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دائرة الامتحانات		

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This Exam Includes Three Exercises. It Is Inscribed on Four Pages Numbered from 1 to 4.
The Use of Non-programmable Calculator Is Allowed.

Answer The Three Following Exercises:

First Exercise (6 points)
Kinetic of Dimerization of Butadiene

At high temperature, butadiene dimerizes in gaseous phase in a complete reaction of which the equation is:

$$2\ C_4H_{6(g)} \rightarrow\ C_8H_{12(g)}$$
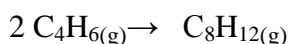
In an evacuated container of constant volume V, maintained at a temperature T = 609K, n_0 mol ofbutadiene gas is introduced. A manometer, attached to this container, measures the total pressure P at different instants of time of the evolution of the reacting system.

The concentration of C_8H_{12} gasis determined at those instants. The results are listed in the table below:

t (min)	8	15	30	60	90	120	150	180
$[C_8H_{12}]\ 10^{-3}$ mol.L^{-1}	1.9	3.0	4.6	6.3	7.2	7.8	8.1	8.4

Given:
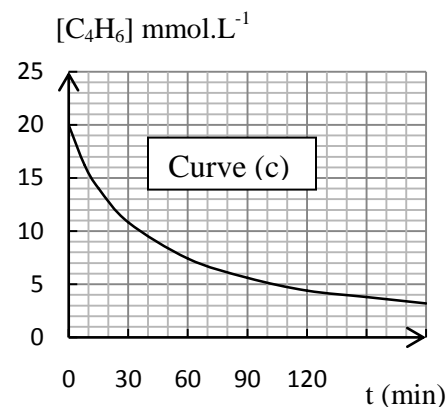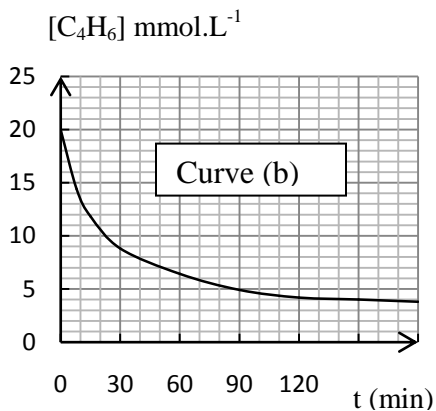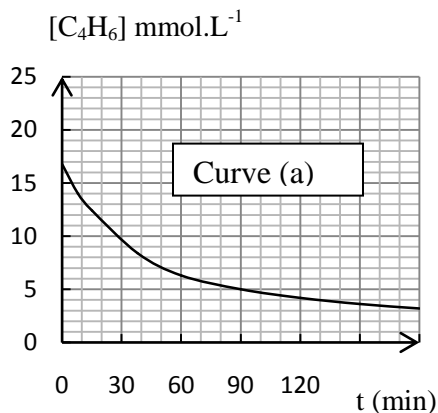- Gases of the reacting mixture are supposed to be ideal.
- Ideal gas constant: R = 0.082 atm.L.mol^{-1}.K^{-1}.

1- Preliminary Study

1.1- Draw up a table representing the composition of the reacting mixture at the initial state and at the instant of time t of its evolution as a function of n_0 and x. (x is the number of moles of C_8H_{12} formed at t).

1.2- Establish the relation among: the concentration of C_8H_{12} gas at the instant of time t, the total pressure P at this instant, and the initial pressure P_0 in the container.

1.3- Show that the concentration of C_8H_{12} at the end of the chemical transformation is equal to 1.0×10^{-2} mol.L^{-1} knowing that the initial pressure inside the container is P_0 = 1.0 atm.

2- Kinetic Study

2.1- Plot the curve representing the change in the concentration of C_8H_{12} as a function of time: $[C_8H_{12}]$ = f (t), in the interval of time: [0 − 180 min]. Take the following scales :
1 cm for 15 min in abscissa and 1 cm for 1.0×10^{-3} mol.L^{-1} in ordinate.

2.2- Deduce, graphically, the change in the rate of formation of C_8H_{12} with time.

2.3- Determine the half-life time of the reaction.

2.4- Consider each one of the three following curvesand specify whether it represents the change in the concentration of C_4H_6 as a function of time.

