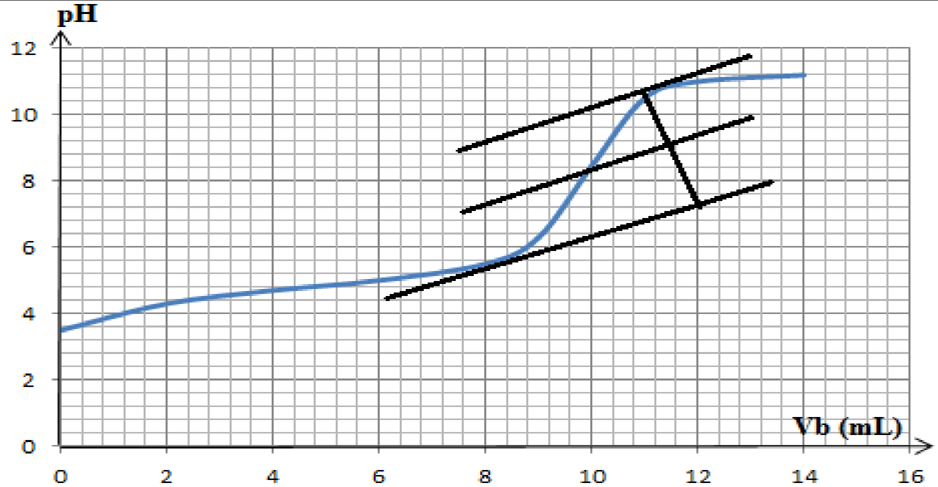
أسس تصحيح مادة الكيمياء

Exercise 1 (7 points)	**The Synthesis of an Organic Compound**	
Part of the Q.	**Answers**	**Note**
1.1	The functional group is an ester group.	**0.25**
1.2	The systematic name of the compound (E) is: 2-methylpropyl methanoate.	**0.5**
2.1	The carboxylic acid (A) is: HCOOH and its name methanoic acid. The alcohol (B) is: $CH_3-\underset{\substack{\vert\\ CH_3}}{CH}-CH_2OH$ and its name is 2-methyl-1-propanol.	**1**
2.2	The alcohol (B) is a primary alcohol.	**0.25**
2.3	The equation of the reaction is: $HCOOH + CH_3-\underset{\substack{\vert\\ CH_3}}{CH}-CH_2OH \rightleftarrows H-\underset{\substack{\Vert\\ O}}{C}-O-CH_2-\underset{\substack{\vert\\ CH_3}}{CH}-CH_3 + H_2O$	**0.5**
2.4.1	Assuming that the reaction is complete; The reacting mixture is stoichiometric since $R(A) = \frac{0.5}{1} = R(B) = \frac{0.5}{1}$ $n(ester)_{theoretical} = n_o(A) = 0.5$ mol.	**0.75**
2.4.2	**Proposition 1:** The reaction is slow since the evolution of the system took more than 50 min to ceases.it takes time to reach the equilibrium state. **Proposition 2:** The reaction is limited since the n(ester) obtained is 0.33 mol less than 0.5 mol.	**0.5** **0.5**
2.4.3	% yield = $\frac{\mathbf{n(ester)\ actual}}{\mathbf{n(ester)\ theorectial}} \times \mathbf{100} = \frac{\mathbf{0.33}}{\mathbf{0.5}} \times \mathbf{100} = \mathbf{66}$ %.	**0.5**
2.5	**Experiment 1:** Starting from an equimolar mixture and since the reaction is athermic reaction; the increase of the temperature does not affect the yield. **Experiment 2:** As one starts from a non-equimolar mixture, the percentage of esterification increases. (The number of moles of the esterified acid increases and therefore the yield of the reaction increases.)	**1**
2.6.1	(D) is methanoyl chloride.	**0.5**
2.6.2	The substitution equation of methanoic acid: $HCOOH + PCl_5 \rightarrow H-COCl + POCl_3 + HCl$	**0.75**

