LEBANESE UNIVERSITY

FACULTY OF ENGINEERING

الجامعة اللبنانية
كلية الهندسة

Entrance Exam 2011-2012 **Time: 1 hour**

Chemistry **03, July 2011**

First exercise (5 points): Identification of some aqueous solutions

Three bottles A, B, C containing each one of the following solutions having the same concentration C_0:

Ethanoic acid solution (CH_3COOH)

Sodium hydroxide solution ($Na^+ + HO^-$)

Hydrochloric acid solution ($H_3O^+ + CL^-$)

It is required to identify the contents of each bottle.

Test tubes and two indicators bromothymol blue and methyl orange are available.

The pH ranges of the two indicators are given in the table below:

Indicator	Bromthhymol blue			Methyl orange		
Color	Jaune	Vert	Bleu	Rouge	Orange	jaune
pH	0 - 6	6 - 7,6	7,6 -14	0 - 3,1	3,1 - 4,4	4,4 - 14

Colorimetric tests, with each one of these solutions are carried out. The results are given in the following table:

	Bromothymol blue	Methyl orange
A	Blue	yellow
B	yellow	yellow
C	yellow	Red

1-In which fields of values are the pH of the solutions contained in bottles A, B and C?

2-Identify the content of each bottle.

3-The pH of the sodium hydroxide solution is $pH_{NaOH} = 11$. Calculate the pH of the hydrochloric acid solution

4-Knowing that the acidity constant of ethanoïc acid is $Ka = 2,0 \times 10^{-5}$, calculate the pH of the solution of this acid.

Given: $[H_3O^+]\,[HO^-] = 1,0 \times 10^{-14}$

Second exercise (10 points): Kinetics of the decomposition reaction of N_2O_5

Dinitrogen pentaoxide, N_2O_5, decomposes at high temperature according to a complete and slow reaction represented by the following equation: $2N_2O_5\,(g) \rightarrow 4\,NO_2\,(g) + O_2\,(g)$

It is required to study the kinetics of this reaction based on the follow up of the pressure change of the mixture at constant volume and constant temperature.

Expérimental procedure

n_0 mol de N_2O_5 are introduced into a closed container of volume V = 1 L at constant temperature T = 318K.
A barometer measures the change of the pressure P in the container during time.
At t = 0, the measured pressure is $P_0 = 4{,}638 \times 10^4$ Pa.
The measurements of the ratio P/P_0 versus time are given in the table below:

Time t in s	0	10	20	40	60	80	100
P/P_0	1,000	1,435	1,703	2,047	2,250	2,358	2,422

We can determine the number of moles of oxygen gas formed versus time and plot the graph $n_{(O2)} = f(t)$ based on these measurements.

Given: Constant of ideal gas R = 8, 31 $J.mol^{-1}.K^{-1}$.

1- **Preliminary study**

1.1- Show that $n_0 = 17, 6$ mmol and $n_{(O2)\infty} = 8{,}8$ mmol.

1.2- Express the total number of moles of the obtained gas (G), n_G, in terms of n_0 and $n_{(O2)}$ at an instant t.

1.3- Deduce the following relation:

$$\frac{P}{P_0} = 1 + \frac{3n(O_2)}{n_0}$$

1.4- Using the result of the part 1.1, calculate the ratio P_{max}/P_0 where P_{max} is the value of the pressure in the container at the end of the reaction. Justify using the above table of measurements that the reaction is not finished at t = 100 s.

2- **Kinetic study**

2.1- Calculate the two missing values in the table below:

Time t in s	0	10	20	40	60	80	100
P/P_0	1,000	1,435	1,703	2,047	2,250	2,358	2,422
$n_{(O2)}$ mmol		2,55	4,12	6,14		7,97	8,34

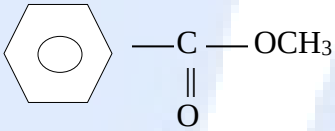
2.2- Plot the curve $n_{(O2)} = f(t)$. Take the following scale: 1grid = 5 s in abscissa and 1 grid = 0.5 mmol in ordinate.

