وزارة التربية والتعليم العالي
المديريّـة العامة للتربية
دائرة الامتحانات الرسمية

امتحانات الشهادة الثانوية العامّة
فرع: علوم الحياة

دورة العام ٢٠١٨ العاديّة
الثلاثاء ١٢ حزيران ٢٠١٨

مسابقة في مادة الكيمياء	الاسم:
المدة: ساعتان	الرقم:

This Exam Includes Three Exercises. It Is Inscribed on Four Pages Numbered from 1 to 4.
The Use of A Non-programmable Calculator Is Allowed.

Answer the Three Following Exercises:

Exercise 1 (7 points) Properties of an Alcohol

Alcohols are products with a great industrial and commercial importance. They undergo many and diverse chemical reactions and are used in the synthesis of many compounds such as esters.
The aim of this exercise is to study the chemical properties of the alcohol (A) and its reaction with methanoic acid.

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

1. Chemical properties of the Alcohol (A)

Available is a saturated and non-cyclic mono-alcohol denoted (A). The quantitative analysis of alcohol (A) shows that the percentage by mass of oxygen is %O = 21.62%

1.1. Show that the molecular formula of the alcohol (A) is $C_4H_{10}O$.

1.2. The condensed structural formula of the alcohol (A) is:

$$
\begin{array}{c}
\qquad\qquad\qquad\quad OH \\
\qquad\qquad\qquad\quad | \\
CH_3 - CH_2 - CH - CH_3
\end{array}
$$

1.2.1. Indicate the class of alcohol (A).
1.2.2. Give its systematic name.
1.2.3. Write the condensed structural formulas of the other three alcohol isomers of alcohol (A).
1.2.4. Justify that the molecule of the alcohol (A) is chiral.
1.2.5. Represent, according to Cram, the two enantiomers of alcohol (A).

1.3. The mild oxidation of the alcohol (A) by a solution of acidified potassium permanganate leads to the formation of an organic compound (B).
Correct the following propositions:

1.3.1. The systematic name of (B) is butanal.
1.3.2. The compound (B) gives white crystals with 2,4- DNPH.

2. Reaction of the Alcohol (A) With Methanoic Acid

A mixture of 0.2 mol of alcohol (A) and 0.2 mol of methanoic acid is heated to reflux, in the presence of few drops of concentrated sulfuric acid as a catalyst.

The esterification reaction is represented by the following equation:

$$\text{methanoic acid} + \text{alcohol (A)} \rightleftharpoons \text{ester (E)} + \text{water}$$

At an instant of time t, the equilibrium is reached. The number of moles of methanoic acid remained at equilibrium is $n_{(acid)} = 0.08$ mol.

2.1. Write, using the condensed structural formulas, the equation of this esterification reaction.
2.2. Determine the number of moles of each constituent of the reacting mixture, at equilibrium.
2.3. Deduce the value of the equilibrium constant Kc.
2.4. The same experiment is carried out again with only one change: "without the addition of concentrated sulfuric acid" .The equilibrium state is reached at an instant of time t'. Choose the correct answer. Justify.
a. $t > t'$ **b.** $t = t'$ **c.** $t < t'$

Exercise 2 (6 points) **Kinetic of the Oxidation of Javel Water with Ammonia**

In an aqueous solution, ammonia (NH_3) reacts with hypochlorite ions ($C\ell O^-$) in a slow and complete reaction that takes place according to the equation below:

$$2\ NH_{3\ (aq)} + 3\ C\ell O^-_{(aq)} \longrightarrow N_{2\ (g)} + 3\ C\ell^-_{(aq)} + 3\ H_2O_{\ (l)}$$

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

- Javel water is a sodium hypochlorite aqueous solution ($Na^+ + ClO^-$).
- Nitrogen gas (N_2) is slightly soluble in water.

Document- 1

1. Preparation of a Javel Water Solution (S_1)

A volume V_1 = 250 mL of the solution (S_1) of molar concentration $C_1 = 0.25\ mol.L^{-1}$ is prepared by diluting 25 times a commercial Javel water solution (S_o).

