مسابقة في مادة الكيمياء المدّة: 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 (7 points)
Chemical Kinetic

In a laboratory session, one decides to identify two organic compounds before carrying out a kinetic study of the reaction taking place in a mixture of these two organic compounds.
These two compounds are liquids and each one of these two compounds is found in a flask of which the label shows the following indications:

Flask (1)	Flask (2)
Saturated non cyclic chain carboxylic acid: HA	Saturated non-cyclic chain Monoalcohol; M = 74 $g.mol^{-1}$

Given: Molar masses in $g.mol^{-1}$: M(H) = 1 ; M(C) = 12 ; M(O) = 16.

1- Identification of The Acid HA

A mass m = 5.0 g of the acid HA is taken from the flask (1) and it is dissolved in distilled water in such a way to obtain a volume of 500.0 mL of a solution noted (S_1).
A volume V_a = 20.0 mL of the solution (S_1) is titrated with a sodium hydroxide solution ($Na^+ + HO^-$) of molar concentration C_b = 0.20 $mol.L^{-1}$.
The equation of the titration reaction is: $HA + HO^- \rightarrow A^- + H_2O$

- 1.1- Determine the molar concentration of the solution (S_1), knowing that the volume of the basic solution added to reach equivalence is V_{bE} = 16.6 mL.
- 1.2- Deduce the molar mass of the acid HA.
- 1.3- Identify the acid HA.

2- Identification of The Content of The Flask (2)

A mild oxidation of the alcohol contained in the flask (2) is carried out in the presence of an excess of oxidizing agent. An organic compound is obtained, which gives a yellow-orange precipitate with 2.4-DNPH, but does not react with Fehling's reagent.

- 2.1- Show that the molecular formula of this alcohol is $C_4H_{10}O$.
- 2.2- Identify this alcohol.

3- Evolution with Time

Eight Erlenmeyer flasks numbered 1 through 8, each containing a mixture of 0.20 mol of the acid HA and 0.20 mol of the alcohol of the flask (2), are maintained at constant temperature T. All these Erlenmeyer flasks are prepared at the instant of time t = 0 and the remaining acid in the mixture is titrated hourly.

The number of moles of the ester formed after each titration is determined. The results are grouped in the table below:

t (hour)	1	2	3	4	5	6	7	15
n (ester) (10^{-2} mol)	4.5	7.8	10	11.2	11.7	12	12	12

3.1- Write the condensed structural formula of the organic compound obtained in this reaction and name it.

3.2- Plot the curve representing the change in the number of moles of the ester formed with time:
n (ester) = f(t) in the interval of time [0 – 7 hours].
Take the following scales: 2 cm for 1 hour in abscissa and 1 cm for 1.0×10^{-2} mol in ordinate.

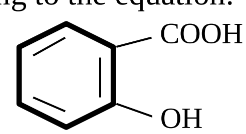
3.3- Determine the rate of formation of the ester at t = 3 hours.

3.4- The kinetic study realized above is carried out again but with one change: each Erlenmeyer flask is prepared by mixing 0.20 mol of the acid HA, 0.20 mol of the alcohol of the flask (2), and few drops of a catalyst (source of H^+ ions).
Plot, on the same graph of the question 3.2-, the shape of the curve n (ester) = g(t). Justify.

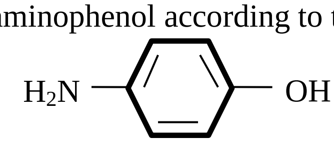
Second Exercise (6 points)
Ethanoic Anhydride

Ethanoic anhydride ($CH_3 – CO – O – CO – CH_3$) is an organic compound that participates in the creation of new functions in the organic chemistry.

It reacts with salicylic acid according to the equation:

Ethanoic Anhydride +  → acetylsalicylic acid + A (reaction 1)

and it can reacts with para-aminophenol according to the equation :

Ethanoic Anhydride +  → paracetamol + A (reaction 2)

1- Preparation of Ethanoic Anhydride

Ethanoic anhydride can be prepared starting from ethanoic acid in the presence of a strong dehydrating agent P_2O_5.

1.1- Write the equation of this reaction.

1.2- Specify the importance of using P_2O_5 in this chemical transformation.

2- About The Reactions 1 and 2

2.1- Name the functional group created in the acetylsalicylic acid molecule.

2.2- Write the condensed structural formula of the compound (A).

