وزارة التربية والتعليم العالي
المديريّـة العامة للتربية
دائرة الامتحانات الرسمية

امتحانات الشهادة الثانوية العامّة
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دورة الـعام ٢٠١٩ العاديّة
الثلاثاء ٢٥ حـزيران ٢٠١٩
مكيفة

This Exam Includes Three Exercises. It Is Inscribed on eleven Pages Numbered from 1 to 11.

The Use of A Non-programmable Calculator Is Allowed.

مسابقة في الكيمياء

(إنكليزي)

المدّة: ساعتان

الاسم:..

الرقم:..

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

The aim of this exercise is to identify a saturated non cyclic chain mono alcohol (A), and to study some of its chemical properties.

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

1. Identification of the Alcohol (A)

The analysis of a sample of a mono 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 $C_4H_{10}O$, knowing that the molecular formula of the monoalcohol is $C_nH_{2n+2}O$

1.2- In order to identify the alcohol **(A)**, the following 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 three experiments **of document-1**.

a- **Copy** and **complete** the table below:

	Results
Experiment 1	The class of the alcohol **(A)** is ……………. or…………….
Experiment 2	The compound **(B)** is ………………or ……………
Experiment 3	Therefore the compound **(B)** is …………and by consequences the class of the alcohol **(A)** is …………..

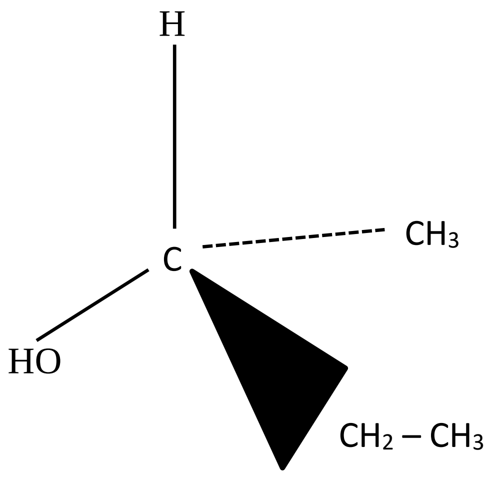
b- Based on the results of each of the three experiments of **document-1.**

Deduce that the alcohol **(A)** is **2-butanol**.

1.3. Verify that the molecule of the alcohol **(A)** is chiral.

1.4. The Alcohol **(A)** has two enantiomers.

One of them is represented according to Cram as:



Represent the second enantiomer of the alcohol **(A).**

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

- The condensed structural formula of 2-butanol is:

$$\begin{array}{c} \qquad\qquad\qquad\mathbf{OH} \\ \qquad\qquad\qquad| \\ \mathbf{CH_3 - CH_2 - CH - CH_3} \end{array}$$

- Alcohols react with carboxylic acids according to the general equation given below:

$$\mathbf{R{-}COOH + R'{-}O\,H \rightleftarrows R{-}COO{-}R' + H_2O}$$

A mixture containing :

- **0.10 mol of 2-butanol,**
- a volume **V= 5.7 mL** of pure ethanoic acid $CH_3 - COOH$ and few drops of concentrated sulfuric acid

is heated to reflux.

2.1. **a- Write**, using condensed structural formulas, the equation of the reaction that takes place.

b- Choose the correct answer:

The systematic name of the ester formed is :	**a-** Butyl ethanoate
	b- 1- metylpropyl ethanoate
	c- Ethyl butanoate

2.2. **Choose**, from the following list, the most appropriate materials (3 materials) needed to construct the reflux heating set-up:

1-	Heating mantle.
2-	Round bottom flask.
3-	Graduated buret.
4-	100 mL beaker
5-	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
- The remaining ethanoic acid is titrated; the number of moles of ethanoic acid is found to be **0.06 mol**.

Given :	Density of ethanoic acid: **d = 1.06 $g.mL^{-1}$.**
	Molar mass of ethanoic acid : **$M(CH_3 – COOH) = 60\ g.mol^{-1}$**

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**	**a- ……..**	**b- …….**	**c- ……**

2.4.3. a- Calculate Q_R of the reaction of the preparation of the ester.

b- Specify whether equilibrium is attained 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.

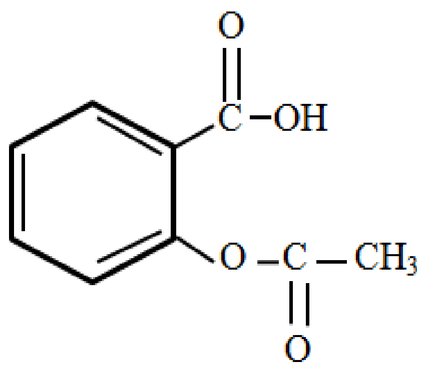
The aim of this exercise is to study the preparation of aspirin and to realize the kinetic of its reaction with bicarbonate ion.

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

1. Preparation of Aspirin

Aspirin can be prepared starting from salicylic acid and ethanoic anhydride.

