مسابقة في مادة الكيمياء — الاسم:
المدّة: ساعة ونصف — 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 of a Slow Reaction

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

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

In order to study the kinetic of this reaction, one introduces a mass m = 0.12 g of magnesium in an Erlenmeyer flask.
At instant t = 0, a volume V = 100.0 mL of a hydrochloric acid solution (S) of molar concentration **C** is poured into the Erlenmeyer flask.
Using an appropriate method, the number of moles of hydrogen gas $n(H_2)$ is determined at different instants t.
The results are grouped in the table of **Document-1**:

t (min)	2	4	6	8	10	12	14	16
n (H_2) 10^{-4} mol	8	14	18.8	22.2	25	26.8	28.2	29

Document-1

<u>Given:</u>
- Molar mass of magnesium (Mg) is: M = 24 $g.mol^{-1}$
- The study is realized at a temperature T = 25°C.
- H_3O^+ is the only chemical species with acid character in the reacting system.

1- Preparation of Hydrochloric Acid Solution (S)

The solution (S) is prepared by diluting 50 times a hydrochloric acid solution (S_0).
Choose, from **Document-2,** the most precise set for the preparation of solution (S). Justify.

Set 1	**Set 2**	**Set 3**
Beaker of 100 mL Graduated cylinder of 10 mL Volumetric flask of 500 mL	Beaker of 100 mL Volumetric pipet of 10 mL Volumetric flask of 500 mL	Beaker of 100 mL Volumetric pipet of 10 mL Volumetric flask of 250 mL

Document-2

2- Preliminary Study

At the end of the reaction, the pH of the obtained solution is: pH = 0.77
2.1. Deduce that magnesium is the limiting reactant.
2.2. Specify whether the instant t = 16 min represents the end time of this reaction.

3- Kinetic Study

3.1. Plot the curve that represents the variation of the number of moles of hydrogen gas (H_2) as a function of time: $n(H_2) = f(t)$ within the interval of time [0 – 16 min]
Take the following scale: Abscissa: 1cm for 1 min
Ordinate: 1cm for 2×10^{-4} mol.

3.2. Determine the half-life time of the reaction $t_{1/2}$.

3.3. Choose the correct answer. Justify.

3.3.1. The rate of the reaction at a given instant t denoted by r_{rxn} and the rate of disappearance of H_3O^+ ions at same instant t denoted by $r_{(H_3O^+)t}$ are related by the following relation:

a) $r_{rxn} = \frac{r_{(H_3O^+)t}}{2}$ **b)** $r_{rxn} = 2r_{(H_3O^+)t}$ **c)** $r_{rxn} = r_{(H_3O^+)t}$

3.3.2. The rate of the disappearance of H_3O^+ at instant t_1 = 6 min is $r_1 = 2.05 \times 10^{-4}$mol.min^{-1}.The rate of disappearance of H_3O^+ at instant t_2 =12 min is:

a) $r_2 = 4.1 \times 10^{-4}$mol.min^{-1} **b)** $r_2 = 2.05 \times 10^{-4}$mol.min^{-1} **c)** $r_2 = 0.86 \times 10^{-4}$mol.min^{-1}

3.3.3. When the above experiment is carried out at a temperature T' >T (as the only modification), the number of moles of H_2 at instant t =12 min is:

a) $n(H_2) > 26.8 \times 10^{-4}$mol **b)** $n(H_2) < 26.8 \times 10^{-4}$mol **c)** $n(H_2) = 26.8 \times 10^{-4}$mol

Exercise 2 (6 points) Sulfamic Acid

Sulfamic acid is a white crystalline solid which is an efficient agent for descaling. It is used for cleaning a number of domestic appliances and industrial equipment.

The aim of this exercise is to study the behavior of sulfamic acid in water and to determine the mass composition of sulfamic acid in a sulfamic acid based powder descaling agent.

