المادة: الكيمياء – اللغة الإنكليزية الشهادة: الثانوية العامة الفرع: علوم الحياة نموذج رقم: 1 / 2019 المدّة: ساعتان	الهيئة الأكاديميّة المشتركة قسم: العلوم	المركز التربوي للبحوث والإنماء

This Exam Includes Three Exercises. It Is Inscribed on Four Pages Numbered from 1 to 4.
Answer the Three Following Exercises:

Exercise 1 (7 points) Ammonium Nitrate Granule

Ammonium nitrate granule is a mineral nitrogen fertilizer based on ammonium nitrate $NH_4NO_{3(s)}$, widely used in agriculture. The nitrogen is presented equally in ammonium ions NH_4^+ and in nitrate ions NO_3^-.
Ammonium nitrate is very soluble in water; it dissolves completely in water according to the following equation:

$$NH_4NO_{3(s)} \rightarrow NH_4^+{}_{(aq)} + NO_3^-{}_{(aq)}$$

On the label of a bag of this fertilizer one reads the following indication « the mass percentage of the element nitrogen N = 30% ».

Document-1

The aim of this exercise is to study the acidic character of the ammonium ions NH_4^+ and to verify the indication of the label by titrating these ions with a sodium hydroxide solution ($Na^+_{(aq)}$+ $HO^-_{(aq)}$) in the presence of convenient colored indicator.

Given: - The study is carried out at T = 25° C.
- pK_a (NH_4^+ / NH_3) = 9.2 ; pK_a (H_2O / HO^-) = 14.
- The molar mass of nitrogen in $g.mol^{-1}$: $M_{(N)}$ = 14.

1. Study of the Acidic Character of the NH_4^+ Ions

The NH_4^+ ions behave in water as monoacid.
1.1. Write the equation of the reaction of NH_4^+ ions with water.
1.2. Determine the constant K_R of this reaction.
1.3. Deduce that the reaction of NH_4^+ ions with water is limited.

2. Preparation of Solution (S) of Ammonium Nitrate

A solution (S) of ammonium nitrate of volume V_S = 500 mL is prepared by completely dissolving a mass m = 3.0 g of this fertilizer in distilled water.
Document-2 represents two sets of material E_1 and E_2 in order to prepare the solution (S).

E_1	E_2
Precision balance, watch glass, spatula, funnel, volumetric flask of 500 mL.	Spatula, watch glass, funnel, 500 mL graduated cylinder.

Document-2

Choose from **document-2** the most convenient set to prepare the solution (S). Justify.

3. Colorimetric Titration of the NH_4^+ Ions Present in the Nitrogen Fertilizer

A sample of volume $V_a = 10.0$ mL of solution (S) is titrated with a solution of sodium hydroxide of concentration $C_b = 0.1$ mol.L^{-1}.
Equivalence is reached after adding a volume $V_{bE} = 7.0$ mL of the base.

3.1. Document-3 represents the set of material used to perform a titration.
Pick out one material which is not necessary to perform this titration. Justify.

pH-meter and its electrode, 100mL beaker, magnetic stirrer and its bar, burette, universal stand.

Document-3

3.2. Write the equation of the titration reaction.
3.3. Based on the species present in the beaker at equivalence. Specify the most convenient indicator in **document-4**, to be used to achieve this titration.

Color indicator	pH range
Methyl Red	Red 4.2 - 6.2 Yellow
Alizarin yellow	Yellow 10 - 12 Purple

Document-4

3.4. Determine the concentration of NH_4^+ ions in the sample taken.
3.5. Show that the total number of moles of nitrogen (N) present in the solution (S) is $n_{(N)} = 0.07$ mol.
3.6. Calculate the mass percentage of the nitrogen element (N) of the ammonium nitrate fertilizer.
3.7. Verify whether the indication of the label is acceptable. Knowing that the percentage of relative error must not exceed 5%.

Exercise 2 (6 points) Kinetic Study of The Reaction

2-Chloro-2-methylpropane $(CH_3)_3C - C\ell$ reacts with water to form an alcohol and hydrochloric acid. The reaction is slow and complete and it is represented by the equation:

$$(CH_3)_3C - C\ell + 2H_2O \rightarrow (CH_3)_3C - OH + H_3O^+ + C\ell^-$$

The aim of this exercise is to study the kinetic of this reaction.

Given: Liquid 2-chloro-2-methylpropane: - Molar mass M = 92.5 g.mol^{-1}.
- Density: $\rho = 0.85$ g.mL^{-1}.

1. Preliminary Study of the Constituents

1.1. Give the systematic name of the alcohol formed.
1.2. Correct the following two propositions. Justify.
1.2.1. The water acts as a catalyst in this reaction.
1.2.2. The alcohol formed gives a ketone by mild oxidation .

