

المادة: الكيمياء الشهادة: الثانوية العامة الفرع: علوم حياة وعلوم عامة نموذج رقم - ١ المدة : ساعتان	الهيئة الأكاديمية المشتركة قسم : العلوم	 المركز التربوي للبحوث والإنماء
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نموذج مسابقة (يراعي تعليق الدروس والتوصيف المعدل للعام الدراسي ٢٠١٦-٢٠١٧ وحتى صدور المناهج المطورة)

This Exam consists of three exercises distributed on four pages numbered from 1 to 4. The use of a non programmable calculator is allowed. Answer the questions on the following exercises.

### Exercise 1 (7 points)

#### Kinetic Study of the Reaction of Ethyl Ethanoate with Sodium Hydroxide

A volume  $V = 8.0 \text{ mL}$  of a sodium hydroxide solution ( $\text{Na}^+_{(\text{aq})} + \text{HO}^-_{(\text{aq})}$ ) of concentration  $C = 0.20 \text{ mol.L}^{-1}$  is poured into a 500 mL beaker containing distilled water. The volume of the resulting solution is 400mL. The combined electrode of a calibrated pH-meter is dipped in the solution and continuous stirring is maintained. At time  $t = 0$ , 0.01 mol of pure ethyl ethanoate is added into the beaker. A slow reaction takes place according to the following equation:



The kinetic study of the reaction is carried out by measuring the values of the pH of the solution by means of a pH-meter. These measured pH values allow to calculate the concentrations of the  $\text{HO}^-$  ions. The results are presented in the following table: (Document 1).

t (min)	0	1	2	4	6	8	10	12	16	20	24	28	34	40
$[\text{HO}^-]$ ( $10^{-3} \text{ mol. L}^{-1}$ )	4.0	3.3	2.8	2.1	1.6	1.3	1.0	0.83	0.6	0.45	0.36	0.3	0.24	0.21

**Document 1**

1.2. Verify that at any instant of time t:  $[\text{CH}_3\text{COO}^-]_t = 4 \times 10^{-3} - (K_w / 10^{\text{pH}})$ , where  $K_w$  is the ion product constant of water.

1.3. Deduce how the concentration of the ethanoate ions  $[\text{CH}_3\text{COO}^-]_t$  varies with pH at constant temperature.

#### 2. Making Use of the Results:

2.1. Plot the curve  $[\text{HO}^-] = f(t)$ . Take the following scales:

abscissa (x-axis): 1cm = 2 min; ordinate (y-axis): 1 cm =  $0.2 \times 10^{-3} \text{ mol.L}^{-1}$ .

2.2. Establish the relation between the rate of disappearance of  $\text{HO}^-$  ions and the rate of formation of  $\text{CH}_3\text{COO}^-$  ions at a given time t.

2.3. The rates of disappearance of  $\text{HO}^-$  ions were measured at  $t=0$  min and at  $t=8$  min using an appropriate method. The following values are obtained:

$1.4 \times 10^{-4} \text{ mol.L}^{-1}.\text{min}^{-1}$  and  $1 \times 10^{-3} \text{ mol.L}^{-1}.\text{min}^{-1}$ .

2.3.1. Assign to each instant of time the corresponding value of the rate.

2.3.2. Specify the kinetic factor involved in this variation.

2.4. Determine graphically the half- life of the reaction.

2.5. Plot on the same graph, the shape of the curve representing  $[\text{CH}_3\text{COO}^-] = g(t)$ , for the time interval (0- 40 min), specifying the coordinates of three remarkable points of abscissas  $t = 0$ ,  $t = t_{1/2}$  and  $t = 40$  min respectively.

## Exercise 2 (7 points)

## Properties of Ammonia Solution

A commercial solution ( $S_0$ ) of ammonia  $\text{NH}_{3(\text{aq})}$  of concentration  $C_0 = 1.1 \text{ mol.L}^{-1}$  can be used as a detergent after dilution.

### 1. Preparation of Solution (S) of $\text{NH}_3$ :

A solution (S) of ammonia of concentration  $C_S = C_0/100$  is prepared starting from the available commercial solution ( $S_0$ ).

