Entrance exam 2001-2002 **Chemistry** **Time: 1 hour**
July 2001

The use of a non-programmable calculator is allowed

Answer the following two questions

I. Titration of ascorbic acid in a vitamin C tablet

The aim of this study is to determine, by titration, the mass of ascorbic acid, $C_6H_8O_6$ (which reacts as a monoacid) in a tablet of vitamin C.

We dissolve one tablet of vitamin C in 100 mL of distilled water. The obtained solution is tittered by a sodium hydroxide solution having concentration of 0.32 $mol.L^{-1}$.

The results of the pH measurements are given in the following table, where V_b is the volume of sodium hydroxide solution.

V_b (mL)	0	1	3	4	5	6	7	8
pH	3,0	3,3	3,8	4,0	4,2	4,4	4,7	5,1

V_b (mL)	8,5	9	9,5	10	11	13	15
pH	5,6	9,6	10,2	10,5	10,8	11,0	11,2

1-Plot on the provided graph paper the curve that represents the variation of pH as function of V_b , $pH = f(V_b)$. Take the following scale: 1 cm for 1 mL on the abscissa and 1cm for each pH unit on the ordinate.

2- From the graph, determine the coordinates of equivalence point.

3- Write the equation of the reaction between ascorbic acid and sodium hydroxide.

4- Determine the mass (in milligram) of ascorbic acid contained in one tablet of vitamin C. Is this result compatible with the indication (500) of the manufacturer « vitamin C 500 »?

Given: $M_{(ascorbic\ acid)} = 176\ g.mol^{-1}$ (18 points)

II- The complete combustion of 2,9 g of an organic compound (A), of formula C_xH_yO, gives 2,7g of water and 6,6 g of carbon dioxide.

1- Show that the molecular formula of (A) is C_3H_6O.

2- Compound (A) gives a white-crystallized solid with sodium bisulfite and a yellow precipitate with DNPH. Identify the functional group of (A) and write the condensed structural formulas of possible isomers of (A).

3- Compound (A) gives by heating, with Fehling solution, a red precipitate. Identify (A).

4- The catalytic hydrogenation of (A) gives a compound (B), whether, the mild oxidation of (A) gives a compound (C). Identify (B) and (C) and write the two equations of the reactions that lead (B) and (C) from (A).

5- We carry out a mixture of 20mL of (B) and 18.5 g of (C) added to 5mL of concentrated sulfuric acid. This mixture is kept at 60 ºC temperature during a few days. The experiment shows that the equilibrium is reached when 2/3 of a limiting reactant react.

a- Write the equation of the reaction that takes place and give the systematic name of the obtained organic product.

b- Specify the role of sulfuric acid.

c- Calculate the number of moles of the organic components of the mixture at equilibrium. The density of compound (B) is equal to 0,8 g. mL^{-1}

d- Suggest a way that increases the yield of this reaction.

H =1 ; C = 12 ; O = 16 (22 points)

Entrance exam 2001-2002 **Solution of Chemistry** **Time: 1 hour**
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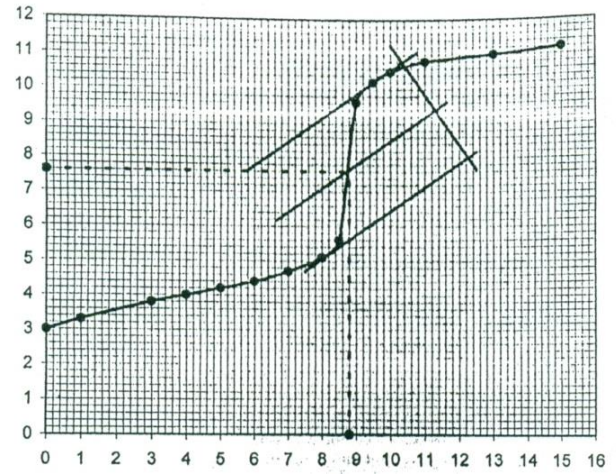
1-



2- The equivalence point (E) is determined by the parallel tangents method, According to the graph, the coordinates of point (E) are: abscissa V_b = 8,8 mL and ordinate PH = 7,6

3- The chemical equation: *NaOH* is a strong base. The pH of the solution, at equivalence, is slightly basic; ascorbic acid $C_6H_8O_6$ is a weak acid.

The chemical reaction is complete and it is given by:

$$C_6H_8O_6 + HO^- \longrightarrow C_6H_7O_6^- + H_2O$$

4- Mass of ascorbic acid contained in a tablet; discuss: Ascorbic acid is monoacid; Sodium hydroxide is a monobase.

- Mass of ascorbic acid: A equivalence, we have : $C_aV_a = C_bV_b$; $n_a = C_aV_a$ is the number of moles of the acid dissolved, and $n_b = C_bV_b$ is the number of moles of the base.

$n_a = n_b = C_bV_b$ = 0,32 x 8,8 x10^{-3} = 2,816 x10^{-3} mol.

m : The mass of ascorbic acid dissolved is :

$m = n_a.M$ (acid) = 2,816 x10^{-3} x 176 = 495.10^{-3} g.

