UNIVERSITE LIBANAISE

FACULTE DE GENIE

الجامعة اللبنانية
كلية الهندسة

Entrance Exam 2014 – 2015 **Duration: 1H**

First Exercice (9 points)
Preparation of an Ester

Consider an organic compound (A), with a saturated open carbon chain, of empirical formula CxHyO.
It is required, starting from this compound, to carry out several chemical reactions producing an ester (E). Represent, in all the reactions requested in this exercise, the organic compounds by their condensed structural formulas.

Given:

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

1- Identification of the Compound (A)

A quantitative analysis carried out on the compound (A) gave the following results:
% mass of carbon = 66.67 and % mass of hydrogen = 11.111.
1.1- Show that x = 4 and y = 8.
1.2- A sample of (A) reacts with the 2,4-D.N.P.H gives a yellow precipitate.
Specify the functional group of (A) and write its possible condensed structural formulas.
1.3- A sample of (A) reacts with Fehling's solution gives a red precipitate.
Deduce the chemical family of (A) and give its name, knowing that its carbon chain is not branched.

2- Chemical Reactions From (A)

The quantity available of (A) is divided into two parts.
The first part is mixed with an excess of an acidified potassium permanganate solution; then the organic compound formed is collected and noted (X).
The second part is heated, in the presence of a catalyst of hydrogenation; then the organic compound formed is collected and noted (Y).
2.1- Give the condensed structural formula and the name of (X).
2.2- Give the condensed structural formula and the name of (Y).

3- Preparation of an Ester

Let react an equimolar mixture of the two compounds (X) and (Y), until having a constant quantity of ester equalizes with 0.4 mol. The equation of the corresponding reaction is:

$$X + Y \rightleftharpoons E + H_2O$$

3.1- Write the condensed structural formula of ester E. Give its name.
3.2- Show that the initial quantity of X (or of Y) is n = 0.6 mol, knowing that the constant of this equilibrium is $K_c = 4.0$.
3.3- We use instead of X the same quantity of its derivative chlorinated to prepare the ester E.
3.3.1- Write the condensed structural formula of this derivative and give its name.
3.3.2- Calculate, then, the quantity of ester formed at the end of this reaction.

Second Exercise (11 points)
Buffer Solution

Starting from a hydrochloric acid solution S of molar concentration $C = 1.0\times10^{-2}$ mol/L, it is required to prepare one liter of a buffer solution of pH = 3.5 by adding a mass m of sodium methanoate solid $HCO_2Na_{(s)}$ which dissociates completely in water according to the following equation:

$$HCO_2Na(s) \rightarrow Na^+_{(aq)} + HCO_2^-(aq) :$$

It is supposed that there is no variation of volume in this preparation.

Given:

- Constant of the conjugate acid/base pair (HCO_2H/ HCO_2^-): pKa = 3.75.
- Molar mass in g/mol: M(H) = 1 ; M(C) = 12 ; M(O) = 16; M(Na) = 23.

1- Calculate the pH of the solution S.
2- Write the equation of the reaction between hydrochloric acid H_3O^+ and $HCO_2^-(aq)$ ion and determine its constant Kr.
3- Justify that hydrochloric acid is the limiting reactant in order to prepare the above buffer solution of pH=3.5.
4- Methanoic acid is a weak acid.
4.1- Write the equation of the reaction between this acid and water.
4.2- Give the expression of the constant of acidity Ka of the conjugate acid/base pair $HCO_2H(aq)/HCO_2^-(aq)$.
5- Knowing that the quantity of matter brought by $HCO_2Na_{(S)}$ is found in HCO_2H (aq) and $HCO_2^-(aq)$:
5.1- Express $[HCO_2^-(aq)]_f + [HCO_2H]_f$ in the term of the mass m of sodium methanoate.
5.2- Determine the value of the concentration $[HCO_2^-(aq)]_f$ in term of m.
6- The solution is electrically neutral.
6.1- Establish the relation between the concentrations of the various species charged in this solution.
6.2- Calculate m.

