


المادة: الكيمياء الشهادة: الثانوية العامة الفرع: علوم الحياة نموذج رقم -3- المدة: ساعتان	الهيئة الأكاديمية المشتركة قسم : العلوم	 المركز العلمي للبحوث والأبحاث
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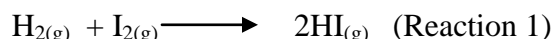
نموذج مسابقة (يراعي تعليق الدروس والتوصيف المعدل للعام الدراسي 2016-2017 حتى صدور المناهج المطورة)

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)

#### Kinetics study of the synthesis of hydrogen iodide (HI)

It is required to carry out a kinetic study of the synthesis of hydrogen iodide HI. The equation of the slow reaction, assumed to be complete, is:



For this purpose, eight round bottom flasks (1L each) are placed at a constant temperature of 350°C; each contains 0.5 mmol of iodine gas and 5 mmol of hydrogen gas.

At time (t), one of the round bottom flasks is cooled suddenly and the remaining iodine is dissolved, using an appropriate method, so as to obtain 200 mL solution. By adding few drops of starch, the solution turns blue. The solution is then titrated with an aqueous sodium thiosulfate solution ( $2\text{Na}^+_{(aq)} + \text{S}_2\text{O}_3^{2-}_{(aq)}$ ) having a concentration of  $5 \times 10^{-2} \text{ mol L}^{-1}$ . The volume of sodium thiosulfate solution added to reach the equivalence point is denoted by V. The same procedure is repeated at different time (t) for the contents of the other flasks.

The following table (document -1) shows the results of the different titrations carried out:

Round bottom flask	A	B	C	D	E	F	G	H
Time t (in min)	50	100	150	200	250	300	350	400
V(in mL)	16.6	13.6	11.4	9.0	7.4	5.6	4.0	3.0
n(HI) in mmol	0.17	0.32	0.43	0.55	0.63	0.72	0.80	

Document-1

#### 1. Preliminary Study:

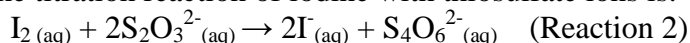
1.1. Determine the number of moles of HI formed at the end of the reaction (1).

1.2. Justify the importance of each of the following steps performed before the titration:

- The sudden cooling of the round bottom flask.
- The addition of starch to the iodine solution.

#### 2. Kinetic study of the synthesis of hydrogen iodide

The net ionic equation of the titration reaction of iodine with thiosulfate ions is:



2.1. Show that, at each time (t), the number of moles of HI formed is related to the volume V of thiosulfate solution, poured at time (t) and expressed in mL, by the following relation:

$$n(\text{HI})_{(t) \text{ in mmol}} = 1 - 5 \cdot 10^{-2} V$$

2.2. Referring to document -1, calculate n (HI) at t= 400 min. Deduce whether the synthesis of HI has gone to completion at this instant of time.

2.3. Plot, on a graph paper, the kinetic curve  $n(\text{HI}) = f(t)$ . Take the following scale:

Abscissa: 1cm for 50 min

Ordinate: 1cm for 0.1 mmol.

2.4. The rate of formation of HI is determined at two instants:  $t_1=150$  min and  $t_2=250$ min. The following values were found:  $r = 2.24 \times 10^{-4} \text{ mmol} \cdot \text{min}^{-1}$  and  $r' = 1.74 \times 10^{-5} \text{ mmol} \cdot \text{min}^{-1}$ .

2.4.1. Assign each value of the rate to the corresponding time.

2.4.2. Specify the kinetic factor that explains this evolution.

2.5. Determine, based on the graph, the half life  $t_{1/2}$  of this reaction.

### 3. Study the effect of some kinetic factors:

In order to study the effect of certain kinetic factors on the rate of reaction (1), two other experiments (2 and 3) are performed. The following table (document-2) summarizes the results of the three experiments (1, 2 and 3). The volume is kept constant for the 3 experiments.

