LEBANESE UNIVERSITY
FACULTY OF ENGINEERING

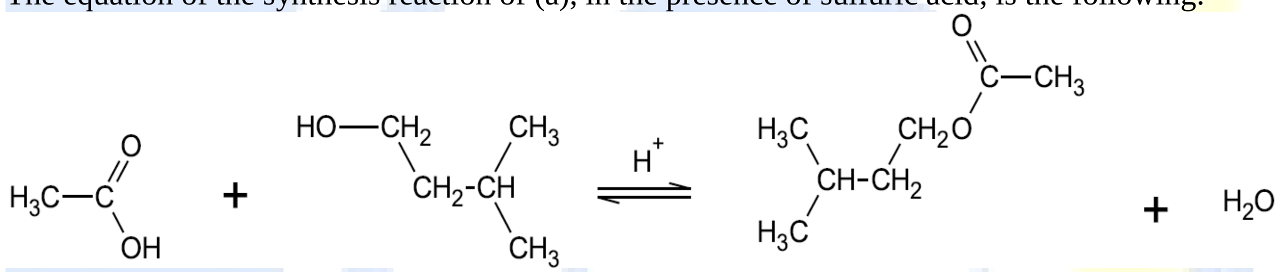
الجامعة اللبنانية
كلية الهندسة

Entrance Exam (2019 – 2020) **Chemistry Exam** **Duration: 1 h**
7 July 2019

Answer the Following two Exercises:

Exercise 1 (10 points)
Isoamyl Acetate

Esters volatile organic compounds often used to produce synthetic flavors and fragrances. They are prepared by action of carboxylic acid molecule on an alcohol. It should be noted that rather the use of the carboxylic acid, acid anhydride or acid chloride can be used. The reactions starting from acyl chlorides are sharp. The mixture needs to be cooled. The reactions starting from acid anhydrides are less sharp and slower (anhydrides are less reactive).
The ester studied in this exercise is isoamyl acetate, an ester whose flavor and odor are those of banana.
The equation of the synthesis reaction of (a), in the presence of sulfuric acid, is the following:



Acetic acid isoamylic alcohol isoamyl acetate (E)

The equation of the synthesis reactions of isoamyl acetate by two other means of synthesis (b and c) are the following:
Synthesis (b): isoamylic alcohol + (B) →. Isoamyl actate (E) + acetic acid
Synthesis (c): isoamylic alcohol + (D) →. Isoamyl actate (E) + HCl
The aim of this exercise is to compare several protocols of synthesis of the noted isoamyl acetate (E).
Given: Physicochemical Characteristics:

Chemical Species	Physical Properties
Isoamylic alcohol	M = 88.1 $g.mol^{-1}$; ρ = 0.81 $g.mL^{-1}$. Slightly soluble in water
Acetic acid	M = 60.1 $g.mol^{-1}$; ρ = 1.05 $g.mL^{-1}$. Very soluble in water
Isoamyl acetate	M = 130.2 $g.mol^{-1}$; ρ = 0.87 $g.mL^{-1}$. Slightly soluble in water
Sulfuric acid	Very soluble in water
Acetic anhydride	M = 130.2 $g.mol^{-1}$; T_{bo} = 139°C; ρ = 1.08 $g.mL^{-1}$. Soluble in water

1. Reaction of Isoamyl Acetate Synthesis

1.1. Give the systematic names of acetic acid, isoamylic alcohol and isoamyl acetate.

1.2. Identify the reactants (B) and (D) in the two syntheses (b) and (c).

2. Synthesis (a) of Isoamyl Acetate

Synthesis (a) is carried out at a laboratory by mixing 20 mL (1.84×10^{-1} mol) of isoamylic alcohol, 15 mL (2.62×10^{-1} mol) of acetic acid, 1 mL of concentrated sulfuric acid, and some grains stone sandpapers in a balloon which is heated maintaining a soft boiling during 30 min to reach the equilibrium state. This synthesis permits to obtain a volume of ester equal to 20.4 mL.

2.1. Determine the value of the volume of ester expected during this synthesis if the transformation were complete.

2.2. If this synthesis is carried out with an equimolar mixture of reactants, the percentage yield will be equal to 65 %. Did the choice to introduce one reactant in excess compared to an equimolar mixture of the two reactants permits to increase the percentage yield of the synthesis? Justify.

