المادة:الكيمياء الشهادة: الثانوية العامة الفرع: علوم الحياة+ العلوم العامة المدّة : ساعتان	الهيئة الأكاديميّة المشتركة قسم : العلوم	المركز التربوي للبحوث والإنماء

نموذج مسابقة(يراعي تعليق الدروس والتوصيف المعدّل للعام الدراسي 2016-2017 وحتى صدور المناهج المطوّرة)

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

Exercise 1 (7 points)

Kinetic study of the decomposition of hydrogen peroxide

Hydrogen peroxide is a strong oxidizing agent used in aqueous solution as as desinfecting agentfor the maintenance of the contact lenses,……………..

Hydrogen peroxide (H_2O_2) decomposes, at ambient temperature T, in a slow and complete reaction according to the following equation:

$$2H_2O_{2(aq)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$$

This decomposition reaction can be accelerated by using a catalyst such a platinum wire, an iron(III) chloride solution(Fe^{3+},$3Cl^-$).

The aim of this exercise is to determine the suitable quantity of an iron (III) chloride for the decomposition of hydrogen peroxide,while still slowtoalmost go to completion in one hour at a constant temperature T.

1. Effect of the quantity of catalyst (Fe^{3+}, $3Cl^-$):

In order to carry out this study, three groups of students: A, B and C are asked to prepare a reaction mixture using the same hydrogen peroxide solution, of concentration $C_0$and the same catalytic solution of iron (III) chloride. Each group is supposed to follow the following procedure:

In a 250mL beaker:

- Pour a volumeV_0=10mL from the commercial solution of H_2O_2.
- Add a volume V_1 of distilled water.
- Add a volume V_2 of (Fe^{3+}+ $3Cl^-$) solution and start the chronometer at this instant.
- The volumes V_1 and V_2 taken by each group are recorded in the following table (Document 1).

	Group A	Group B	Group C
V_1 (in mL)	89	88	85
V_2 (in mL)	1	2	5

Document -1

From the beginning, students found that the release of gas is more abundant in the beaker of group C than in that of group A.

1.1 Specify the effect of the quantity of catalyst on the progress of the reaction.

1.2 The initial concentration of H_2O_2 in the reaction mixture of group A is 0.09mol.L^{-1}. Justify that this concentration is the same as that for reaction mixtures of groups B and C.

1.3 Deduce the concentration (C_0) of the hydrogen peroxide solution.

2. Titration of the prepared hydrogen peroxide solution:

At different times (t), each group takes V=10 ml of the reaction mixture and places it in an Erlenmeyer flask containing ice-cold distilled water. The concentration of the remaining hydrogen peroxide at each instant (t) is titrated by an acidified potassium permanganate solution (K^+, MnO_4^-) of concentration C'=2.10^{-2} mol.L^{-1}.

The net ionic equation of the titration reaction is:

$$2MnO_4^- + 5H_2O_2 + 6H_3O^+ \rightarrow 2Mn^{2+} + 5O_2 + 14H_2O$$

2.1-"If the titration was carried out without adding ice water, the result is not accepted". Justify this statement by indicating the kinetic factors involved after adding ice water.

2.2-Show that, at each time t, the following relation: $[H_2O_2]_t = 5V_3$.

Where $[H_2O_2]_t$ is the concentration of the remaining H_2O_2 (in $mol.L^{-1}$) at time t and V_3 is the volume (in L) of acidified potassium permanganate solution added from buret at equivalence point.

3- Kinetic study of the decomposition of H_2O_2 for group A:

The results of titration for group A are given in the following table (document-2):

t(min)	0	10	20	30	45	60
$[H_2O_2]$in $mol.L^{-1}$	0.09	0.06	0.047	0.039	a	0.025
V_3 in mL	b	12.1	9.4	7.8	5.9	5

Document 2

3.1 Calculate the values of a and b.

3.2 Plot, on a graph paper, the kinetic curve (curve 1): $[H_2O_2] = f(t)$.

Take the following scale:1cm for 10min in abscissa and 1cm for 0.01 $mol.L^{-1}$ in ordinate.

