مسابقة في مادة الكيمياء المدة: ساعتان	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: (6 points) Kinetic of the Reaction of Magnesium with Hydrochloric Acid

Magnesium metal is attacked by a hydrochloric acid solution ($H_3O^+ + C\ell^-$) according to a slow and complete reaction as shown by the equation below:

$$2\ H_3O^+_{(aq)} + Mg_{(s)} \rightarrow Mg^{2+}_{(aq)} + H_{2(g)} + 2\ H_2O_{(\ell)}$$

In order to study the kinetic of this reaction the following experiment is carried out at constant temperature.

A volume V_1=100 mL of a hydrochloric acid solution (S_1) of molar concentration C_1 = 0.20 mol.L^{-1} is introduced into an Erlenmeyer flask.
At instant t = 0, a mass m = 0.15 g of powdered magnesium is added to the Erlenmeyer flask and the chronometer is set to function.
The volume V, of the released hydrogen gas H_2, is measured at different instants t, and then the numbers of moles of hydrogen gas are deduced at these instants. The obtained values are given in document-1.

t (s)	20	40	60	80	100	120
$n(H_2)$ (10^{-5} mol)	50	90	123	152	176	195

Document-1

Given: $M_{(Mg)}$ = 24g.mol^{-1}

1. Preparation of The Acid Solution

Available is a bottle of an aqueous hydrochloric acid solution (S_0) labelled with the following indications: 32.3% by mass of the acid, density d = 1.13g.mL^{-1}, $M_{(HC\ell)}$ =36.5 g.mol^{-1}.

1.1. Show that the molar concentration C_0 of the solution (S_0) is close to 10 mol.L^{-1}.
1.2. The solution (S_1) is prepared starting from the solution (S_0).
1.2.1. Calculate the volume V_0 withdrawn from (S_0) to prepare 200 ml of solution (S_1).
1.2.2. Choose, from document-2, the most precise glassware for the preparation of (S_1)

- Volumetric pipets: 5mL and 10mL
- Graduated pipets: 2mL and 5 mL
- Volumetric flasks:200mL, 250 mL and 500 mL
- Graduated cylinders: 5mL and 10 mL

Document -2

2. Kinetic Study

2.1. Determine the limiting reactant.
2.2. Specify whether the time t = 120s represents the end of the reaction.
2.3. Plot the curve that represents the variation of the number of moles of H_2 gas as a function of time, $n(H_2)=f(t)$ within the time interval [0 ; 120s].
Take the following scale: abscissa: 1cm for 10s ; ordinate: 1cm for 20×10^{-5} mol.
2.4. Deduce, graphically, the variation of the rate of formation of H_2 as a function of time.
2.5. The preceding experiment is repeated with one modification, the solution (S_1) is replaced by hydrochloric acid solution (S_2) of concentration C_2, where $C_2 > C_1$.
Given the following propositions:
2.5.1. The end of the reaction is reached faster.
2.5.2. The number of moles of hydrogen gas produced at the end of the reaction increases.
In the case the proposition is correct. Justify. In the case, the proposition is false. Correct it.

Exercise 2 (7 points) Titration of a Basic Solution

Two flasks are available in the laboratory:
The first contains a white solid of benzoic acid C_6H_5COOH and the second contains sodium hydroxide solution ($Na^+ + HO^-$) of molar concentration C_b mol.L^{-1}.
The aim of this exercise is to determine the concentration C_b of the basic solution.

Given:

- This study is realized at 25°C.
- Molar mass of benzoic acid: M = 122 g.mol^{-1}.

1. Behavior of Benzoic Acid in Water

One prepares a solution (S) of benzoic acid of molar concentration $C_a= 6.5 \times 10^{-3}$mol.L^{-1}. The pH measurement of this solution gives a value of 3.2

1.1. Write the equation of the reaction between benzoic acid and water.
1.2. Determine the dissociation coefficient **α** of benzoic acid. Deduce that benzoic acid is a weak acid.

