مسابقة في مادة الكيمياء
المدة: ساعة ونصف

الاسم:
الرقم:

This Exam Includes Three Exercises. It Is Inscribed on Four Pages, Numbered from 1 to 4.
The Use of A Non-programmable Calculator Is Allowed.
Answer the Three Following Exercises

Exercise 1 (7 points) Kinetic Study

Hydrogen peroxide (H_2O_2) reacts, in acidic medium, with iodide ions (I^-) in a slow and complete reaction that takes place according to the following equation:

$$H_2O_{2\,(aq)} + 2I^-_{(aq)} + 2H_3O^+_{(aq)} \rightarrow I_{2\,(aq)} + 4H_2O_{(l)}$$

The aim of this exercise is to study, at constant temperature T, the kinetic of this reaction.

1. Preliminary Study

In order to study the kinetic of this reaction, one introduces into an Erlenmeyer flask, at a constant temperature T:

- A volume $V_1 = 10.0$ mL of potassium iodide solution ($K^+ + I^-$) of molar concentration $\mathbf{C_1} = 0.1$ mol.L^{-1}.
- A volume $V_2 = 18.0$ mL of sulfuric acid solution considered **in excess**.

At instant t = 0, a volume V = 2.0 mL of hydrogen peroxide solution (H_2O_2) of molar concentration C = 0.1 mol.L^{-1} is added into the Erlenmeyer flask. The number of moles of iodine formed at different instants is determined by an appropriate method. The results are grouped in the table of **Document-1**.

t (min)	0	4	8	12	16	20	24
n (I_2) $\times 10^{-5}$ mol	0	8	12	14	15.2	16	16.6

Document -1

1.1. Show that hydrogen peroxide (H_2O_2) is the limiting reactant.

1.2. Specify whether the instant t = 24 min represents the end time of the reaction.

2. Kinetic Study

2.1. Plot the curve that represents the variation of the number of moles of iodine I_2 as a function of time, $n(I_2) = f(t)$ within the time interval [0 – 24 min].
Take the following scales: abscissa: 1 cm for 2 min;
ordinate: 1 cm for 2×10^{-5} mol.

2.2. Determine, graphically, the half-life time, $t_{½}$, of the reaction.

2.3. The rate of formation of iodine decreases with time.

2.3.1. Justify this statement by referring to the curve $n(I_2) = f(t)$.

2.3.2. Indicate the kinetic factor responsible for this variation.

2.4. The instantaneous rate of formation of iodine at an instant t is denoted $r(I_2)_t$. Choose the relation that corresponds to the rate of disappearance of iodide ions (I^-), $r(I^-)_t$, at the same instant t.

a- $r(I^-)_t = r(I_2)_t$ **b-** $r(I^-)_t = \frac{r(I_2)_t}{2}$ **c-** $r(I^-)_t = 2\,r(I_2)_t$

2.5. The above study is carried out again but with only one modification, the potassium iodide solution is replaced by another solution of concentration $C' > \mathbf{C_1}$. Draw, on the same graph of question **2.1**, the shape of the curve $n(I_2) = g(t)$. Justify.

Exercise 2 (6 points) Caustic Soda

Caustic soda 30% is a commercial sodium hydroxide solution. Caustic soda is a detergent, active, deep-action and strongly alkaline character used for the removal of organic pollution.
The aim of this exercise is to determine the percentage by mass of NaOH in this commercial solution.

Given:
- Molar mass: M(NaOH) = 40 $g.mol^{-1}$
- Density of the commercial solution: d = 1.34 $g.mL^{-1}$
- The study is carried out at 25°C.
- Ion product of water at 25°C: $K_W = 1.0 \times 10^{-14}$

1. Preliminary Study

Sodium hydroxide NaOH is a **strong base.**
The pH of a sodium hydroxide solution ($Na^+ + HO^-$) of molar concentration C is equal to 10.4
Choose, by justifying, the value of the concentration of hydroxide ions $[HO^-]$ in this solution.
a- $[HO^-] = 3.98 \times 10^{-11}$ $mol.L^{-1}$ **b-** $[HO^-] = 2.51 \times 10^{-4}$ $mol.L^{-1}$ **c-** $[HO^-] = 3.98 \times 10^{3}$ $mol.L^{-1}$

2. Dilution of the Commercial Solution

The commercial solution noted as (S_o) is highly concentrated. A sodium hydroxide solution noted (S_1) of molar concentration C_1 is prepared by diluting 125 times the commercial solution (S_o).
Choose, from **Document-1,** the convenient set for the preparation of solution (S_1). Justify.

