وزارة التربية والتعليم العالي
المديرية العامة للتربية
دائرة الامتحانات

امتحانات الشهادة الثانوية العامة
الفرع : علوم الحياة

الدورة الإستثنائية للعام
2009

مسابقة في مادة الكيمياء　　الاسم:
المدة ساعتان　　الرقم:

This Exam Includes **Three** exercises. It Is Inscribed on **Three** Pages Numbered from **1** to **3**.
The Use of A Non-programmable Calculator Is Allowed.

Answer the Three Following Exercises

First Exercise (6 points)
Identification of Some Organic Compounds

In the chemistry laboratory, are available an aqueous solution of a secondary saturated and noncyclic monoamine (B) and two liquid organic compounds, one of which is an alcohol (A) of molecular formula $C_4H_{10}O$ and the other is an ester (E) of molecular formula $C_3H_6O_2$.

1- Identification of Alcohol (A)

1.1- Write the condensed structural formulas of alcohols corresponding to the molecular formula of (A).
1.2- A sample of (A) is mixed with an acidified potassium permanganate solution. A compound (C) is obtained which reacts with 2,4-D.N.P.H. but does not reduce Fehling's solution. Identify the alcohol (A) and write the condensed structural formula of (C).

2- Identification of Ester (E)

2.1- Write the condensed structural formulas of esters of formula $C_3H_6O_2$.
2.2- Hydrolysis of (E), in the presence of concentrated sulfuric acid, produces two compounds, one of which is the ethanoic acid.
  2.2.1- Give the name of (E).
  2.2.2- Write the equation of this hydrolysis reaction.

3- Identification of Amine (B)

Given:

- Molar mass of ethanoic acid: $M = 60$ g.mol^{-1}
- Density of pure ethanoic acid: $d = 1.06$ g.mL^{-1}.

To a volume $V_b = 100$ mL of amine (B) solution of concentration 27 g.L^{-1}, pure ethanoic acid is added drop by drop, in the presence of a convenient indicator. The added volume to reach the equivalence point is 3.4 mL.
Knowing that the equation of the complete reaction between ethanoic acid and amine (B) is:

$$CH_3COOH + B \rightarrow CH_3COO^- + BH^+$$

3.1- Determine, in mol.L^{-1}, the concentration of the solution of amine (B).
3.2- Show that the molecular formula of (B) is C_2H_7N.
3.3- Write the condensed structural formula of the secondary amine (B) and give its name.
3.4- The mixture obtained at equivalence is heated in order to get an amide.
Write the condensed structural formula of this amide and give its name.

Second Exercise (7 points)
Decomposition of Sulfuryl Chloride

Sulfuryl chloride decomposes, in gaseous phase, according to a slow and complete reaction of the following equation:

$$SO_2Cl_{2(g)} \rightarrow SO_{2(g)} + Cl_{2(g)}$$

To follow the kinetics of this decomposition, n_0 mol of sulfuryl chloride are introduced into a container evacuated of air and of constant volume V maintained at a temperature T = 593 K.
A pressure gauge, associated to the container, permits to measure the pressure P_t of the reacting system with time. We deduce the concentration of SO_2 gas at different instants and the obtained results are given in the following table:

t (s)	100	200	300	400	550	700	900
$[SO_2]_t$ (10^{-3} mol.L^{-1})	2.2	4.0	5.2	6.2	7.4	8.0	8.4

<u>Given</u>:

- Take constant of ideal gas: R = 0.082 L.bar.mol^{-1}.K^{-1}.

1- Preliminary Study

1.1- Determine the initial concentration C_0 of sulfuryl chloride, knowing that $P_0 = 0.52$ bar.
1.2- Having the initial pressure P_0 and P_t permits to calculate the concentration of SO_2 gas with time $[SO_2]_t$. Establish the relation among $[SO_2]_t$, P_0 and P_t.
1.3- Calculate the concentration of SO_2 at the end of the reaction.

