

الاسم:	مسابقة في الكيمياء
الرقم:	المدة ساعتان

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 Following Three Exercises:

First Exercise (6 points) Esterification Reaction

Two flasks are available. Their labels show the following indications:

Flask (1): acid (A) of formula R – COOH.

Flask (2): alcohol of formula C₃H₇OH.

The aim of this exercise is to identify the content of each of the two flasks.

Given:

- Molar mass in g.mol⁻¹: M_(H) = 1; M_(C) = 12; M_(O) = 16.

- The value of the equilibrium constant K_c of the esterification reaction

* of a carboxylic acid and a primary alcohol is K_c = 4.2;

* of a carboxylic acid and a secondary alcohol is K_c = 2.2.

I- Identification of the Carboxylic Acid (A)

The dehydration of 1.48 g of (A), in the presence of P₂O₅ as a dehydrating agent, leads to the formation of the anhydride of acid (A) and 0.01 mol of H₂O.

- 1- Write the equation of the above dehydration reaction.
- 2- Determine the number of moles of (A). Deduce its molar mass.
- 3- Show that the molecular formula of (A) is C₃H₆O₂, knowing that R is an alkyl group.
- 4- Write the condensed structural formula of (A) and give its name.

II- Identification of the Alcohol by Esterification Reaction

A mixture of acid (A) and the alcohol is heated for a certain time. A homogenous equilibrium, in the reactional system of volume V, is established. It is represented by the

following equation: $R - COOH + C_3H_7OH \rightleftharpoons R - COOC_3H_7 + H_2O$.

The remaining amount of acid at equilibrium is titrated. This titration permits to determine the number of moles of each constituent at equilibrium. The result is given in the following table:

Constituent	R – COOH	C ₃ H ₇ OH	R – COOC ₃ H ₇	H ₂ O
n _{equilibrium} (mol)	0.111	0.032	0.088	0.088

- 1- Specify the role of heating on the above reaction and its effect on the equilibrium.
- 2- Determine the equilibrium constant K_c and deduce the class of the used alcohol.
- 3- Write the condensed structural formula of this alcohol and give its name.
- 4- Write the condensed structural formula of the obtained ester in this reaction and give its name.

Second Exercise (7 points) Ammonia Solution

Ammonia is commercially sold in dark bottles as concentrated solutions.

Given:

Ammonia is a weak base that corresponds to the pair: $\text{NH}_4^+ / \text{NH}_3$.

I- Titration of a Commercial Solution of Ammonia (S_0)

A commercial solution of ammonia, (S_0), is diluted 100 times to obtain a solution (S). A volume $V_S = 20 \text{ mL}$ of solution (S) is titrated with hydrochloric acid solution of concentration $C_a = 0.1 \text{ mol.L}^{-1}$, in the presence of a coloured indicator. The volume of the acid solution added to reach the equivalence point is $V_{aE} = 21.6 \text{ mL}$.

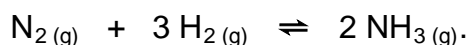
- 1- Write the equation of the titration reaction.
- 2- Determine the concentration of solution (S). Deduce that the concentration of solution (S_0) is $C_0 = 10.8 \text{ mol.L}^{-1}$.
- 3- Specify, by referring to the chemical species present in the beaker, the acid-base nature of pH at equivalence.
- 4- Choose, by justifying, which of the two indicators given in the table below, the one that will be more convenient to detect the equivalence point.

Indicator	pH range
Methyl red	Red : 4.2 – 6.2 : yellow
Phenolphthalein	colorless : 8.2 – 10 : purple

- 5- Indicate the change in color observed during the titration.

II- Synthesis of Ammonia to Prepare (S_0)

Ammonia is synthesized from a mixture composed of $n \text{ mol}$ of N_2 and $3 n \text{ mol}$ of H_2 . This synthesis reaction is reversible and is represented by the following equation:



- 1- Let α be the degree of conversion of N_2 at equilibrium. Rewrite, on the answer sheet, the table below and complete it in terms of n and α .

	$\text{N}_2(\text{g})$	$\text{H}_2(\text{g})$	$\text{NH}_3(\text{g})$	Total number of moles: n_t
Initial state (mol)	n	$3 n$	0	
Equilibrium state (mol)				

- 2- P is the total pressure at equilibrium. Give, in terms of α and P , the expression of the partial pressure of each of the constituents at equilibrium.
- 3- At equilibrium $P(\text{NH}_3) = 2 P(\text{N}_2)$.
 - a) Find the value of α .
 - b) Deduce the value of n needed to prepare 1 L of solution (S_0) of concentration $C_0 = 10.8 \text{ mol.L}^{-1}$.