2. Kinetic Study

A volume V=1.0 mL of 2-chloro-2-methylpropane is introduced in a volumetric flask and a suitable solvent is added to obtain a solution (S) of volume $V_S = 25.0$ mL.

At instant t = 0 min, the chronometer is set to function by adding a volume V'=5.0 mL of solution (S) into a beaker containing an excess of distilled water. Using an appropriate method, the number of moles of H_3O^+ ions formed is determined at different instant t; the results obtained are grouped in the table of **document-1.**

time (min)	0	2.5	5	7.5	10	12.5	15	17.5	20
n (H_3O^+) mmol	0	0.72	1.12	1.35	1.52	1.58	1.61	1.63	1.64

Document-1

2.1. Show that the initial number of moles of 2-chloro-2-methylpropane introduced into the beaker is $n_o = 1.8\times10^{-3}$ mol.

2.2. Plot the curve representing the variation in the number of moles of (H_3O^+) as a function of time: n (H_3O^+) = f (t) within the interval of time [0 - 20 min].
Take the following scales: Abscissas: 1 cm → 2 min and ordinates: 1 cm → 0.2 mmol.

2.3. Specify, graphically, the variation of the instantaneous rate of formation of H_3O^+ ions as a function of time.

2.4. Indicate the kinetic factor responsible for this variation.

2.5. Two propositions are given. In case the proposition is correct justify it and in case it is false correct it.

2.5.1. The rate of the reaction at a given instant (t) is twice the rate of disappearance of water at the same instant.

2.5.2. At the instant t = 7.5 min, the number of moles of 2-chloro-2-methylpropane remained in the reaction mixture is $n_{remained} = 0.45$ mmol.

2.6. Determine the half-life time $t_{1/2}$.

Exercise 3 (7 points) Ester with Jasmine Odor

For the synthesis of the essential ester of jasmine odor, benzyl ethanoate, the following compounds are available in the laboratory:
Ethanoic acid, ethanoic anhydride and benzyl alcohol.

Condensed structural formula
Benzyl alcohol $C_6H_5 - CH_2 - OH$
Benzyl ethanoate $CH_3 - COO - CH_2 - C_6H_5$
Document-1

The aim of this exercise is to compare the action of ethanoic acid and ethanoic anhydride on benzyl alcohol in order to synthesize a benzyl ethanoate and to study the saponification reaction of this ester.

Given: - Molar mass of benzyl alcohol: $M_{(benzyl\ alcohol)} = 108\ g.mol^{-1}$;
- Molar mass of benzyl ethanoate: $M_{(benzyl\ ethanoate)} = 150\ g.mol^{-1}$

1. Preparation of Benzyl Ethanoate by Using Ethanoic Acid

An amount $n_1 = 0.1$ mol of ethanoic acid is mixed with a mass $m_2 = 10.8$ g of benzyl alcohol with a few drops of concentrated sulfuric acid. The mixture is heated to reflux for a certain time. At equilibrium, the recovered ester has a mass $m_{exp} = 9.9$g.

At equilibrium, the percent yield of esterification reaction of equimolar mixture between acid and alcohol is 66% for primary alcohol and 60% for secondary alcohol

Document-2

1.1. Write the equation of the reaction of this synthesis using the condensed structural formulas.
1.2. Choose the correct answer. The esterification reaction between ethanoic acid and benzyl alcohol is:
a. Slow and complete.
b. Fast and complete.
c. Slow and limited.
1.3. Determine the yield of this reaction.
1.4. Deduce the class of benzyl alcohol.
1.5. Specify if the increase in temperature at equilibrium improves the yield of this reaction.

2. Preparation of Benzyl Ethanoate by Using Ethanoic Anhydride

The same experiment is repeated by replacing ethanoic acid with ethanoic anhydride. The reactants are mixed in stoichiometric ratio. At the end of the reaction, a mass m'_{exp} of the same ester is collected.
The nominal equation of this complete synthesis is given by:

Ethanoic anhydride + Benzyl alcohol → Benzyl ethanoate + Compound (B)

2.1. Write the condensed structural formula of the ethanoic anhydride.
2.2. Identify the compound (B).
2.3. Choose the correct answer. Justify.
a. $m'_{exp} = 9.9$ g
b. $m'_{exp} = 15.0$ g
c. $m'_{exp} = 12.0$ g

2.4. Give another advantage of the use of ethanoic anhydride in the synthesis of an ester.

3. Benzyl Ethanoate in Saponification

A mass m = 1.5 g of the ester already prepared is reacted with a sodium hydroxide solution of concentration $C_b = 10.0$ mol.L^{-1} at high temperature. A compound (A) and benzyl alcohol are produced.

