وزارة التربية والتعليم العالي المديرية العامة للتربية دائرة الامتحانات	امتحانات الشهادة الثانوية العامة الفرع : علوم عامة	الدورة العادية للعام 2011
	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 Three Following Exercises:

First Exercise (7 points)
Kinetic of the Reaction Between Hydrochloric Acid and Magnesium

Magnesium reacts, at room temperature, with the H_3O^+ ions of an aqueous solution of hydrochloric acid by a slow reaction according to the following equation:

$$Mg_{(s)} + 2\,H_3O^+_{(aq)} \rightarrow Mg^{2+}_{(aq)} + 2\,H_2O_{(l)} + H_{2\,(g)}$$

A mass of 2 g of magnesium is introduced into a volume V = 100 mL of a hydrochloric acid solution of concentration C = 0.11 mol.L^{-1}. The change of the reacting system is followed in terms of time, by determining the number of moles of hydrogen gas, n(H_2), released at different instants.
The results are given in the following table:

t (min)	0	2	4	6	8	10	14	18	22	26	30	34
n (H_2) (10^{-3} mol)	0	0.85	1.6	2.2	2.9	3.4	4.2	4.7	4.9	5.1	5.2	5.3

Given :

- Molar mass in g.mol^{-1}: M(Mg) = 24
- Ideal gas constant: R = 8.31 J.mol^{-1}.K^{-1}

1- <u>Preliminary Study</u>

This follow-up is carried out by measuring the volume of hydrogen gas released at a temperature of 25 ºC and under a pressure of 9.76×10^4 Pa.

1.1- Show that the concentration of H_3O^+ ions, in the reacting medium, at t = 10 min, is equal to 4.2×10^{-2} mol.L^{-1}. Deduce the pH of this medium at this instant of time.

1.2- Find the limiting reactant.

1.3- Determine the volume of the hydrogen gas evolved at the end of the reaction.

2- <u>Kinetic Study</u>

2.1- Plot, on a graph paper, the curve representing the change of the number of moles of hydrogen versus time: n (H_2) = f (t) in the time interval [0-34 min].

Take the following scale: 1 cm for 2 min in abscissa and 1 cm for 5.0×10^{-4} mol in ordinate.

2.2- Determine the rate of formation of hydrogen at the instant t = 7 min.

2.3- Choose, by justifying without calculation, between the two following values: 6.2×10^{-4}mol.min^{-1} and 8.0×10^{-5} mol.min^{-1}, the one that corresponds to the rate of formation of hydrogen at t = 18 min.

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

2.5- The same experimental study is carried out again, but at a temperature of 40º C. Plot on the same graph of part 2.1, by justifying, the shape of the curve representing the number of moles of hydrogen versus time: n(H_2) = g (t).

Second Exercise (6 points)

A Carboxylic Acid: Ethanoic Acid

The carboxylic acids show a great industrial importance. Ethanoic acid is one of the most important intermediate organic compounds manufactured in large amount worldwide.

Given:

- pKa (CH_3COOH/CH_3COO^-) = 4.75
- [X] is neglected compared to [Y] if $\frac{[Y]}{[X]} \geq 100$

1- <u>Ethanoic acid and calcium carbonate</u>

A volume V of an ethanoic acid solution of concentration C is poured into a beaker containing a powder of calcium carbonate.
Effervescence is appeared. This effervescence decreases with time and ceases after few minutes.
The pH of the obtained solution is equal to 5.2

The equation of the complete reaction that took place is:

$$2\ CH_3COOH_{(aq)} + CaCO_{3(s)} \rightarrow Ca^{2+}_{(aq)} + 2CH_3COO^-_{(aq)} + CO_{2(g)} + H_2O_{(l)}$$

1.1- Extract, from what precedes, how the rate of this reaction changes with time.

1.2- Determine the value of the ratio: $\frac{[CH_3COO^-]}{[CH_3COOH]}$ in the obtained solution at the end of the reaction.

