الدورة الإستثنائية للعام 2011	امتحانات الشهادة الثانوية العامة الفرع : علوم الحياة	وزارة التربية والتعليم العالي المديرية العامة للتربية دائرة الامتحانات
الاسم: الرقم:	مسابقة في مادة الكيمياء المدة ساعتان	

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)
Carboxylic Acid Derivatives

Acid derivatives are more reactive than the corresponding carboxylic acids, especially in the preparation of esters.
The aim of this exercise is to recognize some acid derivatives, their reactions and their preparations.

<u>Given:</u>

- Molar mass in $g.mol^{-1}$: M(H) = 1; M(C) = 12; M(O) = 16; M(Cl) = 35.5
- Density of the liquid compound (B): d = $1.065 g.ml^{-1}$.

1- <u>Structural Formulas of Some Acid Derivatives</u>

The condensed structural formulas of some acid derivatives are given below:

(A): $C_2H_5-\overset{\overset{\large O}{\|}}{C}-O-\overset{\overset{\large O}{\|}}{C}-CH_3$; (B): $C_2H_5-\overset{\overset{\large O}{\|}}{C}-Cl$; (C): $C_2H_5-\overset{\overset{\large O}{\|}}{C}-\overset{\overset{\large C_2H_5}{|}}{N}-C_2H_5$

1.1- Give the systematic name of each (A), (B) and (C).
1.2- Write, using condensed structural formulas of the organic compounds, the equation of one preparation reaction of (C).

2- <u>Preparation of the Compound (A)</u>

The compound (A) is a mixed anhydride less important than acetic anhydride. It is used as an intermediate in the manufacture of many industrial chemicals: perfumes, plastics …
The compound (A) is obtained, in the pure state, by proceeding as follows:
A volume V= 7 mL of liquid compound (B) is introduced into a dry beaker containing an excess of solid sodium ethanoate $CH_3COO\,Na$. A fast reaction occurs according to the following equation:

$$CH_3COONa + (B) \longrightarrow (A) + (F)$$

A mass of 6.9 g of the compound (A) is obtained at the end of the reaction.

2.1- Write the formula of the compound (F).
2.2- Determine the percentage of the compound (B) which has reacted.
2.3- This reaction should be carried out in a dry beaker. Justify.

3- Preparation of an Ester (E) from the Compound (B)

A mixture of the compound (B) and of a saturated non cyclic monoalcohol (D) is heated in the presence of an appropriate catalyst. At the end of the reaction, an ester (E) having a molar mass M= 130g.mol^{-1} is obtained.

3.1- Determine the molecular formula of the ester (E).
3.2- Deduce that the molecular formula of the alcohol (D) is C_4H_9OH.
3.3- Write the possible condensed structural formulas of the alcohol (D).
3.4- Name this alcohol (D) knowing that its molecule contains one asymmetric carbon.
3.5- Identify the ester (E).

Second Exercise (7 points)
Decomposition of Benzene Diazonium Chloride

Benzene diazonium chloride ($C_6H_5N_2Cl$) decomposes, in aqueous solution, as soon as the temperature is higher than 10°C according to the equation:

$$C_6H_5N_2Cl_{(aq)} \longrightarrow C_6H_5Cl_{(aq)} + N_{2(g)}$$

The kinetic of this reaction is followed by measuring the volume $V(N_2)$ of nitrogen gas released, under the pressure of 1 atm and at the temperature of 17 °C, starting with a volume V_0 = 35 mL of benzene diazonium chloride solution of initial concentration C_0 = 8×10^{-2}mol.L^{-1}

Given:
- Ideal gas constant: R = 0.082 L.atm.mol^{-1}.K^{-1}.
- Molar mass in g.mol^{-1}: M(H) =1; M(C) =12; M(N) =14; M (Cl) = 35.5

1- Preliminary Study

1.1- Determine the volume of nitrogen gas formed when the time tends to infinity.
1.2- Show that, at each instant , the concentration of the benzene diazonium chloride solution $[C_6H_5N_2Cl]_t$, in terms of $V(N_2)$ is given by the relation:
$[C_6H_5N_2Cl]_t = 8.0\times10^{-2} - 1.2\times V(N_2)$; Where $V(N_2)$ is expressed in liters.