1.1. Calculate the volume  $V_0$  that should be taken from solution ( $S_0$ ) to prepare 1L of solution (S).

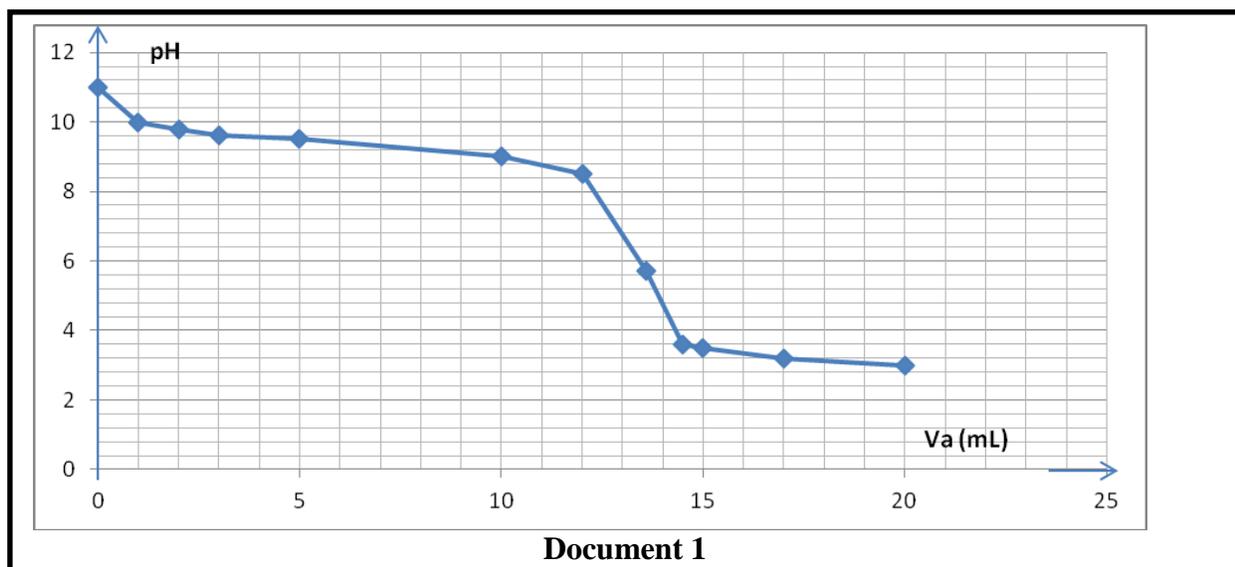
1.2. Choose from the list below, the most precise glassware needed to prepare 1L of (S). You are allowed to withdraw once from ( $S_0$ ).

#### Available Glassware:

- Graduated cylinders : 5, 20 and 50 mL.
- Volumetric flasks : 100, 250 and 1000 mL.
- Volumetric pipettes : 5, 10 and 20 mL

### 2. Titration of Solution (S):

It is required to verify the value of the concentration  $C_0$  of ( $S_0$ ). For this reason, a sample of solution (S) volume  $V_S = 20 \text{ mL}$  is transferred to a beaker containing 100 mL of distilled water. The obtained solution is stirred continuously. This solution is titrated with hydrochloric acid solution ( $\text{H}_3\text{O}^+_{(\text{aq})} + \text{Cl}^-_{(\text{aq})}$ ) of concentration  $C_a = 0.015 \text{ mol.L}^{-1}$ . The pH of the mixture is measured after each addition. The obtained values allowed drawing the curve (Document 1).



2.1. Indicate the suitable glassware needed to :

2.1.1. Transfer the 20 mL of the solution (S).

2.1.2. Add progressively the solution of hydrochloric acid.

2.2. Write the equation of the titration reaction.

2.3. Determine the volume of the acidic solution added till equivalence  $V_{aE}$  .

2.4. Verify, based on graph, the given pKa value of the couple  $\text{NH}_4^+ / \text{NH}_3$  given in document 2.

	$\text{H}_3\text{O}^+ / \text{H}_2\text{O}$	$\text{NH}_4^+ / \text{NH}_3$	$\text{H}_2\text{O} / \text{HO}^-$	<b>Document 2</b>
<b>pKa</b>	0	9.2	14	

2.5. Calculate the concentration  $C_S$  of the titrated solution. Deduce the value of the concentration  $C_0$  of the solution  $S_0$ .

### 3. Another Method to Detect the Equivalence Point:

The same experiment is repeated but this time the titration is carried out by means of an acid-base indicator. Referring to Document 3, what is the most convenient indicator to be used during this titration? Justify.

