وزارة التربية والتعليم العالي المديرية العامة للتربية دائرة الامتحانات	امتحانات الشهادة الثانوية العامة فرع : العلوم العامة	الدورة العادية للعام ٢٠٠٨
	مسابقة في مادة الكيمياء المدة ساعتان	الاسم: الرقم:

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 three following exercises:

First exercise (6 points)
Esterification Reaction

Esterification is a reversible reaction, between a carboxylic acid and an alcohol, represented by the following equation: $R - COOH + R' - OH \rightleftharpoons R - COOR' + H_2O$

Given:

	Formula	M ($g.mol^{-1}$)	d ($g.mL^{-1}$)
Ethanoic acid	$CH_3 - COOH$	60	1.05
Methanol	$CH_3 - OH$	32	0.79

- Concentrated sulfuric acid is a dehydrating agent.

1- Preliminary Study

A mixture of ethanoic acid and methanol, heated in the presence of few drops of concentrated sulfuric acid, leads to the formation of an ester and water.

1.1- Write the equation of this reaction.
1.2- Why is the mixture heated?
1.3- If a mixture of ethanoic acid and methanol is heated in the absence of sulfuric acid, will the reaction take place? Justify.
1.4- Specify the effect of the use of a greater amount of concentrated sulfuric acid on the result of this esterification reaction.

2- Experimental Study

In two balloons A and B, methanol is mixed with ethanoic acid as follows:
* Balloon A contains a mixture of 20.25 mL of methanol and 30 g of acid.
* Balloon B contains a mixture of 20.25 mL of methanol and 60 g of acid.
The two balloons are closed and heated, at the same temperature, till equilibrium is established.
2.1- Show that the reacting mixture in balloon A is equimolar.
2.2- If the reaction is made complete, calculate the number of moles of ester formed in each balloon.
2.3- An acid-base titration permits to determine the number of moles of ethanoic acid remaining in each balloon: in balloon A 0.17 mol and in balloon B 0.58 mol.
2.3.1- Determine the composition in moles of the mixture at equilibrium in each balloon.
2.3.2- Specify if the percentage yield of esterification, in each balloon, changes upon adding few drops of sulfuric acid at the beginning of the experiment.

Second exercise (7 points)
Kinetics at Constant Temperature

Iodide ions react with peroxydisulfate ions according to the following equation:

$$S_2O_8^{2-} + 2\,I^- \rightarrow 2\,SO_4^{2-} + I_2$$

The aim of this exercise is to study the kinetics of this reaction, in the absence and in the presence of iron II ions respectively, at constant temperature.

Given: M (KI) = 166 $g.mol^{-1}$.

1- Preparation of Solutions

Available materials and chemicals

- Sensitive balance	- Spatula
- 100 and 500 mL round bottom flask	- Watch glass
- 50 mL, 100 mL and 200 mL erlenmeyers	- Solid potassium iodide KI
- 50 mL, 100 mL and 200 mL volumetric flasks	- Solution S_0 2 $mol.L^{-1}$ of $Na_2S_2O_8$
- 5 mL, 10 mL and 20 mL volumetric pipets	- Distilled water
- Pipette filler	

1.1- Show, from the above list, the essential materials to prepare a solution S_1 of volume V_1 = 200 mL of potassium iodide of concentration C_1 = 0.8 $mol.L^{-1}$.

1.2- Describe briefly the procedure to prepare, starting with S_0, a solution S_2 of volume V_2 = 200 mL of concentration C_2 = 0.2 $mol.L^{-1}$of sodium peroxydisulfate.

2- Kinetic Study

A reacting system constituted of a volume V_1 = 100 mL of S_1 and a volume V_2 = 100 mL of S_2 is prepared. The system is maintained at a constant temperature T during all the time of the reaction. Samples of the reacting mixture are taken and titrated in order to determine the concentration of the iodine formed.

The same experiment (system identical to the above one) is repeated again, at the same temperature T, but in the presence of few drops of iron II sulfate solution at the beginning of the reaction.

