وزارة التربية و التعليم العالي
المديرية العامة للتربية
دائرة الامتحانات

امتحانات شهادة الثانوية العامة
فرع علوم الحياة

دورة سنة ٢٠٠٤ الاستثنائية الاكمالية

مسابقة في الكيمياء
المدة ساعتان

الاسم:
الرقم:

This Exam Includes **Three Exercises.** It Is Inscribed on **4** Pages Numbered From 1 to 4.
The Use of a Non-programmable Calculator Is Allowed.

Answer The Three Following Exercises:

First Exercise (6.5 points)
Identification of an Organic Compound (B)

A gaseous organic compound (B) has a rotten fish smell. The elementary analysis of (B) shows that it is composed of three elements: carbon, hydrogen and nitrogen.

<u>Given</u>

- Study is performed at 25 ºC.
- Molar volume of a gas: $V_m = 24\ L.mol^{-1}$.
- Ion product of water: $K_w = 10^{-14}$.
- Molar atomic masses in $g.mol^{-1}$: $M_H = 1$; $M_C = 12$; $M_N = 14$.

I- Acid-base nature of (B)

One liter of solution (S) is prepared by dissolving 0.48 L of (B) in distilled water. The pH value of this solution is 11.1.

1- Determine the initial concentration C_B of solution (S).
2- Show that compound (B) is a weak base.
3- The compound (B) reacts with water according to the following equation:

$$B + H_2O \rightleftharpoons HO^- + BH^+$$

Determine the value of pK_a of the pair BH^+/B.

II- Determination of the molar mass of (B)

A solution (S´) is prepared by dissolving 150 mg of (B) in distilled water. The solution (S´) is titrated by a hydrochloric acid solution of concentration $C_a = 0.10\ mol.L^{-1}$. The equivalence point is reached when 25.4 mL of the acid solution are added.

1- Write the equation of the titration reaction.
2- Show that the molar mass of (B) is $M = 59.05\ g.mol^{-1}$.

III- Identification of (B)

The study shows that compound (B) is a saturated monoamine.

1- Verify that the molecular formula of (B) is C_3H_9N.
2- Write the condensed structural formulas of the possible isomers of (B).
3- Identify (B) knowing that it does not react with acyl chlorides.

Second Exercise (7.5 points)
Kinetic of the Reaction Between Hydrochloric Acid and Zinc

Hydrochloric acid solution reacts with zinc according to the following equation:

$$2\ H_3O^+_{(aq)} + Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + H_{2\,(g)} + 2\ H_2O_{(l)}.$$

This exercise aims to study the kinetic of this reaction.

Given

- Molar atomic mass: $M_{Zn} = 65.4$ g.mol^{-1}.
- Molar volume of a gas at the experimental conditions: $V_m = 24$ L.mol^{-1}.

I- Preliminary study

At time t = 0, a volume $V_a = 40$ mL of hydrochloric acid solution of concentration $C_a = 0.500$ mol.L^{-1} is poured into a flask containing a mass m = 1 g of powdered zinc. We admit that the volume of the mixture remains constant.
The volume of the collected hydrogen gas is measured with time.

1- Explain the advantage of the use of powdered zinc instead of a zinc strip in this study.
2- Determine at t = ∞ the concentration of Zn^{2+} ions: $[Zn^{2+}]_\infty$
3- Show that the concentration of H_3O^+ ions, $[H_3O^+]_0$ at t = 0, and that of $[H_3O^+]_t$ at each instant t, are related to the volume of hydrogen gas V_{H_2}, which is formed at each instant t, according to the following relation:

$$[H_3O^+]_t = [H_3O^+]_0 - \frac{V_{H_2}}{480}$$, where V_{H_2} is expressed in mL.