The formula of aspirin is given in **document-1.**

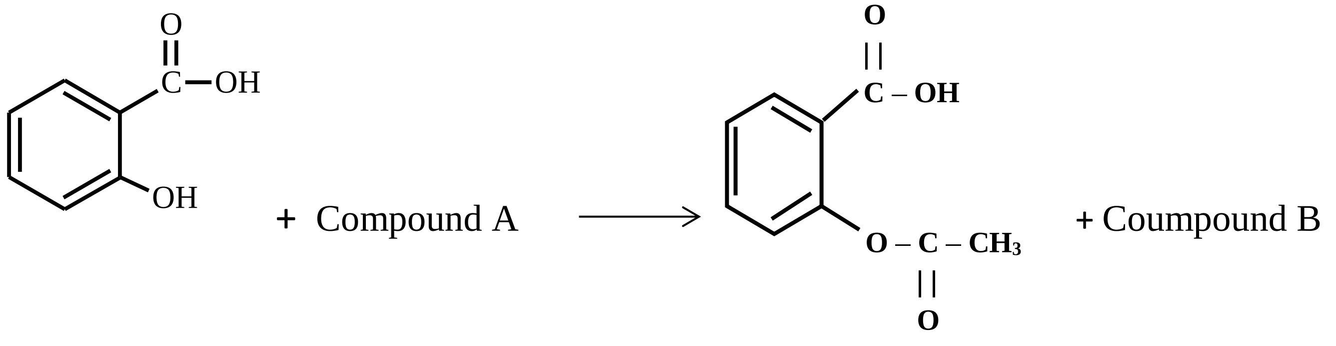


Document-1

1.1. Copy the formula of aspirin,

Circle and **name** its functional groups.

1.2. The reaction of preparation of aspirin is represented by the following equation:



Give the condensed structural formula of each of the compounds A and B.

2. Kinetic Study

Aspirin $C_9H_8O_4$ reacts slowly with bicarbonate ion HCO_3^- according to a reaction, considered complete, which is represented by:

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

2.1. 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.

a. Calculate the initial number of mole of bicarbonate ion and that of aspirin.

b. Deduce that aspirin is the limiting reactant.

2.2. Using an appropriate method, the number of moles of carbon dioxide gas released in the flask at a constant temperature 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)	11.5	17.75	21.00	22.75	23.75	24.5	25.00	25.25	25.55	25.55

Document-2

Plot the curve representing the variation in the number of moles 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 in
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. **a- Give** the number of moles of CO_2 at the end of reaction.

c- Determine the half-life time **($t_{1/2}$)** of the reaction.

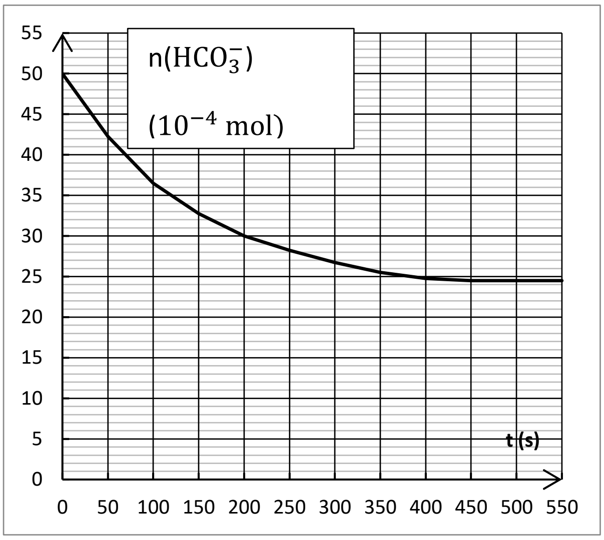
2.5. The number of moles $\mathbf{n(HCO_3^-)_{t\,½}}$ is related to the initial number of moles of $\mathbf{HCO_3^-}$,$\left(\mathbf{n_o(HCO_3^-)}\right)$, and to the initial number of moles of aspirin **n_0(Asp)** by the relation:

$$\mathbf{n\ (HCO_3^-)_{t\,½}\ =\ n_o(HCO_3^-) - \frac{n_o(Asp)}{2}};$$

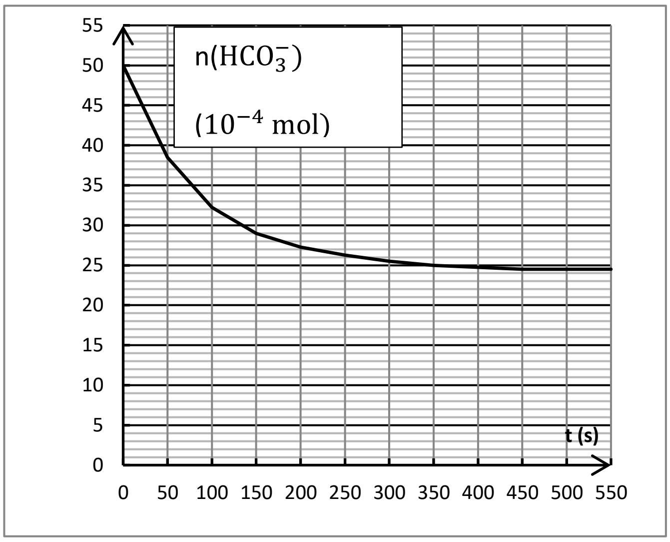
Calculate <u>the number of moles</u> of $\mathbf{HCO_3^-}$ **ions** <u>at the half life time</u> (**$t_{1/2}$**)

