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Entrance Exam 2003-2004 **CHEMISTRY** **Duration: 1 hour**

I. Synthesis of ethyl ethanoate

Synthesis of ethyl ethanoate is an esterification reaction. This esterification is reversible when it takes place between a carboxylic acid and an alcohol

Given :

- Available chemical reactants : pure ethanoic acid, aqueuse solution of éthanoïque acid, ethanol, a dehydrating agent P_4O_{10} : thionyl chloride $SOCL_2$
- The yield of ester synthesis is 67% starting from equimolar initial mixtures of carboxylic acid and primary alcohol.

N.B. Use the condensed structural formulas to write equations of reactions.

1) **Synthesis of ethyl ethanoate**

The synthesis of ethyl ethanoate is carried out, at 60ºC, starting from an equimolar mixture of pure ethanoic acid and ethanoal. When equilibrium is established, we determine, by titration, the number of moles of the remaining acid.

a- Write the equation of synthesis reaction of ethyl ethanoate.
b- Justify the utilization of pure ethanoic acid instead of aqueous ethanoic acid solution in the above synthesis.

2) **Yield of synthesis reaction of ethyl ethanoate**

0.5 mol of ethanol reacts with 2.0 mol of pure ethanoic acid. The number of moles of ethanoic acid in the mixture at equilibrium is 1.535 mol.

a- Determine the yield of this reaction. Compare this yield with that of the reaction where the initial mixture of ethanoic acid and ethanol is equimolar. Interpret the difference between these two yields.
b- Suggest a way that permits to make the yield of the above synthesis total :
 i- By using the same reactants
 ii- By changing of one of the reactants, write the equations of corresponding reactions.

II- Dimerization reaction of 1,3-butadiene

In gaseous state, 1,3- butadiene, C_4H_6 gives a dimer according the slow reaction represented by the following equation:

$$2C_4H_{6(g)} \rightarrow C_8H_{12(g)}$$

Follow the variation of the total pressure, *P*, of the mixture, in a reactor maintained at constant temperature, T = 550K, The results are represented in the following table:

t (min)	0	3	12	24	42	68
P (mm) *Hg*	632	618	584	546	509	474
$[C_8H_{12}]$(mol.L^{-1})						

Given: Constant of ideal gaz :
R = 0.08 L. atm. K^{-1}. mol^{-1} : 1 atm = 760 mm *Hg*

1) Study of the mixture involved in the reaction

a- Explain the global decrease of the pressure, *P*, as the reaction proceeds.

b- Establish the relation between initial pressure, P_0 , total pressure, *P* , at an instant *t* , and the pressure *x* of C_8H_{12} at the same instant *t* .

c- Verify if the dimerization of C_4H_6 is total at instant *t* = 68 min.

2) Kinetic study of dimerization reaction of C_4H_6

a- Show the following relation :
$[C_8H_{12}]_t = 3\times10^{-5}(P_0 - P) mol.L^{-1}$: *where* $[C_8H_{12}]_t$ is the molar concentration of the product C_8H_{12} at instant *t*, *P* and P_0 are expressed in *mm Hg.*

b- Calculate the concentration of C_8H_{12} at the different instants indicated in the above table.

c- Plot the curve [C_8H_{12}] = *f* (*t*). Take the following scales :
Abscissa : 1 cm = 5 min
Ordinate: 1 cm = 5 x 10^{-4} mol. L^{-1}

d- Determine the half-life of the above reaction.

Entrance Exam 2003-2004 | **Solution of CHEMISTRY** | **Duration: 1 hour**

I. Synthesis of ethyl ethanoate

1) a- The equation of the reaction between ethanoic acid and ethanol is:

$$CH_3 - \underset{\underset{O}{\|}}{C} - OH - C_2H_5OH \rightleftharpoons CH_3 - \underset{\underset{O}{\|}}{C} - O - C_2H_5 - H_2O$$

b- Water contained in the aqueous solution of ethanoic acid favors hydrolysis, and our objective is to synthesize ethyl ethanoate, for this reason we prefer to use pure ethanoic acid

2) a- Yield ? Comparison with that of the equimolar mixture:

- the yield :

	alcohol	acid	ester	water
Initial state	0,5 mol	2 mol	0	0
in equilibrium	$0,5 - x$	$2 - x$	x	x

Or $2 - x = 1,535$ as a result, $x = 2 - 1,535 = 0,465$ mol.

$$\text{Yield} = \frac{0,465}{0,5} = 0,93 \text{ or } 93\%$$

- Comparison : Equimolar reactional mixture : yield is 67%

  If the reaction is complete: $R_{ethanol} = \frac{0,5}{1} = 0,5$ *and* $R_{acid} = \frac{2}{1} = 2$

