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مسابقة في مادة 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:

First Exercise (6 points)
Hydrochloric Acid and Calcium Carbonate

It is required to follow-up the progress of the reaction between solid calcium carbonate $CaCO_3$ and an excess of a hydrochloric acid solution ($H_3O^+ + Cl^-$). The equation of this reaction is:

$$CaCO_{3(s)} + 2\,H_3O^+_{(aq)} \rightarrow Ca^{2+}_{(aq)} + CO_{2(g)} + 3H_2O_{(l)}$$

At T = 25 ºC, an excess of a hydrochloric acid solution is introduced into a flask containing a piece of calcium carbonate of mass m = 40 g. The flask is immediately connected to a manometer that indicates an initial pressure P_0 representing the pressure of the air contained in the flask.
We read, then, the pressure P_t measured by the manometer at different times t.
The number of moles of the gas CO_2 released is determined and the results are grouped in the following table:

t (s)	10	20	30	40	60	80	100	120
n (CO_2) (10^{-2} mol)	6.0	10	14	17.5	22.5	26.5	29.5	31.0

Given:

- Molar mass of calcium carbonate: M = 100 g.mol^{-1}.
- Ideal gas constant: R = 0.08 atm.L.mol^{-1}.K^{-1}.
- CO_2 gas is assumed to be an ideal gas.

1- Preliminary study

1.1- Choose, by justifying, among the following terms those which are convenient to describe the mixture at the end of the gas release: heterogeneous, homogeneous, acid, base and neutral.
1.2- Express, in terms of P_0 and P_t, the number of moles of the gas released n(CO_2) where the gaseous mixture occupy a volume of 1 L.
1.3- Verify if the time t= 120 s represents the end-time of the reaction.

2- Kinetic Study

2.1- Plot the curve that represents the change in the number of moles of the gas released as a function of time: $n(CO_2) = f(t)$ in the interval of time: [0 -120 s].
Take the following scale:
1 cm for 10 s in abscissa and 1 cm for 2.5×10^{-2} mol in ordinate.

2.2- Deduce, graphically, the change in the rate of formation of CO_2 with time.

2.3- Determine the half-life time of this reaction.

2.4- The experiment realized at the beginning of the exercise is carried out again but with only one change: the flask is placed in an ice-water bath.
Plot on the same graph of the question 2.1, the shape of the curve representing the new change in the number of moles of the gas released as a function of time: $n(CO_2) = g(t)$. Justify.

Second Exercise (7 points)
Sodium Hydroxide

Sodium hydroxide, an ionic solid of formula unit NaOH, is found generally as white pellets. Sodium hydroxide is highly soluble in water and in ethanol.
In the laboratory, aqueous standardized solutions of sodium hydroxide are used to titrate acidic solutions and the concentrated solutions are used to prepare soaps…

1- Titration of a Scale Removal

Given: The study is carried out at 25 ºC.
List of available glassware in the laboratory

- Beakers: 100, 200 and 500 mL.
- Volumetric flasks: 100, 200 and 500 mL.
- Volumetric pipets: 5, 10 and 20 mL.
- Graduated cylinders: 5, 10 and 20 mL.
- Erlenmeyer flasks: 100, 200 and 500 mL.
- Graduated buret of 25 mL.

It is required to titrate a sanitary liquid scale removal containing hydrochloric acid (assumed to be the only chemical species present with an acid-base character). To do that, one proceeds as follows:

- A sample of this scale removal is diluted 50 times.
- A volume $V_A = 20.0$ mL of the dilute solution is taken and poured into an Erlenmeyer flask containing about 30 mL of distilled water and few drops of an appropriate colored indicator.
- A sodium hydroxide solution of concentration $C_B = 0.10$ mol.L^{-1} is added progressively to reach equivalence.

1.1- Choose, by justifying, from the above list, the essential glassware used for the dilution of the scale removal.

1.2- Write the equation of the titration reaction.

1.3- Determine the concentration of the hydrochloric acid in the dilute solution knowing that the volume of the basic solution added to reach equivalence is $V_{BE} = 9.2$ mL.

1.4- Deduce the concentration of the hydrochloric acid in the scale removal product.

1.5- Specify the effect of the presence of distilled water, in the Erlenmeyer flask, on the volume V_{BE} and on the pH at equivalence pH_E.

2- Preparation of a Soap

Given:
Molar mass of sodium oleate: M = 304 $g.mol^{-1}$.

A mixture of 4.0×10^{-2} mol of olein (a triester of oleic acid) and an excess of a concentrated sodium hydroxide solution is heated in the presence of ethanol as a solvent.
Sodium oleate of formula ($C_{17}H_{33}CO_2^- + Na^+$) and a compound (G) are obtained.

