Chemistry

Secondary Education
Third Year
General Sciences
Life Sciences Sections

ORBITALS Collection

EVISED EDITION

Center for Educational Research and Development
National Textbook
New Curricula

Republic of Lebanon
Ministry of Education and Higher Education

CHEMISTRY

Secondary Education
Third Year
Sections: General Sciences - Life Sciences

Center for Educational Research and Development
National
Textbook
New Curricula

General Coordinator
Moustapha Yaghi

Proof Reader
Edouard Al Alam

CHEMISTRY

Secondary Education
Third Year
Sections: General Sciences - Life Sciences

Ali SAFA (Coordinator)
Jeanne d'Arc HELOU
Hassan ABDALLAH
Abdel Kader BACHIR
Bassam CHAHINE
Elias KAWKABANI
Hussein ZOUGHEIB

Center for Educational Research and Development

■ **Documentary Research :** Iconographic Team, CERD

Layout : Technical Team, SPC s.a.r.l.
Dekwanch - P.O.Box 55530 - Telefax: 01-488775

First Published 2000
15ème Impression 2017

Together We Build Through Education!

The Center for Educational Research and Development (CERD) has embarked on an extensive workshop for assessing and developing the educational framework and curricula which have been placed into effect more than three years ago. With full realization of the fact that the educational cycle must continue normally through its components, and until the development process attains its aspired objectives, we are placing in the hands of students, teachers and directors of public schools, this corrected version of textbooks issued by CERD as part of the National Textbook Series.

This version is an interim stage incorporating the corrected typographical and linguistic errors discovered by CERD specialists as well as teachers and students through their daily dealings with the books. The process of assessment and development of the framework and curricula will take into consideration all the comments that have been made, or will be made, in this regard.

It is expected that once the curricula are developed and aligned with the general and specific objectives set for them, the textbooks will be realigned with the new curricular and framework requirements, including tying the content of a course to the number of teaching hours set for it during the school year, taking into consideration vertical alignment within the same course as well as the horizontal alignment with the rest of the courses.

I take this opportunity to invite all school administrators, teachers and students and all officials concerned in public and private schools alike, to promptly send their comments on these curricula and books as their contribution to enrichment of this momentous national process.

This workshop, which was launched under the kind sponsorship of His Excellency the Minister of Education and Higher Education in implementation of Decree No. 10227 embodying the educational curricula and their objectives, fits in with CERD's proclaimed new motto "Together We Build Through Education".

It is our earnest desire to see this national, all-inclusive workshop attracting the greatest amount of interest and participation to define the safest and soundest educational options that directly affect our children, as we vow to continually modernize education and develop its ways and means to keep abreast of modern developments and progress in science and technology.

Dr. Leila MALEEHA
President CERD

Forward

This chemistry book for the third secondary year covers the programs of the General Sciences section and the Life Sciences section.

For the Life Sciences section, the program includes the following units: gaseous state, chemical kinetics, chemical equilibrium, acid-base reactions in aqueous solutions, pH metry, organic chemistry II, polymers, soaps and detergents, current medicinal drugs and new materials.

The General Sciences program consists of the same program as the life sciences, except the following parts: Amines and α-amino acids, soaps and detergents, current medicinal drugs and new materials.

In writing this book, the same approach has been adopted, as for the second secondary year scientific section, using a simple scientific language and illustrations rich in (figures, schemes, tables, ...). Our aim is to make the comprehension of scientific concepts easy for the students, in addition, to develop their experimental scientific attitude.

The program as a whole can de divided into two main parts, one based on classical conceptual chemistry and the other is based on applied chemistry. In the second part, the following themes are grouped: polymers, soaps and detergents, current medicinal drugs and new materials. These two parts together emphasize the applications of chemistry in everyday life and its importance in modern technologies.

Since at the end of the third year of the secondary cycle, the students will take official examinations, we paid attention to the development of the themes of the program to fit the actual time of study, and the exercises given at the end of each chapter are of the same spirit as the exercises of the exams.
The book is divided into sixteen chapters. Their organization is identical to those presented in the chemistry book for the second secondary year scientific section.

Each chapter is introduced by an illustration and a commentary related to the theme. The objectives to be achieved, the prerequisites and the chapter content are presented as an introductory page.
On the pages reserved for the course, illustrations are given as pedagogical support to the concepts to be studied.

The active learning method, which consists of conducting experimental activities, where the interpretation of the results allows understanding of the scientific concepts, is adopted each time the studied theme permits.

The solved exercises aim to serve as direct application to the preceded scientific notions.

The method sheets are supplements, often necessary, to complete the knowledge of the student on a given subject.

The laboratory investigations (LI), which are more detailed than the experimental activities, are complete experimental applications related to the theme of the chapter. However, these investigations have a supplementary role that will be specified later in this introduction.

The documentary activities fewer in number than those found in the program of the second secondary year scientific section, but they are particularly important for the applied chemistry part of the program.

The activities of the themes of this part constitute a true supplement to the text, because they allow the student to better understand and to extend his knowledge for these themes. The teacher should exploit these activities by asking more questions related to the content of the text.

The exercises given at the end of each chapter are mainly either of the classical type, or of experimental character or taken from everyday life.

At the end of each of the nine units of this book, another group of exercises are given under the heading: Evaluation. They correspond generally according to the length of the unit or to a number of the following three domains of competencies (or to all of them):
Applying of knowledge
Designing an experiment
Communicating.

Because these exercises are few in number, they only serve as simple examples to the kind of exercises that could be proposed in the evaluation method based on the domains of competencies.

The laboratory investigations (or their equivalents) are sometimes proposed as exercises in the domain entitled: Designing experiment.

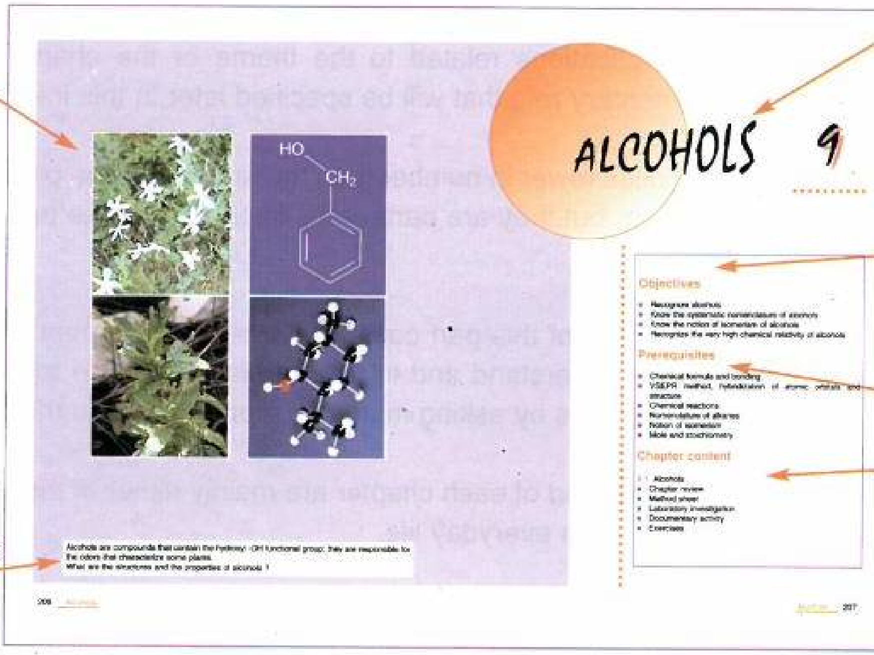
Finally, the comments and suggestions communicated to us by our colleagues about the chemistry textbook of the second secondary year scientific section were of great help. All comments and suggestions about this book are welcome.

The authors

Features of the Book

Unit Opener

- Photos introducing the chapter.
- Commentary introducing the subject of the chapter.
- Title
- Objectives
- Prerequisite
- Chapter content



ALCOHOLS 9

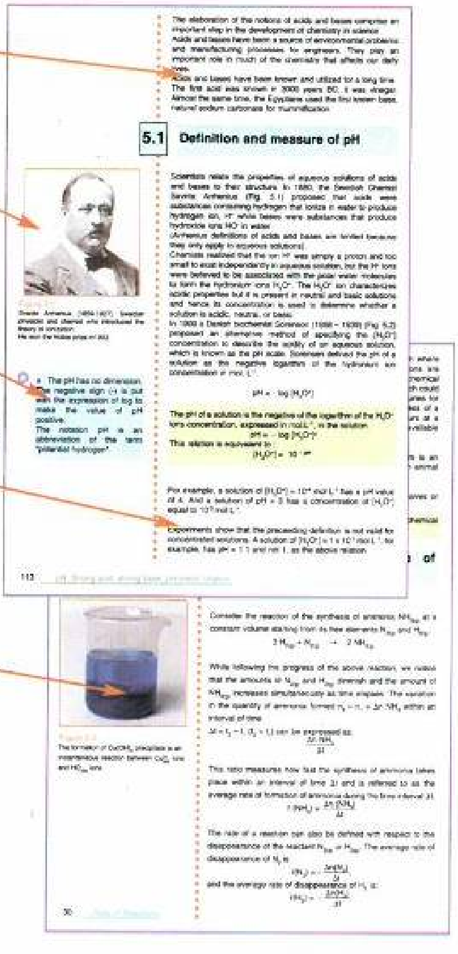
Objectives

Prerequisites

Chapter content

Course

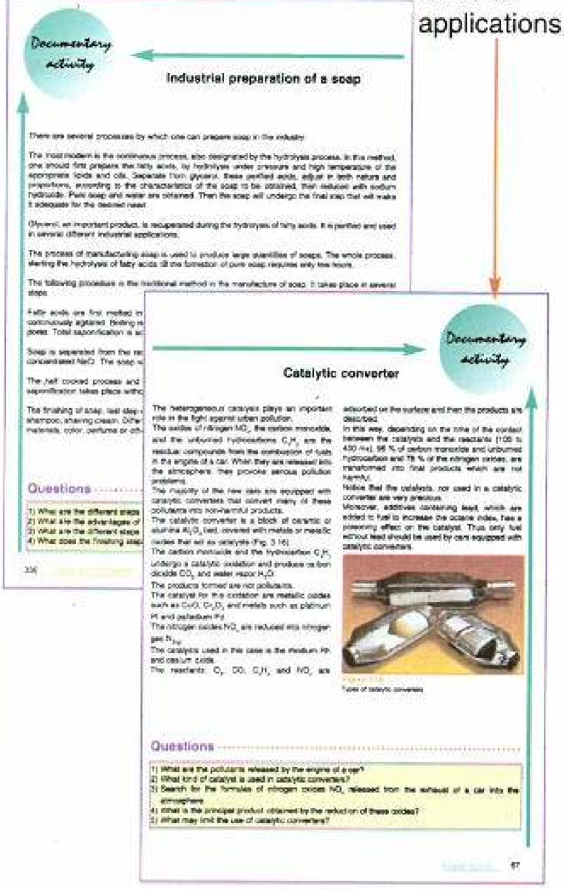
- Introduction to the chapter.
- Light on scientists and on their role.
- Remarks and supplementary information.
- Presents definitions, results and conclusions.
- Illustration



5.1 Definition and measure of pH

Documentary Activities

- To widen the student's knowledge concerning all fields of applications.



Documentary activity

Industrial preparation of a soap

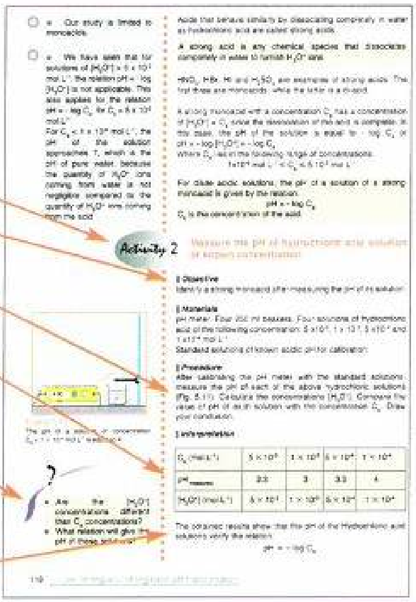
Documentary activity

Catalytic converter

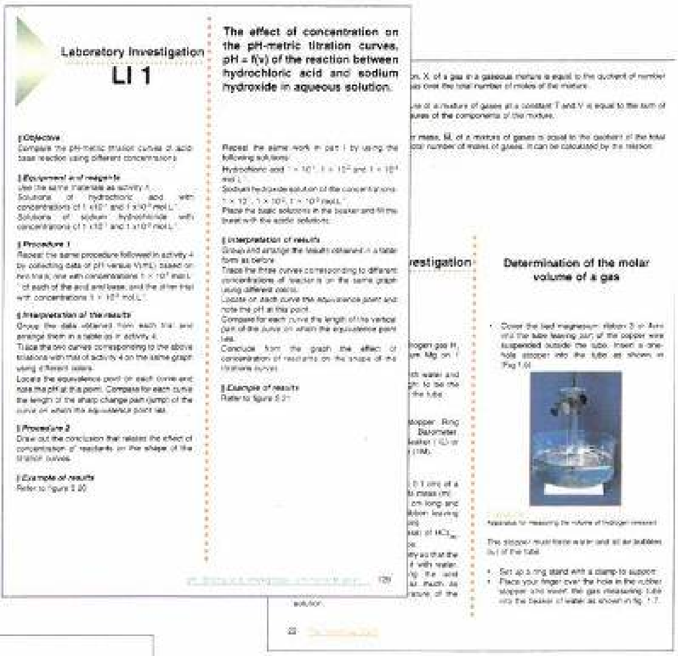
Questions

Experimental Activities

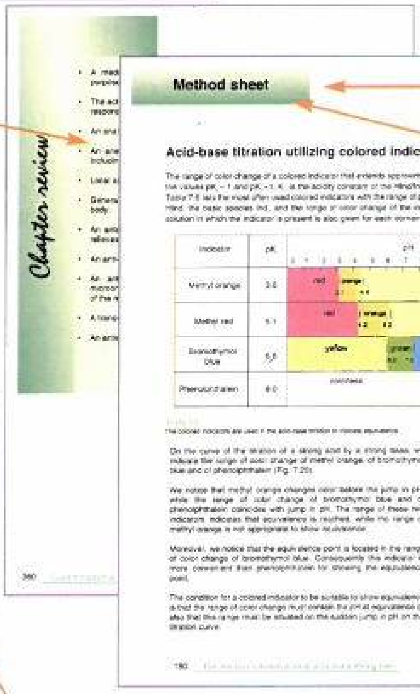
- Title
- Objective
- Procedure
- Results
- Questions leading to interpretation.
- Interpretation



Laboratory Investigations

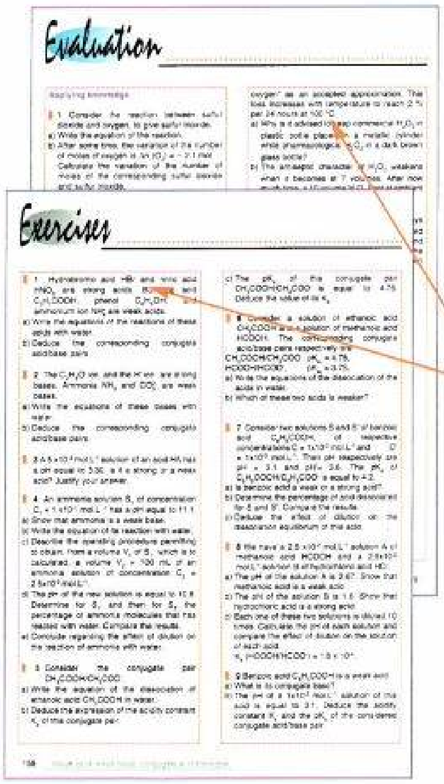


- Chapter review



- Method sheet necessary to complete the student's knowledge.

Exercises



- In addition to exercises, the part entitled Evaluation contains other exercises appropriate to the fields of competencies.

- Solved exercise. Direct application to the preceeded notion.

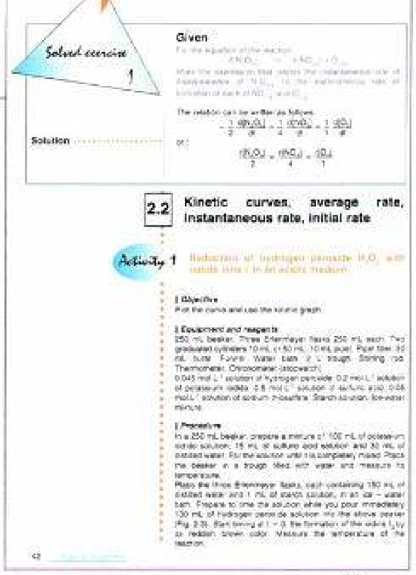
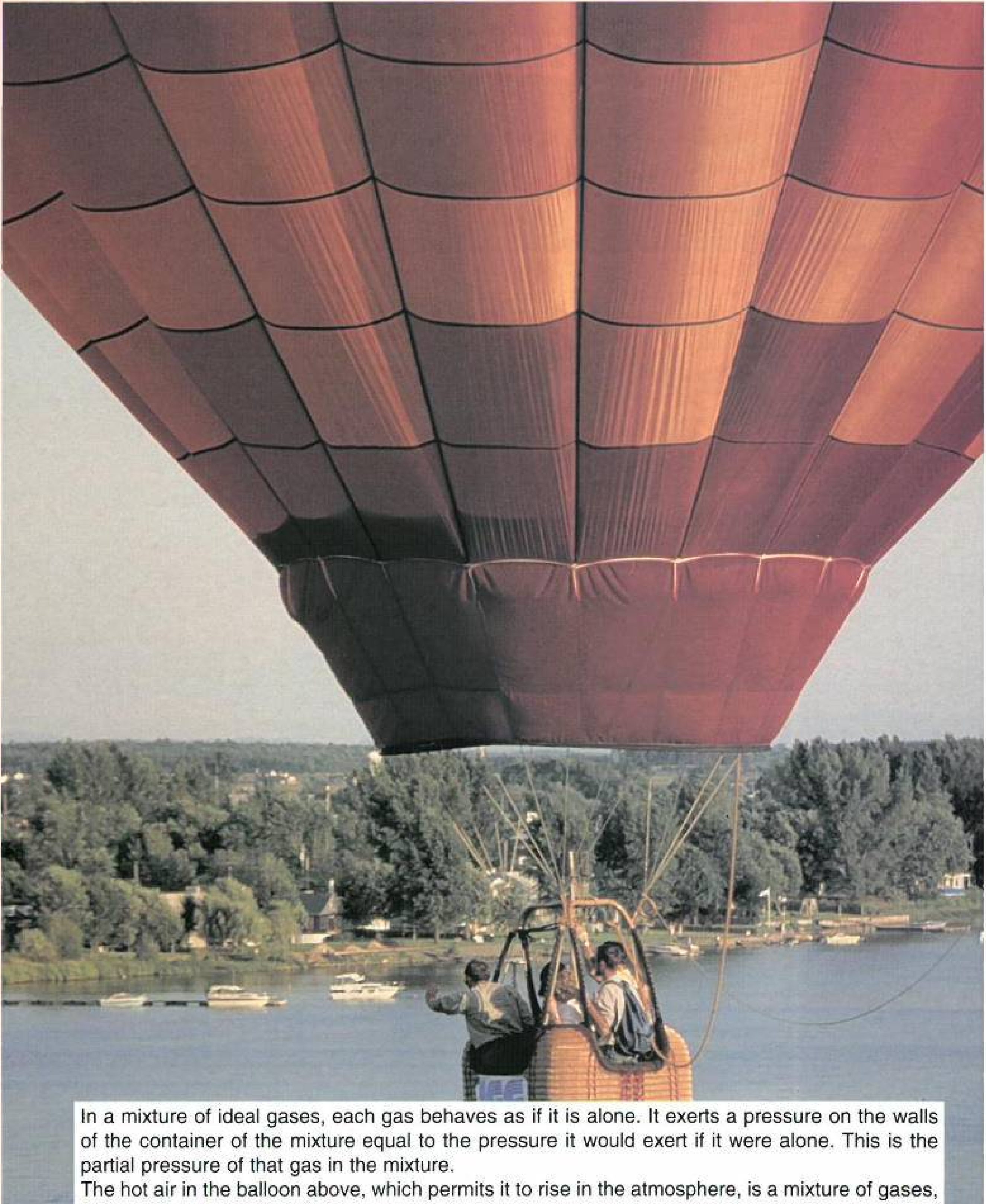


TABLE OF CONTENTS

1

The gaseous state

In the atmosphere, the pressure of the air that enters the lungs is equal to the atmospheric pressure exerted on the thorax.
At the depth of 100 m under sea, the pressure is about 9 times greater than the atmospheric pressure. To breath a mixture of gases where the pressure is equal to that exerted on his thorax, (sea water pressure around him), a diver must suitably adjust the pressure of this mixture, with the aid of a pressure regulator.



In a mixture of ideal gases, each gas behaves as if it is alone. It exerts a pressure on the walls of the container of the mixture equal to the pressure it would exert if it were alone. This is the partial pressure of that gas in the mixture.

The hot air in the balloon above, which permits it to rise in the atmosphere, is a mixture of gases, principally oxygen and nitrogen. Each gas has a partial pressure and the mixture has a total pressure.

What relation exists between the partial pressure of the constituents of a gas mixture and the total pressure of the mixture?

What is the average molar mass of a gas mixture and how can it be calculated?

THE GASEOUS STATE 1

Objectives

- Define the partial pressure of a gas and the total pressure of a mixture of gases.
- Apply the equation of state for ideal gases.
- Identify the composition of gaseous mixture.
- Relate the partial pressure of a gas in a mixture of gases to the total pressure of the mixture of these gases.
- Determine the average molar mass of a mixture of gases.

Prerequisites

- Gas laws.
- Kinetic theory of gases.
- Molar mass.

Chapter content

Gases are distinguished from solids and liquids by their physical behavior. The behavior of a gas is controlled by four variables: volume, pressure, temperature and the number of moles. The physical behavior of gases controlled by these four variables may be observed through different experiments. To explain the observed behavior and predict the results of other experimental observations, a theory is constructed called the kinetic theory of gases. This theory describes the behavior of individual gas particles (atoms or molecules) and is based on the following postulates:

1- The particles in gases are in a continuous, rapid, and random motion in the space available.

2- The particles of a gas are separated from each other by relatively long distances compared to their dimensions so that the volume of these particles is negligible as compared to the volume of space containing them.

3- The forces of attraction and repulsion among the particles of a gas are negligible.

4- The particles of a gas collide with each other and with the walls of the container in an elastic way where the kinetic energy of particles is conserved.

5- The average kinetic energy of particles of a gas is proportional to the absolute temperature of the sample of gas.

- Particles of elements as noble gases exist freely as monoatomic (He, Ne, Ar..) while particles of elements as oxygen, hydrogen, nitrogen... etc. exist freely as diatomic (O_2, H_2, N_2...).

- In an elastic collision, the total kinetic energy of the particles involved in collision remains constant.

1.1 Partial pressure in a mixture of ideal gases

The postulates of the kinetic theory of gases explain the properties of an ideal gas or a perfect gas.

- In our study about gases, we assume all gases to be ideal.

A perfect gas is a hypothetical gas, which obeys the kinetic theory of gases.

A gas approaches closely ideal behavior as the temperature increases and the pressure decreases, that is, when it is far from its liquefaction point.

A mixture of ideal gases, which conforms to the postulates of the kinetic theory and acts as an ideal gas, whether the particles are the same or different, is called an ideal (or perfect) mixture.

Gases are easily compressed at constant temperature; experimental results showed that the pressure of a gas on its surroundings is inversely proportional to its volume (Fig.1.1). The relation between the pressure and the volume of a gas was studied experimentally by Boyle-Mariotte.

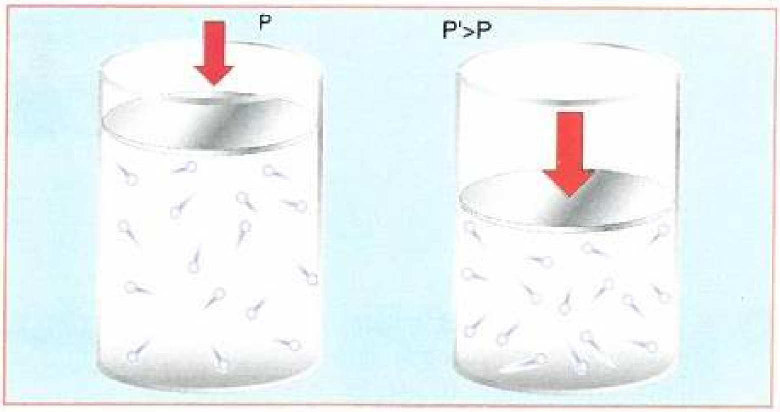


Figure 1.1
Gases are compressible

The compressibility of a gas is due to the very small dimension of its particles relative to the distance among them. In air, for example, at ordinary conditions, the particles occupy 0.1% of the total volume and the rest is empty space.

In an ideal mixture of ideal gases each gas behaves independently and the particles are too far apart from each other to exert a pressure that is the same it would exert if it were alone.

The pressure exerted by a gas on the walls of its container is due to the collision of the particles of the gas with the walls of container (Fig 1.2).

So, in an ideal mixture of ideal gases, each particular gas behaves independently and exerts pressure that results from the collision of its particles with the walls of the container as if it were alone. This pressure is called the partial pressure of the gas in the mixture of gases.

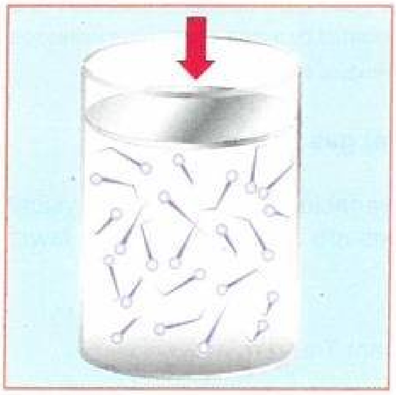


Figure 1.2
The pressure exerted by a gas is due to the collision of its particles with each other and with the walls of the container.

- In our discussion about pressure, the temperature, the volume and the amount of gas are constant.

The partial pressure of a gas in a mixture of gases at a given temperature in a container is the pressure it would exert if it were alone in the container.

1.2 Total pressure in a mixture of gases

The pressure exerted by a gas in a container at a constant temperature depends on the number of collisions among its particles and with the walls of the container. These collisions will increase when the number of particles of a gas increases; this also increases the pressure. At the macroscopic level, the pressure of a gas depends on the number of moles of that gas. Consequently, the partial pressure of a gas in a mixture of gases becomes larger as the number of moles of this gas increases in the mixture (Fig. 1.3).

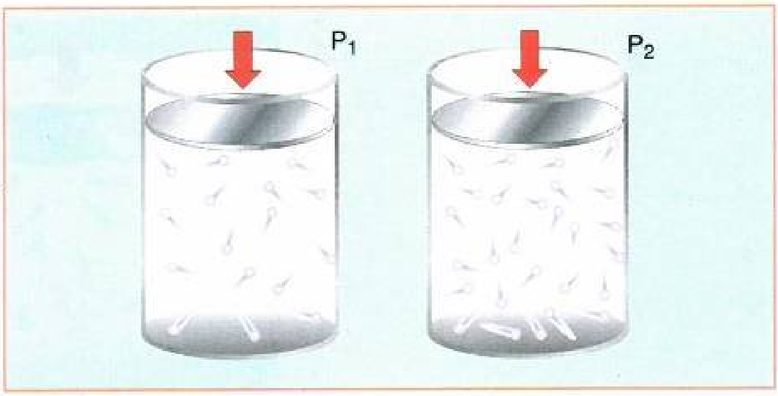


Figure 1.3

The pressure P_2 is higher than pressure P_1 due to the number of particles in the mixture. And because the total pressure exerted by a mixture of gases increases as the number of moles of gases in the mixture increases.

Equation of state of an ideal gas

As pointed out earlier, four variables control the physical behavior of a gas. These variables are described by three laws:

Boyle-Mariotte 's law:

$V \propto \frac{1}{P}$ at constant T and n

Charles' law:

$V \propto T$ at constant P and n

Avogadro hypothesis:

$V \propto n$ at constant T and P

The above three laws can be combined to show how the volume of an ideal gas depends on pressure, temperature and the number of moles of gas present.

$$V = R\frac{nT}{P}$$

This equation can be rearranged into a familiar form of the ideal gas law:

$$PV = nRT$$

The ideal gas law is called equation of state for an ideal gas. It describes a particular state of gas, its volume, temperature, pressure and number of moles. R is the combined proportionality constant called universal ideal gas constant. Its value depends on the units of T, V, P and n. In the international system of units (SI), R has a value of 8.314 $J.mol^{-1}.K^{-1}$. Other values of R are given in table 1.1.

- T is the absolute temperature expressed in Kelvin where zero (0 K) is equivalent to - 273°C.

- The symbol $\propto$ means proportional.

- In the international system for units (SI), the pressure is expressed in Pascal (Pa).
  $1 \text{ bar} = 10^5$ pa
  and $1 \text{ bar} \cong 1$ atm.

Numerical value of R	Unit
8.314	$J.mol^{-1}.K^{-1}$
8.314	$m^3.Pa.mol^{-1}.K^{-1}$
0.082	$L.atm.mol^{-1}.K^{-1}$
1.987	$cal.mol^{-1}.K^{-1}$

Table 1.1

Numerical values of the ideal gas constant R with different units.

Solved exercise 1

Given

A pressurized aerosol can of volume 250 mL contains 2.3 g of propane (C_3H_8).

What is the pressure of gas in the can, in atm and in bar, at the temperature 26°C?

$M(C_3H_8) = 44\ g.mol^{-1}$.
$R = 8.314\ J.mol^{-1}.K^{-1}$.

Solution

Applying the equation of state for an ideal gas:

$$P = \frac{nRT}{V}$$

$n = \frac{2.3}{44} = 0.052$ mol
$T = 26 + 273 = 299$ K
$V = 2.5 \times 10^{-4}\ m^3$

By substitution we get:

$$P = \frac{0.052 \times 8.314 \times 299}{2.5 \times 10^{-4}} = 5.17 \times 10^5\ Pa.$$

$P = 5.17$ bars or $P \cong 5.17$ atm

Solved exercise 2

Given

The molar volume of a gas, at $T_1 = 21$ °C and at $P_1 = 1$ bar, is 24.1 L. mol^{-1}.
Calculate the molar volume of this gas $T_2 = 0$ °C and $P_2 = 1$ bar.

Solution

- The temperature T = 0°C and P = 1 bar ≅ 1 atm are the standard temperature and pressure (S.T.P)

Since the temperature, pressure and volume of gas change while the number of moles remains constant, for 1 mole of gas we use the equation of state for an ideal gas in the following form:

$$\frac{P_1 \times V_1}{T_1} = \frac{P_2 \times V_2}{T_2} = R$$

Then: $V_2 = \frac{P_1 \times V_1}{T_1} \times \frac{T_2}{P_2}$

We are given $P_1 = 1$ bar; $T_1 = 21+273 = 294K$ and $V_1 = 24.1$ L ; $P_2 = 1$ bar, $T_2 = 0°C + 273 = 273$ K

By substitution we get:

$$V_2 = \frac{1 \times 24.1}{294} \times \frac{273}{1} = 22.73\ L.mol^{-1}.$$

1.3 Mole fraction

Consider a gaseous mixture made up of n_1 mole of gas g_1, n_2 mole of gas g_2, and n_3 mole of gas g_3, ... n_i mole of gas g_i (Fig. 1.4). If the sum of the number of moles of gases in the mixture is designated by n_t, then the mole ratios

Figure 1.4

A mixture of gases g_1, g_2, g_3.

$\frac{n_1}{n_t}, \frac{n_2}{n_t}, \frac{n_3}{n_t}, \dots, \frac{n_i}{n_t}$ represent respectively the mole fraction of the gaseous constituents g_1, g_2, g_3, ….g_i.

The mole fraction of a given component of a gaseous mixture is equal to the ratio of the number of moles of the component to the total number of moles in the mixture.

The mole fraction for a given gaseous component g, in a mixture of gases is symbolized by X and has no unit since it is a ratio of the number of moles:

$$X_1 = \frac{n_1}{n_1 + n_2 + n_3 + \dots n_i}$$

$$\Sigma X_i = X_1 + X_2 + \dots + X_i$$

$$\Sigma X_i = \frac{n_1 + n_2 + n_3 + \dots + n_i}{n_t} = \frac{n_t}{n_t} = 1$$

The sum of mole fractions of the components of a gaseous mixture represented by ΣX_i is equal to one.

Solved exercise 3

Given

The percentage composition of dry air by volume at room conditions is given in the following table :

a) Determine the mole fraction of each component of air for the first four components.

b) Determine the percentage composition of dry air by moles for the first four components.

Gas	Percentage by volume
N_2	78.1
O_2	20.9
Ar	9.34×10^{-1}
CO_2	3.15×10^{-2}
Ne	1.82×10^{-3}
He	5.24×10^{-4}
Kr	1.14×10^{-4}
Xe	8.70×10^{-6}

Solution

a According to Avogadro's hypothesis ($V \propto n$, at constant T and P) at the same temperature and pressure, we can write the following equation for any component of the air mixture:

$$\frac{V_i}{100} = \frac{n_i}{n_t} = X_i$$

For example, the mole fraction of nitrogen in dry air is equal to:

$$\frac{78.1}{100} = \frac{n_{N_2}}{n_t} = X_{N_2}$$

Then: $X_{N_2} = 0.781$

Similarly we can find the mole percentage of other components of air (Table 1.2).

Gas	X
N_2	0.781
O_2	0.209
Ar	9.34×10^{-3}
CO_2	3.15×10^{-4}

Since the mole fraction of any component of a gaseous mixture is out of one, then the mole percentage of this component can be directly calculated by multiplying the mole fraction by 100 as follows:

$$100\frac{n_i}{n_t} = 100X_i$$

The mole percentage of oxygen in air is:

$$100 \times \frac{n_{O_2}}{n_t} \text{ or } \frac{100 \times 20.9}{100} = 20.9$$

Gas	Mole Percentage
N_2	78.1
O_2	20.9
Ar	9.34×10^{-1}
CO_2	3.15×10^{-2}

Table 1.2

Mole percentage of dry air in the atmosphere.

We notice that for a given temperature and pressure, the percentage by moles of a component in a mixture of gases is equal to its percentage by volume at the same temperature and pressure.

The composition of a mixture of gases in mole fraction can be written as: X_1, X_2, X_3, ..., X_i and the percentage by mole can be expressed as : $100X_1$, $100X_2$, $100X_3$ ...., $100X_i$.

1.4 Relation between total pressure and partial pressure

The equation of the ideal gas law is the same for a mixture of gases and for a single gas.

The partial pressure P_i of each gas in a mixture of gases at a given T and V is equal to:

$$P_i = n_i \frac{RT}{V}$$

The total pressure P_t of the mixture of gases at same T and V is equal to:

$$P_t = n_t \frac{RT}{V}$$

Equating the above two expressions we get:

$$P_i = \frac{n_i}{n_t} P_t = X_i P_t$$

The partial pressure of a gas in a mixture of gases is equal to the product of its mole fraction and the total pressure.

Figure 1.5
John Dalton (1766-1844). English physicist and meteorologist. He contributed to the development of the atomic theory.

By adding the partial pressures of gases in a mixture we get:

$\Sigma P_i = P_1 + P_2 + P_3 + ... + P_i$

$\Sigma P_i = X_1P_t + X_2P_t + X_3P_t + ... + X_iP_t$

Or

$\Sigma P_i = (X_1 + X_2 + X_3 + ... + X_i)P_t$

$\Sigma P_i = \Sigma X_i \times P_t$

But $\Sigma X_i = 1$

Therefore $\Sigma P_i = P_t$

This relation was obtained experimentally by John Dalton (Fig. 1.5) and stated by a law known as Dalton's law of partial pressures which is expressed as follows:

The total pressure exerted by a mixture of gases in a container is equal to the sum of the partial pressures of the gases in the mixture.

1.5 Mean molar mass of a gas mixture

Consider a mixture of gases g_1, g_2, g_3, ..., g_i, of respectively molar masses M_1, M_2, M_3, ..., M_i and having the respective number of moles n_1, n_2, n_3, ..., n_i. If the mass of each gas is receptively m_1, m_2, m_3, ..., m_i, then the total mass in the mixture is:

$$m_t = m_1 + m_2 + m_3 + ... + m_i$$

It is possible to determine the average molar mass $\overline{M}$ of a mixture by :

$$\overline{M} = \frac{m_t}{n_t} = \frac{m_1 + m_2 + m_3 + ... + m_i}{n_t}$$

The mean (average) molar mass, $\overline{M}$, of a mixture of gases is equal to the quotient of the total mass of the mixture divided by the total number of moles of the gaseous components.

The mass of each component is equal to:

$m_1 = n_1M_1$, $m_2 = n_2M_2$, $m_3 = n_3M_3$,..., $m_i = n_iM_i$

By substitution we get:

$$\overline{M} = \frac{n_1M_1 + n_2M_2 + n_3M_3 + ... + n_iM_i}{n_t}$$

or

$\overline{M} = \frac{n_1}{n_t} M_1 + \frac{n_2}{n_t} M_2 + \frac{n_3}{n_t} M_3 + ... + \frac{n_i}{n_t} M_i$

$\overline{M} = X_1M_1 + X_2M_2 + X_3M_3 + ... + X_iM_i$

$\overline{M} = \Sigma X_iM_i$

This mathematical expression relates the average molar mass of a gas mixture to the molar mass and the mole fraction of each component in the mixture.

Solved exercise 4

Given

The study of the effect of some gases on the growth of plants requires an artificial atmosphere of the following composition: Calculate the average molar mass of the mixture of gases in this atmosphere.

Gas	O_2	CO_2	Ar
Mole percentage	19.0	2.0	79.0

$M(O_2) = 32\ g.mol^{-1}$,

$M(CO_2) = 44\ g.mol^{-1}$ and $M(Ar) = 40\ g.mol^{-1}$.

Solution

The percentage by moles of each constituent in a mixture of gases is equal to 100X where X is the mole fraction of the constituent. The mole fractions of gases in the above mixture are:

Gas	O_2	CO_2	Ar
X	0.19	0.020	0.79

The average molar mass of the mixture is:

$$\overline{M} = (0.19 \times 32) + (0.020 \times 44) + (0.79 \times 40)$$

$$\overline{M} = 38.56\ g.mol^{-1}.$$

Recall that the density of a gas A relative to another gas B at a given T and P is given by the ratio of their molar masses:

$$\frac{d_A}{d_B} = \frac{M_A}{M_B}$$

If gas B is air, then the density of a gas relative to air at ordinary conditions can be expressed as:

$$\frac{d_{(gas)}}{d_{air}} = \frac{M_{(gas)}}{29}$$

Where $29\ g.mol^{-1}$ is the average molar mass of air at ordinary conditions.

Chapter Review

- An ideal gas is a hypothetical gas, which obeys the kinetic theory of gases.
- A mixture of ideal gases behaves as an ideal gas.
- The partial pressure of a gas in a mixture of gases at a specific temperature and volume is the pressure exerted by the gas if it were alone in the same volume at the same T.
- The total pressure of a mixture of gases becomes larger when the number of moles of gases in the mixture increases.
- The temperature, pressure, volume and the number of moles of an ideal gas are related by the relation : $PV = nRT$, called equation of state for an ideal gas.

- The mole fraction, X, of a gas in a gaseous mixture is equal to the quotient of number of mole of the gas divided by the total number of moles of the mixture.
- The total pressure of a mixture of gases at a constant T and V is equal to the sum of the partial pressures of the components of the mixture.
- The mean molar mass, $\overline{M}$, of a mixture of gases is equal to the quotient of the total mass divided by the total number of moles of gases. It can be calculated by the equation: $\overline{M} = \Sigma X_i M_i$

Laboratory Investigation

LI

Determination of the molar volume of a gas

Objective

Determine the molar volume of hydrogen gas H_2 formed by the action of magnesium Mg with 1 $mol.L^{-1}$ hydrochloric acid.
Prepare a beaker (1L) half filled with water and measure the temperature that ought to be the same as that of the acid solution in the tube.

Equipment and reagents

Gas measuring tube. One hole stopper. Ring stand. Clamp. Thermometer. Barometer. Magnesium ribbon. Copper wire. Beaker (1L) or a trough. Hydrochloric acid solution (1M).

Procedure

- Measure a length of 2.5 cm (± 0.1 cm) of a magnesium ribbon and record its mass (m).
- Obtain a copper wire about 15 cm long and tie it around the magnesium ribbon leaving part of the wire free (about 10 cm).
- Pour carefully an amount (excess) of $HCl_{(aq)}$ (1M) into the gas measuring tube.
- Tilt the gas measuring tube slightly so that the air may escape and slowly fill it with water. (Avoid mixing the acid and water as much as possible). Measure the temperature of the solution.
- Cover the tied magnesium ribbon 3 or 4cm into the tube leaving part of the copper wire suspended outside the tube. Insert a one-hole stopper into the tube as shown in (Fig.1.6).

Figure 1.6
Apparatus for measuring the volume of hydrogen released.

The stopper must force water and all air bubbles out of the tube.

- Set up a ring stand with a clamp to support
- Place your finger over the hole in the rubber stopper and invert the gas measuring tube into the beaker of water as shown in fig. 1.7.

The reaction will start after a while till the acid diffuses into the water in the tube to reach the magnesium ribbon.

- When the magnesium ribbon has reacted completely and the evolution of gas has stopped, tap the tube with your finger to dislodge any bubbles attached to the sides of the tube. Wait till the temperature of the solution in the tube is the same as before.
- Place your finger over the hole in the stopper and transfer the tube to a large container of water. Remove your finger and move the tube up and down until the water level is the same outside and inside the tube to equalize pressure.

Read the volume of gases on the seal after the gas measuring tube and record it .

Figure 1.7
Reading the volume of the gas at atmospheric pressure.

Interpretation of the results:

The equation of the reaction that takes place in the gas-measuring tube is:

$$Mg_{(s)} + 2H^{+}_{(aq)} \rightarrow Mg^{2+}_{(aq)} + H_{2(g)}$$

$$n(H_2) = n(Mg) = \frac{m(Mg)}{M(Mg)}$$

If V is the volume of hydrogen gas at, T, the temperature of the experiment, and, P, the barometric pressure, then V_m (molar volume) of H_2 gas at the above condition is:

$$V_m = \frac{V}{n(H_2)} = \frac{V \times M(Mg)}{m(Mg)}$$

Example of results

$m(Mg) = 0.04$ g
$M(Mg) = 24.3$ g.mol^{-1}

$V = 43$ mL

$P_{atm} = 0.993$ bar and $T = 30$ °C

$$V_m = \frac{43 \times 24.3}{0.040 \times 10^{3}} = 26.12 \text{ L.mol}^{-1}$$

To calculate the molar volume at S.T.P, we must first calculate the partial pressure of hydrogen gas in the tube at the temperature of the experiment, taking into account the pressure of saturated water vapor at temperature T. This pressure is given in specific tables.

$p_{H_2} = P_{barometric} - P_{H_2O}$
P_{H_2O} at 30°C $= 0.0424$ bar
$P_{H_2} = 0.993 - 0.0424 = 0.951$ bar

Molar volume at S.T.P. is equal to:

$$V'_m = \frac{26.12 \times 0.951}{303} \times \frac{273}{1}$$

$V'_m = 22.38$ L.mol^{-1}.

Exercises

1 A bicycle tire is filled with air pressure of 6 atm, at a temperature 20°C. Riding the bicycle on asphalt on a hot day at a temperature 42°C makes the volume of the tire increase by 2%. What is the new pressure in the bicycle tire?

2 In the first step of the industrial preparation of nitric acid, ammonia gas reacts with oxygen at T = 850°C and P = 5 bars in the presence of a catalyst. The equation of the reaction is:

$$4NH_{3(g)} + 5O_{2(g)} \rightarrow 4NO_{(g)} + 6H_2O_{(g)}$$

What volume of nitric oxide gas $NO_{(g)}$ will be obtained at the above same condition if 10^6 mole of the limiting reactant ammonia gas are completely oxidized?

Molar volume at S.T.P = 22.4 $L.mol^{-1}$

3 a) What is the mole fraction of each gas in a mixture of 6.00 g of hydrogen H_2 and 7.00 g of nitrogen N_2?

b) What is the total pressure exerted by the above mixture in a volume of 15 L at a temperature of 0°C?

c)What is the partial pressure of each gas in the above mixture?

$R = 8.314\ J.mol^{-1}.K^{-1}$.

4 A) A glass bulb of capacity 4 L contains 0.483 mole of $He_{(g)}$ at T = 30°C. Calculate the pressure of $He_{(g)}$ in the bulb.

B) A second glass bulb of capacity 5 L contains a mixture of 0.306 mole of $Ne_{(g)}$ and 0.113 mole of $Ar_{(g)}$ at the same T = 30°C.

a) Calculate the total pressure of the mixture in the bulb.

b) Calculate the partial pressure of each gas of the mixture in the bulb.

C) We join the above two bulbs with their components to obtain a new mixture of gases.

a) Calculate the partial pressure of each gas of the new mixture in the new volume.

b) Calculate the total pressure of the new mixture of gases.

$R = 8.314\ J.mol^{-1}.K^{-1}$

5 A mixture of gaseous alkanes CH_4, C_2H_6 and C_3H_8 put in a container at T = 0°C and P = 1 bar. The partial pressure of the gases in the container are: $P_{CH_4} = 0.42$ bar ; $P_{C_2H_6} = 0.31$ bar ; $P_{C_3H_8} = 0.27$ bar.

a) Calculate the mean molar mass of the above gaseous mixture.

b) Calculate the density of the above gaseous mixture relative to air.

$M(CH_4) = 16\ g.mol^{-1}$; $M(C_2H_6) = 30\ g.mol^{-1}$;
$M(C_3H_8) = 44\ g.mol^{-1}$; $\overline{M}_{(air)} = 29\ g.mol^{-1}$.

Evaluation

Applying knowledge

1 Fill up the missing information concerning the gas Argon Ar in the following table:

P	V	T	n(mol)	m(g)
---atm	150 mL	30 °C	0.09	---
1.25 bars	5.40 L	40 °C	---	---
3 atm	... L	25 °C	---	84
3 bars	1.32 L	--- K	---	2.8

$M(Ar) = 40\ g.mol^{-1}$
$R = 8.314\ J.mol^{-1}.K^{-1}$.

2 A volume of 850 m^3 of hexane gas $C_6H_{14(g)}$ is decomposed catalytically at T = 480°C and P = 15 bars. We suppose that the reaction is complete and the products are C_6H_6 and $H_{2(g)}$.

a) Write the balanced equation of the reaction.
b) Calculate the total pressure of the gaseous mixture obtained in bars, if the volume becomes $2.3 \times 10^4\ m^3$ and the temperature decreases to 100°C?
c) Calculate the partial pressure of gaseous components of the obtained mixture.
$R = 8.314\ J.mol^{-1}.K^{-1}$.

3 A person takes in a breath of 450 mL of air on a cold day at a pressure of 0.995 atm and a temperature of 15°C. What is the volume of air in the lungs when it warms up to body temperature 37°C and at pressure of 0.988 atm?

4 At a depth of about 100 m, the pressure under seawater is 8.38 atm.
How much must the molar percentage of oxygen $O_{2(g)}$ be in the gas mixture for breathing, which the diver is equipped with, for the partial pressure of O_2 in the mixture to be 0.21 atm (same as in the air at 1 atm)?

Designing an experiment

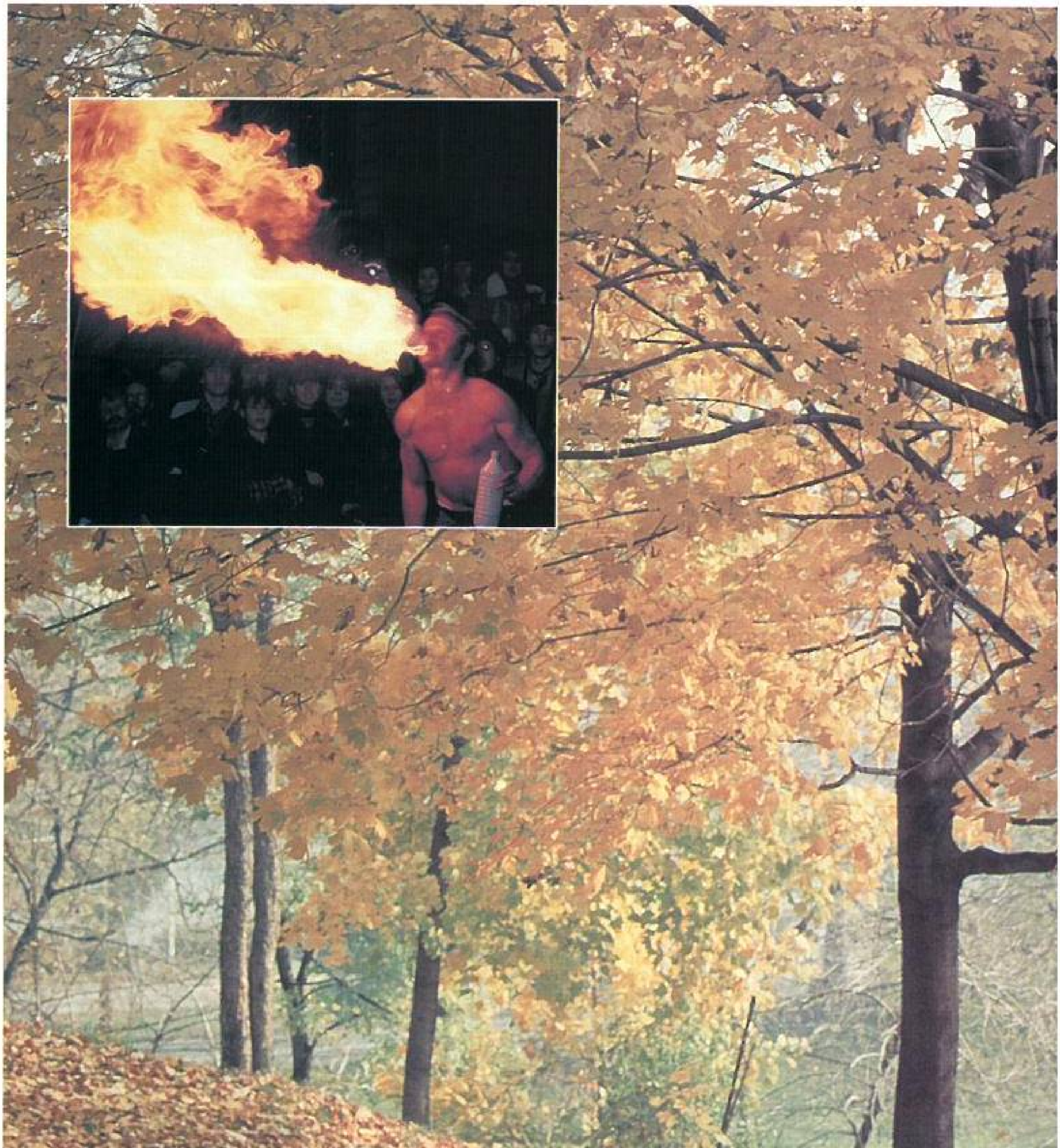
5 Perform an experiment to determine the molar volume of $H_{2(g)}$, obtained by the reaction of a magnesium Mg ribbon with 1 $mol.L^{-1}$ solution of hydrochloric acid HCl, (described in the laboratory method sheet).

- Answer the following questions:
a) Can we not take precautions to stabilize the graduated cylinder which is inverted inside a crystallizing dish filled with water and where the reaction between the HCl and Mg is taking place? Why?
b) The reaction between Mg and HCl is exothermic. Why must we measure the temperature of the gas in this experiment? Why must we wait for the temperature of the collected gas to return to ambient temperature to measure it?
c) Why must we measure the atmospheric pressure? With what type of instrument?
d) Using the results obtained: m(Mg); V_{exp}; T(ambient); $P_{atmospheric}$; P_{H_2O} (from tables), calculate the molar volume of hydrogen at the conditions of the experiment and at S.T.P.

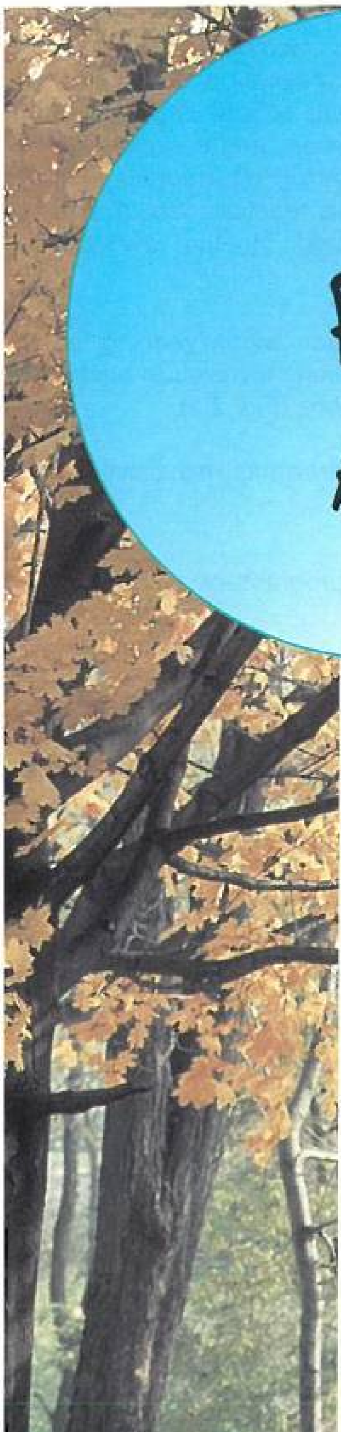
2

Chemical kinetics

Some reactions are very fast. They occur in a flash of a second. The study of their kinetics requires methods different from ordinary laboratory. The explosion of an explosive is an example of such reactions.



The time required for a chemical reaction to take place is an important aspect and of great interest to the research chemists. The study of reaction rates is important because it helps us to choose the most efficient, and the most economical conditions for an industrial operation. It also helps us to understand better how chemical changes take place.
The yellowing of the leaves of a tree is a slow reaction.
Ethanol propelled from the mouth of this man burns instantaneously in the presence of a flame.
What is the role of the parameter time in the progress of a chemical reaction?



RATE OF REACTIONS

2

Objectives

- Define the rate of a reaction.
- Define, by using kinetic curves, the average, instantaneous and initial rate of formation of a product or the disappearance of a reactant.
- Determine graphically the rate of a reaction.

Prerequisites

- Redox reaction titration
- Molar concentration

Chapter content

Figure 2.1

The formation of cellulose $[C_6H_7(OH)_3]_n$ in plants from CO_2 and H_2O is a slow reaction.

A chemical reaction corresponds to a reaction system where reactants are converted into products. Some reactions are naturally fast and others are slow. The progress of a chemical reaction may be measured during intervals of time, which could be seconds, minutes, hours, or even years and centuries for certain slow reactions.The measurement of the progress of a chemical reaction will be feasible if the reaction occurs at a reasonable rate that can be detected by the available instruments.

The corrosion of metals that takes place within years is an example of a slow reaction. Many reactions involved in animal bodies and plant tissues are slow reactions (Fig. 2.1).

Other reactions are very fast such as fireworks, explosives or the formation of a precipitate (Fig. 2.2)... .

Chemical kinetics is the study of the progress of a chemical reaction with time.

2.1 Rate of formation and rate of disappearance of a substance

Figure 2.2

The formation of $Cu(OH)_2$ precipitate is an instantaneous reaction between $Cu^{2+}_{(aq)}$ ions and $HO^-_{(aq)}$ ions.

Consider the reaction of the synthesis of ammonia $NH_{3(g)}$ at a constant volume starting from its free elements $N_{2(g)}$ and $H_{2(g)}$.

$$3\,H_{2(g)} + N_{2(g)} \rightarrow 2\,NH_{3(g)}$$

While following the progress of the above reaction, we notice that the amounts of $N_{2(g)}$ and $H_{2(g)}$ diminish and the amount of $NH_{3(g)}$ increases simultaneously as time elapses. The variation in the number of moles of ammonia formed $n_2 - n_1 = \Delta n\ NH_3$ within an interval of time $\Delta t = t_2 - t_1$ $(t_2 > t_1)$ can be expressed as:

$$\frac{\Delta n\ NH_3}{\Delta t}.$$

This ratio measures how fast the synthesis of ammonia takes place within an interval of time Δt and is referred to as the average rate of formation of ammonia during the time interval Δt.

$$\bar{r}\,(NH_3) = \frac{\Delta n\ (NH_3)}{\Delta t}$$

The rate of a reaction can also be defined with respect to the disappearance of the reactant $N_{2(g)}$ or $H_{2(g)}$. The average rate of disappearance of N_2 is:

$$\bar{r}(N_2) = -\frac{\Delta n(N_2)}{\Delta t},$$

and the average rate of disappearance of H_2 is:

$$\bar{r}(H_2) = -\frac{\Delta n(H_2)}{\Delta t}.$$

The negative sign is placed to obtain a positive value of the rate because Δn is negative in the case of disappearance.
The rate of formation of ammonia at an instant t, is called the instantaneous rate and is obtained when $\Delta t \rightarrow 0$ ($t_2 \rightarrow t_1$). It is represented by:

$$r(NH_3)_{t1} = \frac{dn(NH_3)}{dt}$$

Similarly the instantaneous rate of disappearance of each of $N_{2(g)}$ and $H_{2(g)}$, can be represented respectively by:

$$r(N_2)_t = -\frac{dn(N_2)}{dt} \text{ and } r(H_2)_t = -\frac{dn(H_2)}{dt}$$

■ Units of the rate of a reaction

The synthesis of ammonia being done at constant volume V, the rate above can be expressed in terms of changes in concentration, by dividing each of the previous relations by the volume V.
For the formation of ammonia, we have:

$$r(NH_3)_t = \frac{dn(NH_3)}{V \times dt} = \frac{d[NH_3]}{dt}$$

This implies that the unit of the rate in this case will be $mol.L^{-1}.time^{-1}$ where the unit of time could be (s), (min) or (h).

■ Rate of a reaction and stoichiometry:

The stoichiometric coefficients in the balanced equation of the synthesis of ammonia allow us to write the following:

$$-\frac{dn(H_2)}{3} = -\frac{dn(N_2)}{1} = \frac{dn(NH_3)}{2}$$

In terms of concentration, the variation within an interval of time dt, we can write:

$$-\frac{1}{3}\frac{d[H_2]}{dt} = -\frac{1}{1}\frac{d[N_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$$

For the equation of a reaction of the general form:

$$aA + bB \rightarrow cC + dD$$

The relation between the rate of disappearance of A and B, and the rate of appearance of C and D can be expressed as:

$$-\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

or in another form as:

$$\frac{r(A)}{a} = \frac{r(B)}{b} = \frac{r(C)}{c} = \frac{r(D)}{d}$$

When we speak about the rate of a reaction without specifying a particular reactant or product, we can use the above relation to express the rate of the reaction.

Solved exercise 1

Given

For the equation of the reaction:

$$2\,N_2O_{5(g)} \rightarrow 4\,NO_{2(g)} + O_{2(g)}$$

Write the expression that relates the instantaneous rate of disappearance of $N_2O_{5(g)}$ to the instantaneous rate of formation of each of $NO_{2(g)}$ and $O_{2(g)}$.

Solution

The relation can be written as follows:

$$-\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt} = \frac{1}{1}\frac{d[O_2]}{dt}$$

or :

$$\frac{r(N_2O_5)}{2} = \frac{r(NO_2)}{4} = \frac{r(O_2)}{1}$$

2.2 Kinetic curves, average rate, instantaneous rate, initial rate

Activity 1 Reduction of hydrogen peroxide H_2O_2 with iodide ions I^- in an acidic medium.

Objective

Plot the curve and use the kinetic graph.

Equipment and reagents

250 mL beaker. Three Erlenmeyer flasks 250 mL each. Two graduated cylinders 100 mL and 50 mL. 10 mL pipet. Pipet filler. 50 mL buret. Funnel. Water bath. 2 L trough. Stirring rod. Thermometer. Chronometer (stopwatch).

0.045 mol.L^{-1} solution of hydrogen peroxide. 0.2 mol.L^{-1} solution of potassium iodide. 0.5 mol.L^{-1} solution of sulfuric acid. 0.05 mol.L^{-1} solution of sodium thiosulfate. Starch solution. Ice-water bath.

Procedure

In a 250 mL beaker, prepare a mixture of: 100 mL of potassium iodide solution, 15 mL of sulfuric acid solution. Stir the solution until it is completely mixed. Place the beaker in a trough filled with water and measure its temperature.

Place the three Erlenmeyer flasks, each containing 150 mL of distilled water and 1 mL of starch solution, in an ice – water bath. Prepare to time the solution while you pour immediately 100 mL of hydrogen peroxide solution into the above beaker (Fig. 2.3). Start timing at t = 0, the formation of the iodine I_2 by its reddish brown color. Measure the temperature of the reaction.

- We can use demineralized water.

- Calculate the new concentrations of the species: I^-, H_2O_2, and H_2SO_4.

Figure 2.3
The reddish brown color indicates the formation of I_2.

- Cold water will cause the reaction to stop, this permits to titrate the iodine formed only just when the sample is taken.

- Determine the limiting reactant in the reduction of hydrogen peroxide.

Take 10 mL of the above prepared mixture , at different intervals of time:
T = 30 s, 60 s, 90 s, 120 s, 3 min and pour the contents in an Erlenmeyer flask which is still in the water bath. Titrate the I_2 with sodium thiosulfate solution and record the corresponding volumes V_r to reach the equivalence point.

Interpretation of the results

The hydrogen peroxide solution is reduced by the iodide ions in the acid medium according to the following reaction:

$$H_2O_2 + 2\,I^- + 2\,H^+ \rightarrow I_2 + 2\,H_2O$$

If $n(I_2)$ is the number of moles of iodine I_2 formed at instant t, $n_0(H_2O_2)$ the initial number of moles of H_2O_2 and $n'(H_2O_2)$ is the number of moles that disappeared, then we can write:

$$n'(H_2O_2) = n(I_2)$$

The number of moles of H_2O_2 remaining is equal to :

$$n(H_2O_2) = n_0(H_2O_2) - n(I_2)$$

The iodine formed is titrated with the thiosulfate ions where the following reaction takes place:

$$2\,S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2\,I^-$$

If $n(S_2O_3^{2-})$ is the number of moles of thiosulfate ions consumed during titration and C_r is the concentration of sodium thiosulfate used, then the number of moles of I_2 present in each sample is obtained by:

$$n(I_2) = \frac{1}{2}\,n(S_2O_3^{2-}) = \frac{1}{2}\,C_r \times V_r$$

To find the concentration of I_2 formed or the concentration of H_2O_2 remaining, we divide the corresponding number of moles by the volume measured taken as 10 mL. Table 2.1 summarizes the obtained results

Kinetic curve

curve $n(I_2) = f(t)$

The results of table 2.1 allows us to plot the curve that represents the change of the number of moles of iodine formed versus time, $n(I_2) = f(t)$ (Fig. 2.4).

Time (min)	$n(I_2)$ (mmol)	$n(H_2O_2)$ (mmol)
0	0	4.50
3	1.08	3.42
6	1.56	2.94
9	2.04	2.46
12	2.39	2.11
15	2.64	1.86
18	2.86	1.64
21	3.07	1.58
24	3.18	1.32
27	3.23	1.27
30	3.42	1.08

Table 2.1

- The values of $n(I_2)$ and $n(H_2O_2)$ in table 2.1 correspond to a volume of 215 mL.

- Calculate the number of moles of iodine formed in 10 mL of solution.

- Calculate the number of moles of H_2O_2 remaining in 10 mL solution.

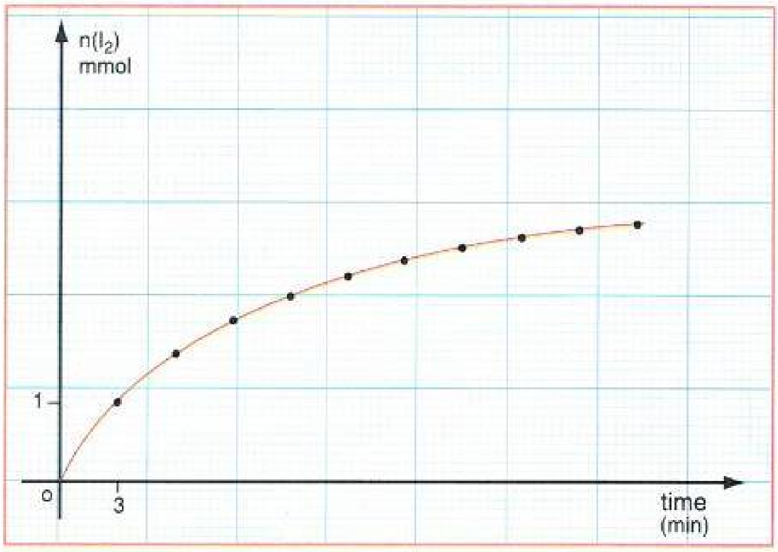


Figure 2.4

Kinetic curve of iodine formed versus time, $n(I_2) = f(t)$.

The above curve shows that the change in number of moles of I_2 formed is fast at the beginning, but decreases little by little to reach a constant value which corresponds to the end of the reaction when the limiting reactant has been consumed completely.

- **curve $n(H_2O_2) = g(t)$**

The results obtained in table 2.1 allow us to plot the curve which represents the change of the number of moles of H_2O_2 remaining versus time, $n(H_2O_2) = g(t)$ (Fig. 2.5).

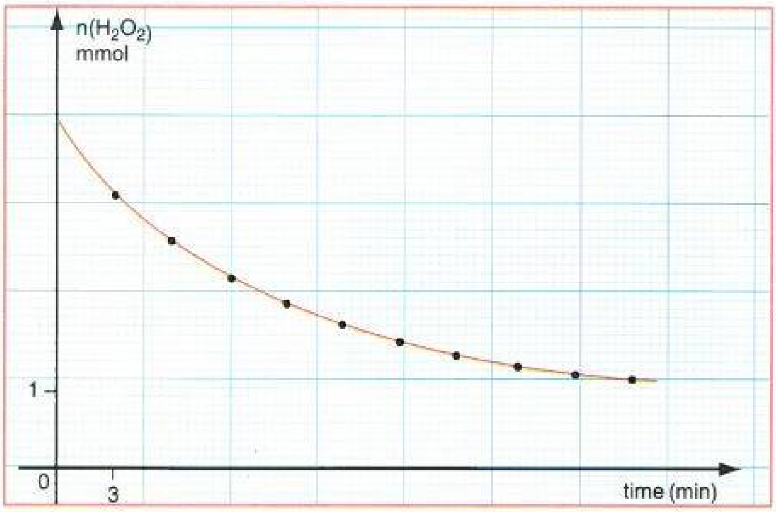


Figure 2.5

Kinetic curve of hydrogen peroxide remaining versus time, $n(H_2O_2) = g(t)$.

The above curve shows the number of moles of hydrogen peroxide left versus time, starting high and decreasing gradually to reach zero, and the hydrogen peroxide is the limiting reactant.

Time (min)	$[I_2]$ ($mmol.L^{-1}$)	$[H_2O_2]$ ($mmol.L^{-1}$)
0	0	20.9
3	5	15.9
6	7.3	13.7
9	9.5	11.4
12	11.1	9.8
15	12.3	8.6
18	13.3	7.6
21	14.3	6.6
24	14.8	6.1
27	15.0	5.9
30	15.0	5.9

Table 2.2

- Calculate the limiting concentration of hydrogen peroxide remaining.

- Calculate the limiting concentration of I_2 formed.

- **$[I_2] = f(t)$ curve**

This curve (Fig. 2.6) is plotted graphically by using the results obtained in table 2.2 .

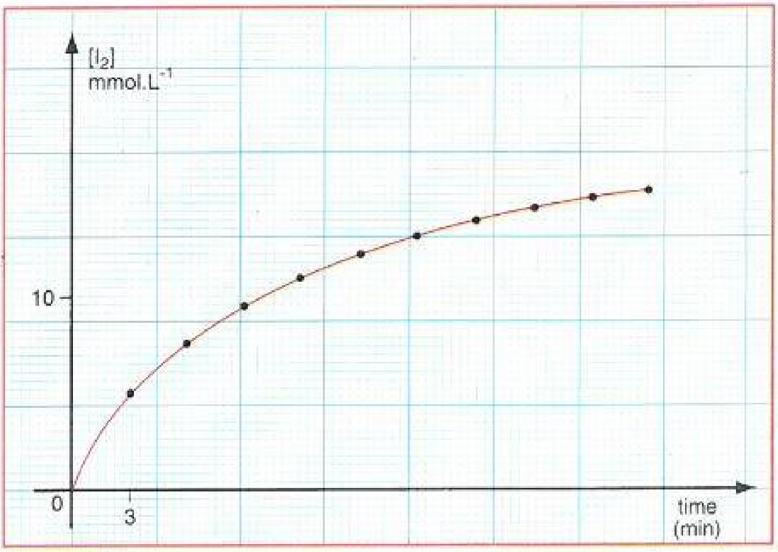


Figure 2.6
Kinetic curve of iodine formed, $[I_2] = f(t)$.

The above curve shows that the concentration of iodine formed with time till it reaches a maximum value, which is determined by the limiting reactant.

- **Curve $[H_2O_2] = g(t)$**

This curve is also plotted by referring to the results obtained in table 2.2 (Fig. 2.7).

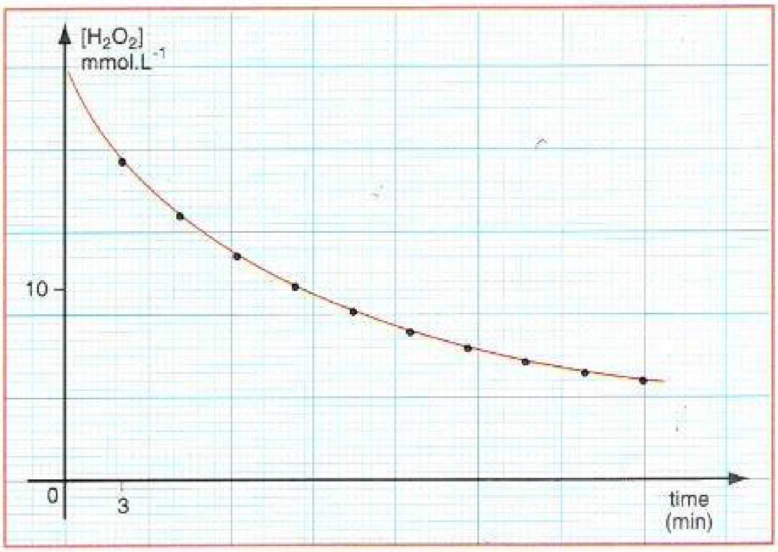


Figure 2.7
Kinetic curve of hydrogen peroxide remaining $[H_2O_2] = g(t)$.

The above curve shows that the concentration of hydrogen peroxide, decreases with time until it reaches zero, it is the limiting reactant.

The shapes of the kinetic curve of the reactant (H_2O_2) and that of the product (I_2) are also observed for the kinetic curves of the reactants and the products for a reaction in general.

The concentration of a reactant decreases with time to reach a limiting value, which is equal to zero, when this reactant is the limiting reactant.
The concentration of a product increases with time until it reaches a limiting value, which is determined by the limiting reactant.

Rate of formation of a product

Average rate

Consider the points M_1 and M_2 corresponding to the abscissas t_1 and t_2 ($t_2 > t_1$) according to Figure 2.8 below.
The concentration of iodine at t_1 and t_2 are respectively $[I_2]_1$ and $[I_2]_2$. The average rate of formation of iodine during the time interval $\Delta t = t_2 - t_1$ is given by the ratio:

$$\bar{r}(I_2) = \frac{[I_2]_2 - [I_2]_1}{t_2 - t_1} = \frac{\Delta[I_2]}{\Delta t}$$

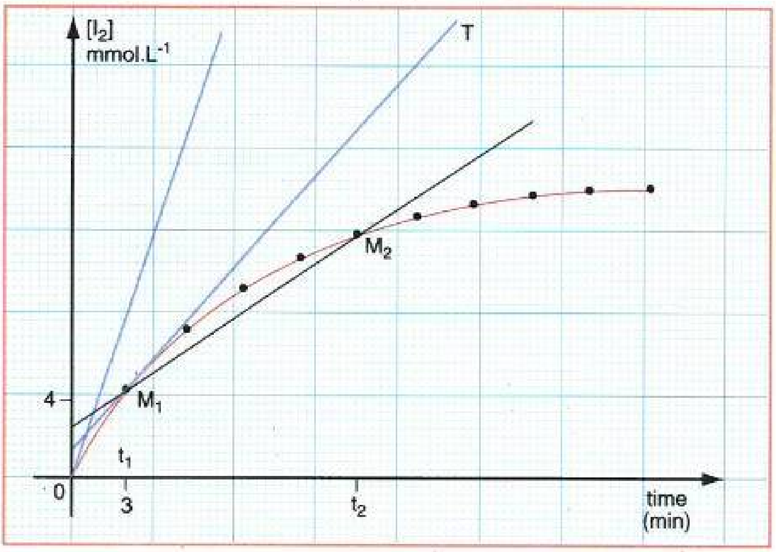


Figure 2.8
Kinetic curve $[I_2] = f(t)$.

From the graph, this rate is equal to the gradient (slope) of the secant M_1M_2 at the points of abscissa t_1 and t_2 (Fig. 2.8).

The average rate of formation of a product P within the interval of time $\Delta t = t_2 - t_1$ is equal to the gradient (slope) of the secant M_1M_2 on the curve $[P] = f(t)$ at the points M_1 and M_2 of abscissa t_1 and t_2, respectively.

Instantaneous rate

The instantaneous rate of formation of iodine at time t_1 is given by the ratio:

$$r(I_2)_{t_1} = \lim \frac{\Delta[I_2]}{\Delta t} \text{ as } \Delta t \rightarrow 0$$

which is equal to the derivative of the function $[I_2] = f(t)$ at time t_1:

$$r(I_2)_{t_1} = (\frac{d[I_2]}{dt})_{t_1}$$

On the curve $[I_2] = f(t)$, when $\Delta t \rightarrow 0$, the secant M_1M_2 tends to form the tangent M_1T at point M_1 of abscissa t_1 (Fig. 2.8). In the case of the instantaneous rate of formation of iodine at instant t_1 is equal to the slope of the tangent M_1T.

The instantaneous rate of formation of a product P at time t is equal to the value of the derivative of the function $[P] = f(t)$, at time t:

$$r(P)_t = \left(\frac{d[P]}{dt}\right)_t$$

Graphically, this rate is equal to the value of the slope of the tangent to the curve $[P] = f(t)$ at the point of abscissa t.

Initial rate

The initial rate of a reaction corresponds to the instantaneous rate determined after the reaction begins (just after $t = 0$) (Fig. 2.8).

The initial rate of formation of a product P is equal to the value of the derivative of the function $[P] = f(t)$ at time $t = 0$:

$$r(P)_{t=0} = \left(\frac{d[P]}{dt}\right)_{t=0}$$

Graphically, this rate is equal to the value of the slope of the tangent to the curve $[P] = f(t)$ at the point of abscissa $t = 0$.

Rate of disappearance of a reactant

Average rate

We take two points M_1 and M_2 on the curve $[H_2O_2] = g(t)$, of abscissa t_1 and t_2 respectively ($t_2 > t_1$) (Fig. 2.9), and of molar concentrations $[H_2O_2]_1$ and $[H_2O_2]_2$. The average rate of disappearance of hydrogen peroxide within the interval $\Delta t = t_2 - t_1$ is given by the ratio:

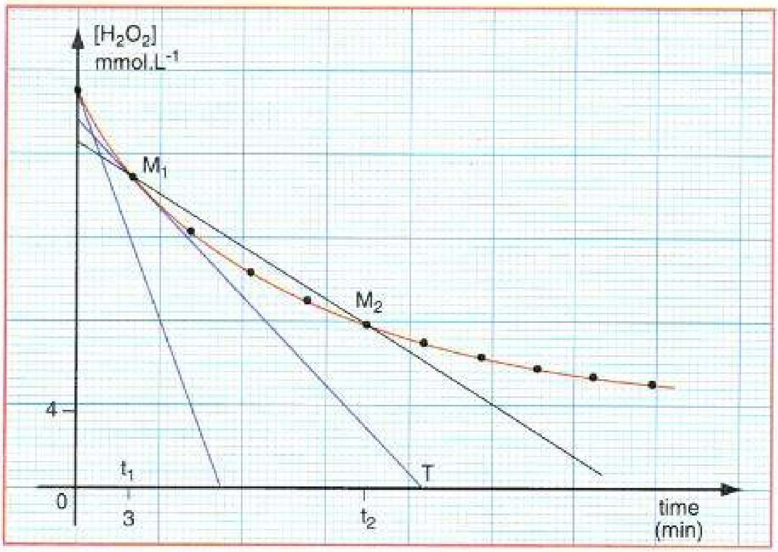


Figure 2.9
Kinetic curve $[H_2O_2] = g(t)$.

$$\bar{r}(H_2O_2) = -\frac{[H_2O_2]_2 - [H_2O_2]_1}{t_2 - t_1} = -\frac{\Delta[H_2O_2]}{\Delta t}$$

From the graph, this rate is equal to the negative slope of the secant M_1M_2 that joins the points of abscissa t_1 and t_2 (Fig. 2.9).

The average rate of disappearance of a reactant R within the interval of time $\Delta t = t_2 - t_1$, is equal to the negative slope of the secant that belongs to the points M_1 and M_2 on the curve $[R] = f(t)$ of abscissa t_1 and t_2 respectively.

- The negative sign (-) is placed in front of the ratio, to make it positive because $[H_2O_2]_2 - [H_2O_2]_1 < 0$.

- **Instantaneous rate**

The instantaneous rate of disappearance of hydrogen peroxide at time t_1 is represented by:

$$\bar{r}(H_2O_2)_{t_1} = \lim -\frac{\Delta[H_2O_2]}{\Delta t} \text{ as } \Delta t \to 0$$

Which is equal to the negative of the derivative of the function $[H_2O_2] = g(t)$ at t_1:

$$r(H_2O_2)_{t_1} = \left(-\frac{d[H_2O_2]}{dt}\right)_{t_1}$$

On the curve $[H_2O_2] = g(t)$, when $\Delta t \to 0$, the secant M_1M_2 tends to approach the tangent M_1T of the curve at point M_1 of abscissa t_1 (Fig. 2.9). In this case, the instantaneous rate of disappearance of hydrogen peroxide at instant t_1 is equal to the negative slope of the tangent M_1T.

The instantaneous rate of disappearance of a reactant R at time t is equal to the negative derivative of the function $[R] = f(t)$, at time t:

$$r(R)_t = \left(-\frac{d[R]}{dt}\right)_t$$

Graphically, it is equal to the negative slope (gradient) of the tangent of the curve $[R] = f(t)$, at the point of abscissa t.

Initial rate

The initial rate of disappearance of a reactant corresponds to the instantaneous rate determined after the reaction begins just after t = 0 (Fig. 2.9), or:

The initial rate of disappearance of a reactant R is equal to the negative of the derivative of the curve [R] = f(t), at t = 0:

$$r(R)_{t=0} = \left(- \frac{d[R]}{dt} \right)_{t=0}$$

Graphically, it is equal to the negative gradient (slope) of the tangent of the curve [R] = f(t) at the point of abscissa t = 0.

Variation of rate with time

Examining the shape of the kinetic curve of the formation of a product (Figure 2.8), shows that the rate of formation is high at the beginning and diminishes with time to become zero at the end of the reaction. This is also observed when comparing the initial rate and the rate at the time t, on the same above curve. For the rate of disappearance of the reactant, the shape of the curve (Figure 2.9) shows this rate is high at the beginning and diminishes with time to become zero at the end of the reaction. This is confirmed, in this case also, when comparing the initial rate and the rate at t_1 on the same curve.

Activity 2 Determination of the rate graphically

Objective

Determine graphically the initial, average, and instantaneous rate.

The rate of formation of a product

Initial rate

On the curve $[I_2] = f(t)$ (Fig. 2.10) draw a tangent to the curve at point t = 0. Choose two distant points on this tangent, M (3; 9) and N (6; 17.6). The initial rate of formation of I_2 is equal to the value of the (slope) gradient of the tangent MN.

$$r\,(I_2)_{t=0} = \frac{17.6 - 9}{6 - 3} = 2.87 \text{ mmol.L}^{-1}.\text{min}^{-1}$$

■ When the two points are apart, the error of the measurement of the line becomes less.

■ Compare the value of the initial rate with that of the instantaneous rate at time t_1. What do you conclude?

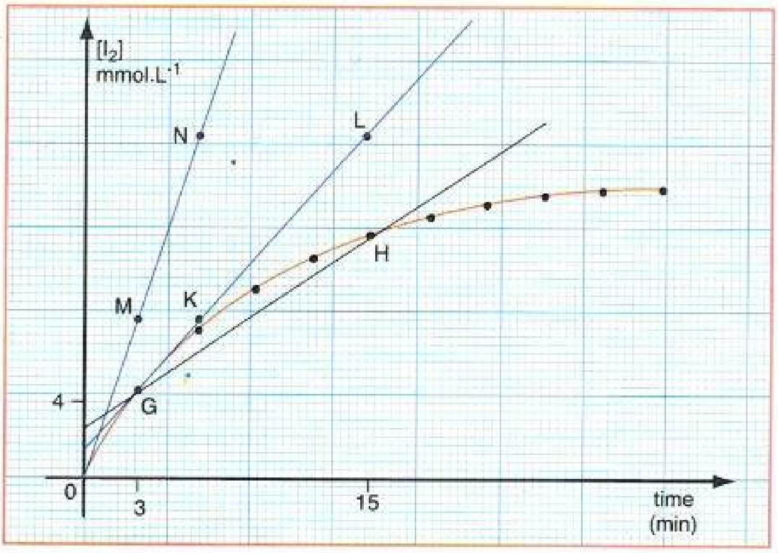


Figure 2.10

Kinetic curve $[I_2] = f(t)$.

■ Average rate

Choose two points on the curve $[I_2] = f(t)$, G (3; 4.8) and H (15; 12.2) (Fig. 2.10). Draw the secant GH. The average rate of formation of I_2 within the interval $\Delta t = (15 - 3)$ min is equal to the gradient of the secant GH:

$$\bar{r}(I_2) = \frac{12.2 - 4.8}{15 - 3} = 0.60 \text{ mmol.L}^{-1}\text{.min}^{-1}$$

■ Instantaneous rate

Draw the tangent of the curve $[I_2] = f(t)$ at the point G of abscissa $t_1 = 3$ (Fig. 2.10). Take two points on this tangent K (6; 8) and L (15;18). The instantaneous rate of formation of I_2 at time t_1 is equal to the value of director coefficient of the tangent:

$$r(I_2)_{t_1} = \frac{18 - 8}{15 - 6} = 1.11 \text{ mmol.L}^{-1}\text{.min}^{-1}$$

■ Rate of disappearance of a reactant

Consider the curve $[H_2O_2] = g(t)$ and follow the same steps as in the preceding section (Fig. 2.11).

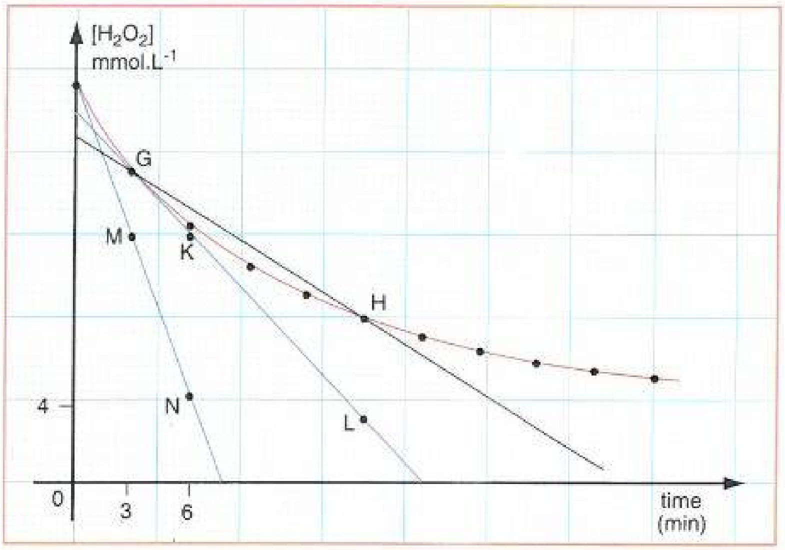


Figure 2.11

Kinetic curve $[H_2O_2] = g(t)$.

■ Compare the value of the initial rate with that of the instantaneous rate at t_1. What do you conclude?

Examples of results

- **Initial rate**

M(3 ; 12.4), N(6 ; 4)

$$r(H_2O_2)_{t=0} = -\frac{4-12.4}{6-3} = 2.80 \text{ mmol.L}^{-1}.\text{min}^{-1}$$

- **Average rate**

G(3 ; 16), H(15 ; 8.6)

$$\bar{r}(H_2O_2) = -\frac{8.6-16}{15-3} = 0.62 \text{ mmol.L}^{-1}.\text{min}^{-1}$$

- **Instantaneous rate**

K(6 ; 12.8), L(15 ; 2.8)

$$r(H_2O_2)_{t1} = -\frac{2.8-12.8}{15-6} = 1.11 \text{ mmol.L}^{-1}.\text{min}^{-1}$$

Solved exercise 2

Given

At the instant t = 0, we mix 5 mL of 0.1 mol.L^{-1} of potassium iodide solution with 1 mL of 0.5 mol.L^{-1} sulfuric acid solution and 5 mL of 0.2 mol.L^{-1} of hydrogen peroxide solution. The iodine formed in the solution is detected by its brown color and its concentration is measured at different intervals of time. The following table shows the data collected:

t(min)	1	2	3	4	5	6	7
$[I_2]$ (mmol.L^{-1})	0.27	0.50	0.71	0.80	0.92	0.99	1.04

a) Write the equation of the reaction.

b) Calculate the initial concentration of each reactant. Deduce the limiting reactant.

c) Plot the curve $[I_2] = f(t)$. Determine graphically the instantaneous rate of formation of I_2 at $t = 0$ and $t = 3$ min. Compare and conclude.

d) Give the stoichiometric relation between the rate of disappearance of H_2O_2 and I^-, and the rate of formation of I_2. Deduce the instantaneous rate of disappearance of I^- at $t = 0$ and $t = 3$ min.

e) Calculate $[I_2]_{t\to\infty}$ and $[I^-]_{t\to\infty}$

Solution

a $2\,I^- + H_2O_2 + 2\,H^+ \rightarrow I_2 + 2\,H_2O$

b We apply the relation $C_1V_1 = C_2V_2$.

$$[I^-]_0 = \frac{0.1 \times 5}{11} = 0.045\ \text{mol.L}^{-1}$$

$$[H_2O_2]_0 = \frac{0.2 \times 5}{11} = 0.091\ \text{mol.L}^{-1}$$

$$[H^+]_0 = \frac{2 \times 0.5 \times 1}{11} = 0.091\ \text{mol.L}^{-1}$$

The initial number of moles of reactants are:

$n_0(I^-) = 0.045 \times 11 \times 10^{-3} = 4.95 \times 10^{-4}$ mol

$n_0(H_2O_2) = 0.091 \times 11 \times 10^{-3} = 10.01 \times 10^{-4}$ mol

$n_0(H^+) = 0.091 \times 11 \times 10^{-3} = 10.01 \times 10^{-4}$ mol

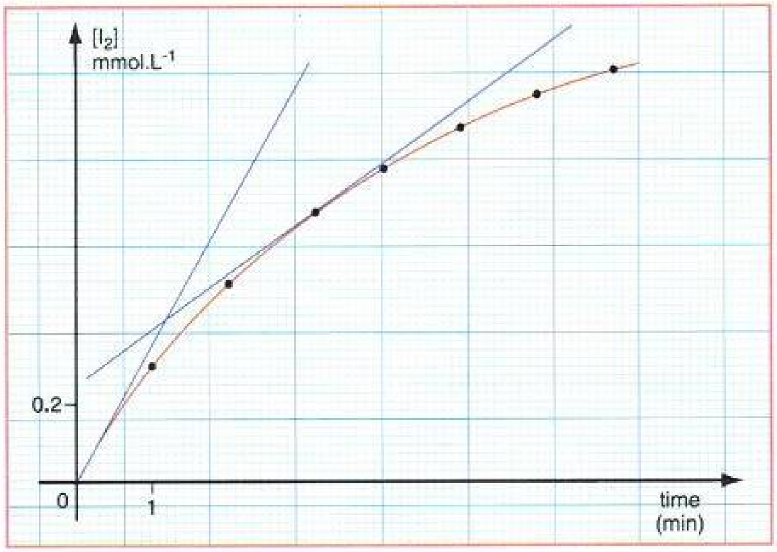
and, the stoichiometric relation among the reactants is:

$$\frac{n_0(I^-)}{2} = \frac{n_0(H_2O_2)}{1} = \frac{n_0(H^+)}{2}$$

We substitute and compare the above calculated values to find that I^- is the limiting reactant:

$$\frac{4.95 \times 10^{-4}}{2} < \frac{10.01 \times 10^{-4}}{2} < \frac{10.01 \times 10^{-4}}{1}$$

c



$$r(I_2)_{t=0} = \frac{(1.05 - 0) \times 10^{-3}}{3 - 0} = 3.5 \times 10^{-4}\ \text{mol.L}^{-1}.\text{min}^{-1}$$

$$r(I_2)_{t=3} = \frac{(1.11 - 0.39) \times 10^{-3}}{6 - 1} = 1.44 \times 10^{-4}\ \text{mol.L}^{-1}.\text{min}^{-1}$$

$r(I_2)_{t=0} > r(I_2)_{t=3}$. We conclude that the rate of formation of a product decreases as the reaction progresses.

d The stoichiometric relation between the rate of disappearance of I^- and H_2O_2 and the rate of appearance of I_2 is:

$$\frac{r(I^-)_t}{2} = \frac{r(H_2O_2)_t}{1} = \frac{r(I_2)_t}{1}$$

or :

$r(I^-)_{t=0} = 7 \times 10^{-4}\ mol.L^{-1}.min^{-1}$.

$r(I^-)_{t=3} = 2.88 \times 10^{-4}\ mol.L^{-1}.min^{-1}$.

e According to the balanced equation and since I^- is the limiting reactant, we can write:

$$[I_2]_{t \to \infty} = \frac{[I^-]_0}{2} = 0.0225\ mol.L^{-1}$$

$$[I^-]_{t \to \infty} = 0.$$

Chapter review

- The rate of a reaction always has a positive value.
- The rate of a reaction is equal to the change of the number of moles of product within a certain interval of time:

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

  or the negative value of the change of the number of moles of a reactant within a certain interval of time:

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

- For the general equation of the reaction:

  $$aA + bB \rightarrow cC + dD$$

  The stoichiometric relation between the rates of disappearance of reactants and the rates of formation of products is:

  $$\frac{r(A)}{a} = \frac{r(B)}{b} = \frac{r(C)}{c} = \frac{r(D)}{d}$$

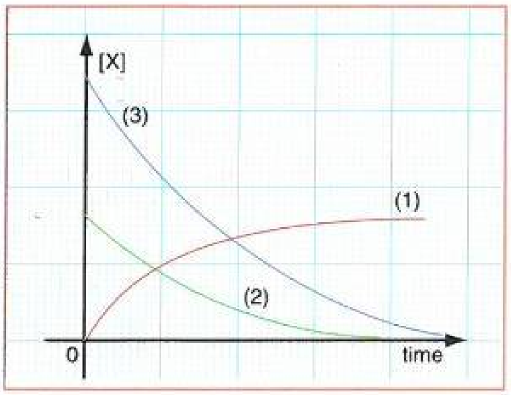
- The concentration of a reactant decreases with time as the reaction progresses.
- The concentration of a product increases with time as the reaction progresses.
- The average rate of formation of a product P within an interval of time $\Delta t = t_2 - t_1$ is equal to the gradient (slope) of the secant on the curve $[P] = f(t)$ at the points of abscissa t_1 and t_2.
- The average rate of disappearance of a reactant [R] within the interval of time $\Delta t = t_2 - t_1$ is equal to the negative slope of the secant on the curve $[R] = f(t)$ at the points of abscissa t_1 and t_2.
- The instantaneous rate of formation of a product P at time t is equal to the value of the derivative of the function $[P] = f(t)$ at time t.
  Graphically, it is equal to the gradient (slope) of the tangent of the curve $[P] = f(t)$ at the point of abscissa t.
- The instantaneous rate of disappearance of a reactant R at time t is equal to the value of the opposite derivative of the function $[R] = f(t)$ at the point of abscissa t.
  Graphically, it is equal to the negative slope of the tangent of the curve $[R] = f(t)$ at the point of abscissa t.
- The initial rate of formation of a product P is equal to the value of the derivative of the function $[P] = f(t)$ at time $t = 0$.
  Graphically, it is equal to the gradient (slope) of the tangent of the curve $[P] = f(t)$ at the point of abscissa $t = 0$.
- The initial rate of disappearance of a reactant R is equal to the opposite derivative of the function $[R] = f(t)$ at $t = 0$.
  Graphically, it is equal to the negative slope of the tangent of the curve $[R] = f(t)$ at the point of abscissa $t = 0$.
- The rate of a reaction decreases with time and becomes zero when the reaction is over.

Exercises

1 Consider a mixture of reactants with stoichiometric proportions according to the equation of the following reaction:

$$2\,A + B \rightarrow C$$

Identify, on the following graph the kinetic curves of each of the reactants and the product.



2 Consider the equation of the reaction:

$$2\,NO_{(g)} + O_{2(g)} \rightarrow 2\,NO_{2(g)}$$

a) During a certain interval of time Δt, the variation of oxygen O_2 moles is $\Delta n(O_2) = -5$ mol.
Calculate the variation of the number of moles of nitrogen monoxide $NO_{(g)}$ and that of nitrogen dioxide $NO_{2(g)}$. during the same interval of time.

b) The duration during which the variation of number of moles O_2 takes place in part (a) is 100 s. Calculate the average rate of disappearance of O_2 during this interval of time. Deduce the rate of disappearance of $NO_{(g)}$ during the same interval of time.

3 At some conditions, diphenyl $C_{12}H_{10}$ is obtained by the reaction of the following equation:

$$2\,C_6H_{12} \rightarrow C_{12}H_{10} + 7\,H_2$$

a) Complete the following table, for the progress of the reaction with time:

Time (s)	$[C_6H_{12}]$ (mol.L^{-1})	$[C_{12}H_{10}]$ (mol.L^{-1})	$[H_2]$ (mol.L^{-1})
0	0.200	0.00	0.00
1	0.159	0.021	.....
2	.....	0.034	.....
3	.....	0.044	.....

b) Calculate the average rate of formation of hydrogen in the interval of time (1s - 2s).

4 Given the reaction:

$$3\,N_2O_{(g)} + C_2H_{2(g)} \rightarrow 3\,N_{2(g)} + 2\,CO_{(g)} + H_2O_{(g)}$$

At an instant t, the rate of formation of H_2O is $r(H_2O)_t = 0.1$ mol.L^{-1}.s^{-1}.

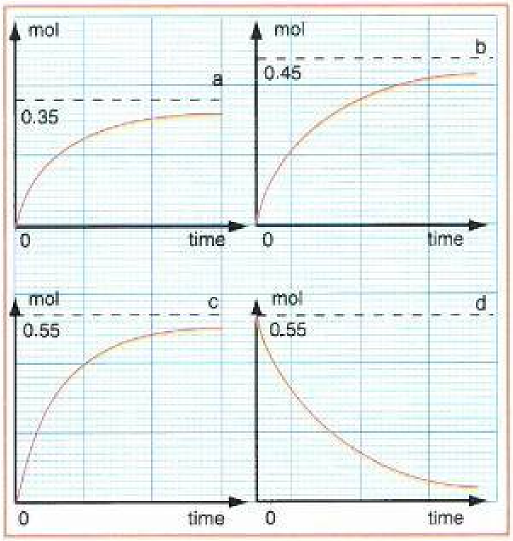
a) Calculate the rate of disappearance of each reactant and the rate of formation of each product at the same instant t.

b) What is the value of the rate of the reaction at this instant?

5 Given the reaction:

$$A + 2\,B \rightarrow C$$

The initial composition of the system being: 0.45 mol of A, 0.70 mol of B and 0.1 mol of C, the evolution of the number of moles of C with time is studied.
Which of the following curves correspond to the system?



6 The oxidation of I^- by peroxydisulfate $S_2O_8^{2-}$ is a slow reaction that takes place according to the following equation:

$$2\,I^- + S_2O_8^{2-} \rightarrow I_2 + 2\,SO_4^{2-}$$

The measurement of the concentrations of I_2 formed at different time intervals are given in the following table:

Time (s)	0	5	10	15	25	35	50	60	80
$[I_2]$ (10^{-2}.mol.L^{-1})	0	0.75	1.25	1.78	2.75	3.22	4.08	4.50	4.90

a) Plot on a graph paper the curve $[I_2] = f(t)$.

b) Determine, by using the curve, the instantaneous rate of formation of I_2 at the instants $t_1 = 10$ s and $t_2 = 32$ s. Compare and conclude.

c) Determine the average rate of formation of I_2 during the interval of time between the instants t_1 and t_2 given in part (b).

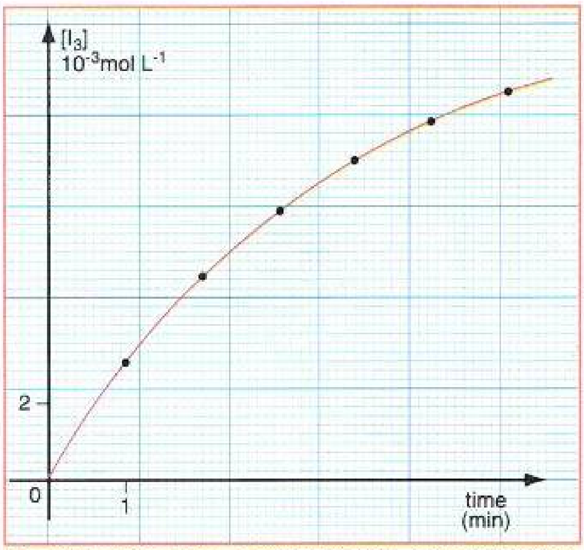
7 At the instant t = 0, a solution (A) is prepared by mixing the following solutions:

- 10 mL of 0.1 mol.L^{-1} potassium iodide solution.
- 2 mL of 1 mol.L^{-1} sulfuric acid solution.
- 10 mL of 0.5 mol.L^{-1} hydrogen peroxide solution.

a) Write the equation of the reaction that takes place. Given: $E^{\circ}_{(I_2/I^-)} = 0.62$ V ; $E^{\circ}_{(H_2O_2/H_2O)} = 1.77$ V.

b) Calculate at instant t = 0, the concentrations of the species I^-, H^+, H_2O_2 in the mixture prepared.

c) What is the maximum concentration of iodine that could be formed?



We follow the rate of change of I_2 concentration formed:

1) Calculate the instantaneous rate of formation of I_2 at the instants t = 0 and $t_2 = 4$ min.

2) Show that at each instant t, $[I]_t = [I]_0 \, . \, 2[I_2]_t$. Plot the curve $[I^-] = g(t)$. Calculate the instantaneous rate of disappearance of I^- at t = 0 and t = 4 min.

3) Compare the rates of formation of I_2 and disappearance of I^- at the instants t = 0 and t = 4 min.

4) Can you predict $r(I^-)_t$ at an instant t at which $r(I_2)_t$ is given?

8 We prepare an aqueous acidified solution of the following species:

$[Cr_2O_7^{2-}] = 0.01$ mol.L^{-1}, $[H_2C_2O_4] = 0.2$ mol.L^{-1}
The equation of the reaction is:

$$Cr_2O_7^{2-} + 3\,H_2C_2O_4 + 8\,H^+ \rightarrow 2\,Cr^{3+} + 6\,CO_2 + 7H_2O$$

a) Which of the above reactants is the limiting reactant?
b) What is the limit of $[Cr^{3+}]$ when t tends to infinity?
c) The values ofconcentrations of Cr^{3+} at different instants of time are given in the following table:

Time (min)	5	10	15	20	25	35	45
$[Cr^{3+}]$ (mmol.L^{-1})	3.25	7.02	9.70	11.80	13.6	16.00	17.00

1) Plot the curve $[Cr^{3+}] = f(t)$.
2) Plot on the same graph paper, the curve $[Cr_2O_7^{2-}] = g(t)$.
3) Compare the shapes of the two curves.

9 Hydrochloric acid reacts with zinc according to the following reaction:

$$2\,H^+ + Zn \rightarrow H_2 + Zn^{2+}$$

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

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

a) Find the relation between the concentration $[Zn^{2+}]_t$ and the volume $V(H_2)_t$. Complete the above table and plot the curve $[Zn^{2+}] = f(t)$.
$V_m = 22.4$ L.mol^{-1}.
b) Determine the average rate of formation of Zn^{2+} within the interval of time $t_1 = 0$ s and $t_2 = 500$ s.
c) Determine the initial rate of formation of $[Zn^{2+}]$.
d) Determine the concentration of $[Zn^{2+}]$ as $t \rightarrow \infty$ and calculate the mass of zinc remaining at the end of the reaction.
M(Zn) = 65.4 g.mol^{-1}.

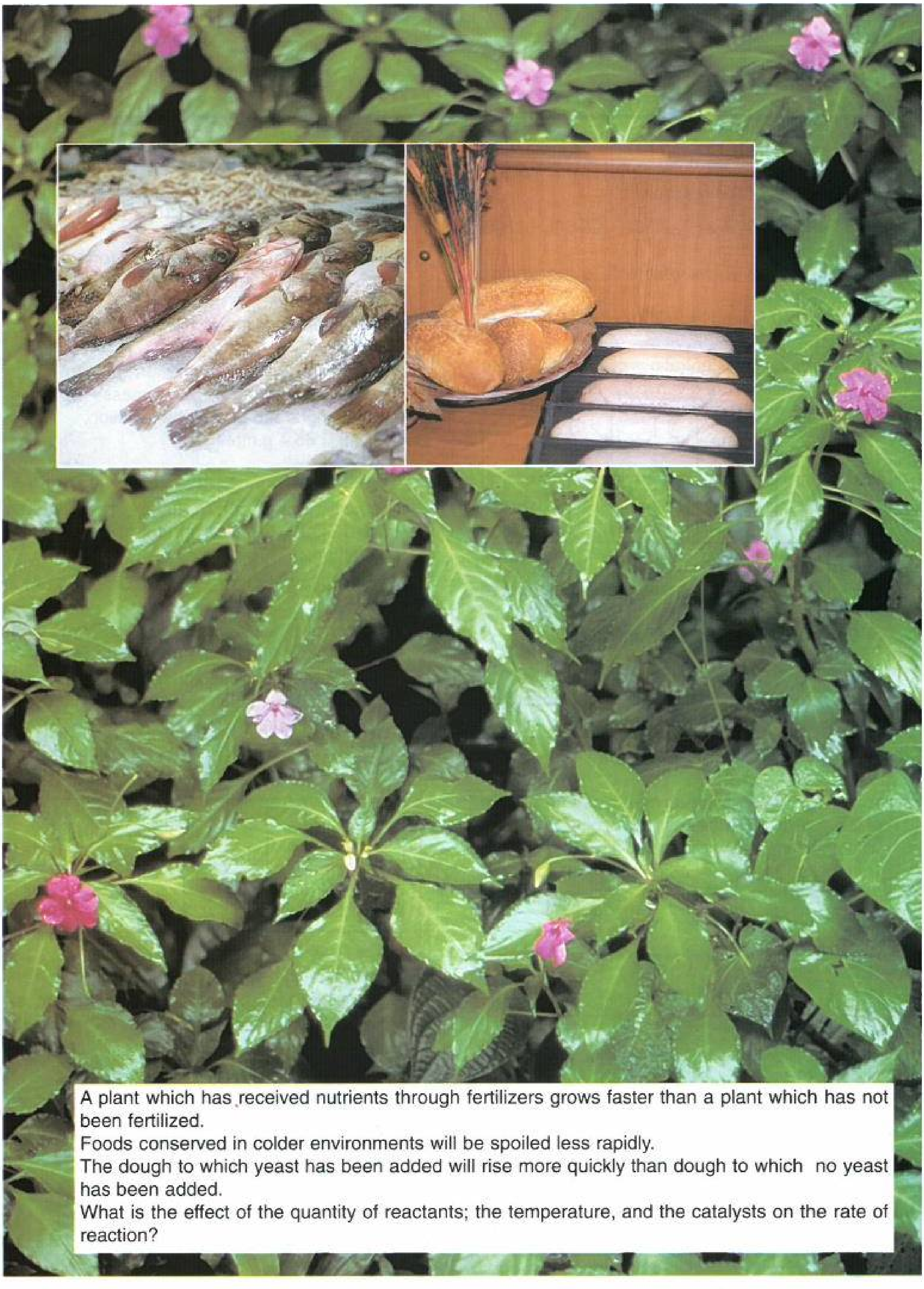
10 It is required to study the kinetic of the saponification of methyl ethanoate CH_3COOCH_3 according to the following equation :

$$CH_3COOCH_3 + HO^- \rightarrow CH_3COO^- + CH_3OH$$

We start with an aqueous solution containing 1×10^{-2} mol.L^{-1} methyl ethanoate and 1×10^{-2} mol.L^{-1} sodium hydroxide and we record the variation of the concentration hydroxyl ions OH^- as a function of time.
The results are given in the following table:

Time (min)	3	5	7	10	15	21	25
$[HO^-]$ (mmol.L^{-1})	7.4	6.3	5.5	4.6	3.6	2.8	2.5

a) Complete the table by adding a row, which shows the variation of the concentration of the ethanoate ion CH_3COO^- formed with time.
b) Plot the curve $[CH_3COO^-] = f(t)$.
c) Deduce the rate of formation of CH_3COO^- at t= 6 min, 12 min and 18 min.
Compare and conclude.



A plant which has received nutrients through fertilizers grows faster than a plant which has not been fertilized.

Foods conserved in colder environments will be spoiled less rapidly.

The dough to which yeast has been added will rise more quickly than dough to which no yeast has been added.

What is the effect of the quantity of reactants; the temperature, and the catalysts on the rate of reaction?

KINETIC FACTORS

3

Objectives

- Identify the kinetic factors.
- Write the expression of the rate law of reaction.
- Acquire the notion of the order of reaction.
- Determine the order of a reaction.
- Identify the half-life of a reaction.
- Know the phenomenon of catalysis.

Prerequisites

- Notion of a catalyst
- Notion of adsorption phenomenon.

Chapter content

3.1 Kinetic factors. Rate constant.
3.2 Order of reaction: zero order, first order and second order.
3.3 Half-life of a reaction.
3.4 Catalysis
- Chapter review
- Documentary activity
- Exercises
- Evaluation

3.1 Kinetic factors. Rate constant

In addition to the nature of reactants and products, other factors affect the kinetic of the reaction system.

The concentration of reactants, the temperature at which the reaction is occurring, and the presence of substances other than the reactants (catalysts, inhibitors...), are among the factors that affect the rate of a reaction.

Influence of concentration

The study of the kinetic curves, disappearance of a reactant (H_2O_2), and the formation of a product, in the previous chapter, all show that the rate of reaction decreases with time during the course of the reaction.

With time, the reactants are consumed and their quantities are decreased. This observation shows that the concentrations of the reactants have an effect on the rate of reaction.

Activity 1

Oxidation of I^- ions by hydrogen peroxide H_2O_2, at constant temperature, starting with different I^- concentrations.

Objective

Study, at constant temperature, the variation of the rate of reaction versus concentration of reactants.

Equipment and reagents

Three beakers of 250 mL each. Three graduated cylinders of 50 mL each. Chronometer.

0.045 $mol.L^{-1}$ hydrogen peroxide solution. 0.250 $mol.L^{-1}$ potassium iodide solution. 1 $mol.L^{-1}$ sulfuric acid solution.

Procedure

Prepare the mixtures A, B and C, using the volumes given in table 3.1:

	KI solution	H_2SO_4 solution	Distilled water	H_2O_2 solution
Beaker A	10 mL	10 mL	70 mL	10 mL
Beaker B	20 mL	10 mL	60 mL	10 mL
Beaker C	30 mL	10 mL	50 mL	10 mL

Table 3.1

Proceed, adding the solution, in the following order:
- Potassium iodide solution
- Sulfuric acid solution
- Distilled water

Homogenize. Add quickly the hydrogen peroxide solution and start the chronometer.

- Calculate the new concentrations: $[H_2O_2]_0$, $[I^-]_0$, $[H^+]_0$.
- Which is the limiting reactant?

Observation and interpretation

Iodine I_2, is formed in the three beakers. At any given instant, the fact that the red-brown color, characteristic of iodine, is darker in beaker C than in beakers B and A, proves that the quantity of iodine formed in beaker C is greater than in beakers B and A (Fig. 3.1).

The concentration of iodine formed, according to the above observation, can be expressed by the relation:

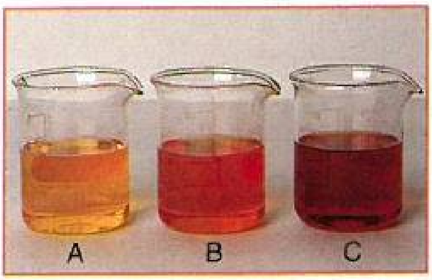


Figure 3.1

The number of moles of iodine formed in beaker C is greater than that formed in beaker B or A.

$$[I_2]_{t(C)} > [I_2]_{t(B)} > [I_2]_{t(A)}$$

The concentrations of hydrogen peroxide and H^+ ions are kept constant. Only the concentration of $[I^-]_0$ is different in the available reaction mixtures.

$$[I^-]_{0(C)} > [I^-]_{0(B)} > [I^-]_{0(A)}$$

Comparing these relations with each other, allow us to deduce that the faster the rate of formation is, and when the initial concentration of a reactant, iodide ion, is greater then the quantity of iodine formed is greater.

The same result is observed when the concentrations of the iodide I^- and H^+ ions are kept constant and the concentration of hydrogen peroxide is changed, this allows us to state:

The rate of reaction (disappearance of reactants and formation of products) increases when the initial concentrations of the reactants increase and vice versa.

Influence of temperature

Activity 2

Reaction of water with magnesium in the presence of phenolphthalein, at different temperatures.

Objective

Study the variation of the rate of reaction with temperature.

Equipment and reagents

Three beakers 250 mL each. Three test tubes. Hot plate. Magnesium ribbon. Phenolphthalein solution. Ice.

Procedure

Fill each test tube halfway with distilled water. Add few drops of phenolphthalein into each test tube.

- Dip the first test tube in a beaker containing a boiling-water bath.
- Dip the second test tube in a beaker containing tap-water, at room temperature
- Dip the third test tube into a beaker containing ice-water (Fig. 3.2).

Introduce into each test tube, at time t = 0, a piece of magnesium ribbon of constant length equal to 1 cm.

Observation

A noticeable release of hydrogen gas is observed in the first test tube. The solution in the tube turns dark pink in color.

In the second tube, the gas released is slower and the solution turns pink slowly.

In the third tube, almost no change is observed (Fig. 3.2).

Interpretation

Magnesium is oxidized by water according to the equation:

$$Mg + 2\,H_2O \rightarrow Mg^{2+} + 2\,HO^- + H_2$$

The rate of hydrogen formation is estimated by the intense release of gas and the rate of formation of HO$^-$ by the intensity of the pink coloration produced in the solution.

This allows us to conclude that the rate of formation of these products is higher at the temperature of boiling water than at room temperature and than the rate at the ice-water bath. For the rate of disappearance of the reactants Mg and H_2O, this allows us to state:

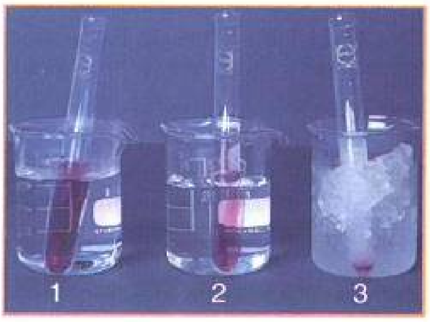


Figure 3.2
The reaction in tube 1 is more rapid than those in tube 2 and in tube 3.

The rate of reaction (disappearance of reactants and formation of products) increases as the temperature of the reaction medium increases and vice versa.

The effect of the concentration of reactants and the temperature of the reaction medium on the rate of reaction is illustrated in the laboratory as well as in industry and in everyday life.

In the laboratory and in industry, we increase the quantities of the reactants to obtain a faster rate of reaction. On the other hand, to get a slower rate of reaction, we dilute the reaction medium.

A process, which consists of suddenly cooling the reaction medium, is a practical way to block a reaction. It is possible to cool and dilute the reaction medium at the same time. In this case, the effect of lowering the temperature is added to the effect of dilution.

In everyday life, foods are cooked quicker in pressure cooking (Fig.3.3) and are conserved for a longer time in the freezer (Fig. 3.4). Thus, in general, we deduce that:

The rate of reaction (disappearance of reactants and formation of products) depends on the concentration of the reactants and the temperature of the reaction medium.

Figure 3.3
In pressure cooking, foods are cooked quickly.

Rate constant

Consider the oxidation reaction of iodide ions, I$^-$, by hydrogen peroxide in acidic medium, and the plot of the kinetic curves, $[H_2O_2] = f(t)$, with different initial concentrations of the reactants H_2O_2 or I$^-$, and with constant H$^+$ ion concentration at a constant temperature, we can determine the initial rate of reaction for different initial concentrations of reactants. An example of such results is given in table 3.2.

Figure 3.4

Frozen food products can be conserved for few months, even for a year.

- We can illustrate the kinetic curves for any reactant or any product in the reaction.

Experiment	$[H_2O_2]_0$ ($mol.L^{-1}$)	$[I^-]_0$ ($mol.L^{-1}$)	$r_{t=0}$ ($mol.L^{-1}.s^{-1}$)
1	0.1	0.1	0.0076
2	0.1	0.2	0.0152
3	0.2	0.1	0.0152

Table 3.2

As we double the value of $[I^-]_0$, keeping $[H_2O_2]_0$ constant, we notice that the value of the initial rate (instantaneous rate at time t = 0) is doubled.

Also, as we double the value of $[H_2O_2]_0$, keeping the $[I^-]_0$ constant, the value of the initial rate is doubled.

This result enables us to establish a relation between the rate of reaction and the concentrations of the reactants H_2O_2 and I^-.

$$r = k\,[H_2O_2]\,[I^-]$$

The rate of the above given reaction is found to be proportional to the product of the concentration of H_2O_2 raised to the power 1 by the concentration of I^- raised to the power 1. The constant k is called rate constant and it depends only on temperature. The relation obtained is called rate law.

Solved exercise 1

Given

Calculate the rate constant for the reaction of oxidation of I^- by H_2O_2 in acidic medium, using the results given in table 3.2

Solution

- In principle, three values of k are calculated and the average value is taken.