II- Kinetic of the reaction

Experimental results are given in the following table:

t (s)	0	100	200	300	400	500	600	800	1000
V_{H_2} (mL)	0	80	132	154	168	178	183	188	192
$[H_3O^+]$ (mol.L^{-1})	x	0.333	0.225	0.179	0.150	0.129	0.119	y	0.100

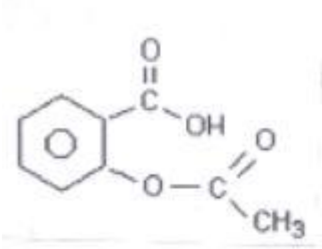
1- Give the value of x, and calculate that of y in the above table.
2- Plot, on the graph paper, the curve $[H_3O^+] = f(t)$.
Consider the following scales: abscissa: 1 cm = 100 s; ordinate: 1 cm = 0.05 mol.L^{-1}.
3- Determine, graphically, the half-life of the reaction.
4- Give, at each instant t, the relation between the rate of formation of Zn^{2+} ions and that of the disappearance of H_3O^+ ions.
5- Trace, on the same graph, the shape of the curve which represents the variation of the concentration of Zn^{2+} ions in terms of time: $[Zn^{2+}] = g(t)$ and passing through the three points of abscissas: t = 0, $t = t_{½}$ and t = 1000 s.

Third Exercise (6 points)
Titration of Aspirin

The aspirin is one of the most consumed drugs in the world. The aim of this exercise is to titrate the acetylsalicylic acid in a tablet of a simple aspirin “300” which is sold in the lebanese market. (“300” represents, in mg, the mass of pure acetylsalicylic acid in one tablet)

<u>Given</u> :

- Condensed structural formula of acetylsalicylic acid:



- pK_a(acetylsalicylic acid/acetylsalicylate ion) = 3.5
- M(acetylsalicylic acid) = 180 g.mol^{-1}.

- An ester, of formula $CH_3 - \overset{\overset{O}{\|}}{C} - O - R'$, reacts with sodium hydroxide solution at high temperature. The reaction that takes place is total and is represented by the following equation:

$$CH_3 - \overset{\overset{O}{\|}}{C} - O - R' \; + \; HO^- \; \rightarrow \; CH_3 - \overset{\overset{O}{\|}}{C} - O^- \; + \; R' - OH$$

I- <u>Acid-base reaction</u>

A weak acid, of formula R – COOH, reacts with sodium hydroxide solution at low temperature, according to a rapid reaction which is represented by the following equation:

$$R - COOH \; + \; HO^- \; \rightarrow \; R - COO^- \; + \; H_2O$$

Verify that this reaction is total, knowing that:

$$pK_a(R - COOH/R - COO^-) < 5 \text{ and } pK_a(H_2O/HO^-) = 14.$$

II- <u>Preparation of acetylsalicylic acid solution</u>

A tablet of a simple aspirin “300” is carefully grinded. The obtained powder is introduced into an appropriate volumetric flask which is partially filled with distilled water. The flask is shaken to dissolve completely the powder. Distilled water is then added to reach the line mark. The obtained solution is called (S).

Show that the appropriate volumetric flask to prepare (S) is of 200 mL capacity, knowing that:

- 50 mL and 200 mL volumetric flasks are only available in the laboratory,
- the solubility of acetylsalicylic acid, in water at 25 ºC, is equal to 3.4 g.L^{-1}.

III- Carrying out titration

The acid-base titration of a 200 mL solution (S) is carried out at low temperature, with sodium hydroxide solution of concentration C_b = 0.10 mol.L^{-1}.

1- The volume added at the equivalence point is V_{bE} = 17 mL. Verify that the mass of acetylsalicylic acid in the tablet of this aspirin is about 300 mg.
2- Rewrite, on the answer sheet, the formula of aspirin. Circle on it, the two functional groups containing oxygen and name them.
3- Name the two reactions that may take place, at high temperature, between hydroxide ions HO^- and aspirin.
4- Conclude why this acid-base titration should be carried out at low temperature.