1.1. Determine the volume V_o withdrawn from solution (S_o) to prepare the solution (S_1).
1.2. Choose, from **document- 2**, the essential glassware needed to carry out the preparation of solution (S_1).

- Beakers : 100ml, 250 ml and 500ml	- Volumetric flasks: 100ml, 250 ml and 500ml
-Graduated cylinders: 5 ml, 10ml and 25ml	- Volumetric pipets: 5 ml, 10ml and 25ml

Document- 2

2. Kinetic Study

A volume V_1=200 mL of a solution (S_1) of Javel water solution of molar concentration C_1 = 0.25mol.L^{-1} is mixed with an excess of ammonia solution at constant temperature T = 27 ^{o}C. Using an appropriate method, the number of moles of nitrogen gas N_2 formed is determined at different instant t, the results obtained are grouped in the table of **document- 3**

t (min)	2	4	6	8	10	12	16
n(N_2) (10^{-3} mol)	4.3	8.0	10.3	12.0	13.3	14.3	15.5

Document-3

2.1. Calculate the initial number of moles of hypochlorite ions $C\ell O^-$.

2.2. Verify whether the instant of time t = 16 min represents the end of the reaction.

2.3. Plot the curve representing the variation in the number of moles of (N_2) as a function of time:

n (N_2) = f (t) within the interval of time [0 – 16 min].

Take the following scales: In abscissas: 1cm for 1 min;

In ordinates: 1cm for 1×10^{-3} mol.

2.4. Deduce, graphically, the variation of the rate of formation of (N_2) as a function of time.

2.5. Choose the correct answer:

The instantaneous rate of formation of N_2 at an instant of time t is denoted as $r_{(N2)t}$ and the instantaneous rate of disappearance of $C\ell O^-$ at the same instant t is denoted as $r_{(C\ell O^-)t}$ are related by the relation:

a. $r_{(ClO^-)t} = 3\, r_{(N2)t}$ b. $r_{(ClO^-)t} = \frac{r(N2)t}{3}$ c. $r_{(ClO^-)t} = r_{(N2)t}$

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

2.7. The same kinetic study is carried out again but with one change: the temperature of the reacting medium is higher than 27 ^{o}C.

Specify, in this study, whether the following statement is true or false:

The number of moles of nitrogen gas (N_2) formed at t = 4 min becomes less than 8.0×10^{-3} mol.

Exercise 3 (7 points) Titration of an Ethanoic Acid Solution

Ethanoic acid is a weak acid of formula CH_3COOH. At room temperature, it is a colorless liquid with a pungent odor and it is highly miscible in water.

The aim of this exercise is to study the behavior of ethanoic acid in water and to determine its molar concentration by pH-metric titration.

Given: - This study is carried out at 25 ^{o}C.

- pKa of the pair (CH_3COOH / CH_3COO^-) = 4.8

1. Study of the Behavior of Ethanoic Acid in Water

In the laboratory, available is a flask containing an ethanoic acid solution (S) of unkown molar concentration C_a.

1.1. Write the equation of the reaction of ethanoic acid with water.

1.2. Knowing that α is the degree of dissociation of ethanoic acid in water ,verify the following relation : $\frac{[CH_3COO^-]}{[CH_3COOH]} = \frac{\alpha}{1-\alpha}$

1.3. Show that the value of α is close to 0.04, knowing that pH of the solution (S) is equal to 3.4

1.4. Based on the value of α, justify that ethanoic acid is a weak acid.

2- Titration of the Ethanoic Acid Solution (S)

Into a beaker, introduce a volume V_a = 20.0 mL of the ethanoic acid solution (S) and a certain volume of distilled water to immerse properly the pH-meter electrode. A sodium hydroxide solution ($Na^+ + HO^-$) of molar concentration $C_b = 2.0\times10^{-2}$ mol.L^{-1} is added progressively. A sample of the experimental results is given in **document-1** :

