

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.

مسابقة في الكيمياء
(باللّغة الإنكليزية)
المدّة: ساعتان


## Answer the Three Following Exercises:

## Exercise 1 (7 points) Properties of an Alcohol

The aim of this exercise is to study the chemical properties of the alcohol (A) and its reaction with methanoic acid.

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

## 1. Chemical properties of the Alcohol (A)

Available is a saturated and non-cyclic mono-alcohol denoted (A).
The quantitative analysis of alcohol (A) shows that the percentage by mass of oxygen is $\% \mathrm{O}=\mathbf{2 1 . 6 2 \%}$
1.1. Knowing that the general molecular formula of saturated monoalcohol is $\mathrm{C}_{\mathrm{n}} \mathrm{H}_{2 \mathrm{n}+2} \mathrm{O}$, calculate in terms of n , the molar mass of alcohol (A).

- Show that the molecular formula of the alcohol (A) is $\underline{\mathrm{C}}_{4} \underline{H}_{10} \underline{\mathrm{O}}$.
1.2.The condensed structural formula of the alcohol (A) is:


## OH


$\mathbf{C H}_{3}-\mathbf{C H}_{2}-\mathbf{C H}-\mathrm{CH}_{3}$
1.2.1. Indicate the class of alcohol (A).
1.2.2 Give its systematic name.
1.2.3. the three alcohol isomers of $(\mathrm{A})$ is:
1- Butanol

2- Methyl-1-propanol

Write the condensed structural formulas of these three alcohol isomers.
1.2.4. Justify that the molecule of the alcohol (A) is chiral.
1.2.5. The alcohol (A) possesses two enantiomers. One of them is represented according to Cram by the following structure:


Represent the second enantiomer of alcohol (A).
1.3. The mild oxidation of the alcohol (A) by a solution of acidified potassium permanganate leads to the formation of an organic compound (B).
Choose the correct answer:
1.3.1.

| The systematic name of (B) is : | butanal |
| :--- | :--- |
|  | butanone |
|  | butanoic acid |

### 1.3.2.

| the compound (B) gives with the 2,4-DNPH : | a white crystals |
| :--- | :--- |
|  | a yellow- orange precipitate |
|  | a black precipitate |

## 2. Reaction of the Alcohol (A) With Methanoic Acid

A mixture of 0.2 mol of alcohol (A) and 0.2 mol of methanoic acid is heated to reflux, in the presence of few drops of concentrated sulfuric acid as a catalyst.

The esterification reaction is represented by the following equation:

$$
\text { methanoic acid }+\operatorname{alcohol}(\mathbf{A}) \rightleftharpoons \text { ester }(\mathbf{E})+\text { water }
$$

2.1. Copy and Complete, by using the condensed structural formula, the equation of the following esterification reaction:
$\mathrm{HCOOH}+\mathrm{CH}_{3}-\mathrm{CH}_{2}-\mathrm{CH} \mathrm{OH}-\mathrm{CH}_{3} \rightleftharpoons$ $\qquad$ $+$ $\qquad$

At an instant $\mathbf{t}$ the equilibrium is reached.
The number of moles of methanoic acid remained at equilibrium is $\mathbf{n}_{\text {(acid) }}=\mathbf{0 . 0 8} \mathbf{~ m o l}$.
2.2. Complete the following table:

|  | methanoic acid + alcohol $(\mathbf{A}) \rightleftharpoons$ ester $(\mathbf{E})+$ water |  |  |  |
| :--- | :--- | :--- | :---: | :---: |
| $\mathbf{t}=\mathbf{0} \mathbf{~ m i n}$ | 0.2 mol | 0.2 mol | 0 | 0 |
| $\mathbf{t}$ at equilibrium | $\mathbf{0 . 0 8} \mathbf{~ m o l}$ | $\ldots \ldots \ldots \ldots$ | $\ldots \ldots \ldots \ldots \ldots$ | $\ldots \ldots \ldots \ldots \ldots$ |

