وزارة التربية والتعليم العالي المديرية العامة للتربية دائرة الامتحانات الرسمية	امتحانات شهادة الثانوية العامة الفرع: علوم عامة	دورة العام ٢٠١٦ العاديّة السبت ١١ حزيران ٢٠١٦

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 (6points)
Preparation of an Ester

Esterification is a chemical reaction during which an ester group (– COOR) is formed, starting from a mixture of an alcohol and a carboxylic acid or a derivative of this carboxylic acid.
The aim of exercise is to approach the preparation of an ester starting from a carboxylic acid noted (A).

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

1- Preparation of The Acid Anhydride

A carboxylic monoacid (A) is heated in the presence of P_2O_5 (a strong dehydrating agent); an acid anhydride (B) is obtained according to the equation below:

$$2\ C_nH_{2n}O_2 \rightarrow H_2O + C_xH_yO_3$$

1.1- Verify the relation: y = 2x-2.

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

1.3- Show that the molecular formula of the acid anhydride (B) is $C_6H_{10}O_3$ knowing that the mass percentage of oxygen in this compound is 37 %.

1.4- Write the condensed structural formula of the acid anhydride and that of the starting carboxylic acid (A).

2- Esterification Reaction

Given: Density of 1- propanol, d = 0.80 g. mL^{-1}.

Into a clean and dry Erlenmeyer flask, a volume V_1 of 1-propanol and a volume containing 0.6 mol of the acid anhydride (B) are introduced. The Erlenmeyer flask is placed in a water bath maintained at 60°C and the mixture is stirred continuously.

2.1- Write, using condensed structural formulas of the organic compounds, the equation of this reaction. Name the ester formed.

2.2- Calculate the volume V_1 of 1- propanol such that the initial mixture of reactants is equimolar.

2.3- Deduce the maximum number of moles of ester that can be obtained at the end of the reaction.

2.4- The experiment, described above, is realized again, but the acid anhydride (B) is replaced with the starting acid (A). Choose among the following values: 0.6 mol, 0.40 mol and 0.67 mol, the one that corresponds to the number of moles of the ester formed at the end of the chemical transformation. Justify.

2.5- Identify an organic compound, other than the acid (A), which can replace the acid anhydride (B) in the preparation of this ester.

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 mole of N_2 gas and 3n moles of H_2 gas in the presence of a 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.

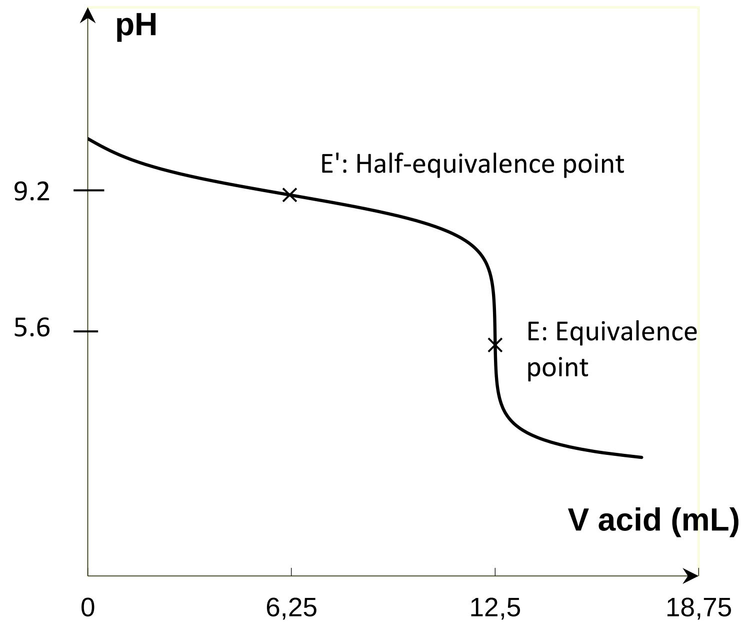
2- Ammonical Household Product

« *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.

