مسابقة في مادة الكيمياء	الاسم:
المدة: ساعة ونصف	الرقم:

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 g.mol^{-1}

1. Preliminary Study

At instant t = 0, a volume V = 280.0 mL of iodine solution (I_2) of concentration $C_o = 2.0\times10^{-2}$ 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 $[Zn^{2+}]_\infty = 18.9 \times10^{-3}$ 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 2.0×10^{-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: **T ' > T**. Trace, on the same graph of question **2.1**, the shape of the curve representing the variation of the concentration Zn^{2+}ions as a function of time at **T '**: $[Zn^{2+}]$ = 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 g.mL^{-1}
- The study is carried out at T = 25°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 $C = 1.0 \times 10^{-2}$ mol.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 2	Set 3
Beaker of 100 mL Graduated cylinder of 10 mL Volumetric flask of 500 mL	Beaker of 100 mL Volumetric pipet of 2 mL Volumetric flask of 1 L	Beaker of 100 mL Volumetric pipet of 2 mL 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 ($H_3O^+ + C\ell^-$) 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 (S_o).
3.5. Choose the value that corresponds to the percentage by mass of the sodium hydroxide in the drain cleaner solution (S_o). Justify.

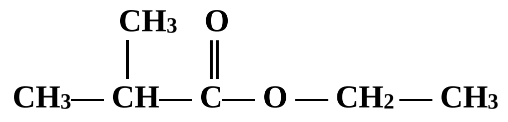
a) 20% **b)** 50% **c)** 35 %

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**:



Document-1

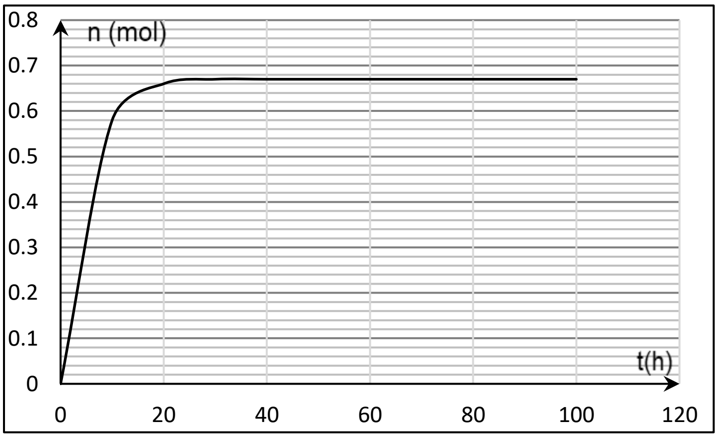
1.1. Recopy the condensed structural formula of isobutyric acid ethyl ester and circle its functional group.
1.2. Give the systematic name of isobutyric acid ethyl ester.
1.3. Isobutyric acid ethyl ester is obtained from the reaction between a carboxylic acid (A) and an alcohol (B). Identify the acid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



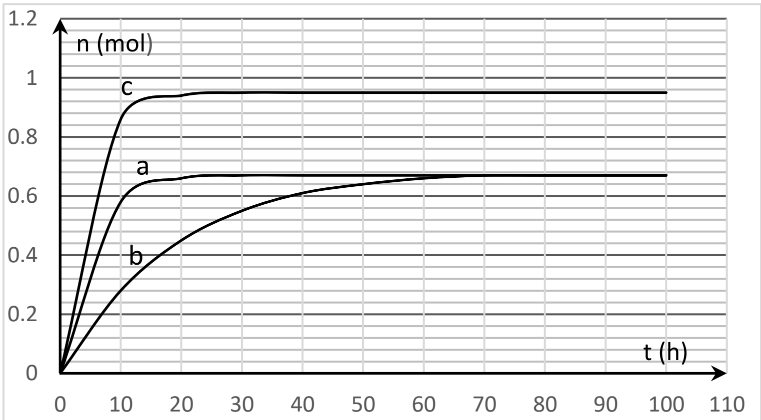
Document-2

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**
M	1.0 mol	1.0 mol	H_2SO_4	a
M′	1.0 mol	1.0 mol		b
M″	1.0 mol	5.0 mol	H_2SO_4	c

