Entrance Exam 2013 – 2014 **Chemistry** **Duration: 1 hour**
July 14/2013

First Exercise (7 points)
Kinetic Study in Gaseous Phase

The decomposition reaction of diterbutyle peroxide in gaseous phase is carried out into a container of constant volume V. It is represented by the following equation:

$$(CH_3)_3C - O - O - C(CH_3)_{3\,(g)} \rightarrow 2\ CH_3 - \underset{\underset{O}{\|}}{C} - CH_{3\,(g)} + CH_3 - CH_{3\,(g)}$$

At 420 K, The measurement of the total pressure P_t of the mixture, at various times, gives the following results:

t(min)	**10**	**50**	**100**	**150**	**200**	**300**
P(bar)	**0.278**	**0.405**	**0.513**	**0.584**	**0.630**	**0.681**

At the end of the reaction, the pressure is constant and is worth P_{final} = 0.718 bar.
We note n_0 the initial quantity of matter of diterbutyle and x the quantity of matter of ethane ($CH_3 - CH_3$) formed at instant t.

1- Express the quantities of matter of different chemical species at time t as function of n_0 and x.
2- Show that the initial pressure P_0 is equal to $P_{final}/3$.
3- Show that at time t: $P_t = P_0\left(1 + 2\frac{x}{n_0}\right)$. Deduce the expression of $\frac{x}{n_0}$ as function of P_t.
4- Find the two missing values in the following table:

t(min)	**10**	**50**	**100**	**150**	**200**	**300**
$\frac{x}{n_0}$	**0.082**	**0.347**		**0.722**	**0.818**	

5- Plot the curve $\frac{x}{n_0} = f(t)$. Take the following scale: 2 divisions for 25 min in abscissa and 2 divisions for $\frac{x}{n_0}$ = 0.1 in ordinate.
6- Determine the half-life time of the reaction.

Second Exercise (13 points)
Preparation and Properties of a Carboxylic Acid

Carbonylation is a reaction permitting to prepare a carboxylic acid starting with an alcohol in the presence of a catalyst according to the following equation:

$$ROH + CO \xrightarrow{catalyst} RCOOH$$

1- Carbonylation of an Alcohol (X)

The carbonylation of 2.5 g of a monoalcohol (X) of an open saturated carbon chain is carried out. The carboxylic acid (HA) obtained is dissolved in water. A solution (S) of volume equal to 250 mL is obtained.
The titration of 20 mL of the solution (S) required 8 mL of a sodium hydroxide solution of concentration Cb = 0.5 $mol.L^{-1}$.

1.1- Write the equation of the titration reaction of acid (HA).
1.2- Determine the number of moles of the acid (HA) in the solution (S).
1.3- Deduce the molar mass of the alcohol (X) knowing that the percentage yield of the carbonylation reaction is 92 %.
1.4- Show that the molecular formula of (HA) is $C_2H_5 - COOH$.

Given:

- Molar mass in $g.mol^{-1}$: M(H) = 1 ; M(C) = 12 ; M(O) = 16.
- Kw = 10^{-14}.
- pKa (C_2H_5COOH/ $C_2H_5COO^-$) = 4.9.
- This study is carried out at 25 ºC.

2- Study of the Solution $S_{E1/2}$ Obtained at the Half-equivalence of the Titration

The solution obtained after the addition of 4 mL of sodium hydroxide solution of concentration Cb = 0.5 $mol.L^{-1}$ to 20 mL of the solution S is called $S_{E1/2}$.

2.1- Make the inventory of the majority chemical species present in the solution $S_{E1/2}$.
2.2- Give the relation between [$C_2H_5COO^-$] and [C_2H_5COOH], in the solution $S_{E1/2}$, by neglecting the reaction of these species with water. Deduce the pH of the solution $S_{E1/2}$.
2.3- Specify the name and the properties of this solution $S_{E1/2}$.
2.4- It is possible to prepare two solutions (S_5) and (S_6), having the same pH as the solution $S_{E1/2}$, by mixing in each case two solutions among those proposed in the table below.