Deduce that calcium carbonate is the limiting reactant.

2- <u>Ethanoic acid and an alcohol (A)</u>

An equimolar mixture of ethanoic acid and an alcohol (A) is heated. A reaction takes place according to the equation:

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A +  CH3 - COOH  ⇄  CH3 – CH – CH2 –CH2 – O – C – CH3  + H2O
                          |                    ‖
                          CH3                  O
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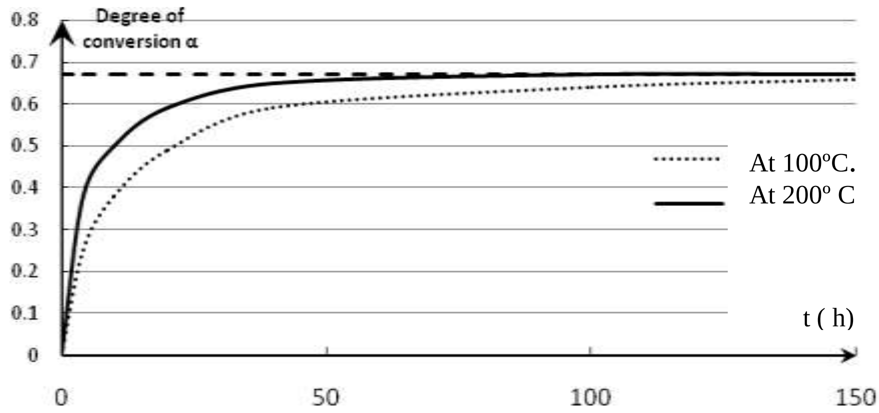
2.1- Give the name of this reaction and that of the organic compound obtained.
2.2- Identify the alcohol (A).
2.3- The two curves given below represent the variation of the degree of conversion (**α**) of the alcohol

(A), in this reaction, as a function of time at two different temperatures: 100º C and 200º C.



Deduce that this reaction is: limited, athermic and slow.

2.4- The above mixture is heated in the presence of a catalyst. Indicate the effect of this catalyst on the degree of conversion **α**.

2.5- In order to obtain a value of **α** close to 1, one of the two reactants, used in the above reaction is replaced by another organic compound (C).

2.5.1- Write the possible condensed structural formulas of (C). Give their names.

2.5.2- Write, by choosing one of the possible formulas of (C), the equation of the corresponding reaction.

2.5.3- Give two characteristics of this reaction.

Third Exercise (7 points)
Identification of an Acid/Base Pair

A solution S containing a weak acid HA, its conjugate base A^- and sodium ions Na^+ is available.
It is required to determine the concentrations of this weak acid HA and that of its conjugate base A^-, in the solution S in order to identify them.
For this purpose, the two following titrations are carried out:

1- Titration of the acid HA

A sodium hydroxide solution of concentration $C_b = 0.10$ mol.L^{-1} is added gradually into a beaker containing a volume $V_1 = 20.0$ mL of the solution S.
A pH-metric follow-up gives the results grouped in the following table:

V_b (mL)	0	1	2	3	4	4.5	5	5.2	5.5	6	7	8	9	10
pH	5.0	5.1	5.3	5.5	5.8	6.1	6.9	9.2	10.9	11.4	11.7	11.8	11.9	12.0

Where V_b is the volume of the basic solution added.

1.1- Choose, among the list giving below, the essential materials needed to carry out this titration.

List of materials:

- 50, 100 and 150 mL Beakers.
- 20 and 50 mL graduated cylinders.
- 25 mL Buret.
- pH-meter and its electrode.
- Sensitive balance.
- 50, 100 and 150 mL Erlenmeyer flasks.
- 10, 20 and 25 mL volumetric pipets.
- Magnetic stirrer and its bar.

1.2- Write the equation of this titration reaction.

1.3- Plot, on a graph paper, the curve representing the variation of pH versus V_b added: $pH = f(V_b)$.
Take the following scale: 1 cm for 1 mL in abscissa and 1 cm for 1 unit of pH in ordinate.

