مسابقة في مادة الكيمياء المدة: ساعتان	الاسم: 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 Three Following Exercises:

Exercise 1 (6 points) Identification of an organic compound

Available is an organic compound (A) of molecular formula C_4H_8O of a saturated non cyclic carbon chain. The aim of this exercise is to identify compound (A) in order to prepare an ester (E).

1. Identification of The Compound (A)

The compound (A) is subjected to the two tests in document-1.

Chemical Test	Experimental Result
Test 1: (A)+ DNPH	Formation of yellow-orange precipitate
Test 2: (A)+ Fehling reagent	Formation of brick-red precipitate

Document-1

1.1. Interpret the result of each of these two tests.
1.2. Write the possible condensed structural formulas of the compound (A).
1.3. Name compound (A) knowing that the carbon chain is non-branched.

2. Preliminary Study

(B) and (C) are two organic compounds used in preparation of the ester (E).
(B) is obtained by catalytic hydrogenation of a sample of the compound (A).
(C) is obtained by mild oxidation of another sample of the compound (A).

2.1. Write, using condensed structural formulas, the equation of the reaction of formation of product (B). Name it.
2.2. Identify the organic compound (C).

3. Esterification Reaction

An equimolar mixture of the compounds (B) and (C) is heated to reflux in the presence of few drops of concentrated sulfuric acid.

3.1- Indicate the role of sulfuric acid.
3.2- Give the condensed structural formula and the name of the ester (E) obtained during this reaction.

3.3- The carboxylic acid used in the preparation of the ester (E) is replaced by its chlorinated derivative.

3.3.1. Identify the derivative used.

3.3.2. Choose, from the three following propositions, the one that corresponds to the characteristics of the above reaction:

a- complete and athermic b-slow and athermic c- complete and exothermic

3.3.3. Write, using condensed structural formulas of the organic compounds, the equation of the reaction of formation of the ester (E) in this case.

Exercise 2 (7points) Sodium Thiosulfate and Hydrochloric Acid

In acidic medium, thiosulfate ions ($S_2O_3^{2-}$) react slowly and completely with the hydronium ions (H_3O^+), according to the following equation:

$$S_2O_3^{2-}{}_{(aq)} + 2\,H_3O^+{}_{(aq)} \rightarrow S_{(S)} + SO_{2(aq)} + 3H_2O_{(\ell)}$$

In order to study the kinetic of the above reaction, the following experiment is carried out, At the instant t = 0, a volume V_1 = 10.0 ml of a hydrochloric acid solution ($H_3O^+ + C\ell^-$) of concentration C_1 = 5.0 mol.L^{-1} is poured into a beaker containing a volume V_2 = 40.0 ml of a sodium thiosulfate solution ($2Na^+ + S_2O_3^{2-}$) of a concentration C_2 = 0.5 mol.L^{-1}.

By an appropriate method the evolution of this reaction is followed and the concentration of the thiosulfate ions is determined at different instants.

The results are grouped in the table of document-1.

t (s)	15	30	60	90	150	210	300
$[S_2O_3^{2-}]$ mol. L^{-1}	0.32	0.26	0.18	0.12	0.06	0.032	0.012

Document-1

1. Preliminary Study

1.1. Show that the initial concentration of the thiosulfate ions is $[S_2O_3^{2-}]_o$ = 0.40 mol.L^{-1} and that of hydronium ions is $[H_3O^+]_o$ = 1.0 mol.L^{-1} in the reactional mixture.

1.2. Identify the limiting reactant.

2. Kinetic Follow-up

2.1. Plot the curve representing the variation of the concentration of thiosulfate ions as a function of time $[S_2O_3^{2-}]$ = f (t) within the time interval: [0 - 300s]. Take the following scales:

abscissa: 1 cm for 30 s ordinate: 1 cm for 0.04 mol.L^{-1}.

