

2023-2024 عام الشهيد السعيد الاستاذ علي احمد سعد

إنه أستاذ الكيمياء المخلص والمضحي والوفي...الأستاذ المحبوب من تلاميذه قبل زمانه...ارتقي شهيدا على طريق القدس...على طريق الحق...ارتقي شهيدا كاتبا بدمائه الطاهرة قصة كيمياء العشق الالهي...قصة كرامة للاجيال...بعض من وفاء لأستاذنا...أن يصبح اسمه ونهاجه عنوان حب لدروسنا...فمنه ننهل كيمياء العطاء والوفاء والاباء...

لله شهيد الاستاذ علي سعد  
العهد بأن نحفظ الوصية...



لفلذات الاكباد وللزملاء  
الاعزة نقدم هذا العمل...  
والشكر والتقدير لمن  
لمن ساهم في انجازه...



Collection of Summaries and Exercises.

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2023-2024 عام الشهيد السعيد الاستاذ علي احمد سعد



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## **ACTION VERBS:**

1. **Analyze:** decompose a whole document into its constituent elements to make evident the variations.
2. **Calculate:** (compute) perform mathematical operation.
3. **State:** express written without explaining.
4. **Compare:** indicate the similarities and/or differences between 2 or more entities.
5. **Complete:** add what is missing
6. **Conclude:** reach to a decision.
7. **Determine:** reach to a decision or a result through logical reasoning, calculation....
8. **Describe:** express, using scientific language, to give the details of an observation, an experiment, a schema, an apparatus...
9. **Show:** prove something is evident by logical reasoning, experimenting, calculating....
10. **Deduce:** draw using logical reasoning new information from given or existing information.
11. **Draw out:** draw from a set of given relation, a role, a law,... without writing the reasoning.
12. **Distinguish (or Differentiate):** recognize or discern one thing from another according to particular traits.
13. **Explain:** clarify, make understandable a phenomenon, a result....
14. **Identify:** recognize something based on its characteristics or its properties, with justification.
15. **Interpret:** analyze and give significance to the result.
16. **Indicate:** designate or state something without justification.
17. **Justify:** give the arguments to prove something.
18. **Specify (precise):** indicate and justify.
19. **Pick out (extract):** select one or more information from a document.
20. **Verify:** confirm using arguments, logical reasoning... whether something is true or not.

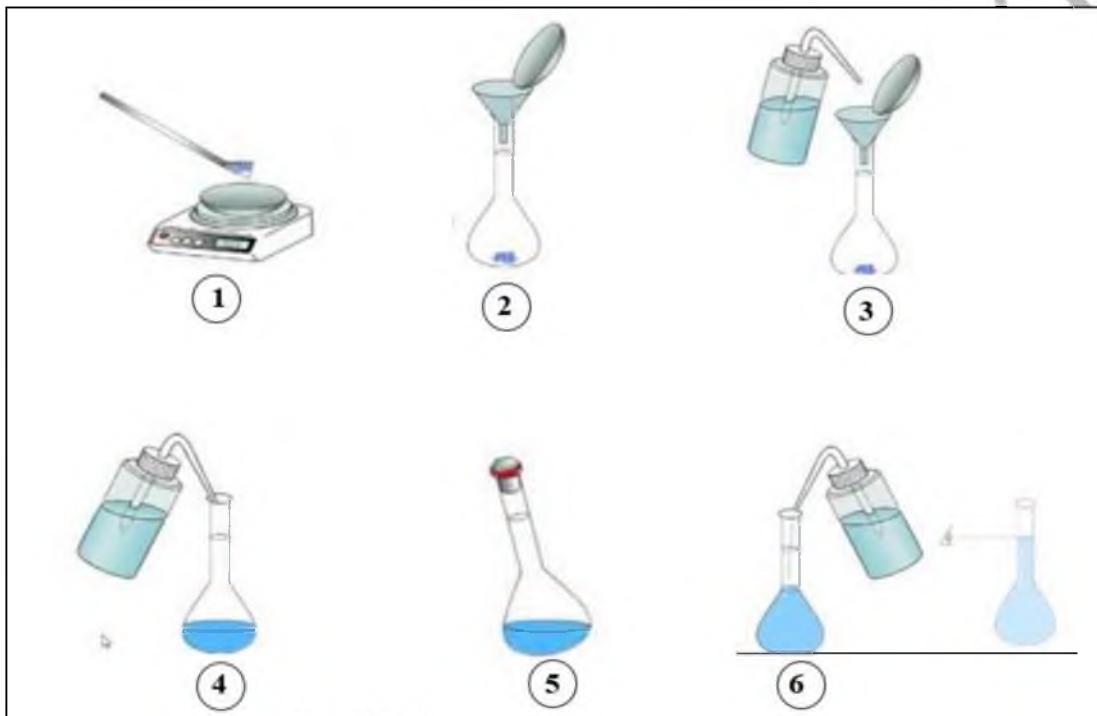


## PREPARATION OF SOLUTION

### I- Preparation of solution from solid sample: dissolution

#### 1- Steps:

- ✓ Rinse all the glassware with distilled water, and allow the watch glass to dry.
- ✓ Weigh using the watch glass, spatula , and digital balance, a mass  $m = \dots$  g of the solute.
- ✓ Introduce the weighed mass into ( $V_s$ ) mL volumetric flask using funnel.
- ✓ Wash the watch glass over the funnel and the funnel over the volumetric flask
- ✓ Add distilled water half the volumetric flask, stopper and swirl to dissolve the solute.
- ✓ Add distilled water to the line mark, stopper and shake to homogenize the solution.



#### 2- Material:

- Digital balance
- $V_s$  mL volumetric flask
- Watch glass and spatula
- Funnel
- Distilled water bottle.

#### 3- Calculations:

Upon preparation number of moles of dissolved solute is conserved:

$$n(\text{solute})_{\text{before preparation}} = n(\text{solute})_{\text{after preparation}}$$

$$\frac{m(\text{solute})}{M(\text{solute})} = C_s V_s$$

Or:

$$n(\text{solute}) = \frac{m(\text{solute})}{M(\text{solute})} \quad \Rightarrow C(\text{solute}) = \frac{n(\text{solute})_{\text{dissolved}}}{V(\text{solution})}$$

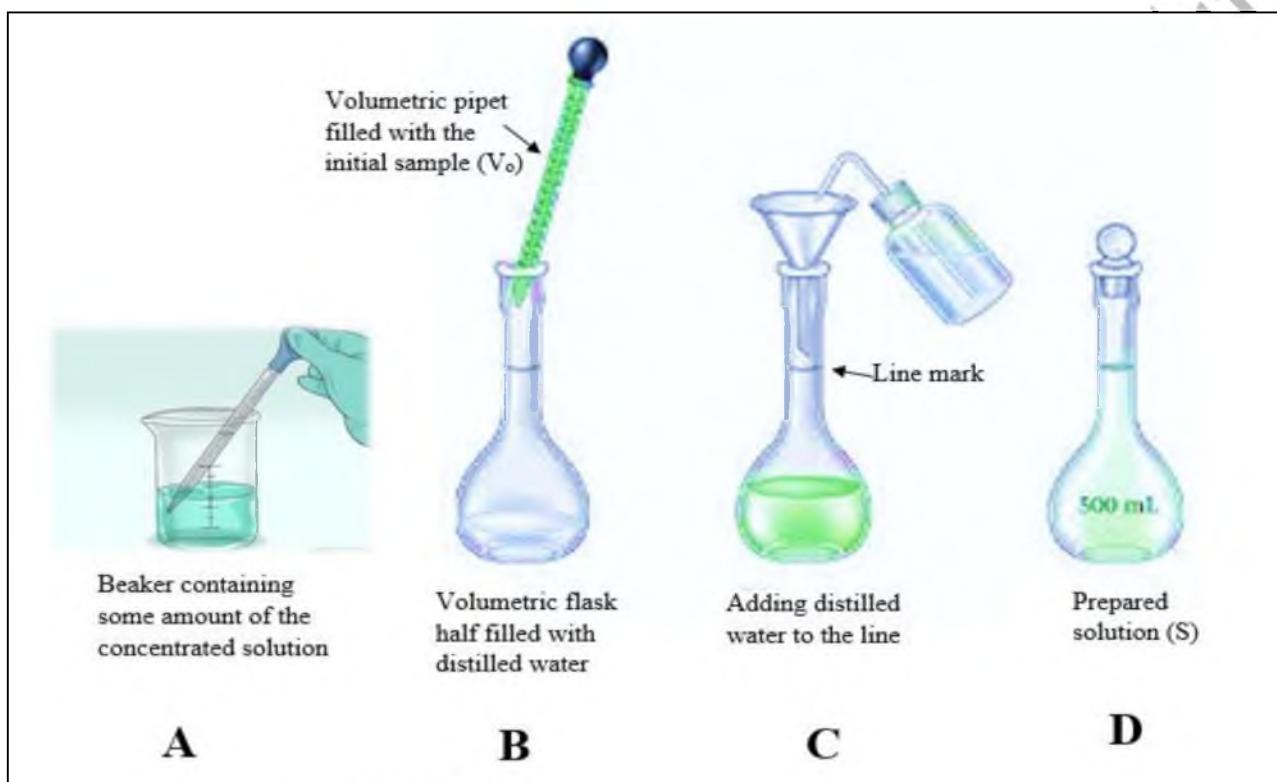


## II- Preparation of solution from initial solution ( $S_o$ ): dilution

### 1. Procedure of dilution:

Preparation of solution (S) from an initial solution ( $S_o$ )

- 1- Rinse all the glassware with distilled water, and then rinse the pipet with the initial solution ( $S_o$ ).
- 2- Take ( $V_o$  mL) of the initial solution ( $S_o$ ) using  $V_o$  mL volumetric (or graduated) pipet, and introduce them into ( $V_s$  mL) volumetric flask half filled with distilled water.
- 3- Add distilled water to the line mark, stopper and shake to homogenize the solution.



### 2. Material:

- $V_o$  mL volumetric pipet (you can choose graduated pipet when necessary)
- $V_s$  mL volumetric flask
- 50 mL beaker
- Pipet filler
- Distilled water bottle.

### 3. Calculations:

Upon dilution, number of moles of initially dissolved solute is conserved:

$$n(\text{solute}) \text{ taken by pipet} = n(\text{solute}) \text{ prepared in the volumetric flask}$$

$$C_o V_o = C_s V_s \quad \text{and} \quad f = \frac{C_o}{C_s} = \frac{V_s}{V_o}$$

### **Exercise 1:**

On the label of a bottle of a commercial Hydrochloric acid (HCl) solution ( $S_0$ ), the following information are written:

Density of the solution:  $1.2 \text{ g/cm}^3$ ; % by mass = 36 %.

12.5mL of ( $S_0$ ) is diluted 20 times to form a solution (S).

1. Determine the volume V of the solution (S) that should be prepared.
2. Among the following materials, choose the appropriate glassware needed to perform this operation:
  - volumetric pipet: 2 mL – 10mL -15 mL
  - graduated pipet: 2 mL – 10mL -15 mL
  - Sensitive balance.
  - Beaker: 50 mL – 100mL – 250 mL
  - volumetric flask: 50 mL – 100mL – 250 mL
  - Graduated cylinder ( 5 mL -10 mL – 20 mL )
  - Watch glass.
  - Rubber bulb ( pipet filler).
3. Determine  $C_0$  of the commercial solution knowing that  $M(\text{HCl}) = 36.5 \text{ g/mol}$ .

### **Exercise 2:**

One liter of solution (X) of iron II hepta hydrated  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  with concentration  $1\text{mol.L}^{-1}$  is to be prepared.

Given: Molar masses in g/mol of: Fe = 56, S = 32, O = 16, H = 1.

#### **1. Preliminary study:**

- 1.1. Calculate the mass of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  crystals needed for the preparation of solution (X).
- 1.2. **Describe** the preparation procedure of solution (X).

#### **2. Dilution of the solution (X)**

During a laboratory session, it is required to prepare 100 mL of solution (Y) from (X) with concentration  $0.1 \text{ mol.L}^{-1}$ .

The following material are available:

- |   |   |                        |
|---|---|------------------------|
| -Volumetric flasks: 50ml-100ml-250ml and 1L | - Watch glass   | - Beakers : 50ml-100ml |
| - Digital Balance                           | - Volumetric Pipettes with pipet filler: 10ml-20ml-25ml | - Spatula              |
| - Funnel                                    | - Graduated pipettes: 20ml                              |                        |

- 2.1. Determine the value of the folds of dilution of solution (Y).
- 2.2. Deduce the volume needed to be taken to prepare the solution (Y).
- 2.3. Choose the appropriate glassware to prepare (Y).

### **Exercise 3:**

It is required to prepare a hydrochloric acid solution (S) by diluting a sample of an initial mother solution ( $S_0$ ) 100 times.

- 1- Choose from the list below the appropriate glassware needed for this preparation.

#### **Available glassware:**

- Volumetric pipet : 1ml – 2mL – 5 mL – 10 mL
- Graduated pipet: 1ml – 2mL – 5 mL – 10 mL
- Volumetric flask: 50 mL – 250 mL - 500 mL
- Beaker: 50 mL – 100mL – 250mL

- 2- **List** the steps of the preparation procedure.

## REVISION SHEET

### **Exercise 1                      Study of the reaction of formic acid with bromine**

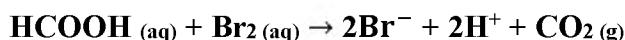
Formic (methanoic) acid (HCOOH) is a colorless corrosive liquid that is secreted by ants and other insects. It is commonly used in paper and textile industries and in the manufacture of insecticides...

The aim of this exercise is to know some of the uses of formic acid in organic synthesis and to study the kinetic of its reaction with bromine liquid at 25°C.

Given: molar volume of a gas at the conditions of this exercise is  $V_m = 24 \text{ L.mol}^{-1}$ .

#### Preliminary study

In aqueous solution, formic acid reacts slowly with molecular Bromine according to the following equation:



Aqueous bromine solution has a red brown color, while hydrobromic acid ( $\text{H}^+ + \text{Br}^-$ ) solution is colorless.

At  $t = 0$ , 50 mL of aqueous solution of bromine of molar concentration  $C_1 = 0.024 \text{ mol.L}^{-1}$  are mixed with 50 mL of formic acid solution of molar concentration  $C_2 = 0.030 \text{ mol.L}^{-1}$ .

1. Determine the concentration of each reactant in the mixture at  $t = 0$ .
2. Determine the limiting reactant.
3. Deduce the number of moles of  $\text{CO}_2$  gas produced when the reaction ends.
4. Prove the following relation:

$$[\text{Br}_2]_t = 0.012 - 4.16 \times 10^{-4} \times V(\text{CO}_2)_t$$

Where  $[\text{Br}_2]_t$  is the molar concentration of Bromine remained at instant  $t$  and  $V(\text{CO}_2)_t$  is the volume of  $\text{CO}_2$  formed at the same instant  $t$  in mL.

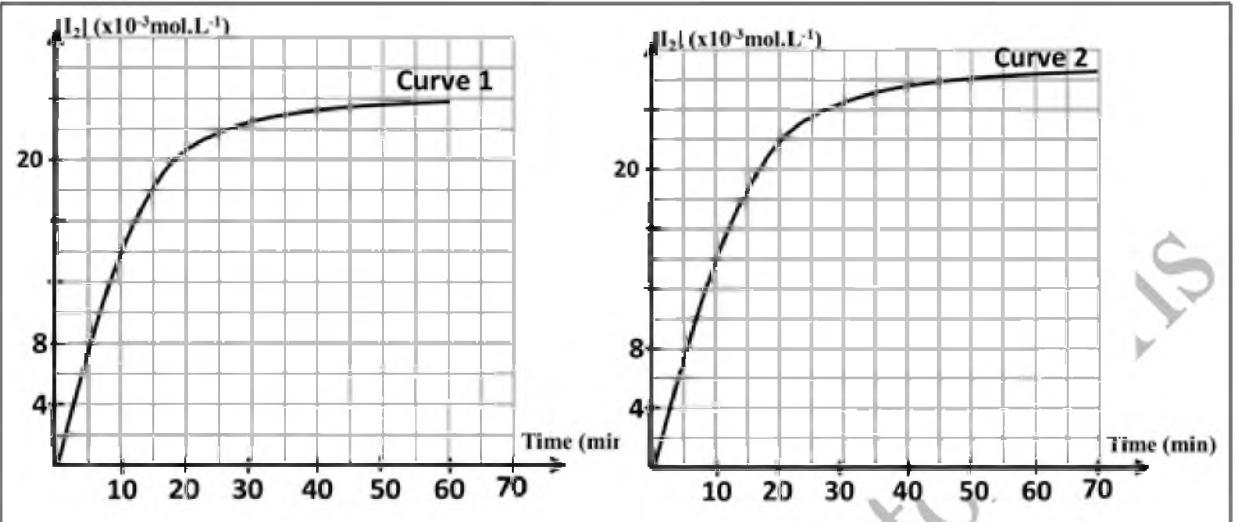
### **Exercise 2                      Oxidation of Iodide Ions by Hydrogen Peroxide**

It is suggested to study the oxidation of iodide ions by hydrogen peroxide solution. This slow reaction takes place according to the following equation:



At time  $t = 0$ , a volume  $V_1 = 60 \text{ mL}$  potassium iodide solution of concentration  $C_1 = 0.1 \text{ mol.L}^{-1}$  is mixed, in a beaker, with a volume  $V_2 = 40 \text{ mL}$  of an acidified hydrogen peroxide solution of concentration  $C_2 = 0.06 \text{ mol.L}^{-1}$ .

Given: molar mass of iodine ( $\text{I}_2$ ) in  $\text{g.mol}^{-1}$  is  $M(\text{I}_2) = 254$



**Doc.1:** concentration of iodine formed versus time

### 1. preliminary Study

- 1.1.Calculate the concentration of iodide ions,  $[I^-]_0$ , and of hydrogen peroxide,  $[H_2O_2]_0$ , in the mixture at  $t = 0$ .
- 1.2.Determine the limiting reactant knowing that  $H_3O^+$  is in excess.
- 1.3.Choose the curve that represents the variation of the concentration of  $I_2$  as a function of time. Justify your answer.
- 1.4.Prove the following relation:  $[H_2O_2]_t = 0.024 - 0.039 \times m(I_2)_t$ , where  $[H_2O_2]_t$  is the concentration of hydrogen peroxide at time  $t$  in the reaction system in  $\text{mol.L}^{-1}$  and  $m(I_2)_t$  represents the mass of iodine formed at time  $t$  in g.

#### Note

**There are many ways to ask about the limiting reactant:**

- 1- **In normal cases:** Determine the limiting reactant.
- 2- **If one of the reactants has color:** Specify the color of the final solution.
- 3- **If one of the reactants has acidic or basic nature:** Specify the acid-base nature of the reaction medium at the end of the reaction.
- 4- **If one if the reactants is solid:** specify whether the final reaction mixture is homogenous or heterogeneous.

# Titration

It is an experimental procedure that aims to determine the concentration of a solution.

## 1. Titration set-up:

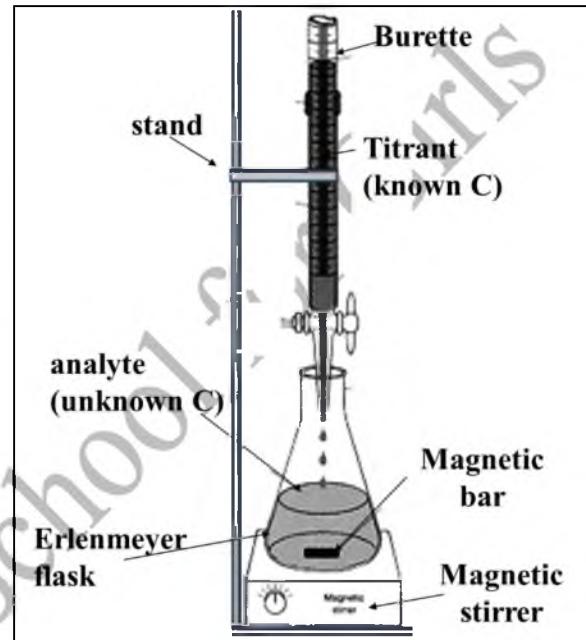
Look at the adjacent figure

## 2. Titration reaction:

Titration depends on a balanced, complete and rapid reaction between the analyte (solution of unknown concentration) and the titrant (solution of known concentration).

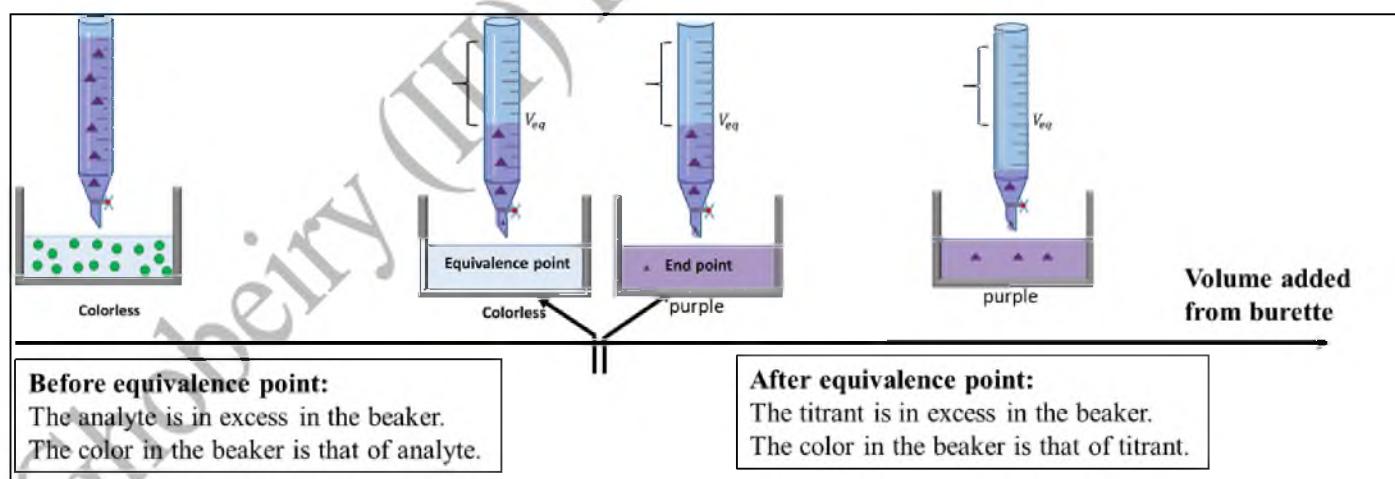
## 3. Characteristics of equation of titration reaction:

- Rapid
- Complete
- Unique



## 4. Titration time line:

Consider the titration between  $\text{MnO}_4^-$  (purple) and  $\text{Fe}^{2+}$  ions (pale green : almost colorless):



- **Equivalence point:** A point during titration where the amount (in mol) of the titrant added from burette is equal to the amount of analyte (in mol) present in the beaker in stoichiometric ratios.

$$\frac{n(\text{Fe}^{2+})_{\text{initially present in the beaker}}}{5} = \frac{n(\text{MnO}_4^-)_{\text{added to reach equivalence}}}{1}$$
$$\frac{C \times V_{\text{Fe}^{2+}}}{5} = \frac{[\text{MnO}_4^-] \times V_E}{1}$$

**End point of titration:** the point at which the color changes in the beaker. At this point the titration stops, the titrant is slightly in excess.

### Exercise 1

### Titration of an iodine solution ( $I_2$ )

The aim of this exercise is to determine the concentration  $C_o$  of a commercial iodine solution ( $S_o$ ) by thiosulfate solution (S).

**Given: molar masses in g.mol<sup>-1</sup> are: Na =23; S= 32; O = 16 ; H = 1.**

$$E^\circ (I_2/I) = 0.54; \quad E^\circ (S_4O_6^{2-}/S_2O_3^{2-}) = 0.08 \text{ V}$$

#### 1. Preparation of thiosulfate solution (S)

Solution (S) of thiosulfate is prepared by dissolving a mass  $m = 4.5 \text{ g}$  of  $Na_2S_2O_3 \cdot 5H_2O$  in 250 mL distilled water. The prepared solution has a concentration ( $C_s$ ).

1.1.List the materials that are needed for this preparation procedure.

1.2.Calculate the concentration  $C_s$  of solution (S).

#### 2. Titration of iodine solution.

In order to determine the concentration of a commercial iodine solution, a volume  $V = 10 \text{ mL}$  of solution ( $S_o$ ) is diluted 100 times to prepare solution ( $S_1$ ).

A volume  $V = 10 \text{ mL}$  of solution  $S_1$  is titrated by the sodium thiosulfate solution (S). Equivalence point is reached when 7.25 mL of solution S were added.

2.1.Label the titration set up. Name the glassware needed to take 10 mL of solution ( $S_1$ ) to be titrated.

2.2.Write the characteristics of titration reactions.

2.3.Write the equation of the titration reaction.

2.4.Show that the reaction is complete.

2.5.Indicate how to detect the equivalence point in this case.

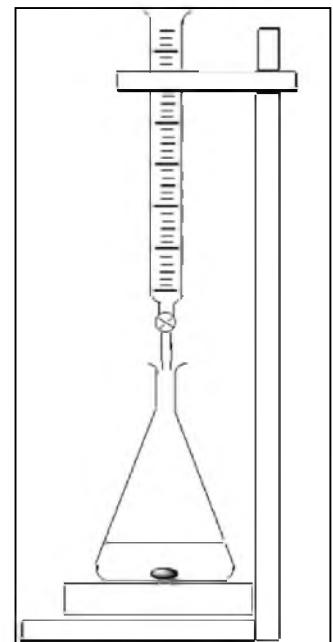
2.6.Explain whether the addition of water before carrying out titration affects the volume of solution (S) needed to reach equivalence.

2.7.Calculate the concentration of solution ( $S_1$ ).

2.8.Deduce the concentration  $C_o$  of solution ( $S_o$ ).

2.9.Determine the percentage by mass of iodine in  $S_o$  solution. Given:

$M(I_2) = 254 \text{ g/mol}$ ; density of  $S_o$  solution is  $1.02 \text{ g/cm}^3$ .



## Exercise 2

### Volumetric Titration

Oxygenated water, is a solution of hydrogen peroxide of formula  $\text{H}_2\text{O}_2$ , it is commercially used as a disinfectant liquid. .

**Document 1** represents the label of a bottle of the commercial solution of oxygenated water ( $\text{S}_0$ ).

The objective of this exercise is to verify the percentage by mass of hydrogen peroxide in ( $\text{S}_0$ ).

**Given:** the redox reaction that involves the pairs:  $\text{MnO}_4^-/\text{Mn}^{2+}$  and  $\text{O}_2/\text{H}_2\text{O}_2$ .

Species	$\text{H}_2\text{O}_2$	$\text{MnO}_4^-$	$\text{Mn}^{2+}$
Color	Colorless	Violet	Colorless

#### Commercial solution $\text{S}_0$ of hydrogen peroxide ( $\text{H}_2\text{O}_2$ )

- Percentage by mass = 3%
- Density = 1012 g/L
- Molar mass of ( $\text{H}_2\text{O}_2$ ) = 34 g.mol<sup>-1</sup>

#### Document 1

#### 1. Dilution of the commercial solution $\text{S}_0$

From the commercial solution  $\text{S}_0$  of hydrogen peroxide, we take a certain volume  $V_0$  which is diluted 10 times to prepare 50mL of a dilute solution S.

1.1. Determine the volume  $V_0$ .

1.2. Three sets of glassware are available in **document-2**.

Set-1	Set-2	Set-3
-Volumetric flask (50mL) -Graduated pipet (5mL) -Beaker 50 mL	-Graduated cylinder -Volumetric pipet (5mL) -Beaker 50 mL	-Volumetric flask (50mL) -Volumetric pipet (5mL) -Beaker 50 mL

#### Document 2

Choose, with justification, the most convenient set necessary to prepare the diluted solution S.

#### 2. Titration of the prepared solution S with solution of potassium permanganate

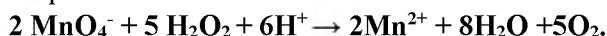
To perform the titration of the dilute solution of hydrogen peroxide, 10 mL of solution (S) of  $\text{H}_2\text{O}_2$  was titrated with potassium permanganate solution ( $\text{K}^{+}_{(aq)}$ ,  $\text{MnO}_4^{-}_{(aq)}$ ) of concentration  $C_1=0.02\text{mol.L}^{-1}$ .

To acidify the medium, few drops of concentrated sulfuric acid ( $2\text{H}^+$ ,  $\text{SO}_4^{2-}$ ) are added.

The volume of the potassium permanganate solution added to reach equivalence point is 17.4mL.

**Document-3** shows the setup of titration.

The net balanced equation of the titration reaction is:



2.1. Referring to document 3

2.1.1. Label glassware 1 and glassware 2.

2.1.2. Give the name of the solutions present in glassware 1 and 2.

2.2. Determine the concentration of solution (S), then show that the concentration of ( $\text{S}_0$ ) is  $C_0=0.87\text{mol.L}^{-1}$ .

2.3. Deduce if the indication on the label (% by mass) of the commercial solution bottle is verified.

2.4. Explain how to detect equivalence point in this case.

2.5. Explain whether the addition of distilled water in glassware 2 before carrying out titration affects  $V_E$ .

2.6. Why do we use diluted solution:

2.6.1. In the Erlenmeyer flask.



Document-3

### 2.6.2. In the burette.

2.7. Choose, with justification, the correct answer.

2.7.1. The color of the solution in glassware-2, after adding 20mL from the above solution is:

- a- Violet      b- Light pink      c- Colorless.

2.7.2. The chemical species present in the solution in glassware-2 before equivalence point are:

- a-  $Mn^{2+}$ ,  $H_2O$ ,  $H^+$ ,  $SO_4^{2-}$ ,  $K^+$ ,  $H_2O_2$ .  
b-  $MnO_4^-$ ,  $H_2O$ ,  $Mn^{2+}$ ,  $H^+$ ,  $SO_4^{2-}$ ,  $K^+$ ,  $H_2O_2$ .  
c-  $H_2O$ ,  $O_2$ ,  $H^+$ ,  $SO_4^{2-}$ ,  $K^+$ ,  $H_2O_2$ ,  $Mn^{2+}$ .

## Exercise 3

### Flash (Madar)

Flash is used to clean and disinfect toilets. It contains concentrated hydrochloric acid solution ( $H^+ + Cl^-$ ). The aim of this exercise is to determine the percentage by mass of HCl in the commercial flash solution.

Given:

- Molar mass in  $g \cdot mol^{-1}$  of HCl is  $36.5 \text{ mol} \cdot L^{-1}$ .
- Density of Flash solution is  $\rho = 1.22 \text{ Kg} \cdot L^{-1}$ .

#### 1. Preparation of a Dilute Solution (S).

A sample of a commercial flash solution ( $S_0$ ) is used to prepare solution (S) which is 100 times diluted. The volume of the prepared solution is  $V_S = 500 \text{ ml}$ .

1.1. Show that the volume of the sample taken from the Flash commercial solution is  $V_0 = 5 \text{ mL}$ .

1.2. Choose from **document-1** the suitable set of glassware to perform the most precise dilution.

Justify.