  Ethanol is the limiting reactant.
  The acid is in excess: the excess of acid favors
  The esterification: for this reason, the yield of the reaction increases.

b- Means to have a yield =100%

- Same reactants: we add a powerful dehydrating agent such as phosphoric anhydride P_2O_5 (its dimers state is P_4O_{10}): The dehydrating agent fixes the water formed.
- Replacing one reactant with another: we replace ethanol with $SOCl_2$

$$CH_3 - \underset{\underset{O}{\|}}{C} - OH + SOCl_2 \longrightarrow CH_3 - \underset{\underset{O}{\|}}{C} - Cl + HCl + SO_2$$

We carry out a reaction between ethanol chloride and ethanol.

$$CH_3 - \underset{\underset{O}{\|}}{C} - Cl + C_2H_5OH \longrightarrow CH_3 - \underset{\underset{O}{\|}}{C} - O - C_2H_5 + HCl$$

II- <u>Reaction of dimerization of but-1,3-diene</u>:

1) Study of the reactional mixture.

a- Explain the decrease of the total pressure P.

$2C_4H_6(g) \longrightarrow C_8H_{12}(g)$

To one mole of C_8H_{12} which appears correspond 2 moles of C_4H_6 that disappear. The number of moles of C_4H_6 decreases during dimerization.

The pressure is proportional to the number of moles: if n decreases then P decreases.

b- Relation between P_0 , P and x :

	C_4H_6	C_8H_{12}	Total
Initial state	n_0	0	n_0
Final state	$n_0 - 2n$	n	$n_0 - n$

According to the table, we can write:

$P_0V = n_0 RT$ and $x V = n RT$

$PV = (n_0 - n) RT = n_0RT - n RT = P_0V - x V$

We simplify by V, then $P = P_0 - x$

c- Verify that if the reaction is complete at $t = 68$ min :

According to the equation of the reaction, the pressure is:

$$\frac{P_0}{2} = \frac{632}{2} = 316\, mm\ Hg$$

At $t = 68$ min, we have $P = 474$ $mm\ Hg$ > 316 $mm\ Hg$, therefore the reaction is not complete.

2) a- show the relation $[C_8H_{12}]_t = 3 \times 10^{-5} (P0 - P)\ mol.\ L^{-1}$

$x V = n RT$ and $n = \frac{xV}{RT}$

$[C_8H_{12}] = \frac{n}{V} = \frac{xV}{RVT} = \frac{x}{RT}$ or $x = P_0 - P$ question (1-b)

$[C_8H_{12}] = \frac{P_0 - P}{RT} = \frac{P_0 - P}{(0{,}08 \times 760) \times 550} = 3 \times 10^{-5}(P_0 - P)$

b- $[C_8H_{12}] = 3 \times 10^{-5}(P_0 - P)$

At $t = 0$ min : $[C_8H_{12}] = 0$

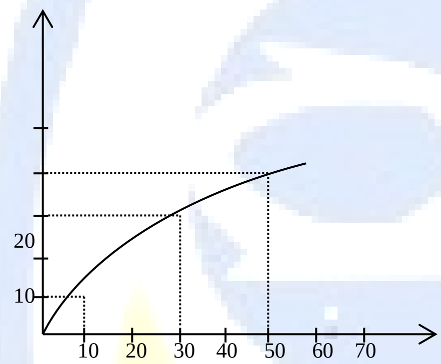
At $t = 3$ min : $[C_8H_{12}] = 3 \times 10^{-5}(632 - 618) = 42.10^{-5} mol.L^{-1}$

Similarly, we continue calculating [C_8H_{12}] at the instants 12 min, 24 min, 42 min and 68 min.

The values thus calculated are shown in the following table:

t (min)	0	3	12	24	42	68
P (*mm*) *Hg*	632	618	584	546	509	474
[C_8H_{12}]($mol.L^{-1}$)10^{-5}	0	42	144	258	369	474

c- The graph demanded is represented below:



d- Determine the half-life time of the reaction :

When the reaction is complete, the number of moles will be divided by 2 and the total pressure well be $x = \frac{P_0}{2}$

[C_8H_{12}]= $3\times10^{-5}(P_0 - P)$

[C_8H_{12}]= $3\times10^{-5}\left(632 - \frac{632}{2}\right) = 948.10^{-5} mol.L^{-1}$

At the half-reaction we should have half this number:

[C_8H_{12}]= $474.10^{-5} mol.L^{-1}$ This corresponds, according to the preceding table to instant *t* = 68 min (see the preceding table)