

Republic of Iraq  
Ministry of Education  
General Directorate of Curricula

# Chemistry

## Fifth Class of Science

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استناداً إلى القانون يوزع مجاناً ويمنع بيعه وتداوله في الأسواق



## Introduction

Chemistry is a practical, theoretical science. These key pillars have grown rapidly and the outcome has covered most aspects of our daily lives, mostly meeting the needs of society Environment and living conditions. The continuous coordination with the rest of the other biological sciences, especially physics, mathematics and life sciences.

The Authoring Committee of the book of chemistry for the fifth grade of science; Interest in enriching the content of the vocabulary of the new curriculum in chemistry to encourage the student and interested to follow up on this vital science, taking into account the sensitive age for the student and taught in previous years of this science starting from the first secondary study. The committee emphasizes the need to support the theoretical material in the book with two main pillars: conducting practical experiments (including the practical needs of the teacher) and linking chemistry as much as possible with daily life and its impact is growing in industry, agriculture, nutrition and medicines cosmetics and others.

The chapters of the book included both horizontal and vertical expansion that these chapters were modern and simple at the same time. Subject to the use of the same symbols, formulas and references used in chemistry books for previous years to facilitate the student and teacher and to be the chemistry curriculum in the secondary stage a coherent gradient (with the addition of the update required by the various unit codes).

The committee assures of the chemistry teachers not to enter any symbols, formulas or terminology, which is waged by confusing the minds of students and adhering, as far as possible, by the quality of the questions and activities mentioned in end of each chapter - direct applied and deductive as well as mentioned exercises In the margins and the accompanying educational information illuminate the ideas of students and not be a stressful part In the exam questions and in order to complete the benefit. The committee considers that it organizes visits to qualitative and annual exhibitions and the establishment of trips - scientific and entertainment at the same time - to a factory near the school and informing students - on the ground - the successive stages of manufacturing raw materials, through to the final product, because it is a goal of great importance.

must be taken care of by teachers and School administrations.

Instruct students to prepare scientific reports for each visit or targeted trip, be an extracurricular activity with an emphasis on investing local environmental resources some of us compensate for certain items that are not available on time. Since this book a new composite needs to be reinforced through feed back of the brothers teachers, educational specialists and parents of students and all who relevant to the implementation of this curriculum in the best way to provide the General Directorate of Curriculum / in the Ministry of education and the books his proposal opinions produced by the field of education to use them in the revision of the Subsequent editions.

## Authers

## Chapter One

### Development of the atomic concept

9

|  |    |
|--|----|
| 1.1 Introduction   | 10 |
| 1.2 Electron Discovery   | 10 |
| 1.3 Proton detection   | 11 |
| 1.4 Estimating the ratio of the charge of the electron to its mass | 12 |
| 1.5 Determination of electron charge                               | 12 |
| 1.6 Detection of the nucleus                                       | 13 |
| 1.7 Detection of atomic number                                     | 14 |
| 1.8 Detection of neutron   | 14 |
| 1.9 The configuration of electrons in an atom                      | 14 |
| 1.10 Electromagnetic radiation                                     | 15 |
| 1.11 Quantum theory  | 15 |
| 1.12 Atomic Spectra  | 16 |
| 1.13 Linear emission spectrum for hydrogen                         | 17 |
| 1.14 The wave nature of the electron                               | 19 |
| 1.15 Wave mechanics  | 20 |
| 1.16 Quantum numbers   | 21 |
| 1.17 How to write an electronic configuration                      | 25 |
| Basic concepts   | 30 |
| Chapter questions  | 31 |

# Content

## Chapter Two

### Bonding forces and the geometric shapes of molecules

35

|                                      |    |
|--------------------------------------|----|
| 2.1 Introduction                     | 36 |
| 2.2 Types of chemical bonds          | 40 |
| 2.3 Resonance                        | 44 |
| 2.4 Geometric shape of the molecules | 45 |
| 2.5 Orbital hybridization            | 49 |
| Basic concepts                       | 59 |
| Chapter questions                    | 60 |

## Chapter Three

61

### Periodic Table and Chemistry of Transitional Elements

|                           |    |
|---------------------------|----|
| 3.1 Periodic table        | 62 |
| 3.2 Transitional elements | 77 |
| 3.3 Iron                  | 90 |
| Basic concepts            | 95 |
| Chapter questions         | 96 |

## Chapter Four

### Solutions

97

|  |     |
|--|-----|
| 4.1 Introduction   | 98  |
| 4.2 Solubility process                                       | 99  |
| 4.3 Types and properties of solutions                        | 100 |
| 4.4 Raoult's Law   | 110 |
| 4.5 Effect of non-volatile solute on some solvent properties | 112 |
| Basic concepts   | 119 |
| Chapter questions  | 120 |

## Chapter Five

### Chemical kinetics

121

|                                     |     |
|-------------------------------------|-----|
| 5.1 Introduction                    | 122 |
| 5.2 Chemical reaction speed         | 122 |
| 5.3 The reaction rate law           | 129 |
| 5.4 Theories of reaction rate       | 135 |
| 5.5 Heat of reaction                | 138 |
| 5.6 Activation energy               | 140 |
| 5.7 Factors affecting reaction rate | 140 |
| 5.8 Reaction mechanism              | 142 |
| Basic concepts                      | 147 |
| Chapter questions                   | 148 |

## Chapter Six

### Acids, Bases and Salts

153

|  |     |
|--|-----|
| 6.1 Introduction                                       | 154 |
| 6.2 Properties of aqueous solutions of acids and bases | 154 |
| 6.3 Molecular concepts of acids and bases              | 156 |
| 6.4 Amphoteric substances                              | 161 |
| 6.5 Acid and base reactions in aqueous solutions       | 162 |
| 6.6 Types of salts                                     | 163 |
| 6.7 Acids and bases indicators                         | 166 |
| 6.8 Acids and bases solutions                          | 166 |
| 6.9 Titration  | 168 |
| Basic concepts   | 171 |
| Chapter questions                                      | 172 |

### Chapter Seven

#### Polymer Chemistry

173

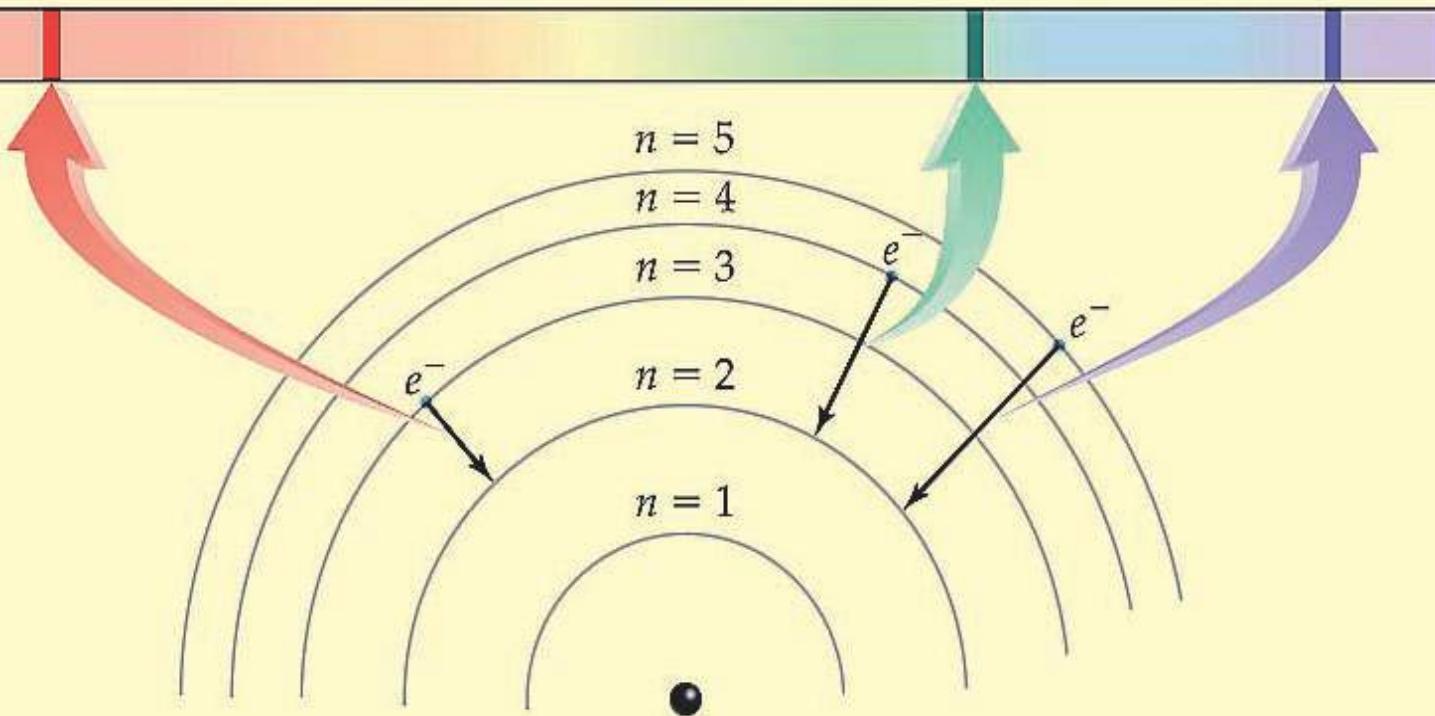
|                           |     |
|---------------------------|-----|
| 7.1 Polymers (plastics)   | 174 |
| 7.2 Polymers Types        | 174 |
| 7.3 Synthetic polymers    | 175 |
| 7.4 The world of plastics | 187 |
| Basic concepts            | 188 |
| Chapter questions         | 189 |

### Chapter Eight

#### Aromatic hydrocarbons

191

|   |     |
|---|-----|
| 8.1 Introduction                                      | 192 |
| 8.2 Benzene composition                               | 192 |
| 8.3 Mechanism of electrophilic substitution reactions | 201 |
| 8.4 Phenols   | 202 |
| 8.5 Preparation of aspirin                            | 205 |
| 8.6 Detection of phenols                              | 205 |
| 8.7 Heterocyclic compounds                            | 205 |
| Basic concepts  | 208 |
| Chapter questions                                     | 209 |



## Chapter One Development of the atomic concept

1

After completing this chapter, the student is expected to:

- Understand the importance of electrical discharge tubes experiments in electron and proton discovery
- Characterize the properties of cathode ray and channel ray.
- Know the value of a single electron's charge, its mass, and how it was found.
- Show the importance of nucleus discovery in the development of atomic structure.
- Know the phenomenon of electromagnetic radiation.
- Understand the meaning of quantum energy and the importance of quantum theory.
- Distinguish the difference between linear and continuous spectrum.
- Show the dual nature of the electron.
- Differentiate between the perception of the principal energy level according to Bohr's theory and mechanics waveform.
- Recognize the four quantum numbers and their importance.
- Determine the four quantum numbers of any electron in an atom.
- Know the principle of exception to Pauli.

### Do you know

Zinc sulfide is a fluorinated substance light flashes when light falls on it.



Figure 1-1

Model for electric discharge tube.

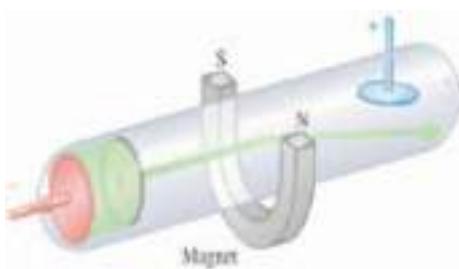


Figure 1-2

Cathode rays were affected by polarity magnetism.

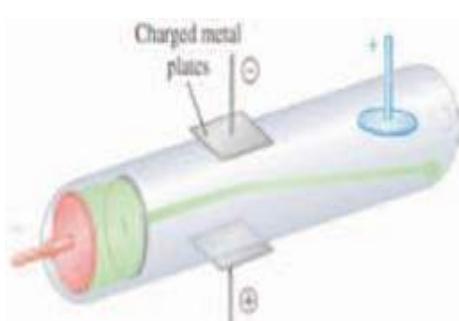


Figure 1-3

Cathode rays were affected by electrical plates.

## 1-1 Introduction

It came in Dalton's atomic theory in one of its clauses stated that "atoms are not able to divide or fragment" but the electrical discharge experiments through gases and radio activity phenomenon particles, meaning that atom is divisible.

## 1-2 Electron Discovery

When supplied with an electric discharge tube, which contains hydrogen gas under low pressure (Figure 1-1), with a zinc sulfate-covered reagent barrier as well as a metal plate near the cathode, with a narrow rectangular incision. When the electrical current passes, we see a luminous line across the barrier, and the explanation for that is beams or electric rays emanate from the cathode, and are moving to anode, the metal plate stops most of them, but a rectangular incision allows to this narrow beam runs through it, and hits the barrier and produces a luminous line. Because the beams appear to be coming from the cathode, they are known as cathode – ray, when a cathode rounded a north pole finder to a magnet from on the side of the tube, the luminous line is curves down, either near south pole finder, the luminous line curves upwards. The deviation trend indicates that the cathode rays are negative electric charge [Figure (1-2)]. The same conclusion can be made when put charging plates electrically above and below the barrier, the illuminated line curves towards the positive plate because opposing charges attract each other [Figure (1-3)].

When studying different gases it was found that these particles compose the luminous line. The luminance has a negative charge of one value as well as its mass and these particles are called electrons. The most important properties of cathode rays:

- 1 - Moving in straight lines emitted from the negative pole towards the positive pole.
- 2 - It consists of particles with a very tiny mass and moving very fast.
- 3 - Affected by the electric field and attracted towards the positive electrode Which indicates it's a negative charge [Figure (1-3)].

4 - Affected by the magnetic field [Figure (1-2)].

5 - Ionize the medium in which it passes.

### 1-3 Proton detection

The first experiments conducted by Goldstein in 1886, to suggest that positive particles are also formed in the electric discharge tubes. In the Goldstein tube [Figure 1-4] there is a positive pole (Anode) towards the right and negative pole (cathode) on the left, which is formed from a piece of metal engraved by a hole, a detector barrier can be placed on the tube, to the left of the cathode. When passing an electric current is formed a luminous line, the formation of this line can be explained as follows: electrons that are emitted from cathode are attracted towards anode and because there is hydrogen gas in the tube, electrons collide with hydrogen neutral gas atoms, if the electrons have enough energy, they can flush away other electrons from the neutral atoms. positive particles remaining in its place are captured mostly by electrons and become neutral, a few numbers of these positive particles slip from the hole to the area behind the cathode "so called a channel ray". It is formed a bundle of particles are affected by the electric field as it deflects toward the plate, which has negative charges and is also affected by the magnetic field. Also, they veer up toward the north finder pole looking up the south pole and curve down the south finder pole. It also found that these particles are usually heavier than electrons where the mass depends on the type of gas in the tube. These particles were later named proton.

From the study of the properties of these rays found the following:

1- Attracted towards the negative pole, which confirms that it is positively charged.

2- It has mass and speed which indicates that it is matter particles and are usually heavier than electrons and its mass depends on the type of gas present in the electric discharge tube.

3- Affected by electric and magnetic fields.

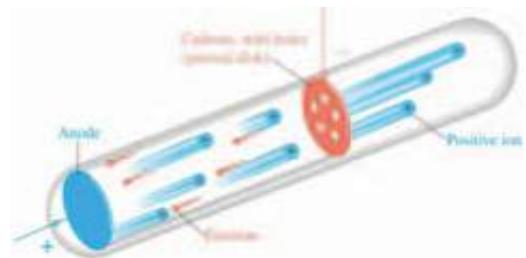


Figure 1-4

Goldstein tube

#### Exercise 1-1

What are the properties of cathode rays?

## 1-4 Estimating the ratio of the charge of the electron to its mass

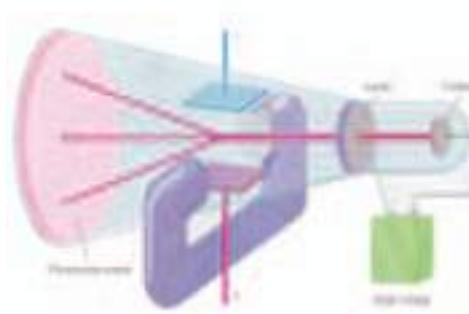


Figure 1-5

Model for Thomson tube.

The first quantitative study on the deviation of electronic beams by electric and magnetic fields was carried out by the scientist Thomson in 1897 and Figure 1-5 illustrates a model, where he used a cathode-ray tube and, by using the properties of these rays. He found that these rays deviate from their straight path under the influence of the magnetic field but returns to its original path when the electric field is set equal to the intensity of the magnetic field in a direction perpendicular to the direction of the magnetic field. From knowing the intensity of the electric and magnetic fields, it was possible to calculate the charge-to-mass ratio of particles. Thomson shows that these constant percentages do not change regardless of the metal which is used to make the cathode or the nature of the gas used inside the cathode ray tube. He has been found the ratio equal to  $1.76 \times 10^{11} \text{ C/kg}$  (coulomb / kilogram).

## 1-5 Determination of electron charge

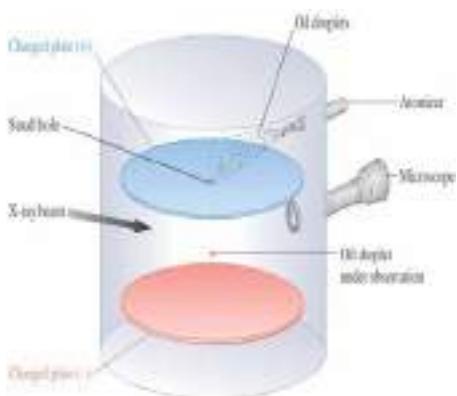


Figure 1-6

A model of the Melican experiment.

In 1909, Millikan assigned an electron charge by placing small negative charge droplets between two electrodes as in Figure 1-6, the positive electrode above tries to attract oil droplets which are charged with negative charge and at the same time droplets tend to descend down by the power of gravity force. When the droplets stabilize in static state between the poles and from the known values of radius, density and the electric field intensity, Millikan enables to calculate the carried charge on these droplets. The value is  $1.6 \times 10^{-19} \text{ C}$  coulombs or one of their simple multiples because droplets can be charged with more than one negative charge. The charge of one electron must be equal the value of the smallest charge carried by the droplet  $1.6 \times 10^{-19} \text{ C}$  and by using this value of the electron charge and the value of the ratio of the charge of the electron to its mass which is calculated by Thomson (paragraph 1 - 4 above) could calculate the mass of an electron from the electron charge found by Millikan:

Electron mass= (The electron charge found by Millican) / (The ratio of the charge of the electron to its mass created by Thomson)

$$\text{Electron mass} = \frac{1.6 \times 10^{-19} \text{ C}}{1.76 \times 10^{11} \text{ C/kg}}$$

$$\text{Electron mass} = 9.1 \times 10^{-31} \text{ kg}$$

### 1-6 Detection of the nucleus

Thomson suggested that the atom could be considered a positive spherical region, and negative electrons are embedded in it (such as a piece of cake filled with currant). The bulk of the atom's mass must be bound by the positively charged spherical region. It is a conclusion arising from a note that positive parts of an atom are heavier than electrons. In 1910 Rutherford conducted the traditional experiment which tested the Thomson model, he was examining the dispersion of alpha particles by a thin slice of metal. According to the Thomson model, the metal consists of atoms as positively charged balls containing negative electrons and because alpha particles are too high energy, they will penetrate through the metal strips as a straight line because the positive charge and the mass is evenly distributed in the metal (according to the Thomson model) and there is little chance of deviation from the original course. As expected, 99% of alpha particles penetrated the slice, some of them skewed sharply and a few of them were reflected along their trajectory [Figure 1-7]. That was not true at all for Rutherford because the Thomson model cannot explain these deviations and as a result Rutherford explained these deviations that the positive charge and mass in the metal slice are centralized in a very small area. According to Rutherford's opinion, the atom has a nucleus or center, where its positive charge and mass are centralized. The quantitative results of dispersion experiments illustrate (such as those carried out by Rutherford) that the nucleus of the atom has a diameter, which is equal to  $10^{-13} \text{ cm}$  and atoms have diameters approximately 100,000 times the diameter of the nucleus ( $10^{-8} \text{ cm}$ ). In other words, the nucleus occupies very little space from the total size of the atom and most of its size is a space occupied by electrons.

#### Do you know

Rutherford's expression was when he saw the results "It was something great, almost unbelievable. It was as if a shell was fired for range 15 inches on a thin translucent piece of paper then she bounced again and hit you."

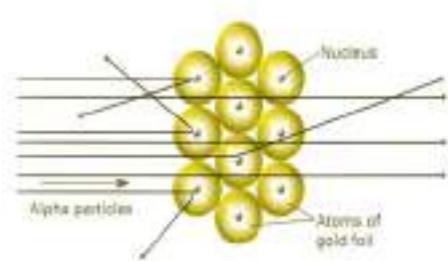
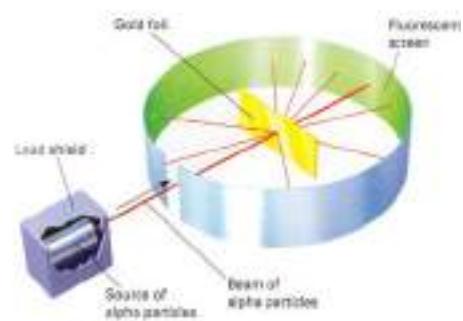


Figure 1-7

A model for the Rutherford experiment

#### Exercise 1-2

Who attributes the discovery of the nucleus of the atom?

#### Do you know

If the atom becomes bigger till the nucleus size as a point (.) then the whole atom would be bigger than a house.

## 1-7 Detection of atomic number

If the nucleus is containing protons, how many protons are exist in a particular nucleus? This question remained until the answer came from scientific observations that are shown by Mossile in 1913 which led to the discovery of the atomic number.

### Do you know

The atomic number (Z) is significant as a special characteristic In chemistry, since it gives a number of protons the positive charge in the nucleus which is equal to the number of electrons out the nucleus which make the atom is neutral. And including (Z) represents the number of protons in a nucleus atom is a nuclear property that provides us with important information about the rest of the atom.

## 1-8 Detection of a neutron

At that time the question was how to interpret isotopes? And how Different blocks of the same element can be obtained, if they are all containing the same number of protons. The answer of this question is that there must be something else in the nucleus. In 1932 Chadwick threw a thin slice of beryllium by alpha particles, there were appeared rays resembling the rays of gamma which has very high energy from metal slice. Subsequent experiments showed that these rays represent the third model of the components of the atom, called by Shadwick as Neutron because its charge is neutral and its mass is roughly equal to that of the proton. The nucleus is now composed of neutrons and protons. The neutron has a mass (atomic mass unit) of 1.00866 amu and charge value equal (0) and the proton has a mass of 1.00727 amu and charge (+ 1). The symbol (Z) of the atomic number, which represents the number of protons in the nucleus of an atom of any element. The symbol (A) represents the number of mass, which is equal to the total number of protons and neutrons in the nucleus of any element.

## 1-9 The configuration of electrons in an atom

The process of arranging the components of atom has gone through several theories. These theories were fading or evolving according to their ability to interpret physical and chemical phenomena. The model is considered to be an atom is consisting of a positive nucleus which the negative electrons are moving around it. This movement of electrons counteract the gravitational force generated by nucleus. Explanation of why these electrons do not radiate energy as they are observed in all other cases.

Moving electric charges under the influence of gravitational forces are losing energy. In the case of electrons, a loss of energy will result in a slow motion of the electron, which will gradually attract it to the nucleus in a spiral path approaching them to fall inside. In this spiral path continuously gives energy as a continuous spectrum that resembles a semi - ray solar spectrum but this does not happen as the atoms are stable in their atomic construction. This atomic stability led scientists to present other theories about atomic construction.

### 1-10 Electromagnetic radiation

This expression includes different types of radiation, such as warm that travels to us from a fireplace or light reflected on bright surfaces, or radiology used in hospitals. They are different but they are common in some intrinsic qualities, all these types of radiation are transmitted in the space in same speed equal to  $3 \times 10^8 \text{ m/s}$ , which is light speed. All of these types are wave-nature and their waves are similar to those which form above the surface of the water in which a stone is thrown [Figure 1-8]. We notice repetition in these waves, that is, the wave is repeated at regular intervals and the regular number of these waves is what is known as the frequency of the wave that occurs per second ,and when radiation passes at a specified point [Figure 1-9]. The waves are small and their frequency is high and the opposite is true and is related to length frequency wave in relation:

$$v = \frac{C}{\lambda}$$

Where  $C$  : The speed of light in unit (m/s)

$v$  : Frequency in unit (1/s)

$\lambda$  : Wavelength in unit (m)

### 1.11 Quantum theory

Max Plank paved the way for the scientific revolution that emerged at the beginning of the twentieth century, by his hypothesis which is considered radiology electromagnetism is like a bundle of small energy groups which he called it Quantum. When he was studying the phenomenon of light emission from hot objects, Planck suggested that hot objects emit energy in small quantities is called (quantum). It is the minimum amount of energy that can be lost or gained by the body The process of losing or acquiring energy is not a continuous process, but rather batches or flows of energy so that the energy is lost or the acquired multiplier is a true multiple of that quantum or quantity.

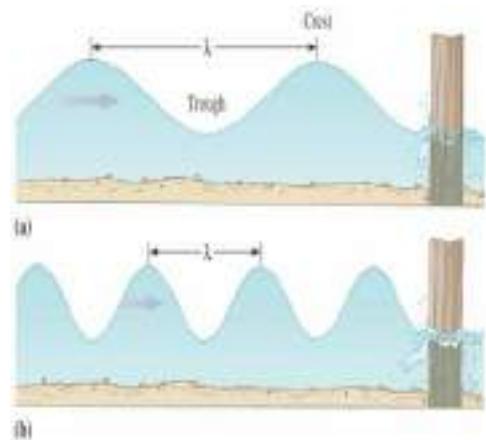


Figure 1-8

Model to form waves above the surface water.

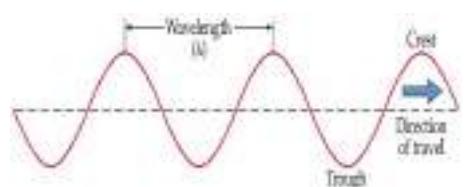


Figure 1-9

A model of the wave nature of light.

### Do you know

Impose a car moving at a certain speed. if we want to increase its speed to reach higher speed the car must pass through all speeds that fall between lower speed and higher speed. It cannot be jump from speed to higher speed, as requires of the idea of quantum leaps.

### Exercise 1-3

What is a photon?

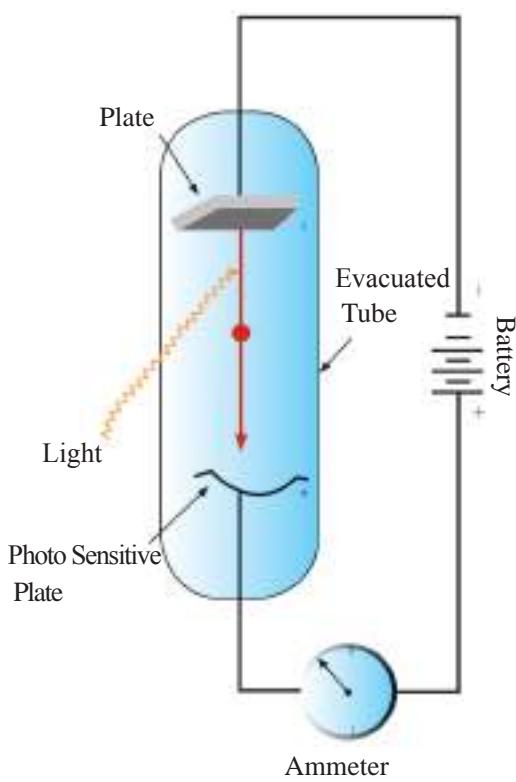


Figure 1-10

Photoelectric effect phenomenon.

The amount of quantum depends upon the frequency of radiation , and is associated with a constant (named Planck constant) and its value  $6.63 \times 10^{-34}$  J.s . Planck's energy is known as:  $E=h\nu$  Where E: Energy in Joule (J) h: Planck constant in unit (J.s)

Einstein then came to expand Planck's theory of interpretation of the photoelectric effect phenomenon, a phenomenon of electrons emitting from a metal when the light is pointed to, [Figure 1-10]. The emission of electrons depends on the frequency of light, ie on its energy, if the frequency of atomic radiation hits the metal surface in low value, we are not observe the emission of electrons. When using increased frequencies, the frequency suddenly reaches at which it begins emitting electrons. Before that, however, the radiation intensity of the low frequency was increased the metal is not affected. If the radiation frequency exceeds that the minimum value of emission does not increase the number of electrons emitted but the energy carried by the electron increases. Einstein has used Planck's equation to calculate the quantum energy of light, which he called (photons) and photon is a particle of electromagnetic radiation has a mass of zero but holds a quantity of energy depends on the frequency of the electromagnetic wave. The photon energy has the lowest frequency needed to emit electrons by overcoming its binding energy that electrons relate to the atom. Einstein's interpretation of this phenomenon was the first application important for quantum theory. This interpretation has also given light a trait particle along with the wave characteristic

## 1-12 Atomic Spectra

The scientific Newton passed ordinary sunlight through a glass prism , he found that the light decomposes into a range of colors firstly from violet and finally to red (Figure 1-11). Because there are no separate areas between one color to another, this spectrum is named with continuous spectrum. But it was observed that if the atoms of a pure element exposure into the gaseous state to heat or in the electric discharge tube in the case of low pressure emits radiation (spectrum) of a glowing element atoms is not connected or continuous but is consisted from a few lines of light separated by relatively large dark distances.