Third Exercise (7 points) Sodium Thiosulfate

Hydrated sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, is a white solid. It undergoes a self oxidation-reduction reaction in a strongly acidic medium. It is a reducing agent when used to titrate iodine solution.

Given:

Molar mass in $\text{g}\cdot\text{mol}^{-1}$: $M_{(\text{H})} = 1$; $M_{(\text{O})} = 16$; $M_{(\text{Na})} = 23$; $M_{(\text{S})} = 32$.

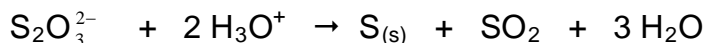
I- Preparation of a Sodium Thiosulfate Solution

A volume of 500 mL of sodium thiosulfate solution of concentration $C = 0.5 \text{ mol}\cdot\text{L}^{-1}$ is to be prepared.

- 1- Determine the mass of hydrated sodium thiosulfate needed for this preparation.
- 2- Choose, from the list below, the appropriate material needed to perform this preparation:
 - sensitive balance
 - 250 and 500 mL beakers
 - 250 and 500 mL volumetric flasks
 - buret
 - funnel
 - 10 and 20 mL volumetric pipets
 - spatula
 - watch glass
 - 50mL and 100mL graduated cylinders

II- Self Oxidation-Reduction of Sodium Thiosulfate

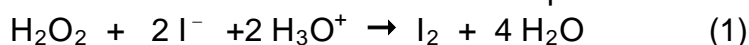
At time $t = 0$, an excess of concentrated hydrochloric acid solution is placed into a beaker containing a volume $V = 40 \text{ mL}$ of a sodium thiosulfate solution of concentration $C = 0.5 \text{ mol}\cdot\text{L}^{-1}$. With time, suspended fine solid particles are progressively formed. The equation of this reaction is:



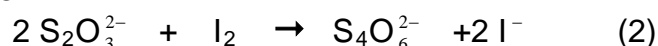
- 1- Show that the number of moles of the sulfur formed at the end of the reaction is equal to $2 \times 10^{-2} \text{ mol}$.
- 2- Draw the shape of the curve that represents the variation of the number of moles of sulfur formed versus time: $n_{(\text{s})} = f(t)$, that passes through the points of abscissa: $t = 0$; $t_{1/2} = 1 \text{ min}$ and the point of the following coordinates: $[t = 5 \text{ min and } n_{(\text{s})} = 2 \times 10^{-2} \text{ mol}]$.
Take the following scale: abscissa 1 cm for 1 min;
ordinate 1 cm for $4 \times 10^{-3} \text{ mol}$
- 3- Specify how the rate of formation of sulfur varies with time.
Deduce the kinetic factor responsible for this variation.

III- Indirect Titration of H₂O₂

At time $t = 0$, hydrogen peroxide solution, an excess of potassium iodide solution, and concentrated sulphuric acid solution, are placed into a beaker. We observe a coloured reactional medium that becomes darker with time. The equation of this reaction is:



In order to determine the amount of H₂O₂ left in the reactional medium at a given time t , the beaker is immersed in an ice-water bath. The iodine formed is then titrated with sodium thiosulfate solution of concentration $C = 0.5 \text{ mol.L}^{-1}$ in the presence of starch. The equation of the reaction is:



1- Specify the reason for immersing the beaker that contains the reactional medium in an ice-water bath.

2- Show that at instant t , we have the relation: $n_t = n_0 - \frac{C \cdot V_E}{2}$ where

$n_0 = n(\text{H}_2\text{O}_2)$ at $t = 0$;

$n_t = n(\text{H}_2\text{O}_2)$ left at instant t ;

C = concentration of sodium thiosulfate solution used in the titration;

V_E = volume of sodium thiosulfate solution added to reach equivalence.

3- Calculate $V_{E\infty}$ that would be added to titrate the iodine formed at the end of reaction (1) when $n_0 = 0.01 \text{ mol}$.

4- Explain the formation of turbidity (fine solid particles) in the beaker when the volume of sodium thiosulphate solution exceeds $V_{E\infty}$.