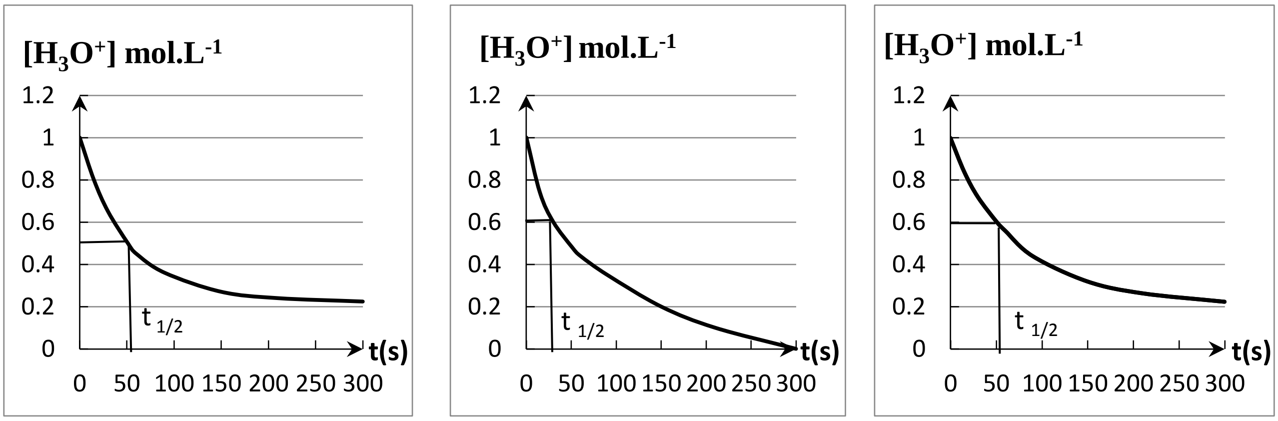
2.2. Determine, graphically, the half-life time $t_{1/2}$.

2.3. Show that at instant t = $t_{1/2}$ the concentration of hydronium ions, $[H_3O^+]_{t_{1/2}}$, is given by the following relation:

$[H_3O^+]_{t_{1/2}} = [H_3O^+]_o - [S_2O_3^{2-}]_o$

2.4. Deduce the value of $[H_3O^+]_{t_{1/2}}$.

2.5. Choose among the three graphs of document-2 the one that corresponds to the shape of the curve that represents the variation of the concentration of H_3O^+ ions as a function of time. Justify.



Graph a Graph b Graph c

Document-2

3. Kinetic Factors

To highlight the effects of the kinetic factors on the duration of this reaction.The three experiments represented in document-3 are carried out, where Δt represents the end time of the reaction in each experiment.

	$[S_2O_3^{2-}]_o$	$[H_3O^+]_o$	Temperature (°C)	Time (t)
Experiment 1	0.4 mol.L^{-1}	1 mol.L^{-1}	40	Δt_1
Experiment 2	0.4 mol.L^{-1}	1 mol.L^{-1}	20	Δt_2
Experiment 3	0.2 mol.L^{-1}	1 mol.L^{-1}	40	Δt_3

Document-3

Compare Δt_2 and Δt_1 as well as Δt_3 and Δt_1 .Justify.

Exercice 3 (7 points) Acid-Base Reactions

The aim of this exercise is to identify aqueous solutions in order to realize a pH-metric study of an acid-base mixture.

Acid/Base pair	H_3O^+ / H_2O	C_6H_5COOH / $C_6H_5COO^-$	NH_4^+ / NH_3
pKa	0	4.2	9.2

- The study is carried out at 25°C.

Document-1

1. Identification of Aqueous Solutions

Available are three beakers numbered 1,2 and 3. Beaker 1 contains a hydrochloric acid solution (H_3O^++ $C\ell^-$). One of the two other beakers contains an aqueous solution of sodium benzoate (Na^+ + $C_6H_5COO^-$) and the other beaker contains an aqueous solution ammonia solution NH_3.

All of the above three solutions have the same molar concentration C.
The pH of each solution is measured. The results are grouped in the table of document-2.

Number of beaker	1	2	3
pH	1.3	11	8.5

Document-2

1.1. Show that the concentration C is equal to 5.0×10^{-2} mol.L^{-1}.

1.2. Identify, by referring to documents (1) and (2), the solution contained in each of the two beakers 2 and 3.

1.3. The ammonia solution of concentration C is prepared from a commercial solution (S_o) of concentration $C_o = 10$ mol.L^{-1}.
Choose, by justifying, from the following two sets a and b of document-3 the appropriate one for the above preparation.