To calculate the value of k, we need only to substitute rate and concentration data into the rate law for any of the three experiments, since they give the same value for k:

$$k_1 = \frac{0.0076}{0.1 \times 0.1} = 0.76\ mol^{-1}.L.s^{-1}$$

3.2 Reaction order: zero order, first order and second order.

The rate law for most chemical reactions is given by the form given below:

$$r = k\,[R_1]^{\alpha}\,[R_2]^{\beta}......$$

The exponents α and β, ... are called partial orders of the reaction with respect to reactants R_1 and R_2, ... And their sum is called the overall order of the reaction.

- Rates involving fractional or negative orders are less frequent.

Thus the preceding reaction, oxidation of I^- ions by H_2O_2 in acidic medium is first order with respect to H_2O_2 and first order with respect to I^-. The overall order of the reaction is 1 + 1 = 2, or overall second order reaction.

In most cases, the partial orders involved in the rate law are limited to the values 0, 1, and 2 and the overall order has values of 0, 1, 2, and 3.

When a reaction is zero order, the rate is constant and is independent of the concentrations of the reactants.

$$r = k$$

In what follows, examples of rate laws are given:

First order reaction

$$2\ N_2O_{5(g)} \rightarrow 4\ NO_{2(g)} + O_{2(g)}$$

$$r = k\ [N_2O_5]$$

Second order reaction

The reaction given according to the equation:

$$CH_3Br + HO^- \rightarrow CH_3OH + Br^-$$

$$r = k\ [CH_3Br]\ [HO^-]$$

is first order in reactant CH_3Br and first order in reactant HO^-.

The reaction given according to the equation:

$$2\ NO_{2(g)} \rightarrow 2\ NO_{(g)} + O_{2(g)}$$

$$r = k\ [NO_2]^2$$

is second order in reactant $NO_{2(g)}$.

The partial orders α, β, ... are determined experimentally and in general are different from the stoichiometric coefficients of the reaction.

■ Simple reaction

When a chemical reaction takes place in a single step, the reaction is called simple reaction and is often called elementary reaction. In this case, the partial orders of the reactants are equal to the stoichiometric coefficients of the reactants involved. For example, the following reaction:

$$NO_{(g)} + O_{3(g)} \rightarrow NO_{2(g)} + O_{2(g)}$$

is a simple (elementary) reaction, since it takes place in a single step. The rate law for this reaction is given as:

$$r = k\ [NO]\ [O_3]$$

where the partial orders are equal to the stoichiometric coefficients.

Rate determining step

Many chemical reactions take place in a sequence of elementary steps. In this case, the rate of reaction is determined by the slowest step in the sequence of steps and is called the rate-determining step.
The rate law obtained experimentally is the rate of the slowest step.
For the equation:

$$NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$$

The rate law is given by:

$$r = k\,[NO_2]^2$$

We consider the reaction taking place in two steps:

- We have chosen the case where the slow step is the first one because it is the simplest case.

Step 1

$$NO_{2(g)} + NO_{2(g)} \rightarrow NO_{3(g)} + NO_{(g)} \qquad \text{(slow)}$$

The expression of rate law:

$$r = k_1[NO_2]^2$$

Step 2

$$NO_{3(g)} + CO_{(g)} \rightarrow NO_{2(g)} + CO_{2(g)} \qquad \text{(fast)}$$

The expression of rate law:

$$r = k_2\,[NO_3]\,[CO]$$

The overall reaction is the sum of the two elementary steps:

$$\begin{array}{lcl} NO_{2(g)} + NO_{2(g)} & \rightarrow & NO_{3(g)} + NO_{(g)} \\ NO_{3(g)} + CO_{(g)} & \rightarrow & NO_{2(g)} + CO_{2(g)} \\ \hline NO_{2(g)} + CO_{(g)} & \rightarrow & NO_{(g)} + CO_{2(g)} \end{array}$$

We notice that the rate law for this reaction is the same as the rate law of the slowest step.

Solved exercise 2

Given

The reaction between nitric oxide $NO_{(g)}$ and bromine Br_2, at 273 °C takes place according to the following equation:

$$2\,NO_{(g)} + Br_{2(g)} \rightarrow 2\,NOBr_{(g)}$$

The determination of the initial rate of formation of $NOBr_{(g)}$, starting from different initial concentrations of the reactants led to the following results:

Experiment	$[NO]_0$ ($mol.L^{-1}$)	$[Br_2]_0$ ($mol.L^{-1}$)	Initial rate ($mol.L^{-1}.s^{-1}$)
1	0.10	0.20	24
2	0.25	0.20	150
3	0.10	0.50	60
4	0.35	0.50	735

a) Determine the partial order of the reaction relative to $NO_{(g)}$, $Br_{2(g)}$ and the overall order of the reaction.
b) Write the rate law for the formation of $NOBr_{(g)}$.
c) Calculate the rate constant k.
d) Calculate the rate of formation of $NOBr_{(g)}$ when $[NO] = 0.075\ mol.L^{-1}$ and $[Br_2] = 0.185\ mol.L^{-1}$.

Solution

a Assume that the rate law is of the form:

$$r(NOBr) = 2k\,[NO]^{\alpha}\,[Br_2]^{\beta}$$

Using the data from experiments 1 and 2, we can write:

$$\frac{150}{24} = \frac{(0.25)^{\alpha}}{(0.10)^{\alpha}}$$

$$6.25 = (2.5)^{\alpha} \Rightarrow \alpha = 2$$

Using the data from experiments 3 and 4, we can write:

$$\frac{735}{60} = \frac{(0.35)^{\alpha}}{(0.1)^{\alpha}}$$

$$12.25 = (3.5)^{\alpha} \Rightarrow \alpha = 2$$

Using the data from experiments of 1 and 3, we can write:

$$\frac{60}{24} = \frac{(0.50)^{\beta}}{(0.20)^{\beta}}$$

$$2.5 = (2.5)^{\beta} \Rightarrow \beta = 1$$

The overall order of the reaction is 2 +1 = 3

b The rate law is:

$$r(NOBr) = 2k\,[NO]^2\,[Br_2]$$

c We can calculate the value of the rate constant using the data from one of the experiments:

$$k = \frac{24}{(0.10)^2 \times (0.20)} = 1.2 \times 10^4\ mol^{-2}.L^2.s^{-1}$$

d

$$r(NOBr) = 2x1.2 \times 10^4 \times (0.075)^2 \times (0.185)$$
$$= 24.98\ mol.L^{-1}.s^{-1}.$$

Unit of the rate constant

The unit of the rate constant depends on the overall reaction order. If the overall reaction order is n, then we have

$$k = \frac{r\ (mol.L^{-1}\ time^{-1})}{[\ ]^n\ (mol^n.L^{-n})}$$

the general form for the unit of k is

$$mol^{(1-n)}.L^{(n-1)}.(time)^{-1}.$$

Thus, for a zero order reaction, k is expressed in $mol.L^{-1}.time^{-1}$
For a first order reaction, k is expressed in $(time)^{-1}$.
For a second order reaction, k is expressed in $mol^{-1}.L.\ time^{-1}$, and consequently, the dimensions of the unit for k depend on the overall reaction order.

3.3 The half-life of a reaction

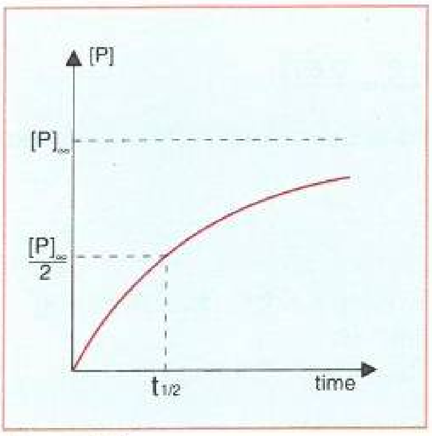


Figure 3.5
Kinetic curve for the formation of product P.

Take for example the kinetic curve for the formation of product P, [P] = f(t) (Fig. 3.5). This graph allows us to know the concentration of product P at any instant of the reaction. The kinetic curve for the disappearance of reactant R, [R] = g(t) (Fig. 3.6), allows us in turn to know the concentration of a reactant at any instant of the reaction.
In case R is the limiting reactant, the time at which its concentration becomes equal to one- half of its initial value,

$$[R]_{t_{1/2}} = \frac{[R]_0}{2}$$

is called half-life of reaction, $t_{1/2}$ (Fig 3.6).

The half-life, $t_{1/2}$ of a reaction is the time required for the concentration of the reactant to decrease to one-half of its initial value.

$$[R]_{t_{1/2}} = \frac{[R]_0}{2}.$$

Since the reactants are not taken according to stoichiometric coefficients, the half-life of a reaction is defined relative to the limiting reactant.

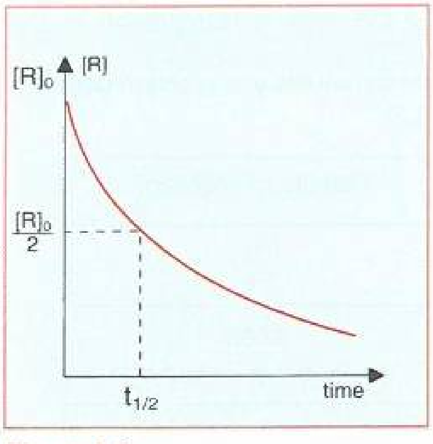


Figure 3.6
Kinetic curve for the disappearance of reactant R.

The half-life of a reaction can also be defined with respect to products. For the product P, for example, if $[P]_\infty$ is the limiting value of its concentration after a long time interval, the half-life $t_{1/2}$ is the time at which (Fig. 3.6)

$$[P]_{t_{1/2}} = \frac{[P]_\infty}{2}$$

Half-life and order of reaction

- **Zero order reaction**

In this case, the integral form of the rate law is:

$$-\frac{d[A]}{dt} = k$$

integration, gives the relation:

$$-[A] = kt + Constant$$

at time t = 0 we have: constant = $-[A]_0$
Hence, $[A]_0 - [A] = kt$

The half-life of a reaction is equal to: $t_{1/2} = \frac{[A]_0}{2k}$

It is proportional to initial concentration of the involved reactant.

- **First order reaction**

In this case, the integral form of the rate law is:

$$-\frac{d[A]}{dt} = k[A]$$

Integration gives the relation:

$$-\text{Ln}\,[A] = kt + \text{Constant}$$

At time t = 0, we have: constant = $-\text{Ln}[A]_0$

Hence, $\frac{\text{Ln}\,[A]_0}{[A]} = kt$

The half-life is equal to:

$$t_{1/2} = \frac{\text{Ln}\,2}{k} = \frac{0.693}{k}$$

It is equal to a constant which is characteristic of the involved reaction (depends on k).

- Ln is the symbol of the mathematical function called natural logarithm. For Ln, remember the following relations:

$\text{Ln}\,(ab) = \text{Ln}\,a + \text{Ln}\,b$

$\text{Ln}\,\frac{a}{b} = \text{Ln}\,a - \text{Ln}\,b$

$\text{Ln}\,a^n = n\,\text{Ln}\,a$

$\text{Ln}\,a^{1/n} = \frac{1}{n}\,\text{Ln}\,a$

These relations are also applicable for the logarithm of base 10 noted log.

- **Second order reaction**

We will consider a reaction involving a single reactant having an integral form of rate law given as:

$$-\frac{d[A]}{dt} = k[A]^2$$

The integration of this expression gives

$$-\frac{1}{[A]} = kt + \text{Constant}$$

At time t = 0, we have constant = $-\frac{1}{[A]_0}$

Hence, $\frac{1}{[A]} - \frac{1}{[A]_0} = kt$ is the integrated second order rate law.

The half-life is equal to: $t_{1/2} = \frac{1}{k[A]_0}$

It is inversely proportional to the initial concentration of the involved reactant.

The previous study shows that the half-life of a reaction depends on the reaction order (Table 3.3).

Reaction order	Half-life of reaction
0	$\frac{[A]_0}{2k}$
1	$\frac{0.693}{k}$
2	$\frac{1}{k\,[A]_0}$

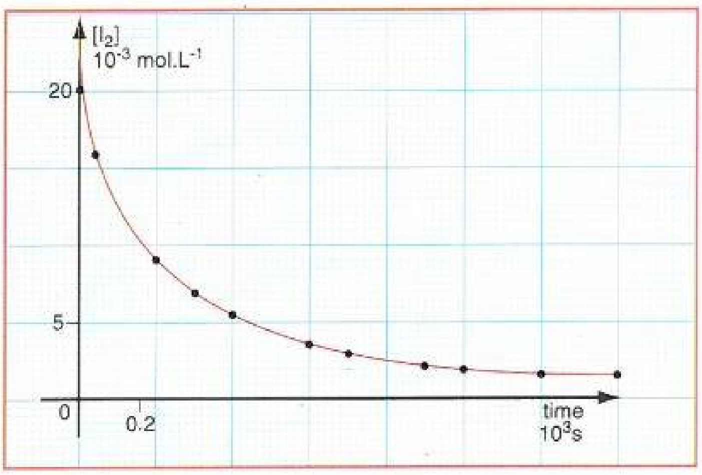
Table 3.3

The half-life of a reaction allows us to determine the concentrations of the reactants and the products from kinetic curves.

Solved exercise 3

Given

We dip a strip of zinc into antiseptic containing iodine I_2, at temperature of 20 °C. Zinc ions Zn^{2+} and I^- ions are formed. The change in the concentration of iodine as a function of time is given in the graph below:



a) Write the equation of the reaction.
b) Determine the half-life of the reaction (iodine is the limiting reactant).
c) Calculate for $t_{1/2}$, the concentrations of the ions present in solution.

Solution

a Equation of the reaction:

$$Zn + I_2 \rightarrow Zn^{2+} + 2\,I^-$$

b Based on the graph, the initial concentration of iodine is 20×10^{-3} mol.L^{-1}. Being the limiting reactant, its concentration is at half-life 10×10^{-3} mol.L^{-1}. From the graph, the time corresponding to this concentration is:

$$t_{1/2} = 200 \text{ s}.$$

c The stoichiometric ratio for the reaction:

$$\frac{n(Zn)}{1} = \frac{n(I_2)}{1} = \frac{n(Zn^{2+})}{1} = \frac{n(I^-)}{2}$$

We can write: $[I_2]_{t_{\frac{1}{2}}} = [Zn^{2+}]_{t_{\frac{1}{2}}} = \dfrac{[I^-]_{t_{\frac{1}{2}}}}{2}$

Or $[Zn^{2+}]_{t1/2} = 10 \times 10^{-3}$ mol.L^{-1}

and $[I^-]_{t1/2} = 20 \times 10^{-3}$ mol.L^{-1}.

- Since, in general, the rate of reaction increases as the temperature is increased, it follows that in this case, the half-life decreases.

Solved exercise 4

Given

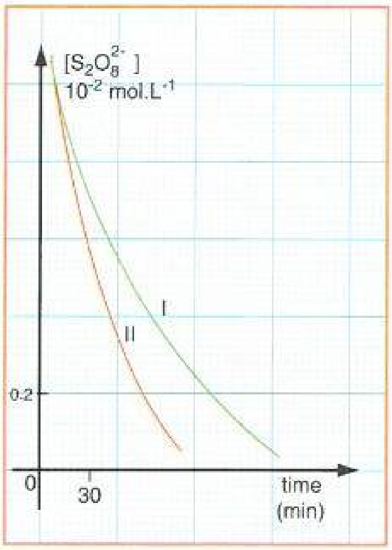
We study experimentally the kinetics for the oxidation of iodide ion I^- by peroxydisulfate ion ($S_2O_8^{2-}$) according to the equation:

$$2\ I^- + S_2O_8^{2-} \rightarrow I_2 + 2\ SO_4^{2-}$$

And the following two curves (I) and (II) are obtained according to the function $[S_2O_8^{2-}] = f(t)$ respectively at temperatures $T_1 = 20\ °C$ and $T_2 = 30\ °C$.

The reactants are taken the stoichiometric ratio, determine graphically the half-life of reaction. Compare the results obtained.

Solution



The two curves (I) and (II) of the function $[S_2O_8^{2-}] = f(t)$.

The reactants satisfy the stoichiometric ratio. We may determine the half-life of a reaction, $t_{1/2}$ from the kinetic curve of the reactant $S_2O_8^{2-}$. This is the time required for the concentration of $S_2O_8^{2-}$ to decrease to half of its initial concentration:

$$[S_2O_8^{2-}]_{t_{1/2}} = \frac{[S_2O_8^{2-}]_0}{2} = 0.5 \times 10^{-2}\ \text{mol.L}^{-1}$$

For $T_1 = 20\ °C$ $\quad t_{1/2} = 60$ min

For $T_2 = 30\ °C$ $\quad t_{1/2} = 32$ min

We notice that $t_{1/2}$ (30 °C) < $t_{1/2}$ (20 °C)

In fact, as temperature increases, the half-life decreases.

3.4 Catalysis

The decomposition of hydrogen peroxide H_2O_2 according to the reaction:

$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2$$

is very slow under ordinary conditions. In the presence of substances such as sodium bromide NaBr, iron (III) chloride $FeCl_3$ or a piece of cow liver, it becomes very rapid (Fig. 3.7).

These substances increase the rate of reaction without being changed at the end of the reaction. These are catalysts of the reaction.

A catalyst is a substance, which accelerates a chemical reaction and remains unaltered, from a chemical point of view, at the end of the reaction.

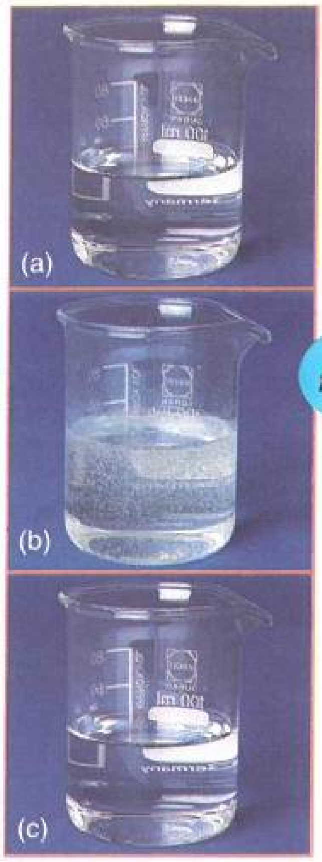


Figure 3.7
Decomposition of hydrogen peroxide in the presence of sodium bromide:
a) Without a catalyst.
b) With a catalyst
c) At the end of the reaction.

Activity 3 Oxidation of iodide ion I^- by peroxydisulfate ion $S_2O_8^{2-}$ in the presence of Fe^{2+} ions.

Objective

Perform a homogeneous catalysis

Equipment and reagents

Two beakers 100 mL each. 10 mL graduated cylinder. Dropper. Chronometer.

0.1 mol.L^{-1} ammonium peroxydisulfate $(NH_4)_2S_2O_8$ solution. 0.1 mol.L^{-1} potassium iodide KI solution. 1 mol.L^{-1} iron (II) sulfate solution $FeSO_4$.

Procedure and observation

Label the two beakers A and B. Into each beaker put 10 mL of ammonium peroxydisulfate solution. In beaker B, add a few mL of iron (II) sulfate solution. Into each beaker, quickly add 10 mL of potassium iodide solution. Homogenize the solutions and immediately set on the chronometer.

Iodine is formed in the two beakers.

After a few minutes, the red-brown characteristic color of iodine in solution is darker in beaker B than in beaker A, proving that the quantity of iodine formed in the first beaker is greater than in the second (Fig. 3.8).

■ Homogeneous catalysis

The reaction in activity 3, between the iodide ions I^- and the peroxydisulfate ions $S_2O_8^{2-}$, as in the equation below:

$$2\,I^- + S_2O_8^{2-} \rightarrow I_2 + 2\,SO_4^{2-}$$

During the same time interval t, more iodine is formed in beaker B than in beaker A. The reaction is faster in beaker B than in beaker A. Thus the reaction, oxidation of iodide ions by peroxydisulfate ions are catalyzed by iron Fe^{2+} ions.

The Fe^{2+} ions, and the reactants I^- ions and $S_2O_8^{2-}$ ions in solution form one single phase. The catalyst in this case is called homogeneous.

Therefore, in a homogeneous catalysis, the reactants and the catalyst form a single phase.

■ A catalyst accelerates a reaction. Substances that slow down a reaction or cease a reaction are called inhibitors.

- What is the difference in the reaction medium in the two beakers?
- In which beaker is the reaction faster?
- How many phases are in beaker B?

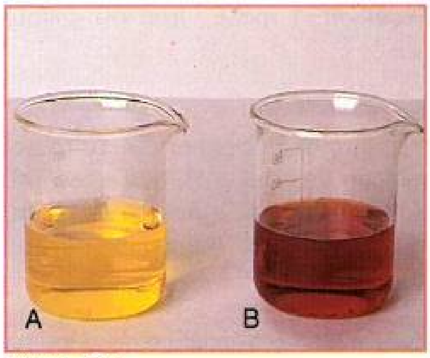


Figure 3.8
In beaker B, the oxidation reaction of iodide ion by peroxydisulfate ion is catalyzed by iron Fe^{2+} ions.

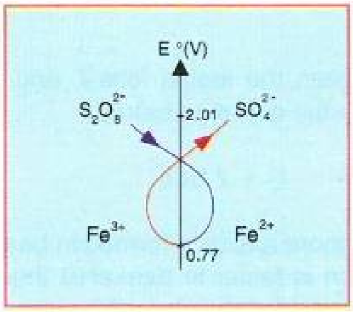


Figure 3.9
The gamma rule predicts the reaction between the $S_2O_8^{2-}$ ions and the Fe^{2+} ions.

- The reaction between the I^- ions and the $S_2O_8^{2-}$ ions is also catalysed by the Fe^{3+} ions.

In a homogeneous catalysis, the catalyst participates in the reaction, without appearing in the equation of the reaction.
In fact, the $S_2O_8^{2-}$ ions and the Fe^{2+} ions react together (Fig. 3.9) according to the following equation:

$$S_2O_8^{2-} + 2\,Fe^{2+} \rightarrow 2\,SO_4^{2-} + 2\,Fe^{3+}$$

The Fe^{3+} ion is an intermediate product of the reaction, which reacts with I^- ion (Fig. 3.10) according to the equation:

$$2\,Fe^{3+} + 2\,I^- \rightarrow 2\,Fe^{2+} + I_2$$

which shows that the catalyst Fe^{2+} is regenerated. The final products present in the reaction medium, due to the oxidation of iodide ions by the peroxydisulfate ions, are the iodine I_2 and the sulfate ions SO_4^{2-}.
The catalyst allows replacing the direct reaction, relatively slowly, by a series of two faster reactions.

Activity 4 Synthesis of water in the presence of platinum moss

Objective

Conduct a heterogeneous catalysis

Equipment and reagents

Pyrex test tubes. Platinum moss. Wooden tongs. A Bunsen burner. A wet rag. An electrolytic cell (source for hydrogen and oxygen gas).

Procedure

Hold the platinum moss for a few seconds in the flame of a Bunsen burner to activate it.
Hold, using the wet rag, the Pyrex tube containing a mixture of hydrogen gas and oxygen gas.
Put the platinum moss into the tube slowly. It will become incandescent-red. Droplets of water will condense on the walls of the tube (Fig. 3.11).
Withdraw the platinum moss and notice that it is chemically unaltered.

Heterogeneous catalysis

A mixture of hydrogen gas and oxygen gas will remain together for a long time without any reaction.
The redness of the platinum moss shows that a strongly exothermic reaction is taking place in the tube between the two gases to form water.
The platinum moss plays the role of a catalyst for the reaction.
The reactants and the catalyst do not form a single phase, thus a heterogeneous catalysis has occurred.

In a heterogeneous catalysis, the reactants and the catalyst do not form a single phase

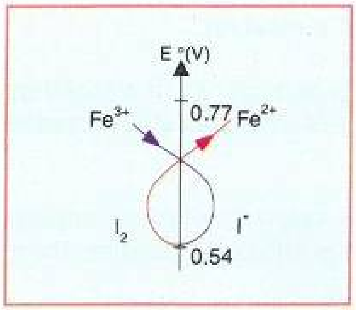


Figure 3.10
The gamma rule predicts the reaction between Fe^{3+} ions and the I^- ions.

- It should be operated with precaution, since the reaction may explode

- Does a mixture of hydrogen gas and oxygen gas react easily under ordinary conditions?
- What does the redness of platinum indicate?
- How many phases will the platinum and the gaseous mixture form?

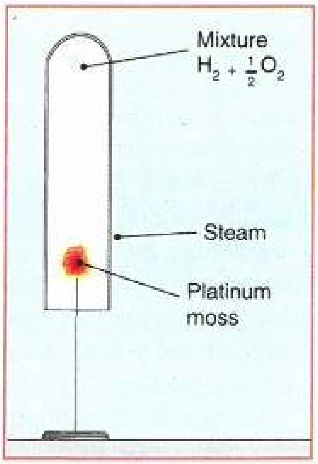


Figure 3.11
The platinum moss catalyzes the synthesis reaction of water.

- **Kinetic role of the catalyst**

The catalyst, in the preceding examples, has speeded up the rate of the reaction significantly, but a catalyst cannot do the impossible by making a reaction happen when the necessary ingredients are missing.
Thus, if we mix I_2 solution and SO_4^{2-} ions, in the absence of a catalyst, no reaction will occur between these two species (Fig. 3.12).

Activity 5 Reaction of oxalic acid with potassium permanganate

Objective

Conduct an autocatalysis

Equipment and reagents

Two beakers100 mL. A 50 mL graduated cylinder. 1mL pipet. Pipet filler. Dropper. Chronometer.
0.02 mol.L^{-1} potassium permanganate solution. 0.1 mol.L^{-1} oxalic acid $H_2C_2O_4$ solution. 1 mol.L^{-1} manganese sulfate $MnSO_4$ solution. 5 mol.L^{-1} sulfuric acid H_2SO_4 solution.

Procedure and observation

Label the two beakers A and B. Put into each beaker 20 mL of oxalic acid solution and 1 mL of sulfuric acid solution. Add few drops of manganese (II) sulfate solution to beaker B. Quickly add into the two beakers 20 mL of potassium permanganate solution. Homogenize and set on the chronometer.
After a few seconds, decolorization in beaker B is produced , whereas the decolorization in beaker A starts a few minutes later, it is less rapid (Fig. 3.13).

- **Autocatalysis**

The reaction between oxalic acid and the permanganate ion in acidic medium occurs according to the following equation:

$$5\,H_2C_2O_4 + 2\,MnO_4^- + 6\,H^+ \rightarrow 10\,CO_2 + 2\,Mn^{2+} + 8\,H_2O$$

The Mn^{2+} ions added to the reaction medium in beaker B plays the role of the catalyst. The reaction in this beaker is faster than in beaker A. These ions, at the same time, are one of the products of the reaction, thus the reaction is catalyzed by one of its products. Such catalysis is called autocatalysis.

In autocatalysis, one of the products is the catalyst for the reaction.

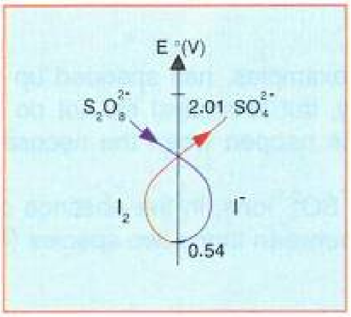


Figure 3.12
The gamma rule does not predict a spontaneous reaction between iodine I_2 and the sulfate ions SO_4^{2-}.

- Which is the limiting reactant?
- To what, is the decolorization of the solution in the two beakers due?
- What are the products formed?

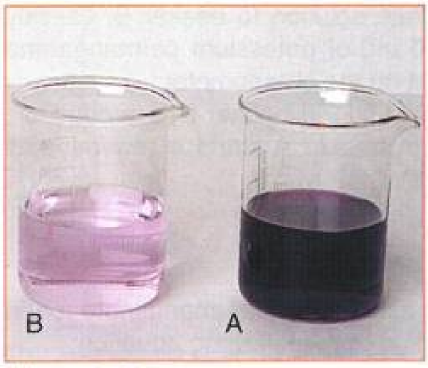


Figure 3.13
The violet color of MnO_4^- ions disappears more rapidly in beaker B than in beaker A.

- The reaction in beaker A starts slowly. Its rate increases with the increase of the quantity of Mn^{2+} ions formed. The curve $[Mn^{2+}] = f(t)$ permits to observe the change of the rate of the reaction with the quantity of Mn^{2+} ions formed without previous addition of Mn^{2+} ions in the solution (Fig. 3.14).

Activity and selectivity of a catalyst.

A catalyst is characterized by its activity. This is defined by the capacity of a minimum quantity of the catalyst to increase the rate of a reaction.

The lesser the quantity of the catalyst, which is capable to cause a noticeable increase in the rate of the reaction, the more active is the catalyst.

In homogeneous catalysis, small quantities of catalyst are sufficient to be added to the reaction medium, since the catalyst is regenerated during the course of the reaction.
However, the more the catalyst in the reaction medium is in contact with the reactants, the more efficient is the catalyst. It is seen in certain types of reactions, for example, in organic chemistry, that large quantities of catalysts are necessary.
A catalyst also is characterized by its selectivity. Starting from the same reactants; the products of a reaction may be different depending on the catalyst used.
The dehydrogenation of ethanol CH_3CH_2OH, for example, gives the compound CH_3CHO, called ethanal where finely divided copper Cu is used as a catalyst,

$$CH_3CH_2OH \xrightarrow[300\ °C]{Cu} CH_3CHO + H_2$$

whereas ethanol gives ethylene $CH_2{=}CH_2$ when the catalyst used is aluminum Al_2O_3.

$$CH_3CH_2OH \xrightarrow[400\ °C]{Al_2O_3} CH_2 = CH_2 + H_2O$$

A given reaction may be catalyzed by a limited number of catalysts.

This property is extensively applied in industrial chemistry to increase the yield of a particular product and to avoid undesirable secondary by products.

Importance of catalysis

Catalysts are used extensively in industry, in the laboratory, and in the majority of the reactions of biological systems.
For example, the oxidation of sulfur dioxide SO_2 into sulfur trioxide SO_3 is a step in the manufacture of sulfuric acid in the contact process. It is catalyzed by vanadium pentoxide V_2O_5.
Ammonia NH_3, an essential component in chemical industry and in agriculture, is manufactured by the reaction of hydrogen gas H_2 with nitrogen gas N_2 in the presence of iron, Fe, as a catalyst.
A large number of catalyst (Ni, Pt ,Cu and zeolites, ...) is used in the manufacture of the majority of organic compounds and compounds of petrochemical origin: fuels, polymers, medical compounds and others.

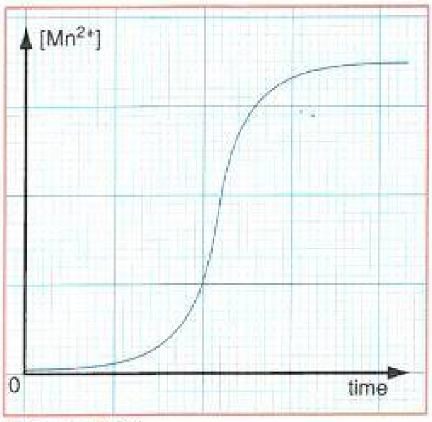


Figure 3.14
Kinetic curve of the formation of product Mn^{2+}, $[Mn^{2+}] = f(t)$ without previous addition of Mn^{2+} ions in the solution.

Reactions that occur in living organism are, in general, complex enough. They take place under proper conditions and have rates that are well controlled. Most of these reactions are catalyzed by enzymes. Enzymes are catalysts, which are very selective. They are also very specific that a given enzyme does not catalyze any other given reaction.

■ Mechanism of heterogeneous catalysis

The catalysts used in heterogeneous catalysis are usually solids (metals and metallic oxides).
The reaction takes place on the surface of the catalyst and it occurs in three steps.
In the first step, molecules of the reactants are adsorbed on the catalyst surface.
The atoms and the ions on the surface of the catalyst possess a certain reactivity, which allows them to form relatively weak bonds with the molecule of the reactants (chemisorption). Practically, not all atoms and ions on the surface of the catalyst have the same reactivity. The more reactive ones are called active site and they play an efficient role in the adsorption process. During the hydrogenation reaction of ethylene, for example, which is catalyzed by finely divided platinum nickel:

$$C_2H_{4(g)} + H_{2(g)} \xrightarrow{\text{Pt, Ni}} C_2H_{6(g)}$$

The molecules of $C_2H_{4(g)}$ and $H_{2(g)}$, in the first step, are adsorbed on the active site on the surface of the catalyst (Fig 3.15 (a)).

In the second step, the reaction occurs on the catalyst surface. For the above reaction, the H-H bond of hydrogen and the π bond of the compound $CH_2 = CH_2$are broken. The two new C-H bonds of ethane $C_2H_{6(g)}$ are formed (Fig. 3.15 (b)).

Finally, in the third step of the process, the products of the reaction separate (desorption) from the surface (Fig 3.15 (c)).
The mechanism of heterogeneous catalysis shows the important role of the surface of solid catalyst.
This is why it is important to increase the contact surface area of the catalyst and increase the number of its active sites. For this reason, the solid catalysts are used as finely divided. The number of active sites depends on the method of preparing the catalyst and how it has to be treated before usage.

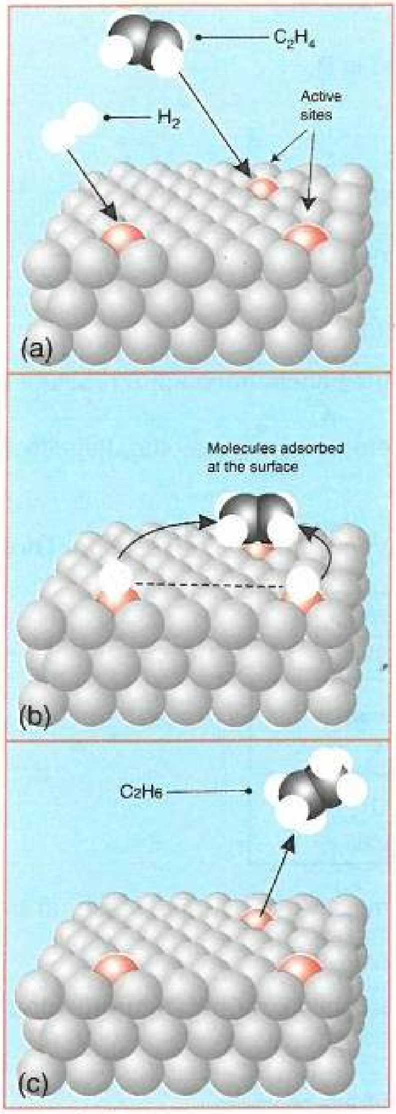


Figure 3.15
a) $C_2H_{4(g)}$ and $H_{2(g)}$ are adsorbed on the surface.
b) Reaction of the adsorbed molecule occurs on the surface.
c) Desorption of the product formed.

■ Catalysis and every day life

The catalysts intervene frequently in the manufacture and action of products for common usage.
The action of hydrogen peroxide as an antiseptic, for example, is based on its decomposition into water and oxygen gas, occurs easily in the presence of an enzyme called catalase, which is found in the blood and the liver of the mammals; it catalyzes the decomposition reaction.

In addition to the many industrial products elaborated by catalyzed reactions, the catalyst, due to its role in the reactions of the living organisms, is involved in food industry (for example in dairy products), in the pharmaceutical industry, in the cosmetic industry, and in many other industries.

- Some substances occupy the active sites of a catalyst and thus cause the catalyst to lose some of its efficiency. These substances cause poisoning of the catalyst.

Chapter review

- The factors that influence the rate of a reaction are: the concentration of the reactants, the temperature, and the catalysts.
- The rate of reaction (disappearance of reactants and formation of products) increases as the initial concentration of the reactants are increased and vice-versa.
- The rate of reaction increases as the temperature of the reaction increases and vice-versa.
- The rate of a reaction is given by the expression: $r = k[A]^{\alpha}[B]^{\beta}$ .....
  called the rate law.
  α and β are the partial orders of the reaction in A and in B.
  The sum $\alpha + \beta$ is the overall order of the reaction.
  k is the rate constant. It depends on temperature.
- The unit of the rate constant is related to the overall reaction order. Thus:

Zero order	k is expressed in $mol.L^{-1}.(time)^{-1}$
First order	k is expressed in $(time)^{-1}$
Second order	k is expressed in $mol^{-1}.L.(time)^{-1}$

- The half-life of reaction, $t_{1/2}$, is the time required for the concentration of a reactant R to decrease to half of its initial concentration.
  When the reactants do not satisfy the stoichiometric proportions, the half-life is defined with respect to the limiting reactant.
- The expression of the half-life, $t_{1/2}$, depends on the overall order of the reaction. Thus:

Zero order	$t_{1/2} = \frac{[A]_0}{2k}$
First order	$t_{1/2} = \frac{0.693}{k}$
Second order	$t_{1/2} = \frac{1}{k[A]_0}$

- A catalyst is a substance, which accelerates a chemical reaction, and which, at the end of the reaction, is not chemically altered itself.
- In a heterogeneous catalysis, the reactants and the catalyst do not form one single phase.
- In autocatalysis, one of the products is the catalyst of the reaction.
- A catalyst is characterized by its activity and selectivity.
- The three steps of a heterogeneous catalysis are adsorption, a reaction occurring at the catalyst surface, and desorption.

Documentary activity

Catalytic converter

The heterogeneous catalysis plays an important role in the fight against urban pollution.

The oxides of nitrogen NO_x, the carbon monoxide, and the unburned hydrocarbons C_xH_y are the residual compounds from the combustion of fuels in the engine of a car. When they are released into the atmosphere, they provoke serious pollution problems.

The majority of the new cars are equipped with catalytic converters that convert many of these pollutants into non-harmful products.

The catalytic converter is a block of ceramic or alumina Al_2O_3 bed, covered with metals or metallic oxides that act as catalysts (Fig. 3.16).

The carbon monoxide and the hydrocarbon C_xH_y undergo a catalytic oxidation and produce carbon dioxide CO_2 and water vapor H_2O.

The products formed are not pollutants.

The catalyst for this oxidation are metallic oxides such as CuO, Cr_2O_3 and metals such as platinum Pt and palladium Pd.

The nitrogen oxides NO_x are reduced into nitrogen gas $N_{2(g)}$.

The catalysts used in this case is the rhodium Rh and cesium oxide.

The reactants: O_2, CO, C_xH_y and NO_x are adsorbed on the surface and then the products are desorbed.

In this way, depending on the time of the contact between the catalysts and the reactants (100 to 400 ms), 96 % of carbon monoxide and unburned hydrocarbon and 76 % of the nitrogen oxides, are transformed into final products which are not harmful.

Notice that the catalysts, used in a catalytic converter are very precious.

Moreover, additives containing lead, which are added to fuel to increase the octane index, has a poisoning effect on the catalyst. Thus only fuel without lead should be used by cars equipped with catalytic converters.

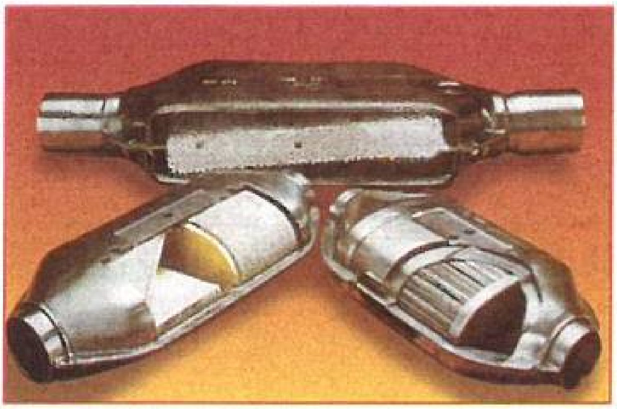


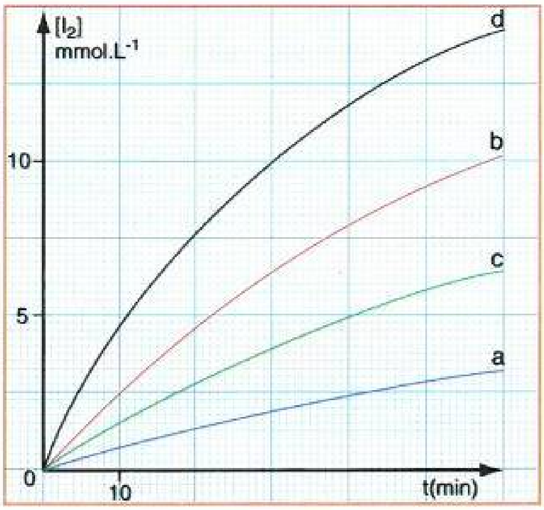
Figure 3.16
Types of catalytic converters

Questions

1) What are the pollutants released by the engine of a car?
2) What kind of catalyst is used in catalytic converters?
3) Search for the formulas of nitrogen oxides NO_x released from the exhaust of a car into the atmosphere.
4) What is the principal product obtained by the reduction of these oxides?
5) What may limit the use of catalytic converters?

Exercises

1 We study the oxidation of iodide ion I^- with peroxydisulfate ion $S_2O_8^{2-}$ in aqueous solution by titrating the iodine formed as a function of time.
The obtained results, according to initial conditions given below, allow us to plot the following curves:



Experiment	$[S_2O_8^{2-}]_0$ mmol.L^{-1}	$[I^-]_0$ mmol.L^{-1}	T °C
1	10	20	18
2	20	40	18
3	10	20	32
4	20	40	32

Assign each curve to an experiment. Justify.

2 The experimental study of the reaction between nitric oxide and hydrogen is given by the equation:

$$2\,NO_{(g)} + H_{2(g)} \rightarrow N_2O_{(g)} + H_2O_{(g)}$$

at a temperature T, and the following table represents the data:

Experiment	$[NO]_0$ mol.L^{-1}	$[H_2]_0$ mol.L^{-1}	$r_0(H_2O)$ mol.L^{-1}.s^{-1}
1	0.12	0.10	0.051
2	0.12	0.20	0.100
3	0.25	0.30	0.313

a) Determine the partial orders of the reaction relative to the reactants $NO_{(g)}$ and $H_{2(g)}$.
b) Calculate the rate constant at temperature T.
c) Calculate the rate of formation of H_2O starting from a mixture where $[NO]_0 = 0.24$ mol.L^{-1} and $[H_2]_0 = 0.4$ mol.L^{-1}.

3 The reaction given by the following equation:

$$NO_{2(g)} + O_{3(g)} \rightarrow NO_{3(g)} + O_{2(g)}$$

is studied at 25 °C.
The following results are obtained:

Experiment	$[NO_2]_0$ 10^{-6} mol.L^{-1}	$[O_3]_0$ 10^{-6}mol.L^{-1}	r_0 10^{-7}mol.L^{-1}.s^{-1}
1	2	2	2.1
2	3	2	3.1
3	4	3	6.2
4	4	4	8.3

Deduce the rate law.

4 The oxidation of oxalic acid $H_2C_2O_4$ by potassium dichromate $K_2Cr_2O_7$ in acidic medium is given by the following equation:

$$Cr_2O_7^{2-} + 3H_2C_2O_4 + 8H^+ \rightarrow 2Cr^{3+} + 6\,CO_2 + 7H_2O$$

The oxidation is carried out using the following solutions:
- Solution A, 0.01 mol.L^{-1} potassium dichromate solution
- Solution B, 0.5 mol.L^{-1} oxalic acid solution
- Solution C, 2 mol.L^{-1} sulfuric acid solution

We prepare the three mixtures 1, 2, and 3 that correspond to the following results:

Mixture	1	2	3
V(A) mL	10	10	10
V(B) mL	10	7.5	5
V(C) mL	2	2	2
V(water) mL	3	5.5	8
$r_0 \times 10^{-3}$ ($mol.L^{-1}.min^{-1}$)	1	0.6	0.25

a) Propose the type of glassware that should be used for transferring each of the volumes mentioned above. Justify.

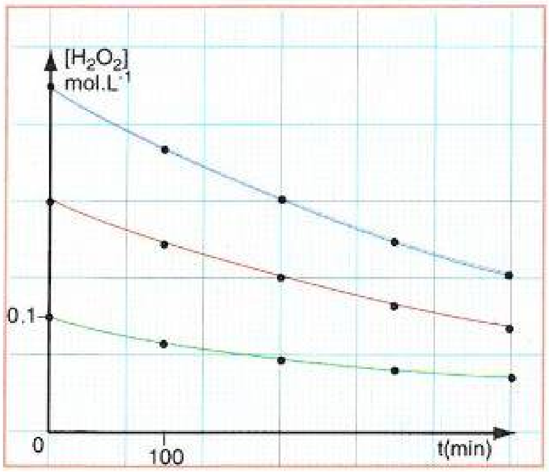
b) Construct a table showing the initial concentrations of the reactants in each mixture.

c) Determine the partial order of the reaction relative to oxalic acid.

5 A) Hydrogen peroxide decomposes slowly at 40 °C according to the following equation:

$$2H_2O_2 \rightarrow 2\,H_2O + O_2$$

The following graph represents the variation of the concentration of hydrogen peroxide as function of time, where only the initial concentration changes.



a) Calculate the initial rate, r_0, for each curve. Conclude.

b) Calculate the half-life of reaction for each curve. Conclude. Give the rate law.

c) Calculate the rate constant.

B) Again we carry out the decomposition of hydrogen peroxide, but at different temperatures: 40, 25, and 4 °C. The variation of the concentration of hydrogen peroxide as a function of time in each experiment is given below:

Time (min)	0	100	200	300	400	500
$[H_2O_2]mol.L^{-1}$ (40 °C)	0.500	0.412	0.340	0.280	0.231	0.191
$[H_2O_2]mol.L^{-1}$ (25 °C)	0.500	0.475	0.451	0.428	0.406	0.385
$[H_2O_2]mol.L^{-1}$ (4 °C)	0.500	0.497	0.493	0.491	0.487	0.484

a) Plot the curves $[H_2O_2] = f(t)$ on a graph paper using the same scale.

b) Calculate the initial rate, r_0, for each curve. Conclude.

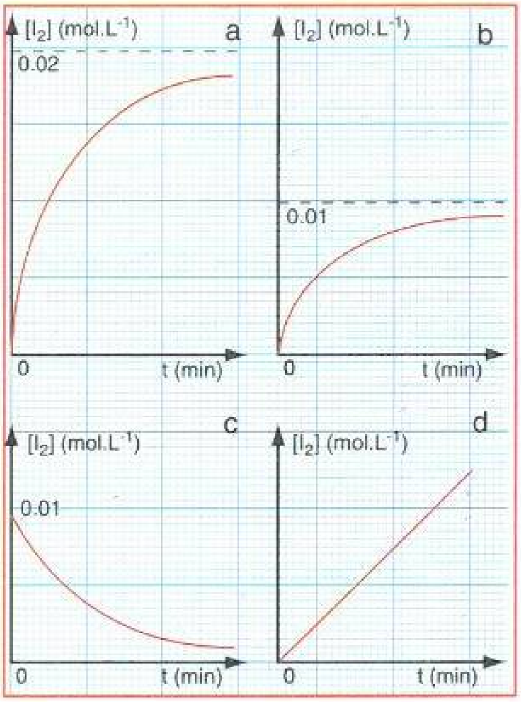
c) Determine the half-life at 40 °C. Compare to $t_{1/2}$ of the experiments of part A. Conclude.

d) Calculate the rate constant at the temperature of 40 °C.

6 We carry out the oxidation of 50 mL of 4×10^{-1} $mol.L^{-1}$ potassium iodide solution KI, with 50 mL of 2×10^{-1} $mol.L^{-1}$ sodium peroxydisulfate $Na_2S_2O_8$ solution in the presence of Fe^{2+} ions as catalyst. The reaction is given by the following equation:

$$2\,I^- + S_2O_8^{2-} \rightarrow I_2 + 2\,SO_4^{2-}$$

Identify using the following four curves, the one which matches with the preceding oxidation.



7 We study the esterification reaction between methanoic acid and ethyl alcohol, at constant temperature, which is given by the following reaction:

$$HCOOH + C_2H_5OH \rightleftarrows \underset{\text{ester}}{HCOOC_2H_5} + H_2O$$

The reaction is carried in the presence of sulfuric acid to insure the presence of H^+ in the reaction medium.

Using the same concentration for the reactants, we perform two experiments, where we double the concentration of H^+ ions in the second experiment.

In the table below, the variation of the concentration of the ester formed as a function of time in the two experiments is recorded.

Time (s)	50	100	150	200	300	400	500
$[ester]_1$ (mmol.L^{-1})	20	41	59	75	101	122	139
$[ester]_2$ (mmol.L^{-1})	40	74	100	121	152	170	182

a) Plot on the same graph paper, using the same axes, the two curves [ester]=f(t).
b) Determine for each curve the rate of reaction at t = 200 s. Compare and draw a conclusion concerning the role of H^+ ions.

8 Hydrogen peroxide decomposes slowly according to the reaction:

$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2$$

The decomposition may be catalyzed by the presence of Fe^{3+} in solution.

To study the kinetic of the decomposition of H_2O_2, we start by determining the concentration of an available commercial solution of H_2O_2.

We use the following materials
Pipets: 5,10 and 25 mL
Volumetric flasks: 100, 250 and 500 mL
Erlenmeyer flasks: 100, 250, and 500 mL
Graduated cylinders: 10, 25, and 50 mL
Beakers: 100, 250, and 300 mL
A buret: 50 mL
A magnetic stirrer
And the following solutions:
2×10^{-2} mol.L^{-1} potassium permanganate $KMnO_4$ solution.
0.1 mol.L^{-1} iron (III) chloride $FeCl_3$ solution.
0.1 mol.L^{-1}sulfuric acid H_2SO_4 solution.

A) Starting with the available commercial solution we prepare 100 mL solution diluted 10 times.

Suggest the glassware to be used to prepare the diluted solution.

B) 10 mL of the prepared solution is titrated with 17.8 mL of the potassium permanganate solution in acidic medium.
a) Describe the procedure and indicate the type of each glassware to be used.
b) Sketch a labelled diagram.
c) Write the ionic equation of the reaction.
d) Calculate the concentration of the dilute solution. Deduce the concentration of the commercial solution.

C) A hydrogen peroxide solution is prepared from 10 ml of the given commercial solution and it is poured into 100 mL volumetric flask. 5 mL of iron (III) chloride solution is added and then the volume is completed exactly to 100 mL.
A change in the concentration of H_2O_2 is recorded as a function of time. After 5min, 10 mL of the H_2O_2 solution is taken and titrated with potassium permanganate solution. We repeat the same procedure after 10, 20, 30, and 40 min. The volume taken is at once placed in 150 mL very cold distilled water.

a) What is the role of diluting in cold water? Which kinetic factors are involved?
b) Is it necessary that the volume of cold water be precise?
c) During the titration, how is the equivalence point recognized?

The results obtained from the titration are represented in the following table:

t (min)	5	10	20	30	40
V (mL)	15.1	12.6	9.2	6.3	4.5

d) Express the concentration of $[H_2O_2]_t$ in terms of the volume V of the potassium permanganate solution added during the titration of the sample taken at the same recorded time .
e) Calculate $[H_2O_2]_t$ for the times mentioned above and plot the curve $[H_2O_2]_t = f(t)$.
f) Determine the rate $r_{t=0}$ and $r_{t=30}$. Compare and conclude.

9 The oxidation of iodide ion I^- with peroxydisulfate $S_2O_8^{2-}$ is given according to the equation:

$$2\ I^- + S_2O_8^{2-} \rightarrow I_2 + 2\ SO_4^{2-}$$

Three experiments 1, 2, 3 are performed starting with the same initial concentration of reactants, but varying the temperature in each experiment, and adding a few drops of iron (III) sulfate $Fe_2(SO_4)_3$ in one of them.

The results are represented in the following table:

Experiment	Temperature (°C)	r_0(mol.L^{-1}min^{-1})
1	T_1	2.05×10^{-4}
2	$T_2 > T_1$	3.65×10^{-4}
3 (presence of Fe^{3+} ions)	T_2	9.75×10^{-4}

Explain the role of the kinetic factors in the values of r_0 for each experiment.

10 Iodide ions are slowly oxidized by hydrogen peroxide, in acidic medium according to the following equation:

$$2\ I^- + H_2O_2 + 2\ H^+ \rightarrow I_2 + 2\ H_2O$$

The time necessary to form n moles of iodine I_2 can be determined by adding in advance a fixed quantity of sodium thiosulfate $Na_2S_2O_3$ which reacts rapidly with the iodine produced according to the following equation:

$$2\ S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2\ I^-$$

To achieve this, a solution is prepared containing:
- 20 mL of 1 mol.L^{-1} potassium iodide KI;
- Enough water to make the final volume of the solution constant;
- A solution which permits to maintain constant H^+ ion concentration;
- 2 mL of 1 mol.L^{-1} sodium thiosulfate solution;
- Some drops of starch solution.

At the instant t = 0.1 mL of 9.88 mol.L^{-1} hydrogen peroxide solution is added. At the instant t_1 = 86 s, the dark blue color of the indicator appears. Then 2 mL of the thiosulfate solution is added, which causes the color to disappear. The color re-appears at the instant t_2 = 183 s. 2 mL of the sodium thiosulfate solution are added again... etc. This allows to construct the following table:

time (s)	86	183	293	419	570	755	996	1341	1955
$n(I_2)$ (mmol)	1	2	3	4	5	6	7	8	9

a) Give 2 examples of the calculation of $n(I_2)$, by using the first two values n_1 and n_2 corresponding to the first two additions of the sodium thiosulfate solution.

b) Plot the curve $n(I_2) = f(t)$.

c) Calculate the rate of formation of iodine in the first reaction, $r = \frac{dn(I_2)}{dt}$ at instant t = 200 s.

d) Explain qualitatively how the rate of formation of iodine varies as a function of time. What kinetic factors intervene in this case and in what direction is it acting?

e) Calculate the number of moles of iodine formed after an infinite time.

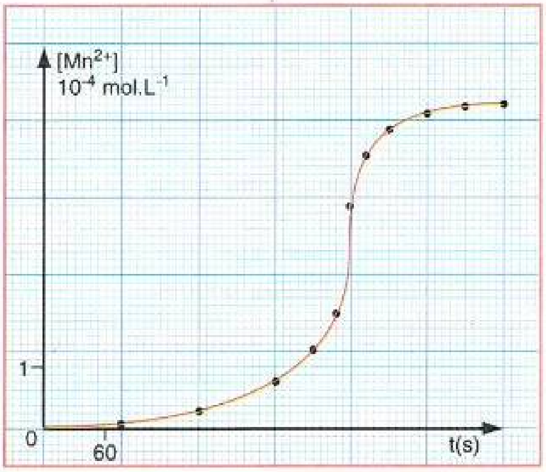
f) What is the value of the rate of formation of iodine after an infinite time?

g) Give two other kinetic factors that may affect the rate of formation of iodine. Explain the effect of each.

11 In our study of the kinetic of the autocatalysis reaction of oxalic acid solution $H_2C_2O_4$ with potassium permanganate $KMnO_4$ solution in acidic medium, the equation of the reaction is:

$$5H_2C_2O_4 + 2MnO_4^- + 6H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

At instant t = 0, 50 mL of 10^{-3} $mol.L^{-1}$ acidified potassium permanganate solution is mixed with 50 mL of 1×10^{-1} $mol.L^{-1}$ oxalic acid solution. The variation of the concentration of Mn^{2+} formed as a function of time, $[Mn^{2+}] = f(t)$ is represented by the following graph:



a) Determine graphically the instantaneous rate of formation of Mn^{2+} at instants:
120 s, 280 s, 330 s.

b) Based on the obtained results, interpret the kinetic of the reaction.

Evaluation

Applying knowledge

1 Consider the reaction between sulfur dioxide and oxygen, to give sulfur trioxide.

a) Write the equation of the reaction.

b) After some time, the variation of the number of moles of oxygen is $\Delta n\ (O_2) = -\ 2.1$ mol
Calculate the variation of the number of moles of the corresponding sulfur dioxide and sulfur trioxide.

c) Ten seconds were needed to observe this change. Calculate the average rate of disappearance of oxygen and sulfur dioxide and the average rate of formation of sulfur trioxide.

2 A constant and slow flow of distilled water from a graduated buret is added to 10 mL of 0.1 mol. L^{-1} potassium permanganate solution placed in a 500 mL beaker containing a magnetic bar.

a) Prior to any addition of distilled water, the color of the solution is dark violet. What happens during the addition of distilled water?

b) What can be said about the concentration of the permanganate ions MnO_4^-?

c) What is the rate of disappearance of the permanganate ions?

3 Hydrogen peroxide decomposes according to the following equation:

$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2$$

A solution is said to be x volumes if 1 L of solution releases x L of oxygen gas (measured at S.T.P).

The decomposition of H_2O_2 is influenced by several factors: temperature, the presence of some metals and their ions, ultraviolet rays, enzymes, ... etc.

It is marketed at 110 volumes and used as antiseptic at 10 volumes.

At 25 °C, H_2O_2 loses 1 % of its "active oxygen" per year as an accepted approximation. This loss increases with temperature to reach 2 % per 24 hours at 100 °C.

a) Why is it advised to keep commercial H_2O_2 in plastic bottle placed in a metallic cylinder while pharmacological H_2O_2 in a dark brown glass bottle?

b) The antiseptic character of H_2O_2 weakens when it becomes at 7 volumes. After how much time, a 10 volume H_2O_2 kept at ambient temperature, can be used as antiseptic?

4 The catalytic converters used nowadays contain a ceramic honeycomb grill, covered with fine particles of platinum (Pt) and rhodium (Rh) which catalyzes the transformation of carbon monoxide, nitrogen oxides and residual hydrocarbons in the gas exhaust.The utilization of the very fine metallic particles on a honeycomb ceramic structure permits to increase the contact surface between the exhaust gases and the metals and to reduce the cost of the converter, by decreasing the amount of metals necessary (platinum and rhodium are among the most expensive metals).

Pour la science
C.Friend, no. 188, June 1993.

Questions

a) Why is it desired to transform carbon monoxide, nitrogen oxides, and the residual hydrocarbons of the exhaust gases?

b) What type of catalysis is made with the fine particles of Platinum and rhodium?

c) Why in this type of catalysis are catalysts generally used in the powder form? Explain why this is more imperative in the case of platinum and rhodium.

d) Using schemes and the simple example of the hydrogenation of ethylene C_2H_4 in the presence of an appropriate catalyst, in the finely divided powder form, show the steps of the mechanism of such catalysis. Name the steps and explain them.

Designing an experiment

5 The kinetic of the reaction between hydrogen peroxide H_2O_2 and the iodide ions I^- from a solution of potassium iodide is to be studied. This reaction is slow and complete. The equation is given below:

$$H_2O_2 + 2\,I^- + 2\,H^+ \rightarrow 2\,H_2O + I_2$$

The titration of iodine formed with time is performed with 2×10^{-2} mol.L^{-1} sodium thiosulfate solution. The titration reaction is complete and instantaneous.
The equation is given below:

$$I_2 + 2\,S_2O_3^{2-} \rightarrow 2\,I^- + S_4O_6^{2-}$$

Given the following solutions:
- 0.5 mol. L^{-1} potassium iodide;
- 0.1 mol. L^{-1} hydrogen peroxide;
- 1 mol. L^{-1} sulfuric acid;
- 2×10^{-2} mol. L^{-1} sodium thiosulfate.

To study the kinetic of the first reaction, a solution S is prepared by mixing:
50 mL of H_2SO_4 + 20 mL of KI + 10 mL H_2O_2 + distilled water to obtain a final volume of S equals 250 mL.
The color of the solution S, maintained at a constant temperature (ambient temperature), turned to red-brown because of the formation of iodine.
The titration of iodine formed with time is done by 10 samples of 20 mL each, at different instants. Each sample is diluted rapidly by cold water and then few drops of starch solution are added.

A- Theoretical study
a) Calculate the initial molar concentration of H_2O_2, I^- and H^+ in solution S.
b) Show that H_2O_2 is the limiting reactant.
c) Calculate the maximum volume of sodium thiosulfate solution required to titrate a sample of solution S.

B- Experimental study
Given the following glassware:
- 100, 250 and 500 mL volumetric flasks;
- 100 and 250 mL Erlenmeyer flasks;
- 10, 20 and 25 mL pipettes;
- 25 and 50 mL graduated cylinders;
- 25 and 50 mL graduated burets.

a) Specify the experimental procedure and the appropriate glassware needed for:
1) Preparation of solution S;
2) Titration of iodine formed.

b) Why is the temperature kept constant? How? Why each sample is diluted with cold water? What is the role of the starch solution?

C- Kinetic study
The measurements performed are summarized in the following table:

t (min)	1	3	5	6	7	8	10	15	20	24
$[I_2]$ mmol.L^{-1}	0.4	1	1.5	1.62	1.83	2	2.25	2.65	2.72	2.8

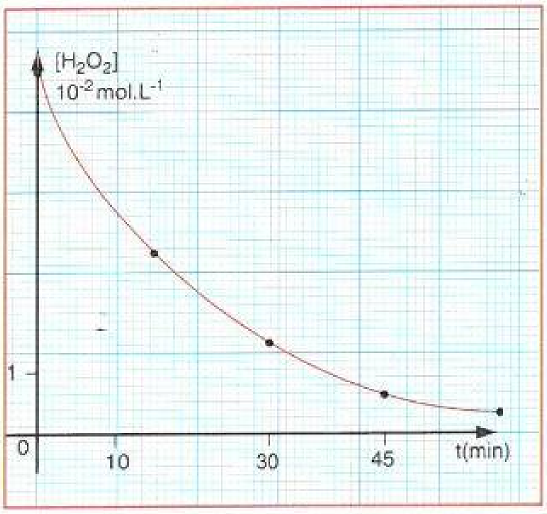
a) Plot the curve $[I_2] = f(t)$.
b) Is the maximum concentration of iodine reached?
c) Based on the curve, indicate how the rate of formation of I_2 with time varies.
d) Explain the reason for the variation.
Scale: abscissa 0.5 cm/min
ordinate 1 cm/0.4×10^{-3} mol. L^{-1}.

Mastery Communicating

6 Hydrogen peroxide decomposes slowly according to the following equation:

$$2\,H_2O_2 \rightarrow 2\,H_2O + O_2$$

The determination of the concentration of peroxide H_2O_2, as a function of time leads to the following graph:



a) Drive from the graph the concentration of H_2O_2 at the following instants:
$t = 0$; $t_1 = 15$ min; $t_2 = 30$ min; $t_3 = 45$ min; $t_4 = 60$ min.

b) Deduce the half-life time.

c) Compare for all the given values of time, the concentrations of hydrogen peroxide $[H_2O_2]$, by considering each time two consecutive instants. Compare the values of the consecutive time intervals. What conclusion can be made concerning the half-life time?

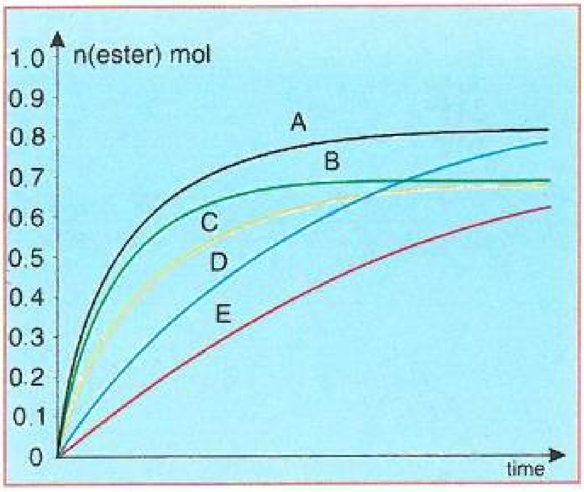
7 The reaction represented by the following equation:

$$\underset{\text{Acid}}{CH_3COOH} + \underset{\text{Alcohol}}{C_2H_5OH} \rightarrow \underset{\text{Ester}}{CH_3COOC_2H_5} + \underset{\text{Water}}{H_2O}$$

Is realized by five different experiments and the number of moles of ester formed with time is determined by an appropriate titration method. The experimental conditions are summarized in the following table:

	Acid	Alcohol	Sulfuric acid	Temperature
Experiment 1	1 mol	1 mol		70 °C
Experiment 2	1 mol	1 mol	2 cm^3	80 °C
Experiment 3	1 mol	1 mol	2 cm^3	70 °C
Experiment 4	1 mol	4 mol	2 cm^3	70 °C
Experiment 5	1 mol	4 mol		70 °C

The results of the variations of the number of moles of ester are represented by the following graph:



Attribute to each experiment its corresponding curve.

Given:

For an equimolar initial mixture of acid and alcohol, the number of moles of ester obtained at equilibrium is 0.67 mol. For an initial mixture of 1 mole of acid and 4 moles of alcohol, the number of moles of ester at equilibrium is 0.80 mol.

8 Nitrogen pentoxide N_2O_5 decomposes in a solution of carbon tetrachloride, according to the following equation:

$$2\ N_2O_5 \rightarrow 4\ NO_2 + O_2$$

NO_2 stays in solution. Its concentration is determined as a function of time from an initial solution of N_2O_5 with initial concentration $[N_2O_5]_0 = 0.25$ mol. L^{-1}. The results are given in the table below:

t (min)	0	5	10	15	20	30	40	60
$[NO_2]$ mmol.L^{-1}	0	90	145	210	250	315	375	437.5

a) Show that $[N_2O_5] = 0.25 - \frac{1}{2}[NO_2]$

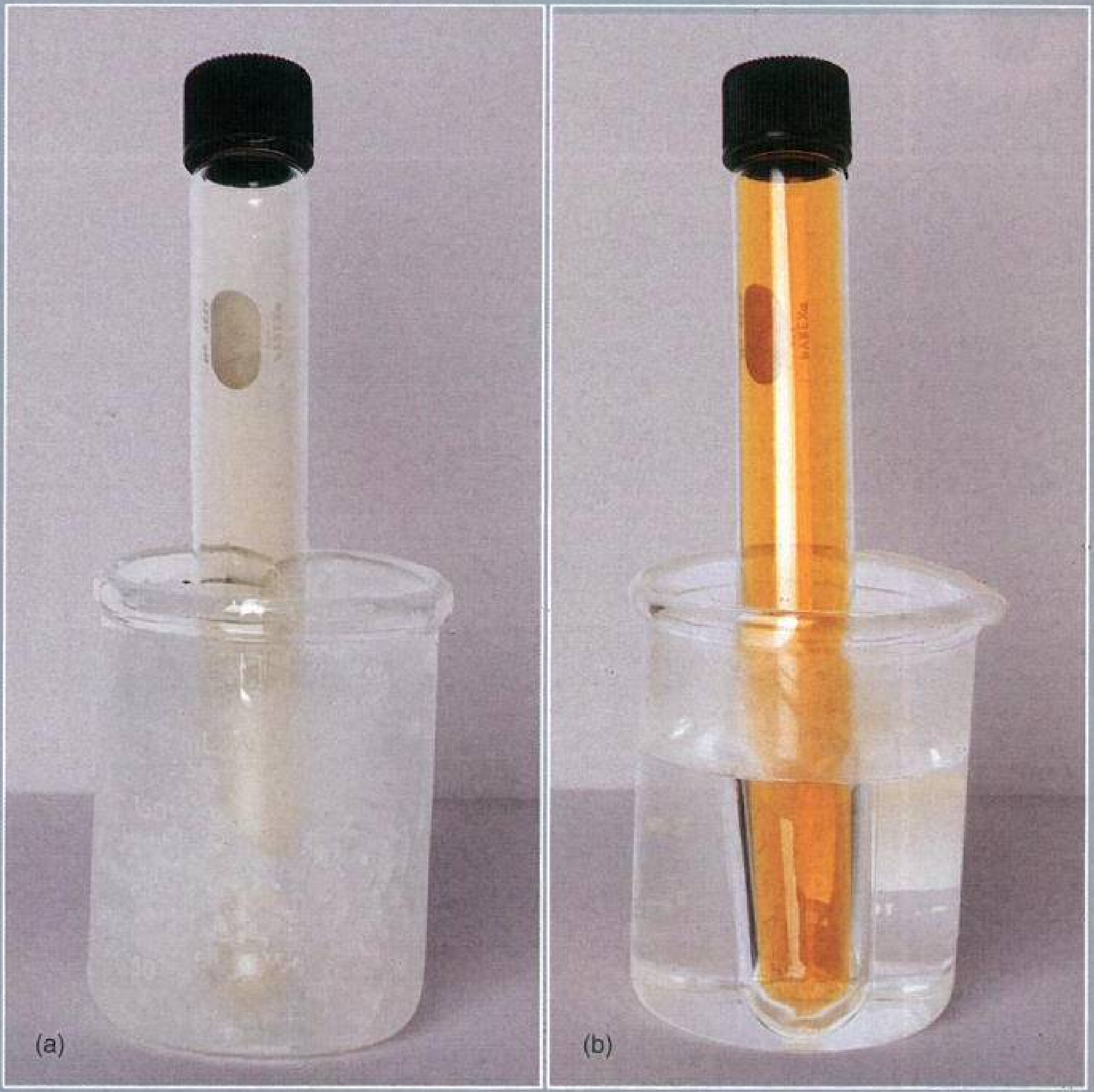
b) Trace the curve representing the variation of the concentration of N_2O_5 as a function of time.

c) Verify that the rate law of the reaction is: $r = 3.46 \times 10^{-2}\,[N_2O_5]$.

3

Chemical equilibrium

In the beaker, a precipitate of lead iodide PbI_2 is in contact with a solution of the same compound surnatant it. An equilibrium is established between the precipitate and the solution. This is a dynamic equilibrium where at each instant t, there is as much of PbI_2 which precipitate from the solution as of this compound passing in the solution, in the form of ions.



The above tube contains a mixture of the two gases: $NO_{2(g)}$ and $N_2O_{4(g)}$

(a) The tube is placed in ice water at temperature 0 °C.
(b) The tube is placed in water at temperature 50 °C.

The extent of dissociation of the colorless gas $N_2O_{4(g)}$ into $NO_{2(g)}$ according to the reaction,

$$N_2O_{4(g)} \rightleftarrows 2NO_{2(g)}$$

can be detected by the intensity of the brown color of $NO_{2(g)}$. The concentration of $NO_{2(g)}$ in an equilibrium mixture of the above two gases is directly related to the intensity of brown color. Can you infer from the above two figures which tube of mixture is more concentrated in NO_2? Can you predict the cause of the difference in the intensity of brown color?

CHEMICAL EQUILIBRIUM

4

Objectives

- Identify the characteristics of equilibrium state in a reaction system.
- Apply the law of mass action.
- Recognize the factors that affect the state of chemical equilibrium.
- Apply Le Chatelier's principle.

Prerequisites

- Molar concentration.
- Heat of a reaction.
- Notion of organic functions
- Dissolution of ionic compounds in water.

Chapter content

4.1 Homogeneous equilibrium in liquid phase - equilibrium constant K_c.
4.2 Homogeneous equilibrium in the gas phase - equilibrium constants K_c and K_p.
4.3 Heterogeneous equilibrium – equilibrium constants K_c and K_p.
4.4 Shifting equilibrium - Le Chatelier's principle.
4.5 Solubility equilibria and Solubility product.

- Chapter review
- Laboratory investigation sheet
- Exercises
- Evaluation

Figure 4.1
M.Berthelot (1827 - 1907) French chemist. He was the first to show that esterification is a reversible reaction.

In the previous chapters we have considered that chemical reactions are almost complete when at least one of the reactants disappears completely. Some reactions do proceed to completion, but many other do not. There are certain reactions that show the capability of the products to react to form the reactants again. Such reactions are called reversible reactions; in such reactions the conversion of products into reactants occurs simultaneously.
Can you predict how the two opposing chemical reactions will proceed with time?

4.1 Homogeneous equilibrium in liquid phase. Equilibrium constant K_c.

Homogenous equilibrium in liquid phase

Activity 1

Study of the kinetic curves for esterification reaction and hydrolysis of ester.

- The experiment described is similar to the experiments performed by Berthelot (Fig. 4.1) to study esterification reactions.

Esterification reaction

Esterification is a reaction between an alcohol and an acid to form an ester and water where all the species involved are in the liquid phase.
We can follow the progress of the esterification reaction by mixing 1 mole of ethanol and 1 mole of acetic acid at time $t_0 = 0$ and a temperature T = 100 °C (Fig. 4.2).
At different intervals of time, we measure the amount of acid present by titrating the acid left with a standard aqueous basic solution. Following the number of moles of acid left with time, we get the following results, which are given, in the following table (table 4.1).

Time (hours)	0	2	4	10	20	40	60	80	100	150	200
n (moles of acid remaining)	1	0.82	0.74	0.62	0.51	0.42	0.39	0.38	0.36	0.33	0.33

Table 4.1

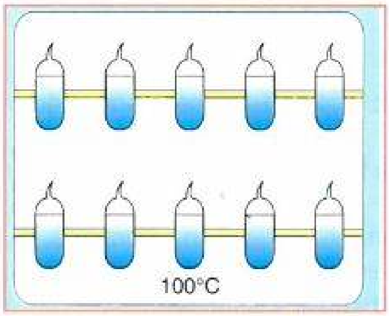


Figure 4.2
The ampules are placed in the oven.

Plotting the number of moles of acid left versus time shows the following curve (Fig. 4.3):

- According to the equation of the reaction, what should the number of moles of the acid, the alcohol, the ester and water be at the end of the reaction?
- From the kinetic curve and the equation, what are these numbers of moles?

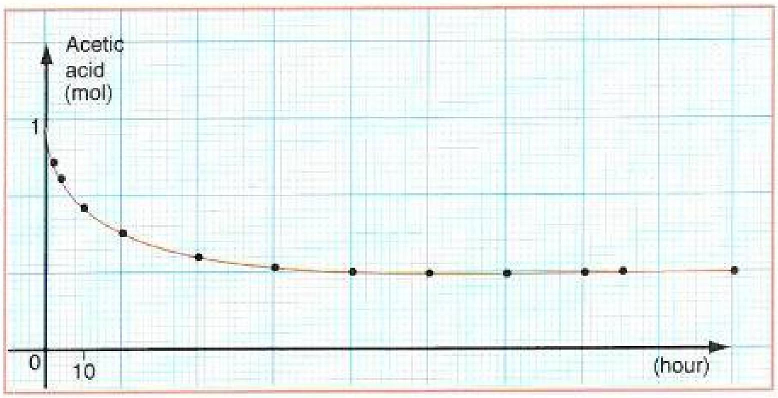


Figure 4.3
Kinetic curve for acetic acid during esterification

From the graph above, we can see that the number of moles of acetic acid has decreased gradually from 1 mole to 0.33 mole. At this point, the disappearance of acid ceases and its amount stays constant after this state, as long as the conditions are not altered. This shows that 0.33 mole of ethanol remains and 0.66 mole of each of the ester and water are produced according to the following equation:

$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethanol}}{C_2H_5OH} \rightleftarrows \underset{\text{Ethyl ethanoate}}{CH_3COOC_2H_5} + \underset{\text{Water}}{H_2O}$$

Therefore esterification is an example of a reaction, which is not complete since all of the components, the reactants and the products, involved are present at the moment where the reaction seems to have stopped.

- Same questions as for the esterification.

Hydrolysis of ester

Hydrolysis of ester is a reaction between ester and water to produce an acid and an alcohol. A mixture of 1 mole of ethyl acetate and 1 mole of water is allowed to react under the same previous conditions. By measuring the amount of acetic acid formed at different intervals of time, the following experimental results are obtained (Table 4.2)

Time (hrs)	0	2	4	10	20	40	60	80	100	150	200
n (moles of acid formed)	0	0.17	0.21	0.24	0.26	0.28	0.29	0.30	0.31	0.33	0.33

Table 4.2

The curve (Fig. 4.4) represents the variation of the amount of acetic acid formed versus time. It shows that the amount of acid increases with time until it reaches a constant value of 0.33 mol.

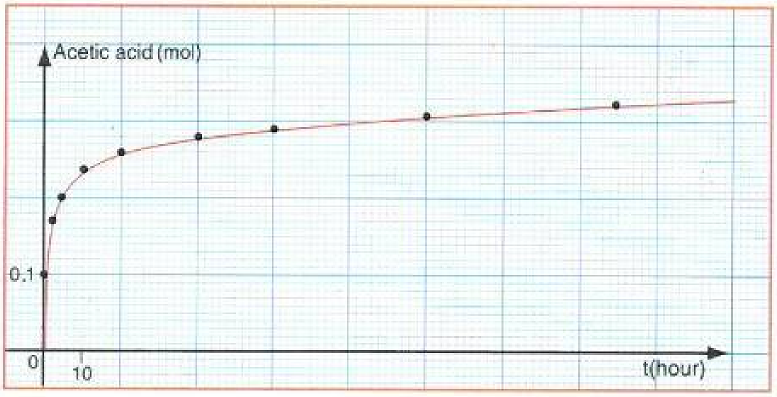


Figure 4.4
The kinetic curve of acetic acid formed during hydrolysis.

According to the equation of the hydrolysis of ethyl ethanoate:

$$\underset{\text{Ethyl ethanoate}}{CH_3COOC_2H_5} + \underset{\text{Water}}{H_2O} \rightleftarrows \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethanol}}{C_2H_5OH}$$

The amounts of other components become: 0.33 mol of ethanol; 0.66 mol of ethyl ethanoate; and 0.66 mol of water.
Therefore, hydrolysis of ester is another example of a reaction, which is not complete because all components involved, namely, reactants and products, are present at the end of the reaction.

From the two preceding experiments, we can see that the products of esterification are the reactants of hydrolysis of ester and vice versa. The two reactions can be represented by the following equation:

$$\text{Acid} + \text{Alcohol} \underset{\text{Hydrolysis}}{\overset{\text{Esterification}}{\rightleftarrows}} \text{Ester} + \text{Water}$$

The two opposite arrows $\rightleftarrows$ indicate that the reaction takes place in two directions forward and reverse, at the same time. Such a reaction is called a reversible reaction.

A reversible reaction is a reaction, which takes place in the forward and reverse direction. Such a reaction is partial, does not go to completion.

In a more general way, for the general equation of a reversible reaction:

$$aA + bB \underset{2}{\overset{1}{\rightleftarrows}} cC + dD$$

The reaction written in the usual way from left to right is called the forward reaction and its direction is referred to as 1. The reaction that takes place from right to left is called the reverse reaction and its direction is referred to as 2. The name and the properties of a reversible reaction are those of the forward reaction.

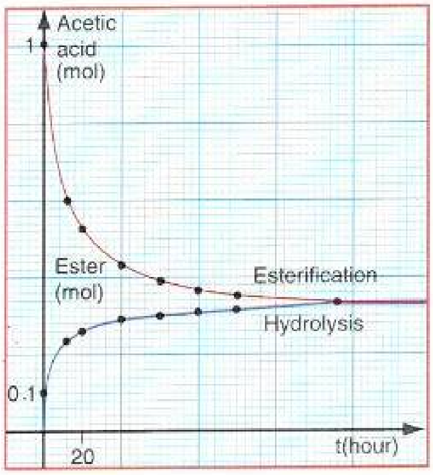


Figure 4.5

Starting from time t = 150 h, there is as much moles of acid disappearing at each instant by esterification, as moles of acid formed by hydrolysis.

Equilibrium state

In the previous section, the study of the experimental data and the graphs of the two opposite reactions (esterification and hydrolysis) tells us that these two reactions counter balance each other and reach a stable state when the amounts (in moles) of reactants and products become constant. This state is called chemical equilibrium, which is characterized by an unchanged overall composition of the chemical system with time.

What happens before a reaction system reaches a state of equilibrium?
Referring to the example of esterification, when ethanol and acetic acid are mixed together to react immediately to form ester and water, the two products begin to react as soon as they are formed to give the acid and the alcohol. At the beginning, the rate of the forward reaction esterification is faster than the reverse reaction hydrolysis because the concentrations of the products are small. As the reaction between the acid and alcohol proceeds, the concentration of ester and water increases and likewise, the rate of the reverse reaction increases. Meanwhile, the concentration of alcohol and acid are becoming less and less, so that the rate of the forward reaction falls off and the rate of the reverse reaction goes up gradually. Consequently, the two reaction rates approach each other and finally become equal, a condition at which the rate of appearance of a component is equal to the rate of its disappearance (Fig. 4.5).

An equilibrium state is characterized by a constant composition of the reaction system.

It may appear here that everything has stopped at equilibrium and the equilibrium state is static. But this is not true because the two opposing reactions will continue to take place in full operation but at the same rate. That is to say that the rate at which a reactant or a product is used up in one reaction is equal to the rate at which that reactant or product is formed by the opposite reaction. For this reason, the state of equilibrium is referred as a state of dynamic equilibrium.

Esterification takes place in one single phase - the liquid phase where the reactants and products are liquids. The equilibrium attained by this reaction is called homogeneous equilibrium in the liquid phase.

Equilibrium for a reaction system involving one single phase is called homogeneous equilibrium.
Equilibrium involving more than one phase is called heterogeneous equilibrium.

The thermal decomposition of calcium carbonate into calcium oxide $CaO_{(s)}$ and carbon dioxide $CO_{2(g)}$ is an example of heterogeneous equilibrium:

$$CaCO_{3(s)} \rightleftarrows CaO_{(s)} + CO_{2(g)}$$

The phases involved in this equilibrium system are solid and gaseous.
Homogeneous equilibrium can be attained also in the gaseous phase as in the synthesis of ammonia gas from its free gaseous elements:

$$3\ H_{2(g)} + N_{2(g)} \rightleftarrows 2\ NH_{3(g)}$$

■ Equilibrium constant K_c

When a system reaches equilibrium, a simple relationship governs the relative proportions of the concentration of reactants and products. This relationship was discovered experimentally by two Norwegian Chemists, Guldberg and Waage in year 1864. They proposed a general description of the equilibrium called the law of mass action. For the general equation of the reaction:

$$aA + bB \rightleftarrows cC + dD$$

it is observed experimentally that at constant temperature, the law of mass action is represented by the following equilibrium expression:

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

This expression is written in such a way that [A], [B], [C] and [D] represent the respective concentrations of species A, B, C and D at equilibrium and a, b, c and d are their respective stoichiometric coefficients in the balanced equation. K_c is a constant characterized by temperature and is called the equilibrium constant relative to concentrations.
This is a mathematical expression of the law of chemical equilibrium which may be stated as follows:

When a reversible reaction has attained equilibrium at a given temperature, the product of the molar concentrations of the products divided by the product of the molar concentration of the reactants, each concentration is raised to the power equal to the stoichiometric coefficient appearing in the balanced equation, is a constant.

Referring to the esterification reaction, when 1 mole of each of acetic acid and ethanol is used, it is found experimentally that the state of equilibrium is reached when the amount of each species is:
ethanol = 0.33 moles; acetic acid 0.33 moles, ethyl ehtanoate = 0.66 moles; water = 0.66 moles.
If the volume of the liquid phase is V liters then K_c:

$$K_C = \frac{[ester][water]}{[acid][alcohol]} = \frac{(0.66/V)(0.66/V)}{(0.33/V)(0.33/V)} = 4$$

■ In the expression of K_c, the concentrations are expressed in $mol.L^{-1}$.

■ K_c has units but conventionally it is given without units in tables.

■ K'_c for the opposite reaction, hydrolysis of ester, is equal to the reciprocal of the equilibrium expression:

$$K'_C = \frac{[Alcohol]\ [Acid]}{[Ester]\ [Water]} = \frac{1}{K_C}$$

at same T.
The equilibrium constants for forward and reverse reactions are the reciprocals of each other.

This value of K_c is constant for esterification reaction as long as the temperature is constant even if the concentrations of the reactants and products are different from those used in the preceding example.

Solved exercise 1

Given

Assume the following amounts are measured experimentally at a certain time for the system:

$$CH_3COOH + C_2H_5OH \rightleftarrows CH_3COOC_2H_5 + H_2O$$

Acetic acid = 1 mole; ethanol = 3 moles ethyl ethanoate = 0.5 mole; water = 2 moles, knowing that K_c for esterification reaction is equal to 4, determine whether the system is at equilibrium or not.

Solution

Taking V (in L) as the volume of the solution, we calculate for the system, the value of the reaction quotient, Q_r:

$$Q_r = \frac{[\text{ester}][\text{water}]}{[\text{acid}][\text{alcohol}]} = \frac{(0.5/V)(2/V)}{(1/V)(3/V)} = \frac{1}{3}$$

Because the value of the reaction quotient given by the mass action expression Q is not equal to 4 (value of K_c), then the system is not at equilibrium.

In general, when the quotient (Q) relative to concentrations is equal to the value of K_c, then the system is at equilibrium. Otherwise when Q_r is not equal to K_c, then the system is not at equilibrium.

$Q_r = K_c$ The system is at equilibrium
$Q_r \neq K_c$ The system is not at equilibrium

4.2 Homogeneous equilibrium in gas phase. Equilibrium constants K_c and K_p.

For reactions involving gases, the partial pressures of the reactants and products are proportional to their molar concentrations. The relationship between the pressure and the concentration of a gas can be obtained from the ideal gas equation PV = nRT, which can be rearranged in the form:

$P = \left(\frac{n}{V}\right) RT$, where $\left(\frac{n}{V}\right)$ represents the molar concentration of the gas. The equilibrium constant expression for these reactions can therefore be written in terms of partial pressures.
For example, for the synthesis of ammonia reaction:

- Partial pressure is expressed in bar or in atm.

- Ordinarily K_P has units, but conventionally it is given without units in the Tables.

$$N_{2(g)} + 3H_{2(g)} \rightleftarrows 2NH_{3(g)}$$

The equilibrium expression K_p can be written in terms of the equilibrium partial pressures of the gases as :

$$K_p = \frac{P^2_{NH_3}}{P_{N_2} \times P^3_{H_2}}$$

K_p depends only on temperature.
It is worth to mention here that a homogeneous equilibrium in the gaseous phase is characterized by K_p and K_c at a given temperature. So, K_c for the synthesis of ammonia from its free gaseous elements can be written as:

$$K_C = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

- **Relation between K_c and K_p**

K_p and K_c for a system in the gaseous phase are related mathematically at constant temperature. For example, in the synthesis of ammonia, the relation can be obtained by the following procedure:

$$K_P = \frac{\left(\frac{n_{NH_3}}{V} RT\right)^2}{\left(\frac{n_{N_2}}{V} RT\right)\left(\frac{n_{H_2}}{V} RT\right)^3} = \frac{[NH_3]^2}{[N_2]\,[H_2]^3} (RT)^{-2}$$

or $K_p = K_c\,(RT)^{-2}$.
The exponent (-2) refers to the difference between the total numbers of the stoichiometric coefficients of the gaseous products as (2) and the total number of coefficients of the gaseous reactants as (4) in the balanced equation (2 − 4 = - 2).
For the general reaction:

$$aA_{(g)} + bB_{(g)} \rightleftarrows cC_{(g)} + dD_{(g)}$$

The relationship can be written as:

$$K_P = K_C(RT)^{\Delta n}$$

where Δn stands for the difference between the total number of moles of gaseous products and the total number of moles of gaseous reactants in the balanced equation:

$$\Delta n = (c + d) - (a + b).$$

It is important to note that when partial pressures of the components of a system at equilibrium are substituted for their concentrations, K_p will be a constant, having usually a different numerical value from K_c.
However, for certain reactions K_p and K_c values are equal. This equality occurs when the sum of coefficients of gases on either side of the balanced equation is identical. That is to say when

$\Delta n = 0$, as in the case of the following equilibrium:

$$N_{2(g)} + O_{2(g)} \rightleftarrows 2NO_{(g)}$$

$\Delta n = n_p - n_r = 2 - 2 = 0$

4.3 Heterogeneous equilibrium - Equilibrium constant K_p and K_c

Consider the following heterogeneous equilibrium that involves two different phases, gas and liquid:

$$CO_{2(g)} + H_{2(g)} \rightleftarrows CO_{(g)} + H_2O_{(l)}$$

Applying the law of mass action, we can write the equilibrium expression:

$$K''_C = \frac{[CO][H_2O]}{[CO_2][H_2]}$$

Because the concentrations of pure liquids and solids are constant at a given temperature, then $[H_2O]$ liquid is constant and can be included in the constant K"c. The expression can be rearranged to give:

$$K_C = \frac{[CO]}{[CO_2][H_2]}$$

where

$$K_C = \frac{K''_C}{[H_2O]} = \text{constant}$$

So, concentrations of substances in their pure condensed phases (liquids and solids) are not included in the equilibrium expression in a reaction system. Similarly, pure liquids and solids are not included in the K_p expression. For the same preceding reaction

$$K_P = \frac{P_{CO}}{P_{CO_2} \times P_{H_2}}$$

Another example of a heterogeneous equilibrium is when solid and gaseous phases are involved as in:

$$CaCO_{3(s)} \rightleftarrows CaO_{(s)} + CO_{2(g)}$$

$$K_C = [CO_2]$$

$$K_P = P_{CO_2}$$

In a heterogeneous equilibrium corresponding to the dissolution of $Ca(OH)_{2(s)}$ in water:

$$Ca(OH)_{2(s)} \rightleftarrows Ca^{2+}_{(aq)} + 2\,HO^-_{(aq)}$$

The concentration of solid $[Ca(OH)_2]$ is not included in the K_c expression and rearranged to be written as :

$$K_{sp} = [Ca^{2+}]\,[OH^-]^2$$

- We will see that K_C of this equilibrium is designated by K_{sp}.

Relation between K_c and K_P

The K_p and K_c for a given system at the same temperature can be related to a heterogeneous equilibrium by the same relationship developed for a homogeneous equilibrium as:

$$K_P = K_C(RT)^{\Delta n}$$

Where Δn represents the difference between the total stoichiometric coefficients of only gaseous products and the total stoichiometric coefficients of gaseous reactants only.
For example, in the decomposition reaction of $CaCO_{3(s)}$, to give $CaO_{(s)}$ and $CO_{2(g)}$:

$$K_P = K_C(RT) = [CO_2]RT, \text{ where } \Delta n = 1.$$

Solved exercise 2

Given

Consider the table given below that shows two sets of data for the reaction at 500 °C:

$$N_{2(g)} + 3H_{2(g)} \rightleftarrows 2NH_{3(g)}$$

	$N_{2(g)}$	$H_{2(g)}$	$NH_{3(g)}$
Experiment 1	1	1	0
Initial concentrations ($mol.L^{-1}$)			
Equilibrium concentrations ($mol.L^{-1}$)	0.921	0.763	0.157
Experiment 2	2	1	3
Initial concentrations ($mol.L^{-1}$)			
Equilibrium concentrations ($mol.L^{-1}$)	2.59	2.77	1.82

a) Calculate K_c the equilibrium constant for the synthesis of ammonia at 500 °C from each of the above two experiments.

b) Compare the two values of K_c and draw your conclusion with respect to the data given.

Solution

a Knowing

$$K_C = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

We calculate the value of K_c for the above two experiments:

First experiment $$K_C = \frac{(0.157)^2}{(0.921)(0.763)^3} = 6.02 \times 10^{-2}$$

Second experiment $K_C = \dfrac{(1.82)^2}{(2.59)(2.77)^3} = 6.02 \times 10^{-2}$

b Comparing the values of K_c in the two experiments which are equal at 500 °C, and considering the different initial concentrations of the species involved for the same system:

$$N_{2(g)} + 3H_{2(g)} \rightleftarrows 2NH_{3(g)}$$

We can conclude that K_c has the same value at 500 °C, regardless of the amounts of the gases that are mixed initially.

From the preceding exercise, a more general conclusion can be drawn namely that for a given system at a given temperature, there are many equilibrium states, but only one value for Kc.

Solved exercise 3

Given

A mixture of two gases NO and Cl_2 is introduced into a flask at a constant volume and a temperature of 25 °C. The following equilibrium is established:

$$2NO_{(g)} + Cl_{2(g)} \rightleftarrows 2NOCl_{(g)}$$

The initial partial pressures of $NO_{(g)}$ and $Cl_{2(g)}$ are 1.25 atm and 0.9 atm respectively, and the equilibrium partial pressure of $NOCl_{(g)}$ is 1.2 atm.

Calculate:

a) The equilibrium partial pressures of $NO_{(g)}$ and $Cl_{2(g)}$.

b) The equilibrium constant K_p for the above system at 25 °C

Solution

a The equation of the above reaction allows us to write:

$$\frac{\Delta n(NO)}{2} = \frac{\Delta n(Cl_2)}{1} = \frac{\Delta n(NOCl)}{2}$$

According to the equation PV = nRT, the partial pressure of a component in a mixture of gases at a constant V and T, is proportional to the number of moles, and so we can write:

$$\frac{\Delta P_{NO}}{2} = \frac{\Delta P_{Cl_2}}{1} = \frac{\Delta P_{NOCl}}{2}$$

Where ΔP_{NO} is the change of pressure of $NO_{(g)}$, ΔP_{Cl_2} is the change of pressure of $Cl_{2(g)}$ and ΔP_{NOCl} is the change pressure of $NOCl_{(g)}$.

But $\Delta P_{NOCl} = +\ 1.2$ atm which implies that $\Delta P_{NO} = -1.2$ atm and $\Delta P_{Cl_2} = -\ 0.6$ atm (the (-) sign corresponds to a decrease in pressure).

At equilibrium, the partial pressures of the different components are:
$P_{NOCl} = 1.2$ atm
$P_{NO} = 1.25 - 1.2 = 0.05$ atm.
And $P_{Cl_2} = 0.9 - 0.6 = 0.3$ atm.

b The equilibrium constant K_p for the above system is expressed as:

$$K_P = \frac{P^2_{NOCl}}{P^2_{NO} \times P_{Cl_2}}$$

By substitution we get:

$$K_P = \frac{(1.2)^2}{(0.05)^2(0.3)} = 1.9 \times 10^3$$

Figure 4.6
Ammonia obtained from hydrogen and nitrogen, by the Haber process, is the principle source of nitrogen fertilizer.

- **The importance of chemical equilibrium**

A great number of chemical reactions involved in industry are reversible. Examples of such reactions are esterification and petrochemical operations, etc. So, it is clear that the principles of chemical equilibrium play an important role in the design and conditions of industrial processes. The production of ammonia by the Haber process, (Fig. 4.6), from inexpensive gases, hydrogen and nitrogen is a good example of the industrial process. Haber carried out experiments and made a careful study by choosing the optimum conditions of temperature and pressure to increase the yield of ammonia (20% by volume), which is limited by the reversibility of the reaction.
Many catalysts are often used in reversible reactions as well as in other chemical reactions. In an equilibrium, the catalyst increases the rate of both reactions (forward and backward), to the same extent, in such a way that it enables equilibrium to be achieved more rapidly without changing the composition of the components.

4.4 Shifting equilibria: Le Chatelier's principle

In a reaction system at equilibrium, any change in the concentration of a component of the system, in the pressure or in the temperature, affects the composition of the system.

- **The effect of a change in concentration**

Consider the synthesis of ammonia by the Haber process:

$$N_{2(g)} + 3H_{2(g)} \rightleftarrows 2NH_{3(g)}$$

Suppose the above system has reached equilibrium by the following concentrations:
$[N_2] = 0.400$ mol.L^{-1}; $[H_2] = 1.197$ mol.L^{-1}; $[NH_3] = 0.202$ mol.L^{-1}.
Upon adding 1 mole of N_2 into the system, at constant

temperature and volume, we will obtain the following concentrations at the new equilibrium:

$[N_2] = 1.340\ mol.L^{-1}$, $[H_2] = 1.044\ mol.L^{-1}$ and $[NH_3] = 0.304\ mol.L^{-1}$.

Comparing the data in the above two equilibrium positions, we can note that the concentration of ammonia has increased and that of hydrogen has decreased upon by adding an extra amount of N_2. The concentration of N_2 has also decreased in the overall amount.

We conclude from this observation that the above equilibrium is shifted in a direction to consume partly the amount of the component added. This observation is general and can be stated as:

When the concentration of a component (reactant or product) of a system at equilibrium is increased, the system is shifted in a direction to consume this component.

The opposite is true. When the concentration of a component is diminished the system is shifted in a direction to produce more of it.

The effect of change in pressure

A change in pressure affects only gaseous equilibrium. This change takes place when the volume of the container is changed at constant temperature.

To study the effect of change in pressure (by changing volume) on a system at equilibrium, let us refer to the table below that shows the effect of increasing pressure (decreasing volume) on the yield of ammonia in the Haber process:

$$N_{2(g)} + 3H_{2(g)} \rightleftarrows 2NH_{3(g)}$$

Total pressure (atm)	1	50	100
% by mole of ammonia in the mixture at equilibrium (500 °C)	0.24	9.5	16.2

From the table above, we can see that the yield of ammonia has increased upon increasing the total pressure on the system. That is, the system has shifted to the right towards forming less number of moles (or reducing the pressure in the container). In fact, when two moles of ammonia are formed, 3 moles of hydrogen gas and one mole of N_2 gas (a total number of four moles) disappear (by reacting) to result in a reduction of less number of moles and hence less total pressure. This observation is general and can be stated as:

For a system in the gaseous phase, an increase in pressure displaces equilibrium towards diminishing the total number of moles (diminishing pressure) and a decrease in pressure displaces the equilibrium towards increasing the total number of moles (increase in pressure).

However, pressure has no effect on a gaseous reaction if there is no change in the number of moles of gaseous reactants and gaseous products on both sides of the balanced equation as in the reaction:

$$N_{2(g)} + O_{2(g)} \rightleftarrows 2NO_{(g)}$$

The effect of a change in temperature

It is important to recognize that although the changes we have just considered may alter the equilibrium position, they do not change the value of the equilibrium constant if the temperature is constant. However, unlike concentration and pressure, temperature affects the value of the equilibrium constant as well as the composition of the components of an equilibrium system. Let us consider the table given below that shows the value of K_p at different temperatures for the synthesis of ammonia, which is an exothermic reaction:

$$N_{2(g)} + 3H_{2(g)} \rightleftarrows 2NH_{3(g)} \qquad \Delta H_1 = -92\ kJ.mol^{-1}$$

The following table shows the variation of K_p with temperature:

T °C	400	500	600
K_P	$1x10^2$	$1.6x10^{-1}$	$3.1x10^{-3}$

From the above experimental data, we can see that the K_p values decrease with an increase in temperature where the equilibrium is shifted to the left side towards forming less ammonia. This observation is general for all exothermic reactions. On the other hand, if we consider the endothermic reaction,

$$N_2O_{4(g)} \rightleftarrows 2NO_{2(g)} \qquad \Delta H = +57\ kJ.mol^{-1}$$

The following table shows the variation of K_p with temperature:

T °C	200	300	400
K_P	$1.9x10^{-6}$	$1.7x10^{-1}$	5.1x10

From the above experimental data, we can see that K_p values increase with a rise in temperature. That is to say that the equilibrium is shifted to the right side favoring the dissociation of N_2O_4. This observation is general for all endothermic reactions. It is worth noting here that K_p and the composition of an equilibrium system for athermic reversible reactions are not affected by change in temperature.


Figure 4.7
H. Le Chatelier (1850-1936). French chemist and metallurgist. Known to have found ways to promote various reactions useful in chemical processes and to increase yields.

Le Chatelier's principle

The effects of different factors on equilibrium were studied experimentally by the French scientist Henri Le Chatelier (Fig. 4.7), who proposed the following generalization to be used in predicting qualitatively the effect of the factors on the position of equilibrium.

If a stress (such as change in concentration, pressure and temperature) is applied to a system at equilibrium, then the equilibrium readjusts itself, if possible, by shifting in a way to reduce or absorb the effect of the stress.

Although Le Chatelier's principle cannot predict the size of the change in the value of the equilibrium constant, yet it predicts correctly the direction of the change.
Let us consider the effect of various changes on the equilibrium position of the endothermic reaction:

$$N_2O_{4(g)} \rightleftarrows 2\ NO_{2(g)} \qquad \Delta H = +\ 57\ kJ.mol^{-1}$$

When $N_2O_{4(g)}$ or $NO_{2(g)}$ is added to the above equilibrium, Le Chatelier's principle predicts that the system is shifted to the side that shows the consumption of part of the added amount of the component.
Or, when a component of the above equilibrium system is removed, the system is displaced to the side that shows the formation of part of this component.

When the pressure on the above equilibrium is increased (by decreasing the volume of container), the equilibrium is shifted to the side that reduces the pressure. That is to say, towards less number of moles (less dissociation of $N_2O_{4(g)}$). Conversely, when the pressure is decreased, the equilibrium is shifted to the side that increases pressure by producing more number of moles towards the formation of more $NO_{2(g)}$ and less $N_2O_{4(g)}$.

To study the effect of change in temperature on the above equilibrium, we treat the heat energy needed for the forward reaction to take place as a reactant and for the reverse reaction as a product as shown in the following equation:

$$N_2O_{4(g)} + \text{Heat} \rightleftarrows 2NO_{2(g)}$$

So, the direction of the shift is predicted in the same way as when an actual reactant is added and when the temperature is increased. That is, the above system is shifted to the right side upon increasing temperature to favor the endothermic reaction in order to consume the heat energy added. Conversely, decreasing temperature favors exothermic reaction to shift the above equilibrium to the left.

Table 4.3 given below summarizes the above ideas and discussion:

Change	Displacement
Addition of $N_2O_{4(g)}$	to the right
Addition of $NO_{2(g)}$	to the left
Elimination of $N_2O_{4(g)}$	to the left
Elimination of $NO_{2(g)}$	to the right
Decrease in pressure (increase in V)	to the right
Increase in pressure (decrease in V)	to the left
Decrease in temperature	to the left
Increase in temperature	to the right

Table 4.3

Displacement of the equilibrium state, for the reaction :

$N_2O_{4(g)} \rightleftarrows 2NO_{2(g)}$ $\quad\quad \Delta H = +57\ kJ.mol^{-1}$

It is important to understand the different factors that influence and control the position of chemical equilibrium to apply their effect on industrial processes. Le Chatelier's principle can be applied to study the effect of changes of these factors on equilibrium systems. The manufacture of a chemical in industry must be based on an economical study by choosing inexpensive reactants and optimum conditions to increase the yield of the product. Chemical engineers, who are in charge of production, study carefully the characteristics of the equilibrium system and choose the proper temperature, pressure and catalyst for maximum yield, at minimum time, and at minimum costs.

Composition of the equilibrium state

When the reaction is reversible in the gaseous phase, we can express the equilibrium position in terms of mole fractions of the components of the gaseous mixture or in terms of mole percentages.

Solved exercise
4

Given

0.05 moles of SO_2 and 0.1 mole of O_2, gases are introduced into a flask of volume one liter at a constant temperature 527 °C. The following equilibrium is established:

$$SO_{2(g)} + \frac{1}{2} O_{2(g)} \rightleftarrows SO_{3(g)}$$

At equilibrium, the number of moles of SO_3 is 0.01 mole and the total pressure of the mixture of gases is 2 atm. Calculate:

a) The mole fraction and the mole percentage of each component at equilibrium.

b) The partial pressure of each component at equilibrium.

Solution

a The mole fraction of a component of a gaseous mixture is equal to:

$$X_i = \frac{\text{Number of moles of component}}{\text{Total number of moles of gases}}$$

The % mole composition is $100X_i$ and the partial pressure of that component is:

$$P_i = X_iP_t.$$

We can put the given information and the results of the solution required in the following table:

b

	$SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftarrows SO_{3(g)}$			Total number of moles
Initial concentration ($mol.L^{-1}$)	0.05	0.1	0	0.15
Change of concentration ($mol.L^{-1}$)	-0.01	-0.005	+0.01	
Equilibrium concentration ($mol.L^{-1}$)	0.04	0.095	0.01	0.145
Mole fraction	0.276	0.655	0.069	
Mole percentage	27.6	65.5	6.9	
Partial pressure (atm)	0.552	1.31	0.138	

Degree of conversion and degree of dissociation

In a chemical reaction the degree of conversion of a substance is defined as the fraction of mole of that substance which reacts out of one mole.

The degree of conversion is referred to as the degree of decomposition when one mole of a reactant only decomposition into different substances. The partial pressures of different gaseous components of a system at equilibrium and the equilibrium constants Kp and Kc can be expressed in terms of the degree of the conversion of a reactant in an equilibrium system.

Solved exercise 5

Given

The equilibrium conversion of methane $CH_{4(g)}$ is established at a constant temperature T according to the following reaction:

$$CH_{4(g)} + H_2O_{(g)} \rightleftarrows CO_{(g)} + 3H_{2(g)}$$

Starting with an equimolar mixture consisting of one mole of each of CH_4 and H_2O, and knowing that the pressure of the mixture of gases at equilibrium is P_e = 1 atm, Express in terms of α, the degree of conversion of methane:

a) The partial pressures of the components of the mixture at equilibrium.

b) The equilibrium constant K_p and K_c at temperature T.

Solution

a Let us represent the information given and the partial pressures of the components of the gases in the mixture of gases at equilibrium in the table below:

	$CH_{4(g)}$ +	$H_2O_{(g)} \rightleftarrows$	$CO_{(g)}$ +	$3H_{2(g)}$	Total number of moles
Initial amounts (mol)	1	1	0	0	2
Change by reaction (mol)	$-\alpha$	$-\alpha$	$+\alpha$	$+3\alpha$	
moles at equilibrium (mol)	$1-\alpha$	$1-\alpha$	α	3α	$2(1+\alpha)$
Partial pressure (atm)	$\frac{1-\alpha}{2(1+\alpha)}$	$\frac{1-\alpha}{2(1+\alpha)}$	$\frac{\alpha}{2(1+\alpha)}$	$\frac{3\alpha}{2(1+\alpha)}$	

b To express K_p in terms of α, we write the equilibrium expression of K_p first, and then substitute the partial pressures of the components in terms of α from the above table.

$$K_p = \frac{P_{CO} \times P^3_{H_2}}{P_{CH_4} \times P_{H_2O}}$$

By replacing each term by its value we get:

$$K_p = \frac{27\alpha^4}{4(1-\alpha^2)^2}$$

To find K_c we write:

$$K_p = K_c\,(RT)^{\Delta n}$$

$$\Delta n = (1 + 3) - (1 + 1) = 2.$$

$$K_p = K_c\,(RT)^2$$

$$K_c = \frac{27\alpha^4}{4(1-\alpha^2)^2}\ (RT)^{-2}$$

The maximum yield of a product in a reversible reaction is obtained at a temperature and a total pressure called optimum conditions which renders maximum α.

4.5 Solubility equilibria and the solubility product

Salts were described before as soluble and insoluble in water. However, most insoluble salts dissolve in water to a small degree; which used to be neglected. When 36 g of sodium chloride are added to 100 g of water at 20 °C, all of the salt dissolves completely. Yet, if you add just a bit more and stir, then none of this extra amount dissolves (Fig 4.8). The point at which the solution can't accept any more sodium chloride to dissolve in is called the saturation point and the solution obtained is referred to as a saturated solution. Therefore, a saturated solution contains the maximum amount of solute for a given amount of solvent at a given temperature. An unsaturated solution contains less solute than a saturated solution.

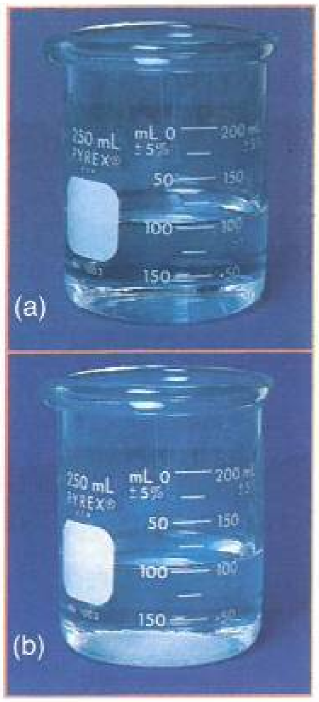


Figure 4.8

a) At 25 °C, 36 g of $NaCl_{(s)}$ dissolve in 100 g of water.

b) An extra mass of $NaCl_{(s)}$ doesn't dissolve in the previous solution.

The maximum amount of a compound that dissolves in a given quantity of solvent at a given temperature to produce a saturated solution, is referred to as the solubility of this compound in the solvent at that temperature.

- Solubility can be expressed in moles of solid solute dissolved in 1 liter of solution

When an ionic solid dissolves in water, it dissociates into separated cations and anions.

A slightly soluble ionic compound as $Ca(OH)_{2(s)}$ dissolves to a little extent in water to form ions and leads to a saturated solution (Fig. 4.9). Any extra amount of this solid added after saturation will precipitate. So, when a saturated solution of a slightly soluble salt is formed, the concentration of the ions becomes constant and hence a state of dynamic equilibrium is established between the solid salt and its dissolved ions. That is to say that at every instant there is as much moles of solid that dissolve as moles which precipitate.

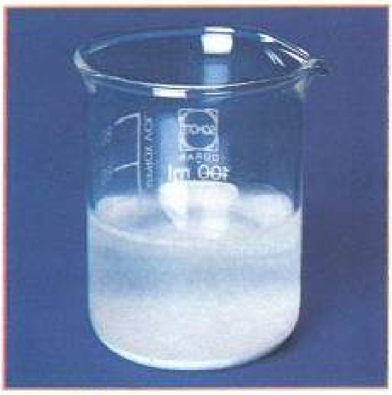


Figure 4.9

$Ca(OH)_{2(s)}$ is slightly soluble in water.

For example when a slightly soluble ionic compound $A_mB_{n(s)}$ is dissolved in water, the equilibrium reaction is represented by the equation:

$$A_mB_{n(s)} \underset{\text{Precipitation}}{\overset{\text{Dissolution}}{\rightleftarrows}} mA^{n+}_{(aq)} + nB^{m-}_{(aq)}$$

At a certain temperature, the law of chemical equilibrium for the above system can be written as:

$$K_{sp} = [A^{n+}]^m \, [B^{m-}]^n$$

Where K_{sp} is the equilibrium constant related to solubility equilibria, and is called the solubility product constant. The K_{sp} constant has one value for a given solid at a given temperature. This value is equal to the product of the concentrations of the ions produced in a saturated solution at a specific temperature.

- Commonly, the constant K_{sp} is called the solubility product.

This product $[A^{n+}]^m [B^{m-}]^n$ is called ionic product (I.P.) of the solution.
For example in the equilibrium system:

$$Ca(OH)_{2(s)} \underset{\text{Precipitation}}{\overset{\text{Dissolution}}{\rightleftarrows}} Ca^{2+}_{(aq)} + 2HO^-_{(aq)}$$

and the solubility product K_{sp} is given by:

$$K_{sp} = [Ca^{2+}]\,[HO^-]^2$$

Remark: The K_{sp} values give us information about the solubility of a salt in water. When a saturated solution of $Ca(OH)_2$ in water is obtained, the concentrations of the ions formed rely on the solubility of the solid in water. For example in the case of $Ca(OH)_2$, the molar concentration of $[Ca^{2+}]$ is equal to the solubility of $Ca(OH)_2$ in water expressed as s mol. L^{-1}. Thus, we can write:

$$[Ca^{2+}] = s \text{ and } [HO^-] = 2s.$$

and consequently $K_{sp} = [s]\,[2s]^2 = 4s^3$

■ Formation of precipitate

A saturated solution of a slightly soluble ionic solid $A_mB_{n(s)}$ exists only when the ion product I.P. is equal to K_{sp}.

$$I.P. = K_{sp}$$

This leads us to say that if I.P. is less than K_{sp}, then the solution is unsaturated because this solution contains less dissolved solute than a saturated solution. On the other hand, when I.P exceeds K_{sp}, some of the salt will precipitate to lower the concentration of ions till I.P. is equal to K_{sp}. Thus, we can summarize the above ideas with the following:

$I.P. = K_{sp}$	Saturated solution
$I.P. < K_{sp}$	Unsaturated solution
$I.P. > K_{sp}$	Precipitation occurs

■ The situation of increasing the concentration of an ion in dissolution - precipitation equilibrium is called common ion effect. It shows that a salt is soluble in water more than in a solution containing any of its own ions.

■ Displacement of dissolution - precipitation equilibrium

Le Chatelier's principle can also be applied to study the effect of change of concentration and of temperature on ionic equilibrium (dissolution precipitation).

Let us consider the equilibrium of the dissolution of calcium carbonate, which is an endothermic reaction, according to following equation:

$$CaCO_{3(s)} + \text{heat} \rightleftarrows Ca^{2+}_{(aq)} + CO^{2-}_{3\,(aq)}$$

■ I.P. is analogous to Q.

Upon increasing the concentration of one of the ions $Ca^{2+}_{(aq)}$ or $CO^{2-}_{3(aq)}$ in the solution, the above equilibrium is displaced to the left side to consume some of the added amounts of ions to cause more precipitation. Conversely, the above equilibrium is displaced to the right side, and moves towards dissolution when one of the ions Ca^{2+} or $CO^{2-}_{3(aq)}$ is removed from the solution.

Upon increasing temperature, Le Chatelier suggests that the endothermic reaction is favored where the above equilibrium is shifted to the right; thus favoring dissolution. Whereas decreasing temperature shifts the above equilibrium to the left; thus favoring precipitation.

The pH of a solution can greatly affect the solubility of compounds in water. For example, magnesium hydroxide $Mg(OH)_{2(s)}$dissolves in water according to the following equilibrium.

$$Mg(OH)_{2(s)} \rightleftarrows Mg^{2+}_{(aq)} + 2HO^{-}_{(aq)}$$

Upon adding HO^{-} to the above solution (an increase in pH), by common ion effect, the above equilibrium is shifted to the left, decreasing the solubility of $Mg(OH)_2$ .On the other hand, an addition of H^{+} ions (a decrease in pH) removes HO^{-} from the solution to shift the equilibrium to the right, and increases the solubility of $Mg(OH)_2$.

Chapter review

- A reversible reaction is a reaction that takes place in two opposite directions; thus it is not a complete reaction. In a reversible reaction, the two opposite reactions reach a stable state called equilibrium.

- An equilibrium state of a reaction system is characterized by an unchanged overall composition of its components over time.

- An equilibrium state of a reaction system is characterized by a constant called equilibrium constant, which is defined by the law of mass action.

- The equilibrium constant relative to concentration is designated by K_c. The equilibrium constant relative to partial pressure is designated by K_p. The two constants are given by the relation:

$$K_P = K_C\,(RT)^{\Delta n}$$

- There are three factors that affect an equilibrium system: concentration of components, pressure, and temperature.
  A catalyst doesn't affect an equilibrium state.

- Le Chatelier's principle can predict qualitatively the effect of changes of different factors on equilibrium by displacing the equilibrium to the side that reduces or opposes the change.

- For the dissolution of a slightly soluble ionic solid in water, we can write:

I.P.$= K_{sp}$	Saturated solution
I.P.$< K_{sp}$	Unsaturated solution
I.P.$> K_{sp}$	Precipitation occurs

Laboratory Investigation

LI

Study of the kinetic curves for esterification of acetic acid CH_3COOH with ethyl alcohol C_2H_5OH

Objective

Study the kinetic curves for the esterification reaction.

Equipment and reagents

Five test tubes with five rubber stoppers with fitted glass tubing to serve as air condenser. 250 mL Erlenmeyer flask. Hot water bath with a thermostat. 15 mL graduated pipet. 1 mL pipet. Digital thermometer. 25 mL buret. 250 mL beaker. Magnetic stirrer. Magnetic bar. Chronometer, 50 mL graduated cylinder.

