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|---|---|---|
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This Exam Includes **Three** Exercises. It Is Inscribed on **4** Pages Numbered From **1** to **4.**
The Use of A Non-programmable Calculator is Allowed.

**Answer the Following Three Exercises:**

## First Exercise (6 points)
## Preparation of an Ester

Consider a compound (A) of formula $C_xH_yO$.
In all the equations of the reactions suggested in this exercise, represent the organic compounds by their condensed structural formulas.

**<u>Given</u>:**

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

### 1- <u>Identification of the Compound (A)</u>

A quantitative analysis carried out on the compound (A) gave the following mass percentages: carbon = 66.67 % and hydrogen = 11.11 %.
1.1- Show that x = 4 and y = 8.
1.2- Write the possible condensed structural formulas of (A) knowing that its carbon chain is saturated and non cyclic.
1.3- (A) is subjected to the following tests:

| Test | Result of the test |
|---|---|
| (A) + 2,4-D.N.P.H | Yellow precipitate |
| (A) + Fehling's solution | Brick-red precipitate |

Deduce the chemical family of (A) and give its name, knowing that its carbon chain is not branched.

### 2- <u>Chemical Reactions with (A)</u>

The available quantity of (A) is divided into two parts.
The first part is treated with an acidified potassium permanganate solution. The formed organic compound is collected and called (X).
The second part is heated, in the presence of a hydrogenation catalyst. The formed organic compound is collected and called (Y).
2.1- Write the equation of the first reaction of (A). Give the name of (X).
2.2- Write the equation of the second reaction of (A). Give the name of (Y).

### 3- <u>Preparation of the Ester (E)</u>

An equimolar mixture of the two compounds (X) and (Y) react until having a constant quantity of ester. This quantity is equal to 0.4 mol. The equation of the corresponding reaction is:

$$X + Y \rightleftharpoons E + H_2O$$

3.1- Write the condensed structural formula of the ester E. Give its name.

3.2- Show that the initial quantity of X (or Y) is n = 0.6 mol, knowing that the equilibrium constant associated to the above equation is Kc = 4.0.

3.3- The compound X is replaced by its chlorinated derivative to prepare the ester E.

3.3.1- Write the condensed structural formula of this derivative and give its name.

3.3.2- Calculate, then, the quantity of ester formed at the end of this reaction using the same quantity of this derivative (0.6 mol).

## Second Exercise (7 points)
## Titration of a Tablet of Vitamin C

The aim of this exercise is to verify the indication of a tablet of vitamin C (ascorbic acid of formula $C_6H_8O_6$) noted as HA.

**<u>Given</u>**:

- This study is performed at 25 ºC.
- M (ascorbic acid: $C_6H_8O_6$) = 176 $g.mol^{-1}$; M (sodium ascorbate: $C_6H_7O_6Na$) = 198 $g.mol^{-1}$.

### 1- <u>Preparation of Aqueous Solutions of Vitamin C and Sodium Hydroxide</u>

A tablet of "VITAMIN C 500"is carefully grinded, and a volume of 100 mL of a solution S of ascorbic acid is prepared from the obtained powder.
It is required to titrate the solution S obtained with a sodium hydroxide solution of molar concentration $Cb = 2.0\times10^{-2}$ $mol.L^{-1}$.
For that, take 10 mL of the solution S which are introduced into a beaker and distilled water is then added to immerse the electrode of the pH-meter.
The following materials are available:
50, 100 and 250 mL volumetric flasks;
100, 250 and 500 mL beakers;
5, 10 and 25 mL volumetric pipets;
25 mL buret;
pH-meter and its electrode;
Magnetic stirrer and its magnetic bar.

1.1- Indicate, from the above list, each material used and its role in the:

1.1.1- Preparation of the solution to be titrated.

1.1.2- Titration procedure.

1.2- The sodium hydroxide solution of concentration $2.0\times10^{-2}$ $mol.L^{-1}$ was prepared, just before its use, by diluting with precision a solution of concentration $1.0\times10^{-1}$ $mol.L^{-1}$.
Choose, by justifying, from the above list the materials used for this preparation.

