Exercise 1 **Esterification reaction**

the instant t_0, 1 mole of an alcohol ROH is mixed with 1 mole of carboxylic acid RCOOH and a little amount of sulfuric acid. This mixture is heated at 100°C; the esterification reaction takes place according to the following equation :

RCOOH + ROH ⇌ RCOOR + H_2O

given :

Compound	RCOOH	ROH
density	1,05 g/ml	0,79 g/ml
Molar mass	60 g/mol	46 g/mol

Note : in an athermic reaction α at equilibrium is not affected by the temperature

1- Prelinimary study :

The remaining carboxylic acid is titrated, with an appropriate method, at different instants. The results are given in the following table:

t(hour)	0	1	5	10	15	20	30	40	50	70	90
n_{RCOOH}(mol)	1	0,89	0,69	0,60	0,54	0,49	0,42	0,38	0,35	0,33	0,33

1.1-calculate the volume of each reagent deduce that the total volume is about **115. 5ml**

1.2-determine the initial concentration of RCOOH in the mixture

-2-Study of equilibrium

2.1- Determine the molar composition of the mixture obtained at equilibrium

2.2- Determine α the degree of conversion of acid RCOOH, deduce the% of RCOOH remaining at equilibrium

2.3- Calculate the constant KC of this reaction.

2.4- Determine the % yield of RCOOR at equilibrium

2.5- Show that $Kc = \alpha^2 / (1 - \alpha)^2$

2.6-at equilibrium we add 0.05mol of ROH

Determine the composition of the mixture at the new equilibrium obtained

2.7-At a time t the number of mol of each remaining reagent is half the number of mol of each product formed

2.7.1. verify if the system is at equilibrium or not.

2.7.2. If it is not at equilibrium, identify the direction in which the reaction proceeds to reach equilibrium.

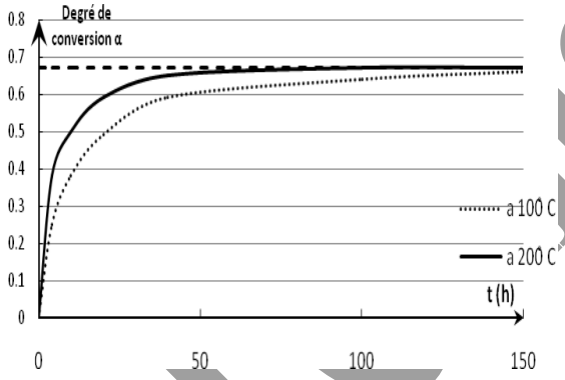
2.8- We give the following 2 propositions, justify if each proposition is correct or not:

2.8.1-in absence of catalyst, the yield of this reaction at equilibrium decreases

2.8.2-when the temperature is increased, the number of mol of acid remaining at an instant t decreases

3-characteristics of the esterification reaction:

Two curves are given below representing the variation in the degree of conversion (α) of RCOOH in this reaction, as a function of time at two different temperatures, 100ºC and 200ºC. Deduce that this reaction is: **reversible , slow, athermic**



Exercise 2 :**A Chlorination Agent : PCl_5**

The phosphorous pentachloride, PCl_5 is a white solid, at room temperature. It is a strong chlorination agent used in organic chemistry.

PCl_5 Is an Unstable Compound

At 100 ºC and above, gaseous phosphorous pentachloride decomposes according to the following equation: $PCl_{5\,(g)} \rightleftharpoons PCl_{3\,(g)} + Cl_{2\,(g)}$.

1mol of PCl_5 is introduced in a thermal reactor of v=1000cm^{3}where the temperature could change from 100 ºC to 350 ºC. The decomposition of $PCl_5$is followed by determining the density of the gaseous mixture relative to air ***(d)***, at different temperatures. The obtained results are given in the following table (1):

Temperature (º C)	120	150	200	350
Relative density ***(d)***	7.2	5.4	4.3	3.6

1- Rewrite the table (2) below, on the answer sheet, and complete it in terms of α, where α is the degree of dissociation of PCl_5 at **a temperature T.**

	PCl_5	PCl_3	Cl_2
Initial state (mol)	1	0	0
Equilibrium state (mol)			

2-Give the expression of Kc as a function of α

3-Show that α = 0.672 if the % by mol of Cl_2 in the mixture at equilibrium is 40.2%

4- Show that % yield of Cl_2 formed =100 α, deduce the value of this yield.