Exercise 2 (7 points)	**Titration of Vinegar**	
Part of the Q.	**Answer**	**mark**
1	During dilution the number of moles of solute is conserved : $f = \frac{Co}{C} = \frac{V}{Vo}$ for $V_{volumetric\ flaks}$ = 250 mL $V_o = \frac{V}{f} = \frac{250}{100}$ = 2.5 mL so the set 2 is convenient since the graduated pipet of 5 mL is used to take the volume V_o.	**1**
2.1		**1**
2.2.1	By using the parallel tangents method: E(10 ; 8.2)	**0.5**
2.2.2	- The curve consists of 4 parts and shows 2 inflection points. - pH_E =8.2 > 7	**0.5**
2.3	The equation of the reaction is : $CH_3COOH + HO^- \rightarrow CH_3COO^- + H_2O$	**0.75**
2.4	At the equivalence point $n(CH_3COOH)_{introduced\ into\ the\ beaker} = n(HO^-)_{added\ to\ reach\ equivalence}$ $Ca \times Va = Cb \times Vb_E$ $Ca = \frac{C_b \times V_{bE}}{V_a} = \frac{2.10^{-2} \times 10 \times 10^{-3}}{20 \times 10^{-3}} = 10^{-2}$ mol.L^{-1}.	**1**
2.5	$f = \frac{Co}{C}$ then $C_o = f \times C = 100 \times 10^{-2} = 1$ mol.L^{-1}. Volume of 100 g of vinegar = $\frac{m_{vinegar}}{d} = \frac{100}{1.02}$ = 98 mL; $m(CH_3COOH) = nxM = C_o \times V \times M(CH_3COOH) = 1 \times 98 \times 10^{-3} \times 60 = 5.9$ g the degree of acidity of this white vinegar solution is 5.9°	**1**
2.6	Since pH_E = 8.2 is not included in the pH change range of this colored indicator, so methyl orange is not an appropriate colored indicator for this titration.	**0.5**
3.1	$K_R = \frac{[CH_3COO^-]\ X\ [CO_2,H_2O]}{[CH_3COOH]X\ [HCO_3^-]}$ x $\frac{[H_3O^+]}{[H_3O^+]} = \frac{Ka(CH_3COOH/CH_3COO^-)}{Ka\ (CO_2,H_2O/HCO_3^-)} = \frac{10^{-4.8}}{10^{-6.4}} = 10^{(-4.8+6.4)} = 10^{1,6}$ $K_R < 10^4$; so the reaction is limited.	**0.5**
3.2	The release of CO_2 gas as the reaction proceeds shifts the equilibrium in the direction of formation of CO_2.	**0.25**

