



**Entrance exam 2002-2003**

**Chemistry**

**Duration: 1 hour**

**Acid Base –Buffer solution.**

**Given:** Molar volume of gas  $V_m = 24 \text{ L.mol}^{-1}$

**1) Strong Acid (2 points)**

The solution of hydrochloric acid, which is a strong monoacid, is obtained by dissolving gaseous hydrogen chloride ( $HCl$ ) in water.

- a- Write the equation of the reaction of  $HCl$  with water.
- b- The pH of a hydrochloric acid solution ( $S$ ) is equal to 2,7.  
Calculate the molar concentration of the solution ( $S$ ).
- c- Calculate the volume of hydrogen chloride needed to prepare 2 L of the solution ( $S$ ).

**2) Weak Acid(2 points)**

We consider a solution ( $S_1$ ) of a monoacid  $HA$  of concentration  $C_1$  and  $pH_1 = 2,4$ . Starting with ( $S_1$ ), we prepare a solution ( $S_1'$ ) of concentration  $C_1' = 0,1 C_1$ . The  $pH_1'$  of ( $S_1'$ ) is equal 2,9.

- a- Show that  $HA$  is a weak acid.
- b- Write the equation of the reaction of  $HA$  with water.

**3) Acidity constant of a couple acid/base (3 points).**

The pH of a solution for the acid  $HA$  of concentration  $0,1 \text{ mol.L}^{-1}$  is equal to 2,4.

- a- Determiner the constant of acidity  $K_a$  of the couple  $HA/A^-$
- b- Verify that the  $pK_a$  of this couple is 3,8.

**4) Preparation of a buffer solution.**

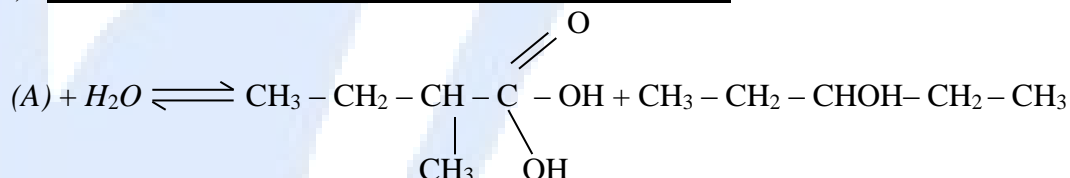
We shall prepare a buffer solution of  $pH = 3,8$  by adding a sodium hydroxide solution of concentration  $0,1 \text{ mol.L}^{-1}$  in 50 mL of  $HA$  acid solution of concentration  $0,1 \text{ mol.L}^{-1}$ .

- a- Determine the volume of the sodium hydroxide solution the twill be added to 50 mL of  $HA$  solution to reach the equivalent point.
- b- Determine the volume of the sodium hydroxide solution the twill be added to 50 mL of  $HA$  solution to obtain a buffer solution of  $pH = 3,8$ .
- c- State the main properties of a buffer solution.



## **II. Identification of some organic compounds.**

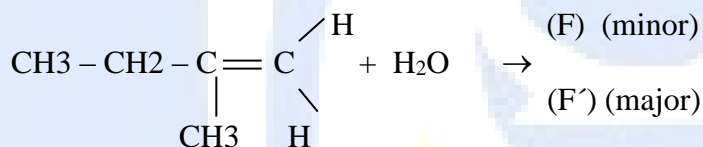
### **1) Hydrolysis of an organic compound (A). (2 points)**



- Identify (A), write the condensed structural formula and give systematic name of (A) according the rules of IUPAC.
- Give two characteristics of the above reaction.

### **2) Hydration of an alkene (2 points).**

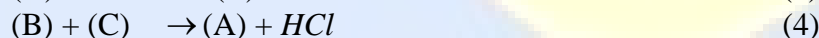
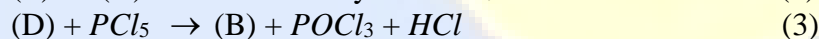
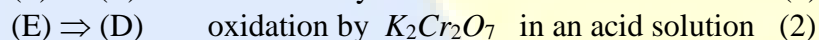
2 – methyl -1-butene undergoes the hydration reaction to gives a minor compound (F) and a compound (F') according the following schematic equation.



Indicate the family of (F) and (F'), write the condensed structural formula, give the systematic name and the class of each one.

### **3) Set of some organic reactions (6 points).**

The organic compounds: (A) , (B) , (C) , (D) , (E) and (F) are reactants or products in the following reactions:



a- Indicate the family of compounds (E) , (D), (B) and (C).

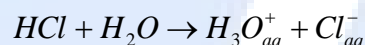
b- Write the condensed structural formula and give the systematic name of each of compounds (E) , (D), (B) and (C).



