	مسابقة في الكيمياء المدة: ساعتان	الاسم: الرقم:

This Exam Includes Three Exercises .It Is Inscribed on Four Pages Numbered From 1 to 4 .
The Use of A Non – programmable Calculator Is Allowed .
Answer the Three Following Exercises :

Exercise 1 (6 points) . Kinetic Study of the Oxidation Reaction of Zinc Metal

Zinc is a metal that reacts with an aqueous solution of hydrochloric acid ($H_3O^+ + Cl^-$) according to the following equation:

$Zn_{(s)} + 2\ H_3O^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2\ (g)} + 2\ H_2O_{(l)}$

In order to study the kinetic of this reaction, the **experiment (I)** described below is carried out.
At T = 25°C, a mass m = 0.5 g of zinc powder metal is added into a flask containing a volume V_a = 75 mL of hydrochloric acid solution of concentration C_a = 0.4 mol.L^{-1}.Using an appropriate method, the volume of the released hydrogen gas H_2 is measured.

Given: - Molar mass of zinc : M(Zn) = 65.4 g.mol^{-1}.
- At the conditions of the experiment , the molar volume of a gas: V_m=24 L.mol^{-1}.

1. **Preliminary Study**

1.1. Determine the limiting reactant.
1.2. Deduce the concentration of Zn^{2+} ions at the end of reaction.
1.3. Establish, at each instant of time t, the relation between the concentration of Zn^{2+} ions, $[Zn^{2+}]_t$, in mol.L^{-1} and the volume of the released hydrogen gas $V(H_2)_t$ in mL.
1.4. At the instant t = 190 min, the volume of released hydrogen gas is 160 mL. Verify whether t = 190 min represents the end time of the reaction.

2. **Kinetic Study**

The volume of the hydrogen gas released, at different instants t, permits to determine the concentration of Zn^{2+} ions at these instants t .The results obtained are grouped in the table in **document-1.**

t (min)	11	20	30	45	60	80	110	140
$[Zn^{2+}]$ (10^{-3} mol.L^{-1})	16	26.6	37.3	52	65.3	78.6	90	96

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), within the interval of time [0 – 140 min].
Take the following scales:
1 cm for 20 min in abscissa and 1 cm for 10×10^{-3}mol.L^{-1} in ordinate.
2.2. Determine the half-life time $t_{1/2}$.
2.3. In order to study the effect of some kinetic factors on the kinetics of this reaction ,two experiments (II) and(III) ,similar to experiment (I) , are carried out but with only one modification in each experiment:

Experiment (II) : the initial concentration of hydrochloric acid solution is 0.5 $mol.L^{-1}$.
Experiment (III) : the temperature of the reacting mixture is T' = 15^0C.

2.3.1. The initial rate of formation of Zn^{2+} ions is determined in each of the experiments (I) and (II) . The results obtained are grouped in the table in **document-2** .

	$[H_3O^+]_0$ in $mol.L^{-1}$	Initial rate
Experiment (I)	0.4	r_0
Experiment (II)	0.5	r_0'

Document-2

Compare r_0 and r'_0. Justify.

2.3.2 . The molar concentration of Zn^{2+} ions at the end of the reaction ($t\infty$), is determined in each of the experiments (I) and (III) . The results obtained are grouped in the table in **document-3**

	Temperature	Molar concentration of Zn^{2+} ions at $t\infty$
Experiment (I)	T= 25 °C	$[Zn^{2+}]_\infty$
Experiment (III)	T'= 15 °C	$[Zn^{2+}]'_\infty$

Document-3

Choose, by justifying , the correct answer :
a- $[Zn^{2+}]_\infty > [Zn^{2+}]'_\infty$ **b -** $[Zn^{2+}]_\infty = [Zn^{2+}]'_\infty$ **c-** $[Zn^{2+}]_\infty < [Zn^{2+}]'_\infty$

Exercise 2 (7 points) Propionic Acid

The production of dry hay can be made difficult when rain is frequent and the hay is conditionally still wet. Propionic acid can be used as a preservative by protecting hay from mildew (fungus) when packed with high water content.

The aim of this exercise is to determine the concentration of propionic acid solution in order to verify whether it can be used to treat the hay.

A solution of propionic acid may be used as a preservative if it contains at least 10 Kg of acid in 100 L of solution.
Document-1

Given: Molar mass of propionic acid: M = 74 $g.mol^{-1}$.