2.3. Give the expression of the equilibrium constant Kc .

Calculate its value.
2.4. The same experiment is carried out again with only one change: "without the addition of concentrated sulfuric acid" .The equilibrium state is reached at an instant of time $t^{\prime}$.
Choose the correct answer. Justify.
a. $\mathrm{t}>\mathrm{t}^{\prime}$
b. $\mathrm{t}=\mathrm{t}^{\prime}$
c. $\mathrm{t}<\mathrm{t}^{\prime}$

## Exercise 2 (6 points) Kinetic of the Oxidation of Javel Water with Ammonia

In an aqueous solution, ammonia $\left(\mathrm{NH}_{3}\right)$ reacts with hypochlorite ions $\left(\mathrm{ClO}^{-}\right)$in a slow and complete reaction that takes place according to the equation below:

$$
2 \mathrm{NH}_{\mathbf{3}_{(\mathrm{aq})}}+3 \mathrm{ClO}_{(\mathrm{aq})}^{-} \longrightarrow \mathrm{N}_{2(\mathrm{~g})}+3 \mathrm{Cl}^{-}{ }_{(\mathrm{aq})}+3 \mathbf{H}_{2} \mathrm{O}_{(\mathrm{l})}
$$

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

Javel water is a sodium hypochlorite aqueous solution $\left(\mathrm{Na}^{+}+\mathrm{ClO}^{-}\right)$

## Document- 1

## 1. Preparation of a Javel Water Solution ( $\mathbf{S}_{\mathbf{1}}$ )

A volume $\mathbf{V}_{\mathbf{1}}=\mathbf{2 5 0} \mathbf{~ m L}$ of the solution $\left(\mathbf{S}_{\mathbf{1}}\right)$ of molar concentration $\mathbf{C}_{\mathbf{1}}=\mathbf{0 . 2 5} \mathbf{~ m o l} . \mathrm{L}^{\mathbf{- 1}}$ is prepared by diluting $\mathbf{2 5}$ times a commercial Javel water solution ( $\mathbf{S}_{\mathbf{o}}$ ).
1.1. Show that the volume $\mathbf{V}_{\mathbf{o}}$ withdrawn from solution $\left(\mathbf{S}_{\mathbf{o}}\right)$ to prepare 10 mL of the solution $\left(\mathbf{S}_{\mathbf{1}}\right)$.
1.2. Choose, from document- 2, the essential glassware needed to carry out the preparation of solution $\left(\mathbf{S}_{1}\right)$ :

- To withdraw: $\mathbf{V}_{\mathbf{0}}$.
- To contain the solution ( $\mathbf{S}_{\mathbf{1}}$ ):

| Beakers | 100 mL | 250 mL | 500 mL |
| :--- | :--- | :--- | :--- |
| volumetric flask | 100 mL | 250 mL | 500 mL |
| graduated cylinder | 5 mL | 10 mL | 25 mL |
| volumetric pipet | 5 mL | 10 mL | 25 mL |

## Document- 2

## 2. Kinetic Study

A volume $\mathbf{V}_{\mathbf{1}}=\mathbf{2 0 0} \mathbf{~ m L}$ of a solution $\left(\mathbf{S}_{\mathbf{1}}\right)$ of Javel water solution of molar concentration $\mathbf{C}_{\mathbf{1}}=\mathbf{0 . 2 5 m o l} \mathbf{L}^{-1}$ is mixed with an excess of ammonia solution at constant temperature $\mathbf{T}$ $=27^{\circ} \mathrm{C}$.

Using an appropriate method, the number of moles of nitrogen gas $\mathbf{N}_{2}$ formed is determined at different instant t , the results obtained are grouped in the table of document- 3:

| $\mathbf{t}(\mathbf{m i n})$ | 2 | 4 | 6 | 8 | 10 | 12 | 16 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $\mathbf{n}\left(\mathbf{N}_{\mathbf{2}}\right)\left(\mathbf{1 0}^{-\mathbf{3}} \mathbf{~ m o l}\right)$ | 4.3 | 8.0 | 10.3 | 12.0 | 13.3 | 14.3 | 15.5 |

## Document-3

2.1. Show that the initial number of moles of hypochlorite ions $\mathbf{C l O}^{-}$is equal $5 \times 10^{-2} \mathrm{~mol}$.
2.2. Calculate the number of moles of $\mathbf{N}_{2}$ expected to be obtained at the end of the reaction.