Set 1	Set 2	Set 3
Beaker of 100 mL	Beaker of 100 mL	Beaker of 100 mL
Volumetric pipet of 5 mL	Graduated pipet of 5 mL	Volumetric pipet of 5 mL
Volumetric flask of 1000 mL	Volumetric flask of 500 mL	Volumetric flask of 500 mL

Document-1

3. pH-metric Titration of Solution (S_1)

A volume $V_{(S1)}$ = 10.0 mL of the solution (S_1) 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 hydrochloric acid solution ($H_3O^+ + C\ell^-$) of molar concentration $C_a = 5.0 \times 10^{-2}$ $mol.L^{-1}$.

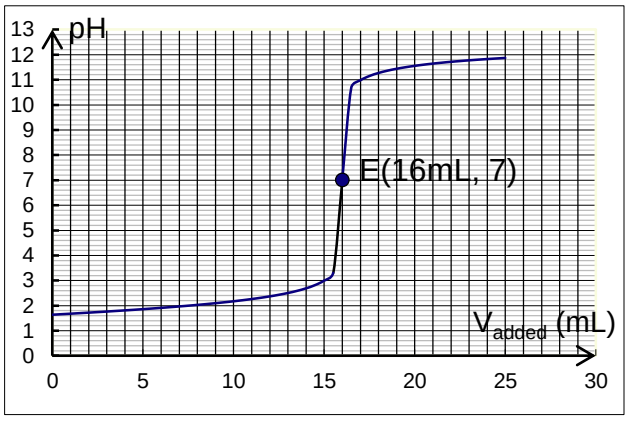
3.1. Write the equation of the titration reaction.

3.2. Choose, from the following, two characteristics of the titration reaction:

Reversible	Complete	Fast	Slow	Unique

3.3. Specify which of the two curves of **Document-2** represents the variation of pH of the solution in the beaker as a function of the volume of the acid added in the above pH-metric titration.

Curve a



Curve b

Document-2

3.4. Justify, based on the chemical species present in solution, that the pH at equivalence is $pH_E = 7$

3.5. Determine the molar concentration C_1 of the sodium hydroxide solution (S_1).

3.6. Show that the molar concentration of sodium hydroxide in the commercial solution is C_o= 10.0 $mol.L^{-1}$.

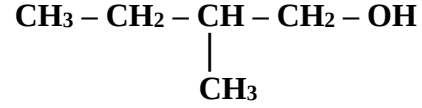
3.7. Determine the percentage by mass of NaOH in the commercial solution.

Exercise 3 (7 points) **Esterification Reaction**

Esters often have a pleasant odor. They are found naturally in fruits and are often responsible for the aroma. Esters are obtained by extraction or by synthesis.
The aim of this exercise is to identify an ester (E) with fruity odor and to study its synthesis reaction.

1. Study of the Structure of an Alcohol (A)

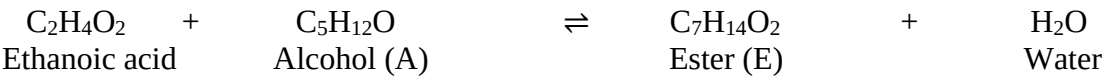
The condensed structural formula of an alcohol (A) is given as follows:



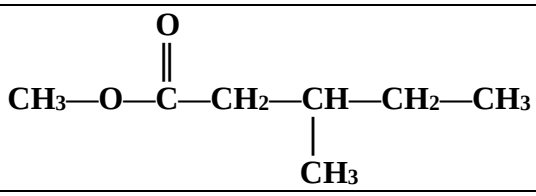
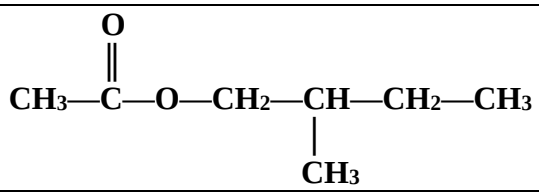
1.1. Copy the structure of the alcohol (A) on your answer sheet then circle and name its functional group.
1.2. Give the systematic name of the alcohol (A).
1.3. Justify the following two statements:
1.3.1. Alcohol (A) is a primary alcohol.
1.3.2. The molecule of the alcohol (A) is chiral.
1.4. Represent, according to Cram, the two enantiomers of the alcohol (A) molecule.

2. Synthesis of the Ester (E)

The ester (E) is a sweet and fruity tasting compound. It can be prepared, in the laboratory, starting from ethanoic acid and the alcohol (A) according to the following equation:



2.1. Give the condensed structural formula of ethanoic acid.
2.2. Choose, from the two condensed structural formulas A and B of **Document-1**, the one that corresponds to the condensed structural formula of the ester (E).

Condensed structural formula A	Condensed structural formula B
	

Document-1

2.3. Give the systematic name of the ester (E).
2.4. A mixture containing 0.1 mol of ethanoic acid and 0.2 mol of the alcohol (A) is heated to reflux for a certain time in the presence of few drops of sulfuric acid as a catalyst.
The mass of the ester obtained at equilibrium is 11.05g.

- For an initial equimolar mixture of a carboxylic acid and a primary alcohol, the yield of the reaction at equilibrium is 67%.
- The molar mass of ester (E) is M = 130 $g.mol^{-1}$.

Document-2

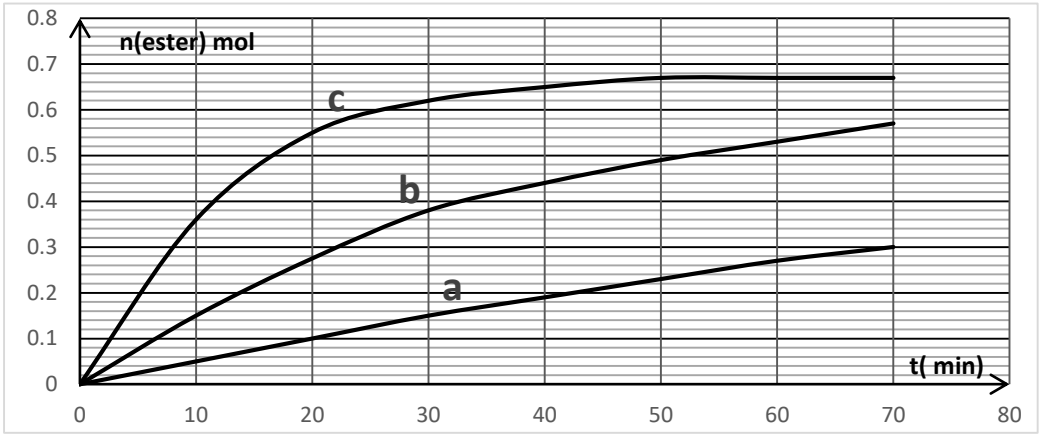
2.4.1. Determine the yield, at equilibrium, of this synthesis reaction.
2.4.2. Deduce the importance of using a non-equimolar initial mixture of reactants on the synthesis reaction of an ester.

3. Factors Affecting the Rate of the Esterification Reaction

In order to study the effect of temperature and that of the presence of a catalyst on the esterification reaction, we realize the three reacting mixtures as given in the table of **Document-3.**

Reacting mixture	Number of moles of ethanoic acid	Number of moles of alcohol (A)	Temperature	Catalyst	Corresponding curve in **Document-4**
M	1.0 mol	1.0 mol	20°C		**a**
M_1	1.0 mol	1.0 mol	70°C		**b**
M_2	1.0 mol	1.0 mol	20°C	H_2SO_4	**c**

Document-3



Document-4

Referring to the table of **Document-3** and graph of **Document-4**, deduce the effect on the rate of the esterification reaction of:

3.1. Increasing the temperature of the reacting medium.

3.2. Using a catalyst.