1.4- Determine graphically the coordinates of the equivalence point.

1.5- Deduce the concentration of HA, [HA], in the solution S.

2- <u>Titration of the base A^-</u>

Another volume $V_2 = 20.0$ mL of solution S is titrated with a hydrochloric acid solution of concentration $C_a = 0.10$ mol.L^{-1}.
Equivalence is reached when the volume of the acid added is $V_{aE} = 9.3$ mL.

2.1- Write the equation of this titration reaction.

2.2- Referring to the chemical species present in the solution obtained at equivalence, specify whether this solution is acidic, basic or neutral.

2.3- Determine the concentration of A^- ions, $[A^-]$, in the solution S.

3- <u>Identification of the Acid HA and its Conjugate Base A^-</u>

The values of pKa of some conjugate acid/base pairs are given below:

Acid/base pair	$HCOOH / HCOO^-$	$C_6H_5COOH / C_6H_5COO^-$	CH_3COOH / CH_3COO^-
pKa	3.75	4.20	4.75

3.1- Identify the species of the pair HA/ A^- present in the solution S.

3.2- In general, the curve representing the titration of a weak acid with a strong base has two inflection points. Specify why the curve of part 1.3 has only one inflection point.

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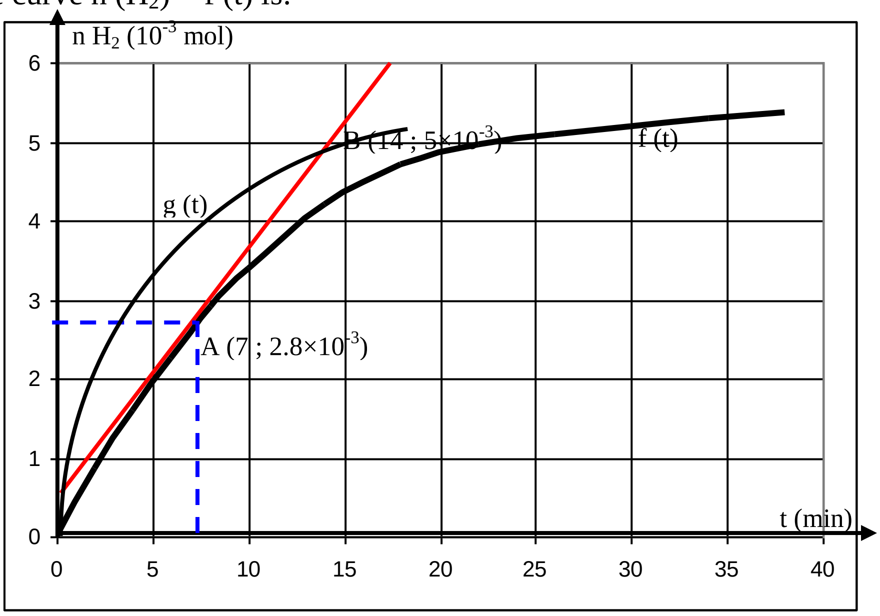
الاسم: الرقم:	مسابقة في مادة الكيمياء المدة ساعتان	مشروع معيار التصحيح

Answer the three following exercises:

First exercise (7 points)