Verify whether the instant of time $t=16$ min represents the end of the reaction.
2.3. Plot the curve representing the variation in the number of moles of $\left(\mathrm{N}_{2}\right)$ as a function of time:
$\mathrm{n}\left(\mathrm{N}_{2}\right)=\mathrm{f}(\mathrm{t})$ within the interval of time [ $\left.0-16 \mathrm{~min}\right]$.
Take the following scales: In abscissas: 1 cm for 1 min ;
In ordinates: 1 cm for $1 \times 10^{-3} \mathrm{~mol}$.
2.4. Deduce, graphically, the variation of the rate of formation of $\left(\mathrm{N}_{2}\right)$ as a function of time.
2.5. Choose the correct answer:
a. $\quad r_{\left(\mathrm{ClO}^{-}\right) \mathrm{t}}=3 \mathrm{r}_{(\mathrm{N} 2) \mathrm{t}}$
b. $\mathrm{r}_{\left(\mathrm{ClO}^{-}\right) \mathrm{t}}=\frac{\mathrm{r}(\mathrm{N} 2) \mathrm{t}}{3}$
c. $\mathrm{r}_{\left(\mathrm{ClO}^{-}\right) \mathrm{t}}=\mathrm{r}_{(\mathrm{N} 2) \mathrm{t}}$

Knowing that:
$r_{(\mathbb{N} 2) t}$ :the rate of formation of $\left(\mathrm{N}_{2}\right)$ at an instant of time t .
$\mathrm{r}_{\left(\mathrm{ClO}^{\circ}\right) \mathrm{t}}$ : the rate of disappearance of $\mathrm{ClO}^{-}$at the same instant t .
2.6. Define the half- life time of the reaction $\mathrm{t}_{1 / 2}$.

Determine graphically this time.
2.7. The same kinetic study is carried out but with one change: it takes place in this case at temperature $\mathrm{T}^{\prime}$ higher than $27^{\circ} \mathrm{C}$.
Specify, in this study, whether the following statement is true or false:
The number of moles of nitrogen gas $\left(\mathrm{N}_{2}\right)$ formed at $\mathrm{t}=4 \mathrm{~min}$ becomes less than $8.0 \times 10^{-3} \mathrm{~mol}$, given value in document- 3 .

Ethanoic acid is a weak acid of formula $\mathrm{CH}_{3} \mathrm{COOH}$.
The aim of this exercise is to study the behavior of ethanoic acid in water and to determine its molar concentration by pH -metric titration.

Given: - This study is carried out at $25^{\circ} \mathrm{C}$.

- pKa of the pair $\left(\mathrm{CH}_{3} \mathrm{COOH} / \mathrm{CH}_{3} \mathrm{COO}^{-}\right)=4.8$


## 1. Study of the Behavior of Ethanoic Acid in Water

In the laboratory, available is a flask containing an ethanoic acid solution (S) of unkown molar concentration $\mathbf{C}_{\mathrm{a}}$.
1.1. Complete the equation of the reaction of ethanoic acid $\mathrm{CH}_{3} \mathrm{COOH}$ with water:

$$
\mathrm{CH}_{3} \mathrm{COOH}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \ldots \mathrm{~A} \ldots+\ldots \text { B ... }
$$

1.2. Knowing that $\alpha$ is the degree of dissociation of ethanoic acid in water.

- Complete the following table :

|  | $\mathbf{C H}_{3} \mathbf{C O O H}+\mathbf{H}_{\mathbf{2}} \mathbf{O} \rightleftharpoons \ldots \mathrm{A} \ldots+\ldots \mathrm{B} \ldots$ |  |  |  |
| :--- | :--- | :--- | :---: | :---: |
| Initial state | $\mathbf{C}_{\mathbf{a}}$ | excès | 0 | 0 |
| Equilibrium state | $\mathbf{C}_{\mathrm{a}}-\mathbf{C}_{\mathrm{a}} \boldsymbol{\alpha}$ | excès | $?$ | $?$ |

