| | 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:

First Exercise (7 points)
Kinetic Study of the Decomposition Reaction of Dinitrogen Oxide

To ensure a suitable atmosphere in the space capsules, the decomposition of N_2O gas is carried out according to a complete reaction of the following equation:

$$2\,N_2O_{(g)} \rightarrow 2\,N_{2\,(g)} + O_{2\,(g)}$$
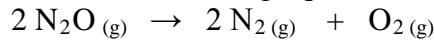
1- Study of the Reacting System

Introduce into an evacuated flask, maintained at $\theta = 600\ ºC$, n_0 mol of N_2O.

1.1- x represents the number of moles of oxygen gas formed at instant t. Copy the following table, on the answer sheet, and complete it in terms of n_0 and x.

Time	N_2O (mol)	N_2 (mol)	O_2 (mol)
0	n_0	0	0
t			
End of reaction			

1.2- Determine the pressure P in the flask at the end of the reaction knowing that the initial pressure is $P_0 = 1.0 \times 10^5$ Pa.

2- Kinetic Study of this Reaction

In order to study the kinetic of this slow reaction, the pressure P inside the flask is measured at different instants. The concentration of oxygen gas, $[O_2]$, is determined based on the measurement of P at each instant t. The results are given in the following table:

t (min)	0	12	25	45	70	100	130	160
$[O_2]_t$ (mol.m^{-3})	0	0.88	1.68	2.68	3.72	4.56	5.12	5.40

2.1- Show that the concentration of O_2 at instant t, $[O_2]_t$, is given by the relation:
$[O_2]_t = 1.38 \times 10^{-4}(P - P_0)$.
Take: $R = 8.3$ Pa.m^3.mol^{-1}.K^{-1}.

2.2- Plot, on a graph paper, the curve $[O_2] = f(t)$. Take the following scale:
abscissa: 1 cm for 10 min and ordinate: 1 cm for 0.4 mol.m^{-3}.

2.3- Describe how to determine, graphically at instant t, the rate of this reaction.

2.4- Deduce the kinetic factor responsible for the change of this rate with time.

2.5- Determine graphically the half-life of this reaction.

2.6- The same study, in the same flask is done, at a temperature $\theta_1 > \theta$.
Specify the effect of the elevation of temperature on:

2.6.1- The rate of the reaction.

2.6.2- The concentration of $O_{2\ gas}$, $[O_2]_\infty$, at the end of the reaction.

Second Exercise (7 points)
Aqueous Solution of Methylamine

The aim of this exercise is to study the acid-base behavior of methylamine in water.

**Given**: Kw is equal to 1.0×10^{-14} at 25 °C.

1- Methylamine in Water

The pH of a solution S of methylamine, CH_3NH_2, of concentration $C_b = 0.010$ mol.L^{-1} is measured and found to be equal to 11.3.

1.1- Write the equation of the reaction between methylamine and water.

1.2- Determine the transformation degree of methylamine in water.

1.3- Show that the pKa of the conjugate acid/base pair ($CH_3NH_3^+$/CH_3NH_2) is equal to 10.7.

2- pH-metric Follow-up

A hydrochloric acid solution of concentration $C_a = 0.020$ mol.L^{-1} is gradually added into a beaker containing a volume $V_b = 40$ mL of solution S of methylamine.

The equation of the reaction which takes place is as follows:

$$CH_3NH_2 \quad + \quad H_3O^+ \quad \rightarrow \quad CH_3NH_3^+ \quad + \quad H_2O \qquad .$$
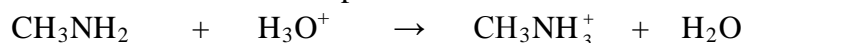
2.1- Determine the volume of the acid solution, V_{aE}, added to reach equivalence.

2.2- The pH of the solution obtained at equivalence is close to 6.1.
Justify the acid character of the solution obtained at equivalence, based on the species present.

2.3- By specifying its remarkable points, trace the shape of the curve representing the variation of pH of the content of the beaker versus the added volume V_a of the acid.
Take the following scale: abscissa: 1 cm for 2 mL and ordinate: 1 cm for 1 unit of pH.

3- Buffer Solution

Consider a buffer solution S_1 where: $[CH_3NH_2] = [CH_3NH_3^+] = 2.0 \times 10^{-3}$ mol.L^{-1}.

3.1- Specify the pH of this solution.

3.2- Add to 1 L of solution S_1, without variation in volume:

3.2.1- 1.0×10^{-3} mol of H_3O^+ ions. Determine the pH_1 of the obtained solution.

3.2.2- 4.0×10^{-3} mol of H_3O^+ ions. The new value of pH is $pH_2 = 2.7$.
Indicate in which case the solution S_1 preserves its buffer properties.

