مسابقة في مادة 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 Following Three Exercises:

First Exercise (7 points)
Hydrolysis of an Ester

The hydrolysis of an ester (E) gives an alcohol (A) and an acid (B). The aim of this exercise is to identify the compounds (A), (B), and (E).

I- Study of the Hydrolysis Reaction

A mixture of ester (E) and water is heated with few drops of concentrated sulphuric acid solution. After a certain time, the established homogenous equilibrium is represented by the following equation:

$$E + H_2O \rightleftharpoons A + B$$

1- Let **x** be the number of moles of (B) formed at equilibrium. Rewrite and complete, on the answer sheet, the following table:

	E	H_2O	A	B
Initial state	1 mol	1 mol	0	0
Equilibrium state				

2- Indicate the role of heating and that of sulphuric acid in performing this hydrolysis reaction.
3- Determine the equilibrium constant K_c knowing that **x** = 0.4 mol.
4- Propose and justify a way to make the hydrolysis of (E) almost complete.

II- Identification of Compounds (A), (B) and (E)

After an almost complete hydrolysis of ester (E), the obtained alcohol (A) and acid (B) are separated.

1- A study shows that (A) is a saturated monoalcohol, with an open carbon chain, and the mass of carbon is 3 times that of oxygen.
   a) Determine the molecular formula of (A).
   b) In order to identify this alcohol, the following tests are carried out:

Test N^o	Initial mixture	Observation and experimental results
Test 1	(A) + Acidified potassium permanganate solution (purple)	- Final solution is colorless. - Formation of an organic compound (C).
Test 2	(C) + 2,4- D.N.P.H.	- Yellow precipitate.
Test 3	(C) + Fehling's solution (blue)	- Blue solution.

Deduce the condensed structural formula of (A) and give its name.

2- A study shows that (B) is an α-amino acid.

a) Write the general formula of an α-amino acid.
b) Deduce the condensed structural formula of acid (B) knowing that its group R is composed of carbon and hydrogen atoms and its molar mass is $M_{(B)} = 89\ g.mol^{-1}$. Given, in $g.mol^{-1}$. $M_{(C)} = 12$; $M_{(H)} = 1$; $M_{(O)} = 16$ and $M_{(N)} = 14$.

3-Write the condensed structural formula of ester (E) and give its name.

Second Exercise (6 points)
Kinetics for the Decomposition of $C_6H_5N_2Cl$

$C_6H_5 – N_2Cl$ is a non-oxygen explosive which is stored at a temperature less than 5^0C. The decomposition of $C_6H_5 – N_2Cl$ in an aqueous medium at a temperature of 25^0C is slow. This decomposition takes place according to the following equation:

$$C_6H_5 – N_2Cl_{(aq)} \rightarrow C_6H_5 – Cl_{(aq)} + N_{2\,(g)}.$$

Given:

- Molar volume of gas at the experimental conditions: $V_m = 25\ L.mol^{-1}$.

I- Preliminary Study

Consider 1 L of $C_6H_5 – N_2Cl$ aqueous solution of concentration $C = 2.0x10^{-3}\ mol.L^{-1}$.

1- Calculate, in mL, the volume of nitrogen gas formed as time tends to infinity.
2- Show, at each instant t, that the concentration of $C_6H_5 – Cl$, expressed in $mol.L^{-1}$ is given by the following expression: $[C_6H_5 – Cl]_t = 4x10^{-5}xV$
where V is the volume, in mL, of nitrogen gas formed at each instant t.

II- Kinetics of this Decomposition

The kinetics of this decomposition reaction in solution (S) is studied by measuring the volume V of the liberated nitrogen gas at different instants. The results are given in the following table:

t (min)	0	3	6	9	12	14	18	22
V (mL)	0	10.5	19	27	33	36	41	45
$[C_6H_5 – Cl]_t\ 10^{-4}\ (mol.L^{-1})$								

1- Rewrite and complete, on the answer sheet, the above table.
2- Plot, on a graph paper, the curve $[C_6H_5 – Cl] = f(t)$.
Take the following scales: abscissa: 1 cm for 2 min; ordinate: 1 cm for $2x10^{-4}\ mol.L^{-1}$.
3- Determine the half-life of the reaction.
4- One liter of $C_6H_5 – N_2Cl$ solution, having a higher concentration than solution (S) is prepared. The kinetics of the decomposition of $C_6H_5 – N_2Cl$ is studied at the same temperature 25^0C
   a) The obtained volume of nitrogen gas at t = 6 min exceeds 19 mL. Justify.
   b) Compare the volume of the liberated nitrogen gas at the end of the reaction ($t \rightarrow \infty$) to the volume of the nitrogen gas obtained in question (**I**- 1-).