2.3- Indicate the effect on the yield of the reaction 1 if the ethanoic anhydride is replaced with ethanoic acid. Justify.

3- Preparation of Paracetamol

A mass m containing 3.3×10^{-2} mol of para-aminophenol is dissolved in acidic medium and an excess of ethanoic anhydride is added drop by drop to this mass.
At the end of the preparation, a quantity of 2.5×10^{-2} mol of pure paracetamol is obtained.

3.1- Write the structural formula of paracetamol.
3.2- Determine the yield of this reaction.

4- Acetylsalicylic Acid and Sodium Hydroxide

The action of an aqueous sodium hydroxide solution on acetylsalicylic acid leads to two types of chemical reactions:

$CH_3 - CO - O - C_6H_4 - COOH + HO^- \rightarrow CH_3 - CO - O - C_6H_4 - COO^- + H_2O$ (reaction A)

$CH_3 - CO - O - C_6H_4 - COO^- + HO^- \rightarrow CH_3 - COO^- + HO - C_6H_4 - COO^-$ (reaction B)

4.1- Assign to each one of the reactions A and B the corresponding qualifying terms among the following: acid-base, oxidation-reduction, hydrolysis in basic medium (saponification), slow or fast.
4.2- Name the ions produced in the reaction B.

Third Exercise (7 points)
Ammonia NH_3

Ammonia, NH_3, is a colorless irritating gas. In addition to its usual cooling properties, it is used in the synthesis of many other compounds as fertilizers…
The aim of this exercise is to approach its industrial synthesis as well as its presence in a household product.

1- Industrial Synthesis of Ammonia

Industrially, the synthesis of ammonia is carried out in gaseous phase according to the following equilibrium:

$$N_{2(g)} + 3\,H_{2(g)} \rightleftarrows 2\,NH_{3(g)}$$

Into a reactor, one introduces a mixture of n moles N_2 gas and 3n moles of H_2 gas in the presence of solid iron catalyst.
This synthesis is carried out at a pressure P = 250 bar and at a temperature of 450°C.

1.1- Indicate the type of this catalysis. Justify.
1.2- Give the molar composition of the mixture obtained at equilibrium in terms of n and α, where α is the degree of transformation of N_2 at equilibrium.
1.3- Specify how one should act on the pressure in order to increase the degree of transformation (α) of the nitrogen gas N_2.

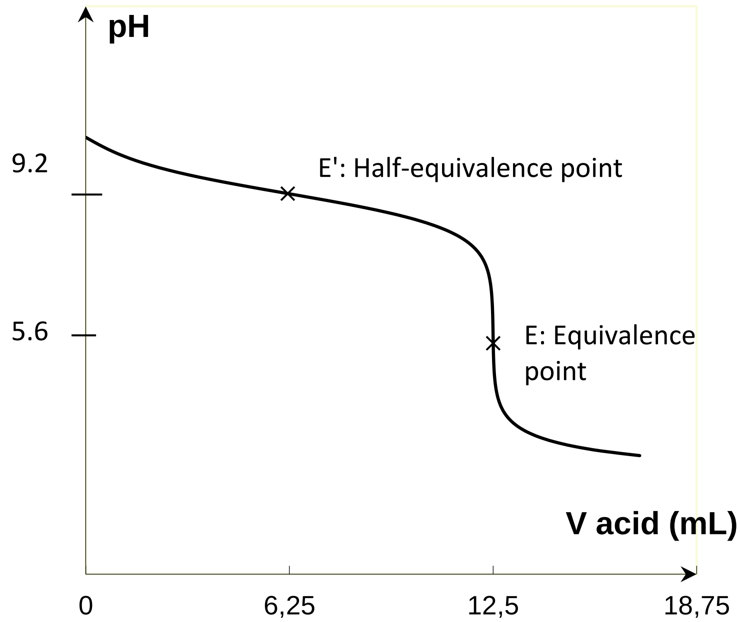
2- Ammonical Household Product

« *Ammoniaque Alcali* » is a commercial ammonia solution used for cleaning carpets, removing fat stains; brighten colors of some fabrics...

In order to determine the percentage by mass of ammonia in this commercial solution, one proceeds as follows:

- The commercial solution is diluted 650 times; the obtained solution is noted (S).
- A pH-metric titration is carried out, at 25 °C, of a volume V_S = 10.0 mL of the solution (S) with a hydrochloric acid solution ($H_3O^+ + Cl^-$) of concentration C = 8.0×10^{-3} $mol.L^{-1}$.

