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

This Exam Includes Three Exercises. It is Inscribed on 4 Pages Numbered from 1 to 4.
The use of Non-Programmable Calculator is allowed.

Answer the three Following Exercises :

Exercise 1 (7 points) Kinetic Study of the Oxidation of an Alcohol

The mild oxidation of 2- propanol by a potassium permanganate solution ($K^+ + MnO_4^-$) in acidic medium takes place according to a slow and complete reaction represented by the equation given below:

$$5\ C_3H_8O\ +\ 2\ MnO_4^-\ +\ 6\ H^+ \rightarrow 5\ C_3H_6O\ +\ 2\ Mn^{2+}\ +\ 8\ H_2O$$

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

Given: The density of 2-propanol: $d(C_3H_8O) = 0.79$ g.mL^{-1}
Molar masses in g.mol^{-1}: $M(KMnO_4) = 158$; $M(C_3H_8O) = 60$

1. Preparation of a Solution (S) of Potassium Permanganate

1.1. Calculate the mass of solid $KMnO_4$ necessary to prepare 250 mL of a solution (S) of potassium permanganate ($K^+ + MnO_4^-$) of concentration C = 0.1 mol.L^{-1}.

1.2. List the essential materials needed to realize the preparation of this solution (S).

2. Kinetic Study

To study the kinetic of this reaction, a volume V = 100 mL of the solution (S) of potassium permanganate of concentration C = 0.1 mol.L^{-1} is introduced into an Erlenmeyer flask then few mL of concentrated sulfuric acid solution are added . (sulfuric acid is in excess)
At instant t = 0, 1 mL of pure 2- propanol is added to the content of the Erlenmeyer flask.
At different instants t, a volume V_1 = 10.0 mL of the reacting mixture is removed and poured into a beaker containing 40 mL of ice water. By an appropriate method, the permanganate ions MnO_4^- contained in the beaker are titrated, and then the number of moles of C_3H_6O formed is deduced at each instant t.
The obtained results are given in the table of **document-1**.

t (min)	1	2	3	4	6	10	15	20
n(C_3H_6O) (mmol)	3.5	5.5	6.8	7.8	9.3	11	12	12.6

Document-1

2.1. Plot the curve representing the variation of the number of moles of (C_3H_6O) as a function of time: $n(C_3H_6O) = f(t)$ in the interval of time [0 – 20 min].
Take the following scales: In abscissa : 1cm for 2 min
In ordinates: 1cm for 1 mmol.

2.2. Show that C_3H_8O is the limiting reactant.

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

2.4. Specify whether each of the following propositions is true or false.

2.4.1. The introduction of volume V_1 = 10.0 mL of the reacting mixture into a beaker containing 40 mL of ice water blocks the oxidation reaction of 2-propanol.

2.4.2. Sulfuric acid plays the role of a catalyst for this reaction.

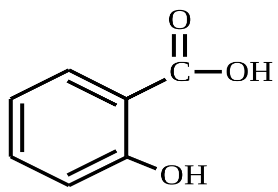
2.5. The experiment realized above is repeated, but with one modification: the volume V = 100 mL of the solution (S) of potassium permanganate is introduced in an Erlenmeyer flask containing initially 100 mL of distilled water. Trace, on the same graph of question 2.1, the shape of the curve representing the variation of the number of moles of (C_3H_6O) as a function of time: $n(C_3H_6O) = g(t)$ in the interval of time [0 – 20 min]. Justify.

Exercise 2 (7points) **Salicylic Acid**

The label of a bottle of wart remover liquid shows, among others, the information listed in **document-1**

- Volume of the solution : 5 mL - Mass of the solution : 4g - Active ingredient: Salicylic acid
Document-1

The aim of this exercise is to determine the mass of salicylic acid in 100 g of the wart remover solution noted as S_o. The condensed structural formula of salicylic acid is given in **document-2**



Document-2

Given:
- Salicylic acid, considered as a monocarboxylic acid, is the only species in the solution (S_0) having an acid- base character.
- The study is carried out at 25 °C.
- Molar mass of salicylic acid: M =138 $g.mol^{-1}$

1. Behavior of Salicylic Acid in Water

Available is a salicylic acid solution of molar concentration C = 1.16×10^{-2} $mol.L^{-1}$. The pH of this solution is found to be 2.52