<b>Acid base Indicator</b>	Acid	pH range of color change	Base
<b>Bromothymol Blue</b>	Yellow	6.0-7.6	Blue
<b>Methyl Red</b>	Red	4.2-6.2	Yellow
<b>Cresol Red</b>	Yellow	7.2-8.8	Red

**Document 3**

### 4. Reaction of Ammonia $\text{NH}_3$ with Water:

Consider the solution (S) of concentration  $C_S = 0.011 \text{ mol.L}^{-1}$ .

1. Write the equation of the reaction between ammonia and water.

2. Calculate  $K_R$  of this reaction.

3. Determine the pH of the solution (S). (Neglect  $[\text{NH}_4^+]$  formed w.r.t.  $[\text{NH}_3]_0$ )

4. Deduce the value of the degree of dissociation of  $\text{NH}_3$  in the solution (S).

**Exercise 3 (6points)****Identification of an Ester**

A number of esters are present in nature. Some natural perfumes are found in flowers and in fruits such as ethyl butanoate in pineapple and isoamyl acetate in banana...

Esters have a pleasant fruity odor, that is why they are used in synthetic aromas. In the following exercise, it is required to identify an ester (E) that has an agreeable odor.

**1. The Condensed Structural Formulas of Natural Esters**

Write the condensed structural formula of the ester:

1.1. Having a pineapple odor.

1.2. Having a banana odor knowing that its systematic name is 3-methyl-1-butylethanoate.

**2. The Molecular Formula of the Ester (E)**

The elemental analysis of the ester (E) gave the following percent mass composition:

62.1% Carbon

10.3% Hydrogen

27.6% Oxygen

**Document 1**

Show that the molecular formula of (E) is  $C_6H_{12}O_2$ . Given the following molar atomic masses:

$M(C) = 12\text{g/mol}$ ;  $M(H) = 1\text{g/mol}$ ;  $M(O) = 16\text{g/mol}$

**3. Identification of the Ester (E):**

The hydrolysis of ester (E) leads to the formation of 2 non-cyclic saturated organic compounds: A monocarboxylic acid (A) and a monoalcohol (B). Using an appropriate technique, acid (A) is separated from alcohol (B).

3.1. Determine the molecular formulas of (A) and (B), knowing that the number of carbon atoms in one molecule of the alcohol (B) is 4.

3.2. Write the condensed structural formula of (A) and give its name.

3.3. In order to identify (B), we allow it to undergo mild oxidation. The obtained compound (C) gives a yellow precipitate with DNPH and does not react with Schiff's reagent.

3.3.1. Write the condensed structural formula of (C) and give its name. Justify.

3.3.2. Identify alcohol (B) and ester (E).

**4. Increasing the Yield of the Esterification Reaction:**

To increase the yield of this reaction, the students gave the following suggestions:

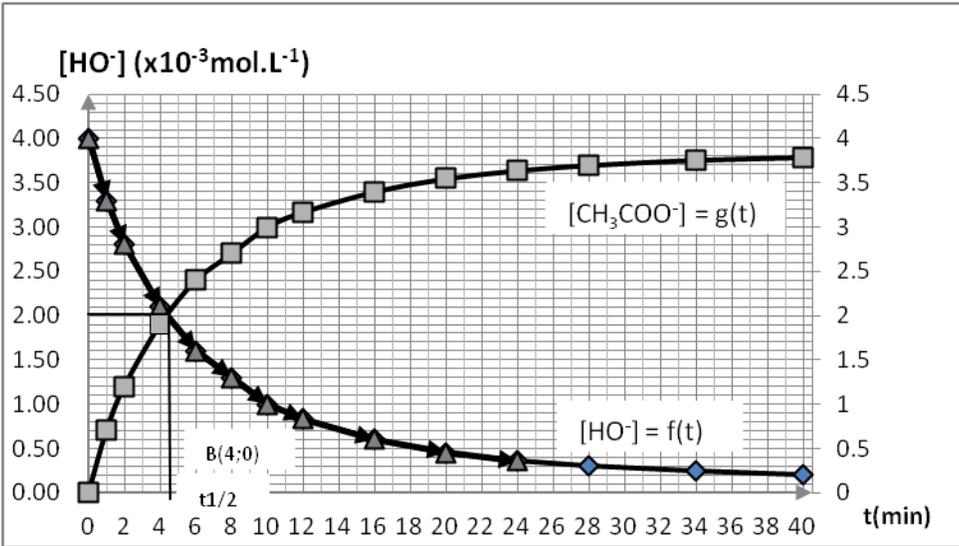
a. Eliminate one of the products formed by distillation.

b. Use an appropriate catalyst.