3.3 Determine, from the graph, the reaction half- life $t_{1/2}$.

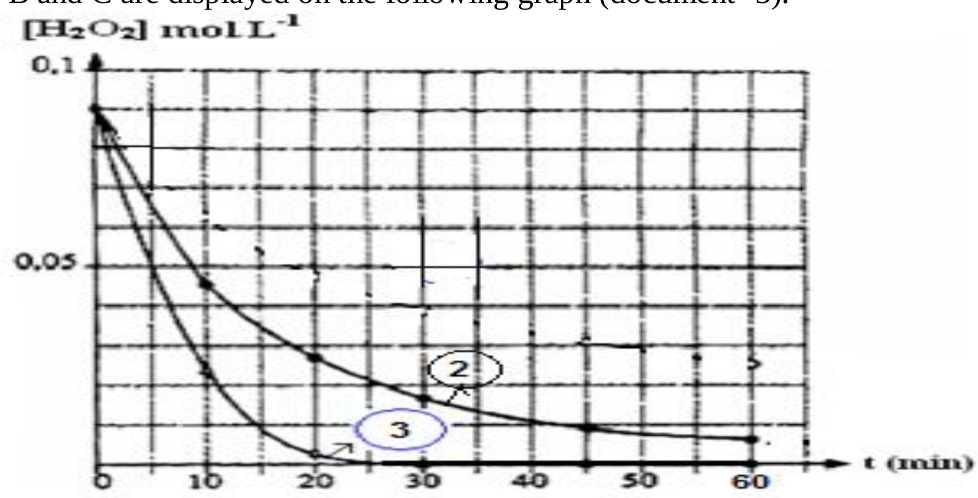
3.4 Show, based on the graph, the variation of the rate of disappearance of H_2O_2 with time.

4- Choosing the suitable amount of catalyst:

The results of titration for groups B and C are displayed on the following graph (document -3).

4.1 Verify that the curves (2) and (3) correspond to the kinetic study for groups B and C respectively.

4.2 Referring to the three curves (1, 2 and 3), deduce the appropriate volume of the catalytic solution to be used to satisfy the required experimental conditions .



Document-3

Exercise 2 (6 ½ points)

Verification the acid degree of Vinegar

Vinegar, used in our meals, is an aqueous solution of ethanoic acid. Document-1 shows the label of a commercial bottle of vinegar solution (S_0).

- Ethanoic acid
- Acidity degreeof vinegar is : 7^0
- Density of vinegar is ρ= 1.02 $Kg.L^{-1}$
- $M(CH_3COOH)$=60$g.mol^{-1}$

Document-1

The degree of acidity of Vinegar is the percentage by mass of ethanoic acid in the vinegar solution.

This exercise aims to verify the label on the bottle "Vinegar 7^0".

Given:

Acid /Base couple	H_3O^+/H_2O	CH_3COOH / CH_3COO^-	H_2O / HO^-
pKa	0	4.8	14

Document -2

1- Reaction between ethanoic Acid and sodium hydroxide solution:

1.1 Write the net ionic equation of the reaction between ethanoic acid solution (CH_3COOH) and sodium hydroxide solution (Na^+, HO^-).

1.2 Calculate the constant K_R of this reaction.

2- Preparation of solution (S) ofethanoic acid:

100mL solution (S) of concentration C is prepared by diluting 10 times the commercial vinegar solution (S_0).

2.1 Determine V_0, the volume to be taken from commercial solution of vinegar to prepare solution (S).

2.2 Choose, from the document-3 given below, the most precise set needed to this preparation. Justify your answer.

Set 1	**Set 2**	**Set 3**
- Beaker (100mL) - Volumetric flask (100mL) - Volumetric pipet (20mL)	- Beaker (100mL) - Volumetric flask (100mL) - Graduated pipet (20mL)	- Beaker (100mL) -Volumetric flask (250mL) - Volumetric pipet (10mL)

Document-3

3- Titration of ethanoic acid solution (S):

A volume V = 20mL of solution (S) is titrated with sodium hydroxide solution ($Na^+_{(aq)}$, $HO^-_{(aq)}$) of concentration C_b= 0.1mol.$L^{-1}$by using a pH meter.

Equivalence point is reached when a volume V_{bE}= 23.4mL of the basic solution is added and pH_E becomes 8.4.