Set a	Set b
- volumetric pipet: 5 mL. -volumetric flask: 500 mL.	- graduated pipet: 5 mL. - volumetric flask: 500 mL.

Document-3

2. pH-metric Follow-up

The hydrochloric acid solution of concentration C is added progressively into a beaker containing a volume $V_b = 20.0$ ml of solution of ammonia of concentration C.

2.1. Write the equation of the reaction that takes place between H_3O^+ ions and NH_3.

2.2. Show that this reaction is complete.

2.3. Determine the volume, V_E, of the acid solution added at equivalence.

2.4. Choose among the three following values:

$$pH_1 = 2 \ ; \quad pH_2 = 7 \ ; \quad pH_3 = 11$$

the one that corresponds to the pH value of the solution obtained after the addition of a volume of the acid equal to 30 mL. Justify without calculation.

2.5. Plot the shape of the curve that represents the variation of pH as a function of the volume of the hydrochloric acid added:

pH = f (V_a), passing through the points of abscissa : $V_a = 0$; $V_a = \frac{V_E}{2}$; $V_a = V_E$ and $V_a = 30$ mL.

Take the following scale: abscissa 1cm for 2 mL and ordinate 1 cm for 1 pH unit.
(Knowing that the pH at equivalence is equal to 5.4)

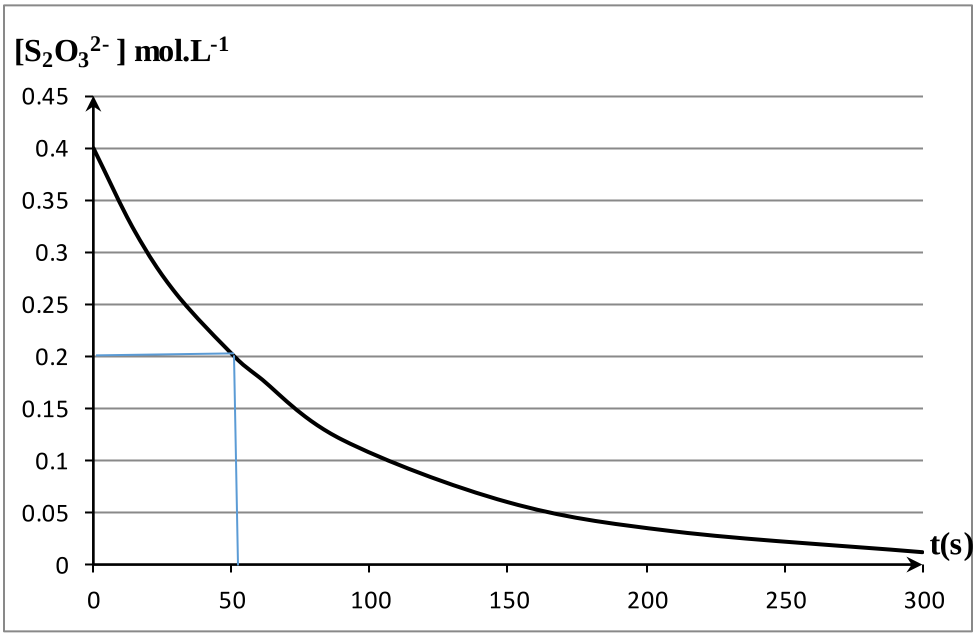
وزارة التربية والتعليم العالي المديرية العامة للتربية دائرة الامتحانات	امتحانات الشهادة الثانوية العامة فرع : علوم عامة	دورة العام 2017 العادية
مشروع معيار التصحيح	مسابقة في مادة الكيمياء المدة : ساعتان	الاسم : الرقم :