Entrance Exam 2014 – 2015 **Solution of Chemistry** **Duration: 1H**

First Exercise (9 points)
Preparation of an Ester

1- Identification of Compound (A)

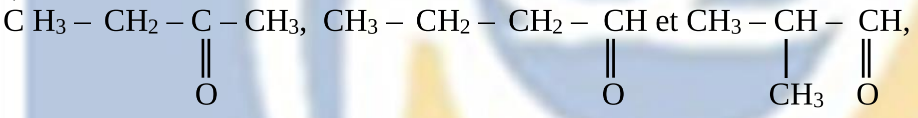
1.1- The law of the definite proportions makes it possible to write:

$$\frac{M}{100} = \frac{12\,x}{66.67} = \frac{y}{11.11} = \frac{16}{22.22}$$

We draw : $x = \frac{16x\,66.67}{22.2x\,12} = 4\,; y = \frac{11.11x16}{22.22} = 8$ (1 point)

1.2- The yellow precipitate identifies the presence of the carbonyl group. (0.25 point).

The carbon chain is saturated and noncyclic. The possible condensed structural formulas of (A) are then:

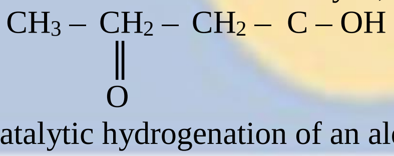


$CH_3 - CH_2 - \underset{\underset{O}{\|}}{C} - CH_3$, $CH_3 - CH_2 - CH_2 - \underset{\underset{O}{\|}}{CH}$ et $CH_3 - \underset{\underset{CH_3}{|}}{CH} - \underset{\underset{O}{\|}}{CH}$, (4× 0.25 point)

1.3- Since (A) reacted with Fehling's solution, it is an aldehyde. (0.25 point)
Its carbons chain is not branched; (A) is thus the butanal. (0.25 point)

2- Chemical Reactions Starting from (A)

2.1- (X) results from the mild oxidation of an aldehyde, (X) is a carboxylic acid it is the butanoic acid of formula:



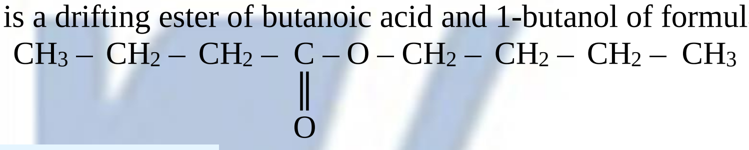
$CH_3 - CH_2 - CH_2 - \underset{\underset{O}{\|}}{C} - OH$ (0.75 point)

2.2- (Y) results from the catalytic hydrogenation of an aldehyde, (Y) is a primairy alcohol it is the butano-1-ol of formula: $CH_3 - CH_2 - CH_2 - CH_2OH$.
(0.75 point)

3- <u>Preparation of an Ester</u>

$$X + Y \rightleftharpoons E + H_2O$$

3.1- E is a drifting ester of butanoic acid and 1-butanol of formula



$$CH_3 - CH_2 - CH_2 - \underset{\underset{O}{\|}}{C} - O - CH_2 - CH_2 - CH_2 - CH_3$$

It is the butyl butanoate. (1 point)

3.2-

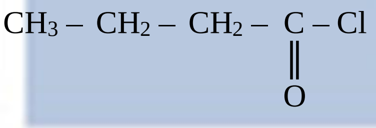
State	Progress (mol)	X +	Y ⇌	E +	H_2O
Initial	x =0	n	N	0	0
Intermediate	x	n –x	n-x	x	x
Equilibrium	xeq	n -0,4	n-0,4	0,4	0,4

$$Kc = \frac{[ester][eau]}{[acid][alc\,ohol]} = \frac{\frac{x}{v} \times \frac{x}{v}}{\frac{n-x}{v} \times \frac{n-x}{v}} = \frac{0.4 \times 0.4}{(n-0.4)(n-0.4)} = 4.\ \text{than :}\ \frac{0,4}{n-0.4} = 2\,.$$

Where : n = 0.6. (2 points)

3.3- .