This titration allows us to plot the curve, given below, representing the change of pH as a function of the volume of the acid added.

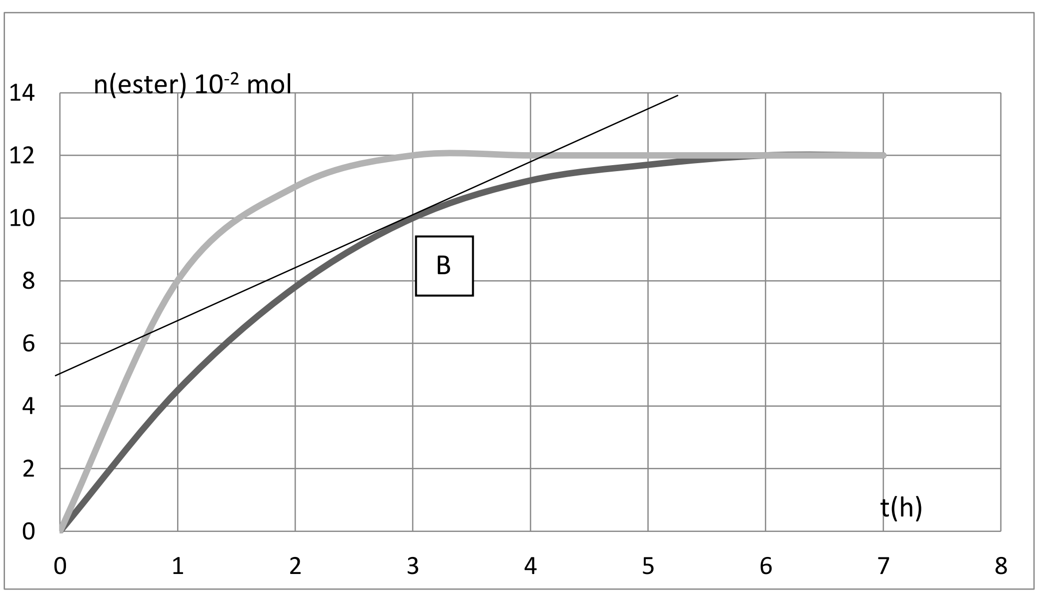


2.1- Draw out, from the graph, two criteria which show that NH_3 is a weak base.
2.2- Write the equation of the titration reaction.
2.3- Determine the molar concentration C_S of the solution (S) in ammonia.
2.4- Deduce the molar concentration of the commercial solution « *Ammoniaque Alcali* » in ammonia.
2.5- Calculate the percentage by mass of ammonia in this commercial solution, knowing that the density of this solution is equal to 0.92 $g.mL^{-1}$.
Given: $M(NH_3) = 17$ $g.mol^{-1}$.
2.6- Extract, from the graph, the pKa of the pair NH_4^+ / NH_3.
2.7- In order to prepare a buffer solution of pH =9.2, one suggests to realize the two following mixtures:

Mixture (a)	Mixture (b)
25 mL of the hydrochloric acid solution of concentration C + 40 mL of the solution (S) of concentration C_S.	25 mL of the hydrochloric acid solution of concentration C + 60 mL of the solution (S) of concentration C_S.

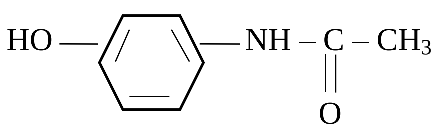
Choose, from these two mixtures, the one that leads to this buffer solution. Justify.

First Exercise

Question	Answer	mark
1.1	At the equivalence point : n (OH^-) added to reach equivalence = n (HA) introduced into the beaker $C_b \times V_{bE} = C_a \times V_a$ The Concentration of the solution (S) is: $C_a = \frac{C_b \times V_{bE}}{V_a} = \frac{0.2\times16.6}{20} = 16.6\times10^{-2}$ mol.L^{-1}	0.75
1.2	n (HA) in 500 mL of solution = $\frac{16.6}{2}\times10^{-2} = 8.3\times10^{-2}$ mol. Molar mass of the acid: M(HA) = $\frac{m(HA)}{n(HA)} = \frac{5}{8.3\times10^{-2}}$ = 60.2 g.mol^{-1}.	0.75
1.3	HA is an alkanoic acid, its genernal formula is $C_nH_{2n}O_2$. M(HA) = 14n + 32 = 60.2 ; therefore n = 2. The acid HA is the ethanoic acid of formula CH_3COOH.	0.75
2.1	The general formula of a saturated non-cyclic chain monoalcohol is $C_xH_{2x+1}OH$. M(alcohol) = 14x + 18 = 74 ; therefore x = 4 and the molecular formula of this alcohol is $C_4H_{10}O$.	0.5
2.2	The product of the mild oxidation of the alcohol is a ketone since it gives a yellow-orange precipitate with 2,4-DNPH but it does not react with Fehling solution. so the alcohol is a secondary alcohol. Its formula is :$CH_3 – CH_2 – CH(OH) – CH_3$ Its name is 2-butanol.	1
3.1	The condensed structural formula of the organic compound obtained is: $CH_3 – C(=O) – O – CH(CH_3) – CH_2 – CH_3$; its name is 1-méthylpropyl ethanoate	0.5
3.2	The curve is: 	1