The results of the two experiments are given in the following table:

t (min)	0	2.5	5	10	15	20	30
$[I_2]$ ($10^{-3}mol.L^{-1}$) without Fe^{2+}	0	9.5	17.2	29.6	38.7	45.7	55.8
$[I_2]$ ($10^{-3}mol.L^{-1}$) with Fe^{2+}	0	15.0	27.0	46.5	61.0	72.7	91.2

2.1- Ice-water is immediately added to each sample before titration. Specify the purpose of this addition.

2.2- Plot on the same graph the curve $[I_2]$ = f(t) of the experiment without Fe^{2+} and the curve $[I_2]$ = g(t) of the experiment with Fe^{2+}. Take the following scale: 1 cm for 2 min in abscissa and 1 cm for $10.0x10^{-3}$ $mol.L^{-1}$ in ordinate.

2.3- Determine the limiting reactant in the reacting system. Ddeduce the concentration $[I_2]$ at $t = \infty$.

2.4- Determine the half-life in each of the two experiments. Conclude the role of Fe^{2+} ions.

2.5- Determine the instantaneous rate of appearance of I_2 at instant t = 20 min in the two experiments. Is the result obtained compatible with the conclusion of the part 2.4.

Third exercise (7 points)
Ethanol

Ethanol is a chemical compound of great industrial and commercial importance. It is used in many chemical reactions and also utilized as an intermediate for the synthesis of several chemical compounds.

1- Industrial Preparation of Ethanol

A gaseous mixture of molar composition of 40 % of ethene and 60 % of water vapor is introduced in an industrial production unit, maintained at a temperature of 300 ^{O}C and under a constant pressure P = 70 atm. A chemical equilibrium is established according to the following equation:

$$C_2H_{4\,(g)} + H_20_{(g)} \rightleftarrows C_2H_5OH_{(g)}$$

The constant K_p of the above equilibrium is equal to $1.54\text{x}10^{-3}$ at 300^{o}C.

1.1- Copy and complete the following table in terms of n and α; where α is the degree of conversion of ethene to ethanol.

	C_2H_4	H_2O	C_2H_5OH
Initial state (mol)	2 n	3 n	
Equilibrium state (mol)			

1.2- Show that the expression of the constant K_p of this equilibrium, in terms of α and P is as follows: $K_p = \frac{\alpha(5-2\alpha)}{(1-\alpha)\times(3-2\alpha)}\times\frac{1}{P}$.

1.3- The mathematical resolution of the quadratic equation found in the preceding question gives the two following values of α: 0.06 and 2.44; deduce the percentage of the transformation of ethene to ethanol at 300 ^{O}C.

1.4- Specify the effect of the increase in temperature on this percentage of transformation, knowing that the above synthesis reaction of ethanol is exothermic.

2- Principle Uses of Ethanol

Ethanol is used in the preparation of several organic compounds such as: ethanal, ethylethanoate …

2.1- In the presence of copper and in absence of air, the oxidation of ethanol, at 300 ºC, to form ethanal is represented by the following equation:

$$CH_3 - CH_2OH \rightarrow CH_3 - CHO + H_2$$

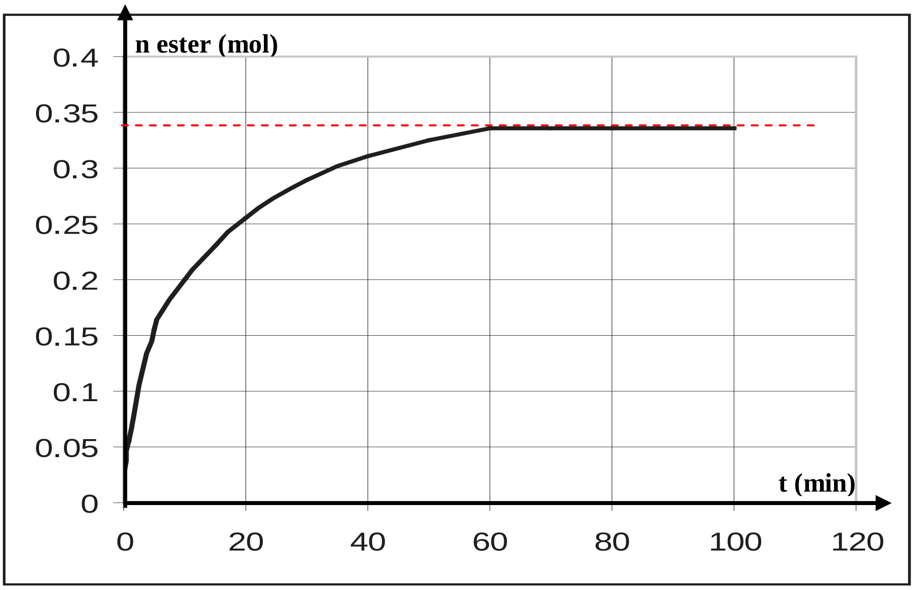
2.1.1- Why is this oxidation described as mild?