Third Exercise (6 points)
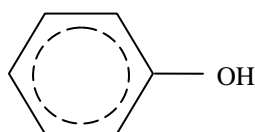## Salicylic Acid

Salicylic acid is used in pharmaceutical and perfume industries.

Given:
  - The structural formula of salicylic acid is:
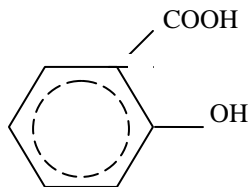
  - The primary raw material of the synthesis of salicylic acid is phenol of formula:

  - M(phenol) = 94 g.mol^{-1} and M(salicylic acid $C_7H_6O_3$) = 138 g.mol^{-1}.

1- Industrial Preparation of Salicylic Acid

This synthesis is carried out in three stages in which the third stage represents the reaction between sodium salicylate ($HO - C_6H_4 - COO^-$) solution and H_3O^+ ions (produced by sulfuric acid).
1.1- Write the equation representing the third stage (assume that this reaction is complete).
1.2- Determine the mass of salicylic acid obtained starting with the total transformation
    of 800 kg of phenol if the percentage yield of all operations covering the three stages is 85 %,
    knowing that one mole of phenol leads to the formation of one mole of salicylic acid.
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2- Salicylic Acid in Cosmetic Industry

Salicylic acid can react with methanol to form an odorous ester called "essential oil of Wintergreen" which is used in perfume industry.
2.1- Write, using the structural formulas of the organic compounds, the equation of the reaction
     between salicylic acid and methanol.
2.2- Give two characteristics of this reaction.
2.3- A mixture of salicylic acid and an excess methanol is subject to reflux heating in the presence
     of few drops of concentrated sulfuric acid.
 2.3.1- State the two kinetic factors involved in this experimental activity.
 2.3.2- Specify the advantage of using an excess of methanol

3- Salicylic Acid in Pharmaceutical Industry

Given:

- Sodium bicarbonate (Na^+, HCO_3^-) is highly soluble in water.
- $pK_a(H_2O/OH^-) = 14$; $pK_a(H_3O^+/H_2O) = 0$; $pK_a(CO_2,H_2O/HCO_3^-) = 6.4$.
- $pK_a(HA_1/A_1^-) = 3.5$ where HA_1 represents acetylsalicylic acid.
- $pK_a(HA_2/A_2^-) = 3.1$ where HA_2 represents citric acid considered as a monoacid.

- A gas is released from a solution only when this solution becomes saturated with it.

Salicylic acid is the essential chemical compound used in the synthesis of aspirin according to the chemical reaction of the following equation:

$$C_7H_6O_3 \ + \ C_4H_6O_3 \ \rightarrow \ C_9H_8O_4 \ + \ C_2H_4O_2$$
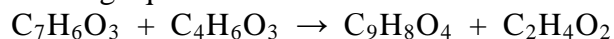
3.1- Write the structural formula of the two compounds: $C_4H_6O_3$ and $C_9H_8O_4$.

3.2- Circle and name the two functional goups in the structural formula of aspirin $C_9H_8O_4$

3.3- Pharmaceutical industry presents aspirin under several formulations. The information concerning the formulation of a buffered effervescent aspirin is given as: acetylsalicylic acid; sodium bicarbonate; citric acid...
A tablet of this aspirin is introduced into a glass of water. A release of gas is observed as the tablet gradually disappears.

3.3.1- Represent on a vertical pK_a axis the conjugate acid/base pairs given before.

3.3.2- Write the equations of the two reactions responsible for the liberation of the gas when the bicarbonate is in an appropriate excess amount.

3.3.3- Justify the two terms ¨buffered¨ and ¨effervescent¨.

وزارة التربية والتعليم العالي
المديرية العامة للتربية
دائرة الامتحانات

امتحانات الشهادة الثانوية العامة
الفرع: علوم الحياة

الدورة الاستثنائية للعام
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مشروع معيار التصحيح	مادة الكيمياء	

First Exercise (7 points)