2.3- Determine graphically the half-life time of the reaction $t_{1/2}$.

Third exercise (5 points): Preparation of an Ester

Into a flask, a mass m = 12, 2 g of benzoïc acid, $C_6H_5 - CO_2H$, and a volume V= 40, 0 mL of methanol $CH_3 - OH$, are heated in the presence of some drops of concentrated sulfuric acid. Methyl benzoate, liquid with strong odor present in some natural flavors, is obtained.

Given: Methyl benzoate has as a condensed structural formula:



Chemical species	Molar mass ($g.mol^{-1}$)	Density ($g.L^{-1}$)	Solubility in water
Benzoic acid	122	1,3	Slightly soluble
Methanol	32	0,8	Soluble
Methyl benzoate	136	1	Insoluble

Answer by « True» or « False » each of the following statements: (*Any « True » answer must be justified*).

1-Sulfuric acid allows to: (a) Increased the yield of the reaction (b) Increased the rate of the reaction (c) Obtain a percentage yield of 100%	2-About the reactants : (a) Methanol is in excess ; (b) Methanol is the limiting reactant ; (c) Methanol and benzoïc acid are in stoechiometric ratios.
3-For the above mixture the percentage yield is : (a) 67 % (b) Higher than 67 % ; (c) Less than 67 %.	4-Starting with an initial mixture where the number of moles of the reactants is doubled and working under the same experimental conditions the yield of the reaction : (a) Increases (b) Decreases (c) Remains the same

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Solution of Chemistry **03, July 2011**

First Exercise (5 points)
Identification of some aqueous solutions

1- The solution A gives a blue color with Bromothymol blue its pH is between 7.6 and 14. This solution gives a yellow color with Methyl orange its pH is between entre 4.4 and 14. That shows pH is between 7.6 and 14.The solution B gives a yellow color with Bromothymol blue its pH is between 0 and 6 and it gives a yellow color Methyl orange it pH is between 4.4 and 14. The pH of this solution is then between 4.4 and 6. The solution C is yellow with the Bromothymol blue and red with the methyl orange its pH is then between 0 and 3. **(1,5 pt)**

2- The pH of the solution A is higher than 7.6 it is then a base solution of sodium hydroxide. The two solutions B and C are acid solutions of the same concentration; which has to the smaller pH corresponds to the stronger acid. Ethanoic acid is that of the solution B and hydrochloric acid is that of the solution C. **(1,5 pt)**

3- Knowing the pH of the solution of the strong base (sodium hydroxide), we can calculate its concentration C_0: $pH = 14 + \log C_0$; $11 = 14 + \log C_0$; $\log C_0 = -3$ and $C_0 = 1.0\times10^{-3}$ mol.L^{-1}. The pH of the hydrochloric acid solution which is a strong acid is: $pH = -\log C_0 = 3$. **(1 pt)**

4- Ethanoic acid reacts with water according to the following equation:

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

Where: $[CH_3COO^-] = [H_3O^+] = x$ and $[CH_3COOH] = C_0 - x \approx C_0$.

$$Ka = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = \frac{x^2}{C_0} = \frac{x^2}{1.0\times10^{-3}} = 2.0\times10^{-5} \ ;$$

$x^2 = 2.0\times10^{-8}$ and $x = (2.0\times10^{-8})^{1/2}$ and pH = 3.85. **(1 pt)**

Second exercise (10 points)
Kinetics of the decomposition reaction of N_2O_5

1.1- The number of moles is given by the equation of ideal gas:

$$n_0 = \frac{P_0 \times V}{RT} = \frac{4{,}638\times10^4 \times 1\times10^{-3}}{8{,}31\times318} = 17{,}6\times10^{-3} \text{ mol.}$$