Exercise 1 (6 points) Identification of an organic compound

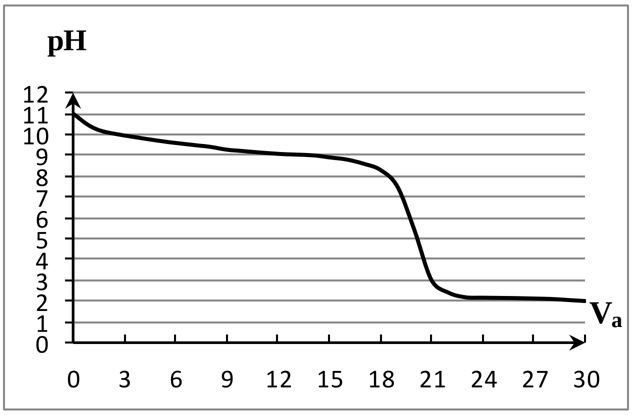
Part of the Q.	Answers	Mark
1.1.	Test 1 : Compound (A) gives with DNPH a yellow orange precipitate ; compound (A) is a carbonyl compound (aldehyde or ketone). Test 2 : Compound (A) gives a red brick precipitate with Fehling reagent ;(A) is an aldehyde.	1
1.2.	The isomers of (A) are: $CH_3 - CH_2 - CH_2 - CHO$ $CH_3 - CH - CHO$ $\quad\quad\;\; |$ $\quad\quad CH_3$	0.5
1.3.	Compound (A) is Butanal.	0.25
2.1.	$CH_3 - CH_2 - CH_2 - CHO + H_2 \rightarrow CH_3 - CH_2 - CH_2 - CH_2OH$ 1-butanol	0.75
2.2.	$CH_3 - CH_2 - CH_2 - COOH$ butanoic acid	0.5
3.1.	The role of sulfuric acid is a catalyst	0.25
3.2.	$CH_3 - CH_2 - CH_2 - COO - CH_2 - CH_2 - CH_2 – CH_3$ Butylbutanoate	0.75
3.3.1.	$CH_3 - CH_2 - CH_2 - COC\ell$ Butanoyl chloride.	0.5
3.3.2.	c- Complete and exothermic.	0.5
3.3.3.	$CH_3 - CH_2 - CH_2 - COC\ell + CH_3 - CH_2 - CH_2 - CH_2OH \rightarrow HC\ell +$ $CH_3 - CH_2 - CH_2 - COO - CH_2 - CH_2 - CH_2 – CH_3$	1

Exercice 2 (7 pts) Sodium Thiosulfate and Hydrochloric acid

Part of the Q.	Answers	Mark
1.1.	$[H_3O^+]_0 = \frac{n_{H_3O^+}}{V_{total}} = \frac{C_1V_1}{V_1+V_2} = \frac{5x10.10^{-3}}{50.10^{-3}} = 1mol.L^{-1}$ $[S_2O_3^{2-}] = \frac{n_{S_2O_3^{2-}}}{V_{total}} = \frac{C_2V_2}{V_1+V_2} = \frac{0,5x40.10^{-3}}{50.10^{-3}} = 0,4mol.L^{-1}$	1
1.2.	$R_{H_3O^+} = \frac{n_{H_3O_0^+}}{2} = \frac{0,05}{2} = 25.10^{-3} > R_{S_2O_3^{2-}} = \frac{n_{S_2O_3^{2-}0}}{1} = 20.10^{-3}$	0.75