V_b (mL)	0	5	10	15
pH	3.5	4.8	pH_E	11.2

Document-1

2.1. From the given material of **document-2**, choose the most suitable ones needed to carry out the titration .

- Volumetric flasks: 50 and 100 mL
- Graduated cylinders: 10, 20 and 50 mL
- Graduated buret : 25 mL
- Precision balance
- Beaker : 100 mL
- Magnetic stirrer and its bar
- pH – meter and its electrode

Document-2

2.2. Write the equation of the titration reaction.

2.3. Based on the chemical species present in the beaker at equivalence. Specify the point that represents the equivalence point:
A (V_{bE} = 10 mL ; pH_E = 8.3) ; B (V_{bE} = 10 mL ; pH_E = 7) ; C (V_{bE} = 10 mL ; pH_E = 5.8).

2.4. Determine the molar concentration of ethanoic acid in the solution (S).

2.5. Plot the shape of the curve representing the change in the pH as a function of the volume of the base added pH = f (V_b) passing by the four remarkable points extracted from the table of **document-1**.
Take the following scales: In abscissa 1 cm = 1 mL;
In ordinates; 1cm = 1 unit of pH.

2.6. Referring to **document-1** and using the predominance axis of the chemical species of the pair CH_3COOH / CH_3COO^-, specify the chemical species which predominates at the end of the titration for V_b = 15 mL.

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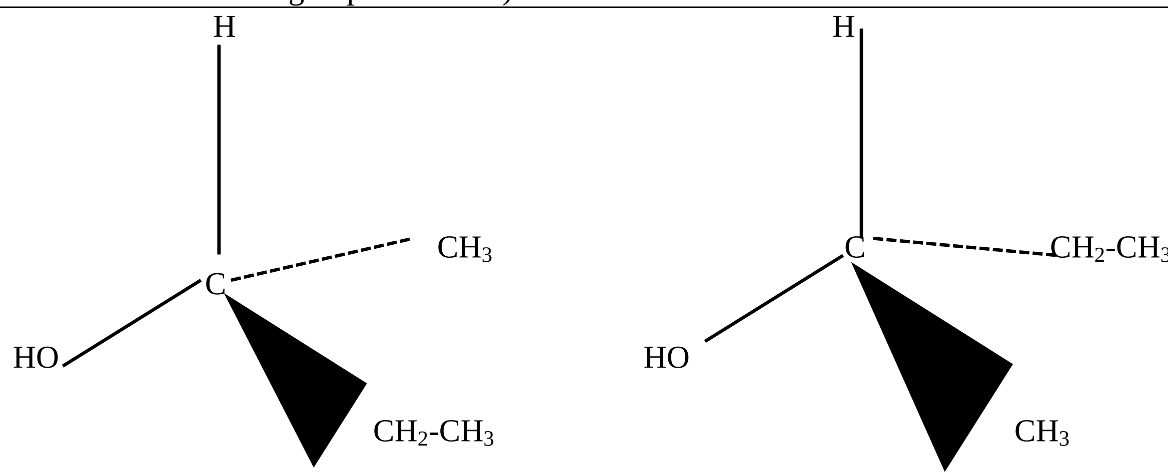
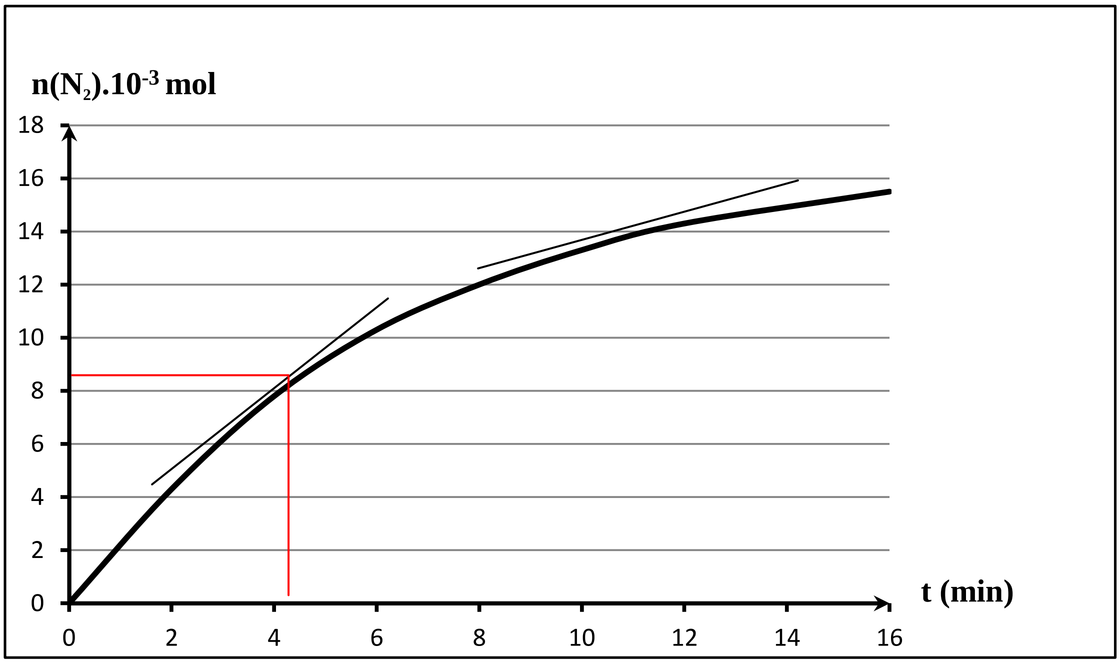
دورة الـعام ٢٠١٨ العادية
الثلاثاء ١٢ حزيران ٢٠١٨