	$n(\text{H}_2)$ initial in mmol	$n(\text{I}_2)$ initial in mmol	Temperature ( $^{\circ}\text{C}$ )	The rate of formation of HI at $t=150\text{min}$ in $\text{mmol}\cdot\text{min}^{-1}$
Experiment (1)	5	0.5	350	$2.24 \times 10^{-4}$
Experiment (2)	8	0.5	350	
Experiment (3)	5	0.5	T	$3.0 \times 10^{-4}$

Document -2

3.1 Specify, based on document -2, whether each of the following statements is true or false.

- The half life of experiment (2) is greater than that of experiment (1).
- At the end of reaction (1), the number of moles of HI in the three experiment reaches the same value.
- The temperature T of the reaction medium in experiment (3) should be greater than  $350^{\circ}\text{C}$ .

### Exercise 2 (6 1/2 points)

#### Determination of the purity of a scale remover

The main constituent of a scale remover for coffee –pot is sulfamic acid. It is sold commercially as white small crystals. Sulfamic acid  $\text{NH}_2\text{SO}_3\text{H}$  is considered as a strong monoacid and it will be denoted by HA in this exercise.

The label on a scale remover reads 94% sulfamic acid by mass. The aim of this exercise is to verify the indication on the label.

#### Given:

- Molar mass of  $\text{NH}_2\text{SO}_3\text{H} = 97 \text{ g}\cdot\text{mol}^{-1}$ ;
- Molar mass of  $\text{CaCO}_3 = 100 \text{ g}\cdot\text{mol}^{-1}$

#### 1- Preparation of solution (S) of Sulfamic acid:

A mass  $m=1.6\text{g}$  of the scale remover is dissolved in distilled water to obtain a solution (S) of volume  $V=200 \text{ mL}$ . The concentration of sulfamic acid in solution (S) is denoted by  $C_a$ .

1.1 Write the equation of the reaction of sulfamic acid with water.

1.2 Describe, by choosing the appropriate glassware from document-1, the experimental procedure for this preparation.

Graduated cylinders: 10, 50 and 100mL	Precision balance	Watch glass	Spatula
Volumetric flask : 50, 100 et 200mL	Funnel		

#### Document-1

#### 2- Titration of sulfamic acid solution (S) with a sodium hydroxide solution:

A volume  $V_1 = 20 \text{ mL}$  of solution (S) is titrated with sodium hydroxide solution ( $\text{Na}^+_{(\text{aq})}$ ,  $\text{HO}^-_{(\text{aq})}$ ) of concentration  $C_b = 10^{-1} \text{ mol}\cdot\text{L}^{-1}$  by using a pH meter.

The obtained results were plotted in the curve shown in Document-2.

2.1. Write the equation of the titration reaction.

2.2. Referring to document -2:

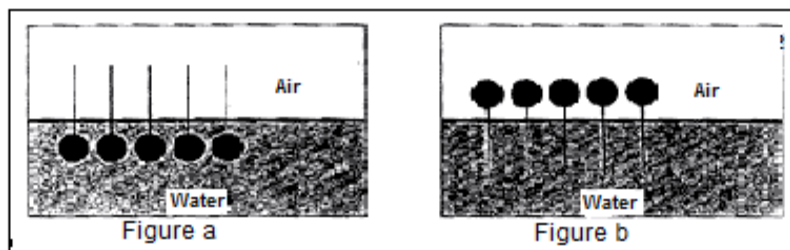
2.2.1 Determine, from the graph, the coordinates of the equivalence point ( $V_{bE}$ ;  $\text{pH}_E$ ).

2.2.2 Verify that sulfamic acid HA is a strong acid.



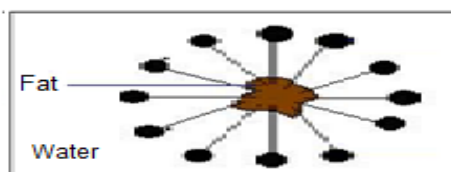
1.1.1 Explain the meaning of these terms.

