Entrance Exam 2005-2006 **CHEMISTRY** **Duration: 1 hour**

Answer the following two exercises

First Exercise (10 points)
Strong Acid and Weak Acid

Consider the following two solutions:

- Aqueous saturated solution (S_1) of benzoic acid (C_6H_5COOH).
- Aqueous solution (S_2) of nitric acid (HNO_3) of molar concentration $C_2 = 8x10^{-3}$ mol.L^{-1}.

The pH of each solution is 3.

Given:

- Solubility of benzoic acid in water: s = 2.4 gxL^{-1}.
- Molar mass of benzoic acid: M = 122 gxmol^{-1}.
- pH range of bromothymol blue : yellow 6 green 7.6 blue.
- The temperature of each of the considered aqueous solutions is 25 °C.

1- Calculate the molar concentration C_1 of the saturated solution (S_1).
2- Show that benzoic acid is a weak acid and nitric acid is a strong one.
3- Write the equation of the reaction of each acid with water.
4- Calculate the ionization coefficient of benzoic acid in (S_1).
5- Show that the pKa of the pair benzoic acid/benzoate ion $C_6H_5COOH/C_6H_5COO^-$) is equal to 4,26
6- Calculate the volume V_2 of nitric acid solution (S_2) that should be added to a volume V_3 = 50 mL of sodium benzoate solution (C_6H_5COONa) of concentration $C_3 = 8x10^{-3}$ mol.L^{-1} in order to obtain a buffer solution of pH = 4,26
Sodium benzoate is completely soluble in water.

Second Exercise (10 points)
Identification of an organic compound

The molecular formula of an organic compound (A) of an open saturated carbon chain is C_4H_8O.

1- Write the condensed structural formulas of possible isomers of (A).
2- Describe a test that allows to identifying the functional group that characterizes these isomers.

3- The mild oxidation of compound (A) with potassium dichromate solution acidified by sulphuric acid solution, gives compound (B). A sample of (B) changes the color of bromothymol blue to yellow. Deduce the systematic name (s) of the isomer (s) that is (are) involved.
4- Compound (B) reacts with $SOCl_2$ to give an organic compound organic (C) of a branched carbon chain. Deduce the condensed structural formula of (A). Write the condensed structural formulas of (B) and (C) and give the systematic name of each.
5- The hydrogenation of (A) gives a compound (D). Write the condensed structural formula of (D) and give its systematic name.
6- Write the equation of the reaction between (C) and (D).

Entrance Exam 2005-2006 **Solution of Chemistry** **Duration: 1 hour**

First Exercise (10 points)
Strong Acid and Weak Acid

1- $n = \frac{n}{M} = \frac{2,4}{122} = 0,01967 mol$

$C_1 = \frac{n_1}{V} = \frac{0,01967}{1} = 0,01967 mol.L^{-1}$

$[C_6H_5COOH] = 0,01967 mol.L^{-1}$

2- Show that HNO_3 is a strong acid?

* S_2 : $C_2 = 10^{-3}$ mol L^{-1}, pH = 3

$[H_3O^+] = 10^{-pH} = 10^{-3}$, $[H_3O^+] = [HNO_3] = 10^{-3}$ mol.L^{-1}

Then the nitric acid is a strong acid.

*Is $[C_6H_5COOH]$ a weak acid? pH = 3

$C_1 = 0,01967 mol.L^{-1}$, there should be $C_1 > [H_3O^+]$

pH = 3 thus $[H_3O^+] = 0^{-pH} = 10^{-3}$ mol.L^{-1} or 0,001 mol.L^{-1}

$C_1 = [C_6H_5COOH] = 0,01967 mol.L^{-1} > [H_3O^+]$

Then benzoic acid is a weak acid.

