المركز التربوي للبحوث والإنماء	الهيئة الأكاديميّة المشتركة قسم : العلوم	المادة: الكيمياء الشهادة: الثانوية العامة فرعا: علوم الحياة / العلوم العامة نموذج رقم -٢- المدّة : ساعتان

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 agent for 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 slow, to be almost **completed in one hour** at a constant temperature T.

1. Effect of the quantity of catalyst:

In order to carry out this study, three groups of students: A, B and C are asked to prepare a reactional mixture using the commercial hydrogen peroxide solution (S_0), of concentration C_0 and the same solution of iron (III) chloride (catalyst). Each group is supposed to perform the following procedure:

Into a 100 mL volumetric flask:

- Pour a volume V_0 = 10mL from the commercial solution of H_2O_2.
- Add a volume V_1 of ($Fe^{3+} + 3 Cl^-$) solution and start the chronometer at this instant.
- Distilled water is then quickly added to the line mark.
- The volumes measured by each group are recorded in the following table (Document-1).

	Group A	Group B	Group C
V_o (in mL)	10	10	10
V_1 (in mL)	1	2	5
V_{total} (mL) of the mixture after adding distilled water	**100**	**100**	**100**

Document -1

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

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 reactional mixture of group A is C'_0=0.09 mol.L^{-1}. Justify that the reactional mixtures of groups B and C have the same initial concentration C'_0 of H_2O_2.

1.3 Deduce the concentration (C_0) of the commercial hydrogen peroxide solution (S_0).

2. Titration of the prepared hydrogen peroxide solution:

At different time (t), each group withdraws a volume V=10 ml from the reactional mixture and places it in an erlenmeyer flask containing ice-cold distilled water. The concentration of remaining hydrogen peroxide at each time (t) is determined by titration with 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 concentration of hydrogen peroxide solution can be expressed by the following relation: $[H_2O_2]_t = 5V_2$.

Where $[H_2O_2]_t$ is the concentration of the remaining H_2O_2 (in mol.L^{-1}) at time t and V_2 is the volume (in L) of acidified potassium permanganate solution added from the buret at the 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_2 in (L) x 10^{-3}	b	12.1	9.4	7.8	5.9	5

Document- 2

3.1 Calculate the values of '**a**' and '**b**' missing in the above table (document-2).

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

Take the following scale: 1cm for 5 min in abscissa and 1cm for 0.01 mol.L^{-1} in ordinate.

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

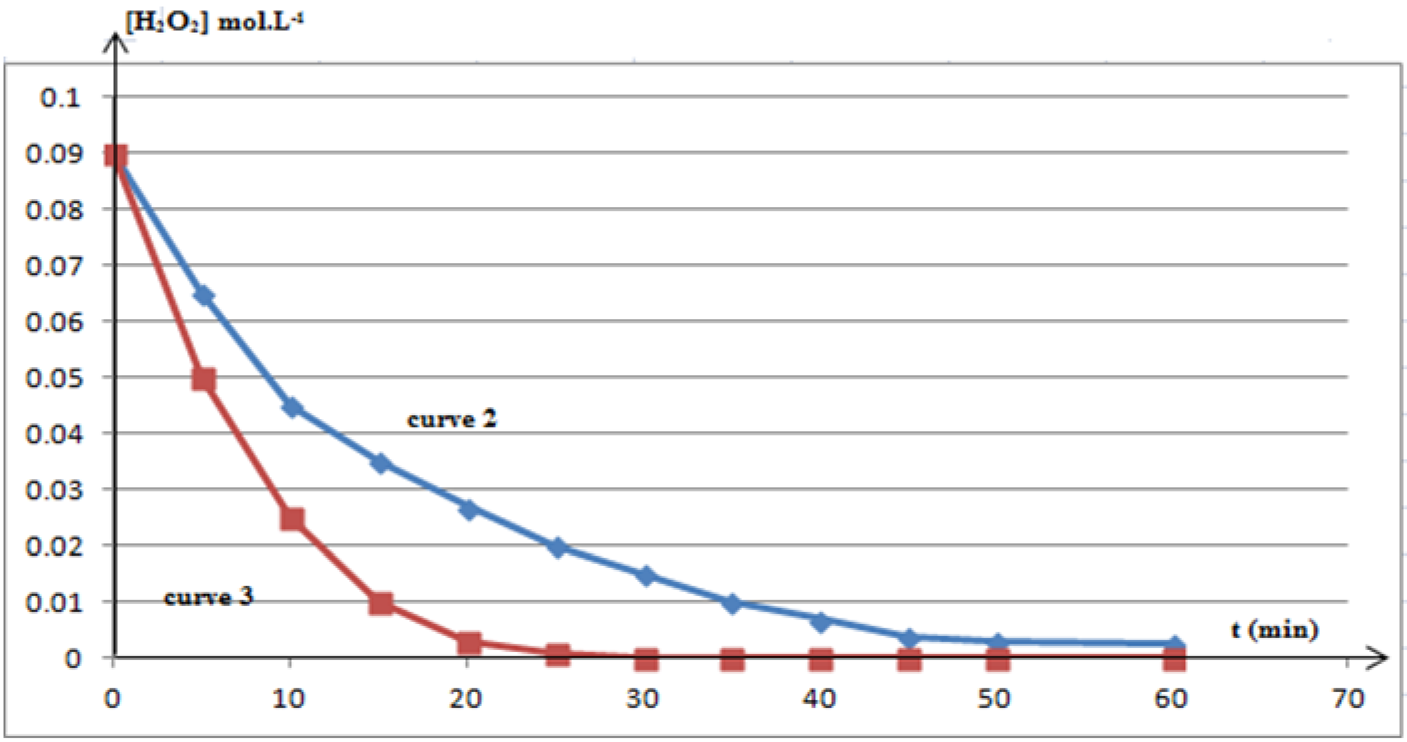
3.4 Show, based on the graph, the variation of the rate of disappearance of H_2O_2 with time.