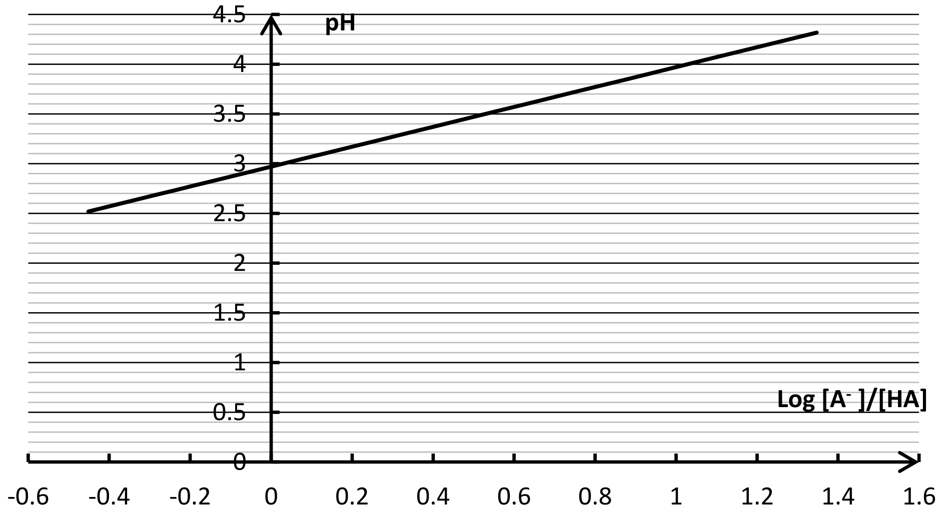
1.1. Verify that salicylic acid is a weak acid.

1.2. Give the condensed structural formula of its conjugate base.

1.3. Write the equation of the reaction of salicylic acid (noted HA) with water.

1.4. Document-3 shows the variation of pH of a solution of salicylic acid as a function of log $\frac{[A^-]}{[HA]}$, where [HA] and $[A^-]$ are the molar concentrations of salicylic acid and its conjugate base respectively.

Deduce, from **document-3**, the value of the pKa of the pair (HA/A^-).



Document-3

2. Preparation of a Dilute Solution (S) of Salicylic Acid

The solution (S_o) is diluted 50 times . A solution (S) is obtained .
Choose, from the sets of the **document-4**, the most convenient one for realizing this dilution. Justify.

Set 1	Set 2	Set 3
10 mL volumetric pipet 500 mL volumetric flask 50 mL beaker	5 mL graduated cylinder 500 mL volumetric flask 50 mL beaker	2 mL volumetric pipet 100 mL volumetric flask 50 mL beaker

Document-4

3. Titration of Salicylic Acid in the Solution (S)

A volume V_1 = 20.0 mL of the solution (S) is introduced into a beaker. Then 20 mL distilled water is added into this beaker to immerse properly the pH-meter electrode , then a pH-metric titration is carried out by adding a sodium hydroxide solution ($Na^+ + HO^-$) of molar concentration $C_B = 1.0\times10^{-2}$ mol.L^{-1} .
The volume of the basic solution added to reach equivalence is found to be V_{BE} = 23 mL.

3.1. Name the glassware needed to:

3.1.1. withdraw the volume V_1 .

3.1.2. add the sodium hydroxide solution.

3.2. Write the equation of the titration reaction. (Salicylic acid is noted as HA)

3.3. Determine the concentration C_1 of salicylic acid in the solution (S). Deduce the value of the concentration C_o of salicylic acid in the solution (S_o).

3.4. Calculate the percentage by mass of salicylic acid in the solution (S_o).

4. Reaction Between Salicylic Acid And Ethanoic Acid

Under specific conditions, salicylic acid undergoes an esterification reaction with ethanoic acid.

4.1. Write, using condensed structural formulas, the equation of this reaction.

4.2. State two characteristics of this reaction.

Exercise 3 (6 points) Organic Compound (A)

Available is a saturated non–cyclic chain monofunctional organic compound (A) having a characteristic fruity odor and a corresponding bittersweet flavor.
Document -1 shows the results of the elemental analysis of the organic compound (A) of formula $C_xH_yO_2$

- Percentage by mass of carbon: % (C) = 54.55 %
- Percentage by mass of hydrogen: % (H) = 9.1%

Document-1

Given: Molar masses in g.mol^{-1}: M (H) =1; M (C) = 12; M (O) = 16

1. Chemical Family of the Compound (A)

1.1. Show that the molecular formula of (A) is $C_4H_8O_2$

1.2. Give the possible chemical families of the compound (A).

1.3. The organic compound (A) is slightly soluble in water. At 25°C, the pH of its solution is equal to 7. Deduce the chemical family of the compound (A).