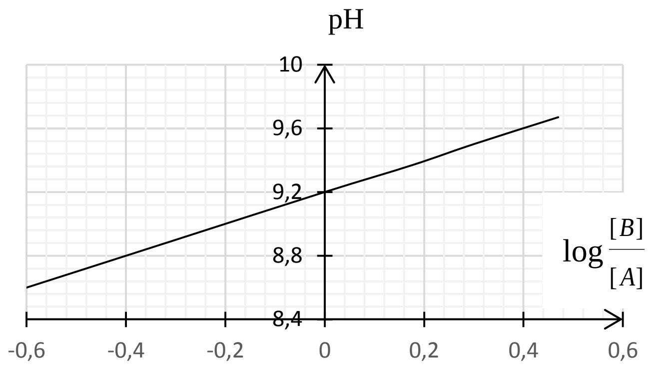
2.3- Determine the molar concentration C_S of the solution (S) in ammonia.

2.4- Deduce the molar concentration of the commercial solution « *Ammoniaque Alcali* » in ammonia.

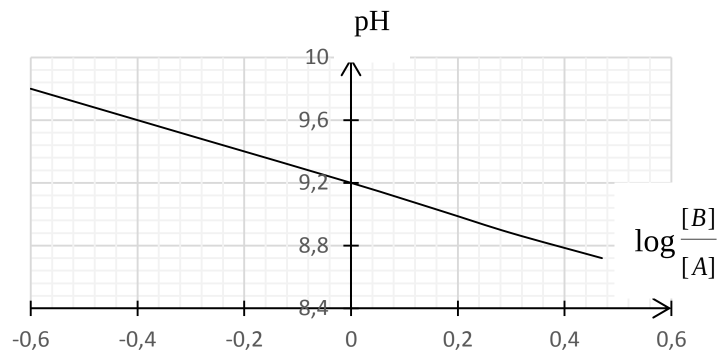
2.5- Calculate the percentage by mass of ammonia in this commercial solution, knowing that the density of this solution is equal to 0.92 $g.mL^{-1}$.
Given: $M(NH_3)$ = 17 $g.mol^{-1}$.

2.6- The molar concentrations of ammonia and its conjugate acid are noted [B] and [A] respectively, one represents graphically the change of pH as a function of $\log\frac{[B]}{[A]}$.

Choose, from the two graphs below, the one that corresponds to this change. Justify.

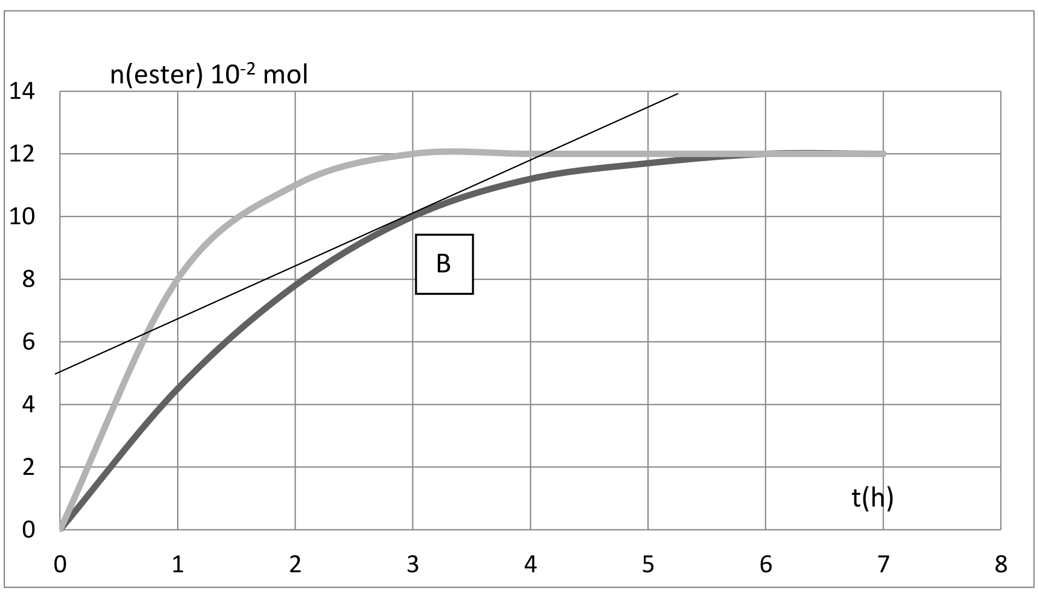


Graph (a)