2.1- Deduce the formula of oleic acid and specify if it is a saturated acid or an unsaturated acid.
2.2- Write the equation of the saponification reaction of olein.
2.3- Give the systematic name of the compound (G).
2.4- Determine the mass of the soap obtained knowing that the yield of the reaction is 95 %.
2.5- Oleate ion possesses two parts: a hydrophilic part and a lipophilic part.
Indicate these two parts on the formula of this ion.

Third Exercise (7 points)
Propanoic Acid

In the laboratory, available are three flasks of which the labels show the following indications:

Flask	1	2	3
Indication of the label	Pure propanoic acid	Aqueous solution of sodium propanoate ($C_2H_5CO_2^- + Na^+$)	2- Butanol

In this exercise, propanoic acid is used to prepare a buffer solution of pH = 5.20 and to synthesize a fruit odor ester.

Given:

- Ion product of water: $K_W = 1.0\times10^{-14}$
- pK_a ($C_2H_5CO_2H$ / $C_2H_5CO_2^-$) = 4.89
- Density of pure propanoic acid: d = 0.99$g.mL^{-1}$.
- Molar mass of propanoic acid: M= 74 $g.mol^{-1}$.

1- Preparation of the Buffer Solution

The pH of the solution contained in the flask 2 is found to be equal to 8.45

1.1- Write the equation of the reaction of the base $C_2H_5CO_2^-$ with water.
1.2- Show that the solution contained in the flask 2 has a concentration $C = 1.0\times10^{-2}$ $mol.L^{-1}$.
(in this solution [$C_2H_5CO_2H$] is neglected compared to C).
1.3- Determine the volume V_1 of pure propanoic acid that should be added to a volume V= 3L of the sodium propanoate solution in order to prepare a buffer solution of pH = 5.20

2- Synthesis of the Ester

An equimolar mixture of propanoic acid and 2-butanol is heated to reflux.

2.1- Write, using condensed structural formulas of the organic compounds, the equation of the reaction that takes place. Name the ester formed.

2.2- List two characteristics of this reaction.

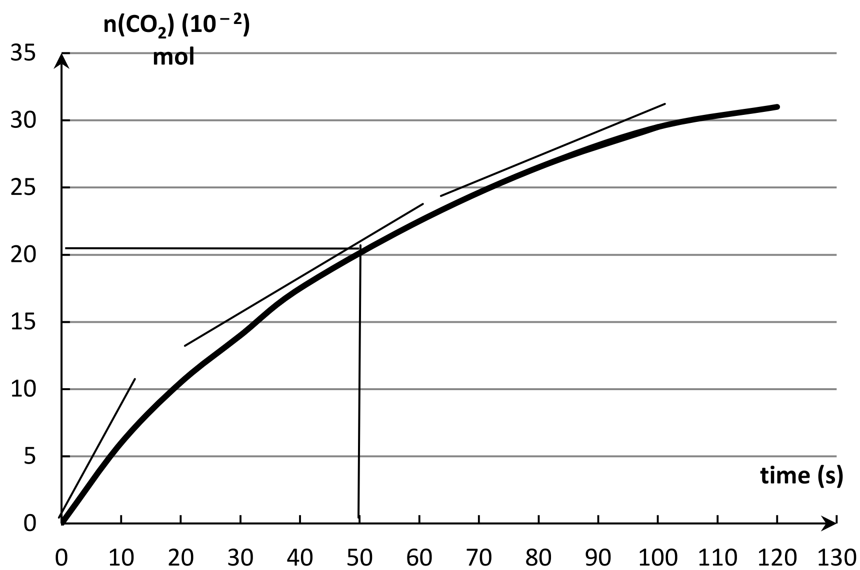
2.3- The ester formed and the 2-butanol have the same type of configuration isomerism. Specify this type of isomerism.