For each suggestion, indicate if it is correct or wrong. Justify.

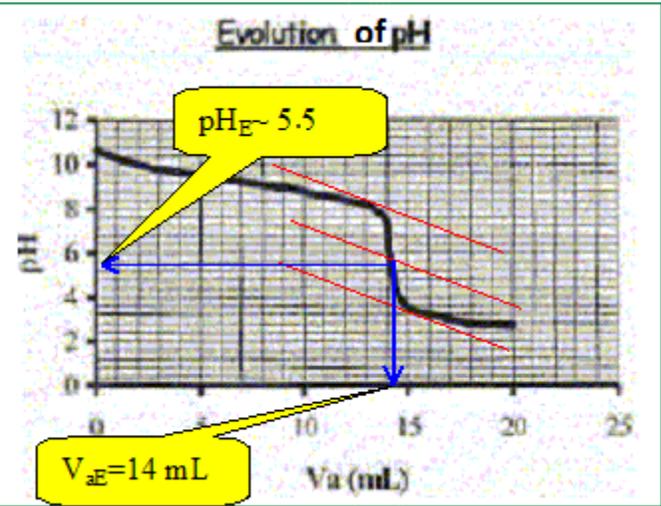
المادة: الكيمياء الشهادة: الثانوية العامة الفرع: علوم حياة + علوم عامة نموذج رقم -١- المدة: ساعتان	الهيئة الأكاديمية المشتركة قسم : العلوم	 المركز العلمي للبحوث والابتكار
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أسس التصحيح (تراعي تعليق الدروس والتوصيف المعدل للعام الدراسي ٢٠١٦-٢٠١٧ وحتى صدور المناهج المطورة)

Exercise 1 (7 points)		
Kinetic Study of the Reaction of Ethyl Ethanoate with Sodium Hydroxide		
Part of Q	Expected Answers	Mark
1.1	$n(\text{HO}^-) = C \times V = 0,2 \times 8.10^{-3} = 1,6 \times 10^{-3} \text{ mol}$ ; $n(\text{ester}) = 1 \times 10^{-2} \text{ mol}$ $R_{(\text{HO}^-)} = \frac{1,6.10^{-3}}{1} < R_{(\text{ester})} = \frac{1.10^{-2}}{1}$ $\text{HO}^-$ is the limiting reactant.	0.75
1.2	At any instant of time t, and according to stoichiometric ratios:: $n(\text{CH}_3\text{COO}^-)_t = n(\text{HO}^-)_{\text{reacted}} = n(\text{HO}^-)_o - n(\text{HO}^-)_t$ Dividing by the volume of the solution : $[\text{CH}_3\text{COO}^-]_t = [\text{HO}^-]_o - [\text{HO}^-]_t$ $[\text{HO}^-]_o = \frac{n_{\text{HO}^-}}{V_s} = \frac{1.6.10^{-3}}{0.4} = 4.10^{-3} \text{ mol.L}^{-1} \quad K_w = [\text{H}_3\text{O}^+][\text{HO}^-]$ $[\text{HO}^-]_t = \frac{K_w}{[\text{H}_3\text{O}^+]_t} = \frac{K_w}{10^{-\text{pH}}}$ then : $[\text{CH}_3\text{COO}^-]_t = 4 \times 10^{-3} - (K_w/10^{-\text{pH}})$ .	0.75
1.3	At constant temperature, $K_w$ is constant. According to the relation, as pH of the solution increases, the ratio $(K_w/10^{-\text{pH}}) = (K_w \times 10^{\text{pH}})$ increases. This indicates that $[\text{CH}_3\text{COO}^-]_t$ decreases.	0.5
2.1		1

