وزارة التربية والتعليم العالي المديرية العامة للتربية دائرة الامتحانات	امتحانات الشهادة الثانوية العامة فرع العلوم العامة	دورة العام 2010 الإستثنائية
	مسابقة في مادة الكيمياء المدة: ساعتان	الاسم: الرقم:

This Exam Includes Three Exercises. It Is Inscribed on 3 Pages Numbered From 1 to 3. The Use of A Non-programmable Calculator is Allowed.
Answer the three following Exercises:

First Exercise (7 points)
A weak Base: Ethanamine

Ethanamine, $C_2H_5NH_2$, is an organic compound highly soluble in water.Its boiling point is 16 °C under a pressure of 1 atm.

Given:

- Ideal gas constant: R = 0.08 L.atm.mol^{-1}.K^{-1}.
-

Conjugate acid/base pair	H_3O^+/H_2O	$C_2H_5NH_3^+ / C_2H_5NH_2$	H_2O/HO^-
pK_a	0	10.8	14

1- Aqueous Solution of this Base

100 mL of a solution (S) are prepared by dissolving, at the temperature of 27 ºC and under a pressure of 1 atm, a volume of 24 mL of ethanamine in distilled water.
The pH of this solution is 11.4

1.1- Specify the physical state of ethanamine used to prepare the solution (S).
1.2- Show that the concentration of the solution (S) is C = 0.01 mol.L^{-1}.
1.3- Write the equation of the reaction between ethanamine and water.
1.4- Establish the relation between α the degree of transformation of ethanamine in water, the pH of the solution and the concentration C. Calculate α.
1.5- A sample of the solution (S) is diluted ten times. The obtained solution is called (S').
Choose, by justifying, the value of the pH of (S') among the three following values:
10.4, 10.9 and 12.4

2- Reaction between ethanamine and hydrochloric acid

A hydrochloric acid solution of concentration C_1 = 0.02 mol.L^{-1}is added progressively, into a beaker containing a volume V = 40 mL of the solution (S) of concentration C = 0.01 mol.L^{-1}.

2.1- Write the equation of the reaction that has occurred. Show that it is a complete reaction.
2.2- Determine the volume, V_E, of the acid solution added to reach the equivalence point.
2.3- Beyond the equivalence, the acid is added until the total volume added reaches 40 mL.
2.3.1- Place, on a vertical pK_a axis, the conjugate acid/base pairs indicated above, writing the acids on the right of the axis.
2.3.2- Write the equation of the more advanced reaction.
2.3.3- Determine the pH of the solution obtained in the beaker.

Second Exercise (6 points)
Synthesis of an Ester

It is required to carry out the synthesis of an ester, benzyl benzoate, starting with: Phenylmethanol (benzylic alcohol) of formula $C_6H_5 - CH_2OH$, potassium dichromate solution, concentrated sulfuric acid and thionyl chloride ($SOCl_2$).

1- <u>Oxidation of the Alcohol</u>

Phenylmethanol is oxidized with potassium dichromate solution in the presence of concentrated sulfuric acid.

1.1- Indicate the class of the alcohol phenylmethanol.

1.2- Write the possible condensed structural formulas of the two organic compounds that can be obtained by this oxidation. Give their names.

1.3- Write the equation of this oxidation reaction if the organic compound obtained is an acid, knowing that $Cr_2O_7^{2-}$ is reduced to Cr^{3+}.

2- <u>Synthesis of Benzyl Benzoate</u>

<u>Given</u>: - M (benzyl benzoate) = 212 $g.mol^{-1}$.
- The acid obtained in the above oxidation is noted as A.

It is required to prepare benzyl benzoate by two different processes.

2.1- **First process:**

A mixture of 0.3 mol of acid A and 0.3 mol of phenylmethanol is heated.
After a certain time, a chemical equilibrium is reached where the mass of the benzyl benzoate formed is equal to 42.4 g.
The equation of the reaction that takes place is:

$$A + C_6H_5 - CH_2OH \rightleftharpoons \text{benzyl benzoate} + H_2O$$

2.1.1- Write the condensed structural formula of benzyl benzoate.

