مسابقة في مادة الكيمياء
المدة: ساعتان

الاسم:
الرقم:

This Exam Includes **Three Exercises**. It Is Inscribed on Three Pages Numbered From **1** to **3.**
The Use of A Non-programmable Calculator Is Allowed

Answer the Three Following Exercises:

First Exercise (6 points)
Determination of the Formula of a Carboxylic Acid

The analysis of an organic liquid compound shows that the molecular formula of this compound is $C_nH_{2n}O_2$. The identification of the properties of this compound shows that it is an acid.

Given :

- Atomic molar mass in $g.mol^{-1}$: $M_H = 1$; $M_C = 12$; $M_O = 16$

I- Preparation of an Aqueous Solution of this Compound

A mass of 4.70 g of this acid (noted as HA) is introduced in enough distilled water to obtain 1 L solution.
Choose, from the following list, the materials used to perform this preparation.
List of Materials:
- 20 mL graduated cylinder;
- 200, 500 and 1000 mL beakers;
- Funnel;
- Electronic balance;
- 200, 500 and 1000 mL volumetric flasks;
- 10 and 25 mL volumetric pipets.

II- Titration of the Aqueous Solution of HA

The titration of 30 mL of the above prepared solution, using a pH-meter, is carried out with an aqueous sodium hydroxide solution of concentration $C_b = 0.10$ $mol.L^{-1}$. The results of the variation of the pH versus V_b (V_b is the volume of base added) are given in the following table:

V_b(mL)	0	5	10	15	20	25	28	30	32	34	36	40
pH	2.4	3.4	3.6	3.7	3.9	4.3	4.8	5.5	10.9	11.4	11.6	11.7

1- Trace on the graph paper the curve pH = f(V_b).
   Take the following scale: abscissa (1 cm for 5 mL) and ordinate (1 cm for 1 unit of pH).
2- Referring to the curve, deduce:
   a) The coordinates of the equivalence point;
   b) The pK_a of the pair HA/A^-.

III- Determination of the Formula of HA

1- Write the equation of the titration reaction.
2- Determine the concentration of the aqueous solution of HA.
3- Deduce the structural formula of HA and give its name.

Second Exercise (7 points)
Esterification and Average Formation Rate

A mixture (G) of 12 g of ethanoic acid and 15 mL of 1-propanol is heated at 100 ºC with an appropriate set-up where the temperature is kept constant.

Given :

- Molar mass in $g.mol^{-1}$: $M_{\text{1-propanol}} = 60$; $M_{\text{ethanoic acid}} = 60$.
- Density of 1-propanol: $d = 0.80\ g.mL^{-1}$.

I- Esterification Reaction

Ethanoic acid and 1-propanol react by an esterification reaction.

1- Write, using structural formulas, the equation of this esterification reaction.
2- Name the ester formed.
3- Give two characteristics of this reaction.

II- Kinetics of this Esterification Reaction

1- Determine the number of moles of each of the reactants in the initial mixture (G).
2- After 10 hours of heating, a sample of the reaction mixture is taken and placed in an ice-water bath. The titration of this sample shows that 0.12 mol of the acid is left. Calculate the number of moles of the formed ester at this time.
3- Specify the role of the use of the ice-water bath.
4- When a mixture of acid and alcohol identical to (G) is heated for 20 hours under the same experimental conditions, 0.10 mol of ester is formed.
   Knowing that, starting from an equimolar mixture of carboxylic acid and a primary alcohol where the yield at equilibrium of the esterification is 67 %, specify if the equilibrium is reached or not.
5- Give the expression that defines the average rate of formation of ester between two instants t and t´. Calculate this rate between t = 10 h and t´ = 20 h.

III- Yield of the Esterification

Explain if each of the following ways is convenient to increase the yield of esterification at equilibrium:

a) Adding a catalyst;
b) Adding an excess of a reactant: alcohol or acid.

Third Exercise (7 points)
Preparation and Titration of Propanone

It is required, in the laboratory, to:

- Prepare propanone ;
- Titrate propanone in the urine of a diabetic patient.

The following materials are available:
1-propanol, 2-propanol, acidified potassium permanganate solution, concentrated sodium hydroxide solution, sodium thiosulfate solution, iodine solution, 2,4-DNPH solution, Schiff's reagent solution, bromothymol blue solution (pH range: yellow 6.1 – 7.5 blue), phenolphthalein solution (pH range: colorless 8 – 10 purple), starch solution and the needed set up to perform the above two activities.

I- <u>Preparation of Propanone</u>

In order to prepare propanone, the oxidation of a sample (A) of 1-propanol and the oxidation of a sample (B) of 2-propanol are carried out separately with an excess of an oxidizing agent chosen from the above list.

1- Indicate the oxidizing agent used in the above two reactions.
2- a) Write the structural formula of the organic compound obtained from the oxidation of sample (A) and give its name.
   b) Referring to the above materials, describe a chemical test that permits to identify this compound.
3- a) Write the structural formula of the organic compound obtained from the oxidation of sample (B).
   b) Referring to the above materials, describe two simple chemical tests to identify this organic compound.