2.2	According to stoichiometric ratios, $n(\text{HO}^-)/1 = n(\text{CH}_3\text{COO}^-)/1$ . The relation between the rate of disappearance of $\text{HO}^-$ and the rate of formation of $\text{CH}_3\text{COO}^-$ , at each instant of time : $r(\text{HO}^-) = r(\text{CH}_3\text{COO}^-)$ .	0.5
2.3.1	$r_{(t=0\text{min})} = 1 \times 10^{-3} \text{ mol. L}^{-1} \cdot \text{min}^{-1}$ , $r_{(t=8\text{min})} = 1.4 \times 10^{-4} \text{ mol. L}^{-1} \cdot \text{min}^{-1}$ .	0.5
2.3.2	The instantaneous rate of disappearance of $\text{HO}^-$ ions decreases with time as the concentration of the reactants, kinetic factor, decreases with time.	0.5
2.4	The half-life time is the time required for the disappearance of half the initial concentration of the limiting reactant.  $[\text{HO}^-]_{t/2} = \frac{[\text{HO}^-]_0}{2} = \frac{4 \cdot 10^{-3}}{2} = 2 \cdot 10^{-3} \text{ mol. L}^{-1}$ from the Graph : $t_{1/2} = 4.4 \text{ min}$ .	1
2.5	According to the relation: $[\text{CH}_3\text{COO}^-]_t = [\text{HO}^-]_0 - [\text{HO}^-]_t$ At $t = t_{1/2}$ : $[\text{CH}_3\text{COO}^-]_{t/2} = 4 \times 10^{-3} - 2 \times 10^{-3} = 2 \times 10^{-3} \text{ mol. L}^{-1}$ . At $t = 40\text{min}$ : $[\text{CH}_3\text{COO}^-]_{t=40} = 4 \times 10^{-3} - 0.21 \times 10^{-3} = 3.79 \times 10^{-3} \text{ mol. L}^{-1}$ .	0.75
2.6	The shape of the curve is shown on the graph. $[\text{CH}_3\text{COO}^-]_{t=0} = 0 \text{ mol. L}^{-1}$ $[\text{CH}_3\text{COO}^-]_{t/2} = 2 \times 10^{-3} \text{ mol. L}^{-1}$ $[\text{CH}_3\text{COO}^-]_{t=40} = 3.79 \times 10^{-3} \text{ mol. L}^{-1}$ .	0.75

<b>Exercise 2 (7 points)</b>		
<b>Properties of Ammonia Solution</b>		
Part of Q.	Expected answers	Mark
1.1	Upon dilution, n (solute) is conserved :  The dilution factor $f = C_0 / C = V / V_0$ $V_0 = 100 / 10 = 10 \text{ ml}$	0.5
1.2	10mL volumetric pipette and 1L volumetric flask.	0.5
2.1.1	20 mL volumetric pipette.	0.25
2.1.2	25 mL Graduated Burette	0.25
2.2	The equation of the reaction : $\text{NH}_3 + \text{H}_3\text{O}^+ \rightarrow \text{NH}_4^+ + \text{H}_2\text{O}$	0.5

2.3	By applying the parallel tangents method :		0.5																							
2.4	<p>At half-equivalence : <math>V_a = \frac{V_{aE}}{2} = \frac{14}{2} = 7\text{mL}</math>.</p> <p>From the Graph, this corresponds to <math>\text{pH} = \text{p}K_a = 9.2</math>  <math>\text{p}K_a (\text{NH}_4^+/\text{NH}_3) = \text{pH}</math> since <math>[\text{NH}_4^+] = [\text{NH}_3]</math></p>	0.5																								
2.5	<p>At equivalence : <math>n(\text{NH}_3)</math> found in the beaker = <math>n(\text{H}_3\text{O}^+)</math> added at equivalence</p> $C_S \times V_S = C_a \times V_{aE} ; C_S = \frac{C_a \cdot V_{aE}}{V_S} = \frac{0.015 \times 14}{20} = 0.0105 \text{ mol.L}^{-1}$ <p><math>C_0 = C_S \times 100 = 0.0105 \times 100 = 1.05 \text{ mol.L}^{-1}</math>.</p>	0.75 0.25																								
3	The pH at the equivalence point (about 5.5) must be included in the pH range of the color change of the indicator, thus methyl red (4.2 – 6.2) is the most convenient one.	0.5																								
4.1	$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{HO}^-$	0.5																								
4.2	$K_R = 10^{\Delta pK_a} = 10^{-4.8} = 1.58 \times 10^{-5}$	0.5																								
4.3	<table style="margin-left: auto; margin-right: auto; border-collapse: collapse;"> <tr> <td></td> <td style="text-align: center;"><math>\text{NH}_3</math></td> <td style="text-align: center;">+</td> <td style="text-align: center;"><math>\text{H}_2\text{O}</math></td> <td style="text-align: center;"><math>\rightleftharpoons</math></td> <td style="text-align: center;"><math>\text{NH}_4^+</math></td> <td style="text-align: center;">+</td> <td style="text-align: center;"><math>\text{HO}^-</math></td> </tr> <tr> <td>Initial state</td> <td style="text-align: center;"><math>C_S</math></td> <td></td> <td style="text-align: center;">solvent</td> <td></td> <td style="text-align: center;">-</td> <td></td> <td style="text-align: center;">-</td> </tr> <tr> <td>Equilibrium state</td> <td style="text-align: center;"><math>C_S - x</math></td> <td></td> <td style="text-align: center;">solvent</td> <td></td> <td style="text-align: center;">x</td> <td></td> <td style="text-align: center;">x</td> </tr> </table> $K_R = K_f = \frac{[\text{NH}_4^+]x[\text{HO}^-]}{[\text{NH}_3]} = \frac{x^2}{C_S - x} = 1.58 \times 10^{-5}$ <p><math>K_R \ll 10^{-4} \quad C_S - x = C_S = 0,011 \quad ([\text{NH}_4^+] = x \text{ is negligible w.r.t. } C_S).</math></p> $\frac{x^2}{C_S} = \frac{x^2}{0,011} = 1.58 \times 10^{-5} ; x = 4.17 \times 10^{-4} \text{ mol.L}^{-1}$ <p><math>\text{pH} = 14 + \log[\text{HO}^-] = 14 + \log 4.17 \times 10^{-4} = 10.62.</math></p>		$\text{NH}_3$	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{NH}_4^+$	+	$\text{HO}^-$	Initial state	$C_S$		solvent		-		-	Equilibrium state	$C_S - x$		solvent		x		x	1
	$\text{NH}_3$	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{NH}_4^+$	+	$\text{HO}^-$																			
Initial state	$C_S$		solvent		-		-																			
Equilibrium state	$C_S - x$		solvent		x		x																			

