مسابقة في مادة الكيمياء	الاسم:
المدة: ساعتان	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) Study of an Alcohol (A)

Alcohols have a long history of several uses worldwide. They have many medical and industrial uses. The aim of this exercise is to identify a saturated non cyclic chain monoalcohol (A), and to study some of its chemical properties.

Given: - Molar masses in $g.mol^{-1}$: M (H) =1; M (C) = 12; M (O) = 16
- Density of ethanoic acid: d = 1.06 $g.mL^{-1}$.

1. Identification of The Alcohol (A)

The elemental analysis of a sample of the alcohol (A) shows that the percentage by mass of oxygen is 21.62 %.

1.1. Show that the molecular formula of the alcohol (A) is $C_4H_{10}O$.
1.2. In order to identify the alcohol (A), the experiments in **document-1** are carried out.

Experiment 1: The alcohol (A) is treated with an acidified potassium dichromate solution ($2K^+ + Cr_2O_7^{2-}$). The color of the medium is changed from orange to green and an organic compound (B) is formed.
Experiment 2: A solution of 2,4-DNPH is added to a sample of compound (B). A yellow orange precipitate is formed.
Experiment 3: A mixture of a sample of compound (B) and a blue Fehling's solution is heated gently. The mixture remains blue and no precipitate is observed.

Document- 1

Based on the results of each of the three experiments of **document-1**, justify that the alcohol (A) is 2-butanol.
1.3. Verify that the molecule of 2- butanol is chiral.
1.4. Represent, according to Cram, the two enantiomers of 2-butanol.

2. Reaction of the Alcohol (A) with Ethanoic Acid

Alcohols react with carboxylic acids according to the following general equation:

$$R—COOH + R'—OH \rightleftarrows R—COO—R' + H_2O$$

A mixture containing 0.10 mol of 2-butanol, a volume V= 5.7 mL of pure ethanoic acid and few drops of concentrated sulfuric acid is heated to reflux.
2.1. Write, using condensed structural formulas, the equation of the reaction that takes place. Give the systematic name of the ester formed.
2.2. Choose, from the following list, the appropriate materials needed to construct the reflux heating set-up: Heating mantle, round bottom flask, graduated burette, 100 mL beaker, and condenser.
2.3. Indicate the importance of the reflux heating for this synthesis.

2.4. After a certain time t, heating is stopped, the reaction medium is cooled and the remained ethanoic acid is titrated; the number of moles of ethanoic acid is found to be 0.06 mol.

2.4.1. Show that the initial number of moles of ethanoic acid is 0.10 mol.

2.4.2. Copy and complete the following table:

	R— COOH	**+ R′— O H ⇄**	**R— COO —R′ +**	**H_2O**
At instant t_o	0.10 mol	0.10 mol	0	0
At instant t	0.06 mol			

2.4.3. Specify whether equilibrium is reached at instant t, knowing that the equilibrium constant of this reaction is $K_C = 2.3$

Exercise 2 (7 points) **Kinetic of a Reaction**

Aspirin is one of the most used medicinal drugs worldwide.
The aim of this exercise is to study the preparation of aspirin and to realize the kinetic of its reaction with bicarbonate ion.

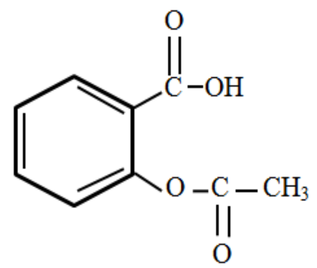
Given: Molar mass of aspirin: $M_{(Asp)} = 180\ g.mol^{-1}$

1. Preparation of Aspirin

Aspirin can be prepared starting from salicylic acid and ethanoic anhydride. The condensed structural formula of aspirin is given in **document-1.**

1.1. Copy the formula of aspirin, circle and name its functional groups.

1.2. Write, using condensed structural formulas, the equation of the preparation reaction of Aspirin.



Document-1

2. Kinetic Study

Aspirin ($C_9H_8O_4$) reacts slowly with bicarbonate ion (HCO_3^-) according to a reaction which is considered complete, and is represented by the following equation:

$$C_9H_8O_4 + HCO_3^- \longrightarrow C_9H_7O_4^- + CO_2 + H_2O$$

A volume $V_1 = 10$ mL of a sodium bicarbonate solution ($Na^+ + HCO_3^-$) of concentration $C_1 = 0.50\ mol.L^{-1}$ is poured into a closed flask containing a mass m = 460 mg of aspirin. Using an appropriate method, the number of moles of carbon dioxide gas released in the flask at constant temperature T can be determined at each instant t.
The results are listed in the table of **document-2**.