Products

Acetic acid ($\rho = 1.05$ kg.L^{-1}). Ethyl alcohol ($\rho = 0.79$ kg.L^{-1}). Concentrated sulfuric acid. 2 mol.L^{-1} sodium hydroxide solution. Phenolphthalein solution.

Procedure

- Place 0.2 mol of acetic acid (11.5 mL measured by the dry graduated pipet) in a 250 mL Erlenmeyer flask and add 1.8 mL of the concentrated sulfuric acid.
- Pour 0.2 mol of ethyl alcohol (11.7 mL taken by a dry pipet) into the flask and quickly stir the mixture and distribute it into five test tubes as 4 mL in each tube. At the instant of mixing where the reaction starts, set on the chronometer.
- Put a stopper on each of the five tubes and place them in the hot water bath maintained at a constant temperature of 40 °C (Fig. 4.10).
- After an interval of fixed time (5 minutes), remove one of the tubes and pour its contents into a 250 mL beaker containing 50 mL of cold water. Make sure you wash the test tube with cold water while pouring its contents into the beaker. Add few drops of phenolphthalein.

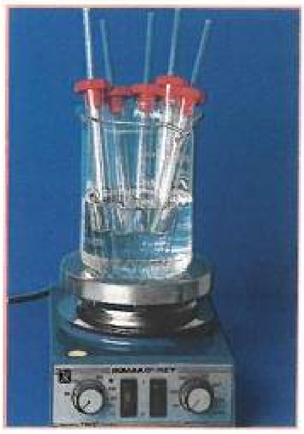


Figure 4.10

The five test tubes placed in a hot water bath maintained at a temperature of 40 ° C.

- Titrate the acid contained in the beaker with the standard NaOH solution and record the volume used to reach the end point.
- Repeat titrating the acid solution present in each of the other four test tubes with the standard sodium hydroxide solution at successive equal intervals of time (5 minutes). Record the volume of the base NaOH used every time (V).

Titration of sulfuric acid

- Prepare a mixture made of 23.2 mL of water and 1.8 mL of concentrated sulfuric acid.
- Stir well and titrate 4 mL of the acidic solution with the standard sodium hydroxide solution. Record the volume needed to reach the end point (V_1).

Titrating the initial quantity of acetic acid in each tube

- Prepare a mixture of 11.5 mL of acetic acid and 11.7 mL of water to which 1.8 mL of concentrated sulfuric acid is added.

- Shake the mixture well and take 4 mL sample to titrate with the standard sodium hydroxide solution. Record the volume of basic solution used to reach the end point (V_2).

Interpretation of the results

$$CH_3COOH + C_2H_5OH \rightleftarrows CH_3COOC_2H_5 + H_2O$$

▪ Sulfuric acid is used in the above reaction as a catalyst to speed up the esterification reaction because it is slow. The amount of sulfuric acid remains unchanged at the end of the reaction. Designating V_1 as the volume of the basic solution used for the titration with the sulfuric acid only and C_b as the concentration of the standard basic solution. The number of moles of NaOH is equal to:

$$n_b = C_b \times V_1$$

This number of moles should be subtracted from the number of moles of NaOH used in every titration made for each test at different intervals of time (5 minutes each) even before the reaction at t_0.

▪ The initial number of moles of acetic acid (pure) present in each tube can be determined by the relation:

$$n_o = C_b(V_2 - V_1)$$

Where V_2 is the volume of the base used for the titration of the total amount of acid (sulfuric and acetic acid).

▪ The kinetic curve of acetic acid represents the variation of the quantity of acetic acid remaining with time as: $n_r = f(t)$ where n_r is the number of moles of acetic acid remained.

Since we started with equal number of moles of acetic acid and ethyl alcohol (equimolar mixture), then according to the overall equation of the reaction, the variation of ethyl alcohol with time is the same as acetic acid and hence the same kinetic curve appears graphically $n_r = f(t)$.

In fact at every instant:

$$n_r(\text{acid}) = n_r(\text{alcohol})$$

Similarly $\quad n_f(\text{ester}) = n_f(\text{water})$

Where n_f is the number of moles of each of the ester and water formed at the same instant.

We can also say that the number of moles of ester formed (or water) is equal to the number of moles of acetic acid (or alcohol) disappeared (n_d) at the same instant.

If V is the volume of sodium hydroxide solution used for the titration in order to determine the amount of acetic acid remaining in each tube at instant t, then we can write:

$$n_r(\text{acid}) = C_b(V - V_1) \qquad (1)$$

and $\quad n_d(\text{acid}) = n_o - n_r(\text{acid})$

$$n_d(\text{acid}) = C_b(V_2 - V_1) - C_b(V - V_1)$$

$$n_d(\text{acid}) = C_b(V_2 - V)$$

This also gives:

$$n_f(\text{ester}) = n_f(\text{water}) = C_b(V_2 - V) \qquad (2)$$

Relation (1) allows us to plot the kinetic curves of acetic acid and ethyl alcohol and relation (2) allows us to plot the kinetic curves of the ester and water.

Example of results

The following table shows the volumes of basic solution used for the titration of the acidic solutions in the five test tubes at equal successive intervals of time. It also gives the values of number of moles of acetic acid (or alcohol) remaining and the number of moles of ester (or water) formed.

Time (min)	V(mL)	n_f(acid) (mmol)	n_f(ester) (mmol)
0	21.4	30.95	0
5	16.7	22.10	8.85
10	14.1	17.00	13.95
15	12.6	14.00	16.95
20	12.0	13.00	17.95
25	10.6	10.30	20.65

Data table

On a graph paper, we trace the kinetic curve of acetic acid (Fig. 4.11) and the kinetic curve of ester formed (Fig. 4.12).

The two curves show that the reaction stops after 25 min where in the 4 mL volume of mixture, only 10.3×10^{-3} mol of acetic acid remains and 20.65×10^{-3} mol of ester is formed.

The percent yield, by moles, of the esterification is equal to:

$$\%\,\text{yield} = \frac{\text{Moles of ester formed (actual)}}{\text{Moles of ester formed (theorotical)}} \times 100$$

$$= 66.7\ \%$$

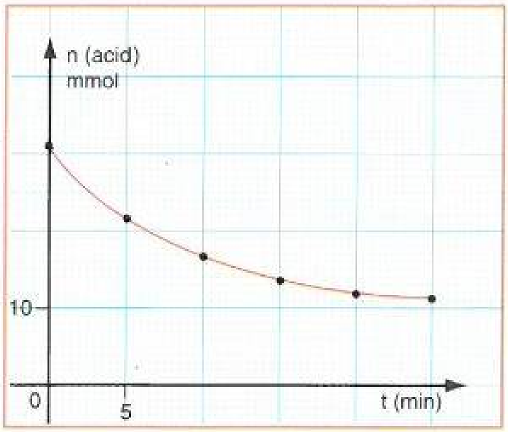


Figure 4.11

Kinetic curve of acetic acid (or ethyl alcohol).

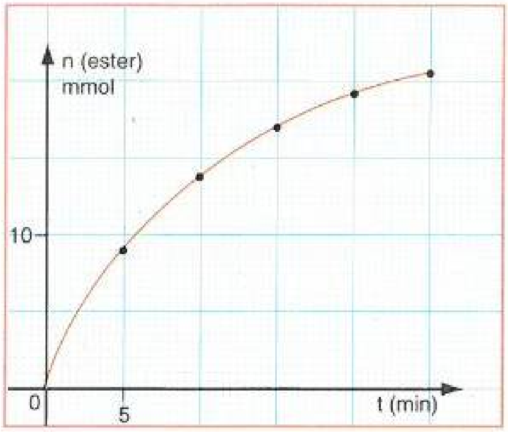


Figure 4.12

Kinetic curve of ester (or water).

Exercises

1 Consider the following table for the equation of the reaction:

$$A_{(g)} + B_{(g)} \rightleftarrows 2\ C_{(g)}$$

Time(s)	0	10	20	30	40	50
[A]	0.080	0.050	....	....	0.015	.....
[B]	0.100	....	....	0.040	....	.....
[C]	0.000	....	0.100	....	....	0.130

At what time does the above reaction system reach equilibrium?

2 Write the equilibrium expression K_c for the following reversible reactions:

a) $Cl_{2(g)} + 2\ NO_{(g)} \rightleftarrows 2\ NOCl_{(g)}$

b) $NH_{3(g)} + H_2S_{(g)} \rightleftarrows NH_4HS_{(s)}$

c) $CO_{2(g)} + H_{2(g)} \rightleftarrows CO_{(g)} + H_2O_{(l)}$

3 Write the expression for K_p for the following equilibrium reactions:

a) $CO_{2(g)} + MgO_{(s)} \rightleftarrows MgCO_{3(s)}$

b) $NH_4Cl_{(s)} \rightleftarrows NH_{3(g)} + HCl_{(g)}$

c) $CO_{(g)} + 3\ H_{2(g)} \rightleftarrows CH_{4(g)} + H_2O_{(g)}$

4 Consider the following:

$$PCl_{5(g)} \rightleftarrows PCl_{3(g)} + Cl_{2(g)}$$

One mole of PCl_5 is placed in a 4 L box to dissociate at a constant temperature T. The number of moles of Cl_2 formed at equilibrium is 0.25 mole.

Calculate the value of K_c of the above system at T.

5 At 100 °C, the equilibrium constant for the reaction system,

$$COCl_{2(g)} \rightleftarrows CO_{(g)} + Cl_{2(g)}$$

is $K_c = 2.19 \times 10^{-10}$

a) Determine whether each of the following mixtures of components of the above system are at equilibrium:

1) $[COCl_2] = 3.50 \times 10^{-3}\ mol.L^{-1}$
$[CO] = 1.20 \times 10^{-5}\ mol.L^{-1}$
$[Cl_2] = 3.30 \times 10^{-6}\ mol.L^{-1}$.

2) $[COCl_2] = 1.50\ mol.L^{-1}$
$[CO] = [Cl_2] = 1.50 \times 10^{-6}$.

b) If the above concentrations are not equilibrium concentrations, in what direction will each system proceed to reach equilibrium?

6 One mole of solid $NH_4Cl_{(s)}$ is heated in a closed box to decompose it partially according to the following reaction:

$$NH_4Cl_{(s)} \rightleftarrows NH_{3(g)} + HCl_{(g)}$$

a) Calculate K_p of the above system at the temperature of the experiment if the partial pressure of ammonia at equilibrium is 1.6 atm.

b) What happens to K_p and the partial pressure of HCl(g) if:

- Some NH_3 gas is pumped into the box at same T.
- More $NH_4Cl_{(s)}$ is added without changing T.
- The volume of the box is reduced 50% at same T.

7 The equilibrium constant K_p for the reaction:

$$CCl_{4(g)} \rightleftarrows C_{(s)} + 2\ Cl_{2(g)}$$

at 700 °C is 0.76 atm.

Determine the initial pressure of carbon tetra - chloride gas that will produce a total equilibrium pressure of 1.2 atm at 700 °C.

8 In a closed container, 0.2 mole of $CO_{2(g)}$ is heated with excess solid carbon. The following equilibrium is established:

$$CO_{2(g)} + C_{(s)} \rightleftarrows 2\ CO_{(g)}$$

The average molar mass of the gaseous mixture at equilibrium is 35.2 g.mol^{-1}.

a) Calculate the mole fraction of CO and CO_2 at equilibrium.

b) Calculate K_p when the total pressure at equilibrium is 10 atm.

9 In a closed container of volume V and at a constant temperature T = 300K, we introduce 2 mol of $NO_{(g)}$ and 1 mol of $O_{2(g)}$. The following equilibrium is established:

$$2\ NO_{(g)} + O_{2(g)} \rightleftarrows 2\ NO_{2(g)}$$

Let α be the degree of conversion of $NO_{(g)}$ to $NO_{2(g)}$ and P_t the total pressure of the mixture of gases at equilibrium:

a) Express in terms of α and P_t the partial pressure of each gaseous component at equilibrium.

b) Calculate α if the partial pressure of $NO_{2(g)}$ at equilibrium is three time that of $O_{2(g)}$.

c) Calculate in terms of α, the mean molar mass of the mixture of gases at equilibrium.

10 Ethylamine $C_2H_5NH_{2(g)}$ is put in an empty flask of volume V, maintained at a constant temperature T = 500K.

The following equilibrium is established:

$$C_2H_5NH_{2(g)} \rightleftarrows C_2H_{4(g)} + NH_{3(g)}$$

Knowing that the initial pressure of ethylamine is 2 atm and the total pressure of the mixture of gases at equilibrium is 3.2 atm, calculate:

a) The degree of dissociation of ethylamine.

b) The equilibrium constant K_p at 500K.

c) How does α, the degree of dissociation vary upon decreasing the volume of the container.

11 Calculate the molar concentration of the ions in a saturated solution of $Ca(OH)_2$ at a temperature T, knowing that K_{sp} of $Ca(OH)_2$ is 4×10^{-6} at that temperature.

12 Given: A saturated solution of $Mg(OH)_2$.

How does the pH vary when the above given solution is treated with few drops of (neglect the volume of drops added) solutions of:

a) $HCl_{(aq)}$

b) $MgCl_{2(aq)}$?

13 The K_{sp} of PbI_2 is 4×10^{-8} at 25 °C.

a) Calculate the solubility of PbI_2 in pure water.

b) What happens when 10 mL of 0.02 mol. L^{-1} of potassium iodide are mixed with 10 mL of 0.02 mol. L^{-1} of lead nitrate $Pb(NO_3)_2$?

c) What happens when the volume of the above mixture is diluted up to 100 mL?

Evaluation

Applying knowledge

1 For the equilibrium:

$$H_{2(g)} + I_{2(g)} \rightleftarrows 2\ HI_{(g)}$$

The equilibrium constant K_c is equal to 50.5 at 448 °C. If $[H_2]_0 = [I_2]_0 = 1$ mol. L^{-1}. What will the concentration of $H_{2(g)}$, $I_{2(g)}$ and $HI_{(g)}$ be at equilibrium?

2 At 25 °C and 1 atmosphere the following equilibrium is established:

$$2\ NO_{2(g)} \rightleftarrows N_2O_{4(g)}$$

the partial equilibrium pressure of $N_2O_{4(g)}$ is 0.7 atm.

a) Calculate K_P of the above system at 25 °C.
b) Calculate the partial pressure of the above two gases at equilibrium when the total pressure at equilibrium becomes 9 atm and the temperature is still 25 °C.

3 A) Silver chromate $Ag_2CrO_{4(s)}$ is dissolved in pure water at 25 °C. Some quantity remains undissolved even after sufficient stirring. Equilibrium is established in the solution between the dissolved quantity and the solid quantity.
What is the resulting solution called?

B) The concentration of Ag^+ ions in the solution is 1.3×10^{-4} mol. L^{-1}.

a) Write the equation of the dissolution.
b) Calculate the concentration of the CrO_4^{2-} in the solution.
c) Calculate the solubility product K_{SP} of silver chromate Ag_2CrO_4.
d) Calculate the solubility of Ag_2CrO_4.

4 Given: the following data for the % by mass of $NH_{3(g)}$ at equilibrium in a mixture of $H_{2(g)}$, $N_{2(g)}$, and $NH_{3(g)}$ as a function of T and P_{total}: (the experiment is based on using initially a mixture of $H_{2(g)}$ and $N_{2(g)}$ in the ratio of 3:1 mole.)

T °C	300 atm	400 atm	500 atm
400	48	55	61
500	26	32	38
600	13	17	21

a) Write the equation for the manufacture of $NH_{3(g)}$.
b) From the above table, what are the values of temperature and pressure that should be used to obtain the maximum yield of ammonia?
c) Based on the above three experiments:

1) Relate the change of yield (shifting equilibrium) to the change of temperature at a constant pressure.
2) Relate the change of yield to the change of pressure at a constant temperature.

Given: The synthesis of ammonia is exothermic.

5 The first step in the manufacture of nitric acid from ammonia involves the exothermic oxidation of ammonia to nitrogen oxide $NO_{(g)}$ and steam.

a) Write the equation of the above reaction.
b) Predict qualitatively the conditions of temperature and pressure for maximum yield of $NO_{(g)}$ in the equilibrium mixture.
c) The Ostwald's industrial process of the manufacture of $NO_{(g)}$ from $NH_{3(g)}$ implies high temperature of 800 °C and pressure of 7 atm.
1) Are these industrial conditions different from those you have predicted in part (b) for maximum yield of $NO_{(g)}$ at equilibrium?
2) In the case of negative response, how do we justify that the experimental conditions used in industry are different than the theoretical conditions that give maximum yield? Suggest a justification for the above reaction.

Mastery Communicating

6 Given the following data for the unbalanced equation for the change of $A_{(g)}$ into $B_{(g)}$:

$$A_{(g)} \rightleftarrows B_{(g)}$$

t(min)	0	2	4	6	8
P_A(atm)	0.6	0.48	0.39	0.345	0.315
P_B(atm)	0	0.04	0.07	0.085	0.095

a) Using the given data, balance the equation with the simplest whole number coefficients.

b) Has the above system reached equilibrium? Justify.

7 Consider the following table for the reaction at a constant temperature T =100 °C;

$$N_2O_{4(g)} \rightleftarrows 2\ NO_{2(g)}$$

time (s)	0	20	40	60	80	100
$P_{N_2O_4}$ (atm)	1	0.60	0.35	0.22	0.22	0.22
P_{NO_2} (atm)	0	0.80	1.3	1.56	1.56	1.56

a) On the same graph trace the curves corresponding to the change of partial pressures of $N_2O_{4(g)}$ and $NO_{2(g)}$ versus time.

b) How long did it take the above system to reach equilibrium?

c) What will be the partial pressure of $NO_{2(g)}$ after 90 seconds?

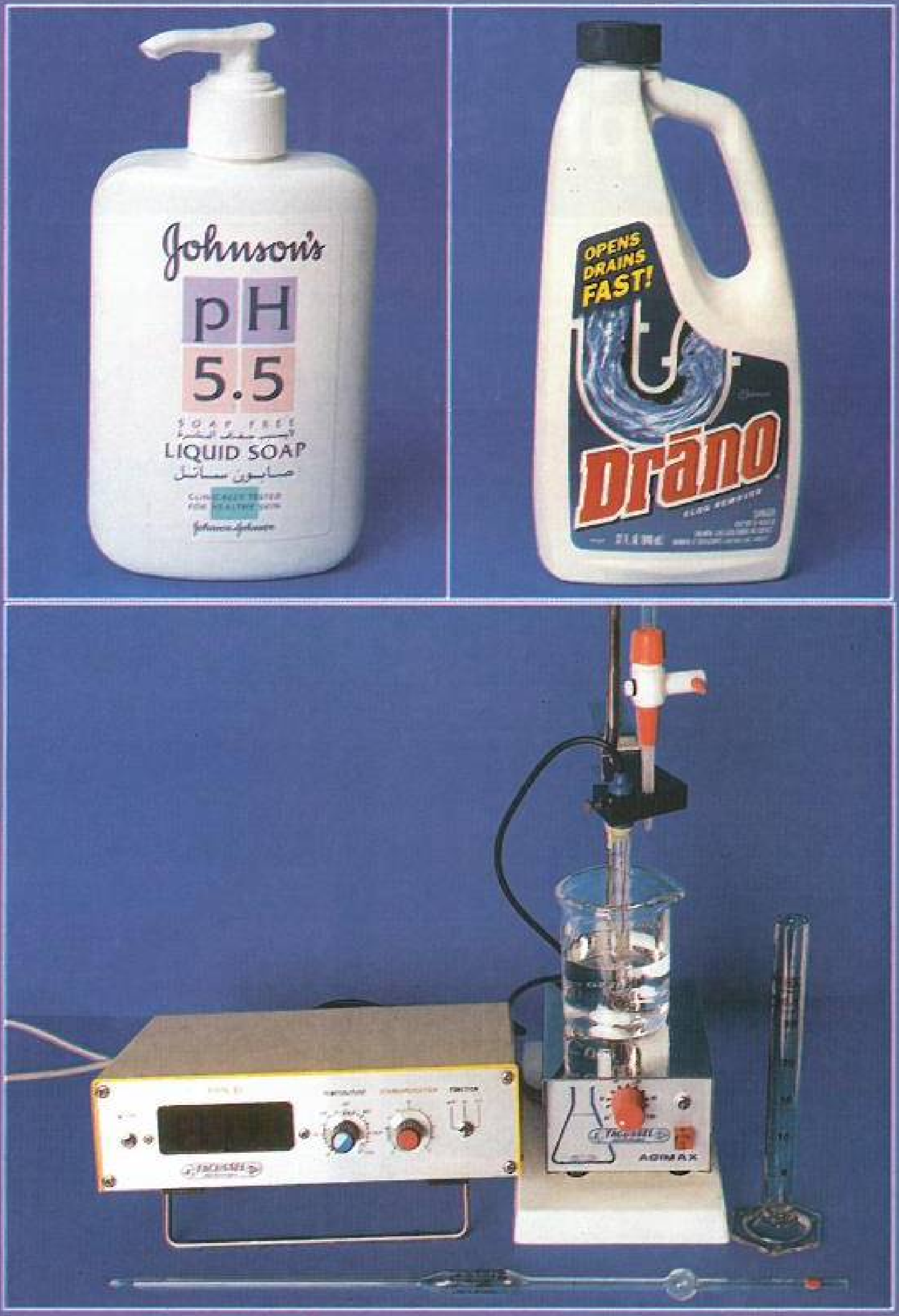
d) Calculate from the above data the equilibrium constant K_p for the system at 100 °C.

e) Compare the rate of disappearance of $N_2O_{4(g)}$ to the rate of formation of $NO_{2(g)}$ during the interval of time 60 - 80 seconds?

4

Acid-Base reaction in aqueous solutions. The pH scale.

Milk, blood, sea water, rain, fruit juice, household products ... are charactarised by their pH whose value is an indication of their acidity, basicity or neutrality.



Bottles of certain common commercial products are labeled with the pH of their solutions. What is pH?

Certain household solutions contain hydrochloric acid or sodium hydroxide. How do these two compounds behave in aqueous solution?

How does the pH of a solution vary in an acid- base titration?

pH. STRONG ACID
STRONG BASE
pH-METRIC TITRATION

5

Objectives

- Measure the pH of an aqueous solution.
- Identify a strong acid and a strong base after measuring the pH of their aqueous solutions.
- Master the experimental study of the pH-metric for the reaction of a strong acid with a strong base in aqueous solution.
- Perform the titration techniques between acidic and basic solutions by using a pH meter.

Prerequisites

- Notion of an acid, a base, and pH.
- Notion of an electrolyte.
- Dissolving properties of water.
- Concentration of a solution.
- Preparation of a solution of given concentration.

Chapter content

5.1 Definition and measurement of pH.

5.2 Study of the pH changes that occur during the reaction between a solution of a strong acid and a strong base. Equivalence point.

5.3 Acid – base titration using pH meter.

- Chapter review
- Method sheet
- Laboratory investigations
- Exercises

The elaboration of the notions of acids and bases comprise an important step in the development of chemistry in science.
Acids and bases have been a source of environmental problems and manufacturing processes for engineers. They play an important role in much of the chemistry that affects our daily lives.
Acids and bases have been known and utilized for a long time. The first acid was known in 3000 years BC; it was vinegar. Almost the same time, the Egyptians used the first known base, natural sodium carbonate for mummification.

5.1 Definition and measure of pH

Figure 5.1
Svante Arrhenius (1859-1927). Swedish physicist and chemist who introduced the theory of ionization.
He won the Noble prize in1903.

Scientists relate the properties of aqueous solutions of acids and bases to their structure. In 1880, the Swedish Chemist Savnte Arrhenius (Fig. 5.1) proposed that acids were substances containing hydrogen that ionize in water to produce hydrogen ion, H^+ while bases were substances that produce hydroxide ions OH^- in water.
(Arrhenius definitions of acids and bases are limited because they only apply to aqueous solutions).
Chemists realized that the ion H^+ was simply a proton and too small to exist independently in aqueous solution, but the H^+ ions were believed to be associated with the polar water molecules to form the hydronium ions H_3O^+. The H_3O^+ ion characterizes acidic properties but it is present in neutral and basic solutions and hence its concentration is used to determine whether a solution is acidic, neutral, or basic.
In 1909 a Danish biochemist Sorenson (1868 – 1939) (Fig. 5.2) proposed an alternative method of specifying the $[H_3O^+]$ concentration to describe the acidity of an aqueous solution, which is known as the pH scale. Sorensen defined the pH of a solution as the negative logarithm of the hydronium ion concentration in mol. L^{-1}.

- The pH has no dimension. The negative sign (-) is put with the expression of log to make the value of pH positive.
The notation pH is an abbreviation of the term "hydrogen potential".

$$pH = -\log [H_3O^+]$$

The pH of a solution is the negative of the logarithm of the H_3O^+ ions concentration, expressed in mol.L^{-1}, in the solution.

$$pH = -\log [H_3O^+]$$

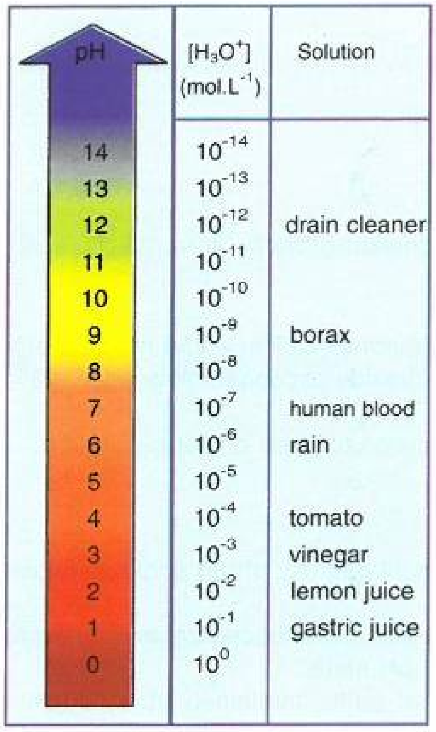
This relation is equivalent to :

$$[H_3O^+] = 10^{-pH}$$

For example, a solution of $[H_3O^+] = 10^{-4}$ mol L^{-1} has a pH value of 4. And a solution of pH = 3 has a concentration of $[H_3O^+]$ equal to 10^{-3} mol L^{-1}.

Experiments show that the preceeding definition is not valid for concentrated solutions. A solution of $[H_3O^+] = 1 \times 10^{-1}$ mol.L^{-1}, for example, has pH = 1.1 and not 1, as the above relation

Figure 5.2
Sören Sörensen (1868-1939)
A Danish Chemist who defined pH as a measure of acidity in aqueous solutions.



pH	$[H_3O^+]$ $(mol.L^{-1})$	Solution
14	10^{-14}	
13	10^{-13}	
12	10^{-12}	drain cleaner
11	10^{-11}	
10	10^{-10}	
9	10^{-9}	borax
8	10^{-8}	
7	10^{-7}	human blood
6	10^{-6}	rain
5	10^{-5}	
4	10^{-4}	tomato
3	10^{-3}	vinegar
2	10^{-2}	lemon juice
1	10^{-1}	gastric juice
0	10^{0}	

Figure 5.3
Theoretical values of pH scale.

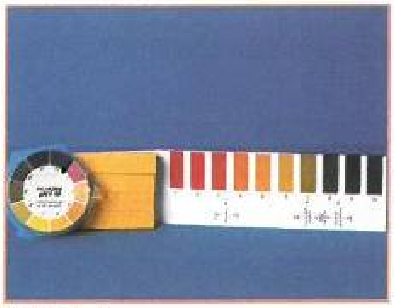


Figure 5.4
pH paper.

- We never immerse the pH paper in the solution.

should have given.
In fact, this relation is not applicable except for concentrations of $[H_3O^+] \leq 5 \times 10^{-2}$ mol.L^{-1}.
Our study is limited to this condition of concentration.
The presence of the – sign in the equation $pH = -\log [H_3O^+]$ indicates that $[H_3O^+]$ and pH vary inversly.

The higher the value of $[H_3O^+]$ concentration, the lower is the corresponding pH value.

pH scale

$[H_3O^+]$ concentrations in most aqueous solutions are quite small and lie between 10^{-14} mol L^{-1} and 1 mol L^{-1}. The range of pH values for these solutions is therefore between 0 and 14. Figure 5.3 shows the pH scale with the approximate pH's of some common substances

Measurement of pH

The pH of a solution can be measured preliminarily by using indicators, which are usually organic compounds that have different colors in acidic or basic solution. Strips of papers (pH papers) imprignated with a mixture of several indicators, then dried, are used to test the pH of a substance (Fig. 5.4).
The indicator undergoes a change in color over a specific range of pH of approximately two units (Fig. 5.5) shows the pH range and the color range of a indicators at 25 °C.

To measure the pH of a solution with a pH paper, you add a drop of the solution to a pH paper strip that can change color. This is then compared to a color chart which reads the approximate pH of the solution.

A more rapid and accurate measurement of pH can be carried out by using a pH meter which is an electronic device that reads usually the pH value within a range of 0.02 units. (Fig. 5.6) (Different pH meters have different ranges of precision)

Auto-ionization of water

Experiments have shown that pure water is a very weak conductor of electricity due to the few limited number of ions formed by the auto-ionization of water as it appears in the following reaction

$$2H_2O \rightarrow H_3O^+ + OH^-$$

The self ionization of water occurs to a very small extent and is limited to the reverse reaction association of ions according to the following:

$$H_3O^+ + OH^- \rightarrow 2H_2O_{(l)}$$

The above two reactions occur simultaneously and lead to the equilibrium of the autoionization of water represented by:

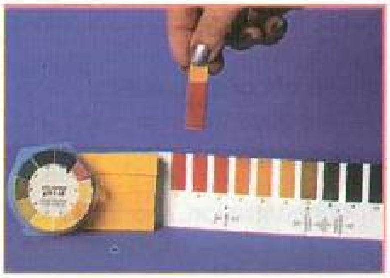


Figure 5.5
The color of the indicator paper is compared to a range of colors corresponding to known values of pH.

$$2H_2O \rightleftarrows H_3O^+ + OH^-$$

This equilibrium is characterized by an unchanged overall composition at a given temperature.
This is represented by the equilibrium constant expression:

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

The concentration of water $[H_2O]$ in pure water and diluted aqueous solutions is constant (55.55 mol L^{-1}). So the expression of K can be written after rearrangement as,

$$K_w = K\,[H_2O]^2 = [H_3O^+]\,[OH^-]$$

where Kw, referred to as the ion-product constant of water, has a very small value that depends on temperature.

Activity 1

Determination of the ion product for water at 25 °C.

Figure 5.6
The precision of pH measurement depends on the performance of the device and the state of the electrodes.

Objective

Determine the ion-product constant of water, K_w at 25 °C.

Equipment and reagents

pH meter. Water bath with a thermostat.Three 250 mL beakers
Three solutions of sodium hydroxide of concentrations 1×10^{-4}, 1×10^{-3} and 1×10^{-2} mol L^{-1}.
Distilled water. Standard solutions of basic pH for calibration.

Procedure

Calibrate the pH meter.
Rinse each beaker with a small quantity of the solution whose pH is to be measured.
Add enough quantity of each solution to each beaker in order to immerse the electrode of the pH meter.
Place the beakers in a water bath maintained at a constant temperature equal to 25 °C.
Measure the pH of each solution (Fig. 5.7)

Interpretation of the results

Calculate $[H_3O^+]$ for each solution and then compute K_w in each case

$[OH^-]$ (mol.L^{-1})	1×10^{-4}	1×10^{-3}	1×10^{-2}
pH	9.94	11.02	11.97
$[H_3O^+]$ (mol.L^{-1})	1.1×10^{-10}	9.5×10^{-12}	1.1×10^{-12}
K_w	1.1×10^{-14}	9.5×10^{-15}	1.1×10^{-14}

At 25 °C the ion product of water K_w is equal to 10^{-14}.

- The concentrations of $[H_3O^+]$ and $[OH^-]$ are expressed in mol L^{-1}.

- K_w possesses a unit but conventionally we use it without a unit.

- Can we do without using the water bath maintained at constant temperature?
- Can we add distilled water in the beakers, in order to immerse the electrode? Justify your answer.

Figure 5.7

Materials used to determine K_w.

- In all solutions studied in this part K_w is taken at 25 °C which is equal to 10^{-14}.

T °C	K_w
5	1.8×10^{-15}
25	1.0×10^{-14}
35	2.1×10^{-14}
60	9.6×10^{-14}

Table 5.1

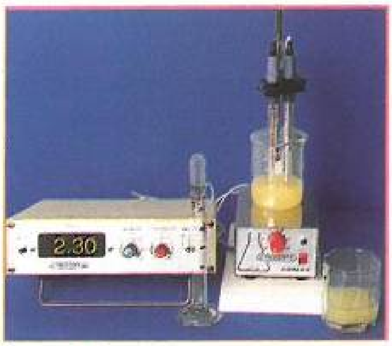


Figure 5.8

Citrus juice has a pH ≅ 2.30

Figure 5.9

Milk of magnesia pH = 9.90

$$K_w = [H_3O^+]\,[OH^-] = 10^{-14}$$

As a conclusion, the ion product of water K_w increases with a rise in temperature as shown in table 5.1.

Classification of aqueous solutions

In pure water, only a minute trace is ionized to give: $[H_3O^+] = [OH^-] = 10^{-7}$ mol. L^{-1} at 25 °C. This implies that the pH of pure water is equal to 7.

In aqueous acidic and basic solutions, H_3O^+ and OH^- ions may arise from sources other than water, but the product $[H_3O^+]\,[OH^-]$ remains constant for all solutions at the same temperature.

$$[H_3O^+]\,[OH^-] = K_w = 10^{-14}$$

Thus, it is possible to determine both the $[H^+]$ and the $[OH^-]$ in any solution. An acidic solution is characterized by the presence of a majority of H_3O^+, that is $[H_3O^+] > [OH^-]$ which makes $[H_3O^+] > 10^{-7}$ mol. L^{-1} and $[OH^-] < 10^{-7}$ mol.L^{-1}.

In terms of pH, an acidic solution is characterized by a pH < 7 (Fig. 5.8).

For example, a solution of hydrochloric acid of $[H_3O^+] = 2 \times 10^{-3}$ mol. L^{-1} possesses a pH equal to 2.67.

A basic solution is characterized by the presence of a majority of OH^-, that is $[H_3O^+] < [OH^-]$ which makes $[H_3O^+] < 10^{-7}$ mol.L^{-1}. In terms of pH a basic solution is characterized by a pH > 7 (Fig. 5.9).

For example, a solution of sodium hydroxide of $[HO^-] = 2 \times 10^{-3}$, possesses a concentration of $[H_3O^+]$ equal to :

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{2 \times 10^{-3}} = 5 \times 10^{-12}\ \text{mol.L}^{-1}$$

The pH is equal to 11.3

A neutral solution is characterized by equal concentrations of the species $[H_3O^+]$ and $[HO^-]$. This solution is characterized by a pH = 7 (Fig. 5.10),

Table 5.2 shows the range of pH value of acidic, basic, and neutral solutions:

Acid solutions	Neutral solutions	Basic solutions
pH < 7	pH = 7	pH > 7
Increasing acidity		Increasing basicity
← Lower pH		Higher pH →

Table 5.2

Classification of aqueous solutions relative to their pH values.

Figure 5.10
Pure water. pH = 7.00

The ion product of water K_w has a very small value and it is convenient to represent its Pk_w as the negative logarithm of base ten as: $PK_w = -\log K_w$

For water: $PK_w = -\log K_w = 14$ at 25 °C

where pK_w depends on temperature. It varies inversely of K_w. PK_w decreases as T increases.

Relative to acidity and as a function of pKw solutions can be divided into three classes:

For an acidic solution we can write:

$$[H_3O^+] > [OH^-]$$
or
$$[H_3O^+]^2 > [HO^-]\,[H_3O^+]$$
$$[H_3O^+]^2 > K_w$$

by taking the negative log form we get:

$$-2\log [H_3O^+] < -\log K_w$$

or $$pH < \frac{1}{2}\,pK_w$$

For a basic solution we can write:

$$[H_3O^+] < [OH^-]$$
or
$$[H_3O^+]^2 < K_w$$

By taking the negative log form we get:

$$-2\log [H_3O^+] > -\log K_w$$
or $$pH > \frac{1}{2}pK_w$$

For a neutral solution we have:
$[H_3O^+] = [OH^-]$ which leads to the relation $pH = \frac{1}{2}pK_w$

Solved exercise 1

Given

Calculate the pH of a hydrochloric acid solution of $[H_3O^+] = 1 \times 10^{-4}$ mol.L^{-1}

Solution

$pH = -\log [H_3O^+]$
By replacing $[H_3O^+]$ by its value we get:
$pH = -\log 10^{-4} = 4$

Solved exercise 2

Given

Calculate the pH of a solution of sodium hydroxide of $[OH^-] = 1 \times 10^{-3}$ mol.L^{-1}

Solution

The ion product of water is $[H_3O^+][OH^-] = K_w = 10^{-14}$

$$[H_3O^+] = \frac{10^{-14}}{[OH^-]} = \frac{10^{-14}}{10^{-3}} = 1 \text{x} 10^{-11} \text{ mol.L}^{-1}$$

or $pH = -\log [H_3O^+] = -\log 10^{-11} = 11$

Solved exercise 3

Given

The label on a bottle of a household product containing ammonium hydroxide solution shows its pH equal to 11.8. Calculate the concentration of H_3O^+ and OH^- in this solution

Solution

The concentration of $[H_3O^+]$ is obtained by the relation,

$$[H_3O^+] = 10^{-pH} = 10^{-11.8}$$

or $[H_3O^+] = 1.58 \text{ x } 10^{-12}$ mol.L^{-1},

since the ion product of water is equal to $K_w = 10^{-14}$, then

$$[OH^-] = \frac{10^{-14}}{1.58 \times 10^{-12}} = 6.33 \times 10^{-3} \text{ mol.L}^{-1}$$

5.1.1 The pH of a solution of a strong acid

When hydrogen chloride $HCl_{(g)}$ gas is dissolved in water, its molecules dissociate completely in water and the following reaction takes place:

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

The solution obtained is acidic and called hydrochloric acid solution. Hydrochloric acid is a strong electrolyte. Each mole of HCl dissociates completely in water to give 1 mole of H_3O^+ ions and 1 mole of Cl^- ions.

- Our study is limited to monoacids.

- We have seen that for solutions of $[H_3O^+] > 5 \times 10^{-2}$ mol.L^{-1}, the relation pH = - log $[H_3O^+]$ is not applicable. This also applies for the relation pH = - log C_a, for $C_a > 5 \times 10^{-2}$ mol.L^{-1}.
For $C_a < 1 \times 10^{-6}$ mol.L^{-1}, the pH of the solution approaches 7, which is the pH of pure water, because the quantity of H_3O^+ ions coming from water is not negligible compared to the quantity of H_3O^+ ions coming from the acid.

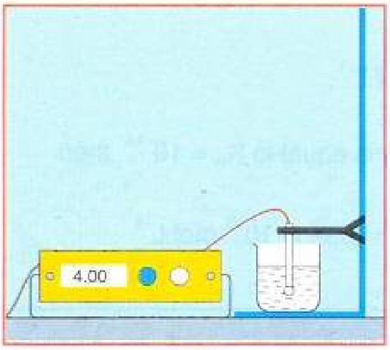


Figure 5.11
The pH of a solution of concentration $C_a = 1 \times 10^{-4}$ mol.L^{-1} is equal to 4.

- Are the $[H_3O^+]$ concentrations different than C_a concentrations?
- What relation will give the pH of these solutions?

Acids that behave similarly by dissociating completely in water as hydrochloric acid are called strong acids.

A strong acid is any chemical species that dissociates completely in water to furnish H_3O^+ ions.

HNO_3, HBr, HI and H_2SO_4 are examples of strong acids. The first three are monoacids, while the latter is a di-acid.

A strong monoacid with a concentration C_a has a concentration of $[H_3O^+] = C_a$ since the dissociation of the acid is complete. In this case, the pH of the solution is equal to - log C_a or pH = - log $[H_3O^+]$ = - log C_a
Where C_a lies in the following range of concentrations:

$$1 \times 10^{-6} \text{ mol.L}^{-1} \leq C_a \leq 5.10^{-2} \text{ mol.L}^{-1}$$

For dilute acidic solutions, the pH of a solution of a strong monoacid is given by the relation:

$$pH = - \log C_a$$

C_a is the concentration of the acid.

Activity 2

Measure the pH of hydrochloric acid solution of known concentration

Objective

Identify a strong monoacid after measuring the pH of its solution.

Materials

pH meter. Four 250 ml beakers. Four solutions of hydrochloric acid of the following concentration: 5×10^{-3}, 1×10^{-3}, 5×10^{-4} and 1×10^{-4} mol.L^{-1}.
Standard solutions of known acidic pH for calibration.

Procedure

After calibrating the pH meter with the standard solutions, measure the pH of each of the above hydrochloric solutions (Fig. 5.11). Calculate the concentrations $[H_3O^+]$. Compare the value of pH of each solution with the concentration C_a. Draw your conclusion.

Interpretation

C_a (mol.L^{-1})	5×10^{-3}	1×10^{-3}	5×10^{-4}	1×10^{-4}
$pH_{measured}$	2.3	3	3.3	4
$[H_3O^+]$ (mol.L^{-1})	5×10^{-3}	1×10^{-3}	5×10^{-4}	1×10^{-4}

The obtained results show that the pH of the Hydrochloric acid solutions verify the relation:

$$pH = - \log C_a$$

5.1.2 The pH of a solution of a strong base

Sodium hydroxide is an example of a strong base. In water it dissociates completely into ions according to the following equation:

$$NaOH \xrightarrow{water} Na^+ + OH^-$$

Sodium hydroxide is a strong electrolyte. Each mole of NaOH dissociates almost completely in water to give 1 mole of Na^+ ions and 1 mole of OH^- ions.

Bases that behave in water solutions as sodium hydroxide are called strong bases.

A strong base is any chemical species which dissociates completely in water to give OH^- ions.

The compounds KOH, $Ca(OH)_2$ are examples of strong bases. The first is a monobase and the second is a di-base.

If C_b is the concentration of a strong monobase, then due to its complete dissociation, we can write:

$$C_b = [OH^-]$$

or :

$$C_b = \frac{K_w}{[H_3O^+]}$$

- Our study is limited to monobases.

By rearranging the relation we get:

$$[H_3O^+] = \frac{K_w}{C_b}$$

Taking the negative log form of the relation we obtain:

$$pH = pK_w + \log C_b$$

or :

$$pH = 14 + \log C_b$$

- For $C_b < 1 \times 10^{-6}$ mol.L^{-1}, the pH approaches 7, the pH of pure water, because the quantity of OH^- ions coming from water is not negligible compared to the quantity of HO^- ions coming from the base.

For the same reasons given before for the limitation of the pH of a strong acid, C_b lies in the following range of concentrations:

$$1 \times 10^{-6} \text{ mol.L}^{-1} \leq C_b \leq 5 \times 10^{-2} \text{ mol.L}^{-1}$$

For dilute solutions, the pH of a solution of a strong base is expressed by the following relation:

$$pH = 14 + \log C_b$$

where C_b is the concentration of the base.

Activity 3 Measure the pH of a solution of sodium hydroxide of known concentration

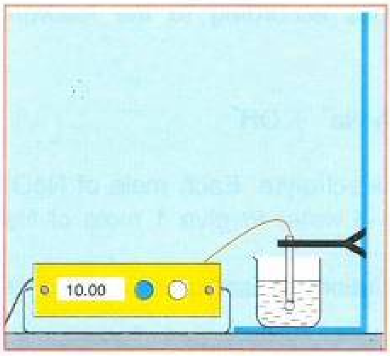


Figure 5.12
The pH of solution of concentration $C_b = 1 \times 10^{-4}$ mol.L^{-1} equals 10.

- Find the relation between the $[H_3O^+]$ and C_b.
- Deduce the relation that gives the pH.

Objective

Identify a strong base after measuring the pH of its solution.

Materials

Same materials as activity 2. Four solutions of NaOH of the following concentrations: 5×10^{-3}, 1×10^{-3}, 5×10^{-4} and 1×10^{-4} mol.L^{-1}.

Procedure

After calibrating the pH meter with the standard solutions, measure the pH of each of the above sodium hydroxide solutions. Record the values (Fig. 5.12). Calculate the concentrations of $[H_3O^+]$. Find a relation between $[H_3O^+]$ and C_b. Draw your conclusion.

Interpretation

C_b (mol.L^{-1})	5×10^{-3}	1×10^{-3}	5×10^{-4}	1×10^{-4}
$pH_{measured}$	11.7	11	10.7	10
$[H_3O^+]$ (mol.L^{-1})	2×10^{-12}	1×10^{-11}	2×10^{-11}	1×10^{-10}
$\frac{K_w}{C_b}$	2×10^{-12}	1×10^{-11}	2×10^{-11}	1×10^{-10}

By comparing the values of $[H_3O^+]$ with the values of the ratio $\frac{K_w}{C_b}$ in the above table, we deduce that the pH of sodium hydroxide solutions can be obtained by the relation:

$$pH = pK_w + \log C_b = 14 + \log C_b$$

5.2 Study of the pH changes that occur during the reaction between a solution of a strong acid and a solution of a strong base. Equivalence point.

- **Reaction between a strong acid and a strong base in an aqueous solution**

In a large beaker, mix 100 mL of 1 mol.L^{-1} hydrochloric acid solution, with 100 mL of 1 mol.L^{-1} sodium hydroxide solution. By stirring and measuring the rise in temperature, the reaction shows that it releases heat energy. After cooling to the same ambient temperature, measure the pH of the resulting mixture.

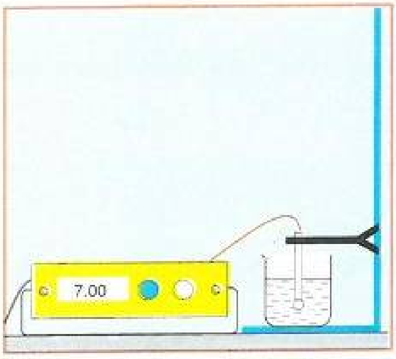


Figure 5.13
The pH at the end of the reaction is equal to 7.

Figure 5.14
White crystals of sodium chloride are obtained after evaporation.

- The proton does not exist in free state in the solution. Its tranfer occurs directly between the reacting species.

The pH meter should read the value 7 to indicate that the solution is neutral (Fig. 5.13).

Take a sample of the resulting mixture and evaporate the solution completely. White crystals of sodium chloride will be formed (Fig. 5.14).

This experimental observation shows that the reaction between a strong acid and a strong base according to the stoichiometric coefficients of the equation, produces a neutral solution. All the ions H_3O^+ and HO^- furnished by the reactants are consumed during the reaction. The Na^+ ions from the base, and the Cl^- ions from the acid, are not involved in the reaction. They are called spectator ions.

▪ Ionic equation of the reaction

The reaction between a strong acid and a strong base in an aqueous solution can be considered as a reaction between the H_3O^+ and OH^- ions which is represented by the equation:

$$H_3O^+ + OH^- \rightarrow 2\,H_2O$$

▪ Nature of the reaction

The above reaction can be explained in two steps. The hydronium ion H_3O^+ donates a proton according to the following equation:

$$H_3O^+ \rightarrow H^+ + H_2O$$

The HO^- ion captures the proton according to the following:

$$OH^- + H^+ \rightarrow H_2O$$

The overall equation for the preceding two steps that represents an acid- base reaction is:

$$H_3O^+ + OH^- \rightarrow 2\,H_2O$$

Consequently, the reaction between an acid and a base in aqueous solution is simply a transfer of a proton from the hydronium ion H_3O^+ to the hydroxide in OH^-.

▪ Characteristics of the reaction

The reaction between a strong acid and a strong base in an aqueous solution according to the stoichiometric proportions is a total and complete reaction. This reaction produces a neutral solution, which results from the complete consumption of H_3O^+ and OH^- furnished by the reactants.

In reality, the reaction is complete, because it is limited to the autoionization reaction of water.

The reaction is exothermic and liberates a constant amount of 57.4 kJ. mol^{-1} of heat energy which is independent of the nature of the strong acid or the strong base.

- **pH-metric study of the reaction**

Activity 4

Changes of pH during the reaction between hydrochloric acid and sodium hydroxide solution.

Objective

pH-metric study of the reaction between a strong acid and a strong base.

Determine the equivalence point.

Equipment and reagents

pH meter. 50 mL buret. 250 mL beaker. 20 mL pipet. Pipet filler. Magnetic stirrer.

10^{-2} mol.L^{-1} hydrochloric acid solution. 10^{-2} mol.L^{-1} sodium hydroxide solution.

Figure 5.15

Set up for the pH-metric study of an acid-base reaction.

Procedure

Calibrate the pH meter and rinse its electrode with distilled water.

Rinse the buret with distilled water then with the sodium hydroxide solution.

Fill the buret to the 0.0 mL reading,

Place, by using a pipet, 20 mL of the above acid in a clean beaker.

Dip the electrode of the pH meter in the acid solution of the beaker and measure its pH. (Fig. 5.15).

Add 2 mL of the basic solution, stir and measure the new pH.

Repeat the addition of the basic solution from the buret progressively and measure the pH corresponding to each additional volume so that the total volume of base added is 30 mL.

During the addition of the basic solution, add 2 mL volumes each time till the pH starts to change more significantly where 0.5 mL volumes are used instead. The data obtained from this experiment are given in the table 5.3.

Plot on a graph the curve representing the pH changes versus the volumes of the basic solution added, pH = f(V_b).

- **curve pH = f(V_b)**

The values in table 5.3 permit us to plot the curve pH = f(V_b) (Fig.5.16).

- Calculate the volume of the sodium hydroxide solution necessary to react completely with the 20 mL of hydrochloric acid solution.
- Locate on the curve pH = f(V_b), the point corresponding to the above volume.

V_b(mL)	pH	V_b(mL)	pH
0	2.0	19	3.6
2	2.1	19.5	4.2
4	2.2	20	7.0
6	2.3	20.5	9.4
8	2.4	21	10.1
10	2.5	22	10.5
12	2.6	24	10.9
14	2.7	26	11
16	2.9	28	11.1
18	3.3	30	11.2

Table 5.3

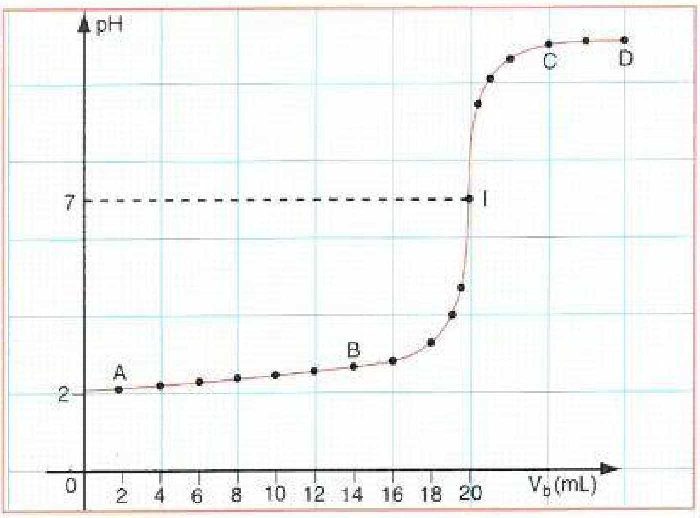


Figure 5.16

The curve representing the changes of pH of hydrochloric acid solution versus the volume of sodium hydroxide solution added is a typical titration curve of a strong acid with a strong base.

This curve is ascending. It consists of three parts.

First, part AB (V_b < 14 mL) which forms a flat-line, where the pH increases very slowly.

Second, part BC (14 mL < V_b < 26 mL) constitutes a jump showing a very sharp change in pH which increases rapidly as the volume approaches and moves beyond V_b = 20 mL. The curve has an inflection point at V_b = 20 mL where the concavity of the curve changes.

Finally, part CD (V_b > 26 mL) shows that the pH increases slowly again approaching a horizontal asymptote and forms a flat-line.

- **curve pH = f (V_a)**

Repeat activity 4 by placing the acidic solution $HCl_{(aq)}$ in the buret instead of the sodium hydroxide solution and replacing the acid in the beaker by the basic solution. The titration curve that shows the change of pH of the basic solution versus the volumes of the acidic solution added progressively appears in the figure 5.17.

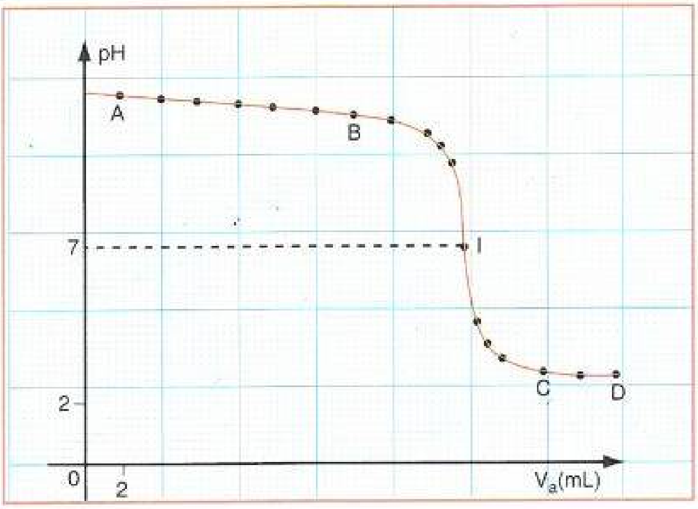


Figure 5.17
Titration curve pH = f(V_a)

This curve is descending. It consists of three parts.
The part AB corresponds to a flat-line of slow change in pH.
The part BC corresponds to a sharp change in pH where a point of inflection exists at $V_a = 20$ mL.
The part CD corresponds to a second flat-line of slow change in pH. In this part the curve approaches a horizontal asymptote.

- **Equivalence point**

The point in the titration at which an amount of base that has been added reacts exactly with all the acid originally used, is called the equivalence point.

At the equivalence point the reactants react in stoichiometric proportions.

On the curve pH = $f(V_b)$ the equivalence point occurs at the volume of base V_{bE}, where exactly enough HO^- has been added to react with all the H_3O^+ originally present.The point on the curve corresponding to V_{bE} is called equivalence point.

The equivalence point on the curve pH = $f(V_b)$ (or the curve pH = $f(V_a)$) corresponds to the volume of the acid or the base which react together according to their stoichiometric proportions.

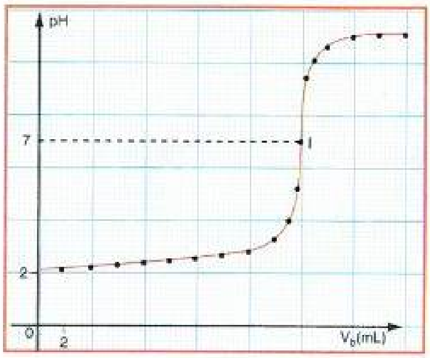


Figure 5.18
The equivalence point corresponds to the point on the curve where pH = 7.

- **Determination of the equivalence point**

For the titration of a strong acid with a strong base in an aqueous solution at 25ºC, the pH of the solution at the equivalence point is equal to 7.
The equivalence point can be determined on the curve pH = $f(V_b)$ at the point of the curve where the pH is equal to 7. (Fig 5.18).
The equivalence point also corresponds to the inflection point of the curve. Another method is used to determine graphically the equivalence point called the parallel tangents. Referring to the graph pH = $f(V_b)$, for example, two parallel tangent lines are drawn to the curve as shown in figure 5.19. Then the point of equivalence is obtained by the intersection of the curve with a parallel line drawn between the two parallel lines and equidistant from them.
At the equivalence point, the number of moles of H_3O^+ ion , $n(H_3O^{+)}$ and the number of moles of OH^-, $n(OH)^-$ which react together are equal.
If V_a is the volume of the acid solution of concentration C_a used in the reaction, and V_{bE} is the volume of the basic solution of concentration C_b needed to reach the equivalence point, then we can write:

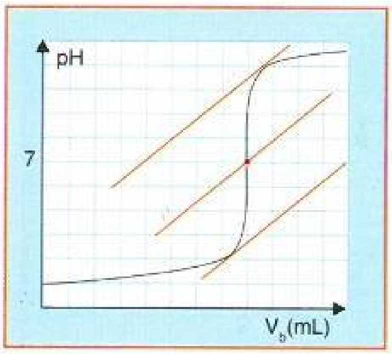


Figure 5.19
The method of parallel tangents permits to determine the equivalence point.

$$n(H_3O^+) = V_a \times C_a$$
$$n(HO^-) = V_{bE} \times C_b$$

- When the acid solution is placed in the buret, the relation that gives the equality of number of moles of H_3O^+ and HO^- ions that reacted at equivalence point is written in the form :

$$V_{aE} \times C_a = V_b \times C_b.$$

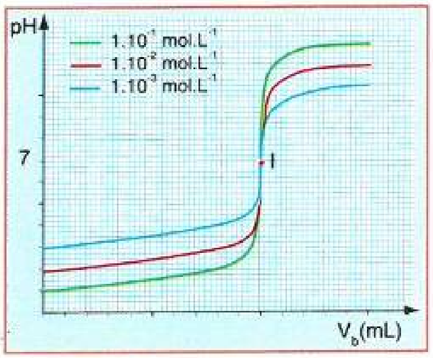


Figure 5.20
The pH of the equivalence point is equal to 7. The height of the pH jump depends on concentrations.

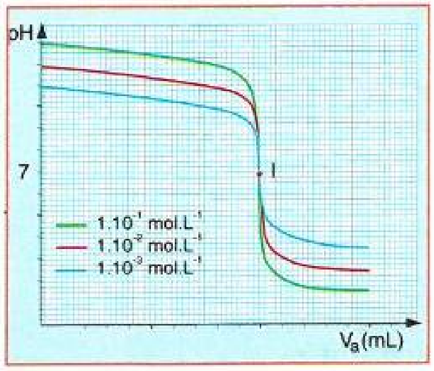


Figure 5.21
Effect of concentration on the shape of the curve pH = $f(V_a)$. The same effect appears on the shape of the curve pH = $f(V_b)$.

At the equivalence point $nH_3O^+ = nHO^-$

That is : $V_a \times C_a = V_{bE} \times C_b$

- **Effect of concentration**

The previous activity 4 is repeated with the same solutions, but using different concentrations as indicated below:

1×10^{-1} mol.L^{-1} hydrochloric acid solution titrated with 1×10^{-1} mol.L^{-1} sodium hydroxide solution.
1×10^{-3} mol.L^{-1} hydrochloric acid solution titrated with 1×10^{-3} mol.L^{-1} sodium hydroxide solution.

On the same graph of activity 4, we plot the two curves pH = $f(V_b)$ corresponding to the above concentrations, we obtain the graph in figure 5.20.
We notice from the graph of figure 5.20 that the pH at the equivalence point is always 7 and the sharp jump of the curve changes where the length of the sharp jump of the curve becomes shorter as the concentrations diminish.

When we reverse the preceding activity by placing the acid in the burette and the base in the beaker, we obtain the graph in figure 5.21 that shows the same previous observation. The pH at the equivalence point is equal to 7 and the length of the sharp change part (jump) of the curve becomes shorter as the concentrations diminish.

5.3 Acid-base titration using pH-meter

The reaction between a strong acid and a strong base in an aqueous solution is actually a reaction between the H_3O^+ furnished by the acid and the HO^- furnished by the base according to the equation:

$$H_3O^+ + OH^- \rightarrow 2\,H_2O$$

This reaction is complete, rapid and unique. It can be used to perform an acid-base titration. The relation between the number of moles used up at the equivalence point: $C_a \times V_a = C_b \times V_b$ permits to determine the concentration of an acidic or basic solution when the concentration of the other reactant is known.
The pH meter allows us to determine the volume of basic solution needed to neutralize a certain volume of an acidic solution.
In this case, we measure accurately a volume of one reactant, the acid for example, and place it in a beaker. The changes of the pH of the solution in the beaker is measured as the basic solution from the buret; is added progressively until we reach the volume of base needed to reach the equivalence point determined on the curve pH = $f(V_b)$.

Figure 5.22

The materials used in acid-base titration.

Titration is a laboratory technique that requires the use of a pH meter, a magnetic stirrer, a pipet (10 or 20 mL) and a buret (25 or 50 mL). (Fig. 5.22).

It is worth noting here that the addition of distilled water to the titrated solution does not change the equivalence point nor the pH at this point.

Solved exercise 4

Given

We titrate 20 mL of sodium hydroxide NaOH solution with a solution of hydrochloric acid $HCl_{(aq)}$ of concentration 0.10 $mol.L^{-1}$.

The equivalence point is reached just after adding a volume $V_a = 21.2$ mL. Determine the concentration of NaOH solution.

Solution

The equation of the reaction is :

$$H_3O^+ + OH^- \rightarrow 2\ H_2O$$

At the equivalence point, the number of moles of H_3O^+ is equal to the number of moles of (OH^-):

$$n(H_3O^+) = n(OH^-)$$

or :

$$C_a \times V_{aE} = C_b \times V_b$$

$$C_b = \frac{C_a \times V_{aE}}{V_b}$$

$$C_b = \frac{0.100 \times 21.1}{20}$$

$$C_b = 0.106\ mol.L^{-1}$$

Chapter review

- The pH of a solution is the negative logarithm to base ten of the concentration of the ions H_3O^+ in the solution expressed in mol. L^{-1}:

$$pH = - \log [H_3O^+]$$

This relation is equivalent to: $[H_3O^+] = 10^{-pH}$

- Water undergoes auto-ionization according to the following equation

$$2\,H_2O \rightleftarrows H_3O^+ + OH^-$$

The ion product of water, referred as K_w, is given by the relation: $K_w = [H_3O^+]\,[OH^-]$
At 25 °C $K_w = 10^{-14}$
This can be represented by the negative log form as $pK_w = - \log K_w$ or $pK_w = 14$

- At 25 °C

An acidic solution is characterized by a $pH < 7$
A basic solution is characterized by a $pH > 7$
A neutral solution is characterized by a $pH = 7$

- In terms of pK_w we can write:

For an acidic solution $pH < \frac{1}{2} pK_w$
For a basic solution $pH > \frac{1}{2} pK_w$
For a neutral solution $pH = \frac{1}{2} pK_w$

- A strong acid is a chemical species that dissociates completely in water to give the H_3O^+ ions. In this case, the pH of the solution is represented by: $pH = - \log C_a$.

- A strong base is a chemical species that dissociates completely in water to give the HO^- ions. In this case, the pH of the solution is represented by: $pH = pK_w + \log C_b$

- The equation of the reaction between a strong acid and a strong base in aqueous solution is:

$$H_3O^+ + OH^- \rightarrow 2\,H_2O$$

This corresponds to the transfer of a proton H^+ from the H_3O^+ ion to the ion OH^-.

- The equivalence point of the reaction between a strong acid and a strong base in aqueous solution is obtained when the two reactants react according to the stoichiometric proportions.

At the equivalence point: $n(H_3O^+) = n(OH^-)$

Or $C_a \times V_a = C_b \times V_b$

- pH-metric titration is an experimental method to determine the equivalence point of the reaction between a strong acid and a strong base in aqueous solution.

- The method of parallel tangents is a way to determine graphically the equivalence point on the curve $pH = f(v)$.

Method sheet

The pH-meter

The pH meter is an instrument, which consists of an electronic millivoltmeter connected to two electrodes: a glass electrode and a reference electrode.

The pH meter gives a direct reading of pH by comparing the two voltages of two electrodes. The glass electrode is sensitive to the ions H_3O^+ and gives the voltage E_v which is a linear function of pH: E_v = (a + b) pH (a and b are constants). The reference electrode (Fig. 5.23) possesses a constant voltage E_r which is constant at a given temperature and independent of pH.

Often, the two electrodes are joined and associated to form a combined electrode (Fig. 5.24) that measures directly the pH of the solution as the voltage difference between the two electrodes.

$E = E_r - E_r = E_r - (a + b.pH) = a' - b.pH$

(a' and b are constants)

pH values depend on temperature; because K_w depends on temperature.

Before using a pH meter, it should be calibrated as described below.

Figure 5.23
The two electrodes of a pH meter: A glass electrode and a reference electrode

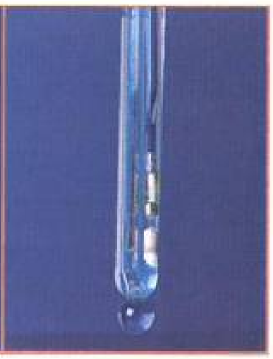


Figure 5.24
The combined electrode of a pH meter.

Calibration of a pH – meter

Measure the temperature of the solution and record it with the pH measured later.

Rinse the electrodes of the pH meter with distilled water and dip them into a standard solution of known pH. Adjust the reading of the millivoltmeter to that pH.

Rinse again the combined electrode with distilled water and dip it into the solution of unknown pH noting its pH.

Use the pH meter carefully by dipping its electrode well into the solution without allowing its extremity to touch the bottom of the container.

Don't discard the standard solution of known pH and keep it for later use.

Measuring the pH

Rinse the electrode with distilled water and immerse it in the solution. Being fragile, handle it with precaution and avoid its tip to touch the bottom of the beaker. Stir to homogenize the solution and record the pH value. At the end, the electrode is rinsed and placed in its cover.

Applications

Measure the pH of certain solutions as:

Mineral water. Tap water. Orange juice. Lemon juice. Tomato juice. Soft drinks ...

Laboratory Investigation

LI 1

The effect of concentration on the pH-metric titration curves, pH = f(v) of the reaction between hydrochloric acid and sodium hydroxide in aqueous solution.

Objective

Compare the pH-metric titration curves of acid-base reaction using different concentrations.

Equipment and reagents

Use the same materials as activity 4.
Solutions of hydrochloric acid with concentrations of 1 x10^{-1} and 1 x10^{-3} mol.L^{-1}.
Solutions of sodium hydroxide with concentrations of 1 x10^{-1} and 1 x10^{-3} mol.L^{-1}.

Procedure 1

Repeat the same procedure followed in activity 4 by collecting data of pH versus V(mL) based on two trials; one with concentrations 1×10^{-1} mol.L^{-1} of each of the acid and base; and the other trial with concentrations 1×10^{-3} mol.L^{-1}.

Interpretation of the results

Group the data obtained from each trial and arrange them in a table as in activity 4.
Trace the two curves corresponding to the above titrations with that of activity 4 on the same graph using different colors.
Locate the equivalence point on each curve and note the pH at this point. Compare for each curve the length of the sharp jump of the curve on which the equivalence point lies.

Procedure 2

Draw out the conclusion that relates the effect of concentration of reactants on the shape of the titration curves.

Example of results

Refer to figure 5.20.

Repeat the same work of part I by using the following solutions:

Hydrochloric acid 1×10^{-1}, 1×10^{-2} and 1×10^{-3} mol.L^{-1}.
Sodium hydroxide solution of the concentrations: 1×10^{-1}, 1×10^{-2}, 1×10^{-3} mol.L^{-1}.
Place the basic solutions in the beaker and fill the buret with the acidic solutions.

Interpretation of results

Group and arrange the results obtained in a table form as before.
Plot the three curves corresponding to different concentrations of reactants on the same graph using different colors.
Locate on each curve the equivalence point and note the pH at this point.
Compare for each curve the length of the vertical part of the curve on which the equivalence point lies.
Conclude from the graph the effect of concentration of the reactants on the shape of the titrations curves.

Example of results

Refer to figure 5.21.

Laboratory Investigation

LI 2

I – pH-metric titration of a solution of nitric acid with a solution of sodium hydroxide

Objective

Titrate a strong acid with a strong base by using pH meter.

Equipment and reagents

pH meter. Magnetic stirrer. 25 mL buret. 250 mL beaker. 10 mL pipet. Pipet filler. 0.1 mol.L^{-1} solution of sodium hydroxide . A solution of nitric acid of unknown concentration. Standard solution of pH = 4.

Procedure

- Calibrate the pH meter
- Fill the burette with sodium hydroxide solution.
- Place 10 mL of the acidic solution in a beaker. Add enough distilled water to dip the electrode of the pH meter and turn on the magnetic stirrer.
- Measure and note the pH of the acidic solution in the beaker.
- Add 1 mL of the basic solution and measure the new pH.
- Repeat the operation till you observe a sudden jump in the pH value.

  This is an indication that the volume (V) of base that has been added has passed the equivalence point and this is a rapid approximate measurement for the volume of the basic solution at equivalence point.
- Repeat the titration. Continue carefully for a more accurate determination of the equivalence point. After the addition of volume equal to (V – 2) mL, then continue adding each time 0.2 mL of the basic solution till the volume (V + 2) mL is reached. Continue adding the basic solution at the rate of 1 mL each time as before to reach finally the volume 20 mL.
- Put the pH meter reading at zero and rinse the electrode with distilled water for later use.

Interpretation of the results

Plot the curve pH = f(V_b).

Determine, by using the methods of parallel tangents, the equivalence point. Note the value of pH at the equivalence point.

Calculate the concentration of the nitric acid solution.

Example

The pH at the equivalence point is equal to 7.

$$V_{bE} = 11.8 \text{ mL.}$$

$$C_a = \frac{C_b \times V_{bE}}{V_a}$$

$$C_a = \frac{0.1 \times 11.8}{10} = 0.118 \text{ mol.L}^{-1}$$

II – pH-metric titration of a household product containing sodium hydroxide with hydrochloric acid solution.

Objective

Titrate a household product solution containing a strong base with a strong acid.

Equipment and reagents

The same materials as part I

Gloves. Goggles for eye protection. A 1L volumetric flask. A bottle of household product solution containing NaOH solution.

A solution of hydrochloric acid of concentration 0.1 mol.L^{-1}

A standard solution of pH = 10

Procedure

We assume that the drain cleaner bottle is labeled: 29%, d = 1.22 kg. L^{-1} (Fig. 5.25). It is necessary to use gloves and goggles in performing this experiment.

Figure 5.25

The household product is a concentrated solution of sodium hydroxide.

Preparation of a dilute solution of the basic solution

- Starting with S_0 a certain volume of the original household cleaning solution, prepare as solution S_1 by diluting S_0 100 times.
- To dilute, measure 10 mL of S_0 using a 10 mL pipette and pour it in a 1L volumetric flask. Add distilled water over S_0 to the line mark, the solution becomes exactly 1 L and name it S_1.

Titrating the diluted solution

- Calibrate the pH meter.
- Take a sample of 10 mL of S_1 and place it in a beaker. Add enough distilled water into the beaker to dip the electrode of the pH meter and set on the stirrer.
- Repeat the procedure of titration followed in part I.
- Put the pH meter reading at zero and rinse its electrode with distilled water for later use..

Interpretation of results

Plot the curve pH = $f(V_a)$. Determine, by using the method of parallel tangents, the equivalence point. Record the value of pH at equivalence point.

Calculate the concentration C_1 of the diluted solution S_1.

Calculate the concentration C_0 of the household cleaning solution S_0.

Determine the % composition by mass of NaOH in S_0 and compare it with that on the label of the bottle.

Example of results

V_{aE} = 8.6 mL

The pH at the equivalence point is equal to 7

$$C_1 = \frac{C_a \times V_{aE}}{V_b} = \frac{0.1 \times 8.6}{10} = 0.086 \text{ mol.L}^{-1}$$

$C_0 = 100 \times C_1 = 8.6 \text{ mol.L}^{-1}$

$C_0 = 28.2$ %.

Exercises

1 Given a hydrochloric acid solution of pH = 3.8 at 25 °C.

a) Calculate the concentration of the H_3O^+ ions in this solution.

b) Deduce the concentration of HO^- ions.

2 Given a solution of sodium hydroxide of pH = 10 at 25 °C.

a) Calculate the concentration of H_3O^+ ions in this solution.

b) 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: $[H_3O^+] = 2.5 \times 10^{-12}$ mol L^{-1},

Solution C: $[HO^-] = 6.3 \times 10^{-12}$ 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 2.4×10^{-14}

a) What is the pH of pure water at 37 °C?

b) 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 pK_w is 12.6.

a) What is the value of ion product of water at 80 °C.

b) Calculate the pH of pure water at 80 °C.

6 Complete the following table :

Solution	$[H_3O^+]$ $(mol.L^{-1})$	$[HO^-]$ $(mol.L^{-1})$	pH	Nature of solution
S_1		2.3×10^{-9}		
S_2	7.5×10^{-4}			
S_3			8.2	
S_4			5.5	

7 Given a solution A of concentration H_3O^+ ions equal to 6.4×10^{-4} mol L^{-1} and a solution B of concentration HO^- ions equal to 7.52×10^{-9} 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.

a) Calculate the molar concentration of solution S.

b) 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 2.5×10^{-3} mol. L^{-1}. The value obtained is pH = 2.6.

a) Show that HA is a strong acid.

b) List the glassware used and write the steps involved in preparing 100 mL of a solution B of concentration 1.25×10^{-4} 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^{-1}.

11 A solution A of the monoacid HA of concentration C_1 has a pH equal to 2.4. From A, we prepare a solution B of concentration $C_2 = 0.1\ C_1$. 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.

a) Calculate the molar concentration of S.

b) Show that HCl is a strong acid.

13 We want to prepare a solution of sodium hydroxide of pH = 12.5

a) What should the concentration of OH^- 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(NaOH) = 40 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?

15 Starting initially with a solution S_0 of hydrochloric acid of concentration 1×10^{-2} mol L^{-1}, we do the following dilutions:

Solutions obtained	S_1	S_2	S_3
V(mL) of S_0	10	10	10
V'(mL) of water	10	30	70

a) Calculate the molar concentrations of S_1, S_2 and S_3 and compare their variations as we move from S_1 to S_3.

b) Calculate the pH of the solutions S_0, S_1, S_2, and S_3.

c) What conclusion can be drawn from the variation of pH versus dilution?

16 Starting from a solution of hydrochloric acid of pH = 2.9, we want to prepare one liter of a solution of pH = 4.2.

Explain briefly the procedure that should be followed to do this operation indicating all the glassware to be used.

17 a) Calculate the pH of a solution of sodium hydroxide of concentration 0.01 mol L^{-1}

b) To 50 mL of the preceding solution we add successively 10, 30, 50 and 100 mL of 0.01 mol L^{-1} hydrochloric acid solution. Calculate the pH of the different solutions obtained after the addition of the above volumes.

18 We want to titrate using a pH-meter a solution (S) of sodium hydroxide with a standard solution of hydrochloric acid of concentration 1×10^{-1} mol L^{-1}. For this experimental activity, we pour 10 mL of solution (S) into a beaker and then add enough distilled water to immerse the electrode of the pH meter. We add progressively the above standard hydrochloric acid (1×10^{-1} mol.L^{-1}) and measure the pH of the solution corresponding to the volumes V_a of the acid added. The following results are obtained.

V_a(mL)	0	2	5	7	8	8.5	8.7	8.9
pH	11.9	11.8	11.6	11.3	11	10.5	10.2	9.2

V_a(mL)	9	9.1	9.3	9.5	10	11	13	15
pH	7	5	4	3.7	3.2	2.7	2.4	2.3

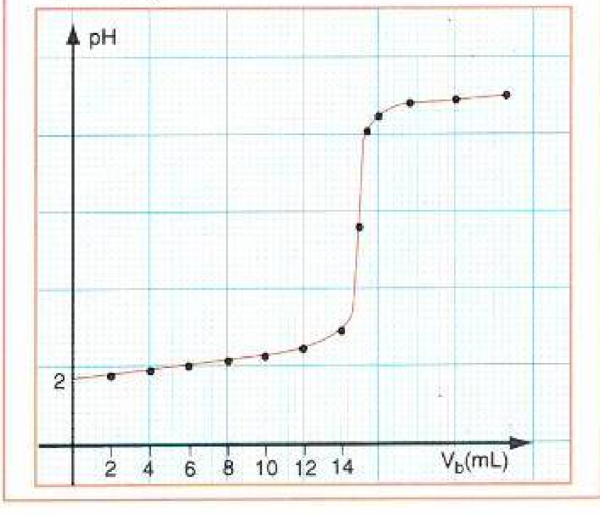
a) Plot the curve pH = f(V_a)

b) Determine graphically the equivalence point.

c) Determine the pH at the equivalence point.

d) Calculate the concentration of the basic solution (S).

19 We titrate a solution of nitric acid HNO_3 with a solution of sodium hydroxide of unknown concentration. The titration of the basic solution with the acidic solution is represented by plotting the following curve pH = f(V).



a) Which of the solutions is placed in the beaker and which fills the buret?
b) Determine graphically the equivalence point.
c) Find the pH at the equivalence point.
d) Write the equation of the reaction involved.
e) If the concentration of nitric acid is 1×10^{-2} mol L^{-1} and the volume of the solution placed in the beaker is 10 mL, calculate the concentration of sodium hydroxide solution.

20 We put 20 mL of a solution A of hydrochloric acid in a 250 mL beaker. We add to it progressively from a burette potassium hydroxide solution of concentration 2×10^{-2} mol.L^{-1}. We measure the values of pH after the addition of different volumes of the KOH solution where the following results are obtained:

V_b(mL)	0	2	4	6	8	10	12	13	14	15	16	17	18	20	22	24
pH	1.8	1.9	2.05	2.15	2.3	2.5	2.7	2.9	3.25	6.95	10.75	11.05	11.2	11.4	11.5	11.6

a) What step precedes the use of pH meter to measure the different pH values?
b) Plot the curve pH = $f(V_b)$.
c) Determine graphically the volume at the equivalence point V_{bE}.
d) Calculate the concentration of the acid solution.

21 A solution of 0.01 mol.L^{-1} hydrochloric acid is titrated with a solution of NaOH of unknown concentration.

A volume of 20 ml of the basic solution is placed in a beaker and titrated with the hydrochloric acid filled in the buret. By using a pH - meter, it is found that the pH in the beaker becomes 7 when V_a = 18 mL.

a) Draw the schema for the titration setup and describe the experimental procedure followed.
b) Describe the shape of the curve pH = $f(V_a)$
c) Determine the concentration C_b of the basic solution.

22 A bottle of a household product is labeled: "sodium hydroxide solution 20%". To verify the labeled information we carry out the following experiment.

1) We take a sample of the above solution S_0 and prepare 1 L of a solution S diluted 100 times.
a) Calculate the volume of the sample S_0 needed for this dilution.
b) Write briefly the steps of the above operation and list the materials used.
2) We take 10 mL of S and titrate it with 0.1 mol.L^{-1} hydrochloric acid solution.
a) The volume of acid solution used to reach the equivalence point is 6 ml. Write the equation of the reaction and calculate the concentration of solution S.
b) Describe the shape of the curve pH = $f(V_a)$ and precise the coordinates of the equivalence point.
3) The density of solution S_0 is 1.22 kg L^{-1}. Calculate the % of pure NaOH in S_0 by mass and compare it with the labeled value.

23 Sulfamic acid 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_2SO_3H that behaves as a strong acid. To determine the percentage composition by mass of this acid in the commercial product used, we prepare a solution S containing 9 g.L^{-1} of the product. We take 20 mL of S and titrate it with 0.1 mol.L^{-1}sodium hydroxide solution. The volume of basic solution added to reach the equivalence point is V_b = 17.4 mL.

a) Write the procedure for the preparation of 250 ml of of solution (S) specifying the glassware used and the precautions taken for this operation.
b) Write the equation of the titration reaction.
c) Determine the concentration of S.
d) Deduce the percentage composition of sulfamic acid by mass in the commercial product.

24 A bottle of commercial hydrochloric acid solution S_0 is labeled 37% composition by mass, density 1.19 kg. L^{-1}.

a) Calculate the concentration of solution S_0.

b) 4.2 mL of S_0 are diluted to 500 mL solution called S. We titrate S with 200 mL of KOH solution of $3x10^{-3}$ mol.L^{-1} placed in a beaker. The results of the measurements of pH versus volumes of acid S are given in the following table:

V_a(mL)	0	1	2	3	4	4.5	5	5.2	5.4	5.6	5.8
pH	11.5	11.4	11.3	11.2	11	10.9	10.7	10.6	10.5	10.3	10

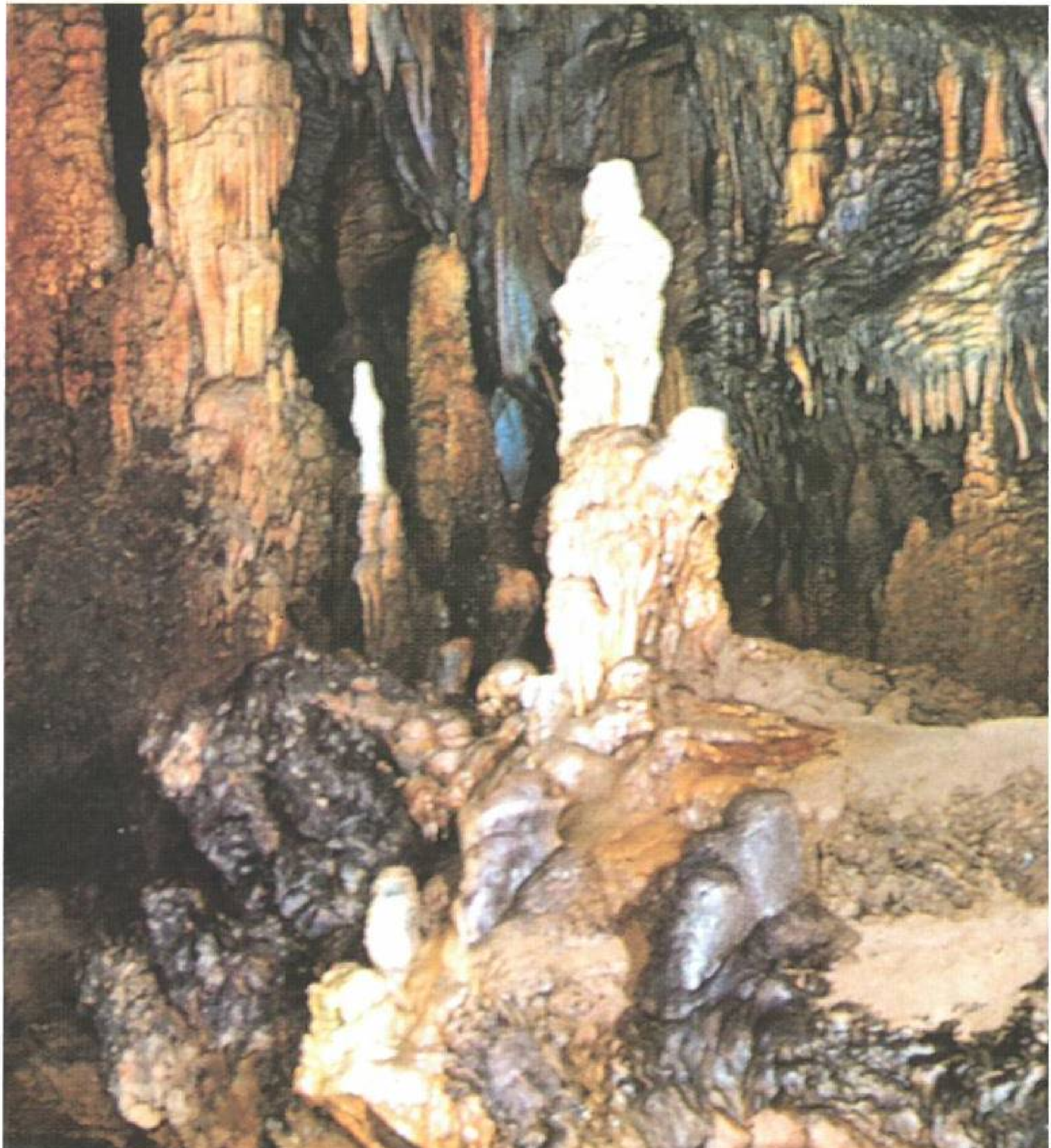
V_a(mL)	6	6.2	6.4	6.6	6.8	7	7.5	8	9	10	11	12
pH	7	4.0	3.7	3.5	3.4	3.3	3.1	3.0	2.8	2.7	2.6	2.5

Trace the curve pH = $f(V_a)$

c) Determine the equivalence point and then find the concentration of solution S.

d) Deduce the concentration of solution S_0 and its % composition by mass. Compare it to the label.

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



The slow formation of stalactites and stalagmites in the grotto of Jeïta is due to reactions involving the conjugate acid/base pair HCO_3^-/CO_3^{2-}.

What is a weak acid, a weak base?

What is a conjugate acid/base pair?

According to which criteria are acid/base pairs classified?

WEAK ACID WEAK BASE CONJUGATE ACID/BASE PAIR

6

Objectives

- Know the Brönsted concept of acid/base.
- Identify a weak acid and a weak base.
- Recognize a conjugate acid/base pair.
- Know the characteristics of acid-base equilibrium.
- Classify conjugate acid/base pairs.
- Predict the direction of an acid-base reaction.
- Identify a quantitative acid-base reaction.

Prerequisites

- Definitions of acid and base according to Arrhenius.
- Dilution of a solution
- Color indicators.

Chapter content

6.1 Weak acid, weak base, conjugate acid/base pair. Acidity constant.
6.2 Classification of the conjugate acid/base pairs.
- Chapter review
- Exercises

6.1 Weak acid, weak base, conjugate acid/base pairs. Acidity constant.

Figure 6.1
Johannes Brönsted, (1879-1947), Danish chemist. He established, at the same time as the English chemist Thomas Lowry (1874-1936) did, but independently, a concept of acids and bases, related to proton transfer, called Brönsted-Lowry theory.

When hydrogen chloride HCl is dissolved in water, it dissociates according to the equation:

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

An acid solution is produced since, according to the Arrhenius concept, the quantity of H_3O^+ ions in water is increased.
The reaction between hydrogen chloride and water corresponds to a transfer of proton H^+ from HCl molecule to H_2O molecule.
In 1923 the Danish chemist Brönsted (Fig 6.1) proposed a definition of acid and base, more general than that of Arrhenius, based on the transfer of proton, but not limited to water as solvent.
According to Brönsted:

An acid is a chemical species capable of donating a proton. A base is a chemical species capable of accepting a proton.

The reaction between HCl and H_2O is thus a reaction between the Brönsted acid HCl that gives up a proton and the Brönsted base H_2O that captures this proton.
In general, the reaction of an acid HA with water is a transfer of a proton H^+ from the acid molecule HA to the base molecule H_2O, according to the equation:

$$HA + H_2O \rightarrow H_3O^+ + A^-$$

The reaction of a base B^- with water is also a transfer of proton from H_2O molecule, acting as an acid, to the base B^-, according to the equation:

$$B^- + H_2O \rightarrow BH + OH^-$$

For example, the reaction between the base CH_3COO^- and water takes place according to the equation:

$$CH_3COO^- + H_2O \rightarrow CH_3COOH + OH^-$$

For a base of the form B, the equation of its reaction with water is represented by:

$$B + H_2O \rightarrow BH^+ + OH^-$$

The reaction of the base NH_3 with water is an example, its equation is:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

Thus, according to Brönsted, the reaction of an acid or a base with water is an acid-base reaction, requiring the simultaneous presence of an acid and a base.

The Brönsted concept of acid and base is not limited to the reactions in aqueous solutions. For example, the reaction between $HCl_{(g)}$ and $NH_{3(g)}$ is an acid-base reaction between the acid HCl that donates a proton to the base NH_3 that accepts this proton, according to the reaction :

- Our study is limited to aqueous solutions.

$$HCl + NH_3 \rightarrow NH_4^+,Cl^-$$

Weak acid

Acetic acid (ethanoic) is a liquid of pungent odor found naturally in the vinegar which is a diluted solution of the acid (Fig 6.2)
What is the behavior of acetic acid in aqueous solution?
Acetic acid does not conduct electric current; therefore, it does not contain ions. On the other hand, an aqueous solution of this acid conducts electric current showing that the acid is ionized in water.
The reaction of acetic acid with water takes place according to equation:

Figure 6.2
Acetic acid is the principal constituent of vinegar, which is a dilute solution of this acid.

$$CH_3COOH + H_2O \rightarrow CH_3COO^- + H_3O^+$$

Measuring the pH of a 1×10^{-2} mol.L^{-1} acetic acid solution gives a value of 3.4. This value of pH indicates that this acid does not behave as a strong acid for which the pH is given by the equation: $pH = -\log C_a$.
The number of moles of H_3O^+ ions produced is less than the quantity of acid dissolved.

$$[H_3O^+] = 10^{-3.4} = 4 \times 10^{-4} \text{ mol.L}^{-1} \neq 1 \times 10^{-2} \text{ mol.L}^{-1}.$$

Consequently, the reaction of acetic acid CH_3COOH with water is partial (does not go to completion).
Acids that behave in aqueous solution like acetic acid are called weak acids.

A weak acid HA is any chemical species that donates a proton H^+ during a partial reaction with water.

$$HA + H_2O \rightleftarrows A^- + H_3O^+$$

In a weak acid solution, $[H_3O^+] < C_a$ and $pH > -\log C_a$.

Weak base

Sodium ethanoate (acetate) CH_3COONa dissociates in water according to the equation :

$$CH_3COONa \xrightarrow{water} CH_3COO^- + Na^+$$

Measuring the pH of a 1×10^{-2} mol.L^{-1} sodium ethanoate solution gives a value of 8.4. This value indicates that this solution is basic. Indeed, HO^- ions are formed by reaction of the ethanoate ion CH_3COO^- with water, according to the equation:

$$CH_3COO^- + H_2O \rightarrow CH_3COOH + OH^-$$

The ion CH_3COO^- accepted a proton donated by water; it is a base.

The pH value shows also that CH_3COO^- is not a strong base the pH is given by the equation:

$$pH = 14 + \log C_b.$$

The number of moles of OH^- ions produced is less than the number of moles of base initially present in water:

$$[HO^-] = \frac{10^{-14}}{10^{-8.4}} = 2.5 \times 10^{-6} \text{ mol.L}^{-1} \neq 1 \times 10^{-2} \text{ mol.L}^{-1}.$$

Consequently, the reaction of the base CH_3COO^- with water is partial. Bases that behave in aqueous solution such as ethanoate ion are called weak bases.

A weak base B^- is any chemical species that accepts a proton H^+ during a partial reaction with water.

$$B^- + H_2O \rightleftharpoons BH + OH^-$$

In a weak base solution, $[HO^-] < C_b$ and $pH < 14 + \log C_b$.

- For a base of the form B, the equation of its partial reaction with water is :

$$B + H_2O \rightleftharpoons BH^+ + HO^-$$

■ Degree of dissociation of a weak acid

The pH value 3.4 of a 1×10^{-2} mol.L^{-1} acetic acid solution allows to calculate the concentration of H_3O^+ ion in the solution :

$$[H_3O^+] = 10^{-3.4} = 4 \times 10^{-4} \text{ mol.L}^{-1}.$$

According to the equation of the reaction of the acid with water:

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

Same number of CH_3COO^- ions as H_3O^+ ions are produced, and this number is equal to the number of CH_3COOH molecules dissociated:

$$[CH_3COOH]_{\text{dissociated}} = [CH_3COO^-] \approx [H_3O^+] = 4 \times 10^{-4} \text{ mol.L}^{-1}$$

- For this acid concentration, the amount of H_3O^+ ions coming from water can be neglected.

The stoichiometry of the reaction allows us to calculate the concentration of remaining acid CH_3COOH:

$[CH_3COOH] = C_a - [CH_3COO^-]$

$$[CH_3COOH] = 1\times10^{-2} - 4\times10^{-4} = 9.6\times10^{-3} \text{ mol.L}^{-1}.$$

Therefore, only 4×10^{-4} mol.L^{-1} of acid have reacted with water.

The ratio:

$$\alpha = \frac{[CH_3COOH]_{\text{dissociated}}}{C_a} = \frac{4 \times 10^{-4}}{1 \times 10^{-2}} = 0.04$$

- The dissociation percentage is equal to 100 α.

α (alpha) is called degree of dissociation (or ionization) of acetic acid in water.

The dissociation degree α of a weak acid is equal to the ratio of the amount of acid dissociated to the amount of acid initially present.

- **Effect of dilution on the pH**

Activity 1

pH measurement of a hydrochloric acid solution and an acetic solution before and after dilution.

Objective

Compare the effect of dilution on the pH of a weak acid solution and a strong acid solution.

- Give the relationship between the pH values of the two hydrochloric acid solutions?
- Does the same relationship between the pH of the two acetic acid solutions hold true?

Equipment and reagents

pH-meter. 250 mL beaker. Two 100 mL volumetric flasks. 10 mL pipet.
1×10^{-2} mol.L^{-1} hydrochloric acid solution.
1×10^{-2} mol.L^{-1} acetic acid solution. Acidic buffer solution(s).

Procedure

Calibrate the pH-meter. Measure the pH of each acid solution.
Prepare a solution 10 times diluted from each one of the acid solutions.
Measure the pH of the two diluted solutions (Fig 6.3).
Calculate, using the pH values, the $[H_3O^+]$ concentration in each of the four solutions.

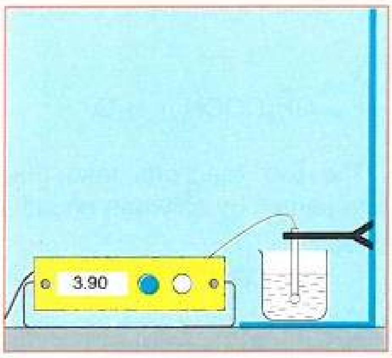


Figure 6.3

When an acetic acid solution is diluted 10 times, its pH does not increase by one unit as is the case for strong acid

Interpretation

The results are arranged in two following tables:

[HCl] (mol.L^{-1})	pH	$[H_3O^+]$ (mol.L^{-1})
1×10^{-2}	2	1×10^{-2}
1×10^{-3}	3	1×10^{-3}

$[CH_3COOH]$ (mol.L^{-1})	pH	$[H_3O^+]$ (mol.L^{-1})
1×10^{-2}	3.4	4×10^{-4}
1×10^{-3}	3.9	1.26×10^{-4}

Such results show that when a hydrochloric acid solution is diluted 10 times, the pH increases one unit as expected for a strong acid solution.
On the other hand, this result is not observed for acetic acid solutions, showing that this acid is not strong acid. In this case, the pH increases less than it does for the same dilution of HCl.

- **Effect of dilution on the dissociation degree**

Using the results of Activity 1, the calculation of the dissociation degree of acetic acid before and after dilution gives:

Before: $\alpha_1 = \dfrac{4 \times 10^{-4}}{1 \times 10^{-2}} = 0.04$ (or 4%)

After: $\alpha_2 = \dfrac{1.26 \times 10^{-4}}{1 \times 10^{-3}} = 0.126$ (or 12.6%)

This shows that the dissociation degree increases with the dilution

Dilution increases the dissociation of a weak acid.

Let us consider again the equation of the reaction of acetic acid with water:

$$CH_3COOH + H_2O \rightleftarrows CH_3COO^- + H_3O^+$$

The dilution of a solution of this acid corresponds to an increase of the amount of the reactant H_2O.
In this case, the equilibrium is shifted in such a manner that it opposes this increase. It is shifted to the right, i.e. to an increase of the acid dissociation.

Conjugate acid/base pair

It has been shown that the acid CH_3COOH reacts with water, to donate a proton, according to the equation:

$$CH_3COOH + H_2O \rightarrow CH_3COO^- + H_3O^+$$

On the other hand, when the base CH_3COO^- is added to a solution containing H_3O^+ ions, a reaction takes place according to the equation:

$$CH_3COO^- + H_3O^+ \rightarrow CH_3COOH + H_2O$$

The base accepts a proton. The two reactions take place simultaneously. They can be represented by only one equation:

$$CH_3COOH + H_2O \qquad CH_3COO^- + H_3O^+$$

This shows that the acid CH_3COOH is associated to the base CH_3COO^- and vice versa.
The two species CH_3COOH and CH_3COO^- are conjugate (associated together), and they constitute a conjugate acid/base pair. CH_3COOH is the conjugate acid of the base CH_3COO^-, and conversely, CH_3COO^- is the conjugate base of the acid CH_3COOH.

The above equation can be represented by a simplified reaction showing the proton transfer between the acid CH_3COOH and its conjugate base CH_3COO^-:

■ It is a simplified representation because the proton H^+ does not exist in the free state in aqueous solution.

$$CH_3COOH \rightleftarrows CH_3COO^- + H^+$$

Considering the example of the partial reaction of the weak base NH_3 with water:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

It is the reverse of the almost complete reaction of the weak acid NH_4^+ with HO^- ions:

$$NH_4^+ + HO^- \rightarrow NH_3 + H_2O$$

The base NH_3 and the acid NH_4^+ are also two conjugate species. They constitute a conjugate acid/base pair. NH_3 is the conjugate base of the acid NH_4^+ and conversely, NH_4^+ is the conjugate acid of the base NH_3.
The two species NH_4^+ and NH_3 are related by the proton transfer between the acid NH_4^+ and its conjugate base NH_3 according to the equation:

$$NH_4^+ \rightleftarrows NH_3 + H^+$$

In general, to each HA is associated a base, which is its conjugate base A^- and conversely, to each B is associated an acid, which is its conjugate acid BH^+. The two conjugate species constitute a conjugate acid/base pair.

A conjugate acid/base pair is constituted of two conjugate species that exchange a proton, according to the relation:

$$\begin{aligned} \text{Acid} &\rightleftarrows \text{Base} + H^+ \\ HA &\rightleftarrows A^- + H^+ \end{aligned}$$

An acid/base pair is represented the writing: Acid/Base where the conjugate acid is written first. Examples:
CH_3COOH/CH_3COO^-, NH_4^+/NH_3, ...etc.

■ Acidity constant K_a

The partial reaction of acetic acid CH_3COOH with water leads to an equilibrium, according to the equation:

$$CH_3COOH + H_2O \rightleftarrows CH_3COO^- + H_3O^+$$

The equilibrium constant K is given by the expression:

$$K = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH][H_2O]}$$

The concentration $[H_2O]$ of water is practically constant in dilute solution, this expression can be arranged under the form:

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

- By convention, K_a is used without unit, when the concentrations are in mol.L^{-1}

K_a is called the acidity constant of the conjugate pair CH_3COOH/CH_3COO^-. It depends only on the temperature. At 25 °C, $K_a = 1.8 \times 10^{-5}$.

The partial reaction of the ethanoate ion CH_3COO^- with water, according to the equation,

$$CH_3COO^- + H_2O \rightleftarrows CH_3COOH + OH^-$$

has also an equilibrium constant K given by the expression :

$$K = \frac{[CH_3COOH][HO^-]}{[CH_3COO^-][H_2O]}$$

It can be arranged under the form:

$$K' = \frac{[CH_3COOH][HO^-]}{[CH_3COO^-]}$$

since concentration of water, $[H_2O]$, is practically constant.

Multiplying the numerator and the denominator of the second member of the relation by $[H_3O^+]$, the acidity constant K_a of the conjugate pair CH_3COOH/CH_3COO^- appears:

$$K' = \frac{[CH_3COOH] \times [HO^-][H_3O^+]}{[CH_3COO^-][H_3O^+]} = \frac{K_w}{K_a}$$

So, the acidity constant K_a of an acid/base pair permits to characterize the reactions of the pair; either by considering the acid or the base of the pair.

- In the expression of K_a, the concentrations are expressed in mol.L^{-1}.

The acidity constant K_a of a conjugate acid/base A/B is the equilibrium constant of the partial reaction of the acid A with water, according to the reaction,

$$A + H_2O \rightleftarrows B^- + H_3O^+$$

given by the expression:

$$K_a = \frac{[H_3O^+][B^-]}{[A]}$$

Each conjugate acid/base pair is characterized by its acidity constant Ka. The table 6.1 gives some conjugate acid/base pairs with their acidity constant Ka values.

Conjugate pair A/B	K_a
HF/F^-	6.8×10^{-4}
$HClO/ClO^-$	5.0×10^{-8}
NH_4^+/NH_3	6.3×10^{-10}
HCN/CN^-	6.2×10^{-10}

Table 6.1

Some conjugate acid/base pairs, with their K_a values.

- **Acid-Base reaction**

The reaction between acetic acid CH_3COOH and ammonia NH_3 in aqueous solution takes place according to the equation:

$$CH_3COOH + NH_3 \rightarrow CH_3COO^- + NH_4^+$$

It is an acid-base reaction between the acid of the conjugate pair CH_3COOH/CH_3COO^- and the base of the conjugate pair NH_4^+/NH_3.

During the reaction the acid donated a proton H^+ to the base to form the species CH_3COO^- and NH_4^+. This permits to give a new definition of acid-base reaction :

An acid-base reaction corresponds to a proton transfer between two conjugate acid/base pairs.

The conjugate acid/base pairs of water

In the reaction of water with acetic acid:

$$CH_3COOH + H_2O \rightleftarrows CH_3COO^- + H_3O^+$$

the species H_2O acts as a base that accepts a proton to form the acid H_3O^+. The two species H_3O^+ and H_2O constitute the acid and the base of the conjugate H_3O^+/H_2O.

In the presence of an acid, water acts as a base, involving the conjugate pair H_3O^+/H_2O.

In the reaction of water with ethanoate ion:

$$CH_3COO^- + H_2O \rightleftarrows CH_3COOH + OH^-$$

the species H_2O acts as an acid that donates a proton to form the base HO^-. The two species H_2O and HO^- constitute the acid and the base of the conjugate pair H_2O/HO^-.

In the presence of a base, water acts as an acid, involving the conjugate pair H_2O/HO^-.

It has a double role: acid in the conjugate pair $H_2O/HO-$ and base in the conjugate pair H_3O^+/H_2O; water has an amphoteric character; it is an ampholyte.

Strong acid, strong base

The reaction between the strong acid HCl and water is complete:

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

The conjugate base of HCl, the Cl^- ion, does not have any practical tendency to accept a proton in aqueous solution.

The base NH_2^-, amide ion, is an example of a strong base that reacts with water completely, according to the equation:

$$NH_2^- + H_2O \rightarrow NH_3 + OH^-$$

The conjugate acid of NH_2^-, the molecule NH_3, does not have any practical tendency to donate a proton in aqueous solution.

These examples show that the stronger an acid, the weaker its conjugate base, and conversely, the stronger the base, the weaker its conjugate acid.

6.2 Classification of conjugate acid/base pairs

The acidity constants K_a have small values, negative powers of 10. It is more convenient to use their logarithms pK_a defined by: $pK_a = - \log K_a$.

The pK_a of a conjugate acid/base pair is the negative of the decimal logarithm of its acidity constant K_a:

$$pK_a = - \log K_a$$

Where $K_a = 10^{-pK_a}$.

The two constants, K_a and pK_a vary in inverse order (Fig 6.4)

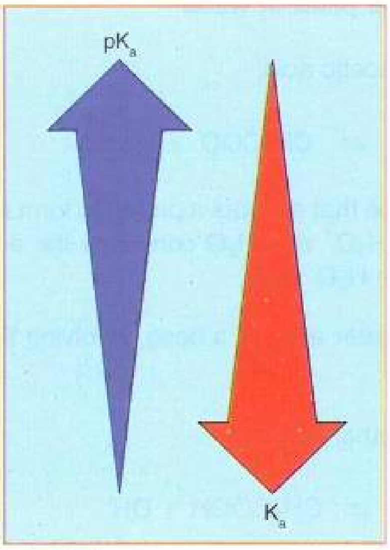


Figure 6.4
The constants K_a and pK_a vary in inverse order.

Relation between pH and pK_a

The expression of the acidity constant of a conjugate acid/base pair A/B,

$$K_a = \frac{[H_3O^+][B^-]}{[A]}$$

gives:

$$[H_3O^+] = Ka \times \frac{[A]}{[B^-]}$$

Taking the negative of the decimal logarithm of the two member of this equality leads to,

$$- \log [H_3O^+] = - \log K_a - \log \frac{[A]}{[B]}$$

$$pH = pK_a + \log \frac{[B]}{[A]}$$

The relation is called the Henderson-Hasselbalch equation. It allows calculating the pH of a weak acid or a weak base solution.

Predominance domains

The relative concentrations of the conjugate species A and B of a conjugate acid/base pair A/B depend on the pH of the solution.

- **When $pH = pK_a$**

$$\log \frac{[B]}{[A]} = 0 \quad \Leftrightarrow \quad \frac{[B]}{[A]} = 1 \quad \Leftrightarrow \quad [B] = [A]$$

The acid and the base of the conjugate pair are present in the solution with equal concentrations.

- **If pH $<$ pK$_a$**

$$\log\frac{[B]}{[A]} < 0 \quad \Leftrightarrow \quad \frac{[B]}{[A]} < 1 \quad \Leftrightarrow \quad [B] < [A]$$

The concentration of the acid in the solution is greater than that of its conjugate base.
By convention, it is considered that the acid A predominates in solution when,

$$\frac{[A]}{[B]} > 10 \qquad \text{or} \qquad [A] > 10\,[B]$$

Since,

$$\frac{[A]}{[B]} = \frac{[H_3O^+]}{K_a} = \frac{10^{-pH}}{10^{-pK_a}}$$

$$\frac{[A]}{[B]} > 10 \quad \Leftrightarrow \quad \frac{10^{-pH}}{10^{-pK_a}} > 10^1 \quad \Leftrightarrow \quad pK_a - pH > 1$$

or also: $pH < pK_a - 1$

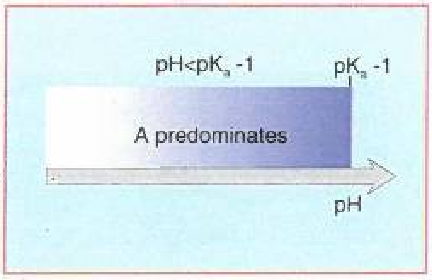


Figure 6.5
For pH $<$ pK$_a$ $-$ 1, the acid A predominates.

The acid A of the conjugate pair A/B predominates in the range of pH lower than (pK$_a$ $-$1) (Fig. 6.5).

- **If pH $>$ pK$_a$**

$$\log\frac{[B]}{[A]} > 0 \quad \Leftrightarrow \quad \frac{[B]}{[A]} > 1 \quad \Leftrightarrow \quad [B] > [A]$$

The concentration of the base in the solution is greater than that of its conjugate acid.
The base B predominates in solution when:

$$\frac{[B]}{[A]} > 10 \qquad \text{or} \qquad [B] > 10[A]$$

Since:

$$\frac{[B]}{[A]} = \frac{K_a}{[H_3O^+]} = \frac{10^{-pK_a}}{10^{-pH}}$$

$$\frac{[B]}{[A]} > 10 \quad \Leftrightarrow \quad \frac{10^{-pK_a}}{10^{-pH}} > 10^1 \quad \Leftrightarrow \quad pH - pK_a > 1$$

or also : $pH > pK_a + 1$

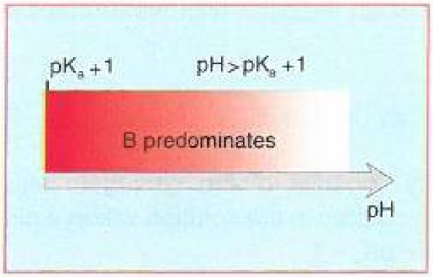


Figure 6.6
For pH $>$ pK$_a$ + 1, the base B predominates.

The base B of the conjugate pair A/B predominates in the range of pH higher than pK$_a$ + 1 (Fig. 6.6).
Figure 6.7 shows the predominance domains of the conjugate species of the conjugate acid/base pair A/B, in solution.

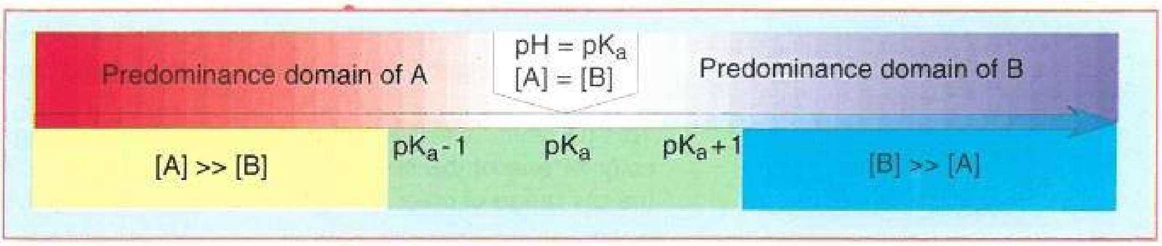


Figure 6.7
Predominance domains of acid A and its conjugate base B, of a conjugate acid/base pair A/B.

pH range of color change of an indicator

An indicator for acid-base reactions is a substance, the color of which depends on the pH of the solution where it is present.
Indicators are mostly weak acids or weak bases, of organic nature.
An indicator is represented by the simplified notation HInd, for example, the corresponding conjugate acid/base pair will be represented by $HInd/Ind^-$.
The acid HInd and its conjugate base Ind- have two different colors (Figure 6.8).

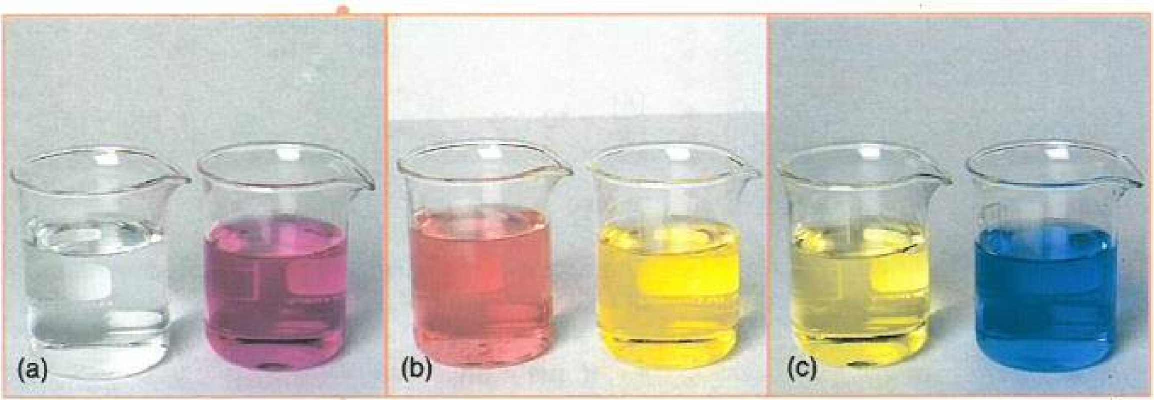


Figure 6.8
Colors of the acidic species (left) and the basic species (right) of: (a) phenolphthalein, (b) methyl orange and (c) bromothymol blue.

The equation of the reaction of an indicator with water can be represented as follows:

$$HInd + H_2O \rightleftarrows Ind^- + H_3O^+$$

Designating by K_i the acidity constant of the conjugate pair $HInd/Ind^-$, the acid HInd predominates in the solution within a pH domain corresponding to $pH < pK_i - 1$.
Within this pH domain the solution has the color of the acidic species HInd.
The base Ind^- predominates within the pH domain corresponding to $pH > pK_i + 1$.
Within this pH domain, the solution has the color of the basic species Ind^-.

Within the zone of pH located between the two values:

$$pH_1 = pK_i - 1 \qquad \text{and} \qquad pH_2 = pK_i + 1$$

corresponding to two pH units, no species predominates; the color of the solution will be intermediate between the colors of the two species.
This pH zone is the pH transition range of the change from the color of one of the species to that of the other one. It is called the pH range of color change of the indicator (Fig. 6.9).

Figure 6.9
The color of bromothymol blue (BTB) in the pH change of color range.

Table 6.1 indicates the color transition pH ranges of three indicators:

Indicator	pK_i	pH range	pH domain	Color of acidic species	Color of basic species
Phenolphthalein	9.0	8.2 – 10	basic	colorless	purple
Methyl orange	3.6	3.1 – 4.4	acidic	red	yellow
Bromothymol blue	6.8	6 – 7.6	neutral	yellow	blue

Table 6.1

Relative strength of acids and bases

Weak acids

A weak acid is stronger when its partial reaction with water

$$HA + H_2O \rightleftarrows A^- + H_3O^+$$

is shifted more to the right, i.e. in the direction of formation of a larger quantity of H_3O^+.

Let us compare the strengths of the acids of the two conjugate pairs: methanoic acid/methanoate ion ($HCOOH/HCOO^-$) and ethanoic acid/ethanoate ion (CH_3COOH/CH_3COO^-), knowing that:

$HCOOH/HCOO^-$, $K_{a_1} = 1.8 \times 10^{-4}$,
CH_3COOH/CH_3COO^-, $K_{a_2} = 1.8 \times 10^{-5}$.

When these two acids HCOOH and CH_3COOH are dissolved in water, with equal concentrations (C_a), their acidity constants K_{a1} and K_{a2} are given by the expressions:

$$K_{a1} = \frac{[H_3O^+]_1\,[HCOO^-]}{[HCOOH]} = \frac{[H_3O^+]_1^2}{C_a - [H_3O^+]_1}$$

$$K_{a2} = \frac{[H_3O^+]_2\,[CH_3COO^-]}{[CH_3COOH]} = \frac{[H_3O^+]_2^2}{C_a - [H_3O^+]_2}$$

Since $K_{a1} > K_{a2}$, this implies:

$$\frac{[H_3O^+]_1^2}{C_a - [H_3O^+]_1} > \frac{[H_3O^+]_2^2}{C_a - [H_3O^+]_2}$$

This corresponds to:
$[H_3O^+]_1 > [H_3O^+]_2$.
Therefore, methanoic acid HCOOH is stronger than ethanoic acid CH_3COOH.

A weak acid is stronger when its acidity constant K_a is greater.

This is equivalent to saying that:

A weak acid is stronger when its pK_a is smaller.

Figure 6.10 shows the comparison of the strength of the acids of the two conjugate pairs $HCOOH/HCOO^-$ and

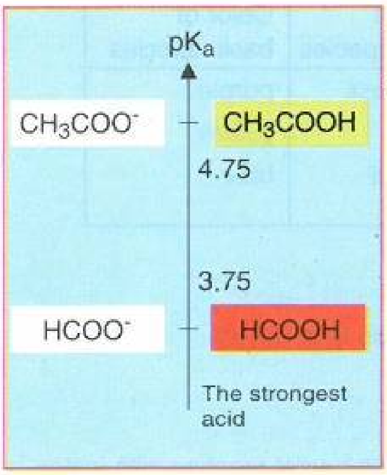


Figure 6.10
Methanoic acid is stronger than ethanoic acid.

CH_3COOH/CH_3COO^-

- **Weak bases**

A weak base is stronger when its reaction with water,

$$B + H_2O \rightleftarrows HB^+ + HO^-$$

is shifted more to the right, i.e. in direction of the formation of a larger quantity of HO^- ions.
Let us compare, for the same conjugate pairs: $HCOOH/HCOO^-$ and CH_3COOH/CH_3COO^-, the relative strengths of their bases, $HCOO^-$ and CH_3COO^-.
The reaction of the base $HCOO^-$, according to the equation,

$$HCOO^- + H_2O \rightleftarrows HCOOH + HO^-$$

is characterized, in dilute solution, by the equilibrium constant K_1:

$$K_1 = \frac{[HCOOH]\,[HO^-]_1}{[HCOO^-]} = \frac{K_w}{K_{a1}}$$

or:

$$K_1 = \frac{[HO^-]_1^2}{C_b - [HO^-]_1} = \frac{K_w}{K_{a1}}$$

C_b being the initial concentration of $HCOO^-$.