2- Kinetic Study of this Decomposition Reaction

The measurement of the volume of nitrogen gas, at different instants, permits to draw up the following table:

time t (s)	0	75	150	225	300	450	600	750	900	1200
$[C_6H_5N_2Cl]_t$ (10^{-2} mol.L^{-1})	8.0	7.0	6.2	5.6	5.1	4.2	3.3	2.6	2.0	1.5

2.1- Plot the curve $[C_6H_5N_2Cl]_t = f(t)$ in the interval of time [0 –1200 s].
Take the following scales: 1 cm for 100 s in abscissa
1 cm for 1.0×10^{-2} mol.L^{-1} in ordinate.
2.2- Determine graphically the half-life time $t_{½}$ of the reaction.
2.3- Calculate the volume of nitrogen gas released at the half-life time $t_{1/2}$
2.4- Determine the rate of disappearance of benzene diazonium chloride at the instant t = 150 s.
2.5- The rate of disappearance of benzene diazonium chloride at $t_{½}$ is equal to 6.0×10^{-5} mol.L^{-1}.s^{-1}. Specify the kinetic factor responsible for its change between t and $t_{1/2}$

Third Exercise (7 points)
Commercial Solution to Decrease the pH of an Aquarium

"... .In fact, certain fishes can't grow except in an acid medium (...), others in a basic medium (...)". According to "Fishes and aquariums" - Larousse Edition.
The aim of this exercise is to study a commercial solution used to decrease the pH of the water in an aquarium.

<u>Given:</u>

- The study is carried out at T = 25° C.
- $K_a(CO_{2\,(aq)}, H_2O\ /\ HCO^-_{3(aq)}) = 4\times10^{-7}$

1- <u>Determination of the Concentration of the Commercial Solution</u>

The commercial solution used to lower the pH of the water of an aquarium is a hydrochloric acid solution of concentration C_0.
To determine C_0, one proceeds as follows:
The commercial solution is diluted 50 times; The solution obtained is noted as S_a.
A volume V_a = 20.0 mL of S_a is titrated with sodium hydroxide solution of concentration $C_b = 4.0 \times 10^{-2}$ mol.L^{-1}. The volume of the base added to reach the equivalence point is V_{bE} = 25 mL.

1.1- Describe, by specifying the material used, the procedure to be followed to prepare 1 L of solution S_a from the commercial solution.
1.2- Write the equation of the titration reaction.
1.3- Specify, based on the chemical species present, the pH of the medium obtained at the equivalence point.
1.4- Determine the concentration of the diluted solution S_a.
1.5- Deduce that the concentration of the commercial solution is 2.5 mol.L^{-1}.

2- <u>Lowering the pH in an Aquarium</u>

It is required to bring the pH of the water in an aquarium to a value close to 6
For that, one follows the instructions of the manufacturer that recommend that it is necessary to pour 20 mL of the commercial solution of concentration C_0 over 100 L of water of an aquarium. (The final volume will be considered 100 L).