Time (s)	50	100	150	200	250	300	350	400	500	600
$n(CO_2)$ (10^{-4} mol)	11.50	17.75	21.00	22.75	23.75	24.50	25.00	25.25	25.55	25.55

Document-2

2.1. Show that aspirin is the limiting reactant.

2.2. Plot the curve representing the variation in the number of moles of carbon dioxide as a function of time: n (CO_2) = f (t) in the time interval [0 – 500 s]. Take the following scales:
Abscissa: 1cm for 50 s ; Ordinate : 1 cm for 2.5×10^{-4} mol.

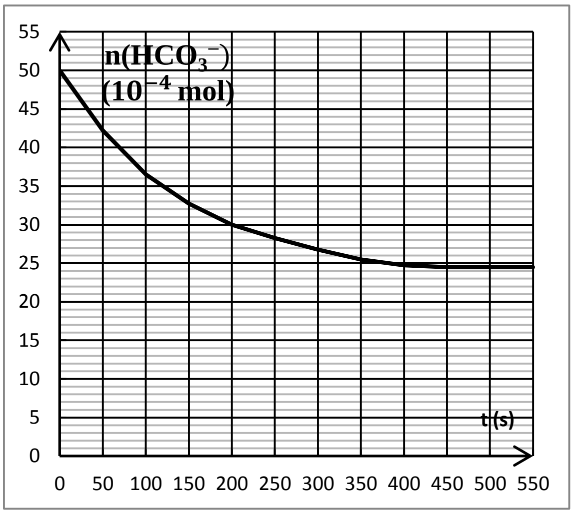
2.3. Deduce, graphically, the variation in the rate of formation of CO_2 as a function of time.

2.4. Determine the half-life time, $t_{1/2}$.

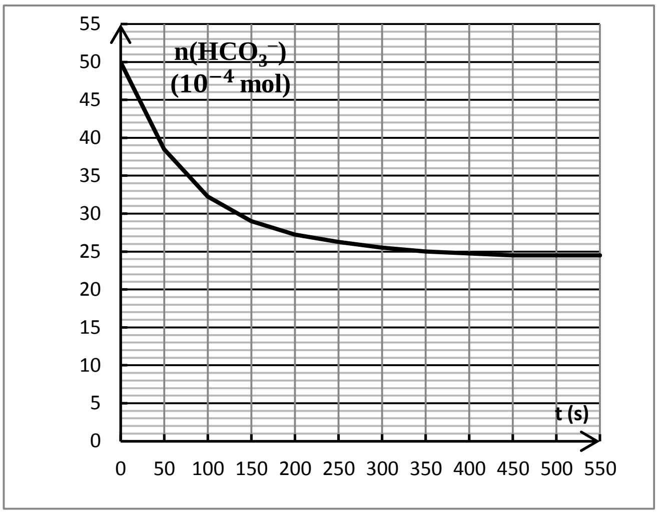
2.5. Show that at the half-life time (t ½) : $n(HCO_3^-)_{t\,½} = n_o(HCO_3^-) - \frac{n_o(Asp)}{2}$;

where $n_o(HCO_3^-)$ is the initial number of moles of HCO_3^- and $n_o(Asp)$ is the initial number of moles of aspirin.

2.6. Consider the two curves given in **document-3**, deduce the one that corresponds to $n(HCO_3^-) = f(t)$.



Curve a



Curve b

Document-3

Exercise 3 (6 points) **Acidic and Basic Solutions**

Available are three flasks containing two weak acid solutions denoted solution (1), solution (2) and a sodium hydroxide solution ($Na^+ + HO^-$) denoted solution (3). The labels on these three flasks show the indications given in the **document -1.**

Solution (1)	Solution (2)	Solution (3)
Monoacid HA_1 C_1= ? pH_1=2.6	Monoacid HA_2 C_2 = ? pH_2 = 2.7	($Na^+ + HO^-$) $C_3 = 4\times10^{-2}$ mol.L^{-1} pH_3= 12.6

Document -1

The aim of this exercise is to study the strength of the two acids.

Given: - This study is carried out at T = 25ºC.

- $K_w = 10^{-14}$

1. Study of The Behavior of Acids and Base

1.1. Verify that sodium hydroxide is a strong base.

1.2. Each of the two solutions (1) and (2) is diluted **ten times**; the solutions (A) and (B) are obtained respectively. The measurements of pH of the obtained solutions are shown in **document-2.**

Solution (A)	Solution (B)
Monoacid HA_1 pH_A = 3.1	Monoacid HA_2 pH_B = 3.2

Document-2

Choose, from the sets of **document-3**, the most convenient one in order to prepare solution (A) from solution (1). Justify.