Given:

- Molar mass of sulfamic acid is: M = 97.0 g.mol^{-1}
- This study is carried out at 25 °C

1. Behavior of Sulfamic Acid in Water

Available is, in the laboratory, a sulfamic acid solution (S) of molar concentration $C = 1.0 \times 10^{-2}$ mol.L^{-1}.
The pH of the solution (S) is measured and found to be $pH_{(S)} = 2.0$

1.1. Calculate the molar concentration of hydronium ions, $[H_3O^+]$, in the solution (S).

1.2. Justify that sulfamic acid is a strong acid.

1.3. For each of the two following statements, justify when the statement is true and correct when it is false:

1.3.1. The equation of the reaction of sulfamic acid(denoted by HA) with water is:

$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$

1.3.2. The dilution 100 times of the solution (S), increases its pH by 2 units.

2. Determination of the Mass Composition of a Descaling Agent

A sample of sulfamic acid based powder descaling agent of mass m = 1.00 g is used to prepare a solution (S′) of volume V = 1.0 L.

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 volume of the basic solution needed to reach equivalence is V_{bE} = 9.8 mL.

2.1. Name the glassware needed to add the basic solution.
2.2. Write the equation of the titration reaction.
2.3. Determine the molar concentration of sulfamic acid in the solution (S′).
2.4. Calculate the mass of sulfamic acid in 1L of the solution (S′).
2.5. Deduce the percentage by mass of sulfamic acid in the descaling agent.

Exercise 3 (7 points) — Isobutyl Propanoate

Esters of general formula RCOOR' are very abundant in nature. Many of them have agreeable characteristic odor and contribute to natural or artificial tastes and flavors of certain fruits, plants, and candies.

The aim of this exercise is to study the preparation reaction of isobutyl propanoate which characterizes the rum odor.

1. Study of the Structure of Propanoic Acid

The molecular formula of propanoic acid is $C_3H_6O_2$
1.1. Write the condensed structural formula of propanoic acid.
1.2. Circle and name the functional group of this acid.

2. Isobutyl Alcohol

The condensed structural formula of isobutyl alcohol is given in **Document-1.**

$CH_3 - CH - CH_2OH$
|
CH_3

Document-1

2.1. Give the systematic name of isobutyl alcohol.
2.2. Identify the class of this alcohol.

3. Synthesis of Isobutyl Propanoate

Isobutyl propanoate can be prepared starting from isobutyl alcohol and propanoic acid.

3.1. Write, using condensed structural formulas, the equation of the preparation reaction of isobutyl propanoate.
3.2. Give the systematic name of the ester formed.
3.3. An equimolar mixture (M) containing 0.1 mol of isobutyl alcohol and 0.1 mol of propanoic acid is heated to reflux for 40 min in the presence of few drops of concentrated sulfuric acid as a catalyst.
The mass of the ester obtained is 8.71g.

- For an initial equimolar mixture of a carboxylic acid and a primary alcohol, the yield of the reaction at equilibrium is 67%.
- Molar mass of isobutyl propanoate is: M = 130 $g.mol^{-1}$.

Document-2

3.3.1. Indicate the importance of the reflux heating.

3.3.2. Determine the yield of this esterification reaction at t = 40 min.

3.3.3. Verify that the reacting system is at equilibrium at this instant.

3.3.4. Another reacting mixture containing 0.1 mol of isobutyl alcohol and 0.1 mol of propanoyl chloride is prepared.

3.3.4.1. Write, using condensed structural formulas, the equation of the preparation of propanoyl chloride starting from propanoic acid.

