مسابقة في الكيمياء
المدة: ساعتان

الاسم:
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:

Exercise 1 (7 points) Lactic Acid

The quantity of free lactic acid contained in commercial yogurt should not be less than 0.7 gram per 100 grams of yogurt when sold to the consumer. It is important to verify regularly that the sold yogurt respects the given standards.
It is assumed that the acidity of the yogurt is only due to lactic acid.

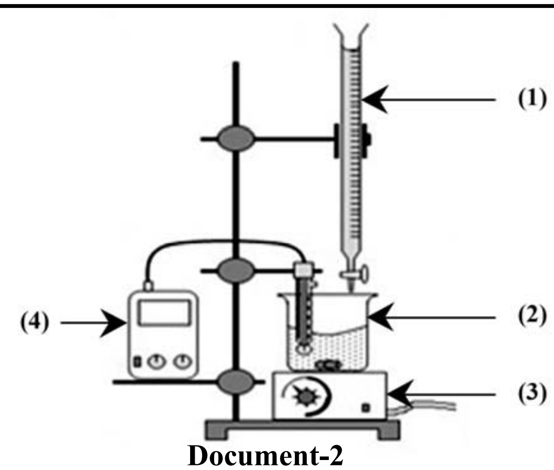
Document-1

The aim of this exercise is to titrate the lactic acid noted HA contained in the commercial yogurt and to study some of its characteristics.

Given: - Molar mass of lactic acid: M = 90 $g.mol^{-1}$
- Lactic acid is a weak acid.

1. pH-metric Titration of Lactic Acid Contained in Commercial Yogurt

Lactic acid contained in a sample of mass m = 10.0g of commercial yogurt is titrated with a sodium hydroxide solution ($Na^+ + HO^-$) of concentration C_b = 0.10 $mol.L^{-1}$. Before starting titration, a sufficient quantity of distilled water is added while stirring to the sample of yogurt to homogenize the solution.
The schema of the titration setup used is shown in **document-2**



Document-2

1.1. Name the parts 1, 2, 3 and 4 of the titration setup of **document-2.**
1.2. Write the equation of the titration reaction.

1.3. Choose which one of the values given below corresponds to the pH of the solution at equivalence. Justify.

a- 5.6 **b-** 7.0 **c-** 8.3

1.4. The equivalence point is reached when the volume of the basic solution added is V_{bE} = 12mL. Determine the number of moles of lactic acid contained in the titrated sample.

1.5. Deduce the mass percentage of lactic acid in the commercial yogurt.

1.6. Referring to **document-1**, specify whether the yogurt respects the above given standards.

2. Characteristics of Lactic Acid

The condensed structural formula of lactic acid is: $CH_3 - CH(OH) - COOH$

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CH3 – CH – COOH
       |
       OH
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2.1. Name the two functional groups present in the above formula.

2.2. Give the systematic name of lactic acid.

2.3. Why lactic acid molecule is chiral?

2.4. Represent according to Cram the two enantiomers of lactic acid.

2.5. Lactic acid undergoes a mild oxidation with an acidified potassium permanganate solution ($K^+ + MnO_4^-$) to produce pyruvic acid.

2.5.1. Indicate in lactic acid molecule the functional group which is involved in this mild oxidation.

2.5.2. Write the condensed structural formula of pyruvic acid.

Exercise 2 (6 points) Chemical Kinetic

In order to follow-up the kinetic of esterification reaction, one proceeds as follows:

- Nine Erlenmeyer flasks each containing 50 mmol of 1-butanol are immersed in a water bath maintained at constant temperature of 60°C.
- At instant t = 0, a quantity of 50 mmol of ethanoic acid is added simultaneously into each flask.
- At intant t, one of the Erlenmeyer flasks is removed and ice-water is added into this flask then the remained acid is titrated with sodium hydroxide solution ($Na^+ + HO^-$) and the number of moles of the ester formed is deduced. This step is repeated at different instants with the other Erlenmeyer flasks.

- The equation of the reaction between a carboxylic acid and a primary alcohol is:

$$RCOOH + R'CH_2OH \rightleftarrows RCOOCH_2R' + H_2O$$

- The equilibrium constant associated with this reaction is $K_C = 4.12$
- The transformation, in each Erlenmeyer flask, takes place without loss of any quantity of constituents of the reactional mixture due to evaporation.