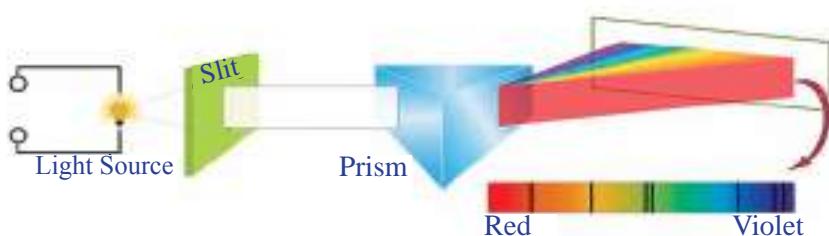


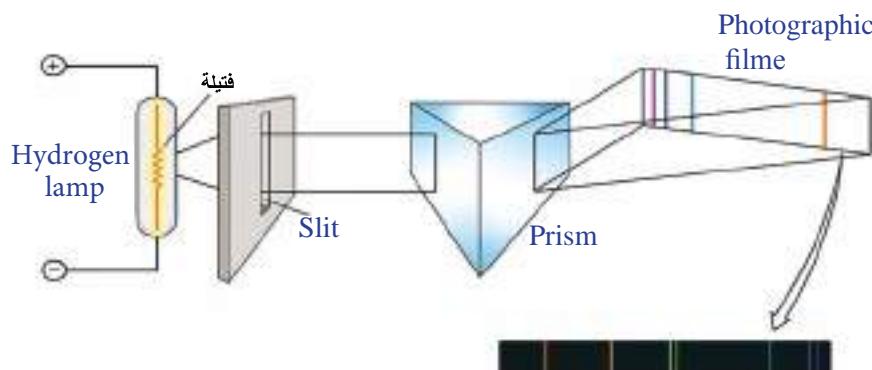
Figure 1-11

Continuous spectrum phenomenon.

call it (the line emission spectrum) because there are spaces between one color and another. It was later discovered that each element had a spectrum linearly distinguishes it from other elements [Figure 1-12]. linear emission spectrum shows that the emitted radiation from an atom emits a specific energy. In other words it is emitted in a quantum style rather than in a continuous manner.

— Do you know —

Each element has a special emission spectrum. Emission spectra are used to designate identities of unknown samples and percentage determination components of stars.



### 1.13 Linear emission spectrum for hydrogen

Classical theory claims that a hydrogen atom can be excited by any amount of energy that it receives. So scientists predicted the emission of a series of continuous spectrum, but the hydrogen atom emits only limited frequencies of light, why, when the current passes in the hydrogen gas under low pressure. The potential energy of some of its atoms increases and the lowest atomic energy level is called (ground state). When the potential energy level of the atom is higher than the ground state led to atom to (excited state).

Figure 1-12

Linear spectrum phenomenon.

— Exercise 1-4 —

That rainbow is a series of colors?

Discuss whether you consider this series of continuous or linear emission spectrum.

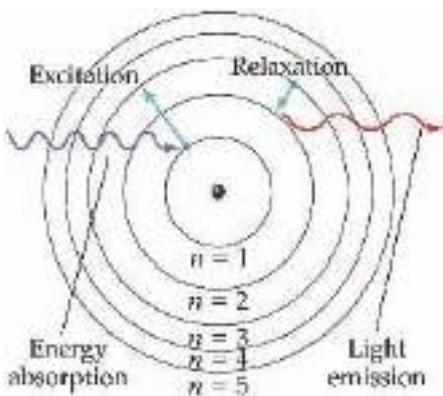


Figure 1-13

The transmission of an electron from a level of less energy to the level of the highest energy and the reverse.

When the atom returns from excited level to the stable level, it loses the gained energy in form of electromagnetic rays (photons) and the energy of this photon is equal to the difference between first and second energy level [Figure 1-13]. Studies showed that hydrogen atoms release only specific frequencies of light. The energy difference between these energy levels of an atom is a specific difference and this means that the hydrogen electron is in limited energy level.

### 1-13-1 Bohr's theory of hydrogen atom

After the discovery of the elements spectra, scientists tried to explain them based on the movement of the electron in the atom, but the attempt failed. Suppose the electron moves around the nucleus at a constant speed, in a curved path and because of laws of physics that require any particle charged as an electron undergo a process acceleration will lose energy on the image of electromagnetic radiation. This slows down the speed of the electron and therefore the electron will collide to nucleus and the atom collapses. Because atoms do not collapse, scientists had to challenge to explain how electrons rotate. The scientist Bohr used ideas of Planck and Einstein mentioned earlier in his theory that he managed of calculating the energy of an electron in hydrogen atom. Bohr was adopted in his theory on two facts: first, the atoms do not collapse and the second is that light emission from an atom is done at a certain frequency, which means that changes in the atom energy are certain and specific.

This shows that the electron exists in areas with specific energy and cannot exist between them because it is forced to specific energy levels in the atom.

In his theory, Bohr assumed that electrons rotate in specific orbits that have constant energy and volume [Figure 1-14]. Bohr theoretical hypotheses can be summarized as follows:-

1. The electron rotates in specific orbit (with a specified diameter) and a specific energy and do not radiate energy as a result of this rotation.
2. Energy is emitted from the atom in one case, which is the transmission of the electron from Specific orbit to another orbit that has less energy than in first orbit.

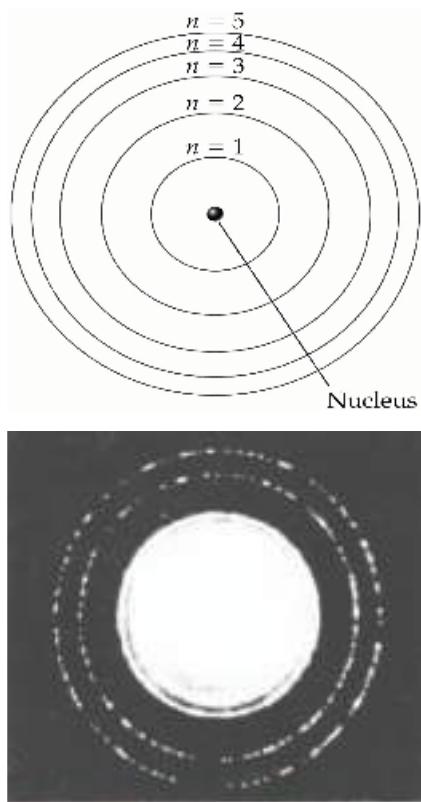


Figure 1-14

Major levels of energy with constant volume and constant energy.

Bohr's theory has proved useful in the structure of a hydrogen atom, but when scientists tried to apply the ideas in Bohr theory to atoms of the other elements was failed because the rest of the atoms contained more electrons so the atomic spectra of these elements are more complex of the atomic spectrum of hydrogen. That means Energy levels is more complex and there are sub-levels of energy starting from the second level so he start thinking about it again and activate search for a more comprehensive theory.

## 1-14 The wave nature of the electron

We said that an electron is a particle with a specific mass and negative charge and light has matter and wave length nature. De Broley (1924) suggested the possibility of duality nature (wavelength and particulate) in the case of the particles also depends on what Einstein and Blank achieved.

$$E = mc^2 \quad \dots \quad (1) \quad \text{Einstein equation}$$

$$E = h\nu \quad \dots \quad (2) \quad \text{Blank Equation}$$

Since equation 1 and 2 are equal

$$h\nu = mc^2 \quad \dots \quad (3)$$

Whereas  $\nu = (c/\lambda)$ , by substituting them into equation (3), we obtain:

$$mc^2 = h \frac{c}{\lambda} \quad \dots \quad (4)$$

By omitting the value of  $c$  from either side in equation (4) it becomes:

$$mc = \frac{h}{\lambda} \quad \dots \quad (5)$$

In order of equation (5) we get:

$$\lambda = \frac{h}{mc} \quad \dots \quad (6)$$

Momentum is known as the following relationship  $mc=p$ :

$$\lambda = \frac{h}{p} \quad \dots \quad (7)$$

Based on this derivation can a torrent of moving electrons that leads to an interfering pattern, that is, a mobile electronic is similar to photons forming rays.

### Exercise 1-5

Why Bohr theory failed?

## 1-15 Wave Mechanics

Despite the success of Bohr theory in the interpretation of the atomic spectrum of hydrogen as well in the interpretation of atomic spectra of systems in which one electron such as ( $\text{He}^+$  and  $\text{Li}^{2+}$ ) but did not produce good results when trying to explain the spectrum of atoms which has more than one electron. In 1936 the scientist Schrodinger used the mathematics to study the hydrogen atom. A science called wave mechanics or quantum mechanics has begun. Schrodinger solved a mathematical equation named after by his name and also called the wave equation. Schrödinger's idea is that instead of thinking about an electron moving circularly in a constant orbit, we have to assume a series of waves move within this stable orbit and that the perimeter of the orbit must be equal a simple multiple of the electron's wavelength. According to the assumption of Schrödinger electron wave behavior gives an estimate of the probability of existence electron within the wavelengths. This new concept is an alternative to the system of the fixed orbits assumed by Bohr in his theory rather than look of an electron as a particle orbiting in a specified radius orbit wave mechanics describes the motion of an electron in terms of the wave function (Figure 1-15), which we call orbital and it depends on the total energy and its potential energy and the coordinates of its location ( $z$ ,  $y$ ,  $x$ ). Nature of this electron wave behavior makes our ability to determine the location of the electron and its momentum (the amount of movement) at the same time not possible. Heisenberg's principle coined known by his name (the principle of inaccuracy) which states it is not possible to locate a particle and its momentum precisely at the same time is able to measure one with greater uncertainty in the accuracy of measuring the other.

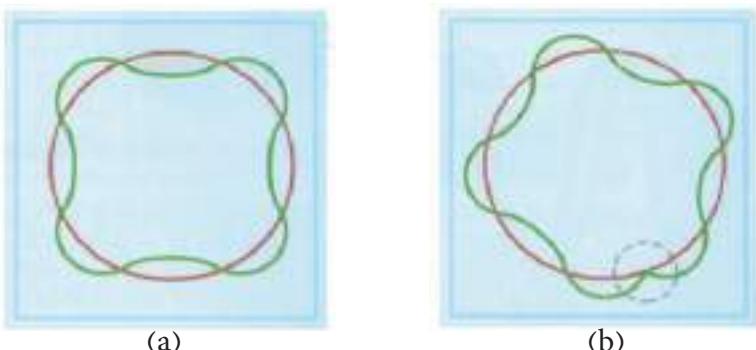


Figure 1-15

The wave motion of an electron.

Since it is not possible to draw a path for electrons, the best thing to do is talking about the probability of finding an electron at a specific location within an atom. The probability of finding an electron at multiple points within an atom is mathematical dilemma is very complicated. Quantum mechanics solves this dilemma as an electron as if it was a wave. In fact, the electrons wave properties appear under some conditions, so that the electron beam moving quickly, for example, appears diffraction, a characteristic of motion waveform. To identify any electron at its atom, solve the wave equation and know the values of the wave function, it requires three quantum numbers. These are real numbers relate to the potential energy and position of electron and shape electronic cloud. Fourth electronic quantum number must be set because the three theoretically quantum numbers were resulting from the solution of the Schrödinger equation are not sufficient to explain all observed properties of electrons in atoms. So the fourth quantum number was entered to fill this deficiency and it is called the electron spin quantum number because the electron can think of it as spinning around its axis as it moves around the nucleus. The fourth quantum number shows the direction of the spinning.

## 1-16 Quantum numbers

To know how electrons will be arranged we must examine the energy levels in the atom by studying the following quantum numbers:

### 1-16-1 Principal quantum number (n)

Energy levels in atom are determined by the principal quantum number and the larger value of n the higher value of energy level and farther the electron from the nucleus. The value of n determines the size of the level and n take integers 1, 2, 3, etc.

### 1.16.2 Momentum quantum number ( $\ell$ )

Determines the shape of orbital in which the electron is likely to be present and it is resulting from the movement of the electron around the nucleus. That each principal level n consists of one or more sub - (secondary) levels. The number of secondary levels in any orbital is equal to the number of principal quantum number, so  $n=1$  consists of one

### Exercise 1-7

How quantum mechanics was able to Explain the presence of an electron in a particular location in atom.

### Do you know

The letters s, p, d, f were selected from the letters the first sequences The main Sharp, principal, diffuse, and fundamental these words represent the forms of lines of linear spectra that are connected energy transitions.

secondary level of energy s. The second principal level  $n=2$  contains two secondary levels is s and p, and the third principal level,  $n=3$ , contains three secondary energy levels are s, p and d as well as the fourth principal level of energy  $n=4$  contains four secondary levels of quantum numbers are s, p, d, and f. Each  $n$  value corresponds to a specific value for the quantum secondary number  $\ell$  are integers starting with zero and ending with  $(n-1)$ . If  $n=1$ , that  $\ell$  will start with zero and end with  $(1-1)$  so there is one value for  $\ell=0$  but if  $n=2$  it is start with zero and end with  $(1-2)$  by 1 so there are two values for  $\ell$  is zero and one. So when  $n=3$  there are three values 0, 1, 2 and when  $n=4$  there are four values: 0, 1, 2, 3 and so on (Table 1-1).

Table (1-1) The values of  $\ell$  and the symbols of the secondary levels indicated

| $\ell$ value               | 0 | 1 | 2 | 3 | 4 | 5 |
|----------------------------|---|---|---|---|---|---|
| The letter signifying them | s | p | d | f | g | h |

In our study we will only consider secondary levels s, p, d, f because they are only ones that are preoccupied with electrons in atoms in ground state. To determine the secondary level from any  $n$  principal level symbolically writes the value of  $n$  for the  $n$  principal level then the character assigned to the secondary level, for example the secondary level s from the second principal level has the symbol  $2s$  and has values( $n=2, \ell=0$ ). The secondary level d of the third principal level is  $3d$  and has quantum values ( $n=3, \ell=2$ ) and so on.

### 1-16-3 Magnetic quantities number ( $m\ell$ )

Atomic orbitals can take the same shape around the nucleus but in different directions. Magnetic quantities number indicates the direction of the orbital around the nucleus where each secondary level consists of one or more orbitals. This number was used to explain the appearance of extra lines in the spectrum when atom placed in a magnetic field. A spatial distribution of an electron, spherical symmetric, ie, the probability of its existence is the same in all trends from the nucleus [Figure 1-16]. On the other hand the probability the presence of the electron p in some directions of the nucleus is more than in other. In fact, the probability of distribution for the electron p of two diffuse lobes to some extent, one on each side of nucleus [figure 1-17]. The p-level consists of three orbitals

Figure 1-16

Secondary level of S.

Figure 1-17

Secondary levels of p

The secondary level d consists of five orbitals and the secondary level f consists of seven orbitals and their spatial distribution is more complex to a large extent [Figure 1-18]. Each value of  $\ell$  matched with the values of magnetic quantum numbers which are positive and negative integers. When the value of  $\ell=0$  there is one value for  $m\ell$  which is (0). If  $\ell=1$ , the values of  $m\ell$  are (+1, 0, -1) and if  $\ell=2$  the values of  $m\ell$  is (+2, +1, 0, -1, -2). When the value of  $\ell=3$  then the value of  $m\ell$  are (+3, +2, +1, 0, -1, -2, -3). Table (1-2) summarizes quantum numbers of primary, secondary and magnetic.

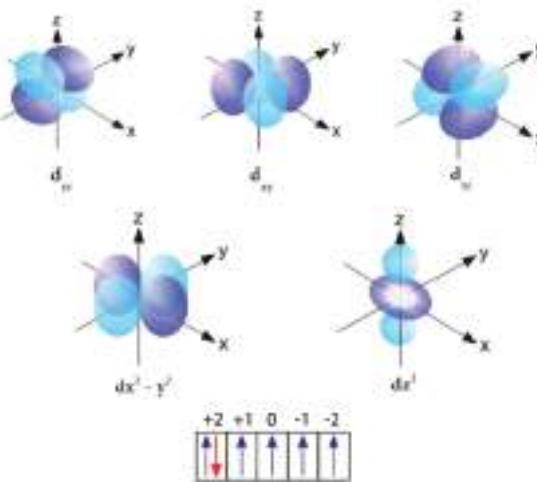


Figure 1-18  
Secondary levels of d

Table (1-2) Values of quantum numbers of primary, secondary and magnetic.

| principal quantum number (n) | Secondary quantum number ( $\ell$ ) | Symbol | Magnetic quantum number ( $m\ell$ ) | Number of orbitals at the secondary level |
|------------------------------|-------------------------------------|--------|-------------------------------------|---|
| 1                            | 0                                   | 1s     | 0                                   | 1   |
| 2                            | 0                                   | 2s     | 0                                   | 1   |
|                              | 1                                   | 2p     | +1, 0, -1                           | 3   |
| 3                            | 0                                   | 3s     | 0                                   | 1   |
|                              | 1                                   | 3p     | +1, 0, -1                           | 3   |
|                              | 2                                   | 3d     | +2, +1, 0, -1, -2                   | 5   |
| 4                            | 0                                   | 4s     | 0                                   | 1   |
|                              | 1                                   | 4p     | +1, 0, -1                           | 3   |
|                              | 2                                   | 4d     | +2, +1, 0, -1, -2                   | 5   |
|                              | 3                                   | 4f     | +3, +2, +1, 0, -1, -2, -3           | 7   |

#### 1-16-4 Electron spin quantum numbers ( $m_s$ )

We explained earlier that there is one orbital for the secondary level S, three orbitals for secondary level p, five for secondary level d and seven for the secondary level f and where these secondary levels can accommodate 2, 6, 10 and 14 electrons respectively. It follows that any orbital can accommodate two electrons but electrons differ in the same orbital by one important thing is that it has opposite spindle rotation. The reason for talking about the spin of the electron comes from sightings the magnetic behavior of the material can be obtained from the behavior of magnetic for single atoms, by Ottostron experiment.

In this experiment [Figure 1-19], a beam of silver atoms Neutralization (resulting from the evaporation of silver) passed between two magnetic electrodes. It was found that the beam splits into two separate beams, that is, half the atoms deflect in a certain direction and the rest deflects in the opposite direction.

To explain this behavior that each electron behaves like a fine magnet. This magnetism is produced by the spin of the negative charge because it is known that the spindle rotation of any charge is generated magnetic field. There are two opposite directions of the spin; we expect each electron to attract each other but that disability of the attraction between the electron orbital repulsion in their charge. Since the movement of the rotation of the two electrons is confined in only two directions so we have two values of the spindle quantum  $m_s$  are  $+1/2$  and  $-1/2$ .

It can summarize the characteristics of the electron in the atom As follows:-

1. The principal quantum number  $n$  and this characteristic indicates the order of the electrons configuration and increase the distance from the nucleus.
2. The momentum quantum number  $m_l$  describes the type of orbital that the electron operates from, where its spatial distribution is similar (for example, the electron  $s$  has spherical distributions are symmetrical and the electrons  $p$  have symmetrical distributions along separated directions in the space).
3. The magnetic quantum number  $m_l$  and this characteristic defines any orbital from orbitals of the secondary level in which an electron is likely to be present.
4. The electron spin quantum number ( $m_s$ ) and this characteristic determines either of the two possible directions of the spin of the electron.
5. When the four characteristics of the electron are determined in an certain atom, it will discover that it cannot exist in the same one atom another electron that has a set similar to those of its the four characteristics. This fundamental definition is known as (the Puli exclusion principle). **This definition states that it cannot two electrons in the same atom have the same values for all quantum four number.**

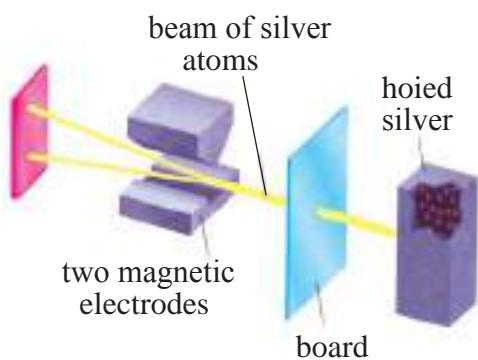


Figure 1-19

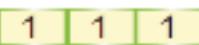
Ottostron experiment.

#### Do you know

To resemble the principal energy levels around an atom by drawer. that does not have a regular dimensional drawer. The distances are very high at first. then gradually diminishing whenever you move away these levels from nucleus.

## 1-17 How to write an electronic configuration

For the purpose of writing the electronic configuration of any atom, you must know the atomic number of that atom, whereas the number of electrons of an atom is equal to their atomic number (number of protons) if electrically equivalent. Well it should we know that the basic process in writing an electronic structure of an atom is that we start by filling the orbitals with electrons of the less energy and then the most energy, thus where they are arranged as follows: 1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f 5d 6p 7s 5f 6d , In the case of secondary levels containing more than one orbital such as levels (p, d and f) electrons enter individually in these orbitals to avoid electric repulsion between charges according to the Hund's rule. This rule states **that there is no duplication between two electrons in the secondary energy level only after orbitals occupies an individual firstly.**

Even if all orbitals of the secondary level now have an one electron in each of them as at the secondary level p<sup>3</sup>  then the fourth electron enters to double with one electron that preceded it to make full orbitals in the secondary level p<sup>4</sup>  and to overcome the repulsion between the two electron charges within a single orbital, the two electrons are represented by two opposite arrows.

### Example 1-1

Write the electronic configurations for the following elements: <sub>23</sub>V • <sub>19</sub>K • <sub>18</sub>Ar

#### Solution

|                  |                                      |
|------------------|--------------------------------------|
| <sub>18</sub> Ar | $1s^2 2s^2 2p^6 3s^2 3p^6$           |
| <sub>19</sub> K  | $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$      |
| <sub>23</sub> V  | $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$ |

### Exercise 1-8

Write the electronic configuration of following elements:

<sub>30</sub>Zn • <sub>20</sub>Ca

If we note in the previous example of the elements that <sub>23</sub>V, <sub>19</sub>K That the electronic configuration of the first 18 electrons of them is ( $1s^2 2s^2 2p^6 3s^2 3p^6$ ). This is the electronic configuration of [Ar] so we can simplify this configuration. So we will write the order of the first 18 electrons of potassium <sub>19</sub>K and vanadium <sub>23</sub>V as well as for the elements beyond which to [Kr]

As follows: <sub>19</sub>K [Ar] 4s<sup>1</sup> , <sub>23</sub>V [Ar] 4s<sup>2</sup> 3d<sup>3</sup>

### Example 1-2

Write the electronic configuration of the elements  $_{29}\text{Cu}$  ,  $_{24}\text{Cr}$

**Solution**



Note that level d needs an electron to become half saturated and atoms when their secondary levels are half full or full be more stable so we write the configuration as follows:  $_{24}\text{Cr} \quad [\text{Ar}] \quad 4s^1 \quad 3d^5$

As for  $_{29}\text{Cu}$



So we write it as follows:



### Example 1-3

Write the electronic configuration for :  $_{47}\text{Ag}$  ,  $_{36}\text{Kr}$

**Solution**

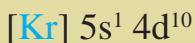


or  $[\text{Ar}] \quad 4s^2 \quad 3d^{10} \quad 4p^6$



5s<sup>1</sup> 4d<sup>10</sup>

or



### Example 1-4

Set the four quantum values of the last electron for each of the following element atoms:  $_{54}\text{Xe}$  ,  $_{23}\text{V}$  ,  $_{17}\text{Cl}$  ,  $_{3}\text{Li}$

**Solution**



$n=2$  because the electronic configuration ended in the second level 2

$\ell=0$  because the electronic configuration ended with the secondary level s

$m\ell = 0$  because the last electron is located in the secondary level s 

$m_s = +1/2$  Because the last electron rotates clockwise (the first electron of the Orbital).

$_{17}^{\text{Cl}}$   $1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^5$

$n=3$  Because the configuration ended with the third principal level 3

$\ell=1$  Because the configuration ended with the secondary level p

$m\ell = 0$  Because the last electron is located in the orbital which has a value of  $\ell = 0$

+1 0 -1



$ms = -1/2$  Because the last electron is the second electron in the orbital.

$_{23}^{\text{V}}$   $1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 4s^2 \ 3d^3$

$n=3$  Because the highest principal level contains electrons at the third

$\ell=2$  Because the electronic configuration ended with the secondary level d

$m\ell = 0$  Because the last electron is located in the orbital whose value is  $m\ell = 0$



$ms = +1/2$  Because the last electron is the first electron in the orbital.

$_{54}^{\text{Xe}}$   $1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 4s^2 \ 3d^{10} \ 4p^6 \ 5s^2 \ 4d^{10} \ 5p^6$

$n=5$  Because the highest principal level contains electrons is the fifth

$\ell=1$  Because the electronic configuration ended with the secondary level p

$m\ell = -1$  Because the last electron is located in the orbital whose value is  $m\ell = -1$



$ms = -1/2$  Because the last electron is the second electron in the orbital.

### Example 1-5

Write the four quantum numbers of the last electron for each of the following ions:  $_{20}^{\text{Ca}}{}^{2+}$ ,  $_{9}^{\text{F}}{}^{-}$

#### Solution

$\text{F}^-$  fluoride ion is a atom that has gained an electron and its number of electrons becomes 10

$_{9}^{\text{F}}{}^{-}$   $1s^2 \ 2s^2 \ 2p^6$

$n=2$  Because the highest principal level contains electrons is the second

$\ell=1$  Because the electronic configuration ended with the secondary level p

### Exercise 1-10

Write the four quantum numbers of the penultimate electron for each of the following atoms:

$_{55}^{\text{Cs}}$ ,  $_{36}^{\text{Kr}}$ ,  $_{26}^{\text{Fe}}$

### Exercise 1-11

Write the electronic configuration of following ions

$_{8}^{\text{O}}{}^{-}$ ,  $_{3}^{\text{Li}}{}^{+1}$

$m\ell = -1$  Because the last electron is located in the orbital whose value is  $m\ell = -1$

+1 0 -1



$ms = -1/2$  Because the last electron is the second electron in the orbital.

### Exercise 1-12

Compare the four quantum numbers of an electron the last of both atomic elements.

$_{14}^{2+}$  Si  $\cdot$   $_{13}^{+}$  Al

The  $\text{Ca}^{2+}$  calcium ion is a calcium atom lost two electrons and the number of electrons become 18

$_{20}^{2+}$  Ca  $1s^2 \quad 2s^2 \quad 2p^6 \quad 3s^2 \quad 3p^6$

$n=3$  Because the highest principal level contains electrons is the second

$\ell=1$  Because the configuration ended with the secondary level p

$m\ell = -1$  Because the last electron is located in the orbital which has a value of  $\ell = -1$

+1 0 -1



$ms = -1/2$  Because the last electron is the second electron in the orbital.

### Example 1-6

Compare the four quantum numbers of the last electron to each of the two element atoms  $_{3}^{+}$  Li and  $_{11}^{+}$  Na

#### Solution

$_{3}^{+}$  Li  $1s^2 \quad 2s^1$

$n = 2$

$\ell = 0$

$m\ell = 0$

$ms = +1/2$

$_{11}^{+}$  Na  $1s^2 \quad 2s^2 \quad 2p^6 \quad 3s^1$

$n = 3$

$\ell = 0$

$m\ell = 0$

$ms = +1/2$

The difference is only in the principal quantum number.

### Example 1-7

If the last electron of an atom of an element has the following four quantum numbers

$n = 3 \cdot \ell = 2 \cdot m\ell = +1 \cdot ms = -1/2$

What is the atomic number of this element?

$n=3$  The principal level will be the third

$\ell=2$  The secondary level is the level and contains five orbitals

$$m\ell = +1$$

Located in the orbital indicator with the letter X

$$+2 \ 1 \ 0 \ -1 \ -2$$



$$ms = -1/2 \text{ is the second electron}$$

$$+2 \ 1 \ 0 \ -1 \ -2$$



So from previous information the last secondary level in the electronic configuration will end with a secondary 3d level which contains seven electrons then become an electronic configuration of secondary levels in this atom as follows:

$$1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 4s^2 \ 3d^7$$

adding the number of electrons above the secondary levels in the electronic configuration and the sum value represents the atomic number of this element.

So      Atomic number = 27

### Exercise 1-14

Write the electronic configuration of  ${}_{11}^5B$  atom

Then write the quantum numbers for all the electrons in which .

### Example 1-8

Write the electronic configuration of the  ${}_{25}Mn$  atom and write the quantum number of the electrons, for the last secondary level.

#### Solution

$${}_{25}Mn \quad 1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 4s^2 \ 3d^5$$

$$+2 \ 1 \ 0 \ -1 \ -2$$



| Electron | Quantum number |        |         |      |
|----------|----------------|--------|---------|------|
|          | n              | $\ell$ | $m\ell$ | ms   |
| First    | 3              | 2      | +2      | +1/2 |
| Second   | 3              | 2      | +1      | +1/2 |
| Three    | 3              | 2      | 0       | +1/2 |
| Four     | 3              | 2      | -1      | +1/2 |
| Five     | 3              | 2      | -2      | +1/2 |

## Basic concepts

### Cathode ray

A bundle of particles emerges from the cathode to the anode direction that when passing a electric current in the electrode discharge tube contains hydrogen gas under low pressure and affected electric and magnetic fields. It has a negative charge and mass.

### Channel ray

A bundle of particles pops up when resulting particles slide that came from the expulsion of electrons from gas neutralized atoms through the hole in the metal into the area behind the cathode. It affected by the electric and magnetic fields and it has a positive charge. Its mass depends on the type of gas used in the electric discharge tube.

### Electromagnetic radiation

An expression used to identify different types of radiation and share in similar properties as transition in the space in same velocity. Each type of radiation has wave property and special frequency of its own and also has a particle property.

### Quantum

The minimum amount of energy that can be lost or gained by the body and the process of loss of energy or gained in the form of fluxes or flows of energy. The amount of energy lost or gained is a multiple integer to this quantum.

### Continue emission spectrum

A group of decaying colors of sunlight which It starts from violet and ends in red and be continuous and connected to each other.

### Line emission spectrum

The decaying group of colors of teased pure element atoms in gaseous state. Each color is separated from other color by large dark spaces and each element has a linear spectrum that distinguishes it from other elements.

### Bohr theory

1. Electron orbits in a specific orbit and a specific energy.
2. Energy is emitted from an atom when an electron is transmitted from a higher energy orbit to a lower energy orbit.

### Uncertainty principle

The location and momentum of an electron cannot be precisely located at the same time if measure one of them increased the lack certainty in the measurement accuracy of the other.

### Principal quantum number

The number determines the electron distance from the nucleus and the amount of energy of an electron at energy levels. The values of these numbers will be positive integer values.

### Momentum quantum number

The number determines the shape of the electronic cloud that probably having an electron in them. This number comes from movement electron around the nucleus for each one principal or more level of the secondary levels are s, p, d, f etc.