Set-1	Set -2	Set-3	Set-4
• 5 mL graduated pipet • 500 mL beaker	• 5 mL volumetric pipet • 500 mL volumetric flask	• 5 mL graduated pipet • 500 mL volumetric flask	• 5 mL graduated cylinder • 500 mL beaker

Document-1

1.3. Describe the procedure of dilution that is performed in this case.

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

In order to determine the concentration of solution (S), a volume  $V_a = 20 \text{ mL}$  of solution (S) is titrated with potassium hydroxide solution ( $Na^+ + HO^-$ ) of concentration  $C_b = 0.1 \text{ mol} \cdot L^{-1}$  in the presence of a suitable indicator. The titration apparatus is shown in **document-2**. The volume needed to reach equivalence point is  $V_{bE} = 12 \text{ mL}$ . Equation of titration reaction is :  $H^+ + HO^- \rightarrow H_2O$ .

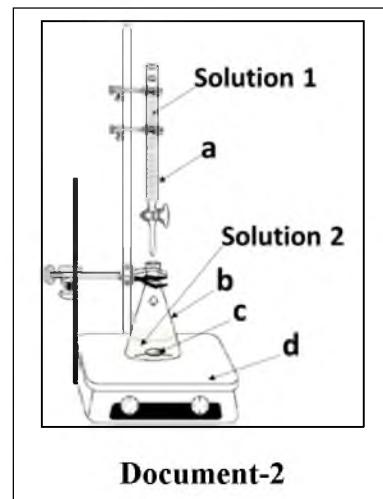
2.1. Give the name of solutions 1 and 2.

2.2. Name the materials a,b,c, and d.

2.3. Before carrying out titration, some distilled water is added to the volume  $V_a$ . Specify whether the added water affects the equivalence volume  $V_{bE}$ .

2.4. Determine the concentration of solution (S):  $C_s$ .

2.5. A student performed the above experiment as directed by his teacher, but he rinsed **material (a)** of document-1 with only distilled water before filling it with



Document-2

solution 1. Choose with justification the correct answer concerning the volume needed to reach equivalence in this case:  $V_{bE}$

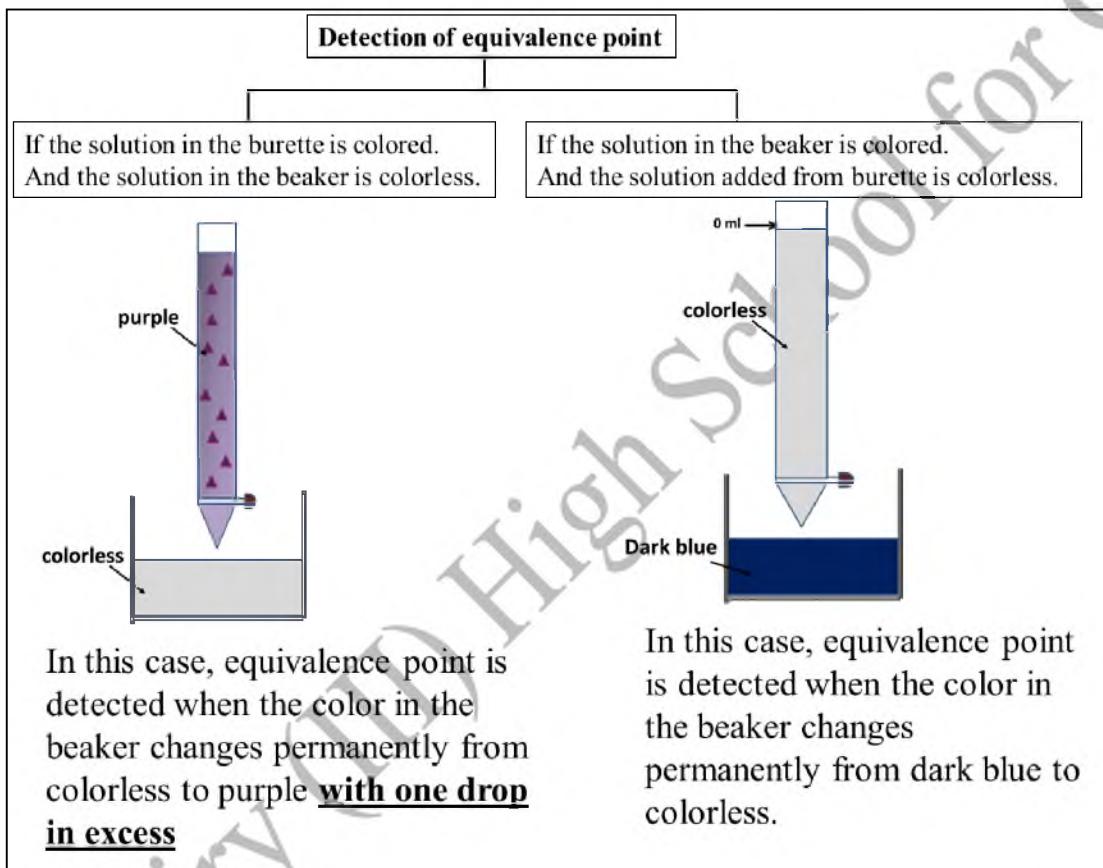
- a)  $V_{bE} = 12 \text{ mL}$       b)  $V_{bE} > 12 \text{ mL}$       c)  $V_{bE} < 12 \text{ mL}$

### 3. Determination of percentage mass of HCl in Flash

3.1.What is the concentration  $C_o$  of flash solution?

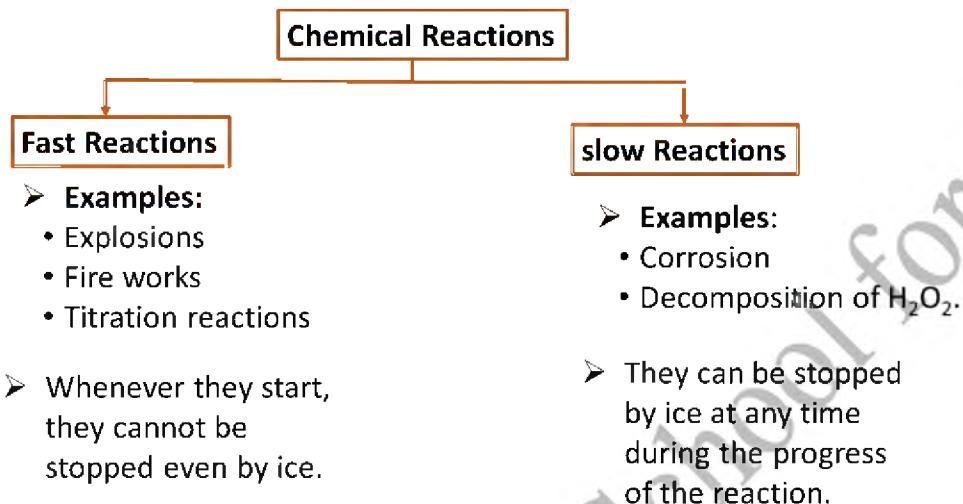
3.2.Determine the percentage mass of HCl in the Flash solution; %m(HCl).

**Note: How to detect the equivalence point during titration?**

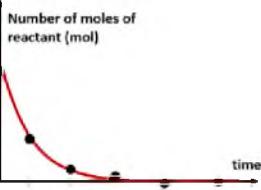
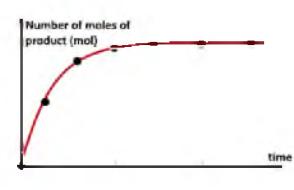


# UNIT 1- CHAPTER 1:CHEMICAL KINETICS

## Introduction

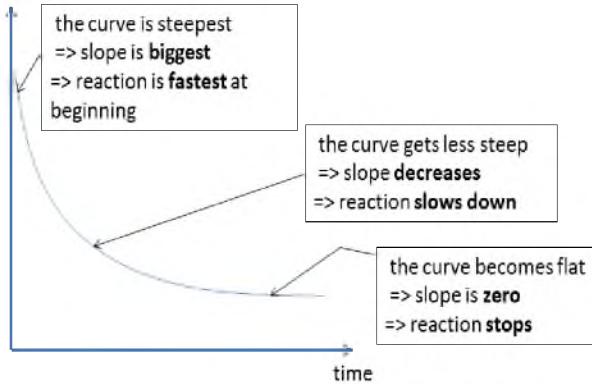


## Variation of amounts of reactants and products during a chemical reaction.

Variation of reactant during the progress of reaction.	Variation of product during the progress of reaction.
Amount of reactant decreases as time passes.	Amount of product increases as time passes.
The corresponding curve is a decreasing curve. 	The corresponding curve is an increasing curve. 
At $\infty$ , the amount of reactant will be zero if the reactant is limiting.	At $\infty$ , the amount of product reached is the maximum amount, and it can be found by S.R from limiting reactant.

### A. Disappearance of a reactant versus time

$n(\text{Reactant})$  or  
[reactant]



### B. Formation of a product versus time

$n(\text{product})$  or  
[product]

the curve becomes flat  
=> slope is zero  
=> reaction stops

the curve is steepest  
=> slope is biggest  
=> reaction is fastest at beginning

the curve gets less steep  
=> slope decreases  
=> reaction slows down

time

#### A.1. Average rate of disappearance of reactant:

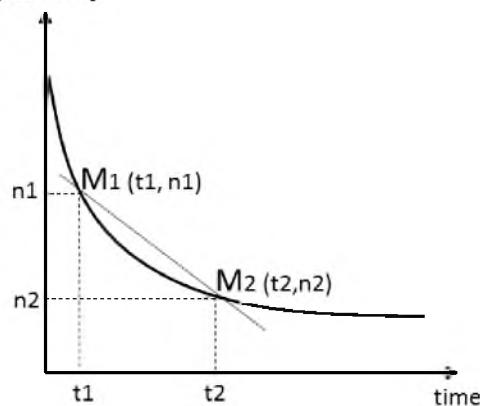
**Definition:** It is equal to the negative slope of the secant ( $M_1M_2$ ) on the curve at points of abscissas  $t_1$  and  $t_2$  respectively.

$$\bar{r}(R) = -\frac{\Delta n(R)}{\Delta t} = -\left(\frac{n(R)_2 - n(R)_1}{t_2 - t_1}\right)$$

Or:

$$\bar{r}(R) = -\frac{\Delta [R]}{\Delta t} = -\left(\frac{[R]_2 - [R]_1}{t_2 - t_1}\right)$$

$n(\text{Reactant})$  or  
[reactant]



#### B.1. Average rate of formation of a product:

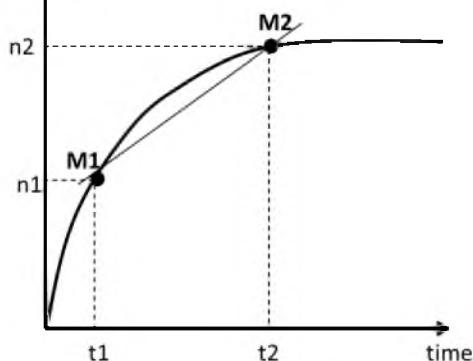
**Definition:** It is equal to the positive slope of the secant ( $M_1M_2$ ) on the curve at points of abscissas  $t_1$  and  $t_2$  respectively.

$$\bar{r}(P) = \frac{\Delta n(P)}{\Delta t} = \left(\frac{n(P)_2 - n(P)_1}{t_2 - t_1}\right)$$

Or:

$$\bar{r}(P) = \frac{\Delta [P]}{\Delta t} = \left(\frac{[P]_2 - [P]_1}{t_2 - t_1}\right)$$

$n(\text{product})$  or  
[product]

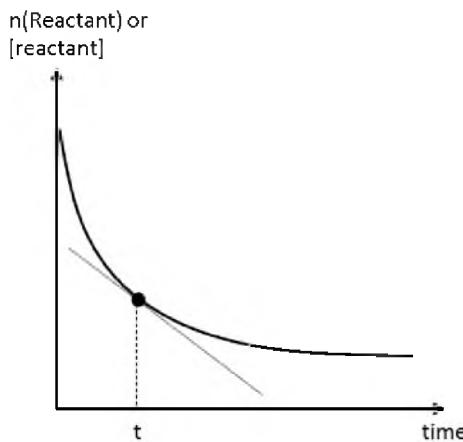


### A.2. Instantaneous rate of disappearance of a reactant:

**Definition:**

- It is equal to the negative slope of the tangent to the curve at point of abscissa t.

$$r(R)_t = - \frac{dn(R)}{dt}$$

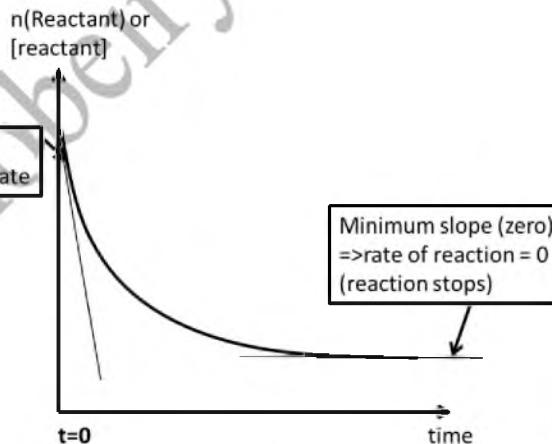


### A.3. Initial rate of disappearance of a reactant:

**Definition:**

- It is equal to the negative slope of the tangent to the curve at point of abscissa t=0.

$$r(R)_{t=0} = - \frac{dn(R)}{dt}$$

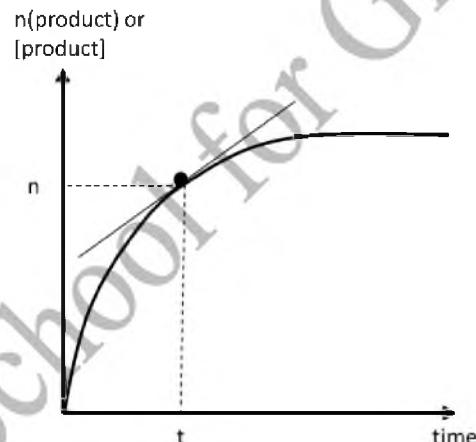


### B.2. Instantaneous rate of formation of a product:

**Definition:**

- It is equal to the slope of the tangent to the curve at point of abscissa t.

$$r(P)_t = \frac{dn(P)}{dt}$$

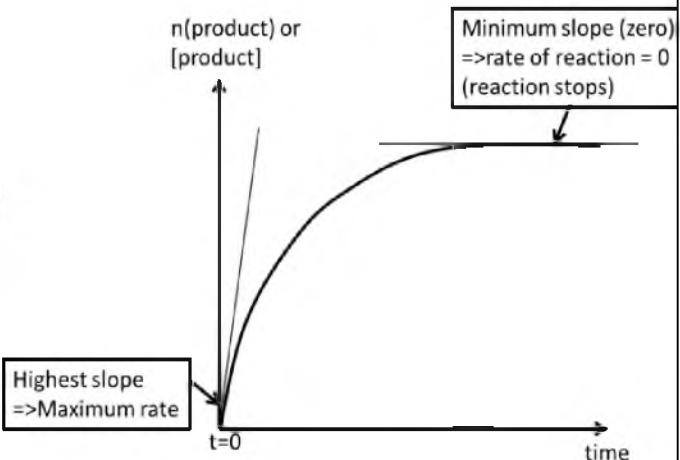


### B.3. Initial rate of formation of a product:

**Definition:**

- It is equal to the slope of the tangent to the curve at point of abscissa t=0.

$$r(P)_{t=0} = \frac{dn(P)}{dt}$$



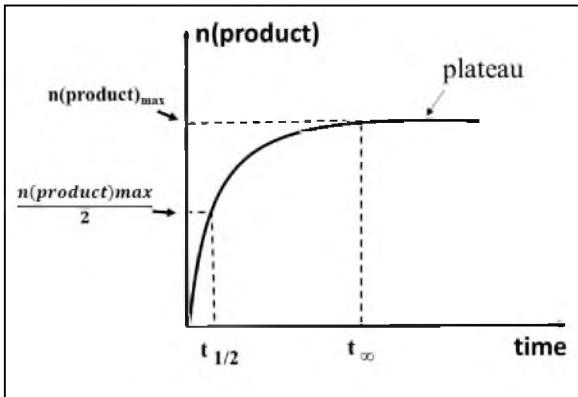
## Half-life of a reaction

### A- If the curve given is increasing:

**Definition:** half-life of a reaction is the time needed for a product to reach half its maximum value.

#### Determination of half-life:

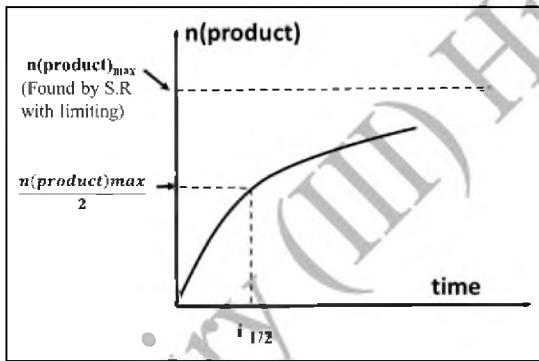
**Case 1:** If the curve becomes constant at  $\infty$



#### Steps of determination:

1. Definition
2. Locate on graph by dotted lines maximum amount of the product, and half max amount.
3. Locate graphically  $t_{1/2}$ .

#### Case 2: If the curve doesn't reach maximum



#### Steps of determination:

1. Definition
2. Calculate  $n(\text{product})_{\text{max}}$  by S.R.
3. Locate on graph by dotted lines maximum amount of the product, and half max amount.
4. Locate graphically  $t_{1/2}$ .

Important note:  $t_{1/2} < \frac{t_\infty}{2}$

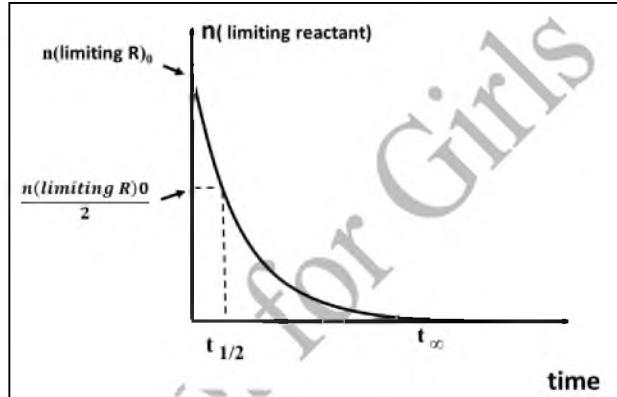
Because the rate of reaction decreases over time due to the consumption of reactants. For this, the first half amount of the product is formed faster (in less time) than the second half.

### B-If the curve given is decreasing:

**Definition:** half-life of a reaction is the time needed for the limiting reactant to reach half its initial value.

#### Determination of half-life:

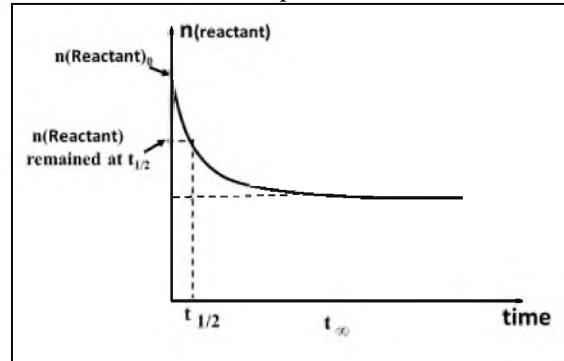
**Case 1:** If the curve corresponds to limiting reactant



#### Steps of determination:

1. Definition
2. Locate on graph by dotted lines:  $\frac{n(\text{lim Reactant})_0}{2}$
3. Locate graphically  $t_{1/2}$ .

#### Case 2: If the curve corresponds to the reactant in excess:



#### Steps of determination:

1. Relation between reactant in excess (E.R) and limiting reactant (L.R): **example:**  

$$n(E.R)_{\frac{t_1}{2}} = n_o(E.R) - n(E.R)_{\text{reac at } \frac{t_1}{2}}$$

$$n(E.R)_{\frac{t_1}{2}} = n_o(E.R) - n(L.R)_{\text{reac at } \frac{t_1}{2}}$$

$$n(E.R)_{\frac{t_1}{2}} = n_o(E.R) - \frac{n_o(L.R)}{2}$$
2. Locate graphically  $t_{1/2}$  from the amount of excess reactant remained at  $t_{1/2}$

## **UNIT 1- CHAPTER 2: KINETIC FACTORS**

### **Definition of Kinetic Factors:**

*A kinetic factor is a parameter that changes the rate of a chemical reaction.*

In this chapter the studied kinetic factors are:

- Temperature
  - Concentration of reactant (s).
  - Catalyst
  - Surface area of contact between reactants.

### 1-Influence of temperature

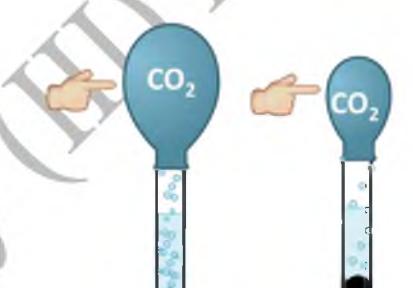
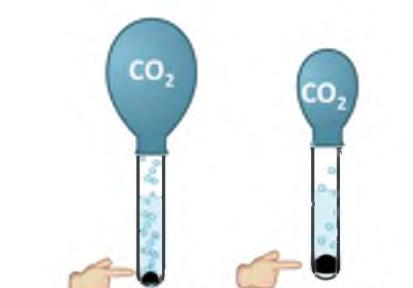
*The reaction rate increases as temperature increases.*

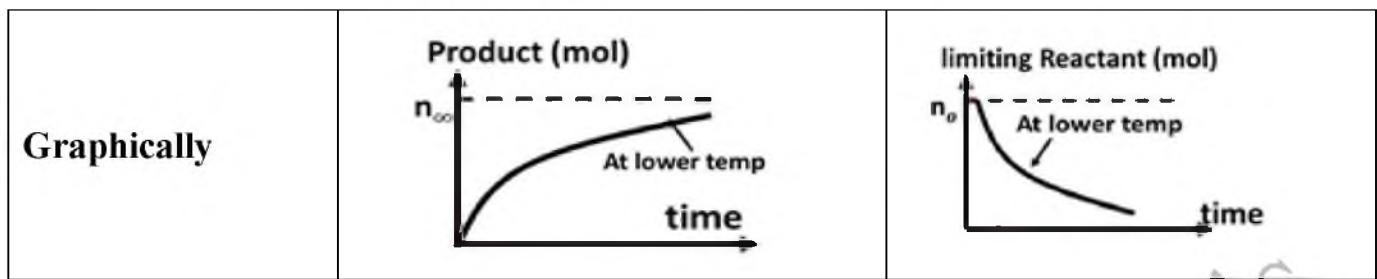
*Explanations: When the temperature increases molecules move faster in the solution. When molecules collide, the shock is more violent and atomic bonds break more easily. This promotes the appearance of products.*

**Example:** Consider the experiment performed at two different temperatures involving the reaction:



**Complete the graphs and comparison in each of the following tables.**

	Focusing on the product	Focusing on the reactant
Illustrating image		
Mathematically :	At any time before $\infty$ : $n(CO_2)p$ $n(CO_2)p$ at high temp      at low temp	At any time before $\infty$ : $n(CaCO_3)rem$ $n(CaCO_3)rem$ at high temp      at low temp



## 2 – Influence of Catalyst

*Definition of a catalyst: A catalyst is a substance that increases the rate of a chemical reaction without being itself changed.*

**Example:** Consider the following the reaction:



Complete the graphs and comparison in each of the following tables.

	<b>Focusing on the product</b>	<b>Focusing on the reactant</b>
<b>Illustrating image</b>	 <b>With catalyst</b> <b>Without catalyst</b>	 <b>With catalyst</b> <b>Without catalyst</b> <div style="border: 1px solid black; padding: 5px; width: fit-content;">           The reactant is invisible in this case because it is colorless.         </div>
<b>Mathematically</b>	At any time before $\infty$ : $n(\text{O}_2)p$ <b>with catalyst</b> <b>without catalyst</b>	At any time before $\infty$ : $n(\text{H}_2\text{O}_2)\text{rem}$ <b>with catalyst</b> <b>without catalyst</b>
<b>Graphically</b>		

**Note:** concentration of catalyst is also a kinetic factor: when the concentration of catalyst increases, rate of reaction increases.

### 3- Influence of concentration of reactant(s)

The rate of product formation (and therefore the disappearance of the reagents) increases with the initial concentration of the reagents.

*Explanations: A chemical reaction occurs only when the reactants collide. As the concentration of the reactants is increased, the molecules are closer to each other; the risk of collision (and therefore of reaction) is greater.*

**Example:** Consider the experiment performed involving the reaction:



If a **new** experiment is done by performing the reaction at the same initial conditions but by changing the concentration of a reactant, We have the following cases:

Complete the graphs in each of the following tables.

Changed factor	Effect on the rate of reaction	Curve corresponding to product	Curve corresponding to reactant
$[A]_0$ is increased	Rate increases		
$[A]_0$ is decreased	Rate decreases		
$[B]_0$ is decreased	Rate decreases		.....
$[B]_0$ is increased	Rate increases		.....

#### 4 - Influence of the contact surface of a solid

The rate of a chemical reaction involving a solid reactant increases when the contact surface of this solid increases.

**Explanations:** The larger the contact surface, the more molecules of the other reagents can attach to the solid; a larger number of reactions can take place simultaneously.

#### **Remark:**

#### **How to block a kinetic reaction?**

There are two ways to block the kinetic reaction:

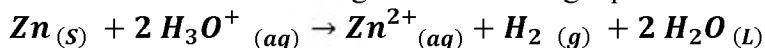
Method	Way 1	Way 2
Effect	Blocking the kinetic reaction (occurring in the beaker)	Blocking the kinetic reaction (occurring in the beaker)
Kinetic factor(s) involved	<ul style="list-style-type: none"><li>Temperature decreasing temperature blocks the reaction.</li></ul>	<ul style="list-style-type: none"><li>Temperature: decreasing temperature blocks the reaction.</li><li>Concentration of reactant(s): pouring the reaction mixture in icy water decreases the concentration of reactant(s) (case of dilution).</li></ul>

## Exercise 1

## Reaction Between Hydrochloric Acid and Zinc Metal

(2010 S<sub>2</sub> GS- Exercise 3)

Hydrochloric acid reacts with zinc according to the following equation:



At time t=0, a mass m of pure zinc granules is introduced into a beaker containing a volume V<sub>1</sub> = 50mL of hydrochloric acid solution (S) of molar concentration C.

A release of gas starts to follow the evolution of this reaction, the volume of hydrogen gas V(H<sub>2</sub>) is measured under the conditions where molar volume V<sub>m</sub> is 25 L.mol<sup>-1</sup>.

The results are given in the table of **document-1**.

t (s)	50	100	200	300	400	500	700	900	1200	....	1500	2000
V(H <sub>2</sub> ) mL	25	50	85	117	142	162	195	220	240	....	250	250

**Document-1**

When the gas release ceases, a solid remains in the beaker.

### 1. Preparation of solution (S)

Solution (S) is prepared by diluting 25 times a commercial solution of hydrochloric acid of concentration C<sub>0</sub>.

Choose, by justifying, from the list given below, the most accurate glassware to carry out this preparation.

#### List of available material:

- 50, 100, 250 mL beakers
- 50, 100, 250 mL volumetric flasks
- 5, 10, 25 mL volumetric pipets
- 5, 10, 25 mL graduated pipets
- 50, 100, 250 mL Erlenmeyer flasks
- funnel
- watch glass and spatula
- pipet filler

### 2. Preliminary Study

2.1. Extract from the experimental study described before, the sentence that shows that H<sub>3</sub>O<sup>+</sup> ion, is the limiting reactant of this reaction.

2.2. Show that the concentration C is equal to 0.4 mol.L<sup>-1</sup>. Deduce the concentration C<sub>0</sub> of the commercial solution.

### 3. Kinetic of this reaction:

3.1. Show that, at any time t, the concentration of H<sub>3</sub>O<sup>+</sup> ions in mol.L<sup>-1</sup>, [H<sub>3</sub>O<sup>+</sup>]<sub>t</sub>, and the volume of H<sub>2</sub> gas in mL, V(H<sub>2</sub>)<sub>t</sub>, are related by the following relation:

$$[\text{H}_3\text{O}^{+}]_t = 0.4 - 1.6 \times 10^{-3} \times V(\text{H}_2)_t$$

3.2. The application of this relation allows to get the following results:

$t(s)$	0	50	100	200	300	400	500	700	900	1200
$[H_3O^+]$ $\times 10^{-1} \text{ mol.L}^{-1}$		3.6	3.2	2.6	2.1	1.7	1.4	0.88	0.48	

Give the value of concentration of  $H_3O^+$  at  $t=0$  and calculate its value at  $t=1200\text{s}$ .

**3.3.** Plot, on a graph paper, the curve representing the variation of  $[H_3O^+]_t$  versus time,  $[H_3O^+] = f(t)$ , in the interval of time  $[0-1200\text{s}]$ . take the following scale: 1cm for 100 s in abscissa, and 1 cm for  $4.0 \times 10^{-2} \text{ mol.L}^{-1}$  in ordinate.

**3.4.** Determine graphically the average rate of disappearance of  $H_3O^+$  between  $t=50$  and  $t=300 \text{s}$ .

**3.5.** The slope of the tangent drawn on the curve at  $t=300 \text{s}$  is  $S_{300} = -4.5 \times 10^{-4}$ . Deduce the rate of formation of ( $H_2$ ) at  $t=300 \text{s}$ .

**3.6.** Deduce graphically how the rate of disappearance of  $H_3O^+$  varies over time.

**3.7.** Determine the half-life time of the reaction.

**3.8.** Specify the kinetic factor responsible for the variation of rate over time.

**3.9.** The same experimental study is repeated again with the same mass of zinc but in a powder form. Plot on the same graph of part 3.3 the shape of the curve  $[H_3O^+] = g(t)$ . Justify.

## Exercise 2

### Reaction of Hydrochloric Acid with Zinc

Hydrochloric acid reacts with zinc according to the following reaction:  $2H^+ + Zn \rightarrow H_2 + Zn^{2+}$

At instant  $t=0$ , we introduce a mass  $m=1.3 \text{ g}$  of Zn powder in a beaker containing 50 ml of  $0.5 \text{ mol.L}^{-1}$  hydrochloric acid solution. We measure the volume of  $H_2$  gas formed at different intervals of time, where the following data is obtained:

Time (s)	0	100	200	300	400	500	600	700	800	900
$V(H_2) \text{ ml}$	0	73	123	157	179	195	207	218	225	235
$[Zn^{2+}] \text{ mol.L}^{-1}$										

**Given:** molar mass of Zn in  $\text{g.mol}^{-1}$  is 65.4

Molar volume of a gas is  $V_m = 22.4 \text{ L.mol}^{-1}$

#### 1. Preliminary Study:

**1.1.** Prove the following relation:  $[Zn^{2+}]_t = \frac{V(H_2)_t}{1120}$  where  $V(H_2)$  is in ml.

**1.2.** Complete the above table.

**1.3.** Show that  $t=900\text{s}$  does not represent the end time of the reaction.

#### 2. Kinetic study of the reaction.

**2.1.** Plot the curve  $[Zn^{2+}]_t = f(t)$  using the following scale:

x-axis: 1cm = 100 s and Y-axis: 1cm =  $0.02 \text{ mol.L}^{-1}$ .

**2.2.** Determine the average rate of formation of  $Zn^{2+}$  between instants  $t=0$  and  $t=500\text{s}$ .

**2.3.** Given that the slope of the tangent on the curve at point of abscissa  $t=600 \text{s}$  is  $S_{600} = 2.87 \times 10^{-4}$ .