Document-1

1. Theoretical Study

1.1. Write, using condensed structural formulas, the equation of the reaction between ethanoic acid and 1-butanol.

1.2. Give the name of the ester formed.

2. Kinetic Study

The results of the realized kinetic study are grouped in the table of **document-2**.

t (min)	2	5	8	12	16	20	25	35	50
n (ester) mmol	9	19	24	29	31.5	32.4	32.8	33.3	33.5

Document-1

2.1. Indicate the effect of adding ice-water to each Erlenmeyer flask. List the two kinetic factors involved.

2.2. Plot the curve that represents the variation of the quantity of the ester formed as a function of time: n (ester) = f (t) within the interval of time [0 – 50 min].
Take the following scale: 1 cm for 5 min in abscissa and 1 cm for 3 mmol in ordinate.

2.3. Deduce graphically the variation of the rate of formation of ester with time.

2.4. Determine the number of moles of each constituent of the reactional mixture at t =50min.

2.5. Show that at time t = 50 min, a chemical equilibrium is reached.

2.6. Specify whether each of the following statements is true or false.

2.6.1. The addition of a quantity of alcohol to the reactional mixture at equilibrium increases the yield of the reaction

2.6.2. Realizing the same above experiment by modifying only the temperature from 60°C to 70°C produces a number of moles of the ester at equilibrium greater than 33.5mmol.

Exercise 3 (7 points) Sodium Hydroxide

An aqueous solution of sodium hydroxide ($Na^+ + HO^-$), also referred as "soda" reacts easily with carboxylic acids.
At high concentrations and temperature, the "soda" can undergo, a saponification reaction with an ester.

1. Sodium Hydroxide in Acid-Base Reaction

Available are two solutions:
- A solution (S_1) of sodium hydroxide ($Na^+ + HO^-$)
- A solution (S_2) of benzoic acid C_6H_5-COOH

Both solutions have the same molar concentration C= 0.01mol.L^{-1}.

Given: Molar mass of NaOH = 40g.mol^{-1};

acid/base pair	H_3O^+/ H_2O	C_6H_5-COOH /C_6H_5-COO$^-$	H_2O/HO^-
pKa	0	4.2	14

1.1. The solution (S_1) is prepared by dissolving a mass m of NaOH in distilled water to obtain 100 mL of an aqueous solution. Calculate the mass m.

1.2. Choose, from **document-1**, the appropriate materials for the preparation of the solution (S_1).

- Volumetric flasks: 50, 100, and 1000 mL;	- watch glass;	- spatula;
- Volumetric pipets: 5,10, and 20 mL;	- buret of 25mL ;	- Precision balance

Document-1

1.3. A solution (S) of pH= 5 is prepared by mixing a volume V_1 of the solution (S_1) and a volume V_2 of the solution (S_2). The equation of the reaction that takes place is:

$$C_6H_5\text{-}COOH + HO^- \rightarrow C_6H_5\text{-}COO^- + H_2O$$

1.3.1. Justify that this reaction is complete.

1.3.2. Place on the pH axis the predominance domains of the species of the pair $C_6H_5\text{-}COOH / C_6H_5\text{-}COO^-$.

1.3.3. Deduce that, at pH=5, HO^- ion is the limiting reactant.

1.3.4. Determine the volume V_2 knowing that V_1 = 54 mL.

2. Sodium Hydroxide in the Saponification Reaction

An excess of a concentrated aqueous solution of sodium hydroxide is introduced into a flask. A certain volume of ethyl benzoate $C_6H_5COOC_2H_5$ is added. A condenser was adjusted to the flask and the mixture was heated to reflux for 20 minutes. Sodium benzoate and ethanol are obtained.

2.1. Ethyl benzoate is prepared by the action of benzoic anhydride on ethanol.

2.1.1. Give the condensed structural formula of benzoic anhydride.

2.1.2. Write, using structural formulas, the equation of this esterification reaction.

2.1.3. Choose the correct answer. This esterification reaction is:

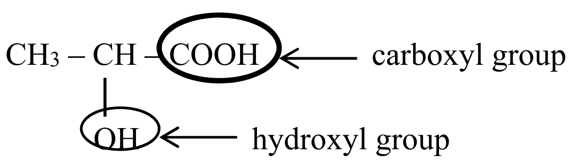
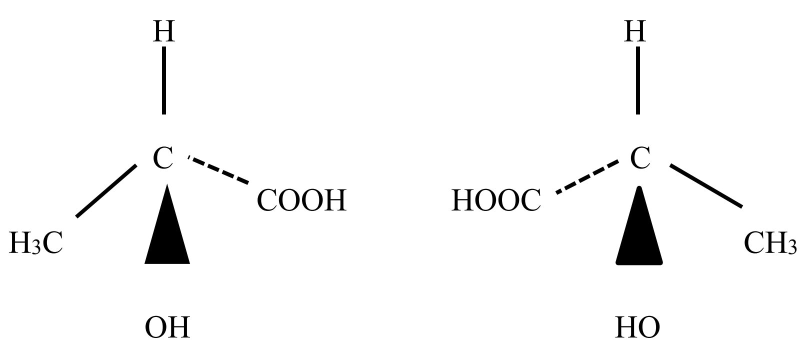
a- limited and athermic **b-** complete and endothermic **c-** complete and exothermic