### Magnetic quantum number

The number determines the direction of the orbital around the nucleus and shows the most probable for a position in any exists orbital and for each secondary level one orbital or more.

### Spin quantum number

The number determines the angular momentum of the electron rotation around himself and this movement is either towards a scorpion clock or counterclockwise.

### Pauli - excluded principle

Two electrons in the same atom cannot be they have one value for all four quantum numbers.

## Chapter One Questions

1

1-1 Describe the model of electric discharge tube with drawing, explain the discovery of the electron?

1-2 What are the characteristics of channel rays.

1-3 What do the symbols (Z and A) mean?

1-4 Explain the effect photoelectric phenomenon. Inter-explanation Einstein to this phenomenon. And what gave this explanation on the nature of light.

1-5 What happens to an electron when it gains energy.

1-6 What is the importance of exposing the electric discharge tube for magnetic and electric fields when studying properties of electrons and protons.

1-7 Talk about the experience of Millikan and what is the important of that have find out.

1-8 How Rutherford discovered the nucleus of an atom. What are the relationship between the size of an atom and its nuclei.

1-9 What are the difference between

A- Rutherford's model and Thomson's model of atomic structure.

B- Rutherford's model and Bohr model of atomic structure

C- Forms of the principal levels of Bohr and quantum theory.

D- Linear and continuous emission spectrum.

1-10 Derive the mathematical relationship  $\lambda = h/p$  based on Planck and Einstein equations.

1-11 What is the difference between the secondary level and the orbital? What are the numbers of orbitals in the first principal four levels.

1-12 What is the frequency wave? What are the units of frequency, then state the mathematical relationship between frequency and wavelength.

1-13 Explain the experience of Autostron, and explain its importance.

1-14 What quantum theory assumes.

1-15 Explain the following

A- Non-repulsion of two electrons in the same orbital

B- Millikan's experience is complementary to the Thomson experience.

C- The secondary level s can accommodate only two electrons either the secondary level p accommodates just six electrons.

D- The position and momentum of an electron in an atom cannot be set in high resolution simultaneously.

E- Secondary level 3p is filled with electrons after secondary level 3s.

F- The strongest attraction of the nucleus on the electron closest to it.

1-16 Define the four quantum numbers (n, l, ml, ms) What do they benefit from each?

1-17 Draw the shape of the orbital when the value of l = 0 and when they are valuable l = 1.

1-18 What we mean by all of what comes.

A- Photon.

B- The wavelength.

C- The double character of the electron.

1-19 What benefits from Hund's base in the electronic configuration.

1-20 show

- A- The Heisenberg principle.
- B- Pauli's exception principle.
- C- How an atom can emit a photon.
- D- How Schrödinger was able to explain the spectrum of atoms which have a higher atomic number of hydrogen.

1-21 What are the values of the principal and secondary quantum numbers and magnetism in the following major levels (third and fourth).

1-22 If you know that the values of the four quantum numbers of the last electron for the atoms (A, B, and C), respectively.

A

$$n = 4 \quad \ell = 2 \quad m\ell = +1 \quad ms = -1/2$$

B

$$n = 2 \quad \ell = 0 \quad m\ell = 0 \quad ms = +1/2$$

C

$$n = 3 \quad \ell = 1 \quad m\ell = -1 \quad ms = -1/2$$

Write the electron configuration of atoms (A, B, and C). What is the atomic number of each.

1-23 Mention at least two elements ends up with distributed electron levels  $s^2 d^6$

1-24 Write the electronic configuration of the following ions  $_{29}Cu^{+2}$ ,  $_{29}Cu^{+1}$

1-25 Write the electronic configuration of atoms and ions of the following  $_{79}Au$ ,  $_{34}Se$ ,  $_{16}S^{-2}$ ,  $_{37}Rb$ ,  $_{50}Sn$

1-26 Compare the four quantum numbers of the last electron for each of the atoms for following elements  $_{38}Sr$ ,  $_{21}Sc$ ,  $_{20}Ca$

1-27 Write the electronic configuration of the atom ( $_{9}F$ ) then write the quantum numbers of all the electrons. Show the principle that corresponds through your feedback to values quantum number for electrons.

1-28 Set the four quantum values for the electrons located in the last major level of each The following atoms  $_{4}Be$ ,  $_{15}P$

1-29 Set the four quantum values for the last electron only for each of the following atoms  $_{78}Pt$ ,  $_{35}Br$ ,  $_{19}K$

1-30 choose the correct answer for the following:

1- When the North Pole finder is rounded to a magnet On cathode rays, the luminous line is curved into:

- A- Down
- B- The highest
- C- Not affected

2- Mass of one electron equal:

- A-  $1.76 \times 10^{11} C/kg$
- B-  $1.6 \times 10^{-19} e$
- C-  $9.1 \times 10^{-31} kg$

3- The discovery of neutron is attributed to the scientist:

- A- Thompson
- B- Henry Mosley
- C- James Chadwick

4- The light wavelength is proportional to its frequency

- A- directly
- B- inversely
- C- equal

5- In the photoelectric effect phenomenon if the radiation exceeds minimum emission value:

- A- The number of emitted electrons increases
- B- The number of electrons emitted decreases
- C- The energy carried by the electron increases

6- Quantum number that determines the shape of the electronic cloud is :

- A- Principal.
- B- Secondary.
- C- Magnetic.

7- The diameter of the atom is greater than the diameter of its nucleus

- A-1000 times
- B-10000 times
- C-100000 times

8. If  $n = 2$ , there are:

- A- one specific value for the secondary quantum number = zero.
- B- two specific values for the number of secondary quantum = 0 and 1
- C- three specific values for the number of secondary quantum = zero, 1 and 2.

9. The principle which states that two electrons cannot exist in the same atom would have the same values, of the four quantum is:

- A- The Heisenberg inaccuracy principle.
- B- The Pauli exclusion principle.
- C- The principle of the rule of Hind.

10. If the electronic configuration ends at the secondary level  $2p^6$  there is a possibility:

- A- The atom should be only one element which is an element.  $_{10}Ne$
- B- That there are two element atoms, namely  $_{9}F$  and  $_{10}Ne$
- C- That there is more than one atom element in addition to  $_{10}Ne$  that these elements are lost or acquired electrons to be rearranged like an atom element  $_{10}Ne$

11- If the electronic configuration of an element's atom ends  $4s^2 3d^5$ , so The four quantum numbers of the last electron be:

- A-  $n = 3 \quad \ell = 2 \quad m\ell = -2 \quad ms = +1/2$
- B-  $n = 4 \quad \ell = 2 \quad m\ell = +2 \quad ms = +1/2$

C-  $n = 4 \quad \ell = 2 \quad m\ell = -2 \quad ms = +1/2$

12- If the values of the four quantum n number for the last electron in the element atom is  $n = 3 \quad \ell = +1 \quad m\ell = 0 \quad ms = +1/2$  The atomic number of the element is:

- A- 12
- B- 13
- C- 14

13- If the values of the four quantum numbers of the penultimate electron in element atom is

$n = 2 \quad \ell = 1 \quad m\ell = 0 \quad ms = -1/2$

The atomic number of the element is:-

- A- 9
- B- 10
- C- 11

14- The electronic configuration of an atom of an element was:-

$1s^2 \quad 2s^2 \quad 2p^6 \quad 3s^2 \quad 3p^3$

The four quantum numbers of electrons are in secondary level  $3p^3$  will only differ in:

- A- Secondary quantum number.
- B- Magnetic quantum number.
- C- Electron spin quantum number.

15- The four quantum numbers of electrons are in secondary level  $4p^2$  will only differ in:

- A- the secondary quantum number.
- B- the magnetic quantum number.
- C- the electron spin quantum number.

16- The four quantum numbers of electrons are in secondary level  $5p^6$  will only differ in:

- A- the secondary and electron spin quantum number.
- B- the secondary and magnetic quantum number.
- C- the magnetic and electron spin quantum number.

17. In his theory, Bohr assumed that electrons orbit at :

- A- specific size and energy orbitals.
- B- specific size and variable energy orbitals.
- C- variable size and specific energy orbitals.

18. In an electrostatic discharge tube positive particles that slides through the hole into an area behind the cathode are called

- A- cathode rays.
- B- channel ray.
- C- x - ray.

19. If we assume that the atom includes only protons in its nucleus, it means:

- A- There is no difference in the atomic number of all elements atoms.
- B- There is no difference in the number of mass of all elements atoms.
- C- There is no difference in the mass number of all atoms for one element.

20. Plank assumed when he was studying a phenomenon of light emission of hot objects:

- A- Hot objects release electromagnetic energy in the form of waves.
- B- Hot objects release electromagnetic energy as specific small amounts.
- C- Hot objects release electromagnetic energy as continuous small amounts.

21. The atom is excited:

- A- when the energy of the atom is at a stable level.
- B- when the potential energy level of atom becomes higher than the stable level.
- C- when energy is lost in the form of electromagnetic radiation (Photon).

22. Quantum number which indicates the direction of the orbital around the nucleus is:

- A- Secondary quantum number.
- B- Magnetic quantum number.
- C- Electron spin quantum number.

23. Principle quantum number is always equal for number:

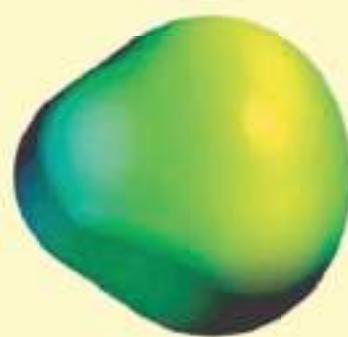
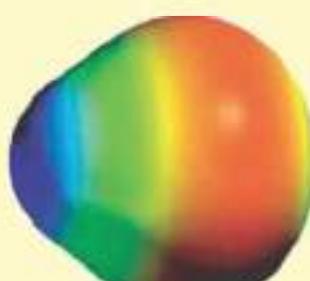
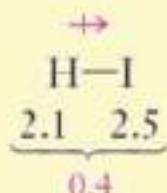
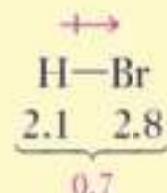
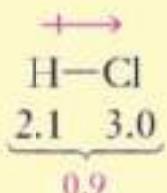
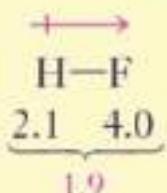
- A-Secondary levels.
- B- Orbitals.
- C- Electrons.

24. The electron orbits in a specific orbit with specific diameter and energy (according Bhor assumption) and as a result of its rotation:

- A- Emit energy.
- B- Absorb energy.
- C- Does not emit energy.

More polarity

Less polarity



## Chapter Two

### Bonding forces and geometric shapes of molecules

2

After completing this chapter, the student is expected to:

- Understand why atoms combine together and the meaning of chemical bonds and their types.
- Understand the factors that determine the type of bonding and know how the atoms combine among them.
- Determine the properties of ionic compounds and distinguishes between their properties and those of covalent compounds
- Realize the absence of molecules in ionic compounds.
- Understand the concept of hybrid orbitals and their types.
- Recognize the principle of resonance and its effect on the effectiveness of some covalent compounds.
- Draw the geometric patterns of some molecules.
- Differentiate the bonds of sigma and the bonds of  $\pi$ .

## 2-1 Introduction

### Do you know

The number of elements already in nature is 94 elements. As for the elements prepared industrially are 26 elements due to chemists' efforts in world. the number of elements are 120 elements.

But the resulting compounds within the various branches of chemistry are in millions. These compounds are increasing with the days and the main and basic reason of that is nature of the atoms that are bonded together to form independent molecules or crystalline structures. Chemical bonds are the ladder, which if the chemist guided in his laboratory to create new materials as we see it in our daily lives.

Before we get into the details of how chemical reactions occur among the atoms of the elements in nature around us, we must review chemical properties of noble or inert elements, this group that we have already studied in previous levels, which include elements of helium He, Neon Ne, Argon Ar, Krypton Kr and xenon Xe has a special and important characteristic that distinguishes it from other elements in nature.

All elements of this group are chemically inert and on most are ineffective in normal circumstances. because the outer energy level has saturated with electrons, unlike the rest of the existing elements in nature. So the formation of electrons saturated orbitals would be the goal of any atom to achieve chemical stability.

It is worth to mention that there are a number of elements found in nature as a single unit (molecule) like oxygen  $O_2$  and nitrogen  $N_2$  and sulfur  $S_8$ , where the atoms are bounded together by bonds to arrived their external orbitals to saturation (which resembles noble gases).

All atoms of the elements except those of noble gases possess uneven chemical activity is under normal conditions and can enter into chemical reactions to saturate the last energy level through loss or acquire or share electrons to access the electronic configuration to the nearest noble (inert) gas.

The term (chemical bonding) are mainly used to know how atoms or ions are bonded together to form covalent or ionic molecules or others, which is mainly used to understand and follow chemical reaction process that lead to creation of new chemical compounds [Figure 2-1].

Here we have to go through our imagination on some logical scientific questions we need to answer, in order to complete the general idea of how these bounds occur:

- \* How and why? Atoms are bound together to form multiple molecules atoms were simple or complex?
- \* Why different chemicals materials possess different physical properties from each other such as color, melting point, boiling point, acidity and thermal conduction, electrical conductivity and solubility in different liquids ....etc?
- \* Why chemicals materials have different chemical qualities in terms of resistance to the effect of acids, bases or various chemical reagents and affected by temperature?

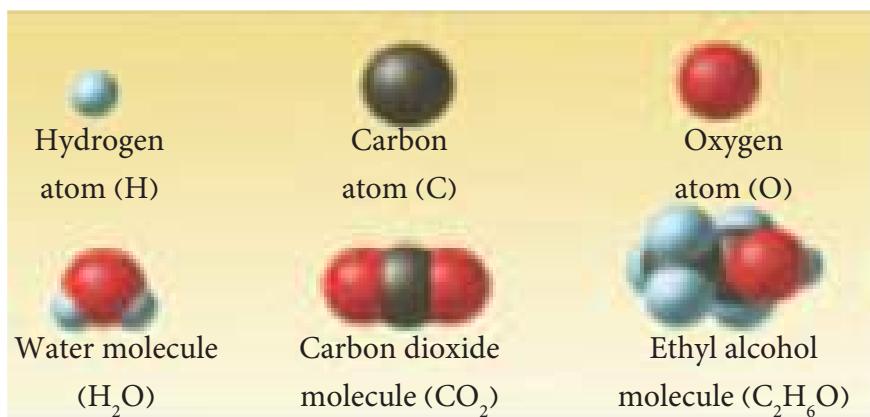


Figure 2-1

Chemical bonding

Many other questions need appropriate scientific answers to them to explain causes, and thus extrapolate other cases where extrapolation is an investigation to the desire of man and his curiosity to uncover the secrets of scientific knowledge. For the purpose of remind students by some of the concepts discussed in the previous year we will review some of them in the following items:

### 2-1-1 Chemical reaction

The chemical reaction between two elements is an interaction between atoms of two elements to form a new compound molecule has chemical and physical properties completely different from the characteristics of the elements involved in the reaction. Its purpose is to form orbitals saturated with electrons to achieve chemical stability. There are many scientific facts and notes must be in the thinking of students, when they are studying and learning of chemical reaction project as follows:

1. The nuclei of elements atoms does not enter the chemical reaction, the same is true for internal electronic orbitals which are saturated and stable.
2. The chemical reaction is limited to the sharing of valence electrons located in the outer shell of unsaturated orbitals.
3. The atoms of the elements involved in the compound composition are strongly associated with abinding on the elements involved. Stability or weakness of bonds in the resulting compound depends on the nature of the bonding force between the atoms; the most important is the electronegativity for involved atoms.
4. When partition the compound into its initial elements, ie separating the two elements from each other with, various chemical or physical methods dismantling of the bonding force (ie, bond breaking) are require. Bond breaking which needs energy equal to that emitted energy to bond formation.
5. When elements are combined, the electronic configuration of external unsaturated orbitals are changed to reach stable state as the atoms which has saturated molecular orbitals.

### Exercise 1-2

Write Lewis symbol for atoms:  $_{16}\text{S}$ ,  $_{11}\text{Na}$ ,  $_{10}\text{Ne}$

### 2.1.2 Lewis symbol and the Octet Rule

You knew from your previous study that electrons in the outer shell of atom element's is configured in Lewis order, so that the symbol of the chemical element is written surrounded by dots each point representing one electron and every two adjacent points are an electronic pair. These points are distributed to the four sides surrounding the symbol so that do not exceed two points on each side.

### Example 2-1

Write the Lewis symbol for magnesium ( $_{12}\text{Mg}$ ) and chlorine ( $_{17}\text{Cl}$ )

#### Solution

Electronic configuration of magnesium atom:



So Louis' symbol for the magnesium atom is: 

Electronic configuration of chlorine atom:



So Louis' symbol for the chlorine atom is: 

These electrons determine the nature of bonds between atoms and also determine chemical formulas for compounds resulting from the atoms union when covalent bonds forms between atoms, they share a number of electrons to be arranged similar to the noble gas closest to them which has eight electrons in its outer shell (except helium who has only two electrons). This can be illustrated by writing Lewis to a number of molecules as follows:

Water molecule ( $\text{H}_2\text{O}$ ) the electronic configuration of an atom (H) is  ${}_1\text{H}: 1\text{s}^1$

Lewis symbol of atom (H) is H.

And atom(O) is  $1\text{s}^2 \ 2\text{s}^2 \ 2\text{p}^4$

Lewis symbol of atom (O) is 

Water molecule is 

Ammonia molecule ( $\text{NH}_3$ ) The electronic configuration of an atom (N) is  ${}_7\text{N}: 1\text{s}^2 \ 2\text{s}^2 \ 2\text{p}^3$   
and the hydrogen atom as mentioned above.

Lewis symbol for the ammonia molecule is 

You may notice that each of the atoms O and N in these compounds, is surrounded by eight electrons and this rule applies to atoms in many compounds. This rule is called the (octet rule), where the central atom in the molecule is surrounded by eight electrons. This rule is not applicable for all the atoms in the molecules as in the phosphorus pentachloride  $\text{PCl}_5$  and Boron trifluoride molecule  $\text{BF}_3$



It notes that the central phosphorus atom was surrounded by ten electrons, as for the boron atom is surrounded by six electrons, so it does not agree with rule of eight. Authorized rule of eight is not general in all cases as there are many atoms that do not agree with this rule.

### Exercise 2-2

Which one of these molecules apply octet rule to Its central atom the  $\text{CH}_4$  or  $\text{BeF}_2$ . Note that the atomic number of F = 9, Be = 4, H = 1, and C = 6

## 2-2 Types of chemical bonds

Chemical bonds are the phenomenon of the presence of atoms coherent together in molecule or crystal. The material atoms are bonded together by chemical bonds, the type and strength of the chemical bond depends on the electronic configuration of the constituent atoms that form bond. There are several types of chemical bonds can form between the atoms of different elements, which are:

### 2-2-1 Ionic bond

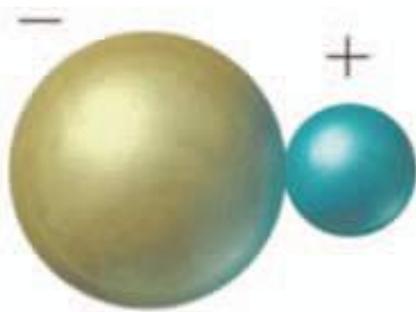


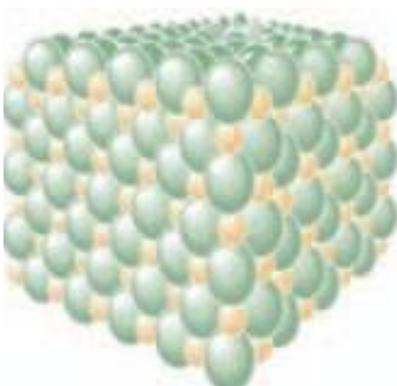
Figure 2-2

Ionic bond of NaCl.

Ionic bonds emerge between a metallic element and a non-metallic element through loss and gain electrons. It results from the interaction of two atoms, one of which have High electronegativity (such as atoms of halogen group elements) and others have low electronegativity (e.g., alkaline earth metals group and alkaline metals group elements). In this case, the valence electron will move completely from the atom of the low electronegative element into the atom of the high electronegative element, and then we have two ions, the first is positive charge ions as a result of the loss of an valence electron , the second is negative ion as a result of the reception of this electron[Figure 2-2]. These different charged ions are then bound as a result of the electrostatic attraction to form the complex and form neutral crystal lattice [Figure 2-3] like; sodium chloride NaCl, potassium chloride, KCl, magnesium chloride MgCl<sub>2</sub> and potassium fluoride KF and calcium chloride CaCl<sub>2</sub> , as well as all hydrides of alkaline metals group elements and alkaline earth metals group elements, such as sodium hydride NaH.

The most important properties of ionic compounds are:

1. It exists in form of a crystalline structures, a regular geometric arrangement of negative and positive ions.
2. It has very high melting and boiling point, to overcome the attraction forces between the negative and positive ions and to break the crystalline structures.
3. Inability of conductive electrical in solid state due to ions connection and their inability to move within the crystalline structures while becomes conductive electrical, when melted or dissolved in water (then the ions will be free to move in the melted and aqueous solution).
4. Soluble in polar solvents such as water and do not dissolve in non-polar organic solvents such as gasoline or ether.



|  |                                    |
|--|------------------------------------|
|  | Sodium ion<br>(Na <sup>+</sup> )   |
|  | Chloride ion<br>(Cl <sup>-</sup> ) |

Figure 3-2

Crystalline structure of sodium chloride.

## 2-2-2 Covalent bond

Covalent bond is formed when the valence electron is difficult to transmit a complete transition from one atom to another, in this case the pair is formed from electronic contribution or participation of both atoms. Charges are not shown on atoms, covalent bonds often occur between non-metals. The difference in the electronegativity value (see electronegativity values for some elements in Table 2.1) plays an important role in the formation of covalent bonds. It can lead to two types of covalent bonds:

### A- Pure covalent bond:

This bond emerge between two atom of non-mittallic elements, where they are similar in electronegativity, or between two elements atoms that are similar in electronegativity, where the difference in electronegativity is zero for the two case. The pair of electrons will spend equal time in the acquisition of both atoms [Figure 2-4].

An example of this type of covalent bond is the bond in the nitrogen molecule  $N_2$ , the chlorine molecule  $Cl_2$  and the oxygen molecule  $O_2$  and in the fluorine molecule  $F_2$ .

### B- Polar covalent bond:

This bond emerge between two elements atom where they are similer electronegativity but in this case the difference must be greater then zero and less than 1.7 to participation with one or more electrons pair [Figure 2-5].

Examples of this type of covalent bonds found in molecules  $H_2O$ , and ammonia  $NH_3$  of water  $H_2O$ , ammonia  $NH_3$ , Hydrogen fluoride HF, aluminum chloride  $AlCl_3$ , and brominde  $HBr$ , In this case one of the atoms carry partial negative change (negative delta  $\delta^-$ ) and the second atom carry partial positive change (positive delta  $\delta^+$ ).

Table (2-1) Electronegative values of some elements of the periodic table.

| Element  | Symbol | Electro-negative | Element   | Symbol | Electro-negative |
|----------|--------|------------------|-----------|--------|------------------|
| Fluorine | F      | 4.0              | Silver    | Ag     | 1.9              |
| Oxygen   | O      | 3.5              | Iron      | Fe     | 1.8              |
| Nitrogen | N      | 3.0              | zinc      | Zn     | 1.6              |
| Chlorine | Cl     | 3.0              | Manganese | Mn     | 1.5              |
| sulfur   | S      | 2.5              | Aluminum  | Al     | 1.5              |
| Hydrogen | H      | 2.1              | Magnesium | Mg     | 1.2              |
| Nickel   | Ni     | 1.9              | Lithium   | Li     | 1.0              |
| Copper   | Cu     | 1.9              | Sodium    | Na     | 0.9              |
| Carbon   | C      | 2.5              | Potassium | K      | 0.8              |



Figure 2-4

Pure covalent bond.

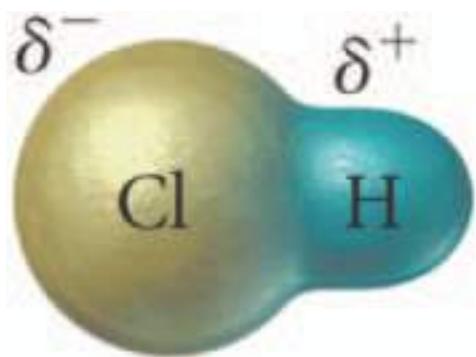
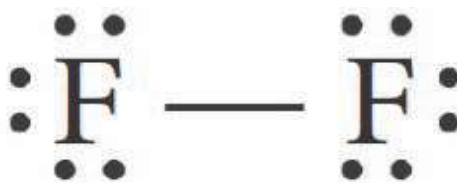
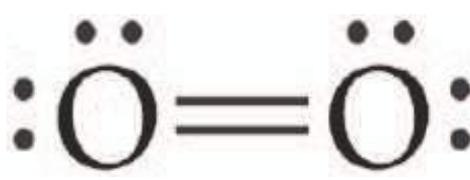


Figure 2-5

Polar covalent bond.



Single covalent bond.



Double covalent bond.



Triple covalent bond.

There are many types of covalent bonds that differ in number of electronic couplings bonding between atoms. most common covalent bonds is a single bond, which share only one electronic pair, such as molecule  $F_2$ . When participating in two electronic pairs, they are called double covalent bonds, In the case of participation in three electronic pairs makes it a triple covalent bond. An example of double bond is what we find in the oxygen molecule  $O_2$ . An example of triple bond is what we find in the nitrogen molecule  $N_2$ . Covalent bonds compounds are characterized by the following:

1. Low melting and boiling point, so do not need high heat energy, because the forces of attraction between their molecules are weak.
2. Do not conducted electric current because they dont form negative or positive ions in their melts or aqueous solutions.
3. Mostly don't dissolve in polar solvents as water while dissolve in organic solvents such as ether and benzene.

### 2-2-3 Coordinate bond

Coordinate bond is formed when one of the atoms provides a pair of electrons to another atom have the ability to receive this electronic pair to form bond. Then this pair will be shared between two atoms. The electron donor atom is the Lewis base and contains a pair of free electron such as oxygen atom in a water molecule or a nitrogen atom in the ammonia molecule. The receiving atom is often a transitional metals (Lewis acid) because they have empty orbitals of the type d such as nickel or hydrogen atom ion.

We can say that coordinate bond Is a special type of covalent bond, except that the source of the electron pair is only from one atom, and the coordinate bond is longer and weaker than covalent bond.

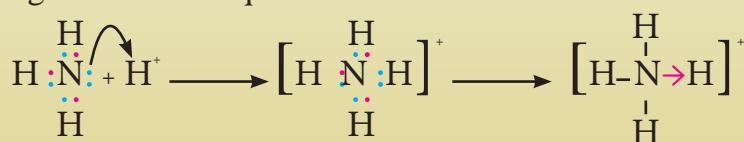
### Exercise 2-3

### Example 2-2

Graphically illustrate the emergence of the coordinate bond in the ammonium ion  $NH_4^+$

#### Solution

This ion consists of the binding of ammonia  $NH_3$  to the hydrogen ion  $H^+$  in aqueous solution:



Use the Lewis symbol for atoms F, O and N to illustrate the formation of covalent bonds single, double and triple.

Note from the previous example that the nitrogen atom has a pair of electrons not involved in the  $\text{NH}_3$  molecule which can be involved. The hydrogen ion has an empty orbital that can receive this pair. When the ammonia molecule is close enough to hydrogen, an attraction occurs and the pair of electrons shared between, as in covalent bond exactly and form  $\text{NH}_4^+$  ion. This type of bond is called coordinate bond and is referred to in the order of the Lewis symbol with an small arrow rather than a line that represents a covalent bond.

#### 2-2-4 Metallic bond

A chemical bond that happens between the atoms of an element of metals, this bond is formed due to the metal atoms possessing electrons in their outer shells contribute to the formation of a crystal and these atoms has free electrons movement in this crystal. When metal atoms are binding together, they do not reach the electronic configuration of noble gases. Atoms of metals such as sodium and potassium, they are easy to lose their equivalent electrons and become positive ions because their electronegativity is low. The strength of the metal bonds is affected by several factors, the most important is the charge density which is equal to the ion charge / ion size (proportional to the number of orbits), where the ion charge is the charge that the metal gains after losing electrons in the last orbit (+1,+2,+3).

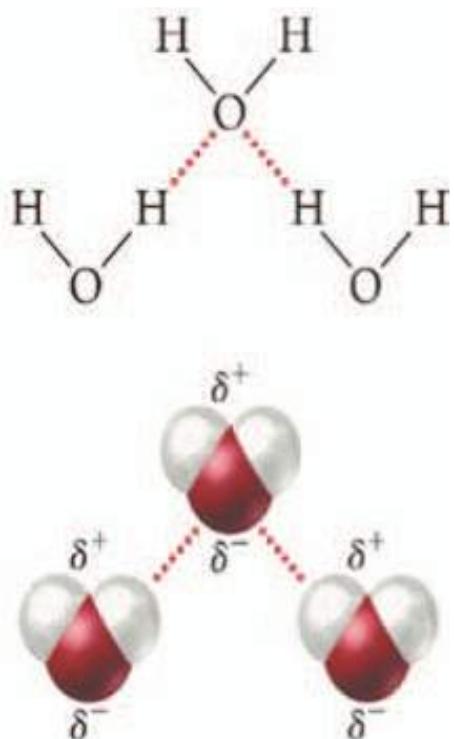
Therefore, the force of the metallic bond depends on the number of the electrons valence beam in the metal atoms, the more electrons of the valence beam, the greater the coherence of the metal to be more solid and higher in boiling point. Higher charge density on the ion increased bond strength and as a result higher melting point obtained. Many of the properties of natural metals depends on the nature of this bond, electrical conductivity and thermal conductivity of metals caused by the movement of free electrons between atoms.