Exercise 3 (6 points)	Kinetic Study of a Slow Reaction	
Part	**Answers**	**Note**
1.1	Hydrochloric acid is a strong acid; $C_0 = [H_3O^+] = 10^{-pH_0} = \frac{1}{10^{pH_0}}$.	**0.5**
1.2	pH = -log $[H_3O^+]$, since the molar concentration of H_3O^+ ions decreases during this transformation (H_3O^+ is a reactant of this transformation) so pH increases.	**0.5**
1.3	At the end of the reaction the reactants are consumed totally (stoichiometric mixture), the reacting mixture contains Zn^{2+} ions and Cl^- ions (spectator ions with no acid or base character) and water (solvent) which is a species which is neutral so pH = 7.	**0.5**
2.1.1	$r_t(Zn^{2+})$ = slope of the tangent drawn to the curve at a point t ; graphically the slopes of the tangents decrease with respect to time, so the rate of formation of Zn^{2+} decreases with time.	**0.5**
2.1.2	By definition t ½ is the time needed to form the half od the maximal concentration of Zn^{2+} ions. So $[Zn^{2+}]_{max.} = 2\times[Zn^{2+}]_{t1/2} = 2 \times 12.5\times10^{-3} = 0.025$ mol.L^{-1}.	**0.5**
2.1.3	According to the stoichiometric ratios: $\frac{n_o(H_3O^+)}{2} = \frac{n(Zn^{2+})max}{1}$ In the same volume : $\frac{Co}{2} = \frac{[Zn^{2+}]max}{1}$ So $C_0 = 2 \times [Zn^{2+}]_{(max)} = 2 \times 0.025 = 0.050 = 50\times10^{-3}$ mol.L^{-1}.	**0.5**
2.2	Answer (**d**) By stoichiometry : $r_o(H_3O^+) / 2 = r_0(Zn^{2+}) = S_0$ and $r_0(Zn^{2+}) = S_0$ So $r_o(H_3O^+) = 2S_0$	**0.5**
2.3.1	According to the stoichiometric ratios and at each instant t of the reaction: $\frac{n(H_3O^+)reacted}{2} = \frac{n(Zn^{2+})formed}{1}$ $n(Zn^{2+})_{formed} = (n_o(H_3O^+) - n(H_3O^+)_{reacted})/ 2$ Divide by $V_{Solution}$: $[Zn^{2+}]_t = ½ ([H_3O^+]_0 - [H_3O^+]_t)$ So $[Zn^{2+}]_t = \frac{1}{2}(C_0 - 10^{-pH})$	**0.75**
2.3.2	A t = 5 min; $[Zn^{2+}] = 6 \times 10^{-3}$ mol.L^{-1} (from the curve) $6\times 10^{-3} = \frac{1}{2}(50 \times 10^{-3} - 10^{-pH})$ $10^{-pH} = 38 \times10^{-3}$ $-\log (10^{-pH}) = - \log (38 \times 10^{-3})$ Therefore pH = 1.42	**0.25**
3.1	False At constant temperature, the concentration of hydrochloric acid solution is a kinetic factor , when it increases the rate of the reaction increases , so at the same instant we have: $[Zn^{2+}]_{2nd\ experiment} > [Zn^{2+}]_{1st\ experiment}$ especially at t = 6 min	**0.75**
3.2	True The concentration of hydrochloric acid increases and it becomes in excess and the initial mass of Zn (limiting reactant) does not change, so the molar concentration of Zn^{2+} ions at the end of the reaction remains the same.	**0.75**

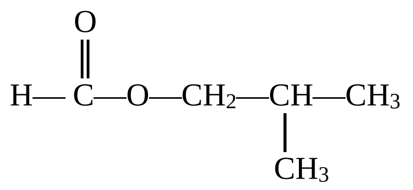
مسابقة في مادة الكيمياء — الاسم:
المدة: ساعتان — الرقم:

This Exam Includes Three Exercises. It Is Inscribed On Three Pages Numbered From 1 to 4.
The Use of a Non-programmable Calculator Is Allowed.

Answer the Following Three Exercises:

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.**



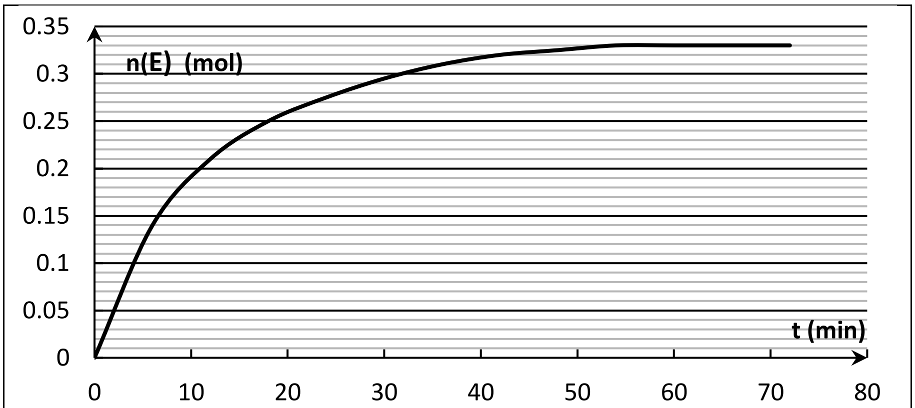
Document-1

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 (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 **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.