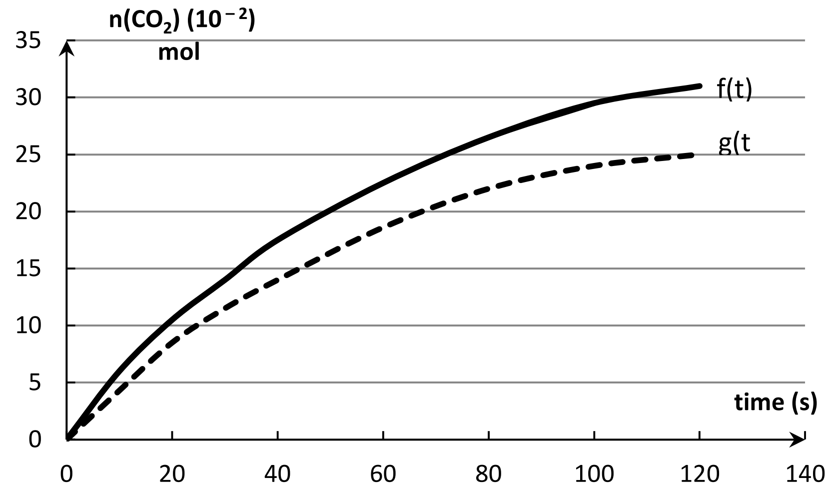
2.4- Indicate the importance of the reflux heating in this synthesis.

2.5- Specify the effect of each of the three following proposals on the yield of this reaction:

- The pure propanoic acid is replaced by an aqueous solution containing the same quantity of the acid.
- A catalyst is added to the initial mixture.
- An initial mixture in which the acid is used in excess with respect to the alcohol.

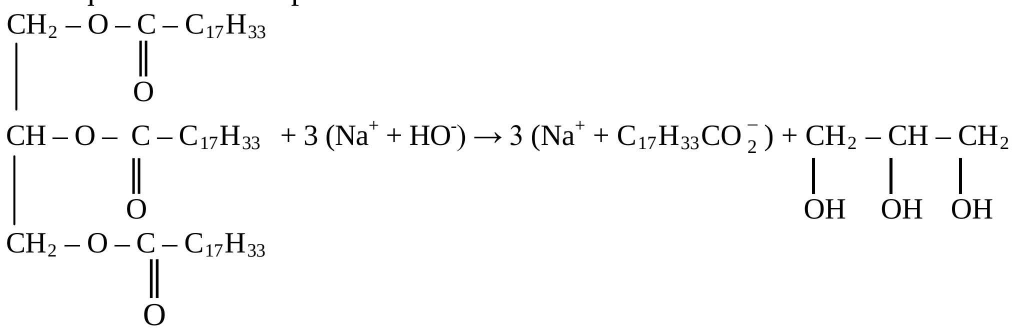
First Exercise (6 points)
Hydrochloric Acid and Calcium Carbonate

Part of the Q	Answer	Mark
1.1	Since the acid is in excess, the terms that describe this mixture are: homogeneous and acid.	0.75
1.2	According to the ideal gas law: $n(CO_2) = \frac{P(CO_2) \times V}{R \times T} = \frac{(P_t - P_o) \times V}{R \times T} = \frac{P_t - P_o}{0.08 \times 298} = \frac{P_t - P_o}{23.84}$ where the pressures are in atm.	0.75
1.3	$n(CO_2)$ formed at the end of the reaction = $n(CaCO_3)$ initial (since H_3O^+ is in excess) ; $= \frac{m(CaCO_3)initial}{M} = \frac{40}{100} = 0.4$ mol. Since at t = 120 s, $n(CO_2)$ formed = 0.31 mol< 0.4 mol, so this time does not represent the end-time of the reaction.	1
2.1		1
2.2	The rate of formation of CO_2 is equal to the slope of the tangent at the curve at the point of abscissa t. This rate decreases with time since, graphically, the slope is maximal at t = 0 then it decreases with time as it shown in the graph 2.1	0.75
2.3	The half-life time is the time needed for $n(CO_2)$ to reach half its maximal value.	

	At $t_{1/2}$, n (CO_2) formed = 0.4 / 2 = 0.2mol. graphically $t_{1/2}$= 50 s.	0.75
2.4	The temperature, which is a kinetic factor, deceases in the ice-water bath and by consequence the rate of formation of CO_2 decreases. At each instant of time t, n(CO_2) formed at 0°C < n(CO_2) formed at 25°C; the shape of the curve is: 	1

Second Exercise (7 points)
Sodium Hydroxide

Part of the Q	Answer	Mark
1.1	During dilution, the number of moles of NaOH is conserved n $_{\text{(before dilution)}}$ = n $_{\text{(after dilution)}}$; $C_o \times V_o = C_A \times V$; where C_o and C_A are the concentrations of the hydrochloric acid in the scale removal and in the dilute solution respectively. Dilution factor F = $\frac{C_o}{C_A} = \frac{V}{V_o}$ = 50 where V is the volume of the volumetric flask to be chosen and V_o is the volume of the pipet. From the list, we choose: a 10 mL volumetric pipet and a 500 mL volumetric flask and a beaker.	1
1.2	The equation of the titration reaction $H_3O^+ + HO^- \rightarrow 2 H_2O$.	0.5
1.3	n (HO^-) added to reach equivalence = n (H_3O^+) introduced into the Erlenmeyer $C_B \times V_{BE} = C_A \times V_A$; $C_A = \frac{C_B \times V_{BE}}{V_A} = \frac{0.1 \times 9.2}{20} = 4.6\times10^{-2}$ mol.L^{-1}.	0.75
1.4	The concentration of the hydrochloric acid in the scale removal is: $C_o = 50 \times C_A = 50 \times 4.6\times10^{-2} = 2.3$ mol.L^{-1}.	0.5
1.5	The presence of water does not affect the initial quantity of H_3O^+ ions. So the volume added to reach equivalence V_{BE} is not affected.	1

