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الجامعة اللبنانية
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Entrance Exam (2016 – 2017) **Chemistry Exam** **Duration: 1 h**
Date: July 2016

Answer the Following Two Exercises:

First Exercise (10 points)
Identification of Some Organic Compounds

Consider four bottles noted A, B, C, and D containing each a mono functional organic liquid different from the other having a saturated non-cyclic carbon chain molecules formed by three carbon atoms. It is required to identify the content of each bottle.

Given: pH range of bromthymol blue is:

Yellow] 6.2 – Green – 7.6 [Blue

A samples of the four bottles are subject of a chemical test. The results are drawn up in the table below:

Test	A	B	C	D
2,4-DNPH	Yellow precipitate	Negative	Yellow precipitate	Negative
Fehling solution	Negative	Negative	Red scurb precipitate	Negative
Bromothymol blue	Green	Yellow	Green	Blue

1- Specify which liquids can be identified without ambiguity. Give the condensed structural formula and the name of each.

2- The content of D is an amine, write the condensed structural formulas of the corresponding possible isomers.

3- The liquid in B gives with the liquid in D the N- isopropylpropanamide (N-1-methyl) ethylpropanamide. Identify the liquid in D.

4- A sample of the bottle C is subject to a catalytic mild oxidation by the oxygen of air, we obtain the product contained in the bottle B. Write, using the condensed structural formula of the organic compounds, the equation of the reaction.

5- Another sample of the bottle C is subject to a hydrogenation reaction, we obtain a product E. Identify E. Write the equation of the reaction of E with the content of B and give the name of the obtained organic product F.

Second Exercise (10 points)
Benzoic Acid and Phenol Behavior in Water

An aqueous solution (S_1) of phenol ($C_6H_5 - OH$) of concentration $C_1 = 1.1\times10^{-2}$ mol.L^{-1} has a $pH_1 = 5.9$. An aqueous solution (S_2) of benzoic acid ($C_6H_5 - COOH$) of the same concentration has a $pH_2 = 3.1$.

1- Write, by justifying the answer, the equation of the reaction of phenol with water.

2- Compare, by justifying the answer, the behavior in aqueous solution of:
   - Phenol and benzoic acid;
   - Phenolate ion and benzoate ion.

3- Locate, on a pKa axis, the pKa_2 of the conjugate acid/base pair phenol/phenolate ion according to the pKa_1 of the conjugate acid/base pair benzoic acid/benzoate ion, knowing they are 4.2 and 10.

4- A solutions of the same volume and the same concentration of sodium benzoate, phenol, benzoic acid and sodium phenolate are mixed.
   4.1- Justify which of two reactions is more advanced that of benzoate ion with phenol or that of benzoic acid with phenolate.
   4.2- Write the equation of the reaction that took place.
   4.3- Calculate the pH of the obtained solution. (Take $10^{2.9} = 800$)

5- Calculate the volume of a sodium hydroxide solution of concentration $C_B = 0.01$ mol.L^{-1} that should be added to 50 mL of the above benzoic acid solution to prepare a buffer solution of pH = 4.2.

Entrance Exam (2016 – 2017) **Chemistry Solution** **Duration: 1 h**
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First Exercise (10 points)
Identification of Some Organic Compounds

1- The compound in A gives a yellow precipitate with 2,4-DNPH, it is an aldehyde or a ketone. It gives a negative test with Fehling solution, it is then a ketone which is neutral (green with BTB). Its chain is saturated, non-cyclic and have 3 atoms of carbon: $CH_3 – CO – CH_3$ it is the propanone.

The compound in B gives a negative test with 2,4-DNPH and with Fehling solution, but, it gives a yellow color with BTB it is then an acid of a saturated carbon chain, non-cyclic and have 3 atoms of carbon: $CH_3 – CH_2 – COOH$, it is the propanoic acid.
The compound in C gives a positive test with 2,4-DNPH and with Fehling solution and a green color with BTB, it is then an aldehyde of a saturated carbon chain, non-cyclic and have 3 atoms of carbon: $CH_3 – CH_2 – CHO$, it is the propanal.
The compound in D gives a blue color with BTB thus it is a base, amine of formula C_3H_9N who cannot be identified without ambiguity.

2- The condensed structural formulas of the possible isomers are:
$CH_3 – CH_2 – CH_2 – NH_2$ and $CH_3 – CH(NH_2) – CH_3$.