Document-2

2.4.1. Determine the theoretical number of moles of the organic compound (E) formed.

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.

2.5. In order to increase the yield of this reaction, the two experiments of **document-3** are suggested:

	Carboxylic acid (A)	Alcohol (B)	Sulfuric acid	Temperature
Experiment 1	0.5 mol	0.5 mol	Few drops	$T_1 > T$
Experiment 2	0.5 mol	2.5 mol	Few drops	T

Document-3

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. Name the compound (D).

2.6.2. Write, using condensed structural formulas, the equation of preparation reaction of (D) from the carboxylic acid (A).

Exercise 2 (7 points) Titration of Vinegar

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 degree of acidity of vinegar corresponds to the mass (in g) of ethanoic acid in 100g of vinegar.
-The condensed structural formula of ethanoic acid is CH_3COOH.

Document-1

Given:

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

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

A commercial white vinegar solution (S_0) is diluted 100 times. A solution (S) is obtained.
Choose from **document-2** the most convenient set in order to prepare the solution (S). Justify.

Set 1	Set 2	Set 3
Volumetric flask of 250 mL Volumetric pipet of 5 mL Beaker of 50 mL	Volumetric flask of 250 mL Graduated pipet of 5 mL Beaker of 50 mL	Volumetric flask of 250 mL Graduated cylinder of 5 mL Beaker of 50 mL

Document-2

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

A volume V_a = 20.0 mL 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 ($Na^+ + HO^-$) of molar concentration $C_b = 2.0 \times 10^{-2}$ $mol.L^{-1}$.
The results are grouped in the table of **document-3**.

V_b (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: pH = f (V_b).

Take the following scales: In abscissa: 1 cm ⟶ 1 mL ; in ordinates: 1 cm ⟶1 pH unit.

2.2. Referring to the curve pH = f (V_b) :

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.

2.4. Determine the molar concentration of ethanoic acid in solution (S).

2.5. Deduce the degree of acidity of the commercial white vinegar solution.

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:

- pKa (CO_2,H_2O / HCO_3^-) = 6.4 ; pKa (CH_3COOH/CH_3COO^-) = 4.8
- CO_2 is a gas slightly soluble in water.

A volume of white vinegar is introduced into a flask containing sodium hydrogen carbonate. A reaction takes place according to the following equation:

$$CH_3COOH + HCO_3^- \rightleftarrows CH_3COO^- + CO_2, H_2O$$

3.1. Verify that this reaction is limited.

3.2. Specify the effect of the CO_2 release on the displacement of equilibrium.

Exercise 3 (6 points) Kinetic Study of a Slow Reaction

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

$$Zn_{(s)} + 2\,H_3O^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + 2\,H_2O_{(l)} + H_{2\,(g)}$$

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

Given:

- The study takes place at 25 ^{0}C.
- Zn^{2+} and $C\ell^-$ are spectator ions with no acid and base character.
- Hydrogen gas (H_2) is insoluble in water.

A mass m of powdered zinc is introduced into a flask containing a volume V_0 = 100 mL of hydrochloric acid solution (H_3O^+ + $C\ell^-$) of molar concentration C_o and pH_o as initial pH. **The reacting mixture is a stoichiometric mixture.**

