دورة المعام ٢٠٢١ الاستثنائيّة الأربعاء ٨ ايلول ٢٠٢١

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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:

Exercise 1 (7 points)

Kinetic of The Reduction of Iodine by Zinc

Zinc metal (Zn) reacts with an aqueous solution of iodine ($I_{2 (aq)}$) in a slow and complete reaction that takes place according to the equation given below:

 $Zn_{(S)} + I_{2(aq)} \rightarrow Zn^{2+}_{(aq)} + 2I^{-}_{(aq)}$ Reaction 1

The aim of this exercise is to study the kinetic of this reaction.

Given: Molar mass of Zinc is: $M(Zn) = 65.4 \text{ g.mol}^{-1}$

1. Preliminary Study

At instant t = 0, a volume V = 280.0 mL of iodine solution (I₂) of concentration $C_0 = 2.0 \times 10^{-2}$ mol.L⁻¹ is poured into a beaker containing a mass m = 346 mg of pure zinc metal.

Reaction 1 is realized at a temperature **T** maintained constant.

- **1.1.** Determine the limiting reactant.
- **1.2.** Establish the relation between the concentration of iodine at instant t, $[I_2]_t$, and the concentration of zinc ions at same instant t, $[Zn^{2+}]_t$.
- **1.3.** Show that the concentration of zinc ions at the end of the reaction is $[Zn^{2+}]_{\infty} = 18.9 \times 10^{-3} \text{ mol.L}^{-1}$.

2. Kinetic Study

Document-1 shows the concentration of Zn^{2+} ions, [Zn^{2+}], obtained at different instants.

t (s)	30	100	200	400	600	800	1000	1200
$[Zn^{2+}]$ (10 ⁻³ mol.L ⁻¹)	2.4	7.9	10.5	13.8	15.8	17.4	17.9	18.4
Document-1								

2.1. Plot the curve representing the variation of the concentration of Zn^{2+} ions as a function of time: $[Zn^{2+}] = f(t)$ in the interval of time: [0 - 1200 s]. Take the following scales: 1 cm for 100 s in abscissa

1 cm for 2.0 $\times 10^{-3}$ mol.L⁻¹ in ordinate.

- **2.2.** Specify, graphically, the variation in the rate of formation of Zn^{2+} ions over time.
- **2.3.** Determine, graphically, the half-life time of the reaction $t_{1/2}$.
- **2.4.** The above kinetic study is carried out but with only one modification: $\mathbf{T} > \mathbf{T}$. Trace, on the same graph of question **2.1**, the shape of the curve representing the variation of the concentration \mathbb{Zn}^{2+} ions as a function of time at $\mathbf{T} : [\mathbb{Zn}^{2+}] = g(t)$. Justify.

Exercise 2 (6 points)

Sodium Hydroxide

Sodium hydroxide solution $(Na^+ + HO^-)$ is colorless and odorless that can react violently with strong acids and water. Sodium Hydroxide is commonly used as a drain cleaner.

The aim of this exercise is to study the behavior of sodium hydroxide in water then to determine its concentration in a commercial drain cleaner.

Given:

- Molar mass of sodium hydroxide: M_(NaOH) = 40 g.mol⁻¹
- Density of commercial drain cleaner solution: $d = 2.13 \text{ g.mL}^{-1}$
- The study is carried out at $T = 25^{\circ}C$
- Ion product of water at 25°C: $K_W = 1.0 \times 10^{-14}$

1. Behavior of Sodium Hydroxide in Water

A mass m = 0.40 g of solid sodium hydroxide are dissolved in distilled water in order to prepare a volume V= 1.0 L of a sodium hydroxide solution (S). The pH of the obtained solution (S) is: pH = 12

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

- **1.2.** Calculate the concentration of hydronium ions, $[H_3O^+]$, in the solution (S).
- **1.3.** Deduce the concentration of hydroxide ions, [HO⁻], in this solution.
- **1.4.** Justify the statement: "Sodium hydroxide is a strong base."

