Entrance Exam (2017 – 2018) **Chemistry Exam** **Duration 1 hour**
9 July 2017

Answer the Following Two Exercises:

First Exercise (10 points)
Chemical Kinetics

The water of dibrome (bromine) is an aqueous solution of a red brown color, the formic acid or methanoic acid is a weak acid, its aqueous solution is colorless.
At instant t = 0 s, an equal volumes of a water dibrome solution of concentration $C_1 = 0.0240$ mol.L^{-1} and formic acid solution of concentration $C_2 = 0.0200$ mol.L^{-1} are mixed. Formic acid reacts with the dibrome to give hydrobromic acid colorless and the gas carbon dioxide which is very slightly soluble in water according to a complete and slow reaction of the following equation:

$$Br_2\,(aq) + HCOOH\,(aq) \rightarrow 2\,H^+_{(aq)} + 2\,Br^-_{(aq)} + CO_2\,(g)$$

By a suitable method we determine, during time, the concentration of dibrome. The obtained result is registered in the following table:

Time (s)	0	50	100	150	200	250	300	350	400
$[Br_2]$ (10^{-3} mol.L^{-1})	12	10	8.5	7.0	6.0	5.0	4.2	3.5	3.0

1- Justify the value of the dibrome concentration given in the above table at t = 0 s.
2- Determine the half-life of the reaction.
3- Plot the curve $[Br_2] = f(t)$. Take the following scale: 1cm (2 squares) for 50 s in abscissa and 1cm (2 squares) for 2.0×10^{-3} mol.L^{-1} in ordinate.
4- Establish the relation between $[HCOOH]_t$ and $[Br_2]_t$.
5- Calculate the two missing values in the following table:

Time (s)	0	50	100	150	200	250	300	350	400
[HCOOH] (10^{-3} mol.L^{-1})	10		6.5	5.0	4.0	3.0	2.2		1.0

6- Plot on the same graph the curve $[HCOOH] = g(t)$.
7- Justify from the graph the value $t_{1/2}$ founded in part 2.
8- Determine the pH of the solution at the end of the reaction.

Second Exercise (10 points)

Identification of an Organic Compound Having Two Functional Groups

The analysis of an organic compound (A) shows that its molecular formula is $C_4H_8O_2$.

1- Identification of the Two Functional Groups of (A)

To identify the two functional groups of (A), a series of chemical tests are carried out with this compound and, the results are given in the following table:

Number of the test	Reagent	Result
1	2,4-DNPH	Positive test
2	Fehling solution	Positive test
3	Excess of an acidified solution of dichromate	A compound (B) is obtained
4	Ethanoic acid	A compound (C) is obtained

1.1- What can you conclude from the result of the test Nº 1 concerning the compound (A)?
1.2- What can you conclude from the result of the test Nº 2 concerning the compound (A)?
1.3- The compound (B), which presents acidic properties, gives a positive test with the 2,4-DNPH and a negative test with ammoniacal silver nitrate. What can you conclude from test Nº 3 concerning the compound (A)?
1.4- The compound (C) contains an ester group. What can you conclude from test Nº 4 concerning compound (A)?

2- The Observations

Indicate, in the case of a positive result, the suitable observations in each of the tests Nº: 1 – 2 and 3.

3- Structural Formula and Name of the Compound (A)

3.1- Write the two possible condensed structural formulas of the identified compound (A).
3.2- Knowing that one of the two functional groups of compound (A) is in position 3, give the systematic name of (A).
3.3- Write, using condensed structural formulas, the equation of the preparation of (C).
3.4- The compound (A) is obtained from ethanal like only reagent, write, using the condensed structural formulas, the equation of the synthesis of (A).