2.1.2- Determine the molar composition of the mixture obtained at equilibrium.

2.1.3- Deduce the yield of this reaction.

2.1.4- Indicate a factor, other than heating, to increase the rate of this reaction. Specify whether this factor affects the yield of the reaction.

2.2- **Second process:**

0.3 mol of acid A reacts with an excess of thionyl chloride. An organic compound B is obtained. An excess of the compound B is slowly added to 0.3 mol of phenylmethanol while cooling the reacting medium.

2.2.1- Write the equation of the reaction of A with thionyl chloride.

2.2.2- Write the equation of the reaction between B and phenylmethanol.

2.2.3- Why the reacting medium is cooled when B is added to phenylmethanol?

2.2.4- Give two advantages for the synthesis of benzyl benzoate by this process.

Third Exercise (7 points)
Reaction between Hydrochloric Acid and Zinc Metal

Hydrochloric acid reacts with zinc according to the following equation:

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

At time t = 0, a mass m of pure zinc granules is introduced into a beaker containing a volume V_1 = 50 mL of hydrochloric acid solution (S) of molar concentration C.
A release of gas starts.

To follow the evolution of this reaction, the volume of hydrogen gas released $V(H_2)$ is measured under conditions where the molar volume V_m is 25 $L.mol^{-1}$.
The results are given in the following table:

t (s)	50	100	200	300	400	500	700	900	1200	….	1500	2000
$V(H_2)$ mL	25	50	85	117	142	162	195	220	240	….	250	250

When the gas release ceases, a solid remains in the beaker.

1- <u>Preparation of the Solution (S)</u>

Solution (S) is prepared by diluting 25 times a commercial solution of hydrochloric acid of concentration C_0.
Choose, by justifying, from the list given below, the most accurate glassware to carry out this preparation.
List of available material:

- 50, 100, 250 mL beakers
- 50, 100, 250 mL volumetric flasks
- 5, 10, 25 mL volumetric pipettes
- 5, 10, 25 mL graduated cylinders
- 50, 100, 250 mL Erlenmeyer flasks
- Funnel
- Watch glass and spatula
- Pipet filler

2- <u>Preliminary Study</u>

2.1- Extract, from the experimental study described before, the sentence which shows that H_3O^+ ion, is the limiting reactant of this reaction.
2.2- Show that the concentration C is equal to 0.4 $mol.L^{-1}$. Deduce the concentration C_0 of the commercial solution.

3- <u>Kinetic of this Reaction</u>

3.1- Show that, at any instant of time t, the concentration of H_3O^+ ions in $mol.L^{-1}$, $[H_3O^+]_t$, and the volume of H_2 gas in mL, $V(H_2)$, are related by the following relation:

$$[H_3O^+]_t = 0.4 - 1.6\times10^{-3}\times V(H_2).$$

3.2- The application of this relation allows to get the following results:

t (s)	0	50	100	200	300	400	500	700	900	1200
$[H_3O^+]_t$ (10^{-1} $mol.L^{-1}$)		3.6	3.2	2.6	2.1	1.7	1.4	0.88	0.48	

Give the value of the concentration $[H_3O^+]$ at t = 0 and calculate its value at t = 1200 s.
3.3- Plot, on a graph paper, the curve representing the variation of $[H_3O^+]_t$ versus time, $[H_3O^+]_t = f(t)$, in the interval of time [0 – 1200 s]. Take the following scale: 1 cm for 100 s in abscissa and 1 cm for 4.0×10^{-2} $mol.L^{-1}$ in ordinate.
3.4- Determine the rate of disappearance of H_3O^+ ions at t = 400 s.
3.5- The value of this rate is 1.0×10^{-3} $mol.L^{-1}.s^{-1}$ at t = 0 and is 2.4×10^{-4} $mol.L^{-1}.s^{-1}$ at t = 700 s. Specify the kinetic factor responsible for the variation of this rate.
3.6- The same experimental study is repeated again with the same mass of zinc but in a powder form. Plot, by justifying, on the same graph of part 3.3, the shape of the curve $[H_3O^+]_t$ versus time.