	مسابقة في مادة الكيمياء	الاسم:
	المدة ساعتان	الرقم:

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 (7 points)
Kinetic Study of the Reaction of Formic Acid with Bromine

:

Formic (methanoic) acid is a colorless corrosive liquid that is secreted by ants and other insects. It is commonly used in paper and textile industries and in the manufacture of insecticides ….
The aim of this exercise is to know some of the uses of formic acid in organic synthesis and to study the kinetic of its reaction with bromine liquid.

Given:

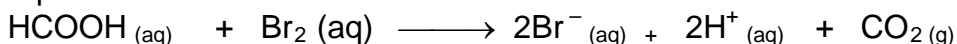- Molar volume of gas: $V_m = 24$ L.mol^{-1}.

1- Formation of Methanoic Acid Derivative

Methanoic acid (HCOOH) reacts with phosphorus pentachloride (PCl_5) to give an acyl chloride (G).
 1.1- Write the equation of this reaction.
 1.2- Give the systematic name of compound (G).
 1.3- Write the formula and give the name of the other reactant which gives with methanoic acid the same compound (G).

2- Preliminary Study

In aqueous solution, formic acid reacts slowly with molecular Bromine according to the following equation:
$$HCOOH_{(aq)} + Br_2 (aq) \longrightarrow 2Br^-_{(aq)} + 2H^+_{(aq)} + CO_{2 (g)}$$
Aqueous bromine solution has a red brown color, while hydrobromic acid ($H^+ + Br^-$) solution is colorless.
At t = 0, 50 mL of aqueous solution of bromine of molar concentration $C_1 = 0.024$ mol.L^{-1} are mixed with 50 mL of formic acid solution of molar concentration $C_2 = 0.030$ mol.L^{-1}.
 2.1- Determine the concentration of each reactant in the mixture at t = 0. Specify whether the reactants are in stoichiometric proportions.
 2.2- Show the following relation:
 $[Br_2]_t = 0.012 - 4.16 \times 10^{-4} \times V(CO_2)_t$; where $[Br_2]_t$ is the molar concentration of Bromine remained at instant t and $V(CO_2)_t$ is the volume of CO_2 formed at the same instant t in mL.

3- Kinetic Study

The measured volumes of CO_2 gas released, at different instants, are given in the following table:

t (sec)	0	50	100	150	200	250	300	350	400
$V(CO_2)$ (mL)	0	4.56	8.50	11.76	14.50	16.80	18.72	20.40	21.70
$[Br_2]$ (10^{-3} mol$\times$L^{-1})		10.1	8.46	7.11		5.01	4.21	3.51	

3.1- Copy, on the answer sheet, the above table and complete it using the preceding relation.

3.2- Plot, on a graph paper, the curve $[Br_2]_t = f(t)$. Take the following scale: abscissa: 1cm for 50 s and ordinate 1cm for 1.0×10^{-3} mol.L^{-1}

3.3- Determine the rate of disappearance of Br_2 at t =150 s. Deduce the rate of formation of Br^- at the same instant t.

3.4- Determine the half-life of the reaction.

3.5- At t =450 s, the volume of carbon dioxide released becomes 22.60 mL. Justify if the obtained solution is colorless or not.

Second Exercise (6 points)
Analysis of an Organic Compound

The aim of this exercise is to identify an organic compound (A) and to recognize some of its properties.

Given: M (H) = 1 g.mol $^{-1}$; M(C) = 12 g.mol $^{-1}$; M(O) = 16 g.mol $^{-1}$

1- Molecular Formula and Isomerism of (A)

The complete combustion of 3.70 g of (A) gives 6.60 g of carbon dioxide and 2.70 g of water vapor. The vapor density of (A) relative to oxygen gas is equal to 2.31.

1.1- Show that the molecular formula of (A) is $C_3H_6O_2$.

1.2- Write the condensed structural formulas of the possible isomers of (A), knowing that these isomers have saturated open carbon chains.