3.1 Justify, by referring to chemical species found in the beaker, the value of the pH at equivalence point.

3.2 Choose the correct answer. Justify.

3.2.1- Solution(S) can be titrated with sodium hydroxide solution since there action between ethanoic acid and the hydroxide ions is:

i- Only complete ii- Complete and slow iii- Complete and fast

3.2.2-After adding 11.7mL of (Na^+; HO^-) solution, the ratio $\frac{[CH3COO-]}{[CH3COOH]}$ becomes:

i- 1 ii- 0.5 iii- 2

3.3 Determine the concentration C of solution (S).

3.4 Show that the value of the concentration C_0 of the commercial solution of vinegar is 1.17 mol.L^{-1}.

3.5 Calculate the acid degree of commercial vinegar solution and verify the amount stated on the label.

Exercise 3 (6 ½ points)

Synthesis of methyl benzoate

Methyl benzoate, a fragrant liquid, is an organic compound used as reagent in perfume.
This compound is an ester obtained by a slow and athermic reaction between benzoic acid and methanol according to the following equation:

Benzoic acid + Methanol $\rightleftarrows$ Methyl benzoate + Water (Reaction 1)

This exercise aims to determine the yield of this esterification reaction.

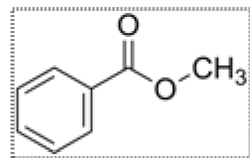
Given:

Density of Methanol = 800 $g.L^{-1}$
M (Benzoic acid) =122 $g.mol^{-1}$; M (Methanol) =32 $g.mol^{-1}$; M (Methyl benzoate)= 136 $g.mol^{-1}$

Document-1

1- <u>Study of the organic compounds of the reaction.</u>

Document-2 shows the condensed structural formula of methyl benzoate.



Document 2

1.1 Write the condensed structural formula of benzoic acid.

1.2 Benzoic acid is prepared by a mild oxidation of compound (A) with acidified potassium permanganate solution. When a sample of compound (A) is heated with a Fehling's solution in basic medium, a red brick precipitate is formed.
Identify the compound (A).

2- <u>Preparation and separation of methyl benzoate:</u>

In order to synthesize methyl benzoate in the laboratory, a mass m=12.2g of benzoic acid and a volume V=4mL of methanol are mixed in a round bottom flask, with few mL of concentrated sulfuric acid. This mixture is heated by reflux at temperature T to reach the equilibrium state.
After cooling, the content of the flask are separate using an appropriate method.

2.1 Indicate the role of reflux heat.
2.2 Specify the effect of using a small amount of concentrated sulfuric acid on the yield of the reaction.
2.3 Sulfuric acid acts as a dehydrating agent when used in large amounts. Justify the effect of using a large amount of concentrated sulfuric acid on the yield of the esterification reaction.

3- <u>The yield of Esterification reaction:</u>

After subsequent treatment of the phase containing the ester, a mass m_E = 8.1 g of methyl benzoate is obtained.
3.1 Verify that the initial reactants are in equimolar mixture.
3.2 Show that the % yield of this reaction is 60%.
3.3 The theoretical percent yield of an equimolar mixture of carboxylic acid and primary alcohol is 67%.

Explain the difference between the theoretical value and the experimental value of percent yield, two suggestions are given:
- Part of the ester is lost during the separation process.
- The temperature of the reaction system should be greater than T.

For each suggestion, specify whether it can explain this discrepancy.

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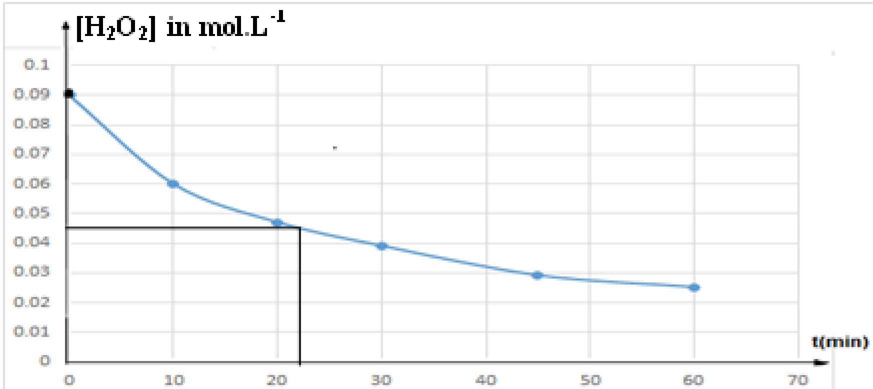
أسس التصحيح (تراعي تعليق الدروس والتوصيف المعدّل للعام الدراسي 2016-2017 وحتى صدور المناهج المطوّرة)

Mark Scheme
Exercise 1 (7 points)

