وزارة التربية و التعليم العالي
المديرية العامة للتربية
دائرة الامتحانات

امتحانات شهادة الثانوية العامة
فرع العلوم العامة

دورة سنة ٢٠٠٤ العادية

مسابقة في الكيمياء
المدة ســاعتان

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 (7 points)
Study of a Household Product "Windex"

Ammonia, NH_3, in aqueous solution is used often in cleaning. "Windex" is a household product used to clean glass. This exercise aims to titrate ammonia in "Windex" and to prepare a buffer solution.
This study is performed at 25 ºC.

<u>Given</u>:

Conjugate acid/base pair	H_3O^+/H_2O	NH_4^+/NH_3	H_2O/HO^-
pK_a	0	9.2	14

- Molar volume of a gas under the experimental conditions is $V_m = 24$ L.mol^{-1}.
- Ammonia gas is very soluble in water.

I- Dilution of a commercial hydrochloric acid solution

A bottle of a commercial hydrochloric acid solution is available. We have, among others, the following indications:
Density: $\rho = 1.12$ g.mL^{-1}; % by mass = 32.13%; $M_{HCl} = 36.5$ g.mol^{-1}.

1- Show that the molar concentration of this solution, noted (S_0), is $C_0 = 9.86$ mol.L^{-1}.
2- A solution (S) is prepared by dilution of the solution (S_0). The solution (S) is titrated with a sodium hydroxide solution. The obtained value of the concentration of (S) is $C_S = 0.07$ mol.L^{-1}.
The two following sets of glassware are available:
Set (a): 1000 mL volumetric flask, 10 mL graduated pipet (graduated 1/10), 50 mL beaker.
Set (b): 100 mL volumetric flask, 2 mL volumetric pipet, 50 mL beaker.
Explain, if each one of the two sets is convenient to perform the above dilution.

II- Titration of the "Windex" solution

A volume V = 25 mL of "Windex" solution is titrated with the hydrochloric acid solution (S) using a pH-meter.
Some of the experimental results are given in the following table:

$V_{(S)}$ in mL	0	22	30
pH	10.2	5.2	2.4

$V_{(S)}$ is the added volume of solution (S) during titration.

1- Write the equation of the titration reaction.
2- At the equivalence point we have: $V_{(S)Equivalence}$ = 22 mL and $pH_{Equivalence}$ = 5.2.
a) Justify the pH value which shows the acid nature of the obtained solution at equivalence.
b) Determine the volume of ammonia gas needed to prepare 1 L of « Windex » solution.
3- Draw the shape of the curve pH = f(V_S) for: $0 \leq V_{(S)} \leq 30$ mL, by locating four remarkable points on this curve.
Take the following scales: abscissa: 1cm for 2 mL and ordinate: 1 cm for 1 unit of pH.

III- <u>Preparation of a buffer solution</u>

The pH-meter, already used, was calibrated with a buffer solution of pH = 7 and another buffer solution of basic nature. The second solution was consumed; it is desired to prepare a buffer solution of pH = 9.2.
An ammonia solution of concentration $C_b = 0.06$ mol.L^{-1} and a hydrochloric acid solution of concentration $C_a = 0.07$ mol.L^{-1} are available.
Determine the volume of ammonia solution V_b added to $V_a = 60$ mL of hydrochloric acid solution in order to prepare this buffer solution.

Second Exercise (6 points)
Kinetic of The Decomposition Reaction of Hydrogen Peroxide

It is suggested to study, at 25 ºC and in the presence of Fe^{3+} ions as catalyst, the kinetic of the decomposition reaction of hydrogen peroxide solution which is sold, in drugstores, in dark flasks.
A volume V = 50 mL of a stabilized hydrogen peroxide solution, of molar concentration C = 0.893 mol.L^{-1}, is poured into a 100 mL volumetric flask; this flask is then placed on a precision balance.
At time t = 0, a volume of 2 mL of iron III nitrate solution ($Fe^{3+} + 3NO_3^-$) is added into the volumetric flask. After a short time, a big amount of gas is observed. This gas is released from the decomposition of hydrogen peroxide according to the following equation:

$$2\ H_2O_{2(aq)} \rightarrow 2\ H_2O_{(l)} + O_{2(g)}$$

With time, the balance indicates a decrease in mass. During the decomposition reaction, the variation of mass Δm represents practically the mass of oxygen gas released at each instant t.