2. Dilution of the Commercial Drain Cleaner Solution

The commercial drain cleaner solution noted (S_o) is too concentrated. A sodium hydroxide $(Na^+ + HO^-)$ solution (S') is prepared by diluting 500 times the commercial solution (S_o) . Choose, from **Document-1**, the most precise set for the preparation of solution (S').

Set 1	Set 1 Set 2			
Beaker of 100 mL	Beaker of 100 mL	Beaker of 100 mL		
Graduated cylinder of 10 mL	Volumetric pipet of 2 mL	Volumetric pipet of 2 mL		
Volumetric flask of 500 mL	Volumetric flask of 1 L	Volumetric flask of 500 mL		
Document-1				

3. pH-metric Titration of Solution (S')

A volume V_b = 10.0 mL of the solution (S') is introduced into a beaker then distilled water is added in order to immerse properly the pH-meter electrode. A pH-metric titration is realized by adding progressively into the beaker a hydrochloric acid solution (H₃O⁺ + C ℓ^-) of molar concentration $C_a = 2.50 \times 10^{-2}$ mol.L⁻¹. The volume of the acid solution needed to reach equivalence is $V_{aE} = 21.3$ mL.

- **3.1.** Write the equation of the titration reaction.
- **3.2.** Specify, based on the chemical species present in the solution, whether the addition of water to immerse properly the pH-meter electrode affects the pH at equivalence, pH_E .
- **3.3.** Determine the molar concentration of the solution (S').
- **3.4.** Deduce the molar concentration of sodium hydroxide in the commercial drain cleaner (S₀).
- **3.5.** Choose the value that corresponds to the percentage by mass of the sodium hydroxide in the drain cleaner solution (S_o) . Justify.

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a) 20%	b) 50%	c) 35 %

Exercise 3 (7 points)

Isobutyric Acid Ethyl Ester

Isobutyric acid ethyl ester is a sweet tasting compound. It is prepared by an esterification reaction between an acid (A) and an alcohol (B).

Outside of the human body, it has been detected in several different foods, such as apples, figs ...

The aim of this exercise is to identify the acid (A) and the alcohol (B) and to study the effect of some factors on the esterification reaction yield.

1. Study the Structure of Isobutyric Acid Ethyl Ester

The condensed structural formula of isobutyric acid ethyl ester is given in **Document-1**:



- **1.1.** Recopy the condensed structural formula of isobutyric acid ethyl ester and circle its functional group.
- **1.2.** Give the systematic name of isobutyric acid ethyl ester.
- **1.3.** Isobutyric acid ethyl ester is obtained from the reaction between a carboxylic acid (A) and an alcohol (B). Identify the acid (A) and the alcohol (B).

2. Synthesis of Isobutyric Acid Ethyl Ester

Isobutyric acid ethyl ester can be prepared starting from carboxylic acid (A) and alcohol (B) according to the following equation:

Carboxylic acid (A) + Alcohol (B) \Rightarrow Isobutyric Acid Ethyl Ester + Water

An equimolar mixture (M) containing 1.0 mol of carboxylic acid (A) and 1.0 mol of the alcohol (B) is heated to reflux for several hours in the presence of few drops of sulfuric acid as a catalyst. **Document-2** represents the change in the number of moles of the ester formed with time.



- **2.1.** Give the importance of heating this reacting mixture.
- **2.2.** Justify, based on **Document-2**, that the system has reached equilibrium state.
- **2.3.** Determine the yield of this synthesis reaction.
- **2.4.** We realize other reacting mixtures given in the table of **Document-3**.

Reacting mixture	Number of moles of (A)	Number of moles of (B)	Catalyst	Corresponding curve
Μ	1.0 mol	1.0 mol	H_2SO_4	а
M′	1.0 mol	1.0 mol		b
M″	1.0 mol	5.0 mol	H_2SO_4	с
Document-3				

Document-4 shows the curves that represent the variation of n(ester) with time in each mixture.



Referring to **Document-3** and **Document-4**:

- **2.4.1.** Deduce the effect of the use of a catalyst on the equilibrium sate.
- **2.4.2.** Suggest a way to increase the yield of the esterification reaction. Justify.