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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 (7 points)
Commercial Solution of Hydrochloric Acid

The aim of this exercise is to verify the indication of the label of a bottle of commercial hydrochloric acid and to identify a weak base by determining the pKa of the corresponding conjugate acid/base pair.

Given:

- This study is carried out at 25 ºC.
- Kw = 10^{-14}.
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Conjugate acid/base pair	pKa
$(CH_3)_3 NH^+/(CH_3)_3N$	9.9
$C_3 H_7 - NH_3^+ / C_3H_7 – NH_2$	10.3
$C_2H_5 - NH_3^+ /C_2H_5 – NH_2$	10.7

1- Dilution of the Commercial Solution

On the label of a commercial hydrochloric acid bottle we read the following indications:
" Hydrochloric acid, density: 1190 kg.m $^{-3}$, percentage in mass of pure acid: 37, molar mass of hydrogen chloride HCl: 36.5 g.mol $^{-1}$ ″.
4.1 mL of acid are taken from this bottle, and distilled water is added to get a volume of 500 mL. The obtained solution is noted as S.
1.1- Determine the number of moles of the solute in 4.1 mL of the commercial solution.
1.2- Deduce that the concentration of solution S is close to 0.1 mol.L $^{-1}$.

2- Titration of the Solution S

In order to verify this concentration, the titration of this acid solution with a solution of a weak base B of concentration C_b = 0.032 mol.L $^{-1}$ is carried out. The hydrochloric acid solution previously prepared is added to a volume V_b = 20 mL of the basic solution.
The table below indicates the various values of pH versus the volume V_a (in mL) of acid added.

V_a	0	1	2	3	4	4.5	5	5.2	5.4	5.6	6
pH	11.4	11.0	10.7	10.4	10.2	10.1	9.8	9.7	9.4	9.3	8.7

V_a	6.2	6.4	6.6	6.8	7	7.5	8	9	10	11	12
pH	8.4	6.8	5.6	3.7	3.2	2.7	2.5	2.2	2.0	1.9	1.8

2.1- Plot, on a graph paper, the curve pH = f(Va). Take the following scale: in abscissa 1 cm for

1 mL and in ordinate 1 cm for 1 unit of pH.

2.2- Determine the co-ordinates of the equivalence point.

2.3- Deduce the concentration of the solution S. Compare it with the value determined in part 1.2.

3- Identification of the Base B

3.1- Determine, graphically, the value of the pKa of the conjugate acid/base pair BH^+/B.

3.2- Verify starting with the concentration of the base and its initial pH the value of the pKa of the above pair BH^+/B.

3.3- Write a possible condensed structural formula of the base B.

Second Exercise (7 points)
Hydrochloric Acid and Zinc

A volume V = 100 mL of a solution S of hydrochloric acid of molar concentration C is poured into a flask. At the instant t = 0, a mass m = 1.3 g of metal zinc is quickly introduced into the flask (without a noticable change in volume V).

A gas is released. The chemical reaction is represented by the following equation:

$$Zn_{(s)} \quad + \quad 2\,H^+_{(aq)} \quad \rightarrow \quad Zn^{2+}_{(aq)} \quad + \quad H_{2\,(g)}$$

Given:

- Gases, in this exercise, are supposed to be ideal and considered under the conditions: θ = 27 ºC and P = 1 atm.
- Ideal gas constant: R = 0.08 atm.L.mol^{-1}.K^{-1}.
- M (Zn) = 65 g.mol^{-1}.

1- Preparation of the Solution (S)

To prepare the solution S, we proceed in the following way:

- Dissolve a volume of 30 L of hydrogen chloride gas in distilled water in such way to have a solution S_0 of volume 1 L.
- Dilute 25 times solution S_0. A solution S of hydrochloric acid of concentration C is obtained.

1.1- Describe, specifying the glassware used, the procedure to prepare 500 mL of solution S starting with solution S_0.

1.2- Show that the molar volume of gas, under the conditions of this exercise, is: V_m = 24 L.mol^{-1}.

1.3- Determine the concentration C_0 of the solution S_0.

1.4- Deduce that the concentration C, of the solution S, is equal to 0.05 mol.L^{-1}.

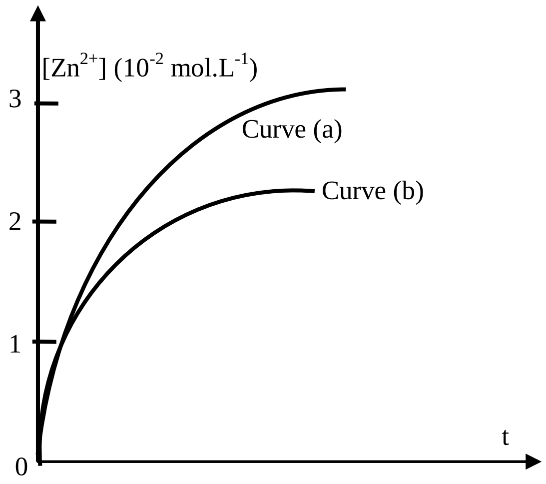
2- Kinetic Study

The progress of the reaction, carried out above, is followed by measuring the volume of hydrogen gas formed by displacement of water, in a graduated cylinder, versus time.