Third Exercise (7 points)
A Scale Product for Coffee-Pot

The main constituent of a scale product is sulfamic acid. It is sold commercially as white small crystals.
The aim of this exercise is to determine the percentage of sulfamic acid in the scale product by pH-metry.

Given:

- Sulfamic acid of formula NH_2SO_3H will be represented as HA in this exercise.
- Molar mass of sulfamic acid in $g.mol^{-1}$: M = 97.1.

Experimental Procedure:

first step: 2.05 g of this scale product are dissolved in distilled water to obtain a solution (S) of volume V = 500 mL.
second step:A volume V_a = 10 mL of solution (S) is put into a beaker. A volume V´ of distilled water is then added to immerse the electrode of the pH-meter.
third step: Titration is carried out by using sodium hydroxide solution of concentration $C_b = 4x10^{-2}$ $mol.L^{-1}$.

I- Preliminary Study

1- Sulfamic acid is a strong acid. Write the equation of the reaction of this acid with water.
2- Indicate the appropriate material used to:
   - weigh the mass of 2.05 g ;
   - prepare the volume V ;
   - withdraw the volume V_a ;
   - add the sodium hydroxide solution.
3- Write the equation of the titration reaction.
4- Based on the chemical species which are present in the beaker, justify the value of pH = 7 at the equivalence point.

II- Make Use of the Titration Results

Part of the titration results is given in the following table:

V_b (mL)	0	10.4	15
pH	2.4	7.0	11.0

1- Draw the shape of the curve $pH = f(V_b)$ for $0 \leq V_b \leq 15$ mL. Take the following scales: abscissa : 1cm for 1mL, ordinate: 1 cm for 1 unit of pH.
2- Determine the concentration C_a of sulfamic acid in solution (S).
3- Deduce the mass percentage of sulfamic acid in this scale product.

III- Effect of Dilution on the pH Measurements

A solution (S') of the scale product is prepared by diluting solution (S) ten times.
1- Among the following kits, choose by justifying, the kit that should be used to carry out the most precise dilution of solution (S).

Kit – 1	Kit – 2	Kit - 3
• 10 mL volumetric pipet ; • 100 mL beaker.	• 10 mL volumetric pipet ; • 100 mL volumetric flask.	• 10 mLgraduated cylinder; • 200 mL volumetric flask.

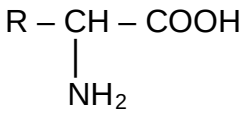
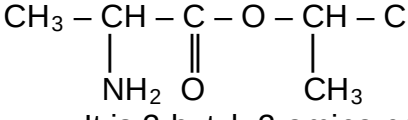
2- Another titration is carried out with (S') by repeating the second step of the above experimental procedure and using another sodium hydroxide solution of concentration $C'_b = 4x10^{-3}$ mol.L^{-1}.

Give, by justifying, the value of pH that corresponds to the volume V_b=10.4 mL.

Official Exam Marking Scheme of Chemistry L. S. 1^{t} session 2006

First Exercise (7 points)