2.1- Supposing that this is a simple dilution of H_3O^+ ions, show that the value of the pH of water in the aquarium will be 3.3
2.2- In fact, the water used in the aquarium is very calcareous; it contains hydrogen carbonate ions (HCO_3^-). The H_3O^+ ions introduced in the aquarium will react with these ions according to the following equation: $HCO^-_{3(aq)} + H_3O^+_{(aq)} \rightleftharpoons CO_{2\,(aq)}, H_2O + H_2O_{(l)}$

2.2.1- Show that this reaction is complete.
2.2.2- Interpret the difference between the value of pH = 3.3 and the required value of the pH of the water of the aquarium which is equal to 6

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Answer the three following exercises:

First Exercise (6 points) (G.S)

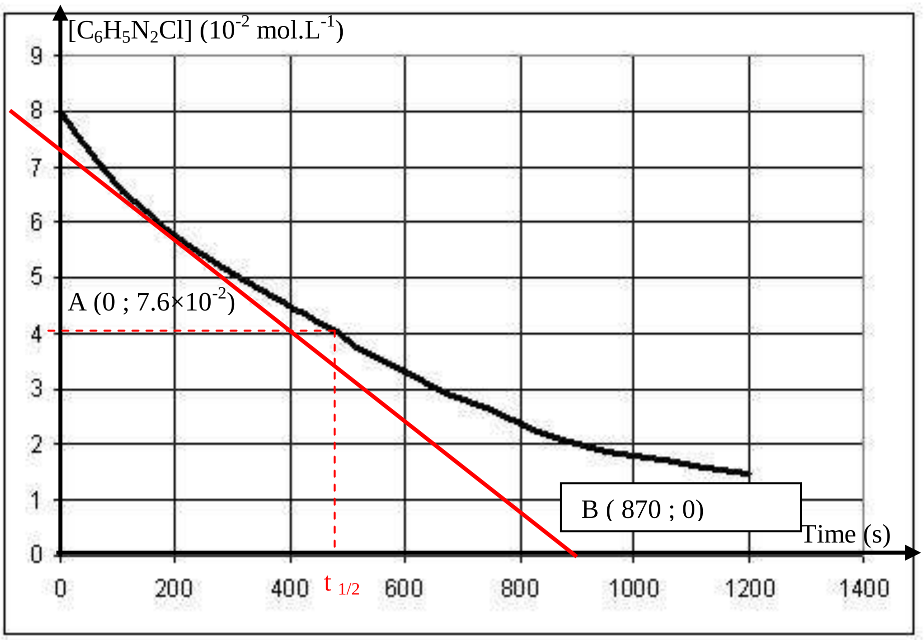
Part of the Q	Answer	Mark
1.1	Name of (A): ethanoic propanoic anhydride Name of (B): propanoyl chloride	0.5
1.2	$C_2H_5-COOH + PCl_5 \longrightarrow C_2H_5-COCl + POCl_3 + HCl$	0.5
2.1	The formula of C is NaCl.	0.25
2.2	$n(B)_{reacted} = = n(A)_{obtained} = \frac{m(A)}{M(A)} = \frac{6.9}{116} = 0.06$ mol . $n(B)_{initial} = \frac{m(B)}{M} = \frac{Volume(B)\times density(B)}{M} =$ $\frac{7\times1.065}{92.5} = \frac{7.455}{92.5} = 0.08$ mol % (B) reacted = $\frac{n(B)reacted}{n(B)initial}\times100 = \frac{0.06}{0.08}\times100 = 75\%$.	1
2.3	The reaction should be carried out in a dry beaker in order to prevent the hydrolysis of the propanoyl chloride.	0.5
3.1	By stoichiometry: n $(ester)_{formed} = n(B)_{initial} = 0.05$ mol . $M(E) = \frac{m(E)}{n(E)} = \frac{\mathbf{5.8}}{\mathbf{0.05}} = 116\ g.mol^{-1}$	0.5
3.2	By law of conservation of mass : $M(C_2H_5COCl) + M(D) = M(E) + M(HCl)$ $M(D) = (116 + 36.5) - 92.5 = 60\ g.mol^{-1}$. The general molecular formula of the alcohol (D) is $C_xH_{2x+1}OH$ $M(C_xH_{2x+1}OH) = 14x + 18 = 60 \Rightarrow x = 3$. So the molecular formula of alcohol (D) is C_3H_7OH.	0.75
3.3.1	Compound (M) is a carbonyl compound: an aldehyde or a ketone since it gives a yellow- orange precipitate with the reagent 2,4-DNPH. Since the compound (M) gives a brick red precipitate with Fehling's solution, so (M) is an aldehyde. Consequently the alcohol (D) is primary alcohol, since it produces an aldehyde by dehydrogenation.	0.5
3.3.2	Compound (D) : $CH_3-CH_2-CH_2OH$: 1-propanol. Compound (M) : CH_3-CH_2-CHO : propanal Compound (E) : $C_2H_5-COO-CH_2-CH_2-CH_3$: propyl propanoate.	1.5

