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 Following Three Exercises:

First Exercise (7 points)
Benzoic Acid and Sodium Benzoate

Benzoic acid (C_6H_5COOH) and sodium benzoate (C_6H_5COONa) are used as food preservatives especially in beverages that do not contain alcohol.
The aim of this exercise is to study the behavior of these two compounds in an aqueous solution.

Given:

- This study is performed at 25 ºC.
- Solubility of benzoic acid: s = 2.5 $g.L^{-1}$.
- Molar mass in $g.mol^{-1}$: benzoic acid M_1 = 122, sodium benzoate M_2 = 144.
- Sodium benzoate is an ionic compound highly soluble in water.
- Ion product of water $K_w = 10^{-14}$.
- pK_a ($C_6H_5COOH/C_6H_5COO^-$) = 4.2.

I- Aqueous Solution of Sodium Benzoate

A mass m = 0.36 g of sodium benzoate is dissolved in distilled water to obtain a volume V of solution of concentration C = 1.0×10^{-2} $mol.L^{-1}$.
The pH of this solution is equal to 8.1.

1- Choose, among the available materials of the list given below, the required set for this preparation. (Calculation is necessary).
   - Sensitive balance.
   - 50, 100 and 250 mL graduated cylinders.
   - Funnel.
   - 50, 250 and 500 mL volumetric flasks.
   - Spatula.
   - Watch glass.
2- Write the equation of the reaction between benzoate ion and water.
3- Determine the degree of conversion of benzoate ion into benzoic acid.

II- Verification of the Solubility of Benzoic Acid

A mass m´ of benzoic acid is introduced into a beaker containing distilled water.
The content of the beaker is stirred; small particles remain in suspension.
After filtration, a solution (S) is obtained.
A volume V_a = 20 mL of (S) is titrated with sodium hydroxide solution ($Na^+ + HO^-$) of concentration $C_b = 3.0\times10^{-2}$ $mol.L^{-1}$, in the presence of a convenient indicator. The added volume to reach the equivalence point is V_{bE} = 13.6 mL.

1- Write the equation of the titration reaction.
2- The following two indicators are available in the laboratory:
    - Methyl orange of pH range: red 3.1 – orange – 4.4 yellow
    - Phenolphthalein of pH range: colorless 8.2 – pink – 10 purple.
    a) Choose, by justifying, the convenient indicator for this titration.
    b) Explain how you detect the equivalence point of this titration.
3- Determine the concentration C_a of solution (S).
4- Verify the solubility of benzoic acid given above.

III- Preparing a Mixture of two Solutions: Benzoic Acid and Sodium Benzoate

A volume V_1 of benzoic acid solution of concentration $C_1 = 5.0\times10^{-3}$ mol.L^{-1} and a volume V_2 of sodium benzoate solution of concentration $C_2 = 5.0\times10^{-3}$ mol.L^{-1} are mixed. The volume of the obtained solution is V = 300 mL and its pH is equal to 4.0.
1- What do you call this solution? Give its characteristics.
2- Determine V_1 and V_2.

Second Exercise (6.5 points)
Identification of an Ester

The analysis of a sample of an ester (A) of molecular formula ($C_xH_yO_2$) gives the following percent mass composition: C = 54.5 % and H = 9.1 %. The objective of this exercise is the identification of (A).

Given:

- Molar mass in g.mol^{-1}: M_H = 1; M_C = 12 and M_O = 16

I Molecular Formula and Isomers of (A)

1- Determine the molecular formula of (A).
2- Write the condensed structural formulas of all esters corresponding to (A).
3- Write the condensed structural formula of a functional isomer of (A) and give its name.

II Hydrolysis Reaction of (A)

The hydrolysis of 0.02 mol of (A) with 0.02 mol of water (H_2O) is carried out in the presence of a convenient catalyst till the system reaches equilibrium.
1- Write the equation of this hydrolysis reaction representing (A) by R – COOR'.
2- Draw the table that represents the initial state and the final state of this hydrolysis in terms of the number of moles, x, of alcohol (B) obtained at equilibrium.
3- The equilibrium constant of the above hydrolysis reaction is 0.25.
   Show that $x = 6.67\times10^{-3}$ mol.