	At equivalence, the pH of the medium is that of the water formed ($pH_E = 7$). An additional quantity of water introduced before titration does not affect the pH_E.	
2.1	The formula of the oleic acid is: $C_{17}H_{33}CO_2H$. This formula does not satisfy the formula $C_xH_{2x}O_2$ or $C_nH_{2n+1}CO_2H$; so this acid is not a saturated acid. It is an unsaturated acid.	0.75
2.2	The equation of the saponification of olein : 	0.75
2.3	The systematic name of the compound G is : 1,2,3-propantriol.	0.25
2.4	n(soap) expected = 3 x n(olein) initial = 3 x 0.04 = 0.12 mol since NaOH is in excess. m(soap) expected = n(soap) x M = 0.12 x 304 = 36.48 g. m(soap) actual = 36.48 x 95 /100 = 34.66 g.	1
2.5	$C_{17}H_{33} - CO_2^-$ lipophilic hydrophilic	0.5

Third Exercise (7 points)
Propanoic Acid

Part of the Q.	Answer	Mark
1.1	The equation of the reaction is: $C_2H_5CO_2^- + H_2O \rightleftarrows C_2H_5CO_2H + HO^-$	0.5
1.2	[$C_2H_5CO_2^-$] initial is equal to C. $C_2H_5CO_2^- + H_2O \rightleftarrows C_2H_5CO_2H + HO^-$ Initial state: C, solvent, -, - At equilibrium: C – x, solvent, x, x $K_r = \frac{[HO^-]\times[C_2H_5CO_2H]}{[C_2H_5CO_2^-]} = \frac{x^2}{C} = \frac{10^{-pKw}}{10^{-pKa}} = \frac{10^{-14}}{10^{-4.89}} = 10^{-9.11}$ Where: $[HO^-] = [C_2H_5CO_2H] = x = 10^{pH-14}$, $[C_2H_5CO_2^-] = C$ So $C = 1.0\times10^{-2}$ mol.L^{-1}.	1.25
1.3	The initial number of moles of each one of the acid and its conjugate base is conserved in the obtained buffer solution.	

	pH(solution) = pK_a ($C_2H_5CO_2H$ / $C_2H_5CO_2^-$) + log $\frac{[C_2H_5CO_2^-]}{[C_2H_5COOH]}$ Where [$C_2H_5CO_2^-$] = $\frac{C \cdot V}{V(mixture)}$ and[$C_2H_5CO_2H$] = $\frac{d \cdot V_1}{M \times V(mixture)}$; So V_1 = $\frac{C \times V \times M}{d \times 10^{pH - pK_a}} = \frac{0.01 \times 3 \times 74}{0.99 \times 10^{5.2-4.89}}$ = 1.1 mL.	1.25
2.1	The equation of this reaction: $CH_3-CH_2-COOH + CH_3-CH_2-\underset{\large OH}{\underset{\vert}{CH}}-CH_3 \rightleftarrows H_2O + CH_3-CH_2-\underset{\large O}{\underset{\Vert}{C}}-O-\underset{\large CH_3}{\underset{\vert}{CH}}-CH_2-CH_3$ The name of the ester is 1-methylpropyl propanoate (2-butylpropanoate).	1
2.2	Two characteristics are: slow and limited.	0.5
2.3	The isomerism is an enantiomerism, since the two molecules of both compounds have an asymmetric carbon.	0.5
2.4	Heating to reflux accelerate the reaction without losing any of the reaction mixture components.	0.5
2.5	Water present at the start of the reaction favors the hydrolysis reaction of the ester (that is formed) and by consequence the yield of the synthesis reaction decreases. The catalyst accelerates both reactions (esterification and hydrolysis) in the same way and by consequence the yield of the synthesis reaction does not changes. The use of an initial mixture with an excess of acid favors the esterification reaction (% of the alcohol reacted increases) and the yield of the reaction increases.	0.5 0.5 0.5