### 2- <u>pH-metric Follow-up</u>

The change of the pH is followed when the sodium hydroxide solution of concentration $Cb = 2.0\times10^{-2}$ $mol.L^{-1}$ is gradually added into the beaker containing the solution S.
The results are given in the table below. (Vb is the volume of the sodium hydroxide solution added).

| Vb (mL) | 0 | 2.0 | 4.0 | 6.0 | 8.0 | 10.0 | 11.0 | 12.0 |
|---|---|---|---|---|---|---|---|---|
| pH | 3.1 | 3.5 | 3.8 | 4.1 | 4.3 | 4.6 | 4.8 | 5.1 |

| Vb (mL) | 13.0 | 13.5 | 14.0 | 14.5 | 15.0 | 16.0 | 18.0 | 20.0 |
|---|---|---|---|---|---|---|---|---|
| pH | 5.6 | 6.3 | 7.5 | 9.1 | 9.8 | 10.2 | 10.6 | 10.8 |

2.1- Write the equation of the titration reaction.
2.2- Plot, on a graph paper, the curve pH = f (Vb). Take the following scale:
1 cm for 1 mL in abscissa and 1 cm for 1 unit of pH in ordinate.
2.3- Determine graphically the co-ordinates of the equivalence point.
2.4- Determine graphically the pKa of the conjugate acid/base pair: ascorbic acid/ascorbate ion.
2.5- Determine the concentration of the solution S. Deduce the mass of ascorbic acid contained in a tablet. Is this result compatible with the indication (500) of the manufacturer "VITAMIN C 500"?

**3- Buffered Vitamin C**

On the label of a bottle of vitamin C we read for one tablet, among others, the following:
Buffered Vitamin C.
Ascorbic acid: 247 mg.
Sodium ascorbate: 284 mg.

3.1- Based on the indications of the label, determine the quantities (in moles) of ascorbic acid and ascorbate ions present in the tablet.
3.2- A tablet of buffered vitamin C is dissolved in distilled water. Determine the pH of the obtained solution.
3.3- Knowing that the pH inside the stomach is close to 1.
3.3.1- Indicate the one, of the two species of the conjugate acid/base pair ($HA/A^-$), that predominates in the stomach.
3.3.2- Justify by calculation the indication "total ascorbic acid: 500 mg "carried also by the label.

## Third Exercise (7 points)
## Kinetics of the Preparation Reaction of Methyl Chloride

Methyl chloride or chloromethane ($CH_3$-Cl) was widely used as a refrigerant, but due to its toxicity this use has been discontinued.
The most important uses of methyl chloride today is as a solvent and as a chemical intermediate in many industries especially in the production of polymers, silicon and rubber…
The aim of this exercise is to study the kinetics of the reaction of the preparation of chloromethane.

**Given** :

- Methyl chloride is a colorless gas with a slightly agreeable odor.
- Molar mass of methyl chloride is 50.5 $g.mol^{-1}$.
- Molar volume of gas at the conditions of the experiment is 24 $L.mol^{-1}$.
- Bromothymol Blue is an indicator of the following change range:

| Acidic color | Neutral color | Basic color |
|---|---|---|
| Yellow | Green | Blue |

**1 – Chlorination of Methanol**

Mostly, the preparation of methyl chloride is done by the action of concentrated hydrochloric acid($H_3O^+ + Cl^-$) solution on methanol according to the following equation:

$$CH_3OH_{(aq)} + H_3O^+_{(aq)} + Cl^-_{(aq)} \longrightarrow CH_3\text{-}Cl_{(aq)} + 2\ H_2O_{(l)}$$

This reaction is slow and complete.
At an instant t = 0, and in a hood, 80 mL of methanol solution of concentration $C_1 = 5$ mol.L$^{-1}$ are mixed with100 mL of hydrochloric acid solution of concentration $C_2 = 3.7$ mol.L$^{-1}$ in a beaker containing 20 mL of distilled water.
The obtained solution is noted as (S).

1.1- Show that the initial molar concentrations of the reactants are respectively: $[CH_3OH]_0 = 2$ mol.L$^{-1}$ and $[H_3O^+]_0 = 1.85$ mol.L$^{-1}$.

1.2- Verify that hydrochloric acid had reacted completely at the end of the reaction.

**2 – Experimental Study**

At different instants t, samples of 20 mL of solution (S) are taken and each sample is added directly into an erlenmeyer flask containing 150 mL of cold water and few drops of bromothymol blue.
The remained quantity of hydrochloric acid in each sample is then titrated with sodium hydroxide solution ($Na^+ + HO^-$) of concentration Cb =0.8 mol.L$^{-1}$. The results obtained are given in the following table:

| Time (min) | 0 | 79 | 158 | 230 | 316 | 405 | 510 | 570 | 632 |
|---|---|---|---|---|---|---|---|---|---|
| $V_{(NaOH)}$ (mL) | 0 | 41.75 | 38.0 | 35.0 | 32.5 | 29.5 | 27.5 | 25.5 | 25.0 |
| $[H_3O^+]$ (mol.L$^{-1}$) | 1.85 | | 1.52 | 1.4 | 1.3 | 1.18 | 1.07 | 1.02 | 0.98 |

2.1- Specify the effect of adding cold water on the kinetics of this reaction.