The concentration of Zn^{2+} ions corresponding to each measured volume of hydrogen is then determined.

2.1- Establish the relation between $V_{(H_2)}$, volume of H_2 gas at instant t expressed in mL, and $[Zn^{2+}]$, concentration of Zn^{2+} ions at instant t expressed in mol.L^{-1}.

2.2- Choose, by justifying, between the two curves given below, which corresponds to $[Zn^{2+}]$ = f (t).



2.3- The observation of the displacement of water in the graduated cylinder shows that it starts fast then slows down to stop at the end of the reaction. Interpret the above observation.

2.4- The following table shows the reacting mixtures (1) and (2).

Reacting mixture	Temperature of the mixture	half-life time
Mixture (1) :100 mL of S + 1.3 g of Zn powder	20°C	t_1
Mixture (2) : 100 mL of S + 1.3 g of Zn plate	40°C	t_2

2.4.1- Define the half-life of the reaction.

2.4.2- Justify if it is possible to compare t_1 to t_2.

Third Exercise (6 points)
Synthesis of an ester

It is required to prepare an ester from some chemical compounds available in the laboratory. These compounds are the following: an alcohol A, ethanoic acid, concentrated sulfuric acid and a dehydrating agent P_2O_5.

Given:

- Molar mass of alcohol A, M (A) = 88 $g.mol^{-1}$.
- Density of alcohol A, d = 0.80 $g.mL^{-1}$.

1- Identification of the Alcohol (A)

(A) is a non cyclic saturated monoalcool.

1.1- Determine the molecular formula of A.

1.2- In acid medium and in the presence of excess oxidizing agent, alcohol A is transformed into an organic compound which reacts with D.N.P.H and does not react with Fehling's solution .

1.2.1- Record your observation in the above two tests.

1.2.2- Specify the class of the alcohol A.

1.2.3- Write the possible condensed structural formulas of alcohol A.

1.2.4- Give the name of the alcohol A, knowing that its carbon chain is branched.

2- Esterification Reactions

Use the condensed structural formulas of the organic compounds to write the equations of the chemical reactions.

An ester is prepared starting with ethanoic acid and the alcohol A.

2.1- Write the equation of the reaction between A and ethanoic acid.

2.2- This reaction is slow. Indicate two ways to increase its rate.

2.3- The same ester can be prepared with a different way by using compounds given in the beginning of this exercise.
Write the equations of the two reactions allowing to prepare this ester.

3- <u>Yield of an Esterification Reaction</u>

A mixture of 0.5 mol of ethanoic acid and a volume V = 39.6 mL of alcohol A is heated in the presence of a few drops of concentrated sulfuric acid.

When the composition of the reacting system becomes non-variable, the remaining acid is titrated and its number of moles is equal to 0.25 mol.

The reaction in this mixture is represented by the following equation:

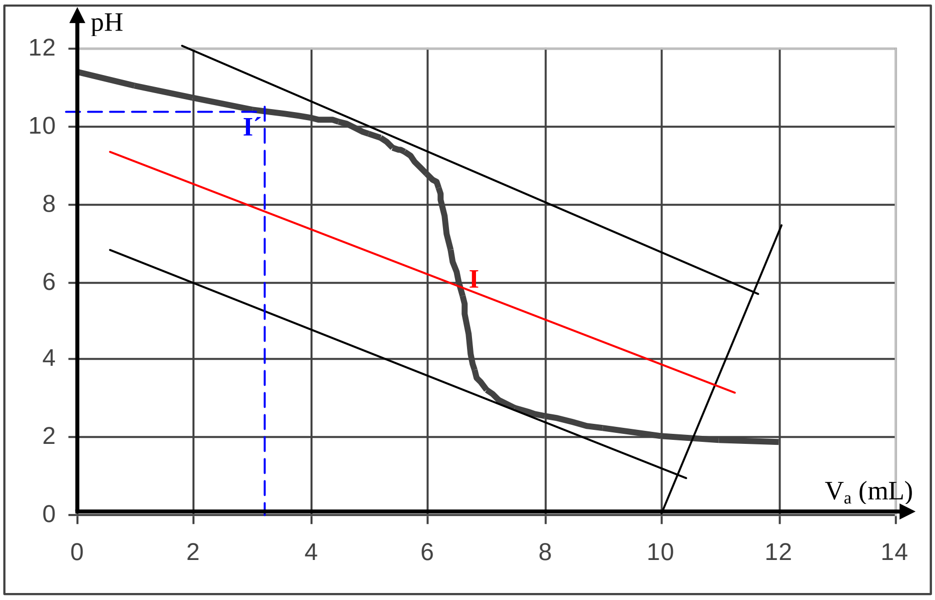
$$A + B \rightleftharpoons E + H_2O$$

Where B represents ethanoic acid.

