This test consists of three exercises. It has four pages numbered 1 to 3.
The use of a non-programmable calculator is allowed.
Solve the following three exercises:

Exercise 1 — Kinetics of base hydrolysis of an ester

We propose to study the kinetics of the reaction between an ester (RCOOR') and sodium hydroxide (NaOH) in solution. This slow and total reaction takes place whose equation is the following:

$$R-COO-R' + HO^- \rightarrow R-COO^- + R'-OH$$

For this, we add to a volume V of sodium hydroxide solution of concentration $C_0 = 2 \times 10^{-2}$ mol.L^{-1}, and an equal volume V of ester solution of the same concentration C_0. This reaction mixture is maintained at a constant temperature θ.

The electrode of a pH meter is immersed in the mixture, which makes it possible to measure the pH on different instants. The concentration of the carboxylate ions $R-COO^-$ is determined at different times during the evolution of the reaction system and the results are grouped in the following **Document-1**:

t (min)	3	6	9	12	15	21	24	30
[RCOO$^-$] (x10^{-3} mol.L^{-1})	1,9	2,8	3,3	3,8	4,2	4,9	5,2	5,6

Document-1

- **Given: Ionic product of water at 25°C,** $K_w = 1{,}0.10^{-14}$

1. Primary Study :

1.1. Calculate the pH of hydroxide solution before adding ester solution.
1.2. Show that the concentration of carboxylate ions [RCOO$^-$] at the end of the reaction is 1×10^{-2} mol.L^{-1}.
1.3. Verify if the instant $t = 30$ min represents the end of the reaction.

2. Kinetic Study

2.1. Plot the curve representing the variation of the concentration of carboxylate ions as a function of time: [RCOO$^-$] = f(t), in the time interval [0 - 30 min].
Take the following scales: 1 cm for 3 min on the abscissa and 1 cm for 1 x 10^{-3} mol.L^{-1} in ordinates..
2.2. Deduce, graphically, the evolution of the rate of formation of carboxylate ions over time.
2.3. Determine the half-life time of the reaction.
2.4. The same study is repeated under the same conditions but at a temperature θ' > θ.
Plot, on the same graph of question 2.1, the shape of the curve representing the new variation in the concentration of carboxylate ions as a function of time : [RCOO$^-$] = g(t). Justify.

Exercise 2 **Acid-base reactions**

The label of a bottle containing a commercial solution of hydrobromic acid includes, among other things, the following indications:

46 % by mass HBr ; density : 1,41 $g.mL^{-1}$.

The purpose of this exercise is to verify the value of the mass percentage indicated above..

- **Given** : M (HBr) = 81 $g.mol^{-1}$. at 25°C, pKw=14

1. Dilution of the Commercial Solution

1.1. Show that the molar concentration of the commercial solution is $C_0 = 8\ mol.L^{-1}$.

1.2. A solution S is prepared by diluting a certain volume of the commercial solution 200 times.
The pH of the solution (S) is equal to 1,39.

1.2.1. Choose, with justification, of the following three sets, the one that is suitable for carrying out this dilution with precision..

Set (a)	Set (b)	Set (c)
- Beaker 50 mL	- Beaker 50 mL	- Beaker 50 mL
- Erlenmeyer flask 1000 mL	- Volumetric flask 1000 mL	- Volumetric flask 1000 mL
- Volumetric pipet 5 mL	- Volumetric pipet 5 mL	- graduated pipet 5 mL

1.2.2. Show that HBr is a strong acid.

1.2.3. Write the equation of its reaction with water.

2. pH- metric titration

A student carried out the titration according to **Document-1**.

- He fills a burette with an aqueous solution of sodium hydroxide ($Na^+ + HO^-$) of concentration $C_1 = 2{,}0.10^{-2}\ mol.L^{-1}$.
- He puts a volume V = 10,0 mL of the acid solution (S) in a beaker of 250 mL.
- He puts the electrode of the pH-meter in the beaker then he adds 40 mL of water so that it is well immersed.
- He adds the basic solution, milliliter by milliliter, noting the pH value with each addition.
- He determines the volume of the base added to the equivalence, this volume is V_{1E} = 19,5 mL.

Document-1

2.1. Write the equation of the titration reaction.

2.2. Determine the concentration C of the solution (S).

2.3. Deduce the mass percentage of HBr in the commercial solution.

2.4. We propose, for this pH-metric monitoring and its results, three proposals.
If the proposition is true, justify it.
If the statement is false, specify the correct answer..

2.4.1. The pH of the solution in the beaker, just before the addition of the basic solution, is equal to 1,39.

2.4.2. The medium obtained at equivalence is neutral.

2.4.3. The pH of the mixture obtained for a volume V_1 greater than V_{1E} of the basic solution is:

$$pH = 12{,}3 + \log\frac{V_1 - V_{1E}}{V_1 + 50}$$

Exercise 3 **Synthesis of an ester**

Esters are neutral organic compounds, poorly soluble in water and soluble in many common solvents. They are often volatile liquids with a pleasant, fruity smell, so they enter into the composition of a number of flavors and fragrances.

Document-1 represents some characteristics of a carboxylic acid (A) and an alcohol (B).

This exercise is devoted to two purposes: to identify the two compounds (A) and (B) and to study the reaction between these two compounds.

Carboxylic acid (A)	**Alcohol (B)**
The carbon chain of each is saturated open	
$M_1 = 60\ g.mol^{-1}$	Oxygen mass percentage is 21,62 %
	Document-1

Given :

- Molar masses in $g.mol^{-1}$: $M(H) = 1$; $M(C) = 12$ and $M(O) = 16$.
- The equilibrium constant K, associated with the equation:

$$RCOOH_{(l)} + R'OH_{(l)} \rightleftarrows RCOOR'_{(l)} + H_2O_{(l)}$$

is equal to 4.12 if the alcohol is primary and 2.25 if the alcohol is secondary.

1. Study of molecules

Referring to **document-1**, answer the following questions.

1.1. Justify the following statements.

1.1.1. Carboxylic acid (A) is ethanoic acid.

1.1.2. The molecular formula of alcohol (B) is $C_4H_{10}O$.

1.2. Write the condensed structural formulas of the alcohol isomers of (B).

2. Synthesis of the ester and identification of (B)

A mixture of 0.5 mol of ethanoic acid and 0.5 mol of alcohol (B) is refluxed. At equilibrium, a quantity of 0.3 mol of an ester E is obtained.

2.1. Give the role of reflux heating.

2.2. Determine the yield (Y) of this reaction.

2.3. Show that $K_c = \frac{(Y)^2}{(1-Y)^2}$, where K_c represents the equilibrium constant of the esterification reaction and R is the corresponding yield. Deduct K_c.

2.4. Give the name of alcohol (B).

2.5. Identify ester (E).

2.6. Verify that the alcohol molecule (B) is chiral. Represent, according to Cram, the two enantiomers of this alcohol (SV).

- Propose two experimental ways which help to increase the yield of this reaction (SG).

2.7. Write, using condensed structural formulas of organic compounds, the equation of the catalytic dehydrogenation reaction of alcohol (B).