2- Kinetic Follow-up

2.1- Plot the curve: $[SO_2] = f(t)$, in the interval of time [0 – 900 s]. Take the following scale: 1 cm for 100 s in abscissa and 1 cm for 1.0×10^{-3} mol.L^{-1} in ordinate.
2.2- Show that the rate of formation of SO_2 at t = 500 s is about 7.4×10^{-6} mol.L^{-1}.s^{-1}. Deduce the reaction rate at this instant.
2.3- Choose, by justifying, which one of the two following values: 3.0×10^{-5} mol.L^{-1}.s^{-1} or 3.0×10^{-6} mol.L^{-1}.s^{-1}, corresponds to the value of the initial rate (t = 0) of formation of SO_2.
2.4- The concentration of sulfuryl chloride versus time is determined. The results are grouped in the following table:

t (s)	100	200	300	400	550	700	900
$[SO_2Cl_2]_t$ (10^{-3} mol.L^{-1})	8.5	6.7	5.5	4.5	3.3	2.7	2.3

2.4.1- Find the relation between the concentration of sulfuryl chloride $[SO_2Cl_2]_t$ and that of sulfur dioxide $[SO_2]_t$ at each instant t during the change of the reacting system.
2.4.2- Plot, on the same graph of part **2.1**, the curve: $[SO_2Cl_2] = g(t)$.
2.4.3- Specify what represents the abscissa of the intersection point of the two curves for the studied reaction.

Third Exercise (7 points)
Buffer Effect

In biochemistry, several chemical reactions require the control of the pH of the reacting medium. The aim of this exercise is to study two solutions (S) and (S´) in order to identify which is the appropriate solution for a reacting medium of controlled pH.

Given :

- This study is carried out at 25 ºC.
- The ionic product of water $K_w = 1.0\times10^{-14}$.
- This study is performed with monoacids and monobases.

1- Study of the Solution (S)

Solution (S) is a solution of a strong base of concentration C_0.
1.1- Calculate C_0 so that the pH of (S) is equal to 9.
1.2- The table below represents three experiments carried out with a volume V_0 = 50 mL of the solution (S):

Experiment	Volume of S in mL	Added reactant	pH
I	50	1.0×10^{-5} mol of a strong base	10.3
II	50	1.0×10^{-5} mol of a strong acid	
III	50	50 mL distilled water	

1.2.1- Write the equation of the reaction that takes place in the experiment II.
1.2.2- Determine the missing values of pH in the above table.

2- Study of the Solution (S´)

1 L of the solution (S´) is prepared by dissolving, in water, 2.25×10^{-2} mol of a weak base (B) and 2.5×10^{-3}mol of hydrochloric acid. The pH of this solution is equal to 9.
2.1- Write the equation of the complete reaction between (B) and the hydrochloric acid solution.
2.2- Show that the value of pKa of the conjugate acid/base pair (BH^+/B) is 8.1.
2.3- The table below represents three experiments carried out with a volume V_0 = 50 mL of the solution (S´):

Experiment	Volume of S´ in mL	Added reactant	pH
IV	50	1.0×10^{-5} mol of a strong base	
V	50	1.0×10^{-5} mol of a strong acid	8.96
VI	50	50 mL distilled water	9

2.3.1- Write the equation of the complete reaction that takes place in the experiment IV.
2.3.2- Determine the missing value of pH in the above table.

3- Choice of the Solution

It is required to perform a reaction in a medium with a controlled pH = 9.
Choose, by justifying, which solution (S) or (S´) permits to perform this task.

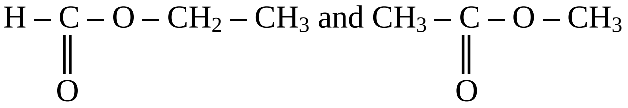
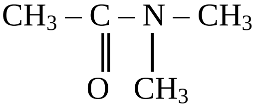
وزارة التربية والتعليم العالي
المديرية العامة للتربية
دائرة الامتحانات