III Identification of (A)

The catalytic dehydrogenation of (B) which is obtained in the above equilibrium, leads to the formation of 387 mg of an organic compound (D) according to the following equation:

$$B \xrightarrow{\text{Catalyst}} H_2 + D.$$

Compound (D) reduces Fehling's solution.

1- Specify the family of (D) and the class of alcohol (B).
2- Determine the molar mass of (D) and that of (B).
3- Deduce the condensed structural formulas of (B) and (A) and give their names.

Third Exercise (6.5 points)
Oxidation of Oxalic Acid by Permanganate Ions

Permanganate ions (MnO_4^-) react with oxalic acid ($H_2C_2O_4$) in an acidic medium according to the following equation:

$$2\ MnO_4^-{}_{(aq)} + 5\ H_2C_2O_{4(aq)} + 6\ H_3O^+{}_{(aq)} \rightarrow 2\ Mn^{2+}{}_{(aq)} + 10\ CO_{2(g)} + 14\ H_2O_{(l)}$$

where (MnO_4^-) is the only colored species in this reactional medium.

I- Kinetic Factors

In order to study the effect of some kinetic factors on the rate of the above reaction, the three following mixtures are prepared. (Potassium permanganate solution is added to each mixture at t = 0).

	Mixture (A)	Mixture (B)	Mixture (C)
$H_2C_2O_4$: C_1 = 0.01 mol.L^{-1}	V_1 = 20 mL	V_1 = 20 mL	V_1 = 20 mL
H_2SO_4 concentrated	V_2 = 10 mL	V_2 = 10 mL	V_2 = 10 mL
Distilled water	0	60 mL	0
Temperature θ	20 ºC	20 ºC	40 º C
$KMnO_4$: C_3 = 5.0x10^{-3} mol.L^{-1}	V_3 = 10 mL	V_3 = 10 mL	V_3 = 10 mL
Δt	$\Delta t_{(A)}$ = 140 s	$\Delta t_{(B)}$ = 190 s	$\Delta t_{(C)}$ = 22 s

Δt is the time needed to obtain the decolorization of the mixture.

1- Interpret the decolorization of the solution at the end of the reaction.
2- With reference to the results obtained in the above table:
   a) Indicate, by comparing the initial state of mixtures, the kinetic factor studied in:
      (A) and (B) on one hand;
      (A) and (C) on the other hand.
   b) Deduce the effect of each factor on the rate of the reaction.
   c) Specify the most convenient experimental condition that should be provided to perform the titration between oxalic acid solution of concentration C_1 and acidified solution of potassium permanganate of concentration C_3.

II- Study of Mixture (B)

The two following mixtures are prepared at the same temperature θ = 20 ºC:

	Mixture (B)	Mixture (D)
$H_2C_2O_4$: C_1 = 0.01 mol.L^{-1}	V_1 = 20 mL	V_1 = 20 mL
H_2SO_4 concentrated	V_2 = 10 mL	V_2 = 10 mL
Distilled water	60 mL	60 mL
Temperature θ	20 ºC	20 ºC
$KMnO_4$: C_3 = 5.0x10^{-3} mol.L^{-1}	V_3 = 10 mL	V_3 = 10 mL
	-	Some grains of manganese (II) sulfate

Δt	Δt $_{(B)}$ = 190 s	Δt $_{(D)}$ = 50 s

The permanganate solution and the grains of manganese II sulfate are introduced at t = 0.

1- Deduce from this study the role of Mn^{2+} ions in mixture (D). Calculate the initial concentration of each : $[MnO_4^-]_0$ and $[H_2C_2O_4]_0$ in mixture (B). Deduce the concentration of Mn^{2+} ions at t = 190 s.
2- Draw the shape of the curve representing the variation $[Mn^{2+}]$ = f(t) in (B) during the interval of time (0 – 190 s).