3- Equation of the reaction of each one of the acid in water : $HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$

While that of C_6H_5COOH, which is a weak acid, is: $C_6H_5COOH + H_2O \rightleftarrows H_3O^+ + C_6H_5COO^-$

4- Let's draw the following table :

	$[C_6H_5COOH]$	$[H_3O^+]$	$[C_6H_5COO^-]$
Initial state	$C_1 = 1,96 .10^{-2}$	0	0
Final state	$C_1 (1-\alpha)$	$C_1 \alpha$	$C_1 \alpha$

$[H_3O^+] = C_1 \alpha$ and $\alpha = \frac{[H_3O^+]}{C_1} = \frac{10^{-3}}{0,0196} \approx 0,05.$ $\alpha = 0, 05$

5- $[C_6H_5COOH] = C_1(1-\alpha) = 0{,}01967\ (1 - 0{,}05) = 0{,}01867$
$[H_3O^+] = [C_6H_5COO^-] = 10^{-3}$

$$K_a = \frac{[H3O^+][C_6H_5COO^-]}{[C_6H_5COOH]} = \frac{10^{-3} \times 10^{-3}}{0{,}01867} = 5{,}356.10^{-5}$$

And $pK_a = -\log Ka = 4{,}26$

6- Buffer solution, pH= $pK_a = 4{,}26$

At half- equivalence; $C_aV_a = \frac{C_bV_b}{2}$

HNO_3 and C_6H_5COONa are totally soluble in water

C_aV_a number of mole of HNO_3 or (H_3O^+)

C_bV_b number of mole of C_6H_5COONa or $(C_6H_5COO^-)$

C_bV_b should be more than C_aV_a in order for $C_6H_5COO^-$ to remain in the solution at the end of the reaction.

$$C_6H_5COO^- + H_3O^+ \rightleftharpoons C_6H_5COOH + H_2O$$

Initial state	C_bV_b	C_aV_a	0
Final state	$C_bV_b - C_aV_a$	0	C_aV_a

The pH of the final solution is written as :

$$pH = pK_a + \log \frac{[C_6H_3COO^-]}{[C_6H_5COOH]} \quad \text{Or,} \quad pH = pK_a$$

we know that $pH = pK_a$: then we deduce that : $\log \frac{[C_6H_3COO^-]}{[C_6H_5COOH]} = 0$

and $[C_6H_3COO^-] = [C_6H_5COOH]$

$C_bV_b - C_aV_a = C_aV_a$ et $C_aV_a = \frac{C_bV_b}{2}$

$C_2\ V_2 = \frac{1}{2}C_3\ V_3\ \ et\ \ V_2 = \frac{C_3V_3}{2C_2} = \frac{8\times10^{-3}\times50}{2\times10^{-3}} = 200mL$

Second Exercise (10 points)
Identification of an organic compound

1- Condensed structural formulas of (A) C_4H_8O and of its isomers :
The carbon chain is saturated on the one hand and non-cyclic on the other hand

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

(A_1): $CH_3 - CH_2 - CH_2 - \underset{\underset{O}{\|}}{C} - H$ aldehyde

or

(A_2): $CH_3 - \underset{\underset{CH_3}{|}}{CH} - \underset{\underset{O}{\|}}{C} - H$ aldehyde

2- Identification :

C_4H_8O + Schiff's reagent $\longrightarrow$ pink color: (A) is an aldehyde

C_4H_8O + Schiff's reactant $\longrightarrow$ remains colorless: (A) is a ketone

3- (A) by mild oxidation $\longrightarrow$ (B)
(B) + Bromothymol blue $\longrightarrow$ yellow color
(B) is an acid and then (A) is an aldehyde

(A_1): $CH_3 - CH_2 - CH_2 - \underset{\underset{O}{\|}}{C} - H$ butanal

(A_2): $CH_3-CH(CH_3)-C(=O)-H$ 2 -methylpropanal

4- Formula of (A):

(B) acid + $SOCl_2$ $\longrightarrow$ compound with a ramified chain (C)

(B) derives from an aldehyde with a ramified chain

$CH_3-CH(CH_3)-C(=O)-H$ 2 -methylpropanal

Condensed structural formulas names

(B) is an acid with a ramified chain

$CH_3-CH(CH_3)-C(=O)-OH$ 2- methylpropanoic acid

(C) is an acyl chloride

$CH_3-CH(CH_3)-C(=O)-Cl$ 2- methylpropanoyl chloride

5- (A) + H_2 $\longrightarrow$ D

$CH_3-CH(CH_3)-C(=O)-H + H_2 \longrightarrow CH_3-CH(CH_3)-CH_2OH$ (D) 2- methyl-1-propan o*l*

6- Equation of the reaction between (C) and (D) is

$$CH_3-CH(CH_3)-C(=O)-Cl + CH_3-CH(CH_3)-CH_2OH \longrightarrow CH_3-CH(CH_3)-C(=O)-O-CH_2-CH(CH_3)_2 + HCl$$

Acyl chloride primary alcohol Ester