<u>Given</u>:

- Molar mass: $M_{O_2} = 32$ g.mol^{-1}.
- Oxygen gas is practically insoluble in water.

I- <u>Preliminary study</u>

1- Specify how the above decomposition reaction will be affected in each one of the two following cases:
a) Performing this study at 40 ºC.
b) Diluting the above hydrogen peroxide solution.
2- Show that, at instant t, the number of moles of hydrogen peroxide $n(H_2O_2)_t$ and the variation of mass Δm (expressed in grams) are related to each other by the following relation:

$$n(H_2O_2)_t = 4.46\times10^{-2} - \frac{\Delta m}{16}$$

II- Kinetic Study of the reaction

The table below shows the number of moles of H_2O_2 at different instants t:

T(min)	0	2	3	4	8	10	15	20	30	35	40
$n(H_2O_2)$ (10^{-2}mol)	4.46	4.46	4.33	4.15	3.33	2.90	2.17	1.83	1.43	1.27	1.21

1- Plot, on graph paper, the curve $n(H_2O_2) = f(t)$.
   Take the following scales: abscissa: 1 cm for 2 min; ordinate: 5 cm for 1.00×10^{-2} mol.
2- Determine the average rate of disappearance of H_2O_2, in $mol.min^{-1}$, between the two instants: $t_1 = 10$ min and $t_2 = 25$ min.
3- Determine graphically the half-life of the reaction.
4- After a certain time t, the value of Δm equals 713 mg.
   Identify the chemical species that are present in the obtained solution at this time.

Third Exercise (7 points)
Identification of an Alcohol and Some Reactions of Alcohols

The analysis, of a monoalcohol (A) of a saturated open carbon chain, shows that the percentage by mass of oxygen is equal to 26.67 %.

Given:

- Molar atomic mass in $g.mol^{-1}$: $M_H = 1$; $M_C = 12$; $M_O = 16$.

N. B.:

Use the condensed structural formulas of the organic compounds to write the chemical equations.

I- Determination of the Molecular Formula of (A)

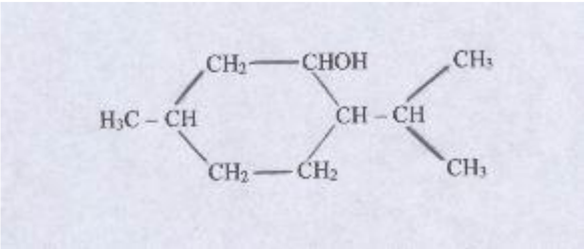
1- Show that the molecular formula of (A) is C_3H_8O.
2- Write the condensed structural formulas of the possible isomers of (A).

II- Identification of (A)

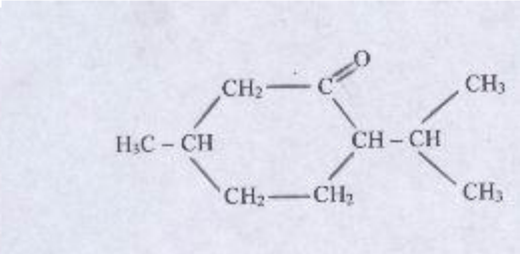
1- The mild oxidation of (A), with an appropriate method, using an acidified potassium dichromate solution ($2K^+ + Cr_2O_7^{2-}$) gives a compound (B). The compound (B) gives a positive test with 2,4 – DNPH solution and a negative test with Fehling solution. Identify (B) and (A).
2- Write the equation of the mild oxidation of (A), knowing that the dichromate ions are reduced into chromium (III) ions Cr^{3+}, in acid medium.