امتحانات الشهادة الثانوية العامة
الفرع : علوم الحياة

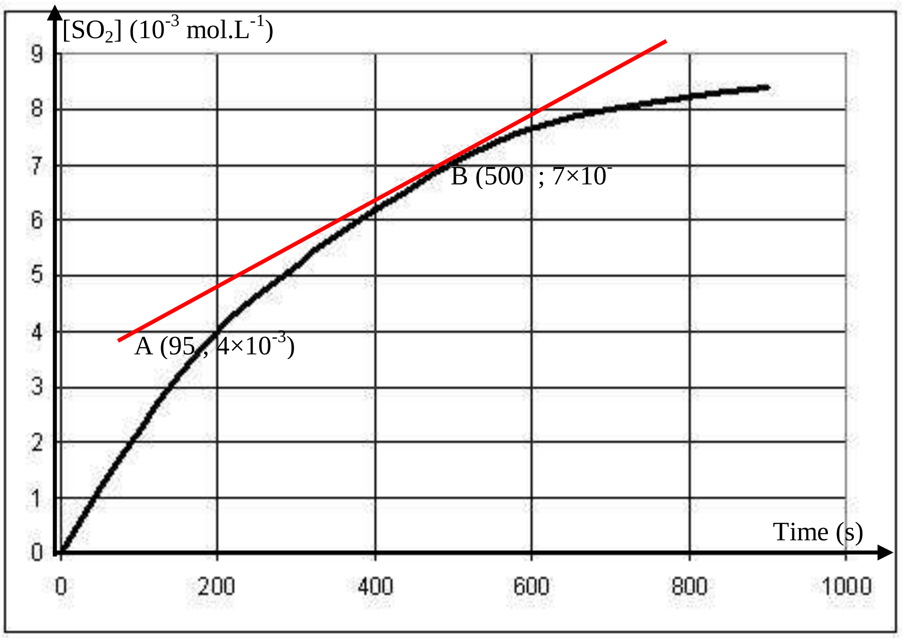
الدورة الإستثنائية للعام
2009

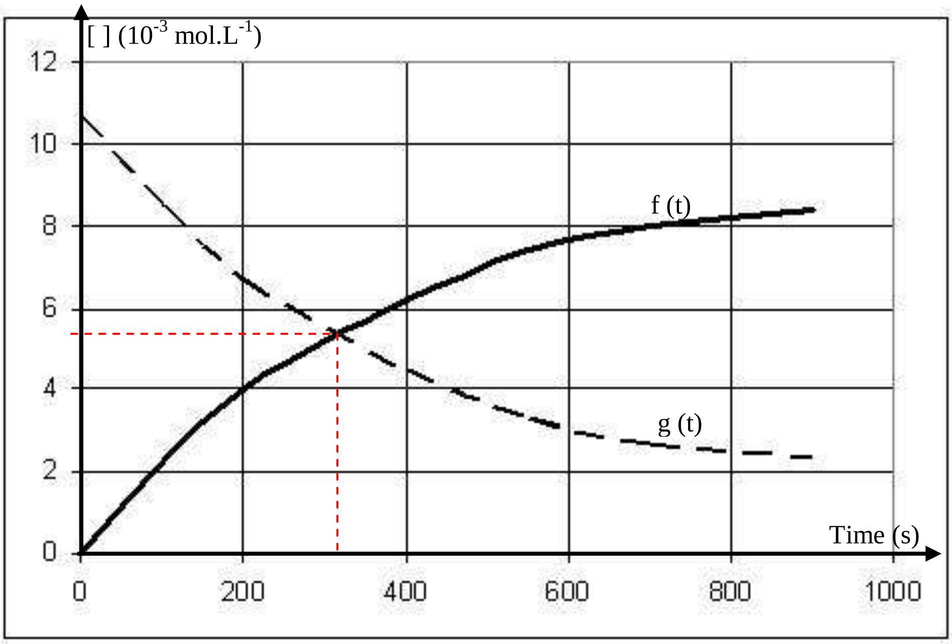
مشروع معيار التصحيح

First Exercise (6 points)
Identification of Some Organic Compounds

Part of the Q	Answer	Mark
1.1	The condensed structural formulas of alcohols are: $CH_3 - CH_2 - CH_2 - CH_2OH$; $CH_3 - CH_2 - CHOH - CH_3$;  $CH_3 - \underset{\overset{\vert}{CH_3}}{CH} - CH_2OH$ and $CH_3 - \underset{\overset{\vert}{OH}}{C}(CH_3) - CH_3$	1
1.2	The mild oxidation of (A) with an acidified potassium permanganate solution gives a compound (C) which reacts with 2,4-DNPH so it contains a carbonyl functional group and since it does not reduce Fehling's solution, this means that (C) is a ketone which comes from a secondary alcohol which is 2-butanol. The condensed formula of C is $CH_3 - CH_2 - CO - CH_3$.	0.75
2.1	The condensed structural formulas of esters having the molecular formula $C_3H_6O_2$ are:  $H - \underset{\overset{\Vert}{O}}{C} - O - CH_2 - CH_3$ and $CH_3 - \underset{\overset{\Vert}{O}}{C} - O - CH_3$	0.5
2.2.1	Hydrolysis of ester gives an acid and an alcohol. The acid obtained is ethanoic acid means that the alcohol is methanol and (E) is methyl ethanoate.	0.5
2.2.2	The equation of the reaction is: $CH_3 - COOCH_3 + H_2O \rightleftharpoons CH_3 - COOH + CH_3 - OH$	0.5
3.1	At equivalence: n(ethanoic acid) in 3.4 mL = n(B) in 100 mL of solution of B. n(ethanoic acid)= $C_b \times V_b$; $\frac{m(acid)}{M(acid)} = \frac{\mu \times V_a}{M} = \frac{1.06 \times 3.4}{60} = C_b \times 100 \times 10^{-3}$ and $C_b = 0.60$ mol.L^{-1}.	1
3.2	The molar mass of B is given by: $C_b = \frac{m}{M \times V}$ and $M = \frac{m}{C_b \times V} = \frac{27}{0{,}60 \times 1} = 45$ g.mol^{-1}. The formula of a noncyclic saturated amine is $C_nH_{2n+3}N$ of molar mass $14n + 17 = 45$ and $n = 2$. The formula of the amine is thus: C_2H_7N.	0.75