Set 1	Set 2	Set 3
Volumetric pipet 10.0 mL Volumetric flask 1000.0 mL Beaker 50 mL	Volumetric pipet 5.0 mL Volumetric flask 50.0 mL Beaker 50 mL	Graduated cylinder10.0 mL Volumetric flask 50.0 mL Beaker 50 mL

Document -3

1.3. Verify, based on the **documents 1 and 2**, that the two acids HA_1 and HA_2 are weak acids.
1.4. Write the equation of the reaction of HA_1 with water.

2. Titration of Solution (1)

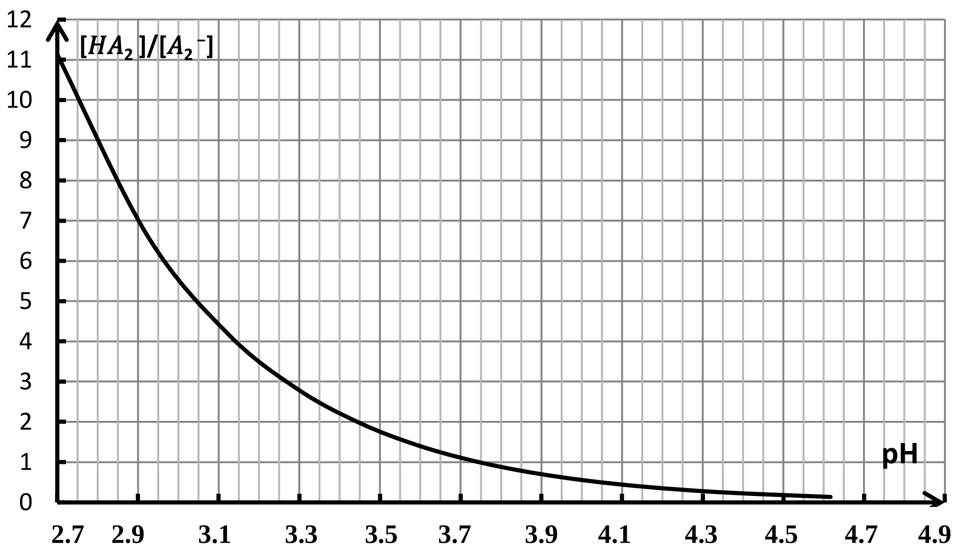
A volume V_1 = 20.0 mL of the solution (1) is taken and introduced into a beaker, and then a certain volume of distilled water is added to immerse properly the pH-meter electrode. The sodium hydroxide solution (3) of concentration C_3= 4×10^{-2} mol.L^{-1} is added progressively.
The volume of the basic solution added to reach equivalence is V_{bE} = 25.0 mL.

2.1. Write the equation of the titration reaction.
2.2. Determine the concentration C_1 of the solution (1).
2.3. At equivalence, $\mathbf{A_1^-}$ ions predominates $\mathbf{HA_1}$ in the solution. Deduce which of the following values corresponds to the pKa of the HA_1 / A_1^- pair, knowing that the pH at equivalence is equal to 8.0

a. 3.9 **b.** 8.0 **c.** 10.0

3. Determination of The pKa of the Pair HA_2 /A_2^-

Document-4 shows the variation of the ratio $\frac{[HA_2]}{[A_2^-]}$ as a function of pH during the addition of the solution (3) to a volume V_2 of the solution (2).



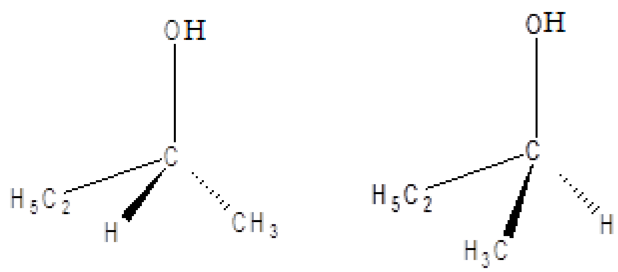
Document-4

3.1. Based on document 4, show that the value of the pKa of the pair HA_2 /A_2^- is 3.75
3.2. Specify, among the three following propositions, the one that corresponds to C_2.

