LEBANESE UNIVERSITY
FACULTY OF ENGINEERING

الجامعة اللبنانية
كلية الهندسة

Entrance exam 2002-2003 **Chemistry** **Duration: 1 hour**

Acid Base –Buffer solution.
Given: Molar volume of gas V_m = 24 $L.mol^{-1}$

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 $mol.L^{-1}$ 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 $mol.L^{-1}$ in 50 mL of HA acid solution of concentration 0,1 $mol.L^{-1}$.

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. <u>Identification of some organic compounds</u>.

1) <u>Hydrolysis of an organic compound (*A*). (2 points)</u>

$$(A) + H_2O \rightleftharpoons CH_3 - CH_2 - \underset{\substack{|\\ CH_3}}{CH} - \overset{\substack{O\\ /\!/}}{\underset{\substack{\backslash\\ OH}}{C}} - OH + CH_3 - CH_2 - CHOH - CH_2 - CH_3$$

a- Identify (A), write the condensed structural formula and give systematic name of (A) according the rules of l'IUPAC.

b- Give two characteristics of the above reaction.

2) <u>Hydratation of an alkene (2 points).</u>

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

$$CH3 - CH2 - \underset{\substack{|\\ CH3}}{C} = \overset{\substack{H\\ /}}{\underset{\substack{\backslash\\ H}}{C}} \quad + \quad H_2O \quad \rightarrow \quad \begin{matrix} (F)\ (minor) \\ (F')\ (major) \end{matrix}$$

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

3) <u>Set of some organic reactions (6 points).</u>

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

(F) ⇒ (E) oxidation by $K_2Cr_2O_7$ in an acid solution (1)
(E) ⇒ (D) oxidation by $K_2Cr_2O_7$ in an acid solution (2)
(D) + PCl_5 → (B) + $POCl_3$ + HCl (3)
(B) + (C) → (A) + HCl (4)

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).

Entrance exam 2002-2003 **Solution of Chemistry** **Duration: 1 hour**

I.

1) Strong acid

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

$$HCl + H_2O \rightarrow H_3O^+_{aq} + Cl^-_{aq}$$

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 $[HCl] = [H_3O^+]$.

$[H_3O^+] = 10^{-pH} = 10^{-2,7} = 0{,}002\ mol.\ L^{-1}$ as a result : $C = 2.10^{-3}\ mol.\ L^{-1}$

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)*.

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

The molar volume is V_m=24 L

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

$C_1 = [H_3O^+] = 10^{-pH} = 10^{-2,4} = 0{,}004\ mol.\ L^{-1}$ (1) .

The same goes for solution (S_1') this leads to:

$C_1' = [H_3O^+] = 10^{-pH} = 10^{-2,9} = 0{,}00126\ mol.\ L^{-1}$ (2).

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

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

Indeed $C_1' = 0{,}1 C_1$ *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) $[HA] = 0,1\ mol.\ L^{-1}$; 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 $[A^-] = [H_3O^+] = x = 10^{-pH} = 10^{-2,4} = 0,004\ mol.\ L^{-1}$

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

$$Ka = \frac{[H_3O]\times[A^-]}{[HA]} = \frac{10^{-2,4}\times 10^{-2,4}}{10^{-1}} = 10^{-3,8} = 1,58.10^{-4}$$

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 :

At equivalence $C_aV_a = C_bV_b$ and $V_b = \frac{C_aV_a}{C_b} = \frac{0,1\times 50}{0,1} = 50mL$

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

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)

$$(A) + H_2O \rightleftharpoons \underbrace{CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle O}{\underset{\|}{C}}-OH}_{\text{acid}} + \underbrace{CH_3-CH_2-CHOH-CH_2-CH_3}_{\text{alcohol}}$$

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:

$$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle O}{\underset{\|}{C}}-O-CH\begin{matrix} \diagup C_2H_5 \\ \diagdown C_2H_5 \end{matrix}$$

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.

III. Hydration of an alkene: $CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2 + H_2O \rightarrow$ (F) (minor) ; (F´) (major)

- Function of F and F´: The hydration of an alkene produces an alcohol: Hence, the function is an alcohol.
  H from H_2O 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') :

$$CH_3-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{C}=CH_2+H_2O \longrightarrow CH_3-CH_2-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_3 \qquad (F') \text{ Major.}$$

$$CH_3-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{C}=CH_2+H_2O \longrightarrow CH_3-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2OH \qquad (F) \text{ minor.}$$

Names :

F : 2-methyl-1-butan o*l* minor

F´: 2-methyl-2-butan o*l* major

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

III. $(F) + K_2Cr_2O_7 + H^+ \longrightarrow (E) \qquad (1)$

$(E) + K_2Cr_2O_7 + H^+ \longrightarrow (D) \qquad (2)$

$(D) + PCl_5 \longrightarrow (B) + POCl_3 + HCl \qquad (3)$

$(B) + (C) \longrightarrow (A) + HCl \qquad (4)$

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 PCl_5 produces compound (*B*) that is an acyl chloride.
Acyl chloride (*B*) reacts with (*C*) to give the compound (*A*) and *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:

$$(E) : CH_3 - CH_2 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - \overset{\displaystyle H}{\overset{/}{\underset{\displaystyle O}{\underset{\backslash\backslash}{C}}}}$$

2-methylbutanal

$$(D): CH_3 - CH_2 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - \overset{\displaystyle OH}{\overset{/}{\underset{\displaystyle O}{\underset{\backslash\backslash}{C}}}}$$

2-methylbutanoic acid

$$(B) : CH_3 - CH_2 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - \overset{\displaystyle Cl}{\overset{/}{\underset{\displaystyle O}{\underset{\backslash\backslash}{C}}}}$$

2-methylbutanoyl chloride

$$(C) : CH_3 - CH_2 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_2 - CH_3$$

3-Pentane o*l*