III- From Menthol to Menthone

Menthone is a component of essential oils for several varieties of mint. It can be obtained by the mild oxidation of menthol which has a strong smell of mint. These two compounds have the following condensed structural formulas:



Menthol



Menthone

Justify the use of mild oxidation in the preparation of menthone starting from menthol.

IV- <u>Esterification reaction of (A)</u>

0.2 mol of ethanoic acid reacts with 0.2 mol of (A) in the presence of some mL of concentrated sulphuric acid solution. After a sufficient long time, the amount of ester, in the obtained homogeneous mixture, shows no more change, and is equal to 0.12 mol.

1- Write the equation of the reaction.
2- Show that the percentage of esterification of this reaction is 60 %.
3- Three experiments are performed, under the same conditions. Their initial states are given in the following table:

Experiment	n ethanoic acid (mol)	n(A)(mol)	n ester (mol)	n_{water} (mol)
1	1	1	0	0
2	2	1	0	0
3	1	1	0.5	0

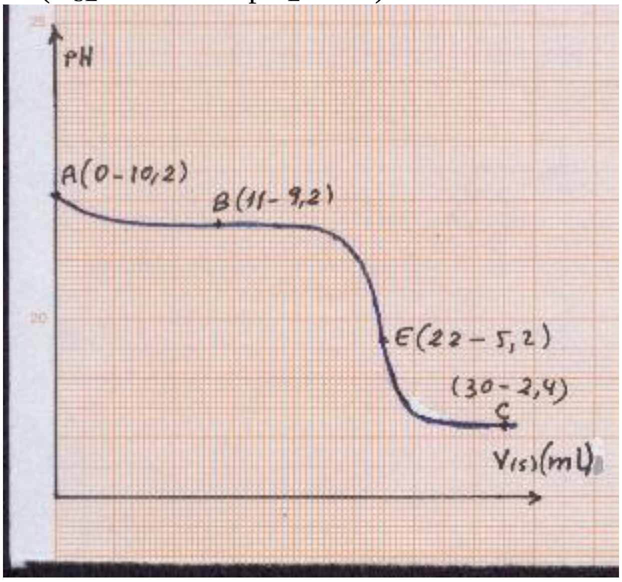
Show that each of the three experiments has a corresponding graph:

Graph (a) *Graph* (b) *Graph* (c)

3- Specify if the yield of the esterification reaction will be affected by a moderate increase of temperature.

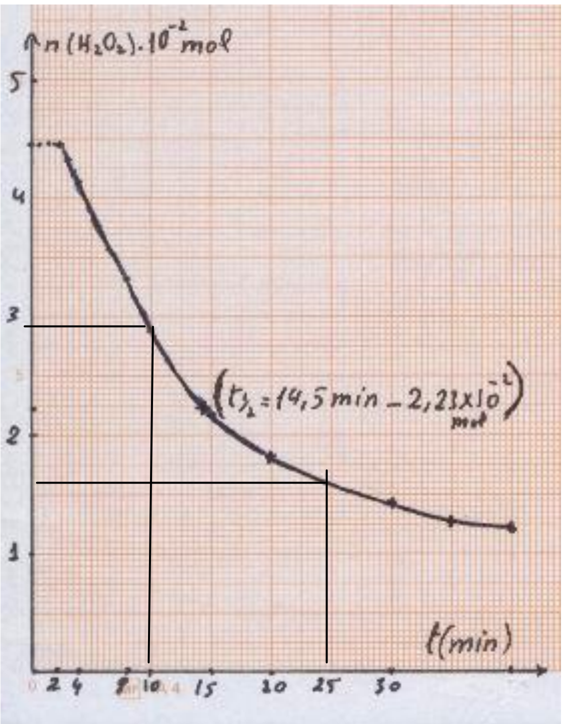
First Exercise (7 points)