#### 2-2-5 Hydrogen bonding

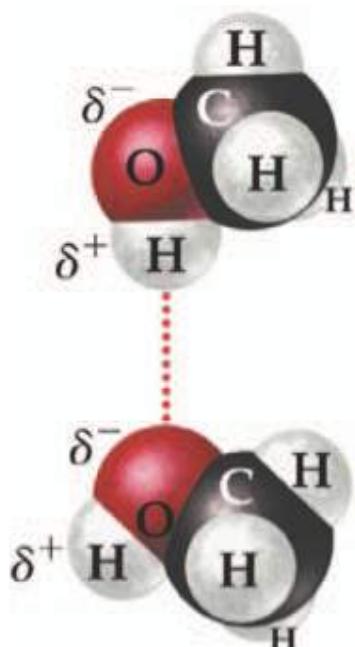
Hydrogen bonds arise due to the attraction that occurs between the positive terminal (hydrogen atom) and the negative terminal atom possess electronic pair or more. These three properties are limited to three elements only are ; oxygen, fluorine and nitrogen atoms. Therefore we find water, ammonia, hydrogen fluoride molecules and others are agglomerated by effect of hydrogen bonds.

#### Exercise 2-4

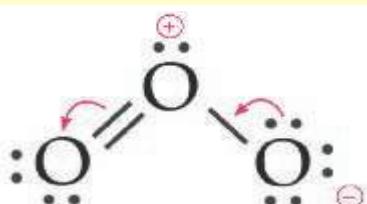
Represent the two ions  $\text{H}_3\text{O}^+$ ,  $\text{BF}_4^-$  using Lewis symbol and interpreted the formation of coordinate bond between them.



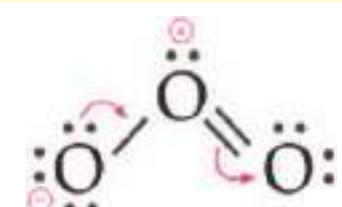
Hydrogen bond in water molecule.



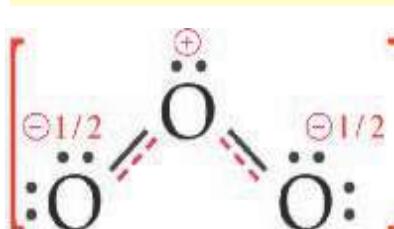
Hydrogen bond.



Composition I



Composition II



Composition III

Hybrid resonance structure between the two structures I,II

Resonance of ozone

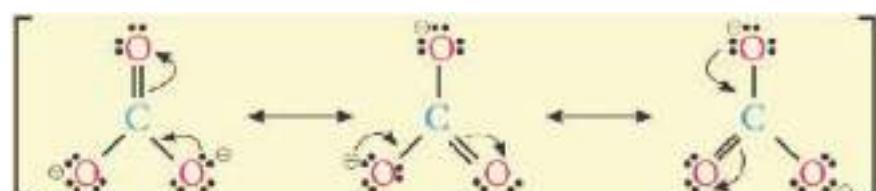
#### Exercise 2-5

Draw the resonant shapes of the sulfate ion( $\text{SO}_4^{2-}$ ) and phosphate ion( $\text{PO}_4^{3-}$ ).

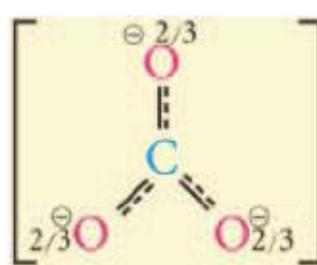
The hydrogen bond is the cause of the high boiling point of water, the melting point of ice and the expansion of the volume of frozen water that led to ice floats on the water. Hydrogen bond is a weak physical bonding force between molecules and not a precise chemical bond: therefore its strength is much lower than other.

### 2-3 Resonance

Some types of bonds can have more than a dot shape such as ozone (composition I, II) in which the central atom has a single bond with one atom and a double bond with another. The dots shape cannot tell us which of the atoms has a double bond. Both atoms have the same chance of a double bond. These two structures are likely to be called resonance structure or resonance. In fact, the structure of ozone is a hybrid resonance structure between its resonance structure (composition III). Rather than having a double bond and a single bond, in fact, the two bonds are equal, which is a middle state between the single bond and double bond, where three electrons are at each all time. Carbonate ion ( $\text{CO}_3^{2-}$ ) can also be drawn by any of the following formulas:



It is clear from the structures above that the central atom (C atom) is connected with the other atoms (O atoms) with two mono bonds and one double bond alternating their position on the three atoms and these potential structures are called resonance. In fact, the ion structure ( $\text{CO}_3^{2-}$ ) is a hybrid resonance structure between the above three structures as following



## 2-4 Geometric shape of the molecules

The molecules of chemical compounds take certain geometric forms that control in its composition a number of factors, the same that control the type of chemical bond (whether ionic, covalent or metallic), which are:

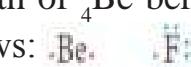
1. Number and type of atoms associated in the molecule.
2. Electronic configuration of element atoms involved in the formation of the molecule.
3. The ability of atoms to acquire, lose or share valence electrons.
4. The presence or absence of an empty secondary outer shell in the atom.

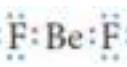
The atom reaches a more stable state and a minimum energy state so that the repulsion between its electrons is minimums in atoms and attracting as much as possible. Theories explain the formation of the bonds and the forms of molecules and recall the most important now, these theories:

### 2-4-1 Valence Shell Electron-pair Repulsion Theory (VSEPR)

This theory explains the configuration of atoms around a central atom based on the repulsion between pairs of electrons involved or not involved in the valence shell of the central atom. The repulsion between these pairs is minimum, when they are as far as possible from each other so as to achieve this greater gravitational attraction of the atoms makes them more stable and less energy. To illustrate, the geometry of some molecules can be studied:

#### BeF<sub>2</sub> molecule:

When Lewis symbol is written for both of <sub>4</sub>Be beryllium atom and the <sub>9</sub>F fluorine atom as follows: 

The Lewis symbol shows that the beryllium atom shares the two fluorine atom by pair of electrons atoms to have a two pairs of electrons shared around beryllium atom. In order for the electrons to be in the lowest state of repulsion, they are distributed on both sides of the beryllium atom and the fluorine atoms are distributed according to the following: 

So you notice that the three atoms are arranged on a straight line so that beryllium falls in the middle and the spatial shape of the molecule is linear and the angle between the two bonds are 180° [Figure 2-6].



Figure 2-6

Linear form of beryllium fluoride molecule.

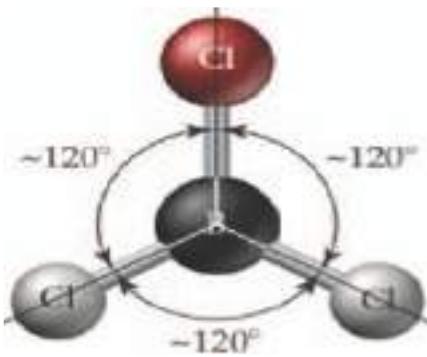


Figure 2-7

Triangle planar.

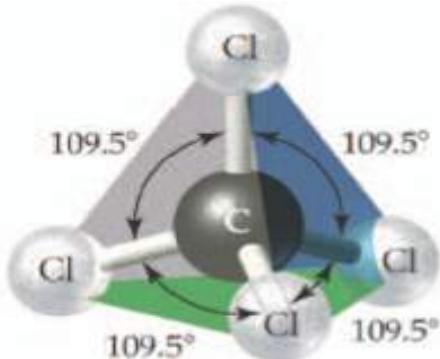


Figure 2-8

Regular tetrahedral.

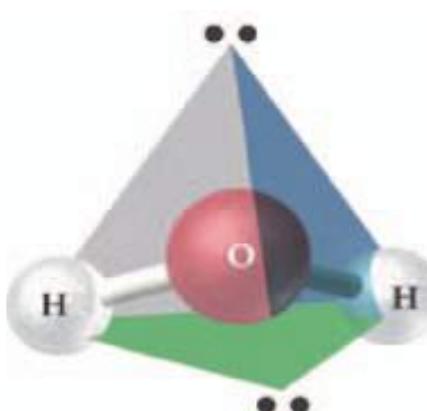


Figure 2-9

Geometric shape of water (angular).

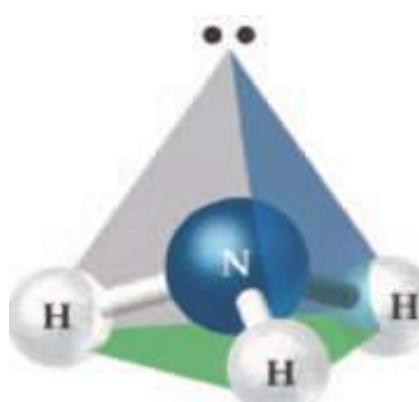
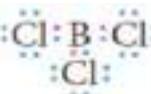


Figure 2-10

Geometric shape of ammonia (trigonal pyramidal).

### BCl<sub>3</sub> molecule:

The Lewis symbol for the boron chloride molecule BCl<sub>3</sub> is written as follows:



It is clear from this symbol that there are three pairs of electrons surrounded boron atom. In order to be less repulsive between pairs of electrons as possible, the chlorine atoms are distributed around the boron atom in the form of a triangle planar. The angles between its bonds are 120° (Figure 2-7).

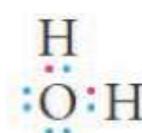
### CCl<sub>4</sub> molecule:

The Lewis symbol for CCl<sub>4</sub> is as follows:



It notes that there are four sets of electron pairs surrounding carbon atom, the repulsion between them at its lowest then chlorine atoms are distributed towards the heads of a regular tetrahedral so that the angle between each pair is 109.5 ° (Figure 2-8).

### H<sub>2</sub>O molecule



It is clear from Lewis symbol of the water molecule that there are four pairs of electrons surround the oxygen atom, further note the composition of the oxygen atom in water molecule is similar to the composition of a carbon atom in CCl<sub>4</sub> molecule. The pairs of electrons are distributed toward a angular shape. The presence of non-participating electronic pairs pushes two hydrogen atoms because they are spread over two vertical sides in a curved shape at an angle of magnitude (Approx.104.5°) [Figure 2-9].

### NH<sub>3</sub> molecule



It is clear from the Lewis symbol that there are four sets of electron pairs surrounded nitrogen atom and it is expected to be distributed as in the case of the CCl<sub>4</sub> molecule toward the form a trigonal pyramidal, but the presence of a non-participating electron pair push the three hydrogen atoms to be distributed on the heads of the three-base pyramid. The angle between the three bonds is about (107.3 °) [Figure 10-2].

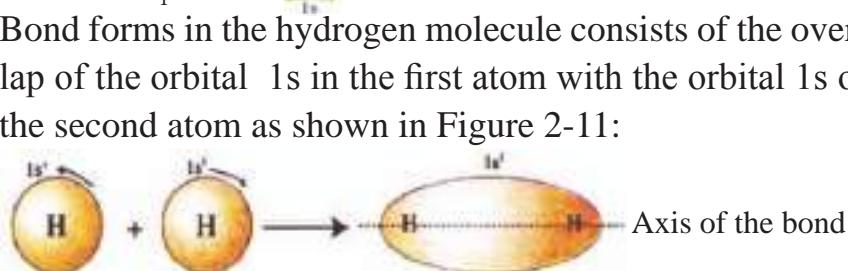
## 2-4-2 Valence bond theory

The theory of repulsion of electrons pairs of valence shell was able to explain different shapes of molecules, but they could not explain how the electrons were distributed between the valence shells of the two constituent atoms of bond. One of the theories that contributed to this clarification theory of the valence bond, which was adopted in its interpretation of the formation of the covalent bond on the interference of atomic orbitals of the valence of the atoms where the electrons move around the nuclei and increase the electronic density in the area of interference between the two atoms. This leads to the two nuclei approaching each other, reducing their energy and increasing their attraction towards the overlap area of the orbitals, thus forming a covalent bond between them. This can be illustrated in the formation of covalent bonds of some simple molecules such as  $H_2$ ,  $HF$ ,  $Cl_2$ ,  $O_2$ ,  $N_2$ . Atomic orbitals overlap as follows:

### A- Orbital overlap S with two hydrogen atoms in the hydrogen molecule

When writing the electronic configuration of the hydrogen atom, we notice that it has one electron at the secondary level (1s):  ${}_1H : 1s^1$

Bond forms in the hydrogen molecule consists of the overlap of the orbital 1s in the first atom with the orbital 1s of the second atom as shown in Figure 2-11:



It is noted from the figure that the electrons of the bond are concentrated between the nuclei of the two atoms, where the electronic density increases in the area of interference around the axis connecting the two nuclei. This bond is called sigma ( $\sigma$ )

### B- Orbital overlap s with orbital p from other atom as in HF molecule

When writing the electronic configuration of hydrogen atom, we note that it has one electron at the secondary level 1s  ${}_1H : 1s^1$

When writing the electronic arrangement of the fluorine atom is as follows:  ${}_9F : 1s^2 2s^2 2p^5$

Figure 2-11

Vertical overlap of Orbitals S.

It notice that there is a single electron in orbital in the fluorine atom, so a sigma bond is created, when the orbital p from the hydrogen atom overlaps with the orbital p (located on the vertical axis) where the electronic density is distributed around the axis connecting the two nuclei. This bond is also named sigma bond [Figure 2-12].

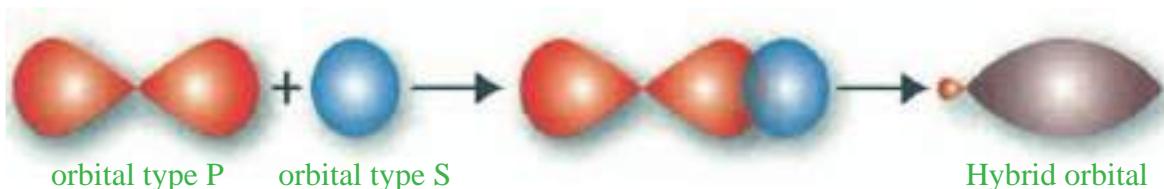


Figure 2-12

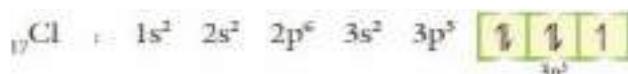
Two orbitals p, s vertical overlap.

**C- Orbital overlap p of the first atom with orbital p of the second atom**

Orbitals p overlap in two ways as follows:

**1- Orbital p overlaps with orbital p on the same axis**

When orbital type p of atom is vertical overlap with orbital type p of another atom (at the same axis), then electronic density is distributed between two nuclei of the two atoms symmetrically along the axis connecting them. This bond is called sigma bond as in  $\text{Cl}_2$  molecule.



Atomic orbital 3p approaches, which contains one electron in both of the two atoms and it overlap between them and arises cloud of electronic density. It represents the sigma bond between the chlorine atoms [Figure 2-13].

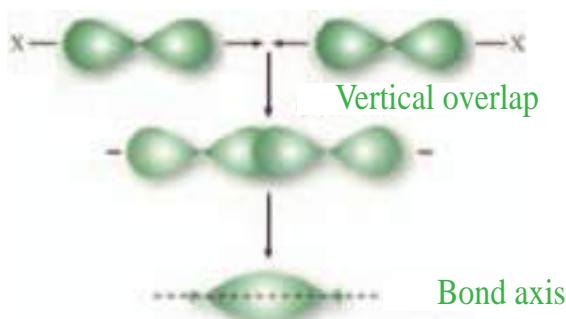


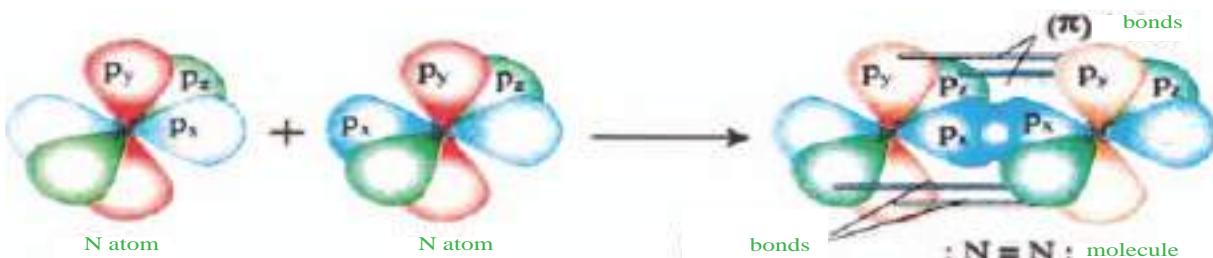
Figure 2-13

Two orbitals p vertical overlap.

**2. Orbital p overlap with orbital p on the side axis**

When an orbital p of an atom overlaps with an orbital p of another atom, the lateral interference occurs vertically, the electronic cloud will be distributed over the bond axis that bonds of the two atoms. These overlap will form a covalent bond type pi ( $\pi$ ), as oxygen molecule.

When lateral interference occurs horizontally, the electronic cloud distributes on the right and left axis of the bond axis that connected the two atoms, that gives bond type pi. Three cases can be found from overlap (vertical, lateral vertical, lateral horizontal) as shown between the two atoms of nitrogen molecule in [Figure 2-14].



## 2-5 Orbital hybridization

The process of overlap can occur between orbitals of one atom which are close in energy to produce a number of atomic hybrid orbitals which are equal to the number of orbitals involved in the interference. This condition is called orbital hybridization, called orbitals that are result from hybrid orbitals. Thus, the hybridization process represents interference atomic orbitals have to produce hybrid orbitals similar in shape and size and equal in energy and more stable and lead to get stronger covalent bonds between atoms involved in molecule formation. Regarding following are some observations regarding the hybridization process and its products:

1. The hybridization process occurs in the same atom orbital after excitation the electrons that fall within the main outer plane and their task reducing the repulsion between electrons of resulted molecules.
2. Hybridization is done between atomic orbitals converging in energy together like (2s,2p), (3s,3p), (4s,4p).
3. The holographic geometry of hybrid atomic orbital differs from Stereoscopic geometry of atomic orbital before hybridization. The hybrid atomic orbital form consists of two lobes, one of which is large; where the cloud is relatively concentrated and the other is small and often neglects while drawing [Figure 2-15].
4. The name of the hybrid orbital is derived from the names and number of pure orbitals, as example the hybrid orbital ( $sp^3$ ) which is involved in the hybridization process. It means the participation of three atomic orbitals of type (p) with one atomic orbital type within the same principal electronic shell.

Figure 2-14

Formation of  $\pi$ bond and sigma bond in nitrogen molecule.

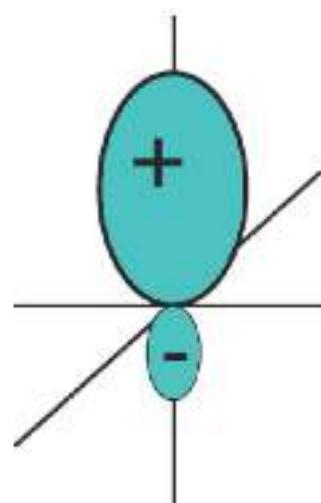


Figure 2-15

Hybrid orbital  $sp$ .

- The number of hybrid atomic orbitals formed is equal to the number atomic orbitals involved in the hybridization process. Based on this is when the hybridization of three atomic orbitals of the type (p) with atomic orbital one of type (s) to form four orbitals of type ( $sp^3$ )).
- The energy of atomic hybrid orbitals formed is equivalent or equal.
- The ability of hybrid orbitals to interfere with atomic orbitals of another atom is greater than the susceptibility of not hybridized atomic orbitals that participate in the hybridization process, because atomic orbitals hybrids orbitals are more extensible in space than the participated atomic orbitals not hybridized.

### 2-5-1 Types of hybrid orbitals

It can get types of hybrid atomic orbitals according to number and type of atomic orbitals involved. The most important will be addressed at the current school level.

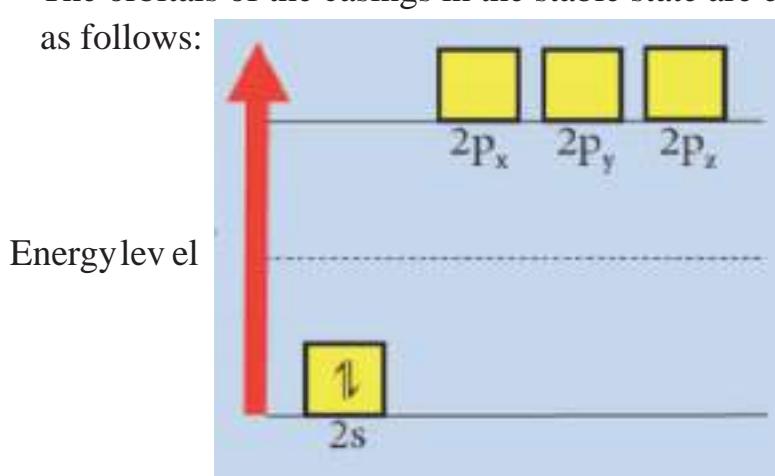
**A-Hybrid orbitals type ( $sp$ ):** According to the above observations, it know that this type of hybrid atomic orbital may be as a result of the participation of two atomic orbitals one of type (s) and the other of type (p).

The overlap of these two atomic orbitals will lead to formation two hybrid orbitals type  $sp$  located on a straight line and at an angle of  $^{\circ}180$  in order to have the least repulsion between the two orbitals like the beryllium hydride molecule  $BeH_2$ . For the purpose of clarifying how that is happen, the following steps are followed:

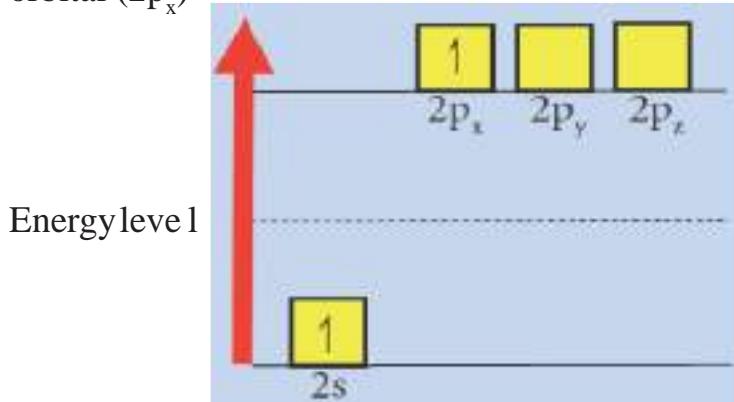
- The electronic configuration of beryllium atom:



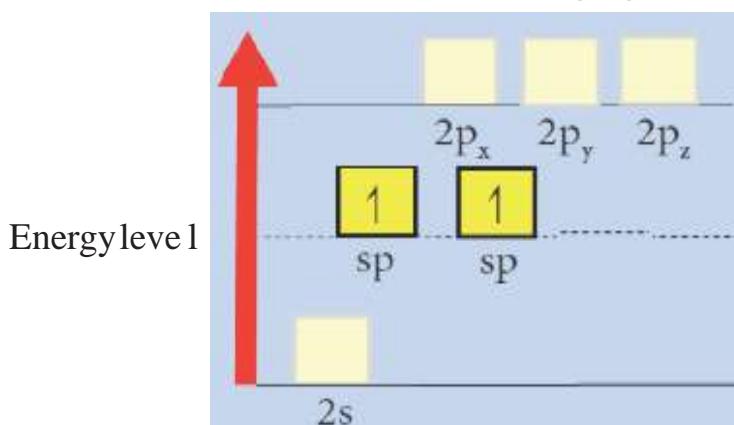
The orbitals of the casings in the stable state are expressed as follows:



2. One of the electrons will rise from the orbital 2s to the orbital (2p<sub>x</sub>)



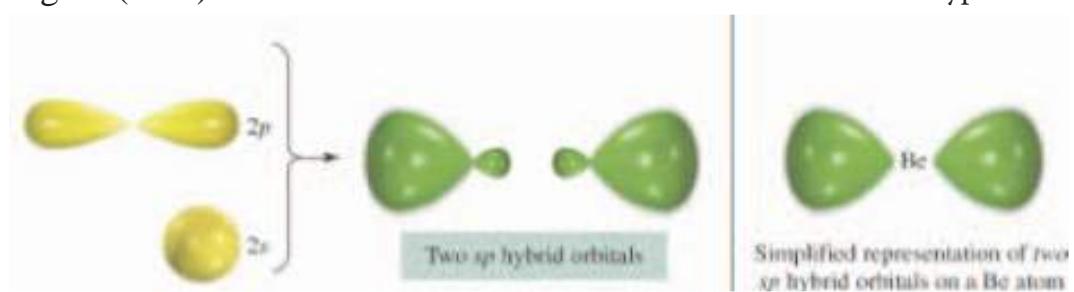
3. Then the interference occurs to generate two hybrid orbitals type sp in equivalent energy less than the energy of atomic orbitals 2p<sub>x</sub>, 2p<sub>y</sub>, 2p<sub>z</sub> and higher than the energy of atomic orbital 2s<sup>2</sup> and on the following figure.



4. These two orbitals have the ability to form molecular orbitals with two hydrogen atoms orbitals (1s<sup>1</sup>) to form two covalent bonds between Be and H and form the beryllium hydride molecule. The four steps above can be illustrated by the representation of stereotypical geometric shapes of atomic orbitals before and after hybridization. In this case we have two hydrogen atoms each one has an orbital (1s<sup>1</sup>), They interfere with the two hybrid orbitals sp of beryllium atom. This overlap is done on one of the coordinates to give the linear shape of the resulting molecule as shown in Figure (2-16).

Figure 2-16

Composition of hybrid orbitals type sp from atomic orbital interference type s with two orbitals type p<sub>x</sub>, p<sub>y</sub> of the s-type .

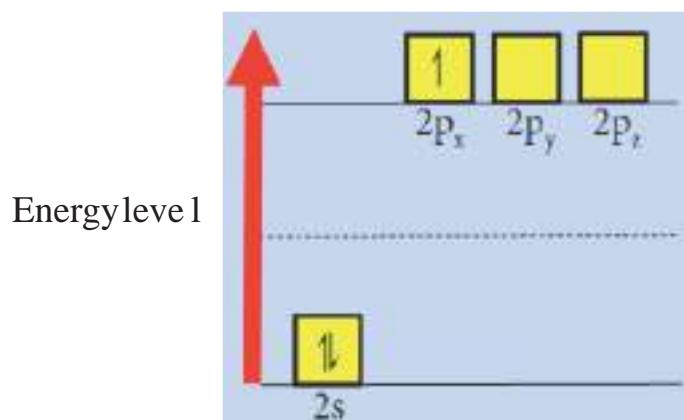


**B- Hybrid orbitals of type ( $sp^2$ ):** This type of atomic orbitals hybridized by the participation of one atomic orbital type (s) with two atomic orbitals type (p) within the same main orbital. The overlap of these three atomic orbitals will lead to formation three hybrid atomic orbitals type  $sp^2$  fall at the same level between them is an angle centered at the center of the central atom of  $120^\circ$ . This will be led to less repulsion between the orbitals as it occurs in a trifluoride boron molecule  $BF_3$ . Below is an explanation of how this hybridization was achieved the following steps:

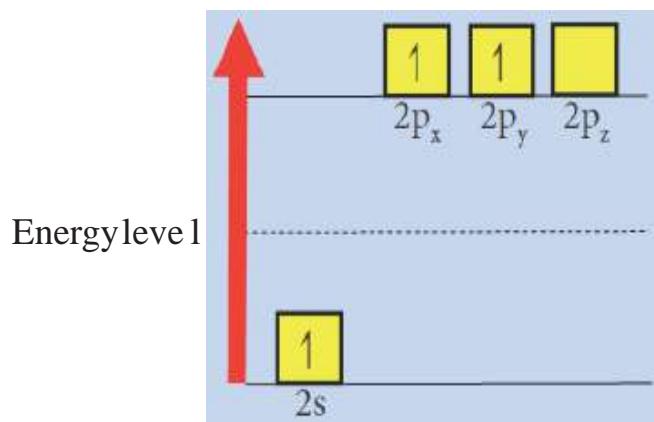
1. The electronic configuration of boron is:



Orbital ( $1s^2$ ) is considered internally and will not participate in hybridization, so the representation of the electronic configuration of the outer shell of this atom is represented as follows:

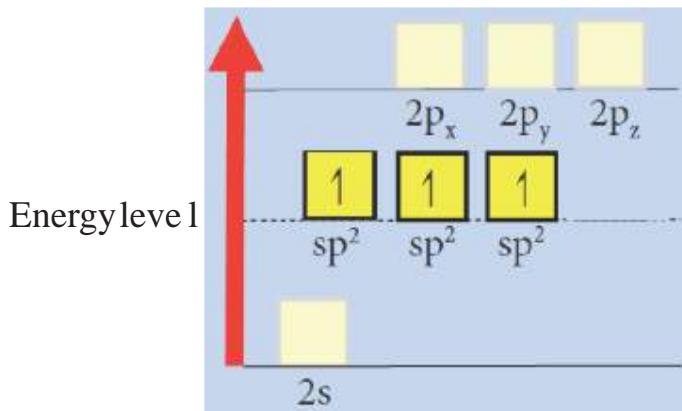


2. One of the two electrons in the orbital ( $2s^2$ ) goes up to the orbital  $p_y$  with the approximate energy:



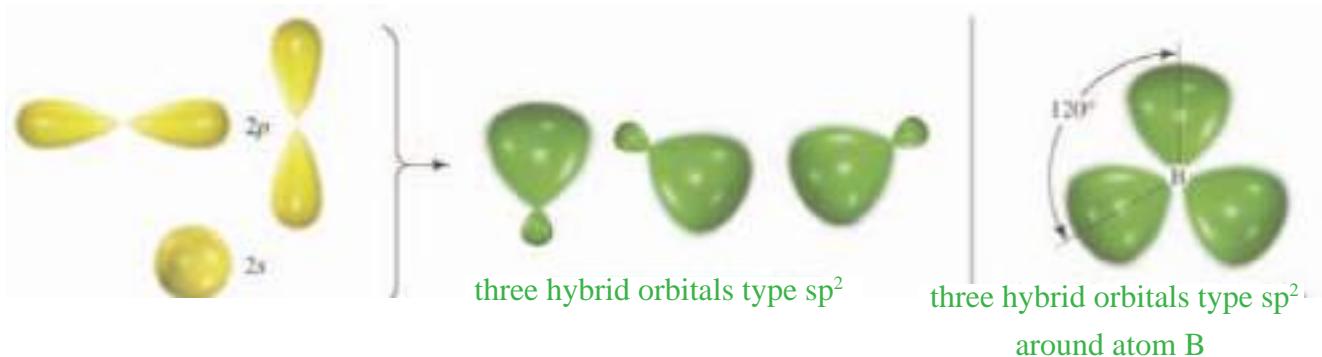
3. Then the interference occurs to generate three hybrid atomic orbitals of type  $sp^2$  has less equivalent energy than non-hybrid atomic orbitals

$2p_x$ ,  $2p_y$ ,  $2p_z$  and higher than non-hybrid atomic orbital  $2s^2$ . These orbitals are distributed around the nucleus in level that shares two coordinates, and they have equal angles.