Similarly, the reaction of the base CH_3COO^- with water,

$$CH_3COO^- + H_2O \rightleftarrows CH_3COOH + HO^-$$

is characterized, for the same concentration C_b, by the equilibrium constant K_2:

$$K_2 = \frac{[HO^-]_2^2}{C_b - [HO^-]_2} = \frac{K_w}{K_{a2}}$$

Since $K_{a1} > K_{a2}$, this implies:

$$\frac{[HO^-]_1^2}{C_b - [HO^-]_1} < \frac{[HO^-]_2^2}{C_b - [HO^-]_2}$$

which corresponds to

$$[HO^-]_1 < [HO^-]_2$$

Therefore, the base, methanoate ion $HCOO^-$ is weaker than the base ethanoate ion CH_3COO^-.

A weak base is stronger when the acidity constant K_a of its conjugate acid/base pair is smaller.

This is equivalent to saying that:

A weak base is stronger when the pK_a of its conjugate acid/base pair is greater.

Figure 6.11 shows the comparison of the strength of the bases

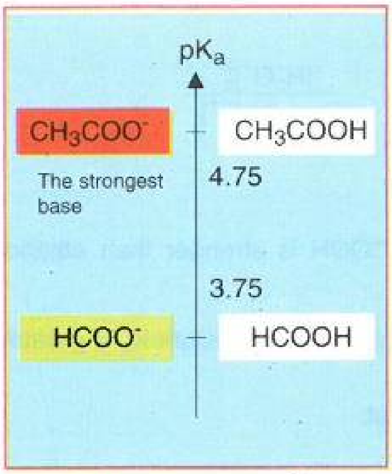


Figure 6.11
The ethanoate ion is a base stronger than methanoate ion.

of the two conjugate pair $HCOOH/HCOO^-$ and CH_3COOH/CH_3COO^-.

This leads to an observation already mentioned before:
The stronger an acid the weaker its conjugate base, and conversely (Fig. 6.12).

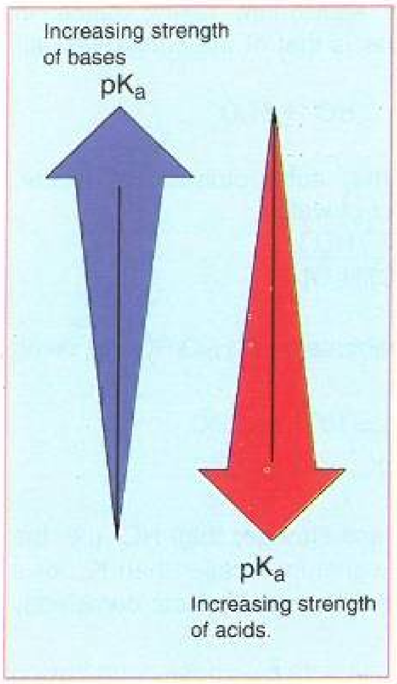


Figure 6.12
Opposite direction of the strength of acids and their conjugate bases of conjugate acid/base pairs.

Acidity scale in water

All the strong acids (HCl, HBr, HNO_3, ...) are completely dissociated in water, according to the equation:

$$HA + H_2O \rightarrow A^- + H_3O^+$$

The aqueous solutions of such acids do not practically contain acid molecules HA. The only strong acid existing in these solutions is the hydronium ion H_3O^+, whatever the strong acid HA is considered.
Thus, the relative strengths of strong acids cannot be distinguished in water. All the strong acids have in water practically the same strength, which is that of the acid H_3O^+.
It is said that water levels out the strength of strong acids to the strength of hydronium ion, which is the only strong acid able to exist in water. Therefore, the only one acid-base equilibrium taking place in aqueous solutions of strong acids is that of the conjugate pair H_3O^+/ H_2O:

$$H_3O^+ + H_2O \rightleftarrows H_2O + H_3O^+$$

This equilibrium is characterized by the constant,

$$K = \frac{[H_2O]\,[H_3O^+]}{[H_3O^+]\,[H_2O]} = 1$$

independent of temperature.

This constant is taken as the acidity constant K_a of the conjugate acid/base pair H_3O^+/ H_2O:
$K_a(H_3O^+/H_2O) = 1$, $pK_a(H_3O^+/H_2O) = 0$

Thus, it is considered that any acid stronger than H_3O^+ (i.e. which conjugate pair has an acidity constant K_a greater than 1, or a $pK_a < 0$) cannot exist in water, and it is completely dissociated there.

Similarly, any strong base B (NaOH, KOH, NH_2^-, $C_2H_5O^-$, ...) reacts completely with water, to give HO^- ions.

$$B + H_2O \rightarrow BH^+ + HO^-$$

The only strong base existing in aqueous solutions of such bases is the hydroxide ion HO^-, whatever the strong base B is considered.
Thus, the relative strengths of strong bases cannot be distinguished in water. All the strong bases have in water practically the same strength, as that of the base HO^-.
It is said that water levels out the strength of the strong bases to that of the hydroxide ion, which is the only strong base able to exist in water.

Therefore, the only acid-base equilibrium taking place in aqueous solutions of strong bases is that of the conjugate pair H_2O/HO^-:

$$H_2O + H_2O \rightleftarrows HO^- + H_3O^+$$

This equilibrium is that of the autoprotolysis of water, characterized by the ionic product of water:

$$K = \frac{[H_3O^+][HO^-]}{[H_2O][H_2O]}$$

The acidity constant of the conjugate pair H_2O/HO^- is taken equal to K_w.

$$K_a\ (H_2O/HO^-) = K_w = 10^{-14} \text{ at } 25°C,$$
$$pK_a\ (H_2O/HO^-) = pK_w = 14 \text{ at } 25°C.$$

- The strengths of the conjugate acid/base pairs of $pK_a > 14$ or $pK_a < 0$ are distinguishable in other solvents such as pure acetic acid or liquid ammonia.

Thus, it is considered that any base stronger than HO^- (i.e. the conjugate pair having an acidity constant smaller than K_w, or a $pK_a > pK_w$) cannot exist in water, and that it reacts completely with water.
Consequently, the strengths of conjugate acid/base pairs having an acidity constant K_a greater than 1 ($pK_a < 0$) or smaller than pK_w ($pK_a > pK_w$; i.e. > 14 at 25°C) cannot be distinguished in water.

Table 6.2 represents some conjugate acid/base pairs, the strengths of which can be distinguished in water, classified by order of their acidity constants K_a and their pK_a.

Name of conjugate acid/base pair	Pair	K_a	pK_a
Water/hydroxide ion	H_2O/HO^-	1.0×10^{-14}	14
Methyl ammonium ion/methylamine	$CH_3NH_3^+/CH_3NH_2$	1.9×10^{-11}	10.7
Phenol/phenate ion	$C_6H_5OH/C_6H_5O^-$	1.0×10^{-10}	10
Hydrogen cyanide/cyanide ion	HCN/CN^-	6.2×10^{-10}	9.21
Ammonium ion/ammonia	NH_4^+/NH_3	6.3×10^{-10}	9.20
Ethanoic acid/ethanoate ion	CH_3COOH/CH_3COO^-	1.8×10^{-5}	4.75
Benzoic acid/benzoate ion	$C_6H_5COOH/C_6H_5COO^-$	6.3×10^{-5}	4.20
Methanoic acid/methanoate ion	$HCOOH/HCOO^-$	1.8×10^{-4}	3.75
Nitrous acid/nitrite ion	HNO_2/NO_2^-	5.0×10^{-4}	3.3
Hydrogen fluoride/fluoride ion	HF/F^-	6.8×10^{-4}	3.17
Hydronium ion/water	H_3O^+/H_2O	1	0

Table 6.2

Classification of some conjugate acid/base pair according to the values of their K_a and pK_a, in aqueous solution at 25°C.

Constant K_R of an acid/base reaction

Let us consider two conjugate acid/base pairs A_1/B_1 and A_2/B_2 of respectively acidity constants K_{a1} and K_{a2}, given by:

$$K_{a1} = \frac{[H_3O^+][B_1]}{[A_1]} \quad \text{and} \quad K_{a2} = \frac{[H_3O^+][B_2]}{[A_2]}$$

A reaction between the acid A_1 and the base B_2 may take place, according to equation:

$$A_1 + B_2 \rightleftarrows B_1 + A_2$$

The equilibrium constant of this reaction, represented by K_R, is given by:

$$K_R = \frac{[B_1][A_2]}{[A_1][B_2]}$$

Multiplying the numerator and the denominator of the second term of this expression by $[H_3O^+]$ leads to:

$$K_R = \frac{[B_1][H_3O^+]}{[A_1]} \times \frac{[A_2]}{[B_2][H_3O^+]}$$

This expression is equivalent to:

$$K_R = \frac{K_{a_1}}{K_{a_2}}$$

In such a case, $K_R > 1$. This means that at equilibrium the amount of base B_1 and acid A_2 formed would be greater than that of base B_2 and acid A_1 remaining. The acid A_1 reacts actually with the base B_2, according to the forward direction of the equation.

$pK_{a_1} < pK_{a_2}$ means that the acid A_1 is stronger than the acid A_2 and the base B_2 is stronger than the base B_1.

The reaction involving two conjugate acid/base pairs takes place between the strongest acid and the strongest base, i.e. between:
The acid of the conjugate pair having the smallest pK_a and the base of the conjugate pair having the greatest pK_a.

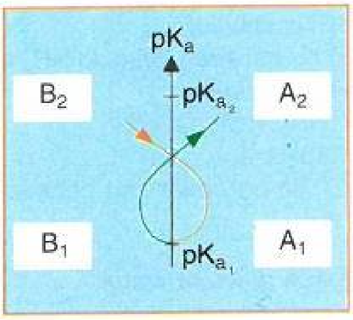


Figure 6.13
Gamma rule used to predict the direction of the reaction between the conjugate acid/base A_1/B_1 and A_2/B_2.

The gamma rule permits us to predict the direction of the reaction between two conjugate acid/base pairs (Fig. 6.13).

■ Complete (quantitative) reaction

An acid-base reaction is considered as complete (quantitative) when its constant K_R is greater than 10^4.
The reaction between the acid A_1 of the conjugate pair A_1/B_1 and the base B_2 of the conjugate pair A_2/B_2 will be quantitative if $K_{a_1} > 10K_{a_2}$, what corresponds to $(pK_{a_2} - pK_{a_1}) > 4$.

■ What happens when $pK_{a_1} > pK_{a_2}$ (or $K_{a_1} < K_{a_2}$)?

In this case, the reaction between the weakest base B_2 and the weakest acid A_1 is of very small extent. It is said that the reaction involving the conjugate acid/base pairs A_1/B_1 and A_2/B_2 is very limited in the forward direction of the equation.
The reaction goes to the forward direction to a small extent as the difference $(pK_{a_1} - pK_{a_2})$ is greater.

On the other hand, this reaction would be appreciable in the reverse direction, i.e. if the acid A_2 and the base B_1 have to react.

Example of reactions between conjugate acid/base pairs

Let us see whether a reaction would take place or not between an aqueous solution of ammonia NH_3 and an aqueous solution of acetic acid CH_3COOH.

The conjugate acid/base pairs to be considered are:

NH_4^+/NH_3 $\quad K_{a_2} = 6.3 \times 10^{-10} (pK_{a_1} = 9.20)$

CH_3COOH/CH_3COO^- $\quad K_{a_1} = 1.8 \times 10^{-5} (pK_{a_2} = 4.75)$

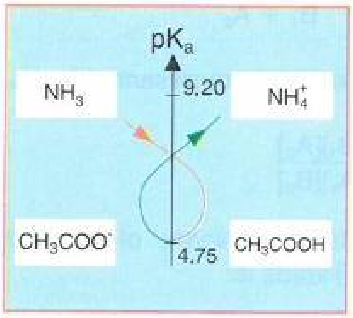


Figure 6.14
Gamma rule shows the possibility of a reaction between the stronger base NH_3 and the stronger acid CH_3COOH.

Let us place these two conjugate pairs on an ascending pK_a axis, the base on the left and the acid on the right (Fig 6.14)

NH_3 is the strongest base and CH_3COOH is the strongest acid. Therefore, a reaction takes place between these two species, when they are present together in an aqueous solution.

$(pK_{a_2} - pK_{a_1}) = 9.20 - 4.75 = 4.45 > 4$.

The reaction is thus complete, and can be written as:

$$NH_3 + CH_3COOH \rightarrow NH_4^+ + CH_3COO^-$$

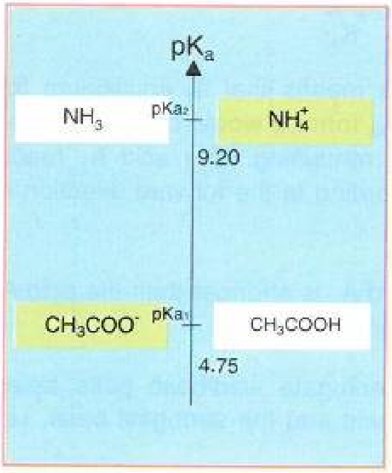


Figure 6.15
The reaction between the acid NH_4^+ and the base CH_3COO^- is very limited.

Does a reaction take place between the acid NH_4^+ and the base CH_3COO^- when two solutions containing these two ions are mixed together?

Let us mix, for example, a solution of ammonium chloride NH_4Cl with a sodium ethanoate CH_3COONa solution.

Figure 6.15 shows that the reaction is between the acid NH_4^+ and the base CH_3COO^- according to the equation,

$$NH_4^+ + CH_3COO^- \rightleftarrows NH_3 + CH_3COOH$$

$(pK_{a_2} - pK_{a_1}) = 4.75 - 9.20 = -4.45 << 4$.

Furthermore, the ions Na^+ and Cl^- do not react and behave as spectator (or indifferent) species.

Role of the conjugate acid/base pairs of water

The prediction and the study of the reactions between conjugate acid/base pairs, in aqueous solution, involves the conjugate acid/base pairs of water H_2O/OH^- and H_3O^+/H_2O.

Solved exercise 1

Given

a) Predict the reaction between nitrous acid HNO_2 and water. $pK_a(HNO_2/NO_2^-) = 3.30$.

b) 2×10^{-2} mol of this acid is dissolved in 1 L of aqueous solution. Calculate the pH of this solution.

Solution

a) Let us place the conjugate pair HNO_2/NO_2^- and the conjugate pairs of water H_2O/HO^- and H_3O^+/H_2O on an ascending pK_a axis (Fig. 6.16).

The ions H_3O^+ and HO^- coming from the autoionization of water are in very small quantity, so they are not involved in the considered reaction.

Figure 6.16 shows that the predominant acid and base in solution are respectively HNO_2 and H_2O. It also shows that the reaction between these two species is taking place to a very small extent:

$$(pK_{a_2} - pK_{a_1}) = 0 - 3.30 = -3.30 << 4.$$

Thus the equation of the reaction can be written:

$$HNO_2 + H_2O \rightleftarrows NO_2^- + H_3O^+$$

b The acidity constant K_a is given by:

$$K_a = \frac{[NO_2^-]\,[H_3O^+]}{[HNO_2]}$$

The initial concentration of HNO_2 is 2×10^{-2} mol.L^{-1}.
Let x be the concentration the concentration of H_3O^+ at equilibrium. It can be written:

$$\begin{array}{lcccccc} & HNO_2 & + & H_2O & \rightleftarrows & NO_2^- & + & H_3O^+ \\ \text{At equilibrium (mol.L}^{-1}) & (2 \times 10^{-2} - x) & & & & x & & x \end{array}$$

Substituting into the expression of K_a gives:

$$K_a = \frac{x^2}{2 \times 10^{-2} - x} = 5 \times 10^{-4}.$$

Solving this equation yields:
$x = [H_3O^+] = 2.92 \times 10^{-3}$ mol.L^{-1}, and pH = 2.54.

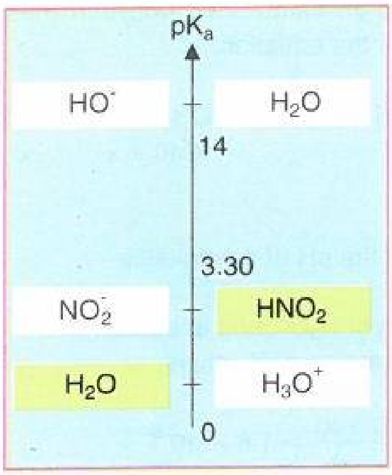


Figure 6.16

■ The acid H_2O of the pair H_2O/HO^- and the base H_2O of the pair H_3O^+/H_2O are predominant in the solution. Their reaction :
$H_2O + H_2O \rightleftarrows H_3O^+ + OH^-$
is more limited than this of HNO_2 with water ($pK_{a_2} - pK_{a_1} = 0 - 14 = -14$).

Solved exercise 2

Given

0.15 mol of HCl, 0.10 mol of NaOH, and 0.15 mol of CH_3COONa are put in 1 L of solution.

Predict the reactions that will take place, and calculate the pH of the solution.

pK_a (CH_3COOH/CH_3COO^-) = 4.75

Solution

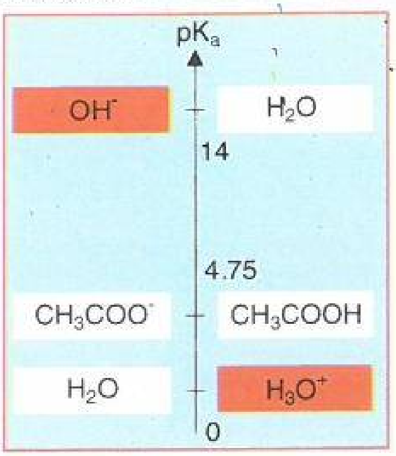


Figure 6.17

Let us place on an ascending pK_a axis the conjugate acid/base pairs present in the solution (Fig. 6.17).
The Na^+ and Cl^- ions being spectator species.
It is noted that H_3O^+ is the strongest acid and HO^- is the strongest base. Since ($pK_{a2} - pK_{a1}$) = 14 >> 4, a complete reaction takes place between these two ions, according to the equation:

$$H_3O^+ + OH^- \rightarrow 2\,H_2O$$

At the end of this reaction, it remains in the solution an excess of 0.05 mol.L^{-1} of H_3O^+ ions.
Hence, Figure 6.17 shows that among the species present in the solution, H_3O^+ is strongest acid and CH_3COO^- base. A complete reaction takes place between these two ions ($pK_{a_2} - pK_{a_1} = 4.75 - 0 > 4$), according to the equation:

$$CH_3COO^- + H_3O^+ \rightarrow CH_3COOH + H_2O$$

0.05 mol.L^{-1} of CH_3COOH is formed and it remains in the solution an excess of 0.10 mol.L^{-1} of CH_3COO^- ions.

Such an approximation has to be justified by comparing the value of x, given by the approximate calculation, with the numbers relatively to which it has been neglected.

An equilibrium state is then established between these two species, according to the equation:

	$CH_3COOH + H_2O$	$\rightleftarrows$	$CH_3COO^- + H_3O^+$	
At equilibrium ($mol.L^{-1}$)	$0.05 - x$		$0.10 + x$	x

This reaction determines the pH of the solution.

x being the concentration of H_3O^+ ions at equilibrium. Substituting into the expression of K_a gives:

$$K_a = \frac{x\,(0.10 + x)}{(0.05 - x)} = 1.8 \times 10^{-5}$$

The small value of K_a allows to neglect x with respect to 0.10 and 0.05, in the equation above. Then, calculation yields:

$[H_3O^+] = x = 9 \times 10^{-6}$ $mol.L^{-1}$ and pH = 5.04.

Chapter review

- According to Brönsted theory, an acid is any chemical species capable of donating a proton, and a base is any chemical species capable of accepting a proton.

- An acid is called a "weak acid" when its reaction with water is partial:

  $$HA + H_2O \rightleftarrows A^- + H_3O^+$$

  In weak acid solution, $[H_3O^+] < C_a$, and $pH > -\log C_a$

- A base B^- is called a "weak base" when its reaction with water is partial:

  $$B^- + H_2O \rightleftarrows BH + HO^-$$

  In weak base solution, $[HO^-] < C_b$, and $pH < 14 + \log C_b$.

- The degree of dissociation α of a weak acid is equal to the ratio of the amount of acid dissociated to the amount of acid initially present.

- A conjugate acid/base pair is constituted of two conjugate species that exchange a proton, according to the relation:

  $$\text{Acid} \rightleftarrows \text{Base} + H^+$$
  $$HA \qquad A^- + H^+$$

- The acidity constant K_a of a conjugate acid/base A/B, is the equilibrium constant of the limited reaction of the acid A of the pair with water :

  $$A + H_2O \rightleftarrows B^- + H_3O^+$$

  It is given by the expression:

  $$K_a = \frac{[H_3O^+][B^-]}{[A]}$$

- An acid-base reaction corresponds to a transfer of proton between two conjugate acid/base pairs.

- Water H_2O is the base of the conjugate pair H_3O^+/H_2O and the acid of the conjugate acid/base pair H_2O/HO^-. It has an amphoteric character.

- The pK_a of a conjugate acid/base pair is the negative decimal logarithm of its acidity constant: $pK_a = -\log K_a$.

  This relation is equivalent to:

  $$K_a = 10^{-pK_a}.$$

- The predominance domains of the acid A and its conjugate base B, of a conjugate pair A/B, in aqueous solution, are determined from the relation:

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

  For $pH = pK_a$, then $[A] = [B]$.

By convention:

A predominates when $[A] > 10\,[B] \Leftrightarrow pH < pK_a - 1$.
B predominates when $[B] > 10\,[A] \Leftrightarrow pH > pK_a + 1$.

- The stronger an acid is, the greater the acidity constant K_a of its conjugate pair and the smaller the pK_a.

- The stronger a base is, the smaller the acidity constant Ka of its conjugate pair and the greater the pK_a.

- The reaction between two conjugate acid/base pairs takes place between the strongest acid and the strongest base.

Exercises

1 Hydrobromic acid HBr and nitric acid HNO_3 are strong acids. Butanoic acid C_3H_7COOH, phenol C_6H_5OH, and ammonium ion NH_4^+ are weak acids.

a) Write the equations of the reactions of these acids with water.

b) Deduce the corresponding conjugate acid/base pairs.

2 The $C_2H_5O^-$ ion and the H^- ion are strong bases. Ammonia NH_3 and CO_3^{2-} are weak bases.

a) Write the equations of these bases with water.

b) Deduce the corresponding conjugate acid/base pairs.

3 A 5×10^{-3} mol.L^{-1} solution of an acid HA has a pH equal to 3.30. Is it a strong or a weak acid? Justify your answer.

4 An ammonia solution S_1 of concentration $C_1 = 1 \times 10^{-1}$ mol.L^{-1} has a pH equal to 11.1.

a) Show that ammonia is a weak base.

b) Write the equation of its reaction with water.

c) Describe the procedure that permits to obtain, from a volume V_1 of S_1, which is to calculated, a volume V_2 = 100 mL of an ammonia solution of concentration $C_2 = 2.5 \times 10^{-2}$ mol.L^{-1}.

d) The pH of the new solution is equal to 10.8. Determine for S_1, and then for S_2, the percentage of ammonia molecules that has reacted with water. Compare the results.

e) Conclude the effect of dilution on the reaction of ammonia with water.

5 Consider the conjugate pair CH_3COOH/CH_3COO^-.

a) Write the equation of the dissociation reaction of ethanoic acid CH_3COOH in water.

b) Deduce the expression of the acidity constant K_a of the conjugate acid-base pair.

c) The pK_a of the conjugate pair CH_3COOH/CH_3COO^- is equal to 4.75. Deduce the value of its K_a.

6 Consider a solution of ethanoic acid CH_3COOH and a solution of methanoic acid HCOOH. The corresponding conjugate acid/base pairs respectively are:

CH_3COOH/CH_3COO^-, $pK_{a_1} = 4.75$,
$HCOOH/HCOO^-$, $pK_{a_2} = 3.75$.

a) Write the equations of the dissociation reaction of the acids in water.

b) Which of these two acids is the weaker acid?

7 Consider two solutions S and S' of benzoic acid C_6H_5COOH, of respective concentrations, respectively $C = 1 \times 10^{-2}$ mol.L^{-1} and $C' = 1 \times 10^{-3}$ mol.L^{-1}. Their pH respectively are pH = 3.1 and pH'= 3.6. The pK_a of $C_6H_5COOH/C_6H_5COO^-$ is equal to 4.2.

a) Is benzoic acid a weak or a strong acid?

b) Determine the percentage of the acid dissociated for S and S'. Compare the results.

c) Deduce the effect of dilution on the dissociation reaction of this acid.

8 We have a 2.5×10^{-2} mol.L^{-1} solution A of methanoic acid HCOOH and a 2.5×10^{-2} mol.L^{-1} solution B of hydrochloric acid HCl.

a) The pH of the solution A is 2.67. Show that methanoic acid is a weak acid.

b) The pH of the solution B is 1.6. Show that hydrochloric acid is a strong acid.

c) Each of these two solutions is diluted 10 times. Calculate the pH of each dilute solution obtained and compare the effect of dilution on the solution of each acid.
K_a $(HCOOH/HCOO^-) = 1.8 \times 10^{-4}$.

9 Benzoic acid C_6H_5COOH is a weak acid.

a) What is its conjugate base?

b) The pH of a 1×10^{-2} mol.L^{-1} benzoic acid solution is equal to 3.1. Deduce the acidity constant K_a and the pK_a of the conjugate acid/base pair.

10 Let S be a solution of HCOOH of concentration C = 1 x10^{-2} mol.L^{-1}. The pH of this solution is 2.9.

a) What is the pH of a solution S' of a strong acid having the same concentration C?
b) Show that HCOOH is a weak acid.
c) Calculate the degree of dissociation α of HCOOH in solution S.

11 Let us consider a solution containing the conjugate acid/base pair HA/A^-.

a) Show that [HA] > [A^-] when pH < pK_a.
b) Show that [A^-] > [HA] when pH > pK_a.

12 50 mL of a 1x10^{-2} mol.L^{-1} solution of acetic acid CH_3COOH are mixed with 50 mL of a 1x10^{-2} mol.L^{-1} solution of hydrochloric HCl.

a) Knowing that pK_a(CH_3COOH/CH_3COO^-) = 4.75, calculate the pH of the solution obtained. Justify your answer.
b) Which of the two chemical species has a higher concentration in the obtained solution: concentration [CH_3COOH] or [CH_3COO^-] is predominant in the solution? Justify your answer.
c) Determine the degree of dissociation α of acetic acid in the obtained solution.
d) Determine the dissociation degree α' of acetic acid in a 5x10^{-3} mol.L^{-1} solution of this acid.
e) Compare α with α' and conclude.

13 Color indicators of acid-base reactions are compounds that form conjugate acid/base pairs HA/A^-.

Determine in terms of pK_a the pH transition interval of color change corresponding to their color in acid and base medium.

14 A conjugate acid/base pair A/B has a pK_a of 9.8.

Which of the species A or B is predominant in solutions of pH respectively equal to: 4, 9.8, and 11.8?

15 Arrange the following conjugate acid/base pairs in an ascending order of the strength of their acids.

Conjugate pairs	K_a
HCO_3^-/CO_3^{2-}	4.8×10^{-11}
CH_3COOH/CH_3COO^-	1.8×10^{-5}
$HCOOH/HCOO^-$	1.8×10^{-4}

16 Arrange the following conjugate acid/base pairs in an ascending order of the strength of their bases.

Conjugate pairs	pK_a
HCO_3^-/CO_3^{2-}	10.32
$HClO/ClO^-$	7.3
$C_2H_5COOH/C_2H_5COO^-$	4.87

17 a) Write the equation of the acid-base reaction that may take place between a solution of ethanoic acid CH_3COOH and a solution of methylamine CH_3NH_2.

b) Calculate the reaction constant K_R.
Given pK_{a_1} (CH_3COOH/CH_3COO^-) = 4.75 and pK_{a_2} ($CH_3NH_3^+/CH_3NH_2$) = 10.7.
c) In which direction does the reaction take place?
d) May the reaction be considered complete?

18 Let us consider the two conjugate acid/base pairs:

HNO_2/NO_2^- $pK_{a_1} = 3.30$
$C_6H_5OH/C_6H_5O^-$ $pK_{a_2} = -10.$

a) Arrange these two conjugate acid-base pairs on a pK_a axis of pH unit scale.
b) Between which species of these two pairs is there a possibility for a reaction?
c) Write the equation of the corresponding reaction.
d) Give the expression of the acidity constant for the two conjugate acid-base pairs.

e) Determine the constant K_R of the reaction. Is this reaction complete?

19 We have 1 L of 1×10^{-1} mol.L^{-1} solution of ammonium chloride, with $pK_a = 9.20$ for NH_4^+/NH_3.

a) Place in an increasing order on a pK_a axis the different conjugate acid/base pairs present in the solution.

b) Write the equation of the different reactions that may take place.

c) Which reaction goes to completion? Deduce the nature of the solution: acidic, basic or neutral.

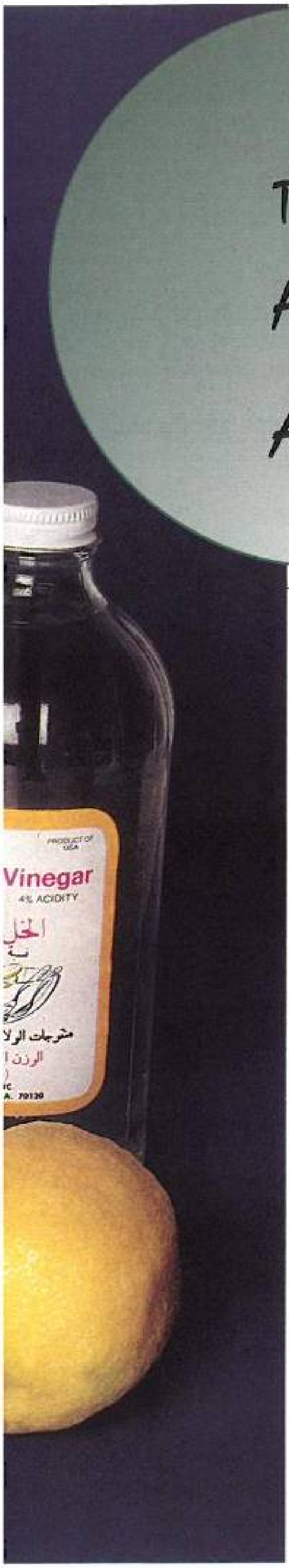
d) Calculate the pH of the solution.

e) 3×10^{-2} mol. L^{-1} of sodium hydroxide is added to the solution given above, without change in volume. Show which reaction will take place in the solution. Is this reaction complete?

f) Write the corresponding equation.

g) Write the equation of the reaction that controls the pH of the solution. Calculate the pH.

Fruits, vegetables and various products of daily use (milk, vinegar, aspirin ...) contain weak acids. Some household products contain ammonia, a weak base.
What are the characteristics of the reaction between a weak acid and a strong base (and vice-versa)?



THE REACTION BETWEEN A WEAK ACID AND A STRONG BASE

7

Objectives

- Master the study of the reaction between a solution of a weak acid and a solution of a strong base by pH-metry.
- Perform titration of a weak acid using pH-meter.
- Master the study of the reaction between a solution of a weak base and a solution of a strong acid using pH-meter.
- Perform titration of a weak base using pH-meter.
- Recognize buffer solutions

Prerequisites

- Acids and bases
- pH of aqueous solutions
- Concentration of solutions

Chapter content

7.1 Study of the pH changes that occur during the reaction between a solution of a weak acid and a solution of strong base

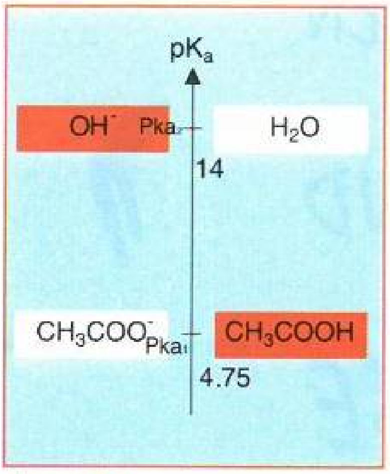


Figure 7.1
The reaction between the species CH_3COOH and OH^- in aqueous solution is complete.

A weak acid HA is characterized by its partial reaction (dissociation) with water, while a strong base is characterized by a complete reaction (dissociation) with water. How does such an acid and such a base react together in an aqueous solution?

- **Reaction between a weak acid and a strong base in an aqueous solution**

- **Equation of the reaction**

When a solution of acetic acid CH_3COOH ($pK_a = 4.75$) reacts with a solution of sodium hydroxide NaOH, the reaction is practically complete:

$$CH_3COOH + HO^- \rightarrow CH_3COO^- + H_2O$$

In fact, the two species present in solution, the stronger acid (CH_3COOH), reacts with the stronger base (OH^-) (Fig. 7.1), in a complete reaction ($pK_{a_2} - pK_{a_1}$)= 14 – 4.75 = 9.25 > 4.

On the other side, the CH_3COO^- ion formed reacts equally with water, in a partial reaction (Fig. 7.2), according to the equation:

$$CH_3COO^- + H_2O \rightleftarrows CH_3COOH + OH^-$$

The two simultaneous reactions could be represented by the equation:

$$CH_3COOH + HO^- \underset{2}{\overset{1}{\rightleftarrows}} CH_3COO^- + H_2O$$

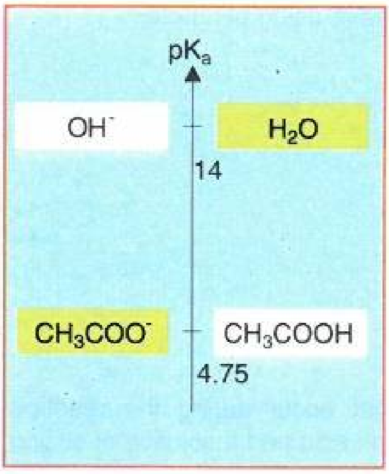


Figure 7.2
The reaction between CH_3COO^- and H_2O in solution does not go to completion.
($pK_{a_2} - pK_{a_1}$) = 4.75 –14
= -9.25 << 4).

which shows that the reaction takes place in direction 1.
Considering, in general, a weak acid HA, the equation of the reaction between an aqueous solution of this acid and an aqueous solution of a strong base is represented by:

$$HA + HO^- \underset{2}{\overset{1}{\rightleftarrows}} A^- + H_2O$$

It shows that the above reaction could be practically complete in the direction1 in a condition to be mentioned later.

- **Relation of K_R with K_a and K_w**

The equation above gives the expression of the constant K_R, of the reaction between the acid HA and a strong base:

$$K_R = \frac{[A^-][H_2O]}{[HA][OH^-]}$$

But since in dilute solutions the concentration of water $[H_2O]$ is constant, the K_R expression becomes:

$$K_R = \frac{[A}{[HA][OH^-]}$$

then multiplying the numerator and the denominator of the second term by $[H_3O^+]$, we obtain:

$$K_R = \frac{[A^-][H_3O^+]}{[HA]} \times \frac{1}{[OH^-][H_3O^+]}$$

or:

$$K_R = \frac{K_a}{K_w}$$

The constant K_R of the reaction between a weak acid HA and a strong base is equal to the ratio of the ionization constant K_a of the conjugate acid-base pair HA/A^- and the ion product constant of water K_w.

The expression of the constant K_R can also be written in the form:

$$K_R = 10^{pK_w - pK_a}$$

It shows that the reaction is quantitative for the acids having $pK_a < 10$ $(pK_w - pK_a > 4)$.

Study of the pH changes during the reaction

Activity 1

Changes of pH of acetic acid solution as a function of the volume of sodium hydroxide added.

Objective

Study the reaction between a weak acid and a strong base by pH-metry.

Equipment and reagents

pH-meter. 50 mL buret. 250 mL beaker. 20 mL pipet. Pipet bulb. Magnetic stirrer. 1×10^{-2} mol.L^{-1} solution of acetic acid. 1×10^{-2} mol.L^{-1} solution of sodium hydroxide.

Procedure

Follow the same procedure of activity 4 in chapter 5 (Fig. 7.3).
Assemble the results obtained in a table.
Trace the curve of the changes of pH of the solution in the beaker as a function of the volume of the base added. $pH = f(V_b)$.

Figure 7.3

The pH-metric study of the reaction between acetic acid and sodium hydroxide.

- How many inflection points are in the curve $pH = f(V_b)$?
- Extract the coordinates of each of these points.

curve $pH = f(V_b)$

The values in table 7.1 permit to plot the curve $pH = f(V_b)$ (Fig. 7.4).

V_b(mL)	pH	V_b(mL)	pH
0	3.4	19	6.1
2	3.9	19.5	6.4
4	4.2	20	8.4
6	4.4	20.5	10.3
8	4.6	21	10.7
10	4.75	21.5	10.9
12	5.0	22	11
14	5.2	24	11.3
16	5.4	26	11.5
18	5.75	28	11.6
18,5	5.9	30	11.7

Table 7.1

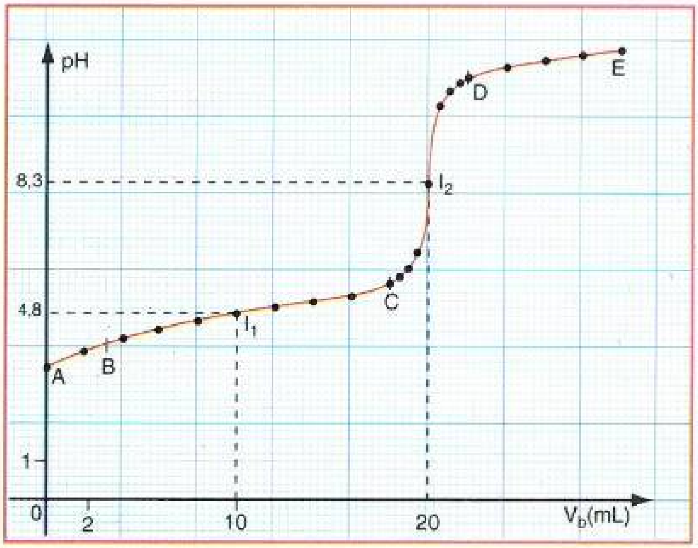


Figure 7.4

Curve of the changes of the pH of the acetic acid solution as a function of the volume of sodium hydroxide added.

The curve is ascending. It consists of four parts:
Part AB ($V_b < 3$ mL). The pH increases relatively rapidly.
Part BC (3 mL $< V_b <$ 18 mL). The pH varies slightly forming a plateau. The curve has an inflection point of coordinates (10 mL; 4.75).
Part CD (18 mL $< V_b <$ 22 mL). The pH increases rapidly. The curve shows a sudden jump of pH and a second inflection point.
Part DE ($V_b >$ 22 mL). The pH varies again slightly, forming a second plateau. The curve approaches a horizontal asymptote.

- **Half-equivalence point**

In activity 1, when we add 10 mL of the 1×10^{-2} mol.L^{-1} sodium hydroxide solution to 20 mL of 1×10^{-2} mol.L^{-1} of acetic acid solution in the beaker, the number of moles of acid consumed in the reaction is equal to half the number of moles of the initial number of moles of the acid. The number of moles of the acid left in the beaker is equal to half the initial amount (number of moles) of the acid.

According to the equation of the reaction,

$$CH_3COOH + HO^- \rightarrow CH_3COO^- + H_2O$$

The number of moles of ethanoate ion CH_3COO^- formed, equals the number of moles of the acid used.
In terms of concentration, after the addition of a volume of the base equal to half the volume at equivalence point ($V_E/2$), the concentrations [CH_3COOH] and [CH_3COO^-] are equal in the solution. This corresponds to half-equivalence point.

During the reaction between a weak acid HA and a strong base, half-equivalence point corresponds to the consumption of half the amount (number of moles) of the acid.

At half-equivalence point and in the equation:

$$pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

the ratio:

$$\frac{[CH_3COO^-]}{[CH_3COOH]}$$

is equal to 1 and the term :

$$\log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

is equal to zero. The pH of the solution is equal to the pK_a of the conjugate acid-base pair CH_3COOH / CH_3COO^- equals in this case to 4.75.

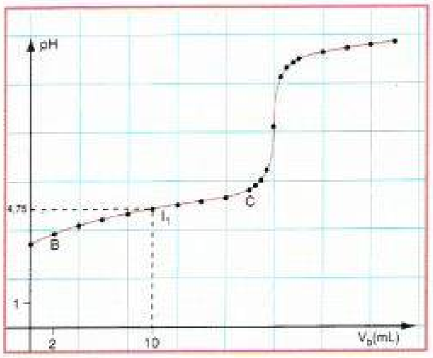


Figure 7.5
The half-equivalence point is the inflection point of the part BC of the curve.

At half-equivalence point of the reaction between a weak acid HA and a strong base, the pH of the solution is equal to the pK_a of the conjugate pair HA /A^- i.e. $pH = pK_a$.

On the curve $pH = f(V_b)$ of activity 1, the half-equivalence, characterized by the volume $V_b = V_{bE}/2$ and pH = 4.75, corresponds to a first inflection point, which is located in the part BC and having the coordinates (10 mL; 4.75) (Fig. 7.5).

- **Equivalence point**

The acid and the base react at equivalence point in stoichiometric proportions because the reaction between the weak acid HA and a strong base is practically complete.

$$HA + OH^- \rightarrow A^- + H_2O$$

Designating C_a and C_b as the respective concentrations of the acid and the base solution, V_a and V_b as the respective volumes of the two solutions utilized to reach equivalence, then the number of moles, n_a and n_b of the acid and the base that react, are given in the following relations:

$$n_a = C_a \times V_a$$
$$n_b = C_b \times V_b$$

The number of moles being equal, then at equivalence point:

$$C_a \times V_a = C_b \times V_b$$

On the curve $pH = f(V_b)$, equivalence occurs in the region of the sudden change in pH (jump of pH).
In fact, before equivalence, the pH is determined by the acid solution in the beaker, which corresponds to part AC of the curve.
After the equivalence point, the pH is determined by the excess of base added to the beaker, which corresponds to part DE of the curve.
In a narrow interval of volumes around the equivalence point, the pH changes suddenly, from acid values to base values. This corresponds to part CD of the curve.
In the region of the pH jump, the equivalence point corresponds specifically to the inflection point on the curve, designated by I_2.
The equivalence point I_2 is determined by the parallel tangents method (Fig. 7.6).

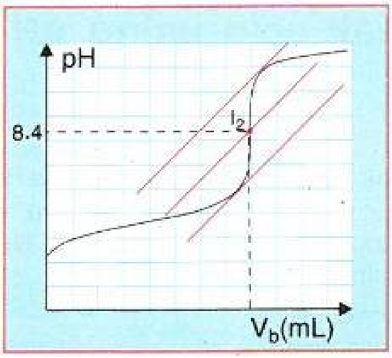


Figure 7.6
The method of parallel tangents permits determining the equivalence point on the curve $pH = f(V_b)$. The pH at equivalence point is greater than 7.

The pH at equivalence point

The curve pH = f(V_b) shows that the pH of the solution at equivalence point is 8.4. This is a basic pH.

In fact, we have seen earlier that the weak base CH_3COO^-, formed by the reaction between acetic acid and sodium hydroxide, reacts partially with water to produce the OH^- in the solution.

This is a general observation of the pH at the equivalence point of the solution resulting from the reaction of weak acid, HA, and a strong base.

For the reaction of a weak acid HA with a strong base, the pH of the solution at equivalence point is > 7.

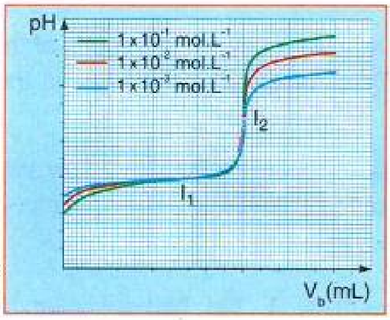


Figure 7.7

The effect of concentration on the curves pH = f(V_b). The pH of the equivalence point decreases as the acid becomes more diluted.

Effect of concentration

The pH metric study of activity 1 can be repeated with different concentrations of acetic acid and sodium hydroxide to study the effect of concentration on the reaction.

For the reactions between the following solutions:

$C_a = C_b = 1 \times 10^{-1}$ mol.L^{-1} from one side, and $C_a = C_b = 1 \times 10^{-3}$ mol.L^{-1} on the other side, we obtain the curves pH = f(V_b) as in Figure 7.7, where the curve of activity 1 is included ($C_a = C_b = 1 \times 10^{-2}$).

We conclude that as the dilution increases, the change in pH, which was relatively rapid at the beginning of the curve, becomes less.

All the curves pass through the same inflection point I_1, corresponding to half-equivalence point. This indicates that the pH at the half-equivalence point is independent of the concentration. It is constant, and it is equal to pK_a (4.75 in the case of these curves).

The jump (steep rise) in pH around the equivalence point decreases as the dilution increases.

All the curves have a pH greater than 7 at equivalence point.

This pH decreases as the dilution of the acid solution increases.

7.2 Titration of a weak acid using pH-meter

The reaction between a weak acid and a strong base in aqueous solution is partically complete, rapid and unique. It could then be utilized for titrating a solution of weak acid. The concentration C_a is then determined from the relation,

$$C_a \times V_a = C_b \times V_b$$

which corresponds to equivalence point.

From the curve pH = f(V) we can determine the volume at equivalence point V_E.

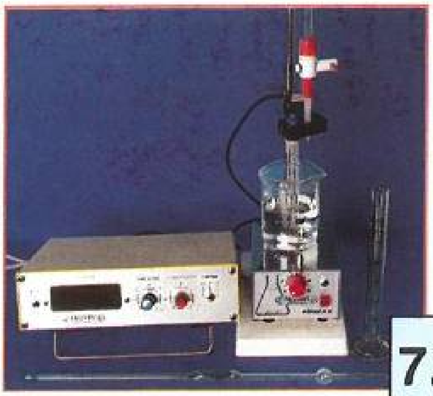


Figure 7.8
Set up for pH-metric titration.

The material and the procedure of the titration are the same for the titration of a strong acid – strong base (Fig. 7.8).
Unlike the titration of a strong acid or a strong base, the addition of distilled water to the beaker in order to immerse the electrode of the pH meter, will affect the pH at equivalence point. But it will not affect the volume of base added to reach the equivalence point.
The laboratory investigation 1 and 2 permits us to perform the titration of some common weak acids.

7.3

Study of the pH changes that occur during the reaction between a solution of a weak base and a solution of a strong acid

■ Reaction between a weak base and a strong acid in aqueous solution

When NH_3 solution ($pK_a = 9.20$) reacts with a solution of hydrochloric acid HCl, according to the following equation:

$$NH_3 + H_3O^+ \rightarrow NH_4^+ + H_2O$$

The reaction is practically complete because NH_3 is the stronger base in the solution and H_3O^+ is the stronger acid (Fig. 7.9) and the constant of the reaction K_R is greater than 10^4 ($pK_{a2} - pK_{a1} = 9.20 - 0 = 9.20 > 4$).

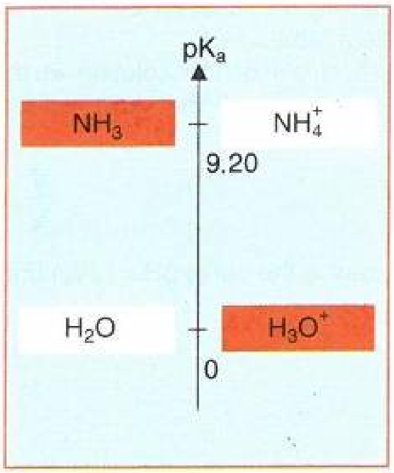


Figure 7.9
The reaction between the base NH_3 and the acid H_3O^+ in aqueous solution is complete .

After the NH_4^+ ion is formed, it reacts with water in a partial reaction (Fig. 7.10) according to the equation:

$$NH_4^+ + H_2O \rightleftarrows NH_3 + H_3O^+$$

The resulting medium is acidic.

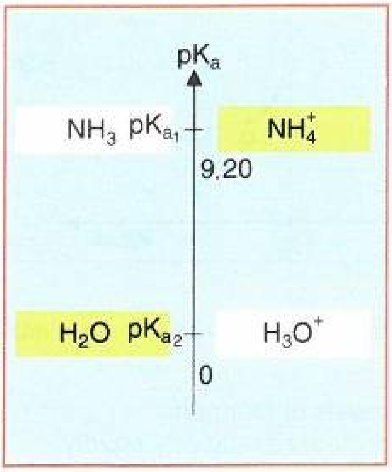


Figure 7.10
The reaction between NH_4^+ and H_2O in solution is partial, it goes to a very small extent.
($pK_{a_2} - pK_{a_1} = 0 - 9.20 = - 9.20 << 4$).

The reaction between ammonia NH_3 and HCl in aqueous solution can be represented by the following equation,

$$NH_3 + H_3O^+ \underset{2}{\overset{1}{\rightleftarrows}} NH_4^+ + H_2O$$

which shows that the reaction proceeds (favored) in direction 1. Considering a weak base B, in general, the equation of the reaction in aqueous solution, between this base and a strong acid is represented by:

$$B + H_3O^+ \underset{2}{\overset{1}{\rightleftarrows}} BH^+ + H_2O$$

It indicates that the reaction is practically complete in direction 1.

- **Study of the pH changes during the reaction**

Activity 2 Changes of pH of ammonia as a function of the volume of hydrochloric acid added.

Objective

Study the reaction between a weak base and a strong acid by pH metery.

Equipment and reagents

Same materials as for activity 1.
1×10^{-2} mol.L^{-1} solution of NH_3. 1×10^{-2} mol.L^{-1} solution of HCl.

Procedure

Follow the same procedure of activity 4 of chapter 5.
Assemble the results obtained in a table.
Trace the curve of the changes of pH of the solution in the beaker as a function of the volume of the acid added, pH = f (V_a).

- Describe the curve pH = f (V_a).
- Determine the equivalence point.
- Is the pH at equivalence point greater, smaller or equal to 7?
  Justify the nature of the solution obtained.

- **curve pH = f (V_a)**

The values in table 7.2 permits tracing the curve pH = f (V_a) (Fig. 7.11).

V_a(mL)	pH	V_a(mL)	pH
0	10.6	19	8.4
2	10	19.5	8.05
4	9.7	20	5.6
6	9.5	20.5	3.15
8	9.35	21	2.9
10	9.2	22	2.6
12	9	24	2.4
14	8.85	26	2.3
16	87	28	2.28
18	8.5	30	2.25

Table 7.2

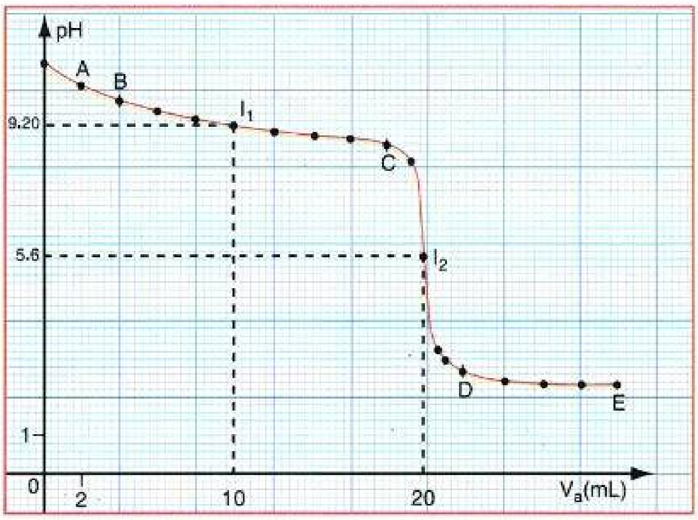


Figure 7.11
Curve of the changes of the pH of ammonia solution as a function of the volume of the strong acid solution added.

The curve is descending. It consists of four parts:
Part AB (V_a < 4 mL). The pH decreases relatively rapidly.
Part BC (4 mL < V_a < 18 mL). The pH varies slightly forming a plateau. The curve has an inflection point of coordinates (10 mL; 9.20).
Part CD (18 mL < V_a < 22 mL). The pH decreases rapidly. The curve shows a sudden drop of pH and a second inflection point.
Part DE (V_a > 22 mL). The pH varies again slightly and forms a

second flatline. The curve approaches a horizontal asymptote.

Half-equivalence point

In activity 2, when we add 10 mL of the 1 x 10^{-2} $mol.L^{-1}$ hydrochloric acid solution to 20 mL of the 1 x10^{-2} $mol.L^{-1}$ of ammonia solution in the beaker, the quantity of consumed base in the reaction is equal to half the quantity of the initial amount of the base. The quantity of the base left in the beaker is equal to half the initial amount of the base.
According to the equation of the reaction:

$$NH_3 + H_3O^+ \rightarrow NH_4^+ + H_2O$$

A quantity of NH_4^+ ions formed equals the quantity of the ammonia used.
In terms of concentration, after the addition of a volume of the acid equal to half the volume at equivalence ($V_E/2$), the concentrations of $[NH_3]$ and $[NH_4^+]$ are equal in the solution. This corresponds to half-equivalence point.

During the reaction between a weak base B and a strong acid, half-equivalence point corresponds to the consumption of half the amount of the base.

At the half-equivalence and in the equation:

$$pH = pK_a + \log \frac{[NH_3]}{[NH_4^+]}$$

the ratio :

$$\frac{[NH_3]}{[NH_4^+]}$$

is equal to1 and the term:

$$\log \frac{[NH_3]}{[NH_4^+]}$$

is equal to zero. The pH of the solution is equal to the pK_a of the pair NH_4^+ / NH_3; equals in this case to 9.20.

At half-equivalence point of the reaction between a weak base B and a strong acid, the pH of the solution is equal to the pK_a of the conjugate pair BH^+ / B.

On the curve pH = f (V_a) of activity 2, the half-equivalence, characterized by the volume V_a = $V_E/2$ and pH = 9.20, corresponds to a first inflection point, which is located in the part BC and having the coordinates (10 mL; 9.20) (Fig. 7.12).

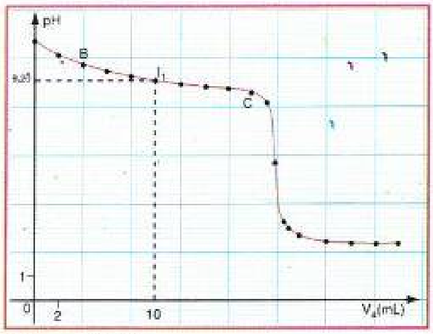


Figure 7.12
The half-equivalence point is the inflection point of the part BC of the curve.

Equivalence point

Designating C_b and C_a as the respective concentrations of the base and acid solution, V_b and V_a as the respective volumes of the two solutions utilized to reach the equivalence point, then the number of moles, n_b and n_a of the base and the acid that react, are given in the following relations:

$$n_b = C_b \times V_b$$
$$n_a = C_a \times V_a$$

The number of moles being equal, then, at equivalence point:

$$C_b \times V_b = C_a \times V_a$$

Like the other curve pH = f (V) studied, the equivalence of the reaction between a weak base NH_3 and the strong acid HCl corresponds to an inflection point located in the region of the sudden drop in the pH.

Graphically, this point is determined by the method of parallel tangents (Fig. 7.13).

From the curve, we can also get the value of pH of the solution at equivalence. It is 5.6. The pH is < 7, the solution is acidic.

In fact, we have seen earlier that the weak acid NH_4^+, formed by the reaction between the base NH_3 and hydrochloric acid, react with water via a very limited reaction to form the H_3O^+ ions in the solution.

This is a general observation of the pH at equivalence of the solution resulting from the reaction of a weak base with a strong acid.

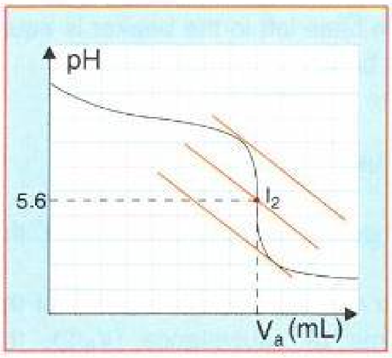


Figure 7.13

The equivalence point is determined graphically by the method of parallel tangents. The pH at equivalence point is <7. It is 5.6. The solution is acidic.

For the reaction of a weak base B with a strong acid, the solution at equivalence point is less than 7, the solution is acidic.

- **Effect of concentration**

Repeating the procedure of activity 2, with different concentrations of ammonia and hydrochloric acid: $C_b = C_a = 1 \times 10^{-1}$ mol.L^{-1} from one side, and $C_b = C_a = 1 \times 10^{-3}$ mol.L^{-1} from the other side and including the obtained results of activity 2 ($C_b = C_a = 1 \times 10^{-2}$ mol.L^{-1}), we can study the effect of the concentration of the basic solution on the pH at equivalence point (Fig. 7.14).

We notice that for the three curves pH = f(V_a), that the pH at equivalence point is < 7. This pH increases as the initial concentration of the base decreases.

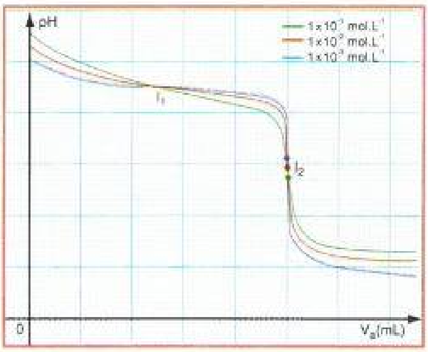


Figure 7.14

The pH at the equivalence point increases as the initial concentration of the base decreases.

7.4 Titration of a weak base using pH-meter

The reaction between a weak base and a strong acid is practically complete, rapid and unique. It could then be utilized for titrating a solution of a weak base. The concentration C_b is then determined from the equation:

$$C_b \times V_b = C_a \times V_a$$

at the equivalence point.

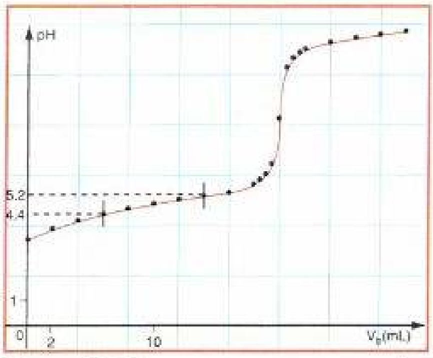


Figure 7.15
The pH of the acetic acid solution varies slightly around the half-equivalence point.

The equivalence point E is determined graphically from the curve pH = f (V).
The material and the procedure of the titration are the same for the titration of strong acid – strong base.
As in the titration of a weak acid with a strong base the addition of distilled water to the beaker to immerse the electrode of the pH meter will affect the pH at equivalence point, but will not affect the volume at equivalence point.
Laboratory investigation 3 permits performing the titration of a household product containing a weak base.

7.5 Buffer solutions

We have seen that at the half-equivalence point of the reaction between the weak acid CH_3COOH and the strong base NaOH, the concentrations $[CH_3COO^-]$ and $[CH_3COOH]$ in the solution are equal. Consequently, the pH of the solution is given by the relation,

$$pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

which is equal to pK_a of the conjugate acid-base pair CH_3COOH / CH_3COO^- (pH = 4.75 in this case).
On the curve pH = $f(V_b)$ corresponding to the reaction, around half-equivalence there is a region where the pH of the solution varies slightly (Fig. 7.15); and it stays constant (Table 7.3). We can say this is the buffer zone of pH.
The solution at half-equivalence point is called buffer solution.

V_b(mL)	pH
6	4.4
8	4.6
10	4.8
12	5.0
14	5.2

Table 7.3
Values of pH extracted from table 7.1 of the acetic acid solution around the half-equivalence point.

The solution obtained at half-equivalence between the reaction of the weak base NH_3 and the strong acid HCl is also a buffer solution. In this solution, $[NH_3] = [NH_4^+]$ and the pH equals to pK_a (pH = 9.20 in this case).
The curve pH = f (V_a) presents around the half-equivalence point, a buffer zone (Fig. 7.16) where the pH is almost constant (Table 7.4).
These observations are general for solutions containing a weak acid HA and its conjugate base A^- or a weak base B and its conjugate acid BH^+, where the concentrations of acid species and the base species are on the same order of magnitude.

A buffer solution is a solution of a weak acid and its conjugate base that gives a slight change in pH upon the moderate addition of a strong acid or a strong base.

- **Characteristics of a buffer solution**

Considering a buffer solution formed from acetic acid CH_3COOH and its conjugate base the ethanoate ion CH_3COO^- where $[CH_3COOH] = [CH_3COO^-] = 1 \times 10^{-1}$ mol.L^{-1}, the pH of the solution is 4.75.

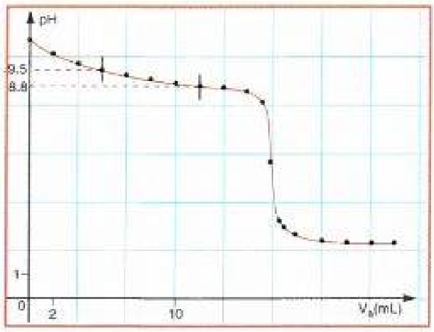


Figure 7.16
The pH of the ammonia solution varies slightly around the half-equivalence point.

V_a(mL)	pH
6	9.5
8	9.35
10	9.2
12	9.0
14	8.85

Table 7.4
Values of pH extracted from table 7.2 of the ammonia solution around the half-equivalence point.

- When we add the H_3O^+ ions, then the concentration of CH_3COO^- ions slightly decreases, and the concentration of CH_3COOH increases by the same magnitude, but the ratio of their concentration in the Henderson-Hasselbalch relation:

$$pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

varies very little so as the pH remains almost constant.

- We often use the Henderson-Hasselbalch equation, with initial concentrations [HA] and [B], of the acid HA and its conjugate base B, to calculate the pH of buffer solutions, without considering the reaction of HA and B with water.

For another buffer solution of composition $[CH_3COOH] = [CH_3COO^-] = 1 \times 10^{-2}$ mol.L^{-1}, the pH is also 4.75.
Furthermore, when the dilution of the buffer solution is increased, the pH will not remain constant, but varies slightly.

A buffer solution is characterized by a constant pH that changes slightly upon dilution.

Also a buffer solution is characterized by its buffer capacity.
The buffer capacity is evaluated by the quantity of a strong acid or a strong base which reacts with the buffer solution before the buffer solution starts to vary noticeably.

The buffer capacity of a buffer solution is high when the buffer is made up of equimolar mixture of the weak acid and its conjugate base.

This capacity becomes higher as the concentration of the acid and its conjugate base increases.
This last observation can be better understood when we monitor the behavior of the buffer solution when a strong acid or a strong base is added moderately.
When we add a small quantity of strong acid to a buffer solution, as with the conjugate acid-base CH_3COOH / CH_3COO^- for example, the ethanoate ion reacts with the H_3O^+ ion added, according to a reaction that is almost complete of equation:

$$CH_3COO^- + H_3O^+ \rightarrow CH_3COOH + H_2O$$

The H_3O^+ ions are consumed in this manner in the solution. This permits the pH of the buffer solution to remain almost constant.
If a small quantity of strong base is added to the buffer solution, the acid CH_3COOH reacts with the HO^- ions added, according to a reaction that is almost complete of equation:

$$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$$

The HO^- ions are also consumed from the solution by the same manner permitting the pH to remain almost constant.
This capacity of the buffer solution to eliminate the H_3O^+ and HO^- ions added to it, to keep the pH almost constant, is higher when the quantity of the weak acid and its conjugate base are higher in the solution; in other words, when the buffer solution is more concentrated.
Pure water, which does not have the capacity to eliminate the H_3O^+ and HO^- ions added to it, is subjected to a high variation of pH even for the moderate addition of such ions.

Solved exercise 1

Given

To 1 liter of a buffer solution of composition: $[CH_3COOH] = 1 \times 10^{-1}$ mol.L^{-1} and $[CH_3COO^-] = 1 \times 10^{-1}$ mol.L^{-1}, we add 2 mL of 5 mol.L^{-1} sodium hydroxide solution.

a) The change of volume of the solution being negligible, calculate the new pH.
b) Calculate the percentage of the change of pH.
c) If this volume of base is added to 1 L of pure water, calculate the pH of the obtained solution and the % of the change of pH.
d) Compare and conclude.
Given: $K_a = 1.8 \times 10^{-5}$

Solution

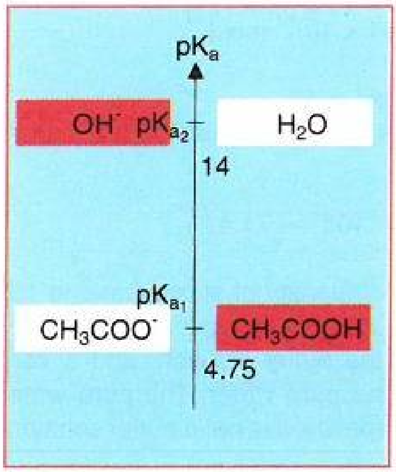


Figure 7.17
CH_3COOH is the stronger acid in the solution and OH^- is the stronger base. The reaction is almost complete because: $pK_{a_2} - pK_{a_1} = 14 - 4.75 = 9.25$.

a We start by calculating the new concentration $[H_3O^+]$ in the solution.

Figure 7.17 shows that the reaction between the acid CH_3COOH and the base HO^- is almost complete:

$$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$$

The number of moles of OH^- ions added is:

$$n(HO^-) = 5 \times 2 \times 10^{-3} = 1 \times 10^{-2} \text{ mol.}$$

This number reacts with an equal number of moles of CH_3COOH to form an equal number of moles of CH_3COO^- ions.

Then the number of moles of the acid after the reaction: $n(CH_3COOH) = 1 \times 10^{-1} - 1 \times 10^{-2} = 9 \times 10^{-2}$ mol.

Hence with this number of moles present in 1 liter, we have:

$$[CH_3COOH] = 9 \times 10^{-2} \text{ mol.L}^{-1}$$

For the CH_3COO^- ions, we have:

$n(CH_3COO^-) = 1 \times 10^{-1} + 1 \times 10^{-2} = 1.1 \times 10^{-1}$ mol.
and $[CH_3COO^-] = 1.1 \times 10^{-1}$ mol.L^{-1}.

After the reaction, the following equilibrium

$$CH_3COOH + H_2O \rightleftarrows CH_3COO^- + H_3O^+$$

At equilibrium (mol.L^{-1}) $9 \times 10^{-2} - x$ $1.1 \times 10^{-2} + x$ x

is established in the solution.

Designating by x the concentration of H_3O^+ in the solution, the expression for the acidity constant K_a allows us to write:

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = \frac{(1.1 \times 10^{-1} + x)(x)}{(9 \times 10^{-2} - x)}$$

But, the small value of the acidity constant (1.8×10^{-5}) permits to neglect x compared to the numerical values inside the parenthesis.

$$K_a = \frac{(1.1 \times 10^{-1})x}{9 \times 10^{-2}} = 1.8 \times 10^{-5}$$

which gives $[H_3O^+] = x = 1.47 \times 10^{-5}$ mol.L^{-1}

The pH of the solution is equal to:

$$pH = -\log(1.47 \times 10^{-5}) = 4.83$$

b The pH of the buffer solution before the addition of the base is equal to pK_a.

$$pH = 4.75$$

The percentage of change of pH of the solution is then equal to:

$$\frac{4.83 - 4.75}{4.75} \times 100 \approx 1.68\ \%$$

c Concentration of OH^- ions in H_2O:

$$[OH^-] = 1 \times 10^{-2}\ \text{mol.L}^{-1}$$

Then the concentration of H_3O^+ ions:

$$[H_3O^+] = 1 \times 10^{-12}\ \text{mol.L}^{-1}$$

The pH is equal to:

$$pH = 12$$

The pH of pure water being 7, the percentage of change of pH of water, then, is:

$$\frac{12 - 7}{7} \times 100 \approx 71.4\ \%$$

d The addition of the same quantity of strong base to 1 L of buffer solution and to 1 L of pure water caused a very slight change of pH in the buffer solution, and a very large change of pH in the pure water. The pure water does not have a buffer capacity; it is not a buffer solution.

Solved exercise 2

Given

To the same solution of the preceding exercise, we add 2 mL of 5 mol.L^{-1} hydrochloric acid instead of the basic solution. Solve, in this case, the same questions a), b), c), and d).

Solution

a Figure 7.18 shows that the reaction between the H_3O^+ ions and CH_3COO^- ions is almost complete, according to the following equation:

$$CH_3COO^- + H_3O^+ \rightarrow CH_3COOH + H_2O$$

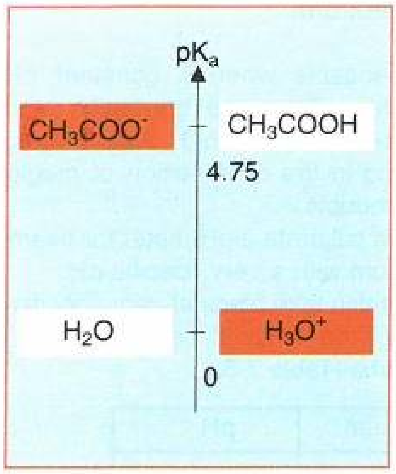


Figure 7.18
H_3O^+ is the stronger acid in the solution and CH_3COO^- is the stronger base. The reaction is complete because $pK_{a_2} - pK_{a_1} = 4.75 - 0 = 4.75$

From the equilibrium occurring in the solution:

$$\begin{array}{llllllll} & CH_3COOH & + & H_2O & \rightleftarrows & CH_3COO^- & + & H_3O^+ \\ \text{At equilibrium} & 1.1 \times 10^{-1} - x & & & & 9 \times 10^{-2} + x & & x \\ (\text{mol.L}^{-1}) & & & & & & & \end{array}$$

and with same previous reasoning, the concentration of H_3O^+ ion is given by the relation:

$$K_a = \frac{(9 \times 10^{-2} + x)x}{(1.1 \times 10^{-1} - x)} = 1.8 \times 10^{-5}$$

$$K_a = \frac{(9 \times 10^{-2})\,x}{(1.1 \times 10^{-1})} = 1.8 \text{x} 10^{-5}$$

$$[H_3O^+] = x = 2.2 \times 10^{-5}\ \text{mol.L}^{-1}$$

The pH of the solution is equal to:

$$pH = 4.66$$

b Percentage of change of pH:

$$\frac{4.74 - 4.66}{4.74} \times 100 \approx 1.68\ \%$$

c Concentration of H_3O^+ ions in H_2O:

$$[H_3O^+] = 1 \times 10^{-2}\ \text{mol.L}^{-1}$$

The pH is equal to: $pH = 2$

d Percentage of change of pH:

$$\frac{7 - 2}{7} \times 100 \approx 71.4\ \%$$

We make the same conclusion as for the preceding exercise but with the addition of an acid.

- We consider the absolute value of the change of pH: $pH_2 - pH_1 = |4.66 - 4.75|$ and $pH_2 - pH_1 = |2 - 7|$

- **Preparation of a buffer solution**

There are three ways to prepare a buffer solution formed by an equimolar mixture of a weak acid and its conjugate base, for example:

- To a volume V of a weak acid solution of concentration C, we add a volume equal to V/2 of a solution of the same concentration of a strong base. We then form the solution of half-equivalence point where the pH is equal to pK$_a$ and where the weak acid and its conjugate base have equal concentrations.
- In the preceding procedure, instead of the weak acid solution, we can use a weak base solution to which we add a strong acid solution, as in the same previous conditions.
- We can also prepare the mixture of volume V of the weak acid solution of concentration C and equal volume of the salt

of this acid, of the same concentration C. The mixture can also be prepared from a solution of a weak base and a solution of one of its salts.

Laboratory investigation 4 permits preparing buffer solutions.

Importance of buffer solutions

Buffer solutions are indispensable when a constant pH is required in a reaction system. They are generally used in laboratories and they have innumerable applications in biochemistry, in medicine and in the composition of medicinal drugs and in the cosmetic products.

In laboratory, they are used to calibrate a pH meter for example, or to ensure a reaction medium with a very specific pH.

The biochemical reactions, which take place at very specific pH, need a buffer medium. Blood, stomach fluid, pancreatic fluid and saliva constitute such mediums (Table 7.5).

Biological medium	pH
Blood	~ 7.4
Stomach fluid	~ 1.5
Pancreatic fluid	~ 7.5
Saliva	~ 7

Table 7.5

The pH of blood for example is constant and equals to about 7.4. It is buffered by the pairs H_2CO_3 / HCO_3^- and $H_2PO_4^-$ / HPO_4^{2-}
Seawater, a vital medium for innumerable living species (Fig. 7.19), is another example of buffer medium. Its pH varies between 8.1 and 8.3 at the surface.

Figure 7.19
Seawater, vital to many living species, is a buffer solution.

Chapter review

- The reaction between a weak acid HA and a strong base in aqueous solution is almost complete. It occurs according to the equation:

  $$HA + OH^- \rightarrow A^- + H_2O$$

  At equivalence point, the pH of the solution is basic because of the partial reaction of the following equation:

  $$A^- + H_2O \rightleftarrows HA + OH^-$$

- The half-equivalence point of the reaction between a weak acid and a strong base corresponds to equal concentrations of the acid and its conjugate base in the solution. The pH of the solution at half-equivalence point is constant and is equal to the pK_a of the acid/base pair considered.

- The pH-metric study of the reaction between a weak acid and a strong base permits us to determine the equivalence point and the half-equivalence point from the curves $pH = f(V_b)$.
  It also permits us to titrate a weak acid of unknown concentration.

- The reaction between a weak base and a strong acid in aqueous solution is practically complete. It occurs according to the equation:

  $$B + H_3O^+ \rightarrow BH^+ + H_2O$$

  At equivalence point, the pH of the solution is acidic because of the partial reaction of the equation:

  $$BH^+ + H_2O \rightleftarrows B + H_3O^+$$

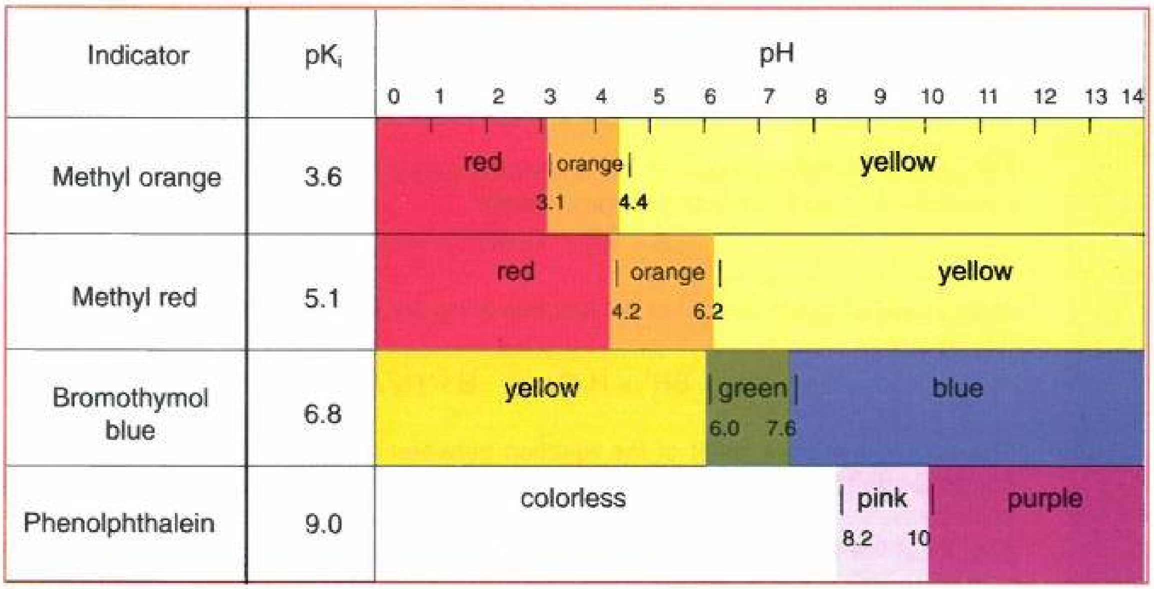
- The half-equivalence point of the reaction between a weak base and a strong acid corresponds to equal concentrations of the weak base and its conjugate acid in the solution.
  The pH of the solution at half-equivalence point is constant and is equal to pK_a of the acid/base pair considered.

- The pH-metric study of the reaction between a weak base and a strong acid permits us to determine the equivalence point and the half-equivalence point from the curves $pH = f(V_a)$.
  It also permits us to titrate a solution of weak base of unknown concentration.

- A buffer solution is a solution containing a mixture of a weak acid and its conjugate base. It is characterized by a constant pH that changes slightly upon dilution or the addition of small quantity of a strong acid or a strong base.

Acid-base titration utilizing indicators

The range of color change for an indicator that extends approximately over two units of pH, between the values $pK_i - 1$ and $pK_i + 1$, K_i, is the acidity constant of the $HInd/Ind^-$ conjugate pair.
Table 7.6 lists the most often used colored indicators with the range of predominance: of the acidic species HInd, the basic species Ind^-, and the range of color change of the indicator. In the table, the color of a solution in which the indicator is present is also given for each domain of predominance.



Indicator	pK_i	pH 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14
Methyl orange	3.6	red | orange | yellow 3.1 4.4
Methyl red	5.1	red | orange | yellow 4.2 6.2
Bromothymol blue	6.8	yellow | green | blue 6.0 7.6
Phenolphthalein	9.0	colorless | pink | purple 8.2 10

Table 7.6
Indicators can be used in the acid-base titration to indicate the equivalence point.

On the curve of the titration of a strong acid by a strong base, we indicate the range of color change of methyl orange, of bromothymol blue and of phenolphthalein (Fig. 7.20).

We notice that methyl orange changes color before the jump in pH, while the range of color change of bromothymol blue and of phenolphthalein coincides with jump in pH. The range of these two indicators indicates that equivalence is reached, while the range of methyl orange is not appropriate to show equivalence.

Moreover, we notice that the equivalence point is located in the range of color change of bromothymol blue. Consequently this indicator is more convenient than phenolphthalein for showing the equivalence point.

The condition for a colored indicator to be suitable to show equivalence is that the range of color change must contain the pH at equivalence or also that this range must be situated on the sudden jump in pH on the titration curve.

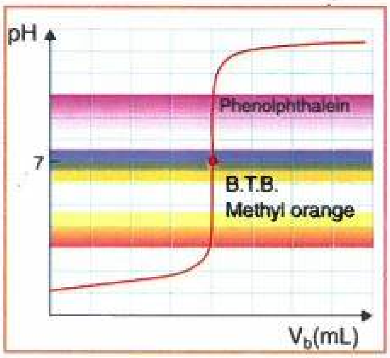


Figure 7.20
Location of pH change range relative to equivalence point.

The titration curve of a weak acid by a strong base (Fig. 7.21) shows that phenolphthalein and bromothymol blue (BTB) are suitable to indicate equivalence of the titration, because their range of color change is situated on the sudden jump in pH. Methyl orange, on the contrary, is not convenient.

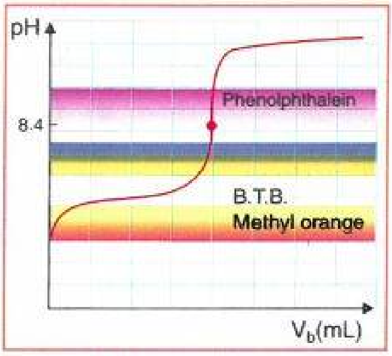


Figure 7.21
pH change range of indicators on a titration curve of a weak acid-strong base.

For the titration of a weak base with a strong acid, the titration curve shows that phenolphthalein and methyl orange are not convenient (Fig. 7.22).

A fourth indicator, methyl red, is more convenient, while BTB can be barely used, because its range of color change is almost situated on the jump in pH.

Indicators are utilized in dilute solutions so as not to affect the pH of the solution in which they are added.

For this reason, during acid-base titration with an indicator, just a few drops of the indicator solution must be added to the solution to be titrated.

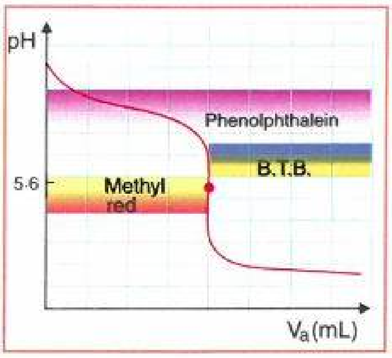


Figure 7.22
Range of color change of indicators on a titration curve of a weak base –strong acid.

To perform an acid-base titration with the aid of an indicator, a rapid titration is done, and an approximate value of volume of titrant is obtained, when the indicator changes color indicating that equivalence point has been reached.

Designating the volume obtained by V, we repeat the procedure by adding rapidly the titrant in order to reach a volume equal to (V-2) mL. At this moment, the titrant must be added slowly drop wise, until one drop causes a persistent color change of the solution.

We can repeat this precise titration to obtain the equivalence volumes V_E, which do not differ by more than 0.1 mL.
Then we report the average of these volumes.

Laboratory Investigation
LI 1

Objective

Titrate using a pH-meter the ascorbic acid ($C_6H_8O_6$) contained in a vitamin C tablet (500 mg).

Equipment and reagents

PH meter. Magnetic stirrer. 50 mL buret. 250 mL beaker. 100 mL graduated cylinder. Porcelain mortar and pestle. Glass rod.

500 mg tablet of vitamin C.

0.2 mol.L^{-1} sodium hydroxide solution.

Procedure

- Calibrate the pH meter.
- Grind the tablet to obtain fine powder. Place the powder in the beaker. Add 100 mL of distilled water and dissolve by stirring with the glass rod (Fig. 7.23).
  Constituents other than ascorbic acid present in the tablet will remain in suspension in the solution. Despite this, make sure that the acid solution is completely dissolved
- Fill the buret with the NaOH solution.
- Immerse the electrode in the solution in the beaker and start the magnetic stirrer.
- Add 1 mL increments of the base and record the pH values of the solution obtained after each addition.
- At the point when the pH changes noticeably, start adding 0.5 mL volume of the base each time.
- Again add 1 mL of the base when the pH varies slightly again.
- Continue the addition until a total volume is 25 mL.
- At the end of the titration, turn the pH-meter off. Rinse the electrode, cover and, store it.

Interpretation of the results

Plot the curve pH = f(V_b).

Determine the equivalence point by using the parallel tangents method. Record the pH value at equivalence point.

Analysis of vitamin C tablet

Figure 7.23

Grind the tablet to a fine powder to facilitate dissolving.

Determine the half-equivalence point and the pH of the solution at half-equivalence point.

Find the pK_a value of ascorbic acid pair from the literature and compare it with your value obtained.

Calculate the number of moles of ascorbic acid in the vitamin C tablet. Knowing that at the equivalence point:

$$n_a = n_b = C_b \times V_{bE}$$

Calculate the mass of ascorbic acid.

Compare this value with the value written on the label of the vitamin bottle.

Example of results

$V_{bE} = 14.1$ mL

At equivalence point; pH ≈ 8.3

$V_{bE}/2 = 7.05$ mL

At the half-equivalence point; pH = 4

Then $pK_a = 4$

$n_a = n_b = 14.1 \times 10^{-3} \times 0.2 = 2.82 \times 10^{-3}$ mol.

$M(C_6H_8O_6) = 176$ g.mol^{-1}, then:

$m_a = 176 \times 2.82 \times 10^{-3} = 0.496$ g.

$m_a < 500$ mg, the mass of ascorbic acid indicated on the label.

Laboratory Investigation

LI 2

Determination of the acid content "degree of acidity" of vinegar

Objective

Titrate using a pH-meter the acetic acid contained in vinegar to determine the acid content "degree of acidity" of vinegar. This degree of activity is equal to the mass of acetic acid present in 100 g of vinegar.

Equipment and reagents

pH meter. Magnetic stirrer. 50 mL buret. 250 mL beaker. 100 mL graduated cylinder. 10 mL pipet. 20 mL pipet. Pipet bulb.

A bottle of white vinegar. 0.1 $mol.L^{-1}$ sodium hydroxide solution.

Procedure

- Obtain 10 mL from the commercial vinegar, and dilute it 10 times (Fig. 7.24).
  To do this dilution, take 10 mL of the concentrated vinegar and dilute it in a 100mL volumetric flask with distilled water. Homogenize the solution.
- Calibrate the pH-meter.
- Fill the buret with NaOH solution and adjust the reading level.
- Place 20 mL of the diluted vinegar solution in the beaker. Immerse the electrode and adjust the magnetic stirrer.
- Proceed titrating the solution in the beaker in the same manner as in the laboratory investigation 1.
  Use a total of 30 mL of the basic solution.
- At the end of the titration, turn the pH-meter off. Rinse the electrode, cover it and store it.

Interpretation of the results

Plot the curve pH = $f(V_b)$. Determine the equivalence point by using the parallel tangents method. Record the pH value at equivalence point.

Determine the half-equivalence point and the pH of the solution at half-equivalence point.

Compare the value of this pH with the pK_a value of the pair CH_3COOH/CH_3COO^- ($pK_a = 4.75$).

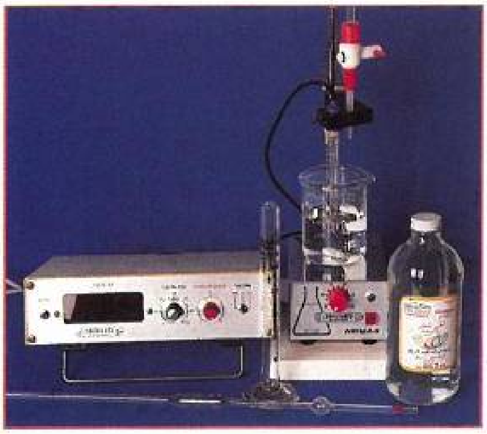


Figure 7.24

Vinegar is a solution of acetic acid.

At the equivalence point,

$$C_a \times V_a = C_b \times V_b$$

calculate the concentration of the diluted solution. Deduce the concentration of vinegar and its degree of acidity.

Example of results

The degree of acidity of vinegar utilized is 4° and $\rho = 1\ kg.L^{-1}$.

$M(C_2H_4O_2) = 60\ g.mol^{-1}$.

At equivalence point; $V_{bE} = 14$ mL, pH $\approx$ 8.6.

At half-equivalence point: $V_{bE}/2 = 7$ mL, pH = 4.8. Then $(pK_a)_{exp.} = 4.8$. The value obtained is very close to 4.75.

Diluted solution:

$$C_a = \frac{0.1 \times 14}{20} = 0.07\ mol.L^{-1}$$

Commercial solution :

$C'_a = 10\ C_a = 0.7\ mol.L^{-1}$.

Degree of acidity determined experimentally is: 4.2°.

Laboratory Investigation

LI 3

Titration of the ammonia contained in a household product

Objective

Titrate a household product containing a weak base.

On the container of the product used, it is indicated: "contains ammonia" and no information about the quantity of ammonia present (Fig. 7.25).

Equipment and reagents

pH meter. Magnetic stirrer. 25 mL buret. 250 mL beaker. 20 mL pipet. Pipet bulb. A bottle of household product containing ammonia. 0.1 mol.L^{-1} hydrochloric acid solution.

Procedure

- Calibrate the pH meter.
- Fill the buret with HCl and adjust the level of buret reading.
- Place 20 mL of the household product in the beaker. Immerse the electrode and adjust the speed of the magnetic stirrer.
- Titrate the solution in the beaker in the same manner as laboratory investigation 1. Use a total of 25 mL of HCl from the buret.
- At the end of the titration, turn off the pH meter. Rinse the electrode, cover it and store it.

Interpretation of the results

Plot the curve pH = f(V_a).

Determine the equivalence point by using the parallel tangents method.

Record the pH value at equivalence point.

Determine the half-equivalence point and the pH of the solution at half-equivalence point.

Compare the pH value with the pK_a for NH_4^+/NH_3 (pK_a = 9.20).

At the equivalence point:

$$C_a \times V_a = C_b \times V_b$$

Calculate the concentration of the ammonia present in the household product.

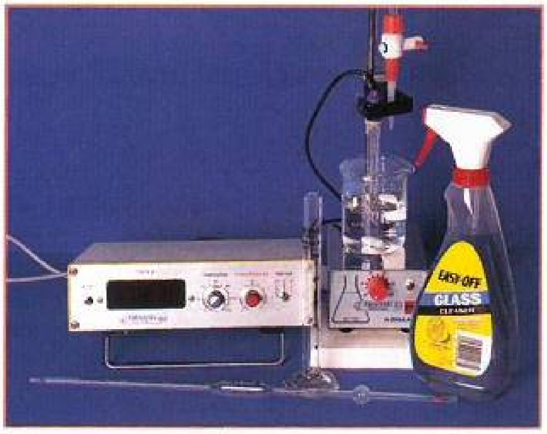


Figure 7.25

The household product containing ammonia, a weak base.

Example of results

At equivalence point:

$V_{aE} = 13$ mL; pH ≈ 5.3.

At half-equivalence point:

$V_{aE}/2 = 6.5$ mL; pH ≈ 9.10

(a value close to the pK_a of NH_4^+/NH_3).

$$C_b = \frac{C_a \times V_{aE}}{V_b} = \frac{0.1 \times 13}{20}$$

$C_b = 0.065$ mol.L^{-1}.

Laboratory Investigation

LI 4

Preparation of a buffer solution from an acetic acid solution and sodium ethanoate solution.

Objective

Prepare a buffer solution from an equimolar mixture of a weak acid and its conjugate base.

Equipment and reagents

25 mL pipet. 250 mL Erlenmeyer flask. 0.2 mol.L^{-1} acetic acid CH_3COOH solution. 0.2 mol.L^{-1} sodium ethanoate CH_3COONa solution.

Procedure

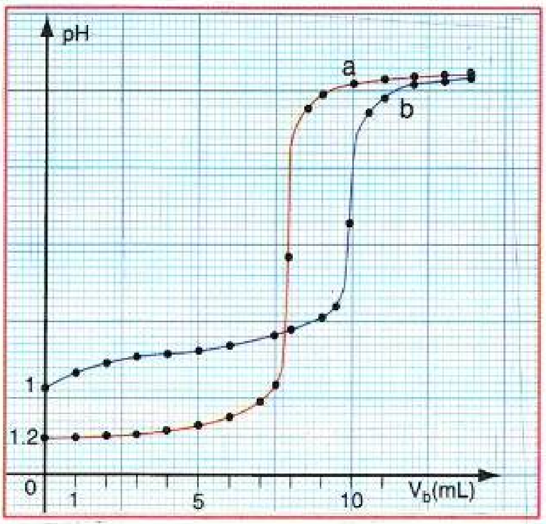
- Rinse the pipet with distilled water and then with acetic acid.
- Introduce 50 mL of the acetic acid solution into a very clean Erlenmeyer flask by using the 25 mL pipet.
- Rinse the pipet with tap water, distilled water, and then with the sodium ethanoate solution.
- Introduce 50 mL of the sodium ethanoate solution into the same Erlenmeyer flask by using the 25 mL pipet.
- Swirl the Erlenmeyer flask to homogenize the solution mixture (Fig. 7.26).
- Transfer into a clean flask, label and store.

Figure 7.26

Equimolar mixture of CH_3COOH and CH_3COO^-, which forms a buffer solution.

Exercises

1 A solution of weak acid HA_1 and a solution of strong acid HA_2 were titrated successively by 1×10^{-1} mol.L^{-1} sodium hydroxide solution. In each case, the sodium hydroxide solution was added progressively to 10 mL of the acid solution and the pH values were recorded. The curve $pH = f(V_b)$ for both solutions are represented on the same graph.



a) Identify on the graph, without calculations, the curve corresponding to each acid. Give the reasons for your choice.

b) Determine the volume at equivalence point for each solution, and calculate the concentration of the corresponding acid.

c) Extract the pH values at equivalence point. Do they agree with the previous identification of the two curves?

d) Using the curve $pH = f(V_b)$, calculate the pK_a of the weak acid.

e) Draw a diagram of increasing pK_a, and calculate the constant K_R of the reaction of each acid with OH^- ions. Do the obtained values justify these reactions for titrating each acid? Why?

2 To obtain an aqueous solution A of monochloroethanoic acid $CH_2ClCOOH$, 1.89 g of this acid were dissolved in a total volume of 2 liters.

a) Calculate the concentration of solution A. $M(CH_2ClCOOH = 94.5$ g.mol.$^{-1}$).

b) The pH of solution A is 2.53. Show that this corresponds to a weak acid. Calculate K_a and pK_a of the corresponding pair.

c) 10 mL of sodium hydroxide solution B were added to 20 mL of solution A to reach equivalence point. Calculate the concentration of solution B. Calculate the concentration of the monochloroethanoate ion CH_2ClCOO^- formed.

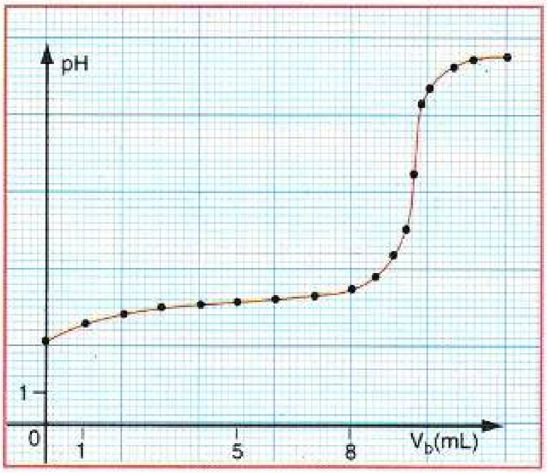
d) Calculate the constant of the reaction between CH_2ClCOO^- ion and water. Conclude. What is the nature of the solution obtained?

e) Calculate the pH of the solution. Conclude.

3 Vitamin C is ascorbic acid of formula $C_6H_8O_6$ which is considered a monoacid HA.

A tablet of vitamin C is dissolved in 100 mL of distilled water and the solution obtained is titrated with 3×10^{-1} mol.L^{-1} sodium hydroxide solution.

The pH values recorded during the titration permit us to trace the curve $pH = f(V_b)$.



a) Is the ascorbic acid a strong or weak acid? From the above curve:
b) Calculate the concentration of the acid solution HA.
c) Determine pK_a.
d) Determine the pH at equivalence point. Is it expected? Justify your answer.

4 A volume of 20 mL of hypochlorous acid HClO solution of unknown concentration C_a, is titrated with 1×10^{-2} $mol.L^{-1}$ sodium hydroxide solution.
The results obtained are given in the following table:

V_b (mL)	0	0.5	1	2	3	4	5
pH	6.0	6.4	6.6	7.0	7.3	7.5	7.6

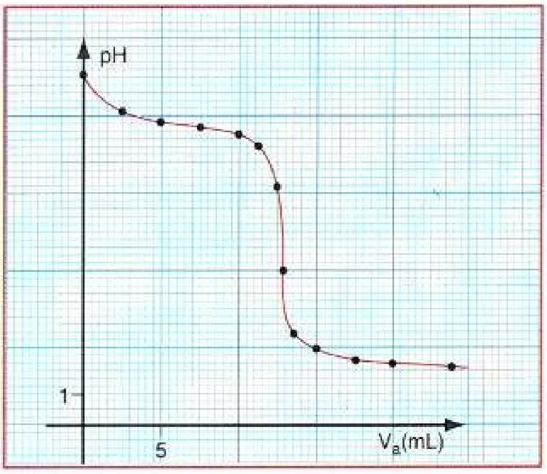
V_b (mL)	6	7	8	9	10	12	14
pH	7.8	8.0	9.5	10.8	11.0	11.1	11.2

a) Trace the curve pH = $f(V_b)$.
b) Determine the equivalence point and deduce the concentration of the acid solution.
c) Determine, from the curve, the pK_a of the pair $HClO/ClO^-$.
d) Deduce the constant K_R of the acid-base reaction. Is this reaction complete?
e) To what limit does the curve pH = $f(V_b)$ approach when an excess of the base is added? Justify your answer.

5 Suppose that the label on a bottle of trimethylamine $(CH_3)_3N$ indicate:
" trimethylamine is 45 % by mass" is to be verified in the laboratory.

A - 1 L of solution S_1, which is 100 times more diluted, is prepared.
a) Calculate the volume to be taken from the bottle to prepare the solution S_1 and suggest the type of glassware to be used? Justify .
b) Describe the experimental procedure to be followed in order to prepare this solution and indicate the safety rules to be respected.

B - Solution S_1 is titrated using a pH-meter. For this, 5×10^{-2} $mol.L^{-1}$ solution of hydrochloric acid is added progressively to 10 mL of solution S_1. This permits us to trace the following curve pH = $f(V_a)$:



a) Write the equation for the reaction of trimethylamine and hydrochloric acid.
b) Determine on the curve the equivalence point and the pH at the half-equivalence point. What does this pH represent?
c) Justify qualitatively the pH value at the equivalence point.
d) Calculate the concentration of solution S_1. Deduce the concentration of the solution in the bottle. Does it agree with the information on the label?
Density = 0.86 $kg.L^{-1}$; $M((CH_3)_3N)$ = 59 $g.mol^{-1}$.
e) If an indicator is utilized during the titration of solution S_1, which of the following indicators would be more convenient? Justify your answer.

Indicator	pH range
Methyl orange	3.1 – 4.4
Methyl red	4.2 – 6.2
Bromothymol blue	6.0 – 7.6
Phenolphthalein	8.2 – 10.0

6 In order to titrate a solution of the base B, a hydrochloric acid solution of concentration $C=1\times10^{-1}$ mol. L^{-1} is added progressively to 10 mL of the base in a beaker and the pH is measured.

The results obtained are given in the following table:

V_a (mL)	0	1	2	3	4	5	6	7
pH	11.0	10.0	9.7	9.4	9.2	9.0	8.7	8.4

V_a (mL)	7.5	8	8.5	9.5	10	13	16	18
pH	8.0	5.3	2.5	2.1	2.0	1.7	1.5	1.4

a) Plot the curve pH = $f(V_a)$.

b) Is the base B strong or weak? Justify as you describe the different parts of the curve.

c) Is the pH at equivalence point an indication of the strength of the base?

d) Determine the equivalence point and deduce the concentration of the solution of B.

e) Deduce graphically pK_a of the conjugate pair of base B.

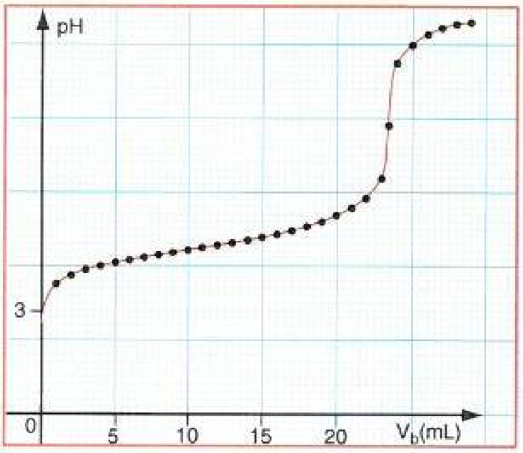
f) Is the reaction between the solution of the base B and HCl complete? Justify.

7 On the label of a 1 L bottle of commercial vinegar to be titrated, is written: "7 degree vinegar". The degree of acidity of vinegar corresponds, in reality, to the mass in grams of acetic acid in 100 g of vinegar.

A – An aliquot of the vinegar from the bottle is diluted 10 times giving solution S_1. What volume of vinegar should be taken from the bottle to prepare 100 mL of S_1?

B – 20 mL of solution S_1 is titrated using pH-meter with 1×10^{-1} mol.L^{-1} solution of sodium hydroxide. The acid solution is placed in the beaker and the base in the buret.

The results obtained permit us to trace the following curve:



a) Draw a diagram of the set-up for the titration, label its components and describe the experimental procedure.

b) Determine, from the graph the equivalence point and the pK_a for the conjugate pair CH_3COOH/CH_3COO^-.

c) Calculate the concentration of solution S_1. Deduce the concentration of the vinegar in the bottle.

d) Calculate the degree of acidity of vinegar, knowing that its density $\rho = 1.02$ kg.L^{-1}. Compare the value obtained with the value on the label.

8 A) A solution containing 1.5×10^{-1} mol.L^{-1} of acetic acid CH_3COOH and 1.2×10^{-1} mol.L^{-1} solution of sodium ethanoate CH_3COONa is prepared.

a) Write the equation of the reaction which determines the pH of the solution.

b) Calculate the pH of the solution knowing that the pK_a of the conjugate pair CH_3COOH/CH_3COO^- is 4.75.

B) 1×10^{-2} mol of HCl is added to 1 L of the above solution without changing the volume.

a) Write the equation of the reaction taking place. Can it be considered complete

b) Calculate the pH of the new solution. What conclusions can be drawn about the properties of this solution?

9 a) It is required to prepare a buffer solution of pH about 9.

Which of the following acid-base pairs given below is more convenient? Justify your answer.

$C_6H_5OH/C_6H_5O^-$	$pK_{a_1} = 10$
HCN/CN^-	$pK_{a_2} = 9.21$

b) 1×10^{-1} mol.L^{-1} solution of the acid HA and 1×10^{-1} mol.L^{-1} of a soluble salt of the base A^- are used. Calculate the volume V_1 of the HA solution that should be added to a volume V_2 of the A^- solution in order to prepare 100 mL of a buffer solution of pH = 9.

c) The pH of the prepared solution is 9.30. Calculate the concentration of the acid [HA] and its conjugate base [A^-] in the buffer solution.

10 A solution of pH = 4.4 is to be prepared from 100 mL of 2.5 x 10^{-2} mol.L^{-1} benzoic acid.

C_6H_5COOH / $C_6H_5COO^-$; $pK_a = 4.20$

a) What volume of 0.1 mol.L^{-1} of sodium hydroxide is to be added?

b) If a solution of sodium benzoate, of the same concentration, is used instead of sodium hydroxide solution, what volume V' should be added?

Evaluation

Applying knowledge

1 A powder used to lower the pH of the water of swimming pools contain sodium monohydrogen sulfate $NaHSO_4$. Suppose the acidic-basic properties of this powder are only due to the presence of HSO_4^- ions that belongs to the conjugate acid-base pair HSO_4^-/SO_4^{2-} of $pK_a = 1.9$ at 25 °C.

I- A mass m = 2 g of this commercial powder is dissolved in distilled H_2O to obtain a clear solution (S) of final volume $V_0 = 100mL$.

a) Indicate the materials needed to be used to prepare (S)?

b) Write the equation of the dissolution reaction, write the equation of the reaction of HSO_4^- with water. Why this product lowers the pH of water in swimming pools?

II- A volume V_A=10 mL of solution (S), is titrated with 0.1 mol. L^{-1} sodium hydroxide solution in the presence of phenolphthalein as indicator. The volume at the equivalence point is V_{BE} = 15 mL.

a) Indicate the materials needed to carry out the titration.

b) Write the equation of the titration reaction. Show that it is complete.

c) Justify the use of phenolphthalein (pH range 8.2 - 10) for this titration.

d) What is the concentration of hydrogen sulfate solution (S)?

e) Deduce the mass fraction of $NaHSO_4$ contained in the powder.
Given: Molar mass M($g.mol^{-1}$):
M(Na) = 23; M(H) = 1; M(S) = 32; M(O) =16.

III- The pH of solution (S) is 1.42. Calculate the degree of dissociation of HSO_4^-. What is / are the predominant species in the solution?

2 A tablet of effervescence aspirin contains acetylsalicylic acid designated by HA and sodium hydrogen carbonate $NaHCO_3$.

The pairs involved in the solution are given in the following table:

Conjugate Pair	H_2O/HO^-	H_3O^+/H_2O	HA/A^-
pK_a	14	0	3.6

Conjugate Pair	HCO_3^-/CO_3^{2-}	$CO_{2(dissolved)}/HCO_3^-$
pK_a	10.3	6.4

a) Arrange in an increasing order on a pK_a scale the different pairs.

b) Locate on this axis, without considering any dissociation, the chemical species introduced initially.

c) Deduce the equation of the principle reaction that occurs when the aspirin tablet is placed in water.

d) In what direction does this reaction occur?

e) Justify after observing the effervescence and the dissolution of the tablet.

3 The color of hydrangea, as well as a number of other flowers, is due to anthocyanes present in different acid-base forms of which some are blue and some are red. Explain this phenomenon.

4 A) The pH of human blood is normally about 7.4 at 37 °C. It can vary, without any risk, between the values 7.35 and 7.45. For this reason, blood is buffered by the following pairs, where their conjugate species are dissolved:

$CO_{2(dissolved)}/HCO_3^-$; $pK_{a_1} = 6.4$
$H_2PO_4^-/HPO_4^{2-}$; $pK_{a_2} = 7.2$

Calculate the ratios:
$[HCO_3^-]/[CO_{2(dissolved)}]$ and $[HPO_4^{2-}]/[H_2PO_4^-]$ in the blood of pH = 7.4.

B) When the pH of blood is below 7.35, this situation is known as acidosis. This is the most usual tendency of blood because the metabolism of the human body produces ordinarily a number of acids.

a) Calculate the ratio: $[HCO_3^-]$ / $[CO_{2(dissolved)}]$ corresponding to the beginning of an acidosis.

b) This situation occurs after a heavy physical activity for example. What spontaneous way does the body perform to eliminate the excess $CO_{2(dissolved)}$ in the blood?

c) Acidosis is fatal for pH < 6.8. Calculate the corresponding $[HCO_3^-]$ / $[CO_{2(dissolved)}]$ ratio.

Designing an experiment

5 Acid-base titration of a household product

Objective

Titrate a household product containing hydrochloric acid (Harpic powder; used for the removal of scales and sediments from pots and kettles).

Equipment and reagents

- 250 mL beaker, 25 mL buret, 5 and 10 mL pipets, 100 mL and 250 mL volumetric flasks.
- Balance.
- Magnetic stirrer; pH meter.
- Harpic powder.
- Indicators; 0.1 mol. L^{-1} sodium hydroxide solution, distilled water; standard solutions.

Principle

From a sample of the household product to be titrated, we prepare a dilute solution using an appropriate indicator, such as bromothymol blue (B.T.B.) and /or pH-meter.

Procedure

- Use safety goggles and gloves, dissolve 7 g of Harpic powder in a volumetric flask and add the necessary quantity of distilled water to obtain a volume V = 100 mL of a homogenous solution (S).
- Rinse the electrode and calibrate the pH-meter.
- Using a pipet bulb and a pipet, take a volume V_A=10 mL of solution (S), put them in the beaker and add about 90 mL of distilled water in order to immerse the electrode, and then add few drops of B.T.B.
- Fill the buret with sodium hydroxide NaOH solution.
- Add NaOH progressively, 1mL at a time, then around the equivalence start adding 0.2 mL increments. Record the corresponding pH values.

Interpretation of the results

- Arrange in a table the changes in pH values recorded as a function of the values of V_B of NaOH added.
- Plot the curve pH = f(V_B).
- Determine the equivalence point and the pH at equivalence point.
- Determine the concentration of the solution (S).
- Calculate the mass percent of hydrochloric acid in the household product. Compare the value obtained to that on the label.

Remark

Handle the household product with precaution since it contains a strong acid.

6 A bottle of unknown concentration of benzoic acid solution was found in a laboratory. Its pH was measured and found to be 2.6.

We then decided to titrate the solution. We have at our disposal 1 mol. L^{-1} sodium hydroxide solution and the following materials:

200 mL volumetric flask, 10 and 20 mL graduated pipets, 250 mL beaker, 50 mL graduated cylinder, 25 mL graduated buret and distilled water.

a) Describe the procedure to be followed to prepare a solution 1 x10^{-1} mol. L^{-1} solution of sodium hydroxide from the original NaOH solution; we proceed to titrate 10 mL of the benzoic acid solution. The pH changes as a function of volume of sodium hydroxide V added are given in the below table:

V(mL)	0	1	2	3	5	6	8	9	9.5
pH	2.6	3.3	3.6	3.9	4.2	4.4	4.8	5.2	5.5

V(mL)	9.8	9.9	10	10.1	11	12	14	16
pH	5.9	6.2	8.5	10.7	11.7	12	12.4	12.7

b) Draw the schema and label the parts of the titration setup used.

c) Trace the curve pH = f(V).

d) Determine from the graph the coordinates of the equivalence point. Deduce the concentration of the studied benzoic acid.

e) Deduce from the curve whether benzoic acid in a strong or weak acid.

Mastery-Communicating

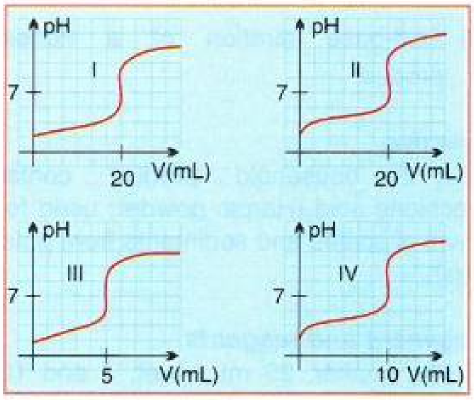
7 Using the four graphs $pH = f(V_{NaOH})$, indicate which correspond to the titration of:

a) 20 mL of 2×10^{-2} mol. L^{-1} ethanoic acid with 4×10^{-2} mol. L^{-1} NaOH.

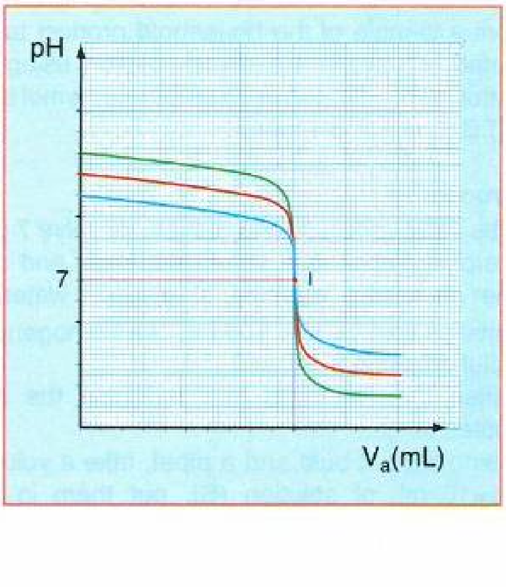
b) 5 ml of 2×10^{-2} mol. L^{-1} hydrochloric acid with 2×10^{-2} mol. L^{-1} NaOH

c) 20 mL of 2×10^{-2} mol. L^{-1} ethanoic acid with 2×10^{-2} mol. L^{-1} NaOH.

d) 10 mL of 2×10^{-2} mol. L^{-1} hydrochloric acid with 1×10^{-2} mol. L^{-1} NaOH.

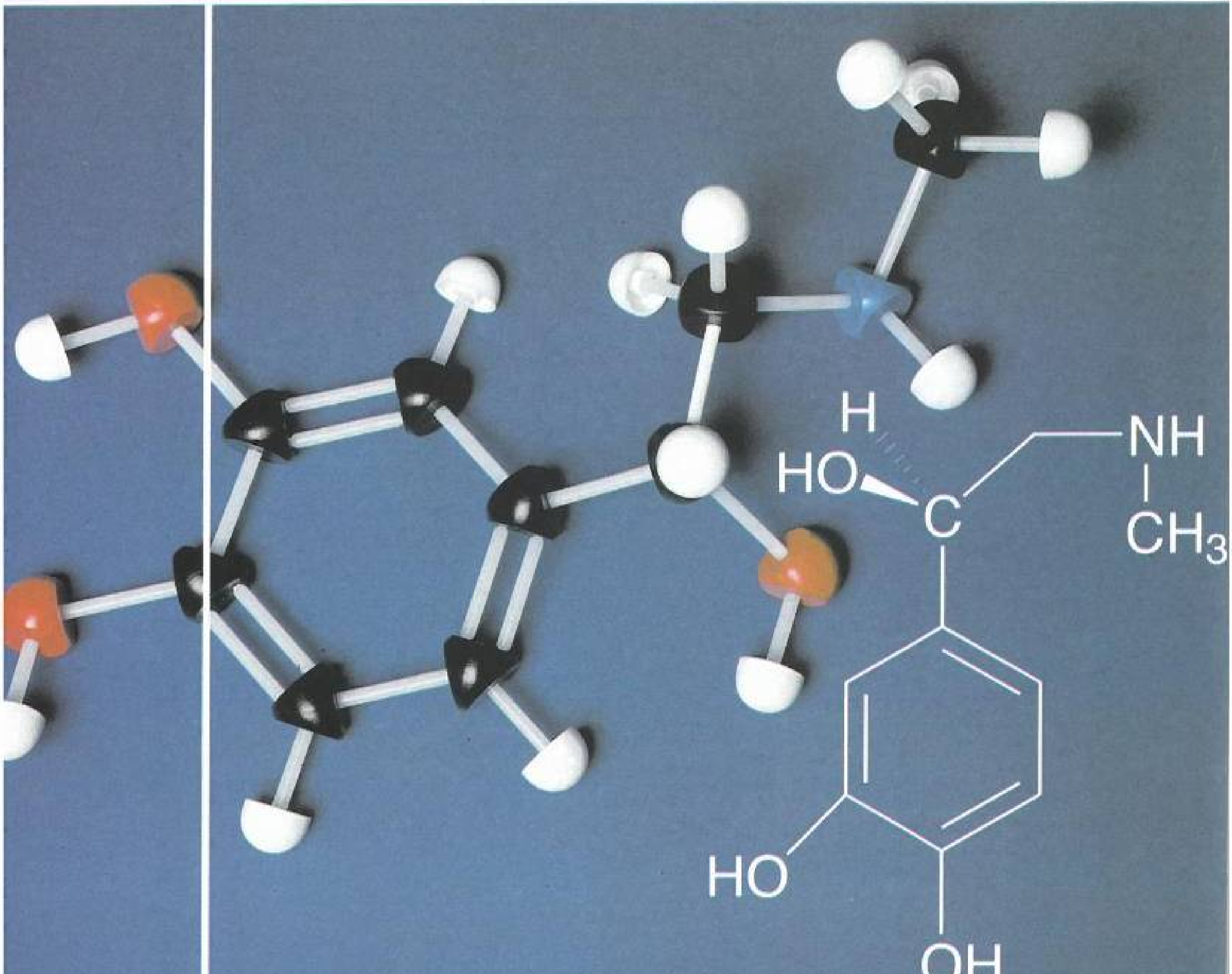


8 The following document shows the effect of concentration on the shape of the curve $pH = f(V_A)$.
Explain this graph

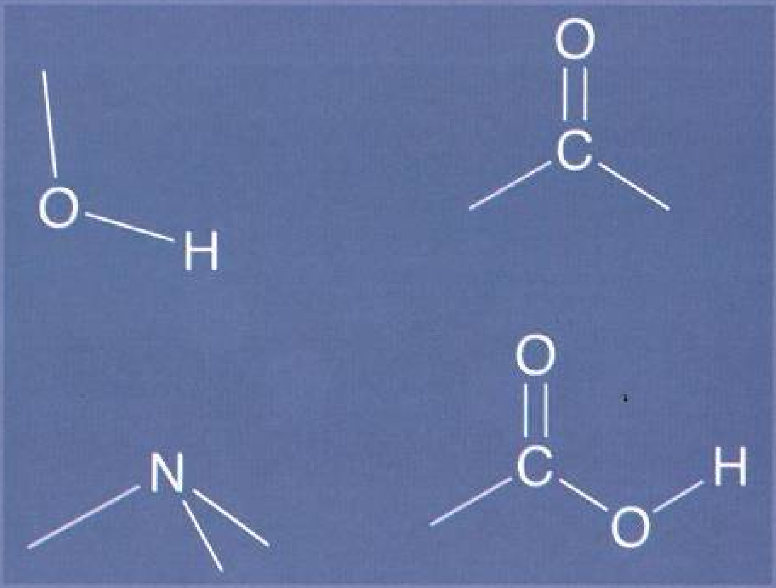


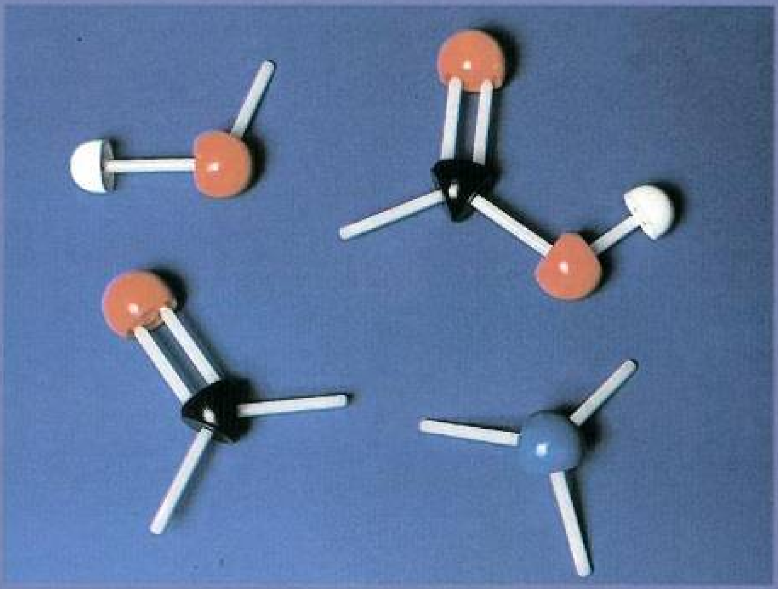
5

Organic chemistry II



Adrenaline is an organic substance that contains, other than carbon and hydrogen, the elements oxygen and nitrogen. It is a powerful stimulant to the central nervous system, which exalts the tone of the cardio-vascular system and raises the temperature of the body.