2- Identification of (A)

The dissolution of a sample of (A) in water gives a solution of pH = 3.1.

2.1- Identify compound (A).

2.2- Indicate the conjugate acid /base pair to which compound (A) belongs.

3- Certain Reactions of (A)

The dehydration of 111 g of (A), in the presence of (P_2O_5), gives according to a complete reaction an organic compound (B).

    3.1- Write, using condensed structural formulas of the organic compounds, the equation of the above reaction. Give the systematic name of (B).

    3.2- Show that the number of moles of (B) formed at the end of the reaction is 0.75 mol.

    3.3- The amount of (B) obtained above is mixed with 2 mol of 2-methyl-1-propanol, in order to prepare an ester (E) which has fruits flavor. A mass of 90 g of ester (E) is obtained.

        3.3.1- Write the equation of this esterification reaction. Give the systematic name of ester (E).

        3.3.2- This reaction is carried out in dry containers. Explain why.

        3.3.3- Determine the yield of this reaction.

Third Exercise (7 points)
Buffer solution

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The aim of this exercise is to prepare a buffer solution.

Given:

- Available materials:
    - Flask containing pure crystals of ammonium chloride NH_4Cl;
    - Sensitive balance, watch glass, spatula, funnel, magnetic stirrer;
    - Beakers: 100, 200 and 500 mL;
    - Graduated cylinders: 100, 200 and 500 mL;
    - Volumetric flasks: 100, 200 and 500 mL;
    - Volumetric pipets: 10 and 20 mL.
- This study is performed at 25 °C.
- $pK_a(NH_4^+/NH_3) = 9.2$; $pK_a(H_3O^+/H_2O) = 0$; $pK_a(H_2O/HO^-) = 14$.
- $M(NH_4Cl) = 53.5$ g. mol^{-1}.

1- pH of an Ammonia Solution

Given an aqueous solution (A) of ammonia of concentration $C_1 = 0.10$ mol.L^{-1}.

    1.1- Write the equation of the reaction of ammonia with water.

    1.2- Determine the constant K_R of this reaction.

    1.3- Determine the pH of the solution (A).

2- Preparation of an Ammonium Chloride Solution

A volume of 500 mL of a solution (B) of ammonium chloride ($NH_4^+ + Cl^-$) of concentration $C_2 = 0.1$ mol.L^{-1} is to be prepared.

    2.1- Describe, briefly, the procedure for the preparation of solution (B) and specify, from the given list, the suitable materials needed.

    2.2- Write the equation of the reaction of the ammonium ion (NH_4^+) with water. Show whether this reaction is complete or not.
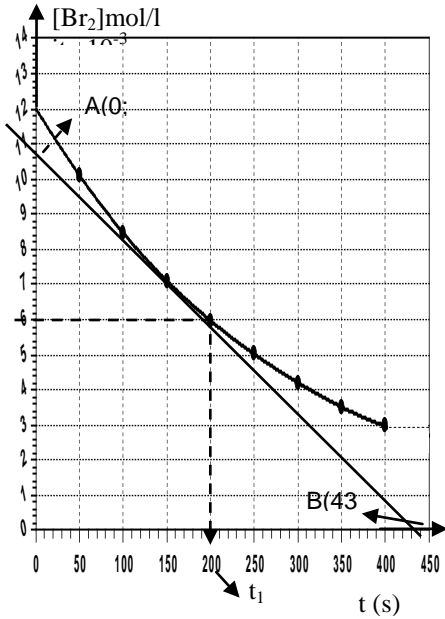
3- Preparation of a Buffer Solution

60 mL of solution (A) and 40 mL of solution (B) are mixed to give a solution noted as (C).

    3.1- Place on a pK_a axis the conjugate acid/base pairs involved in this mixture. Underline the major species introduced in this mixture

    3.2- Write the equation of the predominant (most advanced) reaction.

    3.3- Determine the pH of solution (C).

    3.4- Add 1.0×10^{-3} mol of HCl to solution (C) without a noticeable change in volume.