4. These three orbitals have the ability to form three molecular orbitals with three orbitals for three fluoride atoms to form a triple boron fluoride molecule.

The four steps above can be illustrated by the representation of stereotyped geometric shapes of atomic orbitals before and after hybridization. In this case we have three fluoride atoms interfering with  $sp^2$  hybrid orbitals of boron atom. This overlap is done at one level as shown in Figure (2-17).



**C- Hybrid orbitals type ( $sp^3$ ):** This type of atomic orbitals hybridized by one atomic orbital interference of type (s) with three atomic orbitals of type (p).

The overlap of these the four atomic orbitals will produce four hybrid atomic orbitals type ( $sp^3$ ), these orbitals form a regular tetrahedral shape around the nucleus of the central atom with vertical angles of  $109.5^\circ$ ,

In order to have less repulsion between the orbitals as in the methane molecule  $CH_4$ . Below is an explanation of how the hybridization takes place according to the following steps:

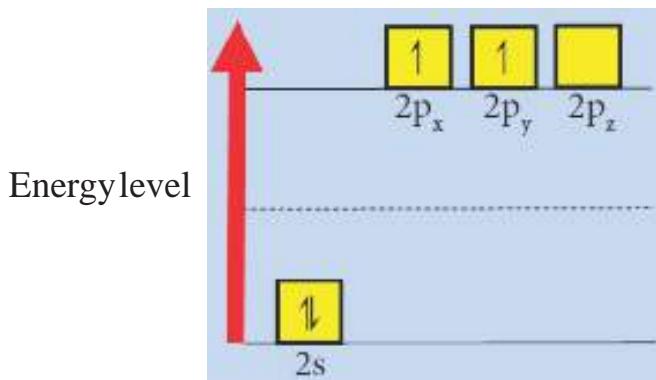
Figure 2-17

Composition of hybrid orbitals type  $sp^2$  of atomic orbital overlap of type  $2s$  with two orbitals  $p_x$  and  $p_y$ .

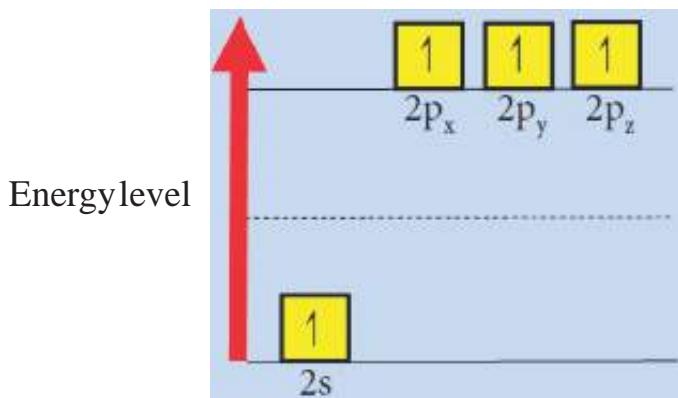
1. The electronic configuration of carbon atom is:



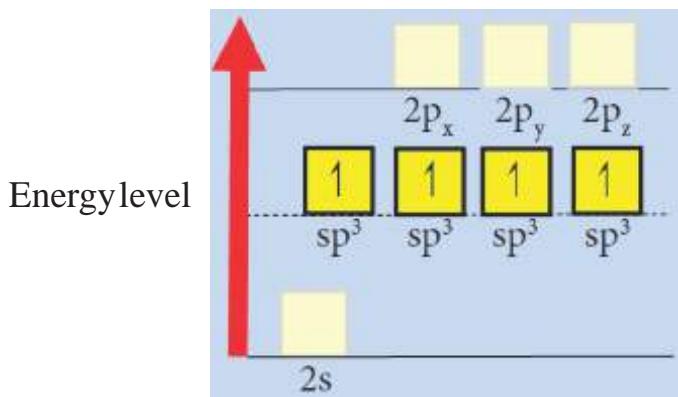
Orbital ( $1\text{s}^2$ ) is considered internally and will not participate in hybridization. So the representation of the electronic configuration of this atom is as follows:



2. One electron from orbital ( $2\text{s}^2$ ) rises to orbital ( $2\text{p}_z$ )



3. The interference is happened to generate four hybrid atomic orbitals from  $\text{sp}^3$  with equivalent energy less than energy of non-hybrid atomic orbitals  $2\text{p}_x$ ,  $2\text{p}_y$ ,  $2\text{p}_z$  and higher atomic orbital energy of  $2\text{s}$ . These hybrid orbitals are distributed in a regular tetrahedral shape around the central carbon atom with equal angles.



4. These four orbitals have the ability to form four molecule orbitals with four atomic orbitals for four hydrogen atoms ( $1s^1$ ) to form a methane molecule. The four steps above can be illustrated by the representation of stereotypes geometric shapes of atomic orbitals before and after hybridization [ Figure 2-18]. In this case we have four hydrogen atoms each one have orbital ( $1s^1$ ) has an overlap with the hybrid orbital  $sp^3$  of carbon atom as shown in Figure (2-18).

#### Exercise 2-6

Explain how hybrids get in molecule for  $SiCl_4$  according to the four steps. that we followed in the hybridization process (atomic numbers Cl = 17 and Si = 14).

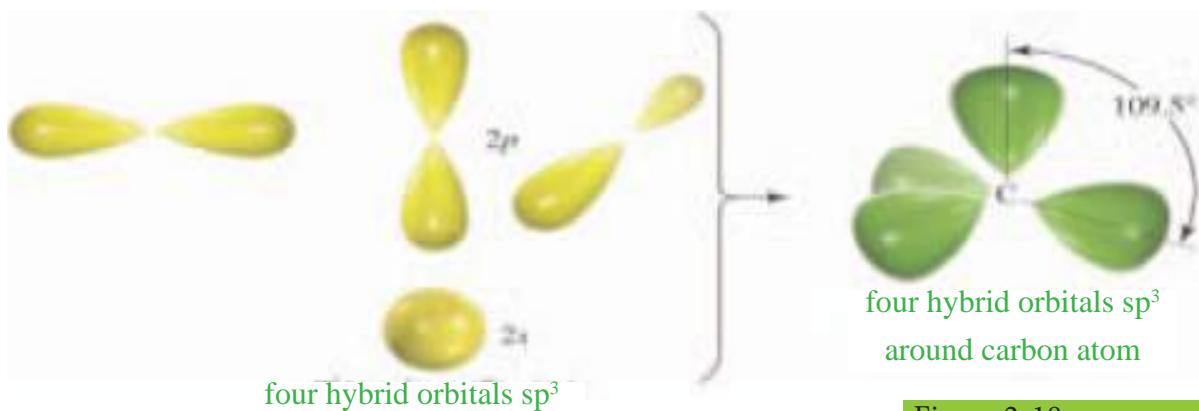


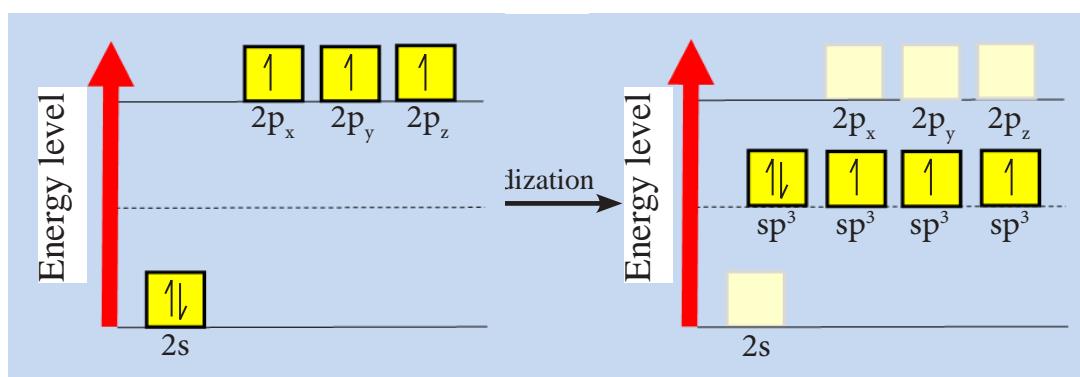
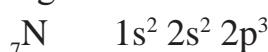
Figure 2-18

Composition of hybrid orbitals  $sp^3$  of orbital overlap from 2s with three orbitals  $p_x$ ,  $p_y$ ,  $p_z$ .

#### 2-5-2 Examples of hybridization and shape geometry

##### 1. Ammonia molecule:

The regularity of hybrid orbitals has a significant impact on the geometry shape of molecule, in other words on the configuration of the nuclei of united atoms. An important example, So what we see happens in the orbitals of some atoms and their formation For molecules with a known geometric shape as we find it in a molecular state of ammonia  $NH_3$ . The nitrogen atom has the following electronic configuration:



### Exercise 2-7

Write the steps of hybridization of atom orbitals of oxygen in water molecule. What is geometry shape and why?

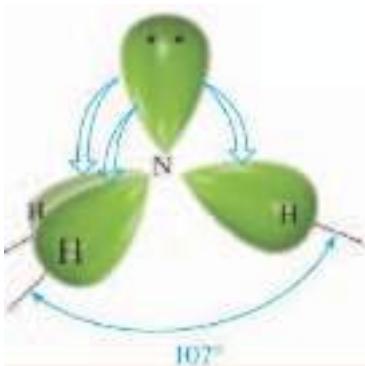
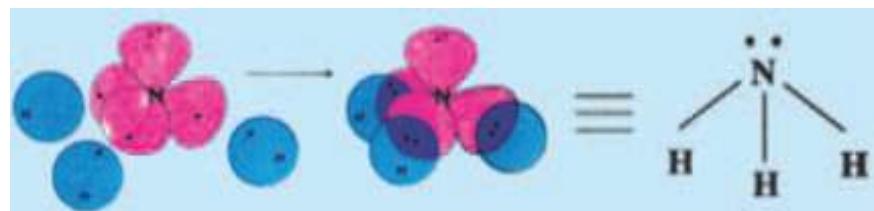


Figure 2-19

Geometry shape of ammonia molecule

When a nitrogen atom approaches three atoms of hydrogen each has an atomic orbital of type  $1s^1$ , then it can hybridize with the external atomic orbitals of the nitrogen atom with each other. This hybridization occurs after the orbital (2s) interferes with the orbital 2p, to give four hybrid orbitals ( $sp^3$ ). They are equivalent in form, energy and possess irregular four-sided geometric shape. The three atomic orbitals ( $1s^1$ ) of the three hydrogen atoms overlap with hybrid atomic orbitals ( $sp^3$ ) which contains one electron in each orbital to form three  $\sigma$  covalent bonds. The hybrid orbital does not participate, that contains an electronic pair in this interference. The geometric shape that this molecule will take will be an irregular tetrahedral pyramid, formed of a central nitrogen atom surrounded by three hydrogen atoms and an unrelated free electronic duplex [Figure 2-19].

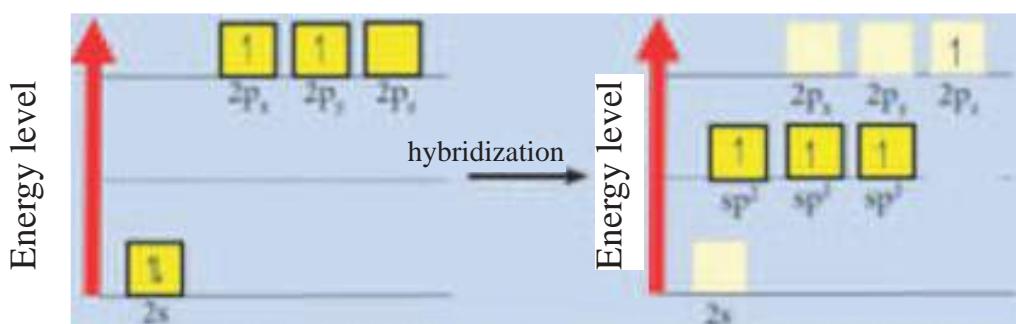


### 2. Ethylene molecule $C_2H_4$ :

The carbon atom has an electronic configuration:

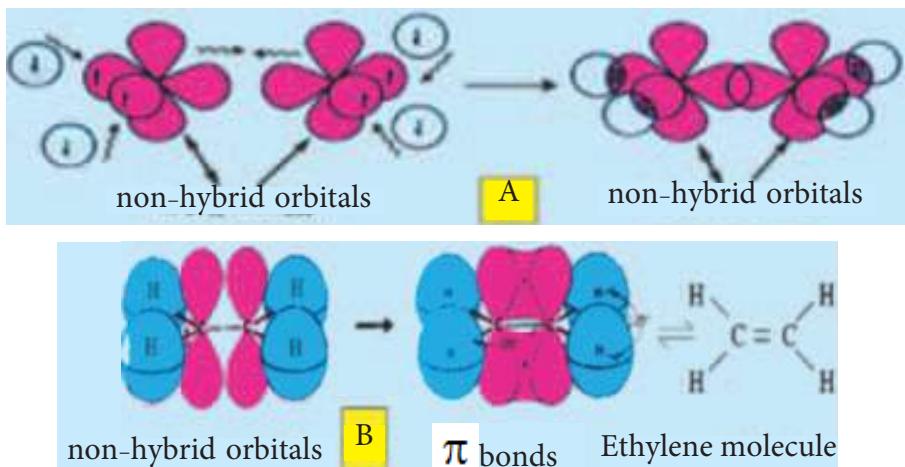


When one of the  $2s^2$  electrons is upgraded to the orbit  $p_z$ , the interference occurs between atomic orbitals we get three hybrid orbitals  $sp^2$  leaving the fourth orbital  $p_z$  non-hybridized.



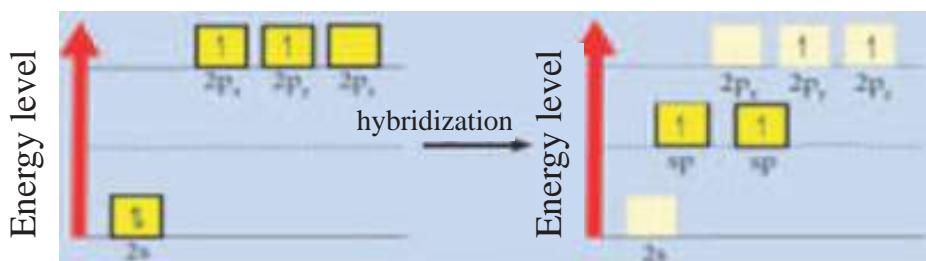
orbitals  $sp^2$  each other, and at the same time, four hydrogen atoms each one have one electron on s [Figure 2-20A] are overlapped and electrons are pairs then five sigma covalent bonds one (C-C) and four (C-H). This is followed by the overlap of non-hybrid orbitals  $p_z$  in two C atoms are

lateral interference and the electrons are duplexed to form  $\pi$  bond between the two carbon atoms that form with the sigma bond double bond between carbon atoms [Figure 2-20B]. This means that the bond of the sigma type is resulted from the interfering of hybrid orbitals  $sp^2$  of two contiguous carbon atoms. Pure  $p_z$  (non-hybridized) orbitals of adjacent carbon atoms, thus, the ethylene molecule is raised. The pi bond was produced by interference pure  $p_z$  (non-hybridized) orbitals of contiguous carbon atoms, where ethylene molecule is created.



### 3. Acetylene molecule:

In the case of the acetylene molecule, that  $2s$  and  $2p_x$  suffer hybridization, while  $p_z$  and  $p_y$  orbitals remain non-hybridized, meaning that hybridization will be of a type  $sp$ .



When two carbon atoms approach this kind of hybridization and two atoms approach at the same time, hydrogen interferes with atomic orbitals, it has three  $\sigma$  covalent bonds of one type C-C and two type C-H, and be connected to a single straightness.

Signal.  $\pi$  bond



Stereosco image of ethylene

Figure 2-20

- Overlap of orbitals to form sigma bonds in the ethylene molecule.
- Orbitals overlap to form  $\pi$  bonds in the ethylene molecule.

As a side overlap occurs for a non-hybrid orbitals  $p_z$ ,  $p_y$  of each C atom and creates two ( $\pi$ ) bonds to form with the ( $\sigma$ ) bond, triple bond and thus creating a straight molecule of acetylene with triple bonds as shown in Figure 2-21.

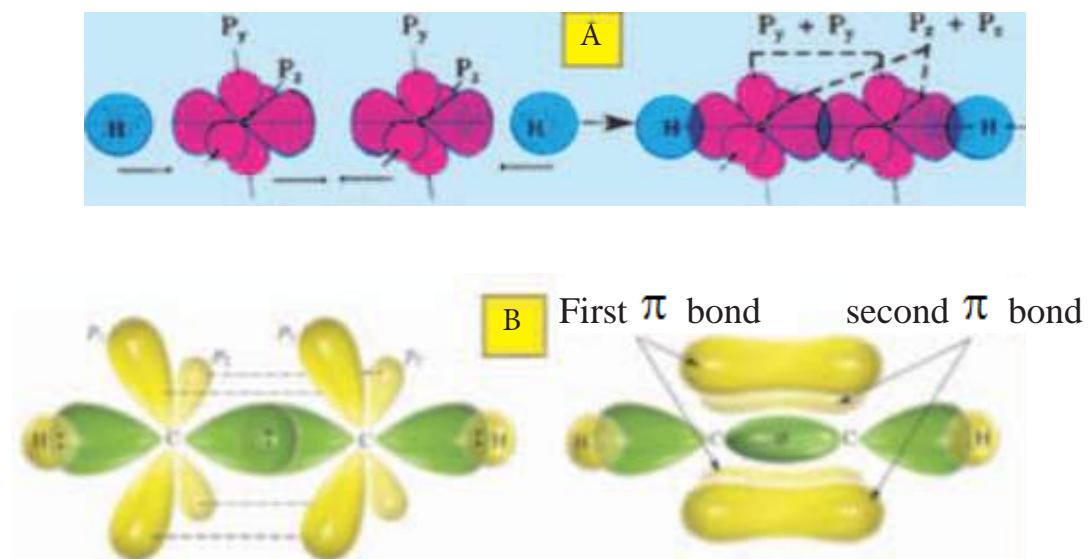


Figure 2-17

- A. Overlap of orbitals to form ( $\sigma$ ) bonds in acetylene molecule.
- B. Orbitals overlap to form bonds ( $\sigma$ ) bonds in acetylene molecule

## Basic concepts

### Chemical reaction

Is the interaction that occurs between atoms of two elements to form the molecule of a new compound possesses chemical and physical properties completely different from the characteristics of the elements involved in the reaction. The purpose of the chemical reaction is to form saturated orbitals with electrons through loss or gain or participate in electrons to achieve chemical stability.

### Chemical bonding

It is the phenomenon of the presence of atoms coherent together in a molecule or crystal within an element or compound, the strength that binds them is called the chemical bond.

### Valence Shell Electron-pair Repulsion Theory (VSEPR)

This theory explains the configuration of atoms around central atom depending on repulsion between participating and non-participating electrons pairs existing in the cavity casing of the central atom, so that it is the repulsion between these pairs is minimal when be as far as possible from each other.

### Valance bond theory

Adopted the theory of parity insistence in its interpretation on the theory of hybridization of orbital where it follows hybrid orbitals of the central atom so that The disharmony between these orbitals is minimal when be as far as possible from each other.

### Orbital hybridization

It is the process of overlapping atomic orbitals to produce hybrid orbitals are equal to the number of orbitals the atomic involved in the hybridization process are similar form, size, equal in energy and more stability than non-hybrid atomic orbitals and lead to stronger covalent bonds between atoms involved in the formation of the molecule.

### Ionic Bond

Is the power of electrical attraction between two ions different in charges, one of which is a metal with a positive charge for the loss of one or more electrons and the other is non-metal that carries a negative charge to acquire one or more electrons.

### Covalent Bond

It is the bonding force between two equal atoms in electronegativity or a slight difference between them, so that each atom shares an electron from its outer shell the two atoms share by this electronic pair by force of attachment is called covalent bonding.

### Polar Covalent Bond

They are covalent bonds of two atoms the difference between electronegativity is relatively significant , the double electronic link is attracted between them towards the highest electronegative atom gain, a second negative charge have partial positive charge.

### Hydrogen Bond

It is the power of electrical attraction between the ends of different charge of molecules with polarized covalent bonds, provided that one part hydrogen.

### Coordinate Bond

It is a special covalent bond between two atoms, one of them is granted the electronic pair of its outer shell to the second atom containing empty orbital in its outer shell.

### Metallic Bond

It is the force that binds the metal atoms together, it results from the sharing of each metal atom with equivalents electrons, and returns them to the metallic properties.

## Chapter Two Questions

2

2-1 Reasons for each of the following:

1. The boiling point of water ( $100^{\circ}\text{ C}$ ) is higher than the boiling point of hydrogen sulfide gas ( $-60^{\circ}\text{ C}$ ).
2. The  $\text{NH}_4\text{Cl}$  ammonium chloride molecule contains three polar covalent bond, coordinate bond and ionic bonds.
3. The angle between the two hybrid orbitals  $\text{sp}^2$  in  $\text{C}_2\text{H}_4$  Molecule is equal to  $120^{\circ}\text{ C}$ .
4. Ionic compounds do not conduct electrical in solid state but for melting or solutions of ionic compound in water has a good ability of electrical conductivity.
5. When you put a piece of ice in the water, float however when you put a frozen piece of gasoline in gasoline immerse.

2-2 Compare between each of the following:

1. Covalent bond and coordinate bond.
2. The sigma ( $\sigma$ ) bond and pi( $\pi$ ) bond.
3. Hybrid orbital and non-hybrid orbital.

2-3 Draw a figure showing a excited carbon atom and an hybrid Carbon atom  $\text{sp}^3$

2-4 What is the hybridization situation in each of the following. Mentioning forms of the resulting compounds:

1. Oxygen in water.
2. Nitrogen in  $\text{HN} = \text{NH}$
3. Nitrogen in Ammonia

2-5 Draw resonance formulas for:



2-6 Why are the atoms of elements combined together? are the combinations of atoms of elements always produce compounds? Discuss your answer scientifically with at least two examples.

2-7 A- What is chemical bond? Identify it accurately.

B- Numbering only types of bonds you know.

2-8 A- What is the ionic bond? What are the conditions of its composition?

B- Why molecules are not formed in ionic compounds?

C- What are the most important characteristics of ionic compounds?

2-9 What do we mean by hydrogen bonding? Explain this in example, draw hydrogen bonds between Methanol ( $\text{CH}_3\text{OH}$ ) molecules.

2-10 Covalent bonds may be polarized, when is that?

2-11 What are the factors that determine the bonding between two atoms covalent or covalent polarized? or Ionic?

2-12 What are the metal bonds? what effect it has on the properties of pure metals?

2-13 Rewrite the following statements as corrected (may) you find it from scientific mistakes:

A- All compounds with covalent bonds didn't dissolve in water.

B- Protons and neutrons are involved in the composition ionic bond.

C- ( $\pi$ ) bond is less energy than ( $\sigma$ ) bond of the same molecule.

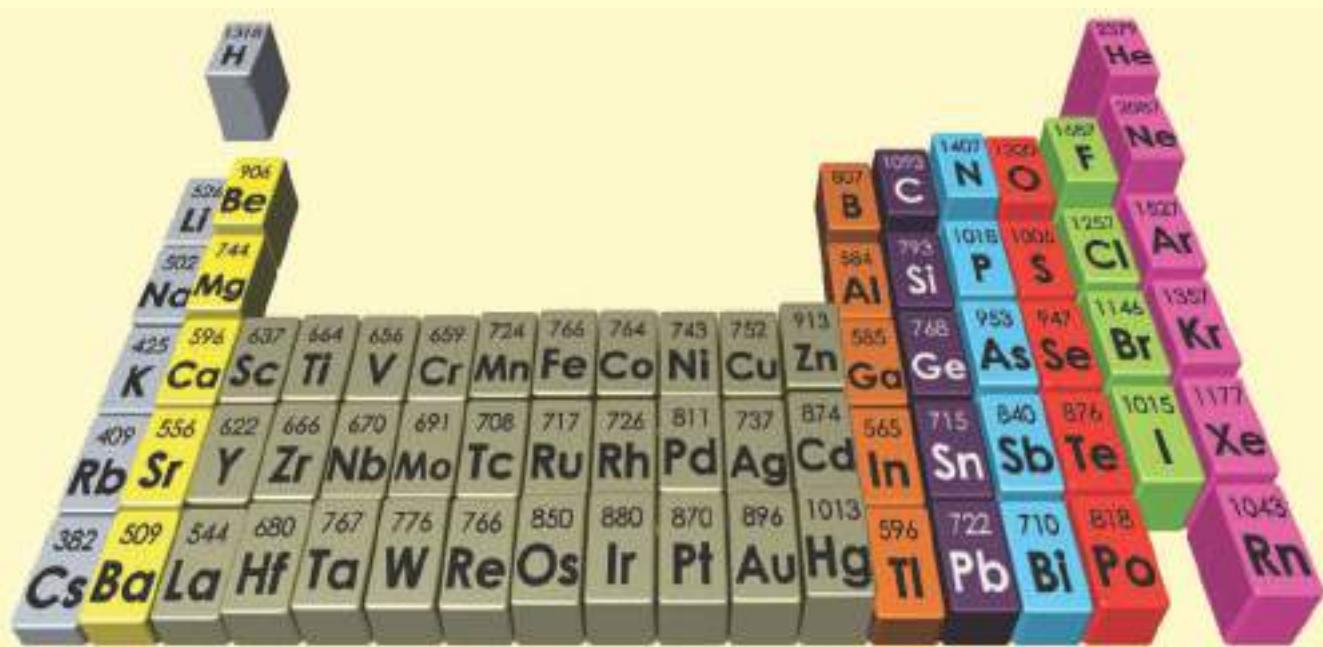
D- The triple bond in ( $\text{C}_2\text{H}_2$ ) contains three types of ( $\pi$ ) bond.

E- The type of hybridization in C atom orbitals in Methan is similar to N atom in ammonia which is ( $\text{sp}^3$ ).

2-14 Draw the geometry of the following particles using hybridization once and using the (VSEPR) theory again:-



2-15 Draw and compare the shapes of the ethylene and acetylene molecules in terms of the hybridized orbitals which of it the bond between the two carbon atoms is stronger.



## Chapter Three

# Periodic Table and Chemistry of Transition Elements

3

After completing this chapter, the student is expected to:

- Recognize the historical sequence of the emergence of the periodic table and attempts made to divide the elements.
- Arrange elements in a modern periodic table based on atomic numbers instead of their atomic masses.
- Able to determine the number of periods included in the periodic table and on the group numbers.
- Recognize the periodic table and can know its parts.
- Understand the periodic properties of elements in the periodic table.
- Understand when an element has an atomic spectrum and that the atomic spectrum is a characteristic for the element.
- Distinguish between a transitional element and a non-transitional element as recognize the internal transition elements.
- Distinguish between the elements that are attracted towards the magnetic field and those that are not attracted.

## 3-1 Periodic Table

### 3-1-1 Introduction

#### Do you know

The word periodic means that The properties of the elements change periodically due to an increase in their atomic numbers.

The emergence and maturation of the periodic table has undergone a series of developments synchronized with the development of scientific concepts in each period, where it came from simple ideas to become a scientific model proud of all Who contributed to the arrangement of these ideas. Those attempts had begun a simple idea for a chemist to arrange the elements in a given table This arrangement then evolved into what it is now.

It seems there is no need in the old to classify items in a special table because the number of elements at that time did not exceed the fingers. After chemistry development and the discovery of more elements, They are beginning to need classification

the elements and scheduling to facilitate their study and facilitate dealing with them were the first Attempts to sort and arrange items in a table are split Items into two groups:

**A- Metals group**

**B- Nonmetals group**

Because there is no boundary dividing the elements into metals and nonmetals, where many share properties between them. There have been other attempts to classify the elements on other bases and most important , those are built on the relationship between the properties of elements and their atomic masses. Following is a summary of these attempts:

1. Dobriner's trilogy: Doeberiner observed in 1817 The differences between the atomic masses of elements such as calcium(Ca), Strontium (Sr) and barium (Ba) are fixed differences as the difference in the atomic mass in these triplets of any element is almost constant for the element that precedes and is attached to it. That the physical and chemical properties of the element in these triplets is the average properties of the two previous and next elements. In other cases such as iron, cobalt and nickel, the elements have approximately equal atomic masses as shown in Table 3-1.

Table (3-1) Atomic mass of some elements and the difference between them

|   | Element        | Atomic mass | Difference                     |
|---|----------------|-------------|--------------------------------|
| 1 | Calcium (Ca)   | 40.07       | 47.56<br>49.74<br>3.10<br>0.25 |
| 2 | Strontium (Sr) | 87.63       |                                |
| 3 | Barium (Ba)    | 137.37      |                                |
| 4 | Iron (Fe)      | 55.84       |                                |
| 5 | Cobalt (Co)    | 58.94       |                                |
| 6 | Nickel (Ni)    | 58.69       |                                |

The previous groups, each of which is composed of three, are called elements are similar in many of their chemical and physical properties are called Dobriner's trilogy.

## 2. Second attempt by the English scientist Newlands

In 1864, he arranged the elements that were known to him and which number 63 elements by increasing their atomic masses in the form of groups, each group has eight elements. It is found if it starts with an element, the eighth element is similar in its chemical properties to the element that began in it. The similarity between this observation and the musical scale it is called of these remarks; (the Law of Eighties of scientific Newlands) the law, is true in the case of the first seventeen elements either the following elements there have been some contradictions due to the lack the accuracy of the atomic masses on the one hand and on the other hand it left no place empty in his schedule for many elements that were not known in it's time as shown in Table 3-2.

