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Entrance Exam 2004-2005 **Chemistry** **Duration: 1 hour**

First Exercise (6 points)
Ionization coefficient; Dilution influence

I- 1) <u>Concentration of an ethanoic acid solution</u>

A solution of one litter of ethanoic acid, CH_3COOH, is prepared by dissolving of 5.7 mL of pure acid in water.
Show that the concentration C_0, of this solution that is noted S_0, is close to $0.1 mol.L^{-1}$.
<u>Given</u>:
- Density of pure ethanoic acid: $\rho = 1.05$ $g.mL^{-1}$.
- Molar mass of ethanoic acid: $M = 60$ $g.mol^{-1}$.

2) <u>Ionisation coefficient of ethanoic acid</u>

A solution S_1 of ethanoic acid is prepared by diluting, 10 times, of the solution S_0. The measurement of the pH of solution S_1 gives the value $pH_1 = 3.4$.

a- Calculate the concentration C_1 of the solution S_1.
b- Show that the ethanoic acid is a weak acid.
c- Calculate the ionisation coefficient α_1 of ethanoic acid in this solution S_1. We remind you that the ionisation coefficient is obtained by the following expression:
$$\alpha = \frac{[CH_3COO^-]}{C}.$$
d- The solution S_1 is diluted to $\frac{1}{100}$; the measurement of the pH of the obtained solution S_2 gives the value $pH_2 = 4,4$.
Calculate the ionisation coefficient α_2 of the ethanoic acid in this solution S_2. Conclude about the effect of the dilution on the ionisation of a weak acid in an aqueous solution.

Second exercise (14 points)
II- Kinetic of an alcoholic fermentation reaction

The beer is obtained by an alcoholic fermentation of an aqueous solution of glucose. The grains of barley, that are mixed with hop which give the flavor to the beer, are essential to prepare this solution.
After ebullition and cooling, this mixture is treated with brewer's yeast. The fermentation of glucose takes place according the reaction of the following equation:

$$C_6H_{12}O_6 \xrightarrow{yeast} 2\ CO_{2\,(g)} + 2\ C_2H_5OH$$

Given:

- Density of ethanol: $\rho = 0.79$ g.mL^{-1}.
- M (ethanol) = 46 g.mol^{-1}.
- Authorized content of ethanol in beer should not exceed 8 % by volume (proof alcohol).

1) Flavor and deterioration of beer

Products, which are obtained in small amount, are formed by metabolism reactions of yeast, play an important role in the final flavor of beer and the deterioration of this flavor:

- Sour beer which burns the throat: acetic fermentation (fermentation of ethanoic acid).
- Free-flowing beer or oily: lactic fermentation (fermentation of hydroxy-2-propanoic acid).
- Rancid flavor: butyric fermentation (fermentation of butanoic acid).

a- Write the condensed structural formulas of ethanoic, lactic and butyric acids.

b- Write the equation of the esterification reaction of ethanol and butanoic acid. Give two characters of this reaction.

c- Among the products mentioned above, there is amyl alcohol, which is a primary alcohol of a non-branched open carbon chain of molecular formula $C_5H_{12}O$.

i) Write the condensed structural formula of amyl alcohol and give its systematic name.

ii) Choose among the two following formulas that of the ester which is obtained by the esterification reaction of amyl alcohol and ethanoic acid:

$$CH_3-\underset{\underset{O}{\|}}{C}-O-(CH_2)_4-CH_3 \quad \text{or} \quad CH_3-\underset{\underset{O}{\|}}{C}-O-CH(CH_3)-(CH_2)_2-CH_3$$

2) Kinetic of the alcoholic fermentation

During an alcoholic fermentation, the concentration of glucose is titrated with an appropriate method, at different instants. The results are grouped in the following table:

t (day)	0	1	2	3	4	5	6	7	8
$[C_6H_{12}O_6]$ x10^{-1}mol.L^{-1}	6.00	4.68	3.64	2.84	2.21	1.72	1.35	1.05	0.82

a- Show the relation: $[C_2H_5OH]_{t} = 2\ ([C_6H_{12}O_6]_0 - [C_6H_{12}O_6]_t)$, where: $[C_6H_{12}O_6]_0$ is the initial concentration of glucose at the instant $t_0 = 0$, $[C_6H_{12}O_6]_t$, the remaining concentration of glucose at an instant t, and $[C_2H_5OH]_t$, the concentration of ethanol formed at instant t.

b- Determine the average formation rate of ethanol between the instants $t_1 = 2$ days and $t_2 = 6$ days

c- Show that, starting from the above solution of glucose we can obtain an alcoholic solution which does not exceed the authorized proof alcohol.

Entrance Exam 2004-2005 **Solution of Chemistry** **Duration: 1 hour**

First Exercise (6 points)
Ionization coefficient; Dilution influence

I- 1) 1 L of solution S_0 ; 5,7 mL of pure acid ; ρ =1,05 g $mol.L^{-1}$

M (CH_3COOH) = 60 g $mol.L^{-1}$

The masse of pure acid is:

$M = \rho . V$ = 1,05 x 5,7 = 5,985 g

$$n = \frac{m}{M} = \frac{5{,}985}{60} = 0{,}09975\,mol$$

$$C_0 = \frac{n}{V} = 0{,}099\,mol.\,L^{-1}$$

$$C_0 \approx 0{,}1\,mol.\,L^{-1}$$

2) a- Calculate the concentration C_1 of solution S_1

$$C_1 = \frac{C_0}{10} = 0{,}01\,mol.L^{-1}$$

b- Prove that ethanoic acid is a weak acid:

$C_1 = 0{,}01\,mol.L^{-1}$ and $pH_1 = 3{,}4$

we should have $[H_3O^+] < C_1$:

$[H_3O^+] = 10^{-pH_1} = 10^{-3{,}4} = 0{,}0004 = 4.10^{-4}$ mol.L^{-1}

Thus $4.10^{-4} < 10^{-2}$

And consequently, ethanoic acid is a weak acid.

c- $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

According to the given data $\alpha_1 = \dfrac{CH_3OO^-}{C_1}$

Now: $\frac{CH_3OO^-}{C_1} = \frac{[H_3O^+]}{C_1} = \frac{4\times10^{-4}}{10^{-2}} = 4.10^{-2}$, $\alpha_1 = 0{,}04$

d- $C_2 = \frac{C_1}{100}$, $pH = 4{,}4$

$$C_2 = \frac{10^{-2}}{100} = 10^{-4}\ mol.L^{-1}$$

$[H_3O^+]$ = $10^{-pH} = 10^{-4,4} = 4.10^{-5}$ mol.L^{-1}

$\alpha_2 = \frac{[H_3O^+]}{C_2} = \frac{4\times10^{-5}}{10^{-4}} = 0{,}4$ $\alpha_2 = 0{,}4$

Conclude: The dilution of an aqueous solution of a weak acid increases its ionization degree.

Indeed α_1 = 0,004 : after ionisation α_2 = 0,4

Second exercise (14 points)

II- Kinetic of an alcoholic fermentation rection

<u>II- Flavor and deterioration of beer</u>

1) a- The condensed structural formulas are :

$CH_3 - C - OH$
||
O

Ethanoic acid

$CH_3 - CH - C - OH$
\ ||
OH OH

Lactic acid: (2-hydroxy propanoic acid)

$CH_3 - CH_2 - CH_2 - C - OH$
||
O

Butyric acid: (or butanoic acid)

b- Equation of esterification+ two characteristics:

$$C_2H_5OH + C_3H_7-\underset{\underset{O}{||}}{C}-OH \rightleftharpoons C_3H_7-\underset{\underset{O}{||}}{C}-O-C_2H_5 + H_2O$$

Two characteristics: The reaction is reversible and athermic

c- i) The condensed structural formula of alcohol $C_5H_{12}O$

According to the data given: primary alcohol open and non-ramified chain.

$CH_3-CH_2-CH_2-CH_2-CH_2-OH$ 1- pentan ol

ii) $CH_3-\underset{\underset{O}{||}}{C}-O-(CH_2)_4-CH_3$ or ester(1)

$CH_3-\underset{\underset{O}{||}}{C}-O-CH(CH_3)-(CH_2)_2-CH_3$ ester(2)

Choose the ester resulting from the reaction between amylic alcohol and ethanoic acid

$CH_3-\underset{\underset{\mathbf{O}}{||}}{C}-O-\mathrm{R}$

Alkyl R derives from an alcohol having an open non- ramified carbon chain.

$-(CH_2)_4-CH_3$ Its chain is open and non- ramified

$-CH(CH_3)-(CH_2)_2-CH_3$ its chain is open and ramified

Thus, ester (1) is convenient.

2) a- Establish the relation $[C_2H_5OH]_t = 2\,([C_6H_{12}O_6]_0 - [C_6H_{12}O_6]_t)$

The equation of the reaction of fermentation is :

$$C_6H_{12}O_6 \xrightarrow{\text{Sour Beer}} 2CO_2 + 2C_2H_5OH$$

To one mole of $C_6H_{12}O_6 \longrightarrow$ 2 moles of C_2H_5OH

$n(C_2H_5OH)_{\text{formed}} = 2\ n(C_6H_{12}O_6)$ reacting

$$n(C_6H_{12}O_6)_0 - n(C_6H_{12}O_6)_t = \frac{n(C_2H_5OH)_t}{2}$$

Dividing the last equality by (V_L) the volume of the reaction mixture we deduce that :

$$[C_2H_5OH]_t = 2([C_6H_{12}O_6]_0 - [C_6H_{12}O_6]_t)$$

b- A t_1 = 2 days we have :

$$[C_6H_{12}O_6]_2 = \frac{3{,}64}{10} = 0{,}364\,\text{mol.L}^{-1}$$

A t_2 = 6 days we have :

$$[C_6H_{12}O_6]_6 = \frac{1{,}35}{10} = 0{,}135\text{mol.L}^{-1}$$

The concentration of ethanol will be

$$[C_2H_5OH] = 2([C_2H_5OH]_2 - [C_2H_5OH]_6)$$

$$= 2\,(0{,}364 - 0{,}135) = 0{,}458\ mol.\ L^{-1}$$

$$\overline{v} = \frac{0{,}458}{6-2} = 0{,}1145\ mol.\ L^{-1}\ J^{-1}$$

c- After the complete fermentation the concentration of ethanol become

$0{,}6 \times 2 = 1{,}2\ mol.\ L^{-1}$

$n_e = C_e V$ and $m_e = M_e \,.\, n_e = M_e \,.\, C_e.\, V$

$V_e = \dfrac{m_e}{\rho_e} = \dfrac{M_e.C_e.V}{\rho_e}$ hence: $\dfrac{V_e}{V} \times 100 = \dfrac{M_e.C_e}{\rho_e} \times 100 = \dfrac{46 \times 1{,}2}{0{,}79 \times 10^3} \times 100 = 0{,}07 = 7\% < 8\%$

This percentage, in alcohol, does not exceed the authorized alcoholic degree that is: 8%.