First Exercise (6 points) (L.S)

Part of the Q	Answer	Mark
1.1	- Name of (A): ethanoic propanoic anhydride Name of (B): propanoyl chloride Name of (C) : N,N-diethylprpanamide.	0.75
1.2	$C_2H_5 -COCl + (C_2H_5)_2-NH \longrightarrow (C) + HCl$	0.5
2.1	The formula of (F) is NaCl.	0.25
2.2	$n(B)_{reacted} = n(A)_{obtained} = \frac{m(A)}{M(A)} = \frac{6.9}{116} = 0.06$ mol . $n(B)_{initial} = \frac{m(B)}{M} = \frac{Volume(B) \times density(B)}{M} =$ $\frac{7 \times 1.065}{92.5} = \frac{7.455}{92.5} = 0.08$ mol % (B) reacted $= \frac{n(B)reacted}{n(B)initial} \times 100 = \frac{0.06}{0.08} \times 100 = 75\%$.	1
2.3	The reaction should be carried out in a dry beaker in order to prevent the hydrolysis of the propanoyl chloride.	0.25
3.1	The general formula of the ester (E) is $C_nH_{2n}O_2$, since it is obtained from a saturated acid derivative and a saturated monoalcohol. M(E) = 14n +32 = 130 ; n = 7; the molecular formula of (E) is $C_7H_{14}O_2$.	0.5
3.2	By law of conservation of mass : n(carbon atoms)in the alcohol (D)= n(carbon atoms) in E – n(carbon atoms)in B = 7-3=4 the molecular formula of alcohol (D) is C_4H_9OH.	0.75
3.3	The possible formulas of (D): $CH_3 -CH_2 - CH_2 -CH_2OH$; $CH_3 -CH_2 -CHOH -CH_3$ $CH_3 -CH(CH_3) -CH_2OH$; $CH_3 -COH(CH_3) -CH_3$	1
3.4	Alcohol (D) : 2-butanol.	0.25
3.5	Compound (E) : $CH_3 -CH_2 -COO -CH(CH_3) -CH_2 -CH_3$ 1-methyl propyl propanoate	0.75

Second Exercise (7 points)

Part of the Q	Answer	Mark
1.1	At t_∞ $n(N_2)$formed = $n(C_6H_5N_2Cl)_{initial} = C_0 \times V_0 = 8\times10^{-2}\times35\times10^{-3}$ $= 2.8\times10^{-3}$ mol $V(N_2)_\infty = \frac{n(N_2) \times R \times T}{P} = \frac{2.8 \times 10^{-3} \times 0.082 \times (273+17)}{1} = 66.6 \times10^{-3}$ L	**1.25**
1.2	n is the number of moles of $C_6H_5N_2Cl$ that reacts at instant t, so: $n(C_6H_5N_2Cl)_t$ = n (initial) – n (reacted) = n (initial) – $n(N_2)$ formed. $n(N_2)$ formed = $P\times V(N_2)/ R\times T = 1\times V(N_2) / (0.082\times 290)$ $= 0.042\ V(N_2)$	**1.5**