أسس التصحيح في مادة الكيمياء

Exercise 1 (7 points) Properties of an alcohol

Part	Answer	Pts
1.1	(A) is a saturated and non-cyclic mono-alcool , Its general formula is $C_nH_{2n+2}O$ So z = 1 $\frac{16x1}{\%O} = \frac{12n+2n+2+16}{100}$; $\frac{16}{21,62} = \frac{14n+18}{100}$; n = 4 So the molecular formula of (A) is $C_4H_{10}O$	**0,75**
1.2.1	(A) is a secondary alcohol	**0,25**
1.2.2	2- butanol	**0,25**
1.2.3	$CH_3 - CH_2 - CH_2 - CH_2OH$ $CH_3 - C(CH_3)(OH) - CH_3$ $CH_3 - CH(CH_3) - CH_2OH$	**0.75**
1.2.4	The molecule of (A) chiral since it posseses an assymetric carbon (the carbon 2 which is connected to four different atoms or groups of atoms)	**0,5**
1.2.5		**0,75**
1.3.1	Butanone	**0,5**
1.3.2	(B) with 2,4-DNPH gives a yellow orange precipitate or (B) with $NaHSO_3$ gives white crystals	**0.5**
2.1	$HCOOH + HO - CH(CH_3) - CH_2 - CH_3 \rightleftharpoons HCOO - CH(CH_3) - CH_2 - CH_3 + H_2O$	**0.75**
2.2	Methanoic acid + (A) ⇌ (E) + H_2O At t = 0: 0.2 mol, 0.2 mol, -, - At t_{eq}: 0.08 mol, 0.08 mol, 0.12 mol, 0.12 mol	**1**
2.3	$K_c = \frac{[E][H_2O]}{[Acide][A]} = \frac{(0.12/V)^2}{(0.08/V)^2} = \frac{(0.12)^2}{(0.08)^2} = 2.25$	**0,5**
2.5	**c.** t < t' the catalyst is a kinetic factor , in absence of a catalyst the rate decreases and the time required to reach the equilibrium state is greater .	**0.5**