4-Choice of 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 kinetics study for groups B and C respectively.

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



Document-3

Exercise 2 (6 ½ points)

Verification of 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	-Acid degree of vinegar is : 7^0
- Density of vinegar is ρ = 1.02 Kg.L^{-1}	-M(CH_3COOH)= 60g.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.

1.3 Deduce that this unique and fast reaction can be used for titration.

2- **Preparation of solution (S) of ethanoic acid:**

100 mL of ethanoic acid 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 withdraw from commercial solution of vinegar to prepare solution (S).

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

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

The equivalence point is reached when a volume V_{bE} = 23.4mL of the basic solution is added and the pH at this point (pH_E) becomes 8.4.

3.1 Justify, by referring to the chemical species found in the reaction mixture, the value of the pH_E at the equivalence point.

3.2 For each of the following, choose the correct answer. Justify.

3.2.1- The suitable acid-base indicator for this titration is:

i- Methyl orange (3.2- 4.4) ii- Bromothymol Blue BTB (6-7.6) iii- Phenolphtalein (8.2-10)

3.2.2- After adding 11.7 mL 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 if it matches the indication 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 reaction (1):

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

Concentrated sulfuric acid acts as a dehydrating agent when used in large amounts.

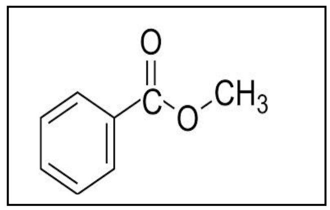
Document-2

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

Document-3 shows the condensed structural formula of methyl benzoate.

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 compound (A)



Document- 3

<u>2 Preparation and separation of the ester:</u>

In order to synthesize methyl benzoate in the laboratory, a mass m=12.2 g of benzoic acid and a volume V= 4 mL of methanol are mixed in a round bottom flask, with few drops 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 is separated using an appropriate method.

2.1 Indicate the role of reflux heat.

2.2. For each of the following statements, choose the correct answer. Justify.

2.2.1 Using a small amount of concentrated sulfuric acid:

i- Increases the rate and the yield of the reaction as well.

ii- Increases the rate without changing the yield of the reaction.

iii-Increases the yield without changing the rate of the reaction.

2.2.2 Using a large amount of concentrated sulfuric acid.

i- decreases the yield of the reaction ii- does not affect the yield iii- increases the yield.

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

The mass of methyl benzoate obtained experimentally is m_E = 8.1 g.

