وزارة التربية والتعليم العالي المديرية العامة للتربية دائرة الامتحانات الرسميّة	امتحانات الشهادة الثانوية العامة فرع: العلوم العامة	دورة العام ٢٠١٦ الاستثنائيّة الجمعة ٥ آب ٢٠١٦
	مسابقة في مادة الكيمياء المدة: ساعتان	الاسم: الرقم:

This Exam Includes Three Exercises. It Is Inscribed on 3 Pages Numbered From 1 to 3. The Use of A Non-programmable Calculator is Allowed.

Answer the three following Exercises:

First Exercise (7 points)
Benzoic Acid

Benzoic acid is a white solid of formula C_6H_5COOH. It is used as a food preservative.

Given:

- M(benzoic acid) = 122 g.mol^{-1}
- pKa(H_3O^+/H_2O) = 0 ; pKa ($C_6H_5COOH/ C_6H_5COO^-$) = 4.2; pKa (H_2O/HO^-) = 14

1- Study of a Benzoic Acid Solution

A volume V= 500.0 mL of an aqueous benzoic acid solution (S) of concentration C = 0.01 mol.L^{-1} is prepared.

1.1- Calculate the mass m of benzoic acid needed for the preparation of the solution (S).
1.2- Choose, from the following list , the materials needed for this preparation :
volumetric flask: 250 and 500 mL ; Erlenmeyer flask 500 mL ; precision balance ; spatula ; watch glass and pH-meter.
1.3- Write the equation of the reaction of benzoic acid with water.
1.4- Justify that benzoic acid is a weak acid knowing that the pH of the solution (S) is equal to 3.1

2- Reaction of Benzoic Acid with a Strong Base

A volume of a sodium hydroxide solution ($Na^+ + HO^-$) is added to a sample of the solution (S) .

2.1- Place, on a pKa axis, the different conjugate acid/base pairs involved.
2.2- Write the equation of the reaction that took place between the strongest acid and the strongest base.
2.3- Show that this reaction is complete.

3 - Reaction of Benzoic Acid with a Weak Base

A volume V_1 of the solution (S) is added to a volume V_2 = 200 mL of a sodium benzoate solution ($C_6H_5COO^-$ + Na^+) of concentration C = 0.01 mol.L^{-1}.
The pH of the obtained buffer solution is equal to 4.0

3.1- Determine the volume V_1.
3.2- List the characteristics of the obtained solution.

Second Exercise (6 points)
Preparation of an Ester

Available is a monofunctional organic compound (A) of saturated non cyclic hydrocarbon chain. The analysis of this compound shows the following results:

- % by mass of (C) = 48.65 ; % by mass of (H) = 8.11 and the remaining is oxygen.
- M(A) = 74 $g.mol^{-1}$.

Given: M (H) = 1 $g.mol^{-1}$; M (C) = 12 $g.mol^{-1}$; M (O) = 16 $g.mol^{-1}$.

1- Molecular Formula of (A)

1.1- Show that the molecular formula of (A) is $C_3H_6O_2$
1.2- Write the condensed structural formulas of the possible isomers of (A).
1.3- Identify the compound (A) knowing that the pH of an aqueous solution of (A) is distinctly less than 7.0

2- Esterification Reaction

A mixture of 0.2 mol of the acid (A) and 0.2 mol of 2-methyl-1-propanol is heated. Heating is stopped after a certain time. (All the constituents of the reacting mixture form one single liquid phase).
The obtained organic compound (B) is extracted. After the purification of this product, it is weighed and its mass is found to be 13 g.

2.1- Write, using the condensed structural formulas of the organic compounds, the equation of the reaction that takes place.
2.2- Give the systematic name of the organic compound obtained.
2.3- Determine the yield of this reaction.
2.4- Specify whether the equilibrium state is reached at the end of heating , knowing that the equilibrium constant K of this reaction is equal to 4.12
2.5- A compound (C) can be used instead of the acid (A) to prepare the organic compound (B).
  2.5.1- Write the possible condensed structural formulas of the compound (C).
  2.5.2- List two advantages of using the compound (C).

Third Exercise (7 points)
Kinetic Study

Ditertbutyl peroxide (A) dissociates in gaseous phase according to a slow and complete reaction, the equation of which is:

$$(CH_3)_3C - O - O - C(CH_3)_{3\,(g)} \rightarrow 2\, CH_3 - CO - CH_{3\,(g)} + C_2H_{6\,(g)}$$

At constant temperature T = 420 K, n_0 mol of the compound (A) is introduced in an evacuated reactor of constant volume V . At different instants of time t of the evolution of reacting system, the pressure P of the gaseous mixture is measured.