1.1.2 A solution containing oleate ions is introduced in distilled water. Identify which of the 2 drawings (document-2) is correct.



Document-2

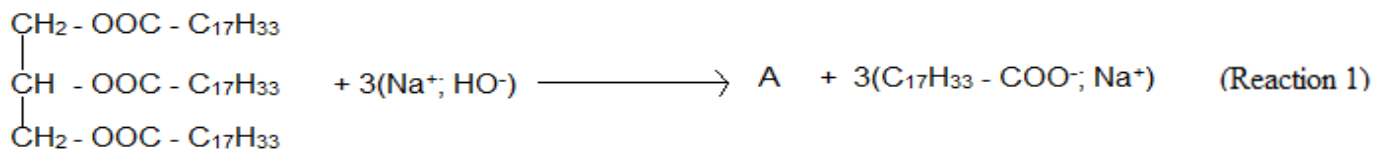
1.1.3 To clean the stain, the oleate ions found in soap are dispersed in water and take the shape represented in document -3. Explain briefly this arrangement.



Document-3

## 2- Study of the reaction between fat and strong base.

Sometimes the piping of the sink is blocked by the greases and the fatty substances, for this purpose an "unblocking product" containing sodium hydroxide is used to unclog it. Sodium hydroxide solution reacts with fat (olein) according to reaction (1).



### **Olein**

By referring to reaction (1), answer the following questions:

2.1 Give the name of this reaction.

2.2 This reaction is complete but also it has 2 other characteristics. State these 2 characteristics.

2.3 Identify the product (A).

2.4 10mL of olein (triester of oleic acid) reacts with an excess of sodium hydroxide solution ( $\text{Na}^+$ ,  $\text{HO}^-$ ). Determine the obtained mass of soap knowing that the percent yield of this reaction is 76%.

## 3- Study of the solubility of soap in water:

Fatty acids, such as oleic acid  $\text{C}_{17}\text{H}_{33}\text{-COOH}$ , are insoluble in water.


### **Document- 4**

A small soap bar is dissolved in a beaker containing 500 mL distilled water. Few mL of a concentrated solution of a strong acid are added to the beaker. A white precipitate appears in the beaker.

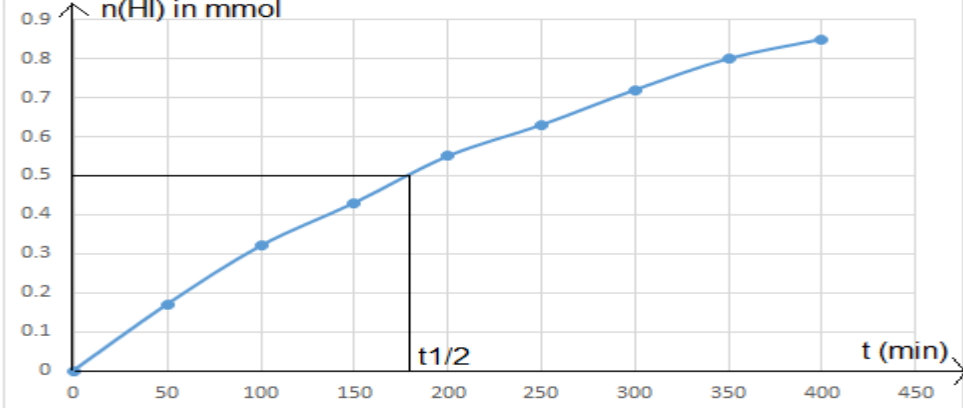
3.1 Referring to document-4, show that oleic acid is an unsaturated carboxylic acid.