Hydrolysis of an Ester

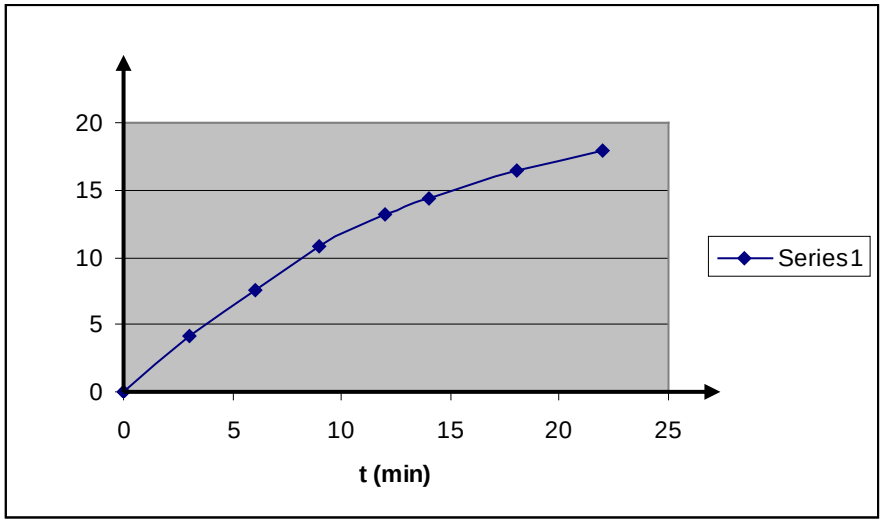
Expected Answer	Mark	Comment
I-		
1- According to the stoechiometric coefficients, we have: $\frac{nE_{reacting}}{1} = \frac{nH_2O_{reacting}}{1} = \frac{nA_{formed}}{1} = \frac{nB_{formed}}{1} = x$	1	
2- Heating increases the rate of the reaction (kinetic factor). Sulphuric acid, which is added in a small quantity, has the role of a catalyst.	0.25 0.25	
3- The equilibrium constant of the above reaction is giving by the following relation: $K_c = \frac{[A][B]}{[E][H_2O]}$. We have then $K_c = \frac{\frac{0.4}{V}\frac{0.4}{V}}{\frac{0.6}{V}\frac{0.6}{V}} = \frac{4}{9} = 0.44$.	1	
4- In order to have a complete hydrolysis, we add a quantity of water. The reaction is then displaced in the forward direction (direction of hydrolysis), according to Le Chatelier's principle, when a stress is applied to a system at an equilibrium state, the system readjust itself by reducing or opposing this stress.	0.5	Any other suitable proposition is acceptable
II-		
1- a) The general formula of a saturated monoalcohol of an open carbon chain is $C_nH_{2n+2}O$. Since $m_{(C)} = 3\ m_{(O)}$, we have then: $12n = 3x16$. $n = 4$. The molecular formula of (A) is then C_4H_9OH.	1	$C_nH_{2n+1}OH$
b) According to test 1, we conclude that (A) is a primary or a secondary alcohol, because it undergoes mild oxidation . According to test 2, (C) is a carbonyl compound (aldehyde or ketone). According to test 3, we conclude that (C) is a ketone. Then (A) is a secondary alcohol of condensed structural formula: $CH_3 - CH_2 - CHOH - CH_3$. Its name is 2-butanol.	1 2x0.25	
2- a) The general formula of an α−amino-acid is: 	0.5	
b) $M_R + 12 + 1 + 14 + 2 + 32 + 12 + 1 = 89$, then: $M_R = 15$. R formed of carbon and hydrogen should be in the form of CH_3.	0.5	
c) The formula of ester (E) is then:  It is 2-butyl -2-amino propanoate .	0.25 0.25	

Second Exercise (6 points)
Kinetics Of the Decomposition of $C_6H_5N_2Cl$

Expected Answer	Mark	Comment
I- 1- According to the stoechiometric coefficients: $n(N_2)_{formed\ at\ t\to\infty} = n(C_6H_5N_2Cl) = CxV = 2x10^{-3}$ mol. The volume of nitrogen is then: $V(N_2) = nxV_m = 2x10^{-3}x25 = 50x10^{-3}$ L=50 mL	1	
2- $n(C_6H_5Cl)_{formed} = n(N_2)_{formed}$. $[C_6H_5Cl]_t = \frac{V(N_2)}{V_m x V_{solution}} = \frac{Vx10^{-3}}{V_m x1} = \frac{Vx10^{-3}}{25} = 4x10^{-5}\ V$	1	
II- 1- We multiply by 0.4, we have then :	0.5	

