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:

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 gasis 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 ofC_8H_{12} gas is 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}gasat 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 to1.0×10^{-2} mol.L^{-1}knowing that the initial pressure inside the container is P_0 = 1.0 atm.

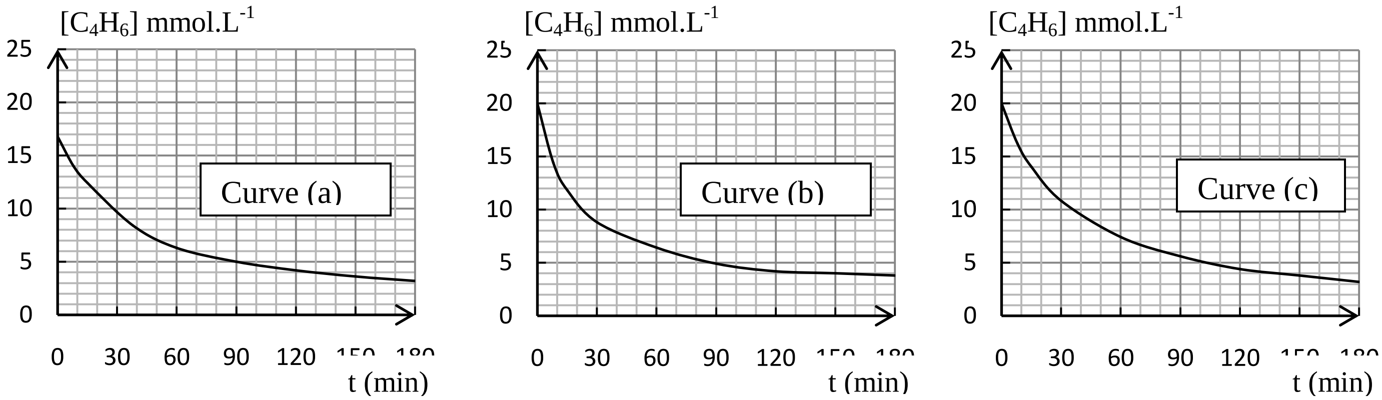
2- Kinetic Study

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.



Second Exercise(7 points)
Hydrolysis Reactions

Water is a universal solvent which plays different roles in chemistry. It can react with carboxylic acid derivatives (R – CO – Z) according to hydrolysis reactions of which the general equation is:

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‖ ||
R – C –Z + H – OH ⇄ R– C– OH +Z–H

Given:

- Starting from equimolar mixture of ester and water, theyield of the hydrolysis reaction of the ester at equilibrium is 33% when a primary alcohol is formed.
- Ethanol and glycerol are miscible with water in all proportions.

1- Hydrolysis of a Dipeptide

The hydrolysis of the dipeptide (Gly-Val), of formula: $H_2N – CH_2 – C(=O) – NH – CH – C(=O) – OH$ (with a substituent bond on CH)

produces two products (A) and (B)

1.1- Name the functionalgroupsthat characterizethe molecule (Gly-Val).
1.2- Write the condensed structural formulas of the products (A) and (B).
1.3- Represent, according to Cram, the two enantiomers of the chiral product of this hydrolysis.

2- Hydrolysis of Esters

2.1- A mixture of 1 mol of ethyl propanoate and of 3mol of water is heated to reflux in the presence of an acid catalyst.
  2.1.1- Write, using condensed structural formulas of the organic compounds, the equation of this hydrolysis reaction.
  2.1.2- One of the following values represents the number of moles of the acid formed at equilibrium: 0.33 mol ; 0.53 mol and 1 mol.Choose, by justifying, the appropriate value.

2.2- A mixture of olive oil and an excess of concentrated aqueous solution of sodium hydroxide in the presence of ethanol as solvent is heated to reflux.

The word equation of this reaction is:

$$\text{Olein + sodium hydroxide} \rightarrow \text{soap + glycerol}$$

2.2.1- Write the condensed structural formula of glycerol and the formula of olein knowing that it is a triester of oleic acid of formula $C_{17}H_{33} - COOH$.

2.2.2- After the relargage of soap in a saturated aqueous sodium chloride solution, two phases are obtained: the soap and the aqueous phase.

List four chemical species,other than water, that exist in the aqueous phase.

2.3- The two statements below are suggested for the above two realized reflux heating and their results :

2.3.1- At the endof the reflux heating, the volume of the reacting medium does not change.

2.3.2- The end of the transformation is reached faster than that when the reacting mixture is kept at room temperature.

When the statement is true, justify it; when it is false, specify the correct answer.

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 todetermine 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.
- $\dfrac{[CO_3^{2-}]}{[HCO_3^-]} = \dfrac{\%(\text{by mol})CO_3^{2-}}{\%(\text{by mol})HCO_3^-}$.
- M ($NaHCO_3$) = 84 $g.mol^{-1}$.