Specify the two solutions used to prepare the solution (S_5) and those used to prepare the solution (S_6).

Solution	Solute	Concentration (mol.L^{-1})	Volume (L)
S_1	Sodium Propanoate	**$C_1 = 0.05$**	**$V_1 = 1.00$**
S_2	Sodium Hydroxide	**$C_2 = 0.05$**	**$V_2 = 0.50$**
S_3	Propanoic Acid	**$C_3 = 0.05$**	**$V_3 = 1.00$**
S_4	Hydrochloric acid	**$C_4 = 0.05$**	**$V_4 = 0.50$**

3- Some Reactions of Propanoic Acid

The derivatives of carboxylic acids have an important role in industry. Write, using the condensed structural formulas of organic compounds, The equations of the reactions permitting to obtain, starting with propanoic acid, propanoyle chloride, methyle propanoate, propanoic anhydride and N-methylpropanamide.

The three parts of this exercise are independent.

Entrance Exam 2012 – 2013 **Solution of Chemistry** **Duration: 1H**
14 July 2013

First Exercise
Kinetic Study in Gaseous Phase

1-The table of the progress evolution of the reaction:

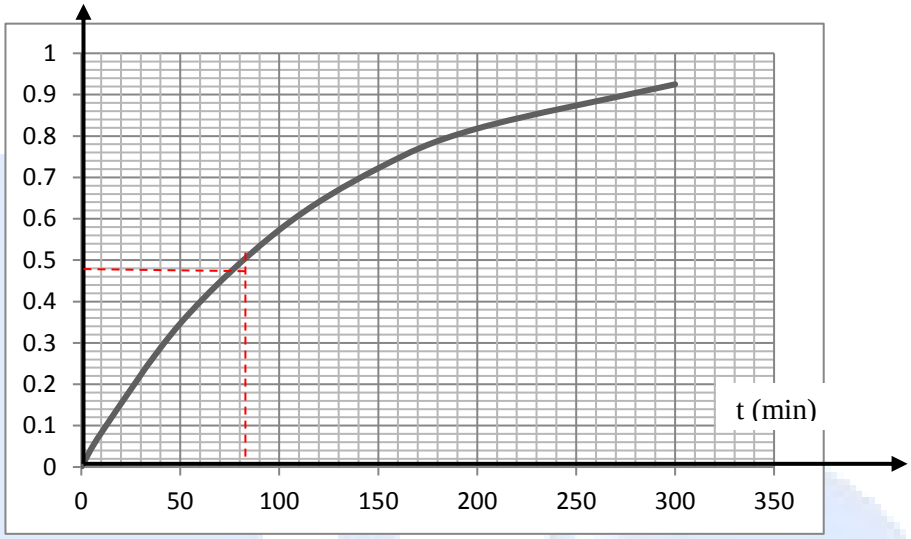
State	progress	$C_8H_{18}O_2$ →	$2\ C_3H_6O$ +	C_2H_6
initial	0	n_0	0	0
Change	x	n_0 -x	2x	X
final	$x_{final} = n_0$	0	$2n_0$	n_0

2- The final number of moles: $n_{final} = 2\ n_0 + n_0 = 3\ n_0$
At a constant volume constant and temperature, we have: $P_t = n_t (RT/V)$ and $P_0 = n_0(RT/V)$, thus : $P_0 = P_{final}/3$.

3- At each instant $n_t = (n_0\text{-}x) + 2x + x = n_0 + 2x = n_0(1 + 2\ x/n_0)$ and
$P_t = P_0 (1 + 2\frac{x}{n_0})$; $P_0 = 0.718/3 = 0.239$ bar; $\frac{x}{n_0} = (P_t - P_0)/2P_0 = 2.09\ Pt - 0.5$.