**I.**

**1) Strong acid**

a- The equation of the reaction between  $HCl$  and water is



b-  $HCl$  in water is a strong acid, Then the reaction is complete.  $pH = 2.7$

According to the equation of the reaction: to one mole of  $HCl$  corresponds one mole of  $H_3O^+$ , hence  $[HCl] = [H_3O^+]$ .

$$[H_3O^+] = 10^{-pH} = 10^{-2.7} = 0,002 \text{ mol. L}^{-1} \text{ as a result : } C = 2.10^{-3} \text{ mol. L}^{-1}$$

c- Volume of  $HCl_{(g)}$  necessary to prepare 2 L of solution (S) :

Let's calculate first the number of moles of  $HCl$  contained in 2 L of solution (S).

$$n_{HCl} + n_{H_3O^+} \text{ therefore } n_{HCl} = CV_s = 2.10^{-3} \times 2 = 4.10^{-3} \text{ mol}$$

The molar volume is  $V_m = 24 \text{ L}$

$$\text{As a result } V_{HCl(gas)} = n. V_m = 4.10^{-3} \times 24 = 96. 10^{-3} \text{ L (gaz).}$$

**2) Weak acid.**

a-  $HA$  is a weak acid :

Solution ( $S_1$ ) :  $HA$  is a monoacid,  $[HA] = C_1$  ;  $pH_1 = 2,4$ .

Solution ( $S'_1$ ) :  $HA$  is a monoacid,  $[HA] = C'_1 = 0,1 C$  ;  $pH' = 2,9$

$HA$  is a monoacid

If  $HA$  is a strong acid, its dissociation in water is then complete and the concentration of  $H_3O^+$  produced should be equal to  $10 [HA]$  initial  $C_1$ , therefore :

$$C_1 = [H_3O^+] = 10^{-pH} = 10^{-2.4} = 0,004 \text{ mol. L}^{-1} \text{ (1) .}$$

The same goes for solution ( $S'_1$ ) this leads to:

$$C'_1 = [H_3O^+] = 10^{-pH} = 10^{-2.9} = 0,00126 \text{ mol. L}^{-1} \text{ (2).}$$

Thus by dividing equations (1) and (2) we get:

$$\frac{C'_1}{C_1} = \frac{0,00126}{0,004} = 0,315.$$

Indeed  $C'_1 = 0,1C_1$  and  $\frac{C'_1}{C_1} = 0,1 \neq 0,315$ , then  $HA$  is a weak acid .

b- The equation of the reaction between  $HA$  and water is :  $HA + H_2O \rightleftharpoons H_3O^+ + A^-$



3)  $[HA] = 0,1 \text{ mol. L}^{-1}$ ;  $pH = 2,4$

a-  $K_a$  of the couple  $HA/A^-$

Let's draw the table that characterizing the equilibrium of the preceding equation:

	$[HA]$	$[H_3O^+]$	$[A^-]$
initial state	0,1	0	0
Final state	$0,1-x$	$x$	$x$

Consequently, we deduce that  $[A^-] = [H_3O^+] = x = 10^{-pH} = 10^{-2,4} = 0,004 \text{ mol. L}^{-1}$

As a result  $[HA] = 0,1-x = 0,1 - 0,004 \approx 0,1$

$$K_a = \frac{[H_3O^+] \times [A^-]}{[HA]} = \frac{10^{-2,4} \times 10^{-2,4}}{10^{-1}} = 10^{-3,8} = 1,58 \cdot 10^{-4}$$

b-Verify that  $pK_a = 3,8$

$$pK_a = -\log K_a = -\log 10^{-3,8} = 3,8$$

4) a-Volume  $V_b$  of the solution of  $NaOH$  solution at equivalence :

$$\text{At equivalence } C_a V_a = C_b V_b \text{ and } V_b = \frac{C_a V_a}{C_b} = \frac{0,1 \times 50}{0,1} = 50 \text{ mL}$$

b- Volume  $V'_b$  of  $NaOH$  solution at  $pH = 3,8$ .

The  $pH$  of the buffer solution is 3,8 :  $pK_a$  of the acid/base couple is equal to 3,8.

So, this solution is obtained at half-equivalence. The volume of  $NaOH$  solution that be

$$\text{added is : } V'_b = \frac{V_b}{2} = \frac{50}{2} = 25 \text{ mL}$$

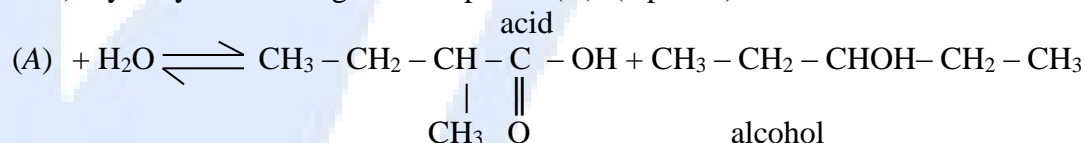
c- The principal properties of this buffer solution are:

- The  $pH$  is equal to  $pK_a$  of the acid/base couple
- The  $pH$  varies a little when adding a moderate amount of strong acid or a strong base or after dilution.