Expected Answer	Mark	Comments
I- 1- The molar concentration of a solution is given by: C = $\frac{n(solute)_{mol}}{V(solution)_L} = \frac{m(solute)_g}{M(solute)_{g/mol} x V x 10^{-3}}$. m(solute)=m(solution)× $\frac{\%}{100} = \rho \times V \times \frac{\%}{100}$. Then : C = $\frac{\% \times \rho}{100 \times M \times 10^{-3}}$. Using the given indications, we obtain: C_0 = 9.86 $mol.L^{-1}$.	1	-0.25 Lack of explanation. Any other correct method is acceptable.
2- By dilution, the number of moles of solute does not change, then : $C_0 \times V_0 = C_S \times V_S$; The factor of dilution: $\delta = \frac{C_0}{C_S} = \frac{V_S}{V_0} = \frac{9.86}{0.07} \approx 141$. The volume V_S must be 141 times that of V_0. Set (a) is convenient to perform the dilution. To use a 1000 mL volumetric flask, it is required a volume of commercial solution: $V_0 = \frac{1000}{141} = 7.1$ mL, that could be removed with a graduated pipet of 10 mL. Set (b) is not convenient to perform this dilution. To use a 100 mL volumetric flask, it is required a volume of commercial solution: $V_0 = \frac{100}{141} = 0.71$mL. This volume cannot be removed with a 2mL volumetric pipet.	1.5	-0,25 if this indication is not mentioned.
II- 1- The equation of the titration reaction is: $NH_3 + H_3O^+ \rightarrow NH_4^+ + H_2O$	0.5	
2- a) The main species at the equivalence point, other than water, are Cl^- and NH_4^+. Cl^- is a spectator ion while NH_4^+ is an acid that reacts with water to make acid solution at equivalence.	0.5	
b) ***<u>the concentration of ammonia in "Windex":</u>*** At equivalence point, the number of moles of NH_3 in 25 mL of "Windex" is equal to the number of moles of H_3O^+ in 22 mL of solution (S): $C(NH_3)xV = C_{(S)}xV_{(S)E}$: $C(NH_3) = \frac{0.07x22x10^{-3}}{25x10^{-3}} = 0.06$ $mol.L^{-1}$. ***<u>The volume of ammonia required to prepare 1 L of "Windex":</u>*** $V(NH_3) = n(NH_3)xV_m = C(NH_3)xVxV_m$:	1.25	

$V(NH_3) = 0.06x1x24 = 1.44$ L. 3- The 4 remarkable points are: A: ($V_S = 0$ – pH = 10.2) B: ($V_S = V_{SE}/2 = 11$ mL – pH = pK_a = 9.2) C: ($V_S = 30$ mL – pH = 2.4) E: ($V_{SE} = 22$ mL – $pH_E = 5.2$)  	1	-0.5 if the half equivalence point is not located. Zero if the given three points are not located.
III- When the pH of a buffer solution is equal to the pK_a of the conjugate acid/base, we have: [acid] = [base]. The equation of the reaction is: $NH_3 + H_3O^+ \rightarrow NH_4^+ + H_2O$ Initial state n_b n_a 0 Final state $(n_b - n_a)$ ~0 n_a . $[NH_4^+] = \frac{n_a}{V}$ and $[NH_3] = \frac{(n_b - n_a)}{V}$. But, in a solution: n_{solute} in mol = C in $mol.L^{-1}$x V in L: $\frac{C_a x V_a}{V} = \frac{(C_b x V_b - C_a x V_a)}{V}$ Since $V_a = 60$ mL so $V_b = 140$ mL.	1.25	

Second Exercise (6 points)

Expected Answer	Mark	Comments
I- 1- a) When the the temperature increases, the rate of the reaction increases because the temperature is a kinetic factor. b) Dilution decreases the concentration of the reactant H_2O_2 , then the rate of the decomposition reaction decreases.	0.5	
2- According to the equation: $2\ H_2O_2 \rightarrow 2\ H_2O + O_2$, we have, at each instant t: $n(H_2O_2)_{reacted} = 2n(O_2)_{formed}$. And, the remaining number of moles of H_2O_2 at instant t is $n(H_2O_2)_t = n(H_2O_2)_{initial} - n(H_2O_2)_{reacted}$	1	