Part of the Q	Answer	Mark
1.1	the table: <table><tr><td>Time</td><td>$2 N_2O$</td><td>$2 N_2$</td><td>O_2</td></tr><tr><td>0</td><td>n_0</td><td>0</td><td>0</td></tr><tr><td>t</td><td>$n_0 - 2 x$</td><td>$2 x$</td><td>x</td></tr><tr><td>End of reaction</td><td>0</td><td>n_0</td><td>$\frac{n_0}{2}$</td></tr></table>	1
1.2	At the end of the reaction, the number of moles is: $n = \dfrac{3n_0}{2}$. However: The ratio in moles is equal to the ratio of the pressures, because the volume and the temperature remain the same. We have: $P = \dfrac{n}{n_0} P_0 = \dfrac{\frac{3n_0}{2}}{n_0} P_0 = \dfrac{3 \times 1.00 \times 10^5}{2} = 1.50 \times 10^5$ Pa.	1
2.1	According to equation of state of ideal gases, we have: $P(O_2) \times V = n(O_2) \times R \times T$; $[O_2]_t = \dfrac{n(O_2)}{V} = \dfrac{P(O_2)}{R \times T}$. Or : at any moment, we have : $P(N_2) = 2 P(O_2)$; $P(N_2O) = P_0 - 2 P(O_2)$; $P = P(N_2O) + P(N_2) + P(O_2) = P_0 + P(O_2)$. Where : $P(O_2) = P - P_0$ and $[O_2]_t = \dfrac{P - P_0}{8.3(600 + 273)} = 1.38 \times 10^{-4}(P - P_0)$ mol.m^{-3}.	1
2.2	- The curve: $[O_2] = f(t)$: 	1
2.3	The rate of this reaction at instant t is equal to the rate of formation of O_2, so: To determine the rate of the reaction at an instant t: - Trace the tangent to the curve $[O_2] = f(t)$, at the point of abscissa t. - Calculate the slope of this tangent.	0.5

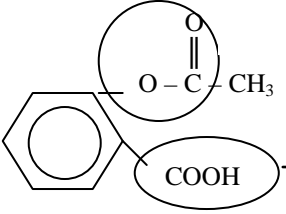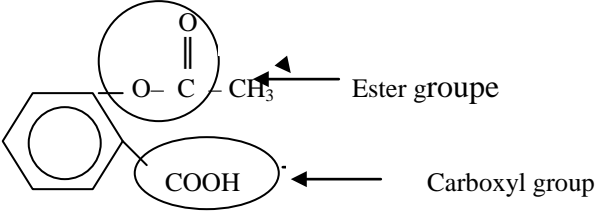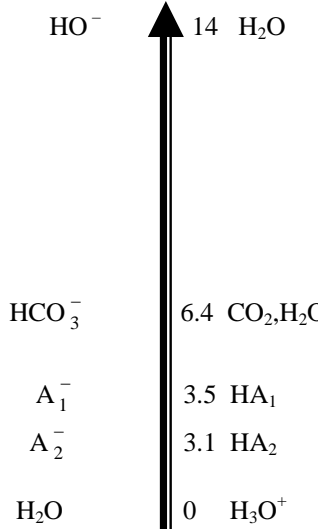|	The rate of the reaction is equal to the value of this slope.	
2.4	The observation of the curve shows that this value decreases when the time passes. This decrease in the rate is due to the decrease in the concentration of the reactant (N_2O).	0.5
2.5	The half-life of the reaction is the time when the concentration of O_2 will be equal to half of its concentration at the end of the reaction. $[O_2]_{t1/2} = \dfrac{[O_2]_{t\infty}}{2} = \dfrac{1.38 \times 10^{-4}(1.50 \times 10^5 - 1.00 \times 10^5)}{2} = 3.45$ mol.m^{-3} According to the graph, this concentration corresponds to : $t_{1/2} = 62$ min.	1
2.6.1	The increase in the temperature increases the reaction rate.	0.5
2.6.2	$[O_2] = \dfrac{n(O_2)}{V}$. Knowing that $n(O_2)_{t\infty}$ and V are constants whatever is the temperature so the final concentration of O_2 does not vary with the temperature.	0.5

Second Exercise (7 points)

Part of the Q	Answer	Mark
1.1	The equation of the reaction between methylamine and water is: $CH_3NH_2 + H_2O \rightleftarrows CH_3NH_3^+ + HO^-$.	0.5
1.2	By definition: $\alpha = \dfrac{n(CH_3NH_2)\,transformed}{n(CH_3NH_2)\,initial} = \dfrac{n(HO^-)\,formed}{n(CH_3NH_2)\,initial} = \dfrac{[HO^-]}{C_b} =$ $\dfrac{10^{pH-14}}{C_b} = \dfrac{10^{-2.7}}{0.01}$; from where $\alpha = 10^{-0.7} = 0.2$.	075
1.3	The acidity constant of this conjugate acid/base pair is: $K_a = \dfrac{[H_3O^+][CH_3NH_2]}{[CH_3NH_3^+]} = \dfrac{10^{-pH} \times C_b(1-\alpha)}{[HO^-]} = 2 \times 10^{-11}$; Where: $pK_a = -\log K_a = -\log 2 \times 10^{-11} = 10.7$.	0.75
2.1	At equivalence, $n(H_3O^+)$ added $= n(CH_3NH_2)$ introduced in the beaker $$C_a \times V_{aE} = C_b \times V_b$$ Where: $V_{aE} = \dfrac{C_b \times V_b}{C_a} = \dfrac{0.01 \times 40}{0.02} = 20$ mL.	0.75
2.2	At equivalence, the species present are: $CH_3NH_3^+$, Cl^- and H_2O. Cl^- is a spectator species in water; $CH_3NH_3^+$ is a weak acid which reacts with water to make the medium acidic.	0.5
2.3	The remarkable points of this shape are: - pH initial = 11.3 ; $V_{aE} = 20$ mL and $pH_E = 6.1$; - $V_{a(1/2\,equivalence)} = 10$ mL and $pH_{(1/2\,equivalence)} =$ $pK_a(CH_3NH_3^+ / CH_3NH_2) = 10.7$ - The pH at which the curve tends is that of the added solution: $pH = -\log C_a = 1.7$ The shape of the curve will be as follows:	1.75