- Discussion :
  The result is compatible with the indication of the manufacturer.
  500 mg $\approx$ 495 mg, the 5 mg difference is due to the measurement error.

II- 1) The molecular formula of (A) is C_3H_6O.

M (C_xH_yO) = (12 x + y +16) g mol^{-1}, M (CO_2) = 44 g mol^{-1} and M (H_2O) = 18 g mol^{-1}

The equation of combustion of compound (A) is written as:

$$C_xH_yO + \left(x + \frac{y}{4} - \frac{1}{2}\right)O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$$

(12x + y +16) g $\rightarrow$ x44y $\frac{y}{2}$.18g

2.9 $\rightarrow$ 6.6g 2,7g

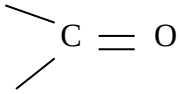
According to the law of defined proportions we can write:

$$\frac{12x + y + 16}{2{,}9} = \frac{44x}{6{,}6} = \frac{\frac{y}{2} \times 18}{2{,}7}$$ hence x = 3 and y = 6

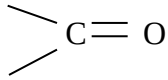
As a result, the molecular formula will be C_3H_6O

2) - Identification the functional group of (A) and the condensed structural formulas of the isomers of (A)

- Identification of the functional group of (A) :
  Compound (A) + sodium bisulfite $\longrightarrow$ white solid

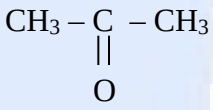
(A) includes the carbonyl group 

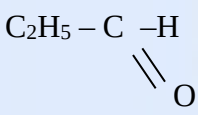
Compound (A) + DNPH ⟶ yellow precipitate:

(A) contains the carbonyl group 

- Condensed structural formulas of the isomers of (A): (A) reacts with sodium bisulfite and with DNPH as well:

(A) can be an aldehyde or ketone. The possible isomers of (A) are:

 ketone : propanone

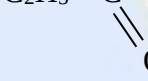
 aldehyde : Propanal

3) Identification of (A):

(A) + Fehling's reagent $\xrightarrow{Heat}$ red brick precipitate

ketone + Fehling's reagent ⟶ No reaction

Aldehyde + Fehling's reagent ⟶ a reaction takes place

Thus, (A) is an aldehyde  propanal

4) Equations of the reactions leading to (B) and (C) starting from (A):

$A + H_2 \xrightarrow{heat} B$

(A) by mild oxidation ⟶ C

(A) is an aldehyde (question 3)

The hydrogenation of aldehyde leads to a primary alcohol, then (B) is a primary alcohol

$C_2H_5 - CH_2OH$ 1- propanol

$$C_2H_5 - \underset{\underset{O}{\|}}{C} - H + H_2 \xrightarrow{N_i} C_2H_5 - CH_2OH \quad (B)$$

The mild oxidation of an aldehyde leads to a carboxylic acid.

$$C_2H_5 - \underset{\underset{O}{\|}}{C} - H + \frac{1}{2}O_2 \xrightarrow{Cu \text{ or } Pt} C_2H_5 - \underset{\underset{O}{\|}}{C} - OH \quad \text{propanoic acid (C)}$$

5) a- Equation of the reaction between 1- propanol (B) and propanoic acid (C) and name of the organic product (E) :

- Equation of the reaction: $C_3H_7OH + C_2H_5COOH \rightleftharpoons C_2H_5 - COOC_3H_7 + H_2O$

The reaction between (B) and (C) is an esterification.

The organic product (E) is propyl propanoate

b- Role of the sulfuric acid:

The concentrated sulfuric acid plays the role of a catalyst by favoring the esterification reaction. Sulfuric acid allows us to reach equilibrium in less time.

c- Composition in moles of organic compounds at equilibrium:

M (C_2H_5COOH) = 74 g mol^{-1}, m = 18,5g, $n = \frac{m}{M} = \frac{18,5}{74} = 0,25mol$

M (C_3H_7OH) = 60 g mol^{-1} , ρ= 0,8 Kg.L^{-1} ; V = 20 mL

$\rho = \frac{m}{M}$ and m = ρ x V = 0,8 x 20 = 16g

Hence, the initial number of moles of (B) is : $n_B = \frac{m_B}{M_B} = \frac{16}{60} = 0{,}266 mol$

$\frac{n_{(Acid)}}{1} = \frac{0{,}256}{1} and \frac{n_{(Alcohol)}}{1} = \frac{0{,}266}{1}$

The acid is the limiting reactant if the reaction is complete. Equilibrium is reached when 2/3 of the limiting reactant have reacted, n acid having reacted = n ester formed.

n acid having reacted = $0{,}25 \times \frac{2}{3} = 0{,}166 mol$

n ester formed = $0{,}166 mol$

n acid remaining = 0,25 - 0,166 = 0,083 mol

n alcohol remaining = 0,266 – 0,166 = 0,1 mol

d) To increase the yield of the reaction we can eliminate water as it is formed.