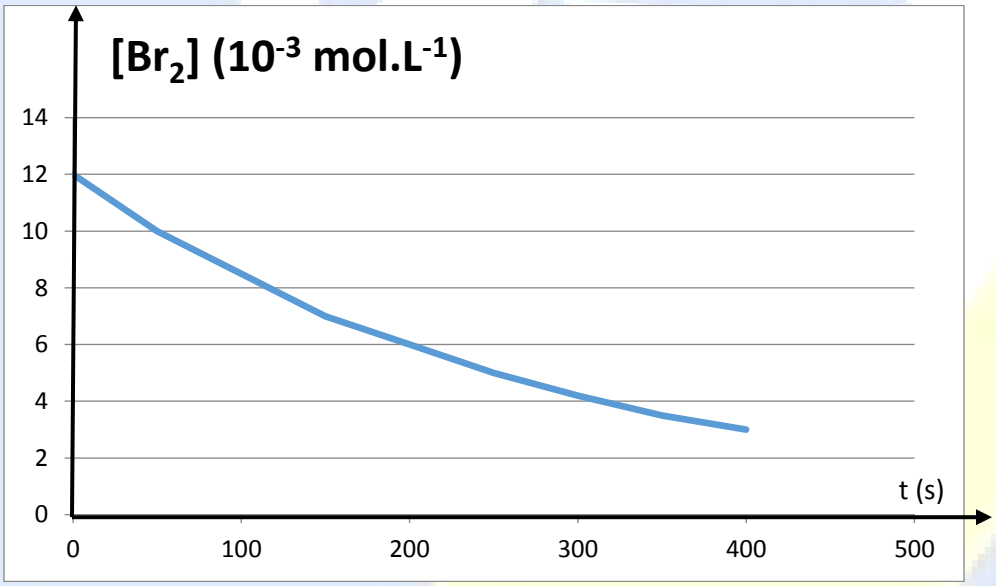
Entrance Exam (2017 – 2018) **Chemistry Solution** **9 July 2017**

First Exercise (10 points)

1- The volume of mixture V = $2V_1$. CV=C_1V_1 where C = $C_1/2$ = 0.012 mol.L^{-1}. (1 point)

2- At half-life $t_{1/2}$ there is disappearance of the half of the limiting reagent.
The limiting reagent is HCOOH because n HCOOH=0.02V< $n\ Br2\ 0.024V$
n HCOOH $_{\text{reacting (t1/2)}}$= $nBr_{2\ \text{reacting (t1/2)}}$ = 0.02 $V_1/2$
and $nBr_{2\ \text{remaining (t1/2)}}$= 0.024$V_1$- 0.02$V_1/2$ = 0.014V_1
Where $[Br_2]_{t1/2}$= 0.014$V_1/2V_1$ = 0.007 mol.L^{-1} and according to the table $t_{1/2}$= 150 s. (2 points)

3- The curve $[Br_2]$ = f(t). (1 point)

