مسابقة في مادة الكيمياء
المدة: ساعتان

الاسم:
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 Following Three Exercises:

First Exercise (7 points)
Identification of an organic compound

Available is an organic compound (A) of molecular formula C_xH_yO. Its carbon chain is saturated and non-cyclic.
The aim of this exercise is to recognize the chemical family of the compound (A) in order to identify it.

1- Identification of the Chemical family of (A)

1.1- List four possible chemical organic families that the compound (A) may represent.
1.2- In order to identify the chemical family of (A), the following two tests are carried out:

First test
The mild oxidation of a sample of (A) is carried out. An organic compound (B) is obtained which, when dissolved in water, gives a solution of pH distinctly less than 7.
Second test
Few drops of 2.4- D.N.P.H are added to another sample of the compound (A). A yellow-orange precipitate appears.
1.2.1- Show that the organic compound (B) is carboxylic acid.
1.2.2- Deduce, from these two tests, the chemical family of (A).

2- Identification of the Compound (A)

Given:

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

Colored indicator	pH range of color change
Methyl orange	3.1 - 4.4
Phenolphtalein	8.2 - 10

In order to identify the compound (A), one proceeds as follows:

- A solution (S) is prepared by dissolving 1.41 g of the acid (B) in distilled water, in such a way to obtain a volume V = 250 mL.
- A volume V_a = 20.0 mL of the solution (S) is titrated with a sodium hydroxide solution (Na^++ HO^-) of concentration C_b = 0.10 $mol.L^{-1}$, in the presence of an appropriate colored indicator.
  The volume of the base added to reach equivalence is V_{bE} = 15.2 mL.

2.1- Choose, from the following material, those needed to carry out this titration: 100 mL beaker, 20 mL graduated cylinder, 25 mL graduated buret, magnetic stirrer, pH-meter and 20 mL volumetric pipet.

2.2- Write the equation of the titration reaction by representing the acid with the formula R – COOH.

2.3- Choose, by justifying, from the two colored indicators given above, the appropriate one to recognize the end point of titration.

2.4- Determine the concentration of the acid (B) in the solution S.

2.5- Show that the molar mass of (B) is about 74 $g.mol^{-1}$.

2.6- Deduce the molecular formula of (B).

2.7- Identify the compound (A).

Second Exercise (6 points)
Kinetic of an Esterification Reaction

It is required to study the kinetic of formation of an ester with banana odor, starting from a mixture of 0.20 mol of ethanoic acid and 0.20 mol of 3-methyl-1-butanol, in the presence of sulfuric acid as a catalyst.

Using an appropriate method, the number of moles of the ester formed, $n_{(Ester)}$, with time is determined. The results are grouped in the following table:

t (min)	2	5	10	15	20	30	45	60
$n_{(Ester)}$ (10^{-2} mol)	4.2	7.4	10.0	11.2	12.0	12.7	13.2	13.4

1- Study of the Esterification Reaction

Ethanoic acid and 3-methyl-1-butanol react according to the general equation:

$$R-COOH + R_1-CH_2OH \rightleftharpoons R-COO-CH_2-R_1 + H_2O$$

The equilibrium constant related to this homogeneous equilibrium is $K_C = 4.12$

1.1- Write the condensed structural formula of ethanoic acid, of 3-methyl-1-butanol and that of the ester formed. Name this ester.

1.2- Show, using the value of the equilibrium constant K_C, that the reacting mixture has reached the equilibrium state at t = 60 min.

1.3- Verify if the esterification reaction stops at t = 60 min.

2- Kinetic Study

2.1- Plot the curve representing the change in the number of moles of ester formed with time: $n_{(Ester)} = f(t)$ in the interval of time [0 – 60 min].
Take the following scale:
1 cm for 5 min in abscissa and 1 cm for 1.0×10^{-2} mol in ordinate.

2.2- Determine the rate of formation of this ester at t = 15 min.

2.3- This kinetic study is carried out again in the same experimental conditions but without using the catalyst. Plot, on the same graph as the question 2.1, the shape of the curve representing the new change: $n_{(Ester)} = g(t)$. Justify.

2.4- In order to make the preparation reaction of this ester faster and complete, a compound (G) is used instead of the ethanoic acid. Write the possible condensed structural formulas of (G).

Third Exercise (7 points)
Acid-Base Reactions

Two flasks are available; each contains one of the following basic solutions:

- S_1: A potassium hydroxide solution ($K^+ + HO^-$) solution of molar concentration C_1.
- S_2: An ammonia solution NH_3 of molar concentration C_2.