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First Exercise (7 points)
Benzoic Acid and Sodium Benzoate

Expected Answer	Mark	Comment
I- <u>Aqueous Solution of Sodium Benzoate</u>		
1- C=n/V. So V = $\frac{0.36/144}{0.01}$ = 0.25L = 250mL The needed materials are: Sensitive balance, spatula and watch glass to weigh mass m; Funnel and volumetric flask of 250 mL to dissolve m and prepare (S).	1	
2- The equation of this reaction is: $C_6H_5COO^- + H_2O \rightleftharpoons C_6H_5COOH + HO^-$	0.5	
3- The value of pH permits to calculate $[HO^-]$: pH = pK_w + log $[HO^-]$ 8.1 = 14 + log $[HO^-]$. So $[HO^-] = 1.26x10^{-6}$ mol.L^{-1}. $\alpha = \frac{n(C_6H_5COO^-)_{reacted}}{n(C_6H_5COO^-)_{initial}} = \ldots = \frac{[HO^-]}{C} = \frac{1.26x10^{-6}}{1.0x10^{-2}} =$ **$1.26x10^{-4}$**	1	
II- <u>Verification of the Solubility of Benzoic Acid</u>		
1- The equation of the titration reaction is: $C_6H_5COOH + HO^- \rightarrow C_6H_5COO^- + H_2O$	0.5	
2- a) Since the titration is between a weak acid and a strong base, then the pH at the equivalence point is greater than 7 (basic medium). The convenient indicator is then phenolphthalein of pH range (8.2 – 10).	0.5	
b) The acid solution is colorless with some drops of phenolphthalein. One drop of the basic solution turns the color into pink. This indicates the equivalence point.	0.5	
3- At the equivalence point, we have: $n(C_6H_5COOH)$ in V_a = $n(HO^-)$in V_{bE}. $C_a x V_a = C_b x V_{bE}$. Where: $C_a = \frac{3.0x10^{-2} x 13.6}{20}$ = $2.04x10^{-2}$ mol.L^{-1}.	0.75	
4- The solubility s = C_axM = $2.04x10^{-2}$x122 = 2.49 g.L^{-1}. The solubility given in the table is then verified.	0.75	
III- <u>Mixture of the Two Solutions: Benzoic Acid and Sodium Benzoate</u>		
1- The pH changes very slightly by dilution or by the addition of a moderate quantity of a strong acid or a strong base.	0.5	
2- The initial amounts of $C_6H_5COO^-$ and C_6H_5COOH are conserved in the obtained solution.	1	

The relation pH = $pK_a + \log\frac{[C_6H_5COO^-]}{[C_6H_5COOH]}$ permits to calculate V_1 and V_2.

$$4 = 4.2 + \log\frac{\frac{C_2xV_2}{V}}{\frac{C_1x(V-V_2)}{V}} = 4.2 + \log\frac{V_2}{V-V_2};$$

$$\log\frac{V_2}{300-V_2} = -0.2 ; \qquad \frac{V_2}{300-V_2} = 063. \text{ Hence:}$$

V_2 = 116 mL and V_1 = 184 mL.

Second Exercise (7 points)
Identification of an Ester

<table>
<tr><th>Expected Answer</th><th>Mark</th><th>Commenta</th></tr>
<tr><td>I- <u>Molecular Formula and Isomers of (A)</u>
1- The law of definite proportion permits to write
$\frac{12x}{54.5} = \frac{y}{9.1} = \frac{32}{100-(54.5+9.1)}$. We conclude then:
x = $\frac{54.5x32}{12x36.4}$ = 4 and y = 8. The molecular formula of (A) is then $C_4H_8O_2$.</td><td>0.5</td><td></td></tr>
<tr><td>2- The condensed structural formulas of the esters are:
$CH_3 – CH_2 – C(=O) – O – CH_3$; $CH_3 – C(=O) – O – CH_2$- CH3 ;
$H – C(=O) – O – CH(CH_3)_2$; $H – C(=O) – O – CH_2- CH_2 – CH_3$.</td><td>4x0.25</td><td></td></tr>
<tr><td>3-The condensed structural formula of the functional isomer of (A) is :
$CH_3 – CH_2 – CH_2 – C(=O) – OH$. Its name is butanoic acid.</td><td>2x0.25</td><td></td></tr>
<tr><td>II- <u>Hydrolysis Reaction of (A)</u>
1- The equation of hydrolysis reaction is:
R – COOR´ + H_2O ⇌ R – COOH + R´ - OH</td><td>0.5</td><td></td></tr>
<tr><td>2-<table><tr><th></th><th>RCOOR´</th><th>H_2O</th><th>RCOOH</th><th>R´OH</th></tr><tr><td>Initial state (mol)</td><td>0.02</td><td>0.02</td><td>0</td><td>0</td></tr><tr><td>Equilibrium state (mol)</td><td>0.02 – x</td><td>0.02 – x</td><td>x</td><td>x</td></tr></table></td><td>0.5</td><td></td></tr>
<tr><td>3- The equilibrium constant of the reaction is:</td><td>0.75</td><td></td></tr>
</table>

