

Duration: 1 hour

Entrance Exam 2005-2006

CHEMISTRY

Answer the following two exercises

First Exercise (10 points)
Strong Acid and Weak Acid

Consider the following two solutions:

- Aqueous saturated solution (S₁) of benzoic acid (C₆H₅COOH).
- Aqueous solution (S₂) of nitric acid (HNO₃) of molar concentration $C_2 = 8x10^{-3}$ mol.L⁻¹.

The pH of each solution is 3.

Given:

- Solubility of benzoic acid in water: $s = 2.4 \text{ gxL}^{-1}$.
- 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 C₆H₅COOH/C₆H₅COO⁻) 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

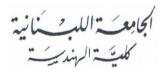
Sodium benzoate is completely soluble in water.

Second Exercise (10 points) Identification of an organic compound

The molecular formula of an organic compound (A) of an open saturated carbon chain is C₄ H₈O.

- 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.

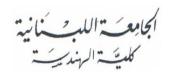




- 3- The mild oxidation of compound (A) with potassium dichromate solution acidified by sulphuric acid solution, gives compound (B). A sample of (B) changes the color of bromothymol blue to yellow. Deduce the systematic name (s) of the isomer (s) that is (are) involved.
- 4- Compound (B) reacts with SOCl₂ 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

$$n = \frac{n}{M} = \frac{2.4}{122} = 0.01967 mol$$

$$C_1 = \frac{n_1}{V} = \frac{0.01967}{1} = 0.01967 mol. L^{-1}$$

$$[C_6 H_5 COOH] = 0.01967 mol. L^{-1}$$

2- Show that HNO₃ is a strong acid?

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

$$[H_3O^+]=10^{-pH}=10^{-3}$$
, $[H_3O^+]=[HNO_3]=10^{-3}$ 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 $C_1 > [H_3O^+]$

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

$$C_1 = [C_6H_5COOH] = 0.01967mol.L^{-1} > [H_3O^+]$$

Then benzoic acid is a weak acid.

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

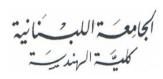
While that of C_6H_5COOH , which is a weak acid, is: $C_6H_5COOH + H_2O \rightleftharpoons H_3O^+ + C_6H_5COO^-$

4- Let's draw the following table:

	[C ₆ H ₅ COOH]	$[H_3O^+]$	$[C_6H_5COO^-]$
Initial state	$C_1 = 1,96 .10^{-2}$	0	0
Final state	$C_1(1-\alpha)$	$C_1 \alpha$	C ₁ α

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





5- $[C_6H_5COOH] = C_1(1-\alpha) = 0.01967(1-0.05) = 0.01867$ $[H_3O^+] = [C_6H_5COO^-] = 10^{-3}$

$$K_a = \frac{[\text{H3O}^+][C_6H_5COO^-]}{[C_6\text{H}_5\text{COOH}]} = \frac{10^{-3} \times 10^{-3}}{0,01867} = 5,356.10^{-5}$$

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

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

At half- equivalence; $C_a V_a = \frac{C_b V_b}{2}$

HNO₃ and C₆H₅COONa are totally soluble in water

 C_aV_a number of mole of HNO₃ or (H₃O⁺)

 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 $C_b V_b$ $C_a V_a$

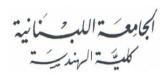
Final state $C_b V_b - C_a V_a = 0$ $C_a V_a$

The pH of the final solution is written as:

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

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





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

$$C_b V_b - C_a V_a = C_a V_a$$
 et $C_a V_a = \frac{C_b V_b}{2}$

$$C_2 V_2 = \frac{1}{2}C_3 V_3 \text{ et } V_2 = \frac{C_3 V_3}{2C_2} = \frac{8 \times 10^{-3} \times 50}{2 \times 10^{-3}} = 200 \text{mL}$$

Second Exercise (10 points) Identification of an organic compound

1- Condensed structural formulas of (A) C₄H₈O and of its isomers:
The carbon chain is saturated on the one hand and non-cyclic on the other hand

$$C H_3 - C H_2 - C - CH_3$$
 ketone $\begin{vmatrix} 1 \\ 0 \end{vmatrix}$

(A₁):
$$C H_3 - C H_2 - C H_2 - C - H$$
 aldehyde

or

(A₂): CH₃ — CH — C — H aldehyde
$$\begin{array}{c|c} CH_3 & O \end{array}$$

2- Identification:

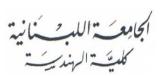
 $C_4H_8O + Schiff's reagent \rightarrow pink color: (A) is an aldehyde$

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

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

(A₁):
$$C H_3$$
— $C H_2$ — CH_2 — C — H butanal C





- 4- Formula of (A):
 - (B) acid + $SOCl_2 \rightarrow compound$ with a ramified chain (C)
 - (B) derives from an aldehyde with a ramified chain

$$CH_3$$
 — CH — C — H 2 -methylpropanal CH_3 — O

Condensed structural formulas

names

(B) is an acid with a ramified chain

$$CH_3$$
 — CH — C — OH 2- methylpropanoic acid CH_3 — OH CH_3 — OH — OH

(C) is an acyl chloride

- 5- (A) + H₂ \rightarrow D CH₃— CH— C — H + H₂ \rightarrow CH₃— CH — CH₂OH (D) 2- methyl-1-propan ol CH₃ O CH₃
- 6- Equation of the reaction between (C) and (D) is

$$CH_{3}-CH-C-Cl+CH_{3}-CH-CH_{2}OH \longrightarrow CH_{3}-CH-C-O-CH_{2}-CH+HCl \\ | | | | | | | | \\ CH_{3} O CH_{3} CH_{3} O CH_{3} O CH_{3}$$

$$Acyl chloride primary alcohol Ester$$