المادة: الكيمياء الشهادة: الثانوية العامة الفرع: علوم الحياة نموذج رقم - ٢ -

لهيئة الأكاديمية المشتركة قسم: العلوم



نموذج مسابقة (يراعي تعليق الدروس والتوصيف المعدّل للعام الدراسي ٢٠١٠-٢٠١٧ 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)

## 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 reaction, assumed to be complete, is:

$$H_{2(g)} + I_{2(g)} \longrightarrow 2HI_{(g)}$$
 (Reaction 1)

For this purpose, eight round bottom flasks (1000mL) are placed at a constant temperature of 350°C; each contains 0,5mmol 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 potassium iodide solution. By adding few drops of starch, the solution turns blue. The solution is then titrated with an aqueous sodium thiosulfate solution  $(2Na^+_{(aq)}+S_2O_3^{2^-}_{(aq)})$  having a concentration of  $5x10^{-2}$  mol L<sup>-1</sup>. The volume of sodium thiosulfate solution added to reach the equivalence point is denoted by V. The same procedure is repeated at different time instants 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	В	С	D	Е	F	G	Н
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	3
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:

$$I_{2\,(aq)} + 2S_2O_3{}^{2\text{-}}{}_{(aq)} {\:\longrightarrow\:} 2\Gamma_{(aq)} + S_4O_6{}^{2\text{-}}{}_{(aq)} \quad \text{(Reaction 2)}$$

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

$$n(HI)_{(t)in mmol} = 1 - 5x10^{-2} V$$

- 2.2. Referring to document -1, calculate n(HI) at t = 400min. 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(HI) = f(t). Take the following scales:

Abscissa: 1cm for 50 min

Ordinate: 1cm for 0.1 mmol.

2.4. The rate of formation of HI is given at two instants:  $r_1 = 2.24 \times 10^{-4}$  mmol.min<sup>-1</sup> at  $t_1 = 150$  min and  $r_2 = 1.74 \times 10^{-5}$  mmol.min<sup>-1</sup> at  $t_2 = 250$ min.

- 2.4.1. Deduce how the rate of formation of HI varies with time.
- 2.4.2. Specify the kinetic factor that explains this variation.
- 2.5. Determine, based on the graph, the half life of this reaction  $t_{1/2}$ .

### 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) sumamrizes the results of the three experiments 1, 2 and 3.

	n(H <sub>2</sub> ) <sub>initial</sub> in mmol	n(I <sub>2</sub> ) <sub>initial</sub> in mmol	Temperature	r( HI) at t= 150min in mmol.min <sup>-1</sup>
Experiment (1)	5	0.05	350°C	$2.24 \times 10^{-4}$
Experiment (2)	8	0.05	350°C	
Experiment (3)	5	0.05	T	$3.0x10^{-4}$

#### **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°C.

### Exercise 2 (6 ½ points)

### **Determining 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 NH<sub>2</sub>-SO<sub>3</sub>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:

-  $M (NH_3SO_3)=97 \text{ g.mol}^{-1}$ ;

 $M(CaCO_3)=100 \text{ g.mol}^{-1}$ 

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

- 1.6g of the scale remover are dissolved in distilled water to obtain a solution (S) of volume V = 200 mL. The concentration of sulfamic acid in solution (S) is denoted by Ca.
- 1.1 Write the equation of the reaction of sulfamic acid with water.
- 1.2 Describe, choosing the appropriate glassware from document-1, the experimental procedure for this preparation.

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

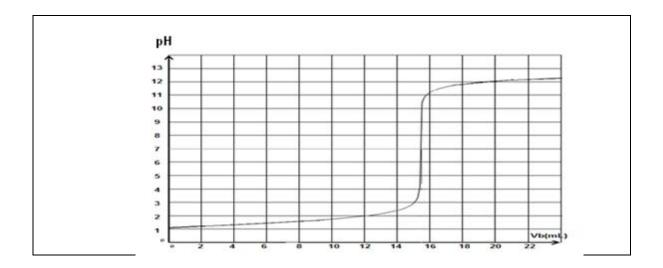
#### **Document-1**

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

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

The obtained results allowed plotting the curve shown below (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  $(V_{BE}, pH_E)$ .
  - 2.2.2 Verify that sulfamic acid HA is a strong acid.