1

$[C_4H_6]$ mmol.L^{-1}

25	
20	
15	Curve (a)
10	
5	
0	

0   30   60   90   120
t (min)

$[C_4H_6]$ mmol.L^{-1}

25	
20	
15	Curve (b)
10	
5	
0	

0   30   60   90   120
t (min)

$[C_4H_6]$ mmol.L^{-1}

25	
20	
15	Curve (c)
10	
5	
0	

0   30   60   90   120
t (min)

Second Exercise(7 points)
The pheromones

Pheromones are organic substances (esters, ketones, alcohols…) very fragrant emitted by most animals (ants, bees …) and act as messengers among the individuals of the same species.
Given, in the table below, the chemical formulas and the names of some pheromones:

Pheromone	Chemical formula or systematic name
A	$CH_3 - C - O - CH_3$ $\parallel$ O
B	3-methylbutyl ethanoate
C	$CH_3 - CH_2 - CH_2 - CH - CH - CH_2 - CH_3$ $\qquad\qquad\quad$ CH_3 OH
D	3-Hexanone

3-hexanone is a liquid compound at room temperature.

1- preliminarystudy

1.1- Name the common functional group of pheromones A and B.
1.2- Write the possible condensed structural formulas of the organic compounds that can react with methanol to produce pheromone A.
1.3- The compound (pheromone) C is subjected to mild oxidation by the reaction with an oxidizing agent. Write the condensed structural formula of the organic compound obtained and give its name.
1.4- Describe two chemical tests that allow identifying the chemical function of compound (pheromone) D, by listing the reagents and the materials used in those tests.

2

2- Preparation of the pheromone B

Given:

- Molar mass in g.mol^{-1}: M (acetic acid) = 60 and M (pheromone B) = 130
- Density of acetic acid : d = 1.04 g / mL.
- Starting from initial equimolar mixture of carboxylic acid and alcohol, the percentage yield at equilibrium is:67% if the alcohol is primary and 60% if the alcohol is

In order to prepare the pheromone B, one proceeds as follows:
- A volume $V_1$of isoamyl alcohol (equivalent to 0.20 mol of this alcohol) is mixed with a volume $V_2 = 30$ mL of acetic acid.
- This mixture is heated for 45 min.
- The pheromone B is extracted from the reacting medium and it is purified and weighed. The mass is found to be m = 17.42 g.
  - 2.1- Write, using the condensed structural formulas of the organic compounds, the equation of the reaction that took place.
  - 2.2- Deduce from the experimental procedure, described above, one of the characteristics of this reaction.
  - 2.3- Calculatethe initial number of moles of acetic acid.
  - 2.4- Determine the yield of this reaction.
  - 2.5- Verify, whether the heating duration (45 min)was sufficient to reach the equilibrium.
  - 2.6- Suggest two experimental ways that help to increase the yield of this reaction (without changing the chemical nature of reactants).

Third Exercise(7 points)

Sodium Bicarbonate

Sodium bicarbonate or sodium hydrogen carbonate, of formula $NaHCO_3$, is used in the production of beverages and carbonated water. Also it is used to reduce the excess stomach acid.

This exercise aims to study the behavior of hydrogen carbonate ions HCO_3^- in water, as well as to determine the percentage by mass (degree of purity) of $NaHCO_3$ in a sample of medicinal sodium bicarbonate.

Given:

- Ionic compounds $NaHCO_3$ and Na_2CO_3 are solids highly soluble in water.
- $\dfrac{[CO_3^{2-}]}{[HCO_3^-]} = \dfrac{\%\,(by\,mol)CO_3^{2-}}{\%\,(by\,mol)\,HCO_3^-}$.
- M ($NaHCO_3$) = 84 g.mol^{-1}.

1- Study of Hydrogen Carbonate Ion

Hydrogencarbonate ion, HCO_3^-, can react with water according to two chemical reactions of equations:

$$HCO_3^- + H_2O \rightleftarrows CO_3^{2-} + H_3O^+ \quad (1) \qquad or \quad HCO_3^- + H_2O \rightleftarrows HO^- + CO_2, H_2O \quad (2)$$
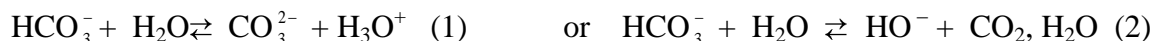
1.1-   Show that hydrogencarbonate ion has an amphoteric character (ampholyte).