2. pH-metric Titration of The Sodium Hydroxide Solution

A volume V_a=10.0 mL of benzoic acid solution of concentration $C_a=6.5\times10^{-3}$ mol.L^{-1}, is taken and introduced into a beaker, then a certain volume of distilled water is added to immerse properly the pH -meter electrode. The sodium hydroxide solution of concentration C_b is added progressively.
Some of the experimental results are shown in document-1.

V_b (mL)	0	10	16.2
pH	3.5	4.4	7.6

Document-1

The equation of the titration reaction is:

$$C_6H_5COOH + HO^- \rightarrow C_6H_5COO^- + H_2O$$

2.1. Indicate the appropriate glassware to:

2.1.1. Withdraw the volume V_a of the benzoic acid solution.

2.1.2. Add progressively the sodium hydroxide solution.

2.2. Determine the concentration C_b of the basic solution, knowing that the volume added at equivalence is V_{bE} =16.2mL.

2.3. Justify, based on the chemical species present, the basic character of the solution obtained at equivalence.

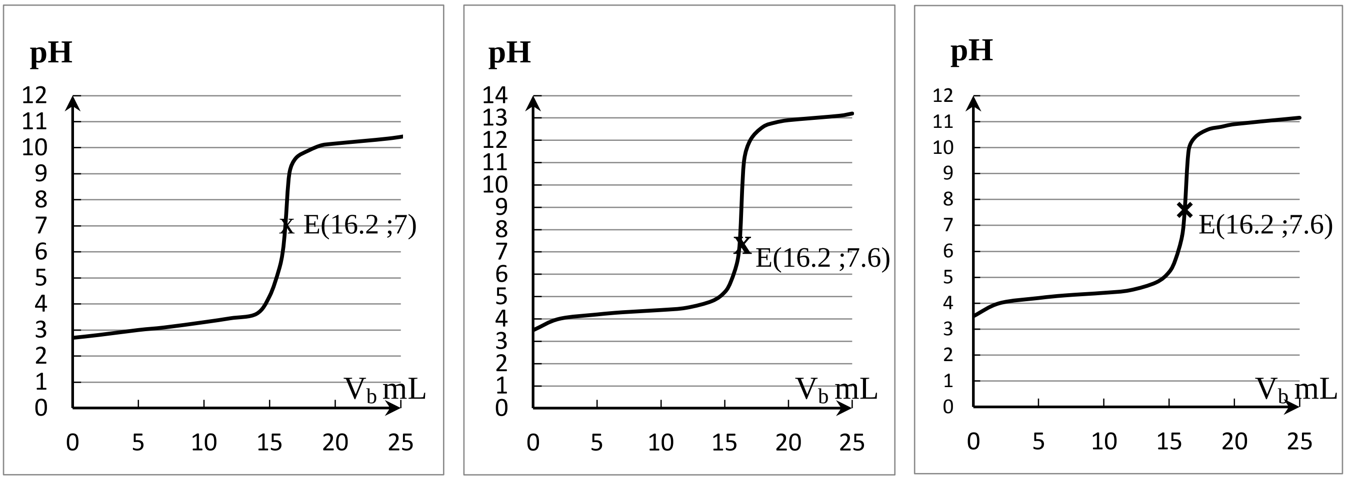
2.4. For a volume V_b of the base added, where $V_b < V_{bE}$.

2.4.1. Show that the pH of the obtained solution is given by the following relation:

$$pH = pK_a + \log \frac{V_b}{V_{bE} - V_b} .$$

2.4.2. Referring to document-1, deduce that the pK_a value of the C_6H_5COOH / $C_6H_5COO^-$ pair is equal to 4.2

2.5. Given the three curves a, b, and c in document-2 which represent the variation of the pH as a function of the volume of the base added. Specify whether each curve corresponds to the above realized titration.



Curve a **Curve b** **Curve c**

Document-2

Exercise 3 (7 points) Study of an Esterification Reaction

Four flasks are available each contains, one of the following organic compounds:
Propanoic acid, 1-propanol, 3-pentanol and 2-butanol.
The available flasks are numbered and their contents are noted as follows:

Number of flask	1	2	3	4
Organic compound	A	B	C	D

Document-1

The aim of this exercise is to identify the content of each flask in order to carry out an esterification reaction.