3. Synthesis (b) of Isoamyl Acetate

Synthesis (b) is carried out by mixing 20 mL of isoamylic alcohol, 25 mL (2.30×10^{-1} mol) of acetic anhydride, 1 mL of concentrated sulfuric acid, and some grains stone sandpapers in a balloon which is heated maintaining a soft boiling during 25 min to reach the final state.

This synthesis permits to obtain a volume of ester equal to 27 mL.

Determine the value of the volume of the ester expected during this synthesis. Conclude.

4. Synthesis (c) of Isoamyl Acetate

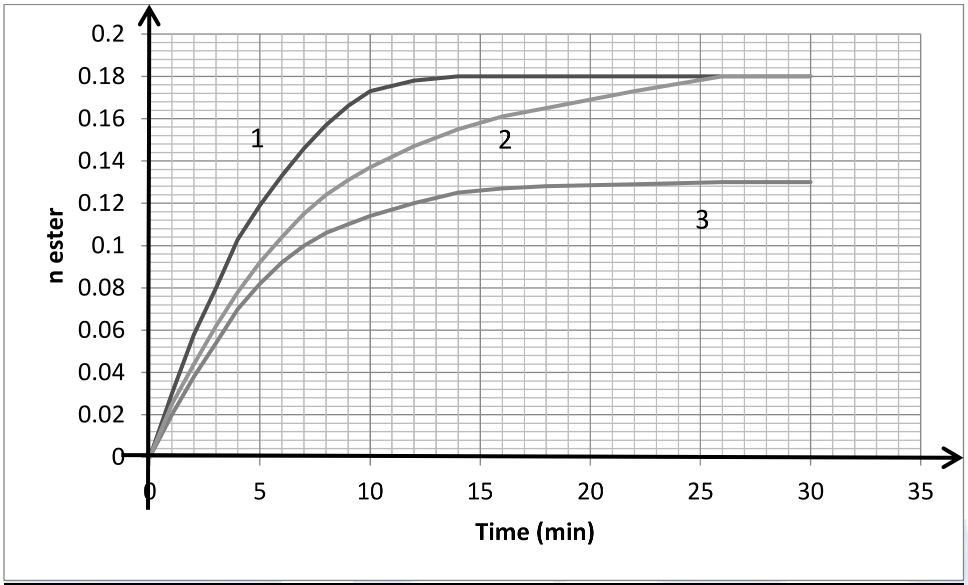
Synthesis (c) is carried out while following the same approach of the synthesis (b) and replacing acid anhydride by the same quantity of acid chloride and by cooling the reactional medium, we obtain the same volume of ester as in the synthesis (b), the final state is reached in a few minutes (about 10 min).

This synthesis permits to obtain a volume of ester equal to 27 mL.

Deduce, from the experimental results of the syntheses (a), (b) and (c) the characteristics of these three syntheses.

5. Kinetic Follow-up of the Esterification Reaction

By suitable protocols we follow the kinetic study of the three synthesis (a), (b) and (c), the results of this study are given in the following graph:



5.1. Associate, with justification, each curve of the graph with the corresponding synthesis.
5.2. Determine graphically the half-life of the reaction for each of the synthesis (b) and (c).

Exercise 2 (10 points)

The Receipt of my Grandmother

Is there limestone around the tap? It is true that is its preferred place! Why? Because it is always that there is a little water which stagnates…Result, $CaCO_3$ limestone settles and it is not easy to remove! Fortunately, my grandmother has an effective trick to eliminate limestone without rubbing during hours. Its tip is to use a mixture of white vinegar and bicarbonate. Look at, it is very simple:

How to make
1. In a clean container, pour one liter of quite hot water.
2. Add 1/4 of withe vinegar glass.
3. Add 1/4 of bicarbonate glass. Attention that foams!
4. Add water in order to have a total volume of two liters.
5. Close it well.
6. Shake it until the bicarbonate is completely dissolved.
7. Pour this domestic product on limestone around the tap.
8. Let act on hour.
9. Rinse with a clean sponge.
10. Wipe with a rag in microfibers.