Graph (b)

First Exercise

Question	Answer	mark
1.1	At the equivalence point : n (OH^-) $_{\text{added to reach equivalence}}$ = n (HA) $_{\text{introduced into the beaker}}$ $C_b \times V_{bE} = C_a \times V_a$ 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 general 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 :$CH_3 – CH_2 – CH – CH_3$ OH Its name is 2-butanol.	1
3.1	The condensed structural formula of the organic compound obtained is: $CH_3 – C – O – CH – CH_2 – CH_3$; its name is 1-méthylpropyl ethanoate O CH_3	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	According to the mass conservation law: x = 2 n and y = 4 n – 2 ; so y = 2 x – 2.	0.5
1.2	P_2O_5 is a strong dehydrating agent, it absorbs water formed in the dehydration reaction of the acid (A), shifting the equilibrium in the direction of formation of the anhydride.	0.5
1.3	$\frac{M(B)}{100} = \frac{3\times 16}{\%O}$; M(B) = 14 x + 46 =129.7 ; therefore x = 6 and the molecular formula of (B) is $C_6H_{10}O_3$.	0.75
1.4	The formula of (A) is: $CH_3 - CH_2 - COOH$. And that of (B) is: $CH_3 - CH_2 - CO - O - CO - CH_2 - CH_3$.	0.5
2.1	The equation of this reaction is: $CH_3 - CH_2 - CO - O - CO - CH_2 - CH_3 + CH_3 - CH_2 - CH_2\,OH \rightarrow$ $CH_3 - CH_2 - CO - O - CH_2 - CH_2 - CH_3 + CH_3 - CH_2 - COOH$. Ester formed is propyl propanoate	0.75 0.25
2.2	An equimolar initial mixture => n (alcohol) initial is equal to 0.6 mol. But n(alcohol) initial = $\frac{d(alcohol)\times V_1}{M(alcohol)}$; with M = 60 $g.mol^{-1}$ and d = 0.80 $g.\,mL^{-1}$, We find V_1 = 45 mL.	1
2.3	From the equation of the reaction: n(ester) maximal = n (alcohol) initial = n (B) initial = 0.6 mol	0.5
2.4	n (ester) at the end of the transformation is 0.40 mol since the corresponding reaction is limited and this value is always less than 0.6 mol.	0.75
2.5	This compound is propanoyl chloride of formula: $CH_3 - CH_2 - COCl$.	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 equivalence : n (H_3O^+) $_{\text{added to reach equivalence}}$ = n (NH_3) $_{\text{introduced into the beaker}}$ $C \times V_E = C_S \times V$ $C_S = \frac{C \times V_E}{V_S} = \frac{8 \times 10^{-3} \times 12.5}{10}$ = 0.01 mol.L^{-1}	1
2.4	The Concentration of the commercial solution is: $C_0 = 0.01 \times 650 = 6.5$ mol.L^{-1}	0.5
2.5	% by mass of the commercial solution in NH_3 = $\frac{C_0 \times M(NH_3)}{d(solution) \times 10}$ avec d(solution) = 0.92 g/mL ; therefore % by mass in NH_3 = 12.0 %	1
2.6	pH (mixture) = pKa (NH_4^+ / NH_3) + log $\frac{[B]}{[A]}$ The graph that corresponds to this change is the graph (a) since : - it is an increasing line (when [B] increases, that of [A] decreases and log $\frac{[B]}{[A]}$ increases ; so pH increases) - it passes in a point of abscissa at the origin equal to 9.2 which is the pKa (NH_4^+ / NH_3) = constant = 9.2 (from the curve pH = f [V (acid)] added.	1