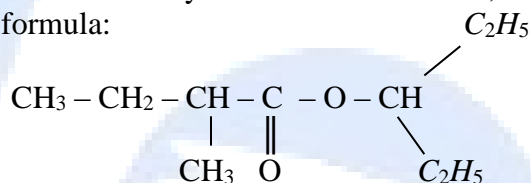
## II. Identification of some organic compounds.

1) Hydrolysis of an organic compound (A). (2 points)



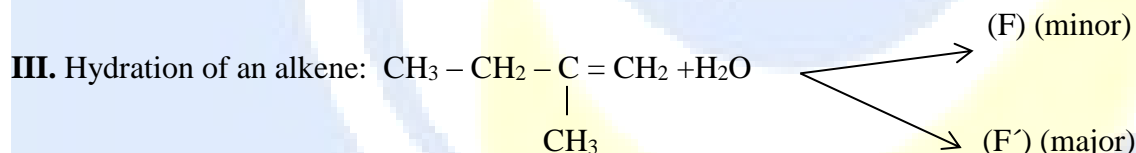
a- Identification of (A) :

The product of hydrolysis of (A) are: A carboxylic acid and an alcohol, hence (A) is an ester having the condensed structural formula:



The name of (A) is 1-ethylpropyl 2-methylbutanoate.

b- The reaction of hydrolysis of the ester is reversible on the one hand and athermic on the other hand.



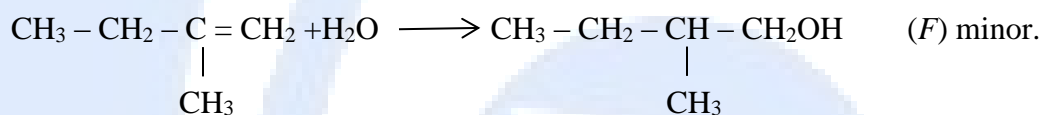
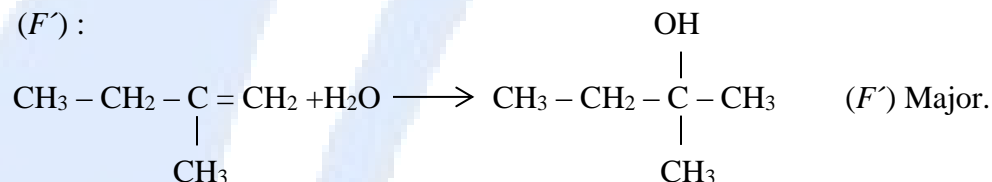
- Function of F and F': The hydration of an alkene produces an alcohol: Hence, the function is an alcohol.

*H* from *H<sub>2</sub>O* is added to one carbon and *HO* is added to the second carbon of the double bond.

According to Markovnikov rule, the hydration of an alkene fixes the hydrogen atom most frequently on the carbon of the double bond that is more hydrogenated, this leads to:



(F') :

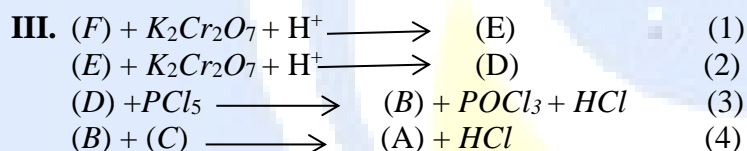


Names :

*F* : 2-methyl-1-butan ol minor

*F'* : 2-methyl-2-butan ol major

Classes: (*F'*) is a tertiary alcohol; (*F*) is a primary alcohol.



a- Functions of each of the compounds (*E*), (*D*), (*B*) and (*C*). Since (*F*) is a primary alcohol, its oxidation produces, first, an aldehyde. hence, (*E*) is an aldehyde.

The aldehyde, in turn, is oxidized into carboxylic acid, therefore, (*D*) is a carboxylic acid.

The reaction between carboxylic acid (*D*) and  $\text{PCl}_5$  produces compound (*B*) that is an acyl chloride.

Acyl chloride (*B*) reacts with (*C*) to give the compound (*A*) and  $\text{HCl}$

(*A*) is an ester, therefore (*C*) is an alcohol.



b- Condensed structural formulas as well as the names of the compounds are :

Formula:

name:

