This Exam Includes Three Exercises. It Is Inscribed on 3 Pages Numbered From 1 to 3. The Use of a Non-programmable Calculator Is Allowed.
Answer the three Following Exercises:

First Exercise (6 points)
Identification of certain Organic Compounds

The mild oxidation of an alcohol (A) leads to the formation of a monocarboxylic acid (B) with a saturated open carbon chain.
The aim of this exercise is to identify (A) and (B) and to study their esterification reaction.

Given:
-   M(H) = 1 g.mol $^{-1}$; M(C) = 12 g.mol $^{-1}$; M(O) = 16 g.mol $^{-1}$
-   The yield of the esterification of an equimolar mixture of carboxylic acid and a primary alcohol is 67 %.

1- Identification of (A) and (B)

The percentage by mass of oxygen in the acid (B) is 36.36 %
   1.1-Show that the molecular formula of (B) is $C_4H_8O_2$. Deduce the molecular formula of (A).
   1.2-Knowing that the carbon chain of (A) is branched, identify (A) and (B),

2- Esterification of Alcohol (A)

A mixture of 1 mol of (A) and 2 mol of (B) is heated in the presence of few drops of concentrated sulfuric acid. After a certain time, a homogeneous equilibrium is established with a constant $K_C = 4$.
   2.1- Write the equation of this reaction. Give the systematic name of the organic compound (C) formed.
   2.2- Determine the number of moles of (C) formed at equilibrium. Deduce the yield of this esterification.
   2.3- This yield exceeds 67 %. Explain, if each one of the three following proposals justifies this fact:
     2.3.1- Heating the reacting medium.
     2.3.2- Presence of few drops of sulfuric acid in the reacting medium.
     2.3.3- Using an initial mixture of reactants which is not equimolar.
   2.4-In order to make the formation reaction of (C) complete, (B) is replaced by one
      of the two compounds (B ') and (B"). The equations of the two reactions are the following:

$$A + B' \rightarrow B + C \qquad\qquad (1)$$
$$A + B'' \rightarrow C + HCl \qquad\qquad (2)$$

   Identify (B ') and (B").

Second Exercise (7 points)
Decomposition Reaction of N_2O_5

Nitrogen pentoxide decomposes completely when heated, in the gaseous phase, according to the following equation: $2 N_2O_{5 (g)} \rightarrow 4 NO_{2 (g)} + O_{2 (g)}$.

Given:

- All gases are considered ideal.
- The ideal gas constant is $R = 0.082$ atm.L.mol^{-1}.K^{-1}.

1- Decomposition of N_2O_5 in a Container of Constant Volume

$n_0 = 1$ mol of N_2O_5 is introduced into a container of constant volume $V = 10$ L, maintained at a temperature $T = 413$ K.

1.1- Calculate, p_0, the initial pressure in the container.

1.2- Show that the total pressure p in the container increases when the reaction of decomposition of N_2O_5 advances.

1.3- Calculate the maximum value of p.

1.4- Show that the concentration of N_2O_5, at instant t, is given by the following relation:

$$[N_2O_5]_t = \frac{5p_0 - 2p}{3RT}.$$

2- Kinetics of the Decomposition Reaction of N_2O_5

The above reaction is slow, to study its kinetics, a certain quantity of N_2O_5 is introduced, at constant temperature, into an evacuated container which is connected to a pressure gauge.
The measurement of the pressure in the container makes it possible to calculate the concentration of $[N_2O_5]_t$ at instant t.
The results are given in the following table:

t(s)	0	200	400	600	800	1000	1200	1400	1600	1800	2000
$[N_2O_5]_t$ (mol.L^{-1})	1	0.88	0.78	0.69	0.61	0.54	0.48	0.43	0.38	0.34	0.30

2.1- Plot, on the graph paper, the curve $[N_2O_5]_t = f(t)$. Take the following scale: abscissa 1 cm for 200 s and ordinate 1 cm for 0.1 mol.L^{-1}.

2.2- Determine graphically the half-life of the reaction.

2.3- Determine the rate of disappearance of N_2O_5 when its concentration becomes 0.8 mol.L^{-1}. Deduce the rate of the reaction at the same instant.