2.2- Specify how to detect the equivalence point in this titration.

**3- Kinetic Study**

3.1- Verify the following relation: $[H_3O^+]_t = 4\times10^{-2}\times$ Vb, knowing that: $[H_3O^+]_t$ is expressed in mol.L$^{-1}$ and Vb is expressed in mL.

3.2- Calculate the missing value in the above table.

3.3- Determine the average rates of disappearance of $H_3O^+$ ions $r_1$ and $r_2$ respectively:

3.3.1- Between $t_1 = 0$ and $t_2 = 158$ min.

3.3.2- Between $t_2 = 158$ min and $t_3 = 316$ min.

3.3.3- Compare $r_1$ and $r_2$. Interpret.

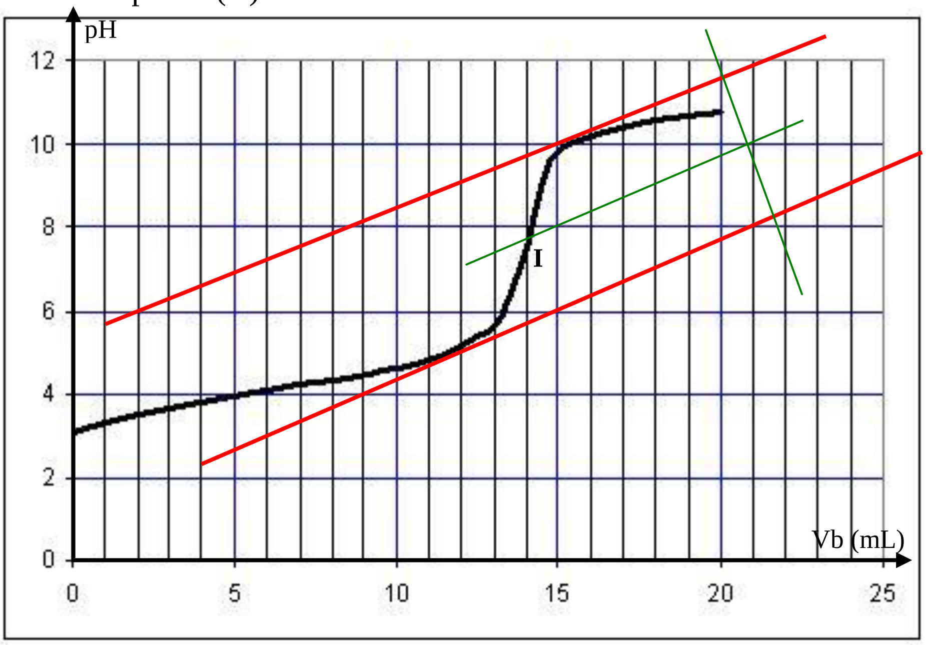
**4- The Released Methyl Chloride Gas**

Determine, at t = 632 min, the released volume of methyl chloride gas, knowing that its solubility in water is 5.325 g.L$^{-1}$at the conditions of the experiment,