3.3	The condensed structural formula of (B) is $CH_3 - NH - CH_3$, it is N-methyl methanamine.	0.5
3.4	The formula of the amide obtained is:  $CH_3 - \underset{\overset{\Vert}{O}}{C} - \underset{\overset{\vert}{CH_3}}{N} - CH_3$ It is N,N-dimethyl ethanamide.	0.5

Second Exercise (7 points)
Decomposition of Sulfuryl Chloride

Part of the Q	Answer	Mark
1.1	According to the equation of the ideal gas: $C_0 = \frac{n_0}{V} = \frac{P_0}{R\times T} = \frac{0.52}{0.082\times 593}$ = 10.7×10^{-3} mol.L^{-1}.	0.5
1.2	$\begin{array}{llll} & SO_2Cl_{2(g)} \rightarrow & SO_{2(g)} + & Cl_{2(g)} \\ \text{At } t=0 & P_0 & - & - \\ \text{At } t & P_0 - P_1 & P_1 & P_1 \end{array}$ $P_t = P_0 + P_1$; where $P_1 = [SO_2]\times R\times T = P_t - P_0$. At the given temperature, knowing P_t and P_0, we can deduce $[SO_2]_t$. $[SO_2]_t = \frac{P_t - P_0}{RT} = \frac{P_t - P_0}{48.63}$	1.25
1.3	At the end of the reaction, $P_t = 2\ P_0$. $[SO_2]_\infty = \frac{2\times 0.52 - 0.52}{48.63}$ = 10.7×10^{-3} mol.L^{-1}.	0.5
2.1	The curve is: 	1
2.2	The rate of formation of SO_2, $r_f\ (SO_2) = \frac{d[SO_2]}{dt}$ at each instant t. $\frac{d[SO_2]}{dt}$ is the slope of the tangent to the curve $[SO_2] = f(t)$ at the point of abscissa 500 s. Two points of this tangent are chosen: A and B, such as: A (95 ; 4×10^{-3}) and B (500 ; 7×10^{-3}). Where, $r_f\ (SO_2) = \frac{(7-4)\times10^{-3}}{500-95}$ = 7.40×10^{-6} mol.L^{-1}.s^{-1}. According to the equation of the reaction: r (reaction) = $r_f\ (SO_2)$ = 7.40×10^{-6} mol.L^{-1}.s^{-1}.	1.25
2.3	The concentration of the reactant, SO_2Cl_2, is a kinetic factor. When this concentration decreases, the rate of formation of SO_2 decreases. So, $r_f(SO_2)$ initial is equal to 3.0×10^{-5} mol.L^{-1}.s^{-1} which is greater than 7.4×10^{-6} mol.L^{-1}.s^{-1}.	0.5