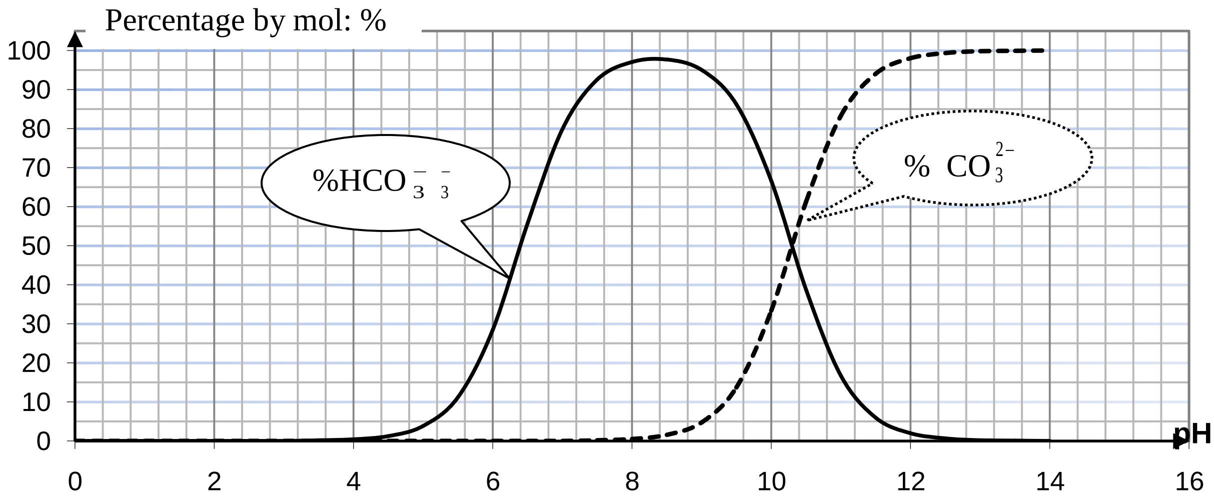
1- Study of Hydrogen Carbonate Ion

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

$HCO_3^- + H_2O \rightleftarrows CO_3^{2-} + H_3O^+$ (1) or $HCO_3^- + H_2O \rightleftarrows HO^- + CO_2, H_2O$ (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:



1.2.1- Calculate, based on the above graph, the ratio $\frac{[CO_3^{2-}]}{[HCO_3^-]}$ 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 powderof 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 = 5.0×10^{-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.

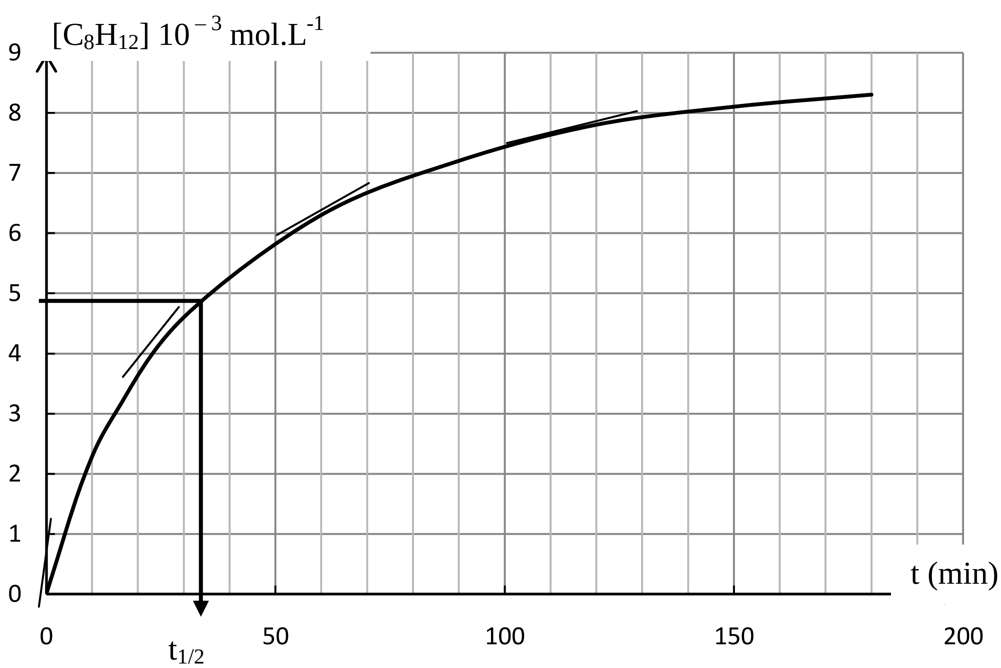
2.2- Determine the molar concentration of HCO_3^- ionsin the solution (S), knowing that the volume of the acid added to reach equivalence is V_E = 16.8 mL.

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.