3. The attempts of Doeberiner and Newlands ended when the scientific Russian Mandeleeff (1869) was developed his known the periodic table it is worth mentioning that Mandeleeff and Meyer worked independently of each other and came to the same conclusion. They arranged the elements ascending according to their atomic masses, They were summarized each the two results of his research in this subject in the following phrase (elements properties are periodically dependent on their atomic masses). This phrase is defined as (Cyclical law). It was taken by Mandeleeff mainly to classify the elements. Mandeleeff spent several years collecting relevant scientific findings elements before he publishes his periodic law, which relies

| Table 3-2 Eighties of scientific Newlands |    |    |       |       |    |      |       |  |
|---|----|----|-------|-------|----|------|-------|--|
| H   | F  | Cl | Co/Ni | Br    | Pd | I    | Pt/Ir |  |
| Li  | Na | K  | Cu    | Rb    | Ag | Cs   | Ti    |  |
| Ga  | Mg | Ca | Zn    | Sr    | Cd | Ba/V | Pb    |  |
| Bo  | Al | Cr | Y     | Ce/La | U  | Ta   | Th    |  |
| C   | Si | Ti | In    | Zn    | Sn | W    | Hg    |  |
| N   | P  | Mn | As    | Di/Mo | Sb | Nb   | Bi    |  |
| O   | S  | Fe | Se    | Ro/Ru | Te | Au   | Os    |  |



In 1869 the Russian Dmitry Ivanovich Mandeleeff developed the first periodic table by arrangement the elements discovered in his time in view tabular by increasing atomic masses relative (atomic weight).

mainly on practical facts and not on theoretical grounds. It is worth mentioning number the elements discovered at the time were limited and therefore left empty places for those elements for possible future discovery. The possibility of Mendeleev in high guess places those elements that have not been discovered. The name of the periodic table have been associated with scientific Mandeleeff because he was able to determine the properties of some undiscovered elements of his time, including the Germanium and named it Similar to silicon.

Mandeleeff also relocated some elements to its new location better aligned with the new neighboring elements. It has been corrected some errors in the development of certain elements depending on the values of atomic masses. As for the weaknesses in a table Mandeleeff are:

**A-Hydrogen Position:** The position of hydrogen in the table remains controversial as it is placed sometimes in the first group above the alkali metals and sometimes above the group seventh (halogens) and that there are some similarities between him and these elements in the two groups mentioned.

**B-Position of internal transition elements (lanthanides):** These fourteen elements are similar in many properties, especially in equivalence (often 3) and their place in the Mandeleeff table in the third group, place element is usually placed at the bottom of the table as well as the case in Actinides.

**C- Disparate arrangement of some elements:**

It is known that the elements are arranged in the Mandeleeff table in ascending order atomic masses, even if this rule in any case strictly followed some elements have occurred in places where their properties are inconsistent with those of the elements in the other group had to be overcome this difficulty of change put these elements regardless of the value of their atomic masses. For example, atomic mass of cobalt Co is 58.94 and the nickel 58.69 is nevertheless placed cobalt Co before nickel as well as in the following pairs of elements:

| Elements  | Atomic mass |
|-----------|-------------|
| Arcon     | 39.94       |
| Potassim  | 39.09       |
| Tellurium | 127.61      |
| Iodine    | 126.93      |

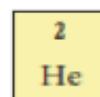
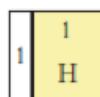
Mandeleeff arranged the elements in ascending order according to their atomic mass so that similar elements in the properties are located below each other. Mandeleeff table included horizontal rows called periods and vertical rows called groups.

| Table 3-3 |        | Mandeleeff table |         |         |        |          |         |                         |      |
|-----------|--------|------------------|---------|---------|--------|----------|---------|-------------------------|------|
|           |        | I                | II      | III     | IV     | V        | VI      | VII                     | VIII |
| 1         | H=1    |                  |         |         |        |          |         |                         |      |
| 2         | Li=7   | Be=9.4           | B=11    | C=12    | N=14   | O=16     | F=19    |                         |      |
| 33        | Na=2   | Mg=24            | Al=27.3 | Si=28   | P=31   | S=32     | Cl=35.5 |                         |      |
| 94        | K=3    | Ca=40            | ?=44    | Ti=48   | V=51   | Cr=52    | Mn=55   | Fe=56,Co=59<br>Ni=59    |      |
| 35        | Cu=6   | Zn=65            | ?=68    | ?=72    | As=75  | Se=78    | Br=80   |                         |      |
| 56        | Rb=8   | Sr=87            | ?Yt=88  | Zr=90   | Nb=94  | Mo=96    | ?=100   | Ru=104,Rh=104<br>Pd=106 |      |
| 7         | Ag=108 | Cd=112           | In=133  | Sn=118  | Sb=122 | Te=127.6 | J=127   |                         |      |
| 8         | Cs=133 | Ba=137           | ?Di=138 | ?Ce=140 |        |          |         |                         |      |
| 9         |        |                  |         |         |        |          |         |                         |      |
| 10        |        |                  | ?Er=178 | ?La=180 | Ta=182 | W=184    |         | Os=195,Ir=197<br>Pt=198 |      |
| 11        | Au=199 | Hg=200           | Tl=204  | Pb=207  | Bi=208 |          |         |                         |      |
| 12        |        |                  |         | Th=231  |        | U=240    |         |                         |      |

### 3-1-2 Modern Periodic Table of Elements

After the discovery of the electron and the appearance of the concept of atomic number by Moseley in 1914, the elements were arranged in ascending order by increasing their atomic numbers rather than by increasing the atomic mass as arranged by Mandeleeff. That is, each element in the modern periodic table exceeds the element preceded by a single electron known as a distinct electron. This arrangement according to the increase in atomic numbers corresponds with the order of elements by increase energy levels from least to most energy. Thus, the image of the modern atomic table, [Figure 3-1] in the form of 7 horizontal periods with groups arranged by columns, their number (18) groups which are:

1. The first short period includes hydrogen and helium.



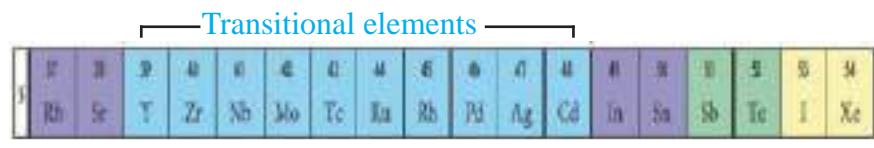
2. The second and third short period, each consisting of 8 elements. They are arranged in the periodic table as follows:



3. The fourth long period consists of 18 elements and they are arranged in the periodic table as follows:



4. The fifth long period consists of 18 elements and they are arranged in the periodic table as follows:



5. The six long period consists of 32 elements and they are arranged in the periodic table as follows:

|   |    |   |   |             |    |    |   |    |    |    |    |    |    |    |    |    |    |    |    |
|---|----|---|---|-------------|----|----|---|----|----|----|----|----|----|----|----|----|----|----|----|
| 6 | He | H | B | La          | Hf | Ta | W | Re | Os | Ir | Pt | Ag | Hg | Tl | Ge | Bi | Po | At | Rn |
|   |    |   |   | Lanthanides |    |    |   |    |    |    |    |    |    |    |    |    |    |    |    |

|    |    |    |    |    |    |    |    |    |    |    |    |    |    |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| He | Pr | Nd | Dy | Eu | Tu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|

6. The seventh long period consists of 24 elements and they are arranged in the periodic table as follows:

|   |    |    |    |           |    |    |    |    |    |    |    |     |     |     |     |     |     |     |     |
|---|----|----|----|-----------|----|----|----|----|----|----|----|-----|-----|-----|-----|-----|-----|-----|-----|
| 7 | Fr | Ra | Ac | 18        | Re | Db | Sp | Bh | Hs | Mt | Ds | 111 | 112 | 113 | 114 | 115 | 116 | 117 | 118 |
|   |    |    |    | Actinides |    |    |    |    |    |    |    |     |     |     |     |     |     |     |     |

|    |    |   |    |    |    |    |    |    |    |    |    |    |    |
|----|----|---|----|----|----|----|----|----|----|----|----|----|----|
| Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr |
|----|----|---|----|----|----|----|----|----|----|----|----|----|----|

| Main group elements |                | transition elements |                |                 |                 |                 |                 |                    |                 |                 |                |                |                |                |                | Main group elements |                |                |               |  |
|---------------------|----------------|---------------------|----------------|-----------------|-----------------|-----------------|-----------------|--------------------|-----------------|-----------------|----------------|----------------|----------------|----------------|----------------|---------------------|----------------|----------------|---------------|--|
|                     |                | 1A (1)              |                |                 |                 |                 |                 |                    |                 |                 |                |                |                |                |                |                     |                | VIIIA (18)     |               |  |
| 1                   | 1 H<br>1,008   | 2                   | 3 Li<br>6,941  | 4 Be<br>9,012   |                 |                 |                 |                    |                 |                 |                |                |                |                |                |                     |                |                | 2 He<br>4,003 |  |
| 3                   | 11 Na<br>22,99 | 12 Mg<br>24,31      | IIIIB (3)      | IVB (4)         | VB (5)          | VIB (6)         | VIIIB (7)       | (8) VIIIB (9) (10) |                 |                 | IB (11)        | IIIB (12)      | 13 Al<br>26,98 | 14 Si<br>28,09 | 15 P<br>30,97  | 16 S<br>32,07       | 17 Cl<br>35,45 | 18 Ar<br>39,95 |               |  |
| 4                   | 19 K<br>39,10  | 20 Ca<br>40,08      | 21 Sc<br>44,96 | 22 Ti<br>47,88  | 23 V<br>50,94   | 24 Cr<br>52,00  | 25 Mn<br>54,94  | 26 Fe<br>55,85     | 27 Co<br>58,93  | 28 Ni<br>58,69  | 29 Cu<br>63,55 | 30 Zn<br>65,39 | 31 Ga<br>69,72 | 32 Ge<br>72,61 | 33 As<br>74,92 | 34 Se<br>78,96      | 35 Br<br>79,90 | 36 Kr<br>83,80 |               |  |
| 5                   | 37 Rb<br>85,47 | 38 Sr<br>87,62      | 39 Y<br>88,91  | 40 Zr<br>91,22  | 41 Nb<br>92,91  | 42 Mo<br>95,94  | 43 Tc<br>(98)   | 44 Ru<br>101,1     | 45 Rh<br>102,9  | 46 Pd<br>106,4  | 47 Ag<br>107,9 | 48 Cd<br>112,4 | 49 In<br>114,8 | 50 Sn<br>118,7 | 51 Te<br>121,8 | 52 I<br>127,6       | 53 Xe<br>126,9 | 54 Kr<br>131,3 |               |  |
| 6                   | 55 Cs<br>132,9 | 56 Ba<br>137,3      | 57 La<br>138,9 | 72 Hf<br>178,5  | 73 Ta<br>180,9  | 74 W<br>183,9   | 75 Re<br>186,2  | 76 Os<br>190,2     | 77 Ir<br>192,2  | 78 Pt<br>195,1  | 79 Au<br>197,0 | 80 Hg<br>200,6 | 81 Ti<br>204,4 | 82 Pb<br>207,2 | 83 Bi<br>209,0 | 84 Po<br>(209)      | 85 At<br>(210) | 86 Rn<br>(222) |               |  |
| 7                   | 87 Fr<br>(223) | 88 Ra<br>(226)      | 89 Ac<br>(227) | 104 Rf<br>(261) | 105 Db<br>(262) | 106 Sg<br>(266) | 107 Bh<br>(262) | 108 Hs<br>(265)    | 109 Mt<br>(266) | 110 Ds<br>(269) | 111            | 112            | 113            | 114            | 115            | 116                 | 117            | 118            |               |  |

|   |             |                |                |                |                |                |                |                |                |                |                |                 |                 |                 |                 |
|---|-------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|-----------------|-----------------|-----------------|-----------------|
| 6 | Lanthanides | 58 Ce<br>140,1 | 59 Pr<br>140,9 | 60 Nd<br>144,2 | 61 Pm<br>(145) | 62 Sm<br>150,4 | 63 Eu<br>152,0 | 64 Gd<br>157,3 | 65 Tb<br>157,3 | 66 Dy<br>162,5 | 67 Ho<br>164,9 | 68 Er<br>167,3  | 69 Tm<br>168,9  | 70 Yb<br>173,0  | 71 Lu<br>175,0  |
| 7 | Actinides   | 90 Th<br>232,0 | 91 Pa<br>(231) | 92 U<br>238,0  | 93 Np<br>(237) | 94 Pu<br>(242) | 95 Am<br>(243) | 96 Cm<br>(247) | 97 Bk<br>(247) | 98 Cf<br>(251) | 99 Es<br>(252) | 100 Fm<br>(257) | 101 Md<br>(258) | 102 No<br>(259) | 103 Lr<br>(260) |

Figure 3-1

Modern periodic table.

The groups in the periodic table and its number (18 groups) divided into Group A (8 groups) and Group B (10 groups) as shown in Figure (3-1). These groups are arranged in vertical columns based on equal number of electrons in the outer shell (external valence electrons). Thus, the elements of a single group are similar in their chemical properties, despite the great difference in their atomic masses so as they equal by number of electrons, these atom can lose or gain, or contribute to during the entry into the chemical reaction. While in a single period the elements where arranged by increase of the atomic number, therefore these elements has convergent in their atomic masses, yet they differ in their physical properties. For example, Nitrogen is near carbon and oxygen in the second period, despite their approximate in the atomic mass, they have different in physical properties, each of the energy shell in elements atoms contain secondary energy shell (sub), its number equal to the number of principal shell. These principal shells are filled with electrons as it increases in the energy where fills the lowest energy level(s) and then the higher energy level. This configuration in filling shell is similar to the configuration of elements in periodic table by increasing atomic number.

### 3-1-3 Periodic Table Parts

The periodic table includes four parts arranged as follows [Figure (3-2)]:

**First part:** includes the first group 1A and the second group 2A and both are ends with (ns) shell known as alkali metals and alkaline earth metals.

**Second part:** include the elements in the groups:

IIIA, IVA, VA, VIA, VIIA, VIIIA (the last group is called 0). The elements of this area (Part I and Part II) are full the electrons in the sub-energy levels (s and p). The first and the second part are called the represented elements.

**Third part:** includes all the elements in subgroups B, namely:

1B, 2B, 3B, 4B, 5B, 6B, 7B, 8B (Group 0) which include (8B, 9B, 10B ) and the outer shell of these elements is type s, d and d is not full of electrons is called transitional elements because they are transite by properties

between elements with the outer shell s (group, 1A, 2A) and elements with outer shell p group (3A, 4A, 5A, 6A, 7A, 8A). They mediate the periodic table.

**Fourth part:** comprises two series of internal transitional elements: which are: Lanthanides and Actinides

The diagram illustrates the periodic table with four distinct parts:

- First part:** Elements H and He.
- Second part:** Elements B, C, N, O, F, and Ne.
- Third part:** Elements Sc through Br, including the lanthanide series (Ce-Lu) and actinide series (Th-Lr).
- Fourth part:** Elements Ga through Lu, including the lanthanide series (Ce-Lu) and actinide series (Th-Lr).

The lanthanide and actinide series are highlighted in pink. The diagram also shows the lanthanide and actinide series as separate blocks below the main table.

Figure 3-2  
Parts of periodic table.

### 3-1-4 Periodicity of properties in the periodic table

Many of the physical properties of the elements change periodically accordingly to position of these elements in the periodic table in terms of group and period, some of these features are discussed below.

**A-Atomic size** Atomic size is a difficult characteristic for several reasons one of the most important reasons is that the probability of electronic distribution is influenced by atoms adjacent in the chemical compound and thus the size of the atom changes somewhat when moving from one case to another. Therefore, when checking any table of atomic radii, it should be remembered that tabulated values may be meaningful only when considering a relative comparison of volumes, Figure (3-3) shows

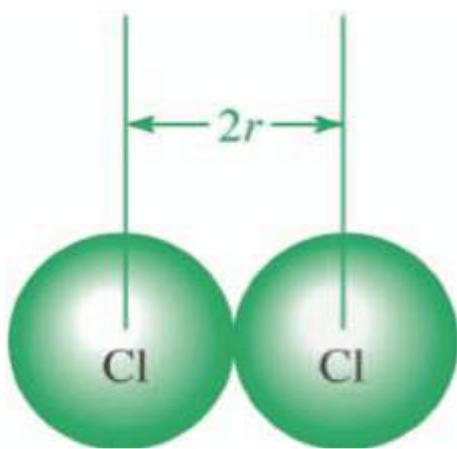


Figure 3-3

Method of measurement of atomic radii of elements.

Method of measurement of atomic radii for elements derived from distances measured from the centers of adjacent atoms in pure elements and on this basis atomic size is defined as half distance between the centers of two identical atoms in a crystal and it is measured using X-rays.

In general, atomic radii are reduced per one period when moving from left to right (ie, atomic number increases) in the periodic table. This behavior can be explained by a table showing the change of atomic radii along the second period.

In the case of the group, the radius increases in one group from top to bottom as the atomic number increases.

The reason for this is the addition of electronic shells with increasing quantum numbers farther from the nucleus as shown in the table of atomic radii[Figure(3-4)].

In the transitional elements

1. The radius decreases gradually in each transition chain until the fifth element, ie to half of the period then gradually increases until the end of the series, where the size decreases due to the increase of attraction force, as the electron, which is added by increasing the number of atomic number from one element to another enters the secondary shell orbitals (d).

2. Observations have shown that adding half of this number, ie 5 electrons, is accompanied by a state of stability and this electronic system block the effect of the nucleus so the attracted force will be less to the electrons that are added , which it explains the increase in size slightly after the fifth element.

|    |    |
|----|----|
| Li | Be |
| Na | Mg |
| K  | Ca |
| Rb | Sr |
| Cs |    |

|    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Sc | Ti | V  | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br |
| Y  | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I  |
| Lu | Hf | Ta | W  | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po |    |

|    |    |    |    |    |
|----|----|----|----|----|
| B  | C  | N  | O  | P  |
| Al | Si | P  | S  | Cl |
| Ga | Ge | As | Se | Br |
| In | Sn | Sb | Te | I  |
| Tl | Pb | Bi | Po |    |

Figure 3-4

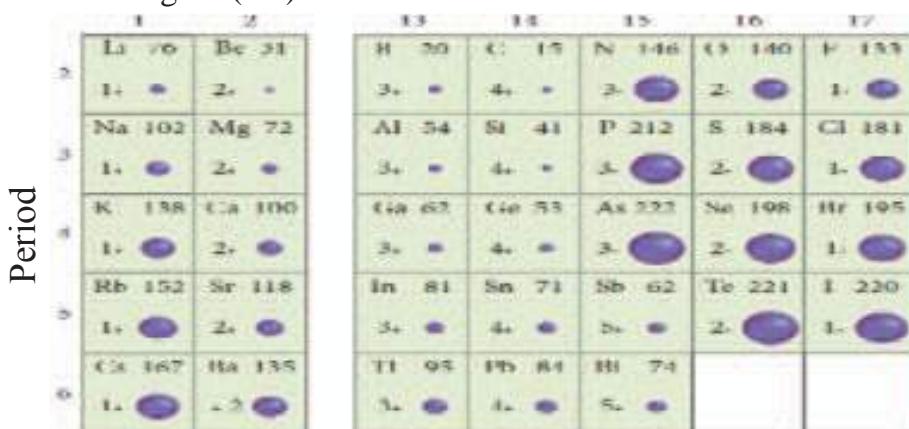
Changing atomic radii (ie. the sizes of atoms) of some elements in the period and group.

In the internal transitional elements, the size also decreases gradually by increasing the atomic number up to the seventh element (ie to half of the chain) and then gradually increasing again and on the same basis of interpretation in point 2

For the radius ions of atoms it is known that atoms can lose or gain one or more electrons to form ions. Electrons have negative charge so atoms gain an extra charge when gain or lose electrons. So the ion is an atom or an atomic group has positive or negative charge.

When an atom loses electrons and is a positive ion is formed, the atom size becomes smaller. This is due to two factors: firstly, the electron that the atom loses often it's an equivalent electron, and the loss of electron led to form an empty external orbit, causing radius decreases. Secondly, electrostatic repulsion decreases between the remaining electrons and increases the attraction between them. The nucleus has a positive charge, allowing the electrons to get closer of the nucleus and figure (3.5a) shows the decrease in the ion radius of sodium atom when it formed a positive ion.

Conversely, when an atom acquires electrons and became negative ions, their size increases because the addition of an electron to the atom generates electrostatic repulsion bigger with the outer-level electrons, and pushes them strongly outward. An increase in the distance between external electrons results in an increase in the amount of radius. Figure 3.5b shows how the radius of the chlorine atom increases, when it forms negative ion. Figure (3.6) shows the ion radius of some elements.



### B- Ionization energy

It is the energy needed to extract an electron from a neutral atom in its gaseous state and to form positive ion as in the following equation:  $M + \text{Energy} \longrightarrow M^+ + e^-$

This energy is consumed in extracting an electron from external valance electrons. The ionization energy is measured in units of electron volts (ev) and electron volts is a small energy equal  $1.6 \times 10^{-19} \text{ J}$ . Energy is needed to remove the first electron is called first ionization energy. The result of that ion with one positive charge.

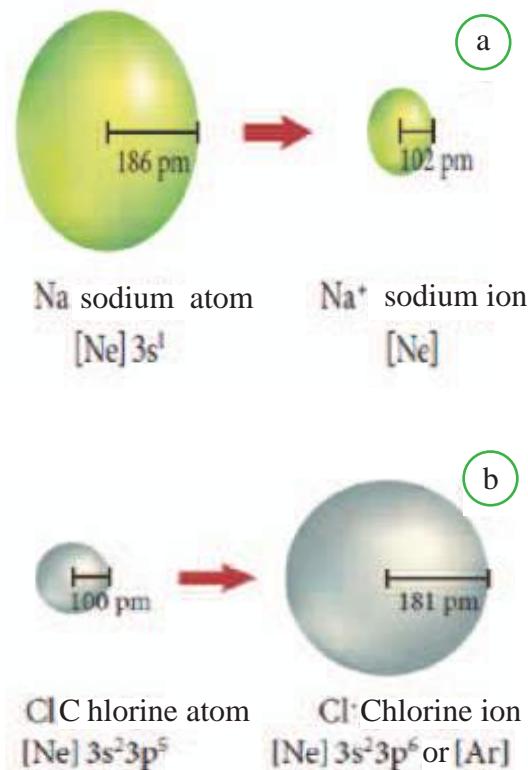


Figure 3-5

A- positive ions smaller than their neutral atoms.

B- negative ions are larger than their neutral atoms.

Figure 3-6

Ion radius of ideal elements measured in pico meters.

(1pm=  $10^{-12} \text{ m}$ )

The energy needed to extract a second electron is also called a second energy ionization. Thus, the second ionization energy is always greater than the first ionization energy because the positive nucleus charge attracts the second electrons strongly larger.

If the relationship between ionization energy and the atomic number of elements is plotted, it is noted that change occurs periodically Figure( 3-7).

The noble elements are located at the great ends of it in order to stabilize their system. The alkaline elements also located on the lower ends due to the large size of the atomic volumes and that the quantum layer penultimate contains (8) electrons are characterized by a high degree of stability and work as a barrier obscures the effect of the charge of the nucleus on the valence electron is easy to extract.

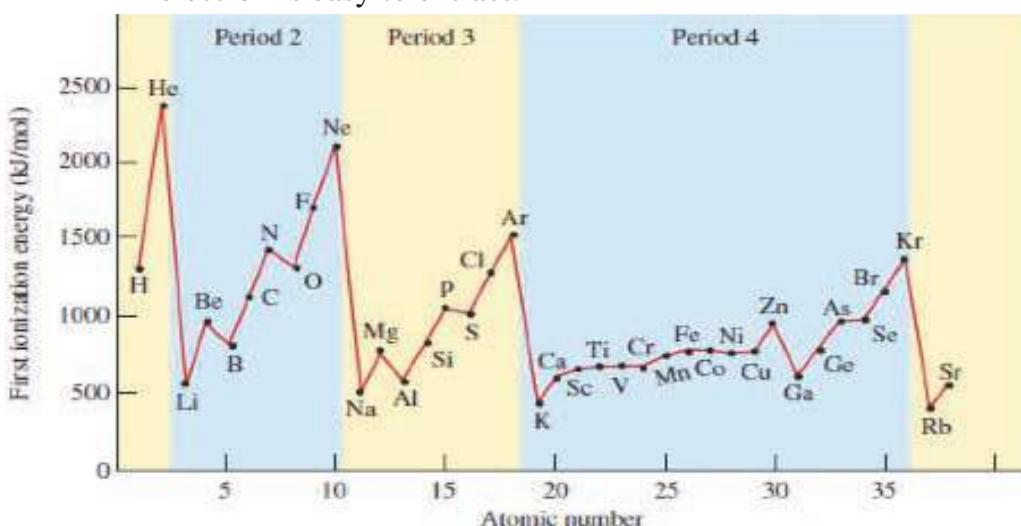


Figure 3-7

The relationship of ionization energy with the atomic number.

It is evident that the ionization energy increases in one period with increasing atomic number because of their small atomic sizes (radii) except atoms whose last shell is saturated or half-saturated, where ionization energy is greater than ionization energy of the next atom. For example, that The ionization energy of <sub>7</sub>N is greater than the ionization energy of <sub>8</sub>O and the reason for this is due to that the last nitrogen shell is half-saturated in which three electrons and to be more stable than oxygen despite being the largest atomic number. As well in the case of manganese <sub>25</sub>Mn and iron <sub>26</sub>Fe the Mn ionization energy is greater than Fe ionization energy for the same previous reason. In one group, ionization energy decreases as atomic number increases due to large atomic size which facilitates extraction the outer electrons of the atom, for example, the ionization energy reduce from lithium to Cesium and from beryllium to radium as shown in Figure (3-8).

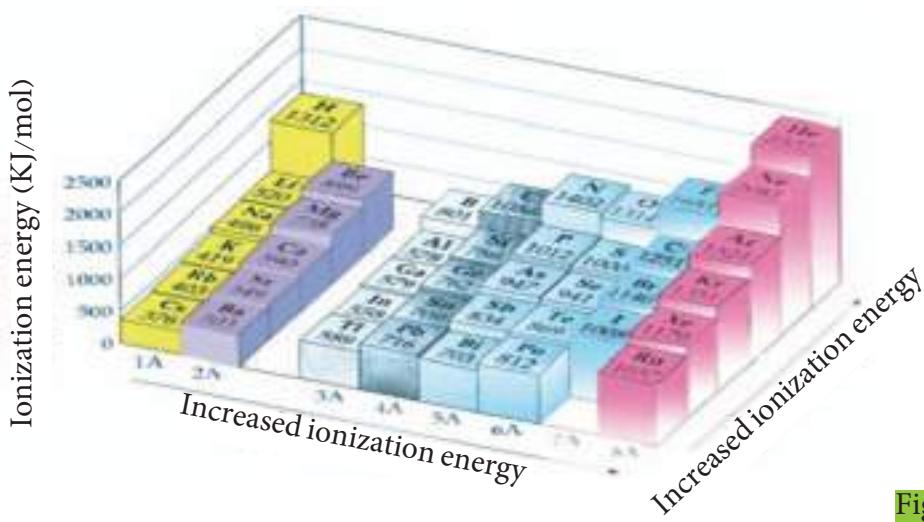
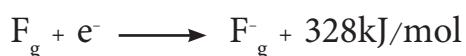


Figure 3-8

Ionization energy changes in one period and group.

### C-Electron affinity

An electronic affinity is known as the amount of energy released from a neutral atom in the gaseous state when it acquires an electron forming negative ions, according to the following equation:



Electronic affinity increases in periods by increasing the atomic number, the small atomic sizes make it easier for the nucleus to attract the electron. Electronic affinity of elements in a single group decreases as atomic number increases because of increasing atomic size. Just as there is first and second ionization energy, so is there first and second electronic attraction whilst some energy is released upon acquisition the first electron often absorbs some energy when second electron is acquired because there is a repulsive force between the negative ion and the acquired electron.

The emission of energy when an electron is added to an atom leads to the transition to lower energy case, ie to a more stable state and this explains the tendency of some atoms to acquire electrons as elements in the VII group in chemical reactions to reach a more stable and minimal state of energy.

The low values in the electronic affinity of noble gases and the elements to the far left of the periodic table are attributable to their inability on the formation of negative ions compared to fluorine (F), chlorine (Cl) and bromine which form easily negative ions as shown in Figure (3-9).

#### Do you know

The electronic affinity measures the severity of additional electron binding to the atom.