3.1 Verify that the initial mixture of reactants is equimolar.

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%. To explain the difference between the theoretical value and the experimental value of percent yield, two suggestions are given:

Suggestion (1): Part of the ester is lost during the separation process.

Suggestion (2) The temperature of the reaction system should be greater than T.

For each suggestion, Specify whether it can explain this discrepancy or not.

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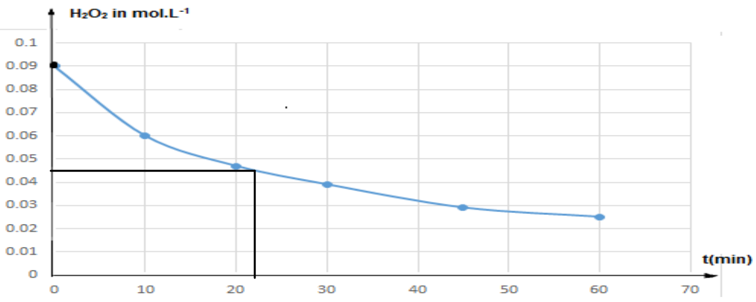
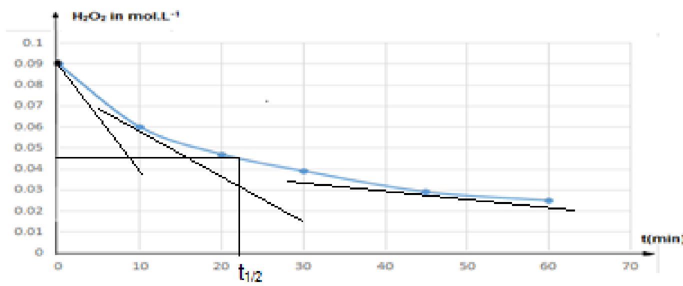
أسس التصحيح (تراعي تعليق الدروس والتوصيف المعدّل للعام الدراسي 2016-2017 وحتى صدور المناهج المطوّرة)

	Exercise 1 (7 points) **Kinetic study of the decomposition of hydrogen peroxide**	
Part of question	**Expected Answers**	**Mark**
1.1	The reaction mixtures for the three groups A, B and C have: - The same initial quantity of hydrogen peroxide. - The same temperature T. - The same total volume of mixture (100mL) - The only difference is the amount of the catalyst used for each group. 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, we have: - The same number of moles of hydrogen peroxide $n(H_2O_2)_0=C_0\ xV_0$ - The same volume of the mixture 100mL. Therefore, for the three groups, the solution has the same initial concentration which is $0.09 mol.L^{-1}$ for the 3.	2(¼)
1.3	At t=0, $n(H_2O_2)_0 = CxV_{Mixture} = C_0xV_0$ therefore $C_0= \frac{0.09x100}{10} = 0.9\ mol.L^{-1}$.	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 reaction. Therefore the titration could not be conducted since one of characteristic of titration reaction is to be unique. Cold water will block the decomposition reaction; this allows only the titration of the remaining hydrogen peroxide to take place. The kinetic factors involved in this decomposition are the concentration of reactants and the temperature.	½ ¼ ¼
2.2	At equivalence: $\frac{n(MnO4-)\text{ added from buret}}{2}=\frac{n(H2O2)\text{found in the beaker}}{5}$: $[MnO_4^-]xV_2/2 = [H_2O_2]xV_0/5$ $[H_2O_2]_t = 5xV_2/2\ x\ 2.10^{-2}/10x10^{-3} = 5V_2$	¾
3.1	In table: $a = 5x5.9x10^{-3} =0.0295\ mol.L^{-1}$. 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 limiting reactant to be 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 negative 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, 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 curves (1, 2 and 3) only curve (2) obtained by group B corresponds to the required experimental conditions, since in one hour, the decomposition of H_2O_2 is almost complete in curve (2). The appropriate volume of catalyst is 2mL (group B).</td><td>½</td></tr>
</table>

	Exercise 2 (6 ½ points) **Verification the acid degree of Vinegar**	
Part of question	**Expected Answers**	**Mark**
1.1	The net ionic equation is : $CH_3COOH_{(aq)} + OH^-_{(aq)} \rightarrow CH_3COO^-_{(aq)} + H_2O_{(l)}$	½
1.2	$K_R = K_a/K_e = 10^{-4,8}/10^{-14} = 10^{9,2} = 1.58x10^9$	½
1.3	Other than unique and fast, this reaction is complete since its constant is greater than 10^4. So, this reaction could be used for titration.	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 $V_0 = V_S/f = 100/10 = 10mL$. The volume withdrawn from S_0 is 10 mL.	¼ ¼