Marking Scheme of Chemistry
First Exercise (6 points)
Esterification Reaction

Expected Answer	Mark	Comments
I- 1- The equation of the dehydration reaction of R – COOH is: $2 R - COOH \rightarrow (R - CO)_2O + H_2O$	0.75	
2- According to the stoichiometric coefficients, we have: $n(R - COOH)_{\text{reacting}} = 2 n(H_2O)_{\text{formed}} = 2 \times 0.01 = 0.02 \text{ mol.}$	0.5	
The molar mass $M = \frac{m}{n} = \frac{1.48}{0.02} = 74 \text{ g.mol}^{-1}.$	0.25	
3- In the formula R – COOH, R is an alkyl group of formula: C_nH_{n+1} , its mass is $14n+1$. Where: $M = 14n+1+12+32+1$. So $n = 2$ and the molecular formula of acid (A) is $C_3H_6O_2$.	0.75	
4- The condensed structural formula of (A) is: CH_3-CH_2-COOH . Its name is propanoic acid.	2x0.25	
II- 1- Heating speeds up the reaction or it decreases the time that is needed to reach the equilibrium. It has no effect on the equilibrium because esterification reaction is athermic.	2x0.25	
2- The equilibrium constant is given by the following expression: $K_c = \frac{[R - COOC_3H_7].[H_2O]}{[R - COOH].[C_3H_7OH]}$. With the given values, we have:	0.25	
$K_c = \frac{\frac{0.088}{V} \times \frac{0.088}{V}}{\frac{0.111}{V} \times \frac{0.032}{V}} = 2.18.$ V is the volume of the reactional medium.	1	
By comparing the value of K_c with the two given values (4.2 and 2.2) we deduce that the alcohol is a secondary alcohol.	0.5	
3- The condensed structural formula is $CH_3 - CHOH - CH_3$ Its name is 2-propanol.	0.25	
4- The condensed structural formula of the ester is: $CH_3 - CH_2 - C(=O) - O - CH(CH_3) - CH_3$. It is the 2-propylpropanoate	0.25	
$CH_3 - CH_2 - \underset{\text{O}}{\parallel}{C} - O - \underset{\text{CH}_3}{ }{CH} - CH_3$	2x0.25	

Second Exercise (7 points)
Ammonia Solution

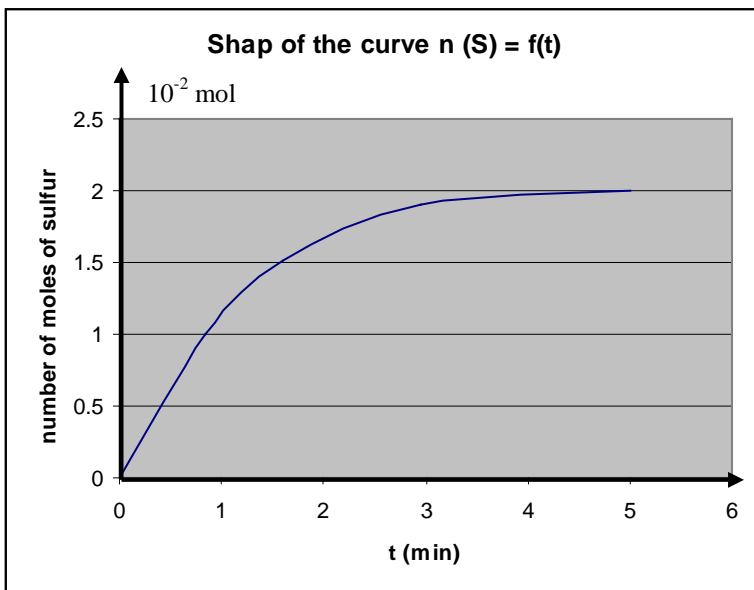
Expected Answer	Mark	Comment
I- 1- The equation of the titration reaction is: $NH_3 + H_3O^+ \rightarrow NH_4^+ + H_2O$	0.5	
2- At equivalence, we have : $n(NH_3)_{\text{in } 20 \text{ mL of (S)}} = n(H_3O^+)_{\text{in } 21.6 \text{ mL of acid solution}}$. Then:	0.25	
$C_{(S)} \times V_{(S)} = C_a V_a$. We conclude: $C_{(S)} = \frac{0.1 \times 21.6}{20} = 0.108 \text{ mol.L}^{-1}.$		