5- Knowing that α and d are related to each other by the following relation: $d = \frac{208,5}{29(1+\alpha)}$.

indicate at which temperature this decomposition reaction is done. Justify

Exercise 3 Synthesis of an ester

Some fishermen use CH_3- $(CH_2)_4OCOCH_3$ amyl acetate noted E to make groundbaits for roaches, small fish from our rivers. This compound can be synthesized by a reaction between ethanoic acid CH_3-COOH noted B and an alcohol (A.)

The reaction equation is: A + B ⇌ E + H_2O (athermic reaction)

Given:

	M ($g.mol^{-1}$)	**ρ ($g.mL^{-1}$)**
Ethanoic acid (B)	60	1.05
Alcohol (A)	88	0.81
Ester (E)	130	0.88

Note: in an athermic reaction the yield at equilibrium in not affected by the temperature

I-preliminary study:

A volume V_1 = 8.6 ml of ethanoic acid of density ρ1 and a volume V2 of alcohol (A) of density ρ2 are introduced into a flask so that the mixture (carboxylic acid-alcohol) is equimolar.

Add a small amount of paratoluene sulfonic acid

This mixture is heated under reflux for about 50 minutes. In addition, ice water is added to the reaction mixture and the ester formed is determined by titration , the mass of the ester formed is m = 11.7 g.

1.1- Paratoluenesulphonic acid is a catalyst for the esterification reaction.

Define a catalyst

1.2- Calculate the value of the volume V_2 of the alcohol (A).

1.3-calculate the number of mol of ester formed at equilibrium

1.4- determine the molar composition of the mixture obtained at equilibrium

II-Determination of the constant Kc and the yield of this synthesis reaction:

2.1- show that $\alpha = 0.6$ (where α is the degree of conversion of A into ester).

2.2- show that the equilibrium constant is $Kc = \alpha^2 / (1- \alpha)^2$ then deduce the value of Kc

2.3-show that the yield of ester formed is 100 α, then deduce the yield of this reaction

2.4- at an instant t the mixture of reactants and products becomes equimolar:

2.4.1 –verify that the reaction system does not reach a state of equilibrium at this instant "t".

2.4.2 Specify in which direction the reaction system will move to reach equilibrium.

III-effect of some factors on the equilibrium of this reaction:

We give the following 3 propositions, justify if each proposition is correct or not:

3.1-the reaction stops at equilibrium

3.2-in absence of the catalyst, the yield of this reaction at equilibrium decreases

3.3-when the temperature is increased; the yield of this reaction at an instant t before equilibrium and at equilibrium does not vary

Exercise 4 Esterification of an alcohol

Esters are very abundant in nature. The simplest, under ordinary conditions of temperature and pressure, are liquid and most often odorous. They are what are commonly called fruit esters.

In order to prepare an ester (E) called ethyl ethanoate ($CH_3COOC_2H_5$), we pour into a container of 1L volume, a volume V1 = 40 mL of ethanol (C_2H_5OH) and 30 g of ethanoic acid (CH_3COOH) .The equation - balance sheet of the preparation reaction of this ester (E) is:

$$CH_3COOH_{(\ell)} + C_2H_5OH_{(\ell)} \rightleftarrows CH_3COOC_2H_{5(\ell)} + H_2O_{(\ell)}$$

The alcohol-acid mixture is heated to a constant temperature of 60^0C in the presence of sulfuric acid. At equilibrium, the acid is titrated and the amount of ethanoic acid remained is 0.115 mol

- **Density of ethanol: μ = 0,82 g.mL^{-1}.**
- **Molar masses: M(CH_3COOH) = 60 g.mol^{-1} ; M (C_2H_5OH) = 46 g.mol^{-1}.**

Notes: - in an athermic reaction the yield at equilibrium does not vary with the variation of temperature.
- Sulfuric acid acts as a catalyst in this reaction.