The molecules of some organic substances are characterized by the presence of particular groups of atoms called functional groups: hydroxyl group, carbonyl group, amino group.....
What is the structure of each of these functional groups?
What type of isomerism does each exhibit?

FUNCTIONAL GROUPS

8

Objectives

- Classify organic compounds into families based on their functional groups.
- Identify the functional groups
- Recognize positional and functional isomerism
- Know the nomenclature of functional groups

Prerequisites

- Chemical formula and bonding
- Stoichiometry and mole
- VSEPR method and hybridization of atomic orbitals
- Notion of isomerism
- Alkyl group (alkyl radical)

Chapter content

8.1 Organic compounds containing oxygen, nitrogen, and isomerism.
- Chapter review
- Method sheet
- Exercises

8.1 Organic compounds containing oxygen or nitrogen and isomerism

Chemical reactivity and other properties of organic substances are directly related to their molecular structures: type of bonds, hybridization of atomic orbitals and to the presence of particular groups of atoms called functional groups in their molecule (Fig.8.1 and 8.2).

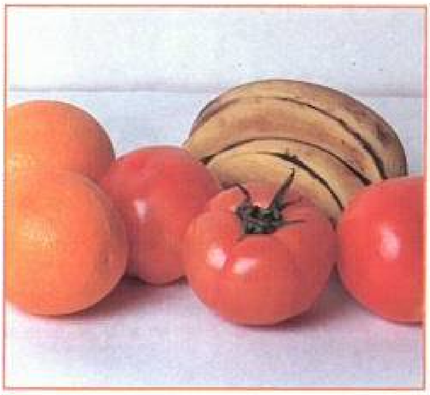


Figure 8.1
Organic molecules containing oxygen atoms are partially responsible for the aroma of fruits and vegetables.

Figure 8.2
Fish conserved badly release strong and disagreeable odor due to a substance called amine..

A functional group has characteristic properties and determines the chemical reactivity of organic substances.

- **Families of organic compounds**

- **Alcohols, aldehydes, ketones and carboxylic acids**

Activity 1

Construction of molecular models of an alcohol (CH_3OH) and an aldehyde (HCHO), a ketone (CH_3COCH_3) and a carboxylic acid (HCOOH)

Objective

Know the substances of functional groups containing oxygen.

Material

Molecular model kit.

Procedure and interpretation

Construct ball-and –stick model of methane CH_4 molecule, model of ethylene CH_2=CH_2 and models of two methyl groups CH_3—.

1- Construct the model of CH_3OH molecule starting from that of CH_4, replacing a hydrogen atom by an oxygen atom connected to another hydrogen atom (Fig.8.3).

$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array} \qquad \begin{array}{c} H \\ | \\ H-C-O-H \\ | \\ H \end{array}$$

Structural formulas of CH_4 and CH_3OH molecule.

The group —OH thus obtained is the hydroxyl group.

All the bonds in the CH_3OH molecule are single bonds. The carbon C and the oxygen O atoms are SP^3 hybridized. The shape of the C-O-H group is bent. The C— atom is tetrahedrally connected to the four atoms that surround it.

- What type of bonds does CH_3OH have?
- What is the type of hybridization for each C and O atoms?
- Write the structural formula of CH_3OH.

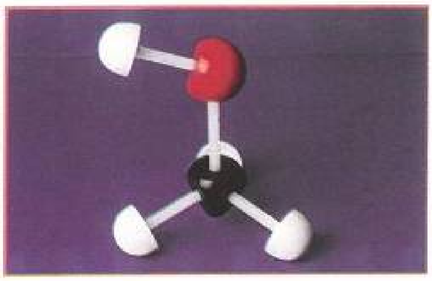


Figure 8.3

Ball -and -stick model of CH_3OH molecule.

- What type of bonds does the CH_2O molecule has?
- What is the hybridization of the C atom connected to the O atom in the CH_2O molecule and in the CH_3COCH_3 molecule?
- Write the structural formulas of the molecules of CH_2O and CH_3COCH_3.

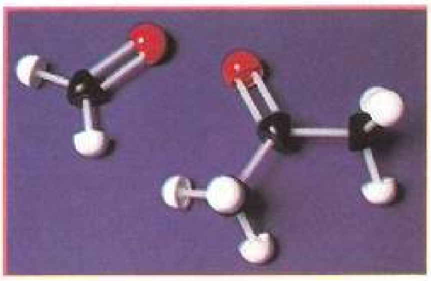


Figure 8.4

Ball-and-stick models of the molecule CH_2O and CH_3COCH_3.

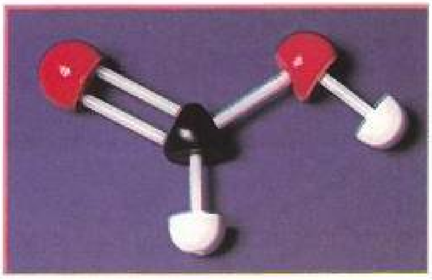
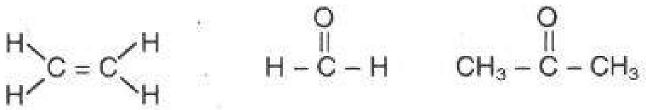


Figure 8.5

Ball-and -Stick model of the molecule HCOOH.

The hydroxyl group connected to a carbon atom characterizes the alcohols. Its shape is bent-planar.

2- Construct the model of a CH_2O molecule. Replace the two hydrogen atoms by two methyl groups $—CH_3$ (Fig. 8.4).



$$H-\overset{\overset{\displaystyle O}{\|}}{C}-H \qquad CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

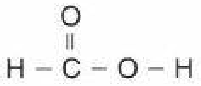
Structural formulas of the molecules $CH_2{=}CH_2$, CH_2O and CH_3COCH_3.

The group —CO— thus obtained is called carbonyl group.

The molecule CH_2O is planar, it has 2 single bonds and one double bond, in the two molecules thus constructed, the carbonyl carbon atom has an sp^2 hybridization and the shape of carbonyl group is plane-triangular.

The carbonyl group, which characterizes the aldehydes and ketones has a plane-triangular structure.

3- Construct a model of the molecule CH_2O. Replace a hydrogen atom by a hydroxyl group —OH (Fig.8.5)



$$H-\overset{\overset{\displaystyle O}{\|}}{C}-O-H$$

Structural formula of methanoic acid molecule.

The carboxylic carbon atom has sp^2 hybridization and the carboxyl group is flat at the corresponding carbonyl part. The oxygen of the OH group has sp^3 hybridization and the corresponding CHO group is bent-planar.

The group —COOH thus obtained is called carboxyl group. It characterizes the carboxylic acids.

- **Ethers and Esters**

- Replacing the hydrogen atom of the hydroxyl group in CH_3OH molecule by a methyl group, the molecule CH_3OCH_3 is obtained (Fig. 8.6).
  This molecule belongs to the family of ethers, characterized by the group C—O—C and has a general formula R—O—R′.
- Replacing the hydrogen of hydroxyl group in the molecule HCOOH, by a methyl group $-CH_3$ the molecule $HCOOCH_3$ is obtained (Fig.8.7).

This molecule belongs to the family of esters, characterized by the group –COOC.

$$\begin{array}{ccccccccc} & & H & & & & H & & \\ & & | & & & & | & & \\ H & - & C & - & O & - & C & - & H \\ & & | & & & & | & & \\ & & H & & & & H & & \end{array} \qquad \begin{array}{ccccccccc} & & O & & & & H & & \\ & & \| & & & & | & & \\ H & - & C & - & O & - & C & - & H \\ & & & & & & | & & \\ & & & & & & H & & \end{array}$$

Structural formulas of the molecules CH_3OCH_3 and $HCOOCH_3$.

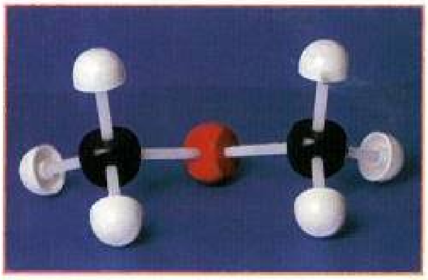


Figure 8.6
Ball-and stick model of the molecule $CH_3–O–CH_3$.

- Ethers are often called alkoxide. When R and R' are different, the ether is called mixed ether.

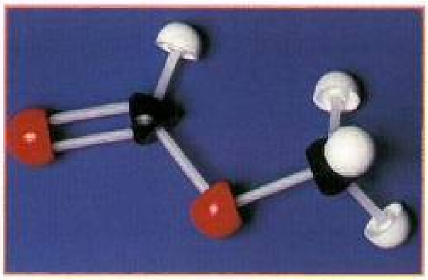


Figure 8.7
Ball- and-stick model of the molecule $HCOOCH_3$.

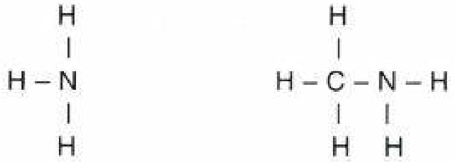
- **Amines**

Activity 2 Construction of the molecular model of an amine (CH_3NH_2)

Objective
Know the structure of a functional group containing nitrogen.

Material
Molecular model kit.

Procedure and interpretation
Construct ball-and-stick models for the molecule NH_3 and methyl group $–CH_3$.
Construct ball-and stick model for the molecule CH_3NH_2.
Replacing a hydrogen atom in the molecule of NH_3 ammonia by the methyl group (Fig. 8.8).



$$\begin{array}{ccc} & & H \\ & & | \\ H & - & N \\ & & | \\ & & H \end{array} \qquad \begin{array}{ccccccc} & & H & & & & \\ & & | & & & & \\ H & - & C & - & N & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

Structural formulas of the molecules NH_3 and CH_3NH_2.

The group $–NH_2$ thus obtained is called amino group.

The molecule NH_3 is pyramidal. The nitrogen atom has an sp^3 hybridization, which is conserved in the molecule CH_3NH_2.
The pyramidal shape is conserved in the amino group .

We note that the hydrogen atoms in the NH_3 molecule can successively be replaced by one, two or three alkyl groups R, thus leading respectively to three molecules, RNH_2, R_2NH and R_3N, that belong to the amine family.

The amino group connected to one, two or three carbon atoms (or alkyl groups), characterizes the amines. It has a pyramidal shape.

- What is the shape of the ammonia NH_3 molecule?
- What is the type of hybridization of the N atom in NH_3 and CH_3NH_2?
- Write the structural formula of the CH_3NH_2 molecule.

The main functional groups studied in this book are:
The hydroxyl group –OH
The carbonyl group –CO–

The carboxyl group –COOH
The amino group $-\underset{\vert}{N}-$

Thus, other groups, which are represented in table 8.1, give a general idea of the corresponding families of organic compounds, their general molecular formula, their characteristic functional groups and an example of each.

Compound's family	General formula	Functional group	Example
Alcohols	$R-OH$	$-OH$	CH_3-OH
Ethers	$R-O-R'$	$-O-$	CH_3-O-CH_3
Aldéhydes*	$(H)R-\underset{\underset{O}{\Vert}}{C}-H$	$-\underset{\underset{O}{\Vert}}{C}-H$	CH_3-CHO
Ketones	$R-\underset{\underset{O}{\Vert}}{C}-R'$	$-\underset{\underset{O}{\Vert}}{C}-$	$CH_3-CO-CH_3$
Carboxylic acids *	$(H)R-\underset{\underset{O}{\Vert}}{C}-OH$	$-\underset{\underset{O}{\Vert}}{C}-OH$	CH_3-COOH
Acyl chlorides*	$(H)R-\underset{\underset{O}{\Vert}}{C}-Cl$	$-\underset{\underset{O}{\Vert}}{C}-Cl$	CH_3-COCl
Acid anhydrides*	$(H)R-\underset{\underset{O}{\Vert}}{C}-O-\underset{\underset{O}{\Vert}}{C}-R'(H)$	$-\underset{\underset{O}{\Vert}}{C}-O-\underset{\underset{O}{\Vert}}{C}-$	$CH_3-\underset{\underset{O}{\Vert}}{C}-O-\underset{\underset{O}{\Vert}}{C}-CH_3$
Esters*	$(H)R-\underset{\underset{O}{\Vert}}{C}-O-R'$	$-\underset{\underset{O}{\Vert}}{C}-O-R'$	$CH_3-COOCH_3$
Amides*	$(H)R-\underset{\underset{O}{\Vert}}{C}-\underset{\underset{H(R'')}{\vert}}{N}-H(R')$	$-\underset{\underset{O}{\Vert}}{C}-\underset{\vert}{N}-$	CH_3-CONH_2
Amines*	$R-\underset{\underset{H(R'')}{\vert}}{N}-H(R')$	$-\underset{\vert}{N}-$	CH_3-NH_2

Table 8.1
R, R'and R" are identical or different alkyl groups.
* The alkyl group R can be replaced by H atom in these molecules.

Isomerism

Activity 3 Construction of molecular models for the isomers of molecular formula C_3H_8O.

Objective

Define positional and functional isomerism.

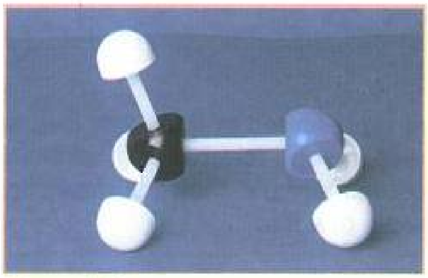


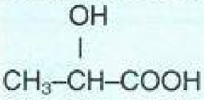
Figure 8.8

Ball-and-stick model of the molecule CH_3NH_2.

- In most cases, the molecules of natural substances have many functional groups. They are called poly functional.

Examples:

Lactic acid of formula:



$$CH_3\text{–}\overset{\overset{\large OH}{|}}{C}H\text{–}COOH$$

contains a hydroxyl group and a carboxyl group. It is bi-functional: the alcohol function and the carboxylic acid function.

Glycine of formula $H_2N\text{-}CH_2\text{-}COOH$ contains an amine group and a carboxyl group; it is bi-functional, amine function and carboxylic acid function.

- How many molecular models can be constructed for the molecular formula C_3H_8O?
- Write the structural formulas of the constructed models
- What structural difference is there among the models?
- To what families of organic compounds do these molecules belong?

Material

Molecular models kit.

Procedure

Construct two ball-and stick models of propane molecule $CH_3\text{–}CH_2\text{–}CH_3$ and the ball-and Stick model of the methyl group $-CH_3$ and ethyl group $CH_3\text{–}CH_2\text{–}$ or $(-C_2H_5)$.

Replace a hydrogen atom of a terminal carbon atom of the carbon chain in the first model, with a hydroxyl group –OH (Fig. 8.9).

Replace a hydrogen atom on the middle carbon atom of the carbon chain in the second model, by a hydroxyl group –OH (Fig. 8.9).

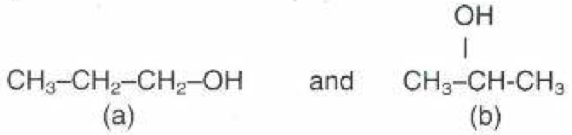
Connect the methyl and ethyl group to an oxygen atom (Fig. 8.10).

Try other combinations satisfying the valence of, C, O, and H atoms. Observe and conclude.

Observation

Three molecular models are constructed.

The first two have a chain formed of three carbon atoms, but differ in the position of the hydroxyl group on the chain. The first holds the hydroxyl group on the terminal carbon atom and the second on the middle carbon atom. Their structural formulas are respectively:



$$\underset{(a)}{CH_3\text{–}CH_2\text{–}CH_2\text{–}OH} \quad \text{and} \quad \underset{(b)}{CH_3\text{-}\overset{\overset{\large OH}{|}}{C}H\text{-}CH_3}$$

(a) and (b) belong to the alcohol family; they differ from each other, by the position of the functional group.

Positional isomers have a main chain containing the same number of carbon atoms, but have the same functional group at different carbon atoms.

A third model is formed by connecting to the oxygen atom a methyl group and an ethyl group, which has the condensed –structural formula of $CH_3\text{–}CH_2\text{–}O\text{–}CH_3$.

(c) belongs to the ether family.

(a) and (b) on one hand, and (c) on the other hand, are isomers that differ in the type of their functional groups. They are called functional isomers.

Functional isomers are compounds that have the same molecular formula but different functional groups.

The physical and chemical properties of ethers are very different from those of alcohols. This is generally observed in functional isomers.

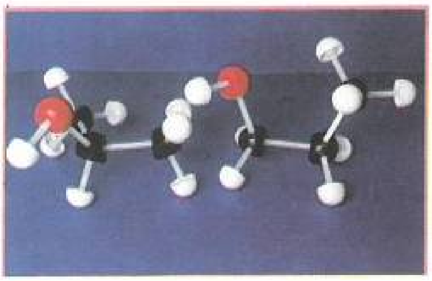


Figure 8.9

Ball-and-stick models of the first two isomers of molecular formula C_3H_8O.

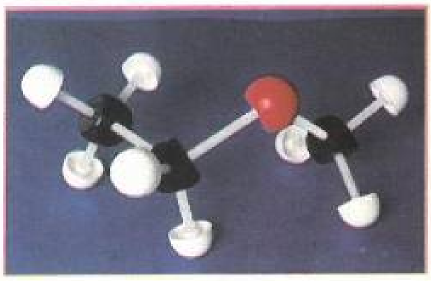


Figure 8.10

Ball-and-stick model for the third isomer of molecular formula C_3H_8O.

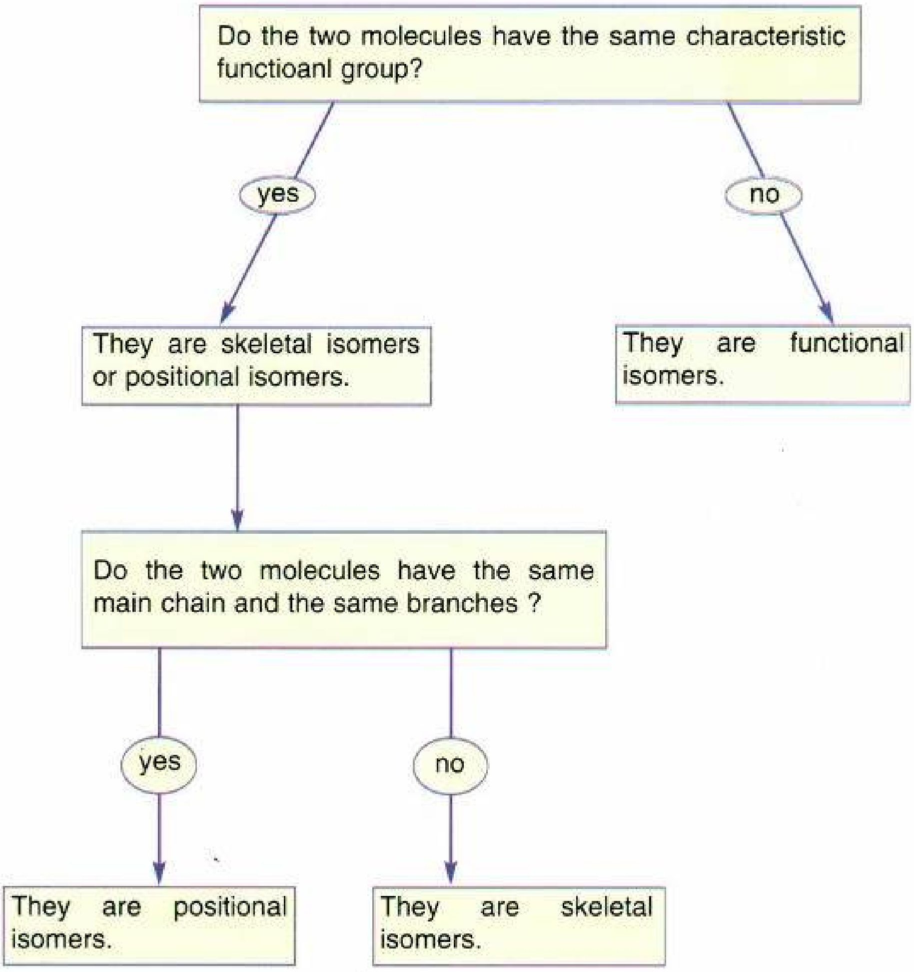
Chapter review

- A functional group has characteristic properties, and determines the chemical reactivity of organic substances.
- The hydroxyl group –OH characterizes the alcohols.
- The carbonyl group –CO- characterizes the aldehydes and ketones.
- The carboxyl group –COOH characterizes the carboxylic acids.
- The amino group $-\overset{|}{N}-$ characterizes the amines.
- Positional isomers differ in the position of the same functional group on the carbon chain.
- Functional isomers have different organic functional groups.

Isomeric relation-I-
Types of structural isomerism

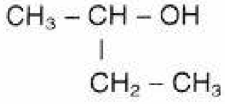
Two molecules that have the same molecular formula, but different structural formulas are structural isomers or constitutional isomers.

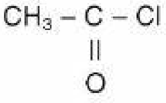
To show their isomeric relation, we proceed by the following sequence of questions and answers.

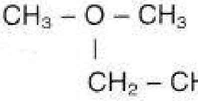


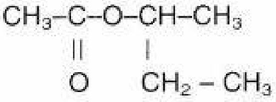
Exercises

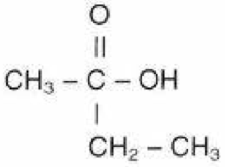
1 From the following structural formulas remove the incorrect one (s) :

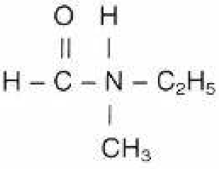
a) 
$CH_3-\underset{\underset{CH_2-CH_3}{|}}{CH}-OH$

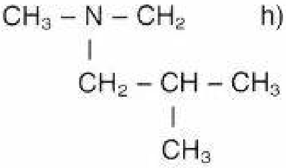
b) 
$CH_3-\underset{\underset{O}{\|}}{C}-Cl$

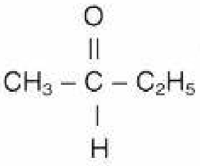
c) 
$CH_3-\underset{\underset{CH_2-CH_3}{|}}{O}-CH_3$

d) 
$CH_3-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{CH_2-CH_3}{|}}{CH}-CH_3$

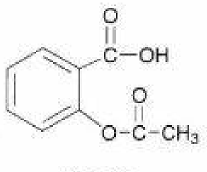
e) 
$CH_3-\overset{\overset{O}{\|}}{\underset{\underset{CH_2-CH_3}{|}}{C}}-OH$

f) 
$H-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{N}}-C_2H_5$

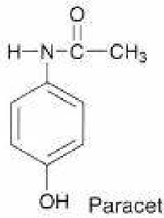
g) 
$CH_3-\underset{\underset{CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3}{|}}{N}-CH_2$

h) 
$CH_3-\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{C}}-C_2H_5$

2 Medicinal drugs are generally mixtures of complex molecules. The following molecules are present in some medications:



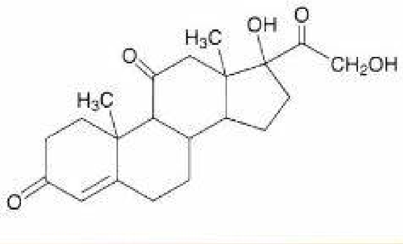
Aspirin



Paracetamol

$(C_6H_5)_2CH-O-CH_2-CH_2-N(CH_3)_2$

Dramamine



Cortisone

Circle the functional groups which contain oxygen and nitrogen atoms in each of the molecules given above.

3 The analysis of an organic substance (S) containing the elements carbon, hydrogen and oxygen gave the following mass composition:

C : 40 %
H : 6.7 %

a) Determine the empirical formula of (S).
b) Determine its molar mass, molecular formula and its structural formula, knowing that its relative density with respect to air is 1.04.
c) What functional group characterizes the molecule (S)? What is the family of the substance (S).

4 The complete combustion of 225 mg of an organic compound (s) containing nitrogen produces 220 mg of carbon dioxide, 135 mg of water, and 61 mL of nitrogen gas measured at 24 °C and a pressure of 1 bar.

a) Calculate the percent mass composition of (S).
b) The vapor density of (S) relative to air is 1.55. Calculate its molar mass and determine its molecular formula.
c) Assuming that compound (S) belongs to the amine family. Write its structural formula.

5 The analysis of an organic substance (S) gives the following mass composition:

C : 30.6 %
H : 3.8 %
Cl : 45.2%

a) Determine the empirical formula of (S).
b) Determine its molecular formula knowing that its molar mass is 78.5 $g.mol^{-1}$.
c) Write its structural formula, knowing that this molecule belongs to the acyl chlorides family.

6 The analysis of a gaseous organic substance containing the elements carbon, hydrogen and nitrogen gives the following mass composition:

C : 38.7 %
N : 45.2 %

a) Determine the empirical formula of this substance.
b) Determine the molar mass, molecular formula and the structural formula, assuming that its density relative to oxygen is 0.97.
c) To which family does this substance belong?

7 115 mg of a carboxylic acid is dissolved in 10 mL of water. The obtained solution is titrated with 10 $g.L^{-1}$ sodium hydroxide solution in the presence of phenolphthalein as indicator. The persistent pink color is attained after adding 10 mL of the basic solution.

a) Write the equation of the reaction.
b) Calculate the molar mass of the acid.
c) Determine the molecular formula and the structural formula of the acid.

Given: H = 1; O = 16; Na = 23 ($g.mol^{-1}$).

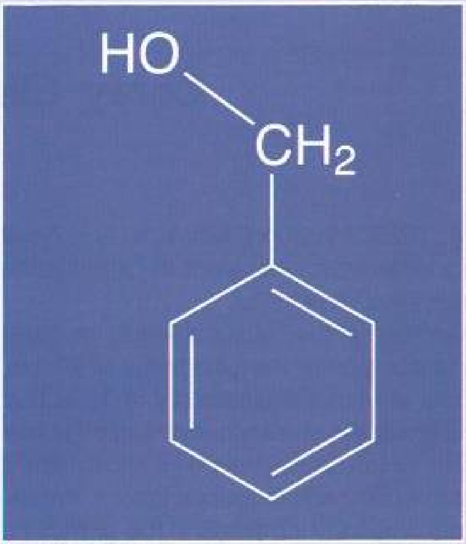
Corey, Elias James (1928-)

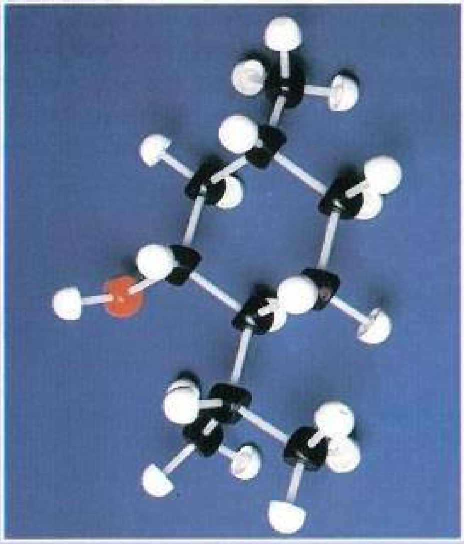
July 12, 1928, Methuen, Mass., U.S.), American chemist, winner of the Nobel Prize for Chemistry in 1990, principally for his work in "retrosynthetic analysis," a technique for simplifying the synthesis of large complex molecules.

Corey studied at the Massachusetts Institute of Technology (B.S., 1948; Ph.D., 1951) and held his first teaching position at the University of Illinois, Champaign-Urbana (1951-59). He became professor of chemistry at Harvard University in 1959 (becoming the Sheldon Emory professor in 1968) and there, with his graduate students, sythesized some 100 molecules hitherto found only in nature. One class of drugs for which Corey was well known is the synthetic prostaglandins--hormonelike compounds used to treat infertility and to induce labour. Another substance first made by Corey is ginkgolide B, an active chemical originally identified in the ginkgo tree, which is used to treat asthma and circulatory problems.

In the retrosynthetic analysis that Corey developed, chemists start with the target molecule and work backward, carefully analyzing its structure and dissecting it piece by piece. By systematically breaking key chemical bonds that join the major components of the target molecule, chemists ultimately arrive at a set of simple precursors. These then can be reassembled into the target molecule in the least possible number of steps using the simplest possible reactions, thereby making the synthesis faster, cheaper, and more efficient.

Microsoft Encarta 99 Encyclopedia





Alcohols are compounds that contain the hydroxyl -OH functional group; they are responsible for the odors that characterize some plants.
What are the structures and the properties of alcohols ?

ALCOHOLS

9

Objectives

- Recognize alcohols
- Know the systematic nomenclature of alcohols
- Know the notion of isomerism of alcohols
- Recognize the very high chemical relativity of alcohols
- Classes of alcohols

Prerequisites

- Chemical formula and bonding
- VSEPR method, hybridization of atomic orbitals and structure
- Chemical reactions
- Nomenclature of alkanes
- Notion of isomerism
- Mole and stoichiometry

Chapter content

9.1 Alcohols
- Chapter review
- Method sheet
- Laboratory investigation
- Documentary activity
- Exercises

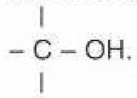
9.1 Alcohols

Definition and general formula

Alcohols are organic substances widespread in plant and animal kingdoms, their molecules contain one or more hydroxyl –OH groups connected to the carbon chain (Fig. 9.1). Those that contain one hydroxyl group are called monoalcohols.

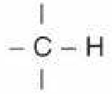
A monoalcohol is a compound which contains one hydroxyl group connected to the carbon chain.

The formula of a monoalcohol can be represented as:



$$\begin{array}{c} | \\ -\mathrm{C}-\mathrm{OH}. \\ | \end{array}$$

It is obtained by replacing a hydrogen atom by a hydroxyl group in the formula of an alkane:



$$\begin{array}{c} | \\ -\mathrm{C}-\mathrm{H} \\ | \end{array}$$

The carbon atom which is connected to the hydroxyl group is the atom which is involved in chemical reactions.

The general formula of a monoalcohol is $C_nH_{2n+1}OH$ and consequently written as $C_nH_{2n+2}O$.
Often a monoalcohol is represented by the formula R–OH.

Nomenclature

According to IUPAC (International Union of Pure and Applied Chemistry), the systematic nomenclature of alcohols is based on those alkanes.

- The name of an alcohol is derived from the name of the alkane having the same number of carbon atoms in the main chain, and that by replacing the final **e** by the ending **ol**:

$$\text{Alkan}\boxed{\text{e}} \Rightarrow \text{Alkan}\boxed{\text{ol}}$$

$$R-H \qquad\qquad R-OH$$

Examples
CH_3OH Methanol or methyl alcohol.
C_2H_5OH Ethanol or ethyl alcohol.

- For n > 2, the carbon atoms of the main chain are numbered such that the position of the –OH group is given the lowest possible number.

Figure 9.1
Orange blossoms.

- Geraniol is the alcohol extracted from the orange blossoms.

- The study is limited to open-chain saturated monoalcohols. These alcohols are very abundant in nature.

- Compounds containing many hydroxyl groups are polyalcohols.
  Examples:
  - glycol (or1,2- ethanediol): CH_2OH-CH_2OH.
  - glycerol (or 1,2,3-propanetriol): CH_2OH-CH_2OH-CH_2OH.

- In an organic molecule having many carbon atoms, the carbon connected to the functional group possesses characteristic reactivity which distinguishes it from other carbon atoms of the chain.

- The main chain is the longest continuous chain of carbon atoms containing the functional group (the hydroxyl group in case of alcohols).

- What structural difference is there among the isomers of formula $C_4H_{10}O$ on the basis of the carbon bearing the functional group?

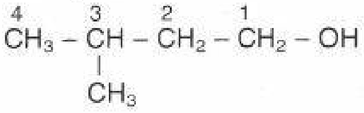
Examples

$\overset{3}{CH_3} - \overset{2}{CH_2} - \overset{1}{CH_2} - OH$ 1-Propanol

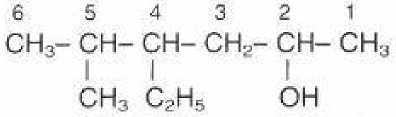
$\overset{3}{CH_3} - \overset{2}{CHOH} - \overset{1}{CH_3}$ 2-Propanol

- When we assign the lowest number, the –OH takes preference over all alkyl groups.

Examples



$\overset{4}{CH_3} - \underset{\displaystyle CH_3}{\overset{3}{CH}} - \overset{2}{CH_2} - \overset{1}{CH_2} - OH$ 3-Methyl-1-butanol



$\overset{6}{CH_3} - \underset{\displaystyle CH_3}{\overset{5}{CH}} - \underset{\displaystyle C_2H_5}{\overset{4}{CH}} - \overset{3}{CH_2} - \underset{\displaystyle OH}{\overset{2}{CH}} - \overset{1}{CH_3}$ 4-ethyl-5-methyl-2-hexanol

- **Structure and isomerism**

Activity 1 Construction of molecular models for isomeric alcohols of molecular formula $C_4H_{10}O$.

Objective

Classify alcohols

Material

Molecular model kit

Procedure

Construct ball-and-stick molecular models for all alcohols of molecular formula $C_4H_{10}O$, starting from a ball-and-stick model of butane molecule and 2-methyl propane molecule of molecular formula C_4H_{10} (Fig. 9.2 and 9.3). Observe.

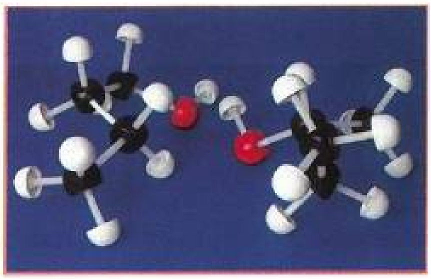


Figure 9.2
Ball-and-stick molecular models of straight chain alcohols $C_4H_{10}O$.

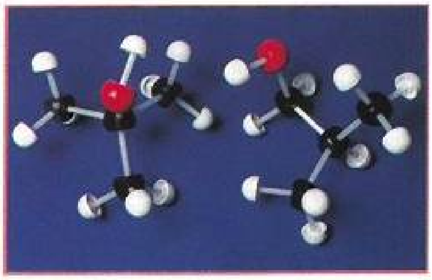
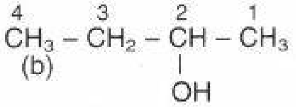


Figure 9.3
Ball-and-stick molecular models of branched-chain alcohols $C_4H_{10}O$.

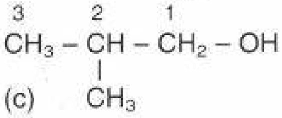
Observation and interpretation

Four molecular models are constructed . They are represented by the following condensed structural formulas:

$\overset{4}{CH_3} - \overset{3}{CH_2} - \overset{2}{CH_2} - \overset{1}{CH_2} - OH$ 1-butanol
(a)



$\overset{4}{CH_3} - \overset{3}{CH_2} - \underset{\displaystyle OH}{\overset{2}{CH}} - \overset{1}{CH_3}$ 2-butanol
(b)



$\overset{3}{CH_3} - \underset{\displaystyle CH_3}{\overset{2}{CH}} - \overset{1}{CH_2} - OH$ 2-methyl-1-propanol
(c)

- Methanol, ethanol and 1-propanol are primary alcohols.
2-propanol is secondary alcohol.
R', R" and R'" are identical or different alkyl groups.

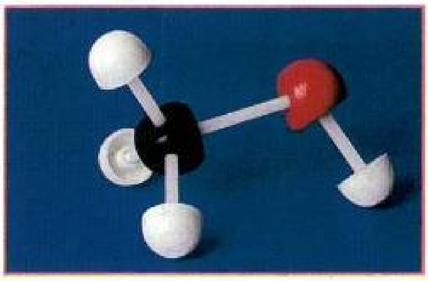
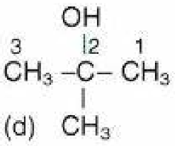


Figure 9.4
A ball-and-stick molecular model of methanol.

- The condensed structural formula does not show the shape of the molecule.

- Skeletal isomerism is also called chain isomerism.

- Hydrogen bond is observed when a hydrogen atom is connected to a very electronegative atom having a small size such as F, O and N.

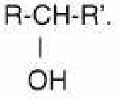


$\overset{3}{CH_3}-\overset{\overset{OH}{2}}{\underset{CH_3}{C}}-\overset{1}{CH_3}$ 2-methyl-2-propanol

The observation of the four models allows to distinguish three classes of alcohols.

- **Primary alcohols.** The carbon bearing the hydroxyl group is connected to one alkyl group according to the formula $R\text{-}CH_2\text{-}OH$.
(a) and (c) are primary alcohols.

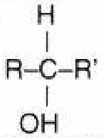
- **Secondary alcohols.** The carbon bearing the hydroxyl group is connected to two alkyl groups according to the general formula R-CH-R'.



$R-\underset{OH}{CH}-R'$

(b)is secondary alcohol.

- **Tertiary alcohols.** The carbon bearing the hydroxyl group is connected to three alkyl groups according to the general formula:



$R-\overset{H}{\underset{OH}{C}}-R'$

(d) is a tertiary alcohol

Structure of methanol

Construct a ball-and stick molecular model of methanol CH_3OH (Fig.9.4). The model presents the following geometric characteristics:

- the carbon atom is tetrahedrally connected to four atoms which surround it, the bond angles are less than 109°.

- The shape of the –C–O–H group is bent with a bond angle $< 109°$.

- The atomic orbitals of the C and O atoms are sp^3 hybridized.

Finally the observation of the constructed molecular models of activity –1 reveals two types of structural isomer of alcohols:

- **Positional isomerism :** (a) and (b) are positional isomers. The same is true for (c) and (d)

- **Skeletal isomerism:** (a) and (c).The same is true for (b) and (d).

Physical properties

The physical properties of alcohols are essentially determined by the presence of the hydroxyl group (OH). The hydroxyl group, as in a water molecule, participates in intermolecular bonds called hydrogen bond, where the hydrogen atom of the hydroxyl

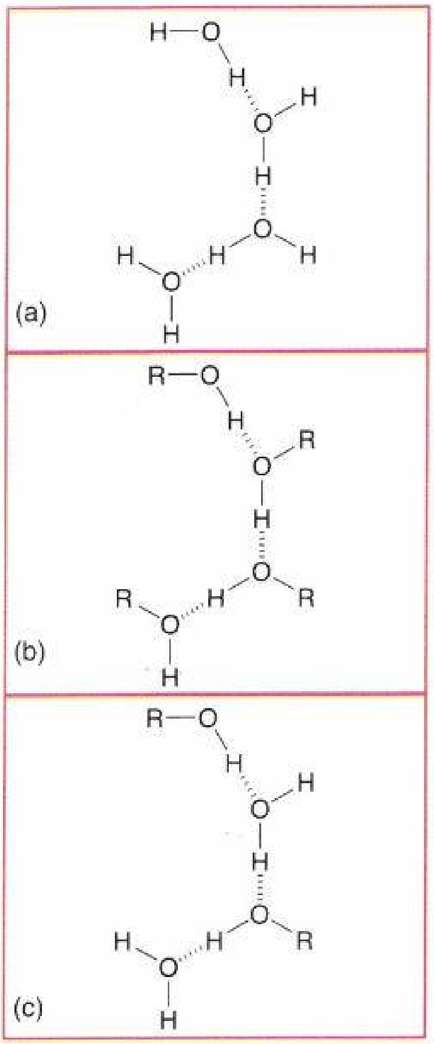


Figure 9.5
Hydrogen bond in:
(a) Pure water.
(b) Pure alcohol.
(c) Water-alcohol mixture.

group of an alcohol molecule is connected to the oxygen atom of another alcohol molecule in the vicinity (Fig. 9.5) .

Thus hydrogen bonding is a consequence of the strong polarity of the OH bond. It leads to a high elevation of the boiling point of alcohols and to a great solubility in water. The effect of hydrogen bond on the boiling point is revealed through comparing the following:

C_2H_5OH (78.5 °C) and CH_3OCH_3 (-25 °C).
$C_2H_5CHOHCH_3$ (99.5 °C) and $C_2H_5OC_2H_5$ (35 °C).

The solubility of alcohols decreases as the carbon chain increases.

Alcohols are liquids or solids at room temperature. Their boiling point generally increases with the increase of their molar mass. Their density is about 0.8 which may vary a little. Some physical properties of alcohols are given in table 9.1

Name	Boiling point (°C)	Solubility (g/kg of water)
Methanol	65	∞
Ethanol	78.5	∞
1-propanol	97	∞
2-propanol	82.5	∞
1-butanol	117	80
2-butanol	99.5	125
2-methyl-1-propanol	108	100
2-methyl-2-propanol	83	∞
1-pentanol	138	23
2-pentanol	119	49
3-pentanol	116	56
2,2-dimethyl-1-propanol	114	∞
1-hexanol	157	6

Table 9.1
Some physical properties of alcohols..

- Ethers do not exhibit hydrogen bonding between their molecules.

However alcohols are good solvents for organic substances and various inorganic substances (I_2, NaOH, KOH ...), methanol and ethanol, especially, have dissolving properties very close to that of water.

Chemical reactions

The electronic structure of the $C-\ddot{O}-H$ group of the alcohols has the following characteristics:

- An $-\overset{\delta^-}{\ddot{O}}-\overset{\delta^+}{H}$ polar bond which makes alcohol behave as a very weak acid.
- A $\overset{\delta^+}{C}-\overset{\delta^-}{\ddot{O}}-$ polar bond, where the lone pair of electrons on the oxygen atom, makes the alcohol behave roughly as a very weak

- Methanol, the most volatile alcohol, is poisonous. Avoid inhaling its vapor.

base. This electronic structure determines the chemical reactivity of alcohols and gives to the reactions an acidic-basic character, and consequently, elimination, substitution or oxidation–reduction reactions will take place.

- **Reaction of absolute ethanol with sodium**

A small piece of sodium (≈ 0.1mg) is added to a test tube containing about 4mL of absolute ethanol. A vigorous reaction is observed with the release of gas ; identifying the hydrogen gas. The solution obtained colors 10mL of distilled water containing 2 drops of phenolphthalein, the obtained solution is basic (Fig. 9.6). Sodium reacts with absolute ethanol to give sodium ethoxide according to the reaction:

$$C_2H_5OH + Na \rightarrow C_2H_5O^-, Na^+ + \tfrac{1}{2}H_2$$

Sodium ethoxide is a strong base and reacts with water according to the equation:

$$C_2H_5O^-, Na^+ + H_2O \rightarrow C_2H_5OH + Na^+ + HO^-$$

In general, an absolute alcohol reacts with sodium to form alkoxides with the release of hydrogen gas according to the equation:

$$ROH + Na \rightarrow RO^-, Na^+ + \tfrac{1}{2}H_2$$

Thus, 2-methyl-2-propanol is slowly reduced by sodium according to the equation:

$$(CH_3)_3COH + Na \rightarrow (CH_3)_3CO^-, Na^+ + \tfrac{1}{2}H_2$$

- **Substitution reactions**

In the presence of some reagents, the hydroxyl group can be substituted by an atom or group of atoms.

The substitution of an alcohol consists of replacing the hydroxyl group by another functional group.

Phosphorous penta chloride PCl_5 reacts with alcohols according to the following equation:

$$ROH + PCl_5 \rightarrow RCl + POCl_3 + HCl$$

The product of the substitution RCl is a chloroalkane (alkyl chloride).

2-propanol, for example, reacts with PCl_5 to give 2-chloropropane according to the following equation:

$$(CH_3)_2CHOH + PCl_5 \rightarrow (CH_3)_2CHCl + POCl_3 + HCl$$

- With a lone pair, the oxygen atom can add a proton H^+. Alcohols are amphoteric.

- The use of absolute alcohol is necessary otherwise, sodium reacts with water.

- Absolute alcohol is also called anhydrous alcohol, that is to say free from water.

- The reaction of sodium with absolute ethanol is less vigorous than that with water. However , to perform this experiment some precautions should be taken, since both absolute alcohol and hydrogen gas are extremely flammable.

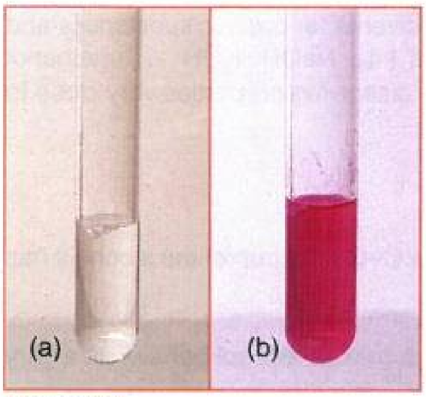


Figure 9.6

(a) Reaction of sodium with absolute ethanol.

(b) Phenolphthalein is colored pink in the obtained solution.

Thionyl chloride $SOCl_2$ reacts with alcohols according to the following equation:

$$ROH + SOCl_2 \rightarrow RCl + SO_2 + HCl$$

to form alkyl chlorides.

- POCl₃ is phosphorous oxytrichloride.

1-butanol, for example, reacts with $SOCl_2$ to form 1-chlorobutane according to the following equation:

$$CH_3CH_2CH_2CH_2OH + SOCl_2 \rightarrow CH_3CH_2CH_2CH_2Cl + SO_2 + HCl$$

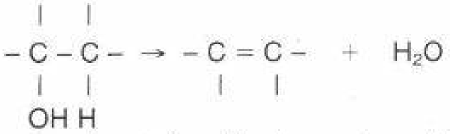
- Alkyl chlorides are commonly used as solvents in organic chemistry. They are also used to manufacture various products; insecticides, polymers ....

Dehydration reactions

The dehydration reaction of an alcohol involves the elimination of a water molecule. Depending on the experimental condition, there are two types of dehydration reaction: intramolecular and intermolecular.

Intramolecular dehydration

The hydroxyl group and a hydrogen atom held by two neighboring carbon atoms , in the same molecule are eliminated to form a molecule of water and a molecule of alkene according to the following equation:



$$-\overset{|}{\underset{\underset{OH}{|}}{C}}-\overset{|}{\underset{\underset{H}{|}}{C}}- \rightarrow -\underset{|}{C}=\underset{|}{C}- + H_2O$$

The reaction is catalyzed by inorganic acids such as H_2SO_4 or H_3PO_4 which also acts as dehydrating agent, or by using alumina Al_2O_3 at a high temperature (350 - 400°C).
The intramolecular dehydration of ethanol leads to the formation of ethylene according to the following equation:

- The experimental conditions, the concentration of the acid, and the temperature of the medium determine the type of the dehydration reaction. In general, high temperatures and concentrations favor intramolecular dehydration.

$$CH_3-CH_2OH \xrightarrow[170\ ^\circ C]{H_2SO_4\ (95\ \%)} CH_2{=}CH_2 + H_2O$$

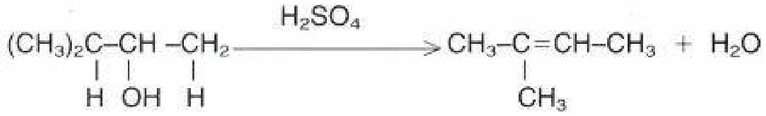
and that of 2-methyl-2-propanol leads to the formation of 2-methylpropene according to the following equation:

$$\underset{\underset{OH}{|}}{(CH_3)_2C}-CH_3 \xrightarrow[85\ ^\circ C]{H_2SO_4\ (20\ \%)} CH_3-\underset{\underset{CH_3}{|}}{C}{=}CH_2 + H_2O$$

- This is the reverse of the hydration of alkenes (studied in the second year secondary).

When intramolecular dehydration gives two isomeric alkenes, the most highly substituted double bond alkene is the major product. According to Zaitev's rule, the more stable alkene is formed.

The dehydration of 3-methyl-2-butanol, for example, gives 2-methyl–2-butene as a major product, the more stable isomer according to the following equation:



$$(CH_3)_2\underset{H}{C}-\underset{OH}{CH}-\underset{H}{CH_2} \xrightarrow{H_2SO_4} CH_3-\underset{CH_3}{C}=CH-CH_3 + H_2O$$

Some alkenes obtained by intramolecular dehydration are Z and E (geometric isomers) in different proportions.

Intermolecular dehydration

The hydroxyl group of an alcohol molecule and the hydrogen atom of the hydroxyl group of another molecule of the alcohol, are eliminated as a molecule of water to form ether. This reaction, is also catalyzed by acids or alumina, takes place according to the following equation:

$$R-O-H + H-O-R \rightarrow R-O-R + H_2O$$

The intermolecular dehydration of ethanol, for example produces ethoxyethane according to the following equation:

$$C_2H_5-OH + HO-C_2H_5 \xrightarrow[130\ °C]{H_2SO_4} C_2H_5-O-C_2H_5 + H_2O$$

Remark

The dehydration of tertiary alcohols does not in general produce ethers. It leads to the formation of alkenes. In fact, the branching at the neighboring carbon to the carbon bearing the hydroxyl group hinders the formation of alkenes.

- The minor product is 3-methyl-1-butene : $(CH_3)_2CH-CH=CH_2$

- C_2H_5-O-C_2H_5 is also called diethylether. It is used as a solvent and as an anesthetic. Other ethers are also used as solvents or as additives in unleaded fuels such as $CH_3OC(CH_3)_3$.

- **Mild oxidation**

Alcohols behave as reductants under certain conditions. They are oxidized, according to their class, into aldehydes, ketones or into carboxylic acids.
The oxidation in this case is called mild oxidation. The oxidation is carried out in a liquid or in a vapor state.

Mild oxidation is a reaction which takes place without breaking the carbon chain.

Mild oxidation of alcohols can be carried out in three ways :

1- Catalytic oxidation in the presence of oxygen gas (of air).
2- Catalytic dehydrogenation in the absence of oxygen.
3- Oxidation by oxidants such as $Cr_2O_7^{2-}$, MnO_4^- ....

- **Mild oxidation of primary alcohols**

Primary alcohols are oxidized to aldehydes and (or) to carboxylic acids (see method sheet page 243).

- During the oxidation, the –COH group of the alcohol is converted into a carbonyl or a carboxyl group.

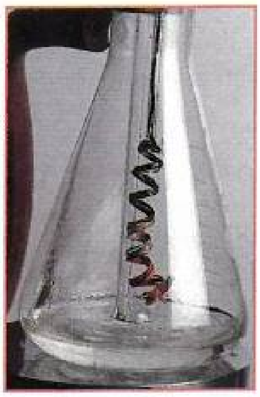


Figure 9.7
Flameless lamp.

Catalytic oxidation

The vapor of a primary alcohol and the oxygen of air react in the presence of a catalyst (Cu, Pt---) to form the aldehyde and the corresponding carboxylic acid according to the following equation:

$$RCH_2OH + \tfrac{1}{2}O_2 \xrightarrow{Cu} RCHO + H_2O$$

and

$$RCH_2OH + O_2 \xrightarrow{Cu} RCOOH + H_2O$$

These two reactions are exothermic. This oxidation is achieved by continuously heating the copper to red-hot; a process called "Flameless lamp" (Fig. 9.7).

Catalytic dehydrogenation

The catalytic dehydrogenation of a primary alcohol in the absence of oxygen leads to the formation of an aldehyde according to the equation:

$$RCH_2OH \xrightarrow{Cu - 300\ ^\circ C} RCHO + H_2$$

Being endothermic, this reaction needs continuous heating of the catalyst to about 300°C (Fig.9.8)

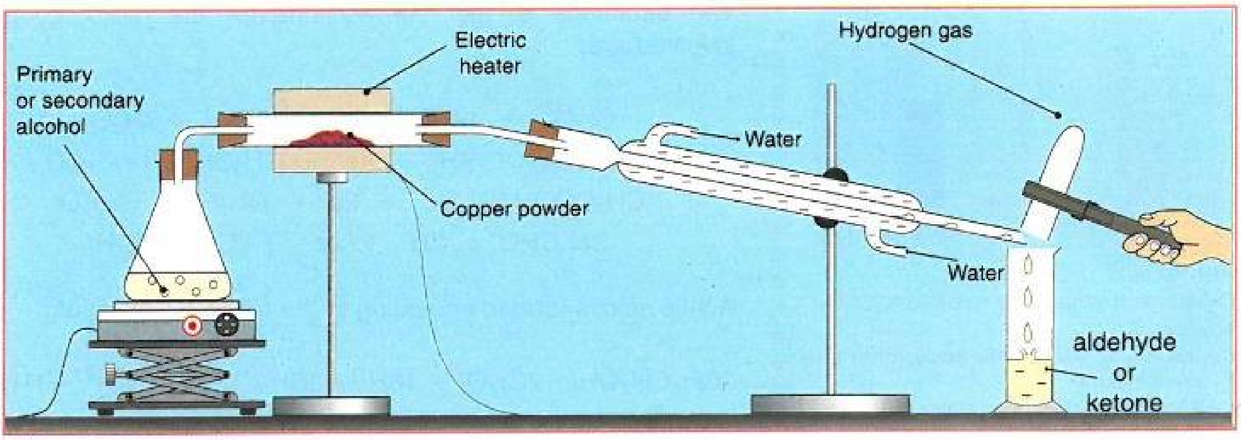


Figure 9.8
Schema of the apparatus used to carry out catalytic dehydrogenation of an alcohol.

Oxidation by potassium dichromate $K_2Cr_2O_7$

Activity 2 Continuous mild oxidation of ethanol by potassium dichromate

- $K_2Cr_2O_7$ is a carcinogenic and toxic product. It should be handled with much precaution.

- What are the colors of the $Cr_2O_7^{2-}$ and Cr^{3+} ions?
- What products do you predict for the oxidation of ethanol ?
- Write the equations for the oxidation and reduction half-reactions taking place in the tube.

- The ethanol is in excess. In fact, it needs a large quantity of the 0.2 mol.L^{-1} $K_2Cr_2O_7$ solution to oxidize the ethanol completely (about 60mL).

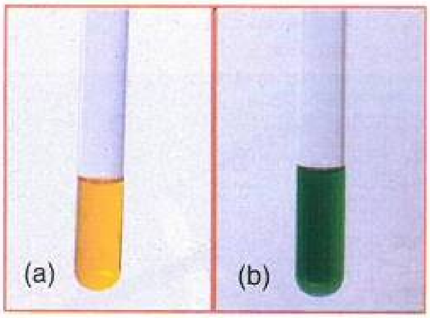


Figure 9.9
Oxidation of ethanol by acidified $K_2Cr_2O_7$ solution:
(a) before the reaction, the solution has an orange color.
(b) after the reaction, the solution becomes green in color.

Objective

Carry out the continuous mild oxidation of a primary alcohol.

Equipment and reagents

Test tube. Two graduated cylinders 10 mL each. 5 mL graduated pipet. Gloves and eye goggles.
Ethanol 95°. Potassium dichromate solution (0.2 mol.L^{-1}). Concentrated sulfuric acid (about 4 mol. L^{-1}). pH paper.

Procedure

Pour into the test tube, respectively, about 3 mL of $K_2Cr_2O_7$ and 0.5 mL of the H_2SO_4 solution. Work with precaution, and cool the mixture. Then pour about 1mL of ethanol. Stir and observe (Fig. 9.9). Heat gently the tube. Hold a wet pH paper close to the mouth of the tube.
Observe (Fig. 9.10).

Observation

The orange color of the $K_2Cr_2O_7$ becomes green after the addition of ethanol. The PH paper changes color.

Interpretation

The orange color is due to $Cr_2O_7^{2-}$ ions.
The green color is due to Cr^{3+} ions.
The change in the color of the pH paper is an indication that an acidic compound is formed.
These observations as well as the standard reduction potentials involved (Fig. 9.11) show that ethanol is oxidized by $Cr_2O_7^{2-}$ ions in acidic medium to form ethanoic acid CH_3COOH.

Reactions with the $Cr_2O_7^{2-}$ ions

The equations of the half-reactions for the redox couples involved are:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$
$$CH_3COOH + 4H^+ + 4e^- \rightarrow CH_3CH_2OH + H_2O$$
$$CH_3COOH + 2H^+ + 2e^- \rightarrow CH_3CHO + H_2O$$
$$CH_3CHO + 2H^+ + 2e^- \rightarrow CH_3CH_2OH$$

Acetic acid is formed according to the following equation:

$$3CH_3CH_2OH + 2Cr_2O_7^{2-} + 16H^+ \rightarrow 3CH_3COOH + 4Cr^{3+} + 11H_2O$$

In general, the oxidation of a primary alcohol by $Cr_2O_7^{2-}$ takes place in two steps:

The alcohol is oxidized to aldehyde according to the following equation:

$$3RCH_2OH + Cr_2O_7^{2-} + 8H^+ \rightarrow 3RCHO + 2Cr^{3+} + 7H_2O$$

Figure 9.10
The color of pH paper changes.

Redox Couple	E°(V)
MnO_4^-/Mn^{2+}	1.51
$Cr2O_7^{2-}/Cr^{3+}$	1.33
CH_3CHO/CH_3CH_2OH	0.19
CH_3COOH/CH_3CH_2OH	0.05
CH_3COOH/CH_3CHO	-0.12

Figure 9.11
Standard reduction potentials.

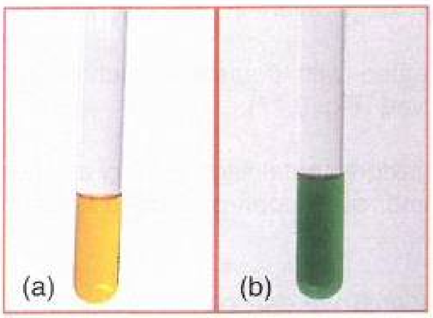


Figure 9.12
Oxidation of ethanol by acidified $K_2Cr_2O_7$:
(a) before the reaction, the solution is orange in color.
(b) after the reaction, the solution becomes green in color.

The aldehyde, which is more reducing than the alcohol (Fig. 9.11), is oxidized in its turn to carboxylic acid (Fig. 9.12) according to the following equation:

$$3RCHO + Cr_2O_7^{2-} + 8H^+ \rightarrow 3RCOOH + 2Cr^{3+} + 4H_2O$$

When the alcohol is taken in large excess, the aldehyde is obtained effectively, whereas the $Cr_2O_7^{2-}$ is in excess, it leads to the formation of carboxylic acid.

The oxidant $Cr_2O_7^{2-}$ used in the preceding activity could be replaced by chromate ion CrO_4^{2-} chromium VI trioxide CrO_3 or permanganate ion MnO_4^-.

In acid medium, for example, the purple color of MnO_4^- is decolorized by ethanol (Fig. 9.13). During the reaction, the solution becomes brown (formation of manganese dioxide MnO_2) before it becomes colorless.

Mild oxidation carried out in the presence of excess oxidant is called continuous mild oxidation.

Remarks

When mild oxidation of ethanol is carried out using the apparatus as in Figure 9.14, the ethanal formed (bp = 21 °C) could be collected by simple distillation in an Erlenmeyer flask containing cold distilled water immersed in ice-water bath. Ethanoic acid is also formed during the reaction which boils at much higher temperature than the alcohol, (respectively, 118 and 78.5 °C).

The apparatus shown in figure 9.15 enables continuous mild oxidation of ethanol into ethanoic acid. This is achieved due to the reflux of the vapor of ethanal which is trapped in the reaction system. Thus, ethanal undergoes oxidation by excess $Cr_2O_7^{2-}$ ion.

- **Mild oxidation of secondary alcohols**

Under the same conditions as those of primary alcohols, the mild oxidation of secondary alcohols ceases upon formation of the corresponding ketones. This result is obtained whatever the mild oxidation is.

Catalytic oxidation of 2-propanol, for example, in the presence of oxygen and copper leads to the formation of acetone according to the following equation:

$$CH_3CHOHCH_3 + \tfrac{1}{2}O_2 \xrightarrow{Cu} CH_3COCH_3 + H_2O$$

The reaction is exothermic as is the case of primary alcohols.

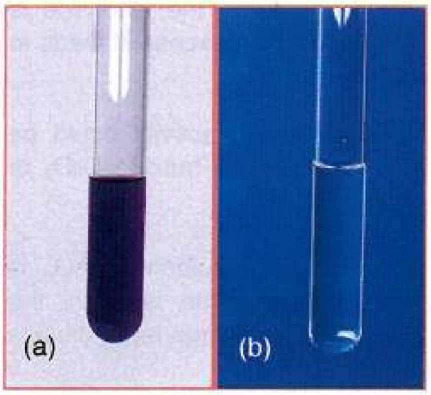


Figure 9.13
Oxidation of ethanol by an acidified potassium permanganate solution $KMnO_4$:
(a) before the reaction, the solution is purple in color.
(b) after the reaction, the solution becomes colorless.

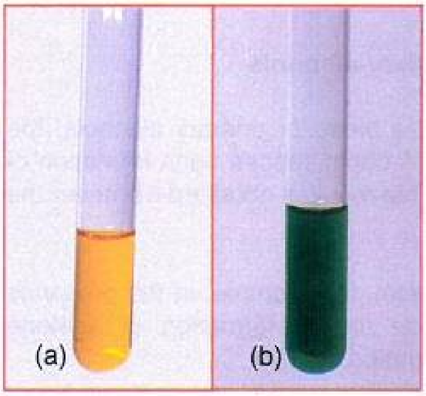


Figure 9.16
Oxidation of 2-propanol by $K_2Cr_2O_7$:
(a) before the reaction, the solution is orange in color.
(b) After the reaction, the solution becomes green in color.

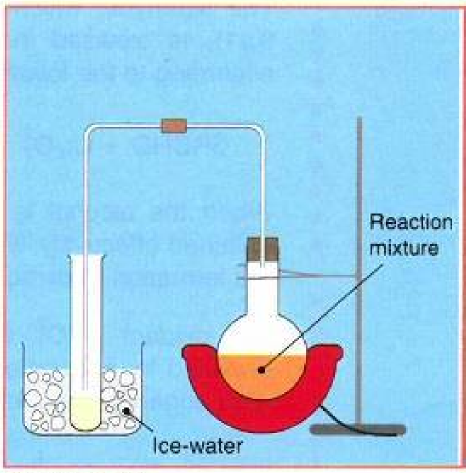


Figure 9.14
Mild oxidation of ethanol and distillation of the ethanal formed.

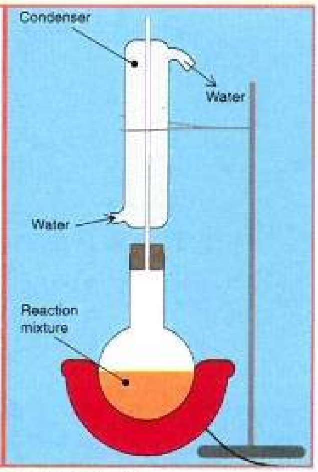


Figure 9.15
Continuous mild oxidation of ethanol. Reflux enables continuous condensation of the vapor of ethanal which is formed as an intermediate compound

The catalytic dehydrogenation (endothermic) of 2-butanol, for example, produces 2-butanone according to the following equation:

$$CH_3CH_2CHOHCH_3 \xrightarrow{Cu - 300\ ^\circ C} CH_3CH_2COCH_3 + H_2$$

Action of $K_2Cr_2O_7$ on 2-propanol, for example, leads to the formation of acetone (Fig. 9.16) according to the following equation:

$$3CH_3CHOHCH_3 + Cr_2O_7^{2-} + 8H^+ \rightarrow 3CH_3COCH_3 + 2Cr^{3+} + 7H_2O$$

Remark

The half-reaction of a ketone (secondary alcohol) redox couple is:

$$RCOR' + 2H^+ + 2e^- \rightarrow RCHOHR'$$

The reaction ceases at this stage even in the presence of excess oxidant.
In fact, when acetone is heated with potassium dichromate solution, no reaction is observed (Fig. 9.17).

Finally, the orange color of a mixture containing a tertiary alcohol and $K_2Cr_2O_7$ remains the same, even upon prolonged heating until boiling (Fig. 9.18).

From the preceding observations, we can conclude that mild oxidation allows to identify the class of an alcohol. These results are summarized in table 9.2.

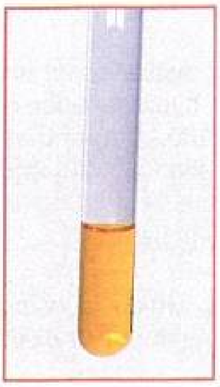


Figure 9.17
Acetone is not oxidized by $K_2Cr_2O_7$.

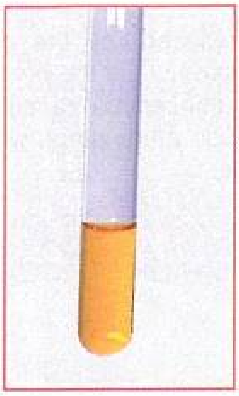


Figure 9.18
No reaction takes place between 2-methyl-2-propanol and $K_2Cr_2O_7$.

Class of alcohol	Product of mild oxidation	Product of continuous mild oxidation
Primary RCH_2OH	Aldehyde RCHO	Carboxylic acid RCOOH
Secondary RCHOHR′	Ketone RCOR'	No reaction
Tertiary RCHOR′R″	No reaction	No reaction

Table 9.2

- **Esterification reaction**

Alcohols react with carboxylic acids to give esters and water according to the following equation:

$$ROH + R'COOH \rightleftarrows R'COOR + H_2O$$

Esterification is the ester formation reaction starting from an alcohol and a carboxylic acid.

Examples:

Formic acid reacts with 2-propanol according to the following equation:

$$HCOOH + CH_3CHOHCH_3 \rightleftarrows HCOOCH(CH_3)_2 + H_2O$$

Acetic acid reacts with 2-methyl-2-propanol according to the following equation:

$$CH_3COOH + (CH_3)_3COH \rightleftarrows CH_3COOC(CH_3)_3 + H_2O$$

The reversible reaction slowly attains an equilibrium state. To accelerate this reaction, heat and an inorganic acid such as sulfuric acid, is used as a catalyst. The proportion of ester formed at equilibrium depends on the initial quantities of the reactants, but also on the class of the alcohol. Higher proportions of ester are obtained with primary alcohols, whereas very little proportions are obtained with tertiary alcohols.

Table 9.3 shows the proportion by mole of the esters formed as a function of the class of the alcohol and starting initially with an equimolar mixture of the alcohol and carboxylic acid.

- **Industrial preparation**

Alcohols are used in large quantities in chemical industry. They are employed as solvents or as intermediate products for organic synthesis; for the manufacture of medicaments; cosmetics ; and polymers ....
The alcohols used mostly are methanol and ethanol.

- Tertiary alcohols when heated in presence of an oxidant in an acidic medium, generally undergo intramolecular dehydration reaction producing alkenes.

- R and R' are two identical or different radicals.

- In carboxylic acids, R' could be replaced by a H-atom.

Class of the alcohol	Mole percentage of the ester
Primary	~ 67 %
Secondary	~ 60 %
Tertiary	1 to 5 %

Table 9.3
The mole percentages of esters formed as a function of the class of the alcohol.

■ The mixture CO + H_2 is called synthesis gas or water gas.

■ Ethylene is one product of petrochemistry. It is obtained by vapor cracking of some petroleum fractions.

■ Methanol

Sometimes methanol obtained by the distillation of wood. It is obtained in large scale by the catalytic hydrogenation of carbon monoxide CO at high pressure (50 to100 bars) and at 250 °C. The reaction takes place according to the following equation:

$$CO + 2H_2 \rightarrow CH_3OH$$

The use of a catalyst is necessary, which is composed of copper Cu, zinc (II) oxide ZnO and chromium (VI) oxide CrO_3.

■ Ethanol

Ethanol is manufactured by the following two processes :

- Since antiquity ethanol is produced, by the alcoholic fermentation of sugar (glucose, fructose ....) in the presence of an enzyme, biologic catalyst. The conversion of sugar into ethanol is complex and passes through many steps which are summarized by the following equation:

$$\underset{\text{(glucose or fructose)}}{C_6H_{12}O_6} \xrightarrow{\text{Enzymes}} 2C_2H_5OH + 2CO_2$$

- A modern process which consists of reacting a mixture of ethylene and water vapor at 300 °C and under a pressure of 70 bars in the presence of an acid catalyst such as sulfuric or phosphoric acid. Actually this is the main process for manufacturing ethanol (Fig. 9.19).

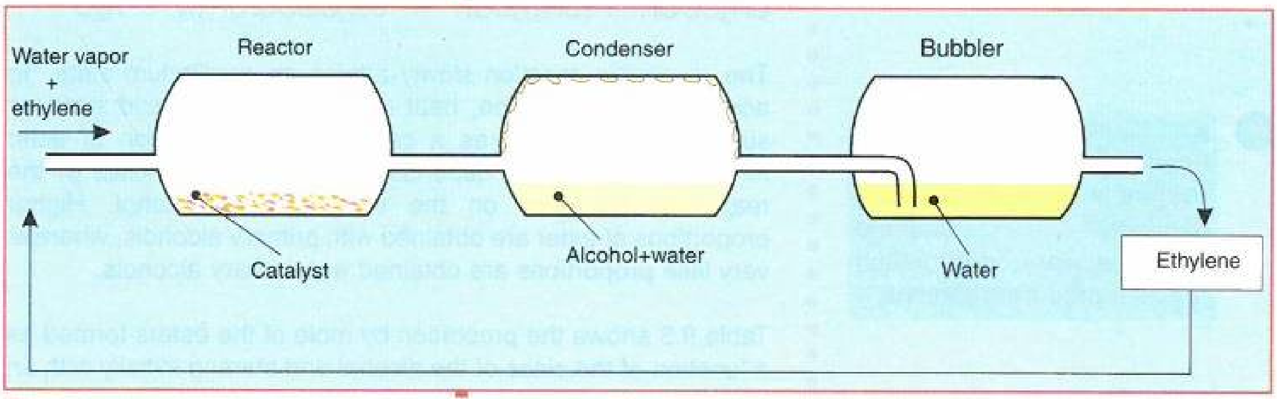


Figure 9.19
The schema shows the principle of manufacture of ethanol starting from ethylene.

$$CH_2{=}CH_2 + H_2O \rightarrow CH_3CH_2OH$$

The worldwide production of methanol and ethanol is many millions of tons for each.

Chapter review

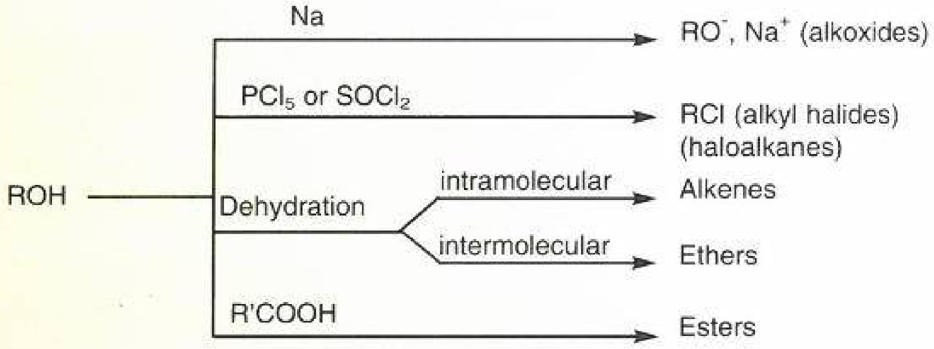
- A straight-chain mono saturated alcohol contains the hydroxyl functional group. It is represented by the general formula R-OH.

- There are three classes of alcohols:

  Primary alcohols of general formula RCH_2OH.
  Secondary alcohols of general formula RCHOHR'.
  Tertiary alcohols of general formula RCOHR'R''.

- The particular high boiling point of alcohols and their great solubility in water is due to the existence of hydrogen bonding.

- Some reactions of alcohols are summarized in the following scheme:



- Primary and secondary alcohols undergo mild oxidation. Tertiary alcohols do not undergo mild oxidation. The following table summarizes the behavior of the different classes of alcohols towards mild oxidation.

Class of alcohol	Product of mild oxidation	Product of continuous mild oxidation
Primary RCH_2OH	Aldehyde RCHO	Carboxylic acid RCOOH
Secondary RCHOHR'	Ketone RCOR'	No reaction
Tertiary RCOHR'R''	No reaction	No reaction

- Methanol (methyl alcohol) is industrially manufactured by the catalytic hydrogenation of carbon monoxide.

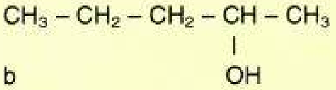
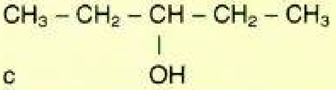
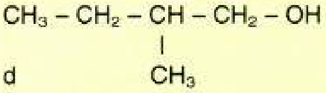
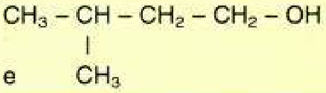
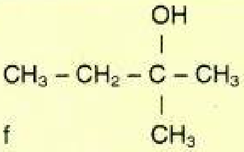
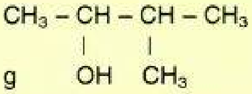
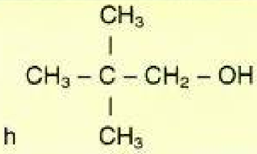
- Ethanol (ethyl alcohol) is industrially manufactured by the fermentation of sugar and by the hydration of ethylene.

Isomeric alcohols: condensed structural formulas, names, classes and isomerism.

It is required to write the condensed structural formula. Give the name, the class, and the type of isomerism of each alcohol of molecular formula $C_5H_{12}O$..

- **Formula, name, and class.**

Table 9.4 lists, isomeric alcohols of formula $C_5H_{12}O$

Formula	Name	Class
$CH_3-CH_2-CH_2-CH_2-CH_2-OH$ a	1-pentanol	Primary
 b $CH_3-CH_2-CH_2-\underset{\overset{\vert}{OH}}{CH}-CH_3$	2-pentanol	Secondary
 c $CH_3-CH_2-\underset{\overset{\vert}{OH}}{CH}-CH_2-CH_3$	3-pentanol	Secondary
 d $CH_3-CH_2-\underset{\overset{\vert}{CH_3}}{CH}-CH_2-OH$	2-methyl-1-butanol	Primary
 e $CH_3-\underset{\overset{\vert}{CH_3}}{CH}-CH_2-CH_2-OH$	3-methyl-1-butanol	Primary
 f $CH_3-CH_2-\overset{\overset{OH}{\vert}}{\underset{\overset{\vert}{CH_3}}{C}}-CH_3$	2-methyl-2-butanol	Tertiary
 g $CH_3-\underset{\overset{\vert}{OH}}{CH}-\underset{\overset{\vert}{CH_3}}{CH}-CH_3$	3-methyl-2-butanol	Secondary
 h $CH_3-\overset{\overset{CH_3}{\vert}}{\underset{\overset{\vert}{CH_3}}{C}}-CH_2-OH$	2,2-dimethyl-1-propanol	Primary

- **Types of isomerism**

Positional isomerism
a, b and c
d and f
e and g

Skeletal isomerism
a, d and h
a, e and h
b and f
c and f

Alcohols d and e are isomers; they differ in the position of branching (methyl group). The same holds true for alcohols f and g.

Six isomeric ethers have the molecular formula $C_5H_{12}O$. They are functional isomers to alcohols that have same molecular formula.

Try to write the condensed structural formulas of these ethers.

Laboratory Investigation

LI

The flameless lamp

Objective

Carry out catalytic oxidation of ethanol.

Equipment and reagents

A 2 mL graduated cylinder. Two glass tubes. A water bath. Gloves and goggles.

Copper wire-turning. Volumetric flask. Hot plate (electrical heater). 95° pure ethanol. pH paper.

Procedure

- Assemble the apparatus shown in figure 9.20.

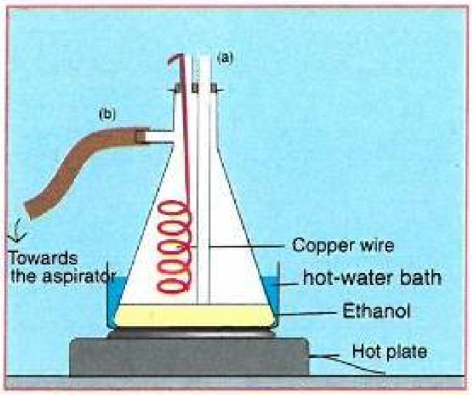


Figure 9.20

The apparatus used to obtain a flameless lamp.

- Introduce in the volumetric flask about 20 mL of ethanol (95°).
- Connect the apparatus to an aspirator.
- Heat the ethanol to lukewarm in a hot-water bath, heated over the hot plate, avoid the use of flame, ethanol is flammable.
- Heat the copper wire to red-hot and quickly introduce it in the volumetric flask in such a way that its end (extremity) is about 1cm from the surface of the liquid. Observe what happens.
- Detach the pipe to the level of exit (b) and approach a wet pH paper. Observe what happens.

Illustration of results

1) Record the observation.
2) In what aspect is the copper wire turning present during the experiment?
3) What is the role of tube (a)?
4) What will be the color of the pH paper?
5) Interpret the observations.
6) Write the equation of the reaction which takes place in this experiment.

Documentary activity

Physiological properties and uses of methanol

Methanol (methyl alcohol, carbinol or wood alcohol), is the most simple mono-alcohol; its formula is CH_3OH. It is a colorless liquid that boils at 65 °C and solidifies at - 98 °C; it is miscible with water in all proportions.

Physiological properties

Methanol is toxic. Prolonged exposure to its vapors may affect vision and, on the long term provokes, blindness (loss of vision).
The high toxicity of methanol is due to its oxidation by enzymes to methanal HCHO. This latter interferes with bimolecules involved in the chemical processes of vision.
The continuous biochemical oxidation of methanol into methanoic acid HCOOH provokes acidosis, which may lead to coma.

Applications

Methanol is largely employed in chemical industry and in everyday life due to its various applications, such as:

- Preparation of methanal which is, in turn, used to prepare various types of products: polymers, solvents, pharmaceutical products,.....
- Preparation of solvents for varnishes and lacquers.
- Preparation of methyltertbutylether (MTBE), which is an additive for unleaded gasoline.
- Preparation of polyesters, plexiglass and other plastic materials (Fig. 9.21).
- Preparation of different chemical products such as chloromethanes and methylamines, ...etc.
- In some countries (North America), methanol mixed with gasoline is used as fuel for cars. The percentage of methanol in these mixtures varies; it may reach up to 85% by volume.

* 50 % of methanol obtained industrially is converted to methanal.

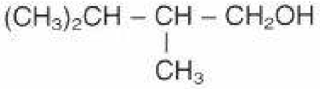
Figure 9.21
Objects made up from polyesters and plexiglass.

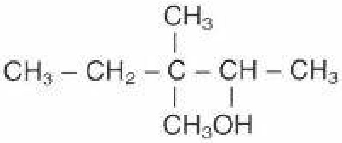
Questions

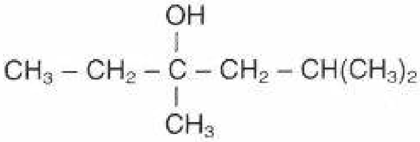
1) Why is methanol toxic?
2) Which organ is the most sensitive to the vapor of methanol?
3) What causes the oxidation of methanol into methanoic acid in an organism?
4) Industrially for what is methanol mainly converted to?

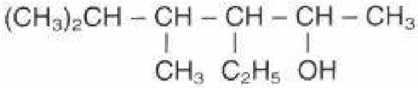
Exercises

1 Give the systematic (IUPAC) name and the class of each of the following alcohols :

a) 
$(CH_3)_2CH-\underset{CH_3}{CH}-CH_2OH$

b) 
$CH_3-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-\underset{OH}{CH}-CH_3$

c) 
$CH_3-CH_2-\overset{OH}{\underset{CH_3}{C}}-CH_2-CH(CH_3)_2$

d) 
$(CH_3)_2CH-\underset{CH_3}{CH}-\underset{C_2H_5}{CH}-\underset{OH}{CH}-CH_3$

2 Write the condensed-structural formulas for the following alcohols. Correct the incorrect names.

a) 4-methyl-1-pentanol.
b) 2-methyl-2-butanol.
c) 3-ethyl-1-butanol.
d) 2,2-diethyl-4-pentanol.
e) 3-ethyl-2-hexanol.

3 a) Express the percentage, by mass of oxygen, in terms of n in an alcohol.
b) Determine the value of n for an alcohol such that the percentage by mass of oxygen equals 21.6 %. Deduce the molecular formula.
c) Write the structural formula and give the name and the class of each of the four isomers.
d) Which of the alcohols gives a ketone upon mild oxidation in the presence of potassium dichromate ?
e) Write the half-reactions and the overall equation of the reaction.

4 Write the equation for each of the following reactions:
a) Reaction of 1-propanol with sodium.
b) Reaction of 1-butanol with phosphorous pentachloride.
c) Reaction of 2-methyl-1-propanol with thionyl chloride.
d) Catalytic oxidation of 3-ethyl-3-methyl-2-pentanol.
e) Oxidation of 3-ethyl-1-hexanol by an excess of potassium dichromate in acidic medium.
f) Action of hot concentrated sulfuric acid with 3-methyl-2-butanol. Three organic products are obtained: an ether and two alkenes one of which is the major product. Specify the major product.

5 Methanol (methyl alcohol) is prepared in industry by the catalytic hydrogenation of carbon monoxide.
a) Write the equation of the reaction taking place.
b) What volume of carbon monoxide, under standard conditions (STP), should be used to manufacture 1000 tons of liquid methanol, if the percent yield of the process is about 88 %?

6 The alcoholic fermentation of 350 g.L^{-1} glucose syrup ceases when the alcoholic degree of the mixture attains 16°. (16 mL ethanol in 100 mL of the solution).
a) Write the overall equation of the fermentation reaction.
b) Consider the fermentation of 100 L of the glucose syrup. Determine the volume and the mass of ethanol formed as fermentation ceases.
c) What mass of glucose remains in the solution?
Hint: the variation of the volume of the solution during fermentation is negligible. The density of ethanol equals 0.79 kg.L^{-1}.

7 A) 9.8 g of an alcohol A completely reacts with an excess of sodium, and a gas is released. When the reaction ceases, the volume of the gas is 1.6 L measured at a temperature of 22 °C and under a pressure of 1 bar.

a) What is the gas released in this reaction ? How can it be identified ?

b) Write the equation of the reaction of alcohol A with sodium.

c) Find the molecular formula of alcohol A.

d) Write the structural formulas of the alcohols which are isomers of A.

B) The dehydration of alcohol A upon heating and in the presence of sulfuric acid produces only two organic compounds B and C. Only the molecule of C contains an oxygen atom. The relative density of B with respect to air equals 1.93.

a) Determine the molecular formulas of the compounds B and C.

b) Assuming that A is branched-chain, write the structural formulas of compounds A, B and C.

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

a) What is this reaction called ? Write the equation of the reaction.

b) Assuming that the equilibrium constant is $K_c = 2.3$, calculate the composition of the mixture at equilibrium.

c) What is the mole % yield of the reaction ? What do you conclude ?

9 A mixture M, containing two moles of water, 23 g of methanoic acid, and n moles of ethanol, is subjected to reflux until equilibrium is attained. 0.23 mol of the acid is left at equilibrium.

a) Write the equation of the esterefication reaction.

b) Calculate the mass of ethanol in the mixture M. The equilibrium constant of the reaction is $K_c = 4$.

10 The complete combustion of 0.25 g of a liquid compound A containing oxygen produce 0.55 g of carbon dioxide and 0.30 g of water.

0.30 g of compound A is changed into vapor. The vapor produced occupies a volume of 158 mL at a temperature of 112 °C and under a pressure of 0.97 bar.

a) Find the molecular formula of A.

b) What structural formulas can be attributed to A ?

c) 2.3 g of sodium reacts completely with a certain quantity of A producing hydrogen. However, the oxidation of A by oxygen in the presence of copper as a catalyst produces a compound which colors a wet litmus paper red.

1) Could we, based on what has taken place in c), find the structural formula of compound A? Explain.

2) Write the equation of the reactions between A and sodium, between A and oxygen.

3) What volume of hydrogen is obtained under standard conditions (STP) ?

11 25 g of ethanol is heated with concentrated sulfuric acid. The alcohol is completely converted into two organic compounds A and B which are separately collected ; A is a gas and B is a liquid.

a) Write the equations of the reactions taking place and indicate their type.

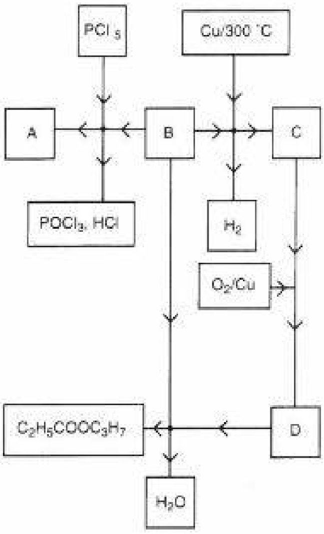
b) Compound A decolorizes the orange color of bromine solution and the purple color of acidified potassium permanganate solution. Write the structural formula of A. Deduce that of B.

c) The complete combustion of compound A produces 8 g of water. What volume measured at 20 °C and under a pressure of 1 bar of compound A is produced in the reaction of ethanol and sulfuric acid ?

d) What fraction of ethanol is changed to A?

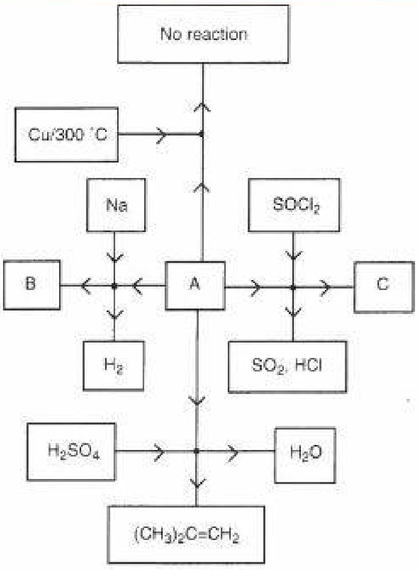
12 How could you prepare:
a) 2-chloropropane from 2-propanol ?
b) 2-butanone from 2-butanol ?
c) ethyl acetate $CH_3COOC_2H_5$ from ethanol ?
d) 2-methyl-2-butene from 3-methyl-2-butanol ?

13 Identify the missing compounds A, B, C and D in the following diagram:



NB. A point (.) stands for the reaction between the reactants. (☐→) a compound entering into reaction and (→☐) a compound resulting from a reaction.

14 Identify the missing compounds A, B, C and D in the following diagram:



15 Some fuels may contain about 5% by volume ethanol. To check the percentage of ethanol in fuel, a sample of this fuel is reacted with acidified potassium permanganate solution. Only ethanol is oxidized, and it is converted to ethanoic acid.

15 mL of the fuel is treated with exactly 85 mL of 0.1 mol.L^{-1} acidified potassium permanganate solution to completely oxidize the ethanol.

a) Write the equations of the half-reactions and the equation of the overall reaction for the oxidation of ethanol with potassium permanganate solution.
b) Determine the percentage by volume of ethanol in this fuel.
Density of ethanol = 790 kg.m^{-3}.

Essential Oils

Any of several chemicals that form the odoriferous essences of a number of plants. The term essential oil is also applied to similar synthetic substances prepared from coal tar chemicals, and semi-synthetic substances prepared from natural essential oils.

Sources

Essential oils come from the flowers, fruits, leaves, roots, seeds, and bark of many plants. Oil of lavender, for example, is derived from a flower, oil of patchouli from a leaf, and oil of orange from a fruit. The oils are formed in the green (chlorophyll bearing) parts of the plant, and with plant maturity are transported to other tissues, particularly to the flowering shoots. The exact function of an essential oil in a plant is unknown; it may be to attract insects for pollination, or to repel harmful insects, or it may be simply a metabolic intermediate.

The essential oils are volatile liquids, mostly insoluble in water, but freely soluble in alcohol, ether, and vegetable and mineral oils. They are usually not oily to the touch. They may be grouped into five classes, according to their chemical structure: alcohols, esters, aldehydes, ketones, lactones and oxides.

Production and Uses

Essential oils are obtained by one of four methods: steam distillation, extraction by volatile solvents, pressing by hand or machine, and defloration, a process in which fat is used as a solvent. In modern practice, essential oils, synthesized or obtained from natural sources by any one of the above four methods, are often purified by vacuum distillation before being used.

Essential oils are used to impart flavour and delicate aroma to coffee, tea, wines, and distilled liquors. They are the basic ingredients in the manufacture of perfumes, and are also used in soaps, disinfectants, and similar products. Essential oils have an important use in medicine, either for their flavouring qualities or for their pain-relieving and physiological value. See articles on many of the specific essential oils mentioned.

Microsoft Encarta 99 Encyclopedia

Aldehydes and ketones are compounds which contain the carbonyl functional group – CO – ; they are responsible for the aroma which characterizes some plants.
What are the structures and the properties of aldehydes and ketones ?

ALDEHYDES AND KETONES

10

Objectives

- Identify aldehydes and ketones.
- Know the systematic nomenclature of aldehydes and ketones.
- Know the notion of isomerism of aldehydes and ketones.
- Recognize the high chemical reactivity of aldehydes and ketones.
- Identify, experimentally, aldehydes, ketones, and the class of an alcohol.

Prerequisites

- Chemical formulas and bonding
- VSEPR method, hybridization of atomic orbitals and structures
- Nomenclature of alkanes
- Notions of isomerism.
- Mole and stoichiometry

Chapter content

10.1 Aldehydes and ketones
- Chapter review
- Method sheet
- Documentary activity
- Exercises.

10.1 Aldehydes and ketones

Figure 10.1
The aroma of the mushroom is due to a ketone.

Definition and general formula

Organic compounds which contain the carbonyl group –CO– in their molecules are called aldehydes or ketones. They are encountered greatly in animal and plant kingdoms.

In an aldehyde, the carbonyl group is connected, at least, to one hydrogen atom.
In a ketone, the carbonyl group is connected to two alkyl groups.

The formula of an aldehyde (or a ketone) can be represented as: $-\overset{O}{\overset{\|}{C}}-$. It is obtained by replacing two CH bonds in the formula of an alkane $H-\underset{|}{\overset{|}{C}}-H$, by the double bond $\underset{|}{\overset{|}{C}}=O$.

The carbon atom of the carbonyl group is the functional carbon of the molecule.
The general formula of an aldehyde (or a ketone), consequently, can be written as $C_nH_{2n}O$.
In general, an aldehyde is represented by the formula: $R-\overset{O}{\overset{\|}{C}}-H$ or simply (RCHO) and a ketone is represented by the formula: $R-\underset{O}{\underset{\|}{C}}-R'$ or simply (RCOR').

- Conventionally, this representation is' used to avoid confusion with alcohols.

Nomenclature

The systematic nomenclature of aldehydes and ketones, as in case of alcohols, is based on those of alkanes.

Nomenclature of aldehydes

- The word aldehyde is a contraction of the expression, dehydrogenated alcohol.

In naming of an aldehyde the terminal **e** of the alkane is substituted with the suffix **al**:

Alkan$\boxed{e}$ ⇨ Alkan$\boxed{al}$

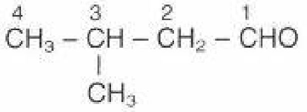
Examples

$H-CHO$	methanal or formaldehyde
CH_3-CHO	ethanal or acetaldehyde.
CH_3-CH_2-CHO	propanal
$CH_3-CH_2-CH_2-CHO$	butanal

C_6H_5-CHO benzaldehyde

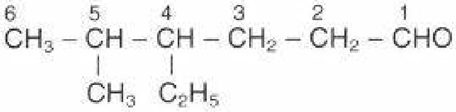
For a branched chain we proceed as for alkanes. The numbering of the carbon chain starts with carbon (functional carbon). The position of the latter is not included in the name of the aldehyde.

Examples



$$\overset{4}{CH_3}-\underset{\underset{\displaystyle CH_3}{|}}{\overset{3}{CH}}-\overset{2}{CH_2}-\overset{1}{CHO}$$

3-methylbutanal



$$\overset{6}{CH_3}-\underset{\underset{\displaystyle CH_3}{|}}{\overset{5}{CH}}-\underset{\underset{\displaystyle C_2H_5}{|}}{\overset{4}{CH}}-\overset{3}{CH_2}-\overset{2}{CH_2}-\overset{1}{CHO}$$

4-ethyl-5-methylhexanal

■ Nomenclature of ketones

Ketones are named by substituting the terminal **e** of the alkane with the suffix **one**:

Alkan$\boxed{e}$ ⇨ Alkan$\boxed{one}$

Examples

$CH_3-CO-CH_3$ propanone or acetone.

$CH_3-CH_2-CO-CH_3$ 2-butanone or ethylmethylketone

$C_6H_5-CO-CH_3$ acetophenone

$C_6H_5-CO-C_6H_5$ benzophenone

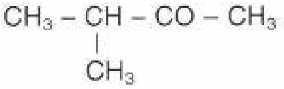
For n > 4, we proceed as in case of alcohols.

Examples

$$\overset{5}{CH_3}-\overset{4}{CH_2}-\overset{3}{CH_2}-\overset{2}{CO}-\overset{1}{CH_3}$$

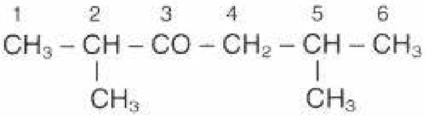
2-pentanone.

$CH_3-CH_2-CO-CH_2-CH_3$ 3-pentanone.



$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CO-CH_3$$

3-methyl-2-butanone.



$$\overset{1}{CH_3}-\underset{\underset{\displaystyle CH_3}{|}}{\overset{2}{CH}}-\overset{3}{CO}-\overset{4}{CH_2}-\underset{\underset{\displaystyle CH_3}{|}}{\overset{5}{CH}}-\overset{6}{CH_3}$$

2,5-dimethyl-3-hexanone.

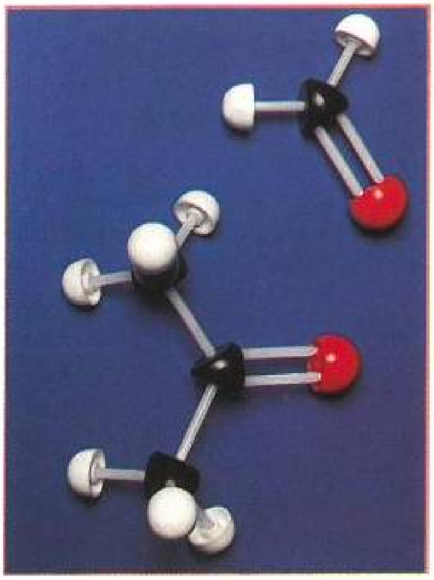


Figure 10.2

Ball-and-stick molecular models of HCHO and CH_3COCH_3.

■ Numbering begins at the end near the carbonyl carbon.

■ Structure and isomerism

Structure of methanal and acetone (propanone)

While constructing the ball-and -stick models for the methanal HCHO and acetone CH_3COCH_3 molecules (Fig.10.2), we conclude that the methanal molecule is coplanar. The atomic orbitals of the carbonyl carbon atom of the molecule is sp^2 hybridized. The same is true with the carbonyl carbon atom of the acetone molecule. In the two structures the value of the bond angles around the carbonyl carbon is approximately 120°.

Isomerism

Aldehydes admit skeletal isomerism, ketones, admit positional isomers with respect to the carbonyl group.

■ Aldehydes and ketones show functional isomerism

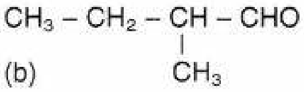
Applications

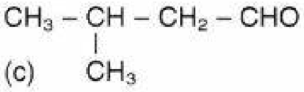
Write the condensed structural formulas and give the names of isomers for the molecular formula $C_5H_{10}O$.
The formulas are written, satisfying the valence of the atoms C, H and O.

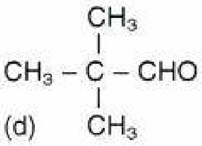
■ Without taking into consideration formulas which contain double bond or cyclic- chain.

Aldehydes

$CH_3-CH_2-CH_2-CH_2-CHO$ pentanal
(a)


$CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-CHO$ 2-methylbutanal
(b)


$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CHO$ 3-methylbutanal
(c)


$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CHO$ 2,2-dimethylpropanal
(d)

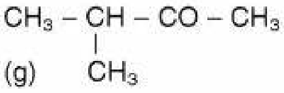
Four aldehyde isomers have the molecular formula $C_5H_{10}O$. (a), (b) and (d) are skeletal isomers. The same is true for (a), (c) and (d).

■ (b) and (c) are isomers that differ in branching position (methyl group).

Ketones

$CH_3-CH_2-CH_2-CO-CH_3$ 2-pentanone
(e)

$CH_3-CH_2-CO-CH_2-CH_3$ 3-pentanone
(f)


$CH_3-\underset{CH_3}{\underset{|}{CH}}-CO-CH_3$ 3-methyl-2-butanone
(g)

Three ketone isomers have the molecular formula $C_5H_{10}O$.
(e) and (f) are positional isomers.
(e) and (g) are skeletal isomers. The same is true for (f) and (g).

■ The four aldehydes are functional isomers for three ketones.

■ Physical properties

Aldehydes and ketones are liquids or solids at room temperature. Their boiling point generally increases with

■ Only methanal is gas at room temperature. An aqueous solution 37% methanal is called formol is commonly used to preserve biological species (Fig. 10.3).

Figure 10.3

A snake preserved in formol.

■ The absence of hydrogen bonding makes the carbonyl compound more volatile than alcohols of comparable molar mass.
CH_3CH_2OH (78.5 °C) and CH_3CHO (21 °C).

■ A lone pair of the oxygen atom allows the carbonyl group to be protonated.

■ The carbonyl functional group is considered as the most important functional group in organic chemistry.

■ Aldehydes in general are more reactive than ketones.

increase of their molar masses. The lower aldehydes and ketones are very soluble in water. This solubility decreases rapidly as the carbon chain increases. Some physical properties of aldehydes and ketones are shown in table 10.1.
The more volatile aldehydes have pungent odor, the ketones have agreeable odor.
Carbonyl compounds are used in perfumes. The first two ketones, acetone, and 2-butanone are good organic solvents. Ethanal which has the odor of an apple, becomes pungent in strong dose.

Name	Boiling point (°C)	Solubility (g/kg of water)
Aldehyde		
Methanal	- 21	Very soluble
Ethanal	21	∞
Propanal	49	160
Butanal	76	70
Pentanal	103	Slightly soluble
Hexanal	128	Slightly soluble
Ketone		
Propanone	56	∞
2-butanone	80	256
2-pentanone	102	63
3-pentanone	102	48
2-hexanone	128	16
3-hexanone	125	15

Table 10.1

Some physical properties of aldehydes and ketones.

■ Chemical reactions

The electronic structure of the carbonyl group has the following characteristics :

- A pi π bond between C and O atom.
- A polar double bond CO, with two lone pairs of electrons on the oxygen atom which gives a weak basic character to the carbonyl compounds,

This electronic structure explains the high chemical reactivity of the aldehydes and ketones which undergo different types of chemical reactions, specially, addition reactions and oxidation –reduction reactions.

■ Addition reactions

The carbonyl group is accessible to addition reaction during which the Pi, π, bond of the group is broken and two sigma, σ, bonds are formed.

Activity 1

Addition of ethanal to a freshly prepared concentrated sodium bisulfite $NaHSO_3$ solution.

Objective

Carry out addition on the carbonyl group of ethanal.

Equipment and reagents

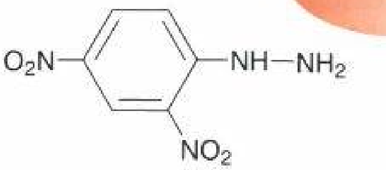
Test tube. 2 (5mL) graduated pipets. Freshly prepared sodium bisulfite solution (2 $mol.L^{-1}$).
Aqueous ethanal solution.

Procedure

Place in the test tube about 3mL of $NaHSO_3$ solution, then add 1 mL of ethanal solution. Shake and observe what happens (Fig. 10.4).

Observation and conclusion

The forming of white crystals in the tube results from the addition of $NaHSO_3$ on the double bond CO of ethanal. The obtained solids are called bisulfite addition compounds. Bisulfite addition reaction is often used in separating and purifying aldehydes and some ketones from other substances.



Formula of DNPH.

Figure 10.4
Addition of ethanal on $NaHSO_3$.

Activity 2

Reaction of ethanal with 2,4-dinitro phenyl hydrazine (DNPH).

- Ketones having branchings on the two carbon atoms attached to the carbonyl carbon do not react with $NaHSO_3$.

Objective

Identify the carbonyl group.

Equipment and reagents

Test tube. 2(5mL) graduated pipets. Alcoholic (DNPH) solution (2 $mol.L^{-1}$).
Aqueous ethanal solution.

Procedure

Place in the test tube about 3mL of DNPH solution. Then add 2-3 drops of ethanal solution (Fig.10.5).

Observation and conclusion

A yellow –orange precipitate is formed. This results from the addition of DNPH on the double bond CO of ethanal. The addition of DNPH on aldehydes and ketones always produces an orange precipitate. This reaction is used to identify the functional carbonyl group of these two families of compounds.

Figure 10.5
A yellow precipitate is formed in the tube.

- To obtain a better precipitate, avoid excess addition of the carbonyl compound since it dissolves the precipitate formed.

- **Catalytic hydrogenation**

Refer to chapter of alkenes and alkynes in the second year secondary. The hydrogenation reaction of an aldehyde or ketone consists of adding a hydrogen molecule to the carbonyl group to produce an alcohol.
For example, hydrogenation of ethanal takes place according to

- This reaction is the reverse of the catalytic dehydrogenation of alcohols, studied in the previous chapter.

- Catalytic hydrogenation of carbonyl compounds is more difficult than those of alkenes and alkynes. For this reason it is carried out with hydrogen under high pressures and high temperatures.

- Ammonical silver nitrate solution is also known as Tollen's reagent.

the equation:

$$CH_3CHO + H_2 \rightarrow CH_3CH_2OH$$

For propanone :

$$CH_3COCH_3 + H_2 \rightarrow CH_3CHOHCH_3$$

Metallic catalysts (Ni, Pt, Pd), in finally divided powdered form, should be used in these reactions. Catalytic hydrogenation of aldehydes produce primary alcohols whereas these ketones produce secondary alcohols.

- **Mild oxidation**

Aldehydes undergo mild oxidation by an oxidant such as potassium permanganate in acidic medium. Also, they can be oxidized by ammonical silver nitrate solution in basic medium or by Fehling's solution.

Mild oxidation of ethanal

Activity 3 Oxidation of ethanal by acidified potassium dichromate solution

- Write the half-reactions of the redox reactions taking place.
- Write the overall equation of the redox reaction taking place in the tube.

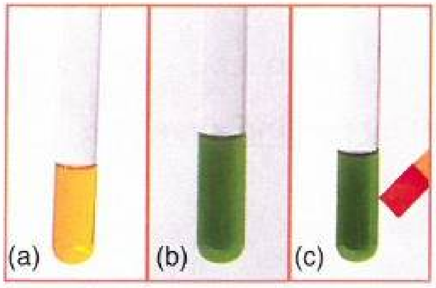


Figure 10.6
Oxidation of ethanal by acidified $K_2Cr_2O_7$ solution:
a) Before the reaction, the solution is orange in color.
b) After the reaction, the solution becomes green in color.
c) The color of pH paper changes.

Objective

Carry out mild oxidation of an aldehyde

Equipment and reagents

Test tube. 2 graduated cylinders10mL each. 5 mL graduated pipet. Heating plate or a steam-bath. Gloves and eye goggles. Aqueous ethanal solution. (0.2 mol.L^{-1}) potassium dichromate solution. Concentrated sulfuric acid (about 4 mol.L^{-1}). pH paper.

Procedure, observation and interpretation

Proceed as with continuous mild oxidation of ethanol (Fig.10.6 and 10.7).

$Cr_2O_7^{2-}$ is reduced to Cr^{3+} according to the half-reaction:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

And ethanal is oxidized to ethanoic acid according to the half-reaction:

$$CH_3CHO + H_2O \rightarrow CH_3COOH + 2H^+ + 2e^-$$

The overall redox reaction is given by the equation:

$$3CH_3CHO + Cr_2O_7^{2-} + 8H^+ \rightarrow 3CH_3COOH + 2Cr^{3+} + 4H_2O$$

Activity 4 Oxidation of ethanal by an ammonical silver nitrate solution

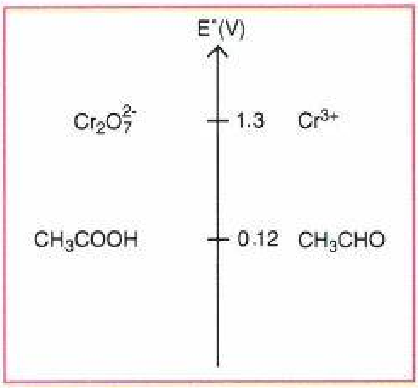


Figure 10.7
Standard reduction potentials of the redox couples involved.

Objective

Carry out mild oxidation of an aldehyde.

Equipment and reagents

Test tube. 10 mL graduated cylinder. 5 mL graduated pipet. Hot plate or steam-bath. Aqueous ethanal solution. Freshly prepared colorless ammonical nitrate solution (Tollen's reagent).

Procedure

In a very clean test tube, put about 3 mL of ammonical silver nitrate solution and 1 mL of ethanal solution. Shake and put the tube in a steam bath about 50 °C. Observe what happens (Fig. 10.8).

Observation and interpretation

The colorless solution gradually blackens, then a mirror develops on the walls of the tube.
The redox couples involved in this reaction are:
$Ag(NH_3)_2^+/Ag$ and CH_3COO^-/CH_3CHO.

Ammonical silver nitrate solution is basic. It contains the complex ion $Ag(NH_3)_2^+$ called silver diammine. This is reduced by ethanal into silver metal, which deposits on the walls of the tube forming silver nitrate according to the half-reaction:

$$Ag(NH_3)_2^+ + 1e^- \rightarrow Ag + 2NH_3$$

Ethanal is oxidized to ethanoate ion (acetate ion) according to the half-reaction:

$$CH_3CHO + 3HO^- \rightarrow CH_3COO^- + 2H_2O + 2e^-$$

The formation of ethanoate ion is due to the fact that the reaction is carried out in basic medium. The overall redox reaction is given by the equation :

$$CH_3CHO + 3HO^- + 2Ag(NH_3)_2^+ \rightarrow CH_3COO^- + 2Ag + 4NH_3 + 2H_2O$$

- What is the redox couple in the ammonical silver nitrate solution ?
- Why ethanal is oxidized to ethanoate ion CH_3COO^-?
- Write the half-reactions involved in the redox reaction taking place.

Activity 5 Oxidation of ethanal by Fehling's reagent

Objective

Carry out mild oxidation of an aldehyde.

Equipment and reagents

Test tube (10 mL). Graduated cylinder. Bunsen burner. 5 mL graduated pipet. Aqueous ethanol solution. Fehling's reagent (blue solution).

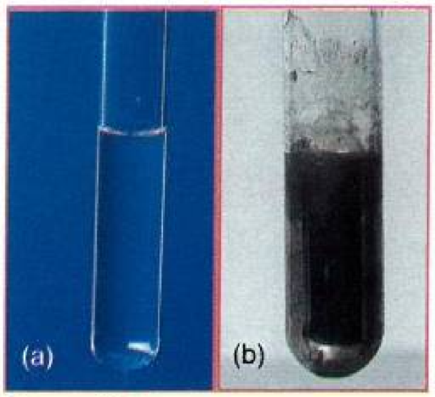


Figure 10.8

The reaction between ethanal and Tollen 's reagent:

(a) before the reaction, the solution is colorless.

(b) after the reaction, there is a formation of a silver mirror.

- Often, instead of silver mirror, formation of a black deposit of silver is observed.

- Write the half-reactions and the overall equation of the reaction taking place in the tube.

- Tartarate ion T^{2-} is a di-anion of formula:

$$\begin{array}{c} HO - CH - COO^- \\ | \\ HO - CH - COO^- \end{array}$$

The redox couples involved in this experiment are: CuT_2^{2-}/Cu_2O and CH_3COO^-/CH_3CHO.

Procedure

Place in a test tube about 3mL of Fehling's reagent and 1mL of ethanal solution. Shake, then gently heat in the flame of the bunsen burner. Observe (Fig.10.9)

Observation and interpretation

The blue coloration of the solution gradually changes then a brick-red precipitate appears in the tube.

Fehling's reagent is a basic solution of copper (II) complex tartarate T^{2-} ions. The complex ions are represented as CuT_2^{2-}, it attributes to the solution its characteristic blue color (royal-blue).

The complex CuT_2^{2-} is reduced by ethanal into copper (I) oxide. It is solid and brick-red in color, according to the half-reaction:

$$2CuT_2^{2-} + 2HO^- + 2e^- \rightarrow Cu_2O + H_2O + 4T^{2-}$$

Ethanal is oxidized to ethanoate (acetate) ion according to the half-reaction:

$$CH_3CHO + 3HO^- \rightarrow CH_3COO^- + 2H_2O + 2e^-$$

The formation of ethanoate ion is due to the fact that the reaction is carried out in a basic medium.

The equation of the overall redox reaction taking place is:

$$CH_3CHO + 5HO^- + 2CuT_2^{2-} \rightarrow CH_3COO^- + Cu_2O + 4T^{2-} + 3H_2O$$

Mild oxidation of aldehydes

In general, aldehydes undergo mild oxidation in an acidic medium or in a basic medium by different oxidants.

In an acidic medium, an aldehyde is oxidized into carboxylic acid by $K_2Cr_2O_7$ according to the following equation:

$$3RCHO + Cr_2O_7^{2-} + 8H^+ \rightarrow 3RCOOH + 2Cr^{3+} + 4H_2O$$

In a basic medium, an aldehyde is oxidized into carboxylate (or alkanoate ion) by ammonical silver nitrate as in the following equation:

$$RCHO + 3HO^- + 2Ag(NH_3)_2^+ \rightarrow RCOO^- + 2Ag + 4NH_3 + 2H_2O$$

By Fehling's reagent according to the following equation:

$$RCHO + 5HO^- + 2CuT_2^{2-} \rightarrow RCOO^- + Cu_2O + 4T^{2-} + 3H_2O$$

Case of ketones

Ketones, when treated under the same conditions of aldehydes, do not undergo mild oxidation (Fig. 10.10 and 10.11).

Generally, aldehydes are good conductors. They undergo mild oxidation whereas, ketones do not undergo mild oxidation. This leads us to the following conclusion:

Mild oxidation allows us to distinguish between aldehydes and ketones.

nitrate solution and Fehling's reagent are used as identification tests for aldehydes.

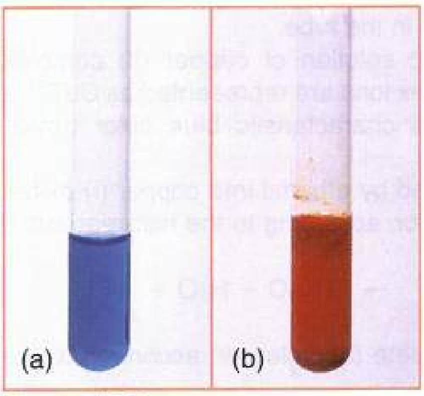


Figure 10.9
The reaction between ethanal and Fehling's reagent:
(a) before the reaction, the solution is blue.
(b) after the reaction, there is a formation of a brick-red solid.

Figure 10.10
Propanone (acetone) is not oxidized by an acidified $K_2Cr_2O_7$ solution

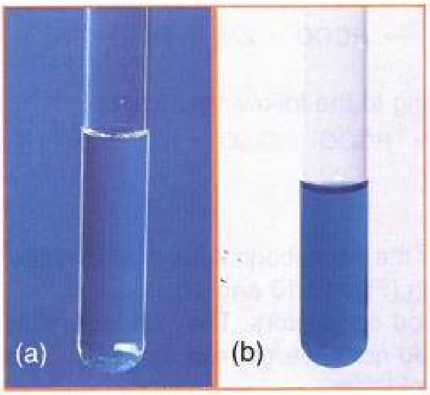


Figure 10.11
Propanone (acetone) is not oxidized by:
(a) Tollen's reagent.
(b) Fehling's reagent.

Activity 6 Reaction of ethanal with Schiff's reagent

Objective

Identify an aldehyde

Equipment and reagents

Test tube. 5 mL graduated pipet. Dropper. Ice-water bath. Aqueous ethanal solution.
Schiff reagent (freshly prepared colorless solution).

Procedure

Place in a very clean test tube about 3 mL of Schiff's reagent. Cool the content of the tube in an ice-water bath (2-3 minutes). Add a drop of ethanal solution. Shake and observe (Fig. 10.12).

Conclusion

Ethanal colors schiff's reagent pink. This observation is general for all aldehydes. Ketones do not color schiff's reagent (Fig.10.13). Thus, we can conclude that the reaction of aldehydes with Schiff's reagent is a simple and efficient test for aldehydes. Finally, the different behavior of alcohols, aldehydes and ketones, with respect to mild oxidation allows us to identify experimentally the class of the alcohol (refer to method sheet).

Industrial preparation

Carbonyl compounds are very important in chemical industry, particularly in methanal, ethanal, and propanone, all of which are manufactured in large quantities.