Part of the Q	Answer	Mark
1.1	According to the equation: $\frac{n(H_3O^+)_{disap}}{2} = \frac{n(H_2)_{formed}}{1} = 3.4\times10^{-3}$ mol at t = 10 min. $[H_3O^+] = \frac{CV - 2n(H_2)_{formed}}{V(S)}$ $= \frac{0.11\times100\times10^{-3} - 2\times3.4\times10^{-3}}{100\times10^{-3}} = 4.2\times10^{-2}$ mol.L^{-1}. pH = -log $[H_3O^+]$ = -log (4.2×10^{-2}) = 1.37	**1.25**
1.2	R (Mg) = $\frac{2}{24} = 8.3\times10^{-2}$ > R (H_3O^+) = $\frac{0.11\times100\times10^{-3}}{2} = 5.5\times10^{-3}$ H_3O^+ is the limiting reactant.	**0.5**
1.3	$\frac{n(H_3O^+)_{disap}}{2} = \frac{n(H_2)_{formed}}{1}$ $n(H_2)_{end\ of\ reaction} = \frac{n(H_3O^+)_0}{2} = 5.5\times10^{-3}$ mol P×V (H_2) = n(H_2) ×R×T $V(H_2) = \frac{n(H_2)\times R\times T}{P} = \frac{5.5\times10^{-3}\times8.31\times298}{9.76\times10^{4}} = 1.4\times10^{-4}$ L.	**1**
2.1	The curve n (H_2) = f (t) is:  	**1**

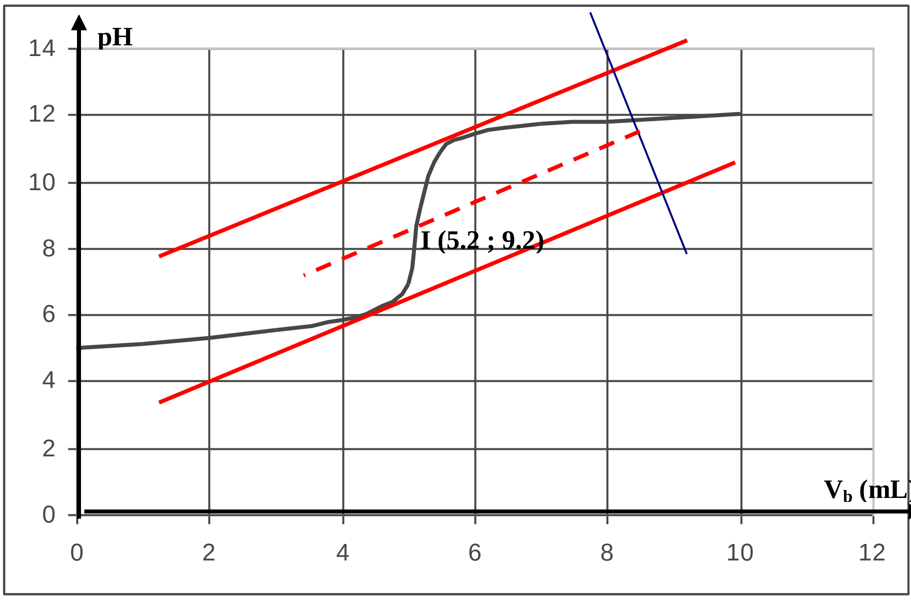
2.2	The rate of formation of H_2 at t = 7 min = $\frac{dn(H_2)}{dt}$ = the slope of the tangent to the curve n (H_2) = f (t) at the point of abscissa t = 7 min. $r(H_2)_{t=7} = \frac{y_B - y_A}{t_B - t_A} = \frac{(5-2.8)\times10^{-3}}{14-7} \approx 3.1\times10^{-4}$ $mol.min^{-1}$.	**1**
2.3	The rate of the reaction decreases with time, because the concentration of H_3O^+ decreases. The rate of formation of hydrogen at t = 18 min< than that at t = 7 min ; The rate of formation of hydrogen at t = 18 min = 8.0×10^{-5} $mol.min^{-1}$.	**0.75**
2.4	The half-life time is the time needed for the formation of half the maximum number of moles of H_2. $n(H_2)_{t1/2} = \frac{5.5\times10^{-3}}{2} = 2.75\times10^{-3}$ mol, which corresponds, according to the graph, to $t_{1/2} \approx 6.9$ min.	**0.75**
2.5	When the reaction is carried out at 40 ºC, the rate of the reaction increases (temperature is a kinetic factor). the number of moles of H_2 formed at an instant of time t at 40ºC is higher than that formed at the same instant at 20ºC. the curve at 40ºC is located above that at 25ºC as it is indicated on the graph above.	**0.75**