The two solutions S_1 and S_2 have the same pH value of 10.6

Given:

- Ion product of water: $K_w = 1.0\times10^{-14}$
- The reaction of ammonia with water is limited.
- NH_4Cl is an ionic compound highly soluble in water.
- $\dfrac{[NH_3]}{[NH_4^+]} = \dfrac{\%(\text{by mol})NH_3}{\%(\text{by mol})NH_4^+}$

1- Strong Base and Weak Base

1.1- Calculate the concentration C_1.

1.2- Compare, by justifying, C_1 and C_2.

2- Determination of the pK_a of the Pair NH_4^+ / NH_3

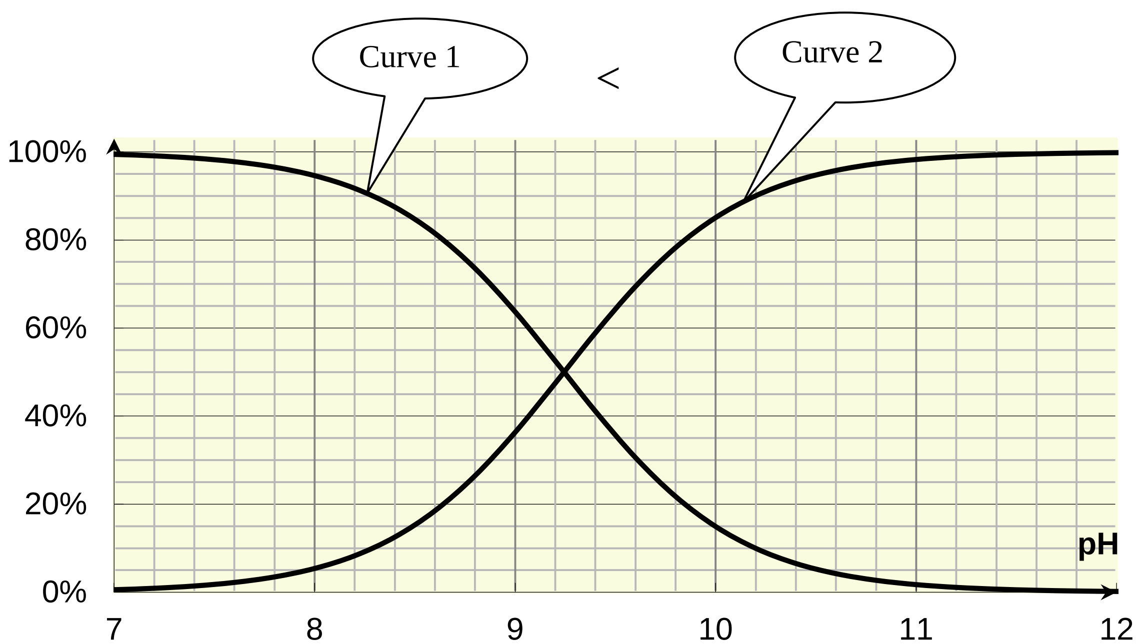
An ammonia solution (S) of concentration $C = 5.0\times10^{-3}$ mol.L^{-1}, is prepared by dissolving ammonia gas in distilled water.

2.1- Write the equation of the reaction between ammonia and water.

2.2- Determine the sum of the concentrations of ammonia, $[NH_3]$, and ammonium ions, $[NH_4^+]$, in the prepared solution.

2.3- Few crystals of ammonium chloride, NH_4Cl, are dissolved in a sample of this solution without changing the volume of the sample.
Specify the change in the pH during this dissolution.

2.4- The following graph represents the change in the percentages (by moles) of the acidic and the basic species of the pair NH_4^+ / NH_3 in the solution (S) as a function of pH.



2.4.1- Identify the two curves 1 and 2.

2.4.2- Determine, using the graph, the pK_a of the pair NH_4^+ / NH_3.

2.5- It is possible to prepare a buffer solution of pH equal to pK_a of the pair NH_4^+ / NH_3 by mixing two of the solutions suggested in the table below.

Solution 1	Solution 2	Solution 3	Solution 4
Ammonia	Potassium hydroxide	Hydrochloric acid	Hydrochloric acid
$C = 5\times10^{-3}$ mol.L^{-1} $V_1 = 400$ mL	$C = 5\times10^{-3}$ mol.L^{-1} $V_2 = 200$ mL	$C = 5\times10^{-3}$ mol.L^{-1} $V_3 = 400$ mL	$C = 5\times10^{-3}$ mol.L^{-1} $V_4 = 200$ mL

2.5.1- Write the equation of the reaction that takes place during the mixing of these two solutions.

2.5.2- Determine the reaction constant, K_R, of this reaction and deduce that it is complete.

2.5.3- Specify the two solutions to be mixed in order to prepare this buffer solution.