- **Methanal**

Methanal (or formaldehyde), is the most important aldehyde because of its various applications. It is manufactured by the catalytic oxidation of methanol at high temperature (600-650 °C) in the presence of silver as catalyst. The reaction takes place according to the following equation :

$$CH_3OH + \tfrac{1}{2}O_2 \rightarrow HCHO + H_2O$$

- **Ethanal**

Ethanal (or acetaldehyde) is manufactured according to the Wacker's process, which consists of carrying out a reaction between ethylene and oxygen in the presence of $PdCl_2$ and $CuCl_2$ in an aqueous solution as a catalyst, and at a temperature of 110-120 °C under a pressure of 4-8 bar. The reaction which takes place is given by the following equation:

$$CH_2{=}CH_2 + \tfrac{1}{2}O_2 \rightarrow CH_2{=}CHOH \rightarrow CH_3CHO$$

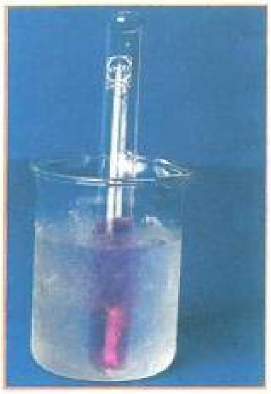


Figure 10.12
Ethanal colors Schiff's reagent pink.

Figure 10.13
Propanone (acetone) does not color Schiff's reagent.

- Methanal is used in many applications, such as in disinfectants, and to manufacture solvents, plastic materials, synthetic resins, pharmaceutical products, and tannins... .
It forms an intermediary unstable compound, which is transformed into ethanal spontaneously.

- Ethanal is also employed to manufacture solvents, pharmaceutical products... .

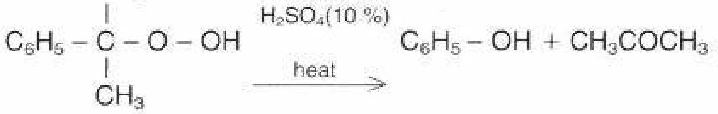
- Acetone is a very good solvent. It is also employed to manufacture rubber, solvents, synthetic resins, and pharmaceutical products.

(unstable intermediate)

- **Propanone**

Propanone(acetone), the most important ketone, is a by-product which forms in the Hock's process which is used to manufacture phenol (refer 2nd year secondary chemistry). The reactions which take place are given by the following equations:

$$C_6H_6 + CH_3-CH=CH_2 \xrightarrow{H^+/heat} C_6H_5-CH(CH_3)_2 \xrightarrow{O_2}$$

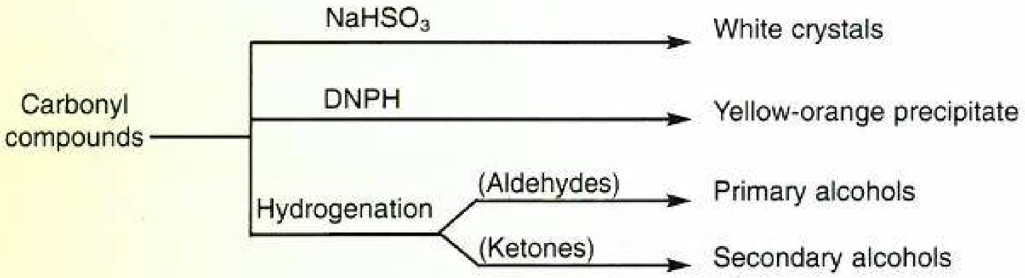


$$C_6H_5-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-OH \xrightarrow[heat]{H_2SO_4(10\ \%)} C_6H_5-OH + CH_3COCH_3$$

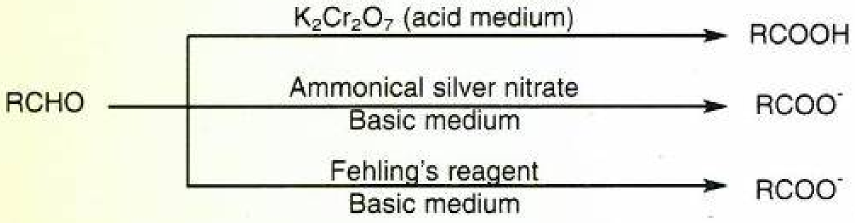
The world wide production of each of these compounds is many million tons.

Chapter review

- An aldehyde is represented by the general formula RCHO.
- A ketone is represented by the general formula RCOR'.
- Aldehydes and ketones have characteristic odors. Some of them are used in perfumes.
- Some addition reactions on the double bond CO of aldehydes and ketones are summarized in the following scheme:



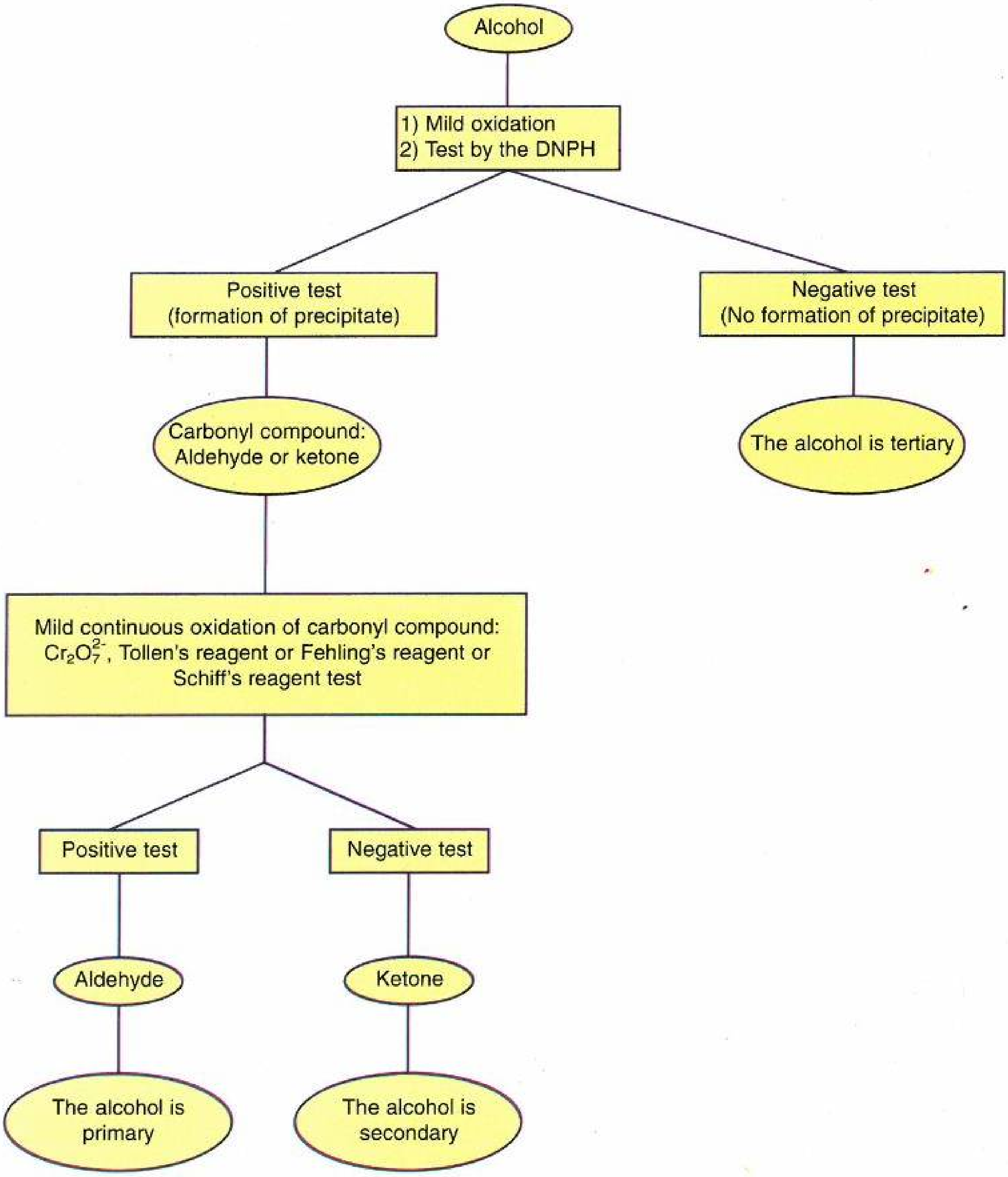
- The reaction with DNPH is a test that allows us to identify the carbonyl group.
- Aldehydes undergo mild oxidation, while ketones do not. The following schema summarizes the mild oxidation reactions of aldehydes.



- Mild oxidation allows to distinguish aldehydes from ketones and to identify the class of an alcohol.
- Methanal (formaldehyde) is manufactured industrially by the catalytic oxidation of methanol.
- Ethanal (acetaldehyde) is manufactured industrially by the catalytic oxidation of ethylene in an aqueous solution.
- Propanone (acetone) is a by-product in the manufacture of phenol according to Hock's process.

Method sheet

Identification of the class of an alcohol
Distinguish between aldehydes and ketones

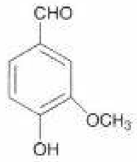


Documentary activity

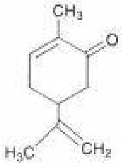
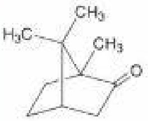
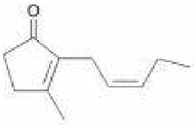
Natural aldehydes and ketones

Molecules of a large number of natural products contain aldehydes and ketones. They are responsible partially for the taste and aroma of many foods and are involved in diverse biochemical processes: hormones, pheromones ….

Aldehydes

Formula	Common name	Origin
 $(CH_3)_2C = CH[CH_2]_2\underset{\underset{CH_3}{\mid}}{C} = CHCHO$	Citral	Citronell
 $(CH_3)_2C = CH[CH_2]_2\underset{\underset{CH_3}{\mid}}{C}HCH_2CHO$	Citronell	Citronellal
$CH_3[CH_2]_2CH = CHCHO$	2-hexenal	Tomato
$C_6H_5CH = CHCHO$	Cinnamaldehyde	Cinnamon
C_6H_5CHO	Benzaldehyde	Bitter almond
	Vanillin	Vanilla bean

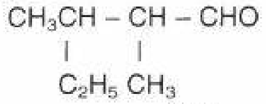
Ketones

Formula	Common name	Origin
$CH_3[CH_2]_3CH = CHCOCH_3$	3-octen-2-one	Mushrooms
$(CH_3)_2C = CH[CH_2]_2\underset{\underset{CH_3}{\mid}}{C} = CH[CH_2]_2COCH_3$	Geranylacetone	Magnolia
	Carvone	Green mint and cumin
	Camphor	Camphor tree
	Jasmone	Essence of jasmine

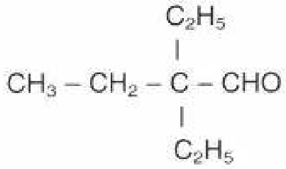
* Systematic name

Exercises

1 Give the systematic (IUPAC) name for each of the following aldehydes and ketones:

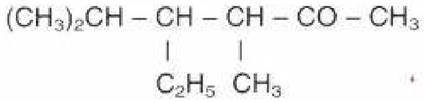
a) 

$CH_3\underset{\substack{|\\C_2H_5}}{CH}-\underset{\substack{|\\CH_3}}{CH}-CHO$

b) 

$CH_3-CH_2-\underset{\substack{|\\C_2H_5}}{\overset{\substack{C_2H_5\\|}}{C}}-CHO$

c) $CH_3-CH_2-CO-CH_2-CH_2-CH_3$

d) 

$(CH_3)_2CH-\underset{\substack{|\\C_2H_5}}{CH}-\underset{\substack{|\\CH_3}}{CH}-CO-CH_3$

2 Write the condensed structural formulas for the following aldehydes and ketones –correct the incorrect names, if there are any.

a) 5-ethyl-2-hexanone
b) 3-ethylpentanal
c) 3-ethyl-2-methylhexanal
d) 3,5-dimethyl-4-hexanone

3 a) In an aldehyde, express the percentage composition, by mass, and the percentage, by mole, of oxygen in terms of n.

b) Determine the value of n so that the percentage by mole of oxygen in the aldehyde is 7.7%. Deduce the molecular formula.

c) Write the structural formula and give the name of each.

4 A) 1m^3 of ethylene measured under the conditions of Wacker' procedure (110 °C and 8 bars) is made to react with oxygen in an aqueous solution and in the presence of $PdCl_2$ and $CuCl_2$ as catalyst.

a) What is the nature of reaction described above and what is the product A obtained under the given conditions?

b) Write the equation of the corresponding reaction.

c) If the % yield of the reaction is 92%, what is the mass of product A obtained?

B) The hydration of an equivalent quantity of ethylene, in the presence of phosphoric acid as a catalyst at 300 °C, leads to the formation of a different product B.

a) What is B? Write the equation of the corresponding reaction.

b) What is the % yield of the process if the mass of product B obtained is 11.5 kg?

c) Could A be converted to B and vice-versa? If yes, describe briefly the reaction that would take place and write the corresponding equation.

5 Five flasks are labeled (I) through (V) each contains a pure liquid compound of four carbon atoms and a functional group containing at least one oxygen atom. Their carbon chain is not branched. The mild oxidation of compound (I), by an acidified potassium dichromate solution, gives compounds (III) and (IV), whereas that of compound (II) gives compound (V).

a) According to the above, can the five compounds be identified? Explain?

b) Only compound (III) reacts with Schiff's reagent as well as with Fehling's reagent.

i) Describe the two experiments.

ii) Write the equation of the reaction of Fehling's reagent with compound (III).

iii) Identify the five compounds and name them. (Except that of compound IV).

6 Two compounds of molecular formula, respectively, C_2H_4O and C_4H_8O produce a yellow-orange precipitate by the reaction with DNPH.

a) Is this indication sufficient to write the structural formulas of these two compounds? Explain.

b) If yes, write the corresponding structural formula. If no, write all the possible structural formulas.

c) What identification tests should further be done to distinguish them? Do these tests allow us to determine definitely the structure of the indicated compounds?

7 It is required to titrate an ethanal solution. Being available a 0.2 mol.L^{-1} potassium dichromate solution and 4 mol. L^{-1} sulfuric acid solution in the presence of a convenient indicator.

a) Indicate the glassware used for the titration.
b) Give a brief description of the procedure followed. How do we detect the equivalence point?
c) Write the half-reaction and the equation of the overall redox reaction.
d) The titration of 10 mL of aqueous ethanal solution required 15mL of dichromate solution to reach the equivalence point. Calculate the molar concentration in mol. L^{-1} and the mass concentration in g.mol^{-1}of ethanal solution.
e) 5 mL of ethanal solution are heated with an excess of an ammonical silver nitrate solution.
  i) Write the oxydation-reduction half reactions and the equation of the overall redox reaction.
  ii) What mass of solid is formed due to the reaction?

8 25 g of a mixture (M) containing ethanol and ethanal are completely oxidized by an excess of a 0.2 mol.L^{-1} acidified potassium permanganate solution. The reaction is assumed to be complete. 11.2 mL of 1 mol.L^{1}sodium hydroxide solution is needed to titrate 1/50 of the ethanoic acid formed.

a) Write the half–reaction and the equation of the overall redox reactions for ethanol and ethanal.
b) Calculate the mass percentage composition of the mixture (M).
c) What volume of the oxidant is just needed to carry out this titration?

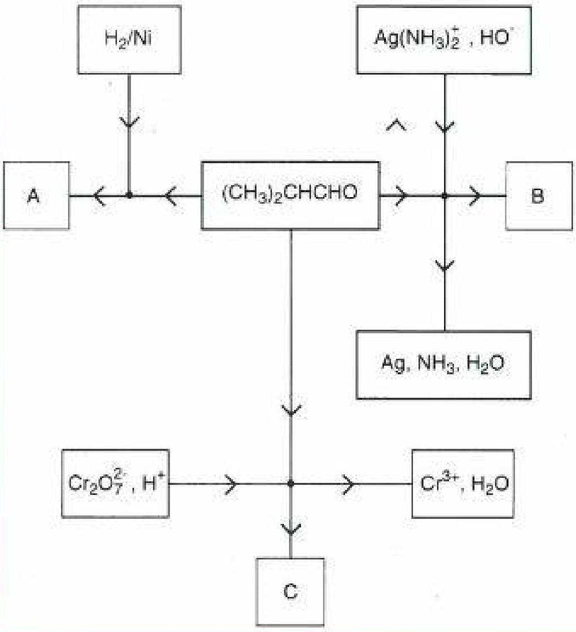
9 When a mixture of methanal and Fehling's solution is heated in a test tube, sometimes it may form a mirror of copper metal on the walls of the tube, besides the brick-red precipitate.

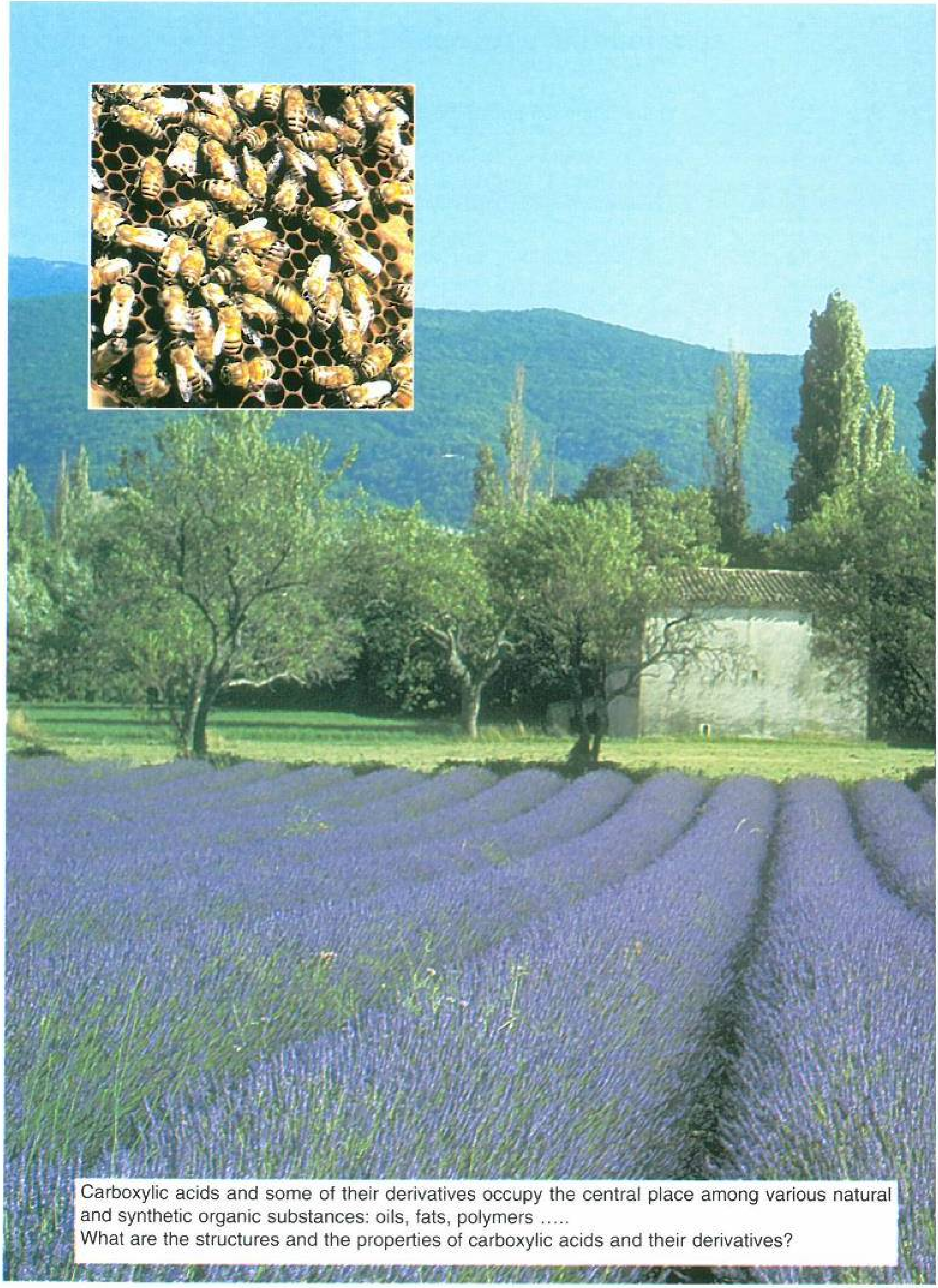
a) What are the redox couples involved in the formation of brick-red solid, and in the formation of the copper mirror?
b) Write the oxydation and reduction half-reactions and the equation of the over-all redox reactions involved.

10 Two isomeric compounds (A) and (B) of molecular formula $C_6H_{12}O$:
Compound (A) can be obtained by the mild oxidation of 3-hexanol.
Compound (B) can be obtained by controlled mild oxidation of 1-hexanol taken in large excess.

a) Name two oxidants commonly used to oxidize alcohols.
b) What mild oxidation of primary alcohols allow to obtain only aldehydes?
c) Write the structural formulas of (A) and (B) and name them:
d) What do you observe if A and B are treated with
1) DNPH solution?
2) Ammonical silver nitrate solution?
3) Fehling's solution?
What organic products are obtained in the two latter cases?

11 Identify the missing compounds A, B and C in the following diagram:





Carboxylic acids and some of their derivatives occupy the central place among various natural and synthetic organic substances: oils, fats, polymers .....
What are the structures and the properties of carboxylic acids and their derivatives?

CARBOXYLIC ACIDS AND DERIVATIVES

11

Objectives

- Identify carboxylic acids and their derivatives.
- Know the systematic nomenclature of carboxylic acids and their derivatives.
- Identify some chemical reactions of carboxylic acids and their derivatives.

Prerequisites

- Chemical formulas and bonding.
- VSEPR method, hybridization of atomic orbitals and structures.
- Chemical reactions.
- Nomenclature of alkanes.
- Notion of isomerism.
- Mole and stoichiometry.

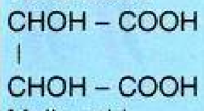
Chapter content

11.1 Carboxylic acids

- Compounds containing two or more carboxyl groups are called polycarboxylic acids.

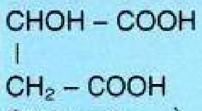
Examples

Tartaric acid



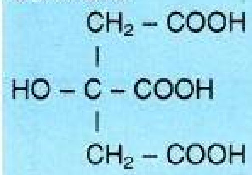
$$\begin{array}{l} CHOH-COOH \\ | \\ CHOH-COOH \end{array}$$

Malic acid



$$\begin{array}{l} CHOH-COOH \\ | \\ CH_2-COOH \end{array}$$

Citric acid



$$\begin{array}{l} \quad\ \ CH_2-COOH \\ \qquad | \\ HO-C-COOH \\ \qquad | \\ \quad\ \ CH_2-COOH \end{array}$$

Figure 11.1.

Some polycarboxylic acids are responsible for the tests of some fruits.
Tartaric acid (grape)
Malic acid (apple)
Citric acid (citron…etc)

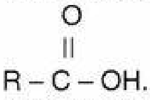
■ Definition and general formula

Carboxylic acids are widespread in nature (Fig. 11.1); they are organic compounds that contain one or more carboxyl groups - COOH.

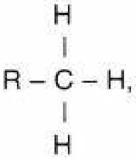
A monocarboxylic acid is a compound, which contains one carboxyl group in its structure.

Compounds containing two carboxyl groups are called dicarboxylic acids and are much encountered in chemistry and in industry, such as in oxalic acid HOOC – COOH and adipic acid, HOOC – $(CH_2)_4$ – COOH, which is used in making nylon-6,6.

The formula of a monocarboxylic acid is represented by:

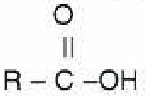


$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH$. It is obtained by replacing the three C-H bond in the formula of an alkane



$R-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-H$, by the double bond C=O and by a single bond C–OH.

The carbon atom of the carbonyl group is the functional carbon of the molecule.
The general formula of carboxylic acids, consequently, is written as $C_nH_{2n}O_2$.
In general, a carboxylic acid is represented by the formula



$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH$ (or simply as RCOOH or also as RCO_2H).

■ Nomenclature

The systematic nomenclature of carboxylic acid is based on that of alkanes.
The name of a carboxylic acid is derived from the name of the corresponding alkane having the same number of carbon atoms by changing the final **e** of alkane with the suffix **oic** and adding the term acid.

Alkan$\boxed{\text{e}}$ ⇨ Alkan$\boxed{\text{oic}}$ acid

Examples

Formula	Systematic name	Common name
H – COOH	methanoic acid	formic acid
CH_3 – COOH	ethanoic acid	acetic acid
CH_3 – CH_2 – COOH	propanoic acid	propionic acid
CH_3 – $(CH_2)_2$ – COOH	butanoic acid	butyric acid

- Formic acid is extracted from ants (from the latin, for mica, or ant) (Fig. 11.2).

- Butyric acid is found in butter, especially when rancid; it is found also in some other foods (Fig.11.3).

Figure 11.2

Ant's nest

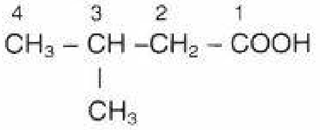
Figure 11.3

Butter and cheese.

- Stearic acid and oleic acid are called fatty acids; they are obtained from the fats of animals and plants (such as olive oil).

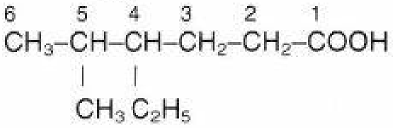
For the branched-chain, we proceed as with aldehydes; the numbering of the carbon atoms of the main chain starts with the carboxyl carbon atom. The position of this latter does not have to be specified in the name of the acid.

Examples



$$\overset{4}{CH_3}-\underset{\substack{|\\ CH_3}}{\overset{3}{CH}}-\overset{2}{CH_2}-\overset{1}{COOH}$$

3 -methyl butanoic acid

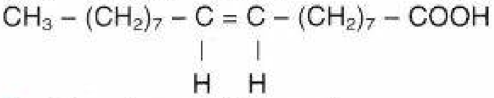


$$\overset{6}{CH_3}-\underset{\substack{|\\ CH_3}}{\overset{5}{CH}}-\underset{\substack{|\\ C_2H_5}}{\overset{4}{CH}}-\overset{3}{CH_2}-\overset{2}{CH_2}-\overset{1}{COOH}$$

4-ethyl-5-methyl haxanoic acid

Some special carboxylic acids:

$C_6H_5 - COOH$	benzoic acid
$C_6H_5 - CH_2 - COOH$	2-phenylethanoic acid
$CH_3 - (CH_2)_{16} - COOH$	stearic acid



$$CH_3-(CH_2)_7-\underset{\substack{|\\ H}}{C}=\underset{\substack{|\\ H}}{C}-(CH_2)_7-COOH$$

(Z)-Oleic acid

Structure and isomerism

Structure of methanoic acid

The ball-and-stick molecular model of methanoic acid HCOOH (Fig.11.4):

The model reveals the following geometric characteristics:

- The axes of the three sigma σ bonds of the carboxyl carbon atom are coplanar. The value of bond angles is less than 120°.
- The atomic orbitals of the carboxyl carbon atom are sp^2 hybrid orbitals.
- The group COH has a bent shape with an angle less than 109°.

Isomerism

Isomeric carboxylic acids exhibit skeletal isomers.

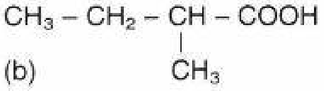
Application

Write the condensed structural formulas and give the names of all possible isomers of carboxylic acids of molecular formula $C_5H_{10}O_2$.

The structural formulas are given as follows :

$CH_3 - CH_2 - CH_2 - CH_2 - COOH$ pentanoic acid

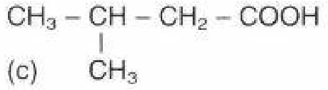
(a)



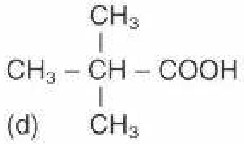
$$CH_3-CH_2-\underset{\substack{|\\ CH_3}}{CH}-COOH$$

2- methyl butanoic acid

(b)



(c) $CH_3-\underset{CH_3}{CH}-CH_2-COOH$ 3-methyl butanoic acid



(d) $CH_3-\overset{CH_3}{\underset{CH_3}{CH}}-COOH$ 2,2-dimethyl propanoic acid

Four isomeric carboxylic acids have the general formula $C_5H_{10}O_2$.
(a), (b) and (d) are skeletal isomers. The same is true for (a), (c) and (d).

■ Physical properties

At room temperature carboxylic acids are liquids or solids. Their boiling point increases generally with the increase of their molecular mass.
The first four acids are miscible with water in all proportions. The solubility in water for the higher members of acids decreases noticeably as the number of carbon atoms in the chain increases.

Some physical properties of carboxylic acids are summarized in table 11.1

Acid	Boiling points (°C)	Solubility (g/kg of water)
Methanoic	101	∞
Ethanoic	118	∞
Propanoic	141	∞
Butanoic	164	∞
Pentanoic	186	~ 50
Hexanoic	205	~ 9.7
Heptanoic	223	~ 2.4

Table 11.1
Some physical properties of carboxylic acids.

The first members of the carboxylic acids are comparatively volatile liquids with sharp or unpleasant odors. The carboxyl group allows the molecules of acids to be associated between each other through hydrogen bonding. In a pure state or in some solvents, the molecules of carboxylic acids associated two by two in structures called dimers (Fig. 11.5); two molecules are held together by two hydrogen bonds. Hydrogen bonding contributes to the high boiling point of carboxylic acids and increases the solubility of the first acids in water.

This strong hydrogen bonding has a noticeable effect on boiling points, giving carboxylic acids much higher boiling than the corresponding aldehydes and alcohols that have approximately

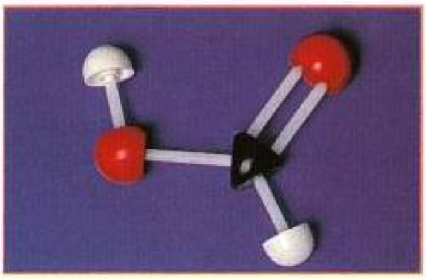


Figure 11.4
The ball-and-stick molecular model of methanoic acid.

■ Carboxylic acids are functional isomers to esters.

■ (b) and (c) are isomers, they differ in the position of the branching methyl group.

■ Nine ester isomers have the general formula $C_5H_{10}O_2$; they are functional isomers for the previous four acids.

■ Attention! methanoic and ethanoic acids cause severe burning when pure or concentrated.

the same molar mass:
CH_3CHO (21 °C), CH_3CH_2OH (78.5 °C) and HCOOH (101 °C).

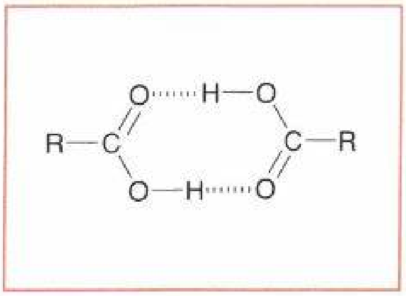


Figure 11.5
Dimers are two molecules of carboxylic acid associated together.

Chemical reactions

The electronic structure of the carboxyl group shows the common characteristics with the hydroxyl group and the carbonyl group.

- A polar-O-H bond.
- A single C-O and a double C=O polar bond.
- A π bond between the atoms C and O which are connected by a double bond.

However, because the close proximity of the two functional groups CO and OH, they contribute to the increase acid character and the base character in comparison, to alcohols.
In general, carboxylic acids undergo acid-base reactions and substitution reactions. They do not undergo addition reactions on the double bond C=O.

Acid properties

Carboxylic acids turn the color of bromothymol blue to yellow and the blue litmus solution to red (Fig. 11.6).

Activity 1 Reaction of vinegar with a marble piece

Objective
Evidence for the acid character of vinegar.

Equipments and reagents
100 mL Erlenmeyer flask. 100 mL beaker. A stopper adjusted to a delivery tube, 50 mL graduated cylinder. Mortar and pestle. Saturated limewater.

Procedure
Assemble the apparatus as shown in figure 11.7. Grind the marble piece and put it in the Erlenmeyer flask. Add about 20 mL of vinegar. Observe what happens.

Observation
Effervescence is observed in the flask, indicating the release of gas. The clear limewater becomes turbid.

Interpretation
The marble is made up of calcium carbonate $CaCO_3$. The vinegar is an aqueous ethanoic acid solution. This latter reacts with calcium carbonate according to the following equation:

$$2CH_3COOH + CaCO_3 \rightarrow 2CH_3COO^- + Ca^{2+} + CO_2 + H_2O$$

to give a soluble salt, calcium ethanoate, water and carbon dioxide that makes clear lime-water turbid.

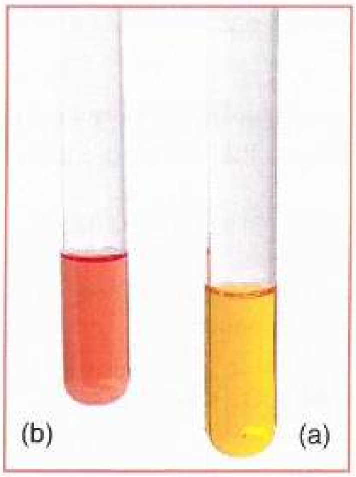


Figure 11.6
Action of aqueous acetic acid on:
(a) bromothymol blue
(b) litmus solution

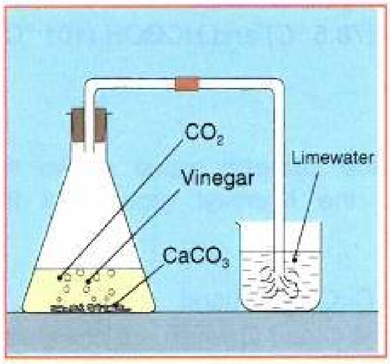


Figure 11.7
The reaction of vinegar with marble.

- This reaction is often used to clean the carbonate formed on a sink or from laboratory glassware.

- The $RCOO^-$ ion is called carboxylate ion or alkanoate ion.

Acid	pK_a
HCOOH	3.77
CH_3COOH	4.76
C_2H_5COOH	4.88
$CH_3(CH_2)_2COOH$	4.82
$(CH_3)_2CHCOOH$	4.86
$CH_3(CH_2)_3COOH$	4.86
$(CH_3)_3CCOOH$	5.05

Table 11.2
PK_a of some conjugate pairs $RCOOH/RCOO^-$

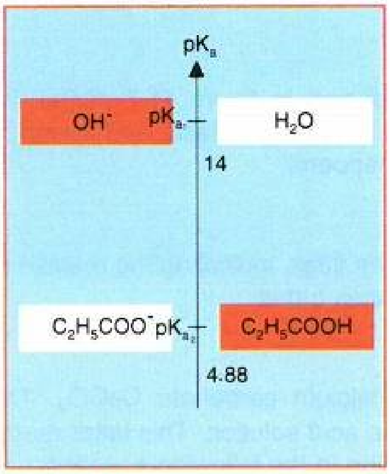


Figure 11.8
The gamma rule and the difference between two pK_a values, show that the reaction between propanoic acid and sodium hydroxide is almost complete.
$(pK_{a_1} - pK_{a_2}) = 14 - 4.88 = 9.12$.

- **Reaction with water**

Carboxylic acids are soluble in water; they are partially ionized in aqueous solution according to the following equation:

$$RCOOH + H_2O \rightleftarrows RCOO^- + H_3O^+$$

The extent to which this acid-base reaction takes place involves an acid-base pair, which is determined by the acidity constant of the conjugate pair $RCOOH/RCOO^-$ and is expressed by:

$$K_a = \frac{[RCOO^-]\,[H_3O^+]}{[RCOOH]}$$

Table 11.2 lists the pK_a values of some conjugate acid-base pairs.

- **Reaction with a strong base**

A carboxylic acid reacts with a strong base, according to almost complete reaction, to produce its conjugate base according to the following equation:

$$RCOOH + HO^- \rightarrow RCOO^- + H_2O$$

The reaction between propanoic acid, for example, with a sodium hydroxide solution (Fig. 11.8) produces sodium propanoate according to the following equation :

$$C_2H_5COOH + HO^- + Na^+ \rightarrow C_2H_5COO^- + Na^+ + H_2O$$

- **Reaction with a metal**

Carboxylic acids react with metals, which are more reducing than hydrogen. The reaction, which is generally, less vigorous than with those of strong acids (HCl, H_2SO_4), produces the carboxylate of the metal and hydrogen gas.

Examples
Magnesium reacts with butanoic acid (Fig. 11.9) to form magnesium (II) butanoate according to the following equation:

$$2CH_3(CH_2)_2COOH + Mg \rightarrow 2CH_3(CH_2)_2COO^- + Mg^{2+} + H_2$$

Iron reacts with methanoic acid (Fig. 11.10) to form iron (II) methanoate according to the following equation :

$$2HCOOH + Fe \rightarrow 2HCOO^- + Fe^{2+} + H_2$$

- **Esterification**

Esterification is the reaction between a carboxylic acid and an alcohol. It takes place according to the following equation:

Figure 11.9

The reaction between butanoic acid and magnesium.

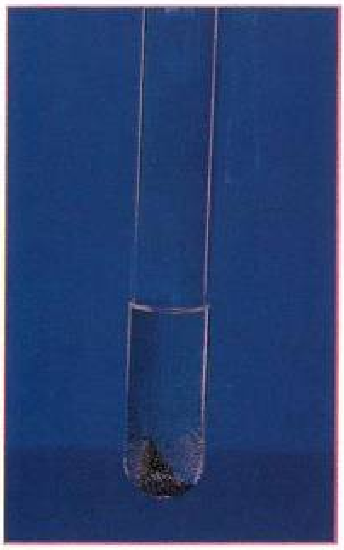


Figure 11.10

The reaction between methanoic acid and iron..

- Carbonylation signifies to insert a carbonyl group into the structure of the molecule.

$$RCOOH + R'OH \rightleftarrows RCOOR' + H_2O$$

Industrial preparation

Carboxylic acids, particularly methaonic and ethanoic acids, have diverse applications in chemical industry, food chemistry, pharmaceutical, ...

Methanoic acid

Methanoic acid (or formic acid) is manufactured according to a simple process, where powder sodium hydroxide is made to react with carbon monoxide under moderately high temperature and pressure (7 bar and 150 °C). The sodium methanoate obtained is then converted to methanoic acid by the action of a strong acid such as HCl in aqueous solution. The reactions taking place are given by the following equations:

$$NaOH + CO \rightarrow HCOO^-, Na^+$$

$$HCOO^- + H_3O^+ \rightarrow HCOOH + H_2O$$

Ethanoic acid

Ethanoic acid (or acetic acid) is manufactured by many procedures.

- Carbonylation of methane according to the equation:

$$CH_3OH + CO \rightarrow CH_3COOH$$

This is known as the Monsanto process. It is carried out under a high pressure (30 to 40 bar) and at 180 °C in the presence of rhodium (III) Rh^{3+} as a catalyst.

- Oxidation of ethanal in the presence of cobalt (III) Co^{3+} as a catalyst according to the following equation:

$$CH_3CHO + \tfrac{1}{2}O_2 \rightarrow CH_3COOH$$

- The process of enzymatic oxidation of ethanol is used to prepare vinegar. The reaction takes place according to the following equations:

$$CH_3CH_2OH + \tfrac{1}{2}O_2 \rightarrow CH_3CHO + H_2O$$
$$CH_3CHO + \tfrac{1}{2}O_2 \rightarrow CH_3COOH$$

Carboxylic acid derivatives

When the hydroxyl group of the carboxylic acid is substituted by an atom or a group of atoms such as: Cl, OR'..... (except H or C), a new functional group is attained characterized by a family

- Ethanal is prepared according to Wacker process.

(class) of compounds called derivatives of carboxylic acids; these possess specific properties.

Acid derivatives are compounds in which the hydroxyl group of the carboxylic acid is replaced by an atom or a group of atoms.

The carbon atom in the functional group of the carboxylic acid derivative is the carbonyl atom of the carboxyl group. Thus, it possesses the same geometric characteristics.

The carbonyl carbon is joined to three atoms by sigma σ bonds, because these bonds utilize sp^2 hybrid orbitals they lie in a plane and are apart about 120°.

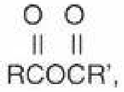
An acid derivative is represented by the general formula

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-Z$$ (or simply as RCOZ).

Four acid derivatives are studied in this book:

acyl chlorides RCOCl,

acid anhydrides



$$R\overset{\overset{\displaystyle O}{\|}}{C}O\overset{\overset{\displaystyle O}{\|}}{C}R',$$

esters RCOOR'

and amides

$$RCO\underset{|}{N}-.$$

Acyl chlorides

An acyl chloride is an acid derivative obtained by replacing the hydroxyl group by a chlorine atom.

Acyl chlorides are more reactive than the carboxylic acids from which are derived. This explains why they are used in organic synthesis reactions rather than the acids.

Acyl chlorides are represented by the general formula

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl$$ (or simply RCOCl) (Fig.11.11).

- As they are highly reactive, acyl chlorides are not encountered in nature.

Nomenclature

The name of an acyl chloride is the combination of two terms: chloride and acyl, this latter stands for the group RCO-.

According to the IUPAC rules, the systematic name of an acyl chloride is derived from the corresponding acid by changing the suffix –**ic** acid with –**yl** and the word acid by chloride.

RCOOH	⇨	RCOCl
Alkanoic acid		Alkanoyl chloride

Examples

HCOCl	methanoyl chloride (formyl chloride)
CH_3COCl	ethanoyl chloride (acetyl chloride)
$CH_3CH_2CH_2COCl$	butanoyl chloride
C_6H_5COCl	benzoyl chloride

- Acyl chlorides are volatile, corrosive, irritating and very reactive. Manipulation with acyl chlorides should be done under the hood and with precaution.

- R can be replaced by a hydrogen atom.
- The general formula of an acid chloride could be written as: $C_nH_{2n-1}ClO$.

- **Preparation of acyl chlorides**

An acyl chloride is prepared by a reaction between a carboxylic acid and phosphorous pentachloride PCl_5 or thionyl chloride $SOCl_2$. These reactions resemble the substitution reactions of alcohols with the same reagents.

Examples

Ethanoic acid reacts with thionyl chloride to produce ethanoyl chloride, sulfur dioxide and hydrogen chloride, according to the following equation:

- HCOCl is unstable, it decomposes into HCl and CO according to the reaction: $HCOCl \rightarrow HCl + CO$

$$CH_3COOH + SOCl_2 \rightarrow CH_3COCl + SO_2 + HCl$$

Benzoic acid reacts with phosphorous pentachloride to produce benzoyl chloride, phosphorous oxytrichloride, and hydrogen chloride, according to the following equation:

- The CH_3CO – group is commonly called acetyl.

$$C_6H_5COOH + PCl_5 \rightarrow C_6H_5COCl + POCl_3 + HCl$$

- **Hydrolysis of acyl chlorides**

Activity 2 Hydrolysis of ethanoyl chloride

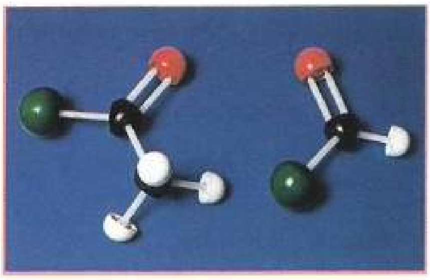


Figure 11.11
Molecular models of methanoyl chloride and ethanoyl chloride.

Objective

Recognize the high reactivity of acyl chloride with water.

Equipment and reagents

100 mL Erlenmeyer flask. 5 mL graduated pipet. Magnetic stirrer. Ethanoyl chloride.
25 mL graduated cylinder. Thermometer. Glass rod. Distilled water. Pipet filler. Eye goggles and gloves. pH paper.

Procedure

Manipulate, with precaution, and under the hood. Place about 10mL of distilled water in the Erlenmeyer flask. Heat to raise the temperature of the medium. Then, add drop-by-drop, 1mL of ethanoyl chloride (Fig. 11.12). Note the new temperature reading. Put one drop of the obtained solution on a pH paper. Observe.

Observation and interpretation

The reaction is vigorous. The temperature of the medium increases. The color of the pH paper indicates that the medium is acidic. The reaction is fast and exothermic. It leads to the formation of ethanoic acid and hydrogen chloride according to the following equation:

- The hydrolysis of an acyl chloride is often a vigorous reaction.

$$CH_3COCl + H_2O \rightarrow CH_3COOH + HCl$$

The hydrolysis of an acyl chloride is complete, fast and exothermic reaction. It produces the corresponding carboxylic

Figure 11.12
Hydrolysis of ethanoyl chloride.

- Acid anhydrides are irritating. They should be manipulated with precaution.
- R and R' are two alkyl groups that can be identical or different and could be replaced by H.
- When R and R' are different, the anhydride is called mixed.
- The general formula of an alkyl acid anhydride can be written as : $C_nH_{(2n-2)}O_3$.

acid and hydrogen chloride according to the following equation:

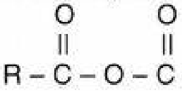
$$RCOCl + H_2O \rightarrow RCOOH + HCl$$

Acid anhydride

An acid anhydride is an acid derivative where the hydroxyl group is replaced by the alkanoate group $RCOO^-$.

Acid anhydrides are commonly used in organic synthesis. The order of reactivity of acid anhydrides is between those of acyl chlorides and carboxylic acids. They react more slowly than acyl chlorides.

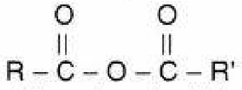
Acid anhydrides are represented by the general formula:



$R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R'$ (Fig.11.13).

Nomenclature

According to the IUPAC rules, the systematic name of an acid anhydride is derived from the corresponding acid by replacing the word acid by anhydride.

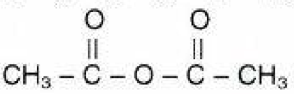


$RCOOH$ ⇨ $R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R'$

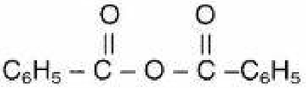
Alkanoic acid — Alkanoic anhydride

Examples

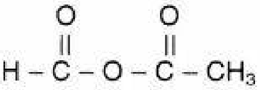
$H-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-H$ methanoic anhydride (formic anhydride).



$CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3$ ethanoic anhydride (acetic anhydride).



$C_6H_5-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-C_6H_5$ benzoic anhydride

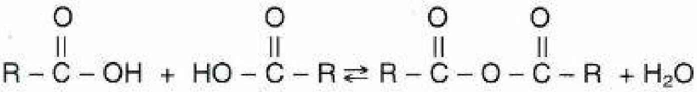


$H-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3$ ethanoic – methanoic anhydride.
(mixed anhydride)

Preparation of acid anhydrides

An acid anhydride is prepared by intermolecular dehydration of two molecules of carboxylic acid.

The hydroxyl group from an acid molecule and the H atom of another carboxyl group from a second molecule are eliminated as water and a molecule of acid anhydride is formed according to the following equation:



$$R-\overset{\overset{O}{\|}}{C}-OH + HO-\overset{\overset{O}{\|}}{C}-R \rightleftarrows R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R + H_2O$$

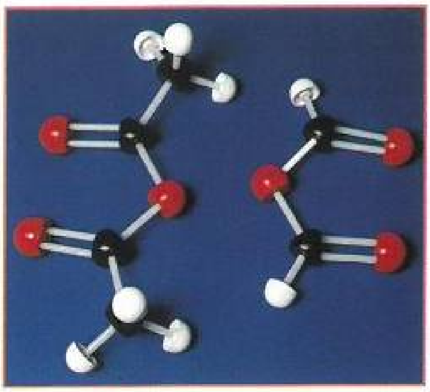
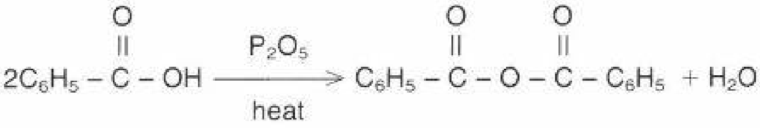


Figure 11.13

The molecular models of methanoic anhydride and ethanoic anhydride.

The reaction is carried out at high temperature in the presence of a powerful dehydrating agent such as phosphorus pentoxide P_2O_5. This latter allows the equilibrium to be displaced in the forward direction, eliminating water and forming the anhydride.

Benzoic anhydride, for example, is prepared according to the following equation:



$$2C_6H_5-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[\text{heat}]{P_2O_5} C_6H_5-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-C_6H_5 + H_2O$$

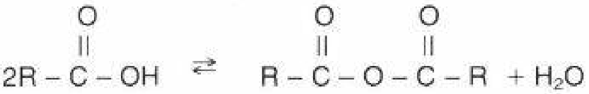
To prepare a mixed anhydride, reaction is carried out under the same conditions as in the preceding case, at high temperature and in the presence of P_2O_5, between a mixture of two different carboxylic acids.
The equation of the reaction is given as:

$$R-\overset{\overset{O}{\|}}{C}-OH + HO-\overset{\overset{O}{\|}}{C}-R' \rightleftharpoons R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R' + H_2O$$

- Methanoic acid could not be prepared by this method.

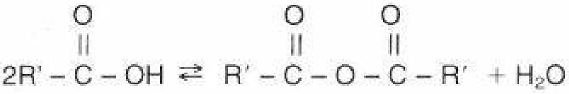
However, the reaction also produces the anhydrides

$R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R$ and $R'-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R'$, according to the following equations:



$$2R-\overset{\overset{O}{\|}}{C}-OH \rightleftharpoons R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R + H_2O$$

and

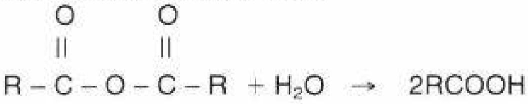


$$2R'-\overset{\overset{O}{\|}}{C}-OH \rightleftharpoons R'-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R' + H_2O$$

- To obtain only the mixed anhydride, a reaction should be carried out between an acyl chloride ROCl and a sodium alkanoate (carboxylate) $R'COO^-Na^+$ in a non-aqueous medium.

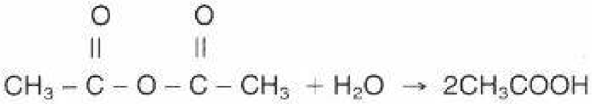
Hydrolysis of acid anhydrides

An acid-anhydride undergoes hydrolysis readily. The reaction is slower and less violent than that of an acyl chloride. The equation of the reaction is given as:



$$R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R + H_2O \rightarrow 2RCOOH$$

The hydrolysis of ethanoic anhydride, for example, produces ethanoic acid according to the following equation:



$$CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3 + H_2O \rightarrow 2CH_3COOH$$

Esters

An ester is an acid derivative where the hydroxyl group of the carboxyl group is substituted by an alkoxy group R'O–.

Esters constitute the most important family of compounds among the derivatives of carboxylic acids.

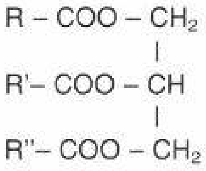
Esters are abundant in nature and have various applications in everyday life such as in perfumes, polymers, food-additives, solvents ....

Esters give to many fruits, flowers, plants and some conserved foods their characteristics odor and taste (Fig. 11.14).


Figure 11.14
The odor (flavor) of different natural and synthetic products is due to esters.

Beeswax is an ester, which consists mainly of long chain alcohols and fatty acids. The same is true for sperm whale oil.

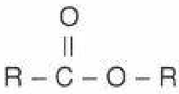
Fats and oils (of animal or plant origin) contain esters of fatty acids and glycerol (called triglycerides) of formula:



$$\begin{array}{l} R-COO-CH_2 \\ \qquad\qquad\quad | \\ R'-COO-CH \\ \qquad\qquad\quad | \\ R''-COO-CH_2 \end{array}$$

However, esters are also found in a number of perfumes, medicinal drugs, aspirin, and antibiotics... (Fig 11.15).

Esters are represented by the general formula:



$R-\overset{\overset{\displaystyle O}{||}}{C}-O-R'$ (or simply RCOOR') (Fig.11.16).


Figure 11.15
Some medicinal drugs and perfumes contain esters..

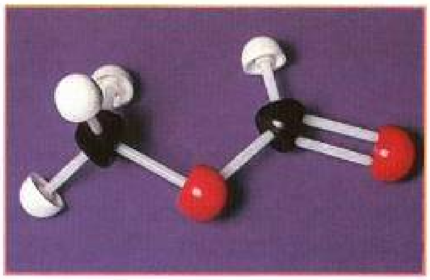


Figure 11.16
The molecular model of methyl methanoate.

Remark

Esters and carboxylic acid have the same general formula: $C_nH_{2n}O_2$. They are functional isomers.

- **Nomenclature**

According to the IUPAC rules, esters are named as alkyl alkanoates. The word alkanoate comes from the carboxylic acid by changing the **ic** of the acid by **ate** and dropping the word acid.

RCOOH	⇨	RCOOR′
Alkanoic acid		alkyl alkanoate

The first word alkyl is the name of the R' group in the alcohol.

Examples

$HCOOCH_3$	methyl methanoate (methyl formate)
$CH_3COOC_2H_5$	ethyl ethanoate (ethyl acetate)
$CH_3COOCH_2CH_2CH_2CH_3$	1-butyl ethanoate (1-butyl acetate)
$C_6H_5COOCH_3$	methyl benzoate

Preparation of esters

The least expensive method to prepare an ester consists of reacting carboxylic acid with an alcohol according to the equation:

$$RCOOH + R'OH \rightleftarrows RCOOR' + H_2O$$

To displace the equilibrium toward the formation of ester, we use an excess of the less expensive component or remove the ester formed from the reaction system.

Two other methods to prepare an ester are usually used: an alcohol is made to react with an acyl chloride or with an acid anhydride. These two reactions are complete, fast and exothermic.

- R and R' are two identical or different alkyl groups. R could be replaced by hydrogen.

Examples

The reaction of ethanoyl chloride with 1-propanol produces 1-propyl ethanoate and hydrogen chloride according to the following equation:

$$CH_3COCl + CH_3CH_2CH_2OH \rightarrow CH_3COOCH_2CH_2CH_3 + HCl$$

The reaction of benzoic anhydride with ethanol produces ethyl benzoate and benzoic acid according to the following equation:

$$C_6H_5\overset{\overset{O}{\|}}{C}O\overset{\overset{O}{\|}}{C}C_6H_5 + C_2H_5OH \rightarrow C_6H_5COOC_2H_5 + C_6H_5COOH$$

- Ethyl acetate and butyl acetate are used as common solvents for varnishes and lacquers. Butyl acetate has the odor of black berry.

Hydrolysis of esters

This is the reverse reaction of esterification; the general equation of the reaction is given as:

$$RCOOR' + H_2O \rightleftarrows RCOOH + R'OH$$

Generally, hydrolysis can take place in acidic medium or in the presence of a strong base. The hydrolysis of some natural esters allows to obtain different acids and alcohols.

Amides

An amide is an acid derivative where the hydroxyl group of the carboxyl group is substituted by amino group. $-\overset{|}{N}-$.

Amides are widespread among the plants and animals. Caffeine is found in coffee and tea, strychnine is found in the seeds of a plant called strychnos nux vomica.
Amides are also found in medicinal drugs such as paracetamol, phenol barbital, penicillin... (Fig.11.17).

- In both cases, it should be worked out in the complete absence of water (anhydride).

Figure 11.17
Some medicinal drugs contain amides.

Depending on the amino group, amides can be represented by the general formula:

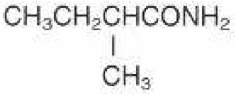
$$R\overset{O}{\overset{\|}{C}}NH_2,\ R\overset{O}{\overset{\|}{C}}NHR' \text{ and } R\overset{O}{\overset{\|}{C}}NR'R''$$

- **Nomenclature**

According to the IUPAC rules, the name of an amide (unsubstituted on the nitrogen atom) is derived from the corresponding acid by replacing the suffix **oic** by the suffix **amide** and dropping the word acid.

$$\begin{array}{ccc} RCOOH & \Rightarrow & RCONH_2 \\ \text{Alkanoic acid} & & \text{Alkanamide} \end{array}$$

Examples

$HCONH_2$	methanamide (formamide)
CH_3CONH_2	ethanamide (acetamide)
 $CH_3CH_2\underset{CH_3}{\underset{\vert}{C}H}CONH_2$	2-methylbutanamide
$C_6H_5CONH_2$	benzamide

- R, R'and R" can be identical or different alkyl groups, R may be replaced by H (Fig. 11.18).

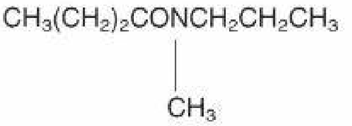
- The general formula of an amide can be written as: $C_nH_{2n+1}NO$.

- In common names, the ending **ic** of the acid name is replaced by the amide suffix: formic: formamide.

Remark
The name of an amide can be derived from the alkane having the same number of carbon atoms in the main chain by replacing the final **e** by the suffix **amide**.

For a substituted nitrogen atom, the name of the amide is preceded by N- (or N,N-) followed by the name of the alkyl group (or groups) depending on their number.

Examples

$HCONHCH_3$	N-methylmethanamide (N-methylformamide)
$C_6H_5CONHC_6H_5$	N-phenylbenzamide
$CH_3CON(C_2H_5)_2$	N,N-diethylethanamide (N,N-diethylacetamide)
 $CH_3(CH_2)_2CO\underset{CH_3}{\underset{\vert}{N}}CH_2CH_2CH_3$	N-methyl-N-(1-propyl)-1-butanamide

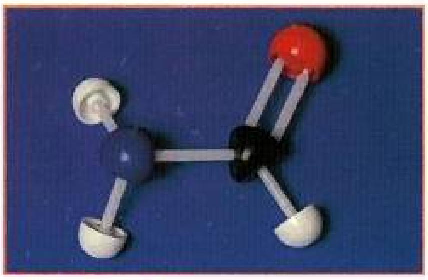


Figure 11.18
The molecular model of methanamide.

- **Hydrolysis of amides**

Amides are the least reactive of the carboxylic acid derivatives. Their hydrolysis occurs with prolonged heating in strong acidic or basic medium. The hydrolysis reaction can be represented by the following equation:

$$RCONH_2 + H_2O \rightleftarrows RCOOH + NH_3$$

In fact, the reaction in the acidic medium occurs according to the following equation:

$$RCONH_2 + H_3O^+ \rightarrow RCOOH + NH_4^+$$

In the basic medium the equation is:

$$RCONH_2 + HO^- \rightarrow RCOO^- + NH_3$$

The hydrolysis of propanamide, for example, produces propanoic acid and an ammonium salt according to the following equation:

$$CH_3CH_2CONH_2 + H_3O^+ \xrightarrow{heat} CH_3CH_2COOH + NH_4^+$$

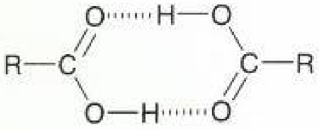
The hydrolysis of benzamide in basic medium produces bezanoate ion and ammonia according to the following equation:

$$C_6H_5CONH_2 + HO^- \xrightarrow{heat} C_6H_5COO^- + NH_3$$

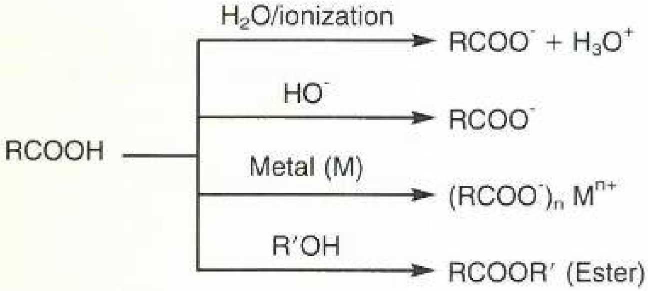
Chapter Review

- A monocarboxylic acid is represented by the general formula RCOOH.
- The presence of hydrogen bonding between molecules of carboxylic acids gives rise to:

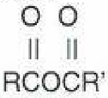
  Unusual increase of the boiling points of carboxylic acid.
  High solubility for the first acids in water.
  Formation of carboxylic acid dimers, in the pure form or in some solvents.



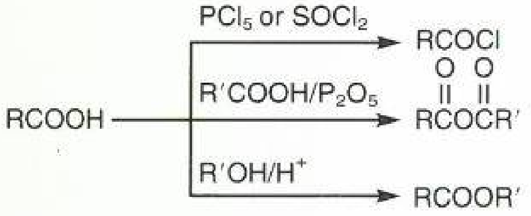
- Some reactions of carboxylic acids are summarized in the following scheme:



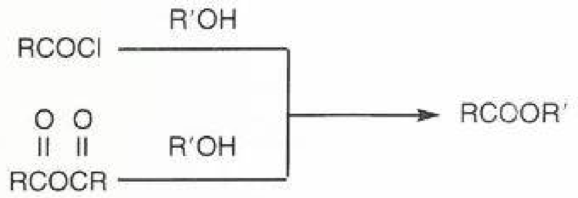
- Methanoic (formic) acid is manufactured in industry by the reaction of carbon monoxide and sodium hydroxide, the product formed ($HCOO^-Na^+$) is treated with a strong acid.
- Ethanoic acid (acetic acid) is manufactured in industry by the carbonylation of methanol, by catalytic oxidation of ethanol, or by enzymatic oxidation of ethanol.
- Carboxylic acid derivatives are:

  - Acyl chorides represented by the general formula: RCOCl
  - Acid anhydrides represented by the general formula:  $RC(=O)OC(=O)R'$
  - Esters are represented by the general formula: RCOOR'
  - Amides represented by one of the three general formulas: $RCONH_2$, RCONHR' and RCONR'R".

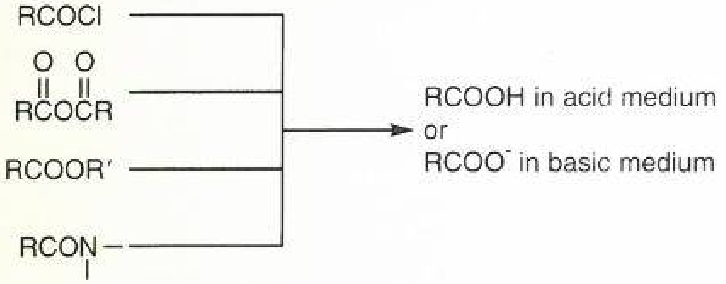
- Carboxylic acid derivatives are obtained from acids by one of the following reactions given in the scheme:



- Esters are most easily prepared when the carboxylic acid is replaced by an acyl chloride or acid anhydride, according to the following scheme:



- Carboxylic acid derivatives undergo hydrolysis to regenerate the corresponding carboxylic acid. This hydrolysis can be carried out more or less easily depending on the nature of the acid derivative.



Documentary activity

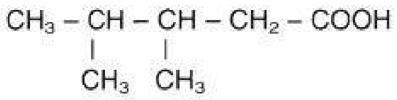
A list of some esters with characteristic odors

Esters of general formula RCOOR' are very abundant in nature. A good number of them have agreeable characteristic odor and contribute to natural or artificial tastes and flavors of certain fruits, plants, and canned foods.

Formula	**Common name**	**Odor**
$HCOOCH_2CH_3$	ethyl formate	Rum
$CH_3COO[CH_2]_3CH_3$	butyl acetate	Blackberry
$CH_3COO[CH_2]_2CH(CH_3)_2$	isoamyl acetate	Banana
$CH_3CH_2COOCH_2CH(CH_3)_2$	isobutyl propanoate	Rum
$CH_3[CH_2]_3COO[CH_2]_2CH(CH_3)_2$	isoamyl valerate	Apple
$CH_3[CH_2]_2COOC_2H_5$	ethyl butyrate	Pineapple
$CH_3[CH_2]_3COO[CH_2]_7CH_3$	octyl valerate	Tangerine
$CH_3COOCH_2C_6H_5$	benzyl acetate	Essence of jasmine
$C_6H_5COOCH_2CH(CH_3)_2$	isobutyl benzoate	Flower of Pittosporum (Australian shrub)

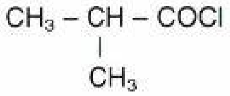
Exercises

1 Give the systematic (IUPAC) nomenclature for each of the following compounds:

a) 
$CH_3-\underset{CH_3}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CH_2-COOH$

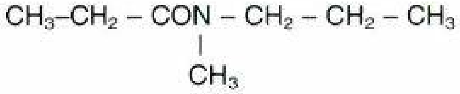
b) $C_6H_5-CH_2-COOH$

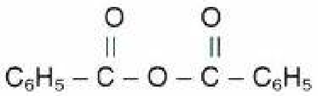
c) $CH_3-CH_2-COO-CH_2-CH_2-CH_3$

d) 
$CH_3-\underset{CH_3}{\underset{|}{CH}}-COCl$

e) $H-CONH_2$

f) $CH_3-CONH-C_6H_5$

g) 
$CH_3-CH_2-CO\underset{CH_3}{\underset{|}{N}}-CH_2-CH_2-CH_3$

h) 
$C_6H_5-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-C_6H_5$

i) $CH_3-CHBr-CH_2-COO-CH_2-CH_3$

j) $ClCH_2-CHCl-CH_2-COOH$

k) CCl_3-COOH

l) $CH_3-CHBr-COOH$

2 Write the condensed structural formulas for the following compounds. Correct the name, if it is wrong.

a) 2,2-dimethylethanoic acid
b) 3-propylheptanoic acid
c) butanoyl chloride
d) propanoic anhydride
e) 2,3-dichlorobutanoic acid
f) N-propylethanamide
g) N,N-diethylbenzamide
h) 2-phenylbutanoyl chloride
i) phenyl ethanoate.

3 A) An organic compound (A) is obtained when 3.5 g of ethanoic acid are reacted with phosphorous pentachloride.

a) Write the equation of the reaction and give the name of compound (A).
b) What mass of phosphorous pentachloride is just needed for the reaction ?

B) Half of the quantity of the obtained compound (A) is reacted with an excess of 1-propanol and an organic compound (B) is formed.
a) Write the equation of the reaction.
b) Name compound B and calculate its mass.
Assume that the preceding reactions are quantitative and the yield is 100%.

C) The other half of the quantity of (A) obtained is reacted with an excess sodium ethanoate. Sodium chloride and an organic compound (C) are obtained.
a) Write the equation of the reaction.
b) Name compound (C) obtained and calculate its mass.
c) In this reaction, as well as, in the preceding reactions, the reactions should be carried out completely in the absence of water. Why ?

D) a) Propose other methods to prepare each of the compounds (B) and (C).
b) Write the equations of these reactions.
c) What advantage does the utilization of (A) have for preparing compounds (B) and (C) as compared to their preparation from ethanoic acid.

E) Could compound (B) be prepared starting from compound (C) ? If yes, write the equation of the reaction.

4 Write the equations of the reactions that allow to convert :

a) 2-methyl-1-propanol to 2-methylpropanoic acid.
b) 1-propanol to 1-propyl propanoate.
c) N-methyl benzamide to benzoyl chloride.

5 20 g of N,N-dimethyl benzamide is heated in an excess of sodium hydroxide solution.

a) Write the equation of the reaction.
b) Calculate the mass of each of the compounds formed.
c) Name compound (A) which contains oxygen, give two methods which lead to the formation of its conjugate acid:
1) Starting from the amide
2) Starting from compound A.
Write in each case, the equation of the reaction taking place.

6 A) It is required to convert, using an enzyme, 100 L of ethanol solution of alcoholic degree 12° into vinegar.

a) Write the equations of the enzymatic oxidations of ethanol.
b) What is the major constituent of vinegar other than water ?
c) What volume of air, measured at conditions where molar volume of gas is 24 L, is needed to carry out this conversion ?
d) What mass of ethanoic acid is obtained ?
e) Calculate the molar concentration of the ethanol solution as well as that of ethanoic acid in vinegar.
Assume that the conversion is complete and that the volume of the solution does not change during the reaction.
Air contains 20% by volume oxygen. The density of ethanol is $0.79 Kg.L^{-1}$. Alcoholic degree represents % volume composition of ethanol solution.

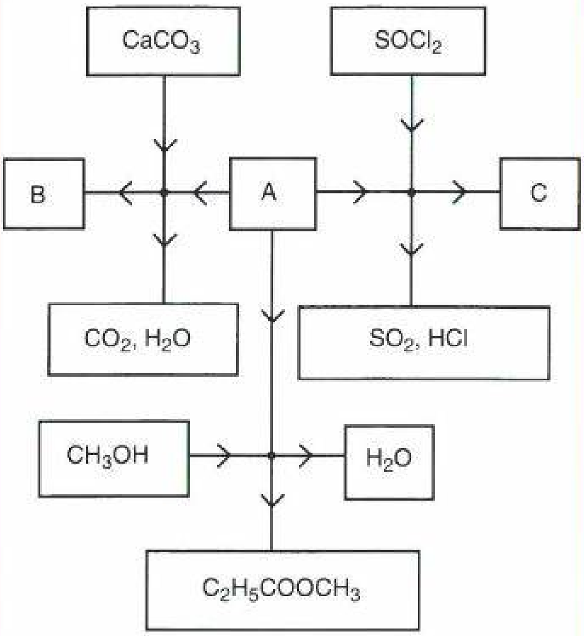
B) The vinegar obtained is titrated with $1 mol.L^{-1}$ sodium hydroxide solution.
We take 10 mL of the vinegar and dilute it with 15 mL of distilled water. The titration is carried out by pH-metry. The sodium hydroxide solution is added gradually to the solution just to attain equivalence.
It is found that 19 mL of the basic solution is added and the pH-meter indicates a pH of 8.9.

a) What is the purpose of adding water to the volume of the vinegar before carrying out the titration ?
b) Write the equation of the reaction taking place.
c) Why is the pH of the reaction medium higher than 7 at the equivalence point?
d) When the volume of sodium hydroxide added is 9.5 mL, the pH of the medium is 4.8. what do these two values correspond to ?
e) Based on the above results, calculate the concentration of ethanoic acid in the vinegar. Deduce the alcoholic degree of the initial ethanol solution.

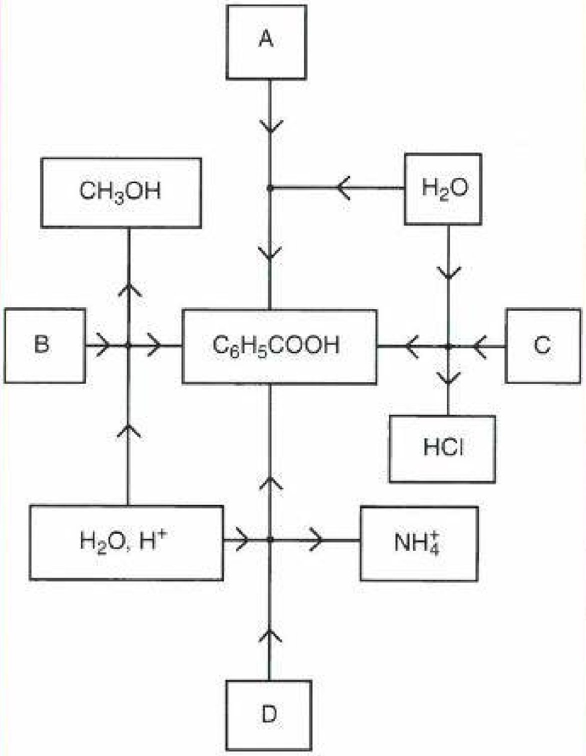
7 The complete oxidation of 2 g of an aldehyde (A) by an acidified potassium chromate solution K_2CrO_4, (CrO_4^{2-} / Cr^{3+}, redox couple) produces 2.1 g of carboxylic acid (B) which is dissolved in 50 mL of distilled water.
The obtained solution reacts with exactly 1.05 g of solid lime (calcium hydroxide) to form a salt (C).

a) Write the equations of the half-reactions and that of the overall reaction of an aldehyde by potassium chromate.
b) Write the equation of the reaction of acid (B) with the lime.
c) Calculate the molar mass of acid (B). Deduce its molecular formula.
d) Write the structural formulas of compounds (A) and (B), and give their names.
e) Name compound (C) and calculate the obtained mass of (C).
f) Calculate the % yield of the oxidation reaction of aldehyde (A).
g) Calculate the volume of the oxidant-solution of concentration $0.2 mol.L^{-1}$, which is just enough to oxidize 2 g of aldehyde (A) into acid (B).
h) The aldehyde (A) is obtained by catalytic dehydrogenation of an alcohol (D).
1) Identify the alcohol (D).
2) Write the equation of the reaction.
3) What volume of $H_{2(g)}$ is obtained, at standard conditions. Assume the reaction is complete and quantitative.

8 Identify the missing compound A, B, C in the diagram given below :



9 Identify the missing compound A, B, C, and D in the diagram given below :

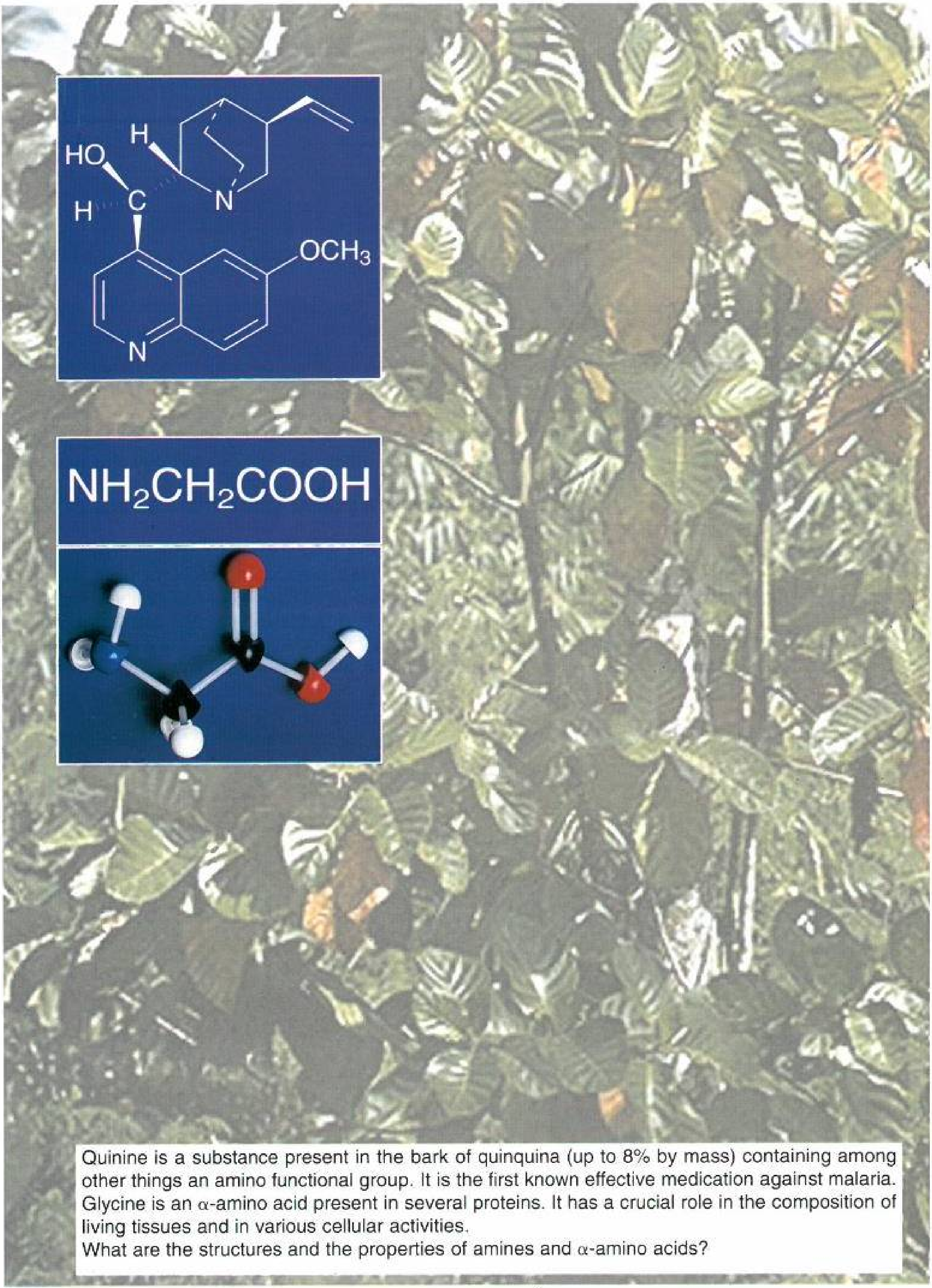


Fatty Acids

common name for a group of organic acids that includes the saturated (hydrogenated), straight-chain acids, with a single carboxyl (COOH) group, that are produced by the hydrolysis of fats. The group also includes all other saturated straight-chain acids and acids with a branched chain or cyclic structure. Methanoic (formic) acid, HCOOH, and ethanoic (acetic) acid, CH_3COOH, are the simplest fatty acids. Both have a sour taste, irritate the skin, and have a sharp smell. Of more complicated structure are butanoic, hexanoic and octanoic acids, all of which have unpleasant odours. Stearic, palmitic, oleic, and naphthenic acids are greasy materials with little odour. A growing source of fatty acids is tall oil, a by-product of the pinewood used to make paper pulp.

Fatty acids are useful in preparing biodegradable detergents, thickeners for paints, and lubricants. Stearic acid is used to combine rubber with other substances, such as pigments, or materials that control the flexibility of rubber products; it is also used in the polymerization of phenylethene (styrene) and butadiene in making artificial rubber. New uses for fatty acids include ore flotation and the manufacture of disinfectants, varnish driers, and heat stabilizers for vinyl resins. Fatty acids are also used in plastic products, such as coatings for wood and metal, and in car parts ranging from air-cleaner housings to upholstery.

Microsoft Encarta 99 Encyclopedia



NH_2CH_2COOH

Quinine is a substance present in the bark of quinquina (up to 8% by mass) containing among other things an amino functional group. It is the first known effective medication against malaria. Glycine is an α-amino acid present in several proteins. It has a crucial role in the composition of living tissues and in various cellular activities.

What are the structures and the properties of amines and α-amino acids?

AMINES AND α-AMINO ACIDS

12

Objectives

- Identify the amines and the α-amino acids.
- Classify amines and α-amino acids.
- Acquire the systematic nomenclature of amines and α-amino acids.
- Identify some chemical reactions of amines.
- Acquire the notions of chirality, asymmetric carbon and enantiomerism.
- Use the three dimensional representation and Fischer representation of enantiomers.
- Identify dipeptides, peptides and proteins.
- Recognize the role of α-amino acids and proteins in the chemistry of living world.

Prerequisites

- Chemical bonding and Formula.
- VSEPR method, hybridization of atomic orbitals and structure.
- Chemical Reaction.
- Nomenclature of alkanes.
- Notion of isomerism.
- Mole and stoichiometry.

Chapter content

12.1 Amino Functional group
12.2 α-Amino acids.
- Chapter review
- Method sheet
- Documentary activity
- Exercises
- Evaluation

12.1 Amines

Definition, classification and general formula

The amino functional group is one of the more widespread functional groups in organic chemistry. It is present, for example, in amino acids, proteins, nucleic acids (DNA, RNA)…., which act as a fundamental part in biochemistry.

■ Biochemistry is the chemistry of the living organisms.

One can consider amines as resulting from the substitution of one, two or three hydrogen atoms in the ammonia molecule NH_3, by one, two or three alkyl groups.

An amine is a compound containing the amino functional group $-\overset{|}{N}-$.

According to the number of substituted hydrogen atoms in the ammonia molecule, three classes of amines are distinguished:

- Primary amines of general formula $R-NH_2$; the amino group is attached to one alkyl group as in CH_3-NH_2 and $C_2H_5-NH_2$ (Fig.12.1).
- Secondary amines of general formula RR'NH; the amino group is attached to two alkyl groups as in $(CH_3)_2NH$ and $(C_2H_5)_2NH$ (Fig.12.2).
- Tertiary amines of general formula RR'R"N; the amino group is attached to three alkyl groups as in $(CH_3)_3N$ and $(C_2H_5)_3N$ (Fig.12.3).

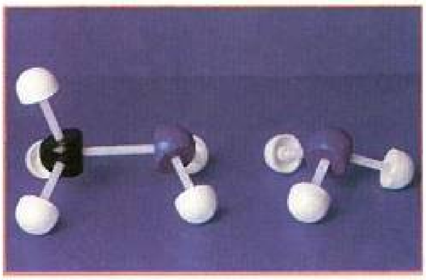


Figure 12.1
Ball-and-stick molecular models of the molecules NH_3 and CH_3NH_2.

■ R, R' and R" are identical or different alkyl groups.

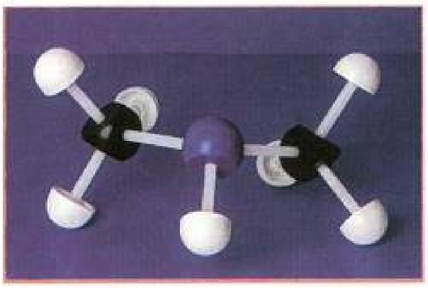


Figure 12.2
Ball-and-stick model of the molecule $(CH_3)_2NH$.

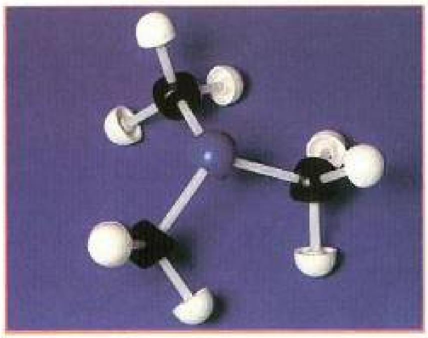


Figure 12.3
Ball-and-stick model of the molecule $(CH_3)_3N$.

The general formula of an amine can be written as $C_nH_{2n+3}N$.

Nomenclature

Primary amines

Primary amines can be named according to either of the two following methods:

1) By replacing the "**e**" ending of the alkane having the same principal carbon chain by the ending "**amine**":

$$\text{Alkan}\boxed{\text{e}} \Rightarrow \text{Alkan}\boxed{\text{amine}}$$
$$R-H \qquad R-NH_2$$

2) By adding the suffix amine to the name of the alkyl substituted group R: alkylamine.

Examples

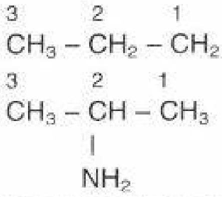
Formula	Method 1	Method 2
CH_3NH_2	methanamine	methylamine

$C_2H_5NH_2$	ethanamine	ethylamine
$C_6H_5NH_2$	benzenamine or	phenylamine (or aniline)

For n>2, one proceeds as for alcohols.

Examples

$\overset{3}{CH_3} - \overset{2}{CH_2} - \overset{1}{CH_2} - NH_2$ 1-propanamine or (1-propylamine)

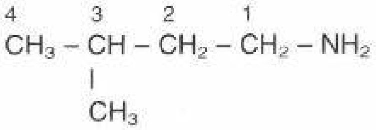


$\overset{3}{CH_3} - \underset{\underset{NH_2}{|}}{\overset{2}{CH}} - \overset{1}{CH_3}$

2-propanamine or (2-propylamine)

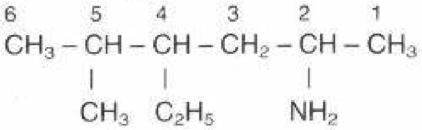
For branched chains, one proceeds as for alkanes using, preferably, the first nomenclature method.

Examples



$\overset{4}{CH_3} - \underset{\underset{CH_3}{|}}{\overset{3}{CH}} - \overset{2}{CH_2} - \overset{1}{CH_2} - NH_2$

3-methyl-1-butanamine



$\overset{6}{CH_3} - \underset{\underset{CH_3}{|}}{\overset{5}{CH}} - \underset{\underset{C_2H_5}{|}}{\overset{4}{CH}} - \overset{3}{CH_2} - \underset{\underset{NH_2}{|}}{\overset{2}{CH}} - \overset{1}{CH_3}$

4-ethyl-5-methyl-2-hexanamine

■ Sometimes, the amines are considered as aminoalkanes; aminomethane, aminoethane, 1-aminopropane.... However, this nomenclature is now reserved for the compounds containing more than one functional group, including the amino group (see aminoacid).

■ Secondary and tertiary amines

The symmetrical secondary and tertiary amines (R_2NH and R_3N) can be named using the name of the substituent alkyl group preceded by the prefix "di" or "tri" as the case may be, and followed by the suffix amine..

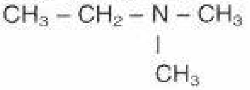
Examples

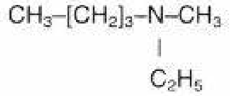
$(CH_3)_2NH$	dimethylamine	$(CH_3)_3N$	trimethylamine
$(C_2H_5)_2NH$	diethylamine	$(C_2H_5)_3N$	triethylamine
$(C_6H_5)_2NH$	diphenylamine	$(C_6H_5)_3N$	triphenylamine

The unsymmetrical secondary and tertiary amines (RR'NH, $R_2R'N$ and RR'R"N) can be named according to two methods:

1) As an N-substituted derivative of a primary amine.
2) Stating the names of all the alkyl substituent groups, followed by the suffix amine.

Examples

Formula	Method 1	Method 2
$CH_3 - CH_2 - NH - CH_3$	N-methylethanamine	ethylmethylamine
$CH_3 -[CH_2]_2- NH - CH_3$	N-methyl-1-propanamine	methyl-1-propylamine
 $CH_3 - CH_2 - \underset{\underset{CH_3}{\vert}}{N} - CH_3$	N,N-dimethylethanamine	ethyldimethylamine



$CH_3-[CH_2]_3-N(C_2H_5)-CH_3$ N-ethyl-N-methyl-1-butanamine
1-butyl(ethyl)methylamine

Structure and isomerism

Let us construct the ball-and-stick molecular model of methylamine CH_3NH_2 (Fig.12.4). The model presents, at the amino group location, a triangular based pyramidal shape, with bond angles close to 109°.

The atomic orbitals of the N atom have an sp^3 hybridization.

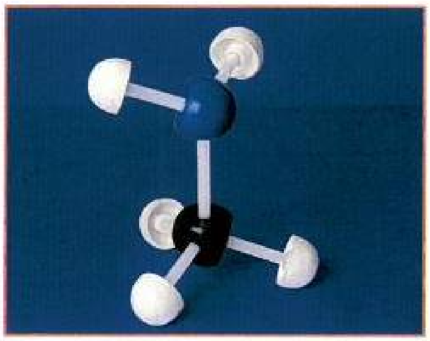


Figure 12.4

Ball-and-stick molecular model of the molecule CH_3NH_2.

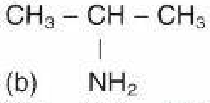
Isomerism

Amines have two types of isomerism: positional isomerism and skeletal isomerism (associated to functional isomerism).

- The functional isomerism of amines is to be considered in the same way as the isomerism between alcohols and ethers, for example. However, the differences in the properties between the amines of different classes are less important compared to the differences in the properties between alcohols and ethers.

Application

Suppose we want to write the structural formulas, name and classify the amine isomers of molecular formula C_3H_9N.

Formula	Name	Class
$CH_3-CH_2-CH_2-NH_2$ (a)	1-propanamine	Primary
 $CH_3-CH(NH_2)-CH_3$ (b)	2-propanamine	Primary
$CH_3-CH_2-NH-CH_3$ (c)	N-methylethanamine	Secondary
$(CH_3)_3N$ (d)	trimethylamine	Tertiary.

(a) and (b) are positional isomers.
(a), (c) and (d) are skeletal isomers. They are also functional isomers since (a) is a primary amine, (c) is a secondary amine and (d) is a tertiary amine.
(b), (c) and (d) are likewise skeletal (and functional) isomers.

Physical properties

At room temperature, the amines are liquids, except methylamine, dimethylamine and trimethylamine, which are gases.
Within a class of amines, the boiling point increases with the molar mass.
The first amines are very soluble in water. However, their solubility decreases when their carbon chain increases.
Table 12.1 lists some physical properties of amines.

Amine	Boiling points (°C)	Solubility (g/kg of water)
Methylamine	- 6.3	Very soluble
Ethylamine	16.6	∞
Propylamine	47.8	∞
Dimethylamine	7.4	Very soluble
Diethylamine	56.3	Very soluble
Dipropylamine	110	Very soluble
Trimethylamine	2.9	910
Triethylamine	89.3	140
Tripropylamine	155	Little soluble

Table 12.1

Some physical properties of amines.

Like ammonia, the molecules of primary amines are held together by hydrogen bonds. So it is with secondary amines, but not with tertiary ones.

The existence of hydrogen bonds explains the high values of boiling points of primary and secondary amines, which are however less important than for alcohols.

The NH bond being indeed less polar than the OH bond, the hydrogen bond is less strong in amines than in alcohols. This is shown in the following comparison of boiling points:

CH_3NH_2 (-6.0 °C) and CH_3OH (65.0 °C)
$C_2H_5NH_2$ (16.6 °C) and C_2H_5OH (78.5 °C)

In other words, the hydrogen bond is stronger in primary amines than in secondary amines. This leads to boiling points of the latter lower than of the primary amines of same molar mass.

$C_2H_5NH_2$ (16.6 °C) and $(CH_3)_2NH$ (7.4 °C)
$CH_3–CH_2–CH_2–CH_2–NH_2$ (77.8 °C) and $(C_2H_5)_2NH$ (56.3 °C)

The absence of hydrogen bond in tertiary amines yields boiling points lower than those of primary and secondary amines.

The hydrogen bond explains also the high solubility of primary and secondary amines in water.

Finally, it is to be noted that the volatile amines have strong and disagreeable odor, and they are toxic.

■ Chemical reactions

The electronic structure of the amine group presents the following characteristics:

- A slightly polar NH bond, less polar than the OH bond.
- The N atom being less electronegative than the O atom, the lone pair of nitrogen makes the amines more basic than the alcohols.

In general, amines participate to acid-base reactions and substitution reactions.

- The chemical properties of amines are very similar to those of ammonia.

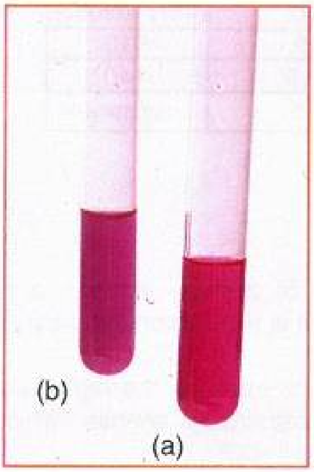


Figure 12.5
Action of an aqueous solution of ethylamine on:
(a) Phenolphthalein.
(b) Litmus solution.

- The alkylammonium salts dissociate in water.

Acid	pK_a
NH_4^+	9.24
$(CH_3)_3NH^+$	9.79
$CH_3NH_3^+$	10.62
$C_2H_5NH_3^+$	10.64
$(CH_3)_2NH_2^+$	10.73
$(C_2H_5)_3NH^+$	10.75
$(C_2H_5)_2NH_2^+$	10.94

Table 12.2
pK_a values of some alkylammonium/alkylamine conjugate pairs.

- These reactions must be performed in the absence of water.

■ Basic properties

Like ammonia, the amines color pink the phenolphthalein and blue the litmus solution (Fig.12.5).
They are weak bases, slightly more basic than ammonia (Table 12.2).
Amines react with strong acids and lead to the formation of alkylammonium salts, according to the equation:

$$-\underset{|}{\text{N}}- + H_3O^+ \rightarrow -\overset{+}{\underset{|}{\text{N}}}\text{H}- + H_2O$$

The reaction is complete, fast and exothermic.

Examples

Ethylamine reacts with hydrochloric acid to give ethylammonium chloride, according to the equation:

$$C_2H_5NH_2 + H_3O^+ + Cl^- \rightarrow C_2H_5\overset{+}{N}H_3 + Cl^- + H_2O$$

Diethylamine reacts with nitric acid to give diethylammonium nitrate, according to the equation:

$$(C_2H_5)_2NH + H_3O^+ + NO_3^- \rightarrow (C_2H_5)_2\overset{+}{N}H_2 + NO_3^- + H_2O$$

Trimethylamine reacts with sulfuric acid to give trimethylammonium sulfate, according to the equation:

$$2(CH_3)_3N + 2H_3O^+ + SO_4^{2-} \rightarrow 2(CH_3)_3\overset{+}{N}H + SO_4^{2-} + 2H_2O$$

■ Reactions of amines with carleoxylic acids

The reaction of an amine with a carboxylic acid leads to the formation of an alkylammonium carboxylate, according to the equation:

$$-\underset{|}{\text{N}}- + RCOOH \rightarrow RCOO^- + -\overset{+}{\underset{|}{\text{N}}}\text{H}-$$

When the amine is primary or secondary, the obtained alkylammonium carboxylate, heated at high temperature, leads to the formation of an amide, according to the equation:

$$RCOO^- + -\overset{+}{N}H_2- \rightarrow RCO\underset{|}{N}- + H_2O$$

However, the amides are more easily formed when an acyl chloride or an acid anhydride replaces the acid. In this case, the reactions are complete, fast and exothermic.

- **Reactions of primary and secondary amines with the acyl chlorides**

A primary amine reacts with an acyl chloride to give, at first, a N-alkylalkanamide and hydrogen chloride, according to the equation:

$$RCOCl + R'NH_2 \rightarrow RCONHR' + HCl$$

The hydrogen chloride formed reacts with the amine to give the alkylammonium chloride, according to the equation:

$$R'NH_2 + HCl \rightarrow R'\overset{+}{N}H_3\ ,\ Cl^-$$

During the reaction, two moles of amine are thus consumed per mole of acyl chloride used, according to the equation:

$$RCOCl + 2R'NH_2 \rightarrow RCONHR' + R'NH_3^+\ ,\ Cl^-$$

Thus, the ethanoyl (or acetyl) chloride, for example, reacts with the 1-butanamine to form the N-butylethanamide and the butylammonium chloride, according to the equation:

$$CH_3COCl + 2CH_3[CH_2]_3NH \rightarrow CH_3CONH[CH_2]_3CH_3 + CH_3[CH_2]_3\overset{+}{N}H_3,Cl^-$$

A secondary amine leads to the formation of a N, N-dialkylalkanamide and a dialkylammonium chloride, according to the equation:

$$RCOCl + 2R'R''NH \rightarrow RCONR'R'' + R'R''\overset{+}{N}H_2,Cl^-$$

Thus, the benzoyl chloride, for example, reacts with the diethylamine to form the N,N-diethylbenzamide and the diethylammonium chloride, according to the equation:

$$C_6H_5COCl + 2(C_2H_5)_2NH \rightarrow C_6H_5CON(C_2H_5)_2 + (C_2H_5)_2\overset{+}{N}H_2,Cl^-$$

- **Reactions of primary and secondary amines with the acid anhydrides**

A primary amine reacts with an acid anhydride to form, at first, a N-alkylalkanamide and a carboxylic acid, according to the equation:

$$R\overset{\overset{O}{\|}}{C}O\overset{\overset{O}{\|}}{C}R + R'NH_2 \rightarrow RCONHR' + RCOOH$$

The carboxylic acid formed reacts with the amine to form the alkylammonium carboxylate (or alkanoate), according to the equation:

$$R'NH_2 + RCOOH \rightarrow R'\overset{+}{N}H_3\ ,\ RCOO^-$$

During the reaction, two moles of amine are thus consumed per mole of acid anhydride used, according to the equation:

$$R\overset{\overset{O}{\|}}{C}O\overset{\overset{O}{\|}}{C}R + 2R'NH_2 \rightarrow RCONHR' + R'\overset{+}{N}H_3\ ,\ RCOO^-$$

Thus, the methanoic (or formic) anhydride, for example, reacts with the ethanamine to form the N-ethylmethanamide (or N-ethyformamide) and the ethylammonium methanoate (or ethyl ammonium formate), according to the equation:

$$H\overset{\overset{O}{\|}}{C}O\overset{\overset{O}{\|}}{C}H + 2C_2H_5NH_2 \rightarrow HCONHC_2H_5 + C_2H_5\overset{+}{N}H_3, HCOO^-$$

A secondary amine leads to the formation of a N,N-dialkylalkanamide and a dialkylammonium carboxylate (alkanoate), according to the equation:

$$R\overset{\overset{O}{\|}}{C}O\overset{\overset{O}{\|}}{C}R + 2R'R''NH \rightarrow RCONR'R'' + R'R''\overset{+}{N}H_2, RCOO^-$$

Thus, the ethanoic (or acetic) anhydride, for example, reacts with the dimethylamine to form the N,N-dimethylethanamide (or N,N-dimethyacetamide) and the dimethylammonium ethanoate (or acetate), according to the equation :

$$CH_3\overset{\overset{O}{\|}}{C}O\overset{\overset{O}{\|}}{C}CH_3+2(CH_3)_2NH \rightarrow CH_3CON(CH_3)_2+(CH_3)_2NH^+_2,CH_3COO^-$$

12.2 α-Amino acids

■ Definition and classification

The name amino acid designates a class of compounds the molecule of which contains an amino functional group and a carboxyl group.
The amino functional group can be primary, secondary or tertiary and can occupy variable positions relative to that of the carboxyll group.

Examples

$H_2N-[CH_2]_4-COOH$ $\quad$ $CH_3-NH-CH_2-CH_2-COOH$

More than 500 natural amino acids are known, among which the α-amino acids occupy an important place in the chemistry of the living organisms.
In the molecule of these acids, the amino group and the carboxyl group are attached to the same carbon atom designated by the letter α.

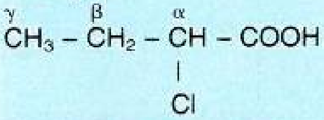
■ Compounds, the molecules of which contain two or many functional groups, are called polyfunctional.

An α-amino acid is a carboxylic acid the molecule of which contains an amino group in α position.

The α-amino acids are represented by the general formula:

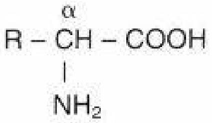
- In a nomenclature system, particularly for biological molecules, the carbons of the chain are designated by the letters α, β, γ starting from the first carbon atom attached to the functional group.

Example:



$\overset{\gamma}{CH_3} - \overset{\beta}{CH_2} - \underset{Cl}{\overset{\alpha}{CH}} - COOH$

α-chlorobutanoic acid
(2-chlorobutanoic acid)



$R - \underset{NH_2}{\overset{\alpha}{CH}} - COOH$

The R group can be an alkyl group or a carbon chain containing a functional group.

Amino acids have a fundamental part in the composition of living tissues and in the diverse functions of plant and animal cells.

With some exceptions, only twenty amino acids are involved in the constitution of proteins. The adult human beings can synthesize twelve of these twenty amino acids. The other eight cannot be synthesized, they must be provided by food; for this reason they are called the essential amino acids.

- The essential amino acids are: valine, leucine, isoleucine, threonine, lysine, phenylalanine, methionine and tryptophane.

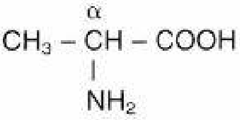
The α-amino acids have common names consecrated by the usage in chemistry literature. In other respects, the amino acids are classified, according to the functional groups contained in the group R, as neutral, acidic or basic amino acids.

- **Neutral amino acids.** The R group does not contain an acidic or a basic functional group (Fig. 12.6).

Examples

Glycine $H_2N - \overset{\alpha}{CH_2} - COOH$

Alanine



$CH_3 - \underset{NH_2}{\overset{\alpha}{CH}} - COOH$

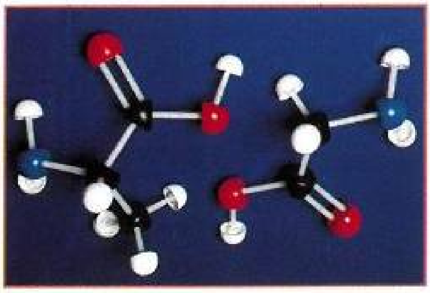


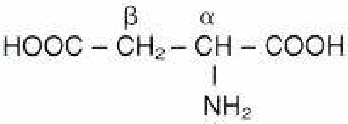
Figure 12.6

Molecular models of glycine and alanine.

- **Acidic amino acids.** The group R contains an acidic functional group.

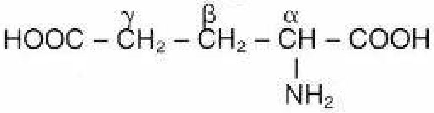
Examples

Aspartic acid



$HOOC - \overset{\beta}{CH_2} - \underset{NH_2}{\overset{\alpha}{CH}} - COOH$

Glutamic acid

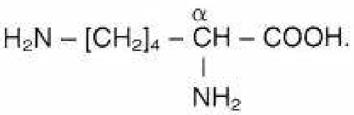


$HOOC - \overset{\gamma}{CH_2} - \overset{\beta}{CH_2} - \underset{NH_2}{\overset{\alpha}{CH}} - COOH$

- **Basic amino acids.** The group R contains a basic functional group.

Examples

Lysine



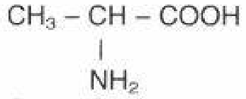
$H_2N - [CH_2]_4 - \underset{NH_2}{\overset{\alpha}{CH}} - COOH.$

Nomenclature

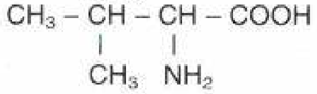
According to the IUPAC rules, an α-amino acid is named as a 2-amino alkanoic acid when the group R does not contain other functional groups.

Examples

$H_2N - CH_2 - COOH$ 2-aminoethanoic (acetic) acid



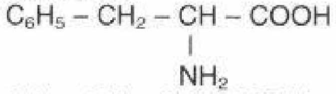
$CH_3-\underset{\substack{|\\ NH_2}}{CH}-COOH$ 2-aminopropanoic acid



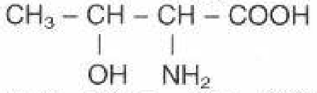
$CH_3-\underset{\substack{|\\ CH_3}}{CH}-\underset{\substack{|\\ NH_2}}{CH}-COOH$ 2-amino-3-methylbutanoic acid

When the group R contains a functional group, the nomenclature becomes complicated.

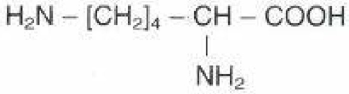
Examples



$C_6H_5-CH_2-\underset{\substack{|\\ NH_2}}{CH}-COOH$ 2-amino-3-phenylpropanoic acid



$CH_3-\underset{\substack{|\\ OH}}{CH}-\underset{\substack{|\\ NH_2}}{CH}-COOH$ 2-amino-3-hydroxybutanoic acid



$H_2N-[CH_2]_4-\underset{\substack{|\\ NH_2}}{CH}-COOH$ 2,6-diamino hexanoic acid

■ Enantiomerism

■ Chirality

Some objects have the property to be non-superimposable on their plane mirror image (or on their symmetrical relative to a plane). It is, for example, the case of the right and left hands (Fig12.7).
Such objects are called chiral (Fig12.8).

Numerous molecules have this property and are said to be chiral.

A chiral molecule is non-superimposable on its mirror image. When the molecule is superimposable on its image, it is said to be achiral.

When a beam of plane-polarized light passes through the solution of a pure substance constituted of chiral molecules, the polarization plane of the light undergoes a rotation of some α angle towards the right or towards the left. The substance is then said to be optically active.

When the rotation of the light polarization plane takes place towards the right, the angle α is counted positively, the substance is said dextrorotary (right) and its name is preceded by the letter (d) or by the sign (+).
In the contrary case, rotation to left, α negative, and the substance is said levorotary (left) and its name is then preceded by the letter (l) or by the sign (-).
The chirality of a molecule is due to its spatial (three-dimensional) structure.
A molecule containing a carbon atom tetrahedrally attached to four different atoms or groups of atoms is indeed chiral, since it is not superimposable on its mirror image.

Figure 12.7
The right hand and the left hand are mirror images and they are not superimposable.

■ The word chiral is derived from the greek word χξιρ (cheir, pronounced kheir) that means hand.

■ Pronounce kiral, kirality.

■ Two objects or molecules are called superimposable, when they are identical and could be superimposed.

Figure 12.8
Chiral objects: gloves, shell, coffeepot,

■ The value of the angle α per unit of light path and per unit of solution concentration is called specific rotation of the substance.

- The chirality is not limited to organic chemistry.

Such a carbon atom is said to be asymmetric (stereogenic).

A carbon atom is said to be asymmetric, when it is attached to four different atoms or groups of atoms.
An asymmetric carbon is represented by C*.

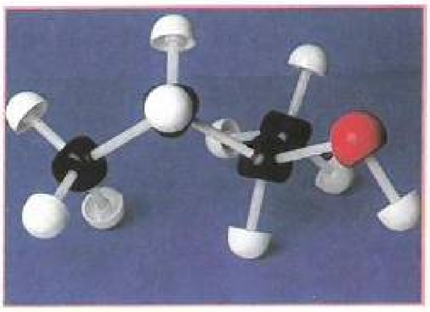
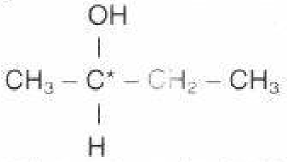


Figure 12.9
Ball-and-stick molecular model of the 2-butanol molecule.

Let us construct a ball-and-stick molecular model of the 2-butanol molecule (Fig.12.9).
The functional carbon (C_2) of the molecule is attached to the H atom and the following groups of atoms: OH, CH_3, C_2H_5, according to the following condensed structural formula:



$$CH_3-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C^*}}-CH_2-CH_3$$

The carbon 2 of the 2-butanol molecule is consequently asymmetric.

Activity 1 Construction of ball-and-stick molecular models of two enantiomers of 2-butanol.

Objective

Define enantiomerism

Equipment

Molecular models kit.

Procedure and conclusion

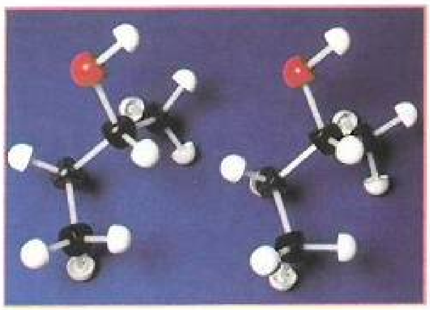


Figure 12.10
The two models of 2-butanol are superimposable.

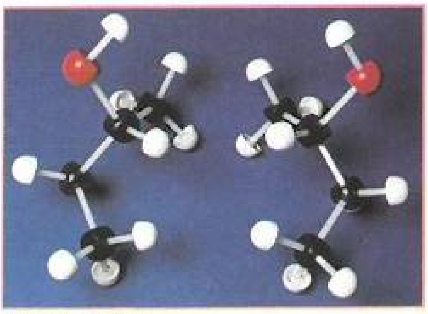


Figure 12.11
The two models of 2-butanol are not superimposable.

Construct two identical ball-and-stick molecular models of 2-butanol. Superimpose them (Fig.12.10).
The two models are superimposable.
Reverse the positions of the H atom and the OH group on the functional carbon of one of the two models. Superimpose the obtained model on the other one remained unchanged (Fig.12.11).
The two models become non-superimposable and they are image one of the other through a plane mirror (or symmetric with respect to a plane).
The two constructed models correspond to two different isomeric configurations. They are called enantiomers.
This phenomenon is called enantiomerism.

Enantiomerism is a configuration isomerism. The enantiomerism relation exists between two molecules, which are non-superimposable and are mirror images.

- **Representations of the enantiomers**

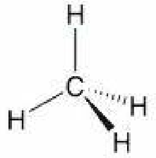
To represent on a paper (or in a plane) a three-dimensional structure, one uses different representations or projections, such as the Cram three-dimensional representation (or perspective representation) and the Fischer representation (or projection).

- **Three-dimensional Cram representation**

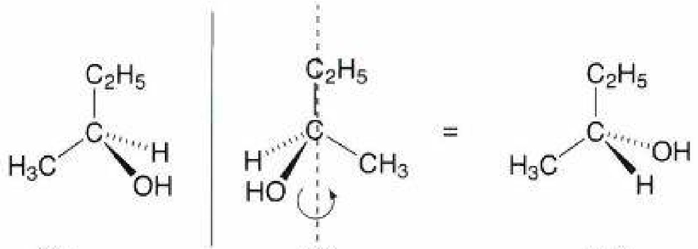
In this representation, the following conventions are adopted:

- The bonds that are in the plane of the figure will be represented by a continuous line (—).
- The bonds that are directed to the front of the plane will be represented by a filled triangle (◀).
- The bonds that are directed behind the plane will be represented by a dotted line (⋯⋯).

The methane molecule, for example, is represented by:



And the two enantiomers of 2-butanol are represented by:



(a) (b) (b')

(a) and (b) are enantiomers; they are mirror images, to each other.

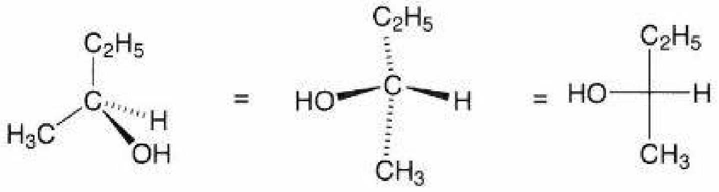
(b) and (b') are identical; (b') is obtained from (b) by rotating it 180° outside the plane of the figure, around the axis of the C-C_2H_5 bond.

- **Fischer representation**

It is generally used when the molecule possesses asymmetric carbons. It is a projective representation. All the bonds are represented by horizontal and vertical continuous lines (—), the principal chain being laid out vertically.

- A vertical line represents a bond in the plane of the paper or directed behind this plane.
- A horizontal line represents a bond directed to the front of the plane.

The Fischer's representation of the two enantiomers of 2-butanol is:



■ The configuration of a molecule is a three-dimensional arrangement of its atoms without taking into account the rotation of some of them around the bond axis.

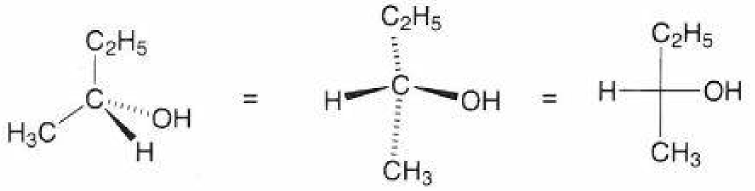
■ The enantiomerism is often called optical isomerism and the enantiomers optical isomers.

■ The word enantiomer is derived from the greek word enantios, which means opposite.

■ Two enantiomers, (d) and (l), possess the same specific rotation α, except the sign.

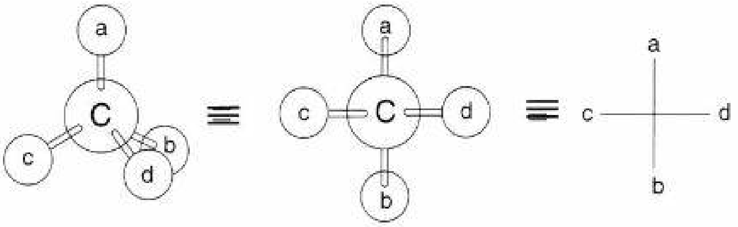
■ An equimolar mixture of two enantiomers is called racemic mixture. It is optically inactive.

■ This projection is commonly used in biochemistry, particularly to represent the molecules of sugar, such glucose, levulose...etc, and the α-amino acids.



The Fischer's representation supposes that the molecule is observed in a definite conventional position:

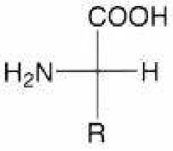
- Two bonds towards the front of a horizontal plane.
- Two bonds behind a vertical plane.



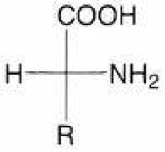
■ **α-amino acids and enantiomerism**

The observation of the structural formulas of the α-amino acids shows that, except glycine H_2N-CH_2-COOH, the carbon α (or carbon 2) is asymmetric. This carbon is indeed attached to four different atoms and groups of atoms: H, NH_2, COOH and R.

According to Fischer's representation, an α-amino acid can be represented by:

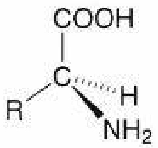


or

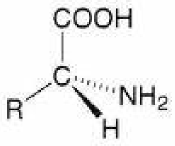


(a) (b)

Which correspond to the following three-dimensional representations:



or

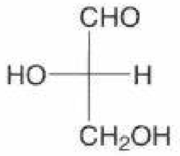


(a′) (b′)

These two representations lead to a classification of the α-amino acids in two series: L and D.

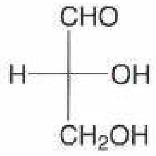
This classification is based on a configuration correlation with the two enantiomers of the glyceraldehyde $HOCH_2-CHOH-CHO$, the Fischer representation of which is the following:

■ (a) and (a') represent the same molecule, likewise (b) and (b').



(a)
(-) Glyceraldehyde
(Series L)

or



(b)
(+) Glyceraldehyde
(Series D)

In the representation of (l or -) glyceraldehyde, the OH group is written at the left. This representation is conventionally taken as the reference of the L series.

In the representation of (d or +) glyceraldehyde, the OH group is written at the right. This representation is conventionally taken as the reference of the D series.

Consequently, the representation (a) corresponds to the α-amino acids of the L series; the NH_2 group being written at the left in the figure, and the representation (b) to the α-amino acids of the D series; the NH_2 group being written at the right in the figure.

■ The systematic name of glyceraldehyde is 2,3-dihydroxypropanal.

Remark

D should not be confused with d, likewise L should not be confused with l.

D and L correspond indeed, simply, to the relative position of the OH group (or another group such as NH_2) on the asymmetric carbon, in the Fischer's representation of a molecule. While d and l correspond respectively to the sign (+) and (-) of the specific rotation of an optically active substance.

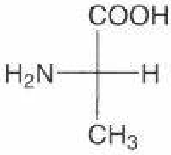
Thus, chiral molecules may belong to D series and be dextrorotary (d,+), and, they may belong to the L series and be levorotary (l,-).

■ The actual configuration of an asymmetric carbon is determined generally by spectroscopic methods such as X-Ray diffraction.

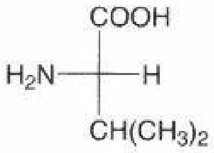
Let us note finally that α-amino acids issued from human proteins and acting a part in the biological process belong to L series.

Examples

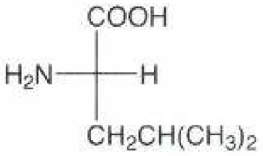
■ The attribution of D and L configurations to the two enantiomers of the glyceraldehyde was made by guess with equal probability to be true or false. In 1951 this attribution proved to be correct.



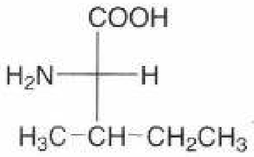
L(+) Alanine



L(-) Valine



L(-) Leucine

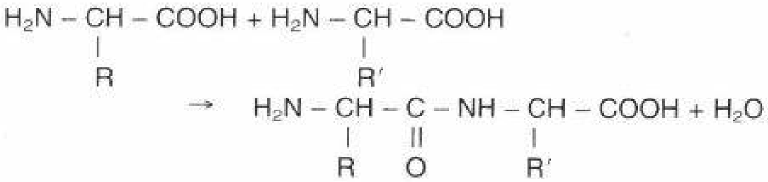


L(+) Isoleucine

- Some α-amino acids issuing from microbiological sources belong to the D series.

