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Entrance exam (2024 - 2025) **Chemistry Exam** **Group (A)** **Time: 1 hour** **10 July 2024**

Answer the Following Two Exercises:

Exercise 1- Esterification and Kinetic Study (10 points)

The two parts A and B are independent.

Part A: Synthesis of an Ester (E)

(E) is an ester used in perfumery for its pleasant smell. To synthesize it, an equimolar mixture formed of a saturated, non-cyclic chain of carboxylic acid of volume V_1 and n_2 mol of ethanol is heated to reflux for 40 minutes and in the presence of 1 mL of concentrated sulfuric acid. The yield of this esterification is 67%. The quantity of ester obtained at equilibrium is $n_3 = 3$ mol.

Given:

- Molar mass in $g.mol^{-1}$: M (H) = 1; M(C) = 12; M(O) = 16
- Density of the carboxylic acid (A): $\rho = 0.97$ $g.mL^{-1}$
- The mass percentage of oxygen in the carboxylic acid (A) is: 36.36%.

Choose the correct answer.

A.1- Carboxylic acid (A):

a) Must be butanoic acid

b) Has the molecular formula $C_4H_8O_2$

c) Has a mass percentage of carbon equal to 63.64%

d) Both a and b are correct

A.2- The carbon chain of the obtained ester is branched. Its systematic name is:

a) Ethyl butanaote

b) Butyl ethanoate

c) Ethyl-2- methyl propanoate

d) 2-methylpropyl ethanoate

A.3- The use of sulfuric acid in this synthesis allows:

a) To increase the yield of the synthesis while increasing its speed

b) To accelerate the reaction without modifying the quantity of ester expected in the final state

c) To direct the reaction towards the synthesis of the desired ester

d) To reduce the duration of this synthesis by avoiding any loss of material

A.4- The characteristics of the esterification reaction that can be extracted from the above synthesis are:

a) Slow and athermic

b) Slow and limited

c) Slow and complete

d) Slow, limited, and athermic

A.5- The quantities used to carry out this synthesis are:

a) V_1 = 272.2 mL and n_2 = 3 mol

b) V_1 = 182.4 mL and n_2 = 2 mol

c) V_1 = 406.2 mL and n_2 = 4.48 mol

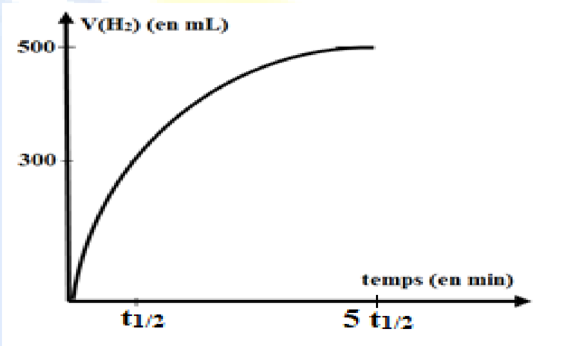
d) V_1 = 406.2 mL and n_2 = 3 mol

<u>Part B:</u> Kinetic study

Into an Erlenmeyer flask initially containing 100 mL of distilled water, a volume V = 100 mL of a solution (A) of hydrochloric acid (H_3O^+ + $C\ell^-$) with a concentration C_a = 1.0 mol. L^{-1} is added. At time t_o and at a constant temperature equal to 25 ºC, a mass m_o of powdered iron is quickly poured into the Erlenmeyer flask. A complete and slow reaction takes place according to the following equation:

$$Fe_{(s)} + 2\,H_3O^+_{(aq)} \rightarrow Fe^{2+}_{(aq)} + H_{2\,(g)} + 2\,H_2O_{(\ell)}$$

Using an appropriate method, the volume of hydrogen gas (H_2) is determined at different instants t, allowing the kinetic curve $V(H_2)$ = f (t) to be plotted as shown below:



Given:

- Gaseous molar volume: Vm = 24 $L.mol^{-1}$
- Molar mass in $g.mol^{-1}$: M(Fe) = 56; M(HCℓ) = 36.5

Choose the correct answer.

B.1- The glassware used to prepare solution (A) from a solution of hydrochloric acid with a mass percentage of HCℓ equal to 37% and a density ρ = 1.19 g.mL $^{-1}$ is:

a) 100 mL volumetric flask; 10 mL volumetric pipette

b) 100 mL volumetric flask; 5 mL volumetric pipette

c) 100 mL volumetric flask; 10 mL graduated pipette

d) 100 mL volumetric flask; 10 mL graduated cylinder

B.2- Referring to the curve $V(H_2) = f(t)$, we can conclude that:

a) The reaction is completed at time $5t_{1/2}$

b) The pH is neutral at $t = 5t_{1/2}$

c) Fe is the limiting reactant

d) The rate of formation of H_2 at t = 0 min is zero

B.3- Knowing that the volume of H_2 formed at each instant (V_{H2}) is expressed in liters, the equation that allows to determine the remaining concentration of H_3O^+ ions at each instant t is:

a) $[H_3O^+]_t = 1.0 - \frac{V_{H_2(t)}}{1.2}$

b) $[H_3O^+]_t = 1.0 - \frac{V_{H_2(t)}}{2.4}$

c) $[H_3O^+]_t = 5.10^{-1} - \frac{V_{H_2(t)}}{2.4}$

d) $[H_3O^+]_t = 5.10^{-1} - \frac{V_{H_2(t)}}{1.2}$

B.4- The molar concentration of the hydrochloric acid solution at $t_{1/2}$ is:

a) 5 times greater than that at $5\ t_{1/2}$

b) Equal to 0.25 mol. L^{-1}

c) Equal to 0.375 mol. L^{-1}

d) Both a and c are correct

B.5- The mass m_o of iron is:

a) 1.17g

b) 1.40g

c) 2.8g

d 5.6g

Exercise 2- Identification of a Solute (10 points)

The information given on the label of a bottle containing a solution (S) are not readable. The solute that was used to prepare this solution is one of the four species **shown in Table 1**.