1.2-   The followinggraph represents the change in the percentages by moles of the chemical species HCO_3^- and CO_3^{2-} in an aqueous solution (A) as a function of pH:

Percentage by mol: %
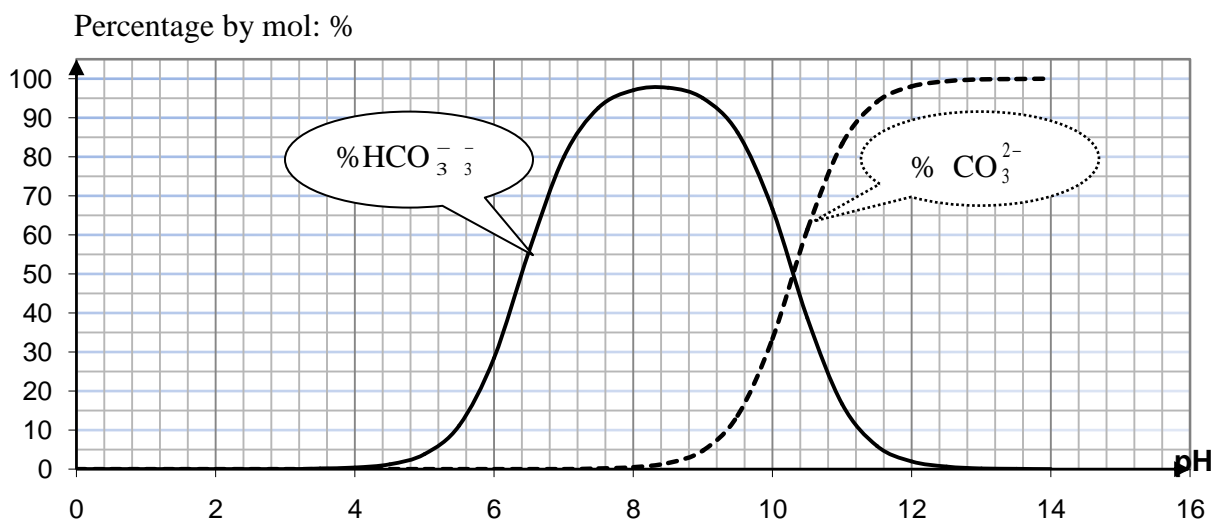
1.2.1- Calculate, based on the above graph, the ratio $\dfrac{[CO_3^{2-}]}{[HCO_3^-]}$ when the pH of solution (A) is equal 10

1.2.2- It is required to prepare a buffer solution of pH = 10 using 3.0×10^{-2} mol of Na_2CO_3 and a mass m of $NaHCO_3$. Determine the mass m needed for this preparation.

2- Degree of Purity of a Sample of Sodium Bicarbonate

In order to determine the degree of purity of a sample of powder medicinal sodium bicarbonate one proceeds as follows:

- A mass m = 1.50 g, of the powder of this sodium bicarbonate, is weighed and dissolved in distilled water in such a way to obtain a volume $V_0 = 200.0$ mL of a solution noted (S).
- A volume $V_1 = 10.0$ mL of the solution (S) is removed and introduced into a beaker then few drops of an appropriate colored indicator are added.
- A hydrochloric acid solution of concentration $C = 5.0\times10^{-2}$ mol.L^{-1} is added progressively to reach equivalence.

The equation of this titration reaction is: $H_3O^+ + HCO_3^- \rightarrow CO_2,H_2O + H_2O$

2.1- Choose, from the list below, the materials needed for the preparation of the solution (S) :
Precision balance, 25 mL graduated buret, 10 mL volumetric pipet, 200 mL volumetric flask, magnetic stirrer, funnel, watch glass and stand.

2.2- Determine the molar concentration of HCO_3^- ionsin the solution (S), knowing that the volume of the acid added to reach equivalence is $V_E = 16.8$ mL.
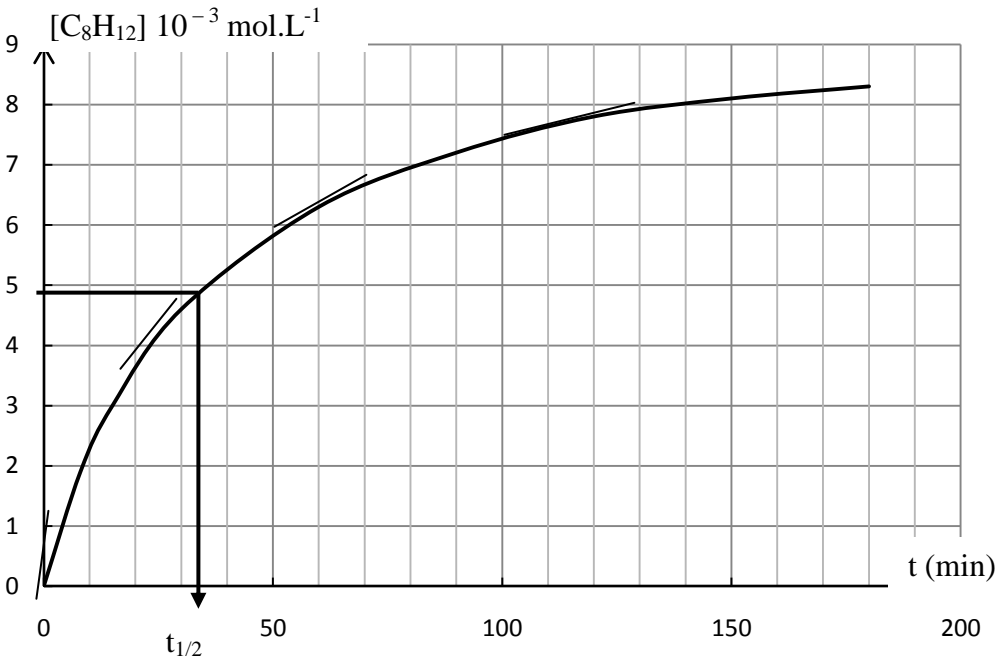
2.3- Deduce the percentage by mass of $NaHCO_3$ in the sample of the medicinal powder.