$= n(H_2O_2)_{initial} - 2\, n(O_2)_{formed}$. Where: $n(O_2) = \frac{\Delta m}{M(O_2)}$, and $n(H_2O_2)_{initial} = Cx50x10^{-3}$ mol = 0,893 × 0.05 $= 4.46x10^{-2}$ mol. Then, we have: $n(H_2O_2)_t = 4.46 \times 10^{-2} - \frac{2\Delta m}{32} = 4.46 \times 10^{-2} - \frac{\Delta m}{16}$, where Δm is expressed in grams. **II-** 1- 	1	
2- The average rate of disappearance of H_2O_2, between the two instants t_1 = 10 min and t_2 = 25 min, is given by: $\bar{r} = - \frac{n(H_2O_2)_{25} - n(H_2O_2)_{10}}{25-10} = - \frac{1.60\times 10^{-2} - 2.9 \times 10^{-2}}{15}$ $= 8.67 \times 10^{-4}$ mol .min^{-1}.	1	
3- The half-life of the reaction is the time needed for half the initial number of moles of H_2O_2 to be decomposed. The corresponding time for this value is $t_{1/2}$ = 14.5 min.(refer to the graph).	1	
4- Based on the question (1- 2-), we obtain: $n(H_2O_2)_t = 4.46x10^{-2} - \frac{713x10^{-3}}{16} \approx 0$. It is concluded that H_2O_2 is decomposed completely; and the chemical species present in the obtained solution are: H_2O: which is a solvent and a product of the reaction; Fe^{3+}: which is a catalyst; NO_3^- : which is a spectator ion.	1.5	

Third Exercise (7 points) L. S.

Expected Answer	Mark	Comments
I- Formula of (A) 1- The formula of (A) can be written as: $C_xH_yO_z$, with z = 6. The law of definite proportions permits to write: $\frac{12x}{\%C} = \frac{y}{\%H} = \frac{16z}{\%O}$. With the given percentages, we obtain: x = 15; y = 26. The molecular formula of (A) is then: $C_{15}H_{26}O_6$. According to the given formula, we conclude that the formula of R contains: $\frac{15-6}{3}$ = 3 atoms of carbon and $\frac{26-5}{3}$ = 7 atoms of hydrogen. The formula of R is then: C_3H_7.	1	
2- Since RCOOH is a fatty acid so it has a non branched carbon chain. $CH_3-CH_2-CH_2$ and the condensed structural formula of (A) is: $CH_3-CH_2-CH_2-\overset{O}{\overset{\Vert}{C}}-O-CH_2$ $CH_3-CH_2-CH_2-\overset{O}{\overset{\Vert}{C}}-O-CH$ $CH_3-CH_2-CH_2-\overset{O}{\overset{\Vert}{C}}-O-CH_2$	0.5	Zero if R is branched.
II- Saponification of (A) 1- The equation of the saponification reaction is: $CH_3-CH_2-CH_2-\overset{O}{\overset{\Vert}{C}}-O-CH_2$ $CH_3-CH_2-CH_2-\overset{O}{\overset{\Vert}{C}}-O-CH + 3\ Na^+ + 3\ HO^- \rightarrow$ $CH_3-CH_2-CH_2-\overset{O}{\overset{\Vert}{C}}-O-CH_2$ $3CH_3-CH_2-CH_2-COO^- + 3\ Na^+$ $+\ CH_2OH-CHOH-CH_2OH$	1	
The name of the formed soap is sodium butanoate.	0.25	
2- This reaction is slow and complete.	2×0.25	
3- The mistake : the condenser is closed from the top with a stopper. Heating increases the pressure inside the flask that causes the setup to explode.	2x0.25	
4- The role of heating is to increase the rate of the saponification reaction (kinetic role).	0.25	