        3.4.1- Write the equation of the reaction that takes place which is considered complete.

        3.4.2- Determine the new value of pH of the resulting solution. Conclude.

        3.4.3-Give two other characteristics of solution (C).

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المديرية العامة للتربية	الفرع : علوم عامة	
دائرة الامتحانات		

مشروع معيار التصحيح	مادة الكيمياء	

First Exercise (7 points)

Part	Expected Answer	Mark
1	**Organic synthesis**	
1.1	The equation of the reaction is: H – COOH + PCl_5 → H – COCl + $POCl_3$ + HCl	0.5
1.2	Compound (G) is methanoyl chloride	0.25
1.3	The formula of this reactant is $SOCl_2$ and its name is thionyl chloride.	0.5
2	**Preliminay Study**	
2.1	$C_0 = \dfrac{n_0}{V_{total}}$. So $[Br_2]_0 = \dfrac{0.024 \times 50}{100} = 0.012$ mol.L^{-1} and $[HCOOH]_0 = \dfrac{0.03 \times 50}{100} = 0.015$ mol.L^{-1}. The stoichiométris proportions are: $R_{HCOOH} = \dfrac{n(HCOOH)_{initial}}{1} = \dfrac{0.03 \text{x} 50 \text{x} 10^{-3}}{1} = 1.5 \text{x} 10^{-3}$ $R_{Br_2} = \dfrac{n(Br_2)_{initial}}{1} = 1,2 \text{x} 10^{-3}$ $R_{HCOOH} \succ R_{Br_2}$ Thus the reactants are not in a stoechiometric proportion. Br_2 is the limiting reactant while HCOOH is in excess	1
2.2	At any instant t we have : $n(Br_2)_{remained\ at\ time\ t} = n(Br_2)_{given\ at\ t=0} - n(Br_2)_{reacted\ at\ time\ t}$ but by stoichiometry $n(Br_2)_{reacted\ at\ time\ t} = n(CO_2)_{formed\ at\ t} = \dfrac{V(CO_2)_t}{V_m}$ then $n(Br_2)_{remained\ at\ time\ t} = n(Br_2)_{taken\ at\ t=0} - \dfrac{V(CO_2)_t}{V_m}$ Divide by V we get : $[Br_2]_t = [Br_2]_{t=0} - \dfrac{V(CO_2)_t}{V_m \times V}$ $[Br_2]_t = [Br_2]_{t=0} - \dfrac{V(CO_2)_{in\ mL}}{24 \times 100}$ then $[Br_2]_t = 0.012 - 4.16 \times 10^{-4} \times V(CO_2)$.	1
3	**Kinetic Study**	
3.1	The table :	0,5

t (s)	0	50	100	150	200	250	300	350	400
V(CO_2) mL	0	4.56	8.50	11.76	14.50	16.80	18.72	20.40	21.70
$[Br_2]_t$ 10^{-3} mol.L^{-1}	12	10.1	8.46	7.11	5.97	5.01	4.21	3.51	2.97

3.2	The graph		1
3.3	Instantaneous rate is the negative slope of the tangent drawn on the curve $[Br_2] = f(t)$ at the instant of abscissa t =150 sec $$r(Br_2) = - \frac{d[Br_2]}{dt} = -\frac{[Br_2]_B - [Br_2]_A}{t_B - t_A} = -\frac{0 - 10,8 \times 10^{-3}}{430 - 0} =$$ 2.51×10^{-5} mol×L^{-1}×sec^{-1}. $r(Br^-) = 2 \times r(Br_2) = 2 \times 2.502 \times 10^{-5} = 5.02 \times 10^{-5}$ mol.L^{-1}.s^{-1}.		1
3.4	Half life of the reaction is the time required for the concentration of the limiting reactant to reach its half of the initial value. $$[Br_2]_{t1/2} = \frac{[Br_2]_{initiale}}{2} = \frac{0.012}{2} = 0.006 \text{ mol.L}^{-1}$$ By projecting for the abscissa we get $t_{t/2}$ = 200 sec		0.75
3.5	At 450 sec, $V(CO_2)$ = 22.6 ml . Applying the relation: $[Br_2]_t$ = 0.012 - 4. ⊠60^{-4} $V(CO_2)$ We get: $[Br_2]_t$ = 0.012 - 4. ⊠60^{-4}×22.6 = 2.6×10^{-3} mol.L^{-1}. Some of the bromine liquid (brown in color) is still unreacted, Thus, the obtained solution is not colorless.		0.5