2.4- The above titration is carried out again but with one change: the volume V_1 is introduced into a beaker containing 20 mL distilled water and the appropriate colored indicator.
By consulting the table below, compare V'_E and V_E on one hand and pH'_E and pH_E on the other hand. Justify.

	Volume of the acid added at equivalence	pH of the mixture at equivalence
Titration without addition of distilled water	V_E	pH_E
Titration with addition of distilled water	V'_E	pH'_E

First Exercise (6 points)
Kinetic of Dimerization of Butadiene

Question	Answer	mark
1.1	$2\ C_4H_{6(g)} \quad \rightarrow \quad C_8H_{12(g)}$ Initial state $\qquad n_0$ - At t $\qquad\qquad n_0 - 2\ xx$	0.5
1.2	Ideal gas law: $P \times V = (n_0 - x) \times R \times T = n_0 \times R \times T - x \times R \times T$ but $[C_8H_{12}] = \dfrac{x}{V} = \dfrac{P_0 - P}{RT} = \dfrac{P_0 - P}{49.998}$ where P is in atm and $[C_8H_{12}]$ in mol.L^{-1}.	1
1.3	At the end of the transformation, $P = P_0 / 2$. $[C_8H_{12}] = \dfrac{P_0}{2 \times 49.938} = 0.010$ mol.L^{-1}	0.5
2.1	The curve is : 	1
2.2	Graphically, the rate of formation of C_8H_{12} is equal to the slope of the tangent at the curve at the point of abscissa t. At t = 0, this slope is maximal and decreases with time.	0.75
2.3	The half-life time of a reaction is the time required for C_8H_{12} to reach half its maximum concentration. At $t_{1/2}$, $[C_8H_{12}] = \dfrac{[C_8H_{12}]\max}{2} = \dfrac{0.01}{2} = 5.0 \times 10^{-3}$ mol.L^{-1}.	0.75

	Graphically : $t_{1/2}$ = 36 min.	
2.4	The curve that represents the change in the $[C_4H_6]$ as a function of time should pass through two specific points: (At t = 0) $[C_4H_6]$ initial = $2 \times[C_8H_{12}]$ at the end of transformation = 0.020 mol.L^{-1}. At $t_{1/2}$, $[C_4H_6]$ should have the value of 0.020 / 2 = 0.010 mol.L^{-1}. The curve (a) is not the convenient one since its initial concentration $[C_8H_{12}]_0$=16.8mmol.L^{-1} The curve (b) is not the convenient one since $t_{\frac{1}{2}}$=20min Therefore, the graph (c) represents this change since $[C_4H_6]_0$= 0.020 mol.L^{-1} and $t_{\frac{1}{2}}$=36 min	1.5

Second Exercise (7 points)
The pheromones

Question	Answer	mark
1.1	The common functional group of pheromones A and B is the ester group.	0.25
1.2	the possible formulas are: $CH_3 - COOH$; $CH_3 - CO - Cl$ and $CH_3 - CO - O - CO - CH_3$.	0.75
1.3	the formula of this product is: $CH_3 - CH_2 - CH_2 - CH - C - CH_2 - CH_3$ $\qquad\qquad\qquad\quad |\quad ||$ $\qquad\qquad\qquad CH_3\ O$ Its name: 4 – methyl-3-heptanone	0.75
1.4	To identify the chemical function of the compound D, the two following tests are carried out: - Few drops of 2.4-D.N.P.H are added into a test tube containing few milliliters of the compound D a yellow-orange precipitate is obtained. - Few drops of Fehling reagent are added into a test tube containing few milliliters of the compound D. After gentle heating, the medium remains blue.	1
2.1	The equation of this reaction is: $CH_3 - CH - CH_2 - CH_2\ OH +\ HO\ - C\ -CH_3 \rightleftarrows CH_3 - CH - CH_2 - CH_2 - O - C - CH_3 + H_2O$ $\qquad |\qquad\qquad\qquad\qquad\quad ||\qquad\qquad\qquad\quad |\qquad\qquad\qquad\quad ||$ $CH_3\ O\ CH_3\quad O$	0.75
2.2	This reaction is slow; from the sentence of the experimental procedure. « This mixture is heated for 45 min ».	0.5
2.3	n(acid) initial = $\dfrac{m(acid)\,initial}{M(acid)} = \dfrac{d \times V_2}{M(acid)} = \dfrac{30 \times 1.04}{60} = 0.52$ mol	0.5