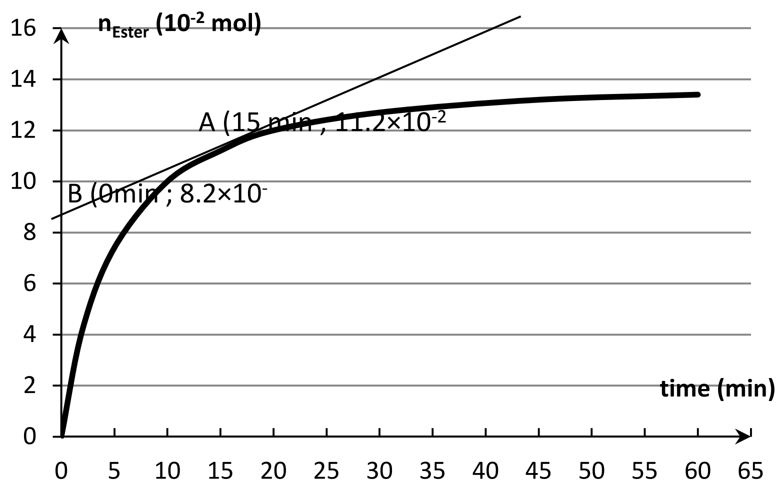
مشروع معيار التصحيح

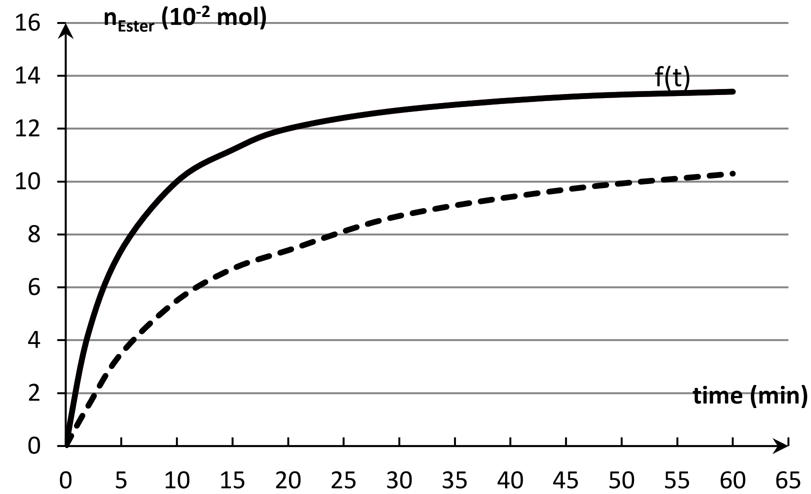
مسابقة في مادة الكيمياء
المدة: ساعتان

First Exercise (7 points)
Identification of an Organic Compound

Part of the Q	Answer	Mark
1.1	The four organic families are : Alcohol, ether, aldehyde and ketone.	1
1.2.1	The aqueous solution of (B) has a pH < 7, so (B) is an acid.	0.25
1.2.2	From the first test, we deduce that the compound (A) could be: a primary alcohol or an aldehyde. From the second test, we deduce that (A) is an aldehyde or a ketone. So, the compound (A) is an aldehyde.	0.75
2.1	The material used are: 100 mL beaker, 25 mL graduated buret, magnetic stirrer and a 20 mL pipet.	1
2.2	The equation of the titration reaction is : $R\,COOH + HO^- \rightarrow R\,COO^- + H_2O$	0.5
2.3	The medium obtained at the equivalence is a basic medium (the reaction is between a strong base and a weak acid). In this case, phenolphtalein is used as a colored indicator since its pH range of color change is basic.	0.5
2.4	At the equivalence point: $n(HO^-)_{\text{added to reach equivalence}} = n(B)_{\text{introduced into the beaker}}$ $C_b \times V_{bE} = C_a \times V_a$. The concentration of the solution (S) is $C_a = \frac{C_b \times V_{bE}}{V_a} = \frac{0.10 \times 15.2}{20} = 7.6.10^{-2}$ mol.L^{-1}	0.75
2.5	n(B) in V = $C_a \times V = 0.076 \times 250 \times 10^{-3} = 1.9 \times 10^{-2}$ mol. Molar mass of (B) = $\frac{m(B)}{n(B)} = \frac{1.41}{0.019} = 74.2$ g.mol^{-1}.	0.75
2.6	The general molecular formula of (B) is $C_nH_{2n}O_2$, since it is obtained by the mild oxidation of a saturated non cyclic aldehyde. Implies 14 n + 32 = 74.2 and n = 3. The molecular formula of (B) is $C_3H_6O_2$.	0.75
2.7	(A) gives the acid (B) upon mild oxidation, so (A) is propanal $CH_3 - CH_2 - CHO$	0.75