	$S_2O_3^{2-}$ is the limiting reactant	
2.1.		**1**
2.2.	Half time :is the time needed for the limiting reactant to lose half of its initial value. $\frac{[S_2O_3^{2-}]_0}{2} = \frac{0,4}{2} = 0,2 mol.L^{-1}$ Graphically $t_{1/2}$ = 52s	**0.75**
2.2.	At each instant of time t : $n_{H_3O^+ remained} = n_{H_3O^+ (o)} - n_{H_3O^+ react}$ $$\frac{n(H_30^+)_{react}}{2} = \frac{n(S_2O_3^{2-})_{react}}{1}$$ $n_{H_3O^+ react} = 2 n_{S_2O_3^{2-} react}$ $n_{H_3O^+ remain} = n_{H_3O^+ o} - 2 n_{S_2O_3^{2-} react}$ At $t_{1/2}$: $n_{H_3O^+_{restant}} = n_{H_3O^+_O} - \frac{2n_{S_2O_3^{2-}{}_O}}{2} = n_{H_3O^+_O} - n_{S_2O_3^{2-}{}_O}$ Divide by the volume of the solution : $[H_3O^+]_{t1/2} = [H_3O^+]_o - [S_2O_3^{2-}]_o$	**0.75**
2.4.	$[H_3O^+]_{t1/2} = [H_3O^+]_o - [S_2O_3^{2-}]_o = 1 – 0.4 = 0.6$ mol.L^{-1}	**0.25**
2.5.	The graph c corresponds to the shape of the curve representing the variation of the concentration of H_3O^+ ions with respect to time , because : At t = 0 we have $[H_3O^+]_o$ = 1mol.L^{-1} At $t_{1/2}$ = 52s we have $[H_3O^+]_{t1/2}$ = 0.6 mol.L^{-1} At t = 300s it does not reach the X- axis ..	**1**
3.	The initial concentration of reactants and the temperature are two kinetic factors . $\Delta t_2 > \Delta t_1$. By comparing the 2 experiments 1 and 2 , we found that the initial concentration of reactants is the same in the 2 experiments but the temperature is higher in experiment 1 than that in experiment 2. The rate of the reaction in experiment 1 is higher than that in experiment 2. $\Delta t_3 > \Delta t_1$. The temperature is the same in the two experiments but the concentration	**1.5**

	of reactant $S_2O_3^{2-}$ is less than that in experiment 3.The rate of the reaction in experiment 1 is higher than that in experiment 3.	

Exercice 3 (7 points) **Acid-Base Reactions**		
Part of the Q.	**Answers**	**Mark**
1.1.	In the beaker 1, hydrochloric acid is a strong acid : pH_1 = - log C ; 1.3 = - log C ; $C = 10^{-1,3} = 5.0.10^{-2}$ $mol.L^{-1}$	**0.5**
1.2.	Ammonia NH_3 and benzoate ion $C_6H_5COO^-$ are two weak bases . Since the two bases have the same concentration C . The base which has the higher pH is the stronger base . Since $pK_a(C_6H_5COOH/C_6H_5COO^-) = 4.2 < pKa(NH_4^+/NH_3) = 9.2$. then NH_3 is a stonger base than $C_6H_5COO^-$. Therefore pH of NH_3 > pH of $C_6H_5COO^-$. Beaker 2 contains solution of NH_3 Beaker 3 contains benzoate ion $C_6H_5COO^-$.	**1**
1.3.	Upon dilution the number of mole of the solute is conserved : $n_o = n$; $C_o \times V_o = C \times V$; $10\ Vo = 5 \times 10^{-2}\ V$; $V = 200\ V_o$; For a volumetric flask of volume V = 500 mL ; Vo = 2,5 mL The appropriate set is b : graduated pipet 5 mL and volumetric flask 500 mL.	**1**
2.1.	$H_3O^+ + NH_3 \rightleftharpoons NH_4^+ + H_2O$	**0.5**
2.2.	$K_R = \frac{[NH_4^+]}{[NH_3][H_3O^+]} = \frac{1}{K_a} = \frac{1}{10^{-pKa}} = \frac{1}{10^{-9,2}} = 10^{9,2} = 1,58.10^9 > 10^4$ Therefore the reaction is complete	**0.75**
2.3.	At equivalence : $n_{H_3O^+ (added)} = n_{NH_3 \text{ present in beaker}}$; $C \times V_E = C \times V_b$; $V_E = V_b = 20$ mL.	**1**
2.4.	V= 30 mL > V_E = 20 mL. The hydrochloric acid becomes in excess in the mixture in the beaker which renders the pH acidic (pH < 7). $pH_1 = 2$.	**0.75**
2.5.	The curve pH = f(V_a) passes through 4 remarkable points initial point: V_a = 0 mL pH = 11 half-equivalence point : $E_{1/2}$: $V_{E1/2}$ = 10 mL pH = pK_a = 9.2 equivalence point E : V_E = 20 mL pH_E = 5.4 Point after equivalence : V = 30 mL pH = 2 	**1.5**