Entrance Exam 2007-2008 **CHEMISTRY** **Duration: 1 hour**

First Exercise (10 points)
Influence of the Concentration of Reactants on the Rate of the Reaction

The aim of this exercise is the study of the influence of the concentration of reactants on the rate of the oxidation reaction of iodide ions with hydrogen peroxide, in acidic medium, according to the reaction of the following equation:

$$H_2O_2 + 2\,I^- + 2\,H_3O^+ \rightarrow I_2 + 4\,H_2O \qquad \textbf{(1)}$$

In order to realize this study, iodine formed during time, in two experiments, is titrated according the reaction of the following equation:

$$I_2 + 2\,S_2O_3^{2-} \rightarrow 2\,I^- + S_4O_6^{2-} \qquad \textbf{(2)}$$

I- Preparation of Two Reactional Mixtures

Experiment 1

The reactional mixture is obtained by dissolving in water: 1.0×10^{-3} mol of hydrogen peroxide, 2.0×10^{-3} mol of potassium iodide and a sufficient quantity of sulfuric acid in order to obtain a solution of total volume equal to 100 mL.

Experiment 2

The reactional mixture having a volume of 100 mL and the following concentrations: $[H_2O_2]_0 = 2.0\times10^{-2}$ mol.L^{-1}; $[I^-]_0 = 4.0\times10^{-2}$ mol.L^{-1}.

In the two experiments, the concentration H_3O^+ ions is closed to 1 mol.L^{-1}, could be considered constant. The two experiments are realized at the same temperature.

1- Calculate the concentration of H_2O_2 and that of I^- in the reactional mixture of experiment 1.
2- Verify if the reactants, H_2O_2 and I^-, in the two mixtures, are in a stoechiometric proportions.

II- Make Use of the Results of the Kinetic Study

The results of this study are given in the following table:

Time (min)	10	20	40	60	80	100	120	180	240	300	360
Ex1 : $[I_2]$ 10^{-3}mol.L^{-1}	0.2	0.4	0.74	1.07	1.4	1.7	2.0	2.65	3.25	3.75	4.2
Ex2 : $[I_2]$ 10^{-3}mol.L^{-1}	0.8	1.5	2.8	3.9	4.9	5.7	6.5	8.4	9.8	11	11.8

1- Plot, on the same graph paper, the two curves $[I_2] = f(t)$ and $[I_2] = g(t)$ respectively related to experiments 1 and 2.
Take the following scales: abscissa: 1 cm for 20 min and ordinate: 1 cm for 1.0×10^{-3} mol.L^{-1}. (Each horizontal or vertical division on the answer sheet corresponds to 0.5 cm).
2- Determine the rate of formation of iodine at instant t = 150 min in each of the two experiments.

3- Compare the values that obtained in question 2 and conclude.
4- Verify if the half-reaction time, in each experiment, is reached or not in the interval of time 0 – 360 min.
5- Indicate another kinetic factor able to modify the rate of formation of iodine.

Second Exercise (10 points)
Identification of an Organic Compound

The identification of an organic compound starts by the determination of its molecular formula then followed by the study of certain of its proprieties.

Given: Molar mass in $g.mol^{-1}$: M (H) = 1; M (C) =12; M (O) = 12

I- Determination of the Formula of the compound (A)

An organic compound (A) of molecular formula C_xH_yO, has the following percentage by mass: C: 64.86% and H: 13.51%. .

1- Show that the molecular formula of (A) is $C_4H_{10}O$.
2- (A) is an alcohol; write the condensed structural formulas of its isomers.
3- (A) reacts with oxygen gas of air, in presence of cupper as catalyst, to give compound (B) which reacts with 2,4-DNPH but not with Schiff's reagent. Identify (A).
4- (A) gives by dehydration water and three compounds (C), (D) and (F). (F) is an oxygenated compound; (D) is in majority compared with (C). Identifier (C), (D) and (F).

II- Reaction of (A) with Acetic Acid

At the room temperature, (A) is a liquid of density d = 0.74 $g.mL^{-1}$.
A volume of 40 mL of (A) is mixed with 24 g of acetic acid in presence of some drops of concentrated sulfuric acid and boiling stones. The mixture is subjected to a reflux heating during 30 minutes.

