degree of acidity of a white commercial vinegar.

- The condensed structural formula of ethanoic acid is $\mathbf{C H}_{\mathbf{3}} \mathbf{C O O H}$.

Document-1

## Given:

- Density of vinegar: $\mathrm{d}=1.020 \mathrm{~g} . \mathrm{mL}^{-1}$.
- The molar mass of ethanoic acid is: $\mathrm{M}=60 \mathrm{~g} \cdot \mathrm{~mol}^{-1}$.
- The study is carried out at $25^{\circ} \mathrm{C}$.


## 1. Preparation of a Diluted Solution (S) of Vinegar

A commercial white vinegar solution ( $\mathrm{S}_{0}$ ) is diluted 100 times. A solution ( S ) is obtained.
a) Choose from doc. 2 the most convenient set in order to prepare the solution (S).
b) Justify your answer.

| Set 1 | Set 2 |
| :--- | :--- |
| - Volumetric flask of 250 mL | • Volumetric flask of 250 mL |
| - Graduated pipet of 5 mL | - Graduated cylinder of 5 mL |
| - Beaker of 50 mL | - Beaker of 50 mL |

## Document-2

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

A volume $\mathbf{V}_{\mathbf{a}}=\mathbf{2 0 . 0} \mathbf{~ m L}$ of the solution ( S ) is introduced into a beaker then distilled water is added in order to immerse properly the pH -meter electrode. A pH -metric titration is realized by adding progressively into the beaker a sodium hydroxide solution $\left(\mathrm{Na}^{+}+\mathrm{HO}^{-}\right)$of molar concentration
$\mathrm{C}_{\mathrm{b}}=2.0 \times 10^{-2} \mathrm{~mol} . \mathrm{L}^{-1}$.

The results are grouped in the table of document-3.

| $\mathrm{V}_{\mathrm{b}}$ <br> $(\mathrm{mL})$ | 0 | 2 | 4 | 6 | 8 | 9 | 10 | 11 | 12 | 14 |  |  |  |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :---: | :---: | :---: |
| pH | 3.5 | 4.3 | 4.7 | 5.0 | 5.5 | 5.8 | 8.2 | 10.8 | 11.0 | 11.2 |  |  |  |
| Document-3 |  |  |  |  |  |  |  |  |  |  |  |  |  |

2.1. Plot the curve that represents the variation of the pH of the solution as a function of the volume of the base added: $\mathbf{p H}=\mathbf{f}\left(\mathbf{V}_{\mathbf{b}}\right)$.

Take the following scales:

## In abscissa: $\mathbf{1 ~ c m ~} \rightarrow \mathbf{1 m L}$; in ordinates: $\mathbf{1 ~ c m ~} \rightarrow \mathbf{1} \mathbf{~ p H}$ unit.

2.2.Referring to the curve $\mathbf{p H}=\mathbf{f}\left(\mathbf{V}_{\mathbf{b}}\right)$ :
2.2.1. Determine the coordinates of the equivalence point.
2.2.2. Give two reasons that verify that ethanoic acid is a weak acid.
2.3. Write the equation of the titration reaction between the ethanoic acid $\mathbf{C H}_{3} \mathbf{C O O H}$ and sodium hydroxide $\left(\mathbf{N a}^{+}+\mathbf{H O}^{-}\right)$.
2.4.Show that the molar concentration of ethanoic acid in solution (S):

$$
\mathrm{C}=1 \times 10^{-2} \mathrm{~mol} \cdot \mathrm{~L}^{-1}
$$

2.5.

The degree of acidity of vinegar corresponds to the mass (in $g$ ) of ethanoic acid in 100 g of vinegar.

## Document - 2

a) Deduce the molar concentration of the commercial solution $S_{0}$ of white vinegar.
b) Deduce, referring to document-2, the degree of acidity of the commercial white vinegar solution $\mathrm{S}_{0}$.
2.6. Methyl orange is an acid - base indicator with a pH change range: red - 3.1-4.4- yellow Justify that methyl orange is not the appropriate indicator for this titration.

## 3. Reaction of Vinegar with Sodium Hydrogen Carbonate

## Given:

- $\mathrm{pKa}\left(\mathrm{CO}_{2}, \mathrm{H}_{2} \mathrm{O} / \mathrm{HCO}_{3}^{-}\right)=6.4 ; \mathrm{pKa}\left(\mathrm{CH}_{3} \mathrm{COOH} / \mathrm{CH}_{3} \mathrm{COO}^{-}\right)=4.8$
- $\mathrm{CO}_{2}$ is a gas slightly soluble in water.

A volume of white vinegar is introduced into a flask containing sodium hydrogen carbonate.

A limited reaction takes place according to the following equation:

$$
\mathrm{CH}_{3} \mathrm{COOH}+\mathrm{HCO}_{3}^{-} \rightleftarrows \mathrm{CH}_{3} \mathrm{COO}^{-}+\mathrm{CO}_{2} \mathrm{H}_{2} \mathrm{O}
$$

3.1.Calculate the reaction constant Kr of this reaction.
3.2. Verify that this reaction is limited.

Zinc reacts with hydrochloric acid solution according to a slow and complete reaction which is represented by the following equation:

$$
\mathrm{Zn}_{(\mathrm{s})}+2 \mathrm{H}_{3} \mathrm{O}_{(\mathrm{aq})}^{+} \rightarrow \mathrm{Zn}_{(\mathrm{aq})}^{2+}+2 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}+\mathrm{H}_{2(\mathrm{~g})}
$$

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

## Given:

- The study takes place at $25^{\circ} \mathrm{C}$.
- $\mathrm{Zn}^{2+}$ and $\mathrm{C} \ell^{-}$are spectator ions with no acid and base character.
- Hydrogen gas $\left(\mathrm{H}_{2}\right)$ is insoluble in water.