3.1- Calculate the initial number of moles of the alcohol (A).

3.2- Determine the yield of this reaction.

First Exercise (7 points)
Commercial Hydrochloric Acid Solution

Part of the Q	Answer	Mark
1.1	The number of moles of the solute is: $n(HCl) = \frac{m(HCl)}{M(HCl)} = \frac{p \times m(solution)}{100 \times M} = \frac{p \times d \times v}{100 \times M}$. With: p = 37 ; d = 1.19 $g.mL^{-1}$; M = 36.5 $g.mol^{-1}$; and v = 4.1 mL, we obtaind: n(HCl) = 0.049 mol	1
1.2	The concentration solution S is : $C_s = \frac{n(HCl)}{V(solution)} = \frac{0.049}{0.5} \approx 0.1 mol.L^{-1}$	0,5
2.1	The curve is: 	1
2.2	The co-ordinates of the equivalence point are given by the method of the // tangents. V_{aE} = 6.5 mL and pH_E = 5.8.	0.75
2.3	The equation of the titration reaction is: $H_3O^+ + B \rightarrow BH^+ + H_2O$ At equivalence, we have : $n(H_3O^+)$ in 6.5 mL = n(B) in 20 mL $C'_a \times V_{aE} = C_b \times V_b$ and $C'_a = \frac{0.032 \times 20}{6.5} = 0.098\ mol.L^{-1} \approx 0.1 = C_a$.	1.25
3.1	pKa = pH at half-equivalence. Graphically, it is the pH which corresponds to volume $V = \frac{V_{aE}}{2} = \frac{6.5}{2} = 3.25$ mL and pKa = 10.3.	0.75
3.2	According to the relation $pH = pKa + \log \frac{[B]}{[BH^+]}$ we can calculate pKa. The equation of the reaction of B with water is: $B + H_2O \rightleftharpoons BH^+ + HO^-$ $pH = 14 + \log [HO^-]$; $\log [HO^-] = - 2 .6$;	1.5

	where : $[BH^+] = [HO^-] = 2.5\times10^{-3}$ mol.L^{-1} and $[B] = 0.032 - 2.5\times10^{-3} = 2.95\times10^{-3}$ mol.L^{-1}. $pKa = 11{,}4 - \log\dfrac{2.95\times10^{-2}}{2.5\times10^{-3}} = 10.3$.	
3.3	A condensed structural formula of the base B: $CH_3 - CH_2 - CH_2 - NH_2$ or $CH_3 - \underset{\displaystyle CH_3}{\underset{\vert}{CH}} - NH_2$	**0.25**

Second Exercise (7 points)
Hydrochloric Acid and Zinc

Part of the Q	Answer	Mark
1.1	The Glassware used to prepare 500 mL of the solution S by diluting S_0 25 times: 500 mL volumetric flask and a 20 mL volumetric pipet because, the factor of dilution F is: $F = 25 = \dfrac{500}{20}$ Take, using the volumetric pipet, 20 mL of the solution S_0. Pour this volume in the volumetric flask. Add distilled water to the line mark and shake to homogenize the prepared solution.	**1**
1.2	According to the equation of ideal gases, we have: $V_m = \dfrac{n\times R\times T}{P} = \dfrac{1\times0.08\times300}{1} = 24$ L.mol^{-1}.	**0.5**
1.3	Concentration of the solution S_0 : $C_0 = \dfrac{n(HCl)\,dissolved}{V(solution)} = \dfrac{\dfrac{V(HCl)\,dissolved}{V_m}}{1} = \dfrac{\dfrac{30}{24}}{1} = 1.25$ mol.L^{-1}.	**0.5**
1.4	Concentration of the solution S: $C = \dfrac{C_0}{F} = \dfrac{1.25}{25} = 0.05$ mol.L^{-1}, because in dilution the number of moles of the solute is conserved.	**0.5**
2.1	According to the equation of the reaction between acid and zinc, we have: At each instant t, $n(Zn^{2+})$ formed = $n(H_2)$formed = $\dfrac{V(H_2)\,formed}{V_m}$ Dividing by the volume V of S, we obtain: $[Zn^{2+}] = \dfrac{V(H_2)\,formed}{V_m\times V} = 4.16\times10^{-4}\times V_{(H_2)}$.	**1**
2.2	Ratio relative to Zn : $R_1 = \dfrac{n(Zn)\,initial}{1} = \dfrac{m(Zn)\ initial}{M(Zn)} = \dfrac{1.3}{65} = 0.02$ Ratio relative to H^+: $R_2 = \dfrac{n(H^+)\,initial}{2} = \dfrac{C.V}{2} = \dfrac{0.05\times100\times10^{-3}}{2} = 2.5\times10^{-3}$ $R_2 < R_1$, H^+ is the limiting reactant. Where, $[Zn^{2+}]$ will be at the end of the reaction $\dfrac{[H^+]\,initial}{2}$ which is equal to 2.5×10^{-2} mol.L^{-1}. Thus the curve b corresponds to the required variation.	**1.25**
2.3	The observation shows that the rate of formation of H_2 is maximal at the beginning then decreases at the end of the reaction.	**1**