## First Exercise (6 points)
## Preparation of an Ester

| Part of the Q | Answer | Mark |
|---|---|---|
| 1.1 | According to the formula of the compound A, we have:<br>$\frac{12x}{\%C} = \frac{y}{\%H} = \frac{16}{\%O}$; the % of oxygen is:<br>100 – (66.67 + 11.11) = 22.22<br>So: $x = \frac{16 \times 66.67}{12 \times 22.22} = 4$ and $y = \frac{16 \times 11.11}{22.22} = 8$. | **0.75** |
| 1.2 | The formulas are:<br>$CH_3 - CH_2 - CH_2 - CHO$ ; $CH_3 - CH_2 - CO - CH_3$ and<br>$CH_3 - CH(CH_3) - CHO$ | **0.75** |
| 1.3 | According to these two tests: A reacts with D.N.P.H and with Fehling's solution, we deduce that A is an aldehyde. Having a non branched chain, its name is butanal. | **0.5** |
| 2.1 | The equation of this reaction is:<br>$5\ CH_3 - CH_2 - CH_2 - CHO + 2\ MnO_4^- + 6\ H^+ \rightarrow 5CH_3 - CH_2 - CH_2 - COOH + 2\ Mn^{2+} + 3\ H_2O$<br>The name of X is: butanoic acid. | **0.75** |
| 2.2 | The equation of hydrogenation reaction is:<br>$CH_3 - CH_2 - CH_2 - CHO + H_2 \rightarrow CH_3 - CH_2 - CH_2 - CH_2OH$<br>The name of Y is: 1-butanol. | **0.75** |
| 3.1 | The formula of E : $CH_3 - CH_2 - CH_2 - C(=O) - O - CH_2 - CH_2 - CH_2 - CH_3$<br>Its name is: butylbutanoate. | **0.5** |
| 3.2 | X + Y ⇄ E + $H_2O$<br>Initial state: n, n, -, -<br>State of equilibrium: n – x, n – x, x, x<br>$K = \frac{[E]\times[H_2O]}{[X]\times[Y]} = \frac{\frac{x}{V}\times\frac{x}{V}}{\frac{(n-x)^2}{V^2}} = \frac{x^2}{(n-x)^2} = 4.0$ ; with $x$ = 0,4 mol, the value of n is: 0.6 mol. | **1** |
| 3.3.1 | The formula of the chlorinated derivative: $CH_3 - CH_2 - CH_2 - COCl$ and its name is butanoyle chloride. | **0.5** |
| 3.3.2 | The reaction is complete; and the quantity of ester obtained is equal to the initial quantity of the acid which is n = 0.6 mol. | **0.5** |

**Second Exercise (7 points)**
**Titration of a Tablet of Vitamin C**

| Part of the Q | Answer | Mark |
|---|---|---|
| 1.1.1 | Preparation of the solution:<br>- 100 mL volumetric flasks to prepare the solution<br>- 10 mL volumetric pipet to take the 10 mL | 0.5 |
| 1.1.2 | Titration procedure :<br>- 50 mL buret to add the sodium hydroxide solution.<br>- Magnetic stirrer and its bar to stir the solution<br>- pH-meter and its electrode to measure the pH<br>- Beaker to perform the titration. | 0.75 |
| 1.2 | The factor of dilution is $f = \frac{C_1}{C_2} = 5$. The volume of the final solution must be 5 times the volume of the initial solution. We can use the following sets:<br>50 mL beaker, 10 mL pipet to take the initial solution which is introduced into the 50 mL volumetric flask add then distilled water to reach the line mark. | 0.5 |
| 1.3 | The equation of the titration reaction is: $HA + HO^- \rightarrow H_2O + A^-$ | 0.5 |
| 1.4 | The curve: pH = f(V)<br><br> | 1 |
| 2.3 | The co-ordinates of the equivalence point are obtained by the // tg method:<br>$Vb_E$ = 14.2 mL and pH = 7.8. | 0.5 |
| 2.4 | pKa = pH when [HA] = [$A^-$]. Its value is obtained considering the pH that corresponds to the half-equivalence point, where $Vb = \frac{14.2}{2}$ and pH = pKa = 4.2. | 0.5 |
| 2.5 | At equivalence the reactants react completely and their quantities are in the stoichiometric proportions, so: | 1 |

| | | |
|---|---|---|
| | $C_aV_a = C_bV_b$ ; $C_a = \frac{14.2\times0.02}{10} = 2.84\times10^{-2}$ mol.L$^{-1}$.<br>(volume of soda at equivalence: 14.2 mL graph reading)<br>The number of moles in a tablet is:<br>$2.84\times10^{-2}\times0.1 = 2.84\times10^{-3}$ mol (in 1 00 mL)<br>Ascorbic acid mass in a tablet: $2.84\times10^{-3}\times 176 = 0.4998$ g = 500 mg.<br>Result conforms to the indication of the manufacturer. | |
| **3.1** | The number of moles, n, is given by the relation $n = \frac{m}{M}$ .<br>So : n (ascorbic acid) = $\frac{247}{176}\times10^{-3} = 1.40\times10^{-3}$ mol.<br>n(sodium ascorbate) = $\frac{284}{198}\times10^{-3} = 1.43\times10^{-3}$ mol. | **0.5** |
| **3.2** | The pH is given by the relation:<br>$pH = pKa + \log\frac{[\text{ascorbate ion}]}{[\text{ascorbic acid}]}$ ; with pKa = 4.2 so:<br>$pH = 4.2 + \log\frac{1.43}{1.40} = 4.21$. | **0.5** |
| **3.3** | pH ≈ 1< pKa - 1 , so the acid HA predominates in the stomach. | **0.25** |
| **3.4** | $\frac{[HA]}{[A^-]} = 10^{pK_a - pH} = 10^{4,2-1} = 10^{3,2} = 1585$ . The basic species are negligible<br>total m of ascorbic acid in a tablet:<br>$(1.40 + 1.43)\times10^{-3}\times176 = 498.1\times10^{-3}$ g ≈ 500 mg | **0.5** |