3.2 Write the equation of the complete reaction between oleate ions and the solution of strong acid.

3.3 Deduce the appearance of a white precipitate in the beaker.

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

Exercise 1 (7 points)		
Kinetics study of the synthesis of hydrogen iodide HI		
Part of the question	Expected Answers	Mark
1.1	According to stoichiometric ratio of the reaction (1): $R(H_2) = \frac{n(H_2)_{initial}}{1} = 5.10^{-3} \quad R(I_2) = \frac{n(I_2)_{initial}}{1} = 0.5.10^{-3}$ $R(I_2) < R(H_2)$ then the reactants are not in stoichiometric proportions and I <sub>2</sub> is limiting reactant.  At the end of the reaction: $\frac{n(I_2)_{initial}}{1} = \frac{n(HI)_{final}}{2}$  $n(HI)_{final} = 2 \times n(I_2)_{initial} = 2 \times 0.5.10^{-3} = 1.10^{-3} \text{ mol} = 1 \text{ mmol.}$	1/4  1/4  1/4
1.2	-The sudden cooling of the flask is necessary to block the progress of the slow reaction (1) in order to determine the quantity of iodine remaining by the titration since titration reaction must be a unique reaction. -Starch is the indicator for the presence of iodine; it allows detecting exactly the equivalence point when the blue color changes to colorless. This means that all the iodine found in the beaker has reacted with the solution poured from burette.	1/2  1/2
2.1	At each instant of time t, $n(I_2)_{remained}(t) = n(I_2)_o - n(I_2)_{reacted}(t)$ . (reaction 1) And $n(I_2)_{remained}(t) = n(I_2)_{titrated}$ (reaction 2) Referring to reaction (2) : According to stoichiometric ratio and at equivalence point : $n(I_2)_{titrated}(t) = [S_2O_3^{2-}]V/2 = 5.10^{-2}V/2 = 2.5.10^{-5} V \quad (V \text{ in mL}).$ According to reaction (1), $n(HI)_{formed} = 2 \times n(I_2)_{reacted} = 2 \times [n(I_2)_o - n(I_2)_{remained}(t)] = 2 [0.5 - 2.5.10^{-2} V].10^{-3} = [1 - 5.10^{-2} V].10^{-3}$ In mmol: $n(HI)_{formed} = 1 - 5.10^{-2} V$	3/4
2.2	Referring to the above expression: $n(HI)_t \text{ formed} = 1 - 5.10^{-2} V$ At t = 400min, $n(HI) = 1 - 5.10^{-2}.3 = 0.85 \text{ mmol.}$ No, because at the end of the reaction the number of moles of HI is 1 mmol > 0.85 mmol	1/4  1/4
2.3		3/4

2.4.1	The rate of the reaction must decrease with time. Since $r$ ( $2.24 \times 10^{-4} \text{ mmol. min}^{-1}$ ) is greater $r'$ ( $1.74 \cdot 10^{-5} \text{ mmol. min}^{-1}$ ), $r$ corresponds to $t = 150 \text{ min}$ and $r'$ corresponds to $t = 250 \text{ min}$ .	1/2
2.4.2	At constant temperature, the kinetic factor involved in this change of the rate of formation of HI is the concentration of reactants. As the concentration of reactants decreases, the rate of the reaction decreases.	1/2
2.5	-The half life is the time needed for the disappearance of the half initial quantity of the limiting reactant ( $I_2$ ), or for the formation of the half maximum quantity of the product (HI). $n(\text{HI})_{\text{produced}} = n(\text{HI})_{\text{final}}/2 = 0.5 \text{ mmol}$ . From the graph, for $n = 0.5 \text{ mmol}$ , $t = 175 \text{ min}$ . Then $t_{1/2} = 175 \text{ min}$ .	1/4 1/4 1/4
3.1	-False, The experiments (1) and (2) have the same temperature and the same concentration of the limiting reactant ( $I_2$ ), but the concentration of the reactant ( $H_2$ ) is higher in experiment (2). Since the concentration of the reactant is a kinetic factor, the rate of the reaction in (2) will be greater than that in (1) and the half life will be smaller.  -True, in the three experiments (1), (2) and (3), there is the same initial quantity of the limiting reactant ( $I_2$ ), then at the end of the reaction; the same number of moles of (HI) will be obtained.  -True, experiments (1) and (3) have the same concentration of reactants but different temperatures. The rate of formation of HI in experiment (3) at $t = 150 \text{ min}$ is $3.24 \times 10^{-4} \text{ mmol. min}^{-1}$ greater than that in experiment (1) ( $2.24 \times 10^{-4} \text{ mmol. min}^{-1}$ ) at the same time $t = 150 \text{ min}$ . Since the temperature is a kinetic factor, so when the temperature increases, the rate of the reaction increases, that's why the temperature $T$ should be greater than $350^\circ\text{C}$ .	1/2 1/2 1/2