1- Determination of the pKa of the Pair (propionic acid / propionate ion)

Available is a propionic acid solution of concentration $C_a = 1.0 \times 10^{-2}$ $mol.L^{-1}$. The measurement of the pH of this solution gives a value of pH = 3.45

1.1. Deduce that propionic acid is a weak acid.
1.2. Write the equation of the reaction of propionic acid denoted HA with water.
1.3. Show that pKa of the pair (HA / A^-) is equal to 4.9 ($[H_3O^+]$ is neglected compared to C_a)

2- Titration of Propionic Acid Solution

Available is a solution (S) of propionic acid of unknown molar concentration C. To determine this concentration, one proceeds as follows:

- The solution (S) is diluted 150 times. The obtained solution is denoted (S_1).
- A volume V_1 = 10.0 ml of solution (S_1) is titrated, in the presence of an appropriate colored indicator, with a sodium hydroxide solution ($Na^+ + HO^-$) of concentration $C_b = 1.0 \times 10^{-2}$ mol .L^{-1}.

2.1. Choose, from **document-2,** the essential materials needed for the titration of solution (S_1).

- Volumetric pipets: 10 mL and 20 mL.	- Graduated cylinders: 5mL and 10 mL.
- Volumetric flasks: 100mL and 500 mL.	- Erlenmeyer Flask: 100 mL.
- pH- meter.	- 25 mL graduated buret .

Document-2

2.2. Write the equation of the titration reaction.

2.3. Knowing that the volume of the basic solution added to reach equivalence is V_{bE} = 10 mL. Determine the concentration of the solution (S_1). Deduce that of the solution (S).

2.4. By referring to **Document-1,** verify that the solution (S) is convenient for treating hay.

2.5. The pH of the obtained solution at equivalence is pH_E = 8.3

2.5.1. Calculate the ratio $\frac{[A^-]}{[HA]}$ in the solution at equivalence.

2.5.2. Deduce the predominant species of the pair (HA/A^-).

2.5.3. Given the two colored indicators in **document -3**

Colored indicator	**pH change range**	**Color of acidic species**	**Color of basic species**
Phenolphthalein	8.2 – 10	Colorless	Purple
Methyl orange	3.1 – 4.4	red	yellow

Document-3

Choose the appropriate colored indicator to carry out the above titration. Justify.

Exercise 3 (7 points) Carboxylic Acids and their Derivatives

Acyl chlorides, acid anhydrides and esters are derivatives of carboxylic acid. Acyl chlorides and acid anhydrides are more reactive than the corresponding carboxylic acids. Esters have agreable odor.

The aim of this exercise is to identify some organic compounds and to prepare an ester.

1. Identification of Carboxylic Acid (A)

The elemental analysis of a saturated non-cyclic chain monocarboxylic acid (A) gives the following result: the percentage by mass of oxygen: % (O) = 43.24

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

1.1. Show that the molecular formula of carboxylic acid (A) is $C_3H_6O_2$.

1.2. Identify the carboxylic acid (A).

2. Identification of an Alcohol (B)

The mild oxidation of a saturated non- cyclic chain monoalcohol (B) gives a compound (C).
Two tests are carried out to identify (C):

- **First test**: compound (C) gives a yellow-orange precipitate with 2,4-DNPH.
- **Second test**: Fehling solution remains blue when added, while heating, to compound (C).

2.1. Specify the class of alcohol (B).

2.2. Identify the organic compounds (B) and (C), knowing that the molecule of the alcohol (B) possesses three carbon atoms.

2.3. The alcohol (B) undergoes the two chemical reactions represented in **document- 1**.

$$CH_3\text{-}CH=CH_2 + H_2O \xleftarrow{Al_2O_3} (B) \xrightarrow{Cu} (C) + H_2$$

Document-1

Referring to **document-1,** deduce one characteristic of a catalyst.

3. Preparation of an Ester

The yield of the esterification reaction of an equimolar mixture of a carboxylic acid and a primary alcohol is 67% and that for an equimolar mixture of a carboxylic acid and a secondary alcohol is 60%.

M (ester)=116 $g.mol^{-1}$

Document-2

We introduce 0.2 mol of carboxylic acid (A) and 0.2 mol of alcohol (B) into a round bottom flask with few drops of concentrated sulfuric acid solution. The reactional mixture is heated to reflux for a certain time. A chemical equilibrium is reached.

3.1. Write, using condensed structural formulas, the equation of the preparation reaction of the ester. Name the ester formed.

3.2. Determine the mass of the ester formed at equilibrium.

3.3. During a laboratory session, two students carry out the previous experimental procedure without initially adding some drops of concentrated sulfuric acid.
The first student thinks that there will be no effect on the mass of the ester formed at equilibrium, while the other student thinks that the mass of the ester formed at equilibrium will be smaller.
Who of the two students is right? Justify.

3.4. In order to improve the yield of this esterification reaction, a third student suggests replacing carboxylic acid (A) by the appropriate acyl chloride.