**2.3.1.** Determine the rate of formation of  $Zn^{2+}$  at  $t=600\text{s}$ .

**2.3.2.** Deduce the following rates:  $r(H_2)_{600}$ ,  $r(H_3O^+)_{600}$ , and  $r(\text{reaction})_{600}$ .

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

**2.5.** Explain graphically how the rate of reaction varies over time.

## Kinetic Questions

### Graphically

#### Example:

- Deduce graphically how the rate changes over time.
- Compare graphically the rate at  $t = 50$  and at  $t = 300$ .

#### Answer:

- Definition of rate:  $r = \text{slope}$
- Draw tangents at different times
- Compare slopes:  $S_{50} > S_{300}$
- Deduce: As time passes rate decreases.

**Numerical:** for the same substance but at different instants.

#### Example:

Given  $r(\text{H}_3\text{O}^+)_{t=300} = 4.5 \times 10^{-4} \text{ mol.L}^{-1.\text{s}^{-1}}$ . choose the value that represents  $r(\text{H}_3\text{O}^+)_{t=50}$ :

- $r(\text{H}_3\text{O}^+)_{t=300} = 4.5 \times 10^{-4} \text{ mol.L}^{-1.\text{s}^{-1}}$
- $r(\text{H}_3\text{O}^+)_{t=50} = 2.5 \times 10^{-4} \text{ mol.L}^{-1.\text{s}^{-1}}$
- $r(\text{H}_3\text{O}^+)_{t=50} = 7.5 \times 10^{-4} \text{ mol.L}^{-1.\text{s}^{-1}}$

#### Answer:

- As time passes rate decreases due to the consumption of reactant(s).
- Deduce the correct answer.

**Numerical:** for two different substances but at the same instant.

#### Example:

For the reaction:



Given:  $r(\text{O}_2)_{t=300} = 3.2 \times 10^{-2} \text{ mol.s}^{-1}$ .

Deduce  $r(\text{H}_2\text{O}_2)_{t=300}$

#### Answer:

- Use stoichiometric Ratios.

### Remark: Determination of concentration of a substance during kinetic study.



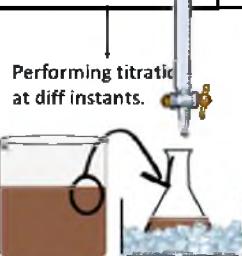
#### 3 ways to find the concentration of species



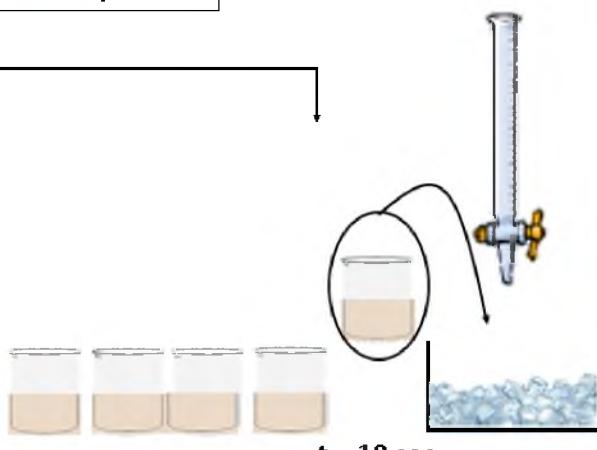
Finds the concentration of colored species.

Time (S)	0	10	20	...
[I <sub>2</sub> ] mol/L	0	0.1	0.2	...

Time (S)	0	10	20	...
[I <sub>2</sub> ] mol/L	0	0.1	0.2	...



Performing titration at diff instants.



Time (S)	0	10	20	30	40	50
[I <sub>2</sub> ] mol/L	0	0.1				

### **Exercise 3:**

### **Kinetics of H<sub>2</sub>O<sub>2</sub> Decomposition**

#### **Available solutions:**

Potassium permanganate solution ( $\text{K}^+ + \text{MnO}_4^-$ ) of concentration  $C = 0.02 \text{ mol.L}^{-1}$ .

Iron III chloride solution ( $\text{Fe}^{3+} + 3\text{Cl}^-$ ).

Commercial H<sub>2</sub>O<sub>2</sub> solution ( $S_0$ ) of concentration  $C_0$

#### **1. Determination of the concentration of the commercial solution ( $S_0$ ).**

1.1. 100 ml solution (S) is prepared starting from the available commercial solution ( $S_0$ ) of hydrogen peroxide, H<sub>2</sub>O<sub>2</sub>, by diluting a sample 10 times.

1.1.1. Suggest the glass ware to be used to prepare the diluted solution.

1.1.2. Describe the procedure.

1.2. 10 ml of the prepared solution (S) is titrated with the available potassium permanganate solution in acidic medium. Equivalence is reached when 17.8 ml of the permanganate solution is added.

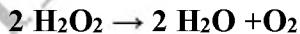


1.2.1. Calculate the concentration of solution (S).

1.2.2. Deduce the concentration of the commercial solution  $S_0$ .

#### **2. Kinetic study of the decomposition of H<sub>2</sub>O<sub>2</sub>.**

Hydrogen peroxide, H<sub>2</sub>O<sub>2</sub>, decomposes slowly according to the reaction :

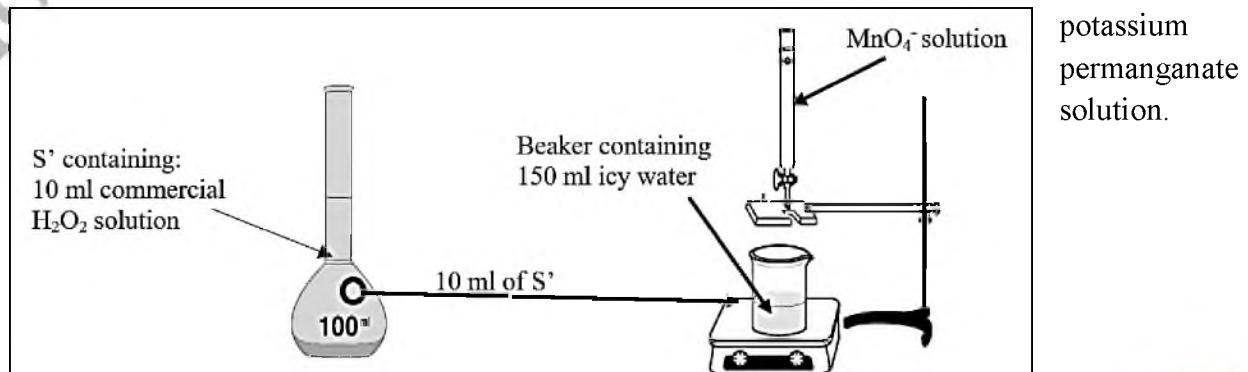


The decomposition is catalyzed by the presence of  $\text{Fe}^{3+}$  in the solution.

To study the kinetic of decomposition of H<sub>2</sub>O<sub>2</sub>, a 100 ml solution (S') is prepared by mixing:

- 10 ml of the commercial H<sub>2</sub>O<sub>2</sub> solution ( $S_0$ )
- 5 ml of Iron III chloride solution ( $\text{Fe}^{3+} + 3\text{Cl}^-$ )
- The volume is completed by distilled water to 100 ml

To follow the change in concentration of H<sub>2</sub>O<sub>2</sub> in solution S', a sample of the solution is taken at different instants of time, and is placed in a beaker containing 150 ml icy water and titrated with the



The volume  $V_E$  of potassium permanganate solution needed to reach equivalence each time is represented in the following table.

Time (min)	5	10	20	30	40
$V_E$ (ml)	15.1	12.6	9.2	6.3	4.5
$[H_2O_2]$ (mol.L <sup>-1</sup> )					

- 2.1.What is the aim of adding the sample into 150 ml icy water.
- 2.2.Is it necessary that the volume of icy water to be precise?
- 2.3.Explain how the equivalence point is detected during titration.
- 2.4.Prove the following relation :  $[H_2O_2]_t = 5 \times 10^{-3} V_E$  (ml)
- 2.5.Complete the above table.
- 2.6.Plot  $[H_2O_2]_t = f(t)$
- 2.7.The rate of disappearance of  $H_2O_2$  at  $t=30$  min is  $r(H_2O_2)_{30} = 1.1 \times 10^{-3}$  mol.L<sup>-1</sup>.min<sup>-1</sup>. choose among the following values the one that represents the rate of disappearance of  $H_2O_2$  at  $t=0$ ,  $r(H_2O_2)_0$  . Justify your answer.
  - $r(H_2O_2)_0 = 1.1 \times 10^{-3}$  mol.L<sup>-1</sup>.min<sup>-1</sup>
  - $r(H_2O_2)_0 = 3.2 \times 10^{-3}$  mol.L<sup>-1</sup>.min<sup>-1</sup>
  - $r(H_2O_2)_0 = 0.1 \times 10^{-3}$  mol.L<sup>-1</sup>.min<sup>-1</sup>
- 2.8.Specify the species present in solution S' when the reaction is over.

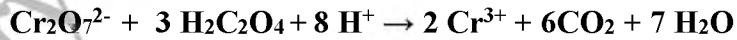
#### Exercise 4

#### Kinetic of Oxidation of Oxalic Acid

We prepare the following aqueous acidified solution containing initially 0.01 mol.L<sup>-1</sup>  $Cr_2O_7^{2-}$  ions and 0.2 mol.L<sup>-1</sup>  $H_2C_2O_4$  molecules.

Given :  $E^0 (Cr_2O_7^{2-}/Cr^{3+}) > E^0 (CO_2/H_2C_2O_4)$

- a. Show that the balanced equation of the reaction taking place is :



- b. Which of the above reactants is the limiting reactant?
- c. What is the limit of  $[Cr^{3+}]$  when t tends to infinity?

The values of concentration of  $Cr^{3+}$  at different instants of time are given in the following table:

Time ( min )	5	10	15	20	25	35	45
$[Cr^{3+}]$ in mmol.L <sup>-1</sup>	3.25	7.02	9.7	11.80	13.6	16.0	17.0
$[Cr_2O_7^{2-}]$ in mmol.L <sup>-1</sup>							

- d. Plot the curve  $[Cr^{3+}] = f(t)$  in the interval [0 -45] . scale: 1 cm = 5 min; 1cm = 2mmol.L<sup>-1</sup>
- e. Compare, graphically, the rate at  $t= 5$  and at  $t=20$  min. Conclude.
- f. Determine the half-life time of the reaction.
- g. Prove the following relation:

$$[\text{Cr}_2\text{O}_7^{2-}]_t = [\text{Cr}_2\text{O}_7^{2-}]_0 - \frac{[cr^{3+}]_t}{2}$$

- h. Complete the table above.
- i. Plot on the same graph, the shape of the curve  $[\text{Cr}_2\text{O}_7^{2-}] = g(t)$
- j. Compare the shapes of the 2 curves.

## **Exercise 6**

## **Kinetic Study**

It is required to follow-up the progress of the reaction between solid calcium carbonate,  $\text{CaCO}_3$ , and hydrochloric acid solution  $\text{HCl} (\text{H}_3\text{O}^{+}_{(\text{aq})} + \text{Cl}^{-}_{(\text{aq})})$ , the equation of the reaction is:



For this aim the following experiment is realized:

At time  $t = 0$  sec, a mass  $m = 2.0$  g of calcium carbonate is rapidly introduced into a flask containing a volume  $V = 50.0$  ml of hydrochloric acid solution, of concentration  $C = 4.0 \times 10^{-2}$  mol.L $^{-1}$ , at temperature

$T = 25^{\circ}\text{C}$ . The **volume** of the heterogeneous reaction mixture is considered constant throughout the experiment.

### **Given:**

- Molar volume of a gas at the conditions of this exercise is  $V_m = 24 \text{ L.mol}^{-1}$ .
- Molar mass of calcium carbonate ( $\text{CaCO}_3$ ) is  $M = 100 \text{ g.mol}^{-1}$ .

### **1. Preliminary study**

- 1.1. Show that, at the end of the reaction, the reaction mixture remains heterogeneous.
- 1.2. Determine at  $t \rightarrow \infty$  the volume of carbon dioxide  $V (\text{CO}_2)_{\infty}$ .

### **2. Kinetic study of the reaction**

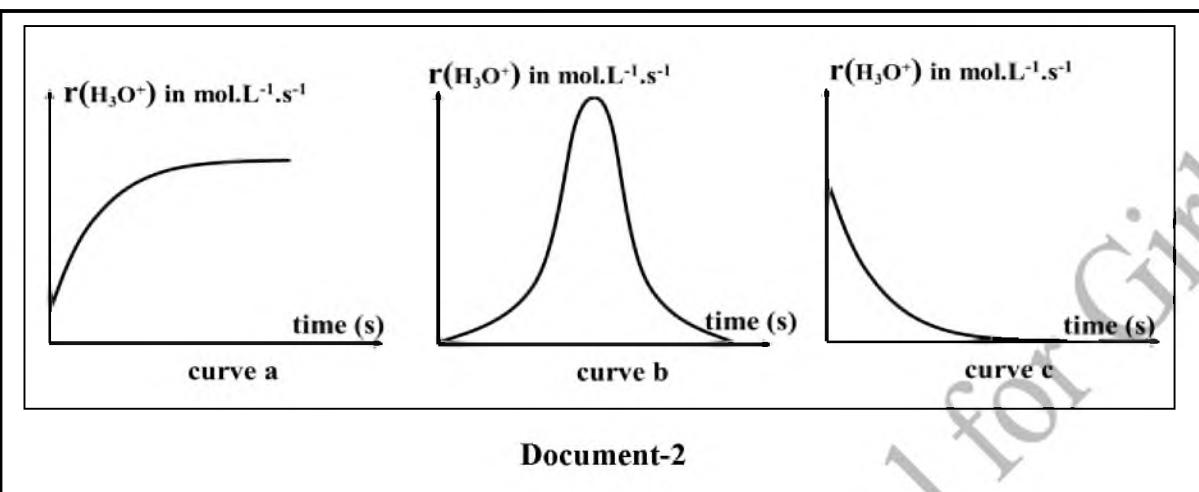
An appropriate method allows us to follow the evolution of the concentration of oxonium ions,  $\text{H}_3\text{O}^{+}$ , with time. The values obtained are shown in **document-1**.

Time (sec)	10	20	30	40	50	60	70	80	90	100
$[\text{H}_3\text{O}^{+}] \times 10^{-2} \text{ mol.L}^{-1}$	3.6	3.2	2.8	2.5	2.3	2.0	1.8	1.7	1.5	1.4

**Document-1**

- 2.1. Draw, on the graph paper, the curve  $[\text{H}_3\text{O}^{+}] = f(t)$  within the time interval:  $[0 - 100 \text{ s}]$ . Take the following scales: 1 cm for 10 s in abscissa and 1 cm for  $0.4 \times 10^{-2} \text{ mol.L}^{-1}$  in ordinate.
- 2.2. Determine graphically the half-life time of the reaction.
- 2.3. The rate of disappearance of  $\text{H}_3\text{O}^{+}$  at  $t = 20 \text{ s}$ :  $r (\text{H}_3\text{O}^{+})_{20} = 2.75 \times 10^{-4} \text{ mol.L}^{-1}\text{s}^{-1}$ . Deduce the rate of reaction at this instant.
- 2.4. During a chemical reaction, the rate changes versus time.

**2.4.1.** One of the three curves in **document-2** represents the variation of the rate of disappearance of  $\text{H}_3\text{O}^+$  versus time,  $r(\text{H}_3\text{O}^+) = g(t)$ . Choose, by justifying, the correct curve.



**2.4.2.** Sami, a student in grade 12, gave the following proposition:

“The amount of  $\text{CO}_2$  produced during the experiment increases as time passes, and thus the rate of formation of  $\text{CO}_2$  increases as function of time”.

Specify whether the proposition given by Sami is true or false.

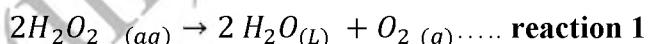
**2.5.** The same experiment realized above, is carried out again, but with one change: the flask is placed in a bath maintained at temperature  $T' < T$ .

On the same graph of part 2.1, plot the shape of the curve representing the new variation of the concentration of  $\text{H}_3\text{O}^+$  ions as a function of time:  $[\text{H}_3\text{O}^+] = h(t)$ . Justify.

### Exercise 7                      Study of the Decomposition of Hydrogen Peroxide Solution

Commercial hydrogen peroxide,  $\text{H}_2\text{O}_2$  solution is an aqueous solution that has many uses.

At  $25^\circ\text{C}$ , hydrogen peroxide decomposes according to a slow reaction represented by the following equation:



Given:  $\text{MnO}_4^-$  is the only colored species in this study, it has a purple color.

#### 1. Preparation of Hydrogen Peroxide Solution (S):

A volume  $V_S = 500 \text{ mL}$  of hydrogen peroxide solution (S) of concentration  $C_S = 5 \times 10^{-2} \text{ mol.L}^{-1}$  is prepared from a commercial solution S<sub>0</sub> of concentration  $C_0 = 1 \text{ mol.L}^{-1}$ .

**1.1.** Choose, among the three sets of document-1, the most precise one to perform the above preparation. Justify.

Set (A)	Set (B)	Set (C)
500 mL volumetric flask 25 mL volumetric pipet 50 mL beaker	500 mL volumetric flask 25 mL graduated pipet 50 mL beaker	500 mL volumetric flask 25 mL graduated cylinder 50 mL beaker

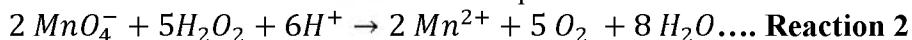
**Document-1**

**1.2.** Describe the preparation procedure.

## 2. Kinetic of the Decomposition of Hydrogen Peroxide

In order to study the kinetics of the slow decomposition reaction of  $\text{H}_2\text{O}_2$ , a beaker containing 200 mL of solution (S) is prepared and few drops of a solution containing  $\text{Fe}^{3+}$  ions are added without affecting the total volume.

At different instants, a volume  $V=20$  mL is taken from the beaker and is poured into icy water, then the remaining  $\text{H}_2\text{O}_2$ , at different instants, is titrated by potassium permanganate solution ( $\text{K}^+$  +  $\text{MnO}_4^-$ ) of concentration  $C = 2 \times 10^{-2} \text{ mol.L}^{-1}$ . The equation of titration reaction is



The volume of the permanganate solution, added to reach the equivalence point,  $V_E$ , is determined. The number of moles of  $\text{O}_2$ , produced at each instant from reaction-, is deduced. The results are grouped in curve -A of document-2.

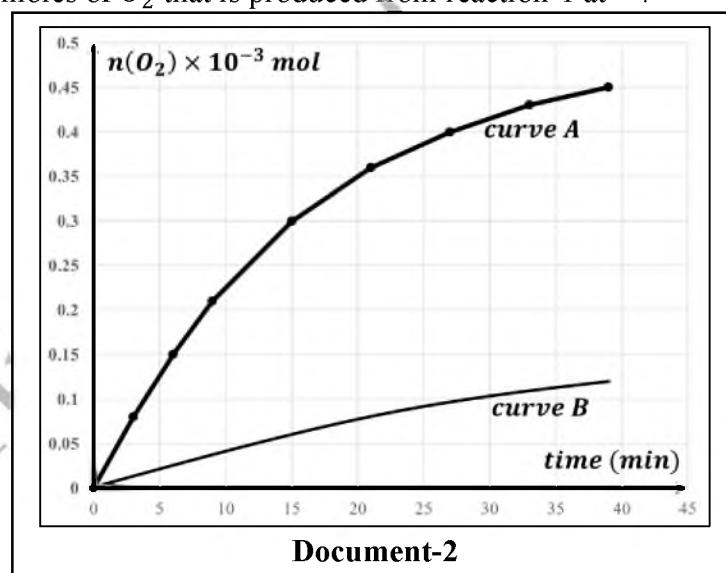
- 2.1.What is the aim of placing the sample in icy water before titration.
- 2.2.Indicate the kinetic factor(s) involved in this case.
- 2.3.Explain how to detect the equivalence point.
- 2.4.Determine the maximum number of moles of  $\text{O}_2$  that is produced from reaction-1 at  $\infty$ .
- 2.5.Prove the following relation for the

reaction taking place in the beaker containing 200 mL solution (S):

$$n(\text{O}_2)_t = 5 \times 10^{-3} - \frac{V_E \times 10^{-3}}{4}$$

Where  $n$  is the number of moles of  $\text{O}_2$  gas produced at a given instant during reaction-1, and  $V_E$  is the volume of  $\text{MnO}_4^-$  added to reach equivalence at the same instant (t).

- 2.6.Determine the rate of the formation of  $\text{O}_2$  between  $t = 6$  min, and  $t=21$  min. in experiment-1.
- 2.7.Explain graphically, how the rate of formation of  $\text{O}_2$  changes over time in experiment-1. Specify the kinetic factor involved in this case.
- 2.8.The same experiment performed above is repeated with only one change, the reaction is allowed to take place without adding few drops of  $\text{Fe}^{3+}$  solution. The corresponding curve of this experiment (experiment-2) is curve (B) of document-2.  
**Deduce** the role of  $\text{Fe}^{3+}$  ions.



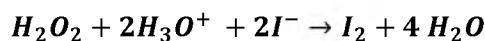
Document-2

## Exercise 8

### Reaction of Hydrogen Peroxide and Iodide Ions

(2010 S<sub>2</sub> LS- Exercise 1)

Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) reacts with iodide ions in acidic medium according to the equation:



In order to study the kinetic of the above complete and slow reaction, three reacting mixtures A,B, and C are prepared at the same temperature (T), where the composition of each is given in the table of document-1:

	<b>Mixture A</b>	<b>Mixture B</b>	<b>Mixture C</b>
Sulfuric acid solution ( $1\text{ mol.L}^{-1}$ )	$V_1 = 10 \text{ ml}$	$V_1 = 10 \text{ ml}$	$V_1 = 10 \text{ ml}$
KI solution ( $0.1 \text{ mol.L}^{-1}$ )	$V_2 = 18 \text{ mL}$	$V_2 = 10 \text{ mL}$	$V_2 = 10 \text{ mL}$
$\text{H}_2\text{O}_2$ solution ( $0.1 \text{ mol/L}$ )	$V_3 = 2 \text{ mL}$	$V_3 = 2 \text{ mL}$	$V_3 = 1 \text{ mL}$
Distilled water	-	$V_4 = 8 \text{ ml}$	$V_4 = 9 \text{ ml}$

### Document -1

In the three mixtures, sulfuric acid is in excess, and  $\text{H}_2\text{O}_2$  is introduced at the same time  $t = 0$ .

The curves 1 and 2 of **document- 2** represent respectively, the variation of the number of moles of iodine  $\text{I}_2$  in the mixtures (A) and (B), within the interval [0-25 minutes]

#### 1. Kinetic Factors

- 1.1.Explain whether  $\text{H}_3\text{O}^+$  is considered as catalyst in this reaction.
- 1.2.Justify based on the graph of **document- 2**, whether the reaction in each of the mixtures A and B has finished at the instant  $t = 25 \text{ min}$ .
- 1.3.Specify the kinetic factor responsible for the difference in shape between curves 1 and 2.
- 1.4.Starting with the reacting mixtures A and B, propose a way that can lessen the difference between the two curves 1 and 2.

- 1.5.The rate of formation of  $\text{I}_2$  in the mixture B is determined at  $t=5 \text{ min}$  and  $t = 15 \text{ min}$ . The obtained values are:  
 $r = 2.77 \times 10^{-6} \text{ mol.min}^{-1}$  and  
 $r' = 12.30 \times 10^{-6} \text{ mol.min}^{-1}$ .

Relate, by justifying, each rate to its corresponding time.

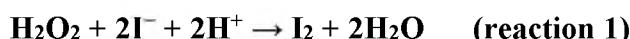
#### 2. Study of mixture C

- 2.1.Determine the number of moles of iodine formed at the end of the reaction in mixture C.
- 2.2.Draw on the graph of document-2 the shape of the curve 3,  $n(\text{I}_2) = f(t)$  corresponding to mixture C. Justify your answer.

#### Exercise 9

#### Iodine Clock Reaction

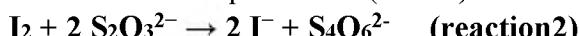
The balanced equation of the reduction of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) by the iodide ions  $\text{I}^-$  is:



This reaction is slow.

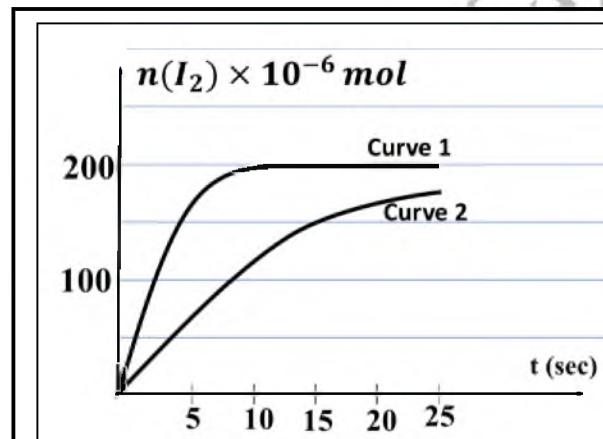
To study the kinetics of reaction 1, we will measure the time required to produce a certain amount of iodine ( $\text{I}_2$ ).

To determine this duration, the very fast oxidation-reduction reaction is used between the iodine ( $\text{I}_2$ ) produced from reaction 1 and the thiosulphate ions ( $\text{S}_2\text{O}_3^{2-}$ ) according to reaction (2).



Reactions (1) and (2) take place successively in the reaction medium.

**Document-1-** summarizes the steps of the experiment.



### Document-2

- At a time  $t = 0$  s, a solution is prepared by mixing 10 ml of hydrogen peroxide solution of concentration  $C = 0.040 \text{ mol.L}^{-1}$  with an excess amount of acidified potassium iodide solution KI ( $\text{K}^+_{(\text{aq})} + \text{I}^-_{(\text{aq})}$ ), 1 ml of sodium thiosulphate solution ( $2\text{Na}^+_{(\text{aq})} + \text{S}_2\text{O}_3^{2-}_{(\text{aq})}$ ) of concentration  $C' = 0.10 \text{ mol. L}^{-1}$  and a few drops of starch paste. The total volume of the reaction mixture is kept constant throughout the experiment ( $V_{\text{total}} = 125 \text{ mL}$ ).
- Since the  $\text{I}_2$  formed by the reaction (1) is consumed instantaneously by the reaction (2), the solution remains colorless until the time  $t_1 = 48$  s, at which the solution is colored blue.
- At the time  $t_1$ , another 1 mL of sodium thiosulfate solution is added, which makes the blue color disappear. The blue color reappears at time  $t_2 = 103$  s.
- A third milliliter of sodium thiosulfate solution is added, and the blue color disappears to reappear again at time  $t_3$  where another milliliter of thiosulfate solution is added, and so on.

#### Document-1

### 1. Preliminary Study.

- Show that the number of moles of iodine reduced by the addition of 1 ml of sodium thiosulfate solution is  $n(\text{I}_2) = 0.05 \text{ mmol}$ .
- Specify whether the acid is considered as catalyst in reaction (1).
- Justify the disappearance of dark blue color every time 1 mL of thiosulfate solution is added.
- Show, without calculation, that the number of moles of  $\text{I}^-$  ions remains unchanged during the progress of the reaction. Deduce the limiting reactant in reaction(1).

### 2. Kinetic study.

The follow up of the experiment allows to draw the table of document-2-:

Time (sec)	$t_0 = 0$	$t_1 = 48$	$t_2 = 103$	$t_3 = 170$	$t_4 = 254$	$t_5 = 366$	$t_6 = 536$	$t_7 = 900$
$[\text{I}_2] (\text{mmol.L}^{-1})$	0	0.4	0.8	1.2	1.6	2	2.4	2.8
$[\text{H}_2\text{O}_2] (\text{mmol.L}^{-1})$	x	2.8	2.4	2.0	y	1.2	0.8	0.4

#### Document-2

- Verify the following relation at each instant  $t$  :  $[\text{H}_2\text{O}_2]_t = [\text{H}_2\text{O}_2]_0 - [\text{I}_2]_t$

Where  $[\text{H}_2\text{O}_2]_t$  represents the concentration of  $\text{H}_2\text{O}_2$  in the reaction mixture, and  $[\text{I}_2]_t$  represents the concentration of  $\text{I}_2$  produced from reaction (1) at any time, both expressed in  $\text{mmol.L}^{-1}$ .

- Find the values of x and y in document-2-. (consider that the total volume of the reaction mixture is constant throughout the experiment)

- Plot the curve  $[\text{H}_2\text{O}_2] = f(t)$  on graph paper in the interval of time  $[0 ; 900]$ .

Take the following scale: x-axis: 1 cm for 50 s ; ordinate axis: 5 cm for  $1 \text{ mmol.L}^{-1}$ .

- Compare, graphically, the rate of disappearance of  $\text{H}_2\text{O}_2$  at  $t= 0$  and  $t = 170$  sec.

Indicate the kinetic factor responsible for this change.

- Determine the half life time of the reaction ( $t_{1/2}$ ).

**2.6.** Another experimental study is performed again, with the same conditions as in the previous one, but under temperature  $T'$ , where  $T' > T$ .

**Plot**, on the same graph of part 2.3, the shape of the curve  $[H_2O_2] = g(t)$  for the experiment taking place at temperature  $T'$ , in the same interval of time  $[0 ; 900]$ . **Justify**.