The role of the reflux is preventing to loose the components of the reaction by condensing their vapours. 5- The two main steps which are followed to separate the soap from other components are successively: relargage (precipitation) and filtration. **III- Synthesis of ester** 1- The equation of the reaction that is supposed to be complete is: $CH_3 - CH_2 - CH_2 - COO^- + H_3O^+ \rightarrow$ $CH_3 - CH_2 - CH_2 - COOH + H_2O$ 2- It is an esterification reaction of equation : $CH_3 - CH_2 - CH_2 - \underset{\underset{O}{\Vert}}{C} - OH + HO - CH_2 - CH_3 \leftrightarrows$ $CH_3 - CH_2 - CH_2 - \underset{\underset{O}{\Vert}}{C} - O - CH_2 - CH_3 + H_2O$ The systematic name of ester (E) is ethylbutanoate. 3- The initial number of moles of (A) is: $n(A)_{initial} = \frac{m_A}{M_a} = \frac{1000}{302}$ mol (M_A= 12x15+26+16x6=302 $g.mol^{-1}$). Based on the series of the the above equations, the number of moles of the ester that could be obtained if the yield is total is: $n(ester)_{formed} = n(acid) = n(soap) = 3\ n(A)_{initial}$. Where the yield is 60 %, then the number of moles of ester obtained is: $n = 3x\frac{1000}{302} \times 0.60 \approx 6$ mol.	0.25 0.5 0.5 0.5 0.25 1	

Third Exercise (7 points) G. S.

Expected Answer	Mark	Comments
I- 1- The general formula of a monoalcohol having a non branched open carbon chain is: $C_nH_{2n+2}O$ of molar mass: M = 14n + 2+ 16, where the percentage by mass of oxygen is: $26.67 = \frac{16x100}{14n+18}$. So n = 3, and the molecular formula of (A) is C_3H_8O. 2- The condensed structural formulas of the possible isomers of (A) are: $CH_3 - CH_2 - CH_2OH$ and $CH_3 - CHOH - CH_3$. **II-** 1- The positive test of (B), with 2,4 – DNPH, shows that (B) is an aldehyde or a ketone. The negative test of(B), with Fehling solution, shows that (B) is a ketone; which is derived from a secondary	0.75 0.25×2 1.5	

alcohol (A). (B) of formula $CH_3 - CO - CH_3$ is: propanone. (A) is 2-propanol.		
2- The equation of the mild oxidation of (A) is: $3\ CH_3 - CHOH - CH_3 + Cr_2O_7^{2-} + 8\ H^+ \rightarrow 3\ CH_3 - CO - CH_3 + 2\ Cr^{3+} + 7\ H_2O$.	0.75	
III- Since menthone is a ketone having the same carbon chain of menthol which is a secondary alcohol, then it is possible to obtain the menthone by a mild oxidation of menthol.	0.75	
IV- 1- The equation of the esterification reaction is: $CH_3 - \overset{\overset{\large O}{\Vert}}{C} - OH + CH_3 - CHOH - CH_3 \leftrightarrows$ $CH_3 - \overset{\overset{\large O}{\Vert}}{C} - O - CH_2 - CH_2 - CH_3 + H_2O$.	0.5	
2- The percentage of esterification is: $\% = \frac{n(acid)reacted}{n(acid)initial} \times 100$ Since the initial mixture is equimolar : n(acid)reacted = n(ester)formed = 0.12 mol. $n(ester)_{theoretically}$ = n(acid) initial = 0.2 mol. We obtain $\% = \frac{0.12 \times 100}{0.2} = 60\%$.	0.5	
3-In the first experiment an equimolar initial mixture of the two reactants and zero mole of ester were used. The curve should begin at 0 and tends to 60 % as a limit. So graph (c) represents this experiment.	0.5	
In the second experiment: 2 mol of acid and 1 mol of alcohol were used, the limit of the reaction increases to exceed 60 %. The curve (a) begins at 0 and tends to a limit >60 % . Graph (a) corresponds to the second experiment.	0.5	
In the third experiment, in the initial state, 0.5 mol of ester is added to 1 mol of alcohol and 1 mol of acid. So the curve will represent the amount of ester that should begin at 0.5 mol. Graph (b) corresponds to the third experiment.	0.5	
4- Increasing the temperature helps to reduce the time required to reach the equilibrium state, but does not change the yield of the reaction at equilibrium.	0.25	