Third Exercise (7 points)
Acid-base Reactions

Given:

Conjugate acid/base pair	$CH_3NH_3^+ / CH_3NH_2$	NH_4^+ / NH_3	HF/ F$^-$	HCOOH/ HCOO$^-$
pK_a	10.7	9.2	3.2	3.8

- The ionic product of water: $K_w = 1.0 \times 10^{-14}$
- Sodium methanoate HCOONa and ammonium chloride NH$_4$Cl are ionic compounds highly soluble in water.

Four beakers contain each an aqueous solution of one of the chemical compounds given in the table below. The solutions have all the same molar concentration C_0.

Number of the beaker	Chemical compound	pH
1	Sodium methanoate	pH_1
2	Ammonium chloride	pH_2
3	Methylamine CH_3NH_2	pH_3
4	Hydrogen fluoride HF	pH_4

1- pH of the Aqueous Solutions

1.1- Classify the pH of these four solutions by ascending order.
1.2- The pH of the solution in beaker N° 4 has the value of 2.65.
1.2.1- Write the equation of the reaction between HF and water.
1.2.2- Show that the molar concentration C_0 is equal to 1.0×10^{-2} mol.L^{-1}.
1.3- Distilled water is added to a volume $V_0 = 10$ mL of the solution of beaker N° 3 until we obtain a solution S of volume V = 100 mL. The pH of the solution of beaker N° 3 and that of solution S are measured. The results are given in the following table:

Solution	Beaker N° 3	S
C (mol.L^{-1})	1.0×10^{-2}	1.0×10^{-3}
pH	11.3	10.7
α	0.2	-

Where α is the coefficient of conversion of methylamine during its reaction with water.
1.3.1- Write the equation of the reaction between methylamine and water.
1.3.2- Name the glassware used to measure with precision the two volumes V_0 and V used in the preparation of solution S.
1.3.3- Determine the value of α in solution S missing in the above table. Conclude?
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2- Preparation of a Buffer Solution

To prepare a buffer solution of pH = 9.0, a volume V_1 of sodium hydroxide solution of concentration $C = 1.0 \times 10^{-2}$ mol.L^{-1} is added to a volume $V_2 = 40$ mL of the solution of beaker N° 2 (ammonium chloride solution).
2.1- Write the equation of the reaction which takes place in this mixture.
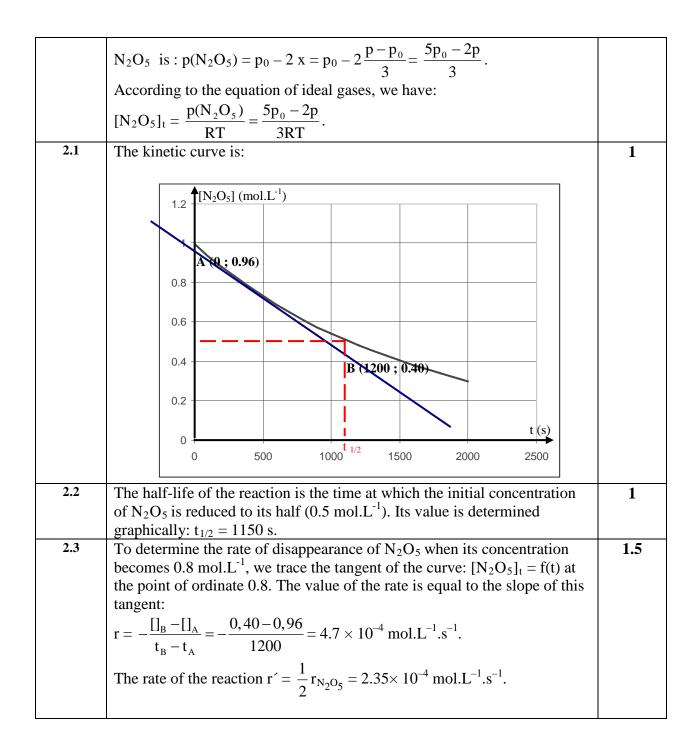2.2- Show that this reaction is total.
2.3- Determine V_1.