	The kinetic factor which explains this change in the rate is the concentration of the H^+ ions; it is maximal at the beginning then decreases with time (limiting reactant).	
2.4.1	The half-life of the reaction is the time necessary so that the initial amount of the limiting reactant (H^+) is reduced to its half.	**0.25**
2.4.2	While passing from the mixture (1) to the mixture (2), we have: - Same concentration of the reactant H^+ - Temperature of the mixture increases; that increases the reaction rate. - Surface contact between the reactants decreases; that decreases the reaction rate. Therefore, we cannot determine the change in the rate and consequently, we cannot compare t_1 to t_2.	**1**

Third Exercise (6 points)

Part of the Q	Answer	Mark
1.1	Being a mono noncyclic saturated alcohol, alcohol (A) has as general formula $C_nH_{2n+1}OH$. M (A) = 14 n + 18 = 88; n = 5, and the molecular formula of A is $C_5H_{11}OH$.	**0.75**
1.2.1	With D.N.P.H we observe a yellow precipitate and with Fehling's solution it remains blue.	**0.5**
1.2.2	Since the mild oxidation of A is done in the presence of excess oxidizing agent, compound A reacts with D.N.P.H and dose not react with Fehling's solution is only a ketone; therefore A is a secondary alcohol.	**0.5**
1.2.3	The possible condensed structural formulas of alcohol A are: $CH_3-CH_2-CH_2-\underset{OH}{\underset{\vert}{CH}}-CH_3$ $\quad$ $CH_3-CH_2-\underset{OH}{\underset{\vert}{CH}}-CH_2-CH_3$ $CH_3-\underset{H_3C}{\underset{\vert}{CH}}-\underset{OH.}{\underset{\vert}{CH}}-CH_3$	**0.75**
1.2.4	Since the carbon chain is branched, its name is then: 3-methyl 2-butanol.	**0.25**
2.1	The equation of the reaction between alcohol A and ethanoic acid. $CH_3-\underset{H_3C}{\underset{\vert}{CH}}-\underset{OH}{\underset{\vert}{CH}}-CH_3 + CH_3-COOH \rightleftarrows CH_3-\underset{O}{\underset{\Vert}{C}}-O-\underset{CH_3}{\underset{\vert}{CH}}-\underset{CH_3}{\underset{\vert}{CH}}-CH_3 + H_2O$	**0.5**
2.2	To increase the rate of this reaction: - Add to the reacting mixture a few drops of sulfuric acid as catalyst. - The reacting medium is heated.	**0.5**
2.3	The equations of these two reactions are: $2\ CH_3-COOH \rightarrow CH_3-CO-O-CO-CH_3 + H_2O$ $CH_3-CO-O-CO-CH_3 + CH_3-\underset{H_3C}{\underset{\vert}{CH}}-\underset{OH}{\underset{\vert}{CH}}-CH_3 \rightarrow$ $CH_3-\underset{O}{\underset{\Vert}{C}}-O-\underset{CH_3}{\underset{\vert}{CH}}-\underset{CH_3}{\underset{\vert}{CH}}-CH_3 + CH_3COOH$	**1**

3.1	n (alcohol)initial $= \frac{m(\text{alcohol})\ \text{initial}}{M(\text{alcohol})} = \frac{d \times V}{M(\text{alcohol})} = \frac{39.6 \times 0.8}{88} = 0.36$ mol.	**0.5**
3.2	Yield of the reaction, $y = \frac{n(\text{ester})\ \text{experimental}}{n(\text{ester})\text{theoretical}} = \frac{n_1}{n_2}$; Calculation of n_1: $n_1 = 0.5 - 0.25 = 0.25$ mol. Calculation of n_2: n_2 = n(alcohol) initial = 0.36 mol. Where, $y = \frac{0.25}{0.36} = 0.694$, and the percentage yield is 69.4.	**0.75**