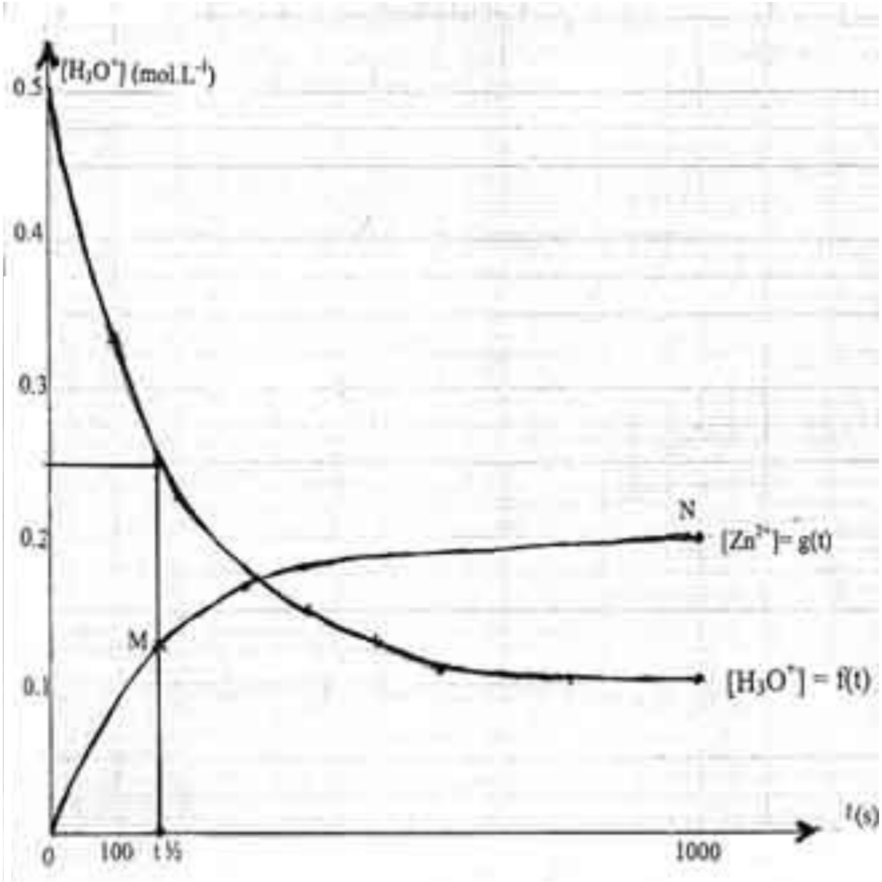
First exercise (6.5 points)

Expected answer	Comments
I- 1- The concentration C_B, expressed in $mol.L^{-1}$, is given by: $C_B = \dfrac{n_{solute} in mol}{V_{solution} in L} = \dfrac{\frac{V_{solute}}{V_m}}{V}$. With; $V_{solute} = 0.48$ L; $V_m = 24$ L -mol^{-1} *and V = 1 L, we have:* $C_B = 0.02$ $mol.L^{-1}$.	
2- The relation $pH = pK_w + \log [HO^-]$ permits to calculate $[HO^-]$. $pH = 11.1$; $pK_w = 14$ we get: $[HO^-] = 1.25x10^{-3}$ $mol.L^{-1} < C_B = 0.02$ $mol.L^{-1}$. The compound (B) is then a weak base.	Each correct reasoning is acceptable.
3- Determination of pK_a: $B + H_2O \rightleftharpoons BH^+ + HO^-$ Initial state ($mol\ L^{-1}$) 0.02 0 0 At equilibrium 0.02 – x x x The relation: $pH = pK_a + \log \dfrac{[B]}{[BH^+]}$ permits to calculate pK_a. $pK_a = pH - \log \dfrac{[B]}{[BH^+]} = 11.1 - \log \dfrac{0.02 - x}{x}$ $pK_a = 11.1 - \log \dfrac{0.02 - 1.25x10^{-3}}{1.25x10^{-3}} = 9.92$	Each correct reasoning is acceptable. ↓
II- 1- The equation of the titration reaction is: $B + H_3O^+ \rightarrow BH^+ + H_2O$ 2- Determination of the molar mass of (B): At the equivalence point, we have: $n_{(acid)}$ added = $n_{(B)}$ contained in (S´). In a solution we have: $n_{(solute)} = C \times V$. $C_A x V_A = n_{(B)}$. with: $0.1x\ 25.4x10^{-3} = n_B = \dfrac{m_B}{M_B} = \dfrac{150x10^{-3}}{M_B}$. We have: $M_B = 59.05$ $g.mol^{-1}$.	//
III- 1- The molecular formula of a saturated monoamine is: $C_nH_{2n+3}N$. M = 12n + 2n + 3 +14 = 59.05. so n = 3 The molecular formula is then: C_3H_9N. 2- The condensed structural formulas of possible isomers of (B) are: $CH_3 - CH_2 - CH_2 - NH_2$; $CH_3 - CH_2 - NH - CH_3$; $CH_3 - \underset{NH_2}{\underset{\vert}{CH}} - CH_3$ and $CH_3 - \underset{CH_3}{\underset{\vert}{N}} - CH_3$. 3- The compound (B) is an amine which does not react with the acyl chloride. (B) is then a tertiary amine of formula: $CH_3 - \underset{CH_3}{\underset{\vert}{N}} - CH_3$ It is trimethylamine or N, N – dimethyl methanamine.	

Second exercise (7.5 points)

Expected answer	Comments
I- 1- The contact surface between the reactants in the case (powder of zinc + hydrochloric acid solution) is bigger than the contact surface between the reactants in the case (strip of zinc + hydrochloric acid solution). Then the rate of the reaction, in the first case, is greater because the rate increases when the contact surface increases. 2- Determination of the limiting reactant: $R\,H_3O^+ = \frac{n(H_3O^+)initial}{2} = \frac{C_a.V_a}{2} = \frac{0.5x40x10^{-3}}{2} = 1x10^{-2}$ $R_{Zn} = \frac{n(Zn)\,introduced}{1} = \frac{m(Zn)\,introduced}{M(Zn)} = \frac{1}{65.4} = 1.5x10^{-2}$. Since $R\,H_3O^+ < R_{Zn}$, then H_3O^+ is the limiting reactant. According to stœchiometric cœfficients of the equation, we write: n(Zn) formed at ∞ = $\frac{n(H_3O^+)initial}{2} = 1x10^{-2}$ mol. Concentration of Zn^{2+}: $[Zn^{2+}]_\infty = \frac{n(Zn^{2+})}{V_a} = \frac{1x10^{-2}}{40x10^{-3}} = 0.25\ mol.L^{-1}$. 3- At instant t: $n(H_3O^+)$ remaining = $n(H_3O^+)$ initial – $n(H_3O^+)$ reacting. According to the stœchiometric cœfficients of the equation, we could write: $n(H_3O^+)$ reacting = 2 $n(H_2)$ formed. So: $n(H_3O^+)$ remaining = $n(H_3O^+)$ initial – 2 $n(H_2)$ formed. Dividing by the constant volume of the solution, $40x10^{-3}$ L, we have then: $[H_3O^+]_t = [H_3O^+]_0 - 2x\frac{n(H_2)}{V}$ $[H_3O^+]_t = [H_3O^+]_0 - 2x\frac{V(H_2)x10^{-3}}{V_m xVx10^{-3}}$ $[H_3O^+]_t = [H_3O^+]_0 - 2x\frac{V(H_2)}{24x40} = [H_3O^+]_0 - \frac{V(H_2)}{480}$. **II-** 1- <u>Value of x</u> : $x = [H_3O^+] = C_a = 0.500\ mol.L^{-1}$. <u>Value of y</u> : $y = [H_3O^+]_{800} = 0.500 - \frac{188}{480} = 0.108\ mol.L^{-1}$.	

2-



3- The half-life of the reaction is the time needed for half the amount of the limiting reactant to be consumed, according to the graph $t_{½} = 170s$ when $[H_3O^+] = 0.25$ mol L^{-1}

4- According to the stœchiometric cœfficients of the equation, The two rates are related by: $R_{disappearance}(H_3O^+) = 2xR_{formation}(Zn^{2+})$.