2. Identification of the Compound (A)

The hydrolysis reaction of the compound (A) takes place according to the following equation:

$$\underset{(A)}{C_4H_8O_2} + H_2O \rightleftharpoons \underset{(B)}{H_2CO_2} + \underset{(C)}{C_3H_8O}$$

2.1. Write the condensed structural formula of B and give its systematic name.

2.2. Give the possible condensed structural formulas of the compound (C).

2.3. In order to identify the organic compound (C), the following experimental activities are carried out:

1st Activity: The compound (C) is oxidized with an acidified potassium permanganate solution ($K^+ + MnO_4^-$). An organic compound (D) is obtained.

2nd Activity: A solution of 2.4-D.N.P.H is added to the compound (D). A yellow-orange precipitate is obtained.

3rd Activity: A mixture of the compound (D) and a blue Fehling's solution is heated gently. A brick-red precipitate is observed.

2.3.1. Based on the results of the three above activities, show that the compound (C) is 1-propanol.

2.3.2. Identify the organic compound (A).

3. Yield of the Preparation Reaction of the Compound (A)

Document-2 shows two reacting mixtures used to prepare the compound (A) starting from the compound (B) and the compound (C)

Number of the preparation	Reacting mixture	Yield
1	Pure compound (C) + Pure compound (B)	$\mathbf{Y_1}$
2	Pure compound (C) + Aqueous solution of compound (B)	$\mathbf{Y_2}$

Document-2

3.1. Compare $\mathbf{Y_1}$ and $\mathbf{Y_2}$ knowing that the two reacting mixtures contain the same number of moles of each reactant. Justify.

3.2. Write, using condensed structural formulas, the equation of another preparation reaction giving a yield higher than $\mathbf{Y_1}$ **and** $\mathbf{Y_2}$**.**

وزارة التربية والتعليم العالي
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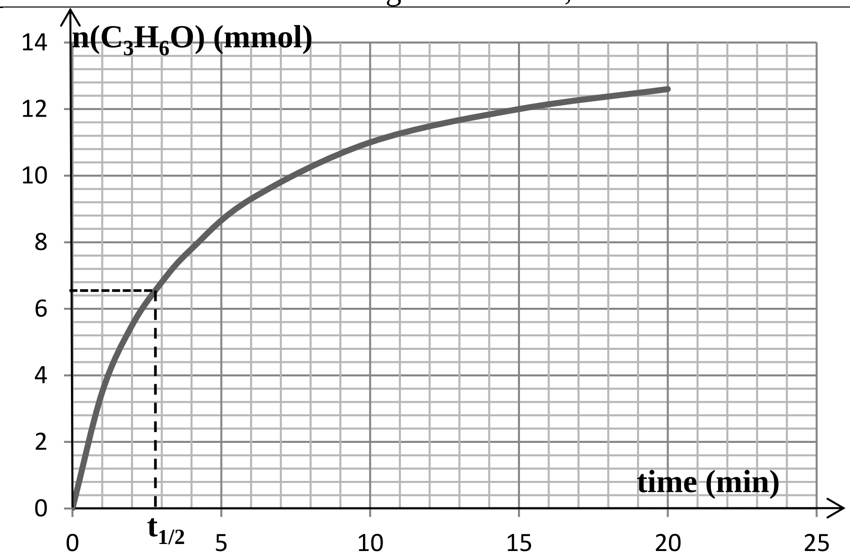
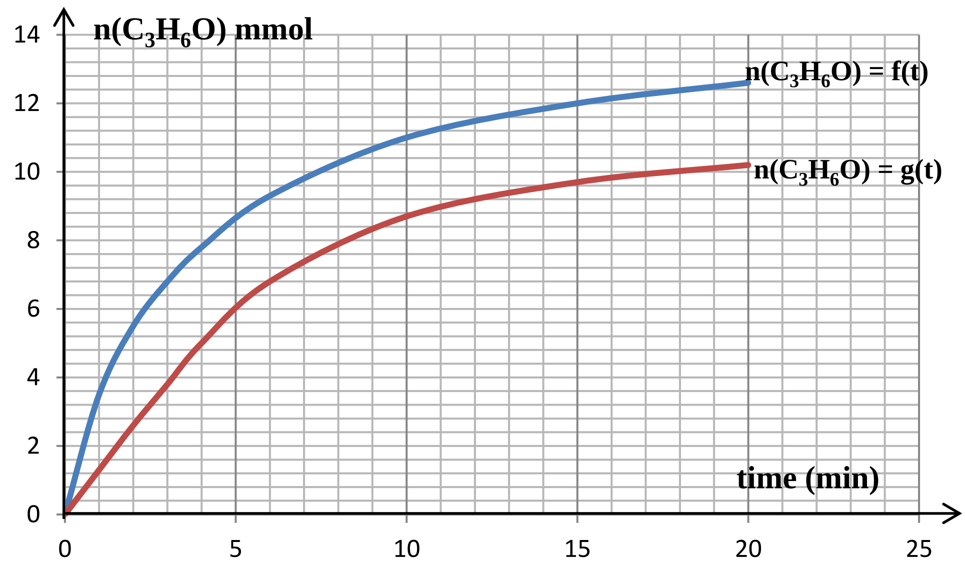
الاثنين ٢٩ تمّوز ٢٠١٩