1- Write the equation of the reaction using the condensed structural formals for the organic compounds.
2- Titration of the acid, after cooling, shows the presence of 0.20 mol of acid. Specify if the mixture reaches the equilibrium knowing that its constant is Kc = 2,25

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Solution of CHEMISTRY

First exercise (10 points)
Influence of the concentration of the reactants on the rate of the reaction

I- Preparation of the two reacting mixtures

1- The molar concentration is given by: $C = \frac{n_{solute}(initial)}{V_{solution}}$. So, we have:

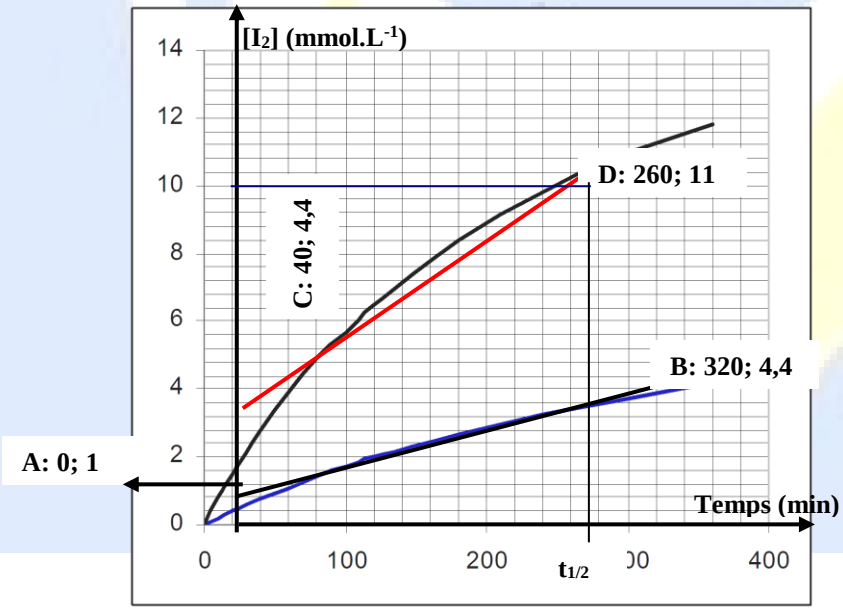
$[H_2O_2]_{initial} = \frac{1.0\times10^{-3}}{100\times10^{-3}} = 1.0\times10^{-2}$ mol.L^{-1} and

$C_{KI} = [I^-]_{initial} = \frac{2.0\times10^{-3}}{100\times10^{-3}} = 2.0\times10^{-2}$ mol.L^{-1}. **(1 point)**

2- In the two mixtures, we have: $\frac{n(H_2O_2)_{initial}}{1} = \frac{n(I^-)_{initial}}{2}$. Then the two reactants (H_2O_2 and I^-) are in the stochiometric ratios. **(1 point)**

II- Make use of the results of the kinetic study

1- The curve is:



(2 points)

2- The rate of formation of I_2 at the instant t = 150 min is defined by:

$r(I_2)_{150} = \frac{d[I_2]}{dt}$. Its value is equal to the slope of the tangent of the curves ($[I_2] = f(t)$ and $[I_2] = g(t)$) on the points of abscissa t = 150 min. We have:

$r_1(I_2)_{150} = \frac{yB - yA}{xB - xA} = \frac{(4.4-1)\times10^{-3}}{320-0} = 1.0\times10^{-5}$ mol.L^{-1}.min^{-1} and

$r_2(I_2)_{150} = \frac{yD - yC}{xD - xC} = \frac{(11-4.4)\times10^{-3}}{260-40} = 3.0\times10^{-5}$ mol.L^{-1}.min^{-1}. **(2 points)**

3- It is noticed that if the concentrations of the reactants are larger the rate of formation of I_2 at the same moment is higher. We draw whereas the concentration of a reactant is a kinetic factor. When this concentration increases the rate of the reaction increases.

(1 point)

4- The half-life of the reaction is the interval of time at the end of which half of $[I_2]_\infty$ is formed.

$[I_2]_\infty = [H_2O_2]_0$

For the first experiment $t_{1/2}$ corresponds to a concentration.