- **Proteins and Peptides**

The α-amino acids may interact together. This reaction is called condensation; it leads to the formation of linear or cyclic chains of various lengths, by elimination of water.
The length of the chain, its geometrical characteristics and its biological properties depend on the number and the structure of the condensed α-amino acids.
The reaction between two molecules of α-amino acid (identical or different) produces a molecule called dipeptide and a molecule of water.
In this reaction, the amino group of an α-amino acid molecule reacts with the carboxyl group of the other molecule, according to the equation:



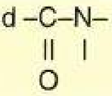
$$H_2N-\underset{\underset{R}{|}}{CH}-COOH + H_2N-\underset{\underset{R'}{|}}{CH}-COOH \rightarrow H_2N-\underset{\underset{R}{|}}{CH}-\underset{\underset{O}{\|}}{C}-NH-\underset{\underset{R'}{|}}{CH}-COOH + H_2O$$

The condensation of several α-amino acid molecules (identical or different) produces a molecule called polypeptide or simply peptide and several molecules of water.
According to the number of condensed molecules of α-amino acid one distinguishes the tripeptides, the tetrapeptides…etc.

A dipeptide results from the condensation of two molecules of α-amino acid.
A peptide results from the condensation of a several number, more or less large, of α-amino acid molecules.

The obtained chain is called peptide chain.
The dipeptide molecule is characterized by the presence of an acylamino functional group, which is the characteristic functional group of a peptide bond.

- R and R' are identical or different groups.



The bond $-\underset{\underset{O}{\|}}{C}-\underset{|}{N}-$ of the acylamino group is called peptide bond.

Conventionally, the term peptide is reserved for chains containing up to 50 amino acid residues ($M \leq 10000 g.mol^{-1}$).
Beyond 50 amino acid residues, the peptide is named protein.

A protein is a peptide resulting from the condensation of more than 50 amino acid molecules.

- A peptide is a polyamide.

The molar mass of a protein may reach many ten millions of $g.mol^{-1}$.
In spite of the limited number of amino acids involved in the constitution of the proteins (twenty common amino acids and some tens of rare amino acids), the diversity of proteins is practically unlimited, due to the infinite number of possible

arrangements of these elementary repeating units.

A peptide formed by the condensation of ten different molecules of amino acids possesses a large number of combinations: 3628800. A protein formed by the condensation of one hundred of amino acid molecules of 15 or 20 different types (the most frequent case), possesses an unimaginable number of combinations.

This explains the fact that each species and even each individual can synthesize its specific proteins, that allow distinguishing it from the other (species or individuals).

- **Nomenclature of the peptides**

■ An amino acid residue is the part of its molecule that remains after condensation. Thus, a dipeptide contains two amino acid residues, a tripeptide, three amino acid residues and so on.

Each residue constitutes an elementary unit of the peptide chain (or of the polyamide).

To name a peptide, it is considered as formed by progressive substitution starting from the amino acid having preserved its carboxyl group free.

The peptide chain is disposed in such a manner that the free terminal -COOH group is located at the right and the free terminal NH_2 group at the left.

This nomenclature of peptides is based on the current names of the α-amino acids.

Only the acid having preserved its carboxyl group preserves its current name, the others are named as radicals, such as glycine becomes glycyl, alanine becomes alanyl and so on. The amino acid residues constituting a peptide are named starting from the left to the right.

■ The diversity of proteins reminds us of the language. An alphabet of only twenty letters allows indeed to composing an unlimited number of words.

This formal resemblance led some scientists to consider the α-amino acids as the letters of the alphabet of the cells chemical language.

Examples

A dipeptide:

$H_2N - CH_2 - CO - NH - CH_2 - COOH$ Glycylglycine (Gly-Gly)

A tripeptide:

$H_2N - CH_2 - CO - HN - CH_2 - CO - HN - CH_2 - COOH$

Glycylglycylglycine (Gly-Gly-Gly)

- **Properties and role of the peptides and the proteins in the chemistry of the living world**

Proteins do not possess definite melting point of fusion. When heated, they undergo diverse irreversible transformations. It said that they are denaturated like the albumin of the egg when heated.

The dissolution of proteins gives colloidal solutions that precipitate by addition of an electrolyte. That is observed with milk, for example, which gives a casein precipitate by adding of acids.

The proteins are the essential constituents of many living tissues: fibrous proteins forming the skin, the muscles, the hair, the silk, the wool...etc

The proteins are involved in diverse vital processes: hormones, globular proteins, blood-plasma...etc:

The rhodopsin, for example, is a photoreceiver of the retina cells acting a crucial part in the vision.

The hemoglobin ensures the transport of oxygen from the lungs to the different organs and cells of the body.

The insulin, secreted by the pancreas, is a protein hormone that acts as an important part in the metabolism of the sugar and is used in the treatment of the diabetes.

The proteins constitute the antibodies responsible of the immunity system.

The enzymes form an important category of proteins. They are selective catalysts involved in all the biological processes on which the life and the organism growth depend.

The enzymes catalyse reactions of various degree of complexity, from the simple hydration of carbon dioxide to the hydrolysis of proteins during the digestion and the duplication of chromosomes.

Finally, the enzymes accelerate some reactions by a multiplying factor of many millions while allowing the realization of these reactions under soft conditions.

■ Collagen is the most abundant fibrous protein in mammal kingdom.

■ The selectivity of a catalyst means that it accelerates a determined chemical reaction rather than another one.

Chapter Review

- An amine contains the amino functional group  $-\overset{|}{N}-$.

- There are three classes of amines:
    - Primary amines of general formula RNH_2.
    - Secondary amines of general formula $RR'NH$.
    - Tertiary amines of formula $RR'R''N$.

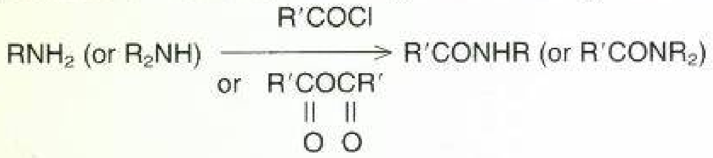
- Molecules of primary (or secondary) amines may bind together by hydrogen bonds.

- Amines are toxic and possess a strong and disagreeable smell.

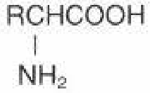
- Amines are weak bases. They react with the acids to give alkyammonium salts, according to following scheme:

$$-\underset{|}{N}- + H_3O^+ \rightarrow -\underset{|}{\overset{+}{N}H}- + H_2O$$

- The primary and secondary amines react with the acyl chlorides and the acid anhydrides to form amides, according to the following schema :



$$RNH_2 \text{ (or } R_2NH) \xrightarrow[\text{or } R'\underset{\underset{O}{\|}}{C}O\underset{\underset{O}{\|}}{C}R']{R'COCl} R'CONHR \text{ (or } R'CONR_2)$$

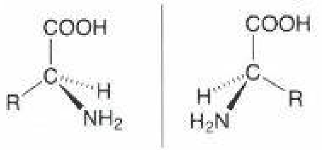
- An α-amino acid contains a carboxyl functional group and an amino functional group attached to the same carbon atom, according to the general formula:  $R\underset{\underset{NH_2}{|}}{CH}COOH$

- A carbon is asymmetric if it is attached to four different atoms or groups of atoms.

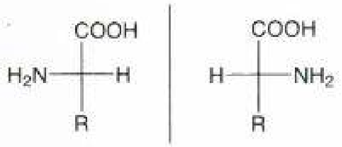
- A molecule containing one or many asymmetric carbons is chiral. In this case, it is not superimposable on its mirror image.

- Two molecules are enantiomers if they are images one of the other through a mirror and are non-superimposable.

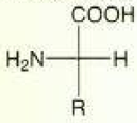
- In the three dimensional Cram representation an α-amino acid is represented by:



- In the Fischer representation, an α-amino acid is represented by:



- The common α-amino acids belong to the L series represented according to Fischer by:

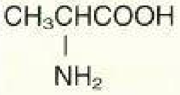
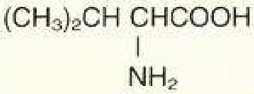
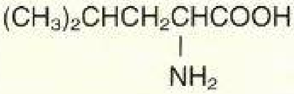
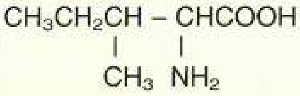
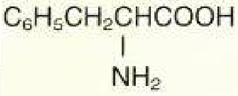
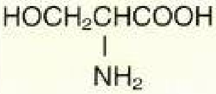
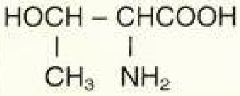
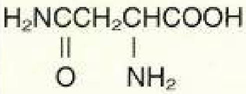
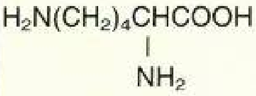
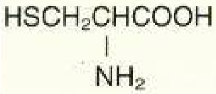
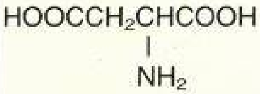
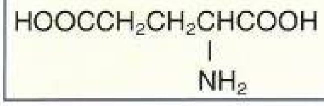


- The peptides and the proteins are natural polyamides formed by the condensation of α-amino acids. They act a fundamental part in the chemistry of the living world.

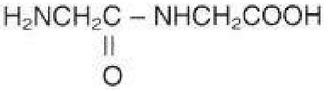
Nomenclature and examples of peptides

The nomenclature of peptides and proteins uses the common names of α-amino acids. The formulas of peptides are written by simply linking the three-letter abbreviation for each amino acid (Table 12.3).
The three-letter abbreviations for the names of the amino acids are used to make the names of peptides more manageable and to help write the formulas of complex peptides in a simple way.
However, it does not show neither the structural formula nor the sequence in the molecule.

Table 12.3

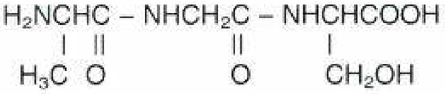
Formula	Name	Three-letter abbreviation
H_2NCH_2COOH	Glycine	Gly
 $CH_3\underset{\substack{\vert\\ NH_2}}{C}HCOOH$	Alanine	Ala
 $(CH_3)_2CH\,\underset{\substack{\vert\\ NH_2}}{C}HCOOH$	Valine	Val
 $(CH_3)_2CHCH_2\underset{\substack{\vert\\ NH_2}}{C}HCOOH$	Leucine	Leu
 $CH_3CH_2\underset{\substack{\vert\\ CH_3}}{C}H-\underset{\substack{\vert\\ NH_2}}{C}HCOOH$	Isoleucine	Ile
 $C_6H_5CH_2\underset{\substack{\vert\\ NH_2}}{C}HCOOH$	Phenylalanine	Phe
 $HOCH_2\underset{\substack{\vert\\ NH_2}}{C}HCOOH$	Serine	Ser
 $HO\underset{\substack{\vert\\ CH_3}}{C}H-\underset{\substack{\vert\\ NH_2}}{C}HCOOH$	Threonine	Thr
 $H_2N\underset{\substack{\Vert\\ O}}{C}CH_2\underset{\substack{\vert\\ NH_2}}{C}HCOOH$	Asparagine	Asn
 $H_2N(CH_2)_4\underset{\substack{\vert\\ NH_2}}{C}HCOOH$	Lysine	Lys
 $HSCH_2\underset{\substack{\vert\\ NH_2}}{C}HCOOH$	Cysteine	Cys
 $HOOCCH_2\underset{\substack{\vert\\ NH_2}}{C}HCOOH$	Aspartic acid	Asp
 $HOOCCH_2CH_2\underset{\substack{\vert\\ NH_2}}{C}HCOOH$	Glutamic acid	Glu

Examples



$$\begin{array}{l} H_2NCH_2C-NHCH_2COOH \\ \qquad\qquad\ \| \\ \qquad\qquad\ O \end{array}$$

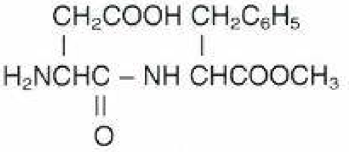
glycylglycine represented as: Gly-Gly



$$\begin{array}{l} H_2NCHC-NHCH_2C-NHCHCOOH \\ \qquad\ |\ \ \| \qquad\qquad\quad \| \qquad\quad\ | \\ \quad H_3C\ \ O \qquad\qquad\ O \qquad\quad CH_2OH \end{array}$$

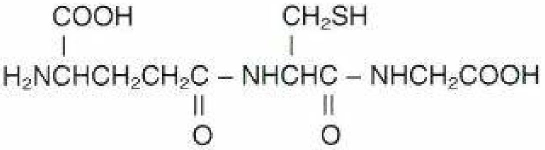
alanylglycylserine represented as: Ala-Gly-Ser.

Examples of some peptides of biological and practical importance.



$$\begin{array}{l} \qquad CH_2COOH\ CH_2C_6H_5 \\ \qquad\ |\qquad\qquad\quad | \\ H_2NCHC-NH\ CHCOOCH_3 \\ \qquad\quad \| \\ \qquad\quad O \end{array}$$

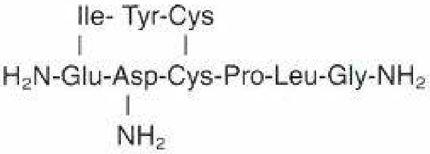
is the methyl ester of aspartylphenylalanine: Asp-phe-OCH_3 called aspartame. High caloric artificial sweetener.



$$\begin{array}{l} \qquad COOH \qquad\qquad\qquad CH_2SH \\ \qquad\ | \qquad\qquad\qquad\qquad\ | \\ H_2NCHCH_2CH_2C-NHCHC-NHCH_2COOH \\ \qquad\qquad\qquad\quad \| \qquad\quad\ \| \\ \qquad\qquad\qquad\quad O \qquad\quad\ O \end{array}$$

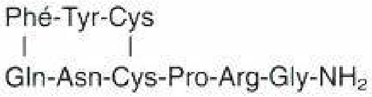
is g-glutamylcysteinylglycine: g-Glu-Cys-Gly called glutathione. It is a tripeptide which is found in all living cells and particularly in the crystal of the eye.

Of the more complex structures, simply represented with the three-letter abbreviation is shown in the following example:



$$\begin{array}{l} \qquad\ \text{Ile- Tyr-Cys} \\ \qquad\ |\qquad\quad\ | \\ H_2N\text{-Glu-Asp-Cys-Pro-Leu-Gly-}NH_2 \\ \qquad\qquad\ | \\ \qquad\quad\ NH_2 \end{array}$$

is oxytocin, a polypeptide involved in diverse physiological functions: egg laying of the hen, lactation of the cow.



$$\begin{array}{l} \text{Phé-Tyr-Cys} \\ \quad |\qquad\quad | \\ \text{Gln-Asn-Cys-Pro-Arg-Gly-}NH_2 \end{array}$$

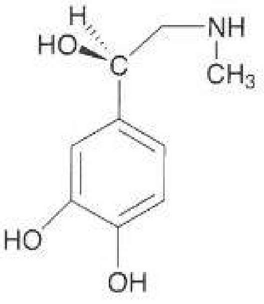
is vasopressin, also called antidiuretic, which is a polypeptide: regulates the excretion of water by the human body.

Tyr : tyrosine, Pro : proline, Arg : arginine, Gln : glutamine.

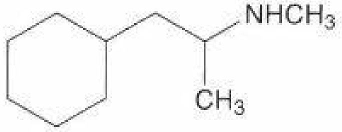
Documentary activity 1

Some physiologically active amines

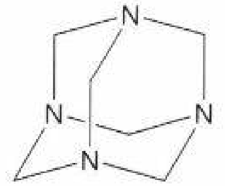
Many physiologically active substances are nitrogen compounds. Among these substances there are simple or polyfunctional amines with nitrogen atoms attached to an open chain or constituting a part of cyclic chain.



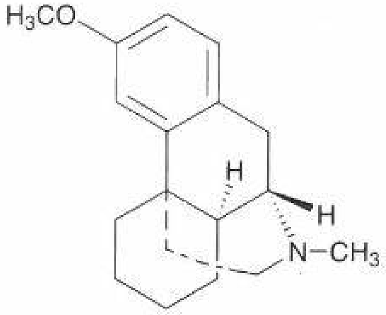
Epinephrine
[Adrenergic stimulant]



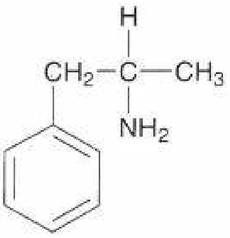
Prophylhexedrine
(Benzedrex)
[Nasal decongestant]



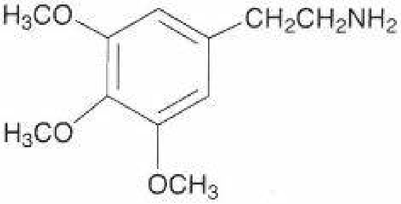
Hexamethyline tetramine
(Urotropine)
[Antibacterial agent]



Dextromethorphane
[Antitussive]



Amphetamine
[Antidepressant, stimulant
for the central nervous
system.]



Mescaline
[Hallucinogen]

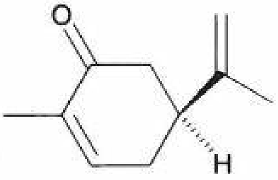
Documentary activity 2

Physiological properties of two enantiomers

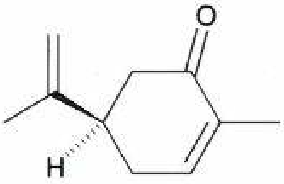
Enantiomers possess generally the same physical properties, except with respect to the polarized light. They have also the same chemical properties except when they react with a chiral molecule where they lead to the formation of two isomers of different configurations called diastereoisomers. This explains partially that the physiological properties of two enantiomers are often different, and may be in some cases opposite.

Examples

1) The two enantiomers of the carvone possess different smells:

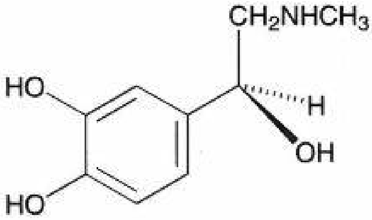


(+)Carvone
Present in the seeds of caraway, fennel and cumin.

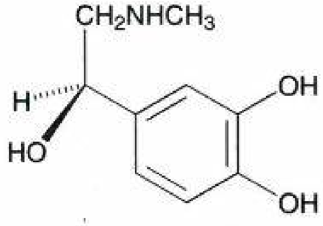


(-)Carvone
present in green mint.

2) Adrenaline is a cardiac stimulating. Only the levorotary (-) enantiomer provokes a physiological response.

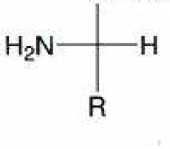


Adrenaline(+)



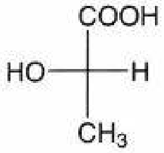
Adrenaline(-)

3) According to Fischer all the common α-amino acids belong to the L series represented by:



$$\begin{array}{c} COOH \\ H_2N - \!\!\!+\!\!\! - H \\ R \end{array}$$

4) The two enantiomers of lactic acid have different origins:

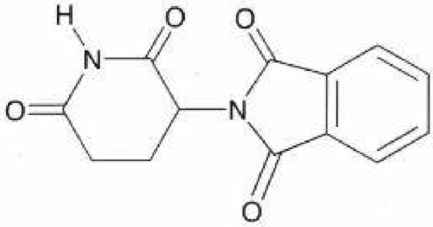


(L) lactic acid

Only the enantiomer L is formed in the muscles during physical activity.
A mixture of the two enantiomers is present in the sour milk or in some fruits and plants.

5) Many medications contain a (racemic) mixture of the two enantiomers. Often, only one of the enantiomers is effective, the second one may provoke serious problems.

Thus in 1960, the thalidomide, which is a sedative, was prescribed in the form of racemic mixture to pregnant women, in Europe. The consequence was the birth of hundreds of babies affected by serious anomaly, (the phocomelia*) provoked by the second enantiomer said « wrong ».



Thalidomide

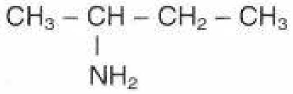
---

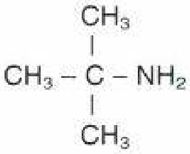
* The phocomelia is a congenital malformation (attacking fetus). It is chracaterized by the appearance of the palms and feet in the trunk (absence of arms and legs).

Exercises

1 Name the following compounds:

a) $CH_3-(CH_2)_4-NH_2$

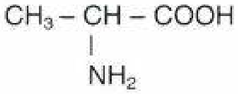
b) 
$CH_3-\underset{NH_2}{\underset{|}{CH}}-CH_2-CH_3$

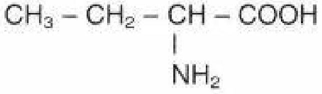
c) 
$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-NH_2$

d) $CH_3-(CH_2)_2-NH-CH_3$

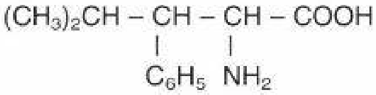
e) $(C_2H_5)_2N-CH_3$

f) $(CH_3)_2CH-CH_2-NH-C_2H_5$

g) 
$CH_3-\underset{NH_2}{\underset{|}{CH}}-COOH$

h) 
$CH_3-CH_2-\underset{NH_2}{\underset{|}{CH}}-COOH$

i) $H_2N-CH_2-CH_2-COOH$

j) 
$(CH_3)_2CH-\underset{C_6H_5}{\underset{|}{CH}}-\underset{NH_2}{\underset{|}{CH}}-COOH$

2 Write the condensed structural formula of each of the following compounds:

a) dipropylamine
b) N,N-dimethyl-2-propanamine
c) N-methyl-2-butanamine
d) N-methyl-N-ethyl-1-butanamine
e) 2-amino hexananoic acid
f) 3-amino-2-phenylpropanoic acid

3 Give the structural formulas and the names of the tertiary amines of molecular formula $C_5H_{13}N$.

4 a) Indicate using an asterisk the asymmetric carbon(s) in each of the compounds of the exercises 1 and 2.

b) Represent according to Cram and according to Fischer the enantiomers of the compounds 1-b), 1-g) and 2-c).

5 A) A carboxylic acid A reacts with a secondary alcohol B to lead to a compound C of formula $C_5H_{10}O_2$.

The reaction of the acid A with the dimethylamine leads to a compound D. Heating D produces a compound E: C_4H_9NO, with formation of water.

a) What are the characteristic functional groups of the products C and E?
b) Propose structural formulas for the compounds A, B, C, D and E.
c) Name the compounds A, B, D and E.
d) Write the equation of the reactions taking place.

B) a) The compounds C and E can be prepared using the derivatives F and G of the acid A. Give their structural formulas and their names.
b) How does one prepare the derivatives F and G starting from the acid A? Write the equations of the corresponding reactions.
c) Write the equations of the reactions of preparation of the compounds C and E starting from the acid derivatives F and G.

6 An amine A of saturated non-cyclic chain has a molar mass of 73 $g.mol^{-1}$.

a) Give its molecular formula.
b) Give the condensed structural formula, the name and the class of each one of the isomers of A.
c) Knowing that A does not react with the ethanoyl chloride, what is its formula and its name?
d) Write the formula of its conjugate acid and express the acidity constant K_a of the corresponding conjugate pair.

7 1.18 g of an amine A are titrated by a 1 $mol.L^{-1}$ hydrochloric acid solution. The equivalence point is obtained when 20 mL of the acid solution is added.

a) Calculate the molar mass of the amine A.
b) Deduce its molecular formula.
c) Give the condensed structural formula, the

name and the class of each amine isomer of A.

d) Knowing that A is a secondary amine, give its name.

e) Write the equation of the reaction between A and the hydrochloric acid.

8 The reaction of the benzoyl chloride C_6H_5COCl with a secondary amine A leads to an organic compound B of molar mass 149 $g.mol^{-1}$.

a) What is the nature of the compound B? Represent its characteristic functional group.

b) What other compound is able to react with amine A, leads to the formation of B?

c) Find the molar mass of amine A.

d) What condensed structural formulas may be attributed to the amine A?

e) Write the equations of the reactions leading to the product B.

9 What are the condensed structural formulas of the α-amino acids of molecular formula $C_4H_9NO_2$?

10 Valine is: 2-amino-3-methanoic acid. Leucine is: 2-amino-3-methylbutanoic acid. Serine is: 2-amino-3-hydroxypropanoic acid.

a) Write the condensed structural formula of each one of these three acids.

b) Indicate using an asterisk the asymmetric carbon atom in the molecule of each of these three acids.

c) Represent the enantiomers of valine and serine according to Cram's representation and Fischer's representation.

d) Relate the two representations.

11 a) Write the condensed structural formula of the 2-pentanol.

b) Is this molecule chiral? Why?

c) If yes, represent the two enantiomers according to Cram and according to Fischer. Relate the two representations.

d) 2-pentanol is oxidized by oxygen, in the presence of copper as catalyst.

1- Write the equation of the corresponding reaction.

2- Name the product formed, does it possess asymmetric carbon atoms? Justify your answer.

N.B. To represent the large (bulky) alkyl groups around the asymmetric carbon atom, use the symbols R_1, R_2, specifying your attribution. E.g. $R_1 = CH_3$, $R_2 = C_2H_5$.

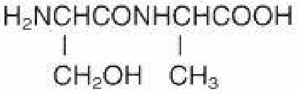
12 a) Name the following dipeptides and the tripeptides:

1) 

$H_2NCH_2CONH\underset{\substack{|\\ CH_3}}{C}HCOOH$

2) 

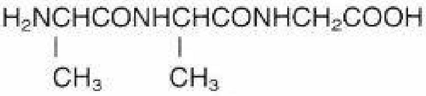
$H_2N\underset{\substack{|\\ CH_3}}{C}HCONHCH_2COOH$

3) 

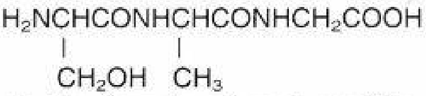
$H_2N\underset{\substack{|\\ CH_2OH}}{C}HCONH\underset{\substack{|\\ CH_3}}{C}HCOOH$

4) 

$H_2NCH_2CONH\underset{\substack{|\\ CH_2OH}}{C}HCOOH$

5) 

$H_2N\underset{\substack{|\\ CH_3}}{C}HCONH\underset{\substack{|\\ CH_3}}{C}HCONHCH_2COOH$

6) 

$H_2N\underset{\substack{|\\ CH_2OH}}{C}HCONH\underset{\substack{|\\ CH_3}}{C}HCONHCH_2COOH$

b) In the formula of each peptide, circle the residues of α-amino acids.

c) Represent the formulas of the compounds using the three letters code symbol.

13 a) Write the condensed structural formulas of the following peptides:

1) Serylglycine.
2) Cystylserylglycine.
3) Serylglycylalanine.

b) Represent the formulas of the compounds using the three letters code symbol.

14 The prodigious superiority of the nature in synthesizing peptides and proteins is evident.

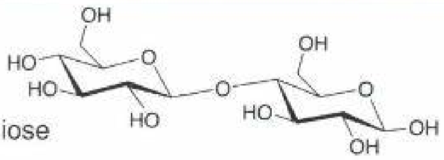
1) The synthesis of a hormone containing 39 amino acids (adrinocortico-tropic hormone) by a team of researchers needs many years.
2) The biosynthesis of a protein of molar mass 10^5 g.mol^{-1} (about 500 amino acids) is done in an organism by enzymatic reaction during 2 minutes and in a well order.

We notice that the sequence of the amino acids in a protein is predetermined by the chromosomes.

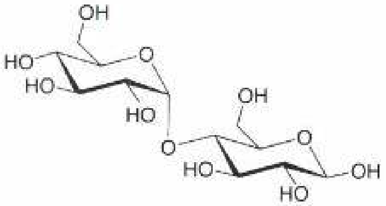
a) Enumerate the type of difficulties which are faced during the synthesis of a peptide in the laboratory.
b) What advantages are there in the biosynthesis of peptides and proteins?
c) Enzymatic reactions are selective. Explain this statement.

15 A) A specific enzyme hydrolyzes the cellobiose but does not hydrolyze the maltose and inversely. Knowing that these two substances are disaccharides (dimerized sugar) which do not have except little structural differences. This observation is made use to find out the configuration of the disaccharide.

β-Cellobiose



β-Maltose



a) Explain why the same enzyme does not hydrolyze two molecules that belong to the same family and which do not have except little structural differences.
b) How do you make use of this observation to find out the configuration of the disaccharide?

B) Enzymes have very active role in the hydrolysis of proteins during digestion.
The specifity of their action explains the fact that the stomach does not digest itself.

a) Why do we have to talk about the risk that the stomach digests itself?
b) Represent the characteristic functional group of peptides and proteins.
c) Name this group and indicate the type of bond which is involved in the hydrolysis.
d) What property of enzymes prevent the autodigestion of the stomach?

Evaluation

Applying knowledge

1 Complete the following table by writing yes or no:

	Formation of a carbonyl compound	Formation of a carboxylic acid	Flameless lamp
1-pentanol			
2-pentanol			
3-pentanol			
2-methyl-2-butanol			
pentanal			
2-pentanone			
pentanoic acid			
	Fehling's solution	Tollen's reagent	DNPH
1-pentanol			
2-pentanol			
3-pentanol			
2-methyl-2-butanol			
pentanal			
2-pentanone			
pentanoic acid			

2 The molecular formula of the lactic acid is $C_3H_6O_3$. It results from the fermentation of some sugars such the lactose of the milk.

a) Propose structural formulas for the lactic acid, knowing that it possesses a hydroxyl group.
b) The systematic name of lactic acid is 2-hydroxypropanoic acid. What is its structural formula?
c) Is lactic acid chiral. Why?
d) Represent its two enantiomers according to Cram and Fischer. Relate the two representations.

3 2-phenylethanol is a constituent of the essential oil of rose. An organic compound A is formed when 2-phenylethanol reacts with an excess of acidified potassium permanganate solution. Compound A reacts with 2-phenylethanol in the presence of sulfuric acid to form a product B which has the scent of jonquil.

a) To which family of organic compounds does A and B belong?
b) Write the equation of the reaction for the formation of A. Name compound A.
c) Draw a diagram for the operation carried out.

4 A) To carry out a breathalyzer (breath-analyzer) (blood alcohol level in g. L^{-1}), the policemen use breathalyzer tests. The driver has to blow into a balloon. The volume of air expired for 10 to 20 seconds passes through a tube containing silica gel impregnated with sulfo-chromic acid mixture, which behaves as an acidified potassium dichromate solution. If the expirated air contains vapors of ethanol, the color of the silica gel changes. The extent of the color change is approximately proportional to the blood alcohol level.

a) What is the role of the sulfo-chromic mixture?
b) What is the color of the silica gel before and after the expiration of the air?
c) What is the name of the reaction used? Write its equation.

B) The determination of blood alcohol level by the breathalyzer being not precise, more accurate quantitative analysis is done with a sample of blood taken from the intoxicated driver.

A specific method of analysis is done in the presence of an enzyme:

Alcohol dehydrogenase (ADH) according to the equation:

$$C_2H_5OH + NAD^+ \xrightarrow{ADH} CH_3CHO + NADH + H^+$$

a) What is the type of this biochemical reaction?
b) What is the role of ADH?
c) What is the role of NAD^+?

Designing an experiment

5 Identification of alcohols having three carbon atoms

Objective
Identify the class of an alcohol.

Equipment and reagents
Two flasks 100 mL each. Ice-water cold bath. Electrical heating mantle. Boiling stones. Two delivery tubes. 4 test tubes.
Potassium permanganate (0.1 mol. L^{-1}). Sulfuric acid solution (4 mol. L^{-1}). DNPH solution. Fehling's solution. Two bottles A and B each containing a liquid substance labeled as alcohol C_3H_8O.

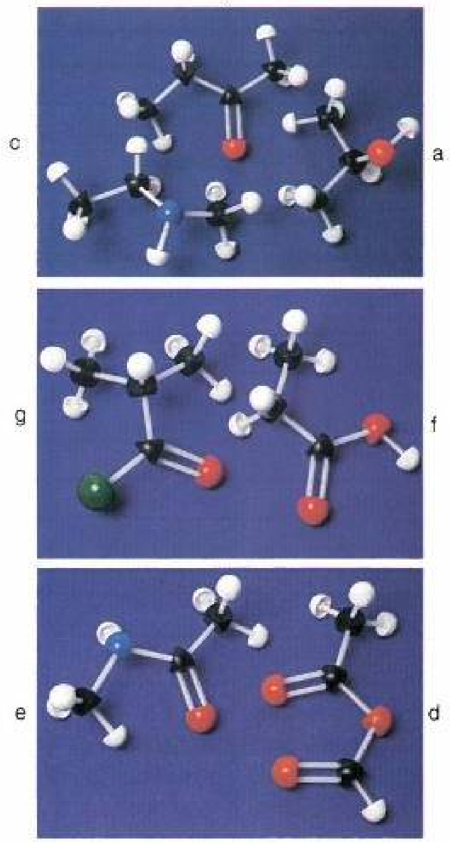
Experiment 1
Step A
Take 5 mL of the liquid from bottle A and place it in a 100 mL flask. Then put 15mL of potassium permanganate solution and 1mL of sulfuric acid solution into the flask. Put 2 pieces of boiling stones into the flask. Observe the changing of color.
Step B
If the color change is not immediate, heat to lukewarm. Then heat the mixture to gentle boiling and collect the distillate by a delivery tube, which is immersed in the ice-water bath.
Step C
Do the following for the identification test with the distillate collected:
Put two drops of the distillate in a test tube containing 1mL of DNPH solution.
Heat to gentle boiling 1mL of the distillate and 1mL of Fehling's reagent.

Experiment 2
The same procedure for the liquid in flask B.

Interpretation of the results
a) Give the structural formulas of the isomeric alcohols of formula C_3H_8O.
b) Give the name and the class for each alcohol.
c) List in a table the results obtained. Deduce the structural formulas of the alcohols studied.
d) Explain how the tests, which allow us to identify the class of an alcohol, are done.

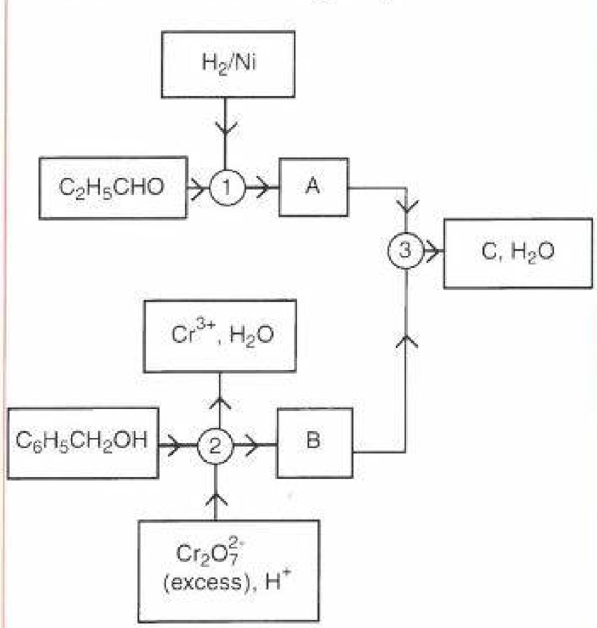
Communicating

6 a) Recognize in the following ball-and-stick or space-filling molecular models the functional groups that characterizes the represented molecules.



b) Write the structural formula of each molecule and indicate to which family of organic compounds it belongs?

7 a) Identify the missing compounds A, B and C in the following diagram:



b) Reaction 1 takes place with a yield of 85%, reaction 2 with a yield of 90% and reaction 3 with a yield of 50% with respect to the limiting reactant.
What mass of C is obtained, starting from 58 g of propanal and 54 g of phenylmethanol (benzylalcohol)?

8 The biological synthesis of peptides and proteins starting with α-amino acids involve enzymes which themselves are proteins. Each condensation between two amino acids requires a specific enzyme.

It is the same for hydrolysis of proteins into amino acids (reverse reaction for the condensation).

All these reactions occur at the body temperature (about 37 °C) relatively low temperature and cease after a short time (about 2-3 hours), these correspond to moderate conditions. The same reactions that carried out in laboratories (known as chemical synthesis), require higher temperature (150 - 200 °C) and longer time (many hours).

In addition, the hydrolysis of a protein requires the use of strong acids such as concentrated sulfuric acid. These conditions are relatively harsher. The hydrolysis (chemical) of protein is very slow even in the presence of sulfuric acid.

a) During the condensation of two amino acids, what are the functional groups involved and what is the functional group formed? What is the bond formed for the corresponding compound called?
b) Give a simple scheme for the condensation reaction of two identical amino acids. What is the product formed called?
c) If the condensation occurs between two different amino acids, three products are obtained. Explain this by means of a scheme.
d) To obtain only the desired product, called heterogeneous peptide, one of the two amino acids is made to react with a derivative of the other amino acid. The amino functional group in this latter undergoes a transformation which changes its properties. That is to say, it does not behave as an amine. It is called protected or camouflaged. However, this function could be regenerated, at the moment needed.
1) What acid derivative could be used?
2) What advantage is there in using an acid derivative? Give a scheme of the corresponding reaction.
3) Why should the amino functional group be camouflaged in the acid derivative used?
e) The utilization of an enzyme renders the condensation of two amino acids fast and specific. Identify the nature of an enzyme. What is its role?
f) In the presence of a certain enzyme, two amino acids A1 and A2 are condensed in the sense A1-A2: In the presence of a second enzyme, their condensation occurs in the opposite sense A2-A1. What characteristics of enzyme intervene in this case?
g) For what reason, is the hydrolysis of a peptide, when done in the laboratory, difficult?

h) What is the role of sulfuric acid in the hydrolysis of peptides?
What differences are there in its action, relative to those of hydrolysis enzymes for protein?

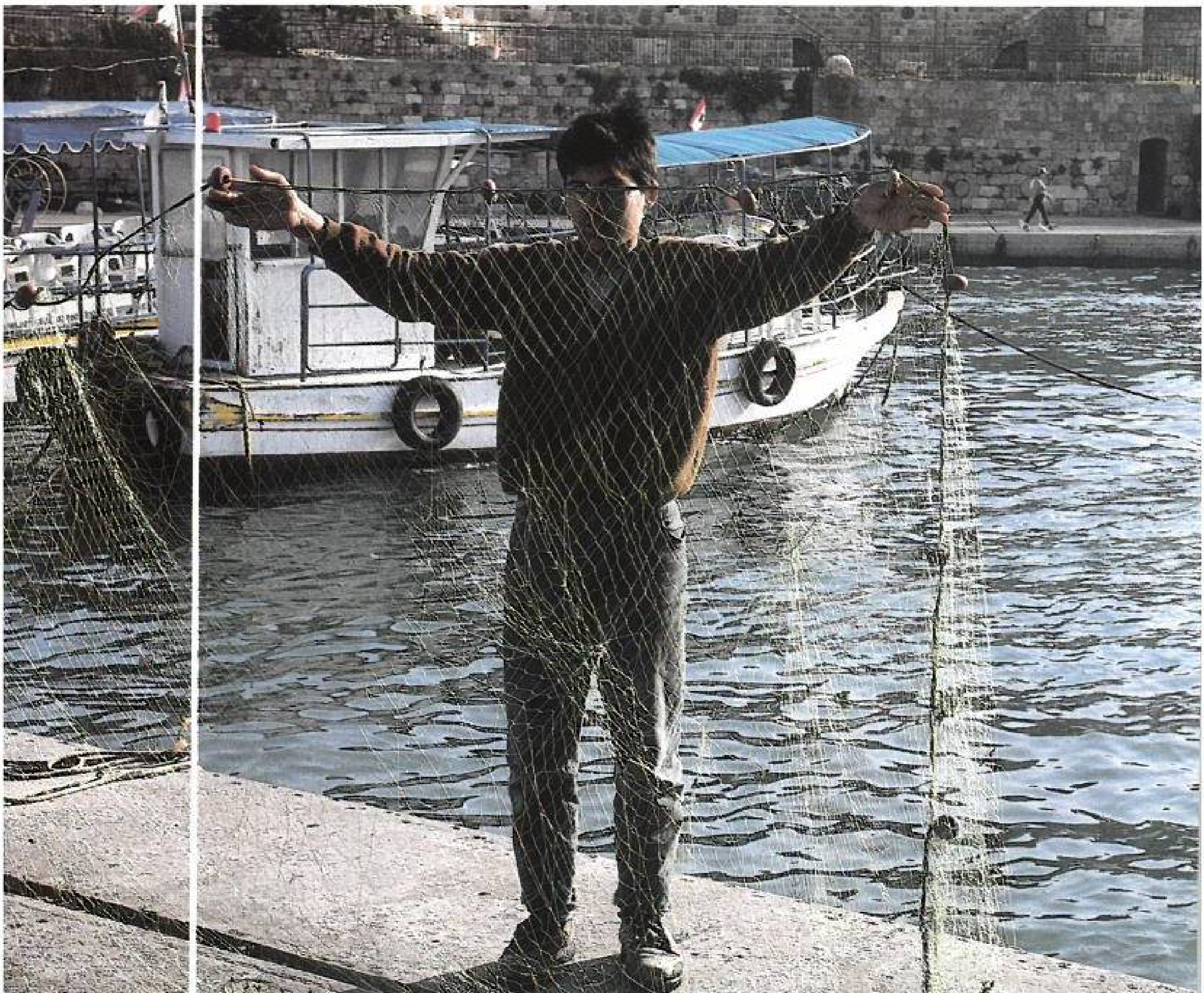
i) Why are enzymatic hydrolysis of peptides called moderate, whereas their hydrolysis when heated and in the presence of sulfuric acid, are called harsh (hard).

h) What is the role of sulfuric acid in the hydrolysis of peptides?
What differences are there in its action, relative to those of hydrolysis enzymes for protein?

i) Why are enzymatic hydrolysis of peptides called moderate, whereas their hydrolysis when heated and in the presence of sulfuric acid, are called harsh (hard).

6

Polymers



Nylon is a synthetic polymer. It is essentially manufactured in the form of fibers, used in textiles. The usage of nylon is not limited to the manufacture of textiles. This polymer is used to make cords, tennis racquets, tooth brush bristles, suture threads, fishing lines and fishing nets.

Polymers, substances characterized by their macromolecules, can be either of natural or synthetic origin.

Cellulose present in wood and cotton, rubber, proteins... are natural polymers.

Plastic materials, a great number of textile fibers, plexiglass, adhesives...are synthetic polymers.

How are synthetic polymers elaborated? What are their characteristics? Are they important for modern societies? Are they considered pollutants?

POLYMERS 13

Objectives

- Distinguish between natural polymers and synthetic polymers.
- Identify the properties and the characteristics of synthetic polymers.
- Recognize the economical importance of the polymers' industry.
- Recognize the impact of polymers on the environment.

Prerequisites

- Polymerization of alkenes.
- Notions on the plastic materials.
- Pollution of the environment.

Chapter content

13.1 Natural polymers and synthetic polymers.
13.2 Characteristics and uses.
13.3 Economic aspect.
13.4 Impact on the environment.
- Chapter review
- Laboratory investigation
- Documentary activities
- Exercises
- Evaluation

13.1 Natural polymers and synthetic polymers

Figure 13.1
Rubber is obtained from a white milky viscous liquid extracted from a certain number of trees.

"Polymer" originated from two Greek words: "poly" which means several, and "meros" which refers to a unit.

Actually, a polymer is a chemical compound formed by only one giant molecule referred to as a macromolecule.

This macromolecule is formed by joining atoms or groups of atoms attached to each other by covalent bonds.

Certain polymers are of natural origin (i.e. produced by living organisms), while others are synthetic.

Wood and cotton, for example, are essentially formed by cellulose, a natural polymer. Starch, resin secreted by certain trees, and rubber (Fig. 13.1) are also examples of natural polymer. Proteins and nucleic acids are two other types of natural polymers, which are produced by living organisms.

Plastic materials, a great number of textiles (Fig. 13.2), Plexiglas, and several type of adhesives... are all examples of polymers that are synthesized by the industry and that we encounter in several applications to our daily life.

Figure 13.2
Synthetic textiles present a great variety of types, properties and uses.

Activity 1 Construction of a molecular model of polyethylene

Objective

Construct the molecular model of a synthetic polymer.

Material

Molecular models kit.

Procedure

Using the appropriate balls and sticks, build the molecular model of ethylene.

Construct 4 or 5 models representing the formula $-CH_2-CH_2-$. Connect these models to each other. Link each extremity of the chain to a hydrogen atom (Fig. 13.3).

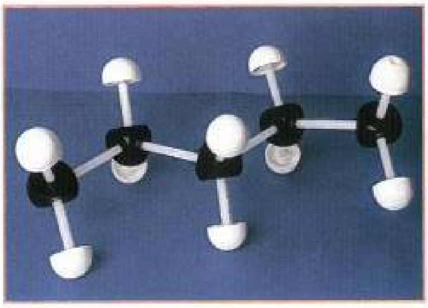


Figure 13.3
Molecular model of polyethylene.

Evolution of the polymers industry

The industry of polymers began at the beginning of the 19th century with the addition of sulfur to the natural rubber at high temperature. This operation is known as "vulcanization", and serves to improve the properties of rubber.

Around 1860, several objects derived from a semi-synthetic resin known as "parkesine", which is a form of plastified nitrocellulose, were synthesized.

The celluloid, another form of plastified nitrocellulose, was elaborated by the Hyatt brothers around 1870, and it enjoyed great commercial success.

Still, the first totally synthesized polymer was known as "bakelite". The Belgian chemist, Leo Baekeland, must be recognized as the first to manufacture it around 1906.

- A polymer is said to be plastified when it is rendered flexible by adding it to a certain substance known as plastifiants.

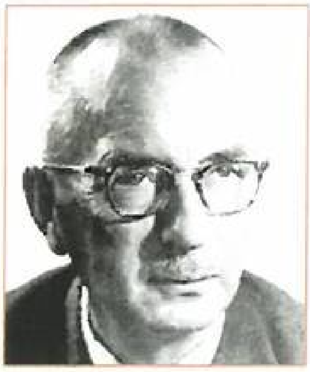


Figure 13.4

Karl Ziegler (1898-1973), a German chemist, received the Nobel Prize in chemistry in 1963. He contributed to the progress of the industry of polymers, by developing catalysts that work by improving the properties of polymers during their synthesis.

Then, starting in1920, a real industry of synthetic polymers was developed, following the achievements of the German chemist Staudinger, who was the first one to claim that polymers were macromolecules.

Between 1920 and 1950, the majority of synthetic polymers known nowadays were already elaborated: acrylic resins, Plexiglas, polystyrene, Teflon, nylon, polyesters, and synthetic rubber...

Two major names contributed to the progress of this industry: Karl Ziegler (Fig. 13.4), who synthesized polyethylene in 1953, and Giulio Natta (Fig. 13.5), who synthesized in the following year polypropene in 1954.

The industry of polymers has contributed to the synthesis of several materials, which are of great importance to society, and which still affect great promise for the future.

■ Synthetic organic polymers

All synthetic polymers that we have mentioned earlier are of organic nature. Actually, organic polymers form the major class of synthetic polymers due to their properties and their applications.

Our study in this chapter is limited to organic polymers.

The products of cracking and reforming of oil, like ethylene, propene, benzene, and their derivatives form the principal raw materials of synthetic organic polymers, due to their abundance and their fair price.

13.2 Characteristics and uses

■ Types of chains

Structure wise, polymers can be linear chains (Fig. 13.6 (a)). A great number of macromolecules possess this structure.

Macromolecules can also have ramifications, which are chains of reduced length attached at certain points to the main chain.

In this case these polymers are said to be branched chains (Fig. 13.6 (b)).

When the branching of these macromolecules takes place in three dimensions of space, polymers are said to be crossed chains. This structure forms a three–dimensional network (Fig. 13.6 (c)).

According to the structure of these chains, polymers behave in different ways vis-a-vis heat.

Figure 13.5

Giulio Natta (1903-1979), an Italian chemist, shared the Nobel Prize in chemistry with Ziegler in 1963, for his achievements in the elaboration of polymers.

■ Thermoplastics

Thermoplastics constitute around 90% of synthetic polymers. They can soften and flow when they are heated at a certain temperature range, and they can harden again when they are taken back to the ordinary temperatures. This property allows them to get their desired forms when they are soft.

The cycle of softening and hardening can in principal be repeated whenever wanted; allows the recycle of thermoplastic articles (Fig. 13.7).

Figure 13.7
These objects of polyethylene are thermoplastic. They can be softened and hardened several times. They can be recycled.

Thermoplastics have a structure of either linear or slightly ramified chains. When heated, these chains can slide past each other, producing a soft state.

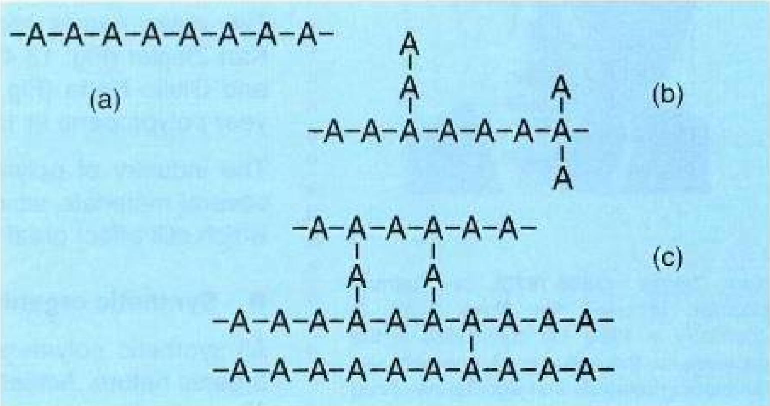


Figure 13.6
The three types of chains in the structure of polymers:
a) linear; b) branched; c) crossed.

Thermosets

Thermosets do not have the property to the soften when they are heated. Above a certain temperature, they undergo decomposition.

Due to this behavior, thermosets are given a definite form when they are synthesized and cannot be recycled in a simple and direct method (Fig. 13.8).

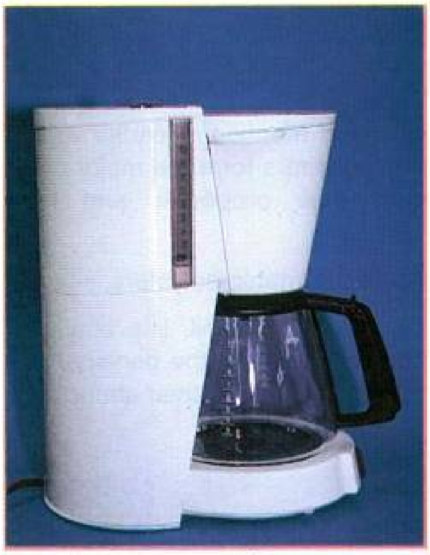


Figure 13.8
The coffee pot is thermoset. Heated above a certain temperature, it will decompose but not soften.

Thermosets possess a structure of crossed chains, which are tightly rigid and attached, so that they cannot slide past each other due to heating; this is why these types of polymers cannot soften under the effect of high temperature.

Elastomers

Elastomers are a class of polymers, which are momentarily distorted; they are not very rigid, still they are not considered thermoplastic.

Actually, elastomers can be stretched out by traction up to 3 to 10 times their initial length, and they can retract to their initial length when the traction stops (Fig. 13.9).

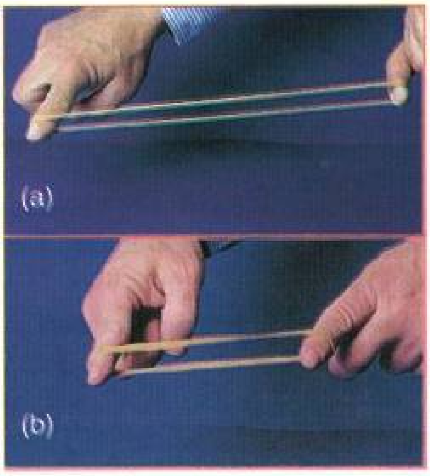


Figure 13.9
The rubber band can be stretched out due to traction (a). It returns to its initial length when the traction is stopped (b).

Elastomers have crossed chains with a weak crossing density. This structure allows them to be elastic but not to soften under the effect of heat (Fig. 13.10).

Mechanisms of polymerization

Synthetic polymers are formed principally by an addition mechanism, known as addition polymerization or a condensation

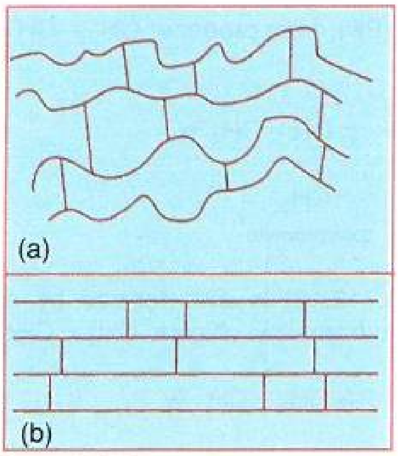


Figure 13.10

Structure of the cross-linked chain of an elastomer:
(a) Before traction
(b) During the reaction

Figure 13.11

Children's gifts made from polystyrene.

- When the degree of polymerization n equals 2, then the polymer is a dimer, and when n equals 3, the polymer is a trimer ...

The value of n can reach 10^6.

polymerization mechanism referred to as condensation polymerization.

Addition Polymerization

The formation of polyethylene (PE) is an example of addition polymerization, where n molecules of ethylene associate with each other to form a macromolecule of the polymer:

$$\underset{\text{ethylene}}{n\,CH_2 = CH_2} \quad \rightarrow \quad \underset{\text{polyethylene}}{-\!\!\left(CH_2 - CH_2 \right)\!\!-_n}$$

In such a mechanism, the reaction should be initiated first. In the second step, the chain of the polymer increases, this is propagation. Finally, the growth of the chain is stopped. This last step is the termination step.

Structural elements

Polyethylene is formed by a series of units of the formula $-CH_2-CH_2-$, known as repeating units and having the molecule of ethylene $CH_2 = CH_2$ as their origin. This molecule is the monomer of polyethylene.

A monomer is the starting molecule from which the polymer is formed. The macromolecule of a polymer is formed by the association of a large number of molecules of the monomer.

Polyethylene is formed by only one type of monomer, ethylene. We will see later on, other examples on which the polymer is formed by two or more types of monomers.

When the polymer is formed by the association of only one type of monomers, it is referred to as homopolymer. When it is formed by the association of two or more types of monomers, it is referred to a copolymer.

The macromolecule of polyethylene is represented by the formula: $-\!\!\left(CH_2 - CH_2\right)\!\!-_n$. The number n is the average number of monomers (or units) in a molecule of the polymer. It designates the degree of the polymerization of the polymer.

In the case of a copolymer of formula $-\!\!\left(A - B\right)\!\!-_n$, for example, the degree of polymerization n, is the average number of units $-\!\!\left(A - B\right)\!\!-$ in the molecule of the polymer.

The degree of polymerization is equal to the average number of units in a molecule of the polymer.

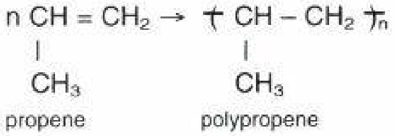
Other examples of addition polymerization are polystyrene (PS) (Fig. 13.11) which is formed from styrene or phenylethylene $C_6H_5 - CH = CH_2$:

styrene polystyrene

Figure 13.12

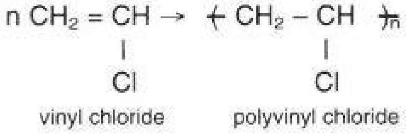
Polyvinyl chloride is used in the manufacture of pipes.

The formation of polypropene (PP), from propene $CH_3-CH=CH_2$:



$$n\,\underset{\substack{|\\ CH_3}}{CH}=CH_2 \rightarrow -\!\!\left[\underset{\substack{|\\ CH_3}}{CH}-CH_2\right]\!\!-_n$$

Polyvinyl chloride (PVC) (Fig. 13.12) is also formed by an addition polymerization reaction from vinyl chloride $CH_2=CHCl$



$$n\,CH_2=\underset{\substack{|\\ Cl}}{CH} \rightarrow -\!\!\left[CH_2-\underset{\substack{|\\ Cl}}{CH}\right]\!\!-_n$$

Table 13.1 summarizes the name, the formula, the symbol and some properties and uses of the preceding polymers.

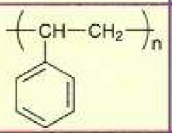
Name	Condensed Structural Formula	Symbol	Properties of usage
Polyethylene	$-\!\!\left[CH_2-CH_2\right]\!\!-_n$	PEHd* PELd*	nonreactive, flexible, impermeable to water vapor. Wrapping gifts , containers ...
Polystyrene		PS	Very hard and thermoplastic. Pots, covers, car dash board.
Polypropene	$-\!\!\left[\underset{\substack{|\\ CH_3}}{CH}-CH_2\right]\!\!-_n$	PP	Low density. Covers, bottles, pipes...
Polyvinyl chloride	$-\!\!\left[CH_2-\underset{\substack{|\\ Cl}}{CH}\right]\!\!-_n$	PVC	Hard and rigid. Tubes, pipes. Made plastic: shower curtains, impermeable synthetic leather ....

Table 13.1

***PEHd** : polyethylene high density: linear chain slightly branched.

***PELd** : polyethylene low density: many branches, less compact and less rigid than PEHd.

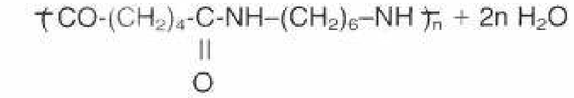
Condensation Polymerization

In condensation polymerization, two or more different compounds react with each other to form the chain of the polymer. In general, the reaction takes place with the elimination of small molecules such as NH_3, HCl, or H_2O.

Polyamides (PA) form a class of polymers synthesized by condensation polymerization. The reaction of polymerization takes place between a dicarboxylic acid $R(CHOO)_2$ and a diammine $R'(NH_2)_2$ with the elimination of molecules of water.

Nylon 6,6 is a polyamide, (Table 13.2) formed by a reaction between hexanedioic acid $HCOO-(CH_2)_4-COOH$ (or adipic acid) and 1,6-diaminohexane $NH_2-(CH_2)_6-NH_2$ (or hexamethylene diamine).

$$n\ HCOO{-}(CH_2)_4{-}COOH + n\ HNH{-}(CH_2)_6{-}NH_2 \rightarrow$$



$$\left[CO{-}(CH_2)_4{-}\underset{\underset{O}{\|}}{C}{-}NH{-}(CH_2)_6{-}NH \right]_n + 2n\ H_2O$$

Nylon 6,6

The second group of the diacid on one extremity of the chain and the second group of the diamine or the other extremity permit the chain to grow.

Nylon 6,6 and a great variety of other nylons have large applications in different fields (Fig. 13.13).

Figure 13.13

The fishing net is made up of nylon.

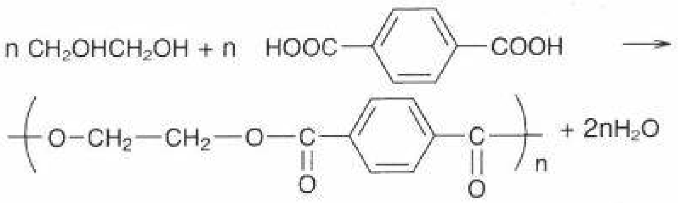
Polyesters form another class of polymers synthesized by condensation. Polymerization takes place between a dicarboxylic acid $R(COOH)_2$ and a diol $R'(OH)_2$, with the elimination of water molecules. This is polyesterification.

A polymer formed by polymerization of 1,2-ethanediol (or glycol) $HOCH_2 - CH_2OH$ and 1,4 dicarboxylic acid benzene (or terephthalic acid) $C_6H_4(COOH)_2$ is known by the name polyethylene tetephthalate (PET) (Table 13.2).

It is known commercially as Tergal or Mylar according to its applications (Fig. 13.14). The polymerization is represented by the following equation:

Figure 13.14

The material of these curtains is made up of Tergal.



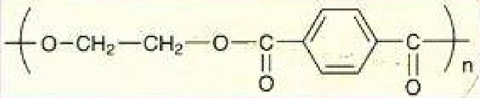
Name	Formula	Symbol
Nylon 6-6	$(CO{-}(CH_2)_4{-}CO{-}NH{-}(CH_2)_6{-}NH)_n$	PA
Polyethylene terephthalate		PET

Table 13.2

Dacron: polyethyleneglycol terephthalate.

Activity 2 Action of some chemical products on synthetic polymers

- For each polymer, and according to the action of each reactant on it , what conclusion can be drawn?

Objective

Study the resistance of polymers vis-a-vis certain chemical products.

Equipment and reagents

Twelve test tubes with stoppers. Wood pincers.
Small portions of each polymer: PE, PVC, PA.
Acetone. Ethanol. Concentrated solution of H_2SO_4. A saturated solution of NaOH.

Procedure

Take 4 test tubes and add 3 mL of acetone in tube 1; add 3 mL of ethanol in test tube 2; add 3 mL of the acid solution in test tube 3, and 3 mL of the sodium hydroxide solution in tube 4.
Add to each tube, a small portion of PE. Close the tube and shake. Observe any changes (Fig. 13.15).
Repeat the same procedure with a portion of the remaining two polymers.

Figure 13.15
Action of concentrated sulfuric acid on PE.

Observation and interpretation

The results of the action of each product with the polymers PE, PVC, and PA are assembled in table 13.3.

Polymer Product	PE	PVC	PA
Acetone	(S+W)*	M	S
Ethyl alcohol	S	S	S
Concentrated sulfuric acid	S	S	W
Saturated sodium hydroxide	S	S	W

Table 13.3
S (strong resistance), M (medium resistance), W (weak resistance).

- The high density PE's are resistant to acetone while the low density PE's are not resistant.

According to the results observed, we can deduce that polymers, polyethene (PE), polyamides (PA) and polyvinylchloride (PVC), are resistant to the action of organic products (acetone, ethyl alcohol) and inorganic products (concentrated H_2SO_4, saturated NaOH).

Characteristics and applications

Synthetic polymers possess a large variety of properties and characteristics according to their chemical composition (nature of monomers), their structure, their mode of manufacture, and the products that are added to them (additives)... .

- **Chemical inertness**

The majority of synthetic polymers are chemically inert.

This property allows them to have several applications such as containers for several products, often reactive or corrosive (Fig. 13.16), and materials for canalization and wrapping, in construction, and in automotive industry, textiles... .

Figure 13.16

Polymers are used as containers for corrosive chemical products.

- **Plastic properties**

Thermoplastics form around 90% of the total number of polymers. The ease by which they can be softened and easily given another shape, in addition to the fact that they can be recycled, are factors that make their applications diverse.

- **Insulating properties**

Polymers are generally very good electric, thermal and acoustic insulators. They are used as sheaths for electric lines and as materials for thermal and acoustic insulation in construction (Tefal, insulating mousse of polyurethane).

- **Hardness and rigidity**

Thermosets polymers, hard and rigid have several applications. Their hardness and their insulating properties, associated together, make them suitable for the synthesis of boards of electric circuits and of insulating parts of utensils (Fig. 13.17), casings for electrical equipment (bakelite)... They are also used as hard covers for the surface of furniture (Formica).

Figure 13.17

The handle of the frying pan is characterized by its hardness and isolation of heat.

- **Impermeability**

Polymers are in general impermeable to water and gases; that is why they are used as canal pipes.

- **Transparency**

Certain polymers are characterized by their transparency, which allows them to be used as contact lenses, or in other applications of glass: containers, windows,..(Plexiglas).

- **Elasticity**

Synthetic elastomers, characterized by their elasticity, replace the natural rubber in a great number of applications; they are used in the manufacture of wheels, pipes, and clothes for protection from water (diving equipment).

- **Lightness**

Polymers have low density, usually close to unity. This lightness, together with their remaining properties is another important factor in their applications.

Additives

Certain products are usually added to synthetic polymers in order to improve their properties or add to them new properties. They are designated by the word "additive".

Antioxidants, for example, protect the polymers from the action of oxygen O_2 and ozone O_3.

UV stabilizers protect them against solar rays and atmospheric agents in general.

Plastifying compounds make these polymers more elastic and flexible. Lubricants reduce the problems of friction. Colored pigments give them colors (Fig. 13.18)...

Other materials and products are added to polymers in order to increase their strength. The polymers resulting constitute what is known as "composites".

This view of the types of synthetic polymers, their characteristics, and their domains of applications show the importance of these compounds in modern societies.

Figure 13.18

Plastic material can be easily colored.

13.3 Economic aspect

The types of polymers that are known, the diversity of their properties, and their applications, exceed the aspects that we have been discussing.

For more than 60 years, the industry of polymers has become a worldwide known sector, and is of major importance to the chemical industry.

At the national level, the synthesis or manufacture of plastic objects has developed and improved in quality. This was achieved by multiplying the nature of the materials treated and the increased different domains of their applications (Fig. 13.19).

Figure 13.19

Water reservoirs, products of the national industry of polymers.

Actually, polymers can replace metals in a great number of ways, for example, in construction, and automotive industry and cans manufacturing.

They can also replace glass (Plexiglas), natural rubber, and natural textile fibers. Their use allows us to safeguard the raw materials to certain extent.

13.4 Impact on the environment

Because of their stability and chemical inertia, synthetic polymers are not dangerous neither to the human health nor to life of fauna and flora. Therefore, the wastes of the polymers do not constitute a major threat to the environment.

However, some raw materials of polymers are dangerous pollutants or are carcinogenic.

Figure 13.20

Plastic wastes thrown away in nature, makes nature a "wastebasket".

Wastes of synthetic polymers, however, constitute visual pollution. If they are thrown in nature, they can last for several years without being degraded, giving to nature the aspect of "waste basket" (Fig. 13.20).

However, we mention one type of pollution due to polymers. When burned in open dump, polymer wastes release toxic and

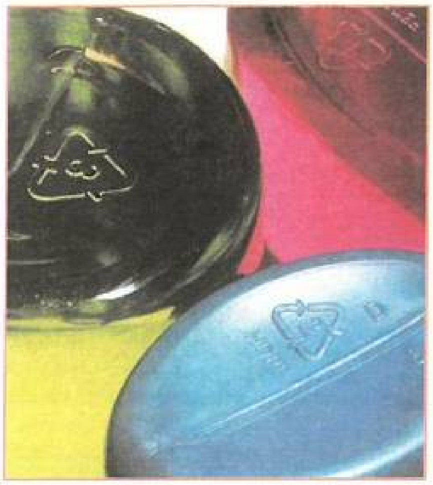


Figure 13.21

The symbol appearing on the plastic article means that this article can be recycled. As the number of internal arrows becomes smaller, the recycling process becomes easier.

polluting gases in the atmosphere: hydrogen chloride $HCl_{(g)}$, carbon dioxide $CO_{2(g)}$ ...

Biodegradable polymers are products synthesized to solve the problem of the polymers waste .

The recycling of synthetic polymers remains nowadays the most practical solution and the most economical way to get rid of the wastes.

The majority of polymers are recyclable (Fig. 13.21).This way they can be used again in the market place and at the same time, raw material can be saved for further use.

Chapter review

- Polymers are of synthetic or natural origin.
- The structure of synthetic polymers can be either of linear chains, or branched or crossed.
- Thermoplastic polymers can soften when they are heated and then harden when taken back to the ordinary temperatures. This property is due to their structure of linear or slightly branched chains.
- Thermoset polymers do not have the property of softening under the effect of heat. This is due to the crossed chain structures.
- Addition polymerization corresponds to the addition of a certain number of molecules in order to form a macromolecule of the polymer.
- Condensation polymerization corresponds to the reaction of several molecules among each other, with the elimination of small molecules, in order to form the macromolecule of the polymer.
- A monomer is the basic molecule of a polymer. When a polymer is formed by one type of monomer, it is called a homopolymer. When it is formed by many types of monomers, it is called a copolymer.
- The degree of polymerization of a polymer is equal to the average number of units in the molecule of the polymer.
- Synthetic polymers are generally characterized by chemical inertness, flexibility, insulating properties (from both electricity and heat), hardness and rigidity, transparency, lightness... All these properties make the applications of polymers diverse.
- Recycling is an economical and profitable way to treat wastes of polymers.

Laboratory Investigation

LI

I – The flame test of PVC and PE

Objective

Detect the presence of chlorine in synthetic polymers.

Equipment

Two wires of copper. Bunsen burner. Two metallic tongs. A piece of PVC. A piece of PE.

Procedure

- Working under hood, grab the copper wire with the tongs and heat it on the Bunsen burner till it turns red.
- Touch the piece of PVC with the hot copper wire until a part of it melts and attaches to the wire.
- Hold the wire with the PVC attached and put it over the flame again. Notice the color.
- Repeat the same procedure for the PE.
- Compare the colors of the flame of the two tests and conclude.

II– Preparation of nylon 6,6

Objective

Prepare a synthetic polymer in the laboratory

Equipment and reagents

100 mL beaker. 10 mL graduated cylinder.
Metallic pincer.
A glass rod.
A solution of 5% adipyl chloride in CCl_4 .
5% aqueous solution of hexamethylenediammine.

Procedure

The experiment is done under the hood.
$ClCO\ (CH_2)_4COCl$ is used instead of adipic acid $HCOO(CH_2)_4COOH$ because it is more reactive. In this case the reaction is fast and complete.

- Add 10 mL of the solution of "adipyl Chloride" to the flask.
- Add slightly (using the glass rod) the solution of hexamethylenediammine, in order to leave the two solutions separated (Fig. 13.22).
- The polymerization reaction takes place at the interface.
- A thin film of the polymer is formed.
- Using the metallic pincer, take away the nylon fiber and try to roll it on the glass rod (Fig. 13.22).
- Rinse with water and leave it to dry.

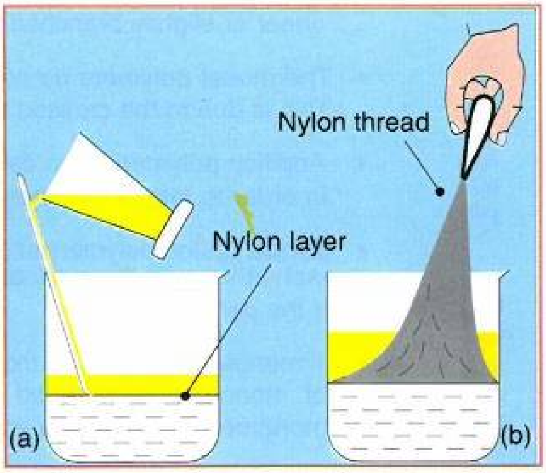


Figure 13.22
(a) The glass rod permits the two solutions to stay separated.
(b) The nylon thread is withdrawn from the interface of the two solutions by a metallic tongs.

Documentary activity 1

Economic importance of the polymers industry

The polymers industry is an important sector in the chemical industry, due to the diversity of the products, the diversity of their characteristics and the domains of their applications, in addition to their impact on the economical status of the country.

The most well known polymers are polyethylene of either high or low density (PEHd, PELd), polyvinyl chloride (PVC), polypropene (PP), polystyrene (PS), polyamides, polyesters, acrylic, and synthetic rubber... are products of great tonnage in industrialized countries.

Their properties, and most importantly their resistance to chemical reagents and bad weather, plasticity, insulation against sound, electricity and heat, lightness, hardness and rigidity (of certain classes), elasticity (elastomers), transparency... make them suitable in a great number of applications.

Polymers can be divided in principle to 4 classes in view of their applications:

Technical plastic: these are polymers used in construction, in the industry of vehicles (autos, planes, trains ...), in electronics, in medical instruments, and in utensils... .

Textile fibers: these are made up of polyamides, polyesters, acrylic, vinylic, polypropene and others... they constitute more than half the worldwide production of textile fibers. They are used in the manufacture of clothes, carpets, textile of furniture... .

Rubbers: these replace natural rubber in all its applications. They are even more usual than the natural ones, and they are also sold more in the market place.

Adhesives: these are used to attach materials together at the level of their surface like the materials used in painting or varnishing.

Questions

1) Cite some properties of synthetic polymers.
2) Cite the different categories of polymers according to their applications.
3) Does the application of polymers cover large domains of life in modern societies?
4) What can we deduce about the importance of these materials?

Documentary activity
2

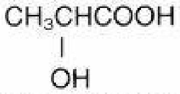
Biodegradable polymers

Nowadays, a biodegradable class of polymers is known commercially. It constitutes of a number of polyesters such as glycolic polyacid (GPA), lactic polyacid (LPA), poly-2-hydroxybutyrate (PHB)..., in addition to their copolymers.

The monomer of each of these polymers contains simultaneously a carboxylic acid function $-COOH$ and an alcohol function $-OH$.

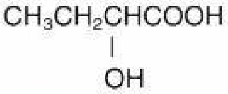
Glycolic acid : $HOCH_2COOH$

Lactic acid :



$CH_3\underset{\underset{OH}{|}}{C}HCOOH$

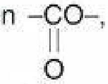
2-hydroxybutyric acid :



$CH_3CH_2\underset{\underset{OH}{|}}{C}HCOOH$

Polymerization is a polyesterification, which takes place by the elimination of one molecule of water from each of the two monomers.

In polyesters, the ester function $-\underset{\overset{\|}{O}}{C}O-$, which attaches two monomers together, is degraded by the action of microorganisms on water.



In the USA and some European countries biodegradable polyesters are used to synthesize flasks, bottles, and wrapping films. They provide, in this way, a partial solution to the problem of plastic wastes.

Polyesters, products of the degradation, being natural products of the metabolism of the human body, have also interesting applications in the surgical domain (sutures) as well as in the wrapping of medications.

Other biodegradable polymers were synthesized by incorporating starch in the structure of known polymers. By this method, the wastes of the polymers ordinarily unchanging with time are made biodegradable. In regard to the cost of the production of these polymers and with respect to the stability problems encountered during their synthesis and usage, this method was not successful.

Questions

1) Is the polyester GPA a homopolymer or a copolymer? Write the synthesis reaction of the dimer formation of glycolic acid.
2) Which part of the macromolecule of the biodegradable polyesters is attacked by the microorganisms?
3) Why do these polymers have medical applications (sutures, wrapping of medications)?
4) Why is the polymer, to which starch is incorporated, not a solution to the problem of plastic wastes?

Exercices

1 Teflon is a polymer of the formula $-\!\left(CF_2-CF_2\right)\!-_n$. It is characterized by its great chemical inertness; its softening temperature is high and has a non-adherent property.

a) Give the formula of the monomer.
b) Write the equation of the polymerization reaction.
c) Is it a polyaddition or polycondensation? Justify your answer.
d) By which means can we stop the growth of the chain?
e) Teflon, used to cover frying pans and casseroles, are known to be made up of Tefal. Explain why it is convenient for such a use?

2 An organic compound contains only carbon and hydrogen. The mass percentages of these elements are:

% C	92.30
% H	7.70

a) Determine the molecular formula of this compound knowing that its molar mass is 104 g.mol^{-1}.
b) Give the structural formula knowing that it contains an aromatic ring C_6H_5-.
c) This compound can be polymerized. Write the formula of the reaction. Identify the type of polymerization.
d) If the average molar mass of the polymer is 624 kg.mol^{-1}, calculate its degree of polymerization.

3 Propene $CH_3-CH=CH_2$ forms a polymer known as polypropene (PP), widely used in the manufacture of plastic articles, containers, pipes, and floor coverings .... .

a) Write the equation of the polymerization reaction.
b) Why does this polymer have these plastic properties? Explain.

4 Nylon 6,6 is produced from the reaction between hexanedioic (or adipic) acid $HCOO(CH_2)_4COOH$ and hexamethyldiammine $H_2N\,(CH_2)_6NH_2$.

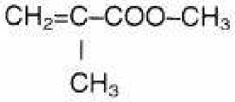
a) Write the equation of the reaction.
b) To which family of polymers does nylon belong?
c) Calculate the molar mass of one repeating unit of this macromolecule.
d) The average molar mass of a sample of nylon is 34000 g.mol^{-1}, calculate the degree of polymerization of this sample.

M(H) = 1 g.mol^{-1}, M(C) = 12 g.mol^{-1}, M(N) = 14 g.mol^{-1}, M(O) = 16 g.mol^{-1}.

5 The monomer of polyethylene is ethylene $CH_2 = CH_2$.

a) Give the formula of this polymer.
b) This polymer is thermoplastic. Explain what this means. Explain the relation between this property and the structure of this polymer.
c) A sample of polyethylene presents an average degree of polymerization equal to 5000. Calculate the molar mass of this sample.

6 Methyl methacrylate:



$$CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-COO-CH_3$$

is the monomer of a commercialized polymer known as Plexiglas. This polymer is known for its remarkable transparency.

a) Write the polymerization reaction. What is the type of polymerization?
b) Is Plexiglas a polyester?

7 Quantitative analysis of a polymer gives the following mass percentages:

% C	63.72
% H	9.73
% N	12.40

a) Determine the empirical formula of the polymer.
b) If the monomer is a monoamino acid with no branched carbon chain, where the carboxyl group –COOH, is at one end and the amino group, $-NH_2$, on the other end. Give the structural formula of the monomer.
c) Write the equation of the polymerization reaction.
d) To what class of polymers does this studied polymer belongs? Justify your answer.
e) Calculate the molar mass of the dimer.

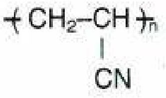
8 The combustion of polyvinyl chloride (PVC) produces carbon dioxide, hydrogen chloride and water.
a) Write the equation of the reaction.
b) If hydrogen chloride is released into the atmosphere by the incineration of plastic bottles in open dumps, what type of pollution is produced?
c) Polyvinyl chloride is a thermoplastic polymer. Cite an effective way to treat the wastes of PVC.

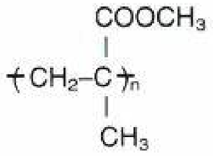
Evaluation

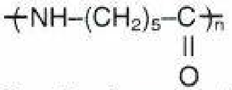
Applying knowledge

1 Given the formulas of the polymers:

1) $\left(CH_2-CH_2 \right)_n$

2)

$\left(CH_2-\underset{CN}{\underset{|}{CH}} \right)_n$

3)

$\left(CH_2-\overset{COOCH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}} \right)_n$

4)

$\left(NH-(CH_2)_5-\underset{O}{\underset{\|}{C}} \right)_n$

1) Give the formula of each monomer of these polymers.
2) Mention, in each case, if this is a polyaddition or a polycondensation.
3) Write the equation for each corresponding reaction.

2 Given the properties in the following table, classify the polymers as either thermoplastic or thermoset.

Polymer	Properties
Nylon 6,6	Mild objects, textile fibers, recyclables.
Formica	Rigid and hard. Tough coverings of furniture. Non recyclables.
Bakelite	Hard and rigid resin. Household appliances covers. Adhesives. Buttons. Non recyclables.
Polypropene	Mild objects. Pipes. Containers. Work clothing. Recyclables.

3 The estimated mass of a household solid waste produced daily in Lebanon is 4 x 10^6 kg. The weight percentage of plastic wastes is 11 %.

It is supposed that 1 % of these wastes is due to mineral water bottles made of PVC, and at least 30 % of these bottles are burned in open dumps.

a) If the products of the combustion of PVC are $CO_{2(g)}$, $H_2O_{(g)}$ and $HCl_{(g)}$, write the corresponding equation of the reaction.
b) If 50 % of $HCl_{(g)}$ are released into the atmosphere, calculate the average mass of hydrogen chloride released every day into the atmosphere by this operation.

4 Mylar is a polyester synthesized from ethylene glycol $HOCH_2CH_2OH$ and terephthalic acid $HCOOC_6H_4COOH$

It is used to cover electric wires, and in the manufacture of photographic films, cassette tapes and beverage bottles.

a) Write the equation of the formation of a repeating unit.
b) Is it an addition polymerization or a condensation polymerization? Justify your answer.
c) Is Mylar a homopolymer or a copolymer? Justify your answer.
d) Cite some of the properties of this polyester that make it convenient for the above uses.

Designing an experiment

5 Procedure

Add 2 mL of styrene and 8 mL of toluene (solvent), while working under the hood, to a test tube.

Add a pinch of benzoyl peroxide to the test tube.

Place the tube in a water bath and heat it until it boils gently. Keep heating it for about 15 minutes.

Cool the tube and then add its contents to 60 mL of ethanol.

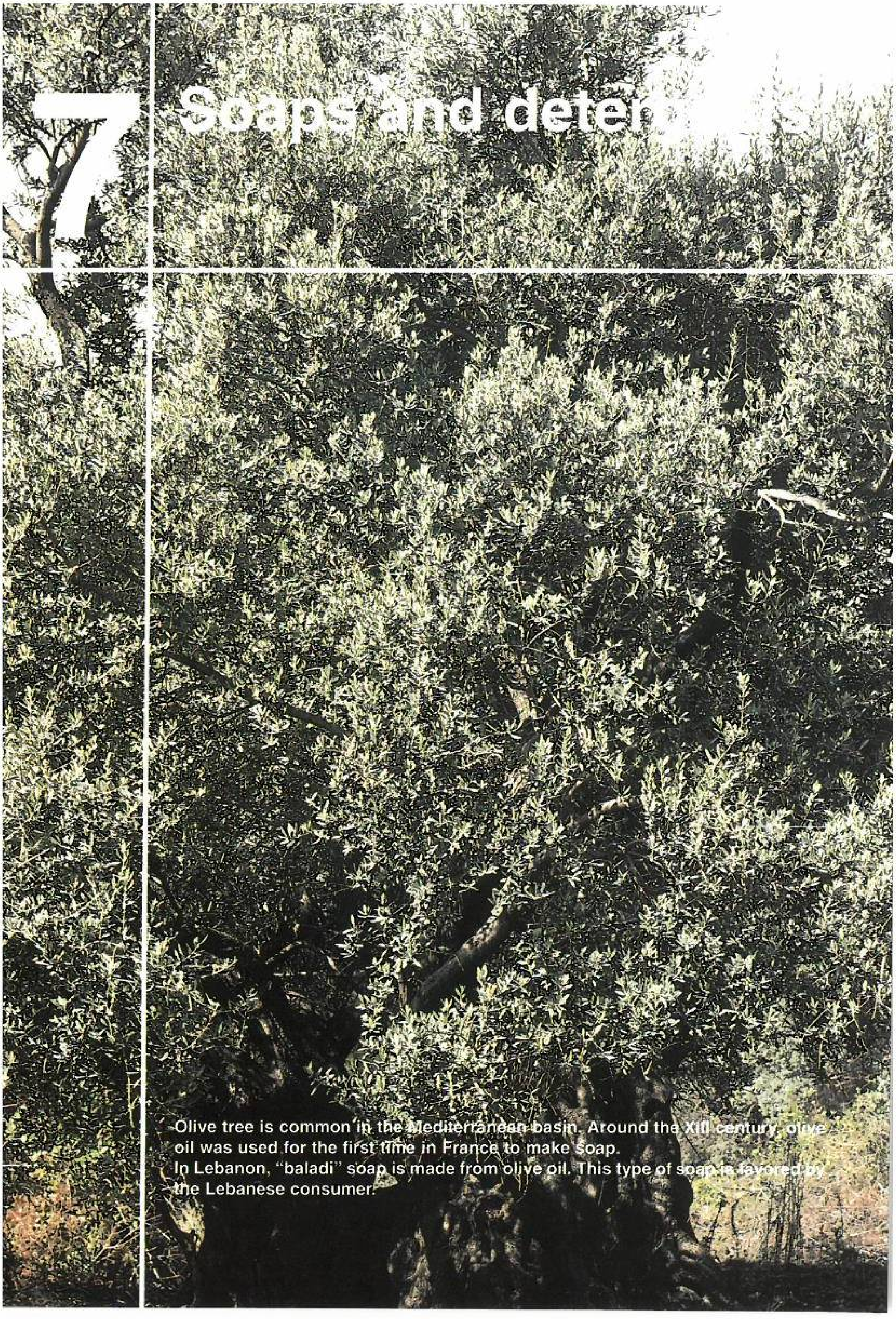
Dry the obtained solid mass.

Questions

a) Why is it necessary to work under the hood?
b) What is the role of benzoyl chloride?
c) What type of polymerization is this? Write the corresponding equation. Name the polymer.
d) How can you verify that the prepared polymer is thermoplastic? Describe how we can proceed.

7

Soaps and detergents



Olive tree is common in the Mediterranean basin. Around the XIII century, olive oil was used for the first time in France to make soap.
In Lebanon, "baladi" soap is made from olive oil. This type of soap is favored by the Lebanese consumer.

Soaps that are manufactured from natural fats have been known for centuries.
Synthetic detergents manufactured from organic raw materials since the beginning of the 20th century, are obtained by synthesis.
The detergent properties of soaps and synthetic detergents depend on their structure.
How are soaps obtained? And how do they act as detergents?
What are the constituents of synthetic detergents?
Do these detergents pose pollution problems?

SOAPS AND DETERGENTS

14

Objectives

- Recognize the raw materials used in the preparation of soaps.
- Recognize the saponification reaction.
- Identify the principle of detergency.
- Identify the constituents of synthetic detergents.
- Recognize the characteristics of surfactants.
- Recognize pollution problems posed by synthetic detergents.

Prerequisites

- Hydrocarbons.
- Organic and petrochemical products.
- Acid-base. pH.
- Organic functional groups.
- Notion of biodegradability.

Chapter content

14.1 Preparation of soaps.
14.2 Principle of detergency.
14.3 Synthetic detergents: composition and properties.
- Chapter review
- Method sheet
- Documentary activities
- Exercises
- Evaluation

14.1 Preparation of soaps

Soaps, known for over 2300 years, were used more for medicine and for purification than as washing detergents.

In the Middle Ages, their use evolved, and since the 19th century, the manufacturing of soap became an important industry, as it became essential for the comfort and hygiene of mankind.

Raw materials

Fatty acids and sodium or potassium hydroxide are the primary raw materials for the manufacturing of soaps.

Fatty acids used in the manufacture of soaps are constitueats of animal fats and vegetable oil.

These fats include cattle's tallow (beef, sheep, goat, horse ...) and fats of some grains and fruits (palm grains, coconut).

Oils of animal and vegetable origin are also used in the manufacturing of soap such as whale oil, copra oil, soya oil, colza oil and olive oil ... .

Glycerol

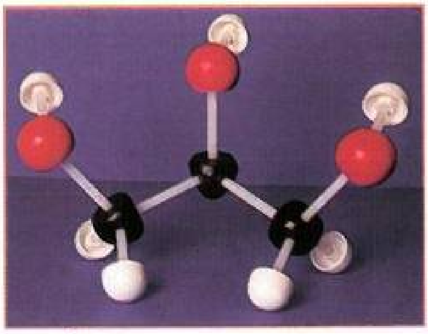


Figure 14.1

The ball-and-stick molecular model of 1,2,3-propanetriol or glycerol.

Glycerol or 1,2,3-propanetriol (Fig. 14.1) has three hydroxyl groups, two are primary and one secondary:

$$\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Natural fatty acids

Natural fatty acids are carboxylic monoacids. They have linear carbon chains with an even number of carbon atoms (C_4 - C_{22}) with some exceptions. The chain may be saturated or unsaturated (Table 14.1), with the latter having Z configuration of the double bond.

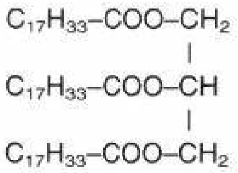
Triglycerides

Triglycerides are triesters produced by esterification of fatty acids and glycerol. The general formula of a triglyceride is given by:

$$\begin{array}{r} R_1\text{–COO–}CH_2 \\ | \\ R_2\text{–COO–}CH \\ | \\ R_3\text{–COO–}CH_2 \end{array}$$

In this case, the triglyceride is mixed, formed from three different fatty acids.

Triglycerides formed from one type of fatty acids are also known. In this case, the three groups R_1, R_2 and R_3 are identical. Example:



$$\begin{array}{c} C_{17}H_{33}-COO-CH_2 \\ | \\ C_{17}H_{33}-COO-CH \\ | \\ C_{17}H_{33}-COO-CH_2 \end{array}$$

Olein

Table 14.1 lists the principal fatty acids used in manufacturing soaps.

Common name	Condensed-structural formula	X : Y
lauric acid	$CH_3-(CH_2)_{10}-COOH$	12 : 0
palmitic acid	$CH_3-(CH_2)_{14}-COOH$	16 : 0
stearic acid	$CH_3-(CH_2)_{16}-COOH$	18 : 0
oleic acid	$CH_3-(CH_2)_7-CH{=}CH-(CH_2)_7-COOH$	18 : 1
linolic acid	$CH_3-(CH_2)_4-(CH{=}CH-CH_2)_2-(CH_2)_6-COOH$	18 : 2
α–linolenic acid	$CH_3-CH_2-(CH{=}CH-CH_2)_3-(CH_2)_6-COOH$	18 : 3

Table 14.1

X, in the third column, represents the number of carbon atoms in the formula of the acid and Y is the number of double bonds.

Table 14.2 gives the mass percentage of fatty acids originated from fats most commonly used in making soap.

x:y	< 16	16:0	18:0	18:1	18:2	18:3
Beef fat	2.5 - 4	24 - 27	15 - 29	30 - 42	2 - 4	0.5 - 2
Soya oil	-	8 - 12	2 - 4.5	20 - 25	51 - 58	5 - 8.5
Colza oil	-	4 - 6.5	1 - 2	55 - 62	19 - 28	7 - 10
Copra oil	77 - 81	1 - 9	2 - 3	7 - 8	1.5 - 3	-
Olive oil	-	8.5 - 14	3 - 5	61 - 80	3 - 15	0 - 0.5

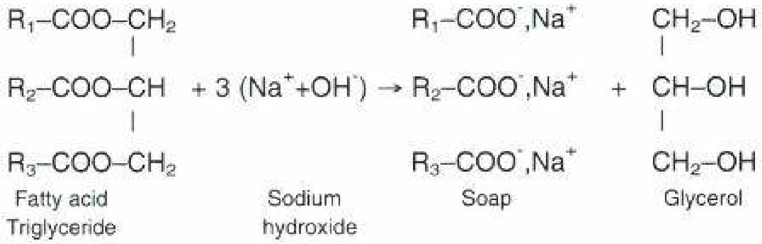
Table 14.2

The minimum and maximum values are given for each mass percentage because the percentage depends on the origin of the fat.
The symbol X:Y are the same as in table 14.1.

Soaps

Sodium (or potassium) carboxylates of fatty acids are called soaps.

Soaps are obtained by a reaction between a triglyceride and a strong alkali sodium (or potassium) hydroxide. For example, with sodium hydroxide, the reaction is given below:



$$\begin{array}{lclcl} R_1\text{–COO–CH}_2 & & R_1\text{–COO}^-,Na^+ & & CH_2\text{–OH} \\ \quad\;\; | & & & & \;\; | \\ R_2\text{–COO–CH} & +\,3\,(Na^+ + OH^-) \rightarrow & R_2\text{–COO}^-,Na^+ & + & CH\text{–OH} \\ \quad\;\; | & & & & \;\; | \\ R_3\text{–COO–CH}_2 & & R_3\text{–COO}^-,Na^+ & & CH_2\text{–OH} \\ \text{Fatty acid Triglyceride} & \text{Sodium hydroxide} & \text{Soap} & & \text{Glycerol} \end{array}$$

- Glycerol, also called glycerin, is a secondary product of the manufacturing of soaps. It has a great number of important industrial applications.

This reaction is called saponification. It takes place at a high temperature. It gives sodium carboxylates (soap) and glycerol. Soaps obtained from sodium hydroxide are hard (Fig. 14.2) and those obtained from potassium hydroxide are soft.

Figure 14.2
Types of hard soaps

Structure of the carboxylate ion

The carboxylate ion of soap is formed of two parts: the hydrocarbon chain R –, often designated by the term "tail" and the negative part carboxylate ion $-COO^-$, designated by the term "head" (Fig. 14.3).
Being charged, the "head" of the carboxylate ion has affinity for the molecule of water, which is polar. It is said to be hydrophilic (water loving). The "tail", formed exclusively of bonded carbon and hydrogen atoms, is not polar and has no affinity for the water molecule. It is said to be hydrophobic (water hating) (Fig. 14.3).
This "tail" has, on the contrary, affinity for fats and oils. It is lipophilic (lipids loving), while the "head" of the carboxylate ion is lipophobic (lipids hating).
The hydrophilic and hydrophobic characters of the carboxylate ion of soap are the cause for the solubility of soaps in water and their detergent property.

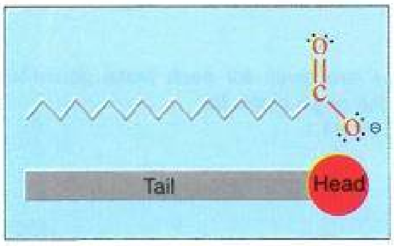


Figure 14.3
Hydrophilic and hydrophobic characters of the carboxylate ions of soap.

Solubility of soaps

Pure water

In general, soaps are moderately soluble in pure water. Table 14.3 gives the solubility of some sodium carboxylates at 25 °C.

	Oleate	Laurate	Palmitate	Stearate
Solubility g/100g of water	180	28	8	1

Table 14.3
Sodium oleate is the most soluble among the considered carboxylates.

The solubility of soaps in pure water is due to the ionic structure. The hydrophilic part of the carboxylate anion is surrounded by the polar water molecules making the ion solvated. The cation Na^+ is strongly solvated. This permits the two ions constituting the soap to disperse in water.

Hard water

Hard water is characterized by the presence of certain amounts of metallic cations, principally Ca^{2+} and Mg^{2+}.

Activity 1 Precipitation of metallic carboxylates in the presence of Ca^{2+}, Mg^{2+}, Cu^{2+}, Fe^{2+}, and Fe^{3+} ions.

Objective

Study the solubility of soaps in hard water.

Equipment and reagents

250 mL beaker. 5 test tubes. Water pump. Vacuum flask. Büchner funnel. Filter paper..

An ordinary soap. 5 solutions of 0.1 mol.L^{-1} each of the following compounds:

Calcium chloride, $CaCl_2$;
Magnesium chloride, $MgCl_2$;
Copper (II) sulfate, $CuSO_4$;
Mohr's Salt, $(NH_4)_2\,Fe(SO_4)_2.\,6H_2O$;
Iron (III) chloride, $FeCl_3$;

Procedure and observation

Dissolve about 3 g of soap flakes in 100 mL of warm distilled water. Filter to obtain clear solution.

Put about 2 mL of the soap solution in each of the test tubes.

In the first tube add a few drops of calcium chloride solution. A white precipitate is formed.

In the second tube add a few drops of magnesium chloride solution. Also a white precipitate is formed.

In the third tube add a few drops of copper (II) sulfate solution. A blue precipitate is formed.

In the fourth tube add a few drops of iron (II) sulfate solution. A green precipitate is formed.

In the fifth tube add a few drops of iron (III) chloride solution. A red-orange precipitate is formed (Fig. 14.4).

- Water hardness is measured by the sum of quantities of Ca^{2+} and Mg^{2+} it contains.
It is expressed either in milliequivalent, as when 1 milliequivalent corresponds to half-mole of the ions Ca^{2+} and Mg^{2+} in m^3, or in French hydrotimetric degree (° TH): 1 French hydrotimetric degree corresponds to 0.1 mol of the ions Ca^{2+} and Mg^{2+} in m^3.

?

- Why do we use warm water to dissolve the quantity of soap?
- What can we conclude from the formation of precipitates?

Figure 14.4

The five precipitates, from left to right are calcium, magnesium, copper (II), iron (II), and iron (III) carboxylates.

The formation of the different metallic carboxylates precipitate showed that soaps are not soluble in the solution containing the metallic ions, in particular, in hard water containing the Ca^{2+} and Mg^{2+} ions.

It is known that hard water diminishes the detergency action of soaps. In fact, all the Ca^{2+} and Mg^{2+} ions present in water must precipitate in the form of insoluble soaps, before the soap solution is formed.

- We add softeners to hard water to engage the Ca^{2+} and Mg^{2+} ions in a soluble complex structure, in order to prevent these ions from reacting with the dissolved soap.

Acid medium

When a solution of HCl, for example, is added by drops, to a soap solution, a solid mass forms and precipitates (Fig. 14.5). These are the insoluble fatty acids of the carboxylate ions of soap. Consider any carboxylate ion, RCOO-, the precipitation of the corresponding acid takes place according to the equation:

$$R\text{–}COO^-_{(aq)} + H_3O^+_{(aq)} \rightarrow R\text{–}COOH_{(s)} + H_2O$$

Soaps are not suitable to use for washing in acidic medium.

Figure 14.5
In acidic medium, there is precipitation of fatty acids corresponding to the soap.

Solution containing sodium ion

Soaps are not soluble in solutions that contain sodium ions Na^+.
The majority of the sodium carboxylate (soaps) have moderate solubility (Table 14.3).
The equilibrium between the carboxylate ions and sodium ions on one side and the solid soap on the other side, in a saturated soap solution, is represented by the equation:

$$R\text{–}COONa_{(s)} \rightleftarrows R\text{–}COO^-_{(aq)} + Na^+_{(aq)}$$

When soap is dissolved in a solution containing Na^+ ions, this equilibrium is shifted to the left; toward the precipitation of soap. This is due to the common ion effect on the solubility of a slightly soluble ionic compound.
The insolubility of soaps in the sodium chloride solutions is used to separate soap from glycerol and other soluble substances present in the reaction medium during their manufacturing.
The method is called flocculation; it consists of adding a concentrated solution of sodium chloride to the medium. Soap is separated in the form of a floating solid. All other substances remain in the solution (Fig. 14.6).

- The concentrated solutions of sodium chloride are called brine.

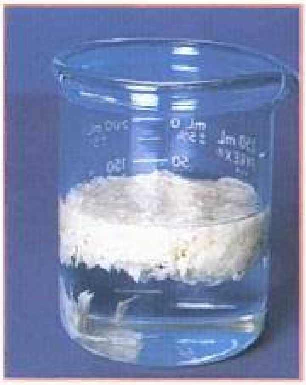


Figure 14.6
Flocculation of soap prepared in the laboratory.

Saponification reaction

Saponification reaction, which yields soap, is a general reaction between esters and hydroxide ions HO^-.

Saponification is the reaction between an ester R-COO-R' and a hydroxide ion HO^-, to form a carboxylate ion $RCOO^-$ and an alcohol R'-OH, according to the equation:

$$R\text{–}COO\text{–}R' + OH^- \rightarrow R\text{–}COO^- + R'\text{–}OH$$

Characteristics

Saponification is a complete reaction, contrary to the hydrolysis of an ester, which is a reversible reaction.
This reaction is slow. It must be heated, generally to 80 °C, to increase its rate.

Moreover, it is faster than the hydrolysis of an ester, and can take place at ordinary temperature.

Activity 2 Measure the pH of a soap solution.

Objective
Identify the pH of an aqueous soap solution.

Materials
pH paper.
Clear soap solution

Procedure and observation
Using universal pH paper, measure the pH of a clear solution of ordinary soap (the solution used in activity 1 or prepared in identical manner). The pH is about 9. This is a basic pH (Fig. 14.7).

- What is the behavior of the carboxylate anions in an aqueous solution?

Figure 14.7
The pH of clear solution of ordinary soap is in the order of 9.

Interpretation
The carboxylate ion R-COO$^-$ is a weak base. In a soap solution, these ions react with water in a partial reaction to produce the OH$^-$ ions.

The reaction of oleate ions $C_{17}H_{33}$-COO$^-$, for example, with water is a partial reaction (PK$_a$ of the oleic/oleate pair, is 4.8) (Fig. 14.8).

It occurs according to the following equation,

$$C_{17}H_{33}-COO^- + H_2O \rightleftharpoons C_{17}H_{33}-COOH + OH^-$$

producing a basic solution.

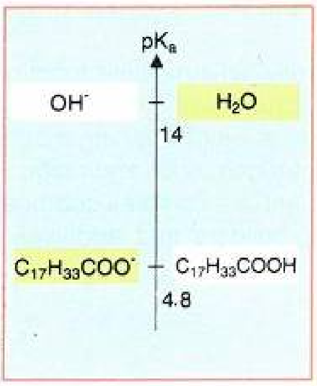


Figure 14.8
The reaction of the oleate ions with water is a limited reaction.

14.2 Principle of detergency

A detergent is a substance, which, when dissolved in water, confers to water the capacity to clean the surfaces from stain.

Soaps are detergents. Their detergent reaction is related to the structure of their carboxylate ions R-COO$^-$. Dissolved in water, these ions have the property to gather water-air, water-fats on the interfaces, directing their hydrophilic head towards water, and their hydrophobic tail away from water (Fig. 14.9). This phenomenon gives the ions their wetting and foaming capacity.

At a certain concentration of the soap solution, the RCOO$^-$ ions initially dispersed, start to assemble, forming in the bulk of the solution spherical agglomerates called micelles.

In the micelle of soap, some tens to hundreds of carboxylate ions agglomerate pointing their charged parts (hydrophilic heads) towards the outside of the micelle, and their hydrocarbon chains (hydrophobic tails) towards the inside (Fig. 14.10),

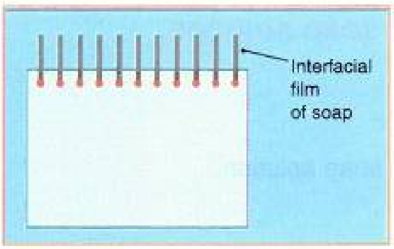


Figure 14.9

Monomolecular layer of $RCOO^-$ ions on the water-air interface of a soap solution.

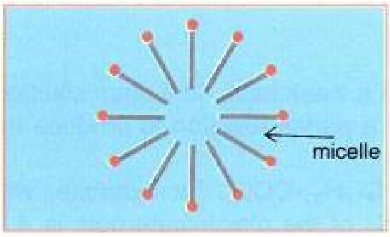


Figure 14.10

The structure of a micelle of a soap.

The formation of micelles confers to soaps a dispersing and emulsifying capacity.

A carboxylate ion possesses, at the same time, a hydrophilic character and lipophilic character. Such a species is called amphiphilic.

Assembled at the water-fat interface of a fat stain (of a tissue, of a plate ...), the carboxylate ions point their lipophilic part towards the fat. Then the hydrocarbon tails penetrate between the fat molecules, which show a similarity to their structure. The hydrophilic parts point toward the aqueous solution (Fig. 14.11). The physio-chemical interactions between these different species, namely, the mechanical agitation, heat ... permit the stains to detach and to get dispersed in the solution, surrounded by the micelles of soap (Fig. 14.12).

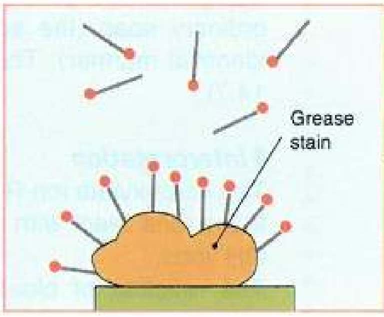


Figure 14.11

The carboxylate ions extend at the water - fat interface.

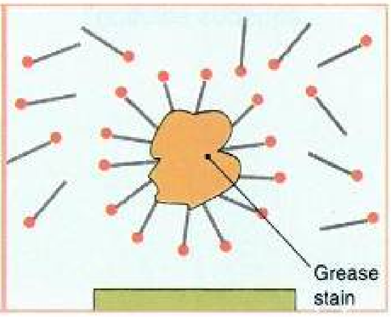


Figure 14.12

The fat stain is dispersed in the solution, surrounded by a soap micelle.

14.3 Synthetic detergents: composition and properties

The scarcity of soap raw materials during World War I led the Germans to manufacture replacements; these were the first synthetic detergents.

The detergents industry began to develop in 1945, with the search for new types of detergents different from soap to fit the new types of textiles (synthetic) and new methods of laundry (washing machines).

A synthetic detergent must generally fulfill multiple functions. It must act as a detergent, soften water used for washing, treat special types of stains, prevent corrosion of washing machines, give laundry pleasant properties of touch, odor and color....

For this reason, a synthetic detergent is a complex composition, formed principally of surfactants, builders and additives (Fig. 14.13).

- **Surfactants**

- **Raw materials**

The fatty alcohols $R\text{-}CH_2OH$ and alkylbenzenes $R\text{–}C_6H_5$, where the radical R- is a linear or slightly branched hydrocarbon chain, are the principal organic raw materials used in the manufacturing of surfactants.

Fatty acids and fatty amines, and other organic raw materials, are also used.

Oleums, chlorosulfonic acid $HClSO_3$, sulfur trioxide SO_3, and sodium hydroxide NaOH are the inorganic raw materials used in the manufacturing of surfactants.

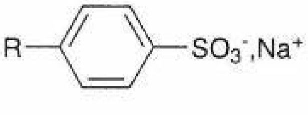
▪ Types of surfactants

Surfactants are of three types: anionic, cationic, and non-ionic. The anionic surfactants are formed of a hydrocarbon chain that is hydrophobic and groups of atoms $-OSO_3^-$ (or SO_3^-), negatively charged and hydrophilic.

Anionic surfactants have various structures. The following two formulas represent two large classes of surfactants:

$$R-CH_2OSO_3^-, Na^+$$

Derivative of fatty alcohols

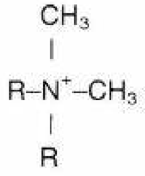


derivative of the alkylbenzene

They show that surfactants are generally sodium salts.

Anionic surfactants are characterized by their detergent action. They enter in the composition of the majority of detergents. They are irritating to the skin.

Cationic surfactants are the cations of salts of fatty amines. They possess a great variety of structures and formulas. The dialkyldimethylammonium ion for example



$$\begin{array}{c} CH_3 \\ | \\ R-N^+-CH_3 \\ | \\ R \end{array}$$

Dialkyldimethylammonium cation

forms a class of cationic surfactants. The alkyl radical R– is a long hydrocarbon chain. The anions associated to this class are Cl^- or $CH_3SO_4^-$.

Cationic surfactants do not have an important detergent action. They are especially used as softeners and conditioners for hair and laundry during washing (Fig. 14.14).

Some are incorporated in disinfectant detergents because of their antiseptic property.

Non-ionic surfactants are products of polyaddition of a fatty alcohol $R-CH_2OH$ and n molecules of ethylene oxide

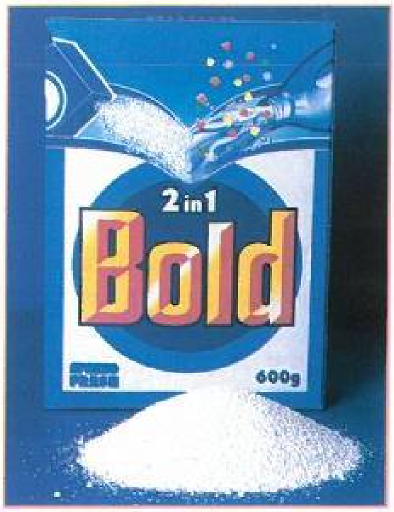


Figure 14.13

A detergent is a complex composition of surfactants, builders and additives.

▪ The radical R – is composed of 8 to 18 carbon atoms.

▪ Oleums possess the general formula:

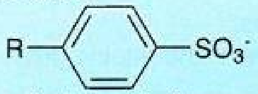
$$H_2SO_4.nSO_3$$

with n > 1.

▪ Soaps are anionic surfactants.

▪ The anion $R-CH_2OSO_3^-$ (or $R'-OSO_3^-$) is called alkyl sulfate.

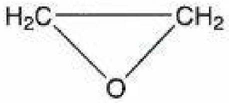
▪ The anion:



is called alkylbenzene sulfonate.

▪ Generally, detergents made of sulfonate are abundant and more used than those made of sulfate.

Figure 14.14
Cationic surfactants enter in the composition of softeners for laundry and conditioners for hair.



Below is the general formula of such a type of surfactants:

$$R{-}CH_2O(CH_2CH_2O)_nH$$

The hydrocarbon chain RCH_2- (or R'-) is the hydrophobic tail, and the part that contains the oxygen atoms is the hydrophilic head.

The non-ionic surfactants have a high detergent capacity. They are not affected by the hardness of water, and they have moderate aggressiveness to the skin and delicate textile fibers. Like the anionic, they are heavily utilized as detergents.

The mechanism of the detergent action of surfactants is identical to that of soaps.

Hence, as detergents, surfactants show a wetting, foaming, dispersing and an emulsifying capacity.

These are achieved because the surfactants are amphiphilic. They assemble at the interface (water-air, water-surface to be cleaned) and draw the stains.

They form micelles, which give them the capacity to draw the stain from the cleaned surface to the bulk of the water, in the form of emulsion.

■ Builders

The function of builders is to reinforce the detergent action of surfactants.

The sodium tripolyphosphate, for example plays the role of softening water by forming soluble compounds with the Ca^{2+} and Mg^{2+} ions. Sodium carbonate, sodium silicilate and sodium pyrophosphate play the same role by forming insoluble compounds with the same ions.

On the other side, sodium hydroxide, sodium carbonate and alkali silicilates reinforce the action of surfactants by saponifying fatty stains and removing them in the form of soaps.

■ Additives

Additives, other than builders, give synthetic detergents specific properties.

Whitening agents remove stains.

Anti-redeposition agents prevent the stains from depositing again on the cleaned surface.

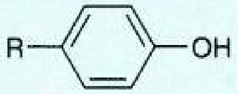
Azure agents absorb UV sunlight and re-emit them with blue shades giving tissues more white and bright aspects.

Appropriate enzymes fragment the protein macromolecules (eggs, blood, milk), starch, and fats....

The foam promoters and regulators increase or control the foam of the detergents.

Colorants and perfumes are added to please the consumers (Fig. 14.15).

■ In addition to fatty alcohols, alkyl phenols are also used.



■ Sodium tripolyphosphate: $Na_5P_3O_{10}$
Sodium pyrophosphate: $Na_4P_2O_7$.

Figure 14.15

This detergent is perfumed by flowers.

- No substance as efficient as phosphate, but less polluting, has been found to replace phosphate as builders. The only way to reduce pollution caused by phosphate is to de-phosphate wastewater.

Figure 14.16

Different types of detergents used for cleaning.

Pollution

The long hydrocarbon chain present in the structure of soaps and detergents are generally very stable.

For the detergents, the branched chain or the chain with aromatic nucleus, is hardly biodegradable. This type of chain makes detergents, present in wastewater, produce foam, which resists biodegradation and accumulates in the water of streams, rivers and even seawater.

In 1960, the use of branched chain hydrocarbons in manufacturing detergents were abandoned, and were replaced totally by linear chain hydrocarbons that are easily biodegradable.

Nowadays, in developed countries, laws prohibit commercial detergents if they do not have a high biodegradability level (90% in France according to Afnor norms).

Phosphates, used as builders, are another source of pollution provoked by detergents.

Phosphates, and nitrogenous substances from fertilizers, constitute nutrient material for algae in the water of lakes, rivers, and streams, which then contributes to their proliferation. This causes the eutrophication phenomenon of areas of water, which poses a threat to aquatic life.

Soap and detergent industries are an important part of the economy. With time, detergents have gradually replaced soaps, because of the large variety of types and characteristics of these products. Nowadays, the production of detergents is estimated at 60 % and soaps at 40 %.

While soaps are reserved specially for toilette, detergents are used for laundry, dishwashing and in diverse products for house cleaning (sanitary, carpets, windows ...) (Fig. 14.16).

In addition, more than half of the total production of soaps and detergents are used in industry. This includes cleaning compounds, germicides surfactants for hospitals, conditioners for manufacturing processes, and emulsifiers for cosmetics ... .

Chapter review

- Soaps are salts of sodium (or potassium) of a variety of fatty acids, called carboxylates.
- The carboxylate ion $RCOO^-$ in soap is formed of hydrophobic and lipophilic part, which is the hydrocarbon chain R-, and a hydrophilic and lipophobic part, which is the $—COO^-$ group.
- Soaps are soluble in pure water. They are insoluble in acidic medium and in water containing Ca^{2+} and Mg^{2+} ions (hard water) and Na^+.
- Saponification is the reaction between an ester and a hydroxide ion HO^-.
- A detergent is a substance, which, when dissolved in water confers to water the capacity to clean the surfaces from stain.
- The carboxylate ion of soaps, because of its hydrophilic and lipophilic characters, is called amphiphilic.
- The detergence of soaps is due to a wetting, foaming, dispersing and an emulsifying capacity of their amphiphilic species.
- A synthetic detergent is a complex composition, formed mainly of surfactants, builders and additives.
- Surfactants are of three types: anionic, cationic and non-ionic.
- Anionic and non-ionic surfactants are detergents. Cationic surfactants do not have a detergent action.
- Builders reinforce the detergent action of surfactants.
- Additives confer to synthetic detergents a number of supplementary and specific properties.

Laboratory Investigation

LI

Preparation of a soap

Objective

Prepare soap in the laboratory.

Equipment and reagents

250 mL Erlenmeyer flask. Magnetic stirrer - hot plate. Condenser. Büchner funnel. Water pump. Support, clamps. 250 mL flask. 100 mL graduated cylinder. 25 mL graduated cylinder. Glass rod. Filter paper. Oil. NaOH Pellets. Ethanol. Sodium chloride NaCl.

Procedure

- Add 20 mL of distilled water in the Erlenmyer flask
- Weigh enough mass of NaOH to prepare 20 mL of a 8 mol.L^{-1} solution. Add continuously in the Erlenmyer flask. Stir.
- Weigh 10 g of oil (ρ = 0.9 kg. L^{-1}). Add it to the Erlenmeyer flask.
- Add 10 mL of ethanol and stir to homogenize the mixture.
- Add a few grains of boiling stones to provide even boiling.
- Adjust the condenser. Place the heating magnetic stirrer and stabilize the whole apparatus with support and clamps (Fig. 14.17).
- Reflux for 30 minutes.
- During this time, prepare a solution of NaCl by dissolving 20 g of the salt in 100 mL of water (distilled cold water). Put 20 mL of this solution aside.
- After the heating has finished, add the hot mixture to the salt solution. Stir using the rod.
- Filter easily the solid soap that is floating. Add 20 mL of the salt solution. Filter and collect the solid and allow it to dry.
- Dry the collected soap by squeezing it between two filter papers.

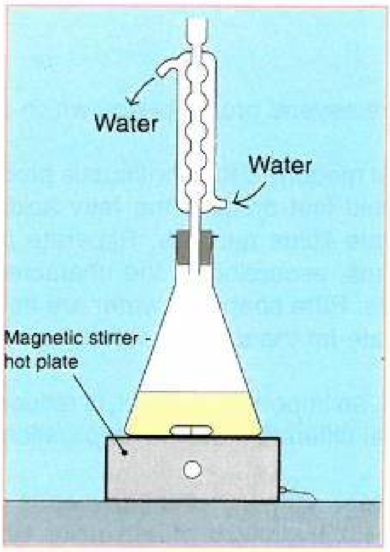


Figure 14.17

Setup for the preparation of soap in the laboratory.

Remarks

Cut a small portion of the prepared soap and dissolve it in water. Foam is formed. The product is a detergent.

Do not clean your hands with this soap because it contains NaOH, and it is caustic for the skin.

Questions

1) What is the role of ethanol?
2) What is the role of salt water?
3) What are the different products that are found in the filtrate?

Documentary activity

Industrial preparation of a soap

There are several processes by which one can prepare soap in the industry.

The most modern is the continuous process, also designated by the hydrolysis process. In this method, one should first prepare the fatty acids, by hydrolysis under pressure and high temperature of the appropriate lipids and oils. Separate from glycerol, these purified acids, adjust in both nature and proportions, according to the characteristics of the soap to be obtained, then reduced with sodium hydroxide. Pure soap and water are obtained. Then the soap will undergo the final step that will make it adequate for the desired need.

Glycerol, an important product, is recuperated during the hydrolysis of fatty acids. It is purified and used in several different industrial applications.

The process of manufacturing soap is used to produce large quantities of soaps. The whole process, starting with hydrolysis of fatty acids till the formation of pure soap requires only few hours.