- 2.3 For each of the following statements, choose the right answer. Justify
  - 2.3.1 After adding 16mL of sodium hydroxide solution, The chemical species found in the reaction system give:

i- An acidic solution

ii- A basic solution

iii- A neutral solution

2.3.2 At equivalence point, the addition of 80mL distilled water to the reaction system:

i- decreases pH<sub>E</sub>

ii- increases pH<sub>E</sub>

iii- has no effect on pH<sub>E</sub>

- 2.4 Show that the concentration Ca of solution (S) is  $7.7 \times 10^{-2} \text{mol.L}^{-1}$ .
- 2.5 Deduce the percent by mass of sulfamic acid in the scale remover.
- 2.6 Compare the value thus calculated to that marked on the label. Justify if the result is accepted knowing that the percent error should not exceed 5%.

#### 3- Action of Scale remover on limestone:

The sulfamic acid solution reacts with limestone containing CaCO<sub>3</sub> according the following equation:

 $2 (H_3O^+ + A^-)_{(aq)} + CaCO_3 (s) \rightarrow Ca^{2+} (aq) + 2A^- (aq) + CO_2 (g) + H_2O_{(l)}$ . (Reaction -1)

It is required to remove a mass m = 2.1 g of limestone (scale) settled on the surface of a coffee maker.

- **3.1** Determine the volume V of sulfamic acid solution  $\hat{S}$  (C=7.7x10<sup>-2</sup>mol.L<sup>-1</sup>) necessary to remove completely the mass m of limestone.
- **3.2** Deduce the mass of the scale remover dissolved in the volume V knowing that it is 94% pure.

# Exercise 3 (6 ½ points)

# Study of the Saponification reaction

A soap bar consists only of sodium oleate  $C_{17}H_{33}$ -COONa. Sodium oleate is derived from an unsaturated oleic acid having the formula  $C_{17}H_{33}$ -COOH.

**Given**: Molar mass of sodium oleate is 304 g.mol<sup>-1</sup>, Molar mass of olein is 884g.mol<sup>-1</sup>.

Density of olein: 0.90 g.mL<sup>-1</sup>

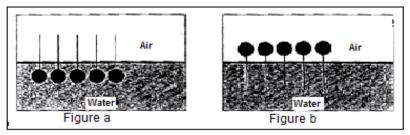
#### 1. Characteristics of oleate ion:

The detergent properties of the soap are due to oleate ion  $C_{17}H_{33}$ -COO.

- 1.1. The figure below (document-1) shows a schematic representation of the oleate ion  $C_{17}H_{33}$ - $COO^-$ . The hydrophilic part is designated by the head and the hydrophobic part is designated by the tail.
- **1.1.1** Explain the meaning of these terms.



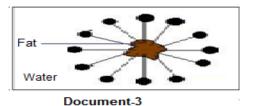
**1.1.2** A solution containing oleate ions is introduced in distilled water. Identify which of the 2 drawings (document 2) is correct.



Document-2

**1.1.3** To clean the stain, oleate ions found in soap are dispersed in water and they take the shape represented in the following document-3.

Explain briefly this arrangement.



#### 2- Evacuation of soapy water

A drain cleaner is a consumer product containing sodium hydroxide that unblocks sewer pipes or helps to prevent the occurrence of clogged drains by dissolving grease or soap/detergent buildups. Sodium hydroxide converts fat into soap which then dissolves in water according to reaction (1).

$$\begin{array}{c} \text{CH}_2 \text{- OOC - C}_{17}\text{H}_{33} \\ \text{CH - OOC - C}_{17}\text{H}_{33} \\ \text{CH}_2 \text{- OOC - C}_{17}\text{H}_{33} \\ \end{array} + 3(\text{Na}^+; \text{HO}^-) \\ \begin{array}{c} \longrightarrow \\ \text{CH}_2 \text{- OOC - C}_{17}\text{H}_{33} \\ \end{array}$$

#### (Reaction 1)

Referring to reaction (1), answer the following questions:

- **2.1** Give the name of this reaction.
- **2.2** This reaction is complete, state another characteristic.
- **2.3** Identify the product (A).
- **2.4** 10mL of olein (trimester of oleic acid) reacts with an excess of sodium hydroxide solution (Na<sup>+</sup>, HO<sup>-</sup>). Determine the obtained mass of soap such as the percent yield of this reaction is 76%.