4- À t = 100 min ; $\frac{x}{n_0} = (P_t - P_0)/2P_0$
$\frac{x}{n_0} = (0.513 - 0.239)/2\times0.239 = 0.573$ bar
At t = 300 min; $\frac{x}{n_0} = (P_t - P_0)/2P_0$
$\frac{x}{n_0} = (0.681\text{-}0.239)/2\times0.239 = 0.925$ bar.

5- The curve:



6 –The half-life of the reaction $t_{1/2}$ is reached when $x_{t1/2} = n_{0/2}$ and $\frac{x}{n_0} = 0.5$ then $t_{1/2} = 80$ min (1 point)

Second Exercise (13 points)
Preparation and Properties of a Carboxylic Acid

1-Carbonylation of an Alcohol (X)

1.1 The equation of the titration reaction of the acid (HA)

$$HA + HO^- \rightarrow A^- + H_2O$$

$n_{acid\ (equivalence)} = n_{base\ added} = CbVb = 0.5 \times 0.008 = 0.004$ mol

$n_{acid\ total} = 0.004 \times (250/20) = 0.05$ mol.

1.2 According to the carbonylation equation $n_{acid\ formed} = n_{alcool\ reacting} = 0.05$ mol

$n_{alcoholused} = 0.05 \times 100/92 = 0.054$ mol.

$M_{alcohol} = m/n = 2.5/0.054 = 46.29\ g.mol^{-1}$.

1.3 The molar mass of the alcohol is 46.3 g it is ethanol CH_3CH_2OH thus the formula of (HA) is $C_2H_5 – COOH$.

2- Study of the Solution $S_{E1/2}$ obtained at the Half-equivalence of the Above Titration

2.1. At the half-equivalence, the majority chemical species, other than water, present in the solution $S_{E1/2}$ are $C_2H_5COO^-$, C_2H_5COOH and Na^+ where:

$n_{C2H5COO} = n_{C2H5COOH,} = CbVbE/2 = 0.002$ mol.

2.2. Where : $[C_2H_5COO^-] = [C_2H_5COOH]$ and pH = pKa = 4.9.

2.3. The solution obtained is a buffer solution whose pH does not vary by addition of water and varies little by moderate addition of a strong acid or a strong base.

2.4. We can obtain a solution of the same pH by mixing:

a- Solution 1 + solution 4

Equation: $C_2H_5COO^- + H_3O^+ \rightarrow C_2H_5COOH + H_2O$; $Kr = 10^{4.9}$ reaction complete

	$C_2H_5COO^-$ +	$H_3O^+ \rightarrow$	C_2H_5COOH +	H_2O
initial	0,05	0,025	0	bcp
final	0,025	0	0,025	bcp

and pH = pKa

b- Solution 2 + solution 3

Equation: $C_2H_5COOH + HO^- \rightarrow C_2H_5COO^- + H_2O$ $Kr = 10^{9.1}$

	C_2H_5COOH +	$HO^- \rightarrow$	$C_2H_5COO^-$ +	H_2O
initial	0,05	0,025	0	bcp
final	0,025	0	0,025	bcp

and pH =pKa.

c- Solution 1 + solution 3

Equation: $C_2H_5COO^- + C_2H_5COOH \leftrightarrows C_2H_5COOH + C_2H_5COO^-$ $Kr = 10^0 = 1$

et pH =pKa

3- Some Reactions of the Propanoic Acid

a- $CH_3—CH_2—COOH + PCl_5 \rightarrow CH_3—CH_2—COCl + POCl_3 + HCl$

b- $CH_3—CH_2—COOH + CH_3—OH \leftrightarrows CH_3—CH_2—COO—CH_3 + H_2O$

c- $CH_3—CH_2—COOH + CH_3—CH_2—COOH \rightarrow$
$CH_3—CH_2—COOOC—CH_2—CH_3 + H_2O$

d- $CH_3—CH_2—COOH + CH_3—NH_2 \rightarrow CH_3—CH_2—CONH—CH_3 + H_2O$.