Second Exercise (6 points)

Part	Expected Answer	Mark
1	**Molecular Formula and Isomerism of (A)**	
1.1	1 Determination of the molecular formula of (A): $$nC = n\, CO_2 = \frac{mCO_2}{MCO_2} = \frac{6.60}{44} = 0.15 \text{ mol and m C} = 0.15 \times 12 = 1.8 \text{ g.}$$ $$m\, H = 2 \times \frac{mH_2O}{MH_2O} \times MH = \frac{2.7}{18} \times 2 = 0.3 \text{ g and m O} = 3.7 - 1.8 - 03 =$$ 1.6 g. Molar mass: M (A) = 32 X 2.31 = 74 g.mol^{-1}. The law of definite proportions allows to write: $$\frac{74}{3.70} = \frac{12x}{1.8} = \frac{1y}{0.3} = \frac{16z}{1.6} \quad C_xH_yO_z \text{ (A)}$$ We have:	1

	$x = 3$; $y = 6$; $z = 2$ and the formula of (A) is: $C_3H_6O_2$.	
1.2	The condensed structural formulas of possible isomers are: $CH_3- CH_2- \overset{\displaystyle \parallel O}{C} - OH$; $H - \overset{\displaystyle \parallel O}{C} - O - CH_2 - CH_3$; $CH_3 - \overset{\displaystyle \parallel O}{C} - O - CH_3$	0.75
2	**Identification of (A)**	
2.1	1- The pH = 3.1 < 7, means that compound (A) reacts with water giving a definitely acid medium, it is thus the propanoïc acid of formula $CH_3 - CH_2 - COOH$.	0.5
2.2	The conjugate acid/base pair is: $CH_3CH_2COOH/CH_3CH_2COO^-$.	0.25
3	**Reaction of dehydration of (A) and Synthesis of Ester (E)**	
3.1	The equation of the dehydration reaction of (A) is: $2\ CH_3–CH_2– \overset{\displaystyle \parallel O}{C} - OH \xrightarrow{\ P_2O_5\ } CH_3 - CH_2 - \overset{\displaystyle \parallel O}{C} - O - \overset{\displaystyle \parallel O}{C} - CH_2 - CH_3 + H_2O$ Compound (B) is propanoic anhydride.	0.75
3.2	According to the stoechiometric proportions of the equation, we have: n (anhydride)formed $= \dfrac{\text{n(acid)reacting}}{2} = \dfrac{m(A)}{2 \times M(A)} = \dfrac{111}{2 \times 74} = 0.75$ mol.	0.5
3.3.1	The equation of the reaction is: $CH_3 - CH_2 - \overset{\displaystyle \parallel O}{C} - O - \overset{\displaystyle \parallel O}{C} - CH_2 - CH_3 + CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle \mid}{CH}} - CH_2OH \rightarrow$ $CH_3 - CH_2 - \overset{\displaystyle \parallel O}{C} - O - CH_2 - \underset{\displaystyle CH_3}{\overset{\displaystyle \mid}{CH}} - CH_3 + CH_3 - CH_2 - \overset{\displaystyle \parallel O}{C} - OH$ 2-methylpropyl propanoate	1
3.3.2	This reaction is carried out in dry containers because the anhydride reacts violently with water to give the corresponding acid.	0.5
3.3.3	The number of moles of ester theoretically formed is equal to the number of moles of anhydride = 0.75 mol. The number of moles of ester obtained in the experiment is: n exp. $= \dfrac{m(E)}{M(E)} = \dfrac{90}{7 \times 12 + 14 + 32} = 0.692$ mol. The yield is: R $= \dfrac{\text{n exp}}{\text{n theoric}} = \dfrac{0.692}{0.75} = 0.92$.	0.75