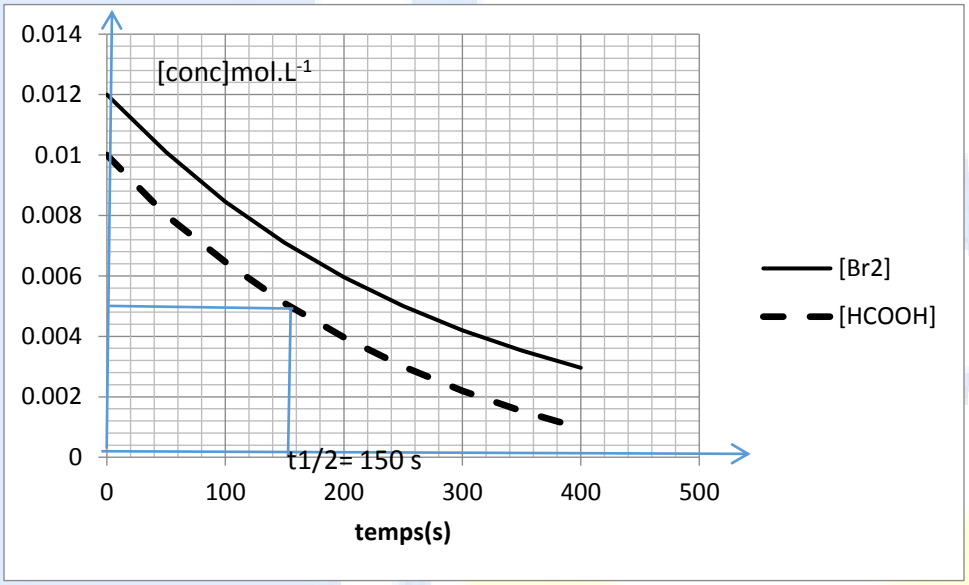


4- n $_{\text{HCOOH reacting (t)}}$= $n_{\text{Br2 reacting (t)}}$
n $_{\text{HCOOH remaining (t)}}$= n $_{\text{HCOOH initial}}$- n $_{\text{HCOOH reacting (t)}}$= n $_{\text{HCOOH initial}}$ - n $_{\text{Br2 reacting (t)}}$ =
n $_{\text{HCOOH initial}}$- n $_{\text{Br2 initial}}$ + n $_{\text{Br2(t)}}$ divvied by V we obtain:
$[HCOOH]_t$ =($[Br_2]_t$- 0.002) mol.L^{-1}. (2 points)

5- Complete the table. (1 point)

Temps (s)	0	50	100	150	200	250	300	350	400
[HCOOH] (10^{-3} mol.L^{-1})	10	**8.0**	6.5	5.0	4	3	2.2	**1.5**	2

6- The curve [HCOOH] = g(t). (1 point)



7- At the half-life: $[HCOOH]_{t1/2} = [HCOOH]_o/2 = 0.005$ mol.L^{-1} which corresponds to the time of 150 s (1 point)

8- At the end of the reaction we have $[H^+] = 2\,[HCOOH]_o = 0.02$ mol.L^{-1}.
Where pH = - log 0.02 =1.7 (1 point)

Second Exercise (10 points)

1- Identification of the Two Functional Groups of (A)

1.1- The reagent 2,4-DNPH identify the presence of the carbonyl group $-C=O$ in the compound (A). (1 point)

1.2- Fehling solution identify that the carbonyl group $H-C=O$ in the compound (A) which corresponds to an aldehyde. (1 point)

1.3- The two functional groups of compound (A) undergo the oxidation.
One is an aldehyde giving an acid (1 point) the other is a hydroxyl group corresponding to a secondary alcohol giving by oxidation a ketone. (1 point)

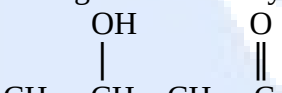
1.4- The test 4 confirmed the presence of hydroxyl group in the compound (A). (1 point)

2. The observations

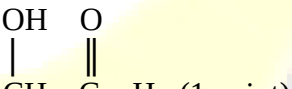
In the test 1 we observe the formation of a yellow precipitate.
In the test 2 we observe the formation of a red precipitate.
In the test 3 we observe a change of color from orange to green. (1.5 point)

3. Structural Formula and Name of Compound (A)

3.1- Having in its formula 4 carbon atoms, a carbonyl group and a hydroxyl group corresponding to a secondary alcohol of the following possible condensed structural formulas:



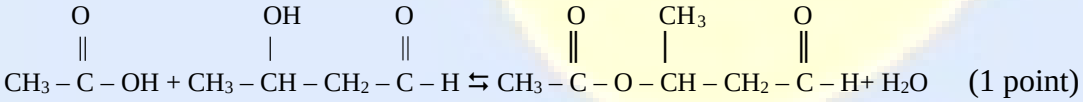
$CH_3-CH(OH)-CH_2-C(=O)-H$;



$CH_3-CH_2-CH(OH)-C(=O)-H$ (1 point)

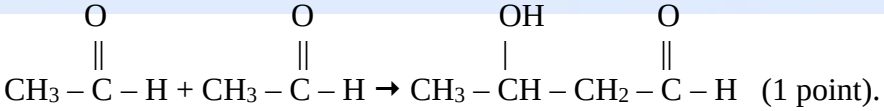
3.2- The name is 3-hydroxybutanal. (0.5 point)

3.3- The equation of the preparation of (C) is:



$CH_3-C(=O)-OH + CH_3-CH(OH)-CH_2-C(=O)-H \leftrightarrows CH_3-C(=O)-O-CH(CH_3)-CH_2-C(=O)-H + H_2O$ (1 point)

3.4- The equation of the synthesis reaction of (A) is:



$CH_3-C(=O)-H + CH_3-C(=O)-H \rightarrow CH_3-CH(OH)-CH_2-C(=O)-H$ (1 point).