1. Preparation of the ester (E):

1.1. show that number of moles of ethanoic acid is 0.5 mol and that `of ethanol is 0.713 mol

1.2. Determine the molar composition of the mixture obtained at equilibrium

1.3. Determine the %yield of ester formed at equilibrium.

1.4. Show that the equilibrium constant (Kc) associated with this synthesis reaction is Kc = 3.93

1.5. Give the expression of Kc as a function of α (α: degree of conversion of ethanoic acid to ester) than deduce the value of α

1.6- before titration of ethanoic acid a cold water is added to the mixture:

1.6.1-Choose from the list below the glassware needed to perform the titration

PH-meter, magnetic stirrer, 10 ml graduated pipette, 100 ml beaker, 50 ml graduated burette

1.6.2- Indicate the two kinetic factors involved in this operation.

1.6.3- Specify the effect of each of these two factors on the kinetics of the esterification reaction

2. study of equilibrium state:

To study the thermal nature of this reaction, the same experiment is repeated for $T_2 = 70\ ^0C$ at constant volume and pressure. The number of mol of ethanoic acid remaining at equilibrium is 0.115 mol.

2.1. Verify that the esterification reaction is an athermic reaction.

2.2. At an instant "t " the amount of each product formed is equal to the double of each remained reactant

2.2.2-Show that the reaction mixture is not at equilibrium at the instant t

2.2.3. Specify in which direction the reaction moves to reach equilibrium.

2.3. Specify whether each of the following statements are true or false.

Proposition 1: Carrying out the same experiment in part 1, in the absence of sulfuric acid, does not affect α at an instant t before equilibrium.

Proposition 2: Carrying out the same experiment in part 1, in the absence of sulfuric acid, decreases the reaction half life.

Exercise 5 :Esterification reaction

In order to prepare ester E, we proceed as follows:

- We mix a volume V_1 = 35ml of primary alcohol (A) and a mass m of ethanoic acid (B)

The equation of the reaction is: $A + B \rightleftharpoons E + H_2O$

-The reaction medium is maintained at a temperature of 25 ºC. The curves C_1 and C_2 of document-1- represent the evolution of the number of moles of acid n (B) and the number of moles of the ester n (E) with time.

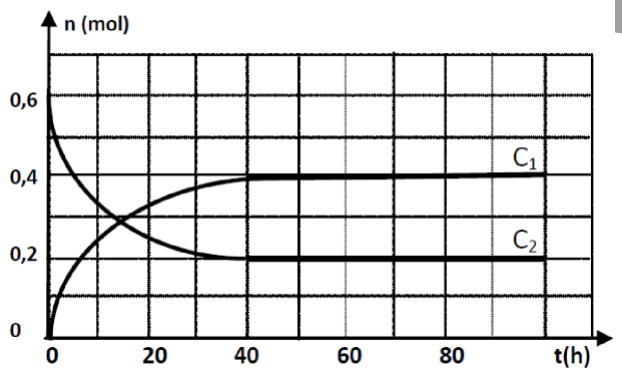
Given: d (alcohol A) = 0.789 g/ml. Molar mass in g.mol^{-1}: M (A) = 46; M(B) =60

1- preparation of reactional mixture:

1.1-show that the initial number of mol of A is 0.6 mol

1.2- calculate the mass m knowing the initial mixture of reactants is equimolar.

1.3--Among the two curves C1 and C2, indicate, with justification, the curve which represents the evolution of n (B) and that of n (E).



Document -1-

1.4-Referring to document-1- specify two characteristics of the synthesis reaction of ester (E).

2-Quantitative Analysis:

2.1-determine the molar composition of the mixture obtained at equilibrium.

2.2-show that the value of KC of this reaction is 4

2.3-at an instant t the molar composition of the reactants and products becomes equimolar

Verify the following statement:**"at this instant the system is shifted forward"**

2.4-determine using the graph the % yield of ester formed at equilibrium.