Second exercise (6 points)

Part of the Q	**Answer**	**Mark**
1.1	The effervescence decreases with time and ceases after few minutes implies the rate of the reaction decreases with time.	0.5
1.2	In the obtained solution, pH (solution) = pK_a ($C_2H_4O_2$ / $C_2H_3O_2^-$) + log $\frac{[CH_3COO^-]}{[CH_3COOH]}$; $\frac{[CH_3COO^-]}{[CH_3COOH]} = 10^{5.2-4.75} = 2.8$; [$CH_3COOH$] is not neglected with respect to [CH_3COO^-] so the acid CH_3COOH exist at the end of the reaction and calcium carbonate is the limiting reactant.	0.75
2.1	The reaction is an esterification reaction. The obtained organic compound is: 3-methylbutylethanoate.	**0.5**
2.2	Alcohol (A) is : $CH_3 - CH(CH_3) - CH_2 - CH_2 - OH$; 3-methyl-1-butanol.	0.5
2.3	The degree of conversion tends towards 0.67 at the end of the evolution of the system: limited reaction. The composition of the system changes with time: slow reaction. At different temperatures, the system tends toward the same value of α: athermic reaction.	1.5
2.4	The presence of a catalyst does not affect α	0.25
2.5.1	Compound (C) could be : - $CH_3 - COCl$; ethanoyl chloride. - $CH_3 - CO - O - CO - CH_3$; ethanoic anhydride.	1
2.5.2	The equation of the reaction is: $CH_3 - COCl + CH_3 - COOH \rightarrow HCl + CH_3 - CH(CH_3) - CH_2 - CH_2 - O - C(=O) - CH_3$	0.5

2.5.3	The reaction is complete and exothermic.	0.5

Third exercise (7 points)

Part of the Q	Answer	Mark
1.1	To carry out this titration, we need: 25 mL Buret, 100 mL beaker, 20 mL volumetric pipet, pH-meter and its electrode and magnetic stirrer and its bar.	**1**
1.2	The equation of the titration reaction is: $HA + HO^- \rightarrow A^- + H_2O$	**0.5**
1.3	The curve is:  	**1**
1.4	According to the method of tangents, the coordinates of the equivalence point are: V_{bE} = 5.2 mL and pH_E = 9.2	**0. 5**
1.5	n(HA) in volume V_1 = n(HO^-) added to reach equivalence $[HA] \times V_1 = C_b \times V_{bE}$ $[HA] = \frac{C_b \times V_{bE}}{V_1} = \frac{0.10 \times 5.2}{20} = 2.6 \times 10^{-2}$ mol.L^{-1}.	**0. 5**
2.1	The equation of the titration reaction is: $A^- + H_3O^+ \rightarrow AH + H_2O$.	**0.5**
2.2	The species present at equivalence are: HA (weak acid), Cl^- and Na^+ (spectator ions) and water. HA reacts with water to make the medium acidic.	**1**
2.3	n (A^-) in the volume V_1 = n(H_3O^+) added at equivalence $[A^-] \times V_2 = C_a \times V_{aE}$ $[A^-] = \frac{Ca \times V_{aE}}{V_2} = \frac{0.10 \times 9.3}{20} = 4.65 \times 10^{-2}$ mol.L^{-1}.	**0. 5**
3.1	pK_a (HA/A$^-$) = pH(solution S) - log $\frac{[A^-]}{[HA]} = 5 - \log \frac{4.65 \times 10^{-2}}{2.6 \times 10^{-2}} \sim 4.75$. By comparing with the given values of pK_a, the conjugate acid/base pair is CH_3COOH / CH_3COO^-. So HA is ethanoic acid and A^- is ethanoate ion.	**1**
3.2	This curve presents one inflection point because the initial pH of the solution S to be titrated is equal to 5 which is higher than the pKa of the studied conjugate acid/base pair (4.75).	**0.5**