وزارة التربية و التعليم العالي
المديرية العامة للتربية
دائرة الامتحانات

امتحانات شهادة الثانوية العامة
فرع العلوم العامة

دورة سنة ٢٠٠٦ الاستثنائية

مسابقة في الكيمياء	الاسم:
المدة ســاعتان	الرقم:

This Exam Includes **Three Exercises**. It Is Inscribed on 3 Pages Numbered from **1** to **3**.

The Use of A Non-programmable Calculator Is Allowed.

Answer The Following Three Exercises:

First Exercise (6 points)

Kinetic for the Oxidation Reaction of Oxalic Acid

Oxalic acid ($H_2C_2O_4$) reacts with dichromate ions ($Cr_2O_7^{2-}$) in acidic medium according to the following equation:

$$Cr_2O_7^{2-} + 3\,H_2C_2O_4 + 8\,H_3O^+ \rightarrow 2\,Cr^{3+} + 6\,CO_2 + 15\,H_2O$$

It is proposed to study the progress of the reaction between a sodium dichromate solution and an oxalic acid solution in the presence of excess sulphuric acid versus time, at constant temperature,

Given

- Molar atomic masses in $g.mol^{-1}$: $M_H = 1$; $M_C = 12$; $M_O = 16$.

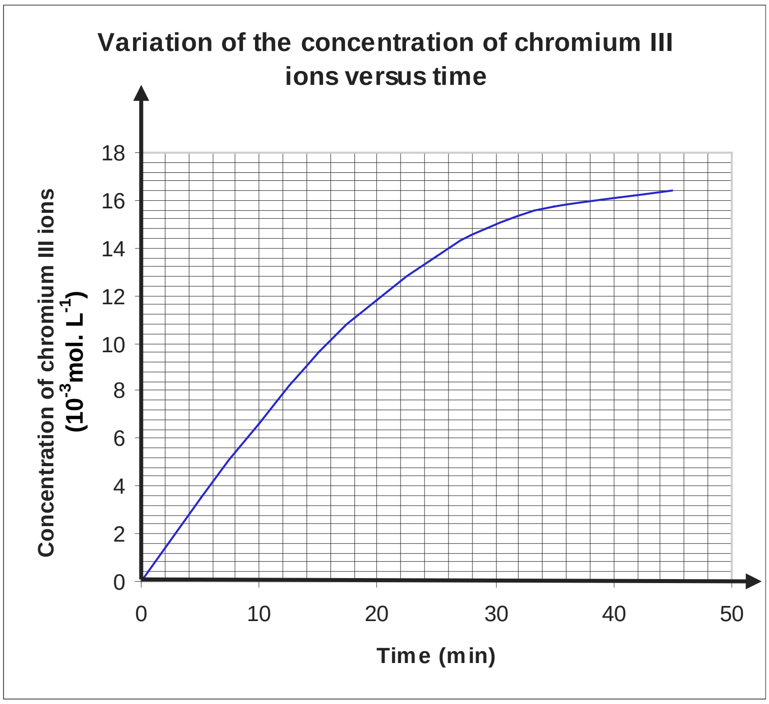
I- Preliminary Study

100 mL of sodium dichromate solution (S_1) of concentration $C_1 = 0.02\ mol.L^{-1}$ are mixed with 100 mL of oxalic acid solution (S_2) containing 5.04 g of hydrated oxalic acid, $H_2C_2O_4.2H_2O$.

1- Show that the concentration of oxalic acid solution (S_2) is $C_2 = 0.4\ mol.L^{-1}$.
2- Specify if dichromate ions and oxalic acid in the initial mixture are in stoechiometric proportions.

II- Kinetic Study

The variation of the concentration of Cr^{3+} ions in the mixture is followed with time. The experimental results permit to construct the following curve:



1- Determine to what limit the concentration of chromium III ions (Cr^{3+}) will tend as time t tends to infinity.
2- Determine the half-life of the reaction.
3- Show that the concentration of $Cr_2O_7^{2-}$ ions and that of Cr^{3+} ions, at instant t, are related by the following relation: $[Cr_2O_7^{2-}]_t = 0.01 - \frac{[Cr^{3+}]_t}{2}$
4- Trace, on a graph paper, the shape of the curve representing the variation of the concentration of dichromate ions versus time, by specifying the points having respectively the following abscissas: t = 0; $t = t_{1/2}$ and t = 45 min.
Take the following scales: abscissa: 1 cm for 5 min; ordinate: 1 cm for 2×10^{-3} mol.L^{-1}.