4.4	$\alpha = \frac{n(NH_3)_{dissoc\acute{e}}}{n(NH_3)_{initial}} = \frac{[NH_4^+]}{[NH_3]} = \frac{4.17 \times 10^{-4}}{0.011} = 0.038$ <p>or 3.8 %.</p>	0.5
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<b>Exercise 3 (6 points)</b>		
<b>Identification of an ester</b>		
Part of Q.	Expected Answers	Mark
1.1	Ester having Pineapple smell : $CH_3 - CH_2 - CH_2 - C - O - CH_2 - CH_3$ $\begin{array}{c} \parallel \\ O \end{array}$	0.5
1.2	Ester having Banana smell : $CH_3 - C - O - CH_2 - CH_2 - CH - CH_3$ $\begin{array}{cc} \parallel &   \\ O & CH_3 \end{array}$	0.5
2	The general formula of a saturated non cyclic ester is $C_nH_{2n}O_2$ According to the law of definite proportions: $\frac{12n}{62.1} = \frac{2n}{10.3} = \frac{2 \times 16}{27.6}$ n = 6 The molecular formula of (E) is: $C_6H_{12}O_2$	0.5
3.1	The general formula of a saturated non cyclic monoalcohol is $C_nH_{2n+2}O$ Sine n=4 ; the molecular formula of (B) : $C_4H_{10}O$ Then the number of carbon atoms for the acid (A) : $6 - 4 = 2$ atoms The general formula of the acid (A) : $C_nH_{2n}O_2$ ; n=2 then (A) : $C_2H_4O_2$	1
3.2	$CH_3 - COOH$ ethanoic acid	0.5
3.3.1	The mild oxidation of (B) gives a compound (C) which becomes yellow in the presence of DNPH; thus (C) could be an aldehyde or a ketone. Since (C) do not react with Schiff's reagent so (C) is a ketone. (C) : $CH_3 - CO - CH_2 - CH_3$ butanone	1
3.3.2	Mild oxidation of (B) gives a ketone, then (B) is a secondary alcohol. (B) : $CH_3 - CHOH - CH_2 - CH_3$ 2- butanol (E) : $CH_3 - C - O - CH - CH_2 - CH_3$ 1-methylpropyl ethanoate $\begin{array}{cc} \parallel &   \\ O & CH_3 \end{array}$	1
4	<b>a.</b> True : When one of the products is removed, the equilibrium shifts in the direction of the formation of this product ; therefore, the yield of the reaction increases in this direction (Le Chatelier principle). <b>b.</b> False : A catalyst is a kinetic factor that increases the rate of both forward and backward reactions but does not displace the equilibrium.	0.5  0.5