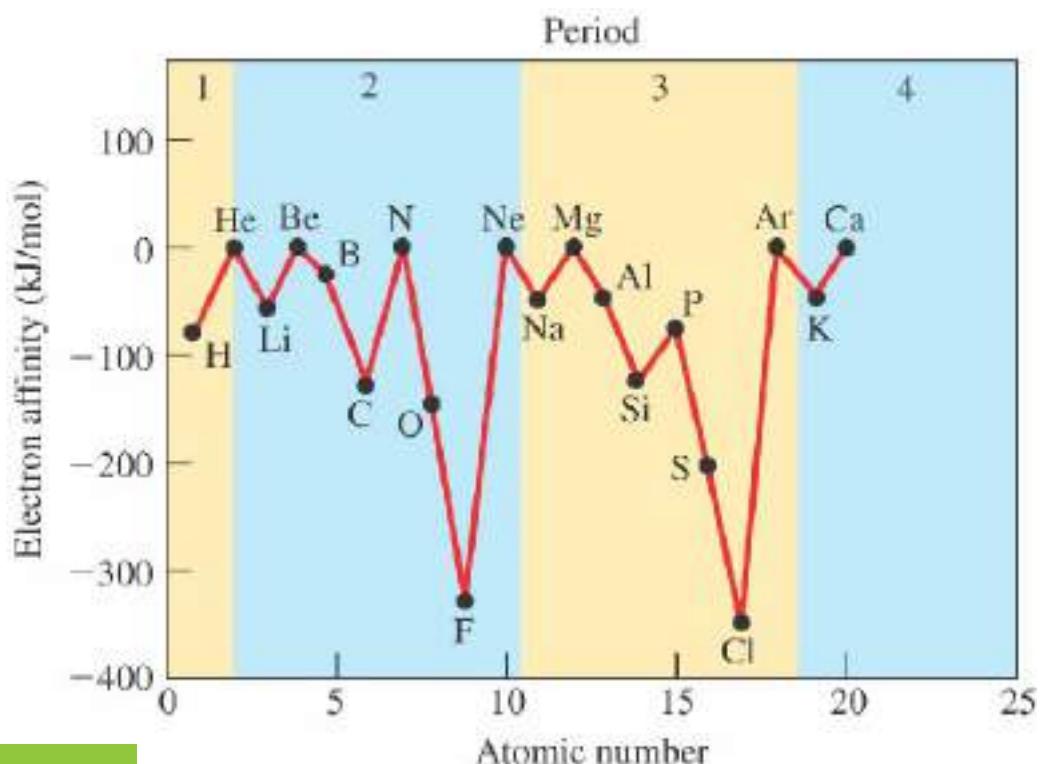


Figure 3-9

The relationship of electronic affinity with the atomic number.

#### D-Electronegativity

Is the ability of atoms in molecules to attract electrons toward them of other atoms associated with them by chemical bond. There are values numerical elements as shown in Figure (3-10) these numbers describe the relative ability of an atom to form a bond, ie turns negative state and shared electron can then attract to it. Fluorine element has high electronegativity relative to any element in the periodic table because it located at the end of its period and on the top of its group. The noble gases elements are not formed chemical bonds and did not agreed on their values yet. In general electronegativity increases in a single period from left to right as the atomic number increases. Existing elements at the far left of the periodic table (group IA, IIA) have low electronegativity.

The elements on the far right except the group (0) has high electronegativity and it is attributed for the elements group (VII) the following electronegativity to:

$$F=4.0, Cl=3.0, Br=2.8, I=2.5$$

The order of decrement in the electronegativity shall be uniform, other than the order of affinity in one group, the electronegativity decreases with increasing atomic number as we move from the top to down of the group.

#### Do you know

And now we ask the benefit of the value of electronegativity the answer to this question that one of these benefits is to predict which bonds are ionic and which covalent. It can also benefit of electronegativity in the polar prediction where two elements apart for electronegativity values whenever necessary. the bonds are more polar and the bond between H and Cl is more polar than those between (Cl and Br).

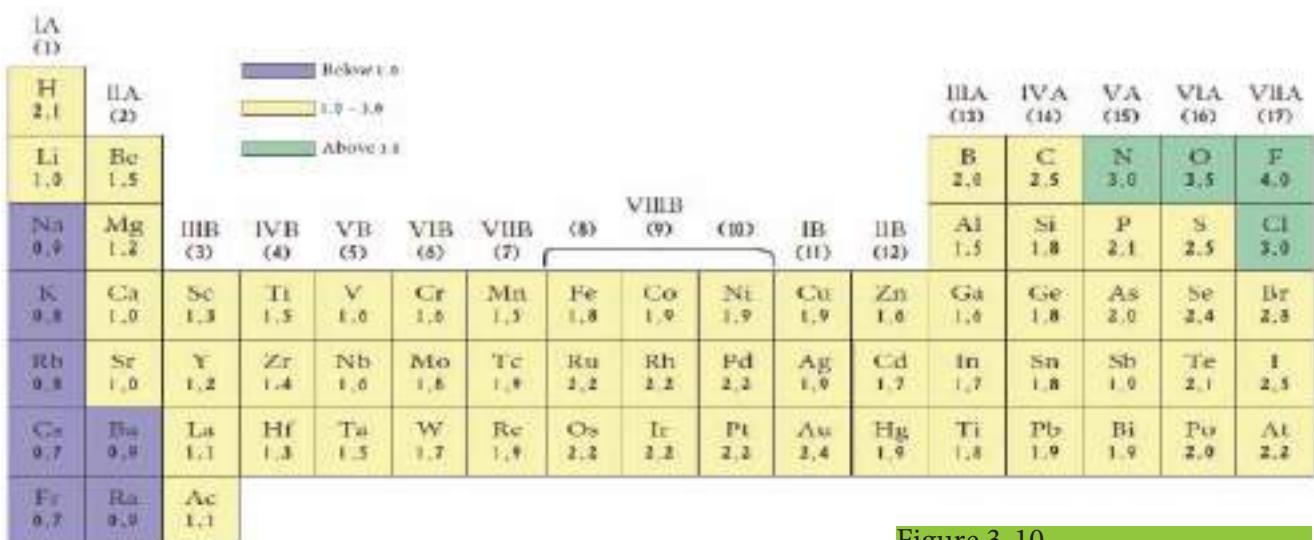


Figure 3-10

Electronegative values for some elements periodic table.

### E- Metallic and non-metallic properties:

Metals have a number of properties including metallic luster and electrical and thermal conductivity and high melting and boiling points such as iron, copper and zinc, while nonmetals, are characterized by no luster and gloss. They are often fragile, with low melting and boiling points such as sulfur, carbon, phosphorus and gases. The metalloid are elements their properties between metals and nonmetals such as boron and silicon. Their properties are graded in the periodic table are as follows:

In one period the metallic properties decrease and the non-metal properties increase as they increase atomic number. We find that the elements of the beginning of the period are all metals and then less this property and a non-metallic property starts to appear as we go to the right of the period, that is, an increase atomic number for example in the second period lithium (<sub>3</sub>Li) and beryllium (<sub>4</sub>Be) metallic properties, while boron (<sub>5</sub>B) shows the properties of semi-metals. The rest comes second period elements such as carbon, nitrogen, oxygen and fluorine to appear properties of nonmetals where the atomic number increases. In one group metallic properties increase and Non - metallic properties decrease with increasing atomic number. All elements of groups (IA and IIA) are metals while elements of groups (VII and 0) are nonmetals. The rest of the groups all elements are not in one class, for example, in the fifth group shows (N) metallic properties, while (S) shows the behavior of semimetals and Bismuth comes the last element in the fifth group with metallic properties.

In periods, the elements of the first period (H and He)(2) are nonmetallic for metals in the next four periods there is a gradual transition from metallic properties to nonmetallic properties of properties. In the sixth period all its elements are metals except the last two elements are non-metallic elements of the seventh period are all metals and show transitional elements and elements Lanthanides and actinides have metallic

.(properties, as shown in Figure (3-11)

Reduction of metal properties

transitional elements

Internal transitional elements

| 1 | IA          | IIA | transitional elements |     |    |     |       |     |     |      |       |      | VIIIA |     |     |     |     |     |     |
|---|-------------|-----|-----------------------|-----|----|-----|-------|-----|-----|------|-------|------|-------|-----|-----|-----|-----|-----|-----|
| 1 | H           | Be  | IIIIB                 | IVB | VB | VIB | VIIIB | (8) | (9) | (10) | IB    | IIIB | 2     |     |     |     |     |     |     |
| 2 | Li          | Mg  | Sc                    | Ti  | V  | Cr  | Mn    | Fe  | Co  | Ni   | Cu    | Zn   | He    |     |     |     |     |     |     |
| 3 | Na          | Mg  | 39                    | 40  | 41 | 42  | 43    | 44  | 45  | 46   | 47    | 48   | 13    | 14  | 15  | 16  | 17  | 18  |     |
| 4 | K           | Ca  | Sc                    | Ti  | V  | Cr  | Mn    | Fe  | Co  | Ni   | Cu    | Zn   | Ga    | Si  | P   | S   | Cl  | Ar  |     |
| 5 | Rb          | Sr  | Y                     | Zr  | Nb | Mo  | Tc    | Ru  | Rh  | Pd   | Ag    | Cd   | In    | Sn  | Sb  | Te  | I   | Xe  |     |
| 6 | Cs          | Ba  | La                    | Hf  | Ta | W   | Re    | Os  | Ir  | Pt   | (222) | Hg   | Ti    | Pb  | Bi  | Po  | At  | Rn  |     |
| 7 | Fr          | Ra  | Ac                    | Rf  | Db | Sg  | Bh    | Hs  | Mt  | Ds   | 110   | 111  | 112   | 113 | 114 | 115 | 116 | 117 | 118 |
| 6 | Lanthanides |     | 58                    | 59  | 60 | 61  | 62    | 63  | 64  | 65   | 66    | 67   | 68    | 69  | 70  | 71  |     |     |     |
| 7 | Actinides   |     | 90                    | 91  | 92 | 93  | 94    | 95  | 96  | 97   | 98    | 99   | 100   | 101 | 102 | 103 | Lr  |     |     |

Figure 3-11

Change of metallic and nonmetallic properties in one period and group.



Sodium flame



Potassium flame



Copper flame



Lithium flame

### F-Flame Spectrum:

The spectrum of an element can be obtained by placing the element or its vapor in an electric discharge tube under low pressure and high voltage that irritates its atoms. It emits linear spectra and each element has a distinct linear spectrum, there is a relationship between the linear spectrum and the atomic structure of the element, that's called the atomic spectrum. For example, the hydrogen atom is in a stable state if the electron is found at the first energy level and when increased energy of an electron moves to a higher energy level and is said to be an atom is excited or irritated when an electron falls from a higher energy level to a lower energy level it loses energy equal to the difference between energy levels.

This energy appears as an electromagnetic radiation (Spectrum) accompanied by a color and has a specific wavelength and frequency for each element, linear spectrum is characteristic of it. when heating a calcium metal on a flame, it flames brick red and strontium is crimson, barium is yellowish green, sodium yellow and potassium violet, cesium blue and rubidium dark red.

## 3-2 Transitional elements

### 3-2-1 Introduction

Transitional elements appear in the fourth, fifth, sixth and seventh periods of the periodic table and has an electronic configuration, orbitals electrons d and f play an important role. These elements can be traditionally divided into two groups:

The set of elements d and the set of elements f

The set of d elements consists of three complete series and a fourth series incomplete. Each series of the third series have ten elements, these are:

**1. The first transition series:** starting from the element scandium (<sub>21</sub>Sc) to zinc element (<sub>30</sub>Zn).

**2. The second transition series:** starting from the element yttrium (<sub>39</sub>Y) to cadmium element (<sub>48</sub>Cd).

**3. The third transition series:** starting from the element lanthanum (<sub>57</sub>La) to gold element (<sub>30</sub>Au).

The fourth transition series starts with actinium element <sub>89</sub>Ac and ends with element darmstadtium <sub>110</sub>Ds, which is composed of (8) elements can be observed these serieses of looking at the periodic table Figure (3-1). The f group consists of two series and in each series 14 elements are called internal transition elements, the first series is called lanthanides and the second series is the actinides, and these two series are:

1. The lanthanide series starts from the cerium Ce atomic number 58 to the lutetium Lu atomic number 71.

2. The actinides series begins with the element thorium Th atomic number 90 to the element lorticium Lr atomic number 103.

In each series, the electronic configuration of the full energy levels remains the same with higher main quantum number is constant while internal energy levels are gradually filled d(n-1) and f(n-2) with increasing atomic number Table (3-4). In the series of transition elements, orbitals 3d, 4d, and 5d are gradually filled, while the internal transitions are gradually filled with orbitals 4f and 5f. The transition element can thus be defined as the element, which has an electronic distribution in which orbitals d or f is partially full in the case of neutral or chemically unified atoms in their compounds.



Ions of salts of transition elements and their solutions from left to right.

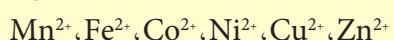


Table (3-4) Electron configuration of transitional elements

| First transitional series  |        |            |   |
|----------------------------|--------|------------|---|
| Atomic number              | Symbol | Name       | Electron configuration  |
| 21                         | Sc     | Scandium   | [ <sub>18</sub> Ar] 3d <sup>1</sup> 4s <sup>2</sup>                   |
| 22                         | Ti     | Titanium   | [ <sub>18</sub> Ar] 3d <sup>2</sup> 4s <sup>2</sup>                   |
| 23                         | V      | Vanadium   | [ <sub>18</sub> Ar] 3d <sup>3</sup> 4s <sup>2</sup>                   |
| 24                         | Cr     | Chromium   | [ <sub>18</sub> Ar] 3d <sup>5</sup> 4s <sup>1</sup>                   |
| 25                         | Mn     | Manganese  | [ <sub>18</sub> Ar] 3d <sup>5</sup> 4s <sup>2</sup>                   |
| 26                         | Fe     | Iron       | [ <sub>18</sub> Ar] 3d <sup>6</sup> 4s <sup>2</sup>                   |
| 27                         | Co     | Cobalt     | [ <sub>18</sub> Ar] 3d <sup>7</sup> 4s <sup>2</sup>                   |
| 28                         | Ni     | Nickel     | [ <sub>18</sub> Ar] 3d <sup>8</sup> 4s <sup>2</sup>                   |
| 29                         | Cu     | Copper     | [ <sub>18</sub> Ar] 3d <sup>10</sup> 4s <sup>1</sup>                  |
| 30                         | Zn     | Zinc       | [ <sub>18</sub> Ar] 3d <sup>10</sup> 4s <sup>2</sup>                  |
| Second transitional series |        |            |   |
| 39                         | Y      | Yttrium    | [ <sub>36</sub> Kr] 4d <sup>1</sup> 5s <sup>2</sup>                   |
| 40                         | Zr     | Zirconium  | [ <sub>36</sub> Kr] 4d <sup>2</sup> 5s <sup>2</sup>                   |
| 41                         | Nb     | Niobium    | [ <sub>36</sub> Kr] 4d <sup>3</sup> 5s <sup>2</sup>                   |
| 42                         | Mo     | Molybdenum | [ <sub>36</sub> Kr] 4d <sup>5</sup> 5s <sup>1</sup>                   |
| 43                         | Tc     | Technetium | [ <sub>36</sub> Kr] 4d <sup>5</sup> 5s <sup>2</sup>                   |
| 44                         | Ru     | Ruthenium  | [ <sub>36</sub> Kr] 4d <sup>7</sup> 5s <sup>1</sup>                   |
| 45                         | Rh     | Rhodium    | [ <sub>36</sub> Kr] 4d <sup>8</sup> 5s <sup>1</sup>                   |
| 46                         | Pd     | Palladium  | [ <sub>36</sub> Kr] 4d <sup>10</sup>                                  |
| 47                         | Ag     | Sllvar     | [ <sub>36</sub> Kr] 4d <sup>10</sup> 5s <sup>1</sup>                  |
| 48                         | Cd     | Cedmium    | [ <sub>36</sub> Kr] 4d <sup>10</sup> 5s <sup>2</sup>                  |
| Third transitional series  |        |            |   |
| 57                         | La     | Lanthanum  | [ <sub>54</sub> Xe] 5d <sup>1</sup> 6s <sup>2</sup>                   |
| 72                         | Hf     | Hafnium    | [ <sub>54</sub> Xe] 4f <sup>14</sup> 5d <sup>2</sup> 6s <sup>2</sup>  |
| 73                         | Ta     | Tantaium   | [ <sub>54</sub> Xe] 4f <sup>14</sup> 5d <sup>3</sup> 6s <sup>2</sup>  |
| 74                         | W      | Tungsten   | [ <sub>54</sub> Xe] 4f <sup>14</sup> 5d <sup>4</sup> 6s <sup>2</sup>  |
| 75                         | Re     | Rhenium    | [ <sub>54</sub> Xe] 4f <sup>14</sup> 5d <sup>5</sup> 6s <sup>2</sup>  |
| 76                         | Os     | Osmium     | [ <sub>54</sub> Xe] 4f <sup>14</sup> 5d <sup>6</sup> 6s <sup>2</sup>  |
| 77                         | Ir     | Iridium    | [ <sub>54</sub> Xe] 4f <sup>14</sup> 5d <sup>7</sup> 6s <sup>2</sup>  |
| 78                         | Pt     | Platinum   | [ <sub>54</sub> Xe] 4f <sup>14</sup> 5d <sup>9</sup> 6s <sup>1</sup>  |
| 79                         | Au     | Gold       | [ <sub>54</sub> Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>1</sup> |
| 80                         | Hg     | Mercury    | [ <sub>54</sub> Xe] 4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> |

| First internal transitional series  |        |              |                                 |
|-------------------------------------|--------|--------------|---------------------------------|
| Atomic number                       | Symbol | Name         | Electron configuration          |
| 58                                  | Ce     | Cerium       | $[\text{Xe}] 4f^1 5d^1 6s^2$    |
| 59                                  | Pr     | Praseodymium | $[\text{Xe}] 4f^3 6s^2$         |
| 60                                  | Nd     | Neodymium    | $[\text{Xe}] 4f^4 6s^2$         |
| 61                                  | Pm     | Promethium   | $[\text{Xe}] 4f^5 6s^2$         |
| 62                                  | Sm     | Samarium     | $[\text{Xe}] 4f^6 6s^2$         |
| 63                                  | Eu     | Europium     | $[\text{Xe}] 4f^7 6s^2$         |
| 64                                  | Gd     | Gadolinium   | $[\text{Xe}] 4f^7 5d^1 6s^2$    |
| 65                                  | Tb     | Terbium      | $[\text{Xe}] 4f^9 6s^2$         |
| 66                                  | Dy     | Dysprosium   | $[\text{Xe}] 4f^{10} 6s^2$      |
| 67                                  | Ho     | Holmium      | $[\text{Xe}] 4f^{11} 6s^2$      |
| 68                                  | Er     | Erblum       | $[\text{Xe}] 4f^{12} 6s^2$      |
| 69                                  | Tm     | Thulium      | $[\text{Xe}] 4f^{13} 6s^2$      |
| 70                                  | Yb     | Ytterbium    | $[\text{Xe}] 4f^{14} 6s^2$      |
| 71                                  | Lu     | Lutatium     | $[\text{Xe}] 4f^{14} 5d^1 6s^2$ |
| Second internal transitional series |        |              |                                 |
| 90                                  | Th     | Thorium      | $[\text{Rn}] 6d^2 7s^2$         |
| 91                                  | Pa     | Protactinium | $[\text{Rn}] 5f^2 6d^1 7s^2$    |
| 92                                  | U      | Uranium      | $[\text{Rn}] 5f^3 6d^1 7s^2$    |
| 93                                  | Np     | Neptunium    | $[\text{Rn}] 5f^4 6d^1 7s^2$    |
| 94                                  | Pu     | Plutonium    | $[\text{Rn}] 5f^6 7s^2$         |
| 95                                  | Am     | Americium    | $[\text{Rn}] 5f^7 7s^2$         |
| 96                                  | Cm     | Curium       | $[\text{Rn}] 5f^7 6d^1 7s^2$    |
| 97                                  | Bk     | Berkelium    | $[\text{Rn}] 5f^9 7s^2$         |
| 98                                  | Cf     | Californium  | $[\text{Rn}] 5f^{10} 7s^2$      |
| 99                                  | Es     | Elnsteinium  | $[\text{Rn}] 5f^{11} 7s^2$      |
| 100                                 | Fm     | Fermium      | $[\text{Rn}] 5f^{12} 7s^2$      |
| 101                                 | Md     | Mendelevium  | $[\text{Rn}] 5f^{13} 7s^2$      |
| 102                                 | No     | Nobelium     | $[\text{Rn}] 5f^{14} 7s^2$      |
| 103                                 | Lr     | Lawrencium   | $[\text{Rn}] 5f^{14} 6d^1 7s^2$ |

The definition of the transitional element by the electronic configuration of neutral atom excludes copper, silver and gold whose electronic configurations are in stabilization  $ns^1$  ( $n-1)d^{10}$  state as well as zinc, cadmium and mercury,  $ns^2$  ( $n-1)d^{10}$  on the other hand if the presence of electrons in chemically united atoms is the only property excluding the elements Y, La and Ac.

### 3-2-2 General characteristics

#### 1 - Physical properties

All transition d elements are generally highly dense metals and low atomic volumes and high melting and boiling points. It is fused and boils the last elements of the group distinctly at lower temperatures as compared to other elements of the group. Mercury is the last element of the transition series represents the observed exception of metals for being fluid under normal condition. Elements of the lanthanide series possesses metallic properties which show a metallic luster and good conductivity of electrical and heat, as well as that the degrees of melting and boiling points as expected.

Table (3-5) melting and boiling point and atomic radii for transition d elements

| First transitional series  |       |      |      |      |      |      |      |      |      |      |
|----------------------------|-------|------|------|------|------|------|------|------|------|------|
|                            | Sc    | Ti   | V    | Cr   | Mn   | Fe   | Co   | Ni   | Cu   | Zn   |
| melting point /K           | 1539  | 1998 | 1988 | 2103 | 1520 | 1801 | 1763 | 1725 | 1356 | 693  |
| boiling point /K           | 2727  | 3533 | 3773 | 2573 | 2363 | 3008 | 3313 | 3113 | 2853 | 1180 |
| atomic radii / pm          | 162   | 132  | 122  | 117  | 117  | 116  | 116  | 115  | 117  | 125  |
| Second transitional series |       |      |      |      |      |      |      |      |      |      |
|                            | Y     | Zr   | Nb   | Mo   | Tc   | Ru   | Rh   | Pd   | Ag   | Cd   |
| melting point /K           | 1509  | 2373 | 2223 | 2870 | 2140 | 2670 | 2240 | 1828 | 1233 | 594  |
| boiling point /K           | 2927  | 3870 | 5370 | 5070 |      | 4470 | 4170 | 3443 | 2453 | 1040 |
| atomic radii / pm          | 182   | 145  | 134  | 129  | 135  | 124  | 125  | 128  | 134  | 141  |
| Third transitional series  |       |      |      |      |      |      |      |      |      |      |
|                            | La    | Hf   | Ta   | W    | Re   | Os   | Ir   | Pt   | Au   | Hg   |
| melting point /K           | 920   | 2570 | 3289 | 3670 | 3420 | 2970 | 2727 | 2047 | 1336 | 234  |
| boiling point /K           | 3469  | 5470 | 6270 | 6070 |      | 4870 | 4770 | 4070 | 2970 | 630  |
| atomic radii / pm          | 187.7 | 159  | 147  | 141  | 137  | 135  | 136  | 139  | 144  | 155  |

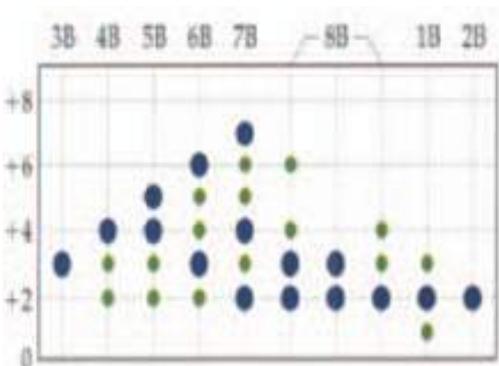
## 2. Chemical properties

### A - Elements of group d:

In general, group d elements are relatively ineffective with oxygen, halogens, sulfur, nitrogen, hydrogen and water vapor at normal conditions but at high temperatures are reacted with these reagents more easily. The group of transition elements reacts with hydrogen under certain conditions to form substances with structures called internal hydrides. This name originally implied that the arrangement of the metal atoms is roughly the same as that of the metal crystallization while the hydrogen atoms enter the distances. Although this is not the reality, the term remains traded. These hydrides occupy a volume larger than the metal volume, where it was formed from it and has a metallic appearance. It is prepared by direct union of metals and hydrogen at high temperatures. For example, platinum, palladium and iron are permeable metals to hydrogen at high temperatures. Tantalum absorbs hydrogen, creating an easily broken product. The elements of group d react directly when the carbon-element mixture is heated at temperatures above about 2200°C produced carbides. The carbides have high melting degrees and are very hardened, which is on two groups with a general formula  $MC$  and  $M_2C$  such as titanium carbides, zirconium, hafnium, vanadium and others. These carbides are characterized by chemical inertness, such as titanium carbide  $TiC$ , it is not affected by water or aqueous solutions of hydrochloric acid even when 600°C.

### B. Elements of group f lanthanides:

Lanthanide metals are soft and more effective with known reagents of group d elements, so lanthanides react slowly with halogens forming  $MX_3$  compounds and with oxygen forming-  $M_2O_3$  at room temperature but easily ignite with these reagents at temperatures above 200°C and react with sulfur at boiling point to form  $M_2S_3$  and nitrogen at a temperature higher than 1000°C to form  $MN$ . At temperatures above 300°C, lanthanides react rapidly with Hydrogen to form a kind of hydride and at high temperatures this reaction with boron and carbon gives borides and carbides respectively.



There are no zero oxidants in the first series of transition elements as shown In the larger circles in the graph.

|    |    |    |    |    |    |    |    |    |    |    |
|----|----|----|----|----|----|----|----|----|----|----|
| 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 |
| Sc | Ti | V  | Cr | Mn | Fe | Co | Ni | Cu | Zn |    |

Transitional elements

series of the first transitional elements.

### 3-2-3 The first transition series

The elements of this series (from scandium to zinc) (Zinc) in the fourth period of the periodic table between calcium Ca in group (IIA), and Galium Ga in group (IIIA). Table (3-4) shows the electronic configuration of these elements. These elements are called transition elements or group of d elements because they possess internal energy level 3d. It is proposed that the transitional elements of the fourth period or the first transition series should end with nickel element because the 3d energy level of the next two elements (copper and zinc) is full, and fact that copper shows multiple characteristics of the transition elements, while zinc shows intermediate characteristics between the transition elements and the main group elements. For this, it is appropriate to include both copper and zinc in the first series of transition elements. That the electronic configuration differences that distinguish transitional elements of other elements, lead to the emergence of special physical and chemical properties of the transition elements. These properties are not necessary unique behavior to the transitional elements. but combined they give transitional elements have a behavior that is distinct from that of any other type of element. These characteristics can be limited to the elements of the first transition series:

#### A- Metallic Characteristics:

One of the most prominent properties of the elements of the first transition series is that they are all of metals with high melting and boiling point and good conductors for heat and electrical. They are generally hard materials and are strong alloys with them and the possession of these qualities gives them a unique technological importance of its kind. Although the transition elements are denser and stiffer and have higher boiling points than the main groups, there is no systematic increase in the degree of these properties as the atomic numbers increase. That metal elements of this series are divided into two groups; first groups from Sc to Mn and the second from Mn to Zn with peaks at Ti and V and at Co, and Ni. The division of the series into two groups has to do with the fullness of orbitals d. The energy level 3d of manganese is half full and then it becomes occupied by individual electrons fills by electrons pairs to become complete fullness at copper and zinc.

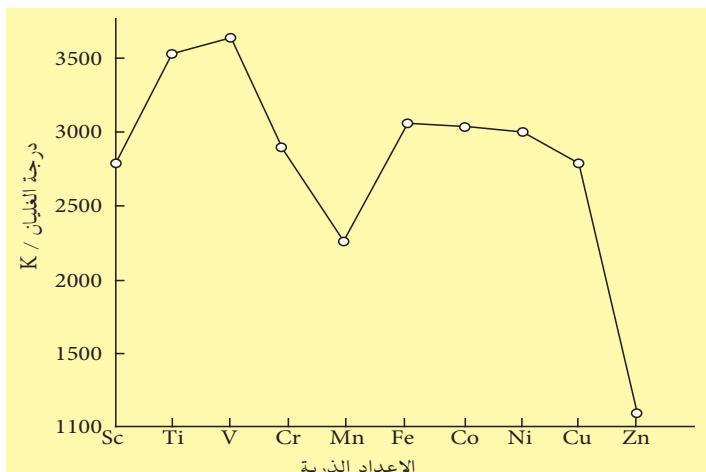


Figure 3-12

The relationship between boiling point and atomic number for elements of the first transition series.

That electronic configuration  $3d^5$  in chrome and  $3d^{10}$  in copper gets by removal of an electron from the  $4s$  level for the purpose of obtaining the most stable ranking. These elements are intended to release the largest number of external valence electrons for metal bonding, that it gives the highest binding energies and is reached in the middle of the series.

#### B - Oxidation cases:

There are more than one oxidation state in all transition elements, for example, iron has two oxidation states, +2 and +3, and an element atom Cobalt has two oxidation states of +2 and +3 and Cr also has numerous oxidation states are +2, +3, +4, +5, and +6 in their ionic and covalent compounds. The oxidation state of the transition elements reaches +7, in the case of manganese as in the compound potassium permanganate  $KMnO_4$  Table(3-6). The cause of the oxidation state is multiple for atoms of the transition elements are due to the number of electrons in the outer shell  $ns$  and  $(n-1)d$  to the atom of that element, where the loss of electrons from  $ns$  begins first and then in terms of the loss of these electrons one after the other, that the number of electrons in  $d$  does not exceed five electrons. Each electron loses an oxidation state appear, so that manganese has an oxidation state of +1, +2, +3, +4, +5, +6 and +7 due to the difficulty of losing all electrons in  $(n-1)d$  because of its need for high ionization energy so prefer to compose coordinate .The resulting ion is a strong oxidizing agent that draws electrons from neighboring atoms. The highest oxidation state of the atoms of the transition elements in the first series depends on:

1. Power of oxidizing agent.
2. Nature of the resulting compound

| Table 3-6 Oxidation states reported by the first transition series |   |                             |                        |                                 |
|--|---|-----------------------------|------------------------|---------------------------------|
| Element symbol   | Electronic configuration of the two orbitals (ns), (n-1) 3d | Multiple oxidative states   | Highest oxidation case | The most stable oxidation state |
| Sc   | 4s <sup>2</sup> 3d <sup>1</sup>                             | +3                          | +3                     | +3                              |
| Ti   | 4s <sup>2</sup> 3d <sup>2</sup>                             | +3 , +4                     | +4                     | +4                              |
| V  | 4s <sup>2</sup> 3d <sup>3</sup>                             | +2 , +3 , +4 , +5           | +5                     | +4                              |
| Cr   | 4s <sup>1</sup> 3d <sup>5</sup>                             | +2 , +3 , +6                | +6                     | +3                              |
| Mn   | 4s <sup>2</sup> 3d <sup>5</sup>                             | +2 , +3 , +4 , +5 , +6 , +7 | +7                     | +2                              |
| Fe   | 4s <sup>2</sup> 3d <sup>6</sup>                             | +2 , +3                     | +6                     | +3                              |
| Co   | 4s <sup>2</sup> 3d <sup>7</sup>                             | +2 , +3                     | +4                     | +2                              |
| Ni   | 4s <sup>2</sup> 3d <sup>8</sup>                             | +2 , +3                     | +4                     | +2                              |
| Cu   | 4s <sup>1</sup> 3d <sup>10</sup>                            | +1 , +2                     | +3                     | +2                              |
| Zn   | 4s <sup>2</sup> 3d <sup>10</sup>                            | +2                          | +2                     | +2                              |

From the Table (3-6) you can see the following:

1-The presence of familiar oxidative state (+2) when electronic loss 4s<sup>2</sup>

2- The increase in the number of oxidation state of scandium (Sc) to (Mn) and in the latter element the oxidation state is consistent with the loss of electrons 4s<sup>2</sup> , 3d<sup>5</sup>

3- The sharp decrease in the number of oxidants after manganese due to the difficulty of removing electrons after doubling.