## 3- Solubility of soap in water:

Fatty acids, such as oleic acid C<sub>17</sub>H<sub>33</sub>-COOH, are insoluble in water.

#### **Document-4**

A small soap bar is dissolved in 500 mL distilled water. The solution thus obtained is poured equally into two beakers (A) and (B). Few mL of oil are added to beaker (A) and few mL of a concentrated solution of a strong acid are added to beaker (B).

A homogeneous solution persists in beaker (A) while a white precipitate appears in beaker (B).

- **3.1** Show that oleic acid is an unsaturated carboxylic acid.
- **3.2** Write the condensed structural formula of oleic acid knowing that it has a double bond between carbons 9 and 10.
- **3.3** Write the equation of the reaction between oleate ions and the strong acid.
- **3.4** Deduce the appearance of a white precipitate in beaker (B).
- **3.5** Explain why the solution remains homogeneous in beaker (A).

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# الهيئة الأكاديمية المشتركة قسم: العلوم



أسس التصحيح (تراعي تعليق الدروس والتوصيف المعدّل للعام الدراسي ٢٠١٦-٧٠١ وحتى صدور المناهج)

# Suggested Mark Scheme Exercise 1 (7 points)

Kinetics study of the synthesis of hydrogen iodide HI

Part of	Suggested Answers	Mark
the		
question		
1.1	According to Stoichiometric ratio:	1.
	$R(H_2) = \frac{n(H_2)initial}{1} = 5.10^{-3}  R(I_2) = \frac{n(I_2)initial}{1} = 0.5.10^{-3}$	1/4
	$R(I_2) < R(H_2)$ then the reactants are not in stoichiometric proportions and $I_2$ is limiting	1/
	reactant.	1/4
		1/4
	At the end of the reaction: $\frac{n(I_2)initial}{1} = \frac{n(HI)final}{2}$	74
	1 2	
	$n(HI) final=2x n(I_2) initial=2x0.5.10^{-3}=1.10^{-3} mol=1 mmol.$	
1.2	- The sudden cooling of the flask is necessary to block the progress of the slow reaction	1/2
1.2	(1) in order to determine the quantity of iodine remaining by the titration since titration	/ 2
	reaction must be a unique reaction.	
	- The starch is the indicator for the presence of iodine, it allows to detect exactly the	1/2
	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.	
2.1	At each instant of time t, $n(I_2)_{\text{remained}}$ (t)= $n(I_2)_{\text{o}}$ - $n(I_2)_{\text{reacted}}$ (t). (reaction 1)	
	And $n(I_2)_{\text{remained}}$ (t)= $n(I_2)_{\text{titrated}}$ (reaction 2)	
	Referring to reaction (2): According to stoichiometric ratio, at equivalence point:	3/4
	$n(I_2)_{\text{titrated(t)}} = [S_2O_3^2]V/2 = 5x10^{-2}V/2 = 2.5x10^{-2} \text{ V (V in mL)}.$	
	Reaction (1), $n(HI)$ formed = $2x$ $n(I_2)$ reacted = $2x$ $[n(I_2)_o-n(I_2)_{remained}(t)]$	
	$= 2 [0.5-2.5x10^{-2} V] = 1-5x10^{-2} V.$	
2.2	Referring to the above expression: n(HI) <sub>t formed</sub> =1-5.10 <sup>-2</sup> V	1/4
	At $t = 400$ min, $n(HI) = 1 - 5x10^{-2}x3 = 0.85$ mmol.	
	No, because at the end of the reaction the number of moles of HI is 1 mmol > 0.85 mmol	1/4
2.3	0.9 \ n(HI) in mmol	1
	0.8	
	0.7	
	0.6	
	0.5	
	0.4	
	0.3	
	0.2	
	t1/2 t (min)	
	0 50 100 150 200 250 300 350 400 450	