3.3.1- The derivative chlorinated used to prepare the ester E is the butanoyle chloride of condensed structural formula:



$$CH_3 - CH_2 - CH_2 - \underset{\underset{O}{\|}}{C} - Cl$$

(1 point)

3.3.2-

The reaction of esterification becomes complete, the mixture is equimolar, the reagents change completely and the number of moles of formed ester is 0.6 mol. (1 point)

Second Exercise (11 points)
Buffer Solution

1- pH = -log[H_3O^+] Since hydrochloric acid is strong we have: [H_3O^+] =C= 1×10^{-2} mol.L^{-1} and pH= 2 (1 point)

2- The equation of the reaction between hydrochloric acid H_3O^+ and HCO_2^- (aq) ion is:

$$H_3O^+ (aq) + HCO_2^- (aq) \rightarrow H_2O_{(l)} + HCO_2H_{(aq)}$$ (0.5 point)

$$Kr= \frac{\{HCO_2H\}}{\{H_3O^+\}\{HCOO^-\}} = \frac{1}{Ka} = 10^{3.75} = 5{,}623\times10^3$$ (1 point)

3- The value of the ration [HCO_2^-]f/[HCO_2H(aq)]f in the buffer solution of pH=3.5.

pH = pKa + log $\frac{[base]}{[acide]}$, 3.75 = 3.5 + log$\frac{[base]}{[acide]}$, $\frac{[base]}{[acide]}$= 0.56, then HCO_2^- doesn't react completely and H_3O^+ (aq) is the limiting reactant. (1.5 points)

4-

4.1- The equation of the reaction between methanoic acid and water is.

$$H_2O_{(l)} + HCO_2H_{(aq)} \rightleftharpoons H_3O^+ (aq) + HCO_2^- (aq)$$ (0.5 point)

4.2- The expression of the acidity constant Ka of the conjugate acid/base pair

HCO_2H(aq)/HCO_2^- (aq) is: Ka = $\frac{[H_3O^+][HCO_2^-]}{[HCO_2H]}$ (0.5 point)

5-

5.1- [HCO_2^- (aq)]f + [HCO_2H (aq)]f in term of the mass of sodium methanoate is as :

$C_{initial}$ = [HCO_2^- (aq)]f + [HCO_2H (aq)]f = $\frac{n}{V} = \frac{m}{M\times v}\ \frac{m}{M\times 1} = \frac{m}{68}$. (1.5 point)

5.2- Value of the concentration [HCO_2^- (aq)]f in term of m is:

[HCO_2^- (aq)]f + [HCO_2H(aq)]f = [[HCO_2^- (aq)]f + $\frac{[HCO_2^-]_{(aq)f}}{0.5678}$]= $\frac{m}{68}$; where :

[[HCO_2^- (aq)]f = 5.28×10^{-3} m mol.L^{-1}. (2 points)

6-

6.1- The relation between the concentrations of the various species charged in solution. The species charged in solution are: Na^+, H_3O^+, Cl^- and HCO_2^- such as:

$[Na^+] + [H_3O^+] = [HCO_2^-] + [Cl^-]$. We neglect $[HO^-]$. (1 point)

6.2- Calculation of m.

$[Na^+]$ = initial = $\frac{m}{68}$; $[H_3O^+] = 10^{-pH} = 10^{-3.5}$; $[Cl^-] = C = 1.0\times10^{-2}$. We have then:

$\frac{m}{68} + 10^{-3.5} = 5.28\times10^{-3}$ m $+ 1.0\times10^{-2}$. Where m = 1.028 g (1.5 point)

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