<b>Exercise 2 (6 1/2 points)</b>		
<b>Determination of the purity of a scale remover</b>		
<b>Part of the question</b>	<b>Expected Answers</b>	<b>Mark</b>
1.1	Sulfamic acid HA is a strong monoacid. It dissociates completely in water according to the following equation: $\text{HA}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightarrow \text{H}_3\text{O}^+_{(\text{aq})} + \text{A}^-_{(\text{aq})}$	1/2
1.2	-Using a precision balance, a watch glass and a spatula, weigh 1.6 g of scale remover. This solid is transferred to a (200mL) volumetric flask by using a funnel. -Using a washing bottle rinse the watch glass into the volumetric flask and shake to dissolve the solid. -Add water till the line mark and shake to homogenize.	1/2
2.1	Since HA is considered to be a strong acid, it is a reaction between a strong acid and a strong base, the equation is then: $\text{H}_3\text{O}^+_{(\text{aq})} + \text{HO}^-_{(\text{aq})} \rightarrow 2\text{H}_2\text{O}_{(\text{l})}$ .	1/2
2.2.1	From the graph and by using the parallel tangent method, the coordinates of the equivalence point (E) are: $V_{\text{bE}} = 15,4 \text{ mL}$ and $\text{pH}_{\text{E}} = 7$	1/2
2.2.2	Choose one of these two reasons to show that the titrated acid is a strong acid: 1- The curve is formed of three parts and one inflexion point (equivalence point). 2- The solution is neutral at the equivalence point and the pH at this point is $\text{pH}_{\text{E}} = 7$ . This is a characteristic of the titration of a strong acid with a strong base.	1/2

2.3.1	ii- A basic solution V(16mL) of sodium hydroxide solution is greater than $V_{bE} = 15.4$ mL, then the species presented in the solution, other than water and spectator ions ( $\text{Na}^+$ and $\text{A}^-$ ), are the ions $\text{HO}^-$ (excess). So, the nature of the solution is basic.	1/4 1/4
2.3.2	iii- The $\text{pH}_E = 7$ (Species found are $\text{H}_2\text{O}$ , neutral, and spectator ions). The convenient indicator is BTB (6-7.6) since $\text{pH}_E$ is included in its pH range.	1/4 1/4
2.4	At equivalence point : $\frac{n(\text{HO}^-)\text{Added from buret}}{1} = \frac{n(\text{H}_3\text{O}^+)\text{ presented in the beaker}}{1}$ $C_b V_{bE} = C_a V_a$ The concentration $C_a$ of solution (S) is: $C_a = \frac{C_b V_{bE}}{V_a} = \frac{0.1 \times 15.4}{20} = 0.077 \text{ mol.L}^{-1}$ .	1/4 1/2
2.5	The mass of sulfamic acid presented in 200 mL of solution (S) is : $m_a = C_a \cdot V \cdot M_{(\text{NH}_2\text{-SO}_3\text{H})} = 0.077 \times 0.2 \times 97 = 1.49\text{g}$ the percent by mass of HA in the scale remover is: $\% m \text{ HA} = \frac{m_{\text{HA}}}{m_{\text{scale remover}}} \times 100 = \frac{1.49}{1.6} = 93.12 \%$	1/4 1/2
2.6	$\text{Discrepancy} = \frac{94 - 93.12}{94} \times 100 = 0.9\% < 5\% \text{ Accepted}$	1/4
3.1	The number of moles of $\text{CaCO}_3$ in a mass $m=2.1\text{g}$ ; $n_{\text{CaCO}_3} = 2.1/100 = 21 \times 10^{-3} \text{ mol}$ . According to stoichiometric ratio : $n(\text{HA})_{\text{reacted}} = 2 \times n(\text{CaCO}_3)_{\text{reacted}} = 2 \times 2.1 \times 10^{-3} = 4.2 \times 10^{-3} \text{ mol}$ . The volume of solution (S) necessary to remove completely 2.1g of $\text{CaCO}_3$ is: $V_S = n(\text{HA}) / C_S = 4.2 \times 10^{-3} / 7.7 \times 10^{-2} = 0.0545 \text{ L} = 54.5\text{mL}$ .	1/4 1/4 1/4
3.2	The mass of sulfamic acid HA necessary to remove 2.1g of limestone $= 4.2 \times 10^{-3} \times 97 = 0.407 \text{ g}$ This corresponds to a mass of scale remover $= \frac{m(\text{HA}) \times 100}{94} = \frac{0.407 \times 100}{94} = 0.433\text{g}$	1/2