The concentration of ethane C_2H_6 is deduced at these instants of time t.
The results are listed in the table below:

t (min)	2	6	10	14	18	26	34	46
$[C_2H_6]$ (10^{-4}mol.L^{-1})	1.5	3.6	5.8	7.8	9.7	13.2	16.0	18.9

Given: Ideal gas constant: R = 0.08 L.atm.K^{-1}. mol^{-1}.

1- Preliminary Study

1.1- Show that the initial concentration of the compound (A) is equal to 71.4×10^{-4} mol .L^{-1}, knowing that the pressure P_0, prevailing in the reactor at t = 0, is equal to 0.24 atm.

1.2- Establish the relation among the pressure P of the gaseous mixture at an instant of time t , the pressure x of C_2H_6 at this instant of time t and the initial pressure P_0 .

1.3- Calculate the pressure of the gaseous mixture at the end of the reaction.

2- Kinetic Study

2.1- Plot the curve representing the change of the concentration of C_2H_6 as a function of time: $[C_2H_6]$ = f(t) in the interval of time [0 - 46 min]. Take the following scales:
1 cm for 4 min in abscissa and 1 cm for 2.0×10^{-4} mol.L^{-1} in ordinate.

2.2- Determine the rate of formation of ethane at the instant of time t = 30 min.

2.3- Deduce the rate of formation of propanone at this instant of time.

2.4- Verify whether the half-life time of the reaction is reached in the interval of time: [0 – 46 min].

2.5- The kinetic study realized above is carried out again at a temperature T_1 > T.
Plot, on the same graph of the part 2.1, the shape of the curve representing the change of the concentration of C_2H_6 as a function of time $[C_2H_6]$ = g(t). Justify.

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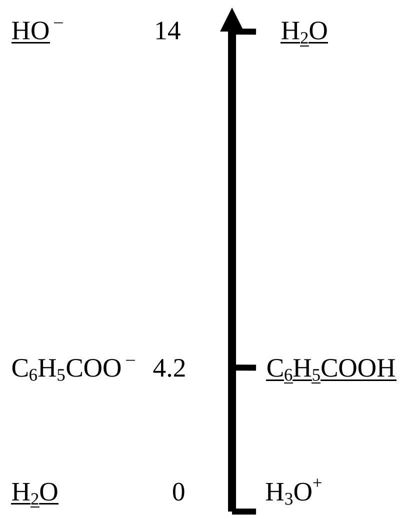
Answer the three following exercises:

First Exercise (7 points)
Benzoic Acid

Part of the Q	Answer	Mark
1.1	n(acid) needed = C ×V = 0.01× 0.5 = 5×10^{-3} mo1 . m(acid) needed = n(acid) ×M(acid) = 5×10^{-3} × 122 = 0.61g .	1
1.2	The materials required for this preparation : Volumetric flask 500 mL ; precision balance ; spatula and watch glass .	1
1.3	The equation of the reaction is: $C_6H_5 - COOH + H_2O \rightleftharpoons C_6H_5 - COO^- + H_3O^+$	0.5
1.4	pH = 3.1 > - log C = - log 0.01 = 2, that characterizes a weak acid. The benzoic acid is a weak acid.	0.75
2.1	The pairs involved on pKa axis are :  pKa axis	0.75
2.2	The equation of the reaction is: $C_6H_5 - COOH + HO^- \rightleftharpoons C_6H_5 - COO^- + H_2O$	0.5
2.3	The constant of this reaction is : $K_r = 10^{pKa(H2O/HO^-) - pKa(C6H5-COO H/C6H5-COO^-)} = 10^{14-4.2} > 10^4$ Therefore , this reaction is complete	0.75
3.1	The initial quantities of the acid $C_6H_5 - COOH$ and its conjugate base $C_6H_5 - COO^-$ are conserved in the solution obtained. According to the relation: $pH = pKa + \log\frac{[C_6H_5COO^-]}{[C_6H_5COOH]}$, then $\frac{[C_6H_5COO^-]}{[C_6H_5COOH]} = 10^{4-4.2} = 0.63$	1