Kinetic study of the decomposition of hydrogen peroxide

Part of question	Suggested Answers	Mark 7
1.1	The reaction mixture for the three groups have: - The same initial quantity of hydrogen peroxide. - The same temperature T. - The same total volume of mixture (100mL) But the quantity of catalyst used in group C is more than the other groups . the release of gas in this group is more abundant than that for the other groups; this means that H_2O_2 decomposes faster. Hence as the amount of catalyst increases, the reaction of decomposition of hydrogen peroxide proceeds faster.	¾
1.2	For the three mixtures prepared: - Same number of moles of hydrogen peroxide $n(H_2O_2)_0=C_0\ xV_0$ - Same volume of the mixture 100mL [10mL+90mL (V_1+V_2)]. Therefore same initial concentration which is $0.09mol.L^{-1}$.	2(¼)
1.3	At t=0, $n(H_2O_2)_0 = CxV_{Mixture} = C_0xV_0$ therefore $C_0 = \frac{0.09x100}{10} = 0.9mol.L^{-1}$.	¼
2.1	If the above titration takes place without adding ice water, two simultaneous chemical reactions take place: first the decomposition of H_2O_2 and second the titration with acidified potassium permanganate solution. Therefore the titration reaction will not be unique. Cold water will block the decomposition reaction; this allows titrating the hydrogen peroxide remaining . The kinetic factors involved in this decomposition are the concentration of reactants and the temperature.	½ ¼ ¼
2.2	At equivalence: $\frac{n(MnO4-)\text{Added from buret at equivalence point}}{2} = \frac{n(H2O2)\text{inthe beaker}}{5}$: $[MnO_4^-]xV_3/2=[H_2O_2]xV_0/5$ $[H_2O_2]_t=2.10^{-2}xV_3x5/10x10^{-3}=5V_3$	¾
3.1	$a = 5x5.9x10^{-3} = 0.0295mol.L^{-1}$. b= 0.09/5 =0.018L =18mL	¼ ¼

<table>
<tr><td>3.2</td><td>Curve (1)

</td><td>1</td></tr>
<tr><td>3.3</td><td>The half life is the time required for the concentration of the reactant to decrease to half of its initial value. From the graph,
At $t_{1/2}$: $[H_2O_2]_{1/2}=[H_2O_2]_0/2=0.045 mol.L^{-1}$ that corresponds graphically to $t_{1/2}$ = 21 min</td><td>¼
¼</td></tr>
<tr><td>3.4</td><td>The instantaneous rate of disappearance of H_2O_2 is the negative slope of the tangent at time t. From the Graph, the slope of the tangent decreases with time, therefore the rate of reaction decreases.</td><td>¼
¼</td></tr>
<tr><td>4.1</td><td>At each time t, the rate of decomposition of H_2O_2 in group C is greater than that in B.
Referring to document 3, the curve 3 is below curve 2; that is at same time t, the rate of disappearance of H_2O_2 in curve 3 is greater than that in curve 2, therefore curve 2 corresponds to group B and curve 3 corresponds to group C.</td><td>¼
¼
¼</td></tr>
<tr><td>4.2</td><td>Among the curves (1, 2 and 3) only curve 2 obtained with group B corresponds to the required experimental conditions. The appropriate volume of catalyst is 2mL (group B), since after one hour, the decomposition of H_2O_2 is almost complete in curve (2).</td><td>½</td></tr>
</table>

Exercise 2 (6.5 points)

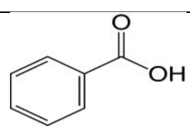
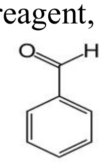
Verification the acid degree of Vinegar

Part of question	Suggested Answers	Mark 6 ½
1.1	The net ionic equation is : $CH_3COOH_{(aq)} + OH^-_{(aq)} \rightarrow CH_3COO^-_{(aq)} + H_2O_{(l)}$	½
1.2	$K_R = K_a/K_e = 10^{-4,8}/10^{-14} = 10^{9,2} = 1.58 x 10^9$	½
2.1	Upon dilution, the number of mole of solute is conserved: The number of folds $f = C_0/C = V/V_0$ therefore $V_0 = V_S/f = 100/10 = 10 mL$. The volume withdrawn is 10 mL.	¼ ¼
2.2	Set 2 is the most convenient: To carry out the most precise preparation, a graduated pipet of 20 mL and a volumetric flask of 100 mL constitute the most convenient glassware because	¼ ½