2.2. Write the equation of the saponification reaction occurring between ethyl benzoate and the hydroxide ions.

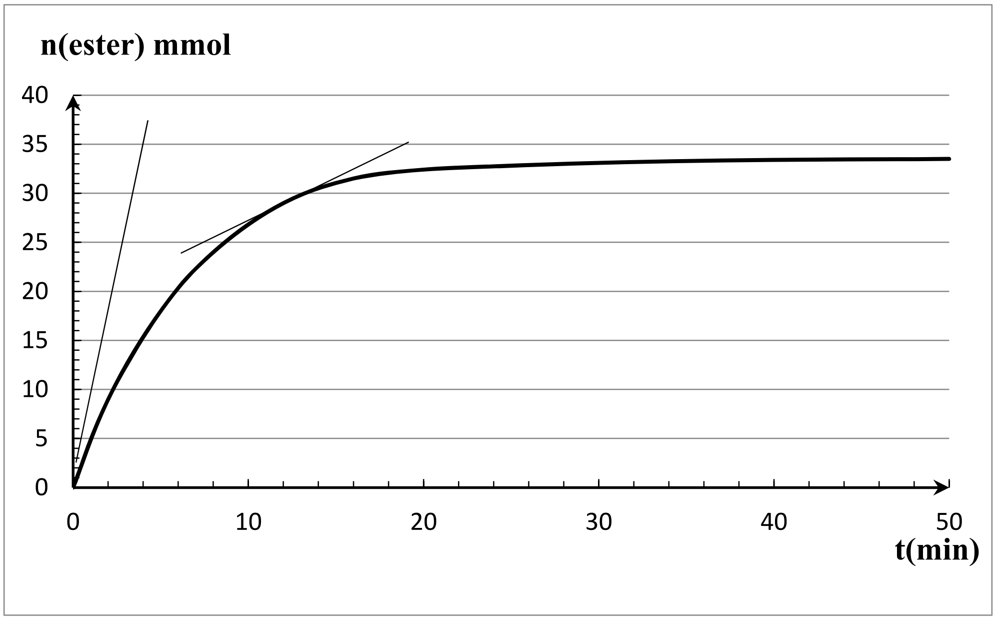
2.3. Indicate the importance of the reflux heating.

مشروع معيار التصحيح
المادة: كيمياء

Exercice 1 (7 points) **Lactic acid**

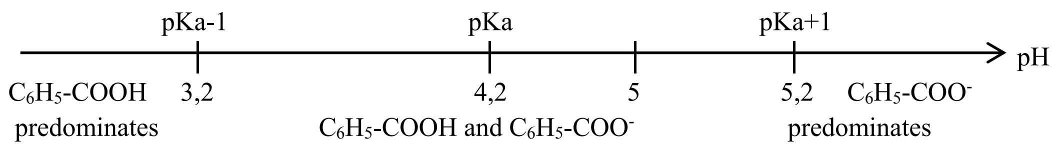
Part of the Q.	Expected Answer	Mark
1.1	(1) : Graduated Buret (2) : Beaker (3) : magnetic stirrer (4) : pH meter	**1**
1.2	$HA + HO^- \rightarrow A^- + H_2O$	**0.5**
1.3	The chemical species present at equivalence in the mixture are: Na^+ (spectator ion), H_2O (neutral) and A^- (weak base) which renders the medium basic with $pH_E > 7$. c- $pH_E = 8,3$.	**0.75**
1.4	At equivalence: $n_{HA(present)} = n_{HO^-(added\ to\ reach\ equivalence)} = C_b \times V_{bE} = 0.1 \times 12\times10^{-3} = 1.2\times10^{-3}$mol.	**0.75**
1.5	The mass of lactic acid contained in the sample = n x M = $1.2\times10^{-3} \times 90 = 0.108$g in 100g yogurt : % lactic acid = 0.108/10 × 100 = 1.08%	**0.5**
1.6	1.08% > 0.7% so the yogurt respects the given standards	**0.5**
2.1		**0.5**
2.2	2-hydroxypropanoic acid.	**0.5**
2.3	The molecule of lactic acid is chiral since the carbon number 2 is an asymmetric carbon (it is bonded to 4 different atoms or group of atoms)	**0.5**
2.4		**0.75**
2.5.1	The hydroxyl group undergoes mild oxidation.	**0.5**
2.5.2	$CH_3 – C – COOH$ ‖ O	**0.5**