Solution (S) is obtained by diluting 100 times the solution (S ₀), then, the concentration of (S ₀) is: C ₀ = 100 x C _(S) = 100 x 0.108 = 10.8 mol.L ⁻¹ .	0.5																
3- The present species at equivalence, other than water, are NH ₄ ⁺ and Cl ⁻ . Cl ⁻ is a spectator ion, but NH ₄ ⁺ is a weak acid that leads to an acidic medium (pH < 7) at equivalence.	0.25																
4- Because the pH at equivalence point is less than 7, the convenient indicator to detect the equivalence point is that having pH range included between two values less than 7. This indicator is the methyl red.	0.75																
5- First the solution is yellow (solution (S) base), it becomes red after the equivalence point.	0.5																
II-																	
<table border="1"> <thead> <tr> <th></th> <th>N₂ (g)</th> <th>H₂ (g)</th> <th>NH₃ (g)</th> <th>n total (mol)</th> </tr> </thead> <tbody> <tr> <td>Initial state</td> <td>n</td> <td>3 n</td> <td>0</td> <td>4 n</td> </tr> <tr> <td>Equilibrium state</td> <td>n (1-α)</td> <td>3 n (1-α)</td> <td>2 n α</td> <td>2 n (2-α)</td> </tr> </tbody> </table>		N ₂ (g)	H ₂ (g)	NH ₃ (g)	n total (mol)	Initial state	n	3 n	0	4 n	Equilibrium state	n (1-α)	3 n (1-α)	2 n α	2 n (2-α)	1	
	N ₂ (g)	H ₂ (g)	NH ₃ (g)	n total (mol)													
Initial state	n	3 n	0	4 n													
Equilibrium state	n (1-α)	3 n (1-α)	2 n α	2 n (2-α)													
2- In a gaseous mixture, the partial pressure P _i = $\frac{n_i}{n_t} \times P$. Then: $P(N_2) = \frac{n(1-\alpha)}{2n(2-\alpha)} \times P = \frac{(1-\alpha)P}{2(2-\alpha)}$ $P(H_2) = \frac{3n(1-\alpha)}{2n(2-\alpha)} \times P = \frac{3(1-\alpha)P}{2(2-\alpha)}$ and $P(NH_3) = \frac{2n\alpha}{2n(2-\alpha)} \times P = \frac{2\alpha P}{2(2-\alpha)} = \frac{\alpha P}{(2-\alpha)}$	1.5																
3- The value of α that verify the relation P (NH ₃) = 2 P (N ₂) is given by the relation : $\frac{\alpha P}{(2-\alpha)} = 2 \frac{(1-\alpha)P}{2(2-\alpha)}$. Where α = 0.5 .	0.5																
4- To prepare 1 L of (S ₀) the needed number of mol is: 1 x 10.8 = 10.8 mol of ammonia. n (NH ₃) = 2 n α. We have then: 10.8 = 2 n α = 2 n x 0.5 so n = 10.8 mol.	0.75																

Third Exercise (7 points)
Sodium Thiosulfate

Expected Answer	Mark	Comment
I-		
1- To prepare this solution, we need n = C x V mol hydrated sodium thiosulfate of mass m = C x V X M, with: M = 2x23+2x32+3x16+2x18 = 194 g.mol ⁻¹ . We have: m = 0.5 x 500 x 10 ⁻³ x 194 = 48.5 g.	0.75	
2- The needed material to carry out this preparation includes: sensitive balance, 500 mL volumetric flask, funnel, watch-glass and spatula.	1.25	
II-		
1- n (S) at the end of the reaction = n (S ₂ O ₃ ²⁻) _{initial} = CxV = 0,4x50x10 ⁻³ = 2x10 ⁻² mol.	0.5	

2- At $t = 0$, $n(S) = 0$ and at $t_{1/2}$, $n(S)_{\text{formed}} = \frac{n(S)_{\infty}}{2} = 1 \times 10^{-2} \text{ mol}$



3- The value of the rate is equal to the slope of the tangent on the curve: $n(S) = f(t)$. An observation shows that this slope decreases when the time increases. We conclude that the rate decreases as time increases.

In fact, when time increases the concentration of the reactants decreases that leads to a decrease in the rate of the reaction. The concentration of reactants is then the kinetic factor which is responsible for this variation.

III-

1- The advantage to put the beaker that contains the reactional medium into an ice-water bath is to block the reaction.

2- Based on the equation of reaction (1)

$n(\text{H}_2\text{O}_2)_{\text{reacting}} = n(\text{I}_2)_{\text{formed}} = n(\text{H}_2\text{O}_2)_{\text{at } t=0} - n(\text{H}_2\text{O}_2)_{\text{remaining at } t}$

$n(\text{I}_2)_{\text{formed}} = n_0 - n_t$

Based on the equation of reaction (2):

$n(\text{I}_2)_{\text{formed (1)}} = n(\text{I}_2)_{\text{reacting in (2)}} = \frac{n(\text{S}_2\text{O}_3^{2-})_{\text{added}}}{2} = n_0 - \frac{C \times V_E}{2}$

Where $n_t = n_0 - \frac{C \times V_E}{2}$

3- At $t \infty$ $n_t = 0 \Rightarrow V = n_0 - \frac{C \times V_{E\infty}}{2} = 0 \Rightarrow V_{E\infty} = \frac{2n_0}{C} = \frac{2 \times 0.01}{0.5}$

= 0,04 L = 40 mL

4- Where volume of thiosulfate exceeds 40 mL, the excess of thiosulfate in the strongly acid medium undergoes self oxidation-reduction that leads to the formation of fine solid particles of sulfur.