The following procedure is the traditional method in the manufacture of soap. It takes place in several steps.

Fatty acids are first melted in large caldrons. NaOH is then gradually added and the mixture is continuously agitated. Boiling is maintained by a current of hot vapors, arriving to the caldron through pores. Total saponification is achieved in few hours. There is formation of soap and glycerol.

Soap is separated from the rest of the mixture by adding to the caldron either solid NaCl or highly concentrated NaCl. The soap will then float. Once taken out, soap is purified.

The half cooked process and the cold process are two varieties of the traditional method where saponification takes place without boiling in the first and cooling in the second.

The finishing of soap, last step of synthesis, consists of producing the final form: toilet soap, medicine, shampoo, shaving cream. Different additives are added to the soap, according to its intended use: fatty materials, color, perfume or others.

Questions

1) What are the different steps in the continuous process of the synthesis of soap?
2) What are the advantages of this process?
3) What are the different steps in the cooking process?
4) What does the finishing step of soap consist of?

Exercises

1 Many fats and oils are glycerides, which means esters of glycerol and fatty acids.

a) Write the structural formula of glycerol or 1,2,3-propanetriol.

b) Oleic acid is the most abundant fatty acid. It forms along with glycerol, a triester: olein of plant oil. Write the formula of olein. The formula of oleic acid can be represented by $C_{17}H_{33}COOH$

c) One ton of oil reacts with excess NaOH, glycerol is formed, in addition to another product S. The oil is composed of olein; write the equation corresponding to this reaction.

d) What do you call this type of reaction? Give its two important characteristics.

e) The product S is recovered and purified. What is the weight of the obtained product S?

f) A certain quantity of S is dissolved in distilled water, is the obtained solution neutral, basic or acidic? Justify your answer

Given:
$M(C) = 12.0\ g.mol^{-1}$; $M(H) = 1.0\ g.mol^{-1}$; $M(O) = 16.0\ g.mol^{-1}$; $M(Na) = 23.0\ g.mol^{-1}$.
$M(olein) = 884\ g.mol^{-1}$.

2 500 g of coconut oil react with KOH. Knowing that coconut oil is mainly formed of triglyceride of lauric acid, a 12-carbon atom saturated acid.

a) Write the condensed structural formula of the triglyceride.

b) Write the equation of the reaction. Name this reaction

c) The obtained soap is soft. Justify why?

d) Part of the structure of the anion produced during this reaction is said to be hydrophilic, and the second part to be hydrophobic.

1) Write the condensed structural formula of the anion

2) Indicate the hydrophilic part and the hydrophobic part.

3) Explain the meaning of these two terms.

e) Calculate the weight of KOH necessary to react with the given weight of oil.

f) Calculate the mass of the obtained soap.

Given:
$M(C) = 12.0\ g.mol^{-1}$; $M(H) = 1.0\ g.mol^{-1}$; $M(O) = 16.0\ g.mol^{-1}$; $M(K) = 39.0\ g.mol^{-1}$.
$M(triglyceride) = 638\ g.mol^{-1}$.

3 Saponification of a tallow of beef gave a mixture of glycerol and sodium carboxylate of three fatty acids; palmitic acid, stearic and oleic acids. The mass percentage of palmitic, stearic and oleic esters of the tallow are respectively: 30%, 25% and 45%.

a) Let us designate by R_1, R_2 and R_3 the alkyl groups corresponding respectively to each of the fatty acids. Give the formula of each group knowing that both palmitic and stearic acids are saturated acids containing respectively 16 and 18 atoms of carbon; and that oleic acid is an unsaturated acid with 18 carbon atoms.

b) Write the equation of saponification of triester of one of the three acids.

c) Determine the mass of the obtained soap by saponification of one ton of tallow by excess NaOH.

Given:
$M(C) = 12.0\ g.mol^{-1}$; $M(H) = 1.0\ g.mol^{-1}$; $M(O) = 16.0\ g.mol^{-1}$; $M(Na) = 23.0\ g.mol^{-1}$.

4 We are supposed to calculate the mass of lost soap in the form of calcium or magnesium carbonate insoluble in natural hard water. The hardness of water used is 27º French hydrotimetric. One degree of French hydrotimetric corresponds to the presence of 0.1mol ions Ca^{2+} or Mg^{2+} in $1m^3$ of water. We use ordinary toilet soap formed by sodium palmitate only.

a) Write the equation of the reaction, which takes place between sodium palmitate and the Ca^{2+} ions present in hard water.

b) The same question for the reaction between sodium palmitate and Mg^{2+} ions. Given:
The formula of palmitic acid $C_{15}H_{31}COOH$

c) Calculate the mass of sodium palmitate lost in the form of precipitates in $1m^3$ of hard water.

d) Calculate the mass of the commercial soap knowing that the mass percentage of lost soap is equal to 33%.

5 Soap is prepared in the laboratory

To do that, the following steps are followed:

Step A

Introduce in a 250 mL Erlenmyer flask, 20 mL of 5 mol.L^{-1} NaOH, 9 g of olive oil and 20 mL of 95º ethanol. Fix the flask on a heating magnetic stirrer. Adjust a condenser to the setup and heat for 30 minutes.

Step B

During heating, prepare 100 mL of saturated NaCl solution. Put aside 20 mL of this solution. After heating, the flask is removed and the hot mixture is added to 80 mL of the salt solution. A yellowish solid separates from the solution and floats. This is the soap.

Step C

Separate the soap by vacuum filtration using Büchner funnel. Then the soap is washed with 20 mL of the salt solution. The soap is obtained on a glass watch and kept between 2 filter papers to be dried. Once dried, it is weighed.

a) Draw the schema of the setup used to prepare soap and the setup of vacuum filtration.

b) Why do we add ethanol to the oil + NaOH mixture?

c) What is the role of the condenser?

d) Why do we heat the mixture to boiling?

e) What is the function of the saturated NaCl solution? What do we call the corresponding process?

f) Explain the principle of formation of solid soap in the solution?

g) Why do we wash the soap with the NaCl solution?

h) If we consider that olive oil is uniquely formed from olein (triester of oleic acid), write the equation of the reaction of saponification.

Given:

Formula of oleic acid is $C_{17}H_{33}COOH$.

i) Determine the % yield of this reaction knowing that the mass of dry soap obtained =7.70g

M (olein) = 884g. mol^{-1}

6 Let us consider the three sodium carboxylates; sodium palmitate, sodium stearate and sodium oleate.

Given the formulas of:

Palmitic acid $C_{15}H_{31}$-COOH

Stearic acid $C_{17}H_{35}$-COOH

Oleic acid $C_{17}H_{33}COOH$ (with a double bond, Z configuration, unsaturated between carbon 9 and carbon 10)

a) Write the condensed structural formula of each sodium carboxylate.

b) These carboxylates are used in aqueous solution to clean greasy surfaces due to their power as detergents. By choosing a carboxylate anion from the previous anions, indicate the parts of the structure of the anion responsible for its power as a detergent, and talk about the characteristics of the elements

c) Dissolve enough of one of the preceding carboxylates in water. Foam is formed at the air-water surface. What is this foam due to? Draw a simplified schema, which shows the formation of this foam.

d) A grease stain, on a surface immersed in a solution of carboxylate, is surrounded by a great number of the carboxylate anion. Draw a simplified schema, which shows the disposition of the anions according to their structure.

e) The solution being relatively hot and after mechanical stirring the grease stain is removed from the surface. It is taken into the solution, surrounded by an agglomeration of soap molecule.

1) What do we call this agglomeration?

2) Draw a simplified schema of grease surrounded by the carboxylate anion in the solution, where you show the disposition of these ions according to their structure.

3) Explain the detergent action of carboxylate anions in solution relatively to the grease stain.

f) A carboxylate anion is said to be amphiphilic . What is the meaning of this term?

7 A synthetic detergent is usually a mixture of complex composition containing surfactants, builders and additives. Surfactants are chemical compounds responsible for the detergent activity.

a) The condensed structural formula below is that of a surfactant:

$$CH_3–(CH_2)_{17}–CH_2O(CH_2CH_2O)_{20}H$$

Indicate the hydrophilic part and the hydrophobic part of this molecule. Is this an amphiphilic molecule? Why?

b) The following compounds are builders:

- sodium tripolyphosphate $Na_5P_3O_{10}$ (forms soluble complexes with Ca^{2+} and Mg^{2+} ions);
- NaOH and sodium carbonate Na_2CO_3 (saponifies fat);
- Sodium pyrophosphate $Na_4P_2O_7$, sodium carbonate, and alkaline silicates (precipitation agents of Ca^{2+} and Mg^{2+} ions);

1) In general, what is the function of the builders of the detergents?
2) Explain the role of each of the preceding builders.

Evaluation

Applying knowledge

1 A) Oleic acid contains principally olein, which is the triester of glycerol and oleic acid.

a) Write the condensed structural formula of glycerol (1,2,3-propanetriol)

b) Oleic acid has the formula $C_{17}H_{33}COOH$. If the carbon chain is linear and presents a double bond between the 9th and 10th carbons (Z configuration). Give the structural formula showing the stereochemistry.

B) We have prepared sodium oleate in the laboratory, by reacting under appropriate conditions, 10 g of olein with sufficient amount of NaOH.

a) What do we call such type of reaction?

b) Write the equation. What is the product obtained with sodium oleate?

c) The reaction mixture is subjected to reflex heating. What can we say about this reaction?

d) The oleate anion is called amphiphilic. Referring to the structure of this anion, explain the meaning of this term and the particularities of its structure.

e) The characteristics of the structure of the oleate anion allow it to be used in important application in daily life. What is this application?

C) After leaving sodium oleate to dry, we collect 9.5 g of the product.

a) Calculate the theoretical mass of sodium oleate that should be obtained.

b) Calculate the % yield of this reaction. What other characteristics can be attributed to the reaction of olein with NaOH.

2 In order to study the solubility of toilet soap in different aqueous solutions, the following experiment was conducted:

Five beakers 100 mL each numbered 1 to 5 were filled respectively by:

Beaker 1: 10 mL distilled water

Beaker 2: 10 mL mineral water of high hardness

Beaker 3: 10 mL of 2 $mol.L^{-1}$ hydrochloric acid solution.

Beaker 4: 10 mL of 0.5 $mol.L^{-1}$ sodium chloride NaCl solution

Beaker 5: 10 mL of highly concentrated NaCl solution.

Add to each beaker 5 mL of a concentrated soap solution, prepared in a water-ethanol mixture. Stir well. Observe the following results:

Beaker 1: Formation of abundant foam

Beaker 2: Absence of foam, the solution is turbid.

Beaker 3: Absence of foam, appearance of a white precipitate

Beaker 4: Formation of abundant foam

Beaker 5: Absence of foam, formation of a precipitate.

a) Using the equation of the dissolution of soap in water and the solubility of each indicated compound, interpret each of the above observations.

b) Deduce in which type of solution does soap have the best detergent action?

c) What makes a synthetic detergent better than soap for detergence in hard water?

3 Olive oil has always been an important agricultural product, in Lebanon.

Olive is a tree that is cultivated on a large scale in the Mediterranean basin.

Owners of large olive fields and olive pressing machines in Lebanon produce, generally, soap from olive oil in a very traditional manufacturing technique.

- They place the oil in large containers and heat it. They add progressively a saturated solution of NaOH and continuously stir allowing soap to form.
- They introduce the solution where soap is formed, still very hot, into large containers filled with brine. They stir and leave it to rest so that soap separates from the rest of the solution.
- They take the floating soap and clean it and decant it in order to separate it from impurities.
- They sometimes mix the soap with traditional fragrant oil originating from the leaves of laurier (ghar), which is appreciated by Lebanese homemakers for laundry.

- Then they place the mass of soaps in molds, cut them into pieces and leave them to dry.

a) Why do the soap makers heat the ingredients? Why do they add progressively the concentrated NaOH solution?
b) What is brine? What is its role?
c) What does the solution separated from soap contains when soap floats in the form of solid layer?
d) Does the process of the preparation described give information on the treatment of this solution?
e) At what step of the manufacture of soap do they add the fragrant oil? Why?

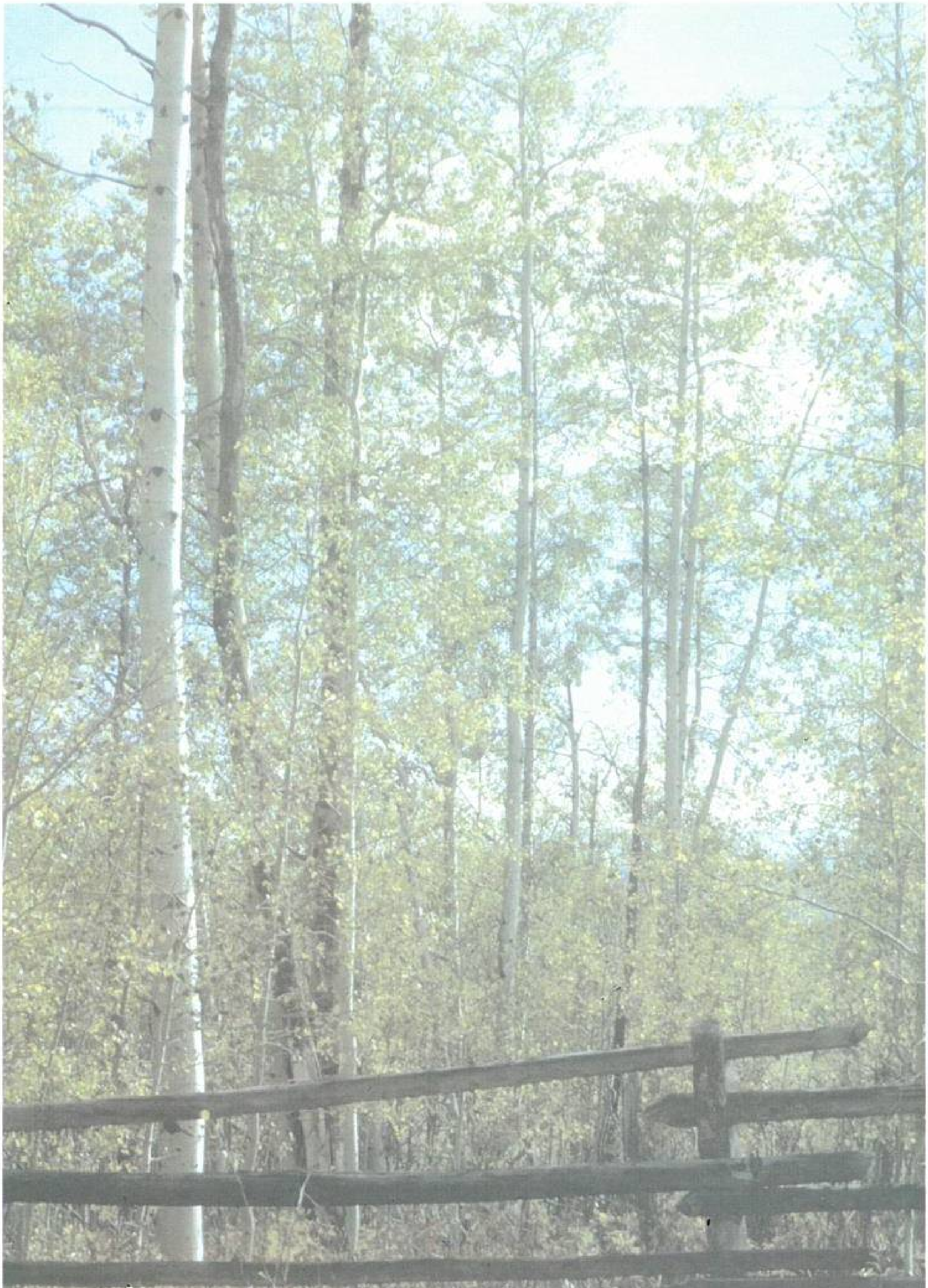
4 Sodium tripolyphosphate $Na_5P_3O_{10}$ and sodium pyrophosphate $Na_4P_2O_7$ are two polluting agents of water.

a) Explain why are they pollutants?
b) These two compounds are builders in the composition of synthetic detergents. Scientific research done to replace them with others less polluting shows that builders with phosphorous base are the most economical and effective. These agents are therefore always used.
c) How can we reduce their polluting effect?

Designing an experiment

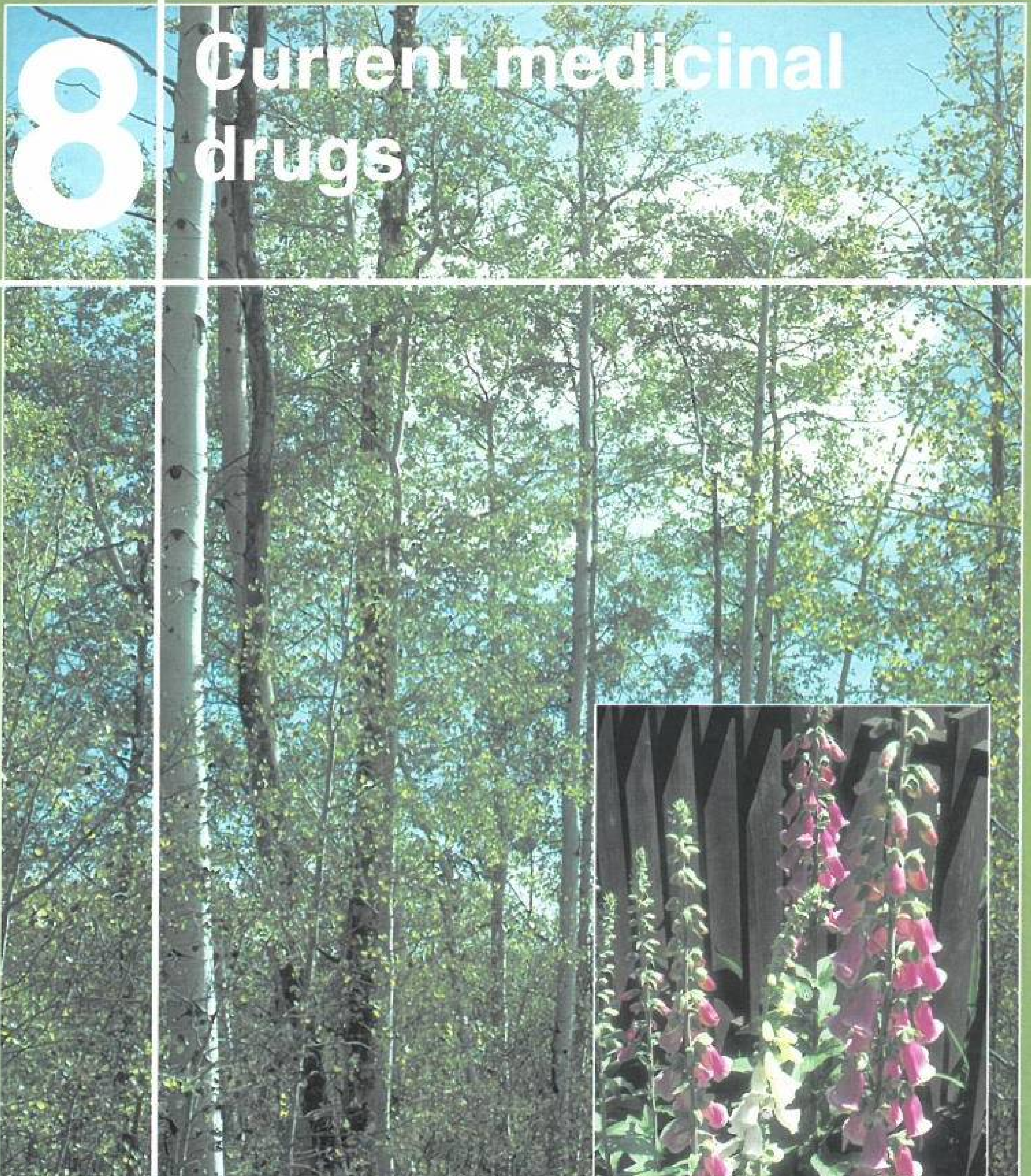
5 Conduct the experiment written in exercise 5 page 338.

a) Answer all the questions of exercise 5.
b) Calculate the % yield by mass, of the soap obtained in this experiment. Compare it, to the result of exercise 5.



8

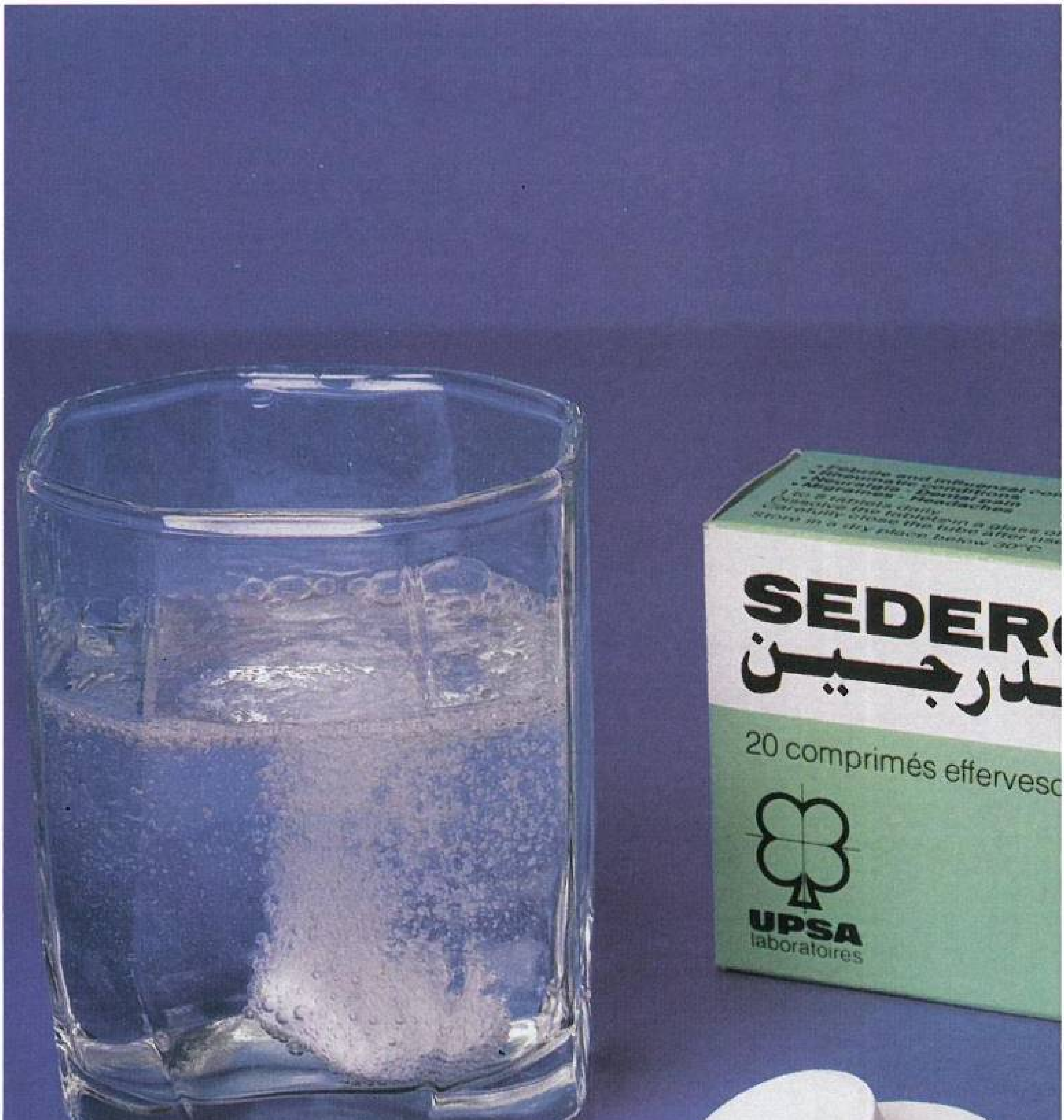
Current medicinal drugs



A great number of plants has therapeutic properties. These plants have been used for longtime for their effects on pains.

Dry leaves from birchwood have essentially diuretic action.

Foxglove has been always used for its therapeutic effect on cardiac pains.



Remedies of natural origin for several illnesses and diseases have been known since antiquity. The study of medicinal drugs and their use (pharmacology) has evolved during several centuries. But since the 19th century it has become a science in itself. Nowadays, the discovery of new drugs remains a hope in order to treat a number of diseases that threaten human life. However, drugs can themselves become a threat to human life, if one ignores their therapeutic effects and their undesirable side effects.

What is a medicinal drug? What are their most common classes? What are their different effects?

CURRENT MEDICINAL DRUGS

15

Objectives

- Define a medicinal drug.
- Classify medicinal drugs according to their pharmacological effects.
- Identify analgesics, anesthetics, antacids, anti-inflammatory, antibiotics, tranquilizers and antidepressants.
- Recognize the overdose effects of some drugs.

Prerequisites

- Acids and bases.
- Oxygen and nitrogen as organic functional groups.

Chapter content

15 Current medicinal drugs

The therapeutic effects of a number of substances of animal, plant and mineral origin on the physiological and psychological functions of human beings have been known by several ancient civilizations. The effect of opium as a tranquilizer, of foxgloves for cardiac cases and of quinquina,... were known a long time ago.
The therapeutic effects of several plants, herbs, and mineral salts are the basic constituents of the "science" of herbatics and apothecarists; the grandfathers of modern pharmacology.
Pharmacology is the modern science of these substances, designated by the term "medicinal drugs". What is a medicinal drug?

A medicinal drug is a chemical compound or substance that affects the functions of the living organism and is used for therapeutic purposes.

- Drugs and poisons affect equally both physiological and psychological functions of human beings.

The chemical synthesis of medicinal drugs started toward the end of the 19th century with that of acetophenetidine (1885), traded as an analgesic. The synthesis of acetylsalicylic acid (aspirin) followed in 1897. From this time, the pharmaceutical industry evolved rapidly with a variety of drugs that were discovered and synthesized.
The pharmaceutical industry takes into account the manufacture of drugs and the research for new drugs as well. Modern biotechnologies are very promising in this field. Pharmaceutical industry is a sector of the chemical industry, and has a great economic importance.

Composition and action of a drug

A drug is formed of a chemical substance, which plays the therapeutic role; other active substances are added in order to stop certain undesirable effects of the drug, and a substance known as excipient, is added to assume the form under which the drug is presented.

- Sodium bicarbonate $NaHCO_3$ (a base) is added, for example, to the composition of a tablet of aspirin, in order to reduce the irritation that might be caused by aspirin on the mucous of the stomach.

Whether the drug is of natural or synthetic origin, its different components are chemical compounds, generally organic, and that is why organic chemistry is very important in the drugs industry.

A drug is administered to the body in different ways: orally, through injection, and by inhalation, in the form of aerosols or scented ointment. The purpose is for the drug to reach its target in the body, with adequate concentration to exert its therapeutic effect.

So, the first stage is the administration of the drug. The second stage is its distribution in the circulatory system and the tissues to reach its target. The third stage is its own action. Afterwards, the drug is eliminated from the body by excretion, in large part through urine.

▪ Forms of drugs

Drugs are traded commercially under different forms, related in principle to their mode of administration and their pharmacological effects: pills, syrup, solutions, aerosols, pomade ...etc (Fig. 15.1).

Figure 15.1
Drugs are traded commercially in the form of tablets, pills, syrups, creams ... .

Information about the composition of the drug and its mode of usage are given on its package: paper, box, bottle ... and on a piece of paper known as the prospectus.

On the prospectus of a drug (Fig. 15.2), there is the name of the drug, the constituent chemical compounds: therapeutic substance, active substances which minimize the side effects, other excipients and their quantities should be mentioned.

Tylenol®

Suppositories 100 mg/200 mg/350 mg
Antipyretic and analgesic for children.

Composition

Suppositories of 100 mg, 200 mg, and 350 mg of paracetamol.

Properties

The analgesic and antipyretic active substance in TYLENOL is N-acetyl-para-aminophenol (paracetamol, acetaminophene).

Its analgesic and antipyretic effects equal those of acetylsalicylic acid. Moreover, TYLENOL is better tolerated and causes less side effects than acetylsalicylic acid. TYLENOL is generally well tolerated. Side effects such as allergic reactions and gastrointestinal disturbances are rarely observed.

Figure 15.2
An example of a medical prospectus.

The form of the drug, the amount inside the box and the therapeutic action of the active substances are also indicated.

Because of the active substance a drug might cause certain negative side effects, especially on some patients, these side effects should be clearly stated on the prospectus under the "secondary effects and contra-indications".

The method of administration and the maximum dose with some precautions are also mentioned. The mode of conservation and the expiration date are also written on the prospectus.

Drugs are used because of their beneficial effects on health, even though these substances can constitute a real danger through their side effects. People are at risk if they take drugs without a doctor's prescription.

▪ All the information given on the prospectus of a certain drug are required by law, in order to prevent serious accidents caused in the past for a large number of people by some drugs.

▪ Classification of drugs

There are many ways to classify drugs. The most common is based on their pharmacological effects.

From this point of view, drugs are classified into analgesics, anesthetics, antiacids, antibiotics, anti-inflammatory, tranquilizers and antidepressants.

Among the substances of which a drug is formulated, one particular substance is responsible for its therapeutic effects. It is an organic chemical compound with a complex formula (Fig. 15.3).

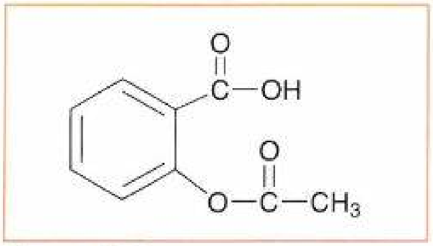


Figure 15.3
Acetylsalicylic acid is the active ingredient of aspirin; it is responsible for aspirin's physiological therapeutic effect.

The active ingredient of a drug is a chemical compound, usually organic and with a very complex structure, which is responsible for the pharmacological effects.

Often, a drug presents more than one pharmacological effect, which allows it to be placed under more than one class.

15.1 Analgesics

An analgesic is a drug that relieves pain.

An analgesic is used to relieve pains of medium intensity and duration, such as headaches, toothaches, periodic pains, rheumatism, ...

It seems, nowadays, that the action of non-opiate analgesics like aspirin and paracetamol, consists of inhibiting the synthesis of prostaglandins in the body: a hormone secreted in the body which is responsible, starting with a certain concentration of their secretion, for the development of pain.

Figure 15.4
The ball-and-stick molecular model of phenol.

Aspirin

Synthesis

Aspirin is the analgesic that is the most widely consumed (20 million kg per year). It is synthesized from phenol C_6H_5-OH (Fig. 15.4).

Phenol reacts with CO_2 to give salicylic acid HO-C_6H_5-COOH (Fig. 15.5). This latter, is transformed by esterification of the –OH group to acetylsalicylic acid. $CH_3COO–C_6H_5–COOH$ (Fig.15.6), is the active ingredient of aspirin, and is responsible for its pharmacological effects. The systematic name of aspirin is acetylsalicylic acid.

The different steps of the synthesis are:

- Phenol is transformed to sodium phenoxide by reacting with sodium hydroxide, according to the following equation:

$$C_6H_5\text{–}OH + Na^+ + HO^- \rightarrow \underset{\text{Crystals of sodium Phenoxide}}{C_6H_5\text{–}O^-, Na^+} + H_2O$$

The reaction is made complete by the elimination of the water. Sodium phenoxide is collected in the form of crystals.

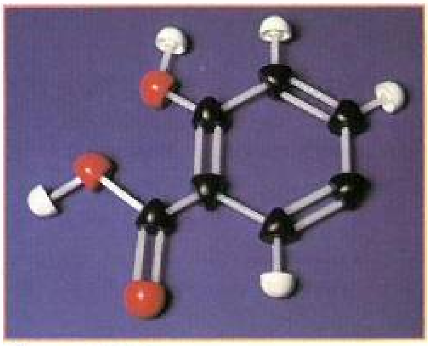


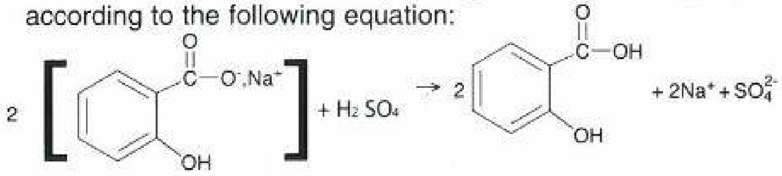
Figure 15.5
The ball-and-stick molecular model of salicylic acid.

- Sodium phenoxide reacts with a current of CO_2 at a temperature kept at less than 100 °C, to give sodium phenylcarbonate according to the following equation:

$$C_6H_5\text{–}O^-, Na^+ + CO_2 \rightarrow C_6H_5\text{–}O\text{–}COO^-, Na^+$$

At a temperature maintained between 130-140 °C and a pressure of CO_2 (~ 7 bars), sodium phenylcarbonate isomerises into sodium salicylate according to the following equation:

- Salicylic acid is obtained in the form of solid precipitate by acidification of sodium salicylate by sulfuric acid H_2SO_4 according to the following equation:



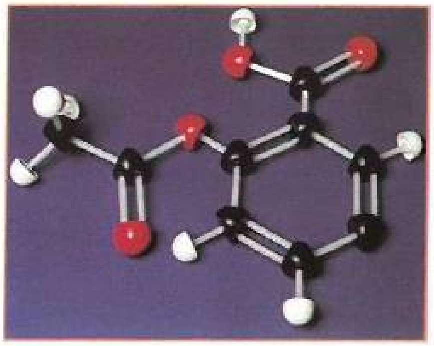
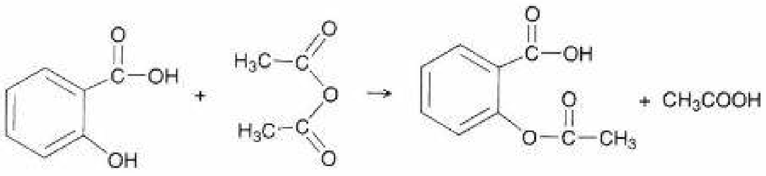


Figure 15.6
The ball-and-stick molecular model of acetylsalicylic acid.

- Salicylic acid, separated and purified, is transformed into acetylsalicylic acid by reaction with acetic anhydride according to the following equation:



The reaction is realized with acetic anhydride instead of acetic acid in order to render the esterification of –OH complete. It is catalyzed by H_2SO_4 and takes place between 50 and 60ºC.
Upon cooling, acetylsalicylic acid is crystallized. It is separated from acetic acid by filtration. Then, it is washed with distilled water and dried in a current of hot air.
The molecule of aspirin contains two organic functional groups: carboxyl group -COOH and the functional group of the ester class $-O-\underset{\underset{O}{\|}}{C}-$ (Fig.15.7).

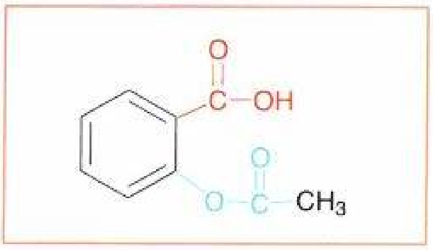


Figure 15.7
The structural formula of aspirin shows both the carboxyl group (red) and the functional group of the ester class, (blue).

Hemisynthesis of aspirin

When aspirin is prepared from salicylic acid and acetic anhydride chemical products, the procedure is called hemisynthesis.

Hemisynthesis of aspirin can be carried out in the laboratory by reacting salicylic acid and acetic anhydride. The reaction takes place between 50 and 60 °C (Fig. 15.8), in the presence of H_2SO_4.

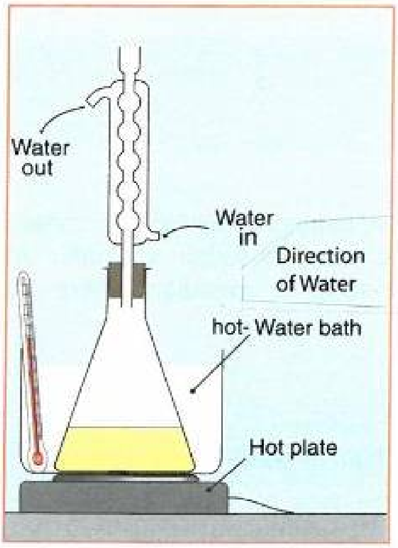


Figure 15.8
The salicylic acid and acetic anhydride mixture is heated between 50 and 60 °C.

Acetic anhydride, being in excess, is transformed by hydrolysis into acetic acid. The acetylsalicylic acid formed, not very soluble in water, is crystallized at a low temperature and separated by filtration. This is aspirin. It is purified by recrystallization in a water-ethanol mixture, separated from the solution by filtration; then it is dried.

The detailed experimental procedure of the hemisynthesis of aspirin is given as a laboratory investigation at the end of this chapter.

Formulation of aspirin

Aspirin is commercialized in a variety of forms, with each form corresponding to a particular use of the analgesic. The tablet of simple aspirin, buffered and effervescent aspirin, and aspirin of pH 8 are known forms of aspirin.

- The simple aspirin tablet (Fig. 15.9) is formed by the agglomeration of aspirin and excipient. Generally, it is diluted in water in order for the acetylsalicylic acid to disperse in the stomach without causing any irritation at the level of the mucous during absorption.

Figure 15.9

A tablet of simple aspirin is the traded form of aspirin.

- Buffered and effervescent aspirin is usually a mixture of aspirin with sodium bicarbonate ($NaHCO_3$), citric acid, ascorbic acid (vitamin C) and an excipient (Fig. 15.10).
  The reaction of the HCO_3^- ion with the acid present in the tablet, when it is placed in water, releases $CO_{2(g)}$, which is the cause of effervescence.
  The simultaneous presence of HCO_3^- ion and its conjugate acid $CO_{2(dissolved)}$, in adequate proportions, form a buffered medium at pH ~ 6.4).

- Aspirin of pH 8 (Fig. 15. 11) corresponds to the coating of acetylsalicylic acid with a substance with low breaking up in water, which takes place when the tablet arrives at the level of the duodenum where the pH is 8. This form is preferable for people who suffer ulcer problems or when the analgesic is used as a long therapy.

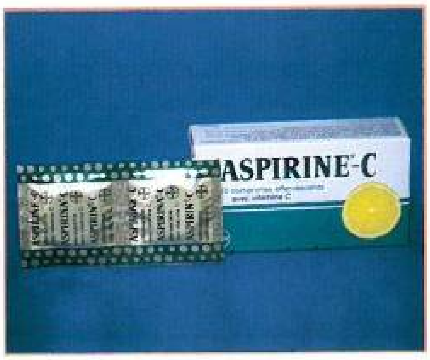
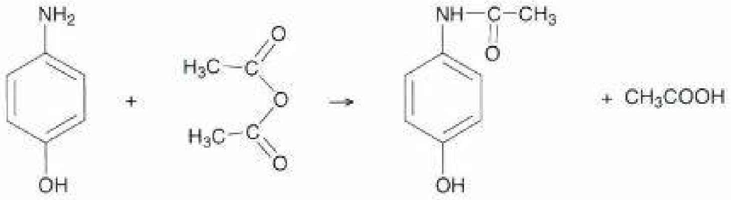


Figure 15.10

Buffered and effervescent aspirin is less irritating to the stomach than the simple aspirin tablet.

Paracetamol

Like aspirin, paracetamol (Fig. 15.12) is a common analgesic in the family pharmacy. It is synthesized by the acetylation of para-aminophenol according to the following equation:



Paracetamol possesses analgesic and anti-fever effects comparable to those of aspirin; but unlike aspirin, paracetamol is not anti-inflammatory.
Hence, paracetamol it is not irritating to the stomach.

15.2 Anesthetics

Figure 15.11

Aspirin of pH 8 is a formulation of this analgesic.

An anesthetic is a substance that causes either local or general loss of sensations, including the sensation of pain. An anesthetic allows to perform surgical operation where the patient does not feel the pain.

Anesthetics are classified into local or general anesthetics.

A local anesthetic provokes the loss of sensation in a very localized part of the body. The patient does not lose consciousness during local anesthesia.

A general anesthesia provokes the absence of perception of all sensations.

During general anesthesia, the patient is in a state of a deep loss of consciousness and his muscles undergo complete relaxation; a state during which long and complex surgical operations can take place.

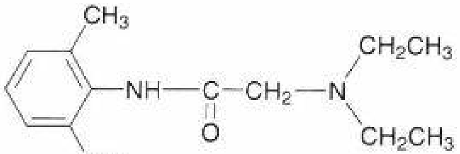
Figure 15.12

The ball-and-stick model of paracetamol.

15.2.1 Local anesthetics

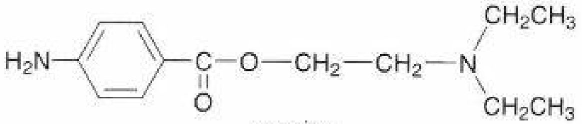
Cocaine is an example of a common local anesthetic (Fig. 15.13). Applied on the part of the body to be anesthetized, it blocks the action of sensitive nerves of this part, preventing it from the conduction of sensational impulses toward the brain.
Local anesthetics that are very common are comparable in structure and action to that of cocaine.
The structure of these anesthetics contains an aromatic nucleus, which is attached by an intermediate chain to an amino group. According to the functional group contained in the chain, one can distinguish esters and amides.

Lidocaine is the most widely used anesthetic. It belongs to a class of amides, as in the formula given:



lidocaine

Procaine, another anesthetic, belongs to the class of esters:



procaine

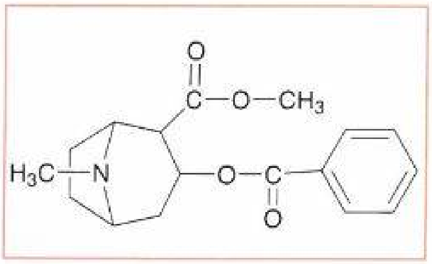


Figure 15.13

Formula of cocaine.

Local anesthetics possess undesirable effects, which can be fatal if administered at a dose which exceeds the allowed dose (overdose).
Overdose can cause, for example, a heart attack, loss of consciousness, intoxication and other fatal accidents or death.

15.2.2 General anesthetics

General anesthetics can be administered by inhalation or by injection.
The first are composed of gases and volatile liquids.
The second are composed of certain barbiturates, substances comparable to morphine (designated as morphinic) and other substances.

- **Inhalation anesthetics**

Nitrous oxide N_2O is a colorless gas, with a mild smell and taste. It has been used as an anesthetic since 1844.
Cyclopropane C_3H_6, is a colorless gas, and diethyl ether

C_2H_5-O-C_2H_5, is a volatile liquid; these are two other anesthetics administered by inhalation.

These compounds are used in the form of mixtures with oxygen, and with appropriate proportions.

Cyclopropane and diethyl ether are flammable, they form with oxygen explosive mixtures. They are actually replaced by other types of anesthetics gaseous or volatile liquids that are more efficient and less dangerous.

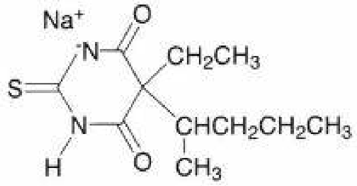
■ Injection anesthetics

Several drugs are administered by injection before a surgical operation to produce certain effects such as the loss of consciousness, relaxation, and control of visceral reflexes.

These drugs compete with the inhalation anesthetics. They permit rapid effects with fewer amounts administered to the patient by inhalation.

■ The technique, as well as the control and the effects of inhalation are more difficult to be controlled than those of the injection.

Thiopental, used in the form of sodium salt:



Sodium thiopental

is the most widely used barbiturate in general anesthesia. It has a rapid action to ensure the loss of consciousness (10 to 20s) and a rapid gaining of the consciousness (20 to 30 min).

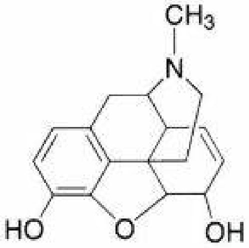
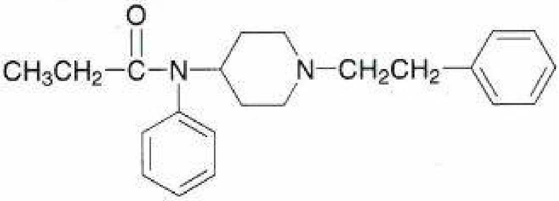


Figure 15.14
Formula of morphine.

Fentanyl possesses certain pharmacological effects of morphine. For this reason, it is considered as a morphinic anesthetic even though its structure differs than the structure of morphine (Fig. 15.14).

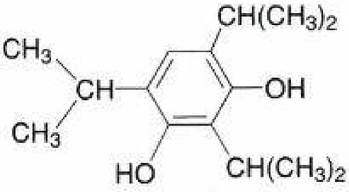


fentanyl

It is the most widely used morphinic anesthetic due to its hypnotic and analgesic effects.

In certain particular situations, propofol is used instead of the two preceding anesthetics:

■ A barbiturate has principally both hypnotic and sedative effects.



propofol

Its anesthetic action is comparable to the two types above.

Inhalation anesthetics are mainly responsible for the deep loss of consciousness and sensations needed for general anesthetics. In addition to this loss caused also by injection anesthetics, it plays the role analgesic role during and after anesthesia. This permits relaxation of muscles, rendering the surgical procedure easier.

Figure 15.15
Some types of antacids traded commercially.

15.3 Antacids

An antacid is a basic compound, administered orally in order to neutralize gastric acids and soothe the pains caused by these acids.

Antacids relieve indigestion, gastritis, and certain forms of ulcers.
Antacids are classified into cationic and anionic.
Cationic are derived from magnesium and aluminum, such as magnesium hydroxide $Mg(OH)_2$ and aluminum hydroxide $Al(OH)_3$ (Fig. 15.15).
Anionic antacids are made from a mixture of sodium bicarbonate $NaHCO_3$ and calcium carbonate $CaCO_3$ (Fig. 15.15).
Sometimes, antacids are mixtures of the two types.
Antiacids are traded commercially either as tablets (sometimes effervescent) or liquids.

15.4 Anti-inflammatory drugs

Inflammation is produced after an aggression to the body by several agents of different nature: wounds, chemical substances, microbes; manifested by fever, redness, pain and swelling.

An anti-inflammatory drug treats inflammations.

Anti-inflammatory drugs have pharmacological effects on the different manifestations of an inflammation. They treat the inflammation and suppress fever and pain.
Anti-inflammatory drugs look like each other when discussing pharmacological effects and undesirable side effects; but they are very different when it comes to their chemical structures. They can be grouped in families; the most important is the family of salicylic, pyrazoles derivatives and propionic derivatives.

Salicylates

Salicylates are derivatives of salicylic acid.

Aspirin is the most widely known and used salicylate. Some salicylates are obtained by the esterification of the hydroxyl –OH group of salicylic acid (Fig. 15.16). This is the case of aspirin (Fig. 15.17). Others are obtained by esterification of the carboxyl functional group –COOH, such as methyl salicylate (Fig. 15.18).

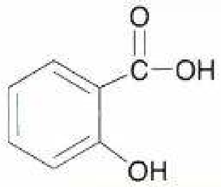


Figure 15.16
Formula of salicylic acid.

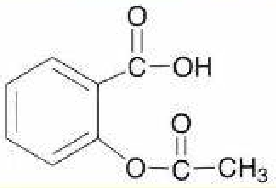


Figure 15.17
Formula of aspirin.

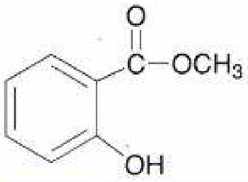
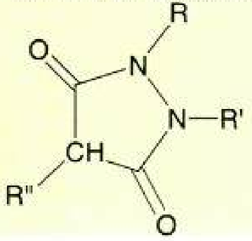


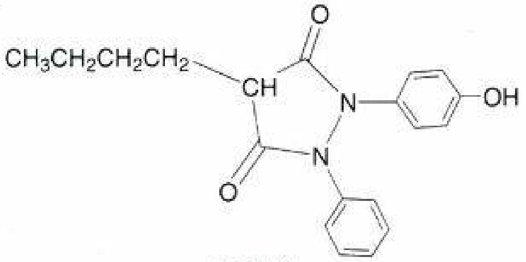
Figure 15.18
Formula of methyl salicylate.

Pyrazole derivatives

Pyrazole derivatives are anti-inflammatory drugs possessing the formula:



Each derivative differs from the others by the nature of radicals R, R' and R". Tanderil (or oxyphenbutazone) is an example of this family:

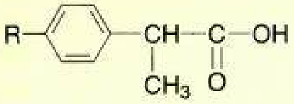


tanderil

Pyrazoles derivatives has some undesirable effects, they cause irritation of the skin, nausea, and insomnia; this is why they are not used as much as other anti-inflammatory drugs.

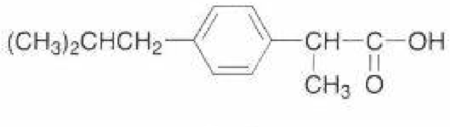
Propionic derivatives

Propionic derivatives are anti-inflammatory drugs possessing the general formula:



$$R-C_6H_4-\underset{CH_3}{\underset{|}{CH}}-\underset{O}{\underset{\|}{C}}-OH$$

These are derivatives of propionic acid. They are distinguished from each other by the R group attached to the phenyl group. Ibuprofen, traded under the name of brufen, is among the most widely used of these derivatives:



brufen

Propionic derivatives are generally more tolerated by the body than other anti-inflammatory drugs. Their undesirable effects are even less than other anti-inflammatory drugs.

15.5 Antibiotics

An antibiotic is a chemical substance produced by a specific species of microorganism (bacteria, fungi ...) that inhibits the growth of certain microorganisms or even destroys them.

It was known, since antiquity, that some molds applied to wounds, carbuncles and furuncles gave therapeutic action. These were antibiotics contained in substances and used to stop the action of germs.

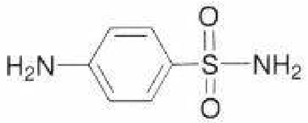


Figure 15.19

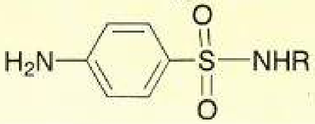
Formula of sulfanilamide.

There is a wide variety of antibiotics that differ remarkably by their chemical structures and their therapeutic properties. The family of sulfonamides, penicillin, and tetracycline are the most widely known antibiotics.
Antibiotics of synthetic or semi-synthetic origin are never produced by microorganisms.

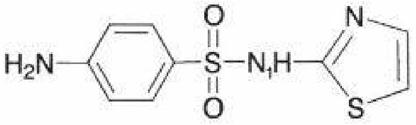
Sulfonamides

Sulfonamides were developed in 1935, when Prontosil was produced, a colored material with antibacterial effects. Sulfanilamide, (Fig. 15.19) a metabolic product of Prontosil, is in reality the compound responsible for the anti-bacterial properties of this stain. Derivatives of substitution of sulfonamide form the family of sulfonamides. Sulfonamides are not produced by microorganisms.

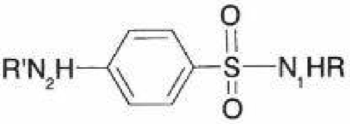
Sulfonamides form a family of antibiotics with sulfanilamide as the basic component. It has the general formula:



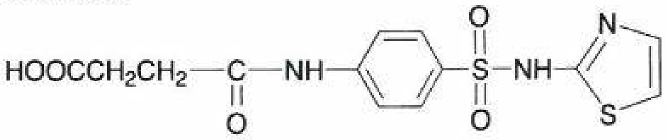
Sulfonamides are mono-substituted derivatives of sulfanilamide.
Sulfathiazole:



is one example of mono-substituted sulfanilamide. In this case, substitution takes place on first nitrogen atom N_1 of sulfanilamide. The compound has the general formula:



We also have di-substituted sulfanilamides. Substitution takes place on the two nitrogen atoms N_1 and N_2 of the sulfanilamide molecule. Succinylsulfathiazole is one example of di-substituted sulfanilamides:



succinylsuflathiazole

Disubstituted sulfanilamides do not have antibiotic effects. However, when administered in the body, they will be metabolized liberating the mono-substituted sulfanilamide corresponding to the antibiotic. These compounds are administered when a retarded effect of sulfanilamide is needed.

Penicillins

Penicillin (Fig. 15.20) and its antibacterial effects were discovered by Fleming (Fig. 15.21) in 1928, but was isolated ten years later. Starting in 1958, a great variety of derivatives of penicillin were largely elaborated and used as antibiotics.

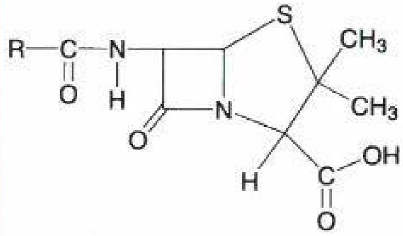


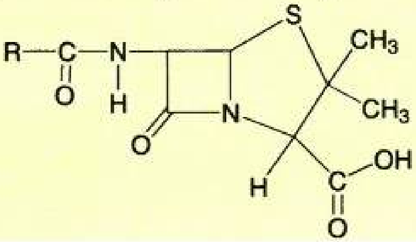
Figure 15.20

Formula of penicillin.

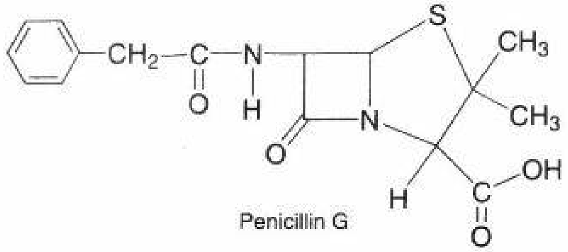
Figure 15.21

Sir Alexander Fleming (1881-1955) an English bacteriologist. He discovered penicillin in 1928. He shared the Nobel Prize with H. Flory and E. Chain in 1945 for isolating this antibiotic in 1938.

Penicillines form a family of antibiotics, which are the derivatives of penicillin and possess the general formula:



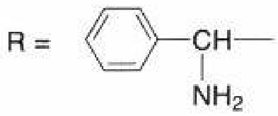
Penicillin G is the first antibiotic of the family that was isolated and marketed:



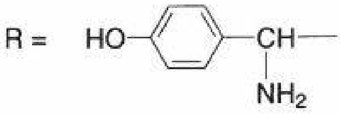
Penicillin G

Figure 15.22
An antibiotic of the tetracycline family. It is administered orally.

Nowadays, ampicillin and amoxycillin are two types of pencillines that are mostly used, because of a number of therapeutic properties, which give them advantage over the other types.



ampicillin

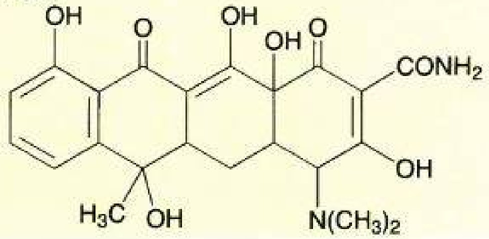


amoxycillin

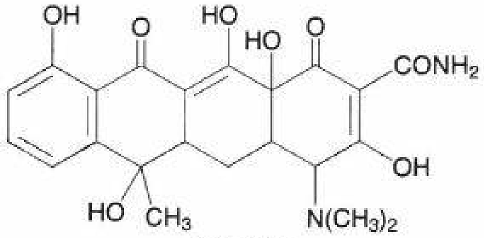
Tetracyclines

Tetracyclines constitute another family of antibiotics after penicillin that are mostly used (Fig. 15.22).

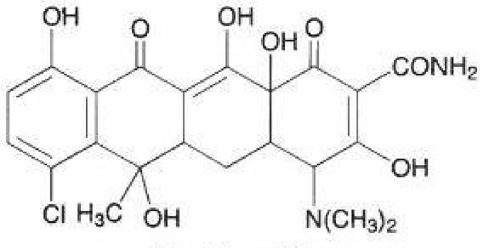
Tetracyclines form a family of antibiotics possessing the general formula:



Tetracyclines are more efficient than penicillins and sulfonamides in treating a great number of diseases caused by microorganisms. Tetracycline and chlorotetracycline are two examples of tetracyclines.



tetracycline



chlorotetracycline

15.6 Tranquilizers

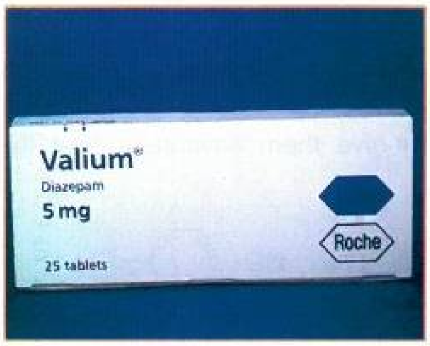
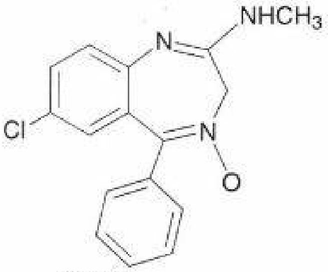


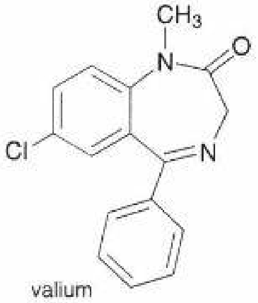
Figure 15.23
Valium is a minor tranquilizer.

A tranquilizer is a drug that relieves anxiety.

A tranquilizer treats several degrees of anxiety: light anxiety, agitation, fear and panic that face an increasing number of people in their daily life and their relationships which makes the tranquilizer the drug most commonly consumed.
Librium and Valium (Fig. 15.23) are two tranquilizers of the same family (benzodiazepins). They are the most widely known and used since the beginning of 1960.



librium



valium

Librium and Valium are of the category of minor tranquilizers, in opposition to major tranquilizers used for mental disorders and highly severe diseases. The tolerance effects caused by the minor tranquilizers are weak compared with those of other drugs generally affecting the mood. These tranquilizers are less dangerous for their toxicity effect and overdoses are rarely fatal unless the tranquilizers is taken with other drugs.

15.7 Antidepressants

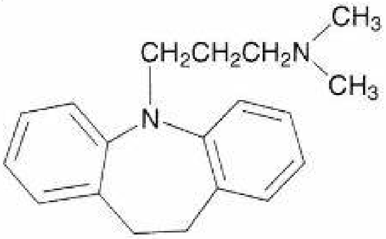
States of depression are characterized by a loss of interest in any activity. Excessive states of depression, considered as diseases, require therapeutic treatment and are characterized by a deep feeling of sadness, despair, guilt and a loss of concentration, in addition to an obsession with suicide and death ....

An antidepressant is a drug used to remedy the cases of acute depression.

The effect of antidepressants is to improve the moral status of the depressed persons. They increase the physical activity, appetite, and the sleeping quality of the patient. They reduce the obsession with suicide, and diminish the depression state.

There are two generations of antidepressants that differ in their chemical structure: tricyclic, which are the oldest type, and the bicyclic, which are more recent (discovered in the1980's).

Tofranil (imipramine) is the most widely used tricylic antidepressant:



tofranil

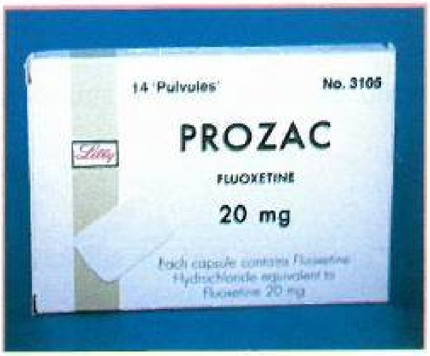
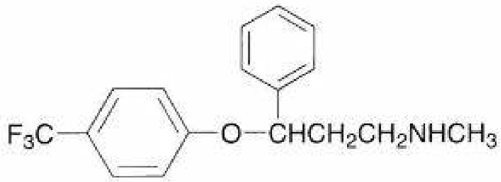


Figure 15.24

Prozac is baptized as "magic drug", but its total effects should be evaluated.

Prozac (fluoxetine) is a well known bicyclic antidepressant, baptized as the "magic drug" since its introduction in 1987 due to its therapeutic effects (Fig. 15.24). However, its total effects should be evaluated:



prozac

Tricyclic antidepressants pose a dangerous effect when overdosed, manifested by heart disfunction, which can lead to heart failure and eventually death.

Chapter review

- A medicinal drug is a chemical compound or substance used for therapeutic purposes.
- The active ingredient of a drug is a chemical compound, usually of complex structure, responsible for the pharmacological effects.
- An analgesic is a drug that relieves pain.
- An anesthetic is a substance that provokes local or general loss of sensation, including pain.
- Local anesthetic provokes a loss of sensation in a localized part of the body.
- General anesthetic provokes an absence of perception in all the sensations of the body.
- An antacid is a basic compound administered orally to neutralize gastric acids; it relieves pain caused by these acids.
- An anti-inflammatory drug is a drug that treats inflammations.
- An antibiotic is a chemical substance produced by a specific species of microorganism (bacteria, fungi ...) that inhibits the growth or leads to the destruction of the microorganism.
- A tranquilizer is a drug that relieves anxiety.
- An antidepressant is a drug used to remedy the states of acute depressions.

Laboratory Investigation

LI

Objective

Perform the hemisynthesis of a drug in the laboratory

Equipment and reagents

250 mL Erlenmeyer flask. Condenser. Water bath (crystallizing dish of water + hot plate). 10 and 20 mL graduated cylinders. Medicine dropper. Vacuum pump. Buckner. Watch glass. Glass rod. Support. Pince. Gloves. Protection goggles.

Salicylic acid. Acetic anhydride. Concentrated sulfuric acid. 95° ethyl alcohol. Cold distilled water. Ice-water mixture.

Procedure

Preparation

- Place 5 g of salicylic acid in a very dry Erlenmeyer flask.
- Add with precaution 6 mL of acetic anhydride with some drops of concentrated sulfuric acid.
- Adjust the condenser on the Erlenmeyer and place the setup in the water bath preheated to about 60 °C. Stabilize the setup by the aid of support and the pince.
- Keep heating for 15 minutes with intermittent agitation.
- Remove the setup from the water bath and add from the top of the condenser 30 mL of cold distilled water.
- Remove the condenser. Stir the mixture in the Erlenmeyer until the appearance of the first crystals. Then add 30 mL of cold distilled water.
- Place in the ice-water bath for 10 minutes.
- Filter the crystals. Wash with small volume of cold water then squeeze the crystals between two filter papers.

This is aspirin (acetylsalicylic acid). It is not pure. It is purified by recrystallization.

Purification

- Place the crystals in the well dry Erlenmeyer. Add 3 mL of ethyl alcohol and dissolve by introducing the Erlenmeyer in the water-bath preheated to 80°C. If the re-dissolution is not complete, re-add alcohol to a total volume of 5 mL.
- Then add 15 mL of lukewarm distilled water and let it cool, first in air then in the ice-water bath.
- Filter the crystals. Wash with small volume of cold and collect on an already watch glass.
- Dry in the oven at 80°C. Weigh. Calculate the yield.

Example of results

M(salicylic acid) = 138 $g.mol^{-1}$
M(acetic anhydride) = 102 $g.mol^{-1}$
M(aspirin) = 180 $g.mol^{-1}$
ρ(acetic anhydride) = 1.08 $kg.L^{-1}$
Salicylic acid is the limiting reactant.
$m(aspirin)_{exp} = 3.10$ g
Then, the yield is ~ 79 %.

Documentary activities

Secondary effects and contra-indications of aspirin

Because of the acidity of the gastric fluid (HCl and pH ~ 1.5), aspirin (acetylsalicylic acid) is absorbed by the mucous membrane of the stomach in its acid form HA. This causes local irritation and provokes weak bleeding.

To avoid this undesirable effect of aspirin, a tablet of this analgesic must not be taken unless it is disintegrated in a cup of water.

The buffered and effervescent form of aspirin permits this previous disintegration by the effervescence. The buffered medium plays a role, by increasing at least locally, the pH of the gastric fluid during absorption.

The pH 8 form of aspirin is also made to treat this effect of gastric irritation of aspirin.

Often, in the composition of aspirin, some antacids are added. Because of its irritation in the stomach, aspirin is not given for persons suffering from ulcer.

Aspirin has the effect of reducing blood clotting. This reduces the risk of heart attacks and formation of blood clots. This is why half a tablet of aspirin is advised daily for people exposed to such a risk.

This second effect of aspirin increases the risk of hemorrhage during wounds or surgical operations.

Questions

1) Cite two reasons: the first related to the structure of aspirin, the other to the nature of the medium of the stomach, which cause aspirin to irritate the stomach.
2) What are the positive secondary effects of aspirin? How can a person at risk benefit from these effects?

Undesirable effects of local and general anesthetics

If local anesthetics arrive across the skin, the tissues and the capillaries of the blood stream, they can be toxic due to their metabolic products formed in the blood, the liver and the kidney .... For this reason local anesthetics and its quantity must be chosen precisely so as not to invoke danger.

Among general anesthetics, inhalation anesthetics as nitrogen dioxide, diethyl ether, cyclopropane may provoke irritation of the lungs.

Their overdose can induce coma or death.

Anesthetics administered by injection are generally less dangerous.

The barbiturates among general anesthetics do not have undesirable effects unless they are given with some other drugs.

Morphinics, like morphine, have addiction effect.

General anesthetics have some effects that appear after the patient regains consciousness: headache, nausea, vomiting, drowsiness ... .

Questions

1) What is the danger of local anesthetics? How can we remedy this problem?
2) Why is the overdose of general inhalation anesthetics dangerous?
3) What is an addiction to a drug or to a substance?
4) What are the general undesirable effects observed after the patient wakes from general anesthesia?

- **Undesirable effects of antacids**

Antacids composed of magnesium (hydroxide and salts) are laxatives while antacids composed of aluminum provoke constipation.

So, according to the predispositions of the person using antacids, the appropriate type should be chosen. So we can use one of the two types or make a mixture of the two.

On the other side, a person suffering from hypertension or cardiac disorders should not use antacids with large amounts of sodium.

The usage of antacids can sometimes can be harmful because it delays the time needed to discover the true reason for stomach pain: grave ulcer, stomach cancer ...

Questions

1) Give three undesirable effects of antacids.
2) How using antacids can sometimes be dangerous instead of being beneficial for a person?

- **Undesirable effects of anti-inflammatory drugs**

The undesirable effects of anti-inflammatory drugs are identical to those of aspirin, which belongs to this class of drugs: irritation of the stomach, risk of hemorrhage when there are wounds and during surgical operations.

The anti-inflammatory drugs can sometimes manifest some toxicity, which is presented in the form of allergy, difficulty in respiration, eruption of skin, headache and hepatic complications...

The toxicity is due to the toxins produced during the metabolism of the anti-inflammatory drugs.

Questions

1) What are the undesirable effects of anti-inflammatory drugs that are common with those of aspirin?
2) Search for the meaning of the expression: metabolism of a drug.
3) Search for the meaning of the terms: eruption of skin, toxin.

- **Undesirable effects of antibiotics**

Sulfonamides possesses, to a certain point, light toxicity, which limits their use to a particular case of infections or diseases.

The undesirable effects of penicillin are very limited. However, allergic shocks felt by some people due to penicillin and which may be very dangerous should be mentioned. To a lesser degree, the following allergic effects are observed: eruption of skin, nausea, vomiting.

Tetracycline provokes gastric irritation and some toxicity of the liver and the kidneys.

An antibiotic has a wider zone of action over bacteria and microbes that is it has an effect over a great number of germs; it has an inhibiting effect on the growth and development of all the bacteria that are found in the intestines. Among these bacteria, some play the immunizing role. Thus, antibiotics can reduce the immune system in the intestines.

Questions

1) What makes the use of sulfonamides limited to particular case of infections and diseases?
2) What is the most dangerous undesirable effect of penicillin?
3) Are the undesirable effects of tetracycline noticeable or important?
4) What is the undesirable effect of antibiotic, which has a wider zone of action over bacteria and microbes?

Undesirable effects of tranquilizers and antidepressants

The minor tranquilizers (Librium and Valium) do not have dangerous effects. They are considered relatively non-dangerous or "safe". Sometimes, light discomfort is observed due to their absorption: headache, nausea, and dizziness.

These tranquilizers have weak effect of addiction. The association of alcohol or some drugs to these tranquilizers is dangerous, especially in the case of overdose.

Among the antidepressants, the tricyclic has the effects of a dry mouth, bitter taste of saliva, gastric discomfort, constipation, tachycardia, urinary retention ….

The overdose of tricyclic antidepressants is lethal.

The bicyclic antidepressants, designated also as antidepressants of the second generation, are replacing more and more the tricyclic antidepressants because they have weaker undesirable effects.

Prozac, the mostly used bicyclic antidepressant, has a small range of undesirable effects. In a number of persons, the following effects are observed: light nausea, diarrhea, fever, anxiety and insomnia.

Questions

1) Why are the minor tranquilizers designated as "safe" drugs?
2) Is it comfortable to use tricyclic antidepressants?
3) Why are bicyclic antidepressants designated as second generation?
4) Are the undesirable effects of the two generations of antidepressants comparable?

Exercises

1 A) In an autoclave, 300 kg of phenol react with just the necessary quantity of NaOH. Water, a product of the reaction, is removed while being formed (by evaporation), to render the reaction complete.

a) Write the equation of the reaction. What type of reaction is it?
b) Name compound A obtained, other than water.
c) Calculate the obtained mass of compound A.

B) Carbon dioxide current is passed through compound A under a pressure of 7 bars and at temperature 100 °C and then 130 °C. Compound B is obtained with 95 % yield.

a) Write the equations of the reactions taking place.
b) Name compound B and calculate its mass.

C) B is dissolved in water and sulfuric acid is added to the solution. A precipitate C is obtained. It is separated by filtration and then purified.

a) Name compound C.
b) Calculate its mass if the yield is 92 %.

D) Compound C reacts with the just necessary quantity of acetic anhydride, in the presence of sulfuric acid. By cooling, we obtain aspirin in the form of crystals. Separated, washed and dried, it weighs 500 kg.

a) Write the equation of the reaction. What type of reaction is it?
b) Give the systematic name of aspirin.
c) What is the role of sulfuric acid?
d) Calculate the yield of the reaction.

Given in g . mol^{-1}:
M(H) = 1; M(C) = 12 ; M(O) = 16 ; M(Na) = 40

2 On the prospectus of a drug (Excedrin), it is indicated that it contains aspirin, paracetamol, caffeine and an excipient.

a) Caffeine is a stimulating substance, added because of an undesirable effect of the drug. Suggest what may this effect be.
b) Aspirin and paracetamol are the active ingredients of the drug. Define an active ingredient.
c) Give the formula of each of the two compounds. Give the systematic name of aspirin.
d) What are the pharmacological effects of each active ingredient of the Excedrin?

3 A) To prepare aspirin in the laboratory, 5 g of salicylic acid are placed in a well dry Erlenmeyer flask and 8 mL of acetic anhydride are then added. A condenser is adapted to the Erlenmeyer, which is heated in the water bath, between 50 and 60°C, for 15 minutes.

a) Write the equation of the reaction.
b) Why do we use acetic anhydride instead of acetic acid?
c) What is the role of the condenser?

B) At the end of heating, the reaction is finished. The Erlenmeyer is removed from the water bath, and 6 mL of distilled water are added from the top of the condenser. Boiling occurs. When it is calmed, 25 mL of cold water are added. We stir. Aspirin crystals appear. 25 mL of cold water are added again and the Erlenmeyer is placed in the ice-water bath.

a) What reaction takes place when the 6 mL of water are added? Write its equation.
b) Why are the 25 mL of cold distilled water added after the appearance of the crystals?
c) Why was the Erlenmeyer placed in the ice-water bath?

C) The crystals are filtered and collected. To purify them, they are re-crystallized. For this, they are placed in a clean and dry Erlenmeyer, and they are dissolved in 6 mL of 95° ethanol at 80°C. 15 mL of warm water are added. They are cooled in air and then in the ice-water bath. The crystals are collected by filtration and are dried in an oven at 80°C. 5 g of aspirin are obtained.

a) What is the role of ethanol? What is the role of water? Where did the impurities, mixed with aspirin, go?

b) Determine the limiting reactant in the preparation of aspirin.

c) Calculate the yield of the preparation.

Given :

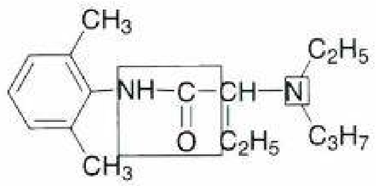
M(salicylic acid) = 138 g.mol^{-1}

M(acetic anhydride) = 102 g.mol^{-1}

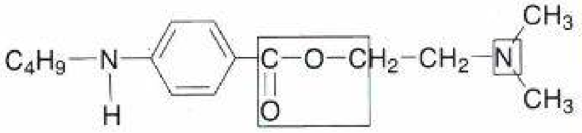
M(aspirin) = 180 g.mol^{-1}

ρ (acetic anhydride) = 1.08 kg.L^{-1}.

4 Etidocaine:



and tetracaine:



are two local anesthetics.

a) Identify the boxed functional group in each formula.

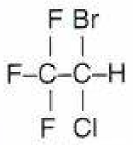
b) Identify the three principal parts of the structure of these two anesthetics.

c) Indicate to which class does each of the two belongs: ester, amide ...

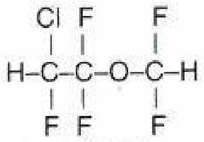
d) What is the overdose effect of such local anesthetics?

5 a) Name three common general inhalation anesthetics.

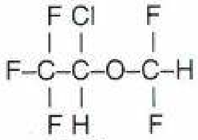
b) Halothane, enflurane, isoflurane and methoxyflurane:



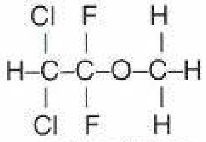
halothane



enflurane



isoflurane



methoxyflurane

are 4 volatile gases which possess anesthetic effects. They are inert, non-irritating and their mixtures with air or with oxygen are neither flammable nor explosive. Cite two inhalation anesthetics that must be preferably replaced by one of the four compounds above. Why?

6 a) Classify the following antacids as cationic or anionic:

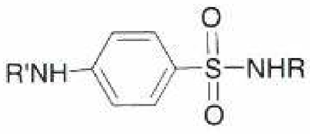
$Mg(OH)_2$, $NaHCO_3$, $CaCO_3$, $MgCO_3$, $Al(OH)_3$.

b) Write, for each of them, the equation of a reaction that shows its antacid effect.

7 a) A drug is said to be anti-inflammatory if it has three characteristic pharmacological effects. What are these effects?

b) Among the following drugs:
aspirin, penicillin G, paracetamol, tanderil and brufen.
Which is/are anti-inflammatory drug(s)?

8 The general formula of a di-substituted sulfonamide is given by:



a) Does a di-substituted sulfonamide have antibiotic effect? Explain.

b) Give the general formula of a sulfonamide which has antibiotic effects.

9 Tetracyclines are a family of common antibiotics.

a) Name two other commonly used antibiotic families.
b) Define an antibiotic.
c) Are all antibiotics produced from microorganisms?
d) Compared to the two most common families of antibiotics, the family of tetracylines has specific characteristic relative to its antibiotic effects. What is this characteristic?

10 Valium and Librium are two very commonly used tranquilizers.

a) Define the pharmacological effect of a tranquilizer.
b) Valium and Librium are designated as minor tranquilizers. What are the uses of major tranquilizers?
c) In what conditions is the overdose of a tranquilizer such as Valium and Librium dangerous?

11 a) Cite four or five common effects which characterizes an acute depression state.

b) Cite the principal effects of an antidepressant.
c) Which of these two antidepressants is more recent: tofranil, prozac?
d) Which has less undesirable effects?
e) For which of the two is the overdose effect more dangerous? What are the consequences of the overdose in this case?

Evaluation

Applying knowledge

1 Classify the following drugs relative to their pharmacological effects:

Indocid: Inhibiting agent of the synthesis of prostaglandin, with marked analgesic and antipyretic properties.

Atarax: To relief anxiety and tension.

Suprane: it is indicated as inhalation agent to provoke and maintain anesthesia for adults and infants.

Ampiclox: it is indicated for the immediate treatment of severe bacteria infections before the infection agent is identified.

Trilafon: At small doses, to calm the manifestation of anxiety.

Athymil: To relief the symptoms of depression.

Floxapen: It is indicated for treatment of infections such as acne, eczema, furoncles, and infected wounds....

(Extracts from MEPPO-VIDAL, 1997)

2 Paracetamol is obtained by the reaction between (para) aminophenol and acetic anhydride.

a) Write the corresponding equation.
b) Put a box around two functional groups of the formula of paracetamol. Name each functional group.
c) Cite two pharmacological effects of this drug. Is it an anti-inflammatory? Why?

3 a) What is generally the role of an anesthetic?

b) Compare the pharmacological effects produced by local and general anesthetics.

4 A person has the habit of keeping the drugs he used for some common diseases: cold, influenza, allergy, cough, fever, overwork, kidney stones ... He wants to use them later in the same situation or advise his entourage.

What are the risks, which result from such an attitude? Explain why.

5 A very emotional adolescent feels distressed and anxious in situations such as: preparation of an exam, goes out with friends of her age, speaks with adult person or with people responsible for her ...

To get rid of her stress and to get assurance, she got used to take some common tranquilizers.

a) Is this an appropriate way to remedy her state?

b) What probable risk is she exposed to by her behavior?

Designing an experiment

6 Preparation of paracetamol in the laboratory

(La Reunion 1998, Extracts)

Paracetamol is prepared by the reaction of (para) aminophenol with ethanoic anhydride.

Step A: 2.18 g of (para) aminophenol and about 20 mL of distilled water are introduced into an Erlenmeyer flask. The mixture is acidified. A condenser is adapted and the mixture is heated and stirred to dissolve the (para) aminophenol. It is then cooled.

Step B: The Erlenmeyer is placed in ice-water bath and 3.0 mL of ethanoic anhydride are slowly added. Crystals appear. They are filtered with a Buchner and rinsed with small amount of cold water.

Step C: The crystals are introduced into 15 mL of boiled water. If needed, water is added again in order to have complete dissolution. The system is cooled to ambient temperature, and then in an ice-water mixture. Crystals appear. They are filtered and dried.

Step D: The crystals are weighed.

Questions

a) What is the role of the condenser?

b) Step B is done in ice-water bath. Why? Why are the crystals washed with small amounts of cold water?

c) What is the goal of step C? Propose a way to dry the crystals rapidly and at a temperature of about 80 °C.

d) Write the equation of the reaction of the preparation of paracetamol.

e) Calculate the quantity of the introduced reactants. Calculate the yield knowing that 1.7 g of crystals are collected.

Given:

M((para)aminophenol) = $109\ g.mol^{-1}$

M(ethanoic anhydride) = $102\ g.mol^{-1}$

M(paracetamol) = $151\ g.mol^{-1}$

ρ (ethanoic anhydride) = $1.08\ kg.L^{-1}$.

Communicating

7 On the prospectus of a drug, it is indicated, that it contains paracetamol, aspirin, aluminum hydroxide $Al(OH)_3$ and magnesium hydroxide $Mg(OH)_2$.

a) To what class does this drug principally belong?

b) What undesirable effect of aspirin is indicated when paracetamol is added?

c) What are the roles of the two compounds: $Al(OH)_3$ and $Mg(OH)_2$?

d) Search for the reason for using a mixture of these two compounds?


93496

9

New materials

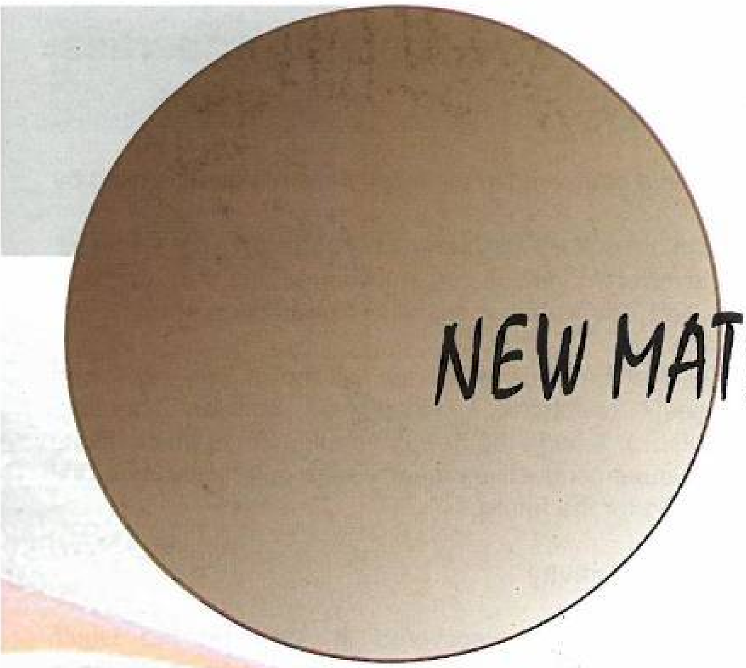
Composites are new materials. They have wide applications in the manufacture of spatial and nautical vehicles.

The husk of a sailboat is made from composite material, constituted of a synthetic polymer and of fiberglass.

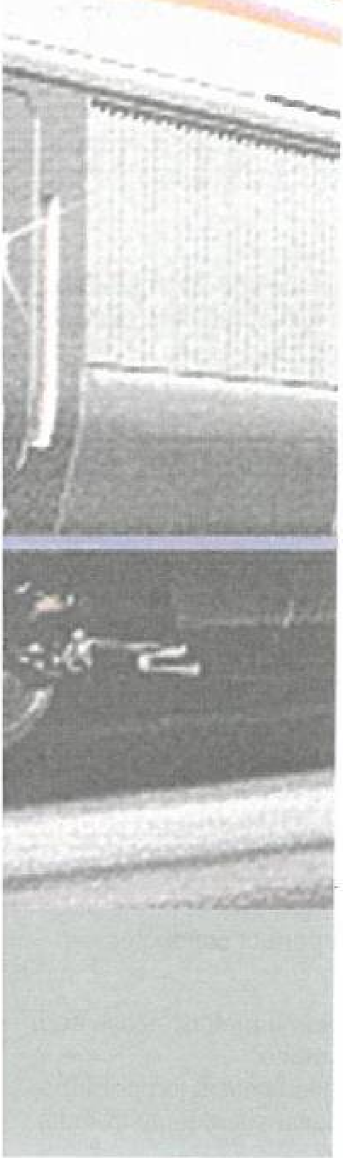
Superconductive ceramics belong to the ceramics category called "new" or "technique". They are characterized by particular electric and magnetic properties.

Composite materials, formed by the association of materials of different nature: organic polymers, metals, and ceramics; they have the useful and favorable characteristics of the materials they come from, but without their undesirable characteristics.

Research of new materials is a very important branch of modern chemistry and physics. The development of a number, continuously increasing, of new technologies, depends greatly on discovering and manufacturing such materials.



NEW MATERIALS 16



Objectives

- Define superconductivity.
- Identify superconductive ceramics.
- Identify composite materials.
- Recognize the importance of superconductive ceramics and composite materials.

Prerequisites

- Cements and glass.
- Electricity and magnetism.
- Metals and alloys.

Chapter content

16.1 Ceramics; development, properties and uses.

Ceramics have been among the most ancient materials used by mankind.

First known in pottery (earthenware, porcelain, potteries....), their use evolved to include construction material (tile, sanitary, bricks,..) and traditional industries (refractory ceramics for furnaces).

Nowadays, technique ceramics are utilized in very advanced technologies (electronic, weapons, nuclear, motors, biomaterials....). Among the new generation of ceramics, those possessing superconductive properties are potentially important and promising for the future.

Superconductivity

Figure 16.1

Heike Kamerligh Onnes (1853-1926) a Dutch physicist who received the Noble prize in 1913. He liquefied helium in 1907 and discovered superconductivity in 1911.

Superconductivity was discovered in 1911 by the Dutch physicist H. Onnes (Fig. 16.1) who noticed that when cooled to a temperature of - 269 °C (4.2 K) mercury loses all resistance to conduct electric current.

A number of metals and alloys (known or manufactured since 1911) possess the property of losing all resistance to conduct electric current, when brought to ultra cool temperatures (below 23 K).

Superconductivity is a phenomenon manifested by materials that do not show any resistance to conducting electric current below a critical temperature designated by T_c.

The flow of an electric current through a body acting as a conductor (a metal for example) is due to the circulation of a set of electrons through that body.

Normally, the interactions between the mobile electrons, which are responsible for flow of current, and the rest of the matter of the conducting body (positive ions, impurities ...) constitute an obstacle to electrons circulation. This is the origin of the electric resistance of a conductor and the loss of energy by Joule's effect during current flow.

In a superconducting material, the electrons do not face any obstacle during their circulation. This material does not possess electric resistance and there is no energy loss when current passes through them.

A superconductor can be qualified as a perfect conductor.

Superconductivity is a characteristic of some metals, alloys and ceramics, but not a general property of matter.

It is manifested below a temperature, called critical temperature T_c, of the material where this material passes suddenly from its normal state to become superconductor.

Ceramics

Traditional ceramics, used in pottery, construction and as refractory materials of some industries, have clay, which is a source of silicates, as their raw materials.
On the other hand, technique ceramics have more diversified composition and more rigorous norms of manufacture and structure.
A modern identification of ceramics tends to include both categories (traditional and technique).

Ceramic is an inorganic non-metallic material, having a crystalline and rigorously controlled structure; it is manufactured from very pure raw materials, which gives it its very specific characteristics.

Depending on the raw materials used, the composition of the ceramic, and on the method of manufacture, ceramic is obtained to be used: in electronics, for example, to be a superconductive ceramic, or for biomedical uses... .

Powder	Examples
Non-metals	C, B, Si
Oxides	SiO_2, Al_2O_3, BaO, MgO, ZrO_2, TiO_2
Carbides	TiC
Nitrides	AIN
Silicides	$MoSi_2$
Borides	TiB_2

Table 16.1
Examples of powders; raw materials for ceramics.

Principle of manufacturing ceramics

The raw materials of ceramics such as non-metals, oxides, carbides, nitrides, silicicides and borides, are used in the powder form (Table 16.1).
For technique ceramics, the preparation of the powder follows strict norms and sophisticated procedures to get ultra pure compounds and microstructures consistent with the desired dimensions and forms of grain.
The different powders are mixed. For technique ceramics, it is important that the mixture is totally homogenous.
For traditional ceramics, the powder is kneaded with water to form the paste. The mixture (dry or paste) is shaped to the desired form of the ceramic, and then fired at a temperature between 900 °C and 2000 °C. During firing, a chemical reaction occurs between the components.
Also, for technique ceramic, reaching the firing temperature and returning to ambient temperature, must be done slowly.

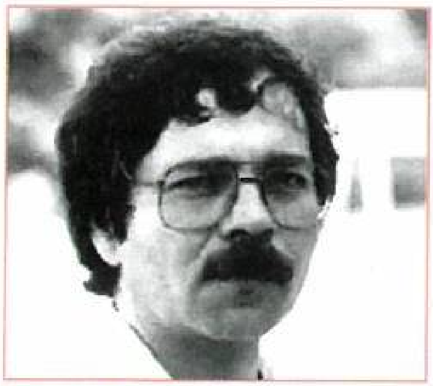


Figure 16.2
Georg J. Bednorz (1950-   ) is German physicist who shared with his colleague the Swiss K. Müller, the Nobel Prize in physics in 1987 for discovering a superconductive ceramic.

Superconductive ceramics

Since the discovery of superconductivity in1911 and until 1986, there was no superconductor known with critical temperature T_c higher than 23 K (-250 °C) (T_c of Niobium-Germanium alloy).
In 1986, G. Bednorz (Fig. 16.2) and K. Müller announced the discovery of a superconductive ceramic with a critical temperature T_c = 35 K (-238 °C), which earned them, the next year, (a record time) the Nobel prize in physics (1987). This ceramic was a mixed oxide of lanthanum and copper doped with barium (La_2CuO_4).
In 1987, the same scientists discovered the ceramic $YBa_2Cu_3O_7$ with critical temperature T_c = 93 K (-180 °C) and the superconductive ceramics era became wide open.

Superconductive ceramics possess specific and important electronic and magnetic properties of superconductors.

This ceramic has no resistance to the flow of electric current. They can conduct very high currents for a very long time (100,000 years), without any noticeable loss of electric energy.

When placed in a magnetic field, and rendered superconductive, by bringing them to a temperature lower than their T_c, they can have two behaviors: either expel any magnetic flux (Meissner effect) (Fig. 16.3), or become a center of intense magnetic field. These two behaviors give ceramics their vast important applications.

Uses of ceramics

The large diversity of ceramics and their properties make the fields of their application vast.

The large quantity of ceramics manufactured corresponds to traditional ceramics, used in construction, in confection of domestic objects, and for refractory materials of some industries.

Industrial ceramics have diversified applications. Some of these are:

- Thermomechanic ceramics (motors, gas turbines, ...). They replace traditional materials.
- Electronic ceramics (emission and detection of ultrasound, microphones, gauges, pulse generators, support and cover for integrated circuits ...).
- Ceramics for diverse use (cutting devices, temperature exchangers, heating elements).

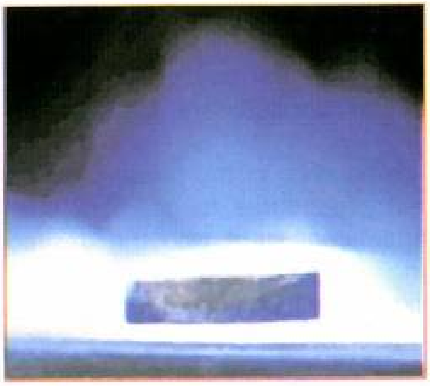


Figure 16.3

The small magnet is levitated above this superconductive ceramic, because it has the property to repel the lines of the magnetic field of the magnet.

The class of superconductive ceramics is of interest because of the many possible applications they will provide in the future.
With critical temperatures T_c higher than the liquefaction of nitrogen (77 K), it is possible to replace liquid helium (rare and expensive fluid) by liquid nitrogen to induce the superconductivity of ceramics.
Superconductive ceramics are used to manufacture small magnets, which create a powerful magnetic field, utilized in medical imaging (MRI) (Fig. 16.4).
Their property of expelling magnetic fields can be utilized in the future to manufacture, on large scale, magnetic levitated trains. They also permit the manufacture of superconductive chips that conduct powerful current, hence the manufacturing of ultra rapid computers.

Figure 16.4

Medical imaging of the MRI type will have improved performance by using superconductive ceramics.

16.2 Composite materials: development, properties, and uses.

Developing composite materials at the end of the 1950's was a response to the need in the space program for light and thermally stable materials.
Nowadays, the applications of these materials are enhanced, and there have been improvements in their manufacturing, and progress in research for new types; it is an important field in materials science.

A composite material is formed of two or more different materials, associated together to give superior characteristics to those of their separate constituents.

A composite material is usually made up of fibers (reinforcements), embedded in a matrix. The matrix plays the role of a joint between the fibers, which gives solidity to the composite.
The reinforcements may be fiberglass, graphite, silicone, carbides, polyamides, alumina or others.
The matrices are of three types: organic polymers, metals or ceramics.
Organic polymers are thermosets and thermoplastics. The composites corresponding to this type of matrices are made for uses where temperatures do not exceed 300 °C.
Composites in which matrices are metallic can stand higher temperatures without decomposing (to 600 °C).
To obtain stable composites at temperatures reaching 3000 °C, for example, the matrices must be constructed of ceramics.

■ Properties of composite materials

Composite materials are characterized by their lightweight. Compared with steel, of similar strength, composite materials are three or four times lighter than these alloys.
They are hard and rigid.
They are more resistant to traction than steel.
They conduct electricity and heat.
They are thermally stable.
They are resistant to fatigue and wear.
Composites with organic polymer matrices are resistant to chemical agents.
Those with ceramic matrices are refractory and resistant to corrosion.

■ Fatigue of a material is due to its prolonged and excessive usage, which alters some of its properties (generally, physical). A metallic cable breaks suddenly for example).

■ Principal uses

Composite materials have their greatest utilization in the aerospace industry. Being light, rigid, and thermally stable, they are suitable for construction of any kind of space engines: aircrafts, satellites, rockets .... . They constitute the material of choice to reinforce the cover of motors, the wings, the doors and the shutters of airplanes.

These materials are utilized in the automotive, trains, ships and yachts industries.

Because of their rigidity and their lightness, they are utilized in sport equipments: skis, rackets, surfing boards, jumping poles (Fig. 16.5).

Plastics reinforced with fiberglass are used in the manufacturing of utensils and household objects.

The utilization of composite materials includes construction fields' equipment, where they constitute reinforcements used in the pillars of bridges and highways and for biomedical uses such as prosthesis.

Figure 16.5

Composite materials are used in manufacturing sport equipments.

Chapter review

- Superconductivity is a phenomenon manifested by materials that do not show any resistance to conduct the electric current, below a critical temperature designated by T_c.
- Ceramic is an inorganic material, non-metallic, with a crystalline structure and a rigorously controlled structure.
- Superconductive ceramics have no electric resistance.
- Placed in a magnetic field, superconductive ceramics can either expel any magnetic flux, or become a center of intense magnetic field.
- A composite material is formed of two or more different materials; they are associated together to give characteristics superior to those of their separate constituents.
- A composite material is usually made of reinforcements and a matrix.
- The reinforcements can be fiberglass, graphite, silicone, carbides, polyamides, or alumina.
- The matrices are of three types: organic polymers, metals or ceramics.
- Composite materials are characterized by their hardness, lightness, thermal and electrical conductivities, thermal stability and resistance to traction and wear.

Documentary activity 1

Manufacture of the ceramic : $YBa_2Cu_3O_7$

The raw materials are the oxides: Y_2O_3, BaO and CuO, in a finely divided (powdered) state. Instead of barium oxide, you can use barium carbonate $BaCO_3$. You can realize a stoichiometric mixture relative to metals, without taking into consideration the quantity of oxygen, because the mixture will undergo roasting during which the amount of oxygen will be adjusted.

You realize a homogeneous mixture of oxides using adequate mixers for powders; a turbo mixer like the one you use to prepare coffee for example. The mixture is then placed in a cast. If you wish to prepare a ceramic in the form of a small cylinder for example, the mixture should be placed in a cast with this form.

The powder is a strongly pressed using a compression system with a screw. A solid blok is then formed, which is still very friable.

The solid is placed in refractory crucible; in porcelain or in alumina. It is then heated very slowly to a very high temperature (950°C for example). It is healed at this temperature between 24 and 48 hours, and then brought back slowly to room temperature. The progressive elevation of temperature can last for ten hours or more. It would be the same when bringing it back to ambient temperature.

During heating and cooling, a chemical reaction takes place between the raw materials and the ceramic $YBa_2Cu_3O_7$ where its characteristic crystalline network is formed.

In order to show the superconductivity of the ceramic $YBa_2Cu_3O_7$, you can place it on a magnet and lower its temperature using liquid nitrogen to reach 77 K (a temperature less than its $T_c = 93$ K). The ceramic is then raised few millimeters above the magnet. At a temperature equals or less than its T_c, the ceramic becomes superconductive. This can repel any magnetic flux (Meisner effect), which provokes the levitation of the ceramic away from the magnetic field.

Questions

1) Explain why you can replace a metallic oxide by carbonate, in the manufacture of ceramic. Write down the corresponding chemical reaction?
2) Why is it necessary, in the synthesis of ceramic $YBa_2Cu_3O_7$, that all oxide powders are slender and their mixture is homogeneous?
3) With what process is the powder mixture given a certain shape in the cast?
4) Search the meaning of friable?
5) Why should the crucible be refractory?
6) Why should both the heating of the powders mixture and the return of the product formed to ambient temperature be very slow?
7) What happens if we place a small magnet over superconductive ceramic and then lower the temperature to $T \leq T_c$?

Documentary activity 2

Possible applications of superconductor ceramics

The usage of superconductor ceramics is very promising, it would be possible to apply and improve in the future. This depends on two factors that remain to be realized in this domain: prepare ceramics of high critical temperatures (T_c) (in other words with T_c close to ambient temperature) and make easy and practical the use of low temperature (that of liquid nitrogen for example) at the level of large applications.

The use of ceramics is based on their electric and magnetic properties. They are able to transport high electrical energy by Joule effect. They can, according to the type of magnet they are a part of, either expel any magnetic flux or be the siege point of intense magnetic fields.

Nuclear magnetic resonance

Atomic nuclei with an odd number of protons (Z is odd) or an odd number of neutrons (A is odd) can act as small magnets. The phenomenon of nuclear magnetic resonance is due to the magnetic behavior of such nuclei.

Nuclear magnetic resonance is realized when a substance is put under an elevated and fixed magnetic field, and then brought back to absorb a radiation of the region of spectrum of radio waves, equal to a natural radiation of certain nuclei of atoms that form it (nuclei of either odd Z or A). When the magnetic field is omitted, these nuclei will emit a radiation that is transformed into a pulse of energy.

The applications of nuclear magnetic resonance are based in the exploitation of radiation absorbed and emitted by the nuclei. Nuclear magnetic resonance is applied to the study of structure of chemical substances. It is also applied to the study of structure of living tissues, especially smooth tissues; muscles, brain, lungs, kidneys, blood, visceral mass.... The radiations used in this domain are those of the nuclei of the most abundant isotope hydrogen ^1H, that are found abundantly in the tissues and that participate in the constitution of their molecules. H_2O, lipids, proteins, glucose and sugars.

Computers transform the signals (radiation or pulses of energy) received from the tissue into precise images of these tissues and their structures. These images allow conceiving abnormalities, diseases... In the tissues. This is the principle of imaging by magnetic resonance (MRI) applied in the medical field since 1983. This method even though it is more expensive than other methods in medical imaging, it is the most performing and effective in the diagnosis of diseases. In addition to this, it is the least dangerous to the body.

MRI requires strong magnets, able to create intense and stable magnetic field, in the living tissues to make images. Superconductor ceramics can, due to their property of being the site of intense magnetic field, assume the elaboration of such magnets.

Questions

1) On which properties of superconductor ceramics will the eventual applications of ceramics in the future be based?
2) What are the difficulties that are faced in the use of ceramics in high scale applications?
3) Explain why nuclei with odd A can act as small magnets?
4) Explain why the isotope ^1H is the most adequate nucleus, in order to exploit the magnetic behavior in medical imaging of the body, by the MRI method?
5) What does the application of superconductor ceramics consists of in the MRI method?

Magnetic levitated trains

Magnetic levitated trains are trains with very high speeds that circulate above rails without touching them. They are propelled due to magnetic forces, in sort that they circulate few millimeters or centimeters above the rails (Fig. 16.6). Such trains, having a speed of 100 Km/h are manufactured in England since 1984.

They run between the airport of Birmingham and train stations.

The magnetic lift of trains is released by intense magnetic fields; with superconductors being the site or that are created by giant electromagnets. The lift of the train by superconductors leads to a more stable system than that of electromagnets, which do not need a continuous adjustment of the distance between the train and the tails. Still, this technique is more expensive than that of electromagnets and demands the presence of a system of refrigeration in the train to the superconductors below the T_c.

Figure 16.6

Magnetic levitated train in experimentation stage, in Germany.

The superconductor ceramics discovered up till now, which have the highest known T_c, in addition to the hope of elaborating ceramics with higher T_c, open a new way for the project of construction of magnetic levitated trains and the generalization of their use.

Magnetic levitated trains have great number of advantages relative to ordinary trains, which use wheels and rails of steel. They are fast; their speed can exceed 500 Km/h. They have the facility of acceleration and braking, a great capacity to go uphill and function in bad weather conditions; temperature, rain, snow, frosts... They don't make any noise. They consume less fuel or energy than ordinary trains or other vehicles. They are less polluting for the atmosphere than other vehicles.

Questions

1) How was the magnetic levitated trains realized?
2) What advantages does superconductors present in the techniques of magnetic levitated trains?
3) What advantages does superconductor ceramics present?
4) List the advantages of trains with magnetic lift relative to ordinary trains and other vehicles.

Other applications

The tendency in the manufacture of modern computers is toward microminiaturaization:
diminish the dimensions of circuit elements and pile up millions of elements on a «chip» of 1 to 2 cm^2 . This increases considerably the speed of operations and propagation of signals giving rise to ultra fast computers with reduced size.
Superconductor ceramics can replace in some cases silicon and other semi-conductors in the manufacture of "chips". The advantage of superconductor ceramics is to assume the circulation of intense electric current in ultra reduced spaces, without any loss in energy.
Moreover. their use can not be generalized to personal micro-computers because such computers can not be easily equipped with a liquificator of helium or nitrogen. Their application is suitable for large computers because in this case their power is considerably increased and their volume is considerably reduced. The most seducing application of superconductor ceramics is to constitute generators and transporters of electric current.
This application seems difficult to be realized because of the fragility of ceramic: they resist shocks and they break easily.

Questions

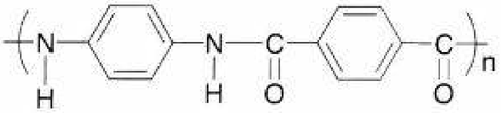
1) What does microminiaturizing mean in the manufacturing of computers? What is its advantage?
2) What is the advantage of using superconductor ceramics in this domain?
3) Why is it difficult to use ceramics as transporters of electric current?

Documentary activity 3

The Kevlar

Kevlar is not a composite material because it is not constituted of fibers, playing the role of reinforcement and a matrix where fibers are embedded. Still, it is not a new material relative to its remarkable characteristics.

Kevlar is an organic polymer of formula:



Hydrogen bonds are formed between the atoms of oxygen of the $-\underset{\underset{O}{\|}}{C}-$ groups and the hydrogen atoms of the $-\underset{|}{N}-$ groups of different chains creating a plain network and a sheet structure of the polymer.

The remarkable properties of Kevlar, which can be resumed by its resistance to heat, its great rigidity and its hardness higher than those of steel, are due to the existence of strong bonds in the individual chains, also to the strength of the hydrogen bonds in the plain network of sheet structure, and finally to the regular disposition of sheets in the material.

The cords of Kevlar have replaced the cables of steel in several applications, more particularly in the platforms for the offshore oil drilling. For the same diameter, Kevlar cables are 20 times more resistant than steel cables, in the seawater.

Kevlar is used to make skis of good quality (Fig. 16.7) and anti-bullets vests.

Due to its great thermal stability, Kevlar is used in the manufacture of tunics, worn by firemen, for protection against fire.

Figure 16.7
Kevlar, robust and light, is used in the manufacture of high quality skis.

Questions

1) Is Kevlar a composite material? Why?
2) What are the most remarkable properties of Kevlar?
3) Cite the important applications of Kevlar.
4) For what reason is Kevlar used in the manufacture of anti-bullets vests, tunics worn by firemen for protection against fire?
5) What are the remarkable properties of Kevlar due to?

Some applications of composite materials

- **Prosthesis**

Prosthesis is the replacement of a lost limbs of the body by an artificial limbs. The use of artificial limbs has been known for long time. In the 19th century, wood was the principle material used in the manufacture of such limbs. Later on, an alloy of aluminum, duraluminum and fiber materials were used. These latter made the manufacture of artificial limbs light and solid. Composite materials, due to their remarkable properties and lightness, rigidity, resistance to traction or usury, are convenient to construct such limbs. Composite materials with ceramics matrix for example, are used in the manufacture of femur heads, artificial legs, arms ... .

- **Aeronautics structures**

Composite materials have wide applications in the manufacture of spatial and nautical structures. In addition to their rigidity, properties such as lightness, thermal stability, resistance to high temperatures and resistance to corrosion, render these materials convenient to manufacture such structures.

Materials with metallic matrix are used in the making of coaches. They are lighter than metals.
Materials with ceramic matrices are used to cover the exterior body of satellites and rockets, some parts of the structure of military planes and supersonics planes, to protect them from high temperature to which their engines are exposed.
Materials resistant to corrosion are used in nautical structures. They are essential for the matrices of polymers, reinforced by ceramics, graphite or metals.

In general, most parts of spatial engines (planes, helicopters, shuttles ...) and nautical ships..... are made from composite materials.

Questions

1) What are the particular properties of composite materials that make them suitable for the manufacture of artificial limbs in prosthesis?
2) Lightness, thermal stability, resistance to high temperatures and to corrosion are principal properties for a material to be adequate for aeronautic structure.
Justify, using specific examples, why each property is important in the aeronautic structures.

Evaluation

Applying knowledge

1 A) Copper metal Cu, as all metals, conducts electric current. What is the reason for the flow of electric current through a copper wire?

B) Titanium Ti is a transition metal. It conducts electric current. Below a certain temperature T_c (inferior to 23 K), titanium is superconductor.

a) What distinguishes the behavior of titanium as conductor as compared to being superconductor?

b) What is the temperature T_c called?

c) Suggest a possible way, which allows to reach a temperature inferior to 23 K.

Given:
4.2 K; temperature of liquid helium
77 K; temperature of liquid nitrogen.

d) Describe a simple procedure to obtain titanium metal in a superconductor state.

2 A ceramic, part of the structure of an electronic piece is to be manufactured.

A) The raw material, mixed oxides of barium and titanium (IV) (TiO_2 and BaO), was prepared by a sophisticated method called sol-gel, which produced ultra pure powder, having well controlled structural characteristic (size of the grain ...).

Why is there a need to proceed in a rigorous and controlled manner to prepare the raw material of such ceramic? Do we proceed in an identical manner to prepare pottery ceramic?

B) With the obtained powder, the desired form of the piece of ceramic is shaped in the dry state and then slowly heated to 1000°C. It is heated for 24 hours, and is returned slowly to ambient temperature. This describes the cooking of the ceramics.

a) What happens generally during the cooking of a ceramic?

b) The procedure of shaping and cooking a pottery ceramic is different in one aspect than this described in B. State what is this aspect.

3 $YBa_2Cu_3O_7$ is a superconductive ceramic of $T_c = 93$ K (the highest known temperature).

a) Explain the behavior of a superconductor when an electric current passes through it.

b) What distinguishes this behavior from that of an ordinary conductor?

c) When a small element of the ceramic $YBa_2Cu_3O_7$ is placed on a magnet and cooled to a temperature T_c, it is levitated few millimeters above the magnet.

1) To what magnetic property of superconductors is this due?

2) Explain the significance of the temperature T_c.

3) Name an application of great economic importance that allows to profit from the magnetic behavior of such a ceramic.

4 2 g of $YBa_2Cu_3O_7$ ceramic are prepared.

a) List the principal steps of the preparation.

b) Calculate the mass of the following oxides: Y_2O_3, BaO and CuO that were used.

c) Why is it not necessary to consider the mass of oxygen in the ceramic, when the mass of the powder oxides used in the preparation are to be determined?

d) In a second procedure, BaO is replaced by $BaCO_3$ to prepare the same mass of the ceramic.

Why is it possible to use $BaCO_3$ instead of BaO? Explain using a chemical reaction. Write the equation of the reaction.

Given the molar masses in $g.mol^{-1}$:
M(Ba) = 137.3; M(Cu) = 63.5; M(O) = 16 ;
M(Y) = 88.9.

5 A) A composite material is used in an application to withstand a temperature of 2000 °C. What type of matrix should it have?

B) Using light materials is sought in the manufacture of airplanes. Aluminum alloys are used because of the lightness of this metal. Composite materials permit to reduce the weight of such vehicles even more.

a) What are the structural elements of a composite material?

b) Suggest a type of composite material convenient for the manufacture of the exterior of an airplane and identify its elements.

6 The MRI method (Magnetic Resonance Imaging) is widely used in medicine. It permits to get very precise images of living tissues, especially soft tissues: heart, kidneys, lungs, … . The method consists of subjecting the body to an intense and stable magnetic field, then permitting the nucleus of the hydrogen isotope ^1H (the most abundant isotope of this element and which participates in the human body in the structure of all the tissues, because it participates quantitatively in the structure of water, lipids, proteins and carbohydrates) to absorb a radio radiation equal to one of their natural radiations.

When the field is cancelled, the ^1H isotope nuclei emit radiations, which are analyzed by a very high performance computer and transformed to images of the tissues to be examined.

a) The human body being made of 70% by mass of water, the lipids being constituted essentially of fats, the muscles, of proteins, and carbohydrates, of long chains of general formula $C_x(H_2O)_y$, explain how this information permit to justify the choice of ^1H isotope to study the structure of living tissues by MRI method.

b) What does the term radio radiation or (radio wave) mean?

c) In MRI, superconductors are used to obtain intense and stable magnetic fields, why are these materials appropriate for such a use?

d) Superconductive ceramics have an advantage over known superconductors. What is this advantage?

7 In electronics, the "chips" are very small surfaces (1 to 2 cm^2) where millions of microelements of circuits are stacked. They are used in microcomputers, to pass high electric current in short times.

The current "chips" are manufactured from semi-conductors (silicon or others). Superconductive ceramics have replace semi-conductors in the manufacture of such "chips".

a) Why can these ceramics replace the current "chips"?

b) Superconductive ceramics have an advantage over semi-conductors. What is it?

8 Kevlar is a new material in the sense it has a number of characteristics of great importance, which permit its usage in diverse applications.

a) Nowadays, Kevlar replaces steel in the manufacture of cables used in offshore oil drilling. Cite these characteristics that permit the use of Kevlar in replacing steel cables.

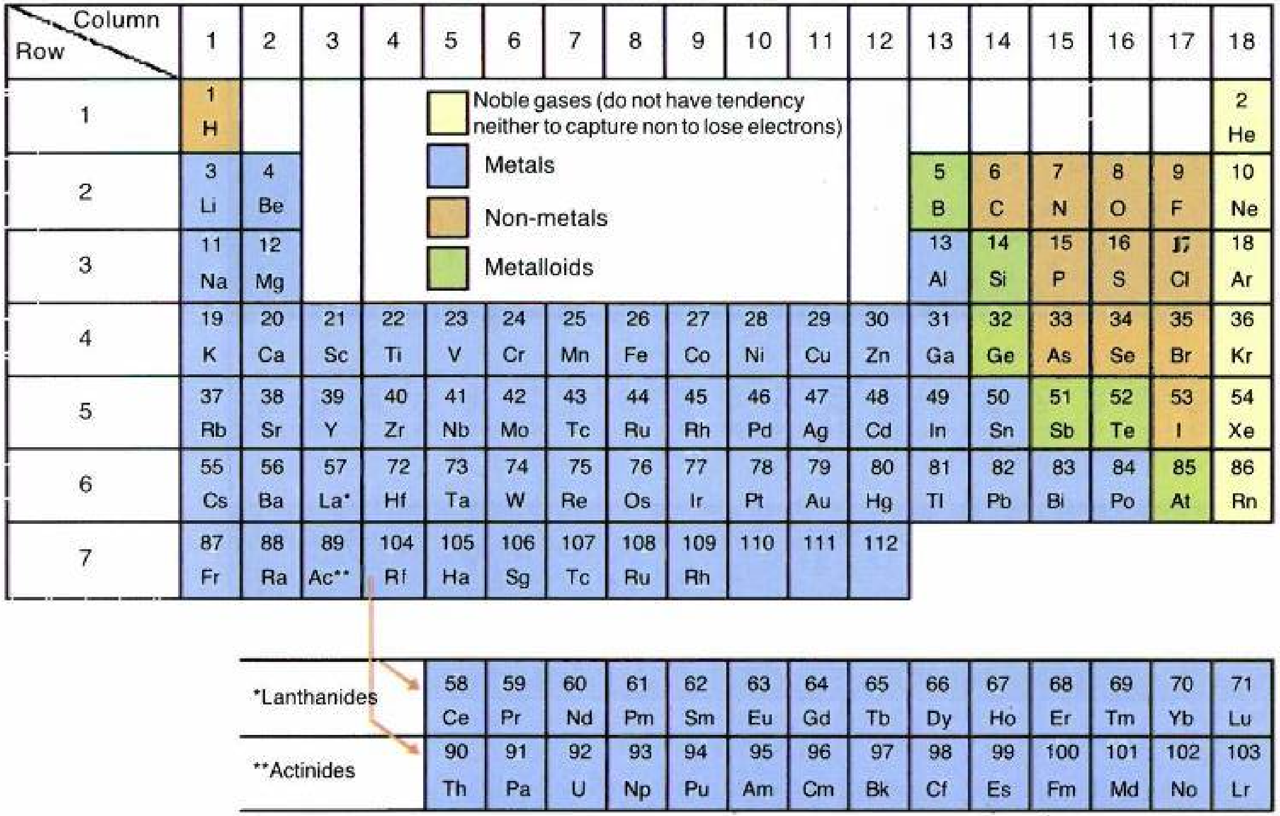
b) Kevlar is used to manufacture sport equipment such as skis, surfing boards, jumping poles … . Cite two characteristics that make it appropriate for such use.

c) This same material is used in the manufacture of anti-bullet vests and tunics used by firemen for protection from fire. Cite two characteristics of Kevlar necessary for each use.

Water vapor pressure (kPa)

T (°C)	p (kPa)	T (°C)	p (kPa)
0	0.61	35	5.63
5	0.87	40	7.37
10	1.23	45	9.59
12	1.40	50	12.33
14	1.60	55	15.73
16	1.82	60	19.92
17	1.94	65	25.00
18	2.06	70	31.16
19	2.20	80	47.34
20	2.34	90	70.10
21	2.49	92	75.59
22	2.64	94	81.45
23	2.81	96	87.67
24	2.98	98	94.30
25	3.17	100	101.32
26	3.36	102	108.78
27	3.57	104	116.67
28	3.78	106	125.04
29	4.01	108	133.92
30	4.24	110	143.27

PERIODIC CLASSIFICATION OF ELEMENTS



Row \ Column	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac**	104 Rf	105 Ha	106 Sg	107 Tc	108 Ru	109 Rh	110	111	112						

🟨 Noble gases (do not have tendency neither to capture non to lose electrons)

🟦 Metals

🟧 Non-metals

🟩 Metalloids

*Lanthanides	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
**Actinides	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Atomic masses of principal chemical elements

Name	Symbol	Approximate molar atomic mass (g. mol^{-1})	Name	Symbol	Approximate molar atomic mass (g. mol^{-1})
aluminum	Al	27	magnesium	Mg	24.3
antimony	Sb	122	manganese	Mn	55
argon	Ar	40	mercury	Hg	200.6
arsenic	As	75	molybdenum	Mo	96
barium	Ba	137.3	neon	Ne	20
beryllium	Be	9	nickel	Ni	58.7
bismuth	Bi	209	nitrogen	N	14
boron	B	11	oxygen	O	16
bromine	Br	80	palladium	Pd	106.4
cadmium	Cd	112.4	Phosphorus	P	31
calcium	Ca	40	platinum	Pt	195
carbon	C	12	potassium	K	39
cesium	Cs	133	radium	Ra	226
chlorine	Cl	35.5	radon	Rn	222
chromium	Cr	52	rubidium	Rb	85.5
cobalt	Co	59	silicon	Si	28
copper	Cu	63.5	silver	Ag	108
fluorine	F	19	sodium	Na	23
germanium	Ge	72.6	strontium	Sr	87.6
gold	Au	197	sulfur	S	32
helium	He	4	tin	Sn	118.7
hydrogen	H	1	titanium	Ti	48
iodine	I	127	tungsten	W	184
iridium	Ir	192	uranium	U	238
Iron	Fe	56	vanadium	V	51
krypton	Kr	84	xenon	Xe	131.3
lead	Pb	207	zinc	Zn	65.4
lithium	Li	7	zirconium	Zr	91.2

7SS085