1. Identification of The Content of Each Flask

The following tests are carried out:

Chemical test	Experimental result
Mild oxidation of compound (A) by an acidified potassium permanganate solution.	An organic compound (F) is obtained which reacts with DNPH and Fehling solution.
The pH of an aqueous solution of compound (B) is measured.	The pH is clearly less than 7.0

Document-2

1.1. Referring to document-2, identify the organic compounds (A) and (B).

1.2. Knowing that the molecule of compound (C) is chiral:

1.2.1. Write its condensed structural formula. Justify its chirality.

1.2.2. Represent according to Cram its two enantiomers.

1.3. Give the condensed structural formula of the compound (D).

2. Esterification Reaction

- For an initial equimolar mixture of a carboxylic acid and a secondary alcohol, the yield of the reaction at equilibrium is 60%.
- Density of the propanoic acid is d = 0.99 $g.mL^{-1}$.
- Molar masses in $g.mol^{-1}$: M (propanoic acid) = 74 ; M (E) = 130.

Document-3

A mixture of 0.25 mol of 2-butanol and a volume V = 30 mL of propanoic acid is heated to reflux. At instant t, heating is stopped. The mass of the ester (E) obtained at instant t is 19.5 g.

2.1. Write, using condensed structural formulas, the equation of the esterification reaction taking place. Name the obtained ester (E).

2.2. Calculate the initial number of moles of propanoic acid.

2.3. Determine the yield of this reaction at instant t.

2.4. Referring to document-3, verify whether the equilibrium is reached at this instant t.

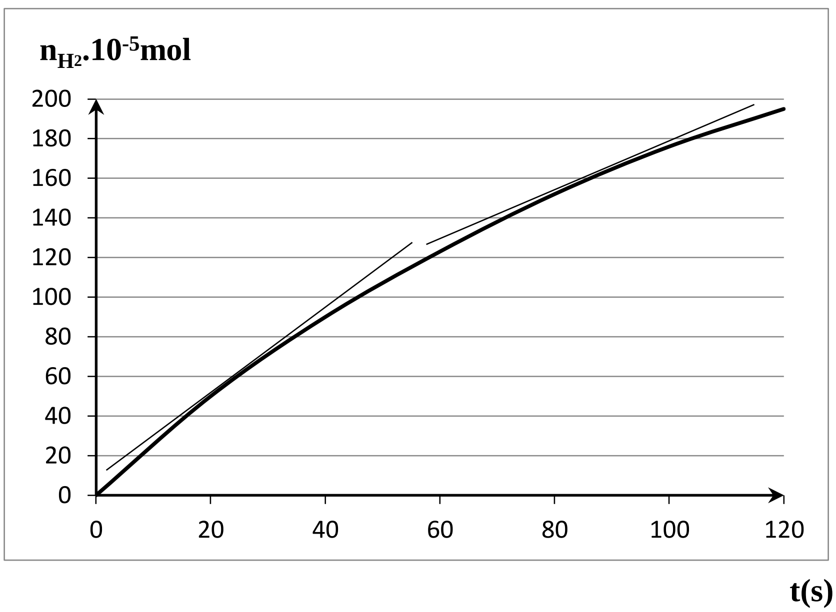
2.5. It is suggested to realize the following modifications during this study:

- Modification 1: Extend the duration of heating.
- Modification 2: Add a catalyst to the initial mixture of the reactants.

Specify the effect of each modification on the yield of this reaction.