Second Exercise (6 points)
Kinetic of an Esterification Reaction

Part of the Q.	Answer	Mark
1.1	Ethanoic acid: CH_3-COOH; 3-methyl-1-butanol: $CH_3-CH(CH_3)-CH_2-CH_2OH$ The ester formed $CH_3-C(=O)-O-CH_2-CH_2-CH(CH_3)-CH_3$: 3-methylbutylethanoate.	1
1.2	At t = 60 min, if $n_{(Ester)}$ = 0.134 mol and from the equation of the reaction: n (water) = 0.134 mol and n(acid) remaining = n(alcohol) remaining = 0.066 mol. At t = 60 min, the quotient of the reaction is: $Q_R = \frac{[ester]\times[water]}{[acid]\times[alcohol]} = \frac{n_{(Ester)}\times n(water)}{n(acid)\times n(alcohol)} = \frac{(0.134)^2}{(0.066)^2} = 4.12$ Since $Q_R = K_C$; the reacting mixture is at equilibrium state.	1
1.3	At the equilibrium state, the evolution of the system stops but the esterification reaction and the hydrolysis reaction still occurring simultaneously (dynamic equilibrium).	0.5
2.1		1
2.2	By definition : r (ester) = $\frac{dn_{(Ester)}}{dt}$ at t $\frac{dn_{(Ester)}}{dt}$ is the slope of the tangent at the curve at the point of abscissa t = 15 min.	1

	A and B are two points of the tangent where A (15 min ; 11.2×10^{-2} mol) and B (0 min ; 8.2×10^{-2} mol). r (ester) = $\frac{(11.2-8.2)\times10^{-2}}{15-0}$ = 2×10^{-3} $mol.min^{-1}$.	
2.3	The catalyst is a kinetic factor. Without catalyst the rate of formation of the ester decreases. At each instant of time t, $n_{(Ester)}$ (without catalyst) < $n_{(Ester)}$ (with catalyst). The shape of the curve is: 	1
2.4	The possible condensed structural formulas of (G) are: CH_3 –COCl and CH_3 –CO – O – CO – CH_3.	0.5

Third Exercise (7 points)
Acid-Base Reactions

Part of the Q.	Answer	Mark
1.1	KOH is a strong base ; pH = 14 + log C_1 and $C_1 = 10^{\,pH-14} = 10^{10.6-14}$ $= 4.0\times10^{-4}$ $mol.L^{-1}$	0.5
1.2	The two solutions have the same pH value: $C_1 = [HO^-]$ provided by the ammonia. The reaction of ammonia and water is limited: $C_2 > [HO^-]$ provided by the ammonia. So: $C_2 > C_1$.	0.75
2.1	The equation of this reaction is $NH_3 + H_2O \rightleftarrows HO^- + NH_4^+$	0.5
2.2	$NH_3 + H_2O \rightleftarrows HO^- + NH_4^+$ Initial state: C, solvent, -, -, in $mol.L^{-1}$ Obtained solution: C - x, solvent, x, x, in $mol.L^{-1}$ So: $[NH_4^+] + [NH_3] = C - x + x = 5.0\times10^{-3}$ $mol.L^{-1}$.	0.75
2.3	By adding NH_4Cl solid, $n(NH_4^+)$ increases and the equilibrium is shifted backward (according to Le Chatelier's principle); $n(HO^-)$ decreases in a constant volume of	0.75

	solution and $[HO^-]$ decreases. By consequence pH of the solution decreases.	
2.4.1	Curve 1: % decreases with the increase in pH so it represents the change in the percentage of NH_4^+ as a function of pH. Curve 2: % increases with the increase in pH so it represents in the percentage of NH_3 as a function of pH.	0.75
2.4.2	pK_a (NH_4^+/ NH_3) = pH (solution) + log $\frac{[NH_3]}{[NH_4^+]}$ = pH(solution) + log $\frac{\%NH_3}{\%NH_4^+}$ but at the intersection point of the curve : % NH_3 = % NH_4^+ pK_a (NH_4^+/ NH_3) = pH (solution) at this point= 9.25	0.75
2.5.1	The equation of the reaction : (solution 1 + H_3O^+ ions) $NH_3 + H_3O^+ \rightleftarrows NH_4^+ + H_2O$	0.5
2.5.2	The reaction constant : $K_R = \frac{[NH_4^+]}{[NH_3]\times[H_3O^+]} = \frac{1}{K_a} = 10^{9.25} = 1.8 \times 10^9$ $K_R > 10^4 \Longrightarrow$the reaction is complete.	0.75
2.5.3	To prepare this solution we must choose a mixture in which H_3O^+ is the limiting reactant in such a way that $n(H_3O^+)$ initial be the half of $n(NH_3)$ initial. This condition is satisfied only in the mixture of the two solutions 1 and 4 since $C.V_1 = 2\ C.V_4$	1