Second Exercise (7 points)
Determination of the degree of Purity of ″Bicarbonate of Soda″

The sodium hydrogencarbonate ($NaHCO_3$) known in the market as bicarbonate of soda, is commonly used in every day life:
- It reduces the duration of cooking;
- It is recommended in the case of indigestion especially in the excessive stomach acidity.

It is required to study the acid-base character of the sodium hydrogencarbonate and to determine the degree of purity of a sample of commercial ″Bicarbonate of Soda ″.

Given:
- Atomic molar masses in g.mol^{-1}: $M_H = 1$; $M_C = 12$; $M_O = 16$; $M_{Na} = 23$.

Conjugate acid/base pair	HCO_3^-/CO_3^{2-}	$(CO_2,H_2O)/HCO_3^-$	H_2O/HO^-	H_3O^+/H_2O
pK_a	10.3	6.4	14	0

- **Available material list**: stirrer, sensitive balance, burette, 100 mL graduated cylinder, 100 mL Erlenmeyer flask, 100 mL volumetric flask, 20 mL volumetric pipette, spatula and watch glass.

I- Behaviour of $NaHCO_3$ in Water

960 mg of ″Bicarbonate of Soda″ are dissolved into a volumetric flask of 100 mL containing distilled water. More distilled water is then added to reach the line mark. Solution (S) is thus obtained.

1- Choose, among the above list, the material used to weigh the mass of 960 mg of ″Bicarbonate of Soda″.
2- Place on a vertical axis of pK_a the four conjugate acid/base pairs given above.
3- Write the equations of the reactions between the hydrogencarbonate ions (HCO_3^-) and water. Deduce the character of HCO_3^-.
4- Calculate the constant K_R for each of these reactions.
5- Justify the fact that the ″Bicarbonate of Soda″ is recommended to reduce the excessive acidity in the stomach.

II- Titration of $NaHCO_3$ in the ″Bicarbonate of Soda″

In order to determine the degree of purity of ″Bicarbonate of Soda″, a volume V_b = 20 mL is taken from the solution (S) and placed into a beaker. Hydrochloric acid solution of concentration C_a = 0.10 mol.L^{-1} is then added progressively from a burette into the beaker. The change in the pH is followed with a calibrated pH-meter.
The results are given in the following table:

V_a(mL)	0	1	2	4	6	10	12	14	16	17	18	19	20	21	22	25

pH	8.0	7.2	7.0	6.8	6.6	6.3	6.2	6.1	6.0	5.8	5.3	4.0	2.8	2.4	2.3	2.1

1- Write the equation of the titration reaction.
2- Plot, on a graph paper, the curve pH = $f(V_a)$. Take the following scales: abscissa: 1 cm for 2 mL; ordinate: 1 cm for one unit of pH.
3- Determine the coordinates of the equivalence point.
4- Verify, graphically, the value of pK_a of the pair $(CO_2,H_2O)/ HCO_3^-$.
5- Determine the degree of purity of ″Bicarbonate of Soda″ in the used sample.

Third Exercise (7 points)
Synthesis of an Ester

It is required to prepare an ester (E), 2-methylbutyl ethanoate, by different chemical ways.
List of available chemicals:
Ethanoic acid, 2-methylbutanoic acid, 2-methyl-1-butanol, 3-methyl-1-butanol, ethanol, dehydrating agent P_4O_{10}, thionyl chloride $SOCl_2$, acidified potassium dichromate solution, Fehling solution, ethanamine $C_2H_5 – NH_2$, Tollens reagent and 2, 4 – DNPH.

I- <u>Esterification of an alcohol by an acid</u>
In order to synthesize the ester (E), a 0.50 mol of an acid (A) and a 0.50 mol of an alcohol (B) chosen from the above list are heated in the presence of some drops of concentrated sulphuric acid. At equilibrium, a 0.33 mol of (E) is obtained.
1- Write the condensed structural formula of (E).
2- Write the condensed structural formula of each of (A) and (B).
3- Indicate the class of (B). Describe briefly the steps that will be followed to identify this class by using the convenient chemicals from the above list.
4- Write the equation of the reaction between (A) and (B).
5- Calculate the yield for this synthesis reaction of (E).