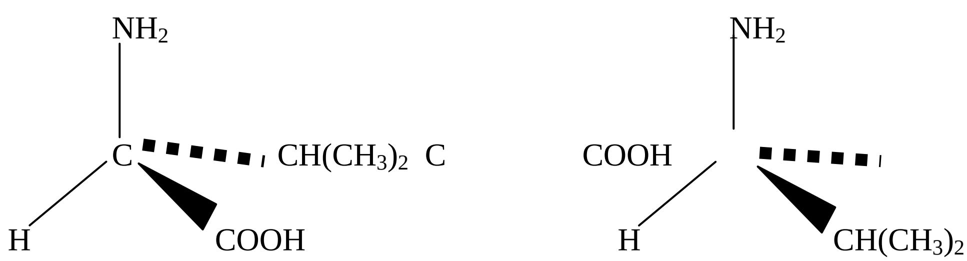
	Volume of the acid added at equivalence	pH of the mixture at equivalence
Titration without addition of distilled water	V_E	pH_E
Titration with addition of distilled water	V'_E	pH'_E

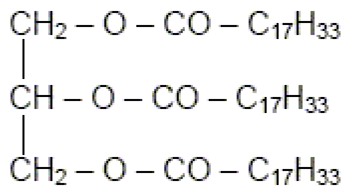
First Exercise (6 points)
Kinetic of Dimerization of Butadiene

Question	Answer	mark
1.1	$2\ C_4H_{6(g)} \rightarrow C_8H_{12(g)}$ Initial state n_0 - At t $n_0 - 2\ xx$	0.5
1.2	Ideal gas law: P×V = ($n_0 - x$) ×R×T = n_0 ×R×T – x ×R×T but $[C_8H_{12}] = \frac{x}{V} = \frac{P_{0-P}}{RT} = \frac{P_{0-P}}{49.998}$ 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. $[C_8H_{12}] = \frac{P_0}{2\times 49.938} = 0.010\ mol.L^{-1}$	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 $t_{1/2}$, $[C_8H_{12}] = \frac{[C_8H_{12}]max}{2} = \frac{0.01}{2} = 5.0\times10^{-3}\ mol.L^{-1}$.	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 ×$[C_8H_{12}]$ 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 $[C_8H_{12}]_0$=16.8$mmol.L^{-1}$ 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)
Hydrolysis Reactions

Question	Answer	mark
1.1	The functional groups are:carboxyl group, amidegroupand amino group.	**0.75**
1.2	the formulas are**:** $H_2N - CH_2 - COOH$ and $NH_2 - CH(COOH) - CH(CH_3)_2$	**0.5**
1.3	The twoenantiomeresare:  	**0.75**
2.1.1	The equation of this reaction is: $CH_3 - CH_2 - COO - CH_2 - CH_3 + H_2O \rightleftarrows CH_3 - CH_2 - COOH + CH_3 - CH_2OH$	**0.75**
2.1.2	This reaction is a limited reaction, n (acid) formed at equilibrium could not be1 mol. The initial mixture is not equimolar, n (acid) formed at equilibrium could not be 0.33 mol.Therefore n (acid formed) is 0.53 mol.	**1**
2.2.1	The condensed structural formula of glycerol is: $CH_2OH - CHOH - CH_2OH$. That of olein is:	**0.25**

		**0.5**
2.2.2	The chemical species that exist in the aqueous phase are: Na^+, OH^- ,Cl^- , ethanol and glycerol.	**1**
2.3.1	During the reflux heating the volume of the reacting mixture does not change since the vapors released from the flask are condensed andreturned back to the flask.	**0.75**
2.3.2	Temperature is a kinetic factor, when it increases, the rate of the reaction increases.Therefore the end time of reaction is reached faster when the reacting medium is heated.	**0.75**

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 molof HCO_3^- is 67 ; that of CO_3^{2-} is 33 $\frac{[CO_3^{2-}]}{[HCO_3^-]} = \frac{\%\text{by mol } CO_3^{2-}}{\%\text{by mol } HCO_3^-}$ = 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. $\frac{[CO_3^{2-}]}{[HCO_3^-]} = \frac{\frac{n_1}{V(solution)}}{\frac{n_2}{V(solution)}} = \frac{n_1}{n_2}$ 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 = $\frac{m(NaHCO_3)initial}{M(NaHCO_3)} = \frac{m}{84}$ 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	1

	equivalence. Therefore [HCO_3^-]×V_1=C×V_E; [HCO_3^-]=$\frac{C\times VE}{V1}$=$\frac{0.05\times 16.8}{10}$=$8.4\times10^{-2}$mol.$L^{-1}$	
2.3	n ($NaHCO_3$) in the sample = n (HCO_3^-) dissolved in V_0 = $8.4\times10^{-2}\times 0.2$ =1.68×10^{-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 = $\frac{m(NaHCO_3)\ pure}{m(sample)}\times 100 = \frac{1.41}{1.50}\times 100$ = 94 %.	1.5
2.4	V'_E= $\frac{n(HCO_3^-)\, initial\, in V_1}{C}$. 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