2.1.2- Write the equation of the reaction of the mild oxidation of ethanol into ethanal in the presence of air.

2.2- In the laboratory, a mixture of 0.5 mol of ethanoic acid and 0.5 mol of ethanol is heated, in the presence of concentrated sulfuric acid.

2.2.1- Write the equation of this reaction.

2.2.2- The study of the variation of the number of moles of ester formed versus time gives the following result:



Draw out from this experiment two characteristics of this reaction.

2.2.3- Calculate the percentage yield of this reaction.

2.2.4- Study the effect of each one of the following proposals on the percentage yield of this reaction:

- The water formed is removed progressively from the reactional medium.
- Use an initial mixture of 5 mol of ethanoic acid and 5 mol ethanol under the same experimental conditions.

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مشروع معيار التصحيح	مسابقة في مادة الكيمياء المدة ساعتان	الاسم: الرقم:

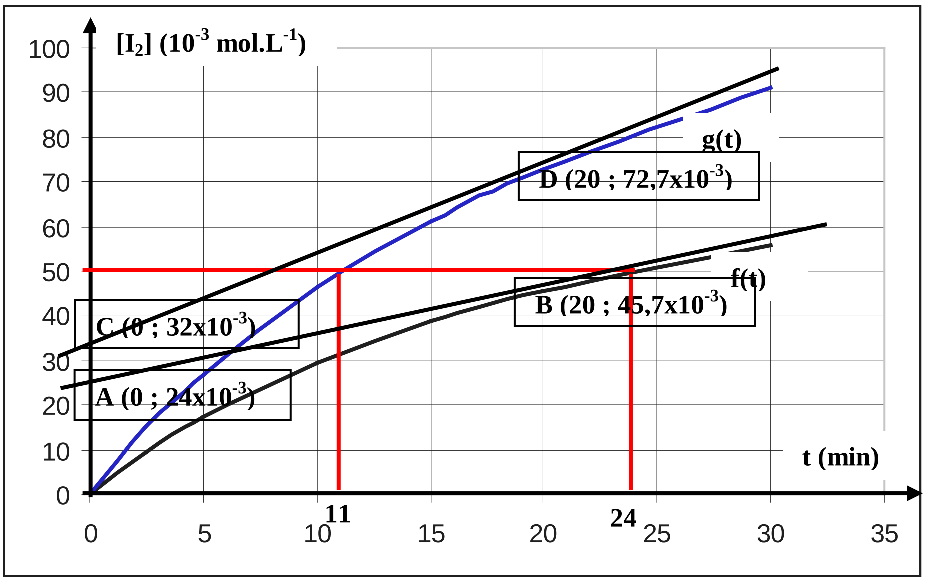
Marking scheme

First exercise (6 points)