3.1. Write the equation of the saponification reaction.
3.2. Give the systematic name of the compound (A).
3.3. The saponification reaction is slow and complete. Determine the minimum volume of used sodium hydroxide solution to have complete saponification.

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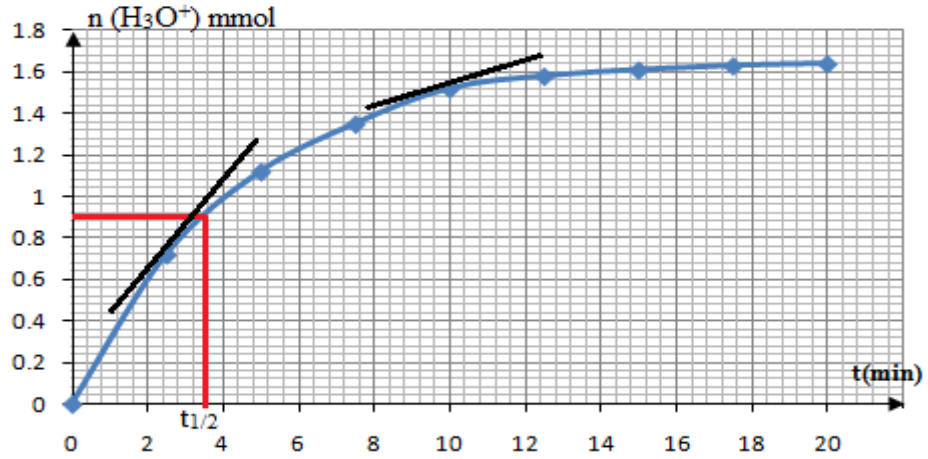
أسس التصحيح:

Part of question	Exercise 1 (7 points) Ammonium Nitrate Granule Expected Answer	Mark
1.1.	$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$	**0.5**
1.2.	$K_R = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = Ka = 10^{-pKa} = 10^{-9.2} = 6.3x10^{-10}$	**0.5**
1.3.	$K_R < 10^{-4}$ thus the reaction is limited.	**0.5**
2.	The E_1 set is the most precise one since ones need: - a precision balance, spatula, watch glass to weigh the mass m = 3.0g of the fertilizer. - a 500 mL volumetric flask and a funnel to prepare the volume of 500 mL; the volumetric flask is more precise than the graduated cylinder to measure the volume V_S.	**1**
3.1.	In a colorimetric titration, a colored indicator is needed to detect the equivalence. So, we do not need a pH meter and its electrode.	**0.75**
3.2.	$NH_4^+ + HO^- \rightarrow NH_3 + H_2O$	**0.5**
3.3.	The chemical species present in the beaker at equivalence are: NH_3(weak base), H_2O (neutral), NO_3^- and Na^+ (spectator ions). So the medium is basic at equivalence point. Since the $pH_E > 7$ then the most convenient indicator is alizarin yellow [10 - 12] because pH_E is included in its pH range.	**1**
3.4.	At equivalence point: $\frac{n_{NH_4^+(present\ in\ Va)}}{1} = \frac{n_{HO^-(added\ in\ V_{bE})}}{1}$; $C_aV_a = C_bV_{bE}$; $C_a = \frac{0.1x7}{10} = 0.07$ mol.L^{-1}	**0.75**
3.5.	In 500mL solution (S): $n(NH_4^+) = C_a \times V_S = 0,07 \times 0,5 = 0,035$ mol. According to S.R: $n(NH_4^+) = n(NO_3^-) = 0,035$ mol. Thus the total number of moles of nitrogen (N) present in the solution (S): $n_{(N)} = 0,035 + 0,035 = 0,07$ mol.	**0.75**
3.6.	$m_{(N)} = n_{(N)} \times M_{(N)} = 0.07 \times 14 = 0.98$ g $\%\ by\ mass\ of\ N = \frac{m_{(N)}}{m_{(fertilizer)}} x100 = \frac{0.98}{3} x100 = 32.7\%$	**0.5**
3.7.	$\%Relative\ error = \left\lvert\frac{30 - 32.7}{30}\right\rvert x100 = 9\% > 5\%$ So the indication of the label is unacceptable	**0.25**