Document-3

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

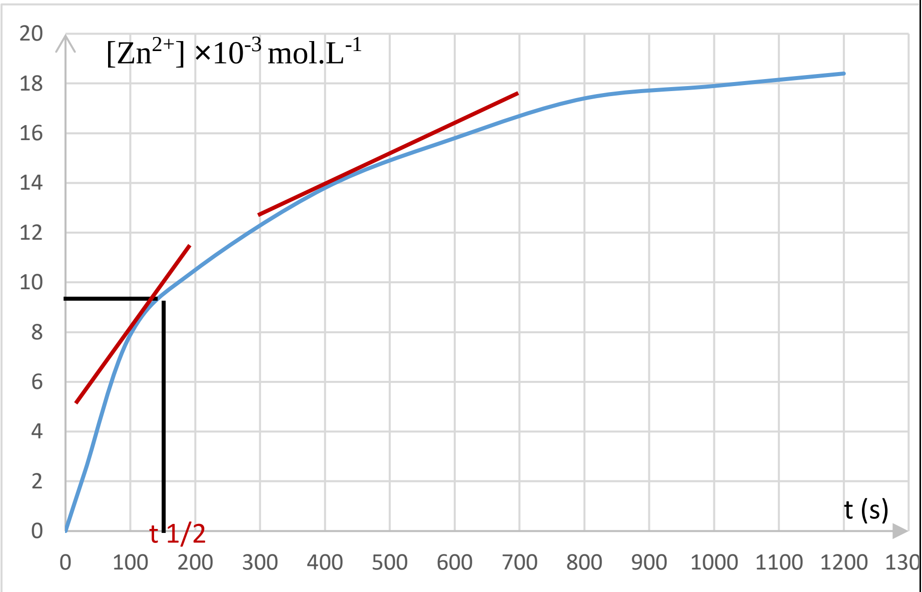


Document-4

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.

Exercise 1 (7 points) **Kinetic of The Reduction of Iodine by Zinc**

Part of the Q	Answer	Mark
1.1	R (I_2) $=\frac{n(I_2)initial}{1}=\frac{C\times V}{1}=\frac{2\times10^{-2}\times280\times10^{-3}}{1}=5.6\times10^{-3}$. R (Zn) $=\frac{n(Zn)initial}{1}=\frac{m}{M}=\frac{346\times10^{-3}}{65.4}=5.29\times10^{-3}$. R ($I_2$) > R (Zn) therefore Zn is the limiting reactant.	1
1.2	$n(I_2)_{\text{remained at t}} = n(I_2)_{\text{initial}} - n(I_2)_{\text{reacted at t}}$, at each instant, $n(I_2)_{\text{reacted}} = n(Zn^{2+})_{\text{formed}}$; $n(I_2)_{\text{remained at t}} = n(I_2)_{\text{initial}} - n(Zn^{2+})_{\text{formed at t}}$; Divide by $V_{solution}$: $[I_2]_t = [I_2]_o - [Zn^{2+}]_t$	1
1.3	$n(Zn)_o = n(Zn^{2+})_\infty = 5.29\times10^{-3}$mol; $[Zn^{2+}] = \frac{n(Zn^{2+})\infty}{V_{solution}} = \frac{5.29\times10^{-3}}{280\times10^{-3}} = 18.9\times10^{-3}$mol.L^{-1}	0.75
2.1		1
2.2	The rate is equal to the positive slope of the tangent drawn on the curve $[Zn^{2+}] = f(t)$. The slope of the tangent at instant t_1 > the slope of the tangent at instant t_2 . (Shown on curve). Then the rate at t_1 > the rate at t_2 and thus the rate decreases with time.	1
2.3	Half life time ($t_{1/2}$) is the time needed for half the maximum amount of the product to be formed.	1

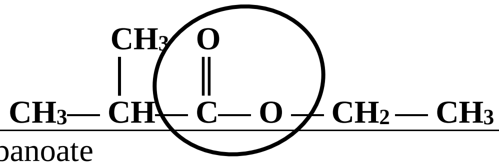
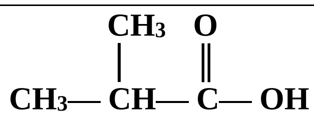
	At $t_{1/2}$: $[Zn^{2+}] = \frac{[Zn^{2+}]\infty}{2} = \frac{18.9\times10^{-3}}{2} = 9.45\times 10^{-3}$ mol.L^{-1}. Graphically $t_{1/2}$ = 150s	
2.4	Temperature is a kinetic factor. As temperature increases, the rate of the reaction increases. At each instant the rate at **T'** > the rate at **T**. and then at each instant $[Zn^{2+}]$ at **T'** > $[Zn^{2+}]$ at **T**. The curve $[Zn^{2+}]$ = g(t) is above $[Zn^{2+}]$ =f(t)	**1.25**