2.4.1	The rate at $t_1$ =150 min (2.24x10 <sup>-4</sup> mmol. min <sup>-1</sup> ) is greater than the rate at $t_2$ =250 min (1.74.10 <sup>-5</sup> mmol. min <sup>-1</sup> ). Therefore the rate of the reaction decreases with time.	1/4
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 half the initial quantity of the limiting reactant ( $I_2$ ), or to the formation of half the maximum quantity of the product. $n(HI)_{produced} = n(HI)_{final}/2 = 0.5 \text{mmol}.$ From the graph, for $n = 0.5$ mmol, $t = 175$ min therefore $t_{1/2} = 175$ min .	3/4
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 ( $I_2$ ) 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.	1/2
	- True, in the three experiments (1), (2) and (3), there is the same initial quantity of the limiting reactant (I <sub>2</sub> ), then at the end of the reaction, the same number of moles of (HI) will be obtained.	1/2
	- True, experiments (1) and (3) have the same concentration of reactants but different temperatures. The rate of formation of HI in experiment (3) at $t = 150$ min is $3.24 \times 10^{-4}$ mmol. min greater than that in experiment 1 ( $2.24 \times 10^{-4}$ mmol.min 1) at same time 150min. Therefore the temperature is a kinetic factor and increasing temperature increases the rate of the reaction at same time t, then T should be greater than $350^{\circ}$ C.	1/2

# Exercise 2 (6.5 points)

# Determining the purity of a scale remover

Part of the	Suggested Answer	Mark
question		
1.1	Sulfamic acid HA is a strong monoacid. It dissociates completely in water according to the following equation:	1/2
	$HA_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + A^{(aq)}$	
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 volumetric flask (200mL) by using a funnel.	1/2
	- 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.	
2.1	Since HA is considered to be a strong acid, it is a reaction between a strong acid and a	1/4
	strong base, the equation is then:	
	$  H_3O^+_{(aq)} + HO^{(aq)} \rightarrow 2 H_2O_{(1)}.$	
2.2.1	From the Graph and according to parallel tangent method, the coordinates of the	1/2
	equivalence point (E) are:	
	$V_{bE} = 15.4$ mL and pH <sub>E</sub> = 7	
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 only one inflexion point (equivalence point).	1/2

	2- The solution is neutral at the equivalence point and the pH at this point is $pH_E = 7$	
2.3.1	ii- A basic solution $V(16\text{mL})$ 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 (Na <sup>+</sup> and A <sup>-</sup> ), are the ions HO <sup>-</sup> (excess), Therefore the nature of the solution is basic.	1/4
2.3.2	iii- has no effect on pH <sub>E</sub> .	1/4
	After adding 80mL distilled water, the species remain the same: water and spectator ions (Na <sup>+</sup> and A <sup>-</sup> ). Then the solution remains neutral.	1/4
2.4	At equivalence point: $ \underline{n(HO-)Added from\ buret\ at\ equivalence\ point}\underline{n(H_3O^+)in\ the\ sample\ in\ beaker} \ . $	1/4
	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1/2
2.5	The mass of sulfamic acid present in 200 mL of solution (S) is:	1/4
	$m_a = C_a$ . V. $M(NH_2-SO_3H) = 0.077 \times 0.2 \times 97 = 1.49g$ the percent by mass of HA in the scale remover is:	1/2
	% m HA= Error!x 100=Error! =93.12 %	72
2.6	$Discrepancy = \frac{94 - 93.12}{94} x100 = 0.9\% < 5\%$ Accepted	1/4
3.1	The number of moles of CaCO <sub>3</sub> in a mass $m = 2.1$ g of limestone: $n_{CaCO3} = 2.1/100 =$	1/4
	$21.10^{-3}$ mol. According to stoichiometric ratio: $n(HA)_{reacted} = 2 n(CaCO_3)_{produced}$	1/ <sub>4</sub> 1/ <sub>4</sub>
	$= 2 \times 2.1 \times 10^{-3} = 4.2 \times 10^{-3} \text{ mol.}$	,
	The volume of solution (S) necessary to remove completely 2.1g of limestone is: $V_S = n(HA)/C_S = 4.2 \times 10^{-3}/7.7 \times 10^{-2} = 0.0545 \text{ L} = 54.5 \text{mL}.$	
3.2	The mass of sulfamic acid HA necessary to remove 2.1g of limestone	1/4
	$= 4.2 \times 10^{-3} \times 97 = 0.4 \text{g}$ that corresponds to scale remover mass = <b>Error!</b> = <b>Error!</b> = 0.43 g	1/2
	mar corresponds to scale remover mass -Error: - Error: - 0.43g	