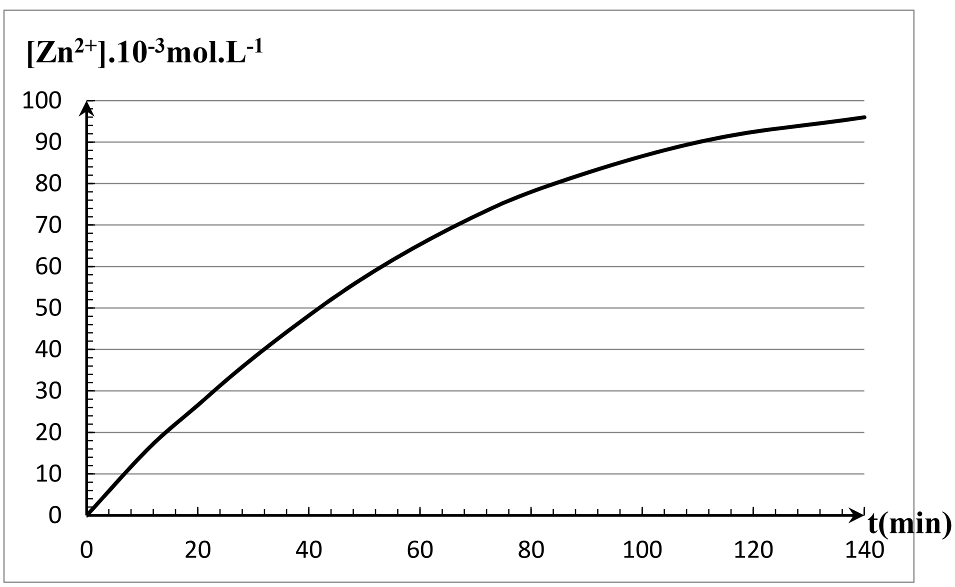
3.4.1. Justify this proposition.

3.4.2. Write, using the condensed structural formulas, the equation of the corresponding reaction.

وزارة التربية والتعليم العالي المديرية العامة للتربية دائرة الامتحانات الرسميّة	امتحانات الشهادة الثانوية العامّة فرع: العلوم العامّة	دورة العام ٢٠١٧ الاستثنائيّة الاثنين في ٧ آب ٢٠١٧

مشروع معيار التصحيح
مادة: الكيمياء

Exercise 1 (6 points) Kinetic study of oxidation of zinc metal

Part of the Q	Expected Answers	Mark
1.1	$n_{(Zn)0} = \frac{m}{M} = \frac{0.5}{65.4} = 0.0076$ mol. $n_{(H3O+)0}$=CaVa=0.4x0.075=0.03mol R(Zn)= $\frac{0.0076}{1}$ < R(H_3O^+) = $\frac{0.03}{2}$ = 0.015 then Zn is the limiting reactant.	0.75
1.2	Acc.to S.R $n(Zn)_0 = n(Zn^{2+})_\infty = 0.0076$mol. $[Zn^{2+}]_\infty = \frac{n_{Zn^{2+}}}{V_S} = \frac{0.0076}{0.075} = 0.1 mol.L^{-1}$	0.5
1.3	At each instant t : $n_{(Zn^{2+})\text{formed at t}} = n_{(H2)\text{formed at t}}$; then $n_{(Zn^{2+})\text{formed at t}} = \frac{V_{H_2}}{V_m}$ Divided by V=75mL then : $[Zn^{2+}]_t = \frac{V_{H_{2(t)}}}{V_m x V_S} = \frac{V_{H_{2(t)}}.10^{-3}}{24 \times 0,075} = 5.55x10^{-4} V_{H_{2(t)}}$	0.75
1.4	$[Zn^{2+}]_{t=190min}$ = $5.55x10^{-4}$ x 160 = 0.089 mol.L^{-1} < $[Zn^{2+}]_\infty$ = 0.1 mol.L^{-1} , Then this instant does not represent the end of the reaction.	0.75
2.1		1
2.2	It is the required time to produce the half of the final concentration of Zn^{2+} ions obtained at the end of the reaction. At $t_{1/2}$:$[Zn^{2+}]_{1/2}$=:$[Zn^{2+}]_{max}$/2 =0.1/2 =50 x10^{-3} mol.L^{-1} that corresponds graphically to $t_{1/2}$ = 43min	0.75
2.3.1	The concentration of reactants is a kinetic factor, when the initial concentration of the reactants increases the initial rate of formation of Zn^{2+} ions will increase. $r_0' > r_0$	0.75

2.3.2	The temperature does not affect the concentration of Zn^{2+} ions at the end of the reaction, because by decreasing the temperature from 25 to 15^0C, the rate of formation of Zn^{2+} ions decreases but the concentration of these ions at t∞ does not change . **b-** $[Zn^{2+}]_{\infty} = [Zn^{2+}]'_{\infty}$.	**0.75**