<table>
<tr><th>Part of the Q</th><th>Answer</th><th>Mark</th></tr>
<tr><td>1.1</td><td>The equation of the reaction is:
$CH_3 - COOH + CH_3 - OH \rightleftharpoons CH_3 - COOCH_3 + H_2O$</td><td>0.5</td></tr>
<tr><td>1.2</td><td>Heating is to increase the rate of the reaction.</td><td>0.25</td></tr>
<tr><td>1.3</td><td>If a mixture of ethanoic acid and methanol is heated in the absence of sulfuric acid, the reaction would take place. Indeed, sulfuric acid is a catalyst which is necessary to increase the rate of a possible reaction. But it cannot make a reaction take place.</td><td>0.5</td></tr>
<tr><td>1.4</td><td>Sulfuric acid is a dehydrating agent, it eliminates water, which is one of the products of the reaction. This makes this reaction move in the direction of the formation of ester (Le Chatelier' principle: a system in equilibrium, undergoes a modification, partly hinders, if it is possible, this modification). Thus, the yield of the esterification increases.</td><td>0.75</td></tr>
<tr><td>2.1</td><td>The number of moles of methanol is:
$n_{alcohol} = \frac{m(alcohol)}{M(alcohol)} = \frac{\mu \times V}{M} = \frac{0.78 \times 20.25}{32}$ = 0.5 mol.
$n_{acid} = \frac{m(acid)}{M(acid)} = \frac{30}{60}$ = 0.5 mol. The two numbers are equal, the mixture is equimolar.</td><td>1</td></tr>
<tr><td>2.2</td><td>If the reaction is made complete:
In balloon A, n(ester) = n = 0.5 mol.
In balloon B, alcohol is the limiting reactant (0.5 mol and 1 mol), n(ester) = n = 0.5 mol.</td><td>0.75</td></tr>
<tr><td>2.3.1</td><td>n(ester) formed = n(water) formed = n(acid)reacting = n – n remaining.
n(alcohol) remaining = n - n(acid) reacting.
<table>
<tr><th></th><th>Alcohol</th><th>Acid</th><th>Ester</th><th>Water</th></tr>
<tr><td>Balloon A</td><td>0.17</td><td>0.17</td><td>0.33</td><td>0.33</td></tr>
<tr><td>Balloon B</td><td>0.08</td><td>0.58</td><td>0.42</td><td>0.42</td></tr>
</table></td><td>1.75</td></tr>
<tr><td>2.3.2</td><td>By adding, at the beginning, few drops of sulfuric acid, the yield of the reaction does not vary; equilibrium is reached in a shorter time, because sulfuric acid is a catalyst.</td><td>0.5</td></tr>
</table>

Second exercise (7 points)

Part of the Q	Answer	Mark
1.1	The mass of KI necessary to prepare 200 mL of solution S_1 is: m = n (KI)×M(KI) = C_1×V×M (KI) = $0.8\times200\times10^{-3}\times166$ = 26.56 g. The materials to prepare S_1 comprise: **sensitive balance;** spatula and watch glass to weigh 26.56 g of solid KI and a 200 mL **volumetric flask to measure 200 mL** volume of S_1.	**0.75**
1.2	By dilution n of solute does not change: n = C×V = C_2×V´. Thus, to prepare 200 mL of S $_2$ starting with S_0 it is necessary to take away:	**0.75**

	$V = \frac{C_2 \times V_2}{C} = \frac{0.2 \times 200}{2} = 20$ mL. Using a **volumetric pipette of 20 mL** provided with a pipette filler, take 20 mL of solution S_0; pour them in a **200 mL volumetric flask;** fill this flask, to the line mark, with distilled water; stopper it and shake it several times to homogenize.	
2.1	The immediate addition of ice-water makes the concentration of the reactants decreases and lowers the temperature. The concentration of reactants and the temperature are two kinetic factors. This addition blocks the reaction.	**0.75**
2.2	The two curves are:  	**1.25**
2.3	Limiting reactant: $R(I^{-}) = \frac{0.8 \times 100 \times 10^{-3}}{2} = 0.04 > R(S_2O_8^{2-}) = \frac{0.2 \times 100 \times 10^{-3}}{1} = 0.02.$ $S_2O_8^{2-}$ is thus the limiting reactant. According to the stoichiometric coefficients of the equation, we have: $[S_2O_8^{2-}]_0 = [I_2]_\infty = \frac{0.02}{200 \times 10^{-3}} = 0.1$ mol.L^{-1}.	**1**
2.4	The half-life is the time needed to consume half of the limiting reactant, or the time needed to form half of $[I_2]_\infty$. $[I_2]_{t1/2} = \frac{0.1}{2} = 50.0\text{x}10^{-3}$ mol.L^{-1}. This concentration corresponds to: $t_{1/2}$ (without Fe^{2+}) = 24 min and $t_{1/2}$ (with Fe^{2+}) = 11 min. We conclude that the presence of Fe^{2+} ions increases the reaction rate at a constant temperature. It is a catalyst.	**1**
2.5	Instantaneous rate $r_{t = 20\ min}$ is equal to the slope of the tangent to the curve $[I_2] = f(t)$ and that of the tangent to the curve $[I_2] = g(t)$ at the points of abscissa t = 20. Without Fe^{2+}, $r_{t = 20} = \frac{(45.7 - 24) \times 10^{-3}}{20} \approx 1.1 \times 10^{-3}$ mol.L^{-1}.min^{-1}. With Fe^{2+}, $r_{t = 20} = \frac{(72.7 - 33) \times 10^{-3}}{20} \approx 2.0 \times 10^{-3}$ mol.L^{-1}.min^{-1}. The comparison of the two values shows that the result obtained is compatible with the conclusion of the part 2.4.	**1.5**