Part of question	Exercise 2 (6 points) Kinetic Study of The Reaction Expected Answer	Mark
1.1.	2-methyl-2-propanol	**0.25**
1.2.1.	Water is a reactant because it participates in the reaction and changes its nature.	**0.5**
1.2.2.	The alcohol formed is tertiary and does not undergo mild oxidation.	**0.5**
2.1.	In 25 mL of solution(S), the number of moles of 2-chloro-2-methylpropane is : $n = \frac{m}{M} = \frac{\rho x V}{M} = \frac{0.85x1}{92.5} = 0.0092 mol;$ In 5mL of solution(S) ; $n_{(0)} = \frac{n\,x\,5}{25} = \frac{0{,}0092\,x\,5}{25} = 1{,}8.10^{-3}\,mol$.	**0.5**
2.2.		**1**
2.3.	The instantaneous rate of formation of H_3O^+ ions is equal to the slope of the tangent drawn on the curve at a point of abscissa t. It starts maximum at t = 0 and decreases with time because the slope of the tangent at each point of the curve decreases with time.	**0.75**
2.4.	The concentration of the reactants is the kinetic factor responsible for this variation because it begins maximum and decreases with time.	**0.25**
2.5.1.	False. at any instant t and according to the stoichiometric ratios: $\frac{r_{(reaction\ )t}}{1} = \frac{r_{(H_2O)t}}{2}$ So, the rate of the reaction at a given instant is half the rate of disappearance of water at the same instant t	**0.75**
2.5.2.	True. At t = 7.5min and according to stoichiometric ratios: $\frac{n_{(reacted)t=7.5}}{1} = \frac{n_{(H_3O^+)t=7.5}}{1} = 1.35\ mmol$ $n_{(remained)} = n_{(0)} - n_{(reacted)t=7.5} = 1.8 - 1.35 = 0.45$ mmol	**0.75**
2.6.	$t_{1/2}$ is the time required for the disappearance of half the amount of limiting reactant. According to stoichiometric ratios: $\frac{n_{(0)}}{1} = \frac{n_{(H_3O^+)\infty}}{1} = 1.8x10^{-3}\,mol$; $\frac{n_{(H_3O^+)\infty}}{2} = 0.9x10^{-3}\,mol = 0.9$ mmol. Graphically $t_{1/2}$ = 3.5 min	**0.75**

Part of questions	Exercise 3 (7 points) Ester with jasmine smell Expected Answer	Mark
1.1	$CH_3 – COOH + HO – CH_2 – C_6H_5 \rightleftharpoons CH_3 – COO – CH_2 – C_6H_5 + H_2O$	**0.5**
1.2	**c.** Slow and limited.	**0.5**
1.3	$n_{(alcohol)} = \frac{m_2}{M} = \frac{10.8}{108} = 0.1mol$ The mixture of reactants is equimolar $n_{(acid)} = n_{(alcohol)} = 0.1$ mol According to stoichiometric ratios: $n_{(acid)} = n_{(ester)theoretical} = 0.1$ mol $m_{(ester)\ theoretical} = n_{(ester)theoretical} \times M = 0.1 \times 150 = 15$ g. The yield of the reaction is then: $\%Y = \frac{m_{(ester)experimental}}{m_{(ester)theoretical}} x100 = \frac{9.9}{15} x100 = 66\%$	**1**
1.4	The mixture of the reactants is equimolar and the yield of the esterification reaction is 66% thus the benzyl alcohol is a primary alcohol.	**0.5**
1.5	The increase in temperature does not modify the yield at equilibrium because the reaction is athermic, but the rate of the reaction increases.	**0.5**
2.1	$CH_3 – \overset{\overset{O}{\|}}{C} – O – \overset{\overset{O}{\|}}{C} – CH_3$	**0.5**
2.2	(B): $CH_3 – COOH$ ethanoic acid.	**0.5**
2.3	**b.** $m'_{exp} = 15.0$ g The reactants are equimolar and the reaction is complete. At the end of the reaction we have: $\frac{n_{(alcohol)}}{1} = \frac{n_{ester(formed)}}{1} = 0.1mol$ $m'_{(ester)\ formed} = n \times M = 0.1 \times 150 = 15$ g.	**1**
2.4	The synthesis which is carried out in the presence of an acid anhydride is faster than that which is carried out with a carboxylic acid.	**0.5**
3.1	$CH_3 – COO – CH_2 – C_6H_5 + (Na^+ + HO^-) \rightarrow (CH_3 – COO^- + Na^+) + HO–CH_2–C_6H_5$	**0.5**
3.2	Sodium Ethanoate.	**0.25**
3.3	According to stoichiometric ratios: $\frac{n_{(ester)}}{1} = \frac{n_{sodiumhydroxide}}{1} = \frac{m}{M} = \frac{1.5}{150} = 0.01mol;$ $C_b = \frac{n_{sodiumhydroxide}}{V};\ V = \frac{n_{sodiumhydroxide}}{C_b} = \frac{0.01}{10} = 10^{-3}L\ or\ 1mL$	**0.75**