Exercise 2 (7 points) **Propionic Acid**

Part of the Q	Expected Answers	Mark
1.1	An acid is weak when it has pH > -log C_a with -log C_a = log10^{-2} = 2 pH = 3.45 > 2 then propionic acid is weak acid	**0.5**
1.2	$HA + H_2O \rightleftarrows A^- + H_3O^+$	**0.5**
1.3	$HA + H_2O \rightleftharpoons A^- + H_3O^+$ À t = 0: Ca, excess, -, - À t_{eq}: Ca – x, excess, x, x Ka = $Ka = \frac{[A-].[H_3O^+]}{[HA]} = \frac{[H_3O^+]^2}{Ca-[H_3O^+]} = \frac{[H_3O^+]^2}{Ca-[H_3O^+]} = \frac{(10^{-3,45})^2}{10^{-2}} = 1.26\times10^{-5}$ and pKa = -log Ka = 4.9	**1 .25**
2.1	The necessary materials are: Erlenmeyer flask 100 mL, graduated buret of 25 mL and volumetric pipet 10 mL.	**0.75**
2.2	The titration equation is : $HA + HO^- \rightarrow A^- + H_2O$	**0.5**
2.3	At equivalence : n_0(HA) in 10 mL = n(HO^-)added in V_{bE} $C_1 \times V_a = C_b \times V_b$ $C_1 = C_b \times V_b / V_a = 10^{-2}$ mol.L^{-1} and that for solution (S) : C = 150 x C_1 = 1.5 mol.L^{-1}.	**1**
2.4	The mass concentration of solution (S) is given by C_m = Cx M (HA) C_m = 1.5 x 74 = 111 g.L^{-1} The mass of propionic acid contained in 100L of solution (A) is : m = C_m x V = 111 x 100 = 11100 g = 11.1 kg > 10 Kg The solution (S) is suitable for treating hay.	**1**
2.5.1	The pH of the solution obtained at equivalence is given by the following relation : pH = pKa + log $\frac{[A^-]}{[HA]}$, $\frac{[A^-]}{[HA]} = 10^{pH-pKa} = 10^{8.3-4.9} = 10^{3.4} = 2512$	**0.5**
2.5.2	Since $[A^-]$ = 2512 [HA] ; $[A^-]$ > 10 [HA] so the basic species A^- predominates.	**0.5**
2.5.3	pH_E = 8.3 is included in the pH range of the phenolphthalein [8.2 – 10] so the appropriate indicator to carry out the above titration is phenolphthalein .	**0.5**

Exercise 3 (7 points) **Carboxylic Acids and their Derivatives**

Part of the Q	Expected Answers	Mark
1.1	Let $C_nH_{2n}O_2$ the formula of a saturated non-cyclic monocarboxylic acid, According to the law of definite proportions: $\frac{M(CnH2nO2)}{100} = \frac{2\,M(O)}{\%(O)}$ then M ($C_nH_{2n}O_2$) = $\frac{2 \times 16 \times 100}{43,24}$ = 74 g.mol^{-1}	**0.75**

	So $12n + 2n + 32 = 74$ then $n = 3$. The formula of propanoic acid is $C_3H_6O_2$	
1.2.	Condensed structural formula: $CH_3 – CH_2 – COOH$ Systematic name : propanoic acid	**0.5**
2.1	Since the mild oxidation of alcohol (B) gives a compound (C) which gives yellow orange precipitate with DNPH and negative test with Fehling solution so (C) is a ketone and (B) is a secondary alcohol.	**0.75**
2.2	B: CH_3-CHOH-CH_3 2-propanol C: CH_3-CO-CH_3 propanone	**1**
2.3	Selectivity of a catalyst, since the same reactant gave two different products according to the choice of the catalyst.	**0.5**
3.1	CH_3-CH_2-COOH + CH_3-CHOH-CH_3 $\leftrightarrow$ CH_3-CH_2COOCH$(CH_3)_2$ +H_2O 1-methylethylpropanoate or 2-propyl propanoate.	**1**
3.2	A + B $\rightleftharpoons$ ester + water At t= 0 n_0 0.2 0.2 0 0 At eq 0.2-x 0.2-x x x The mixture is equimolar without excess. $n_{(ester)the} = n_A = 0.2$ mol $n_{(ester)exp}$ = yield x $n_{(ester)the}$ = 0.6 x 0.2 = 0.12mol m = n x M = 0.12 x 116 = 13.92g	**1**
3.3	The addition of few drops of sulfuric acid accelerates the esterification reaction in order to reach the equilibrium shortly without modifying neither the yield nor the quantity of ester formed at equilibrium (play the role of a catalyst). The first student is right.	**0.5**
3.4.1	If he replaces the carboxylic acid (A) by an appropriate acyl chloride the reaction becomes complete and the yield of the esterification increases.	**0.5**
3.4.2	CH_3-CH_2-COCℓ + CH_3-CHOH-CH_3 $\rightarrow$ CH_3-CH_2COOCH$(CH_3)_2$ + HCℓ	**0.5**