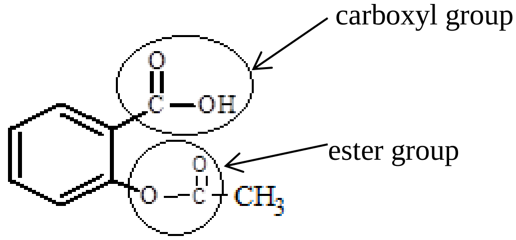
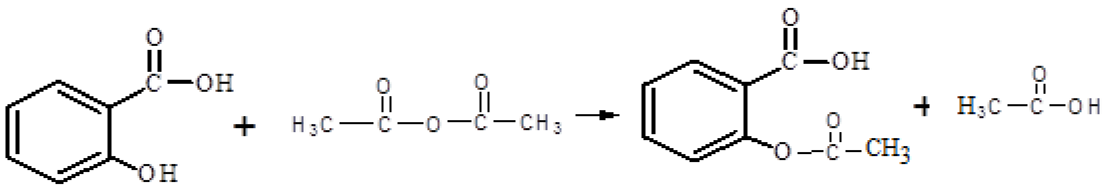
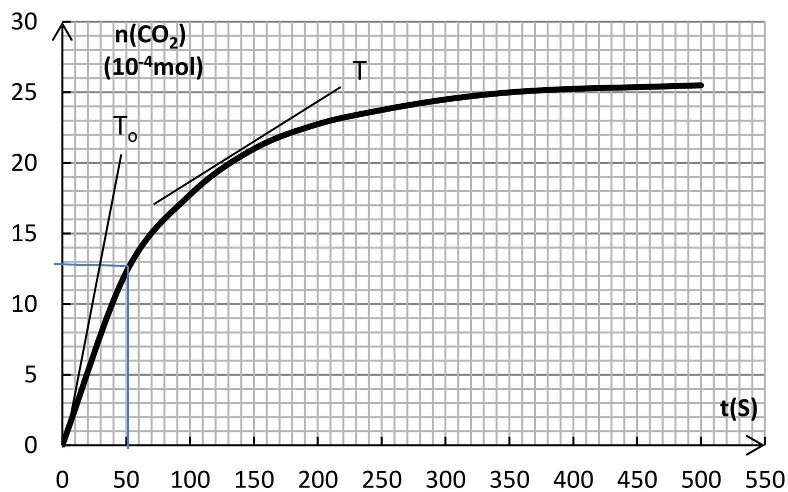
a. $C_2 > C_1$ **b.** $C_2 = C_1$ **c.** $C_2 < C_1$

أسس التصحيح في مادة الكيمياء

Exercise 1 (7 points) Study of an Alcohol (A)

Part of the Q	Answer	Mark
1.1	The general formula of a saturated non cyclic chain alcohol is $C_nH_{2n+2}O$. %O = 21.62 %. $\frac{M(A)}{100} = \frac{16}{\%O}$, with M(A)= 14n+18 n = 4 and the molecular formula of (A) is $C_4H_{10}O$	**0.5**
1.2.	From experience 1: (A) is oxidized so we deduce that it is not a tertiary alcohol, it is a primary or a secondary alcohol. From experience 2: since a yellow orange precipitate id formed so (B) is a carbonyl compound (aldehyde or ketone). From experience 3: we deduce that (B) is a ketone since it does not react with Fehling's solution ; So (A) is a secondary alcohol that 2-butanol	**1**
1.3	Since the molecule of the 2-butanol contains an asymmetric carbon atom (a tetrahedral carbon atom linked to 4 atoms or group of atoms all different)	**0.5**
1.4.		**0.75**
2.1.	The equation of the reaction is: $CH_3 - CHOH - CH_2 - CH_3 + CH_3 - COOH \rightleftarrows CH_3 - C(=O) - O - CH(CH_3) - CH_2 - CH_3 + H_2O$ The systematic name of the ester is: 1-methylpropylethanoate	**1**
2.2.	The most appropriate materials needed to carry out the reflux heating: Heating mantle, round bottom flask, and condenser.	**0.75**
2.3.	The importance of reflux heating is to accelerate the reaction without any loss in the constituents of the reacting mixture.	**0.5**
2.4.1.	$n(alcohol)_{initial} = \frac{m(alcochol)initial}{M(alcohol)} = \frac{V(alcohol).d(alcohol)}{M(alcohol)} = \frac{5.7\times1.06}{60} = 0.10 mol$	**0.5**
2.4.2	Acid + alcohol ⇌ ester + water Initial state: 0.1 mol, 0.1 mol, -, - At t: 0.06, 0.06, 0.04, 0.04	**0.75**
2.4.3	$Q_r = \frac{[ester]\times[water]}{[alcohol]\times[acid]} = \frac{\frac{0.04^2}{V^2}}{\frac{(0.06)^2}{V^2}} = 0.44 < Kc$; system does not reached the equilibrium yet.	**0.75**