Students of the final years have to carry out this receipt according to the following approaches:

- They prepare 100 mL of a solution S_1 by diluting 5 times of a withe vinegar containing 7 % by mass of acetic acid CH_3COOH and of density $\rho = 1.05$ g.mL^{-1}.
- They prepare 100 mL of a solution S_2 by dissolving 0.21 g of sodium bicarbonate $NaHCO_3$ in water in order to obtain 100 mL of solution.
- **Given:**

Molar mass in g.mol^{-1}: $NaHCO_3$ $M_1 = 84$, $CaCO_3$ $M_2 = 100$

Solubility in g·L^{-1}: $NaHCO_3$ $s_1 = 87$, $Ca(HCO_3)_2$ $s_2 = 400$

$pKa_1 = 4.76$ (couple CH_3COOH/ CH_3COO^-)

$pKa_2 = 6.33$ (couple $CO_{2\ dissolved}, H_2O / HCO_3^-$)

$pKa_3 = 10.33$ (couple HCO_3^- / CO_3^{2-})

1- Preparation of Solutions S_1 and S_2

1.1. Indicate, from the opposite list, the essential materials to prepare the solutions S_1 and S_2.

- Balance, spatula, watch glass, funnel, glass stirrer.
- Beckers100 mL, Erlenmeyer 200 mL, Volumetric flasks 50 mL, 100 mL,
- Graduated cylinders 50 mL.
- Pipet 2 mL, 10 mL, 20 mL.

1.2. Show that the concentration of S_1, in ethanoic acid, and that of S_2, in sodium bicarbonate, is almost equal $C = 2.5\times10^{-2}$ mol.L^{-1}.

2- Study of Solutions S_1 and S_2

2.1. Write the equation of the reaction of ethanoic acid with water.
2.2. Show that the pH of solution S_1 is is greater than 1.6.
2.3. Verify the value of the pH of S_1, $pH_1 = 3.2$.
2.4. Evaluate an order of the size (±2) of pH of solution S_2. Justify

3- Scaling Power

Into acid medium, calcium carbonate converts into calcium bicarbonate $Ca(HCO_3)_2$, very soluble in water. This transformation is done in naturel environment starting from carbonic acid H_2CO_3:

$$CaCO_3 \text{ (insoluble)} + H_2CO_3 \text{ (soluble)} \rightarrow Ca(CO_3H)_2 \text{ (soluble)}$$

Dissolved in water, the ion HCO_3^- avoid the precipitation, usually so easy, of Ca^{2+} ions giving calcium carbonate or limestone. Here is the origin of its lenitive properties.

S_1 and S_2 are mixed and the mixture is poured on a tap covered by layer of fur $CaCO_3$.

3.1. Place on a vertical axis of pKa the couples intervening by pouring the solution of the mixture on the tartar tap.
3.2. Write the equation of formation of H_2CO_3 in the mixture of solutions S_1 and S_2.
3.3. Calculate the mass of the limestone removed by the mixture of S_1 and S_2.

Entrance Exam (2019 – 2020) **Solution of chemistry** **7 July 2019**

Exercice 1 (10 points) **Isoamyl Acetate**

Q	Expected Answer	Mark
1.1	- Acetic acid is ethanoic acid. - Isoamylic alcohol is 3-mthyl-1-butanol. - Isoamylic acetate is 3-methylbutylethanoate.	3×0.5
1.2	**(D)** Ethanoyle chloride: CH_3—C (=O)Cl **(B)** Etanoic anhydride: CH_3—C (=O)—O –C(=O)—C H_3	2×0,5
2.1	If the reaction is complete and according to the equation of the reaction, to consume 1 mol of isoamylic alcoholmol 1 mol of acetic acid should be introduced. Thus when 0.18 mol of alcohol is consumed, 0.18 mol of acid is consumed. There would remain 0.26 – 0.18 = 0.08 mol of acid. The acetic acid is well in excess. If the reaction is complete and according to the equation of the reaction, the quantity of ester formed is equal that of the limiting reactant consumed which is isoamylic alcohol. Therefore n(E) = 0.18 mol of ester . $n_E = \frac{\rho_E . V_E}{M_E}$ then $V_E = \frac{n_E . M_E}{\rho_E}$ $V_E = \frac{0,18 \times 130,2}{0,87}$ = 28 mL	1. 1
2.2	A volume of 20.4 mL of ester is obtained whereas with a percentage yield of 100 % we could hope obtain 28 mL. The yield is: $R = \frac{V_{E\ Réel}}{V_E}$ $R = \frac{20.4}{28} = 0.74 \text{ or } 74\%$. It is noted that this yield is higher than the 65% obtained with an equimolar mixture. The introduction of a reagent in excess makes it possible to improve the yield of the synthesis.	1.5
3.	According to the stoichiometric ratios, alcohol is the limiting reactant and n(E) = n(alcohol) = 0.183 mol and its volume is: $V_{(b)} = \frac{nM}{\rho} = \frac{0.183 \times 130.2}{0.87} = 27.38 mL$. The expected volume attendu is almost equal that of the obtained volume, the yield is: $R_{(b)} = \frac{27}{27.38} = 0.9861 = 98.61\%$. The reaction is almost complete.	1.5