Part of the Q	Answer	Mark
3.1	An equimolar mixture of the acid and its conjugate base has a pH equal to pK_a of this pair; thus the pH of the solution S_1 is 10.7.	0.5
3.2.1	$$CH_3NH_2 \ + \ H_3O^+ \ \rightarrow \ CH_3NH_3^+ \ + \ H_2O$$ Initial state $\quad$ 2.0×10^{-3} mol $\quad$ 1.0×10^{-3} mol $\quad$ 2.0×10^{-3} mol $\quad$ solvant Obtained solution $\quad$ $\sim 1.0 \times 10^{-3}$ mol $\quad$ ~ 0 $\quad$ $\sim 3.0 \times 10^{-3}$ mol $\quad$ solvant $$pH(solution) = pK_a(CH_3NH_3^+ / CH_3NH_2) + \log \frac{[CH_3NH_2]}{[CH_3NH_3^+]}$$ $$= 10.7 + \log 0.333 = 10.2.$$	1
3.2.2	The solution S_1 conserves its buffer properties in the case of question 3.2, because the variation of its pH is relatively little.	0.5

Third Exercise (6 points)

Part of the Q	Answer	Mark
1.1	The equation of this reaction is: Or $HO - C_6H_4 - COO^- \ + \ H_3O^+ \ \rightarrow \ HO - C_6H_4 - COOH + H_2O.$	0.5
1.2	n(salicylic acid) formed = n(phenol) initial $\times \dfrac{85}{100}$ m(salicylic acid) formed = $0.85 \times$ m (phenol) $\times \dfrac{M(\text{salicylic acid})}{M(\text{phenol})}$ $= 0.85 \times 800 \times \dfrac{138}{94} = 998.3$ kg.	0.5
2.1	The equation of this reaction is: $HO - C_6H_4 - COOH + CH_3OH \ \rightleftarrows \ HO - C_6H_4 - COOCH_3 + H_2O$	0.5
2.2	This reaction is athermic, slow, reversible.	0.5

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2.3.1	The two kinetic factors which are involved in this activity are: The temperature and the catalyst represented by concentrated sulfuric acid.	0.5
2.3.2	The excess of methanol favors the formation of the ester so the yield of the reaction increases.	0.5

3.1	The condensed structural formula of compound $C_4H_6O_3$ is:
	$CH_3 – C – O – C – CH_3$
	     $\|$ $\|$
	     O O
	That of compound $C_9H_8O_4$ is:
	
	O
	$\|$
	O – C – CH_3
	(benzene ring)
	COOH
		0.5

3.2	O $\|$ O– C – CH_3 ← Ester groupe (benzene ring) COOH ← Carboxyl group	0.5
3.3.1	$NaHCO_3$ completely ionized in water gives the ions: Na^+ and HCO_3^-. The conjugate acid/base pairs placed on the pK_a axis: HO^- ↑ 14 H_2O HCO_3^- 6.4 CO_2, H_2O A_1^- 3.5 HA_1 A_2^- 3.1 HA_2 H_2O 0 H_3O^+	0.5
3.3.2	The two equations of the two reactions responsible for the release of gas: $HA_1 + HCO_3^- \rightleftharpoons A_1^- + CO_{2(g)} + H_2O$ $HA_2 + HCO_3^- \rightleftharpoons A_2^- + CO_{2(g)} + H_2O$	1
3.3.3	The release of gas justify the term: " effervescent ". Since HCO_3^- is in excess and the solution is saturated by CO_2 gas; the mixture formed by acid CO_2 dissolved an its conjugated base HCO_3^-, in the final solution, justify the term " buffered ".	0.5

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