2.2	Set 2 is the most convenient: To carry out the most precise preparation, a volumetric pipet of 10 mL and a volumetric flask of 100 mL constitute the most convenient glassware because with this pipet we can withdraw a volume V_0 = 10mL, then dilute this volume in 100 mL volumetric flask.	¼ ¼ ¼
3.1	At equivalence, the pH_E = 8.4 >7. The chemical species found in the solution other than water (neutral), are: Na^+(spectator ion), and CH_3COO^- (weak base) that reacts with water to produce HO^- as the following equation: $CH_3COO^- + H_2O \rightleftarrows CH_3COOH + HO^-$ therefore the medium becomes basic.	¼ ½
3.2.1	(iii)- is the correct answer. The pH_E must be included in the pH range of the indicator. Since 8.2 < 8.4 < 10, therefore phenolphthalein is the convenient indicator	¼ ¼
3.2.2	(i) is the correct answer. The volume V=11.7 mL represents the volume of strong base added at half equivalence point ($11.7=V_{bE}/2$); therefore $[CH_3COOH]_{remaining} = [CH_3COO^-]_{formed} = [CH_3COOH]_{initial}/2$ (in the same total volume), so $\frac{[CH3COO-]}{[CH3COOH]}$ =1.	¼ ½
3.3	At equivalence point, the reactants react completely in stoichiometric proportions : $n(OH^-)_{\text{added at equivalence point}} = n(CH_3COOH)_{\text{present in the beaker}}$. $C_bV_{bE} = C_1V_1$, $C_1 = \frac{0,10x23.4}{20}$=0.117 mol.$L^{-1}$.	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 1.17x1=1.17mol that corresponds to $m_{(ethanoic\ acid)}$=nxM = 1.17x60 =70.2g - The mass of 1 L of vinegar is: $m_{(Vinegar)}$ = ρx1 = 1x1020 g/L=1020 g. therefore 1020 g of vinegar contains 70.2 g of ethanoic acid - % by mass of ethanoic acid in vinegar = $\frac{100x70.2}{1020}$ = 6.88% = 6.88^0. -The acidity degree $6.88^0$is very close to the value on the label.	4x(¼)

	Exercise 3 (6 ½.points) **Synthesis of methyl benzoate**	
Part of question	**Expected Answers**	**Mark**
1.1	The condensed structural formula of benzoic acid is : $C_6H_5 – COOH$	½
1.2	The compound A is an aldehyde because it undergoes a mild oxidation with Fehling's reagent. The condensed structural formula of A is: $C_6H_5– CHO$ Its name is benzaldehyde.	¼ ¼ ¼
2.1	-Reflux heating increases the temperature thus increases the rate of the 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.	¼ ¼
2.2.1	The correct answer is (ii) Concentrated sulfuric acid, when used in small amounts, acts as a catalyst that increases the reaction rate without changing the yield.	¼ ½

2.2.2	The correct answer is (iii) 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 (Le Chatelier); this increases the yield of the esterification reaction.	¼ ½
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. so the mixture is equimolar since $n_{(Benzoic\ acid)}$ = $n_{(Methanol)}$=0.1 mol	1
3.2	Suppose that the reaction is complete, the mixture of reactants is stoechiometric (R_{acid} = $R_{methanol}$= 0.1), n(Ester)$_{theoretical}$ = 0,1 mol Then m (Ester)$_{theoretical}$ = 0,1 x136=13.6g The percent yield is y = $\frac{m(ester)\,experimental}{m(ester)\,theoretical} x100 = \frac{8.1}{13.6} x100 = = \mathbf{60\%}$ **(N.B: the yield can also be determined using the number of moles).**	¼ ½
3.3	- <u>Suggestion 1</u> :True The yield of reaction is proportional to the experimental mass of ester. When part of the experimental mass of the 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 is an athermic reaction. Therefore it increases only the rate of reaction of both directions and does not change the yield.	¼ ½ ¼ ½