2.4	The yield of this reaction: yield = $\dfrac{n(ester)\,actual}{n(ester)\,theoretical} = \dfrac{n_1}{n_2}$ with	1
	$n_1 = \dfrac{m(ester)\,actual}{M(ester)} = \dfrac{17.42}{130} = 0.134$ mol.	
	$n_2 = n(alcohol)\ initial = 0.2$ mol. So yield = 0.67, or 67%.	
2.5	The initial mixture is not equimolar, the yield at equilibrium must exceed 67%. So, the duration of min is not sufficient to reach the equilibrium of this reaction.	0.5
2.6	The two ways are: - removing the water from the reacting medium as long as it is formed. - using an initial mixture where the difference between the two reactants exceeds the value of 0.32 (0.52 – 0.20).	1

Third Exercise(7 points)
Sodium Bicarbonate

Question	Answer	mark
1.1	Hydrogen carbonate ion has an amphoteric character since it belongs to two acid/base pairs: HCO_3^- / CO_3^{2-} and $CO_2, H_2O / HCO_3^-$.	0.5
1.2.1	From the graph, the % by mol of HCO_3^- is 67 ; that of CO_3^{2-} is 33 $\dfrac{[CO_3^{2-}]}{[HCO_3^-]} = \dfrac{\%\,by\,mol\,CO_3^{2-}}{\%\,by\,mol\,HCO_3^-} = 33/67 = 0.5$	0.75
1.2.2	The introduced quantity of HCO_3^- ions (produced by $NaHCO_3$) and that of CO_3^{2-} ions (produced by Na_2CO_3) are conserved in the obtained solution. $\dfrac{[CO_3^{2-}]}{[HCO_3^-]} = \dfrac{\dfrac{n_1}{V(solution)}}{\dfrac{n_2}{V(solution)}} = \dfrac{n_1}{n_2}$ With $n_1 = n(CO_3^{2-})$ formed in the solution = $n(Na_2CO_3)$ initial = 3.0×10^{-2} mol and $n_2 = n(HCO_3^-)$ formed in the solution = $n(NaHCO_3)$ initial = $\dfrac{m(NaHCO_3)\,initial}{M(NaHCO_3)} = \dfrac{m}{84}$ mol. By calculation m= 5.04 g.	1.25
2.1	The materials needed for the preparation of the solution (S) is : Precision balance, watch glass, funnel and 200 mL volumetric flask.	1
2.2	n ($NaHCO_3$) dissolved in V_1 = n (HCO_3^-) initial in V_1 = n (H_3O^+) added to reach equivalence. Therefore [HCO_3^-]$\times V_1 = C \times V_E$; [HCO_3^-]$=\dfrac{C\times VE}{V1}=\dfrac{0.05\times16.8}{10}=8.4\times10^{-2}$ mol.L^{-1}	1
2.3	n ($NaHCO_3$) in the sample = n (HCO_3^-) dissolved in $V_0 = 8.4\times10^{-2} \times 0.2 = 1.68\times10^{-2}$ mol.	

	m (NaHCO$_3$) in the sample = n (NaHCO$_3$) × M(NaHCO$_3$) = 1.68×10^{-2} × 84 = 1.41 g. Degree of purity = $\dfrac{m(NaHCO_3)\ pure}{m(sample)} \times 100 = \dfrac{1.41}{1.50} \times 100 = 94\ \%$.	1.5
2.4	$V'_E = \dfrac{n(HCO_3^-)\ initial\ in\ V_1}{C}$. the dilution of solution does not change the initial quantity of HCO$_3^-$ and C is the concentration of the acid solution in the buret, therefore $V'_E = V_E$ The solution obtained at equivalence is acidic, the dilution of an acidic solution increases its pH, therefore pH$'_E$>pH$_E$.	0.5 0.5