The reaction is total, than we have: $n(O_2)_\infty = \frac{1}{2}\times n_0 = \frac{1}{2}\times17{,}6\times10^{-3} = 8{,}8\times10^{-3}$ mol. **(1 pt)**

1.2- The following table represents the composition of the gaseous mixture : **(2 pts)**

State	N_2O_5 (mol)	NO_2 (mol)	O_2	n_G (mol)
Initial state t = 0	n_0	0	0	0
State t > 0	$n_0 - 2\,n(O_2)$	$4\,n(O_2)$	$n(O_2)$	$n_0 + 3\,n(O_2)$

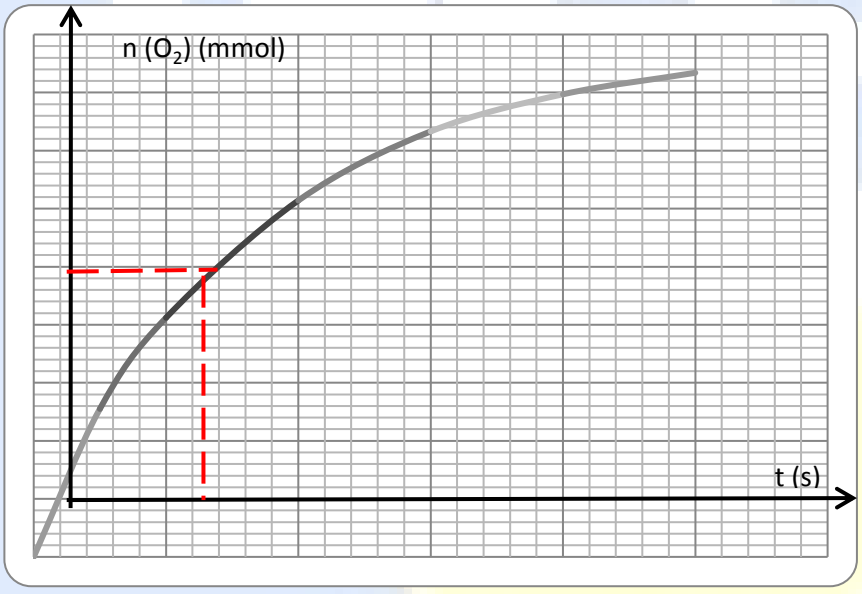
1.3- Same T and V, where: $\frac{P}{P_0} = \frac{n}{n_0} = \frac{n_0 + 3n(O_2)}{n_0} = 1 + \frac{3n(O_2)}{n_0}$. **(1,5 pts)**

1.4- $\frac{P_{max}}{P_0} = \frac{n_\infty}{n_0} = \frac{4.375\times10^{-2}}{1.75\times10^{-2}} = 2.5.$

At t = 100 s, we have $\frac{P}{P_0} = 2.422 < 2.5$. That shows the reaction dose not finished at this time. **(2 pts)**

2- 2.1- The two values are: $n(O_2)_0 = 0$ and 7.33 mmol. **(1 pt)**

2.2- The curve is: **(1 pt)**



2.3- The half-life time of the reaction corresponds to the time during it there is formation the half of the maximal amount of oxygen, at $t_{1/2}$ we have $n_{(O2)} = 4.4$ mmol. According to the curve this amount corresponds to t = 21.5 s. **(2 pts)**

Third exercise (5 points)
Preparation of an Ester

1- A little amount of sulfuric acid acts as a catalyst in order to increase the rate of the slow reaction. **(1,25 pt)**
2- The reaction is not complete (reversible). There is no limiting or excess reactant. The mixture is not stoechiometric. **(1,25 pt)**
3- n acid (initial) = 0.1 mol. n alcohol (initial) = 0.67 mol the mixture is not stœchiomitric, The alcohol is primary the % exceeds 67% **(1,25 pt)**
4- Working under the same experimental conditions Kc remains the same and the yield of the reaction remains the same. **(1,25 pt)**