$K=\frac{[RCOOH][R'OH]}{[RCOOR'][H_2O]}=\frac{x^2}{(0.02-x)^2}$ = 0.25; $\frac{x}{0.02-x}$ = 0.5 . So	0.25	
x = 6.67x10^{-3} mol.	0.25	
III- <u>Identification of (A)</u> 1- Since (D), that is obtained by dehydrogenation of alcohol (B), reduces Fehling's solution, so it is an aldehyde. (B) is a primary alcohol because when dehydrogenated it gives an aldehyde	1	
2- According to the equation, we have: n (D)$_{formed}$ = n (B)$_{reacted}$; n (D) = $\frac{m(D)}{M(D)}=\frac{387x10^{-3}}{M(D)}=6.67x10^{-3}$. M (D) = $\frac{387x10^{-3}}{6.67x10^{-3}}$ = **58.0 g.mol^{-1}**. The molar mass of (B) is then: M (B) = 58 + 2 = **60 g.mol^{-1}**.	0.5	
3- (B) is a saturated alcohol of general formula $C_nH_{2n+2}O$ (because it is obtained by the hydrolysis of an ester of formula $C_xH_{2x}O_2$) . Its molar mass M = 14 n + 18 = 60.	2x0.25	
n = $\frac{60-18}{14}$ = 3. The molecular formula of (B) is then C_3H_8O. Its condensed structural formula is: $CH_3 - CH_2 - CH_2OH$; it is 1-propanol. By the law of conservation of atoms: The number of carbon atoms of the acid is: 4 – 3 = 1. Its formula is: H – COOH. The condensed structural formula of (A) is: $H - COOCH_2 - CH_2 - CH_3$. 1-propyl methanoate.	0.75	

Third Exercise (6 points)
Oxidation of Oxalic Acid by Permanganate Ions

Expected Answer	Mark	Comment
I- <u>Kinetic Factors</u>		
1- In each of these mixture, MnO_4^- is the only colored species. At the end of the reaction, there is a complete disappearance of this species and formation of colorless species, that interprets the decolorization of the solution.	0.5	
2- a) By comparing of the initial states, it is noted that: * For the two mixtures (A) and (B), The kinetic factor is the concentration of reactants, because the two mixtures are different only by the volume of 60 mL of distilled water added to mixture (B);	0.5	
* For (A) and (C), the kinetic factor is the temperature, because the other components of the two mixtures are the same;	0.5	
b) For (A) and (B), the needed time to obtain decolorization is less. So the reaction is then faster. We conclude that the rate of the reaction increases when the concentration of reactants increases.	0.5	

For (A) and (C), the time needed for decolorization is less in (C). We conclude that, the rate of the reaction increases when the temperature increases.	0.5	
c) Knowing that titration reaction must be fast. We conclude that the titration of oxalic acid solution of concentration C_1 with an acidified solution of $KMnO_4$ of concentration C_2 should be performed at a temperature about 40 ºC.	0.5	
II- <u>Study of Mixture (B)</u> 1- There is one difference between the two mixtures (B) and (D) (presence of manganese ions from manganese II sulfate). This difference is responsible for the decrease in time to obtain decolorization. We conclude then Mn^{2+} ions plays the role of a catalyst	0.5	
2- The total volume is V = 20 + 10 + 10 + 60 = 100 mL. The concentration is given by: $C_i = \frac{C_i x V_i}{V}$ $[H_2C_2O_4]_0 = \frac{2.0x10^{-2} x20}{100} = 4.0x10^{-2}$ mol.L^{-1} and $[MnO_4^-]_0 = \frac{1.0x10^{-2} x10}{100} = 1.0x10^{-3}$ mol.L^{-1}.	1	
MnO_4^- is the limiting reactant $R(MnO_4^-) < R(H_2C_2O_4)$ (or it disappears completely at the end of the reaction), then the final concentration of Mn^{2+} is: $[Mn^{2+}]_{final} = [MnO_4^-] = 1.0x10^{-3}$ mol.L^{-1}. This is the limit of the curve at t = 190 s.	0.5	
3- The shape of the curve is:	1