5- The three points: O (t = 0s; $[Zn^{2+}] = 0$ mol L^{-1}); M ($t = t_{1/2} = 170$ s; $[Zn^{2+}] = 0.125$ mol L^{-1}) and N (t =1000 s; $[Zn^{2+}] = 0.2$ mol L^{-1}).

Third exercise (6 points)

Expected answer	Comments
I- 1- The equation of the reaction is: $$RCOOH + HO^- \rightarrow RCOO^- + H_2O$$ $$K_R = \frac{[RCOO^-]}{[RCOOH][HO^-]} = \frac{[RCOO^-][H_3O^+]}{[RCOOH][HO^-][H_3O^+]}$$ $K_R =$ $$\frac{K_a(RCOOH/RCOO^-)}{K_a(H_2O/HO^-)} = \frac{10^{-pK_a(RCOOH/RCOO^-)}}{10^{-pK_a(H_2O/HO^-)}} = 10^{pK_a(H_2O/HO^-) - pK_a(RCOOH/RCOO^-)}$$	Direct application of the formula :1.

$K_R > 10^9 >> 10^4$. The reaction is then total.

II-

1- The solubility of aspirin is 3.4 g, so the minimum volume of water needed to dissolve 300 mg = 0.3 g of aspirin is then: $V = \frac{0.3x1}{3.4} = 0.088$ L. which is >50 mL and < 200mL.

Hence the capacity of the volumetric flask should be 200 mL.

Any reasonable answer is accepted.

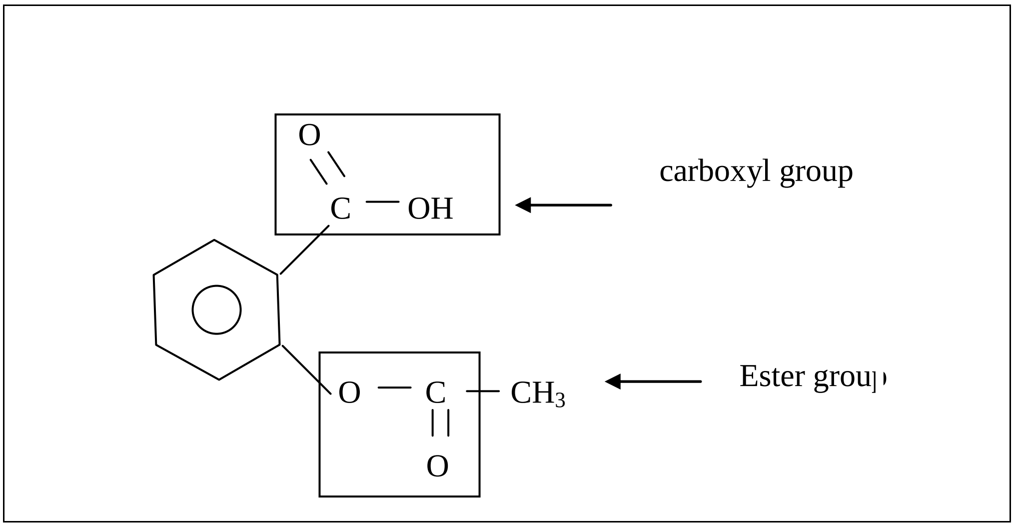
III-

1- At equivalence : n(aspirin) in the solution = n (HO^-) added

$\frac{m}{180} = C_b \text{ x } V_{bE} = 0.1 \text{ x } 17 \text{ x } 10^{-3}$

so m = 0.306g. ≅ 300 mg.

2-



3 – The reaction between the HO^- ions and the carboxyl group is an acid-base reaction.
The reaction between the HO^- ions and the ester group is a saponification reaction.

4- The acid-base titration is carried out at low temperature in order to avoid the saponification reaction that takes place at high temperature.