-verify the following relation:

$$
\frac{\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]}{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]}=\frac{\alpha}{1-\alpha}
$$

1.3. Show that the value of $\alpha$ is close to 0.04 , knowing that:

- pH of the solution ( S ) is equal to 3.4
- The pH is calculated by this relation $\mathrm{pH}=\mathrm{pKa}$ (acide $/$ base) $+\log \frac{\text { [base] }}{\text { [acide] }}$
1.4. Based on the value of $\alpha$, justify that ethanoic acid is a weak acid.


## 2-Titration of the Ethanoic Acid Solution (S)

Into a beaker, introduce a volume $\mathrm{V}_{\mathrm{a}}=20.0 \mathrm{~mL}$ of the ethanoic acid solution ( S ) and a certain volume of distilled water to immerse properly the pH -meter electrode. A sodium hydroxide solution $\left(\mathrm{Na}^{+}+\mathrm{HO}^{-}\right)$of molar concentration $\mathrm{C}_{\mathrm{b}}=2.0 \times 10^{-2}$ mol. $\mathrm{L}^{-1}$ is added progressively. A sample of the experimental results is given in document-1 :

| $\mathrm{V}_{\mathrm{b}}(\mathrm{mL})$ | 0 | 5 | 10 | 15 |
| :---: | :---: | :---: | :---: | :---: |
| pH | 3.5 | 4.8 | $\mathrm{pH}_{\mathrm{E}}$ | 11.2 |

## Document-1

2.1.Choose, From the given material of document-2, the most suitable ones needed to carry out the titration.

- Volumetric flasks: 50 and 100 mL
- Beaker : 100 mL
- Graduated cylinders: 10, 20 and 50 mL
- Magnetic stirrer and its bar
- Graduated buret: 25 mL
- pH - meter and its electrode
- Precision balance


## Document-2

2.2. Write the equation of the titration reaction between $\mathbf{C H}_{3} \mathbf{C O O H}$ and $\mathbf{H O}^{-}$ions.
2.3.Based on the chemical species present in the beaker at equivalence. Specify the point that represents the equivalence point:
$\mathrm{A}\left(\mathrm{V}_{\mathrm{bE}}=10 \mathrm{~mL} ; \mathrm{pH}_{\mathrm{E}}=8.3\right)$;
$\mathrm{B}\left(\mathrm{V}_{\mathrm{bE}}=10 \mathrm{~mL} ; \mathrm{pH}_{\mathrm{E}}=7\right)$;
$\mathrm{C}\left(\mathrm{V}_{\mathrm{bE}}=10 \mathrm{~mL} ; \mathrm{pH}_{\mathrm{E}}=5.8\right)$.
2.4.Determine the molar concentration of ethanoic acid in the solution (S).
2.5.Plot the shape of the curve representing the change in the pH as a function of the volume of the base added $\mathrm{pH}=\mathrm{f}\left(\mathrm{V}_{\mathrm{b}}\right)$ passing by the four remarkable points extracted from the table of document-1.

Take the following scales: In abscissa $1 \mathrm{~cm}=1 \mathrm{~mL}$;

$$
\text { In ordinates; } 1 \mathrm{~cm}=1 \text { unit of } \mathrm{pH} \text {. }
$$

2.6. - Plot the predominance axis of the chemical species of the pair $\mathrm{CH}_{3} \mathrm{COOH} / \mathrm{CH}_{3} \mathrm{COO}^{-}$.

- Referring to document- $\mathbf{1}$ and using the predominance axis specify the chemical species which predominates at the end of the titration for $\mathrm{V}_{\mathrm{b}}=15 \mathrm{~mL}$.