Exercice 2 (6 points) **Chemical Kinetic**

Part of the Q	Expected Answer	Mark
1.1	The equation of the reaction is : $CH_3 - COOH + CH_3 - CH_2 - CH_2 - CH_2OH \rightleftarrows CH_3 - COO - CH_2 - CH_2 - CH_2 - CH_3 + H_2O$	0.75
1.2	The ester obtained is butyl ethanoate.	0.25
2.1	To block the slow esterification reaction. Temperature and the initial concentration of the reactants.	0.75
2.2		1
2.3	The instantaneous rate of the formation of the ester, is equal to the slope of the tangent drawn on the curve at a point of abscissa t. Graphically, the slope of the tangent at each point on the curve decreases with time then the rate decreases.	0.75
2.4	Acid + Alcohol ⇄ Ester + water A t = 0 0.05 mol 0.05 mol - - A t = 50 0.05-x 0.05-x x x With x = 0.0335 mol = $n_{(ester)} = n_{(water)}$ $n_{(acid)} = n_{(alcohol)}$ = 0.05-0.0335 = 0.0165 mol	0.75
2.5	Quotient of the reaction at t = 50 min : $Q_r = \frac{[ester]\times[water]}{[alcohol]\times[acid]} = \frac{\frac{n(ester)}{V}\times\frac{n(water)}{V}}{\frac{n(acid)}{V}\times\frac{n(alcohol)}{V}} = \frac{(0.0335)^2}{(0.05-0.0335)^2} = 4.12$ The quotient Q_r is equal to the equilibrium constant K_C, thus the reactional medium reaches chemical equilibrium	0.75
2.6.1	True. The addition of alcohol at equilibrium displaces the equilibrium in the forward direction according to Le Chatelier's principle which results in increasing the experimental quantity of ester formed whereas theoretical quantity of ester remains the same. Then the yield of esterification increases.	0.5
2.6.2	False. The increase in temperature doesn't affect the yield at equilibrium since the reaction is athermic.	0.5

Exercice 3 (7 points)

Sodium Hydroxide

Part of the Q.	Expected Answer	Mark
1.1	m = n × M = C × V × M = 0.01× 0.1× 40 = 0.04g	**0.5**
1.2	- volumetric flask 100mL - watch glass - spatule - precision balance.	**1**
1.3.1	$K_R = 10^{\Delta pKa} = 10^{9.8} > 10^{4}$ the reaction is complete.	**0.5**
1.3.2		**0.75**
1.3.3	For pH = 5 the two species C_6H_5-COOH and C_6H_5-COO^- exist with close concentration. Since the reaction is complete, C_6H_5-COOH doesn't disappear so it is in excess while HO^- is the limiting reactant.	**0.5**
1.3.4	C_6H_5-COOH + HO^- → C_6H_5-COO^- + H_2O at t=0 CV_2 CV_1 - excess at t_f CV_2-CV_1 0 CV_1 excess $pH = pKa + \log\frac{[C_6H_5COO^-]}{[C_6H_5COOH]} = pKa + \log\frac{CV_2/V_t}{(CV_1 - CV_2)/V_t} = pKa + \log\frac{V_2}{V_1 - V_2}$ $\mathbf{\log\frac{V_2}{V_1 - V_2} = pH - pKa = 5 - 4.2 = 0.8; \frac{V_2}{V_1 - V_2} = 10^{0.8} = 6.3}$ V_2= 6.3×(V_1-V_2) ; 7.3V_2 = 6.3V_1 ; V_2=1.16V_1=1.16×54=62.6 mL	**1**
2.1.1	C_6H_5-C-O-C- C_6H_5 ‖ ‖ O O	**0.5**
2.1.2	C_6H_5-C-O-C- C_6H_5 + CH_3-CH_2-OH → C_6H_5-COO-C_2H_5 + C_6H_5-COOH ‖ ‖ O O	**0.75**
2.1.3	c- total and exothermic.	**0.5**
2.2	$C_6H_5COOC_2H_5$ + HO → $C_6H_5COO^-$ + C_2H_5OH	**0.5**
2.3	Heating under reflux increases the rate of the reaction without losing any quantity of reactants or products by condensing the vapors escaping and returning them to the reactional mixture.	**0.5**