Q	Expected Answer
<b>1.1</b>	According to S.R (reaction 2): $\frac{n(I_2)_{\text{reacted}}}{1} = \frac{n(S_2O_3^{2-})_{\text{reacted}}}{2}$ $\Rightarrow n(I_2)_{\text{reduced}} = \frac{[S_2O_3^{2-}] \times V_{\text{added}}}{2} = \frac{0.1 \times 1 \times 10^{-3}}{2} = 0.05 \times 10^{-3} \text{ mol} = 0.05 \text{ mmol}$
<b>1.2</b>	The acid is not considered as a catalyst since a catalyst must be regenerated at the end of reaction. In reaction 1 $H^+$ ions are converted into $H_2O$ .
<b>1.3</b>	Throughout the experiment, iodine produced by reaction (1) is consumed by $S_2O_3^{2-}$ by the fast reaction (2) when 1 mL of sodium thiosulfate is added. Until the number of moles of $S_2O_3^{2-}$ added in the 1ml are totally consumed, at this instant, $I_2$ produced will directly complex with starch to give dark blue color
<b>1.4</b>	According to S.R (reaction 1): $\frac{n(I^-)_{\text{reacted}}}{1} = \frac{n(I_2)_{\text{produced}}}{2}$ $\Rightarrow n(I^-)_{\text{reacted in (1)}} = 2 n(I_2)_{\text{produced in (1)}}$ According to S.R (reaction 2): $\frac{n(I_2)_{\text{reacted}}}{1} = \frac{n(I^-)_{\text{produced}}}{2}$ $\Rightarrow 2 n(I_2)_{\text{reacted in (2)}} = n(I^-)_{\text{produced in (2)}}$ But: $n(I_2)_{\text{produced in (1)}} = n(I_2)_{\text{reacted in (1)}}$ Thus: $n(I^-)_{\text{reacted in (1)}} = n(I^-)_{\text{produced in (2)}}$ Then the concentration of $I^-$ ions remains the same, and $H^+$ is in excess. Therefore, $H_2O_2$ is the limiting reactant.
<b>2.1</b>	$n(H_2O_2)_{\text{remaining}} = n(H_2O_2)_0 - n(H_2O_2)_{\text{reacted}}$ According to S.R : $\frac{n(H_2O_2)_{\text{reacted}}}{1} = \frac{n(I_2)_{\text{produced}}}{1}$ $\Rightarrow n(H_2O_2)_{\text{remaining}} = n(H_2O_2)_0 - n(I_2)_{\text{produced}}$ At each instant $t$ : $n(H_2O_2)_t = n(H_2O_2)_0 - n(I_2)_{(t)}$ Divide by constant volume of solution : $[H_2O_2]_t = [H_2O_2]_0 - [I_2]_{(t)}$
<b>2.2</b>	<ul style="list-style-type: none"> <li>• <math>x = ?</math></li> </ul> Upon mixing number of moles of species ( $H_2O_2$ ) is conserved: $n(H_2O_2)_0 = C \times V = 0.04 \times 10 \times 10^{-3} = 0.4 \times 10^{-3} \text{ mol} = 0.4 \text{ mmol}$ . $[H_2O_2]_0 = \frac{n(H_2O_2)_0}{V_{\text{total}}} = \frac{0.4 \times 10^{-3}}{125 \times 10^{-3}} = 3.2 \times 10^{-3} \text{ mol.L}^{-1} = 3.2 \text{ mmol.L}^{-1} \Rightarrow x = 3.2$ <ul style="list-style-type: none"> <li>• <math>y = ?</math> <math>y</math> is at <math>t = 254 \text{ s}</math>; from table : <math>[I_2]_{(t=254)} = 8 \text{ mmol.L}^{-1}</math></li> </ul> Substitute in relation of part 2.2 then $y = 18 - 8 = 10 \text{ mmol.L}^{-1} \Rightarrow y = 1.6$

2.3	<p><math>[H_2O_2] = f(t)</math></p> <p><math>[H_2O_2] = g(t)</math></p> <table border="1"> <caption>Data points estimated from the graph</caption> <thead> <tr> <th>Time (sec)</th> <th>[H<sub>2</sub>O<sub>2</sub>] (f(t))</th> <th>[H<sub>2</sub>O<sub>2</sub>] (g(t))</th> </tr> </thead> <tbody> <tr><td>0</td><td>3.2</td><td>3.2</td></tr> <tr><td>100</td><td>2.8</td><td>2.5</td></tr> <tr><td>200</td><td>2.4</td><td>2.0</td></tr> <tr><td>300</td><td>2.0</td><td>1.5</td></tr> <tr><td>400</td><td>1.7</td><td>1.2</td></tr> <tr><td>500</td><td>1.5</td><td>1.0</td></tr> <tr><td>600</td><td>1.3</td><td>0.8</td></tr> <tr><td>700</td><td>1.1</td><td>0.6</td></tr> <tr><td>800</td><td>0.9</td><td>0.4</td></tr> <tr><td>900</td><td>0.7</td><td>0.3</td></tr> <tr><td>1000</td><td>0.5</td><td>0.2</td></tr> </tbody> </table>	Time (sec)	[H <sub>2</sub> O <sub>2</sub> ] (f(t))	[H <sub>2</sub> O <sub>2</sub> ] (g(t))	0	3.2	3.2	100	2.8	2.5	200	2.4	2.0	300	2.0	1.5	400	1.7	1.2	500	1.5	1.0	600	1.3	0.8	700	1.1	0.6	800	0.9	0.4	900	0.7	0.3	1000	0.5	0.2
Time (sec)	[H <sub>2</sub> O <sub>2</sub> ] (f(t))	[H <sub>2</sub> O <sub>2</sub> ] (g(t))																																			
0	3.2	3.2																																			
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800	0.9	0.4																																			
900	0.7	0.3																																			
1000	0.5	0.2																																			
2.4	<p>Draw a tangent on the curve at point of abscissa <math>t = 0</math> and at point of abscissa <math>t = 170</math> s. The negative slope of tangent to the curve at <math>t=0</math> is greater than that at <math>t = 170</math> min. The rate of disappearance of <math>H_2O_2</math> equals negative slope of the tangent to the curve at point of abscissa <math>t</math>. Therefore <math>r(H_2O_2)_0 &gt; r(H_2O_2)_{170}</math></p> <p>The kinetic factor responsible for this change is the concentration of reactants <math>H_2O_2</math> and <math>I^-</math>.</p>																																				
2.5	<p>Half life: it the time needed for half amount of the limiting reactant to be consumed.</p> $[H_2O_2]_{t/2} = \frac{[H_2O_2]_0}{2} = \frac{3.2}{2} = 1.6 \text{ mmol.L}^{-1}$ <p>Graphically it corresponds to <math>t_{1/2} \approx 254</math> sec</p>																																				
2.6	<p>The conditions and concentration of reactant is the same in the two experiments except temperature.</p> <p>Temperature is a kinetic factor, as temperature increases, rate of disappearance of <math>H_2O_2</math> increases. Then <math>H_2O_2</math> disappears faster at <math>T'</math>.</p> <p>At each instant <math>t</math>: <math>[H_2O_2]_{t \text{ left at } T'} &lt; [H_2O_2]_{t \text{ left at } T}</math></p> <p>The curve <math>[H_2O_2]=g(t)</math> will be below <math>[H_2O_2]=f(t)</math></p> <p>(The two curves tend to the same limit value at the end of reaction(same initial amounts of reactants)).</p>																																				

## **Chemistry Extra sheet**

### **Grade 12 LS and GS**

#### **Mathematical relations joining two chemical equations.**

##### **Exercise 1.**

A volume  $V_{\text{total}} = 50 \text{ ml}$  is prepared by mixing 0.1856 mol alcohol (B) and 0.383 mol of carboxylic acid (HA)

Equation of reaction:  $\text{B} + \text{HA} \leftrightarrow \text{ester} + \text{water}$

In order to follow up the progress of esterification reaction, we proceed as follows:

- At a definite time  $t$ , take a volume  $V=3\text{ml}$  from the reaction mixture of  $V_{\text{total}} = 50 \text{ ml}$  and pour them in ice water.
- The acid (HA) present in volume  $V= 3\text{ml}$  is titrated with sodium hydroxide solution of  $C = 1 \text{ mol.L}^{-1}$ . Equation of titration :  $\text{HA} + \text{HO}^- \rightarrow \text{A}^- + \text{H}_2\text{O}$

##### **Question :**

Prove the following relation in total volume.

$$n(\text{ester})_t = 0.383 - \frac{V_E}{60} . \text{ Where } V_E \text{ in ml}$$

##### **Exercise 2**

In a beaker few zinc granules are added into 100 ml of hydrochloric acid solution of concentration  $C_a = 0.01 \text{ mol.L}^{-1}$ .



In order to study the progress of the reaction, at different instants ( $t$ ), a sample of volume  $V=2\text{ml}$  is taken from the reaction mixture and titrated with sodium hydroxide solution of concentration  $C_b = 1 \text{ mol.L}^{-1}$ . Equation of titration is :  $\text{H}_3\text{O}^+ + \text{HO}^- \rightarrow 2 \text{H}_2\text{O}$

- a. Prove the following relation in  $V_{\text{total}}$

$$n(\text{Zn}^{2+})_t = 0.5 \times 10^{-3} - 25 \times 10^{-3} V_{bE} . \text{ where } V_{bE} \text{ is expressed in ml}$$

##### **Exercise 3**

At instant  $t=0$  , 10 tubes, each contains  $10^{-4} \text{ mol}$  of ester ( E ) and large excess of water , are placed in a water bath at  $40^\circ\text{C}$ :  $\text{E} + \text{water} \leftrightarrow \text{HA} + \text{alcohol}$

At instant of time  $t$ , one of the tubes is taken and is immersed in the ice, and the formed acid (HA) is then titrated using sodium hydroxide solution of  $C_b = 0.01 \text{ mol.L}^{-1}$ :  $\text{HA} + \text{HO}^- \rightarrow \text{A}^- + \text{H}_2\text{O}$

Show that :  $n(\text{ester})_t = 10^{-4} - 10^{-5} V_{\text{E}(t)}$  . where  $V_{\text{bE}}$  is expresssd in ml

#### Exercise 4

At  $t=0$ , a solution of ethyl ethanoate is mixed with sodium hydroxide solution. The initial concentration of each reactant in the mixture is  $C = 5 \times 10^{-2} \text{ mol.L}^{-1}$ :



The mixture is divided into 5 parts, each part has a volume  $V = 10 \text{ ml}$ . at different instants ( $t$ ), and in presence of colored indicator, the  $\text{HO}^-$  remained in each volume  $V$ , are titrated with hydrochloric acid solution of  $C_a = 10^{-2} \text{ mol.L}^{-1}$ :  $\text{H}_3\text{O}^+ + \text{HO}^- \rightarrow 2 \text{ H}_2\text{O}$

Let  $V_a$  be the volume of acidic solution needed to reach equivalence point at each instant.

Prove the following relation for the reaction taking place in 10 mL

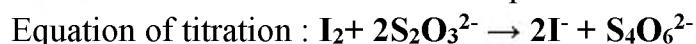
$n(\text{ethanol})_t = 5 \times 10^{-4} - 10^{-2} V_a(t)$  . where  $V_a$  is expresssd in L.

#### Exercise 5



At  $t=0$ , a mixture (S) is prepared by mixing a volume  $V_1 = 10 \text{ ml}$  of potassium iodide (KI) solution of  $C_1 = 0.50 \text{ mol.L}^{-1}$ , and a volume  $V_2 = 10 \text{ ml}$  of sodium peroxydisulfate ( $\text{Na}_2\text{S}_2\text{O}_8$ ) solution of  $C_2 = 5 \times 10^{-3} \text{ mol.L}^{-1}$ . The total volume of mixture (S) is noted as  $V_t$ .

- A volume  $V = 5 \text{ ml}$  of the reaction mixture is introduced into a beaker containing ice water.
- The iodine present in the volume  $V$  is titrated with sodium thiosulfate solution ( $2\text{Na}^+ + \text{S}_2\text{O}_3^{2-} \rightarrow \text{I}_2 + \text{S}_4\text{O}_6^{2-}$ ) of  $C' = 2.0 \times 10^{-3} \text{ mol.L}^{-1}$ . In presence of few drops of starch solution. The volume of thiosulfate added to reach equivalence is  $V_E$ .

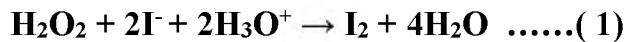


Prove the following relation for the reaction taking place in solution (S) of volume  $V_t$ :

$$n(I^-)_t = n(I^-)_0 - 8 \times 10^{-6} V'_E \text{ (0)} ; V'_E \text{ is expressed in ml}$$

### Exercise 6

At time  $t=0$ , 10 identical beakers are prepared by mixing  $\text{H}_2\text{O}_2$  solution , an excess of KI solution, and commercial sulfuric acid solution. The equation of reaction is:



In order to determine the amount of  $\text{H}_2\text{O}_2$  left in the reaction medium at a given time  $t$ , a beaker is immersed in an ice- water bath. The iodine formed is then titrated with sodium thiosulfate solution ( $2\text{Na}^+ + \text{S}_2\text{O}_3^{2-}$ ) of  $C= 0.5 \text{ mol.L}^{-1}$  in presence of starch.

The equation of titration is :  $2\text{S}_2\text{O}_3^{2-} + \text{I}_2 \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{I}^-$

Prove the following relation:

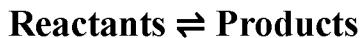
$$n(\text{H}_2\text{O}_2)_t = n(\text{H}_2\text{O}_2)_0 - 0.25 V_E . \text{ where } V_E \text{ is expressd in L.}$$

# UNIT 2-CHAPTER 3: CHEMICAL EQUILIBRIUM

## 1) Introduction

Chemical reactions are either complete or incomplete.

- **Complete reactions** are those that stop when at least one reactant (limiting reactant) disappears completely from the reaction medium.
- **Incomplete reactions** (also called reversible reactions) are those whose reactants are never fully consumed when their evolution stops. These reactions show capability of products to react to form the reactants again. They are represented by:



Note: in reversible reactions, the point at which the evolution of the reaction system stops is called equilibrium state.

## 2) What are the characteristics of equilibrium state?

The equilibrium state is characterized by a:

- constant composition of the reaction system (the amounts of reactants and products become constant at equilibrium , or we can say **the evolution of the reaction system stops at equilibrium**)
- forward and backward reactions take place simultaneously (at same time) with the same rate in case of dynamic equilibrium.
- The rate of formation of a compound is equal to its rate of disappearance.

## 3) Explain why equilibrium is said to be dynamic?

The equilibrium is said to be dynamic because the reaction doesn't stop. In fact, it occurs in both directions but with the same rate.

## 4) Equilibrium constant K<sub>c</sub>

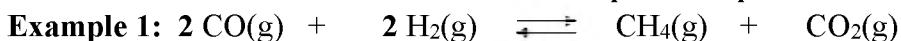
At constant temperature the ratio of [product]<sub>eq</sub> over [reactants]<sub>eq</sub> is a constant number whatever the initial amount of reactants are.

$$K_c = \frac{[\text{products}]_{\text{equil}}}{[\text{reactants}]_{\text{equil}}} = \text{constant value (at constant temperature).}$$

- K<sub>c</sub> is called equilibrium constant.
- It changes only if the temperature of the reaction system changes.

Consider the following reversible reaction: aA + bB  $\rightleftharpoons$  cC + dD

$$K_c = \frac{[C]_{\text{eq}}^c \times [D]_{\text{eq}}^d}{[A]_{\text{eq}}^a \times [B]_{\text{eq}}^b}$$



$$K_c = \dots$$

## 5) Reaction quotient (Q)

Reaction quotient (Q) helps us to know if the reaction system is at equilibrium or not.

Consider the following reversible reaction:  $aA + bB \rightleftharpoons cC + dD$

	$\text{CH}_3\text{OH}$	$\text{HCOOH}$	$\text{HCOOCH}_3$	$\text{H}_2\text{O}$
$n_o (\text{mol})$	$n_o$	$n_o$	0	0
<b>Change to reach equilibrium</b>				
<b>At equilibrium</b>				

$$Q = \frac{[C]_t^c \times [D]_t^d}{[A]_t^a \times [B]_t^b}$$

Interpretation of the value of Q : Three cases are possible:

- $Q = K_c$  : The system is at equilibrium; there is no movement.
- $Q > K_c$  : The reaction shifts from right to left (reverse reaction is favored) to reach equilibrium.
- $Q < K_c$ : The reaction shifts from left to right (direct reaction is favored) to reach equilibrium.

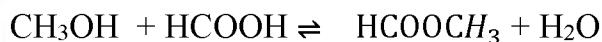
## 6) Degree of conversion (transformation or dissociation) of a reactant $\alpha$ :

$$\alpha = \frac{n(\text{reactant})_{\text{reacted}}}{n(\text{reactant})_{\text{initial}}}$$

Note: for complete reactions  $\alpha = 1$ , for incomplete reactions  $\alpha < 1$ .

### Exercise 1

The following table of variation corresponds to the reversible reaction:

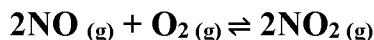


- Copy and complete the table in terms of  $n_o$  and  $\alpha$ , the degree of conversion of HCOOH.
- Knowing that at equilibrium, the total number of moles is considered the sum of the equilibrium number of moles of all reactants and products. Deduce the total number of moles at equilibrium:  $n_t$  in terms of  $n_o$ .
- Determine the value of  $\alpha$  knowing that the percentage yield of  $\text{HCOOCH}_3$  at equilibrium is  $\%Y = 67\%$ .

## Exercise 2:

## Chemical equilibrium

In a closed container of volume ( $V$ ), and at constant temperature, we introduce  $2n$  moles of NO gas and  $n$  moles of O<sub>2</sub> gas. The following equilibrium is established:



Let  $\alpha$  be the degree of conversion of NO to NO<sub>2</sub>.

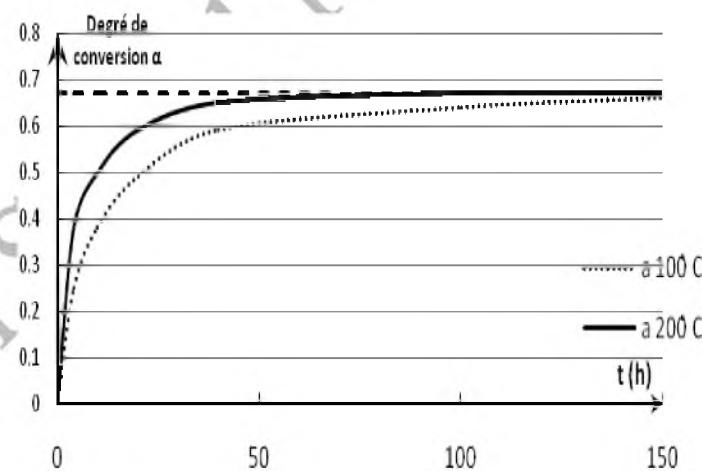
- Express in terms of  $\alpha$  and  $n$  the number of mole of each reaction component at equilibrium.
- Knowing that at equilibrium, the total number of moles is considered the sum of the equilibrium number of moles of all reactants and products. Deduce, in terms of  $\alpha$  and  $n$ , the total number of moles ( $n_t$ ) of the reaction mixture at equilibrium.
- Show that  $K_c = \frac{\alpha^2}{n(1-\alpha)^3} \times V$
- Find the % yield of the reaction in terms of  $\alpha$ .

## **Exercise 3**

Equimolar mixture of carboxylic acid (A) and an alcohol (B) is heated. A reaction takes place according to equation:

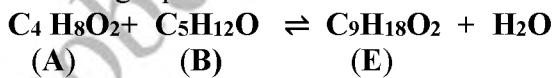


- The two curves in the adjacent graph represent the variation of the degree of conversion ( $\alpha$ ) of the alcohol (B), in this reaction, as a function of time at two different temperatures: 100°C and 200°C.  
Deduce that this reaction is: limited, athermic and slow.
- The above mixture is heated in the presence of a catalyst. Indicate the effect of this catalyst on the degree of conversion  $\alpha$ .



## **Exercise 4**

Pentyl butanoate (E) is an ester that is obtained by an esterification reaction represented by the following equation:



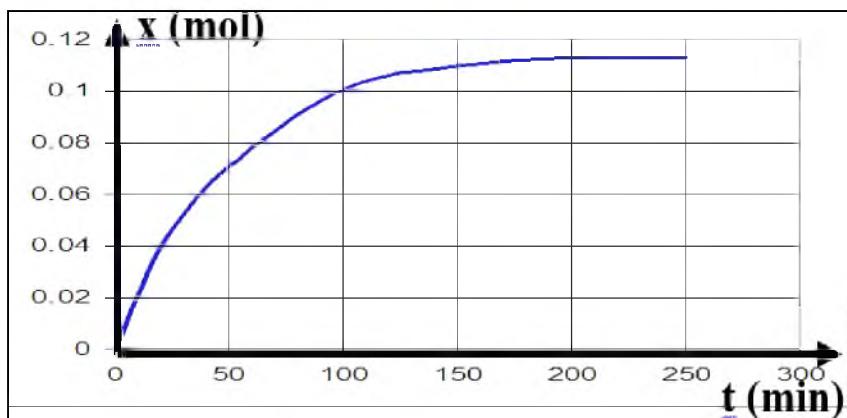
16 mL of acid (A) and 0.17 mol of alcohol (B) are mixed in the presence of a few mL of concentrated sulfuric acid. This mixture is divided into identical parts which are placed into Erlenmeyer flasks that are then heated at constant temperature. The remaining acid, in each Erlenmeyer flask, is titrated at regular intervals of time.

**Given :** For carboxylic acid (A) : density :  $\rho_A = 0.96 \text{ g.mL}^{-1}$ ; Molar mass :  $M_A = 88 \text{ g.mol}^{-1}$ .

- Show that the initial reactional mixture is equimolar
- Indicate the reason for which the Erlenmeyer flasks are immersed in ice-water before carrying out the titration

- 3- knowing that  $x$  represents the number of moles of ester formed at each instant in the initial mixture. The results of titration permit to plot the curve below:  $x = f(t)$

Answer, by justifying, whether the proposals given below are true or false



-**Proposal 1** : The instantaneous rate of the reaction increases with respect to time.

-**Proposal 2** : The percentage of the esterification of alcohol, at  $t = 100$  min, is 33 %.

-**Proposal 3** : We can obtain "more ester" by eliminating the water formed during the transformation.

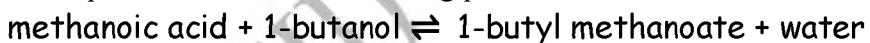
### Exercise 5

**Given :**

- Molar mass in g.mol<sup>-1</sup>: M (methanoic acid) = 46 ; M (1-butanol) = 74 and M(ester) = 102 ;
- density 1-butanol :  $\mu = 0.8 \text{ g.mL}^{-1}$

We heat a mixture of 30 g of methanoic acid and a volume  $V = 38 \text{ mL}$  of 1-butanol. After a certain time, we stop the heating and we find the amount of acid left. The result show that the quantity of acid left is equal to 0.40 mol.

The equation of the reaction taking place is :



- 1.1- Choose the convenient terms to characterize this reaction: athermic, endothermic, total, slow and rapid.
- 1.2- Verify if the initial mixture of reactants is stoichiometric.
- 1.3- Determine the yield of this reaction.
- 1.4- We realize the following three mixtures : Compare  $R_1$ ,  $R_2$  and  $R_3$ . Justify.

Mixture	Yield of the reaction at equilibrium
<b>Mixture 1</b> : 0,2 mol of methanoic acid + 0,2 mol of 1-butanol	$R_1$
<b>Mixture 2</b> : 0,2 mol of methanoic acid + 0,2 mol of 1-butanol + some drops of concentrated sulfuric acid	$R_2$
<b>Mixture 3</b> : 0,4 mol of methanoic acid + 0,4 mol of 1-butanol	$R_3$

# **Organic Chemistry**

Organic compound has molecules that contain covalently bonded carbon and hydrogen atoms. They can contain additional elements like oxygen, nitrogen, chlorine, bromine ....

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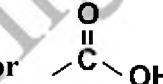
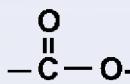
## UNIT 4 - CHAPTER 6: FUNCTIONAL GROUPS

**Definition:** A functional group determines the characteristic properties and the chemical reactivity of an organic substance.

**Main functional groups:**

- Hydroxyl group: (-OH)
- Carbonyl group: (- CO-)
- Carboxyl group: (-COOH)
- Amino group: (-N-)

|

Family	Functional group	Example	Nomenclature
Alcohol	Hydroxyl : – OH	$\text{CH}_3 - \text{CH}_2 - \text{OH}$	x-Alkanol
Aldehyde	Carbonyl : (- CO-) or 	$\text{CH}_3 - \text{CH}_2 - \text{CHO}$	Alkanal
Ketone	Carbonyl : (- CO – ) or 	$\text{CH}_3 - \text{CO} - \text{CH}_3$	x-Alkanone
Carboxylic Acid	Carboxyl : (- COOH) or 	$\text{CH}_3 - \text{COOH}$	Alkanoic Acid
Ester	Ester : – COO – or 	$\text{CH}_3 - \text{COO} - \text{CH}_3$	Alkyl alkanoate

## Isomers:

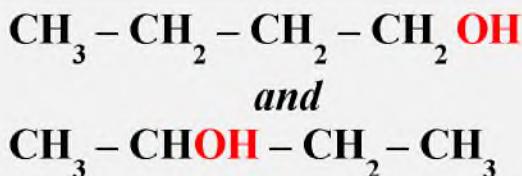
Organic compounds that have:

**Same molecular formula but different arrangement**

Positional isomerism

Functional group isomerism

- *have Same molecular formula, same carbon chain, but different position of the functional group, ex :*

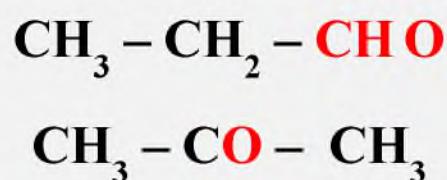


**Common:** -molecular formula:  $\text{C}_4\text{H}_{10}\text{O}$   
- linear chain

**Difference:** Location of the functional group (hydroxyl).

⇒ **Positional isomers.**

- *Have Same molecular formula, but different functional group, ex:*



**Common:** molecular formula:  $\text{C}_3\text{H}_6\text{O}$

**Different:** functional groups      =>  
different families

=>**Functional isomers.**

**Note:**

**How to find the molecular formula of an organic compound:**

- 1- If the molar mass of the unknown organic compound (X) is given + % masses of C,H. and O.  
Use law of proportionality:

Let the molecular formula of compound (A) be:  $\text{C}_x\text{H}_y\text{O}_z$

$$\frac{12x}{\%m(C)} = \frac{1y}{\%m(H)} = \frac{16z}{\%m(O)} = \frac{M(X)}{100}$$

- 2- If the family of the unknown organic compound (X) is given + % masses of C,H. and O.

Use law of proportionality:

Let the molecular formula of compound (A) be:  $\text{C}_x\text{H}_y\text{O}_z$

$$\frac{12x}{\%m(C)} = \frac{1y}{\%m(H)} = \frac{16z}{\%m(O)} = \frac{M(X)}{100}$$

- If (X) is an alcohol, aldehyde or ketone, then  $z = 1$

- If (X) is a carboxylic acid or ester, then  $z = 2$
- If (X) is an acid anhydride, then  $z=3$

**3- If the family of the unknown organic compound (X) is given + its molar mass then:**

**Example:** determine the molecular formula of an alcohol whose molar mass is  $74 \text{ g.mol}^{-1}$

Let the molecular formula of (X) be  $C_nH_{2n+2}O$

$$M(X) = 12n + 2n + 2 + 16 = 14n + 18$$

$$74 = 14n + 18$$

$$\Rightarrow \text{So } n = 4$$

$\Rightarrow$  Molecular formula of (X) is  $C_4H_{10}O$

---

### Exercise 1

The analysis of an organic substance (S) containing the elements carbon, hydrogen and oxygen gave the following mass composition: C:40%; H : 6.7%.

- Determine the empirical formula of (S).
- Deduce the molecular formula of (S) knowing that its molar mass is  $30 \text{ g.mol}^{-1}$ .
- Write its condensed structural formula. Circle and name its functional group.

### Exercise 2

- A-** The analysis of an organic substance (X) gives the following mass composition: C: 30.6% ; H: 3.8% ; Cl: 45.2%.
- Determine the empirical formula of (S).
  - Determine its molecular formula knowing that its molar mass is  $78.5 \text{ g.mol}^{-1}$ .
- B-** The analysis of another organic compound (Y) containing the elements: C,H, and nitrogen gives the following mass composition: C: 38.7% ; N: 45.2%.
- Determine the empirical formula of this compound (Y).
  - Knowing that this organic compound contains 1 nitrogen per molecule. Deduce its molecular formula.

### Exercise 3

The complete combustion of 1.1 g of an organic compound (A) of formula  $C_xH_yO_z$  gives 2.75 g  $CO_2$  and 1.35 g water vapor.

- Calculate the percent composition of (A).
- Determine its empirical formula.
- Verify that the molecular formula of (A) is  $C_5H_{12}O$  knowing that its molar mass is  $88 \text{ g.mol}^{-1}$ .

### Exercise 4

The complete combustion of 225 mg of an organic compound (S) containing nitrogen produces 220 mg carbon dioxide and 135 mg water vapor. And 61 mL nitrogen gas.

- Calculate the percent mass composition of (S).
- Knowing that  $M(S) = 45 \text{ g.mol}^{-1}$ , Determine its molecular formula.

### Exercise 5

The complete combustion of 0.295 g of an organic compound (S) containing nitrogen produces 0.44g  $CO_2$ , 0.225 g  $H_2O$ , and 0.0697 g nitrogen gas ( $N_2$ ).

- Calculate the percent mass composition of (S).
- Determine the molecular formula of (S) knowing that its molar mass is  $59 \text{ g.mol}^{-1}$ .

### Exercise 6

115 mg of a carboxylic acid (HA) is dissolved in 10mL water. The obtained solution is titrated with 10 g.L<sup>-1</sup> sodium hydroxide solution ( $\text{Na}^+ + \text{HO}^-$ ) in the presence of a suitable indicator. Equivalence point is reached when 10 mL of NaOH solution is added.

The equation of the titration reaction is :  $\text{HA} + \text{HO}^- \rightarrow \text{A}^- + \text{H}_2\text{O}$

- Determine the molar mass of carboxylic acid (HA).
- Deduce the molecular formula of (HA).

### Remark: Enantiomers

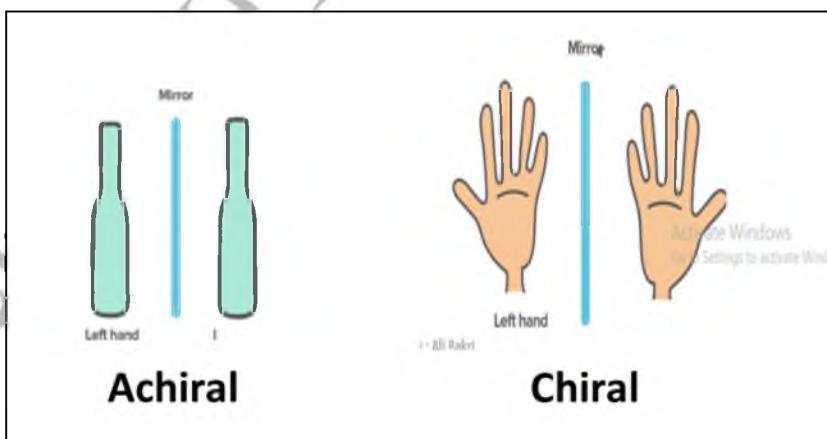
#### Enantiomerism

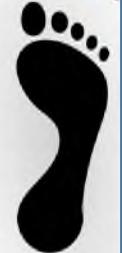
**Enantiomers** are objects that are mirror images of each other but cannot appear identical simply by reorientation.

Mirror images may be identical or not:

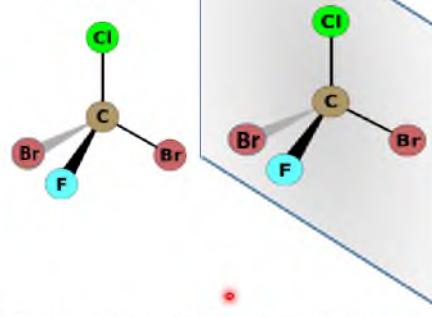
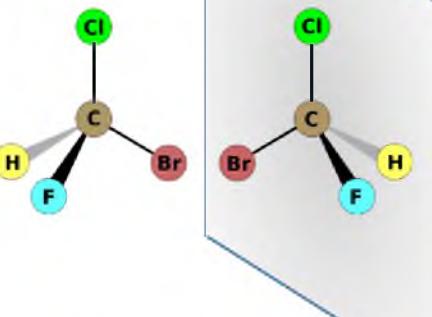
- If they are identical i.e, they can be superimposed, then they are the same (not isomers).
- If they cannot be superimposed, then the object and its mirror image are not identical, rather they are isomers, and are called enantiomers.