	with this pipet we can withdraw a volume V_0 = 10mL and dilute this volume in 100 mL volumetric flask.	
3.1	The chemical species found in the solution other than water (neutral), Na^+(spectator ion), and CH_3COO^- (weak base) that reacts with water to produce HO^- as the following limited equation $CH_3COO^- + H_2O \rightleftarrows CH_3COOH + HO^-$ therefore $[HO^-] > [H_3O^+]$ and the medium becomes basic pH_E=8.4 more than 7.	¾
3.2.1	iii- is correct Titration reaction is characterized by complete and fast reaction.	¼ ¼
3.2.2	(i) is correct: The volume V=11.7 mL represents the volume of strong base added at half equivalence point (11.7 = V_{Be} /2) thenpH =pKa and according to Handerson Hasselbalch pH =pKa + log$\frac{[CH3COO-]}{[CH3COOH]}$ then log$\frac{[CH3COO-]}{[CH3COOH]}$=0 therefore$\frac{[CH3COO-]}{[CH3COOH]}$=1.	¼ ½
3.3	At equivalence point, the reactants react in stoichiometric proportion : $n(OH^-)_{\text{added at equivalence point}} = n(CH_3COOH)_{\text{presented in the beaker}}$. $C_bV_{bE}=C_1V_1$, $C_1=\frac{0,10x23.4}{20}$=0,117 mol.L^{-1}.	¼ ½
3.4	The vinegar is diluted 10 times to prepare solution (S) : $C_0=10xC_1$=1,17 mol.L^{-1}	¼
3.5	- In one liter of vinegar, the number of moles of ethanoic acid is 1.2x1=1.2mol that corresponds to $m_{(\text{ethanoic acid})}$=nxM = 1.17x60 =70.2g - The mass of 1 L of vinegar is $m_{(\text{Vinegar})}$ = ρx1 = 1x1020 g/L=1020 g. therefore 1020 g of vinegar contains 72 g of ethanoic acid - %by mass of ethanoic acid in vinegar= $\frac{100x70.02}{1020}$= 6.88% = 6.88^0. The acidity degree $6.88^0$is very close to the labeled value.	5x(¼)

Exercise 3 (6.5 points)

Synthesis of methyl benzoate

Part of question	Suggested Answers	Mark 6 ½
1.1	 The condensed structural formula	½
1.2	The compound A is oxidized with Fehling's reagent, then A is an aldehyde.  The condensed structural formula of A is:	¼ ¼
2.1	- Reflux heating increases the temperature thus increases the rate of the	½

	esterification reaction (T is a kinetic factor). - The condenser condenses the vapors thus prevents the loss of the components by condensing their vapors hence minimizing losses upon heating.	½
2.2	Concentrated sulfuric acid, when used in small amounts, actsas a catalyst that increases the reaction rate without changing the yield.	¼ ¼
2.3	Concentrated sulfuric acid, when used in large amounts, acts as a dehydrating agent that eliminates water from the reaction medium and thus displaces the equilibrium in the forward direction (according to Le Chatelier) ; this increases the yield of the esterification reaction.	1
3.1	The initial number of moles of each reactant: $n_{(Benzoic\ acid)}$ = m/M = 12,2/122 =0,1 mol $n_{(Methanol)}$ = m/M = ρ xV/M=800x4x10^{-3}/32= 0.1mol. then they are in equimolar mixture since $n_{(Benzoic\ acid)} = n_{(Methanol)}$.	¼ ¼ ¼
3.2	If the reaction is complete, according to stoichiometric ratio: n(Ester)$_{theoretical\ obtained\ at\ final\ time}$= 0,1 mol since the mixture is stoichiometric (R acid = R methanol= 0.1) Then m (Ester)$_{theoretical\ obtained\ at\ final\ time}$ = 0,1 x136=13.6g The yield is y = $\frac{m(ester)\exp erimental}{m(ester)theoretical} x100 = \frac{8.1}{13.6} x100 = = \mathbf{60\%}$	¼ ½
3.3	- <u>Suggestion 1</u> :True The yield of reaction is proportional to the experimental mass of Ester. When part of experimental mass of ester is lost, the percent yield decreases. - <u>Suggestion 2 :</u> False The temperature is a kinetic factor but does not shift equilibrium since it's an athermic reaction. Therefore it increases only the rate of reaction of both directions and does not change the yield.	¼ ½ ¼ ½