A mass m of powdered zinc is introduced into a flask containing a volume $\mathrm{V}_{0}=100 \mathrm{~mL}$ of hydrochloric acid solution $\left(\mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{C}^{-}\right)$of molar concentration $\mathrm{C}_{\mathrm{o}}$ and $\mathrm{pH}_{\mathrm{o}}$ as initial pH . The reacting mixture is a stoichiometric mixture.

## 1. Preliminary Study

Knowing that the pH of a solution is determined by the relation $\mathbf{p H}=-\log \left[\mathbf{H}_{3} \mathrm{O}^{+}\right]$:
Choose, with justification the answer:
1.1.the relation between $\mathrm{pH}_{0}$ and $\mathrm{C}_{\mathrm{o}}$ :

$$
\mathrm{C}_{\mathrm{o}}=\frac{1}{\mathrm{pH}_{0}} \quad \mathrm{C}_{\mathrm{o}}=\frac{1}{10^{\mathrm{pH}_{0}}}
$$

1.2.the variation of pH with time pH increases
pH decreases
1.3. Knowing that the reaction is complete.
a) Specify the chemical species present in the reacting mixture at the end of the reaction
b) Deduce that the value of the pH at the end of the reaction is equal to 7 .

## 2. Kinetic Study

The follow-up of the evolution of the molar concentration of the $\mathrm{Zn}^{2+}$ ions as a function of time, using an appropriate method, permits to plot the curve $\left[\mathrm{Zn}^{2+}\right]=\mathrm{f}(\mathrm{t})$ represented by the document-1.


Document-1
2.1. By referring to document-1:
2.1.1.Deduce the variation of the rate of formation of $\mathrm{Zn}^{2+}$ ions with time.
2.1.2.Show that the value of the concentration of $\mathrm{Zn}^{2+}$ ions at the end of the reaction is equal to $25 \times 10^{-3} \mathrm{~mol} . \mathrm{L}^{-1}$
2.1.3. Show that the concentration $\mathrm{C}_{0}=50 \times 10^{-3} \mathrm{~mol} . \mathrm{L}^{-1}$
2.2 Choose the relation between the initial rate of disappearance of $\mathrm{H}_{3} \mathrm{O}^{+}$ions $\mathrm{r}_{\mathrm{o}}\left(\mathrm{H}_{3} \mathrm{O}^{+}\right)$and the slope $\mathrm{S}_{\mathrm{o}}$ of the tangent.

By referring to the equation of the reaction:

$$
\mathrm{Zn}_{(\mathrm{s})}+2 \mathrm{H}_{3} \mathrm{O}_{(\mathrm{aq})}^{+} \rightarrow \mathrm{Zn}_{(\mathrm{aq})}^{2+}+2 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}+\mathrm{H}_{2(\mathrm{~g})}
$$

a. $\mathrm{r}_{\mathrm{o}}\left(\mathrm{H}_{3} \mathrm{O}^{+}\right)=2 \mathrm{~S}_{0}$
b. $\mathrm{r}_{\mathrm{o}}\left(\mathrm{H}_{3} \mathrm{O}^{+}\right)=\mathrm{S}_{\mathrm{o}}$
c. $\mathrm{r}_{\mathrm{o}}\left(\mathrm{H}_{3} \mathrm{O}^{+}\right)=-2 \mathrm{~S}_{\mathrm{o}}$
2.3 The concentration of the $\mathrm{Zn}^{2+}$ ions, noted $\left[\mathrm{Zn}^{2+}\right]_{(\mathrm{t})}$ formed at each instant of time t of the evolution of the reacting system is related to the pH of the solution by the relation:

$$
\left[\mathrm{Zn}^{2+}\right]_{\mathrm{t}}=\frac{1}{2}\left(\mathrm{C}_{\mathrm{o}}-10^{-\mathrm{pH}}\right) .
$$

2.3.1 Determine, by referring to the document -1 , the molar concentration of the[ $\left.\mathrm{Zn}^{2+}\right]$ at $\mathrm{t}=5 \mathrm{~min}$.
2.3.2 Deduce the pH of the solution at $\mathrm{t}=5 \mathrm{~min}$, knowing that $\mathrm{C}_{\mathrm{o}}=50 \times 10^{-3} \mathrm{~mol} . \mathrm{L}^{-1}$

## 3 Study of The Effect of a Kinetic Factor

The previous experiment is carried out again but with only one modification: a volume $\mathrm{V}_{\mathrm{o}}=100 \mathrm{~mL}$ of a hydrochloric acid solution is used of molar concentration $\mathrm{C}_{1}>\mathrm{C}_{\mathrm{o}}$ is used

For each proposition answer by true or false. Justify you answer.
3.1.The molar concentration of $\mathrm{Zn}^{2+}$ ions at $\mathrm{t}=5 \mathrm{~min}$ remains equal to $6 \times 10^{-3} \mathrm{~mol} . \mathrm{L}^{-1}$.
3.2. The molar concentration of $\mathrm{Zn}^{2+}$ ions at the end of the reaction is equal to that found in the question (2.1.2), knowing that Zn remains the limiting reactant.