$[I_2]_{t½\,(1)} = \frac{1\times10^{-2}}{2} = 5\times10^{-3}$ mol.L^{-1}.

In the interval of the time given in table (0; 360 min) we did not arrive at this concentration of I_2. We cannot thus determine the time of half-life of the reaction in the first experiment for the values given. For the second experiment $t_{1/2}$ corresponds to a concentration

$[I_2]_{t½\,(2)} = 10\times x10^{-3}$ mol.L^{-1}. We find $t_{1/2\,(2)} = 250$ min. **(2 points)**

5- The temperature is another kinetic factor. The rate of the reaction increases when the temperature increases. **(1 point)**

Second exercise (10 points)
Identification of an organic compound

I- <u>Determination of the compound</u>

1- Determination of the molecular formula of (A):

The mass percentage of oxygen is: 100 – (64.86 + 13.51) = 21.63.

The law of the definite proportions permits to write: $\frac{12x}{64.86} = \frac{y}{13.51} = \frac{16}{21.63}$

We draw then: $x = \frac{64.86\times16}{12\times21.63} = 4$ and $y = \frac{13.51\times16}{21.63} = 10$. From where the formula is: $C_4H_{10}O$.

(1point)

2- The condensed structural formulas are:
$CH_3 – CH_2 – CH_2 – CH_2OH$;
$CH_3 – CH_2 – CHOH – CH_3$;
$CH_3 – CH(CH_3) – CH_2OH$;

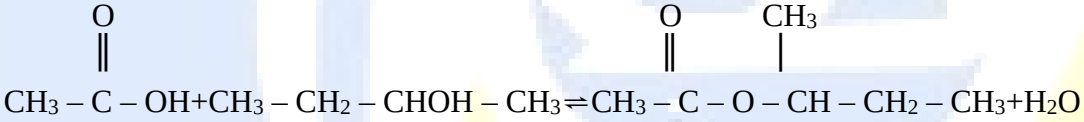
$CH_3 – C(CH_3)_2$; **(1 point)**

3- The compound (A) undergoes the mild oxidation in the presence of copper; it is a primary or secondary alcohol. The product of oxidation (B) reacts with the 2,4-DNPH, it is thus an aldehyde or a ketone. (B) does not react with the reagent of Schiff, it is a ketone and (A) is secondary alcohol. It is then 2-butanol of formula $CH_3 – CH_2 – CHOH – CH_3$. **(2 points)**

4- The intermolecular dehydration of (A) gives two compounds: one majority (D) of formula $CH_3 – CH = CH – CH_3$: 2-butene, The other minority one (C) of formula $CH_3 – CH_2 – CH = CH_2$: 1-butene (according to Zaytzev).
The intermolecular dehydrationn gives the ether (F) of formula
$CH_3 – CH_2 – CH(CH_3) – O – CH(CH_3) – CH_2 – CH_3$: di (1-methyl)propyle oxide.
(3 points)

II- Reaction of (A) with acetic acid

1- The equation of the reaction between ethanoic acid and (A) is the following:



$$CH_3 – C(=O) – OH + CH_3 – CH_2 – CHOH – CH_3 \rightleftharpoons CH_3 – C(=O) – O – CH(CH_3) – CH_2 – CH_3 + H_2O$$

(1 point)

2- $n(\text{alcohol})_i = \frac{m(\text{alcohol})}{M(\text{alcohol})} = \frac{\rho \times V}{M(\text{alcohol})} = \frac{0.74 \times 40}{74} = 0.40$ mol.

$n(\text{acid})_i = \frac{m(\text{acid})}{M(\text{acid})} = \frac{24}{60} = 0.40$ mol. The mixture is stœchiomtric.

The table shows the composition

	Acid	Alcohol	Ester	Water
Initial state	0.40	0.40	0	0
State where n(acid) = 0.20	0.40-0.20 = 0.20	0.40-0.20 = 0.20	0.20	0.2

The ratio $Q = \frac{[\text{ester}]x[\text{eau}]}{[\text{acide}]x[\text{alcool}]} = \frac{(\frac{0.20}{V})^2}{(\frac{0.20}{V})^2} = 1 < K_C = 2.25$, the system does not reach the equilibrium. **(2 points)**