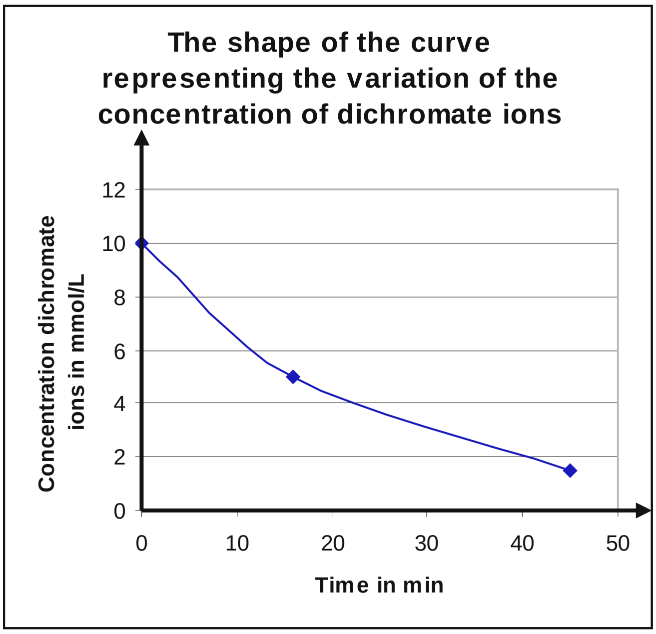
II- <u>Synthesis of (E) From the Derivatives of Acid (A)</u>
1- Formation of the derivatives of acid (A).
a) Acid (A) reacts with a reactant from the above chemicals, to give an acyl chloride (C). Write the equation of this reaction and give the name of (C).
b) Heating acid (A) with the dehydrating agent (P_4O_{10}) leads to the formation of the derivative (D). Write the condensed structural formula of (D) and give its name.
c) An amide (F) can be obtained by a reaction between (A) and ethanamine. Write the condensed structural formula of (F) and give its name.

2- Formation of ester (E).
a) Indicate the derivative(s) of the acid (A) that could react with the alcohol (B) in order to synthesize (E).
b) Write the equation of the reaction of (B) with a convenient derivative to obtain (E).
c) Compare the characteristics of this reaction with those of the esterification reaction mentioned in part **I** of this exercise.

First exercise (6 points)

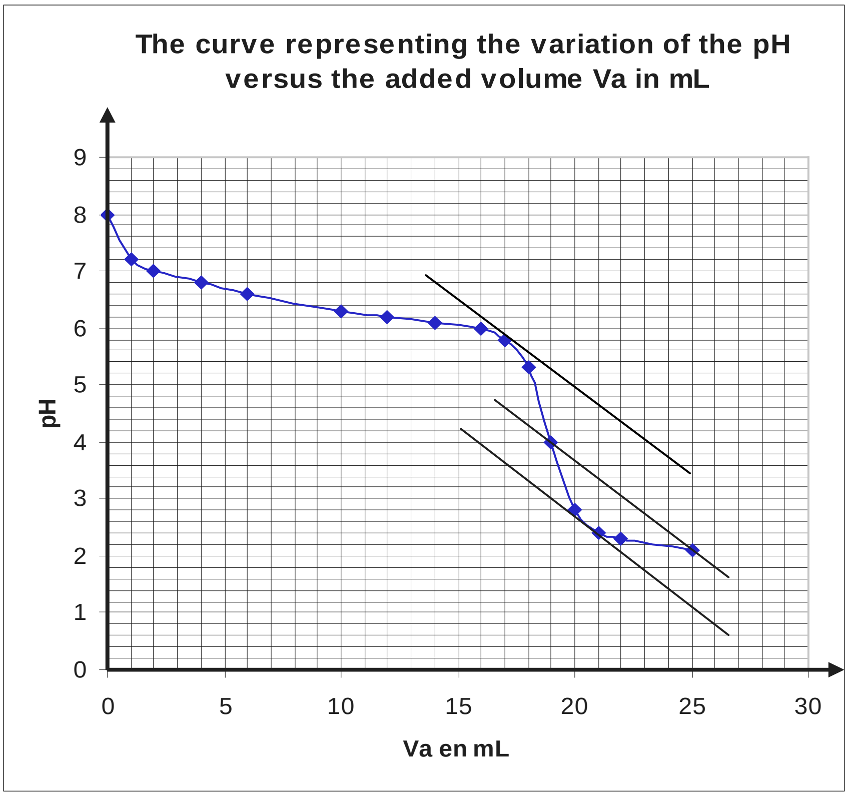
Kinetic of the Oxidation of Oxalic Acid by Dichromate Ions