First Exercise (6 points)

Part of the Q	Answer	Mark
1.1	The formula of a carboxylic acid with saturated acyclic carbon chain is $C_nH_{2n}O_2$. The % of oxygen is: $\dfrac{32}{12n + 2n + 32} \times 100 = 36.36$. $3200 = 509.04\,n + 1163.52$; $n = 4$. The formula of (B) is then $C_4H_8O_2$ and that of (A) is $C_4H_{10}O$, because by mild oxidation the carbon skeleton remains the same.	**1**
1.2	The carbon chain is branched, the condensed structural formulas are then: CH_3 $\qquad\qquad\qquad$ CH_3 $\mid$ $\qquad\qquad\qquad\qquad$ $\mid$ $CH_3 - CH - CH_2OH$ $\qquad$ $CH_3 - CH - C - OH$ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \parallel$ (A) $\qquad\qquad\qquad\qquad$ (B) $\qquad$ O 2-methyl-1-propanol $\qquad$ 2-methylpropanoic acid	**1**
2.1	The equation of the reaction between (A) and (B) is: $CH_3 \qquad CH_3 \qquad\qquad\qquad CH_3 \qquad\qquad CH_3$ $\mid \qquad\quad \mid \qquad\qquad\qquad\qquad \mid \qquad\qquad\quad \mid$ $CH_3 - CH - COOH + CH_3 - CH-CH_2OH \rightleftharpoons H_2O + CH_3 - CH - C - O - CH_2 - CH - CH_3$ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \parallel$ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad O$ (C) is 2-methylpropyl-2-methylpropanoate .	**0,75**
2.2	The law of mass action is: $K_c = \dfrac{[ester][water]}{[acid][alcohol]}$ The composition of the system is: |	Acid	Alcohol	Ester	Water
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Initial state	2	1	0	0
$\rightleftharpoons$ state	2 – x	1 – x	x	x | We have then: $\dfrac{(\frac{x}{V})^2}{\frac{(1-x)(2-x)}{V^2}} = 4.$ the following equation : $3x^2 - 12x + 8 = 0$, gives to x the acceptable value : x = 0.845. The number of moles of (C) formed is 0.845 mol. The yield of the esterification is: $R = \dfrac{n(ester)\,exp}{n(ester)\,the}$ n(ester)the = n(alcohol)ini(limiting reactant) $R = \dfrac{0.845}{1} = 0.845$ or 84.5 %.	**1,25**

2.3.1	The reaction of esterification is athermic, thus heating does not affect the equilibrium (the limit does not vary), it simply increases the rate to reach this equilibrium.	0,25
2.3.2	the presence of few drops of sulfuric acid does not change the yield of esterification because, in small quantity, this acid acts as a catalyst and has only kinetic role	0,25
2.3.3	Introducing an initial mixture whch is not equimolar supports the reaction in the direction of formation of ester and consequently increases the yield of esterification to exceed 67 %.	0,25
2.4	The two compounds which can replace this acid in the reaction of synthesis of ester are:

$$CH_3\text{–}CH\text{–}CH_2OH + B' \rightarrow CH_3\text{–}CH\text{–}C\text{–}OH + CH_3\text{–}CH\text{–}C\text{–}O\text{–}CH_2\text{–}CH\text{–}CH_3$$

(with CH_3 branches on the CH groups and $\|O$ on the C groups)

The formula of (B´) is then:

$$CH_3\text{–}CH\text{–}C\text{–}O\text{–}C\text{–}CH\text{–}CH_3$$

(with CH_3 branches and $\|O$ on both C groups)

2-methylpropanoic anhydride.
By the same way, the formula of (B´´) is:
$CH_3 – CH(CH_3) – COCl$. It is 2-methylpropanoyl chloride. | 1.25 |

Second Exercise (7 points)

Part of the Q	Answer	Mark
1.1	The ideal gas equation makes it possible to calculate p_0 : $$p_0 = \frac{n \times R \times T}{V} = \frac{1 \times 0.082 \times 413}{10} = 3.387 \text{ atm.}$$	0.5
1.2	The change of the pressure can be represented by the following table: | Instant	$p(N_2O_5)$	$P(NO_2)$	$p(O_2)$
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0	p_0	0	0
t	$p_0 - 2x$	$4x$	x | The total pressure is: $p = p_0 - 2x + 4x + x = p_0 + 3x > p_0$. The pressure increases throughout the reaction.	1
1.3	The maximum value of p is obtained when N_2O_5 reacts completely and its pressure is cancelled: $$p_0 - 2x = 0 \; ; \; x = \frac{1}{2}p_0 \text{ and } p = p_0 + 3\frac{p_0}{2} = 2.5\,p_0 = 8.467 \text{ atm}$$	0.75
1.4	The total pressure $p = p_0 + 3x$, where $x = \frac{p - p_0}{3}$ and the pressure of	1.25