3- Since this amine gives the amide N- (1-methyl) ethylpropanamide (isopropylpropanamide), it is a primary amine of formula:
$CH_3 – CH(NH_2) – CH_3$ which is: 2-aminopropane (amino-2-propane).

4- The equation of the reaction is:
$CH_3 – CH_2 – CHO + ½ O_2 \rightarrow CH_3 – CH_2 – COOH$

5- The hydrogenation of the propanal gives the compound (E) which is 1-propanol of formula: $CH_3 – CH_2 – CH_2OH$. The equation of the reaction with propanoic acid is:
$CH_3 – CH_2 – COOH + CH_3 – CH_2 – CH_2OH \rightleftarrows CH_3 – CH_2 – COO – CH_2 – CH_2 – CH_3 + H_2O$
The organic product F is the propyl propanoate.

Second Exercise (10 points)
Benzoic Acid and Phenol Behavior in Water

1- The equation of the reaction of phenol with water is:

$C_6H_5 – OH + H_2O \rightleftarrows C_6H_5 – O^- + H_3O^+$.

The concentration is $C_1 = 1.1\times10^{-2}$ mol.L^{-1} and $pH_1 = 5.9$. Phenol is a weak acid because $[H_3O^+] = 10^{-5.9} = 1.26\times10^{-6}$ mol.L^{-1} < ١.١×10^{-2} mol.L^{-1}.

2- The solutions having equal concentrations, we can compare their respective pH: $pH_2 = 3.1$ and $pH_1 = 5.9$. The solution of the strongest acid corresponds to the solution of the smallest pH. Benzoic acid is then the strongest acid. Conversely, phenolate is a base stronger than the benzoate.

3- The smallest acidity constant $pKa_1 = 4.2$ corresponds thus to the strongest acid which is benzoic acid, and the constant $pKa_2 = 10$ corresponds to the weakest acid the phenol :

$$\underset{pKa_1 = 4.2}{C_6H_5 – COOH \mid C_6H_5 – COO^-} \qquad \underset{pKa_2 = 10}{C_6H_5 – OH \mid C_6H_5 – O^-} \longrightarrow$$

4-

4.1-We have $pKa_2 – pKa_1 = 10 – 4.2 = 5.8 > 4$. It is thus the benzoic acid which reacts on phenolate ion and not the inverse, because the constant of the inverse reaction is: $Kr = 10^{-5,8}$.

4.2- The equation of the reaction is:

$C_6H_5 – COOH + C_6H_5 – O^- \leftrightarrows C_6H_5 – COO^- + C_6H_5 – OH$.

4.3- $C_6H_5 - COOH + C_6H_5 - O^- \leftrightarrows C_6H_5 - COO^- + C_6H_5 - OH$.

C	C	C	C
C(1-x)	C(1-x)	C(1+x)	C(1+x)

$10^{5,8} = \frac{C(1+x)C(1+x)}{C(1-x)C(1-x)} = \frac{(1+x)^2}{(1-x)^2}$; $10^{2,9} = \frac{(1+x)}{(1-x)}$; 800 (1-x) = (1+x) ; x = $\frac{799}{801}$;

According to the relation: pH = pKa +log$\frac{[base]}{[acide]}$. We have:

- pH = 10 + log $\frac{1-\frac{799}{801}}{1+\frac{799}{801}} = 10 + log\frac{2}{1600}$ =7,1 or

- pH = 4,2 + log $\frac{1+\frac{799}{801}}{1-\frac{799}{801}} = 4{,}2 + log\frac{1600}{2}$ =7,1

5- According to the relation: $pH = pKa_1 + \log\frac{[C_6H_5 - COO^-]}{[C_6H_5 - COOH]}$. Since $pH = pKa_1 = 4.2$,

we have: $\log\frac{[C_6H_5 - COO^-]}{[C_6H_5 - COOH]} = 0$ and

The equation is: $C_6H_5 - COOH + HO^- \rightarrow C_6H_5 - COO^- + H_2O$

Initial S	CV	C_BV_B	0
Final S	$CV - C_BV_B$	0	C_BV_B

$$\log\frac{\frac{C_BV_B}{V_t}}{\frac{CV - C_BV_B}{V_t}} = \frac{0.01V_B}{1.1\times10^{-2}\times50 - 0.01V_B} = 0 \text{ and}$$

$\frac{0.01V_B}{0.55 - 0.01V_B} = 1$. D'où V_B = 27.5 mL.