أسس التصحيح

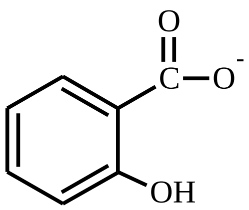
مسابقة في مادة الكيمياء

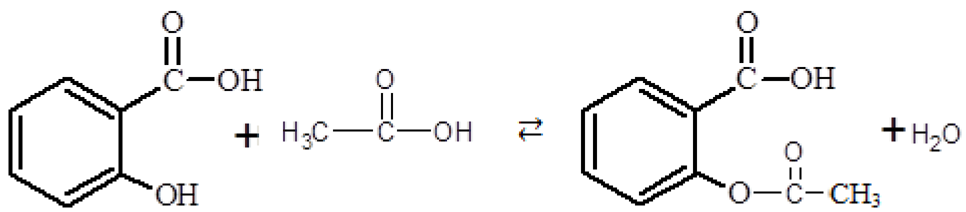
Exercise 1 (7 points) Kinetic Study of the Oxidation of an Alcohol

Part of the Q	Answers	Note
1.1	$C = \frac{n(KMnO_4)}{V(solution)}$ so $n(KMnO_4) = C \times V = 0.1 \times 250.10^{-3} = 0.025$ mol $m(KMnO_4) = n \times M = 0.025 \times 138 = 3.95$ g.	0.75
1.2	The essential materials are :digital balance , volumetric flask of 250 mL	0.5
2.1		1
2.2	$n(KMnO_4) = C \times V = 0.1 \times 0.1 = 0.01$ mol; $n(C_3H_8O) = \frac{m}{M} = \frac{\rho \times V}{M} = \frac{0.79 \times 1}{60} = 0.013$ mol; $R(KMnO_4) = \frac{0.01}{2} = 5 .10^{-3}$ $R(C_3H_8O) = \frac{0.013}{5} = 2.6.10^{-3}$ $R(KMnO_4) > R(C_3H_8O)$ so C_3H_8O is the limiting reactant	1
2.3	The half-life time is the time needed to the formation of the half of the maximal number of moles of the product. According to the stoichiometry of the reaction : $\frac{n(C_3H_8O)_o}{5} = \frac{n(C_3H_6O)_\infty}{5}$ so $n(C_3H_6O)_\infty = 0.013$ mol At $t_{1/2}$: $n(C_3H_6O)_{t1/2} = \frac{0.013}{2} = 6.5.10^{-3}$ mol = 6.5 mmol. Graphically $t_{1/2} = 2.8$ min	1
2.4.1	True The presence of 40 mL of ice water decreases the temperature and the concentration of reactants .The temperature and the concentration of the reactants are kinetic factors so when they decrease the rate of the reaction decreases.	0.75
2.4.2	false Because sulfuric acid is one of the reactants in this reaction.	0.75
2.5		

	 In the presence of 100 mL of distilled water, the total volume of the reacting mixture increases so the initial concentrations of the reactants decrease. And since the initial concentration of the reactants is a kinetic factor so the rate of formation of C_3H_6O decreases. at each instant : $n(C_3H_6O)$formed in the 2^{nd} experiment $<$ $n(C_3H_6O)$ formed in the 1^{st} experiment therefore the curve $n(C_3H_6O) = g(t)$ must be below that of $n(C_3H_6O) = f(t)$	1.25