II- <u>Titration of Propanone</u>

The titration of propanone, present in the urine of a diabetic patient, is performed by the oxidation of propanone with iodine in a basic solution. The reaction of this titration is represented by the following equation:

$$CH_3 - CO - CH_3 \ + \ 3\,I_2 \ + \ 4\,HO^- \ \rightarrow \ CH_3 - COO^- \ + \ 3\,I^- \ + \ CHI_3 \ + \ 3\,H_2O$$

This reaction is carried out with excess iodine. The non reacted iodine is then titrated with sodium thiosulfate solution, in the presence of starch solution.
A volume V_1 = 10 mL of urine and a volume V_2 = 25 mL of iodine solution of concentration C_2 = 0.08 mol.L^{-1} are mixed in a beaker in a basic medium, in order to perform this titration.
The titration with sodium thiosulfate solution shows that the non reacted iodine in the beaker is $8\text{x}10^{-4}$ mol.

1- Justify if the oxidation of propanone by iodine, in this reaction, is a mild oxidation.
2- What is the importance of using starch during the titration of iodine with sodium thiosulfate solution?
3- Determine the concentration of propanone in the urine of this patient.

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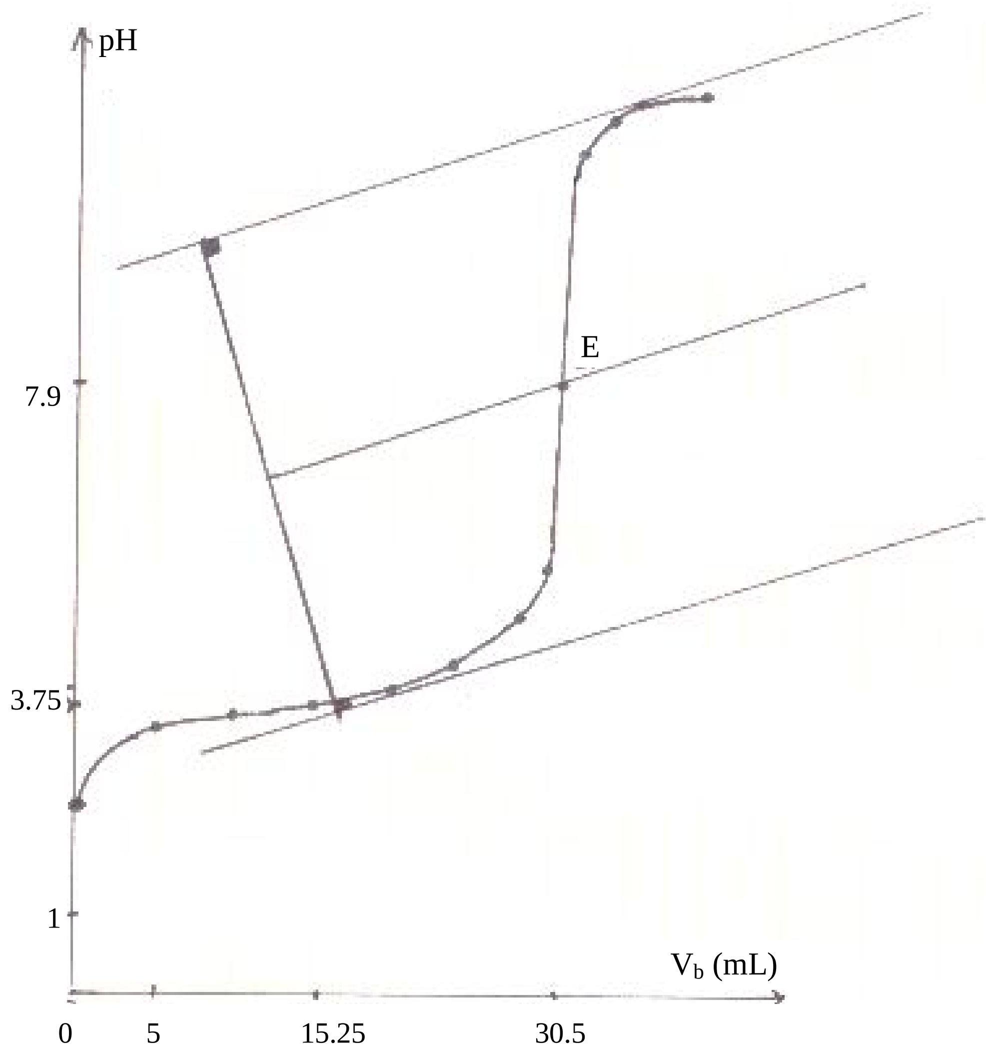
First Exercise (6 points)
Determination of the Formula of a Carboxylic Acid