2.6. a- Referring to the questions **(2.4.b and 2.5)**

b- **Choose** the curve that corresponds to **$n(HCO_3^-)$ = f(t).**



Curve a



Curve b

Document-3

Exercise 3 (7 points) **Acidic and Basic Solutions**

Available are **3** 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 **3** flasks show the indications given in the **document -1.**

Solution (1)	Solution (2)	Solution (3)
Monoacide HA_1 $C_1 = ?$ $pH_1 = 2.6$	Monoacide 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. Referring to **C_3** and **pH_3** of **document-1**, **show** that sodium hydroxide is a strong base.

1.2. Each of the two solutions **(1)** and **(2)** is diluted **10 times**, two solutions **(A)** and **(B)** are obtained respectively.

Choose, from the sets of **document-2**, 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-2

1.3. The dilution of the two solutions **(1)** and **(2)**, give respectively the two solutions the solutions **(A)** and **(B)**.

The measurements of **pH** before and after the dilution for each acid (HA_1 and HA_2) are shown in **document-3.**

Solution (1)	**Solution (2)**
$pH_1 = 2.6$	$pH_2 = 2.7$
Solution (A)	**Solution (B)**
Monoacide HA_1 $pH_A = 3.1$	Monoacide HA_2 $pH_B = 3.2$

Document-3

Verify, based on the **document-3** and by comparing **pH_1 to pH_A** and **pH_2** to **pH_B** 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)** of the acid **(HA_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 **($Na^+ + HO^-$)** solution of concentration **$C_3 = 4\times10^{-2}$ 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 between the acid **HA_1** and the sodium hydroxide **($Na^+ + HO^-$).**

2.2- Determine the concentration **C_1** of the solution **(1)**.

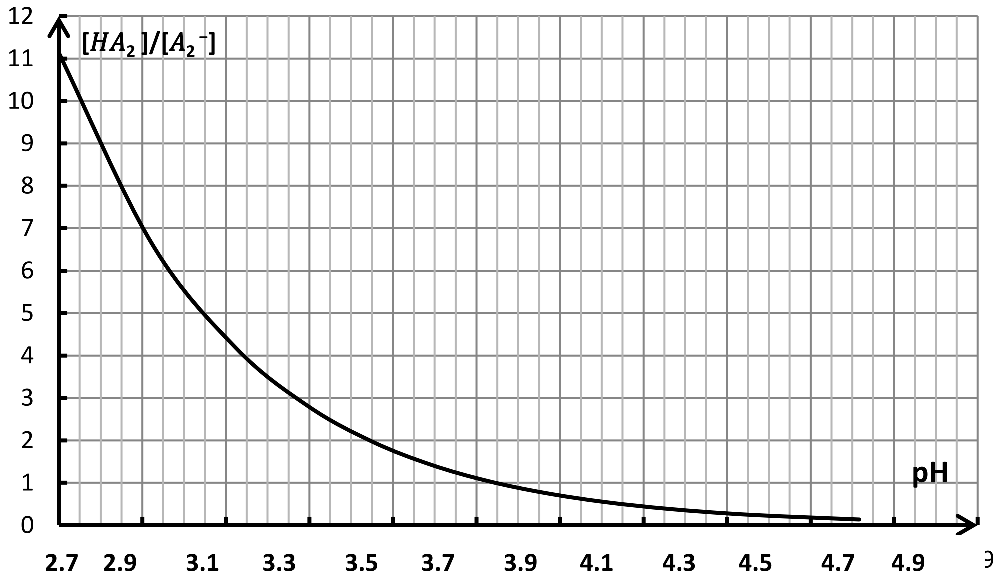
2.3- At equivalence **A_1^-** predominates **HA_1** in the solution.

By applying the relation **pH = pKa₁ +log** $\frac{[A_1^-]}{[HA_1]}$ **,** and knowing that the pH at equivalence is 8.0, **deduce** from the following values the one that corresponds to pKa_1 of the pair $\mathbf{HA_1/A_1^-}$

a. 3.9 **b.** 8 **c.** 10

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 $\mathbf{V_2}$ of the solution **(2)**



Document-4

3.1- Based on **document 4**,

a- Give the **pH** of the solution that corresponds to the ratio $\frac{[HA_2]}{[A_2^-]}$ = 1

b- Deduce the value of **pKa_2** of the pair $\mathbf{HA_2 / A_2^-}$.

3.2- Specify, among the 3 following propositions, the one that corresponds to C_2.

a. C2 > C1 **b. C2 = C1** **c. C2 < C1**