3.3	The rate of formation of the ester is: r = $\frac{d\,n(ester)}{dt}$ at t = 3 hours. Graphically, it is equal to the slope of the tangent at the curve at the point of abscissa 3 hours. A(0 ; 5.10^{-2} mol) and B(3 heures; 10.10^{-2} mol) $r = \frac{Y_B - Y_A}{X_B - X_A} = \frac{(10-5)\times 10^{-2}}{3} = 1.6\times 10^{-2}\,mol.h^{-1}$	1
3.4	The presence of the catalyst increases the rate of this reaction. At each instant of time t, n (ester) formed (in the presence of H^+) is greater than n (ester) formed (in the absence of H^+).	0.75

Second Exercise

Question	**Answer**	**mark**
1.1	The equation of the reaction: 2 $CH_3COOH \rightarrow (CH_3CO)_2O + H_2O$	0.75
1.2	P_2O_5 is a strong dehydrating agent that absorbs the water formed in this reaction therefore shifting the equilibrium in the direction of formation of the anhydride.	0.5
2.1	Chemical function created in the reaction 1: ester function	0.5
2.2	When ethanoic acid replaces ethanoic anhydride, the yield of the reaction decreases since the reaction becomes limited.	0.75
2.3	The formula of A is CH_3COOH	0.5
3.1	The structural formula of paracetamol is:  	0.5
3.2	The yield of this reaction: yield = $\frac{n(paracetamol)\,experimental}{n(paracetamol)\,theorietical} = \frac{n_1}{n_2}$ n_2 = n(para-aminphenol) initial = 0.033 mol. with n_1 = 0.025 mol, the yield is eqaul to 0.757, or 75.7 %.	1
4.1	Reaction A : acid-base and fast. Reaction B : hydrolysis in basic medium.	1
4.2	the produced ions: ethanoate ion and salicylate ion.	0. 5

Third Exercise

Question	Answer	mark
1.1	This is a heterogeneous catalysis since the reactants and the catalyst are in different phases.	0.5
1.2	N_2 : n(1 – α) mol ; H_2 : 3n(1 – α) mol and NH_3 : 2 nα mol	1
1.3	In order to increase the degree of transformation α, one should increase the total pressure under which the synthesis is carried out (Le Chatelier's principle).	1
2.1	The two criteria are: - The curve shows two inflection points. - The pH at equivalence is less than 7.0	0.5
2.2	The equation of the titration reaction is: $H_3O^+ + NH_3 \rightarrow NH_4^+ + H_2O$	0.5
2.3	At the equivalence : n (H_3O^+) added to reach equivalence = n (NH_3) introduced into the beaker $C \times V_E = C_S \times V$ $C_S = \frac{C \times V_E}{V_S} = \frac{8 \times 10^{-3} \times 12.5}{10}$ = 0.01 mol.L^{-1}	1
2.4	The Concentration of the commercial solution is: C_0 = 0.01×650 = 6.5 mol.L^{-1}	0.5
2.5	% by mass of the commercial solution in NH_3 = $\frac{C_0 \times M(NH_3)}{d(solution) \times 10}$ with d(solution) = 0.92 g/mL ; therefore % by mass in NH_3 = 12.0 %	1
2.6	pKa (NH_4^+ / NH_3) = pH (mixture) at half-equivalence = 9.2	0.25
2.7	in order to obtain a buffer solution of pH = 9.2, the ratio of the volume of the base over that of the acid should be equal to 6.25/10 the mixture (a) is the appropriate one since the ratio in this mixture is equal to 25/40 = 6.25/10	0.75