## Third Exercise (7 points)

## Kinetics of the Preparation Reaction of Methyl Chloride

| Part of the Q | Answer | Mark |
|---|---|---|
| **1.1** | The mixture obtained represents a case of dilution, where the number of moles of each solute remains unvaried , thus<br>C.V = C'V'. (Total volume is V = 80 + 100 + 20 = 200 mL)<br>$[CH_3OH]_0 = \frac{5\times80}{200} = 2$ mol.L$^{-1}$ .<br>$[H_3O^+]_0 = \frac{3.7\times100}{200} = 1.85$ mol×L$^{-1}$ . | **0.75** |
| **1.2** | $\frac{[CH_3OH]_0\times V}{1} = 2\times200\times10^{-3} > \frac{[H_3O^+]_0\times V}{1} = 1.85\times200\times10^{-3}$<br>0.4 > 0.37 hence hydrochloric acid is the limiting reactant. Since this reaction is complete so, hydrochloric acid disappears completely at the end of reaction. | **0.75** |
| **2.1** | The effect of the cold water is to stop the reaction immediately by decreasing the temperature of the system and decreasing the concentration of the reactants since they are kinetic factors. | **0.75** |
| **2.2** | The change in color of the solution in the beaker permits to detect the equivalence point. The change of the yellow color into green color indicates the equivalence point. | **0.5** |
| **3.1** | At equivalence point , and according to the stoichiometric proportions:<br>$n(H_3O^+)_{\text{remained in the beaker}} = n(HO^-)_{\text{added}}$ .<br>Hence $C_a.V_a = C_b.V_{bE} \Rightarrow C_a = \frac{0.8\times V_{b(\text{in mL})}}{20\text{ mL}} = 0.04\times V_{bE(\text{in mL})}$ | **1** |

| | | |
|---|---|---|
| **3.2** | Using the relation $C_a = 0.04 \times V_{bE(\text{ in ml })}$, the missing value is: 1.67 $mol.L^{-1}$ at t = 79 min. | **0.5** |
| **3.3.1** | The average rate of the disappearance of the $H_3O^+$ is obtained by:<br>$\overline{r}(H_3O^+) =$<br>$r_1 = -\frac{\Delta[H_3O^+]}{\Delta t} = -\frac{1.52-1.85}{158} = 2.1\times10^{-3}\ mol.L^{-1}.min^{-1}$ | **0.5** |
| **3.3.2** | $r_2 = -\frac{1.30-1.52}{316-158} = 1.4\times10^{-3}\ mol.L^{-1}.min^{-1}$ | **0.25** |
| **3.3.3** | $r_2 < r_1$. The average rate of disappearance of $H_3O^+$ ions decreases with time. This decreasing is due to the decreasing in the concentration of the reactants (kinetic factor). | **0.75** |
| **4** | At t=632 min , $[H_3O^+] = 0.98\ mol.L^{-1}$.<br>By stoichiometric proportion , $n(CH_3\text{-}Cl)_{\text{totally obtained}} = n(H_3O^+)_{\text{reacted}}$<br>But $n(H_3O^+)_{\text{reacted}} = n(H_3O^+)_o - n(H_3O^+)_{\text{rem}} =$<br>$= ([H_3O^+]_o - [H_3O^+]_{\text{rem}})\times V_{\text{total}} = (1.85 - 0.98)\times 0.2 = 0.174$ mol<br>Hence $n(CH_3\text{-}Cl)_{\text{totally obtained}} = 0.174$ mol<br><br>But according to the solubility :<br>$m(CH_3 - Cl)_{\text{totally dissolved}} = S_{g/L}.V = 5.325 \times 0.2 = 1.065$ g ,<br>$n(CH_3\text{-}CL)_{\text{totally dissolved}} = \frac{\mathbf{m}}{\mathbf{M}} = \frac{\mathbf{1.065}}{\mathbf{50.5}} = 0.021$ mol<br>$n(CH_3\text{-}Cl)_{\text{collected after 632 min}} = 0.174 - 0.021 = 0.153$ mol<br>$V(CH_3\text{-}Cl)_{\text{collected after 632 min}} = 0.153 \times 24 = 3.67$ L**.** | **1.25** |