	Divide by the volume of the solution: $[C_6H_5N_2Cl]_t = C_0 - 0.042\ V(N_2)/ 0.035 = 8.0\times10^{-2} - 1.2 \times V(N_2)$.	
2.1	the curve  	**1**
2.2	The half-life time of the reaction $t_{1/2}$ is the time needed for the decomposition of half the initial quantity of $C_6H_5N_2Cl$. $[C_6H_5N_2Cl]t_{1/2} = 0.08 / 2 = 0.04\ mol.L^{-1}$. Graphically $t_{1/2} = 480$ s.	**1**
2.3	At the time $t_{1/2}$:$V(N_2) = V(N_2)_\infty/2 = 6.66\times10^{-2} / 2 = 3.33\times10^{-2}$ L	**0.5**
2.4	The instantaneous rate of disappearance of benzene diazonium chloride is $r = - d[C_6H_5N_2Cl]/dt$. It is equal to the opposite of the slope of the tangent to the curve at the point of abscissa t = 150 s. $r_{150} = -\dfrac{y_B - y_A}{x_B - x_A} = -\dfrac{(0-7.6)\times10^{-2}}{870} = 8.7\times10^{-5}\ mol.L^{-1}.s^{-1}$.	**1**
2.5	The decrease in the rate between t and $t_{1/2}$ is explained by the decrease in the concentration of the reactant with time. This concentration is a kinetic factor.	**0.75**

Third Exercise (7 points)

Part of the Q	Answer	Mark
1.1	During dilution: n (solute) is conserved. $C_0 \times V_0 = C_a \times V$; implies $V/V_0 = C_0/C_a = 50$ $V_0 = 1000/50 = 20$ mL. Take, using a 20 mL volumetric pipet and a pipet filler, 20 mL of the commercial solution. Introduce this volume into a volumetric flask of 1 L, filled partially with distilled water. Complete the volume with distilled water to reach the line mark. Shake several times to homogenize.	**1.5**
1.2	The equation of the reaction between a strong acid and a strong base is: $H_3O^+ + HO^- \rightarrow 2\ H_2O$	**0.5**

1.3	the chemical species in the medium at the equivalence point are : Na^+, Cl^- and H_2O. Na^+ and Cl^- are spectator ions. The pH at the equivalence point at T= 25°C ; The pH = 7	**1**
1.4	At the equivalence point: $n(H_3O^+)$ in 20 mL of S_a = $n(HO^-)$ added to reach equivalence. $C_a \times V_a = C_b \times V_{bE}$ and $C_a = \frac{4\times10^{-2}\times25}{20} = 5.0\times10^{-2}$ mol.L^{-1}.	**1**
1.5	The solution S_a is obtained by diluting 50 times the commercial solution S, we draw that C = 50 C_a = 2.5 mol.L^{-1}.	**0.5**
2.1	By neglecting the variation of volume we draw: $[H_3O^+] = \frac{n(H_3O^+)\text{initial}}{V(\text{solution})} = \frac{20\times2.5\times10^{-3}}{100} = 5.0\times10^{-4}$ mol.L^{-1}. pH = -log $[H_3O^+]$ = - log 5.0×10^{-4} = 3.3	**0.75**
2.2.1	the reaction constant is $Kr = \frac{[CO_{2(aq)}]}{[HCO^-_{3(aq)}][H_3O^+]} = \frac{1}{K_a} = \frac{1}{4\times10^{-7}} = 2.5\times10^6$. $K_r > 10^4$; the reaction is complete	**1.25**
2.2.2	In fact, n (H_3O^+) introduced into the aquarium is not conserved. They react completely with HCO_3^- ions in a constant volume. $[H_3O^+]$ decreases. The pH of the medium is greater than 3.3; it will be equal to $pK_a + \log\frac{[HCO^-_{3(aq)}]}{[CO_{2(aq)}]}$; with $\frac{[HCO^-_{3(aq)}]}{[CO_{2(aq)}]} < 1$. The pH reach a value close to 6 as the instructions of the manufacturer indicate.	**0.5**