THE OBJECT THAT IS NOT SUPER IMPOSABLE TO ITS MIRROR IMAGE IS CALLED **CHIRAL OBJECT**, OTHER WISE IT IS **ACHIRAL**



<b>achiral</b> 		<b>chiral</b> 	
<ul style="list-style-type: none"> <li>✓ The object and its mirror image are identical (not enantiomers)</li> <li>✓ This is achiral object.</li> </ul>		<ul style="list-style-type: none"> <li>✓ The object and its mirror image are not superimposable=&gt;They are enantiomers</li> <li>✓ The foot is chiral object</li> </ul>	

By: Zeinab Al Hoson- Reviewed by : Ali Balkhi

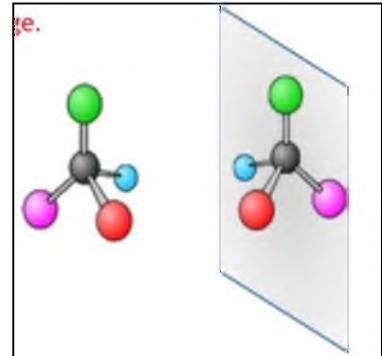
<b>achiral</b> 	
<ul style="list-style-type: none"> <li>✓ The molecule and its mirror image are identical (not enantiomers)</li> <li>✓ This is achiral molecule.</li> </ul>	
<ul style="list-style-type: none"> <li>✓ The molecule and its mirror image are not super imposable=&gt; they are enantiomers.</li> <li>✓ Then this molecule is chiral.</li> </ul>	

By: Zeinab Al Hoson- Reviewed by : Ali Balkhi

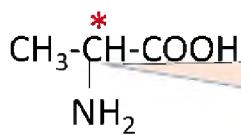
### Chiral molecule:

A molecule containing a carbon atom attached to **4 different atoms or group of atoms** is said to be **chiral**, since it is not superimposable on its mirror image.

The object and its mirror image are called enantiomers.



**Example:**



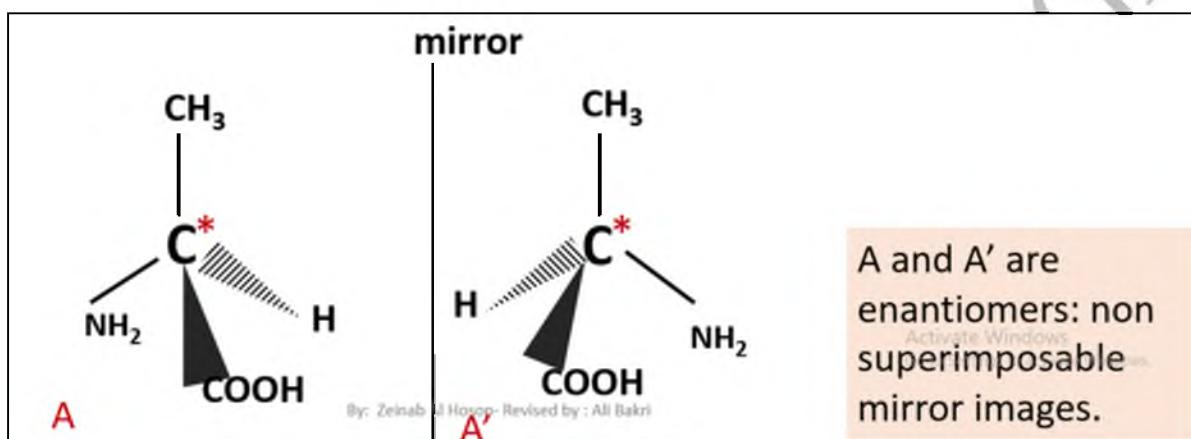
This carbon is attached to 4 different groups, it is:

- ✓ Chiral center
- ✓ Asymmetric carbon

**How to represent enantiomers?**

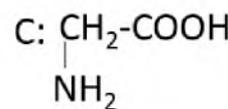
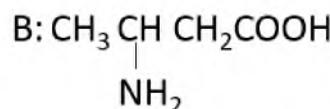
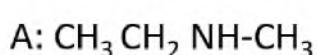
Using Cram representation

**Example:**



### Application

Consider the following molecules:



- 1- Specify among these the chiral molecule.
- 2- Represent the chiral molecule and its mirror image using Cram representation.
- 3- Specify the type of isomerism that exists between these compounds.

## UNIT 4- CHAPTER 7 : ALCOHOLS

**1- Definition:** A saturated, open-chain mono alcohol is an organic compound having one hydroxyl group (- OH) connected to a carbon chain. Hence, they are represented by the general formula R—OH or by: C<sub>n</sub>H<sub>2n+1</sub>OH or C<sub>n</sub>H<sub>2n+2</sub>O, where n represents the number of carbon atoms.

### 2- Nomenclature of alcohols:

Rule of naming alcohols: Alkane → Alkanol

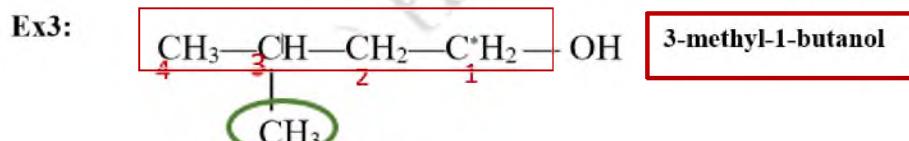
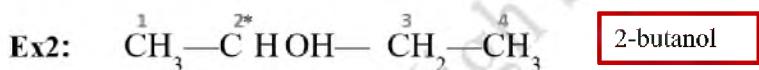
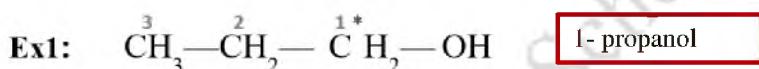
#### Simple Alkanes :

- CH<sub>3</sub>- OH : methanol
- CH<sub>3</sub>- CH<sub>2</sub>- OH : ethanol

Note : The Carbon which is linked to the functional group is called " **functional carbon**".

#### Alkanes having longer carbon chains :

In an alkane whose carbon chain is made up of more than 2 carbon atoms, the carbon atoms must be numbered since the position of the (-OH) must be mentioned.



### 3- Structure and Isomerism :

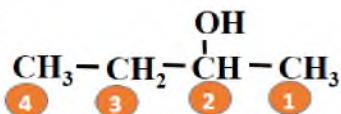
Let us draw all the possible condensed structural formula of C<sub>4</sub>H<sub>9</sub>OH



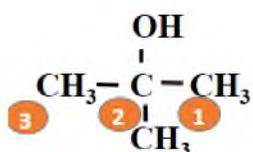
(a) 1-butanol



(c) 2-methyl-1-butanol



(b) 2-butanol



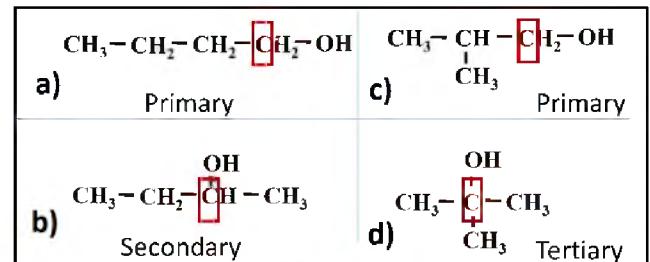
(d) 2-methyl-2-propanol

Let us classify these isomers into positional and skeletal isomers.

Positional isomers:	Skeletal isomers
• (a) and (b)	• (a) and (c)
• (c) and (d)	• (b) and (d)

#### 4- Classes of Alcohols

- **Primary:** The functional carbon carries only 1 alkyl group
- **Secondary:** The functional carbon carries only 2 alkyl groups.
- **Tertiary:** The functional carbon carries only 3 alkyl groups.



#### 5- Chemical reactions: Mild oxidation

Mild oxidation is a reaction that takes place without breaking of carbon chain.

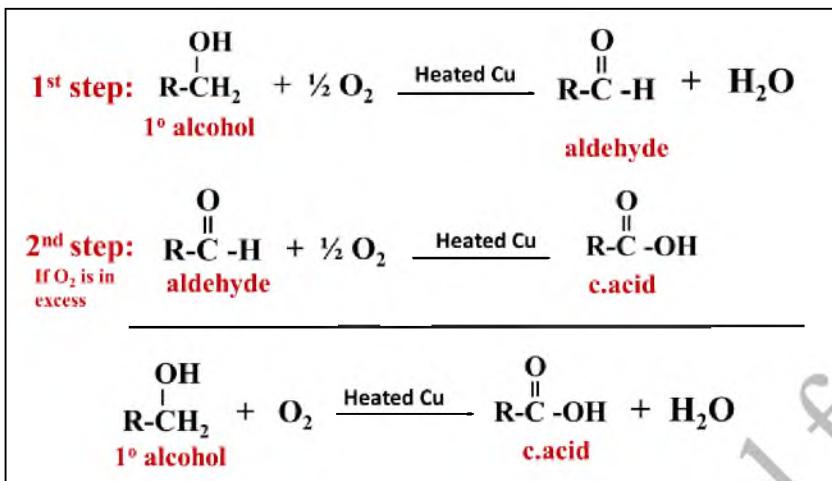


1° alcohol $\xrightarrow{\text{oxidation}}$ Aldehyde $\xrightarrow{\text{oxidation}}$ c.acid 2° alcohol $\xrightarrow{\text{oxidation}}$ Ketone 3° alcohol No oxidation reactions
---

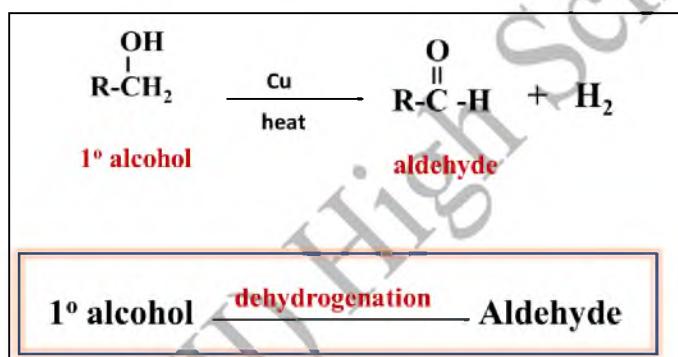
Changes occur only on the functional carbon. The carbon chain remains unchanged during mild oxidation.

## I- Mild oxidation of primary alcohols

- I. A- Catalytic oxidation in presence of oxygen : (O<sub>2</sub>)

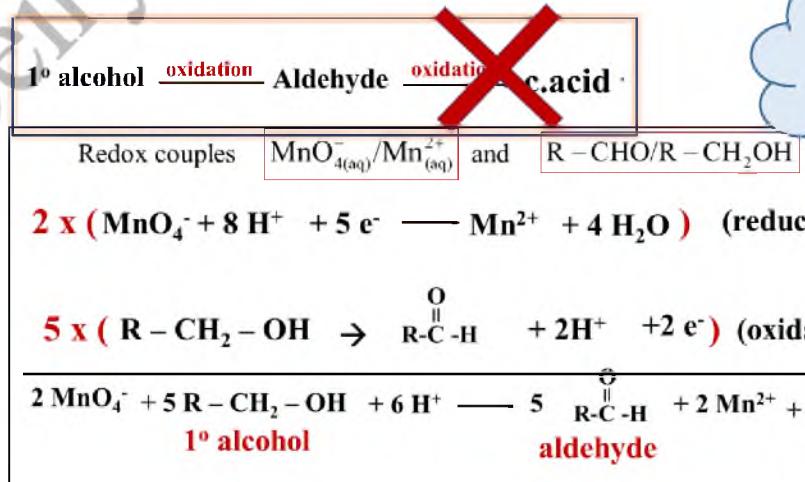


- I. B- Catalytic dehydrogenation in absence of oxygen :



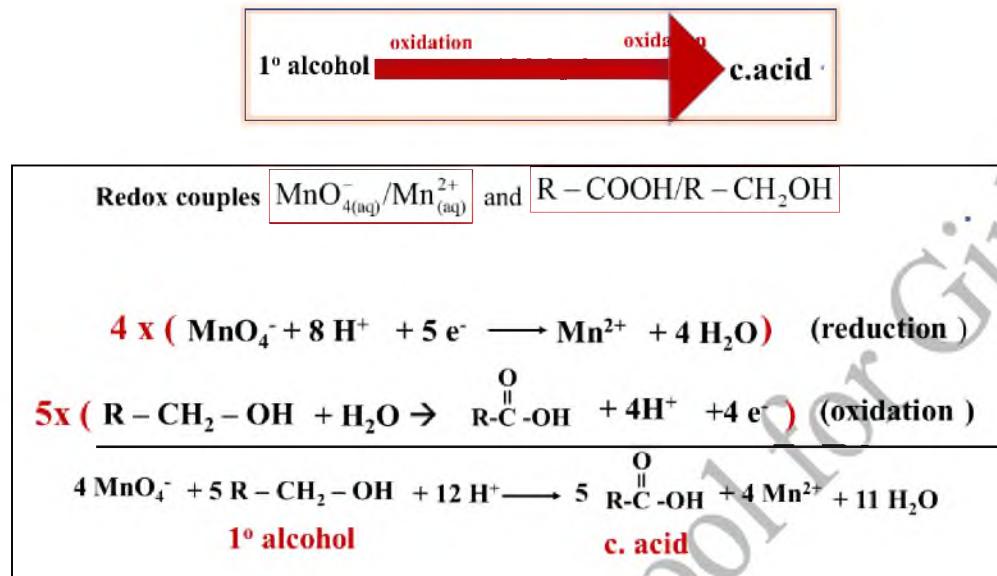
- I. C- By using oxidants ( MnO<sub>4</sub><sup>-</sup> or Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> ,... )

- 1° alcohol with MnO<sub>4</sub><sup>-</sup> (limiting) : **reaction stops at aldehyde**



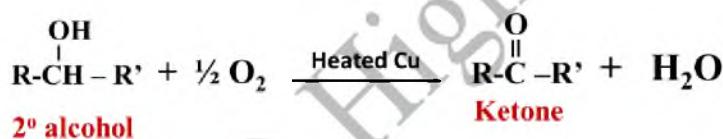
In this case, oxidation of primary alcohol stops at aldehyde.

- **1° alcohol with MnO<sub>4</sub><sup>-</sup> (excess) :**



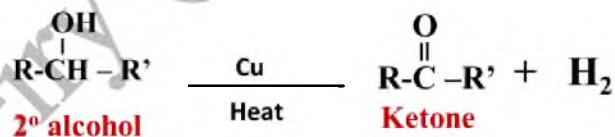
**II- Mild oxidation of secondary alcohols**

**II.A. Catalytic oxidation in presence of O<sub>2</sub>:**



Reaction stops at ketone even if O<sub>2</sub> is in excess.

**II.B- Catalytic dehydrogenation in absence of O<sub>2</sub>:**

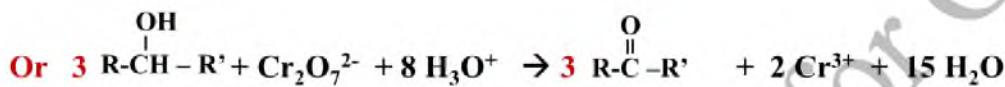
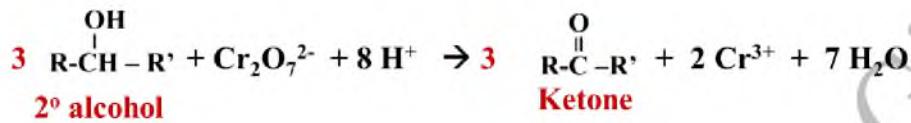
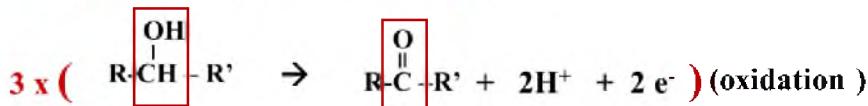


**II.C- In presence of an oxidant ( MnO<sub>4</sub><sup>-</sup> or Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>...) in acidic medium:**

Whether the oxidation is controlled or continuous, reaction stops at ketone.

Case of dichromate ion Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> (yellow –orange ) in acidic medium:

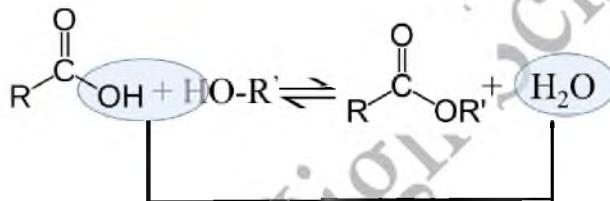
Redox couples are: (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>/Cr<sup>3+</sup>) and (Ketone/ 2° alcohol)



### Remark:

Other than mild oxidation reactions, alcohols can also undergo several chemical reactions including esterification reaction.

**Equation of esterification reaction: carboxylic acid + alcohol  $\rightleftharpoons$  ester + water**



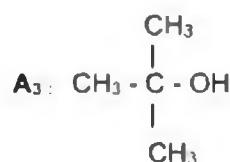
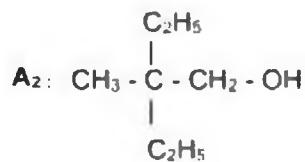
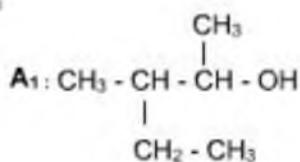
### Exercise 1

Give the systematic names of the following alcohols.

- $(\text{CH}_3)_2\text{CH}-\text{CH}(\text{CH}_3)-\text{CH}_2\text{OH}$
- $\text{CH}_3-\text{CH}_2-\text{C}(\text{CH}_3)_2-\text{CH}(\text{OH})-\text{CH}_3$
- $\text{CH}_3-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)_2$
- $(\text{CH}_3)_2\text{CH}-\text{CH}(\text{CH}_3)-\text{CH}(\text{C}_2\text{H}_5)-\text{CH}(\text{OH})-\text{CH}_3$

### Exercise 2

There are three alcohols A<sub>1</sub>; A<sub>2</sub> and A<sub>3</sub> of respective condensed structural formulas:



- Give the name and the class of each alcohol.

2. The mild oxidation of one of the above alcohols was performed by an acidified solution of potassium dichromate ( $2\text{K}^+ + \text{Cr}_2\text{O}_7^{2-}$ ), the product (B) formed is ketone.
- 2.1. Indicate the alcohol studied.  
 2.2. Write the equation of the reaction

### **Exercise 3**

The complete combustion of 7.4 g of a non-cyclic saturated monohydric alcohol (A) gives 17.6 g of carbon dioxide.  $M(\text{C}) = 12 \text{ g.mol}^{-1}$ ,  $M(\text{H}) = 1 \text{ g.mol}^{-1}$  and  $M(\text{O}) = 16 \text{ g.mol}^{-1}$ .

#### **1. Molecular formula and isomerism:**

- 1.1. Give the general molecular formula of a non-cyclic saturated chain mono alcohol in terms of n.  
 1.2. Write the equation complete combustion reaction of (A).  
 1.3. Show that the Molecular formula of (A) is  $\text{C}_4\text{H}_{10}\text{O}$ .  
 1.4. Write the condensed structural formula of all possible isomers of compound (A).

#### **2. Identification of the organic compound (A)**

The following tests were performed to samples of compound (A)

Test number	Added reagent	Result obtained
Test 1	Few drops of acidified potassium permanganate solution	Decolorization of the solution
Test 2	Excess amount of acidified permanganate solution	<ul style="list-style-type: none"> <li>• The color of the solution fades.</li> <li>• formation of an acidic organic compound in the product</li> </ul>

- 2.1. Give the conclusion that can be drawn from test 1.  
 2.2. Identify the class of alcohol (A) by referring to the test 2.  
 2.3. Deduce the systematic name of (A) knowing that it has a non-branched chain.

#### **3. Reactions of alcohol (A)**

- 3.1. Write the two half reactions and the overall equation of the reaction taking place between alcohol (A) and permanganate ion in test 2.

**Given** ( $\text{MnO}_4^-/\text{Mn}^{2+}$ )

- 3.2. Alcohol (A) undergoes dehydrogenation reaction.  
 3.2.1. Write the equation of the reaction taking place.  
 3.2.2. Indicate the family of organic compound obtained.

### **Exercise 4**

One mole of 2-propanol is mixed with one mole of propanoic acid.

- Name the reaction taking place.
- Write the equation of the reaction using condensed structural formulas.
- Assuming that the equilibrium constant  $K_c = 2.3$ , calculate the composition of the system at equilibrium.
- Determine the percentage yield of the reaction at equilibrium.

### **Exercise 5**

A saturated open chain monoalcohol (A):  $\text{C}_x\text{H}_y\text{O}$  has the following mass percent composition:

$$\%m(\text{H}) = 13.51\% \quad \%m(\text{O}) = 21.62\%$$

Density of (A) is  $d = 0.81\text{g/mL}$ .

### 1. Identification of alcohol (A)

- 1.1. Show that the molecular formula of (A) is  $\text{C}_4\text{H}_{10}\text{O}$ .
- 1.2. Write the condensed structural formula of all possible isomers of compound (A).
- 1.3. One unbranched isomer of (A) undergo dehydrogenation reaction at a temperature of  $300^\circ\text{C}$  and in absence of oxygen using Cu as catalyst. The obtained product is an aldehyde.
  - 1.3.1. Give the systematic name of alcohol (A).
  - 1.3.2. Write using condensed structural formula the equation of the reaction that took place.
  - 1.3.3. This reaction is called mild oxidation. Explain.

### 2. Esterification reaction

A mixture of 0.2 mol of ethanoic acid and a volume  $V = 20\text{ mL}$  of alcohol (A) is heated in presence of few drops of concentrated sulfuric acid until reaching equilibrium. The amount of ester obtained is found to be 0.13 mol. Given: density of (A) =  $0.74\text{g/mol}$

- 2.1. Write, using condensed structural formulas, the equation of the reaction taking place.
- 2.2. Verify that the initial mixture of the two reactants is equimolar.
- 2.3. Calculate the equilibrium constant  $K_c$ .
- 2.4. At a time ( $t$ ), the percentage yield was 65%. Determine whether the reaction has reached equilibrium at time  $t$ .

### Exercise 6

The aim of this exercise is to identify an alcohol (A) using esterification reaction.

Given: Starting from equimolar mixture of a monoalcohol and a monocarboxylic acid, the percentage yield of an esterification reaction is as follows:

Class of alcohol	Primary alcohol	Secondary alcohol	Tertiary alcohol
%Y	67%	60%	5%

The elemental analysis of alcohol (A) shows that the percentage by mass of oxygen in (A) is 21.62%.

### 1. Identification of alcohol (A).

- 1.1. Show that the molecular formula of (A) is  $\text{C}_4\text{H}_{10}\text{O}$ .
- 1.2. Write all possible condensed structural formulas of (A).
- 1.3. 0.2 mol of alcohol (A), and a volume  $V_2$  of ethanoic acid are mixed together in presence of concentrated sulfuric acid as catalyst. The mixture is subjected to reflux heating for 30 minutes where equilibrium is reached. The amount of ethanoic acid left after 30 minutes is 0.08 mol.
  - 1.3.1. Write the general equation of esterification reaction.
  - 1.3.2. Determine the volume  $V_2$  knowing that the initial mixture of the two reactants is equimolar. Given:  $M(\text{ethanoic acid}) = 60\text{ g/mol}$ , density of ethanoic acid =  $1.05\text{ g/mL}$ .
  - 1.3.3. Calculate the %Y of the reaction.
  - 1.3.4. Deduce the systematic name of alcohol (A) knowing that it has no branches.

### 2. Study of esterification Reaction

In a second experiment, 2 mol of alcohol (A) and 1 mol of ethanoic acid are mixed together. The mixture is heated for 1 hour, the number of moles of ester obtained during this time is 0.60 mol.

- 2.1. Write the equation of reaction using condensed structural formulas.
- 2.2. Name the ester obtained.
- 2.3. Verify whether the heating duration (1 hour) was sufficient to reach equilibrium.
- 2.4. Suggest two experimental ways to increase the yield of the reaction.

### Exercise 7

The aim of this exercise is to identify organic compounds (A) and (B), and to study esterification reaction.  
An organic compound (A) has the following mass percentages:

$$\%C = 40\%, \%H = 6.66\%.$$

#### 1. Identification of (A) and (B):

- 1.1. Determine the empirical formula of (A).
- 1.2. Show that the molecular formula of compound (A) is  $C_2H_4O_2$  knowing that the molar mass of (A) is 60 g/mol.
- 1.3. (A) is obtained by continuous mild oxidation of an alcohol (B).
  - 1.3.1. Determine the molecular formula of (B).
  - 1.3.2. Write the condensed structural formula of (B). Circle and name its functional group.

#### 2. Reaction between (A) and (B):

We mix 28.57 mL of (A) and 29.11 mL of (B) and few drops of concentrated sulfuric acid.  
The following reaction takes place:



At equilibrium, the number of moles of ester (E) obtained is 0.33 mol.

Given:

Compounds	(A)	(B)
Density g.mL <sup>-1</sup>	1.05	0.79
Molar mass in g.mol <sup>-1</sup>	60	46

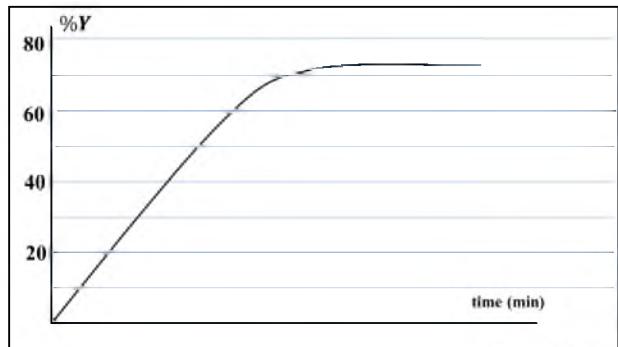
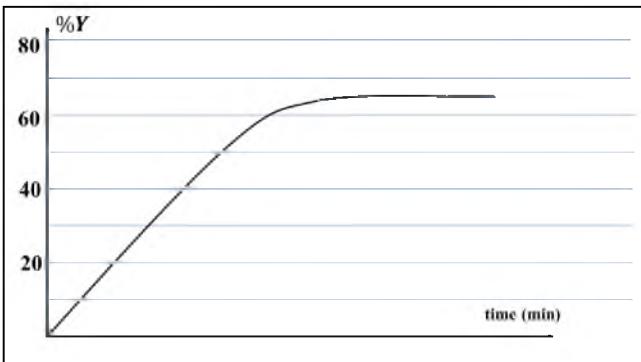
- 2.1. Write the equation of the reaction taking place between (A) and (B).
- 2.2. Name the ester obtained
- 2.3. Show that the initial mixture is equimolar.
- 2.4. Determine the degree of conversion of (A) at equilibrium.
- 2.5. Verify that the percentage yield of the reaction is 66%.

#### 3. Experimental Study:

Two experiments are performed under the same conditions as the previous experiment with changing the initial amounts of (A) and (B).

Experiment	n(A)	n(B)	n(E)	n(H <sub>2</sub> O)
1	1	1	0	0
2	0.5	1	0	0

The following curves are given:



Associate for each experiment the corresponding curve. Justify your answer.

### Exercise 8 Study of an Esterification Reaction

A reaction takes place between 1 mol of carboxylic acid (A) and 1 mol of alcohol (B) in presence of sulfuric acid as catalyst. The mixture is subjected to reflux heating at temperature (T) until the amounts become constant.

**Given:**

- Carboxylic acid (A) is methanoic acid
- Alcohol (B): 2-methyl-1-propanol.

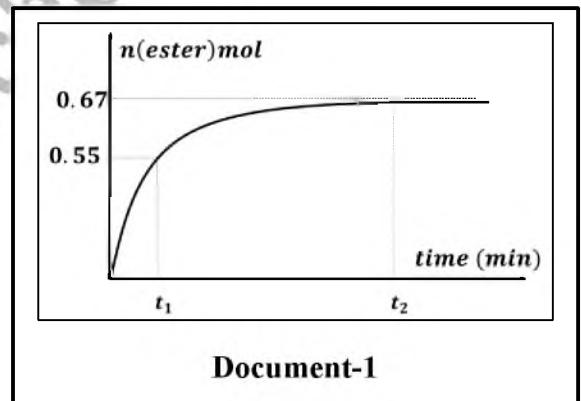
The amount of ester produced over time is given in **document-1**.

#### 1. Preliminary study:

- 1.1. Give the condensed structural formulas of (A) and (B).
- 1.2. Specify the class of alcohol (B).
- 1.3. Write the equation of the reaction taking place.
- 1.4. Name the ester (E) produced.

#### 2. Quantitative Study:

- 2.1. Calculate the percentage yield of the reaction at instants  $t_1$  and  $t_2$ .
- 2.2. The same experiment is repeated several times with one change each time. Specify how the percentage yield varies in each case at instants  $t_1$  and  $t_2$ .
  - 2.2.1. The reaction mixture is subjected to heating at temperature  $(T') > (T)$ .
  - 2.2.2. The reaction takes place in absence of sulfuric acid. (*note at  $t_2$  equilibrium is reached in the new experiment*)
  - 2.2.3. The mixture contained initially 2 mol of (A) and 1 mol of (B).
  - 2.2.4. The mixture contained initially 2 mol of each of the two reactants. (without  $t_1$ )
  - 2.2.5. Using dehydrating agent (excess amount of concentrated sulfuric acid). (without  $t_1$ )
  - 2.2.6. Using 1 mol of aqueous methanoic acid instead of pure methanoic acid. (without  $t_1$ )



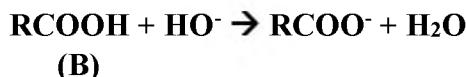
**Document-1**

## Exercise 9

## Alcohols

The oxidation of a mass  $m=0.55\text{ g}$  of non-cyclic, saturated, non-branched primary alcohol (A) gives an acid (B) of general molecular formula  $\text{RCOOH}$ .

The carboxylic acid (B) that is obtained is titrated with aqueous solution of sodium hydroxide ( $\text{Na}^+ + \text{HO}^-$ ) of  $C_b = 0.5\text{ mol.L}^{-1}$ . The volume needed to reach equivalence point is  $V_{bE} = 12.5\text{ mL}$ . The equation of reaction taking place is:



### 1. Determination of Alcohol (A):

- 1.1.Determine the molecular formula of alcohol (A).
  - 1.2.Write the condensed structural formula of (A) and give its IUPAC name.
  - 1.3.Deduce the condensed structural formula of (B) and give its IUPAC name.
- ### 2. Alcohol (A) is subjected to catalytic dehydrogenation reaction.
- 2.1.Write the equation of the reaction.
  - 2.2.Give the family and the name of the product obtained.
  - 2.3.When alcohol (A) is heated in presence of  $\text{Al}_2\text{O}_3$  as catalyst an alkene is formed. Specify the property of catalyst revealed in this case.

### 3. Esterification Reaction:

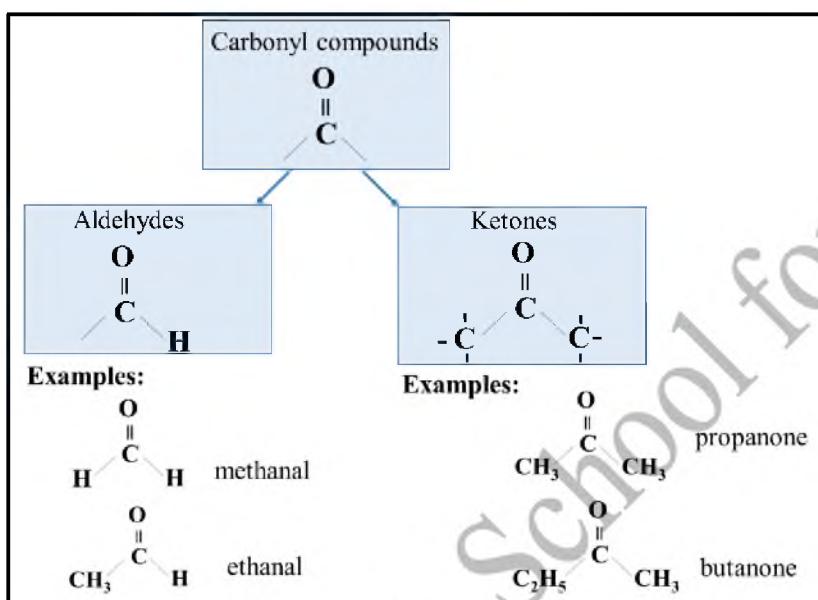
- A mixture is prepared by mixing 1 mol of alcohol (A) and 1 mol of carboxylic acid (B).
- 3.1.Write the equation of the reaction taking place. Give the characteristics of the reaction.
  - 3.2.Name the ester obtained.
  - 3.3.The reaction takes place in presence of sulfuric acid. Give the role of sulfuric acid.
  - 3.4.Knowing that  $K_c = 4.12$ , determine the percentage yield of the reaction at equilibrium.
  - 3.5.Suggest two ways to increase the yield of the reaction at equilibrium.