4.	With the same quantity of chloride we obtained same volume of ester but during a shorter time. We then draw the characteristics from the three syntheses as follows: Esterification with: - the carboxylic acid is slow, reversible (limited) and athermic; - the acyle chloride is fast, complete and exothermic; - the acid anhydride is complete with a mean rate.	1.5
5. 1	The curve 1 corresponds to the synthesis (**c**), the curve 2 corresponds to the synthesis (b) and the curve 3 corresponds to the synthesis (a). Indeed, the two syntheses (b) and (c) give the same quantity of ester (two curves 1 a nd 2 have the same limit, with an almost complete reaction). But the synthesis (c) is faster, the limit is reached with a duration shorter than with the synthesis (b), moreover at any moment the rate in the synthesis (c) is greater than in the synthesis (b). The synthesis (a) leads to a smaller quantity (the reaction is not complete in this case) and the limit is reached for a longer length of time.	0. 5
5. 2	The half-life time of the reaction is time with the end of which the quantity of formed ester is equal to half of its quantity obtained at the end of the reaction. For the two syntheses (b) and (c) we have: $n(E)_{1/2} = \frac{0.183}{2} = 0.0915$mol which corresponds, according the curve 2, to $t(b)_{1/2}$= 5 min and according the curve 1, to $t(c)_{1/2}$ = 3.2 min.	0.5

Exercise 2 (10 points)

The Receipt of my Grandmother

Q	Expected Answer	Mark
1.1.	To prepare S_1, the equipment comprises the volumetric pipet of 20 mL, the volumetric flask of 100 mL and a beaker. To prepare S_2, the equipment comprises the volumetric flask of 100 mL, the balance, the watch glass, the spatula, the funnel, the glass stirrer and a beaker.	1.5
1.2.	A volume of 2 mL of vinegar weighs 2×1.05 = 2.1 g and contains 2.1×7/100 = 0.147 g of acetic acid. the concentration of S_1 is then: $C_1 = \frac{n}{V} = \frac{m}{M \times V} = \frac{0,147}{60 \times 100 \times 10^{-3}} = 2.45 \times 10^{-2}$ mol.L^{-1}. $C_2 = \frac{0.21}{84\ X\ 100\ X 10^{-3}} = 2.5\ X\ 10^{-2}\ mol.L^{-1} \approx\ C_1 = C$	1.5

2.1.	The equation is: $CH_3COOH + H_2O \rightleftarrows CH_3COO^- + H_3O^+$.	0.5
2.2.	Since it is a weak acid, pH> -logC, pH> -log 2.5×10^{-2}, pH is higher than 1.6.	1
2.3.	$Ka_1=10^{-pka1}=10^{-4.76}=1.74\times10^{-5}$ $Ka1 = \frac{[H3O+][Ch3COO-]}{[CH3COOH]} = \frac{10^{-3,2}x10^{-3,2}}{(2,510^{-2}-10^{-3,2})} = 1.63\times10^{-5}$	1
2.4.	Draw the prevalence axis of the species of the conjugate acid/base pairs: pKa_2= 6.33 (couple CO_2 dissolved,H_2O / HCO_3^-) pKa_3=10.33 (couple HCO_3^- / CO_3^{2-}) pH axis → H_2CO_3 dissolved 6.3 $HCO3^-$ 10.3 CO_3^{2-} HCO_3^- is the prevalence species and $6.3 < pH < 10.3$	1
3.1.	pKa **Axis of pKa** ↑ HO- 14 H2O CO_3^{2-} 10.33 HCO_3^- HCO_3^- 6.3 CO_2 H_2O ,H_2CO_3 CH_3COO^- 4.76 CH_3COOH H_2O 0 H_3O^+	1
3.2.	The equation of the formation reaction of H_2CO_3: $HCO_3^- + CH_3COOH \leftrightarrows CH_3COO^- + H_2CO_3$	1
3.3	$nCaCO_3$ reacting = n H_2CO_3 reacting=2.5×10^{-3}mol. m $CaCO_3$ reacting = $2.5\times10^{-3}\times100 = 0.25$ g	1.5