Exercice 1 (6 points)

Kinetic of the Reaction of Magnesium with Hydrochloric Acid

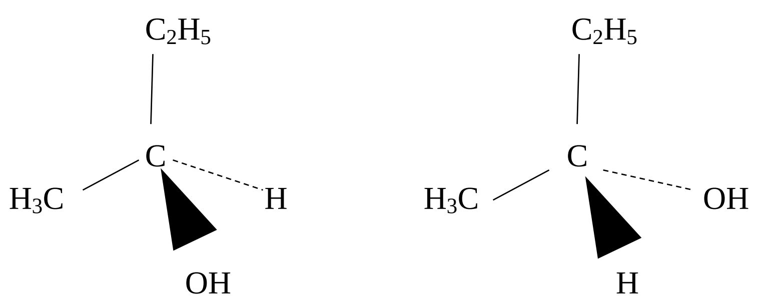
Part of the Q.	Answer	Mark
1.1	$C_0 = \frac{n_{HCl}}{V_S} = \frac{m_{HCl}}{MxV_S} = \frac{dxV_SxP}{MxV_Sx100} = \frac{1130x32.3}{36.5x100} = 10mol.L^{-1}$	0.75
1.2.1	upon dilution the number of moles of solute is conserved $n_0 = n_1$; $C_0V_0 = C_1V_1$; $V_0 = \frac{C_1V_1}{C_0} = \frac{0.2x0.2}{10} = 0.004L$ ou 4mL	0.5
1.2.2	Graduated pipet of 5mL, and volumetric falsk 200mL	0.5
2.1	$n_{Mg} = \frac{m_{Mg}}{M} = \frac{0.15}{24} = 6.25x10^{-3}mol$ $n_{H_3O^+} = C_1V_1 = 0.2x0.1 = 0.02mol$ $R_{Mg} = \frac{n_{Mg}}{1} = 6.25x10^{-3} < R_{H_3O^+} = \frac{n_{H_3O^+}}{2} = 10x10^{-3}$; Mg is the limiting reactant	0.75
2.2	At the end of the reaction: $\frac{n_{H_2(\infty)}}{1} = \frac{n_{Mg(0)}}{1} = 6.25\times 10^{-3} = 6.25\times10^{-5}$ mol From the table $n(H_2)_{120} = 195\times10^{-5}mol < 625\times10^{-5}mol$. Then the time t = 120s doesn't represent the end of the reaction.	0.75
2.3		1
2.4.	The rate of formation of hydrogen gas is equal to the positive slope of the tangent drawn on the curve $n(H_2) = f(t)$ at point of abscissa t. From the curve the slope of the tangent 1 is greater than the slope of tangent 2 therefore the rate of formation of H_2 decreases with time.	0.75
2.5.1	True. Concentration is a kinetic factor. When concentration of H_3O^+ increases the rate of the reaction increases and hence the end of the reaction is attained rapidly (faster).	0.5

2.5.2	False. The number of mole of hydrogen H_2 at the end of the reaction depends only on the limiting reactant, since the limiting reactant Mg doesn't change, then the number of mole of H_2 final remains the same.	**0.5**