## UNITE 4- CHAPTER 8: ALDEHYDES AND KETONES

### 1. Definition

Organic compounds that contain the carbonyl group (-CO-).

- **Aldehydes:** -CHO
- **Ketones** -CO-



### 2. Nomenclature of aldehydes:

Naming unbranched aldehydes	
H-CHO	Methanol
CH <sub>3</sub> -CHO	Ethanol
CH <sub>3</sub> -CH <sub>2</sub> -CHO	propanal
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CHO	butanal

Naming branched aldehydes	
$\begin{array}{c} \text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \text{CHO} \\   \\ \text{CH}_3 \end{array}$	2-methylpropanal
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 - \underset{\text{CH}_3}{\text{C}} - \text{CH}_2 - \text{CHO} \\   \\ \text{CH}_3 \end{array}$	3,3-dimethylbutanal

#### Notes:

- Start numbering from the functional carbon
- Do not mention the number of the position of the aldehyde group, it is always on carbon number 1

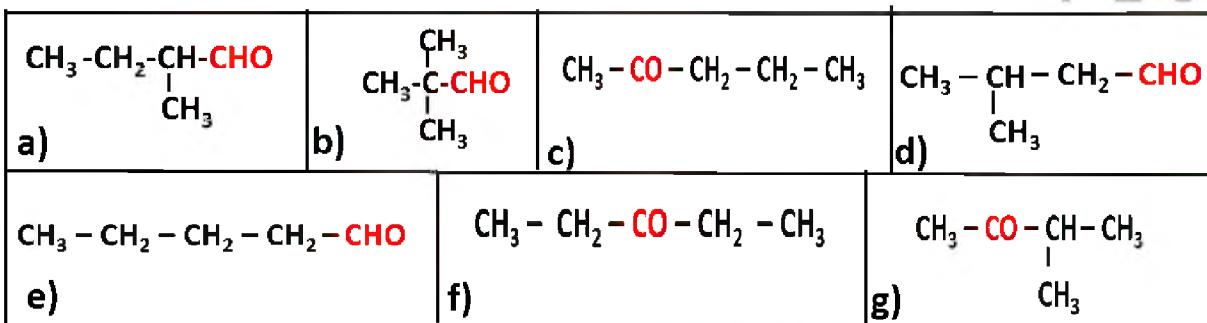
### 3. Nomenclature of Ketones:

Examples	
CH <sub>3</sub> -CO-CH <sub>3</sub>	propanone
CH <sub>3</sub> -CO-CH <sub>2</sub> -CH <sub>3</sub>	2 - butanone

$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CO} - \text{CH}_2 - \text{CH}_3$	3- hexanone
$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CO} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$	4- heptanone
$\text{CH}_3 - \text{CH}(\text{CH}_3) - \text{CH}_2 - \text{CO} - \text{CH}_2 - \text{CH}_3$	5-methyl-3-hexanone

#### 4. Isomerism:

Consider the following carbonyl compounds, all admitting the molecular formula:  $\text{C}_5\text{H}_{10}\text{O}$ .



1- Indicate, among these compounds, the aldehydes and ketones, and arrange them in a table.

Aldehydes	Ketones

2- Deduce the type of isomerism that exists between aldehydes having same molecular formula.

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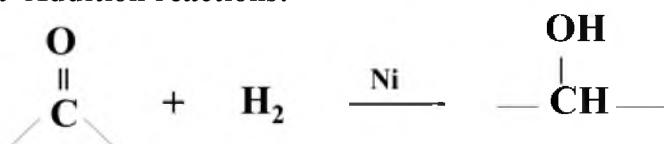
3- Give the type of isomerism that exists between compounds ( c ) and ( f ) , and between ( c ) and ( g ).  
Give a conclusion.

.....

.....

#### 5- Chemical reactions:

##### 5-a- Addition reactions:



Both aldehydes and ketones can undergo addition reactions.

### 5-b- oxidation reactions

Note: Ketones can not undergo oxidation reactions.

**Application:** Write the equation of oxidation reaction of an aldehyde ( $\text{R}-\text{HO}$ ) with  $\text{MnO}_4^-$ .

.....  
.....  
.....  
.....  
.....

### 6- Identification tests:

- The fact that both aldehydes and ketones can undergo addition reactions is used to identify them from other organic compounds.
- The fact that aldehydes can undergo oxidation while ketones can't is used to identify aldehydes from ketones.

#### How to perform a test:

Add few drops of the testing reagent (DNPH,  $\text{NaHSO}_3$ , Fehling's solution, ...) to a test tube containing some amount of the organic compound. Any change in color indicates a positive test.  
Summary of identification tests:

	$\text{NaHSO}_3$	DNPH	Tollen's reagent	Fehling's reagent	Schiff's	$\text{MnO}_4^-$	$\text{Cr}_2\text{O}_7^{2-}$
<b>Aldehyde</b>	White crystals	Yellow-orange precipitate	Formation of silver mirror	Formation of brick red precipitate	Pink color	Disappearance of purple color	Change of color
<b>Ketone</b>	White crystals	Yellow-orange precipitate	No change	No change	No change	No change	No change

#### Application Exercises:

##### Exercise 1:

Compound (A) is a colorless, flammable liquid with a punget odor. It is immiscible with many organic solvents. Quantitative organic analysis of a compound (A) of formula  $\text{C}_x\text{H}_y\text{O}$  gave the following results:

$$\%m(\text{C}) = 66.67\%$$

$$\%m(\text{H}) = 11.11\%$$

Given molar masses in  $\text{g}\cdot\text{mol}^{-1}$  of  $\text{H} = 1$ ,  $\text{C} = 12$ , and  $\text{O} = 16$ .

##### 1. Identification of compound (A):

1.1. Show that the molecular formula of (A) is  $\text{C}_4\text{H}_8\text{O}$ .

1.2. Write the possible condensed structural formula of the possible isomers of (A) and give their names knowing that the carbon chain is saturated and non-cyclic.

**1.3.** The following test are carried out:

Test 1: (A) + 2,4-D.N.P.H → yellow-orange precipitate

Test 2: (A) + fehling solution → brick red precipitate.

**1.3.1.** Describe the procedure of test 2.

**1.3.2.** Deduce the family of (A).

**1.3.3.** Identify (A), knowing that its carbon chain is branched.

**2. Some chemical properties of (A)**

A certain quantity of (A) is divided into two parts. The first part is treated with an acidified solution of potassium permanganate ( $K^+ + MnO_4^-$ ). The organic compound formed is denoted (B). The second part is heated in the presence of a hydrogenation catalyst. The organic compound formed is denoted (C).

**2.1.** Write the equation of the first reaction. Identify the functional group of (B).

**2.2.** Write the equation of the second reaction. Name (C).

**Exercise 2:**

An oxygen-containing compound is an organic pure compound whose molecule contains at least one oxygen atom. Four flasks are labeled 1 to 4, each containing one of the following organic compounds:

- 2-methyl -2- propanol
  - 2-pentanol
  - Butanone
  - Butanal
1. Write the condensed structural formula of each of the above organic compounds.
  2. A series of chemical tests are carried out to identify each compound. The test is considered (+) if a reaction occurs, and (-) if no reaction occurs. The results are shown in document-1.

Test	Flask (1)	Flask (2)	Flask (3)	Flask (4)
Dichromate solution	-	+	-	+
2,4- D.N.P.H	-	+	+	-
Fehling's reagent	-	+	-	-

Document-1

Identify the content of each flask.

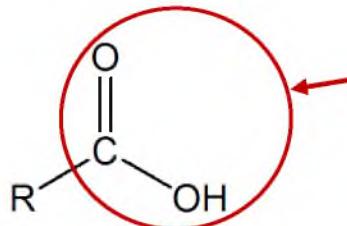
Ghobeyri (Institute for Ghobeyri)

## UNIT 4- CHAPTER 9 -CARBOXYLIC ACIDS:

### Introduction

Carboxylic acids represent a class of organic compounds

Their general molecular formula of saturated mono carboxylic acids is represented by:



- Where R is mostly an alkyl group of general molecular formula:  $\text{C}_n\text{H}_{2n+1}$  where n is the number of carbon atoms.
- General molecular formula of saturated monocarboxylic acids is then:  $\text{C}_n\text{H}_{2n}\text{O}_2$
- Functional group of carboxylic acids is: carboxyl group (-COOH)

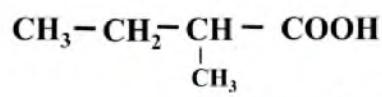
### Nomenclature of carboxylic acids:

Rule of naming carboxylic acids: Alkane → Alkanoic acid

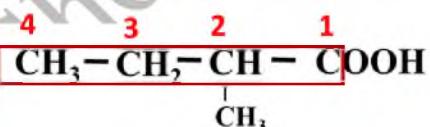
### Examples :

- H-COOH : Methanoic acid
- $\text{CH}_3\text{-COOH}$ : Ethanoic acid
- $\text{CH}_3\text{-CH}_2\text{-COOH}$ : Propanoic acid

### Naming branched chain carboxylic acids:



- Choose the main chain.
- Number it starting from the carbon of the functional group.
- Do not mention the position of the functional group.



Name: 2-methyl butanoic acid

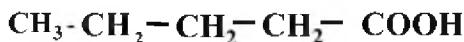
### Isomerism:

Carboxylic acids have no positional isomers: the carboxyl group is always on carbon number 1.

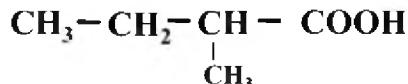
They only have skeletal isomers:

**Example:**

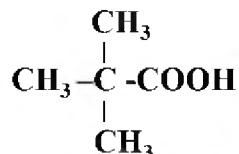
Consider the following three compounds:



**M.F:** C<sub>5</sub>H<sub>10</sub>O<sub>2</sub>  
Pentanoic acid



**M.F:** C<sub>5</sub>H<sub>10</sub>O<sub>2</sub>  
2-methylbutanoic acid



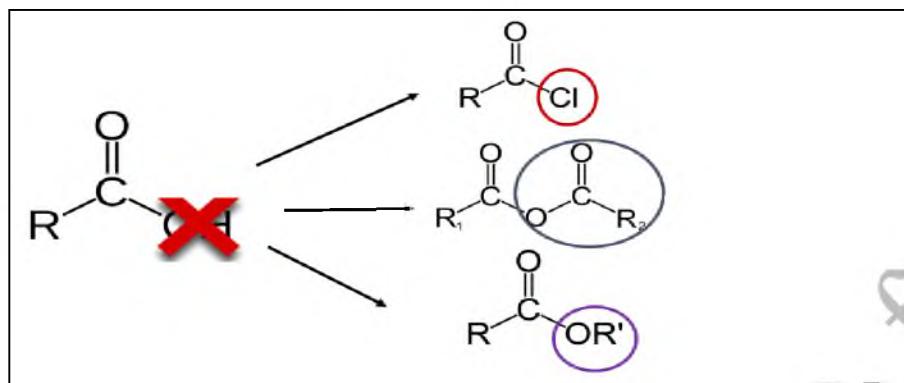
**M.F:** C<sub>5</sub>H<sub>10</sub>O<sub>2</sub>  
2,2-dimethylpropanoic acid

These three compounds have same molecular formula, same functional group, but different arrangement of carbon atoms, thus these compounds are **skeletal isomers**.

## Carboxylic Acid Derivatives

Carboxylic acid derivatives are compounds in which the -OH group of the carboxylic acid is replaced by an atom or a group of atoms.

Three carboxylic acid derivatives are required in this chapter.



## Esters

Esters are organic compounds that are found naturally, or synthesized. They have fruity odors.

They are derived from carboxylic acids when  $-\text{OH}$  group of the carboxylic acid is replaced by  $-\text{OR}'$  group.



### III- 1) Nomenclature of esters

They are named as alkyl alkanoates:

- a)  $\text{CH}_3 \text{COO-CH}_3 \rightarrow$  methyl ethanoate
- b)  $\text{HCOO CH}_2\text{CH}_3 \rightarrow$  ethyl methanoate
- c)  $\text{C}_6\text{H}_5\text{COO-CH}_3 \rightarrow$  methyl benzoate
- d)

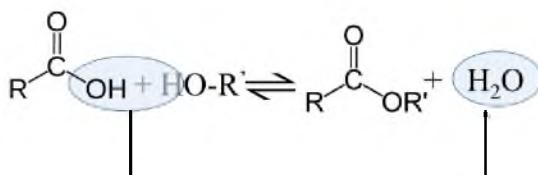


- e)
- 
- The chemical structure of ethyl 2-methylpropanoate is shown. It consists of an ethyl group ( $\text{CH}_3\text{CH}_2-$ ) attached to a propanoate group ( $\text{COO-CH}_2\text{CH}-\text{CH}_3$ ). The carbons in the propanoate group are numbered 1, 2, and 3, starting from the methyl group at position 1. A methyl group ( $\text{CH}_3$ ) is attached to the second carbon of the propanoate group. An arrow points to the right, followed by the name "Ethyl 2-methylpropanoate".

### III- 2) Preparation of esters

Three methods to prepare esters:

**Method 1:** by mixing carboxylic acid with alcohol



**Characteristics of esterification reaction:**

- Slow
- Incomplete (reversible)
- Athermic

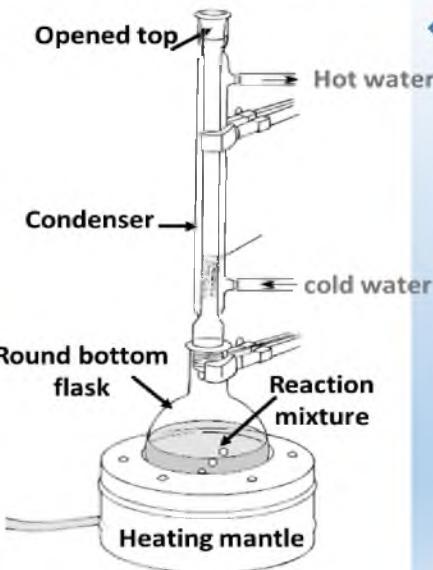
To increase the yield of the reaction you have to favor direction 1 by:

- Use excess amount of one of the reactants.
- Remove one of the products from the reaction medium as it is formed.



To speed up the reaction:

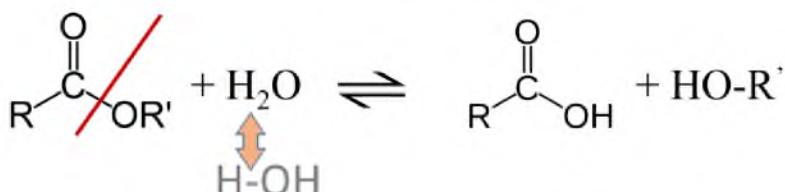
- Use catalyst : kinetic factor
- Heat the reaction mixture by using reflux heating (Heating with a condenser to speed up the reaction prevent the loss of reaction components by condensing the vapors and returning them to the reaction medium).



**Reflux heating apparatus:** heating in presence of a condenser.

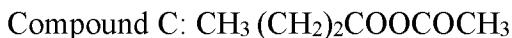
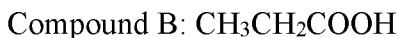
- Heating: speeds up the reaction.
- Condenser : prevent the loss of reaction components by condensing their vapors and returning them to the reaction medium.

### III-3) Hydrolysis of esters



### **Exercise 1**

Consider the following compounds:



1. Name each of the above compounds.
2. Write the 2 equations of formation of compound E from benzoic acid.
3. Write the equation of hydrolysis of compound C. Give its characteristics.
4. Compound C is produced by the reaction of compound A and sodium ethanoate.
  - 4.1. Write the chemical formula of sodium ethanoate.
  - 4.2. Write the equation of the reaction taking place.
  - 4.3. This reaction must take place in a well dry beaker. Justify.
5. Compound D can be produced by reaction of benzoic acid with an alcohol X.
  - 5.1. Give the condensed structural formula of alcohol X. and name it.
  - 5.2. Write the equation of reaction taking place.
  - 5.3. Give the characteristics of the reaction.
  - 5.4. Specify the effect of catalyst and heat on yield of reaction.
  - 5.5. Give 2 ways that can be used to increase yield.
  - 5.6. Write the equations of reactions that allow to obtain maximum yield of the ester by choosing two suitable compounds from the list given above.

### **Exercise 2**

Consider the following organic compounds

A: ethanoic acid

B: ethanoyl chloride

C: ethanoic propanoic anhydride

1. Give the condensed structural formula of A, B, and C.
2. Write the equation of formation of compound (B) from (A).
3. A mixture of ethanoic acid and propanoic acid is heated in presence of  $\text{P}_2\text{O}_5$ .
  - 3.1. Give the condensed structural formula of all the possible organic products that will be produced in this case.
  - 3.2. Write the equation of reaction that produces compound (C).
  - 3.3. Explain the role of  $\text{P}_2\text{O}_5$  in this reaction.
4. Compound (C) can be produced by the reaction of compound (B) and sodium propanoate in absence of water.
  - 4.1. Write the equation of reaction that takes place in this case.
  - 4.2. Explain the importance of carrying the reaction in absence of water.

### Exercise 3

### Preparation of an Ester

The aim of this exercise is to identify some organic compounds and to study different methods of preparation of ester (E).

**Given :** molar masses in g.mol<sup>-1</sup> : H = 1, C = 12, O = 16.

#### 1. Identification of compound (A)

The complete combustion of 7.4 g of an organic compound (A):  $C_3HxOy$  gives 13.2 g of carbon dioxide and 5.4 g of water.

- 1.1. show that the molecular formula of (A) is  $C_3H_6O_2$ .
- 1.2. Write all the possible condensed structural formula of (A).
- 1.3. (A) turns litmus red. Deduce the chemical family of (A) and give its systematic name.

#### 2. Identification of compound (B)

The mild oxidation of an alcohol (B) in presence of heated copper and excess oxygen gas leads to the formation of the above compound (A).

- 2.1. Define mild oxidation.
- 2.2. Identify the class and the condensed structural formula of (B).
- 2.3. Write the equation of the oxidation reaction.

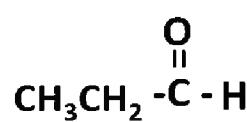
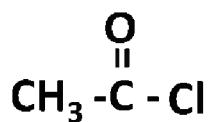
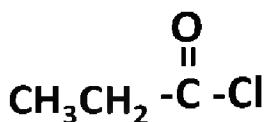
#### 3. Preparation of an ester by different methods:

The table of document 1 summarizes the chemical reagents that are used in the synthesis of ester and their amounts in each of the two methods:

	1 <sup>st</sup> reactant	2 <sup>nd</sup> reactant	Other additives	Ester produced	%Y
<b>Method 1</b>	(A): 0.3 mol	(B): 0.3 mol	Sulfuric acid : catalyst	(E) : 0.2 mol	%Y <sub>1</sub>
<b>Method 2</b>	Derivative of (A) : 0.3 mol	(B): 0.3 mol	-	(E) : 0.3 mol	%Y <sub>2</sub> ≈ 100%

**Document-1**

- 3.1. Write the equation of the reaction taking place in method 1.
- 3.2. Give the systematic name of (E).
- 3.3. Determine the value of %Y<sub>1</sub>.
- 3.4. Choose, from the following compounds, the one that is used as the 2<sup>nd</sup> reactant in method 2.



- 3.5. Write the equation of the reaction of method 2.

**Exercise: 4****Organic Chemistry**

- **Given:** The boiling points of any series of isomeric organic compounds decrease with the degree of branching.

**1- Identification of alcohol (A)**

(A) is an alcohol containing 21.6 % by mass oxygen, and having a saturated, noncyclic carbon chain.

**1.1.** Show that the molecular formula of (A) is  $C_4H_{10}O$ .

**1.2.** Give all the possible condensed structural formulas of (A)

**1.3. Document-1** summarizes two tests that are used to identify (A):

	Chemical test	Result
<b>Test-1</b>	(A)+ few drops of $MnO_4^-$ solution	Decolorization of $MnO_4^-$ solution
<b>Test-2</b>	(A)+ excess $MnO_4^-$ solution	Formation of an organic compound that turns wet litmus paper red.

**1.3.1.** Interpret the results of each test.

**1.3.2.** Identify alcohol (A) knowing that it admits a boiling point which is the highest among all alcohols having molecular formula  $C_4H_{10}O$ .

**2. Esterification reaction:**

- $K_c$  of esterification reaction involving primary alcohol is  $K_c = 4.2$ , and that of esterification reaction involving secondary alcohol is  $K_c = 2.25$ .
- Molar masses in  $g \cdot mol^{-1}$  of ester (E) =  $130 \ g \cdot mol^{-1}$ , M(C) = 12, M(H) = 1, M(O) =  $16 \ g \cdot mol^{-1}$

A mixture (mixture 1) consisting of 0.20 mol of compound (A), 0.20 mol of propanoic acid, and 1.00 mL of sulfuric acid solution is subjected to reflux heating maintained at constant temperature (T). After a specific time (t), reflux heating is stopped, and the mass of ester (E) formed is  $m(E) = 15.6 \ g$ . the % yield of the reaction in this mixture is  $Y_1$ .

Sulfuric acid acts as catalyst in this chemical reaction.

**2.1.** Write the equation of reaction using condensed structural formulas.

**2.2.** Specify whether equilibrium is reached at time “t”.

**2.3.** It is advised to use, instead of propanoic acid, the corresponding chlorinated derivative (B) to prepare the ester (E).

**2.3.1.** Give the condensed structural formula of (B) and the corresponding name.

**2.3.2.** Explain the advantage of using compound (B) instead of propanoic acid for the preparation of this ester.

**Exercise 5****Synthesis of an Ester**

We intend to prepare an ester whose taste and smell are like those banana. This ester is 3-methyl butyl ethanoate (iso amyl acetate) of formula:



It is used to flavor some syrups.

### 1- Principle of manipulation:

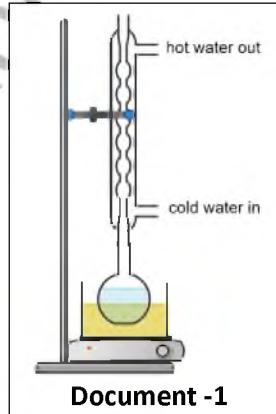
This ester is prepared by the action of an acid (A) on an alcohol (B). The reaction takes place at a high temperature. The ester formed is extracted by fractional distillation.

The chemicals that are used are acid (A), alcohol (B) and sulfuric acid.

Compounds	Solubility in water	Density ( $\text{g.L}^{-1}$ )	Boiling points ( $^{\circ}\text{C}$ )	Molar mass ( $\text{g.mol}^{-1}$ )
Acid (A)	Soluble	$1.05 \times 10^3$	118	60
Alcohol (B)	Almost insoluble	$8.10 \times 10^2$	128	88
Ester	Almost insoluble	$8.70 \times 10^2$	143	130

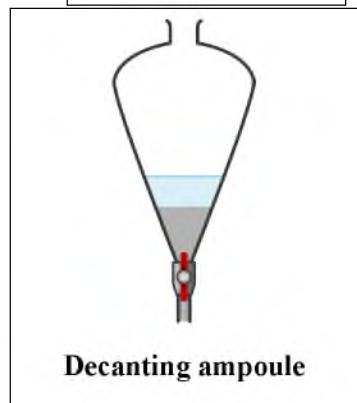
#### First step

In a round bottomed flask of  $100\text{mL}$ , we pour a volume  $V_1 = 44.0\text{ mL}$  of alcohol (B) and a volume  $V_2$  of acid (A). we add cautiously 1 mL of concentrated sulfuric acid and a few grains of boiling stones. We adjust the condenser and we reflux (document-1).



#### Second step

After cooling we pour the content of the flask in water, we stir, and we pour the mixture into a decanting ampoule. Two layers of immiscible liquids are formed, one of which contains ester and the alcohol that did not react. We collect the content and subject it to fractional distillation.



#### 1. Study of first step:

1.1.Name and write the condensed structural formula of acid (A) and of alcohol (B) used. Specify the class of alcohol (B).

1.2.Write the equation of the reaction taking place between acid (A) and alcohol (B). List the characteristics of the reaction.

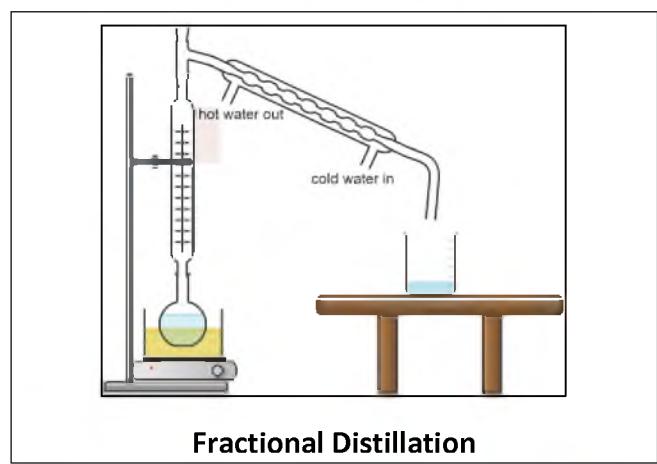
1.3.Knowing that the mixture is equimolar, calculate the volume  $V_2$  of the acid needed to react with  $44.1\text{ mL}$  of alcohol (B).

1.4.What is the role of the boiling chips?

1.5.Give the role of the condenser ?

#### 2. Study of second step:

2.1.Deduce, with justification, the phase to which isoamyl acetate exists during decanting.



- 2.2.** Why is it necessary to monitor the temperature during distillation? Name the liquid that vaporizes first during fractional distillation.  
**2.3.** What mass of ester would be obtained if the reaction was complete?  
**2.4.** The real mass obtained is 26.3 g. Calculate the percentage yield of the reaction.

### Exercise 6

### Esterification Reaction and Percentage yield

#### Given

Starting from an equimolar mixture of two reactants, the percentage yield of esterification reaction involving primary alcohol is 67 % and that involving secondary alcohol is 60%.

The aim of this exercise is to study the esterification reaction between 2,2-dimethyl-1-propanol (A) and ethanoic acid (B)

#### 1. Study of Experiments 1 and 2:

Two experiments (1 and 2) were performed. The conditions of these two experiments are given in the table of document-1.

Experiment number	Number of moles of (A) in moles	Number of moles of (B) in moles	dehydrating agent	Number of moles of (E) in moles at time t
1	1	1	-	0.67
2	1	1	Present	??

- 1.1.** Give the condensed structural formula of (A) and (B).
- 1.2.** Write the equation of the esterification reaction taking place.
- 1.3.** Name, according to systematic nomenclature, the produced ester (E).
- 1.4.** Show that equilibrium is reached at time t in experiment 1.
- 1.5.** Choose, with justification, the value that represents n (E) at equilibrium in experiment 2.
  - a) 0.55
  - b) 0.67
  - c) 0.78

#### 2. Performing the Experiments with New Conditions

Experiments 3 and 4 were performed in order to study the effect of presence of excess of one of the reactants on percentage yield. The table of document-2 summarizes these experiments:

Experiment number	Number of moles of (A) in moles	Number of moles of (B) in moles	dehydrating agent	Percentage yield at equilibrium
3	1	2	-	%Y <sub>3</sub>
4	1	5	-	%Y <sub>4</sub>

- 2.1.** Compare %Y<sub>3</sub>, %Y<sub>4</sub> and %Y<sub>1</sub>.
- 2.2.** Draw out a conclusion.

## Exercise 7

Consider the organic compounds given in the table of document-1.

Compound (A)	Compound (B)	Compound (C)	Compound (D)	Compound (E )
1-butanol	2-butanol	Carboxylic acid	butanal	Ester of molecular formula C <sub>6</sub> H <sub>12</sub> O

**Document-1**

**Given:** For an esterification reaction starting from equimolar mixture of the two reactants, the percentage yield is 67 % if the involved alcohol is primary, and 60 % if the involved alcohol is secondary.

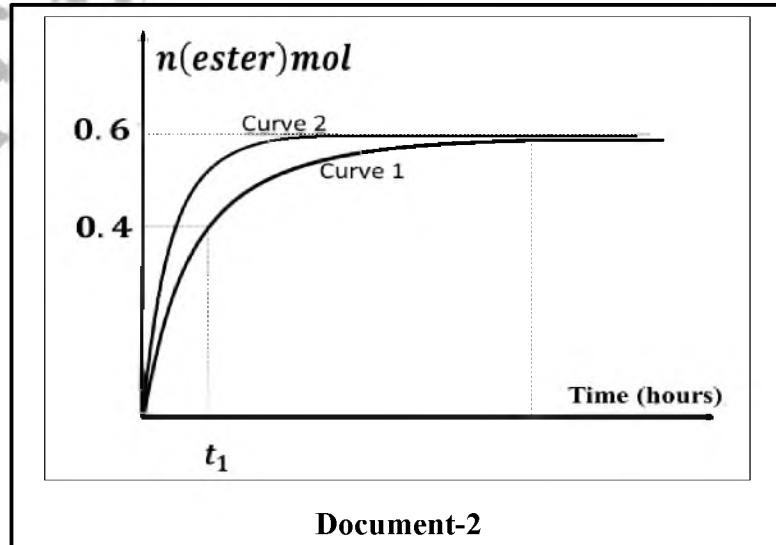
### 1. Preliminary study:

- 1.1. Write the condensed structural formula of compounds A, B, and D.
- 1.2. Circle and name the functional group of A, B, and D.
- 1.3. Specify the type of isomerism existing between compounds A and B.
- 1.4. Compound (D) can be obtained from (A) by dehydrogenation reaction. Write using condensed structural formulas the equation of the reaction taking place.
- 1.5. Verify that compound (B) has an asymmetric carbon.
- 1.6. Draw the Cram representation of (B) and its mirror image (B'). Specify the type of isomerism that exists between (B) and (B').

### 2. Esterification reaction:

Ester (E) is obtained, during experiment-1, by the reaction of equimolar mixture consisting of 1 mol of compound (C) and 1 mol of an open chain saturated monoalcohol of molecular formula C<sub>4</sub>H<sub>10</sub>O. The mixture is heated at temperature (T). The follow up of this reaction allows to draw **curve (1)** of document-2.

- 2.1. Identify compound (C).
- 2.2. Determine the equilibrium constant K<sub>c</sub> of this reaction.
- 2.3. The alcohol that is involved in this reaction is one of the two alcohols of **document-1**. Specify the alcohol involved in this esterification reaction.
- 2.4. Deduce the condensed structural formula and the name of ester (E).
- 2.5. Two other experiments were performed in order to study the effect of some kinetic factors on esterification reaction. The conditions of the two experiments are summarized in **document-3**.



**Document-2**

Experiment	Amount of alcohol	Amount of (C)	Temperature	catalyst
2	1 mol	1 mol	T'>T	Absent
3	1 mol	1 mol	T	Present

**Document-3**

**2.5.1.** Curve (2) of document-2 corresponds to experiment-2. Deduce from curve (2) the effect of temperature on esterification reaction.