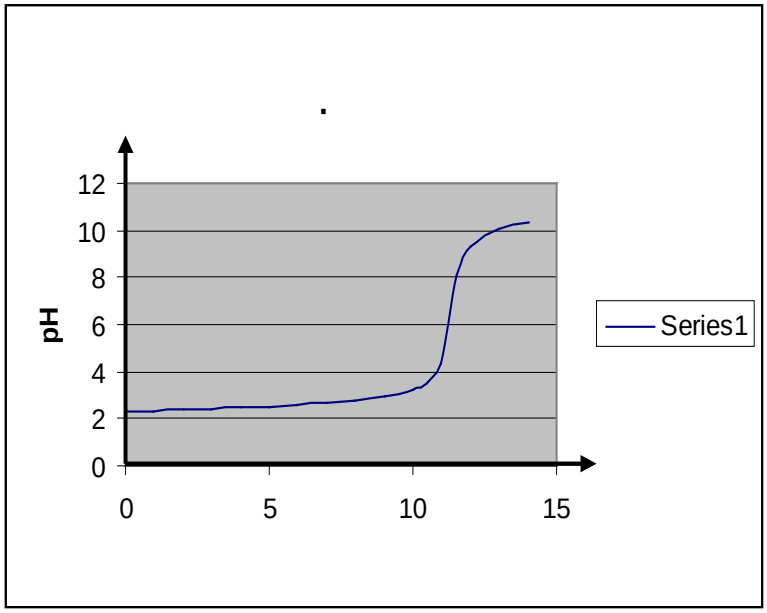
t (min)	0	3	6	9	12	14	18	22
$[C_6H_5N_2Cl]x10^{-4}$ mol.L^{-1}	0	4.2	7.6	10.8	13.2	14.4	16.4	18.0

2- The curve $[C_6H_5Cl] = f(t)$.



	1	
3- The half-life of the reaction is the time needed for half the amount of $C_6H_5N_2Cl$ to disappear . So the time that corresponds to the concentration $[C_6H_5Cl]_{t1/2} = 10x10^{-4}$ mol.L^{-1} is $t_{½} = 8.2$ min.		or the time needed for half the maximum amount of C_6H_5Cl to appear .
4- a) Since the new solution has a higher concentration than solution (S), so the rate of the reaction is greater. Starting from the same volume 1 L, the obtained volume of nitrogen is greater than 19 mL at t = 6 min.	0.75	
b) Because the solution has a higher concentration, starting from the same volume 1 L, the number of moles of the reactant is greater and consequently the volume of nitrogen gas at $t \to \infty$ is greater than the volume obtained in the first case.	0.75	

Third Exercise (7 points)
Scale Product for Coffee-Pot

Expected Answer	Mark	Comment
I- 1- The equation of the reaction of sulfamic acid with water is: $HA + H_2O \rightarrow H_3O^+ + A^-$ 2- To weigh: sensitive balance (1/100). To prepare V = 500 mL: 500 mLvolumetric flask. To take V_a: 10 mL volumetric pipet. To add NaOH: buret. 3- Since, it is a reaction between a strong acid and a strong base, the equation is then: $H_3O^+ + HO^- \rightarrow 2\ H_2O$. 4- The species that are present at equivalence point, other then water, are Na^+ and A^-, which are spectator ions (neutral particles). The pH is then equal to 7. **II-** 1-	0.5 4x0.25 0.5 0.5	
	1	
2- At equivalence point, we have: $n_{H_3O^+ \text{ (in beaker)}} = n_{HO^- \text{ (poured)}}$. Knowing that, in a solution: n = CxV, where: $C_aV_a = C_bV_{bE}$; we conclude: $Ca = \frac{4x1o^{-2}x10.4}{10} = 4.16x10^{-2}$ mol.L^{-1}.	0.25 0.75	
3- n (HA) = $4.16x10^{-2}x0.5 = 2.08x10^{-2}$ mol ; m (HA) = $2.08x10^{-2}$ x97.1 = 2.02 g ; and the percentage by mass is: % = $\frac{2.02}{2.05}x100 = 98.53$ %.	1	
III- 1- When the solution is diluted ten times, the final volume becomes ten times greater than the initial volume. The suitable		

glass-ware that should be used are: 10 mL volumetric pipet and 100 mL volumetric flask, so kit-2- is convenient. 2- Because the titration takes place between a strong acid and a strong base and both have been diluted 10 times, the pH at the equivalence point, where V_{bE} = 10.4 mL remains the same, is equal to 7. Or $C'_b V'_b = C'_a V'_a \Rightarrow V'_b = \frac{\frac{C_a}{10}}{\frac{C_b}{10}} x10 = \frac{4.16x10^{-2}}{4x10^{-2}} x10 = 10.4mL$ So the pH that corresponds to this volume is 7.	1 0,5	