Expected Answer	Mark	Comment
I- 1- The materials that will be used to carry out this preparation are : 20 mL graduated cylinder, balance, funnel and 1000 mL volumetric flask.	1	0 if the balance or the 1000 mL volumetric flask are not used.
II- 1- 	1	
2- a) The coordinates of equivalence point, as shown on the graph, are: V_{bE} = 30.5 mL and pH = 7.9.	0.75	0 if the parallel tangents method is not shown.
b) The pK_a of the pair AH/A^- is equal to pH that corresponds at $V_b = V_{bE}/2$ = 15.25 mL, and pK_a = 3.75.	0.5	
III- 1- The equation of the titration reaction is: $HA + HO^- \rightarrow A^- + H_2O$.	0.5	0 for $H_3O^+ + HO^- \rightarrow 2H_2O$
2- At equivalence point, we have: n_{HA} in 30 mL = n_{HO^-} in the added volume to reach equivalence point. Then, in solution $n_{(solute\ in\ mol)} = C_{mol.L^{-1}} \times V_{solution\ in\ L}$.	0.75	

Where: $C = \frac{0.10x30.5}{30} = 0.102$ mol.L^{-1}. 3- The dissolved mass of 4.70 g in 1 L (S) correspond to 0.102 mol. The molar mass of HA is then: $M = \frac{4.70}{0.102} = 46.07$ g.mol^{-1}. The formula is $C_nH_{2n}O_2$, we have then: 14n + 32 = 46 and n = 1. The molecular formula is CH_2O_2. It is an acid of condensed structural formula: H – C – OH it is methanoic acid. ‖ O	1.5	

Second Exercise (7 points)

Esterification and Average Formation Rate

Expected Answer	Mark	Comment
I-		
1- The equation of the esterification reaction is: $CH_3 - \underset{\substack{\vert \\ OH}}{C} = O + CH_3 - CH_2 - CH_2OH \rightleftarrows CH_3 - \underset{\substack{\vert \\ O - CH_2 - CH_2 - CH_3}}{C} = O + H_2O$	0.75	
2- The ester is propyl ethanoate.	0.25	
3- This reaction is: slow, reversible, athermic.	0.25$\times$2	
II- 1- The number of moles n is given by: n = m in g/ M in g.mol^{-1}. $n_{acid} = \frac{12}{60} = 0.2$ mol.	0.25	
$n_{alcohol} = dxV/M = \frac{0.80x15}{60} = 0.2$ mol.	0.5	
2- According to the equation: n_{ester} formed = n_{acid} react = n_{acid} initial – n_{acid} remaining. n_{ester} formed = 0.2 – 0.12 = 0.08 mol.	0.75	
3- The role of ice-water bath is to stop any reaction other than titration.	0.5	
4- a) The mixture (G) is equimolar, its esterification yield at equilibrium is then 67% ($R = \frac{n_{ester} \exp erimental}{n_{ester} theoretical} x100$). After 20	0.25	
hours of heating, 0.1 mol of ester is obtained that corresponds to the following yield: $R = \frac{0.1x100}{0.2}$ = 50 %. This yield is lower then 67 %, then equilibrium is not reached.	0.75	
5- The average rate of formation of ester between instants t and t´is given by the following expression: $r = \frac{n_{ester(t')} - n_{ester(t)}}{t' - t} = \frac{0.1 - 0.08}{20 - 10} = 2x10^{-3}$ mol.h^{-1}.	0.5x2	
III- 1- a) The addition of a catalyst does not increase the yield of esterification at equilibrium, because the catalyst makes the	0.75	

system reach equilibrium in a shorter time without shifting equilibrium to any side. b) The addition of an excess of one of the two reactants shifts equilibrium to the right side. Consequently, this addition increases the yield of esterification at equilibrium.	0.75	

Third Exercise (7 points)
Preparation and Titration of Propanone

Expected Answer	Mark	Comment
I- 1- a) The oxidizing agent used to perform oxidation of the two alcohols is acidified potassium permanganate solution.	0,5	
2- a) The structural formula of the organic compound obtained from the oxidation of (A) with excess oxidant is: $CH_3 - CH_2 - \underset{\underset{\displaystyle O}{\parallel}}{C} - OH$, it is propanoic acid	0,75	
b) This compound gives a yellow color with B.T. B.	0,5	
3- a) The structural formula of the compound obtained is: $CH_3 - \underset{\underset{\displaystyle O}{\parallel}}{C} - CH_3$	0,5	
b) The compound is treated with 2,4-DNPH. A yellow precipitate is formed (the compound carries a carbonyl group). This compound gives a negative test with Schiff's reagent.	1	
II- 1- In a mild oxidation reaction, the carbon chain is conserved, while in this oxidation reaction the carbon chain has changed. So this oxidation is not a mild oxidation reaction.	1	
2- The use of starch solution is to detect the equivalence point sharply because starch gives a blue color with iodine even with traces.	1	
3- $n_{\text{iodine reacting with propanone}} = n_{\text{iodine initial}} - n_{\text{iodine in excess}} =$ $C_2xV_2 - 8x10^{-4}$ According the equation, we have: $n_{\text{propanone}}$ in 10 mL of urine = $n_{\text{iodine reacting with propanone}}/3$ C_1 is the concentration of propanone in urine. $C_1xV_1 = \frac{C_2xV_2 - 8x10^{-3}}{3}$ hence $C_1 = \frac{0.08x25x10^{-3} - 8x10^{-4}}{3x10^{-3}} =$ 0.04 mol.L^{-1}.	1,75	