2.5-Explain whether each of the following statements is correct:

2.5.1- the reaction stops at 40h

2.5.2- if a catalyst is added to the mixture the %yield at each instant and at equilibrium will increases.

2.5.3-the % of A remained at equilibrium is 33.33%

2.6- We perform two experiments; the experimental conditions are given in the table of

document- 2- below:

Experiments	**n_0 of acid**	**n_0 of alcohol**	**T (°C)**	**Catalyst (H_2SO_4)**	**%yield at equilibrium**
1	0.6 mol	0.6 mol	80	Absent	66.6
2	0.6 mol	1.2 mol	80	absent	80

Suggest by referring to document 2 a method used to increase the yield of an esterification at equilibrium. Justify

Exercise 6: esterification reaction

A volume V_1 = 28,57 ml of ethanoic acid CH_3COOH and a volume V_2 = 29,11 ml of ethanol C_2H_5OH are introduced into around bottom flask, few mls of sulfuric acid are added the system is bheated at 60 ^{0}C and the following equilibrium takes place:

CH_3COOH + C_2H_5OH ⇌ $CH_3COOC_2H_5$ + H_2O

Compound	Ethanoicacid	Ethanol
Density	1,05 g/ml	0,79 g/ml
Molar mass	60 g/mol	46 /mol

I-Study of the esterification reaction

1.1Show that the initial mixture is equimolar.

1.2-Determine the molar composition of the mixture at equilibrium If n(ester)formed is 0.33 mol

1.3-at an instant a mixture of 0,2mol of ethanoic acid and 0.2 mol of ethanol, 0.3 mol of ester and 0.3 mol of water is obtained

1.3.1-verify that the system is not at equilibrium

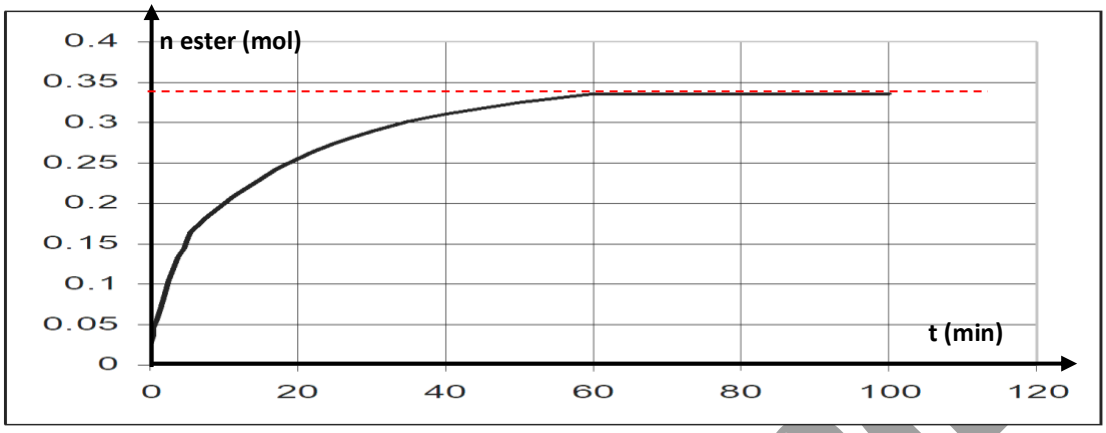
1.3.2- explain in which direction the reaction should proceed to attain equilibrium

1.4-identify using the above given the two kinetic factors used in the preparation of ester

II-Yield of esterification reaction

2.1-Show that % yield of estirification reaction is 66%.

2.2- the graph below shows the variation of number of mol of ester with time



Deduce using the graph two characteristics of this reaction

2.3- We give the following 3 propositions, justify if each proposition is correct or not:

2.3.1-the reaction stops at equilibrium

2.3.2-in absence of the catalyst, the yield of this reaction at equilibrium decreases

2.3.3-the conversion degree of acid at equilibrium is $\alpha = 0.67$