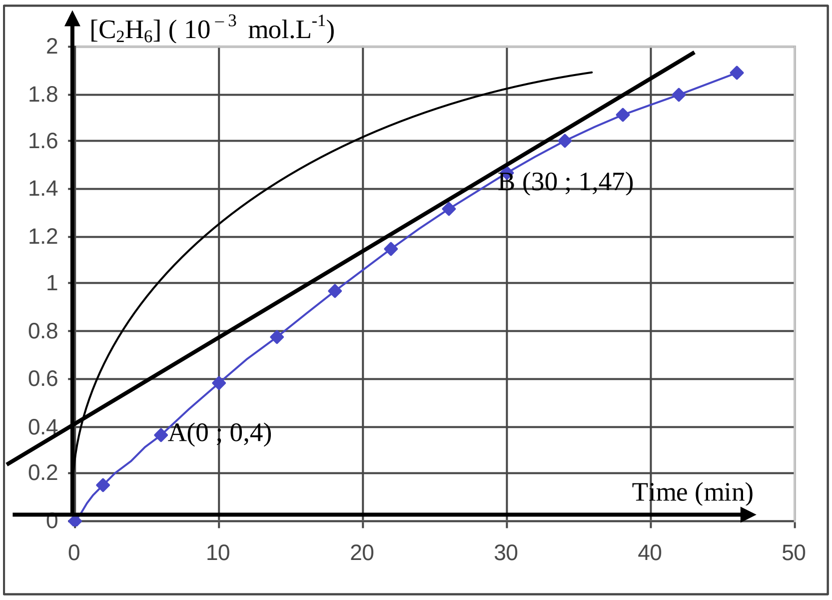
	with $\frac{[C_6H_5COO^-]}{[C_6H_5COOH]} = \frac{C.V_2 / V(mixture)}{C.V_1 / V(mixture)} = \frac{V_2}{V_1}$ where V_1 = 317.4 mL.	
3.2	It is a buffer solution , the pH of which varies slightly upon: - addition of a moderate quantity of a strong acid; - addition of a moderate quantity of a strong base; - or by dilution.	**0.75**

Second Exercise (6 points) G.S
Preparation of an Ester

Part of the Q	Answer	Mark
1.1	let $C_xH_yO_z$ be the molecular formula of the compound (A). According to the law of definite proportions : $\frac{M(A)}{100} = \frac{12x}{\%(C)} = \frac{1y}{\%(H)} = \frac{16\,z}{\%(O)}$ with %(O) = 100 – (% C + % H) = 100 –(48.65 + 8,11) = 43,24 and M(A) = 74. then : x = 3 ; y = 6 ; z = 2 and the molecular formula of (A) is : $C_3H_6O_2$.	**0.75**
1.2	The condensed structural formulas of the possible isomers are: CH_3– CH_2– C– OH ; H – C – O – CH_2 – CH_3 and CH_3 – C – O – CH_3 ‖ ‖ ‖ O O O	**0.75**
1.3	pH = 3.1 < 7, this means that compound (A) has an acid character. So (A) is propanoic acid of formula $CH_3 – CH_2 – COOH$.	**0.5**
2.1	The equation of the reaction is: CH_3 – CH_2 – C – OH + CH_3 – CH – CH_2OH ⇌ CH_3 – CH_2 – C – O – CH_2 – CH – CH_3 + H_2O ‖ | ‖ | O CH_3 O CH_3	**0.75**
2.2	Its systematic name is : 2-methylpropylpropanoate	**0.25**
2.3	The yield of the reaction is: Yield $= \frac{n(ester)\,actual}{n(ester)\,theoretical} = \frac{n_1}{n_2}$ With $n_1 = \frac{m(ester)\,actual}{M(ester)} = \frac{13}{130} = 0.1 mol.$ and n_2 = n(acid) initial = 0.2 mol. Where Yield = 0.5 , the % yield is 50%.	**1**

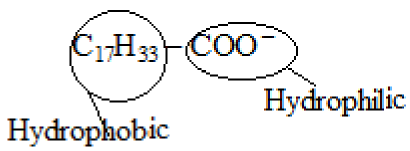
2.4	Alcohol + acid ⇌ ester + water Initial state 0.2 mol 0.2 mol 0 0 final state 0.1mol 0.1 mol 0.1 mol 0.1mol The quotient of this reaction : $Q_r = \frac{[ester][water]}{[acid][alcohol]} = \frac{n(ester)/V \times n(water)/V}{n(acid)/V \times n(alcohol)/V} = \frac{0.1 \times 0.1}{0.1 \times 0.1} = 1$ Since $Q_r < K$, therefore the equilibrium is not reached.	**1**
2.5.1	The possible formulas are: $CH_3 - CH_2 - CO - Cl$ and $CH_3 - CH_2 - CO - O - CO - CH_2 - CH_3$	**0.5**
2.5.2	The two advantages are : The esterification reaction becomes complete and fast.	**0.5**