Expected Answer	Mark	Comment
I- Preliminary Study		
1- n ($H_2C_2O_4$) = $\frac{m(H_2C_2O_4)hydrated}{M(H_2C_2O_4.2H_2O)} = \frac{5.04}{126}$ = 4x10^{-2} mol ;	0.5	
$[H_2C_2O_4]_0 = \frac{n(H_2C_2O_4) in mol}{V(solution) in L} = \frac{4x10^{-2}}{100x10^{-3}}$ = 0.4 mol.L^{-1}.	0.5	
2- R($H_2C_2O_4$) = $\frac{n(H_2C_2O_4)}{3} = \frac{0.04}{3}$ = 0.0133 and R($Cr_2O_7^{2-}$) = $\frac{0.02x0.1}{1} = 0.002$ mol. The two reactants are not in the stoechiometric ratio.	0.5	
II- Kinetic Study		
1- R($Cr_2O_7^{2-}$) < R($H_2C_2O_4$). The dichromate ion is then the limiting reactant. According to the stoechiometric relation, we have: n (Cr^{3+}) $_{\text{formed at infinity}}$ = 2 n ($Cr_2O_7^{2-}$) $_{\text{initial}}$ = 2 x 0.002 = 0.004 mol. We conclude: $[Cr^{3+}]_\infty = \frac{n(Cr^{3+})_\infty}{V_{total}} = \frac{0.004 mol}{0.2 L}$ = 0.02 mol.L^{-1} = 20 mmol.L^{-1}.	1	
2- The half-life of the reaction is the time taken for half the maximum concentration of the Cr^{3+} ions to be formed at t = ∞ . $[Cr^{3+}]_{t1/2} = \frac{[Cr^{3+}]_\infty}{2} = 0.01$ mol.L^{-1}. Based on the curve, the obtained value is $t_{1/2} \approx 16$ min.	1	
3- According to the equation we could write: $\frac{n(Cr_2O_7^{2-})_{reacting}}{1} = \frac{n(Cr^{3+})_{formed}}{2}$: n $(Cr_2O_7^{2-})_0$ – n$(Cr_2O_7^{2-})_t$ = $\frac{n(Cr^{3+})_t}{2}$. Dividing by the volume V, we have: $[Cr_2O_7^{2-}]_0 - [Cr_2O_7^{2-}]_t = \frac{[Cr^{3+}]_t}{2}$ and $[Cr_2O_7^{2-}]_0$ = 0.01 mol.L^{-1}. So $[Cr_2O_7^{2-}]_t = 0.01 - \frac{[Cr^{3+}]_t}{2}$.	1	
4- The curve representing the variation of $[Cr_2O_7^{2-}]_t$ passes in the remarkable points: t = 0 $[Cr_2O_7^{2-}]_0$ = 0.01 mol.L^{-1} = 10 mmol.L^{-1} ; t = $t_{1/2}$ $[Cr_2O_7^{2-}]_{t1/2}$ = 0.005 mol.L^{-1} = 5 mmol.L^{-1} ; t = 45 min $[Cr_2O_7^{2-}]_{45}$ = 0.01 – 0.085 = 0.0015 mol.L^{-1} = 1.5 mmol.L^{-1}. The shape of the curve:	1.5	

Second Exercise (7 points)
Determination of The Degree of Purity of "Bicarbonate of Soda"

Expected Answer	Mark	Comment
I- Behaviour of $NaHCO_3$ in water		
1- The material used in order to weigh the sodium hydrogencarbonate is: sensitive balance, spatula and watch glass.	0.75	
2- The 4 conjugate acid/base pairs on a vertical axis of pK_a: **Base** **pK_a** **Acid** HO^- 14.0 H_2O CO_3^{2-} 10.3 ,HCO_3^- HCO_3^- 6.4 CO_2,H_2O H_2O 0.0 H_3O^+	0.5	
3- The equation of the reaction where the hydrogen carbonate has the role of an acid: $HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$.	0.5	
The equation of the reaction where the hydrogen carbonate has the role of a base: $HCO_3^- + H_2O \rightleftharpoons CO_2,H_2O + HO^-$.	0.5	
HCO_3^- has the amphoteric character.	0.25	
4- Calculation of the constants: $K_R = 10^{pKa\ (base) - pKa\ (acid)}$. $K_{R1} = 10^{0 - 10.3} = 5x10^{-11}$; $K_{R2} = 10^{6.4 - 14} = 10^{-7.6}$=$2.5x10^{-8}$	0.5	