2.4.1	According to the equation, $n(SO_2Cl_2)_{\text{reacting}} = n(SO_2)_{\text{formed}}$; dividing by the volume of the solution, we have: $[SO_2Cl_2]_0 - [SO_2Cl_2]_t = [SO_2]_t$; $[SO_2Cl_2]_t = [SO_2Cl_2]_0 - [SO_2]_t = 10.7\times10^{-3} - [SO_2]_t$	**0.5**
2.4.2	Two curves:  	**0.75**
2.4.3	The point of intersection of the two curves has as abscissa the half-life of the reaction, because the ordinate of this point corresponds to: $[SO_2Cl_2] = [SO_2] = \dfrac{[SO_2Cl_2]_0}{2} = 5.35\times10^{-3}$ mol.L^{-1}. The half-life of the reaction is: $t_{1/2} = 310$ s.	**0.75**

Third Exercise (7 points)
Buffer Effect

Part of the Q	**Answer**	**Mark**
1.1	The pH of the solution (S) of a strong base is given by the relation: pH = 14 + log C_0 ; log C_0 = 9 – 14 = - 5 hence $C_0 = 1.0\times10^{-5}$ mol.L^{-1}.	**0.5**
1.2.1	The equation of the reaction between hydrochloric acid and a strong base is: $H_3O^+ \quad + \quad HO^- \quad \rightarrow \quad 2\,H_2O$	**0.5**
1.2.2	In the experiment II $n(H_3O^+)_o = 10^{-5}$ mol. $n(HO^-)_o = 10^{-5}\times0.050 = 5\times10^{-7}$ mol. Since HO^- is the limiting reactant. 95×10^{-7} mol H_3O^+ remain at the end of the reaction in 50 mL of solution we have: $[H_3O^+] = 19\times10^{-5}$ mol.L^{-1} and pH = 3.72. In the experiment III the volume of the solution is doubled by dilution, the number of moles of the solute does not vary and the concentration of HO^- is divided by 2, it becomes: $[HO^-] = 0.5\times10^{-5}$ mol.L^{-1} and pH = 14 + log 0.5×10^{-5} = 8.7.	**2**
2.1	The equation of the reaction is: $B \quad + \quad H_3O^+ \quad \rightarrow \quad BH^+ \quad + \quad H_2O$	**0.5**
2.2	The pKa is given according to the relation: pH = pKa + log $\dfrac{[B]}{[BH^+]}$.	**1**

	$R(H_3O^+) = 2.5\times10^{-3} < R(B) = 22.5\times10^{-3}$. $\Rightarrow$ H_3O^+ is the limiting reactant. We have: $n(BH^+) = n(H_3O^+)$ and $n(B) = n(B)_{initial} - n(H_3O^+)$ and V = 1 L. Where: $[BH^+] = 2.5\times10^{-3}$ mol.L^{-1} and $[B] =22.5\times10^{-3} - 2.5\times10^{-3} = 20\times10^{-3}$ mol.L^{-1}. $9 = pKa + \log\frac{20\times10^{-3}}{2.5\times10^{-3}}$ hence pKa = 8.1.	
2.3.1	HO^- reacts with BH^+ according to the following equation: $HO^- + BH^+ \rightarrow B + H_2O$	**0.5**
2.3.2	At the end of the reaction: $n(B) = n(HO^-)_{added} + n(B)_{inital} = 1.0\times10^{-5} + 20\times10^{-3}\times 0.050 = 101\times10^{-5}$ mol. $n(BH^+) = n(BH^+)_{initial} - n(HO^-)_{added} =$ $2.5\times10^{-3}\times0.050 - 1.0\times10^{-5} = 11.5\times10^{-5}$ mol. $pH = 8.1 + \log\frac{\frac{101\times10^{-5}}{V}}{\frac{11.5\times10^{-5}}{V}} = 9.04.$	**1**
3	The same quantities (acid, base and water) are added to the same volume (50 mL) during the study of each solution (S) and (S´): - the pH of solution (S) varies in a noticeable way in the first three experiments. - the pH of solution (S´) varies very little and remains practically equal to 9 in the last three experiments. So the solution (S´) is the suitable solution to control the pH of the reacting medium.	**1**