Exercise 2 (7 points) **Kinetic of a Reaction**

Part of the Q	Answer	Mark
1.1.		**1**
1.2.		**1**
2.1.	$n(HCO_3^-) = C \times V = 0.5 \times 0.01 = 5 \times 10^{-3}$ mol ; $R(HCO_3^-) = 5\times10^{-3}$ $n(asp) = \frac{m(asp)}{M(asp)} = \frac{0.460}{180} = 25.5 \times 10^{-4}$ mol; $R(asp) = 25.5\times 10^{-4}$ $R(HCO_3^-) > R(asp)$ implies aspirin is the limiting reactant.	**0.75**
2.2.	The curve: 	**1**
2.3.	The rate of formation of CO_2 is equal to the slope of the tangent to the curve at the point of abscissa t. Slope of tangent T_o > slope of tangent T Therefore the rate of formation of CO_2 decreases with time.	**0.75**
2.4.	The half-life time of a reaction is the time needed for the formation of half the maximum number of moles of CO_2 $n(CO_2)_{max} = n_o(asp) = 25.5 \times 10^{-4}$ mol. $n(CO_2)_{t1/2} = 25.5\times10^{-4}/2 = 12.75\times10^{-4}$ mol. Graphically t ½ = 55 s	**1**

2.5.	$C_9H_8O_4$ + HCO_3^- → $C_9H_7O_4^-$ + CO_2 + H_2O At t = 0 $n_o(Asp)$ $n_o(HCO_3^-)$ At t1/2 $\frac{no(Asp)}{2}$ $n_o(HCO_3^-)- \frac{no(Asp)}{2}$ $n(HCO_3^-)_{t1/2} = n_o(HCO_3^-) - \frac{n0\ (Asp)}{2}$	**0.75**
2.6	The curve that represents $n(HCO_3^-) = f(t)$ starts from $n_o = 50\times10^{-4}$ mol, $n\ (HCO_3^-)_{t\ ½} = n_o(HCO_3^-) - \frac{no(Asp)}{2} = 50\times10^{-4} - \frac{25.5\times10^{-4}}{2} = 37.25\times10^{-4}$ mol with t1/2 = 55 s Therefore curve b.	**0.75**

Exercise 3 (6 points) **Acidic and Basic Solutions**

Part of the Q	Answer	Mark
1.1	$14 + \log C_3 = 14 + \log 4\times10^{-2} = 12.6$ $\Rightarrow$ pH = 14 + log C_3 ; therefore sodium hydroxide is a strong base.	**0. 75**
1.2	During dilution, the number of moles of solute is conserved $\frac{C_1}{C_A} = \frac{V_A}{V_1} = 10$ $\Rightarrow V_A = 10 \times V_1$; with V_A = volume of volumetric flask and V_1 = volume of the pipet; so set 2 must be used (pipet of 5 mL and volumetric flask of 50 mL)	**1**
1.3	For the solution (1); when the solution is diluted 10 times, pH has increased by less than 1 unit (3.1 – 2.6 = 0.5), so HA_1 is a weak acid. The increase of pH in the solution (2) is also less than 1, therefore HA_2 is a weak acid.	**0.75**
1.4	$HA_1 + H_2O \rightleftharpoons A_1^- + H_3O^+$	**0.5**
2.1	The equation of the titration reaction is: $HA_1 + HO^- \rightarrow A_1^- + H_2O$	**0.5**
2.2	At the equivalence point: n (HA_1) introduced into the beaker = n (HO^-) added to reach equivalence $C_1 \times V_1 = C_3 \times V_E$; so the concentration of the solution (1) is : $C_1 = \frac{\mathbf{C_3 \times V_E}}{\mathbf{V_1}} = \frac{\mathbf{4\times10^{-2}\times25}}{\mathbf{20}} = 5\times10^{-2}$ mol.L^{-1}.	**1**
2.3	Since the species A_1^- predominates so pH > pKa +1 For pH = 8.0 , pKa should be less than 8 => pka = 3.9 answer (a)	**0.5**
3.1	pKa of the pair HA_2 / A_2^- = pH when $\frac{[HA_2]}{[A_2^-]} = 1$ graphically $\frac{[HA_2]}{[A_2^-]} = 1$ for a pH = 3.75; pKa of the pair $HA_2 / A_2^- = 3.75$	**0.5**
3.2	HA_2 is a stronger acid than HA_1 (since pKa(HA_2 / A_2^-) < pKa (HA_1 / A_1^-) $pH_1 < pH_2$, The [H_3O^+] in the solution (1) is greater than that in solution (2) even though HA_2 is a stronger acid than HA_1 : this can be explained only by the fact that the concentration C_1 is greater than the concentration C_2 The answer is c	**0.5**