**2.5.2.** Choose the correct answer in each of the following cases. Justify.

- The number of moles of ester produced in experiment-3 at time  $t_1$  is:  
a) 0.3                  b) 0.4                  c) 0.7                  d) 0.5
- The amount of ester produced at equilibrium in experiment-3 is:  
a) 0.5 mol              b) 0.6 mol              c) 0.7 mol              d) 1 mol

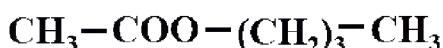
### Exercise 5

### The Aroma Of Banana

The aroma of banana is due the presence of natural banana extracts, or the presence of an artificial compound, butyl acetate.

#### Document-1

The condensed structural formula of butyl acetate is :



	A	B	E	H <sub>2</sub> O
Molar mass (g.mol <sup>-1</sup> )	60	74	116	18
Density (g.mL <sup>-1</sup> )	1.05	0.81	0.87	1.00

#### Document-2

**Given:** starting with equimolar amounts of the two reactants, the yield of esterification reaction involving primary alcohols is 67% and that involving secondary alcohols is 60 %.

#### 1. Preliminary study

The synthesis of butyl acetate (E) can be carried out from a carboxylic acid (A) and an alcohol (B). The equation associated with the reaction modeling the synthesis of E is written:



**1.1.** Give the names and condensed structural formulas of compounds A and B.

**1.2.** Indicate the family of organic compounds to which these chemical species belong to?

#### 2. Laboratory synthesis of Butyl Acetate

It is proposed to synthesize butyl acetate (E) in the laboratory from compounds A and B and to carry out kinetic monitoring of this synthesis. For this, an experiment, named experiment-1, consisting of three parts is performed. **document – 3** summarizes these parts.

**Part 1:** In a beaker placed in an ice-water bath, we introduce:

- a volume of carboxylic acid A:  $V_A$
- a volume of alcohol B:  $V_B = 9.2 \text{ mL}$
- a few drops of concentrated sulfuric acid added as catalyst.
- The total volume of the reaction mixture is  $V_{\text{total}} = V_A + V_B$

**Part 2:** The mixture is accurately, **equally distributed in 10 test tubes** placed in an ice-water bath, and all the tubes are then simultaneously placed in a bath at  $100^\circ \text{C}$ . The chronometer is then started

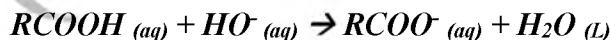
**Part 3:** The quantity of remaining carboxylic acid (A) in each tube is determined at given instants by titrating it with a solution of sodium hydroxide ( $\text{Na}^+ + \text{HO}^-$ ) of molar concentration of  $C_B = 1.0 \text{ mol L}^{-1}$ , in the presence of a colored indicator. Before each titration, each tube is

**Note: Correct in the above document  $C_B = 0.1 \text{ mol/L}$  and not  $1.0 \text{ mol/L}$ .**

2.1. Indicate the aim of initially placing the beaker in an ice-water bath.

2.2. Knowing that the initial mixture of carboxylic acid and alcohol is equimolar, show that the volume of carboxylic acid is  $V_A = 5.8 \text{ mL}$ .

2.3. Determine the maximum amount of ester that would be formed if the reaction is complete:  $X_{\text{max}}$ . The chemical equation associated with the titration of the carboxylic acid alone with sodium hydroxide is as follows:



Let  $X_{(t)}$  be the amount of ester produced, in mole, in the total volume  $V = 15 \text{ mL}$ .

2.4. Verify, at a given instant (t), that X is related to  $V_{\text{eq}}$ , expressed in mL, by the following relation:

$$X_{(t)} = X_{\text{max}} - 10^{-2} \cdot C_b \cdot V_{\text{eq}(t)}$$

2.5. At  $t = 20 \text{ min}$ ,  $V_{\text{eq}} = 40 \text{ mL}$ . Determine the % Y of this reaction at  $t=20 \text{ min}$ :  $Y_{20}$ .

2.6. Deduce whether equilibrium is reached at this instant.

Another experimental study is performed with same initial amounts of the two reactants as in experiment-1, but in absence of catalyst. The tubes are also placed in a bath maintained at  $100^\circ \text{C}$ . The yield at  $t = 20 \text{ min}$  in this case is  $Y'_{20}$ . Choose, with justification the correct answer.

- a)  $Y'_{20} = Y_{20}$       b)  $Y'_{20} > Y_{20}$       c)  $Y'_{20} < Y_{20}$

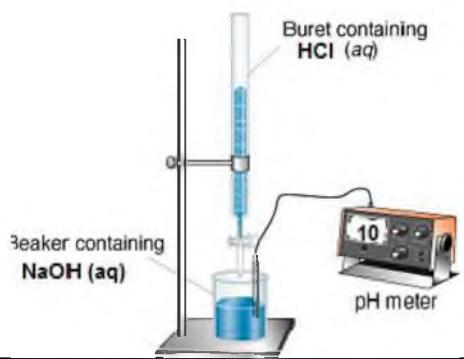
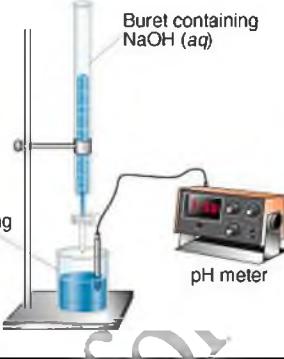
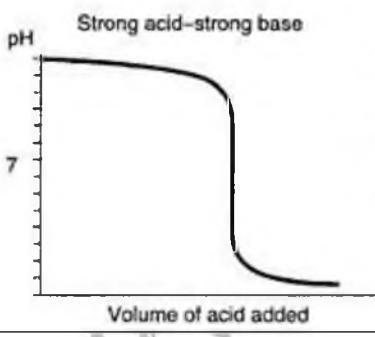
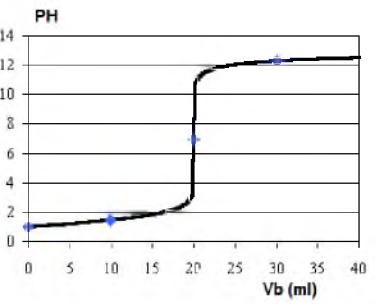
To synthesize butyl acetate by a rapid and complete chemical reaction, it is possible to replace the carboxylic acid A with one of its derivatives.

- 2.7.**Give the name and condensed structural formula of this derivative.  
**2.8.**Write the new synthesis equation.

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## UNIT 3- CHAPTER 4 : ACIDS AND BASES – ACID BASES TITRATIONS

<b>Strong acids:</b>	<b>Strong bases:</b>																
<b>Arrehenius definition:</b> -An acid is a substance that dissociates in water to give $\text{H}_3\text{O}^+$ ions. -A strong acid is a substance that dissociates <b>completely</b> in water to give $\text{H}_3\text{O}^+$ ions.	<b>Arrehenius definition:</b> -A base is a substance that dissociates in water to give $\text{HO}^-$ ions. -A strong base is a substance that dissociates <b>completely</b> in water to give $\text{HO}^-$ ions.																
Example: $\text{HCl} + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{O}^{+}_{(\text{aq})} + \text{Cl}^{-}_{(\text{aq})}$ <table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td>t=0</td> <td><math>n_a</math></td> <td>0</td> <td>0</td> </tr> <tr> <td><math>t=\infty</math></td> <td>0</td> <td><math>n_a</math></td> <td><math>n_a</math></td> </tr> </table>	t=0	$n_a$	0	0	$t=\infty$	0	$n_a$	$n_a$	Example: $\text{NaOH}_{(\text{s})} \longrightarrow \text{Na}^{+}_{(\text{aq})} + \text{HO}^{-}_{(\text{aq})}$ <table border="1" style="margin-left: auto; margin-right: auto;"> <tr> <td>t=0</td> <td><math>n_b</math></td> <td>0</td> <td>0</td> </tr> <tr> <td><math>t=\infty</math></td> <td>0</td> <td><math>n_b</math></td> <td><math>n_b</math></td> </tr> </table>	t=0	$n_b$	0	0	$t=\infty$	0	$n_b$	$n_b$
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for strong acids: $n(\text{H}_3\text{O}^+) = n_a$ <b>for strong acids:</b> $[\text{H}_3\text{O}^+] = C_a$	for strong bases: $n(\text{HO}^-) = n_b$ <b>for strong bases:</b> $[\text{HO}^-] = C_b$																
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<b>Concentration of strong acids:</b> From PH = $-\log [\text{H}_3\text{O}^+]$ $[\text{H}_3\text{O}^+] = 10^{-\text{PH}}$ for strong acids: $[\text{H}_3\text{O}^+] = C_a$ $C_a = 10^{-\text{PH}}$	<b>Concentration of strong bases:</b> From PH = $14 + \log [\text{HO}^-]$ $[\text{HO}^-] = 10^{\text{PH}-14}$ for strong bases: $[\text{HO}^-] = C_b$ $C_b = 10^{\text{PH}-14}$																
<b>Identification of strong acids:</b> There are two ways : <b>1<sup>st</sup> way:</b> If PH and $C_a$ are given: -Compare : PH ...?... $-\log C_a$ If they are equal => It is a strong acid. <b>2<sup>nd</sup> way:</b> If a strong acid is diluted: 10 times => its PH increases by 1 unit 100 times => its PH increases by 2 units	<b>Identification of strong bases:</b> There are two ways : <b>1<sup>st</sup> way:</b> If PH and $C_b$ are given: -Compare : PH ...?... $14 + \log C_b$ If they are equal => it is a strong base. <b>2<sup>nd</sup> way:</b> If a strong base is diluted: 10 times => its PH decreases by 1 unit 100 times => its PH decreases by 2 units																

<u>Titration of strong base with strong acid</u>	<u>Titration of strong acid with strong base</u>
<b>Titration apparatus</b> 	<b>Titration apparatus</b> 
<b>Equation of titration</b> $\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$ $\text{NaOH} \rightarrow \text{Na}^+ + \text{HO}^-$ Na <sup>+</sup> and Cl <sup>-</sup> ions are spectator ions: Ionic equation of titration reaction is: $\text{H}_3\text{O}^{(\text{aq})} + \text{HO}^{(\text{aq})} \rightarrow 2\text{H}_2\text{O}_{(\text{L})}$	<b>equation of titration</b> $\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$ $\text{NaOH} \rightarrow \text{Na}^+ + \text{HO}^-$ Na <sup>+</sup> and Cl <sup>-</sup> ions are spectator ions: Ionic equation of titration reaction is: $\text{H}_3\text{O}^{(\text{aq})} + \text{HO}^{(\text{aq})} \rightarrow 2\text{H}_2\text{O}_{(\text{L})}$
<b>Characteristics of the reaction :</b> The reaction is complete, fast, and exothermic <b>Titration curve : PH = f(V<sub>a</sub>)</b> 	<b>Characteristics of the reaction :</b> The reaction is complete, fast, and exothermic <b>Titration curve : PH = f(V<sub>b</sub>)</b> 
<b>Description of the curve</b> The curve is a descending (decreasing) and made up of three parts: <b>1<sup>st</sup> part:</b> the curve forms a plateau, PH decreases v. slightly. <b>2<sup>nd</sup> part:</b> PH decreases sharply, the curve forms a jump and contains an inflection point. <b>3<sup>rd</sup> part:</b> the curve forms a plateau, PH decreases v. slightly.	<b>Description of the curve</b> The curve is an ascending (increasing) and made up of three parts: <b>1<sup>st</sup> part:</b> the curve forms a plateau, PH increases v. slightly. <b>2<sup>nd</sup> part:</b> PH increases sharply, the curve forms a jump and contains an inflection point. <b>3<sup>rd</sup> part:</b> the curve forms a plateau, PH increases v. slightly.

- 1** Given a solution of hydrochloric acid of pH = 3.8 at 25 °C.
- Calculate the concentration of the ions  $\text{H}_3\text{O}^+$  in this solution.
  - Deduce the concentration of  $\text{HO}^-$  ions.
- 2** Given a solution of sodium hydroxide of pH = 10 at 25 °C.
- Calculate the concentration of  $\text{H}_3\text{O}^+$  ions in this solution.
  - Deduce the concentration of the above basic solution  $C_b$ .
- 3** Given the following solutions A, B and C:
- Solution A: pH = 2.7,  
 Solution B:  $[\text{H}_3\text{O}^+] = 2.5 \times 10^{-12} \text{ mol L}^{-1}$ ,  
 Solution C:  $[\text{HO}^-] = 6.3 \times 10^{-12} \text{ mol L}^{-1}$ .  
 Arrange the above acids in an increasing order of acidity.
- 4** At 37 °C the ion product of water is equal to  $2.4 \times 10^{-14}$
- What is the pH of pure water at 37 °C?
  - If the pH of saliva at body temperature 37 °C is equal to 6.85, specify whether saliva is acidic or basic.
- 5** At 80 °C, the value of  $\text{pK}_w$  is 12.6.
- What is the value of ion product of water at 80 °C.
  - Calculate the pH of water at 80 °C.
- 6** Complete the following table :

Solution	$[\text{H}_3\text{O}^+]$ (mol.L <sup>-1</sup> )	$[\text{HO}^-]$ (mol.L <sup>-1</sup> )	pH	Nature of solution
S <sub>1</sub>		$2.3 \times 10^{-9}$		
S <sub>2</sub>	$7.5 \times 10^{-4}$			
S <sub>3</sub>			8.2	
S <sub>4</sub>			5.5	

- 7** Given a solution A of concentration  $\text{H}_3\text{O}^+$  ions equal to  $6.4 \times 10^{-4} \text{ mol L}^{-1}$  and a solution B of concentration  $\text{HO}^-$  ions equal to  $7.52 \times 10^{-6} \text{ mol L}^{-1}$ . Determine if solutions A and B are acidic, basic or neutral.
- 8** A solution S of nitric acid of pH = 3.5.
- Calculate the molar concentration of solution S.
  - What value of pH does this solution tend to reach upon extreme dilution?
- 9** We measure the pH of an aqueous solution A of an acid HA of concentration  $2.5 \times 10^{-1}$  mol. L<sup>-1</sup>. The value obtained is pH = 2.6.
- Show that HA is a strong acid.
  - List the glassware used and write the steps involved in preparing 100 ml of a solution B of concentration  $1.25 \times 10^{-4} \text{ mol L}^{-1}$  from solution A.
- 10** a) Write the equation of the reaction of HBr with water.  
 b) Knowing that HBr is a strong acid and the pH of an aqueous solution of this acid is 2.2 calculate its concentration in mol L<sup>-1</sup>.
- 11** A solution A of the monoacid HA of concentration C<sub>1</sub> has a pH equal to 2.4. From A, we prepare a solution B of concentration C<sub>2</sub> = 0.1 C<sub>1</sub>. The pH of B is 3.4.  
 Is HA a strong acid? Justify your answer.
- 12** We prepare 200 ml of a solution S of hydrochloric acid by dissolving 0.112 L of hydrogen chloride gas in distilled water. The pH of this solution is 1.6.
- Calculate the molar concentration of S.
  - Show that HCl is a strong acid.  
 $V_m = 22.4 \text{ mol L}^{-1}$
- 13** We want to prepare a solution of sodium hydroxide of pH = 12.5
- What should the concentration of  $\text{HO}^-$  ions be in the above solution?

- b) What mass of solid NaOH must be used to prepare one liter of the above solution?
- c) What will be the pH if we dilute the preceding solution with an equal volume of distilled water?  
 $M(\text{NaOH}) = 40 \text{ g.mol}^{-1}$ .

- 14 a) Write the equation of the reaction of potassium hydroxide with water.
- b) The pH of a solution of KOH is 11. Calculate the concentration of this solution.
- c) We dilute the preceding solution 100 times. What will be the pH of this obtained solution?

### Exercise 15

We want to titrate using a pH-meter a solution (S) of sodium hydroxide ( $\text{Na}^+ + \text{HO}^-$ ) with a standard solution of hydrochloric acid ( $\text{H}_3\text{O}^+ + \text{Cl}^-$ ) of concentration  $C_a = 1 \times 10^{-1} \text{ mol.L}^{-1}$ . For this experimental activity, we pour a volume  $V_b = 10 \text{ mL}$  of solution (S) into a beaker and then 30 mL of distilled water is added. Titration begins when we added progressively the above standard hydrochloric acid solution. The pH of the solution in the beaker is measured after each addition of the acidic solution. The results are shown in the following table:

Va (mL)	0	2	5	7	8	8.5	8.9	9	9.1	9.3	9.5	10	11	13	16
pH	11.9	11.8	11.6	11.3	11	10.5	9.2	7	5	4	3.7	3.2	2.7	2.4	2.3

- Trace the curve  $\text{pH} = f(V_a)$ .  
 Take the following scales: y-axis: 1cm  $\rightarrow$  1 pH unit ; x-axis: 1cm  $\rightarrow$  1 mL
- Indicate the aim of adding water to the beaker before carrying out titration.
- Explain whether the added amount of water affects : a)  $V_{aE}$ , b)  $\text{pH}_E$
- Determine graphically the equivalence point.
- Write the equation of titration reaction.
- Determine the concentration of the basic solution.
- Explain to what limit the curve may approach upon addition of large amount of acidic solution.
- Derive a relation between pH and  $V_a$  (in mL):
  - For  $V_a < V_{aE}$
  - For  $V_a > V_{aE}$

### Exercise 16

We put a volume  $V_a = 20 \text{ mL}$  of a solution (A) of hydrochloric acid ( $\text{H}_3\text{O}^+ + \text{Cl}^-$ ) in a 250 mL beaker. We add to it progressively from a burette potassium hydroxide solution ( $\text{K}^+ + \text{HO}^-$ ) of concentration  $C_b = 2 \times 10^{-2} \text{ mol.L}^{-1}$ . We measure the values of pH after the addition of different volumes of the basic solution where the following results are obtained.

<b>V<sub>b</sub> (mL)</b>	0	2	4	6	8	10	12	13	14	15	16	17	18	20	22	24
<b>pH</b>	1.8	1.9	2.05	2.15	2.3	2.5	2.7	2.9	3.2	6.9	10.7	11	11.2	11.4	11.5	11.6

1- What step precedes the use of pH meter to measure the different pH value.

2- Trace the curve  $pH = f(V_b)$ .

Take the following scales: y-axis: 1cm  $\rightarrow$  1pH unit ; x-axis: 1cm  $\rightarrow$  1 mL.

3- Determine graphically the equivalence point.

4- Write the equation of the titration reaction.

5- Determine the concentration of the acidic solution.

6- The acidic and basic solutions that are used in this titration are diluted solutions. Explain the importance of using diluted solutions during titration.

7- Derive a relation between pH and V<sub>b</sub> (in mL):

i- For  $V_b < V_{bE}$

ii- For  $V_b > V_{bE}$

8- A student repeated the same titration as the one performed above. But he rinsed the burette only with distilled water. Indicate whether the volume  $V_{bE}$  in this case is equal to, greater than, or less than the value obtained in part 3. Justify your answer.

### Exercise 17

A bottle of household product is labeled :

**Sodium hydroxide solution:** %m = 20% ; M (NaOH) = 40 g.mol<sup>-1</sup>; d = 1.22 Kg.L<sup>-1</sup>

The aim of this exercise is to verify the label of the bottle.

#### 1. Dilution of the household product:

A sample of the above household product (S<sub>o</sub>) is taken to prepare 1L of a solution (S) diluted 100 times.

1.1.Calculate the volume (V<sub>o</sub>) of solution (S<sub>o</sub>) needed for this dilution.

1.2.List the materials needed for this dilution.

1.3.Write briefly the steps.

#### 2. Verification of the label:

A volume V<sub>b</sub> = 10 mL of solution (S) is taken into a beaker, and it is titrated with a hydrochloric acid solution (H<sub>3</sub>O<sup>+</sup> + Cl<sup>-</sup>) of concentration C<sub>a</sub> = 0.1 mol.L<sup>-1</sup>. The volume of the acidic solution needed to reach equivalence point is V<sub>aE</sub> = 6 mL .

2.1.Write the equation of the titration reaction.

2.2.Determine the concentration of solution (S).

2.3. Calculate the %m of NaOH in the household product. Compare it to the label.

2.4.Verify, qualitatively, that the value of pH<sub>E</sub> = 7.

2.5.Derive a relation between pH and V<sub>a</sub> (in mL) for V<sub>a</sub> > V<sub>aE</sub>.

2.6.Complete the following table and sketch the curve  $pH = f(V_a)$  indicating three important points:

<b>V<sub>a</sub> (mL)</b>	0	6	11
<b>pH</b>	-----	7	-----

### Exercise 18

Sulfamic acid (HA) is a constituent of a commercial product, which is used for the removal of scales and sediments from pots and kettles. It is a white solid of formula NH<sub>2</sub>SO<sub>3</sub>H that behaves as a strong acid. The aim of this exercise is to determine the percentage composition by mass of this acid in the commercial product.

### **1. Preparation of solution (S).**

A mass (m) of the commercial product is used to prepare a volume  $V_s = 250$  mL of solution (S) of  $C_m = 9\text{ g.L}^{-1}$

**1.1.**Determine the mass (m).

**1.2.**List the materials needed for this preparation.

**1.3.**Describe the steps of the preparation procedure.

### **2. Determination of the percent composition:**

A volume  $V_a = 20$  mL of of solution (S) is taken into a beaker, and is titrated by a sodium hydroxide solution ( $\text{Na}^+ + \text{HO}^-$ ) of concentration  $C_b = 0.1 \text{ mol.L}^{-1}$ . The volume of basic solution needed to reach equivalence is  $V_{BE} = 17.4$  mL.

**2.1.**Write the equation of the titration reaction.

**2.2.**Determine the concentration of solution (S).

**2.3.**Deduce the percentage composition of sulfamic acid in the commercial product.

**2.4.**Derive a relation between pH and  $V_b$  (in mL):

i- For  $V_b < V_{BE}$

ii- For  $V_b > V_{BE}$

### **Exercise 19**

A bottle of commercial hydrochloric acid solution ( $S_o$ ) is labeled 37% composition by mass, density =  $1.19 \text{ Kg.L}^{-1}$ ;  $M(\text{HCl}) = 35.5 \text{ g.mol}^{-1}$ .

### **1. Preparation of diluted solution (S):**

A volume  $V_o = 4.2$  ml of solution ( $S_o$ ) is diluted to prepare 500 ml solution (S).

**1.1.**Choose from the following sets of glassware the most suitable one to prepare solution (S).

Set A	Set B	Set C
5 ml graduated pipet 500 ml beaker	5 ml graduated pipet 500 ml volumetric flask	10 ml graduated pipet 500 ml volumetric flask/

### **2. Titration od solution (S).**

In order to determine the concentration of solution (S), we filled the burette with the prepared solution (S), and a volume  $V_b = 200\text{ml}$  of potassium hydroxide solution ( $\text{K}^+ + \text{HO}^-$ ) of concentration  $C_b = 3 \times 10^{-3} \text{ mol.L}^{-1}$  is placed in a beaker. Solution (S) is progressively added and the  $pH$  value is found after each addition. The results are grouped in the table below:

<b>V<sub>a</sub> (mL)</b>	0	1	3	4	5	5.4	5.6	5.8	6	6.2	6.4	6.6	7	8	9	10	11	12
<b>pH</b>	11.5	11.4	11.2	11	10.7	10.5	10.3	10	7	4	3.7	3.5	3.3	3	2.8	2.7	2.6	2.5

**2.1.**Trace the curve  $pH = f(V_a)$

**2.2.**Determine graphically the equivalence point.

**2.3.**Write the equation of the titration reaction.

**2.4.**Determine the concentration of solution (S).

**2.5.**Deduce the percentage by mass of HCl in the commercial solution. Compare it to the label.

**2.6.** We replace solution (S) by a nitric acid solution (strong acid) of same concentration. Will the curve  $pH = f(V_a)$  change? Justify your answer.

### Exercise 20

### Study of a Household Product: ‘FLASH’

“Flash” is a household product used to disinfect and clean the WC toilets. It is a commercial concentrated solution of hydrochloric acid. On the label of a “flash” bottle, the following information is noted: *contains hydrochloric acid solution of 18 % by mass*.

The determination of the density of this liquid gives the following value:  $d = 1.22 \text{ Kg.L}^{-1}$ .  
The aim of this exercise is to verify the indication 18 % by using pH – metric titration.

#### Given:

Molar mass of HCl =  $36.5 \text{ g.mol}^{-1}$

$\text{pK}_w = 14$  at  $25^\circ\text{C}$

#### 1. Preliminary Study:

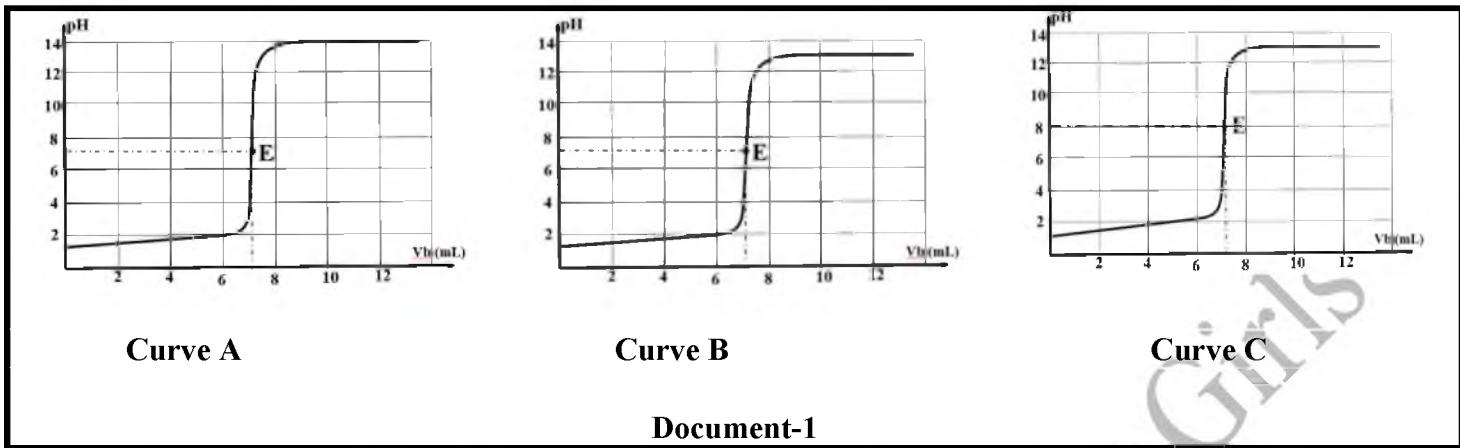
- 1.1. Show that the concentration of the commercial solution according to the label “flash” is about  $C_0 = 6.02 \text{ mol.L}^{-1}$
- 1.2. Determine the volume  $V_0$  that should be taken from the “Flash” solution to prepare the solution (S).
- 1.3. The pH of the prepared solution is 2 units greater than that of “Flash”. Deduce whether HCl is a strong or weak acid.
- 1.4. Write the equation of dissociation of HCl in water.

#### 2. Titration of solution (S).

In order to verify the percentage composition of HCl in “Flash” the following procedure is carried out.

- A volume  $V_a = 10 \text{ mL}$  of solution (S) is poured into a beaker and enough distilled water is then added to immerse the combined electrode of the pH-meter.
- A pH-meter is used to titrate solution (S) with a potassium hydroxide solution ( $\text{K}^+ + \text{HO}^-$ ) of molar concentration  $C_b = 8.5 \times 10^{-2} \text{ mol.L}^{-1}$ .
- The volume of the basic solution added to reach equivalence point is  $V_{bE} = 7 \text{ mL}$ .

- 2.1. Write the equation of the titration reaction.
- 2.2. Give the characteristics of this reaction.
- 2.3. Calculate the pH of the potassium hydroxide solution.
- 2.4. One of the following curves represent the titration curve  $pH = f(V_b)$  of the performed titration. Choose the curve that best represents the titration studied in this exercise. Justify your answer.



2.5. Determine the concentration of solution (S).

2.6. Verify if the indication 18 % is accurate or not.

### Exercise 21

### Sulfamic Acid

A commercial product is a powder used for the removal of scales and sediments from pots and bottles contains sulfamic acid of formula  $\text{NH}_2\text{SO}_3\text{H}$ .

**Given:** Molar mass of sulfamic acid  $\text{NH}_2\text{SO}_3\text{H}$  is  $M=97 \text{ g/mol}$

**Sulfamic acid is a strong acid, it will be represented as HA in this exercise.**

#### 1. Preparation of solution (S)

A solution (S) of sulfamic acid is prepared by dissolving a certain mass (m) of the **commercial product** whose mass concentration is  $C_m=4\text{g/L}$

1.1. Determine the mass (m) needed for the preparation of 500ml of solution (S).

1.2. Describe the procedure needed to prepare the solution (S) and specify the materials required during the process.

#### 2. pH-metric titration of solution (S)

20ml of solution (S) is transferred into a 250ml beaker. Distilled water is then added to immerse the pH meter. Titration is carried out using a solution of sodium hydroxide ( $\text{Na}^+, \text{OH}^-$ ) of concentration  $C_b=0.06\text{mol/L}$ .

equivalence point is reached when 12 ml of the base is added.

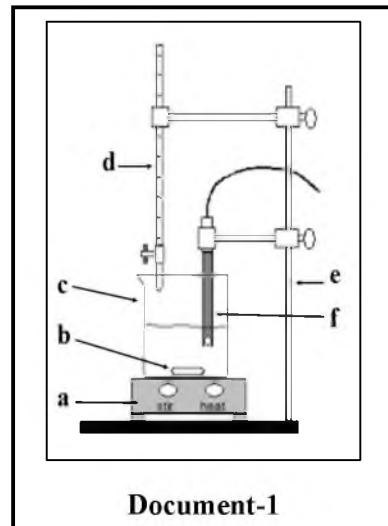
2.1. **Document-1** represents the titration apparatus. Label the parts (a) through (f).

2.2. Write the equation of titration reaction.

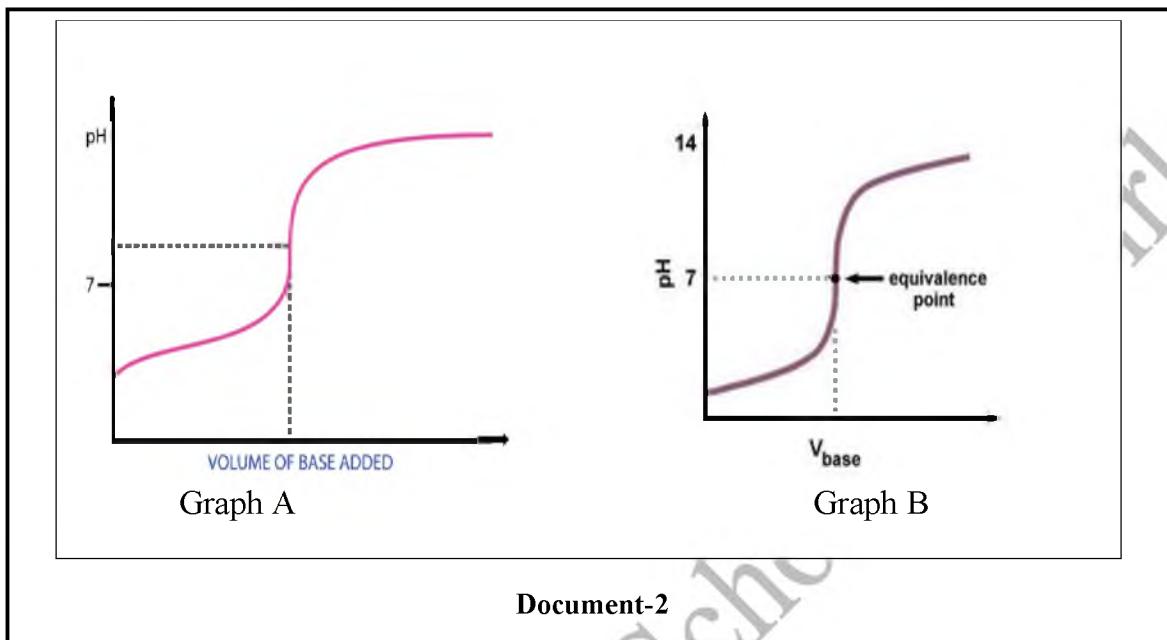
2.3. Determine the concentration of solution (S).