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	N_2O_5 is : $p(N_2O_5) = p_0 - 2\,x = p_0 - 2\dfrac{p - p_0}{3} = \dfrac{5p_0 - 2p}{3}$. According to the equation of ideal gases, we have: $[N_2O_5]_t = \dfrac{p(N_2O_5)}{RT} = \dfrac{5p_0 - 2p}{3RT}$.		
2.1	The kinetic curve is: 		**1**
2.2	The half-life of the reaction is the time at which the initial concentration of N_2O_5 is reduced to its half (0.5 mol.L^{-1}). Its value is determined graphically: $t_{1/2} = 1150$ s.		**1**
2.3	To determine the rate of disappearance of N_2O_5 when its concentration becomes 0.8 mol.L^{-1}, we trace the tangent of the curve: $[N_2O_5]_t = f(t)$ at the point of ordinate 0.8. The value of the rate is equal to the slope of this tangent: $r = -\dfrac{[]_B - []_A}{t_B - t_A} = -\dfrac{0{,}40 - 0{,}96}{1200} = 4.7 \times 10^{-4}$ mol.L^{-1}.s^{-1}. The rate of the reaction $r' = \dfrac{1}{2}\,r_{N_2O_5} = 2.35\times 10^{-4}$ mol.L^{-1}.s^{-1}.		**1.5**

Part of the Q	Answer	Mark
1.1	Starting with the same initial concentration, the smallest value of pKa corresponds to the most strong acid and consequently the lowest value of pH: $pK_a (HF/F^-) < pK_a (NH_4^+/NH_3)$ thus $pH_4 < pH_2 < 7$. Starting with the same initial concentration, the smallest value of pKa corresponds to the most weak base and consequently the lowest value of pH: $pK_a (HCOOH/HCOO^-) < pK_a(CH_3NH_3^+ / CH_3NH_2)$ thus $7 < pH_1 < pH_3$. The order of increasing pH is then: pH_4, pH_2, pH_1, pH_3.	1.25
1.2.1	The equation of this reaction is: $HF + H_2O \rightleftharpoons F^- + H_3O^+$	0.5
1.2.2	According to the equation of this reaction, we can write: $[F^-] = [H_3O^+] = 10^{-pH} = 10^{-2.65} = 2.23 \times 10^{-3}$ mol.L^{-1} and $[HF] = C_0 - [F^-]$. In addition, $K_a (HF/F^-) = \dfrac{[H_3O^+] \times [F^-]}{[HF]}$ and $C_0 = \dfrac{(2.23 \times 10^{-3})^2}{6.31 \times 10^{-4}} + 2.23 \times 10^{-3} = 1.01 \times 10^{-2}$ mol.L^{-1}.	1
1.3.1	The equation of this reaction is: $CH_3NH_2 + H_2O \rightleftharpoons OH^- + CH_3NH_3^+$	0.5
1.3.2	To take V_0, we use a volumetric pipette of 10 mL and to have volume V, we use a volumetric flask of 100 mL.	0.5
1.3.3	In solution S: $\alpha = \dfrac{n(CH_3NH_2)transformed}{n(CH_3NH_2)initial} = \dfrac{n(OH^-)formed}{n(CH_3NH_2)initial} = \ldots = \dfrac{[OH^-]}{C} =$ $\dfrac{10^{pH-14}}{10^{-3}} = 0.5$. The dilution of the solution of ethylamine favors its reaction with water.	0.75
2.1	The equation of this reaction is: $OH^- + NH_4^+ \rightleftharpoons NH_3 + H_2O$.	0.5
2.2	The constant K_r of this reaction is: $K_r = 10^{14-9.2} = 6.4 \times 10^4 > 10^4$; thus this reaction is complete.	0.75
2.3	Calculation of V_1, knowing that $C = C_0$: Since the solution is buffer, NH_4^+ and NH_3 coexist, HO^- is the limiting reactant. $\qquad\qquad OH^- + NH_4^+ \rightarrow NH_3 + H_2O$ Initial state $\quad C \times V_1 \qquad C_0 \times V_2 \qquad 0 \qquad$ solvent Obtained solution 0 $\qquad C(V_2 - V_1) \qquad C \times V_1 \qquad$ solvent $pH (solution) = pK_a (NH_4^+/NH_3) + \log \dfrac{[NH_3]}{[NH_4^+]}$; so : $\log \dfrac{V_1}{V_2 - V_1} = 9 - 9.2 = -0.2$ and $V_2 = 40$ mL, hence $V_1 = 15.5$ mL.	1.25