Exercise 2 (6 points) Sodium Hydroxide

Part of the Q	**Answer**	**Mark**
1.1	$C = \frac{n(naOH)}{V\ solution} = \frac{m}{M\times V} = \frac{0.4}{40\times1} = 1\times 10^{-2}$ mol.L^{-1}	**0.5**
1.2	$pH = -\log[H_3O^+]$; $[H_3O^+] = 10^{-pH} = 10^{-12}$ mol.L^{-1}	**0.5**
1.3	$Kw = [HO^-][H_3O^+]$; $[HO^-] = \frac{10^{-14}}{[H_3O^+]} = \frac{10^{-14}}{10^{-12}} = 1\times 10^{-2}$ mol.L^{-1}	**0.5**
1.4	Since $[HO^-] = 1\times 10^{-2}$ mol.L^{-1} = C, then NaOH is a strong base	**0.5**
2.	Upon dilution: n(solute) is conserved Then $\frac{V}{V_0}$ = dilution factor = 500. For a volumetric flask of volume V = 1 L, $\frac{1}{500}$ = 2 mL to be taken by a volumetric pipet. Set 2 is the most precise set.	**0.75**
3.1	$H_3O^+{}_{(aq)} + HO^-{}_{(aq)} \rightarrow 2H_2O_{(\ell)}$	**0.5**
3.2	At equivalence, the chemical species present in the solution are: Na^+, H_2O and $C\ell^-$. Na+ and $C\ell^-$ are spectator ions. H_2O is a neutral species, then pH_E remains 7 after the addition of distilled water.	**0.75**
3.3	At equivalence: $n(H_3O^+)$ added to reach equivalence $= n(HO^-)$ introduced into the beaker $C_a\times V_{aE} = C_b\times V_b$; $C_b = \frac{2.5\times10^{-2}\times21.3}{10} = 0.053$ mol.L^{-1}	**0.75**
3.4	$C_o = 500 \times C_b = 500 \times 0.053 = 26.625$ mol.L^{-1}	**0.5**
3.5	$\% m = \frac{m\ solute}{msolution} \times 100 = \frac{n\times M}{d\times V} \times 100 = \frac{C_o\times M}{d} \times 100$ $= \frac{26.625\times40}{2.13\times10^3} \times 100 = 50\ \%$ **Answer b**	**0.75**

| **Part of the Q** | **Answer** | **Mark** |

Exercise 3 (7 points) Isobutyric Acid Ethyl Ester

1.1		**0.5**
1.2	Ethyl 2-methylpropanoate	**0.75**
1.3	(A) :  **2-methylpropanoic acid** (B): **CH_3—CH_2OH** **Ethanol**	**1.5**
2.1	Heating increases the rate of the slow esterification reaction.	**0.5**
2.2	Esterification reaction is a reversible reaction, referring to **Docment-2** and starting from t = 20hrs n(ester) remains constant and doesn't change, then it reaches the equilibrium state.	**0.5**
2.3	From **Document-2** n (ester) = 0.66 mol, this is an equimolar mixture and $R_A = R_B$, n(ester) theoretical = 1.0 mol = $n(A)_o = n(B)_o$ % yield $= \frac{n\ actual}{ntheoretical} \times 100 = \frac{0.66}{1} \times 100 = 66$ %	**1**
2.4.1	Comparing mixtures M and M': Starting with the same equimolar mixture. A catalyst is added to Mixture M, from **Document-4** the rate of the reaction in mixture M (represented by curve a) is greater than the rate of the reaction in mixture M' (represented by curve b) where mixture M reaches the same equilibrium state as in mixture M' but in less time, so the catalyst increases the rate of esterification reaction to reach equilibrium faster.	**1.25**
2.4.2	Using Documents 3 and 4 curve c reaches equilibrium state at a value: n (ester) = 0.96 mol which is greater than 0.66 mol and thus yield increases, therefore using a non-equimolar mixture as (M'') increases the yield of an esterification reaction.	**1**