2.4. Deduce the number of moles of sulfamic acid present in 500ml of solutions (S).

2.5. Calculate the percentage by mass of sulfamic acid in the commercial product.



**2.6.** The following curves represent the variation of pH as a function of the base added from the buret. choose, with justification, the one that corresponds to the above titration.



Document-2

### Exercsie 22

### A Scale Product for Coffee-Pot

The main constituent of a scale product is sulfamic acid. It is sold commercially as white small crystals.

The aim of this exercise is to determine the percentage of sulfamic acid in the scale product by pH-metry.

#### Given:

- Sulfamic acid of formula  $\text{NH}_2\text{SO}_3\text{H}$  will be represented as HA in this exercise.
- Molar mass of sulfamic acid in  $\text{g}\cdot\text{mol}^{-1}$ :  $M = 97.1$ .

#### Experimental Procedure:

**first step:** 2.05 g of this scale product are dissolved in distilled water to obtain a solution (S) of volume  $V = 500 \text{ mL}$ .

**second step:** A volume  $V_a = 10 \text{ mL}$  of solution (S) is put into a beaker. A volume  $V' = 30 \text{ mL}$  of distilled water is then added to immerse the electrode of the pH-meter.

**third step:** Titration is carried out by using sodium hydroxide solution of concentration  $C_b = 4 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$ .

#### 1- Preliminary Study

- 1- Sulfamic acid is a strong acid. Write the equation of the reaction of this acid with water.
- 2- Indicate the appropriate material used to:
  - 2.1.weigh the mass of 2.05 g ;
  - 2.2.prepare the volume  $V$  ;
  - 2.3.withdraw the volume  $V_a$  ;
  - 2.4.add the sodium hydroxide solution.
- 3- Write the equation of the titration reaction.

- 7- Based on the chemical species which are present in the beaker, justify the value of pH = 7 at the equivalence point.

## **II- Make Use of the Titration Results**

Part of the titration results is given in the following table:

V <sub>b</sub> (mL)	0	10.4	15
pH	2.4	7.0	pH = ?

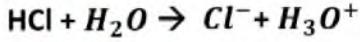
1. Show that, at each time after equivalence point, the pH of the solution in the beaker is related to V<sub>b</sub> by the following relation:  $pH = 12.6 + \log \frac{V_b - 10.4}{V_b + 40}$
2. Deduce the value of pH at V<sub>b</sub> = 15 mL.
3. Draw the shape of the curve pH = f(V<sub>b</sub>) for  $0 \leq V_b \leq 15$  mL. Take the following scales: abscissa : 1cm for 1mL, ordinate: 1 cm for 1 unit of pH.
4. Determine the concentration C<sub>a</sub> of sulfamic acid in solution (S).
5. Deduce the mass percentage of sulfamic acid in this scale product.

## **UNIT 3- CHAPTER 5 : WEAK ACIDS AND BASES**

### **Introduction:**

#### **Bronsted definition of acids and bases:**

A **Bronsted-Lowry acid** is any species that is capable of donating a proton H<sup>+</sup>. Example HCl is a Bronsted acid:



A **Bronsted-Lowry base** is any species that is capable of accepting a proton, H<sup>+</sup>. Example NH<sub>3</sub> is a Bronsted base:



### **I- Characteristics of weak acids:**

- a) Weak acids dissociate incompletely in water to give H<sub>3</sub>O<sup>+</sup>:  $\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{A}^- + \text{H}_3\text{O}^+$ .
- b) The pH of a solution of a weak acid:  $\text{pH} > -\log C_a$ , where C<sub>a</sub> represents the concentration of the weak acid initially dissolved.
- c)  $[\text{H}_3\text{O}^+]_{\text{in solution}} < C_a$
- d) The degree of dissociation of weak acid in water:  $\alpha = \frac{n(\text{HA})_{\text{changed}}}{n(\text{HA})_o} < 1$ .
- e) Dilution of a weak acid solution increases  $\alpha$  ( dilution favors the dissociation of a weak acid).
- f) Dilution of a weak acid solution:
  - 10 times increases pH by less than 1 unit.
  - 100 times increases pH by less than 2 units.

## II- Characteristics of weak bases:

- weak bases react with water incompletely to give  $\text{HO}^-$ :  $\text{B} + \text{H}_2\text{O} \rightleftharpoons \text{BH}^+ + \text{HO}^-$ .
- The pH of a solution of a weak base is  $pH < 14 + \log C_b$  where  $C_b$  represents the concentration of the weak base initially dissolved.
- $[\text{HO}^-]_{\text{in solution}} < C_b$
- The degree of conversion of weak acid in water:  $\alpha = \frac{n(\text{B})_{\text{changed}}}{n(\text{B})_0} < 1$
- Dilution of a weak base solution increases  $\alpha$ .
- Dilution of a weak base solution:
  - 10 times decreases  $pH$  by less than 1 unit.
  - 100 times decreases  $pH$  by less than 2 units.

## III- Conjugate Acid-Base Pairs

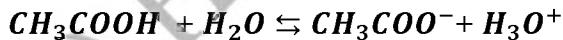
A conjugate acid/base pair is constituted of two conjugate species that are associated together through exchange of proton ( $\text{H}^+$ ).

A conjugate acid/base pair is represented by  $(\text{HA}/\text{A}^-)$  or  $(\text{BH}^+/ \text{B})$ , examples:  $\text{HF}/\text{F}^-$  ,  $\text{NH}_4^+/\text{NH}_3$  ,  $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$

Each acid-base reaction constitutes two pairs. For example, the following reaction :  $\text{HF} + \text{NH}_3 \rightleftharpoons \text{F}^- + \text{NH}_4^+$  constitutes the two pairs:  $\text{HF}/\text{F}^-$  and  $\text{NH}_4^+/\text{NH}_3$ .

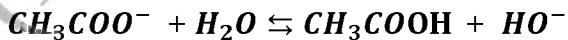
Note:

- Water acts as a conjugate base in the following reaction because it accepts a proton ( $\text{H}^+$ ):



The corresponding conjugate acid base pair of water in this reaction is  $\text{H}_3\text{O}^+/\text{H}_2\text{O}$

- Water also acts as a conjugate acid in the following reaction because it donates a proton ( $\text{H}^+$ ):



The corresponding conjugate acid base pair of water in this reaction is  $\text{H}_2\text{O}/\text{HO}^-$

- For this water is called an **amphoteric substance** or **ampholyte**.

## IV- Acidity constant: Ka

- Each acid/base pair is characterized by its  $K_a$ .  $K_a$  is a constant number (at constant temperature), that is derived from the equilibrium constant of the following reaction:  $\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{A}^- + \text{H}_3\text{O}^+$ .

$$K_a (\text{HA}/\text{A}^-) = \frac{[\text{A}^-] \times [\text{H}_3\text{O}^+]}{[\text{HA}]} = \text{cte}$$

The value of  $K_a$  is very small and it is difficult to deal with it, for this we mostly use  $pK_a$  where:

$$pK_a = -\log K_a$$

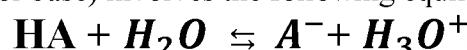
- Remember: if  $pK_a = -\log K_a$  then  $K_a = 10^{-pK_a}$ .
- Henderson- Hasselbalch equation is an equation that is used to find pH of a solution containing a weak acid and its conjugate base. It is derived from  $K_a$  expression.

**Henderson- Hasselbalch equation:**

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

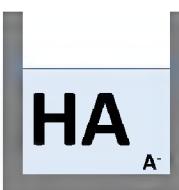
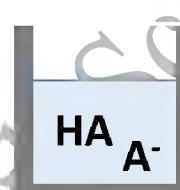
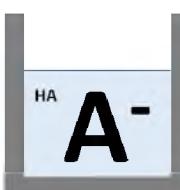
## V- Predominance domains of conjugate acid base pairs

Any solution of a weak acid (or base) involves the following equilibrium:



This means that any solution of a weak acid (or a weak base) contains both the weak acid and its conjugate base:

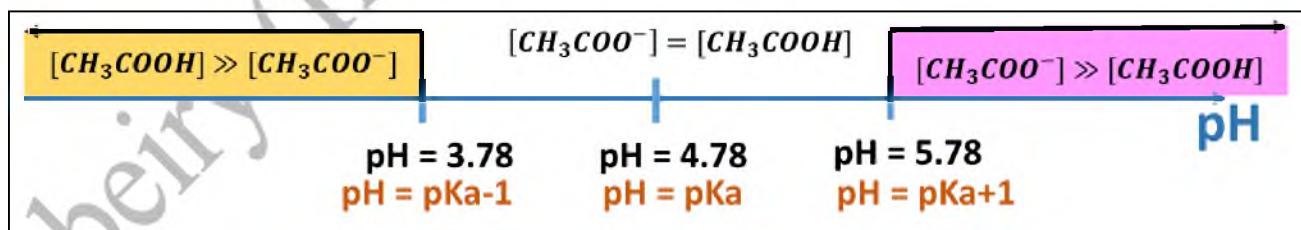
The pH of the solution determines the predominant species:

If $pH < pK_a - 1$	If $pH = pK_a$	If $pH > pK_a + 1$
$[HA] \gg [A^-]$	$[HA] = [A^-]$	$[HA] \ll [A^-]$
		
HA predominates	No predominance	$A^-$ predominates

The predominance domain of an acid/base pair is represented by the an axis. Example:

Consider the acid/base pair  $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$  whose  $pK_a$  at  $25^\circ\text{C}$  is  $pK_a = 4.78$ .

The corresponding predominance domain can be represented by:



### Note:

An indicator is a solution of a weak acid and its conjugate base, where the acid and its conjugate base have different colors.

The acid base pair of an indicator is represented as  $(\text{HInd}/\text{Ind}^-)$ , and its  $pK_a$  is written as  $pK_i$  ('i' for indicator).

**Example:** Bromothymol blue is an indicator such that:

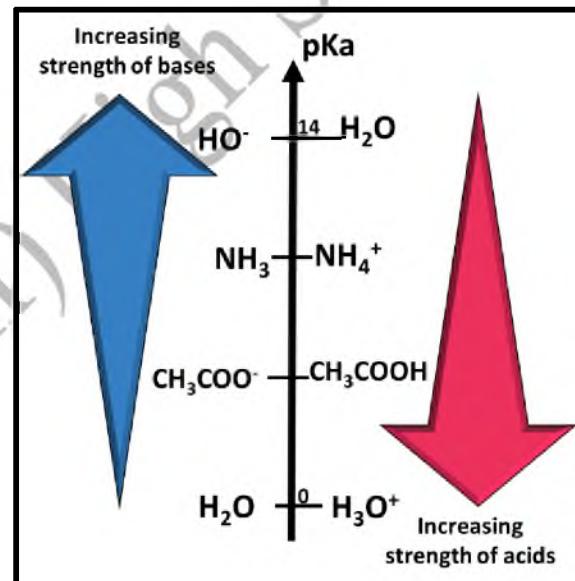
- HInd has yellow color.
- Ind<sup>-</sup> has blue color
- pKi = 6.8 at 25°C.

For pH < 5.8 ( pKi -1)	HInd predominates	The solution takes the color of HInd
For pH > 7.8 ( pKi +1)	Ind <sup>-</sup> predominates	The solution takes the color of Ind <sup>-</sup>
For 5.8 < pH < 7.8	No predominance: Both HInd and Ind <sup>-</sup> are present.	The color of the solution is intermediate between the two colors.

## VI- Relative Strength of Acids and Bases

A weak acid is stronger when its acidity constant Ka is greater. This means when its pKa is smaller.

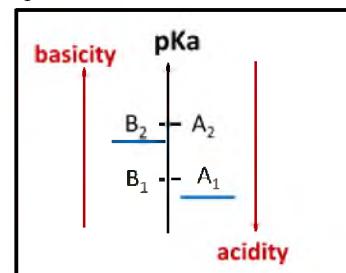
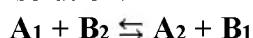
A weak base is stronger when the acidity constant Ka of its conjugate acid/base pair is smaller. This means when its pKa is greater.



## VII- Acid-Base Reactions

Consider two conjugate acid base pairs: A<sub>1</sub>/B<sub>1</sub> and A<sub>2</sub>/B<sub>2</sub> where pKa<sub>2</sub> > pKa<sub>1</sub>.

- To write the equation of the reaction that takes place between these two pairs, place them on pKa axis:  
The reaction takes place between stronger acid (A<sub>1</sub>) and stronger base (B<sub>2</sub>) present in solution:



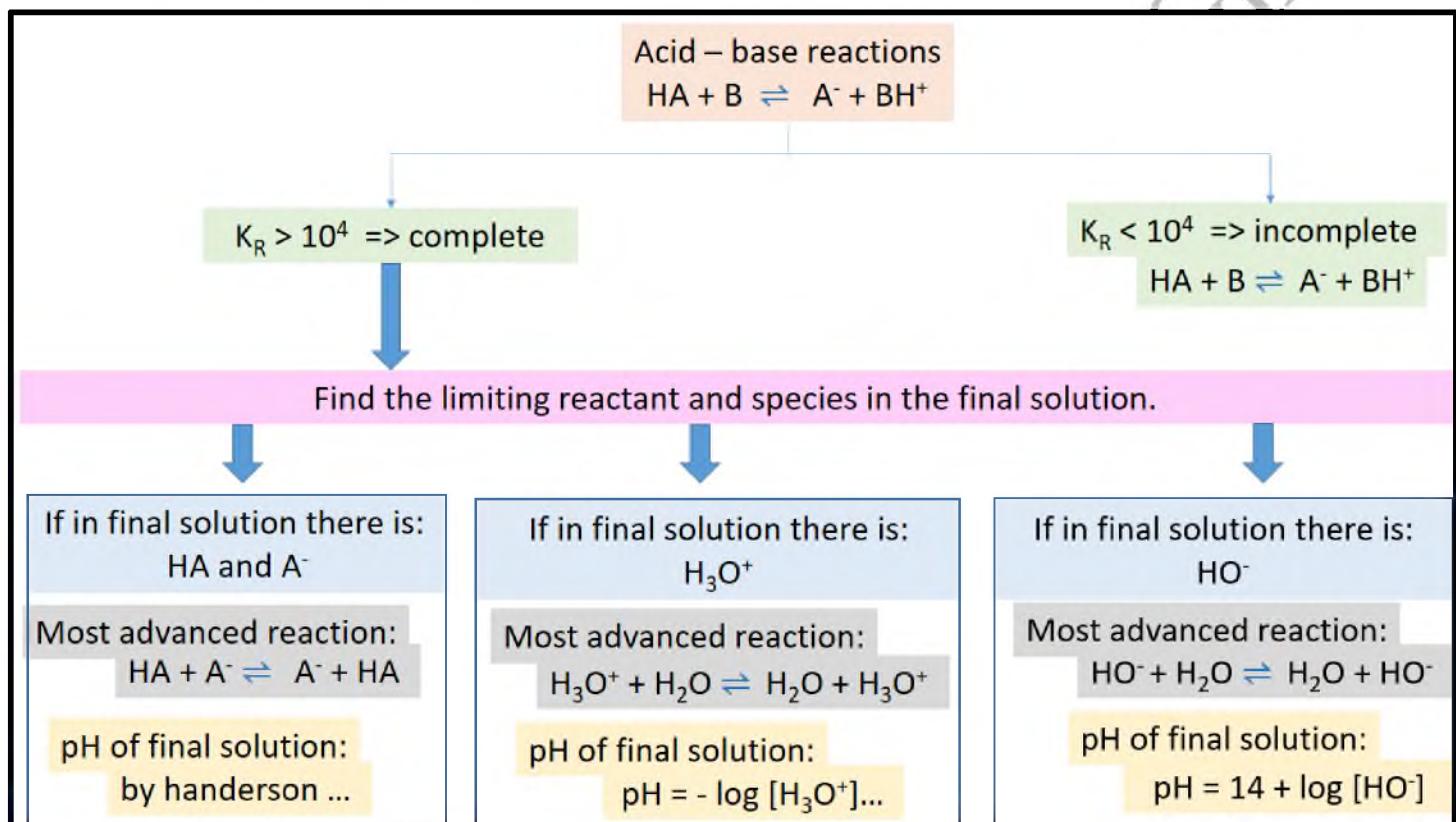
To determine whether the reaction is complete or not, calculate the value of  $K_R$  :  $K_R = \frac{[A_2] \times [B_1]}{[A_1] \times [B_2]}$

Multiply by  $\frac{[\text{H}_3\text{O}^+]}{[\text{H}_3\text{O}^+]}$

$$\Rightarrow K_R = \frac{[\text{A}_2] \times [\text{B}_1]}{[\text{A}_1] \times [\text{B}_2]} \times \frac{[\text{H}_3\text{O}^+]}{[\text{H}_3\text{O}^+]} = \frac{[\text{B}_1] \times [\text{H}_3\text{O}^+]}{[\text{A}_1]} \times \frac{[\text{A}_2]}{[\text{H}_3\text{O}^+] \times [\text{B}_2]} = \frac{K_{a1}}{K_{a2}} = 10^{pK_{a2} - pK_{a1}}$$

If  $K_R > 10^4$ , the reaction is complete:  $\text{A}_1 + \text{B}_2 \rightarrow \text{A}_2 + \text{B}_1$

If  $K_R < 10^4$ , the reaction is incomplete:  $\text{A}_1 + \text{B}_2 \rightleftharpoons \text{A}_2 + \text{B}_1$



## How to determine the values of pH, pKa, Ka, a, or C<sub>0</sub> for a weak acid or a weak base solution.

Follow the following steps:

**1<sup>st</sup> step:** write the equation of reaction with water (remember, it is incomplete)

**2<sup>nd</sup> step:** Fill the table of conversion in terms of concentration (not number on moles).

	HA	+	H <sub>2</sub> O	↔	A <sup>-</sup>	+	H <sub>3</sub> O <sup>+</sup>
<b>Initially (mol.L<sup>-1</sup>)</b>	C <sub>a</sub>		Solvent		0		0
<b>Change</b>	-x				+x		+x
<b>At equilibrium</b>	C <sub>a</sub> -x		Solvent		x		x

**3<sup>rd</sup> step:** calculate the value of (x) using the given values

## I- Applications involving weak acids:

### Application 1:

Consider methanoic acid solution ( $\text{HCOOH}$ ) of concentration  $C_a = 0.01 \text{ mol.L}^{-1}$ .

Given :  $pK_a (\text{HCOOH}/\text{HCOO}^-) = 3.8$

- a- Write the equation of reaction of  $\text{HCOOH}$  with water.
- b- Determine the value of pH of the solution.
- c- Deduce the value of  $\alpha$ .

### Application 2:

Consider ethanoic acid solution ( $\text{CH}_3\text{COOH}$ ) of  $\text{pH} = 3.4$

Given :  $pK_a (\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-) = 4.8$

- a- Write the equation of reaction of  $\text{CH}_3\text{COOH}$  with water.
- b- Determine the concentration of the above the solution.
- c- Deduce the value of  $\alpha$ .

### Application 3:

Consider hydrofluoric acid solution ( $\text{HF}$ ) of concentration  $C_a = 10^{-3} \text{ mol.L}^{-1}$ .

Given :  $pK_a (\text{HF}/\text{F}^-) = 3.3$

- a- Write the equation of reaction of  $\text{HF}$  with water.
- b- Determine the value of pH of the solution.
- c- Deduce the value of  $\alpha$ .

### Application 4:

Consider a weak acid solution ( $\text{HA}$ ) of concentration  $C_a = 0.75 \text{ mol.L}^{-1}$ , and  $\text{pH} = 1.6$

- a- Write the equation of reaction of  $\text{HA}$  with water.
- b- Determine the value of  $pK_a$  of the pair ( $\text{HA}/\text{A}^-$ ).
- c- Calculate %  $\alpha$ .

### Application 5:

Consider a weak acid solution ( $\text{HA}$ ) of concentration  $C_a = 1 \text{ mol.L}^{-1}$ , and its %  $\alpha = 2\%$ .

- a- Write the equation of reaction of  $\text{HA}$  with water.
- b- Determine the value of  $K_a$  of the pair ( $\text{HA}/\text{A}^-$ ).
- c- Calculate pH of the solution.

## II- Applications involving weak bases:

### Application 6:

Available is sodium methanoate ( $\text{HCOONa}$ ) solution, having a concentration  $C_b = 0.001 \text{ mol.L}^{-1}$ .

**Given :**  $pK_a (\text{HCOOH}/\text{HCOO}^-) = 3.8$ ,  $pK_w = 14$

- a- Write the equation of reaction of  $\text{HCOO}^-$  with water.
- b- Determine the value of pH of the solution.
- c- Calculate the value of the degree of conversion of  $\text{HCOO}^-$  ion ( $\alpha$ ).

#### **Application 7:**

A solution of concentration  $C = 0.015 \text{ mol.L}^{-1}$  is obtained by dissolving a sample of sodium ethanoate ( $\text{CH}_3\text{COONa}$ ) in water.

**Given :**  $pK_a (\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-) = 4.8$ ;  $pK_w = 14$

- a- Write the equation of reaction of ethanoate ions with water.
- b- Determine the value of pH of the solution.
- c- Calculate the value of the degree of conversion of  $\text{CH}_3\text{COO}^-$  ion ( $\alpha$ ).

#### **Application 8:**

A solution of weak base (B) of concentration  $C = 10^{-2} \text{ mol.L}^{-1}$  has a  $\text{pH} = 9.1$ .

**Given:**  $pK_w = 14$

- a- Write the equation of reaction of B with water.
- b- Determine the value of  $K_a$  of the pair ( $\text{BH}^+/\text{B}$ ).
- c- Calculate the value of the degree of conversion of B ion ( $\alpha$ ).

### **Reactions involving weak acids and weak bases:**

#### **Application 1: weak acid and weak base**

A solution contains  $\text{NH}_3$  and  $\text{CH}_3\text{COOH}$  mixed together.

**Given:**  $pK_a (\text{NH}_4^+/\text{NH}_3) = 9.2$  and  $pK_a (\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-) = 4.75$

- 1- Arrange all species present in solution on  $pK_a$  axis.
- 2- Predict the reaction that takes place in the reaction medium.
- 3- Specify type of the reaction taking place.
- 4- Verify if the reaction is complete or not.

#### **Application 2: weak acid and weak base**

A solution is prepared by mixing 0.05 mol of  $\text{ClO}^-$  and 0.05 mol of  $\text{C}_2\text{H}_5\text{COOH}$ . The total volume of the solution is 1 L.

**Given:**  $pK_a (\text{HClO}/\text{ClO}^-) = 7.3$  and  $pK_a (\text{C}_2\text{H}_5\text{COOH}/\text{C}_2\text{H}_5\text{COO}^-) = 4.87$

- 1- Write the equation of the reaction taking place.
- 2- Specify the type of the reaction.
- 3- Specify whether the reaction is complete.
- 4- Determine the pH of the final solution.

#### **Application 3: weak acid and weak base**

A mixture of volume (V) is prepared by mixing 0.4 mol of  $\text{NH}_3$  and 0.6 mol of  $\text{HCOOH}$ .

**Given:**  $pK_a(NH_4^+/NH_3) = 9.2$  and  $pK_a(HCOOH/HCOO^-) = 3.75$ .

- 1- Write the equation of the reaction that takes place.
- 2- Is the reaction complete?
- 3- Write the equation of the most advanced reaction in the final solution.
- 4- Determine the pH of the final solution.

#### **Application 4: weak acid and strong base**

A reaction mixture is prepared by mixing  $2 \times 10^{-2}$  mol of sodium hydroxide ( $NaOH$ ) and  $6 \times 10^{-2}$  mol of  $CH_3COOH$ .

**Given:**  $pK_a(CH_3COOH/CH_3COO^-) = 4.75$ ;  $pK_a(H_2O/HO^-) = 14$ ;  $pK_w = 14$ .

- 1- Write the equation of the reaction.
- 2- Is the reaction complete or not?
- 3- Specify the type of the reaction.
- 4- Write the equation of the most advanced reaction in the final solution.
- 5- Determine the pH of the final solution.

#### **Application 5: weak acid and strong base**

A reaction mixture is prepared by mixing  $5 \times 10^{-3}$  mol of potassium hydroxide ( $KOH$ ) and  $8 \times 10^{-3}$  mol of  $C_2H_5COOH$ .

**Given:**  $pK_a(C_2H_5COOH/C_2H_5COO^-) = 4.87$ ;  $pK_a(H_2O/HO^-) = 14$ ;  $pK_w = 14$ .

- 1- Write the equation of the reaction.
- 2- Is the reaction complete or not?
- 3- Specify the type of the reaction.
- 4- Write the equation of the most advanced reaction in the final solution.
- 5- Determine the pH of the final solution.

#### **Application 6: weak base and strong acid**

A reaction mixture is prepared by mixing 0.3 mol of ammonia ( $NH_3$ ) and 0.01 mol of hydrochloric acid solution ( $H_3O^+ + Cl^-$ ).

**Given:**  $pK_a(NH_4^+/NH_3) = 9.2$ ;  $pK_a(H_3O^+/H_2O) = 0$ ;  $pK_w = 14$ .

- 1- Write the equation of the reaction.
- 2- Is the reaction complete or not?
- 3- Specify the type of the reaction.
- 4- Write the equation of the most advanced reaction in the final solution.
- 5- Determine the pH of the final solution.

#### **Application 7: weak acid and weak base**

A reaction mixture is prepared by mixing 0.2 mol of ammonia ( $NH_3$ ) and 0.6 mol of  $CH_3COOH$ .

**Given:**  $pK_{a1}(CH_3COOH/CH_3COO^-) = 4.75$ ;  $pK_{a2}(NH_4^+/NH_3) = 9.2$ ;

- 1- Write the equation of the reaction.
- 2- Is the reaction complete or not?
- 3- Determine the pH of the final solution.
- 4- Write the equation of the most advanced reaction that takes place in the final mixture.

#### **Application 8: weak base and strong acid**

A reaction mixture is prepared by mixing 0.03 mol of ammonia ( $NH_3$ ) and 0.1 mol of hydrochloric acid solution ( $H_3O^+ + Cl^-$ ). The total volume of the solution is 1L.

**Given:**  $pK_a(NH_4^+/NH_3) = 9.2$ ;  $pK_a(H_3O^+/H_2O) = 0$ ;  $pK_w = 14$ .

- 1- Write the equation of the reaction.
- 2- Is the reaction complete or not?
- 3- Write the equation of the most advanced reaction in the final solution.
- 4- Determine the pH of the final solution.

**Application 9: weak acid and strong base**

A reaction mixture is prepared by mixing  $5 \times 10^{-3}$  mol of potassium hydroxide (KOH) and  $2 \times 10^{-3}$  mol of  $C_2H_5COOH$ . The total volume of the solution is 1L.

**Given:**  $pK_a(C_2H_5COOH/C_2H_5COO^-) = 4.87$ ;  $pK_a(H_2O/HO^-) = 14$ ;

- 1- Write the equation of the reaction.
- 2- Is the reaction complete or not?
- 3- Write the equation of the most advanced reaction in the final solution.
- 4- Determine the pH of the final solution.

**Application 10: weak acid and strong base**

A reaction mixture is prepared by mixing  $2 \times 10^{-2}$  mol of sodium hydroxide (NaOH) and  $2 \times 10^{-2}$  mol of  $CH_3COOH$  in a 1 L solution.

**Given:**  $pK_a(CH_3COOH/CH_3COO^-) = 4.75$ ;  $pK_a(H_2O/HO^-) = 14$ ;  $pK_w = 14$ .

- 1- Write the equation of the reaction.
- 2- Is the reaction complete or not?
- 3- Write the equation of the most advanced reaction in the final solution.
- 4- Determine the pH of the final solution.

**Application 11 (official exam 2013 S1 Ex:2)**

Four flask are numbered and an aqueous solution of one of the species below is introduced into each of these flasks.

Number of the flask	Chemical species	
	Name	Formula
1	Hydrogen fluoride	HF
2	Sodium methanoate	$HCOONa$
3	Ammonia	$NH_3$
4	Ammonium Chloride	$NH_4Cl$

**These solutions have the same concentration C.**

**Given:**

- The following table:

Acid/base pair	$NH_4^+/NH_3$	$HF/F^-$	$HCOOH/HCOO^-$
pKa	9.2	3.2	3.8
- Sodium methanoate and ammonium chloride are both ionic compounds that are highly soluble in water.

**1- Classify the above four solutions as acidic and basic.**

**2- Preparation of the solution of flask 3**

The solution in the flask 3 of molar concentration C, has been prepared from a commercial ammonia solution of which the label shows the following indications:

$$\%m = 25\% \quad d = 0.91 \text{ g.mL}^{-1} \quad M(\text{NH}_3) = 17 \text{ g.mol}^{-1}$$

A volume  $V_o = 1.5 \text{ mL}$  of this commercial solution is taken and distilled water is added to this volume in a way to obtain a solution of volume  $V = 2.0 \text{ L}$ .

**2.5.**Determine the molar concentration  $C_o$  of the commercial solution.

**2.6.**Show that the molar concentration  $C = 1.0 \times 10^{-2} \text{ mol.L}^{-1}$ .

**2.7.**Choose, among the following glassware, those that are essential for the preparation of the solution in the flask 3.

**2 mL volumetric pipet – 2 mL graduated cylinder – 2 mL graduated pipet – 2 L graduated cylinder – 2 L volumetric flask.**

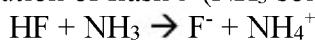
### **3- Study of the solution in Flask 1**

**3.1.**Write the equation of the reaction between HF and water.

**3.2.**Determine the degree of ionization of HF in the solution of flask 1. ( $[\text{F}^-]$  is neglected compared to the concentration C).

### **4- Mixture of two solutions:**

A volume  $V_1 = 40 \text{ mL}$  of solution of flask 1 (HF solution) is mixed with a volume  $V_2 = 30 \text{ mL}$  of the solution of flask 3 (NH<sub>3</sub> solution) the equation of the reaction that takes place is:



**4.1.**Justify that this reaction is complete.

**4.2.**Specify the limiting reactant.

**4.3.**Deduce the pH of the obtained mixture.



Element	Atomic number	Atomic mass
Hydrogen	1	1
Helium	2	4
Lithium	3	6.94
Beryllium	4	9.01
Boron	5	10.81
Carbon	6	12.01
Nitrogen	7	14.01
Oxygen	8	15.99
Fluorine	9	19
Neon	10	20.18
Sodium	11	22.99
Magnesium	12	25.31
Aluminium	13	26.98
Silicon	14	28.09
Phosphorus	15	30.97
Sulphur	16	32.07
Chlorine	17	35.45
Argon	18	39.95
Potassium	19	39.1
Calcium	20	40.08
Scandium	21	44.96
Titanium	22	47.87
Vanadium	23	50.94
Chromium	24	52
Manganese	25	54.94
Iron	26	55.85
Cobalt	27	58.93
Nickel	28	58.69
Copper	29	63.55
Zinc	30	65.41