1. Preliminary Study

1.1. Choose , with justification , the relation between pH_o and C_o :

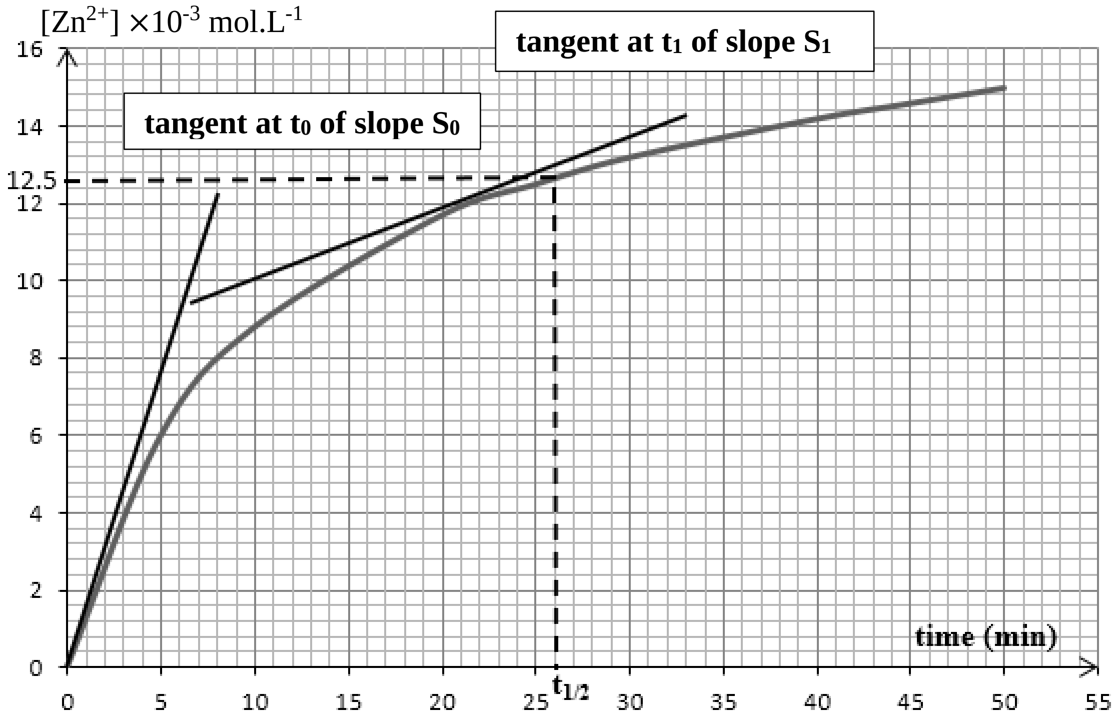
a. $C_o = \frac{1}{pH_0}$ **b.** $C_o = \frac{1}{10^{pH_0}}$ **c.** $C_o = \frac{1}{10^{-pH_0}}$

1.2. Indicate how the pH of the solution varies with the evolution of the reaction. Justify.

1.3. Specify, based on the chemical species present in the reacting mixture, the value of the pH at the end of the reaction.

2. Kinetic Study

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

2.1.2. Determine the value of the concentration of Zn^{2+} ions at the end of the reaction.

2.1.3. Show that the molar concentration C_o is equal to 50×10^{-3} mol.L^{-1}.

2.2. By referring to **document-1** and to the equation of the reaction, choose the relation between the initial rate of disappearance of H_3O^+ ions $r_o(H_3O^+)$ and the slope S_o of the tangent. Justify.

a. $r_o(H_3O^+) = -S_o$ **b.** $r_o(H_3O^+) = -2S_o$ **c.** $r_o(H_3O^+) = S_o$ **d.** $r_o(H_3O^+) = 2S_o$

2.3. The concentration of the Zn^{2+} ions is related to the pH of the solution.

2.3.1. Show that the molar concentration of the Zn^{2+} ions, denoted by $[Zn^{2+}]_{(t)}$, formed at each instant of time t of the evolution of the reaction is related to the pH of the solution by the following relation:

$$[Zn^{2+}]_t = \frac{1}{2}(C_o - 10^{-pH}).$$

2.3.2. Deduce the pH of the solution at t = 5 min.

3. Study of The Effect of a Kinetic Factor

The previous experiment is carried out again but with only one modification: a volume $V_o = 100$ mL of a hydrochloric acid solution is used of molar concentration $C_1 > C_o$ is used

For each proposition answer by true or false. Justify you answer.

3.1. The molar concentration of Zn^{2+} ions at t = 5 min remains equal to 6×10^{-3} mol.L^{-1}.

3.2. The molar concentration of Zn^{2+} ions at the end of the reaction is equal to that found in the question **(2.1.2).**