3.3.4.2. Choose, with justifying, the correct answer.
The mass m of the ester obtained at the end of the reaction is:

a) m= 8.71g **b)** m < 8.71 g **c)** m > 8.71 g

أسس التصحيح

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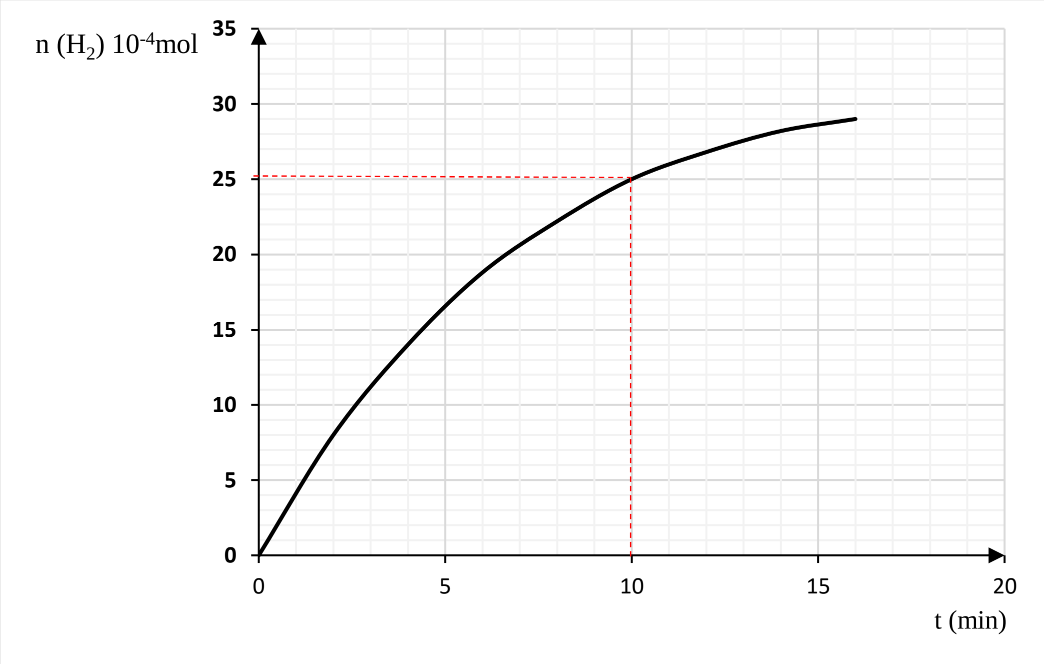
Exercise 1 (7points)

Kinetic Study of a Slow Reaction

Part of the Q.	Answer	Mark
1	During dilution, the number of moles of solute is conserved Dilution factor = $\frac{C_o}{C} = \frac{V}{V_0}$ For V = 500 mL ; $V_o = \frac{V}{F} = \frac{500}{50} = 10$ mL We must use a volumetric pipet of 10 mL and a volumetric flask of 500 mL Then set 2	**1**
2.1	Since the pH of the obtained solution is 0.77 < 7 so, the final medium is acidic, therefore the hydrochloric acid is in excess and magnesium is the limiting reactant.	**0.75**
2.2	$n(Mg) = \frac{m(Mg)}{M(Mg)} = \frac{0,12}{24} = 50\times10^{-4}$ mol $\frac{n(Mg)_o}{1} = \frac{n(H_2)_\infty}{1}$ Then $n(H_2)_\infty = 50\times10^{-4}$ mol > $n(H_2)_{at\ t\,=\,16\ min} = 29\times10^{-4}$ mol So t = 16 min does not represent the end time of the reaction.	**1**
3.1		**1**
3.2	The half-life time of the reaction is the time needed for the formation of half the maximum quantity of the product. $n(H_2)_{t1/2} = \frac{n(H_2)_\infty}{2} = \frac{50\times10^{-4}}{2} = 25\times10^{-4}$ mol Graphically $t_{1/2}$ = 10 min	**1**
3.3.1	a since from the stoichiometric ratios:	**0.75**

	r(reaction) = $\frac{r(disappearance\ of\ H_3O^+ ions\ )}{2}$	
3.3.2	c $[H_3O^+]$ decreases with time (kinetic factor) so the rate of disappearance of H_3O^+ ions deceases with time.	**0.75**
3.3.3.	a Since the temperature increases, the rate of formation of hydrogen increases. Therefore at t = 12 min: $n(H_2)_{\text{formed at temperature T}'} > n(H_2)_{\text{formed at temperature T}}$	**0.75**