Exercise 3 (6.5 points)
Study of the Saponification reaction

Part of	Suggested Answer	Mark
the		
question		
1.1.1	The hydrophilic head is the part attracted by water and repelled by oil.	1/2
	The hydrophobic tail is the part attracted by oil and repelled by water.	1/2
1.1.2	Therefore figure (a) is the correct one.	
	The head is the hydrophilic part of the RCOO ion, it loves water, so this part must be	1/2
	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.	
1.1.3	In this arrangement, in the water-fat interface, the tails (hydrophobic parts) penetrate the	1/2
	fat molecules and are immersed in oil stain because they like lipids. The heads	

	(hydrophobic parts) are directed towards the aqueous solution.	
	However, the heads (hydrophilic part), because love water then they are immersed in	
	water.	
2.1	It is a saponification reaction.	1/4
2.2	Slow reaction	1/2
2.3	The condensed structural formula of A is CH <sub>2</sub> OH – CH <sub>2</sub> OH – CH <sub>2</sub> OH	1/4
	The product A is 1,2,3-propantriol.	1/4
2.4	$m_{\text{olein}} = \rho \text{ xV}_{\text{olein}} = 0.9 \text{ x } 10 \text{ mL} = 9 \text{ g}$	
	we calculate the theoretical mass of soap according to stoichiometric ratio in the reaction	
	1:	1/2
	$m_{\text{olein}} / M_{\text{olein}} = m_{\text{soap theoretical}} / 3 M_{\text{soap}};$	
	$n_{olein}$ nsoap molein $m_{soap}$ $3xM_{soap}xm_{oleine}$ $3x304x9$	
	$\frac{n_{olein}}{1} = \frac{nsoap}{3}; \frac{molein}{M_{oleine}} = \frac{m_{soap}}{3M_{soap}}; m_{soap(theo)} = \frac{3xM_{soap}xm_{oleine}}{Molein} = \frac{3x304x9}{884}$	1/2
	therefore $m_{theoretical soap} = 9.285 g$	
	The % yield = $\frac{m_{\text{soap}}(exp)}{m_{\text{soap}}(theo)}$ x 100 = 76%	
	$m_{soap}(exp) = 76 \text{ x } m_{soap}(theo)/100 = 7.05 \text{ g}$	
3.1	Oleic acid is a carboxylic acid because it has the functional group carboxyl – COOH.	1/2
	Then, Oleic acid is unsaturated since the radical R of formula C <sub>17</sub> H <sub>33</sub> does not correspond to	
	$C_nH_{2n+1}$	
3.2	Oleic acid CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>7</sub> -CH=CH-(CH <sub>2</sub> ) <sub>7</sub> -COOH	1/4
3.3	$C_{17}H_{33}\text{-COO}^- + H_3O^+ \to C_{17}H_{33}\text{-COOH} + H_2O$	1/2
3.4	The formation of oleic acid that is insoluble in water gives the white precipitate in beaker B.	1/2
3.5	Since soap is soluble at the same time in water and in oil, this leads to the formation of the	1/2
	homogeneous solution obtained in beaker A.	