Exercise 2 **Kinetics of the oxidation of Javel water with ammonia**

Part	Answers	Note
1.1	By dilution , the number of moles of solute is consvred : $n_0 = n_1$; $C_0 \times V_0 = C_1 \times V_1$; $F = \frac{C_0}{C_1} = \frac{V_1}{V_0}$; $V_0 = \frac{V_1}{F} = \frac{250}{25} = 10\,mL$.	**0,5**
1.2	The glassware needed to prepare te solution (S_1) : Volumetric flask :250 mL, volumetric pipet : 10 mL and (beaker 100 mL).	**0,5**
2.1	n ($C\ell O^-$) initial = $C_1 \times V_1 = 0.25 \times 0.2 = 5 \times 10^{-2}$ mol.	**0,5**
2.2	According to ST. R. : $n(C\ell O^-)_0 / 3 = n(N_2)_\infty$; $n(N_2)_\infty = 5\times10^{-2} / 3 = 16.6\times10^{-3}$ mol Or at t = 16 min , we have $n(N_2) = 15.5\times10^{-3}$ mol < 16.6×10^{-3} mol. So t = 16 min does not correspond to the end of the reaction .	**0,75**
2.3		**1**
2.4	The instantaneous rate of formation de N_2 is equal to the slope of the tangent drawn to the on the curve at a point of abscissa t. The slope of the tangent decreases at each point So the intantaneous rate of formation de N_2 deacreases with time.	**0,75**
2.5	**a.** $r_{(C\ell O^-)t} = 3\, r_{(N_2)t}$.	**0,5**
2.6	The half life time is the time needed to for the la quantity of N_2 to become the half of of its maximal value At $t_{1/2}$: $n(N_2)_{t1/2} = n(N_2)_\infty / 2 = 16.6\times10^{-3} / 2 = 8.3\times10^{-3}$ mol. Graphically $t_{1/2} = 4.3$ min.	**1**
2.7	False . The temperature is a kinetic factor , when it increases the rate of the reaction increases so the number of moles of N_2 at instant t = 4 min becomes greater than to 8.0×10^{-3} mol.	**0,5**

Exercise 3 (7 points) Titration of an Ethanoic Acid Solution

Part	Answer	pts
1.1	$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$	**0,5**
1.2	a t = 0 C_a solvent 0 0 a t⇌ $C_a - C_a\alpha$ solvent $C_a\alpha$ $C_a\alpha$ According to the table : $\frac{[CH_3COO^-]}{[CH_3COOH]} = \frac{Ca\alpha}{Ca(1-\alpha)} = \frac{\alpha}{1-\alpha}$ Verified	**0,75**
1.3	$pH = pKa + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$ $3.4 - 4.8 = \log \frac{[CH_3COO^-]}{[CH_3COOH]}$ $-1.4 = \log \frac{\alpha}{1-\alpha}$ $\frac{\alpha}{1-\alpha} = 10^{-1.4}$; $\alpha = 0.038$, it is close to 0.04 Verified	**0,5**
1.4	Since $\alpha = 0.04 < 1$ So the ethanoic acid CH_3COOH is a weak acid .	**0,25**
2.1	The most suitable material needed to carry out the titration are : - Beaker : 100 mL - Graduated buret : 25 mL - pH – meter and its electrode . - Magnetic stirrer and its bar	**1**
2.2	$CH_3COOH + HO^- \rightarrow CH_3COO^- + H_2O$	**0,5**
2.3	The chemical species presents in the beaker at the equivalence are : Na^+ (spectator ion) ; H_2O (neutral) and CH_3COO^- (ion of basic character so $pH_E > 7$) , we deduce that the point that corresponds to the equivalence point is : A (V_{bE} = 10 mL ; pH_E = 8.3).	**0,75**
2.4	At equivalence : $n(CH_3COOH)_{\text{introduced in the beaker}} = n(HO^-)_{\text{added to reach equivalence point}}$ $C_aV_a = C_bV_{bE}$ $C_a = (C_b.V_{bE})/V_a = (2.10^{-2} \times 10.10^{-3})/20 \times 10^{-3} = 10^{-2}$ mol.L^{-1}.	**1**
2.5		