Exercice 2 (6points) **Sulfamic Acid**		
Part of the Q.	**Answer**	**Mark**
1.1	$[H_3O^+] = 10^{-pH} = 10^{-2}$ mol.L^{-1}	**0.5**
1.2	Since $[H_3O^+]$ = C then sulfamic acid is a strong acid.	**0.5**
1.3.1	$HA + H_2O \longrightarrow A^- + H_3O^+$	**0.5**
1.3.2	When the solution is diluted 100 times, its concentration becomes $C = \frac{C_o}{100} = \frac{10^{-2}}{100} = 10^{-4}$ mol.L^{-1} pH = -log C = -log 10^{-4} = 4 pH – pH$_o$ = 4 – 2 = 2 So the pH increases by 2 units.	**0.75**
2.1	Graduated buret	**0.5**
2.2	$H_3O^+ + HO^- \rightarrow 2H_2O$	**0.75**
2.3	At the equivalence point : $n(H_3O^+)_{\text{introduced into the beaker}} = n(HO^-)_{\text{added to reach equivalence}}$ $C_a \times V_a = C_b \times V_{bE}$ $Ca = \frac{C_b \times V_{bE}}{V_a} = \frac{2\times10^{-2} \times 9.8 \times 10^{-3}}{20 \times 10^{-3}} = 0.0098$ mol.L^{-1}	**1.25**
2.4	n (sulfamic acid) = C × V = 0.0098 × 1 = 0.0098 mol m(sulfamic acid) = n . M = 0.0098 × 97 = 0.9506 g	**0.5**
2.5	$\% = \frac{m(sulfamic\ acid)}{m(\text{descaling})} \times 100 = \frac{0.9506}{1} \times 100 = 95.06\%$	**0.75**

Exercise 3 (7 points) **Isobutyl Propanoate**		
Part of the Q.	**Answer**	**Mark**
1.1	The condensed structural formula of propanoic acid is **$CH_3 – CH_2 – COOH$**	**0.5**
1.2	**$CH_3 – CH_2 – COOH$** (COOH circled) The functional group of this acid is carboxyl group.	**0.5**
2.1	The systematic name of isobutyl alcohol is : 2-methyl-1-propanol	**0.5**
2.2	This alcohol is a primary alcohol since the functional carbon is connected to one alkyl	**0.5**

	group.	
3.1	$\mathbf{CH_3 - CH_2 - COOH + CH_3 - CH - CH_2OH \rightleftharpoons CH_3 - CH_2 - COO - CH_2 - CH - CH_3 + H_2O}$ | | $\mathbf{CH_3}$ $\mathbf{CH_3}$	**1**
3.2	the systematic name of the ester formed is 2-methylpropylpropanoate	**0.5**
3.3.1	The reflux heating accelerates the rate of the esterification reaction without any loose of reactants or products due to evaporation.	**0.5**
3.3.2	$\%Yield = \frac{n(ester)actual}{n(ester)theoratical} \times 100$ $n(ester)_{actual} = \frac{m(ester)actual}{M} = \frac{8.71}{130} = 0.067$ mol assuming that the reaction is complete: $R(alcohol) = \frac{n(alcohol)}{1} = 0.1$ $R(acid) = \frac{n(acid)}{1} = 0.1$ Then the mixture is stoichiometric $n(ester)_{theoretical} = n(alcohol) = 0.1$ mol $\%Yield = \frac{n(ester)actual}{n(ester)theoratical} \times 100 = \frac{0.067}{0.1} \times 100 = 67\ \%$	**1**
3.3.3	Since the initial mixture of a carboxylic acid and a primary alcohol is equimolar and the yield of the reaction at equilibrium is 67% then the reacting system is at equilibrium at this instant.	**0.5**
3.3.4.1	True Since this mixture is an equimolar mixture.	**0.75**
3.3.4.2	False $\%Yield = \frac{n(ester)actual}{n(ester)theoratical} \times 100$ $n(ester)_{actual} = \frac{\%Yield \times n(ester)theoratical}{100} = \frac{67 \times 0.2}{100} = 0.134$ mol $m(ester)_{actual} = n \times M = 0.12 \times 130 = 17.42$ g	**0.75**

Special part LS

3.3.4.1	$CH_3 - CH_2 - COOH + PCl_5 \longrightarrow CH_3 - CH_2 - COCl + HCl + POCl_3$	**0.75**
3.3.4.2	c since the esterification reaction using propanoyl chloride instead of propanoic acid becomes complete.	**0.75**