Third exercise (7 points)
Kinetic Study

Part of the Q	Answer	Mark
1.1	According to the equation of ideal gases , $[A]$ initial $= \frac{P_o}{RT} = \frac{0.24}{0.08 \times 420} = 71.4 \times 10^{-4}$ mol.L^{-1}.	**0.75**
1.2	At each instant t, we have: $P(A) = P_0 - x$; P(propanone) = 2 x and P(ethane) = x. The total pressure is therefore : $P = P_0 - x + 2x + x = P_0 + 2x$.	**1**
1.3	At the end of reaction , P(gaseous mixture) = $3 \times P_o = 3 \times 0.24 = 0.72$ atm.	**0.75**
2.1	The curve is :  	**1**
2.2	The rate of formation of ethane is defined by: $r = \frac{d[C_2H_6]}{dt}$. It is value is equal to the slope of the tangent drawn on the curve $[C_2H_6] = f(t)$ at a point of abscissa t = 30 min. $r\,(C_2H_6)_t = \frac{y_B - y_A}{t_B - t_A} = \frac{(1.47 - 0.4) \times 10^{-3}}{30} = 3.57 \times 10^{-5}$ mol.L^{-1}.min^{-1}.	**1**

2.3	From the equation, the coefficient of propanone is twice that of ethane; consequently, r (propanone) = 2 r(C_2H_6) = 7.14×10^{-5} mol.L^{-1}.min^{-1}.	**0.5**
2.4	Half-life time of the reaction is the time at which the concentration of C_2H_6 attains half its maximal value. [C_2H_6] at $t_{1/2}$ = [C_2H_6] max / 2 = [A] initial / 2 = 35.7×10^{-4} mol.L^{-1} > [C_2H_6] at t = 46 min. So the half-life time is not reached.	**1**
2.5	When the temperature increases, the rate of formation of ethane increases. At each instant, [C_2H_6] at T_1 > [C_2H_6] at T.	**1**

Second Exercise (6 points) L.S
Hydrolysis of esters

Part of the Q	**Answer**	**Mark**
1.1	The systematic name of isoamyl acetate is: 3- methylbutylethanoate.	**0.25**
1.2	The molecule of isoamyl acetate is not chiral since it does not contain an asymmetric carbon.	**0.5**
1.3	The equation of this hydrolysis reaction is : $CH_3 - CO - O - CH_2 - CH_2 - CH(CH_3) - CH_3 + H_2O \rightleftharpoons CH_3 - COOH + HOCH_2 - CH_2 - CH(CH_3) - CH_3$	**0.5**
1.4	the two products are : ethanoic acid and 3-methyl-1-butanol.	**0.5**
2.1	the convenient materials needed to realize reflux heating are: Heating mantle, round bottom flask and condenser.	**0.75**
2.2	The saturated solution of sodium chloride helps the precipitation almost complete of soap since soap is insoluble in this solution.	**0.5**
2.3.1	Hydrophilic: loves water. Hydrophobic: hates water.	**0.5**
2.3.2	The formula is : 	**0.5**
2.4	$\text{yield} = \frac{n(\text{soap})\ \text{actual}}{n(\text{soap})\ \text{theoretical}} = \frac{n_1}{n_2}$ With $n_1 = \frac{m_{act}}{M(\text{soap})} = \frac{11.2}{304} = 3.7\times10^{-2}$ mol. and $n_2 = 3 \times n(\text{olein initial}) = 3 \times 2.0\times10^{-2} = 6.0\times10^{-2}$ mol. then yield = 0.616	1
2.5	- Using an initial quantity of oleine less than 2.0×10^{-2} mol: n_1 decreases and n_2 decreases but the ratio of these two quantities does not change (at the same experimental conditions); then the yield of reaction does not change . - Extend the heating time: n_1 increases but the quantity n_2 does not change (at the same experimental conditions); then the yield of the reaction increases.	0.5 0.5