Exercise 2 (7points) **Salicylic Acid**

Part of the Q	Answers	Mark
1.1	For a strong acid pH=-log C $-\log C = -\log 1.16 \times 10^{-2}$ mol.L^{-1} = 1.93< pH Therefore salicylic acid is a weak acid.	**0.5**
1.2	The formula of its conjugate base. 	**0.5**
1.3	The equation of the reaction of salicylic acid with water : $HA + H_2O \rightleftarrows A^- + H_3O^+$	**0.5**
1.4	$pH = pKa\ (HA/A^-) + \log \frac{[A^-]}{[HA]}$ when $\log \frac{[A^-]}{[HA]} = 0$; $pH = pKa\ (HA/A^-)$ graphically $pH = pKa\ (HA/A^-) = 2.95$	**0.5**

2	During dilution, the number of moles of solute is conserved $\frac{C_0}{C_S} = \frac{V_S}{V_0} = 50$ $\Rightarrow V_A = 50 \times V_1$; with V_A = volume of volumetric flask and V_1 = volume of the pipet; so set 3 must be used (pipet of 2 mL and volumetric flask of 100 mL) (total volume of wart remover solution is 5 mL)	**0.75**
3.1.1	To take V_1: a 20 mL pipet is needed.	**0.25**
3.1.2	To add the sodium hydroxide solution: a 25 mL graduated buret is needed.	**0.25**
3.2	The equation of the titration reaction is: $HA + HO^-_{(aq)} \rightarrow A^- + H_2O_{(l)}$	**0.5**
3.3	At the equivalence point : $n(HO^-)_{\text{added to reach equivalence}} = n(HA)_{\text{introduced into the beaker}}$ $C_B \times V_{BE} = C_1 \times V_1$ $C_1 = \frac{0.01 \times 23 \times 10^{-3}}{20 \times 10^{-3}} = 0.0115$ mol.L^{-1} $C_o = 50 \times C_1 = 50 \times 0.0115 = 0.575$ mol.L^{-1}	**1**
3.4	Mass of salicylic acid in 5 mL solution = $C_o \times V \times$ M(salicylic acid) $= 0.575 \times 0.005 \times 138 = 0.39675$g % (HA) $= \frac{\text{m (HA)in a volume V of } S_o}{\text{m of the volume V of } S_o} \times 100 = \frac{0.39675}{4} \times 100 = 9.92\% \cong 10\%$	**1**
4.1		**0.75**
4.2	Slow, reversible and athermic	**0.5**

Exercise 3 (6 points) Organic Compound (A)

Part of the Q	**Answer**	**Mark**
1.1	The formula of the compound (A) is $C_xH_yO_2$ %O = 100-(54.55+9.1) = 36.35% $\frac{12X}{54.55} = \frac{Y}{9.1} = \frac{32}{36.35}$, So the molecular formula of (A) is $C_4H_8O_2$	**0.75**
1.2	The molecular formula of compound (A) is of the form $C_nH_{2n}O_2$; Therefore the possible chemical families of this compound are carboxylic acid or ester.	**0.5**
1.3	Since the pH of the solution of compound (A) is 7, so this compound does not have an acid character, therefore it is an ester.	**0.5**
2.1	the compound (B) is a carboxylic acid of molecular formula H_2CO_2 O ‖ methanoic acid H—C –OH	**0. 5**

2.2	The possible structural formulas of (C): $CH_3—CH_2—CH_2OH$ OR $CH_3—CHOH—CH_3$	**0.5**
2.3.1	From activity 2: we deduce that (D) is a carbonyl compound (aldehyde or ketone). From activity 3: we deduce that (D) is an aldehyde. From activity 1: the mild oxidation of (C) produces an aldehyde, so (C) is primary alcohol ; therefore it is 1-propanol	**1**
2.3.2	$\underset{\underset{O}{\Vert}}{H-C}-O-CH_2-CH_2-CH_3$ Propyl methanoate	**0.75**
3.1.	The two reacting mixtures contain the same number of moles of the two reactants, but in the preparation number 2 an aqueous solution of the methanoic acid is used. The presence of water in the reacting medium shifts the esterification reaction backwards resulting in a yield less than that when a pure methanoic acid is used. So $Y_1 > Y_2$	**0.75**
3.2.	To increase the yield of the esterification reaction, (higher than **Y_1 and Y_2.)**, an acid derivative must be used. The equation of the reaction is: $CH_3-CH_2-CH_2OH + H-COC\ell \rightarrow H-\underset{\underset{O}{\Vert}}{C}-O-CH_2-CH_2-CH_3 + HC\ell$	**0.75**