5- An excessive acidity in the stomach is due to the increase of the concentration of H_3O^+ ions in the gastric fluid. Hydrogencarbonate has a basic character and it decreases the concentration of H_3O^+. For this reason it is recommended to reduce the excessive acidity in the stomach.	0.5	
II- Titration of $NaHCO_3$ in the ″Sodium Bicarbonate″ 1- The equation of the titration reaction is: $HCO_3^- + H_3O^+ \rightarrow H_2O + CO_2,H_2O$.	0.5	
2- The graph:  	1	
3- Based on the parallel tangents method, we determine the coordinates of the equivalence point: E (19 – 4).	0.5	
4- At half-equivalence, we have: $pH = pK_a + \log \frac{[base]}{[acid]}$. With [base] = [acid], we have $pH = pK_a$. For V_a = 9.5 mL, we conclude: pK_a = 6.4.	0.5	
5- At the equivalence point, we have: n (acid) $_{added}$= n (base)$_{beaker}$., In a solution we have: n (solute) = CxV. We have then: $C_a x V_{aE} = C_b x V_b$. We conclude : $C_b = \frac{0.10x19}{20}$ = 0.095 $mol.L^{-1}$. m ($NaHCO_3$) = n (HCO_3^-) x M ($NaHCO_3$) = $0.095x100x10^{-3}x84$ = 0.798 g = 798 mg. The degree of purity : $\frac{798}{960}$x100 = 83 %.	1	

Third Exercise (6 points) Synthesis of an Ester

Expected Answer	Mark	Comment
I- Esterification of an alcohol by an acid 1- The condensed structural formula of (E) is ; $CH_3 - C(=O) - O - CH_2 - CH(CH_3) - CH_2 - CH_3$.	0.5	

2- (A) of condensed structural formula $CH_3 - COOH$ (B) of formula $CH_3 - CH_2 - CH(CH_3) - CH_2OH$.	2x0.25
3- (B) is a primary alcohol. The oxidation of (B) by acidified potassium dichromate solution gives a carbonyl compound	0.25
which is identified by the DNPH reagent by giving a yellow precipitate. The carbonyl compound reduces the Fehling solution by giving a red brick precipitate (or with Tollens reagent), so it is an aldehyde and alcohol (B) is a primary alcohol.	0.75
4- The equation of the reaction between (A) and (B) is: $CH_3 - COOH + CH_3 - CH_2 - CH(CH_3) - CH_2OH \rightleftharpoons$ $CH_3 - \underset{\underset{O}{\|}}{C} - O - CH_2 - CH(CH_3) - CH_2 - CH_3 + H_2O$.	0.5
5- The mixture is stoechiometric, the number of moles of the ester is: n (ester) $_{theoritical}$ = 0.5 mol. The yield is then: $R = \frac{n(ester)_{experimental}}{n(ester)_{theoritical}} = \frac{0.33}{0.5} = 0.66$ or 66 %.	1
II- Synthesis of (E) from the derivatives of acid (A) 1- ***Formation of the derivatives of acid (A)*** a) The acid (A) reacts with thionyl chloride to give the compound (C) according the following equation: $CH_3 - COOH + SOCl_2 \rightarrow CH_3 - COCl + SO_2 + HCl$	0.5
(C) is the ethanoyl chloride.	0.25
b) The condensed structural formula of (D) is: $CH_3 - \underset{\underset{O}{\|}}{C} - O - \underset{\underset{O}{\|}}{C} - CH_3$.	0.25
Its name is ethanoic anhydride.	0.25
c) The formula of (F) is: $CH_3 - \underset{\underset{O}{\|}}{C} - NH - C_2H_5$	0.25
(F) is N- ethylethanamide.	0.25
2-***Formation of ester (E)*** a) The ethanoyl chloride or the ethanoic anhydride could react with alcohol (B) to give the ester (E).	2x0.25
b) The equation of the reaction of formation of (E) may be: $CH_3 - COCl + CH_3 - CH_2 - CH(CH_3) - CH_2OH \rightarrow$ $CH_3 - \underset{\underset{O}{\|}}{C} - O - CH_2 - CH(CH_3) - CH_2 - CH_3 + HCl$. Or: $CH_3 - \underset{\underset{O}{\|}}{C} - O - \underset{\underset{O}{\|}}{C} - CH_3 + CH_3 - CH_2 - CH(CH_3) - CH_2OH \rightarrow$ $CH_3 - \underset{\underset{O}{\|}}{C} - O - CH_2 - CH(CH_3) - CH_2 - CH_3 + CH_3 - COOH$.	0.5
c) The reactions in part (b) are rapid, total and exothermic, while the esterification reaction is slow, reversible and athermic.	0.75