Solution	Acidic or basic character	pKa of the corresponding acid/base pairs
Sodium benzoate (C_6H_5COONa)	Weak Base	4.20
Sodium Hydroxide (NaOH)	Strong Base	
Ammonia (NH_3)	Weak Base	9.22
Ethanoic Acid (CH_3COOH)	Weak Acid	4.75

Table 1- Characteristics of some chemical species

The aim of this exercise is to determine the solute that was used to prepare the solution (S) and then study its chemical reactivity.

Given:

- The study is carried out at 25 °C
- The ionization constant of water is $K_w = 10^{-14}$

1. Identification of the solute in solution (S)

The molar concentration of the solution (S) is $C = 1.0 \times 10^{-2}$ mol. L^{-1}.

The molar concentration of the solution (S) in hydronium ions (H_3O^+) is $[H_3O^+] = 2.51 \times 10^{-11}$ mol. L^{-1}.

1.1. Among the four solutions present in **Table 1**, indicate which one(s) were not used to prepare solution (S). Justify.

In the rest of this exercise, the solute used to prepare the solution (S) is denoted by B.

1.2. Write the equation of the reaction of solute B with water.

1.3. Show that the degree of conversion α of solute B in water and the pH of this solution are related by the following relation: $\alpha = 10^{pH-12}$

1.4. Calculate α.

1.5. Identify the solute that was used to prepare the solution (S).

2. Acid-base reaction

Solution (S) can be used to prepare a chemical fertilizer solution of acidic pH.

To do this, a volume V_1 = 20 mL of solution (S) is added to a solution (S_a) of hydrochloric acid ($H_3O^+ + C\ell^-$) with a molar concentration Ca = $2.0\text{x}10^{-2}$ mol. L^{-1}.

2.1. Write the equation of the reaction which takes place by mixing the two solutions (S) and (Sa), knowing that it is complete.

2.2. Determine the minimum volume of solution (Sa) that must be added to obtain a chemical fertilizer solution with a pH less than 7.

Good Work

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Solution **Group (A)** | **10 July 2024**

Exercise 1- Esterification and Kinetic study (10 points) **group (A)**

Questions	Expected Answers	mark
A.1.	**B**	**1**
A.2.	**C**	**1**
A.3.	**B**	**1**
A.4.	**B**	**1**
A.5.	**C**	**1**
B.1.	**C**	**1**
B.2.	**C**	**1**
B.3.	**C**	**1**
B.4.	**C**	**1**
B.5.	**B**	**1**

Exercice 2- Identification of a solute (10 points)

Questions	Expected Answers	mark
1.1.	The pH of the solution (S) is pH = $-\log[H_3O^+] = -\log(2.51.10^{-11})$ pH = 10.6 > 7 then the solution (S) is a basic solution, the ethanoic acid is first eliminated. On the other hand NaOH is a strong base, the pH of such a solution of concentration C = $1.0.10^{-2}$ mol. L^{-1} is pH = pKw + log C pH = 14 + $\log(1.0.10^{-2})$ = 12 ≠ 10.6. So NaOH must be eliminated	**1** **1**
1.2.	$B + H_2O \rightleftharpoons HB^+ + HO^-$	**1**
1.3.	$\alpha = \frac{n(B)reacted}{n(B)initial} = \frac{n(HO^-)formed}{C \times V} = \frac{[HO^-] X V}{c X V} = \frac{Kw}{[H_3O^+]x c}$ $\alpha = \frac{10^{-14}}{10^{-pH} x 0.01} = 10^{pH-12}$	**1**
1.4.	$\alpha = 10^{10.6-12} \approx 0,04$	**1**
1.5.	The composition of the system at equilibrium is: | | B + | $H_2O \rightleftharpoons$ | HB^+ + | HO^- | | Initial state | C | Solvent | 0 | 0 | | Final state | C(1 – α) | | C.α | C.α | On the other hand,	

	$K_A\ (HB^+/B) = \frac{[B]x\,[H_3O^+]}{[HB^+]} = \frac{C(1-\alpha)x\ 2{,}51.10^{-11}}{C.\alpha}$ $K_A\ (HB^+/B) = \frac{(1-0{,}04)x\ 2{,}51.10^{-11}}{0{,}04} = 6{,}024.10^{-10}$ $p\,K_A\ (HB^+/B) = -\log K_A\ (HB^+/B) = -\log (6{,}024.10^{-10}) = 9{,}22$ the solute is ammonia NH_3	**2**
2.1.	$NH_3 + H_3O^+ \rightarrow NH_4^+ + H_2O$	**1**
2.2.	The minimum volume (Va) of hydrochloric acid solution that must be added to have an acidic mixture is that which makes the mixture stoichiometric because following this addition, the NH_4^+ ion predominantly present, makes the environment acidic. so $\frac{n(NH_3)inital}{1} = \frac{n(H_3O^+)initial}{1}$ $C \times V_1 = C_a \times V_a$ $,V_a = \frac{C\,x\,V_1}{C_a} = \frac{10^{-2}\,x\,20}{2.10^{-2}} = 10$ mL	**2**