<b>Exercise 3 (6 1/2 points)</b> <b>Study of the Saponification reaction</b>		
<b>Part of the question</b>	<b>Expected Answers</b>	<b>Mark</b>
1.1.1	The hydrophilic head is the part attracted by water and repelled by oil. The hydrophobic tail is the part attracted by oil and repelled by water. <b>Note: any other definition is accepted: water loving, water hating, ..</b>	1/2 1/2
1.1.2	Figure (a) is the correct one. The head is the hydrophilic part of the $\text{RCOO}^-$ ion, it loves water. So, this part must be immersed in water and repelled from oil. On the other hand, the tail is the hydrophobic part, so, it hates water and must be attracted by the oil.	3/4
1.1.3	In this arrangement, water-fat interface, the tails of oleate ion (hydrophobic parts) penetrate into the fat molecules and are immersed in oil stain because they love lipids. However, the heads (hydrophilic part) are immersed in water because they love water .	3/4
2.1	It is a saponification reaction.	1/2

<b>2.2</b>	Other than complete reaction, it's a slow and athermic reaction.	1/2
<b>2.3</b>	The condensed structural formula of A is CH <sub>2</sub> OH – CH <sub>2</sub> OH – CH <sub>2</sub> OH The product A is 1, 2, 3-propantriol.	1/4 1/4
<b>2.4</b>	$m_{olein} = \rho \times V_{olein} = 0.9 \times 10 \text{ mL} = 9 \text{ g}$ we calculate the theoretical mass of soap according to stoichiometric ratio in the reaction 1: $m_{olein} / M_{olein} = m_{soap \text{ theoretical}} / 3 M_{soap}$ ; $\frac{n_{olein}}{1} = \frac{n_{soap}}{3} ; \frac{m_{olein}}{M_{olein}} = \frac{m_{soap}}{3M_{soap}} ; m_{soap(theo)} = \frac{3 \times M_{soap} \times m_{olein}}{M_{olein}} = \frac{3 \times 304 \times 9}{884}$ therefore $m_{theoretical \text{ soap}} = 9.285 \text{ g}$ The % yield = $\frac{m_{soap(exp)}}{m_{soap(theo)}} \times 100 = 76\%$ $m_{soap(exp)} = 76 \times m_{soap(theo)} / 100 = 7.05 \text{ g}$	1/2  1/2
<b>3.1</b>	Oleic acid is a carboxylic acid because it has the functional group carboxyl – COOH. Furthermore, Oleic acid is unsaturated since the radical R- of formula C <sub>17</sub> H <sub>33</sub> - does not correspond to C <sub>n</sub> H <sub>2n+1</sub> .	1/2
<b>3.2</b>	$C_{17}H_{33}COO^- + H_3O^+ \rightarrow C_{17}H_{33}COOH + H_2O$	1/2
<b>3.3</b>	The formation of oleic acid which is insoluble in water is the responsible of the observation the white precipitate in the beaker.	1/2