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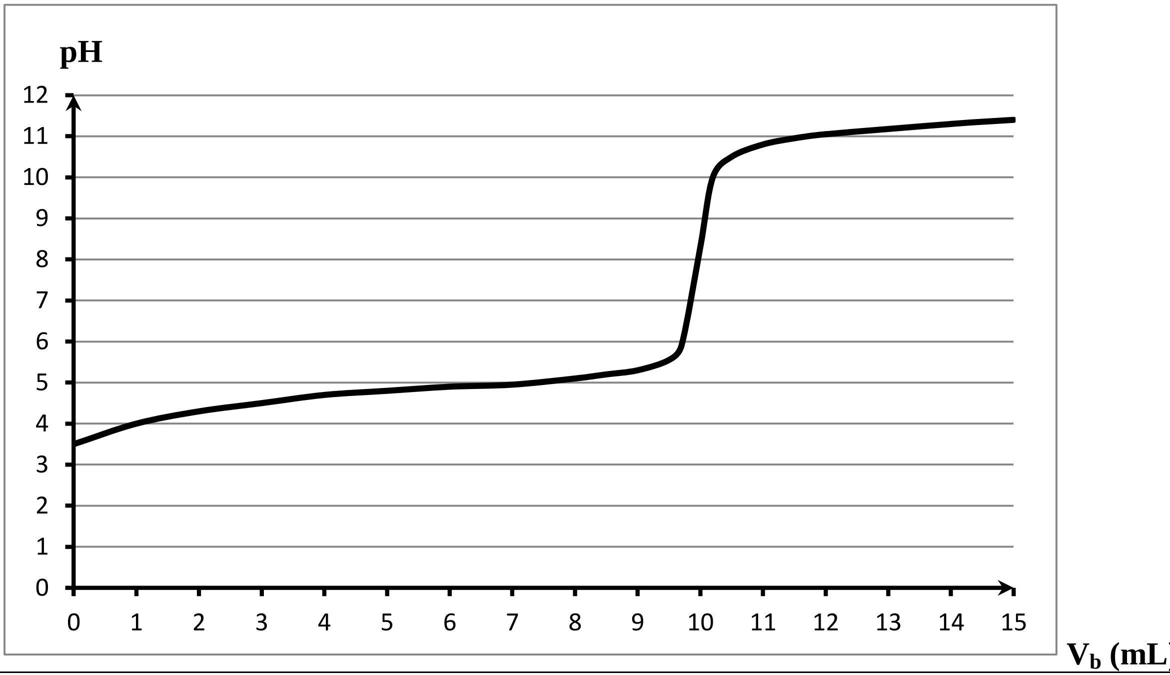
<tr><td></td><td>
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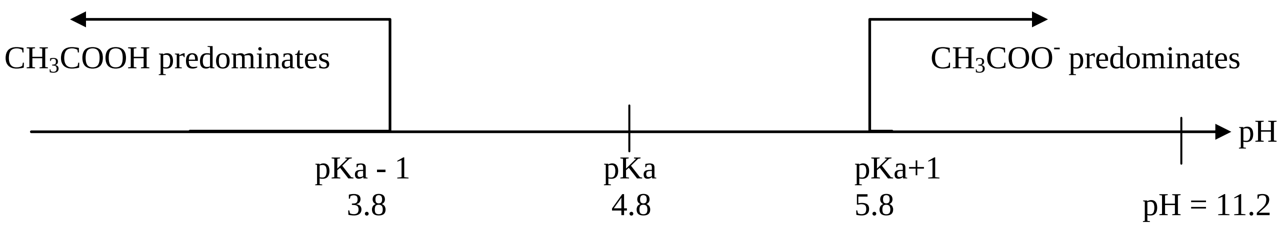
<tr><td>2.6</td><td>

For V_b = 15 mL; pH = 11.2 > pKa + 1 = 5.8 so CH_3COO^- is the predominant species .</td><td>0,75</td></tr>
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