Third exercise (7 points)

<table>
<tr><th>Part of the Q</th><th>Answer</th><th>Mark</th></tr>
<tr><td>1.1</td><td>According to the value of α which is equal to $\frac{n(C_2H_4)_{transformed}}{n(C_2H_4)_{initial}}$, it is deduced that $n(C_2H_4)$ transformed = 2 n.α
And according to the equation of the reaction, we can write:
<table>
<tr><th></th><th>C_2H_4</th><th>H_20</th><th>C_2H_5OH</th></tr>
<tr><td>Initial state (in mol)</td><td>2 n</td><td>3 n</td><td>0</td></tr>
<tr><td>Euilibrium state (in mol)</td><td>2 n – 2 n α</td><td>3 n – 2 nα</td><td>2 nα</td></tr>
</table>
</td><td>1.75</td></tr>
<tr><td>1.2</td><td>$$K_p = \frac{P_{C_2H_5OH}}{P_{C_2H_4}.P_{H_2O}} = \frac{\frac{2n\alpha}{n(5-2\alpha)}\times P}{\frac{2n(1-\alpha)}{n(5-2\alpha)}\times P.\frac{n(3-2\alpha)}{n(5-2\alpha)}\times P} = \frac{\alpha(5-2\alpha)}{(1-\alpha)(3-2\alpha)}\times\frac{1}{P}$$
With n(5- 2α) = n(gaseous mixture) obtained at equilibrium.</td><td>0.5</td></tr>
<tr><td>1.3</td><td>The value of α could not exceed the value 1; according to the two values given, we choose α = 0.06. The percentage of transformation is equal to 6 %.</td><td>0.5</td></tr>
<tr><td>1.4</td><td>According to Le Chatelier's principle, the increase in the temperature supports the endothermic reaction; it is the reaction of dehydration of ethanol. Thus the percentage of transformation of ethene decreases.</td><td>0.5</td></tr>
<tr><td>2.1.1</td><td>The oxidation is known as being mild because the carbon chain of alcohol is preserved and only the functional carbon undergoes oxidation.</td><td>0.5</td></tr>
<tr><td>2.1.2</td><td>The equation of this reaction is:
$CH_3 - CH_2OH + \frac{1}{2}O_2 \rightarrow CH_3 - CHO + H_2O$</td><td>0.5</td></tr>
<tr><td>2.2.1</td><td>The equation of this reaction is:
$CH_3 - CH_2OH + CH_3 - COOH \rightleftharpoons CH_3 - COO\ CH_2 - CH_3 + H_2O$</td><td>0.5</td></tr>
<tr><td>2.2.2</td><td>According to the graph, we deduce that:
After 60 min, the quantity of ester formed does not vary and is equal to 0.33 mol lower than the awaited maximum quantity: thus this reaction is slow and limited.</td><td>0.75</td></tr>
<tr><td>2.2.3</td><td>The percentageyield of this reaction :
$R = \frac{n(ester)equilibrium}{n(ester)maxim\ expected} x100 = \frac{0.33}{0.50} x100 = 66\ \%$.</td><td>0.5</td></tr>
<tr><td>2.2.4</td><td>- If water is progressively removed as it is formed:
The equilibrium moves in the direction of formation of ester and water and the yield of the reaction increases.
- If the mixture remains equimolar under the same experimental conditions, n(ester) formed at equilibrium increases and n(ester) maximum expected increases but the ratio of these two amounts does not change; thus the yield of the reaction does not change.</td><td>1</td></tr>
</table>