Third Exercise (7 points)

Part of the Q	Answer	Mark
1	**pH of an Ammonia Solution**	
1.1	The equation of the reaction of ammonia with water is: $NH_3 + H_2O \rightleftharpoons HO^- + NH_4^+$	0.5
1.2	The constant K_R : $K_R = \dfrac{[HO^-]\ [NH_4^+]}{[NH_3]} \cdot \dfrac{[H_3O^+]}{[H_3O^+]} = \dfrac{10^{-14}}{10^{-9,2}} = 10^{-4.8}$ $K_R = 1.58 \times 10^{-5}$.	0.5

1.3	$K_R = \dfrac{[HO^-]^2}{[NH_3]} = \dfrac{x^2}{0.1-x} = 1.58 \times 10^{-5}$. We obtain: $[HO^-] = 1.26 \times 10^{-3}$ mol L^{-1}, $[H_3O^+] = 7.9 \times 10^{-12}$ mol L^{-1} and pH = 11.1	0.5
2	**Preparation of an Ammonium Chloride Solution**	
2.1	In order to prepare 500 mL of solution (B), the needed mass is: m = 0.1 x500x10^{-3} x53.5 = 2.675 g. Using the sensitive balance, the spatula and the watch glass, to weigh 2.675 g of $NH_4Cl_{(s)}$. Introduce, using the funnel, this solid into a volumetric flask of 500 mL, partially filled with distilled water, shake to dissolve the solid, add more distilled water to fill the volumetric flask till the line mark. Shake to homogenize.	1
2.2	The equation of the reaction of the ammonium ion with water is: $NH_4^+ + H_2O \; \rightleftharpoons \; H_3O^+ + NH_3$ $K_R = \dfrac{[H_3O^+][NH_3]}{[NH_4^+]} = K_a = 10^{-9.2}$. The reaction is not complete.	1
3	**Preparation of a Buffer Solution**	
3.1	Placement of the species on an axis of pK$_a$ HO^- 14 — H_2O NH_3 9.2 — NH_4^+ H_2O 0 — H_3O^+	0.5
3.2	The most advanced reaction takes place between the strongest acid (NH_4^+) and the strongest base (NH_3) which are introduced. The equation of this reaction is: $NH_4^+ + NH_3 \rightleftharpoons NH_4^+ + NH_3$.	0.5
3.3	The preceding equation shows that the initial amounts of NH_4^+ and NH_3 do not vary. Where: $pH = pK_a + \log \dfrac{[NH_3]}{[NH_4^+]} = pK_a + \log \dfrac{\frac{C_1 \times V_A}{V}}{\frac{C_2 \times V_B}{V}} = 9.2 + \log \dfrac{0.1 \times 60}{0.1 \times 40} = 9.38$.	0.75
3.4.1	The equation of the reaction is: $NH_3 + H_3O^+ \rightarrow H_2O + NH_4^+$.	0.5
3.4.2	$n(NH_3)_{introduced} = 0.1 \times 60 \times 10^{-3} = 6 \times 10^{-3}$ mol.	0.75

	$n(H_3O^+)_{introduced} = 10^{-3}$ mol. It is the limiting reactant. After reaction, 5×10^{-3} mol NH_3 and $(4 \times 10^{-3} + 10^{-3})$ mol of $NH_4^+ = 5 \times 10^{-3}$ mol of NH_4^+ are remained pH = 9.2 + log $\dfrac{\dfrac{5 \times 10^{-3}}{V}}{\dfrac{5 \times 10^{-3}}{V}}$ = 9.2. the variation of the pH is not significant. So the solution is buffer.	
3.4.3	The two other characteristics of solution (C) are : - The variation of pH is not significant upon dilution -The variation of the pH is not significant upon adding few amount of a base.	0.5