Exercise 2 (7 points) Titration of a Basic Solution

Part of the Q	Answer	Mark
1.1.	The equation of the reaction: $C_6H_5COOH + H_2O \rightleftarrows C_6H_5COO^- + H_3O^+$	**0.5**
1.2	$\alpha = \frac{n_{C_6H_5COOH(reacted)}}{n_{C_6H_5COOH(initial)}} = \frac{n_{H_3O^+(formed)}}{n_{C_6H_5COOH(initial)}} = \frac{[H_3O^+]xV(s)}{[C_6H_5COOH]xV(s)}$ $\alpha = \frac{[H_3O^+]_{(formed)}}{[C_6H_5COOH]_0} = \frac{10^{-pH}}{C_a} = \frac{10^{-3.2}}{6.5x10^{-3}} = 0.097$ or 9.7% $\alpha < 1$ then benzoic acid is a weak acid	**1** **0.25**
2.1.1.	Pipet of 10 mL	**0.25**
2.1.2.	Graduated buret	**0.25**
2.2	At equivalence : $n(HO^-)_{\text{added from the burette}} = n(C_6H_5COOH)_{\text{Introduced into the beaker}}$ C_b x V_{bE} = C_a x V_a ; then $C_b = \frac{C_a x V_a}{V_{bE}} = \frac{6.5x10^{-3}x10}{16.2} = 4.0\times10^{-3}$ mol.L^{-1}	**1**
2.3	At equivalence, the chemical species present are: Na^+, $C_6H_5COO^-$ and water. Na^+ is spectator ion, H_2O neutral and $C_6H_5COO^-$ is the conjugate base which renders the nature of the solution basic.	**0,75**
2.4.1	$C_6H_5COOH + HO^- \rightarrow C_6H_5COO^- + H_2O$ Initial state: C_aV_a ; C_bV_b ; - ; solvent Obtained solution: $(C_aV_a - C_bV_b)$; 0 ; C_bV_b ; solvent HO^- is the limiting reactant since $V_b < V_{bE}$. pH (solution) = $pK_a(C_6H_5COOH / C_6H_5COO^-) + \log \frac{[C_6H_5COO^-]}{[C_6H_5COOH]}$ $pH = pK_a + \log \frac{\frac{C_bxV_b}{V(S)}}{\frac{C_axV_a - C_bxV_b}{V(S)}} = pK_a + \log \frac{V_b}{V_{bE} - V_b}$ with $C_aV_a = C_bV_{bE}$	**1**
2.4.2	$pK_a = pH - \log \frac{V_b}{V_{bE} - V_b} = 4.4 - \log \frac{10}{16,2 - 10} = 4.2$	**0,5**
2.5.	- The curve (a) doesn't correspond to the realized titration, since it shows one inflection point, then it corresponds to the titration of a strong acid with a strong base. - The curve (b) doesn't correspond to the realized titration, although it represents two inflection points, but the pH exceeds the limited value $pH = 14 + \log Cb = 14 + \log 4.10^{-3} = 11.6$ - The curve (c) corresponds to the realized titration, since it shows two inflection points and the pH doesn't exceed the value 11.6	**0,5** **0,5** **0,5**

Exercise 3 (7 points) **Study of the esterification reaction**

Part of the Q.	Answer	Mark
1.1.	- The mild oxidation of compound (A) produces a compound (F), since (F) reacts with DNPH and with Fehling's reagent, then (F) is an aldehyde and the compound (A) is a primary alcohol. - (A) is 1-propanol of condensed structural formula: $CH_3 – CH_2 – CH_2OH$ The solution of compound (B) gives a value of pH < 7. Then (B) is a carboxylic acid. (B) is propanoic acid of condensed structural formula: $CH_3 – CH_2 – COOH$	1.5
1.2.1.	The compound (C) is 2-butanol of a condensed structural formula: $CH_3 – CH_2 – {}^{*}CH(OH) – CH_3$ It is chiral molecule since it contains an asymmetric carbon (carbon number 2) which is attached to 4 different atoms or groups of atoms.	0.75
1.2.2		0.75
1.3	(D): $CH_3 – CH_2 – CH(OH) – CH_2 – CH_3$	0.25
2.1	The equation of this reaction is: $CH_3 –CH_2–COOH+CH_3 – CHOH –CH_2 –CH_3 \rightleftharpoons CH_3 – CH_2 – COO – CH(CH_3)–CH_2–CH_3+H_2O$ The name of (E) is : 1-methylpropyl propanoate or 2-butyl propanoate	0.75 0.25
2.2	$n_{acid(initial)} = \frac{m(acid)}{M(acid)} = \frac{d(acid)xV(acid)}{M(acid)} = \frac{0.99x30}{74} = 0.40mol.$	0. 5
2.3	The yield of this reaction: $Y = \frac{n(ester)experimental}{n(ester)theoretical} = \frac{n_1}{n_2}$; and $n_1 = \frac{m(ester)experimental}{M(ester)} = \frac{19.5}{130}$ =0.15 mol and $n_2 = n(alcohol)_{initial}$= 0.25 mol. then Y = 0.60 or 60%.	0.75
2.4	The initial mixture of reactants isn't equimolar; the yield of this reaction at equilibrium should be greater than 60% therefore the equilibrium isn't reached yet.	0. 5
2.5	- Extended duration of heating increases the $n(ester)_{formed}$ and as a result the yield increases. - Adding a catalyst to the initial mixture of reactants: increases the rate of the reaction without affecting the yiled.	0.5 0.5