### C-Acid and base properties

The acidic and basic properties of the transition elements are based on Lewis' concept of oxidation state, so the higher the oxidation number of element, the lower the basic and the more acidity as shown in Table 3-7 for manganese in its oxides.

| Table 3-7 Acid and base properties for magnesium transition element in its oxides |              |                                |                       |
|---|--------------|--------------------------------|-----------------------|
| Oxidation number  | property     | formula                        | Oxide name            |
| +2  | basal        | MnO                            | Manganese oxide       |
| +3  | Weak basic   | Mn <sub>2</sub> O <sub>3</sub> | Trioxide dimagnesium  |
| +4  | Amphoteric   | MnO <sub>2</sub>               | Dioxide magnesium     |
| +6  | Acidity      | MnO <sub>3</sub>               | Trioxide magnesium    |
| +7  | Rich acidity | Mn <sub>2</sub> O <sub>7</sub> | Heptoxide dimagnesium |

## D-Formation of coordinate Complexes

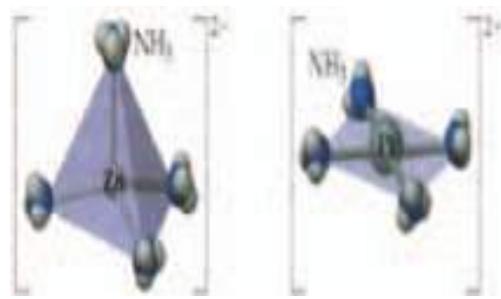
The positive ions of the transition elements shed strong electrostatic attraction on molecules or ions that contain one or more pairs of non-bonding electrons are known as such molecules or ions by (ligands). The result of this attraction is the so-called complex coordinate. Thus, we can say that the coordinate complex is an centralized atom is often a transitional element surrounded by a group of atoms, molecules, or ions are called ligands. The central atom often, they are transition metals, but ligands may be a negative ion of signal atom, such as a halide ion, or may be a polyatomic molecule, or an ion containing a donated atom belonging to oxygen or nitrogen group such as  $\text{H}_2\text{O}$  or  $\text{NH}_3$  or  $\text{CN}$  or  $\text{NO}_2$  and others. The term coordinate number uses to refer to the number of atoms that donated electrons related to the central atom. The coordinate number of the iron atom in the coordinate ion  $[\text{Fe}(\text{CN})_6]^{4-}$  equals 6, and the oxidation state of iron equals +2. The number -4 represents the complex ion charge, which is equal to (algebraic sum of the coordinate charge number and the central ion charge), where the sum of coordinate charge number equal (-6) and central ion charge equal (+2) so, the difference between them is (-4) representing the complex ion charge. The coordinate number varies from one element to another but in the complex compounds of the transition elements in oxidation states +2 and +3 is usually 4 or 6. Examples of such complexities are  $[\text{Co}(\text{NH}_3)_6]^{+3}$  and  $[\text{Ni}(\text{CO})_4]^{+2}$ . Common forms of such complexes are octahedral of the coordinate number (6), and tetrahedral of the coordinate numbers 4. There are other forms such as linear, binary, triangular, and others. These complex shapes will the student is informed about it in his university studies.

## H- Color

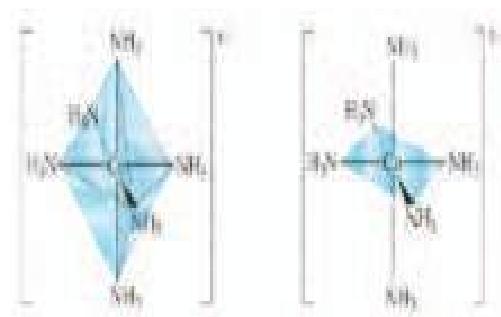
All complexes of the transition elements are characterized by their distinctive bright colors, for example  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  copper sulphate has a light blue color, while  $\text{Ni}(\text{OH})_2$  light green color and copper fourth ammonia (II)  $[\text{Cu}(\text{NH}_3)_4]^{+2}$  dark blue and others.

## I- Magnetic properties

Electrons have a charge and their motion creates two magnetic effects one is associated with the quantum number (l) and the other is accompanied by the quantum number (s) and these two effects give each electron the characteristics of a small magnetic pole.

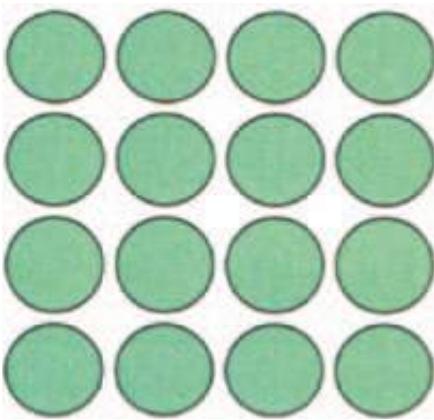


A) octahedral complex.

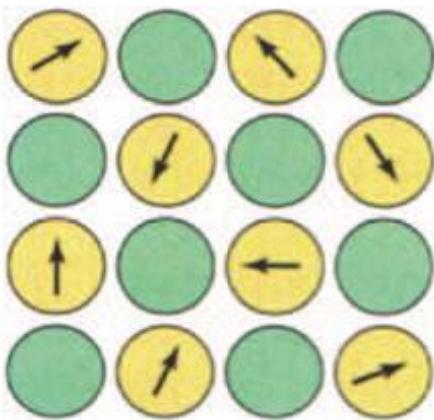


B) tetrahedral complex.

### Types of magnetic behavior



Diamagnetism

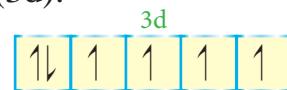


Paramagnetism

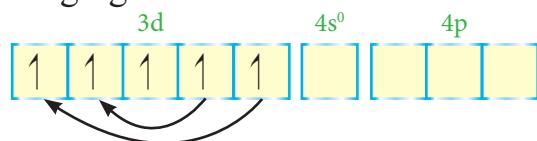
### Information

The green color represents the electron pairs And the yellow color represents single electrons.

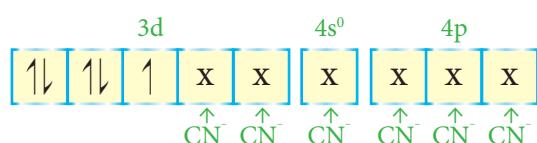
A magnetic moment in electron-filled shell is equivalent to the magnetic moment of each other and the atom as a whole will possess the resultant magnetic moment only if there are individual electrons in the valence orbit. When this happens it will make the outer magnetic field projected to direct the magnetic moment of the atoms toward that this field and this such behavior is called (paramagnetism). When all electrons are double in external orbitals, in this case a magnetic fields induced that reflect the magnetic field that generated it. This makes material repel with the external magnetic field, and this behavior is known as (diamagnetism). For example, we find iron as an element is attracted towards the magnet field because of its existence individual electrons in its outer shell where the outer shell is for the iron atom (3d).



If the iron is within the coordinate ion as in  $[\text{Fe}(\text{CN})_6]^{4-}$  (Hexaciano ferrate(II)) it is not attracted to the magnetic field because the orbitals the outer shell of the iron ion (II) has been saturated with electrons granted by ligands. For the component  $[\text{Fe}(\text{CN})_6]^{3-}$  (Hexaciano ferrate(III)), it is where the triple iron ion gravitates toward the magnetic field (paramagnetism) due to the presence of a single electron in the outer orbital shell 3d of triple iron ion as shown in the following figure:

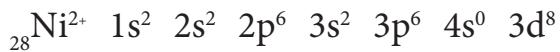


At the approach of the ligand(coordinate group), such as  $(\text{CN}^-)$  has a high rang of orbits 3d of triple iron ion works on duplex electrons in 3d orbitals for iron ion as shown in following figure:

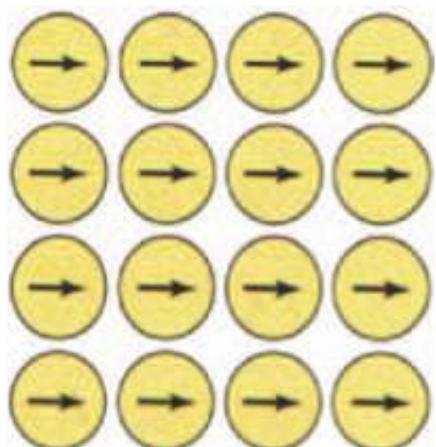


The electrons given by the coordinate groups are placed in the form of (X) differentiated from electrons not granted by coordinate groups (  $\uparrow\downarrow$  )

A complex ions that have a paramagnetic property is  $[\text{NiCl}_4]^{2-}$ , where the outer shell (3d) of the  $\text{Ni}^{2+}$  ion contains two single electrons, so it shows a single paramagnetic property



in orbitals



ferromagnetism

If we take the zinc component ( ${}_{30}\text{Zn}$ ) we observe from its electronic configuration that all the electrons in its outer shell are in pairs and so it is not attracted to the magnetic field.



A third type of magnetic behavior is ferromagnetism, which is actually very rare but it is extremely importance. a special case of paramagnetism occurs in compounds that contain a large part of atoms or ions containing single electrons.

For this type of components and in appropriate conditions, the single electrons of each atom interact and regulate themselves with electrons. This process is repeated during all atoms in the component. Therefore, the effect leads to the construction of permanent magnets. Ferromagnetic behavior can be observed mainly among metals, alloys and transition elements oxides and less impact in internal transition elements oxides.



Permanent magnets made of materials ferromagnetism

## Gouy balans

The material with dia or paramagnetic properties can be identified using a sensor called (Gouy balance). This device has a very sensitive balance attached in one hand the material whose magnetic properties are to be defined and the equivalent weights are placed the material in the second cuff as shown in Figure (3-13).

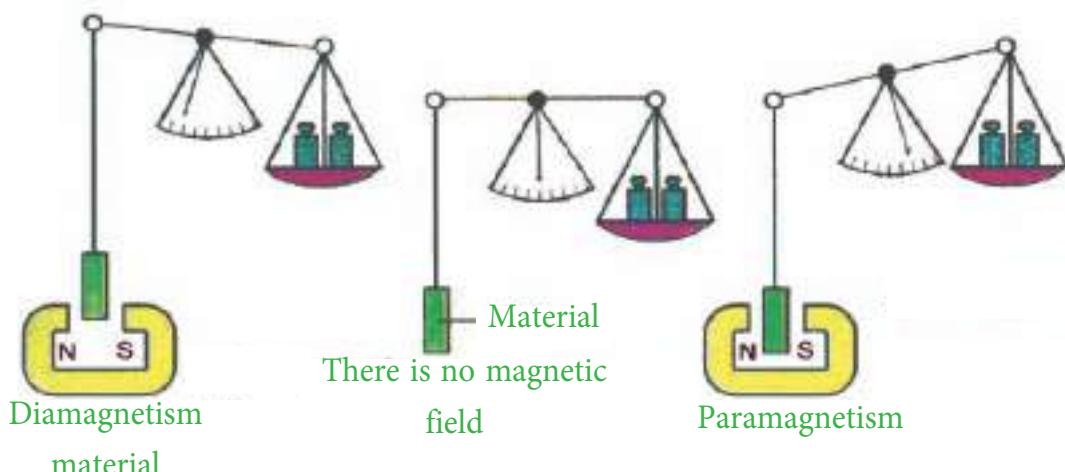


Figure 3-13

Gouy balans.

where the material is placed in a strong magnetic field, if it has paramagnetism properties, it will gravitate towards the magnetic field and increase the scale reading, but if the material diamagnetism it will repel with the field and decrease the scale reading

#### I-Effectiveness as catalysts:

The catalysts derived from the transition elements has great importance in many biological processes and systems and are indispensable in chemical industries too. Almost all of the transition elements ability to behave as catalysts either in their free states or in component forms. This ability is likely to come from the use of d orbital or from the formation of compounds that can absorb and activate reactants. The ability of these compounds to behave as catalysts by ability to create low-energy pathways for reactions by either oxidation-induced changes or by the formation of suitable intermediate compounds.

### 3-2-4 Lanthanides and Actinides

#### 1.Lanthanides

Lanthanum (La) (atomic number 57) shows the first element in the third series of transition elements which has electronic configuration  $[_{36}\text{Kr}] 4\text{d}^{10} 5\text{s}^2 5\text{p}^6 5\text{d}^1 6\text{s}^2$  .

The next element is cerium and its atomic number is 58 and electronic configuration  $[_{36}\text{Kr}] 4\text{d}^{10} 4\text{f}^1 5\text{s}^2 5\text{p}^6 5\text{d}^1 6\text{s}^2$ . Where electrons begin to fill the energy level (peak level) 4F until we get to the element lutetium (Lu) has an atomic number (71) and then the 4d level returns to fullness. Elements from lanthanum to lutetium are called lanthanides the first internal transition series consists of 14 elements.

|    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 | 72 |
| Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |    |

Lanthanides series

These elements are called a Rear earth because they exist in uncommon mixtures as they were thought to be elements of soil or oxides.

The elements of lanthanides are very similar to each other, and their separation is a major problem because all their compounds are very similar, where the oxidation state (+3) appears and this state shows the predominant ionic properties are similar to the alkaline earth metal ions except that they are positive trilogy and not positive dualism. There is no aerobium (Eu) (one of the elements in this series) free in nature and can only be discovered when obtained within an nuclear fission output.

## 2. Actinides:

Similarly to the lanthanide series, the actinides begin with an element actinium (Ac) has an atomic number of 89 and has an electronic configuration:  $[\text{Xe}] 4f^{14} 5d^{10} 6s^2 6p^6 6d^1 7s^2$  Before we know about the possibility of the presence of elements after uranium has developed heavier natural elements such as thorium, erotectinium and uranium in the sixth period of periodical classification in tandem elements of hafnium, tantalum and tungsten. It was inferred that these elements were the beginning of a new series of four ten elements in which the sixth quantum level is filled in exactly the same way that the fifth quantum level is full by hafnium, tantalum and tungsten elements. The discovery of several post-uranium elements and the study of their qualities in fact demonstrate the emergence of a new internal transitional series that begins after actinium. So post-actinium elements are now called actinides. Whatever the extent of oxidants possessed by oxidants, they always have an oxidative state (+3) within oxidants.

In the actinides, the element curium is one of the elements, its inner subshell casing is probably half-filled, and the vast majority, for its compounds curium (Cm) is a positive trilogy, while the elements are above americium have many oxidative states behave like +2, +3, +4, +5, +6 and an Berkelium element (Bk) after curium exhibits oxidative states +3, +4. Polymorphism in oxidative states of actinides elements to extent amersium elements makes the chemistry of the elements of this series very complex.

|    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 | 72 |
| Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb |    | Lu |
|    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |

actinides series.



magnetite



limonite



hematite

In addition, in cadolinium (Gd) the subshell level is filled in half with electrons. This is known particularly represents electronic configuration and ionization. Cadolinium forms  $\text{Gd}^{+3}$  ions only, (with the loss of three external electrons) and does not show inclination to add or lose electrons in a half-filled inner level. This behavior can be compared with the element that comes before cadolinium is an aerobium (Eu), and this element exhibits an oxidation state of +2 and also +3, the next element, terbium (Tb), exhibits oxidative states +3 and +4. We will take iron as an example of transition elements.

### 3-3- Iron

#### 3-3-1 Introduction

Iron is the second metal after aluminum and the fourth element after oxygen, silicon and aluminum in proportion to the crust of the earth, believed to be the center of the earth, consists mainly of iron and nickel. Iron is spread in the earth's crust, united with other elements forming multiple ores; hematite which contains  $\text{Fe}_2\text{O}_3$  and magnetite contains  $\text{Fe}_3\text{O}_4$  and limonite contains  $\text{FeOOH}$  and siderite contains  $\text{FeCO}_3$ .

Iron is also the most important transitional element, it is one of the elements involved in the synthesis of blood hemoglobin and is also found with molybdenum in the synthesis of the nitrogen fixing enzyme. It is one of the necessary elements that are Chlorophyll for the food industry in the plant.

#### 3.3.2 The location of iron in the periodic table

Iron falls in the periodic table and in the fourth period the eighth group B, and has the following electronic configuration:  $_{26}\text{Fe} : 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

The fact that the iron element of the transitional valence fall within the two outer shell [ns, (n-1) d] but it does not show an oxidation state equal to this number (8).

The most common oxidation states in iron are +2 and +3, the process of losing two electrons from the iron atom to form an iron ion (II) or the loss of three electrons to form iron ion (III) depends on the reactants nature. The relationship between the oxidation states can be represented the following equation below:

$$\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + \text{e}^-$$

The equation above shows that the iron ion(II) can oxidize (lose an electron) to become an iron ion(III), or the iron ion(III) reduces (acquires an electron) to the iron ion(II).

### 3-3-3 Properties of iron

Iron is a shiny white metal that is pure and is characterized by all the properties of metals such as hardness, good thermal and electrical conductivity, and ability of hammering and , extrusion and other properties. It is a magnetized metals with melting point 1528°C, boiling point 2861°C and density 7.86 g/cm<sup>3</sup> at 25°C

### 3-3-4 Iron reactions

1. Iron does not react in normal temperatures with dry air and does not react with water free from dissolved air, but reacts with oxygen in moist air to form a brownish reddish layer called rust.

This layer of iron is separated in the form of crusts, which is aqueous iron oxide and does not stop rust at the outer surface of the iron piece (due to permeability and incoherence of the oxygen layer formed)

This layer of iron is separated in the form of crusts, which is aqueous iron oxide (III) and does not stop rust at the outer surface of the iron piece (due to permeability and incoherence of the oxygen layer formed)



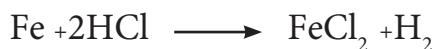
2. Iron is oxidized when heated to high temperatures (degree of redness) and in the presence of air forming iron oxide magnetic  $\text{Fe}_3\text{O}_4$  as in the following equation:



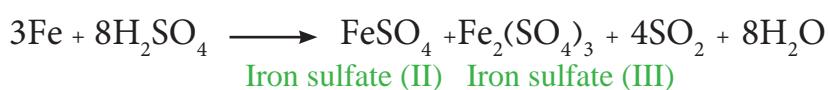
3. Iron reacts with water vapor, forming magnetic iron oxide and realizing hydrogen gas as in the following equation:



4. Iron reacts easily with dilute acids such as hydrochloric acid and sulfuric acid forming iron salt (II) and realizing hydrogen gas as in the following equations:



It reacts with concentrated acids such as hot concentrated sulfuric acid and nitric acid, forming iron salts and water, and rising  $\text{SO}_2$  gas as in the following equation.



#### Do you know

that the most famous iron sulphate is iron pyrite  $\text{FeS}_2$ , which is known as gold false because of the color similar to the color of gold, which is used in cheating gold without easily detected.

5. When heating a mixture of iron filings and sulfur powder form Iron sulfide (II) as in the following equation:



That iron enters into a lot of the most famous cyanide compounds  $\text{Fe}_4[\text{Fe}(\text{CN})_6]$  is called a blue tincture Prussia which is used to remove yellowing water from sediment salts iron, called locally (Jweet).

#### Do you know

6. Iron reacts with halogens (fluorine, chlorine and bromine) to produce iron halides (III) according to the equation:



For example, iron chloride (III) is produced from the passage of chlorine gas on the heated iron filings to the redness temperature as in the following equation:



#### 3-3-5 Iron extraction

Iron is produced industrially in the bloating oven by reducing iron ores, especially hematite and magnetite with carbon at  $2000^{\circ}\text{C}$ .

The method involves mixing iron ore with coke and limestone (mostly calcium carbonate) and add the mixture from the top hole of the bloating oven [Figure (3-14)].

Then the hot air from the nozzles is blown. In a result of the high temperature of the mixture, many reactions happen which can be summarized. Firstly coal combustion to heat the oven and form a carbon monoxide:



Carbon monoxide reduces iron ore to produce fusible iron and carbon dioxide:



The oven heat also caused the decomposition of calcium carbonate into calcium oxide and carbon dioxide according to the equation:



Then calcium oxide combines with sand to be molten calcium silicate according to the equation:

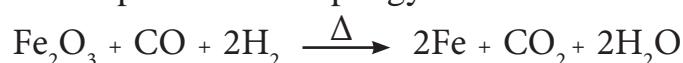


The calcium silicate molten floats above the iron molten, because its density less than the density of iron, forming a layer called slag that prevents mixing of iron fusion with the material above it. The molten iron is drawn from time to time from the bottom of the oven, where it is poured into special molds and then called cast iron, which is used as iron ore in the following stages of iron manufacturing.

The slag formed is also pulled from special holes below oven, which is used in cement, concrete or concrete roads and other construction. Due to environmental concerns about the use of coke, alternative methods of iron processing have emerged, one of which is the reduction of iron using natural gas. Iron is produced in the form of a powder called spongy iron, which is used in steel industry. The process consists of two main interactions namely: oxidation of natural gas with the help of auxiliary agent and heat.



the resulting  $\text{H}_2$  and  $\text{CO}$  gases then at 800-900°C reduction of iron ore to produce iron spongy.



The sand is then removed by adding calcium carbonate in the next step to form slag as in the previous method.

This method of iron production is characterized by:

1. Does not require expensive coke and is not available.
2. The cost of its creation is much lower than the cost of setting up the blower oven.
3. Technology is simple and easy to use.
4. The iron produced is carbon-free while the cast iron is produced from the lower oven contains approximately 4% carbon.

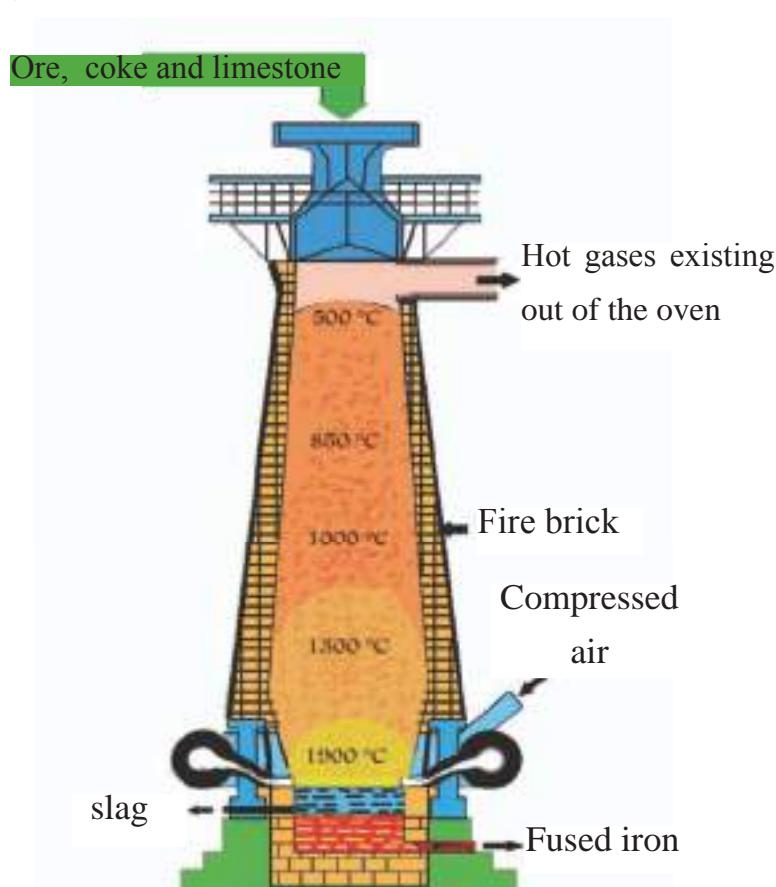


Figure 3-14

Bloating oven.

### 3-3-6 Iron types

We learned that the iron produced from the bloating oven is called cast iron contains impurities ranging from (6% to 8%) mostly carbon and silicon. Percentage change these impurities can get different types of iron ones:

#### A- Casting Iron

When re-melting cast iron and pouring into molds to make the required tools then it is called cast iron and it has two types depending on casting and cooling method. If you use metal molds for casting the casting process is quick and the output is called white cast iron. If sand molds are used then the solidification process is slow and the product is called gray cast iron. In general, cast iron, known locally as 'Aheen', is characterized very rigid but brittle and does not withstand strong shocks. It is often used in making some parts for fireplaces, pipes and sewage covers.

#### B) casting (steel):

Iron produces steel from cast iron after oxidation of existing impurities in a special oven, add the required amount of carbon (0.2% to 1.5%) and other elements according to the desired qualities of the desired steel quality. The properties of iron and steel depend on the ratio of carbon and other additives.

## Basic concepts

### Periodic Table Parts

The modern periodic table consists of four parts, the first part includes the elements that end its outer shell with s type orbitals. The second part includes elements whose outer shell ends with orbitals of type s and p while elements are whose outer shell ends with a type of orbital s or d the third part of the periodic table. Internal transitional elements series (lanthanides and actinides) fourth part of the periodic table, whose outer shell ends with s and f orbitals

### Atomic Volume

It is half the distance between the centers of two atoms two consecutive crystals are measured using radiology X-ray. Atomic radii are lower in the one period when you move from left to right but they are increase when moving from top to bottom in one group.

### Ionization Energy

Is the energy needed to extract an electron from an neutral atom in its gaseous state and positive ion formation. The energy needed to extract the first electron is called the first ionization energy is called the energy needed to extract the second electron is the second ionization energy and so on.

### Electron Affinity

It is the amount of energy released from the neutral atom in gaseous state when acquired electron creating negative ions. This trait increases in the one period by increases the atomic number while decreasing in the group by increasing atomic number.

### Electronegativity

It is the ability of atoms in molecules to attract electrons towards it from other atoms connected with it chemical bond. Electronegativity is increased by increasing the atomic number in one period and decreased by increasing atomic number.

### Transition element

An element that has an electronic configuration that is orbitals d or f are partially full in the neutral or chemically bonding in their compounds.

### Coordinated Complexes

It is a central atom and is often for a transitional element surrounded by a group of atoms or molecules or ions are called actinides. Actinides may be a single atom negative ion like a halide ion or it could be polyatomic molecule or an ion that contains donation atom and belong to the atom of the Oxygen or Nitrogen group such as  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{CN}$  and  $\text{NO}_2$  and others.

### Coordinated number

It is the number of atoms, molecules or ions that donor of the electrons related to the central atom. The number of symmetric elements changes to another but in the transition elements is equal to commons 4 or 6.

### Magnetic Properties

The electron has properties as the result of the movement of qualities small magnetic rod with magnetic momentum. In the case of materials contain full orbitals with electrons, the magnetic moment of one electrons are equivalent to the magnetic moment of the other electron. Thus is not attracted to the outer magnetic field, and it is said to be a diamagnetic material.

## Chapter Three Questions

3

3-1 After trying to divide the elements into metals and nonmetals, attempts were made to classify them. Mention these attempts and on what basis those attempts were built.

3-2 Indicate the periodic law reached by each of From Lands and Mandeleeff.

3-3 What are the weaknesses of the scientific Mandeleeff table

3-4 What is the difference between the Mendeleev table and the new periodic table.

3-5 How the atomic size of the elements of the single period and single group change by increasing the atomic number and why.

3-6 Which atoms in each of the following pairs are larger atomic size (<sub>3</sub>Li, <sub>4</sub>Be) (<sub>16</sub>S, <sub>8</sub>O), (<sub>17</sub>Cl, <sub>35</sub>Br).

3-7 Arrange the following according to the ionization energy increasing, mentioning reason. Al, Al<sup>+</sup>, Al<sup>2+</sup>, Al<sup>3+</sup>.

3-8 If you have the following elements (<sub>17</sub>Cl, <sub>15</sub>P, <sub>11</sub>Na) answer the following questions:

A- Any of the elements have a larger atomic size and which the smallest atomic size.

B- Arrange these elements as increasing electronegativity, mentioning the reason for this arrangement.

C- Arrange them according to the increasing attraction electronic affiliation, mentioning the reason

D- Any of these elements in which the metallic properties are expected.

3-9 You have atoms <sub>34</sub>Se, <sub>16</sub>S, <sub>8</sub>O arranged them according to the following with the reason.

- A- Electronic affinity.
- B- Increasing electronegativity
- C- Atomic radius increasing
- D- Increasing ionization energy

3-10 Explain

- A- There is no need in the old to classify the elements in periodic table.
- B- The division of elements into metals and nonmetals did not last long.
- C- High ionization energy <sub>17</sub>Cl compared to ionization energy <sub>12</sub>Mg
- D- Energy is released when the first electron is acquired, but many often absorb some energy when gaining the second electron.
- E- Fluorine ionization energy is greater than oxygen ionization energy.

3-11 How to obtain a spectrum for the element. Does the spectrum of the element appear when it absorbs energy or when it emits energy.

3-12 What is the coordinate number of the central atom and complex Ion charge of each of the following:

A- Hexaciano ferrate [Fe(CN)<sub>6</sub>](III)

B- Quaternary ammonia copper

[Cu(NH<sub>3</sub>)<sub>4</sub>](II)

C- Quaternary chloro Nickel [NiCl<sub>4</sub>](II)

3-13 Mention methods of industrial extraction of iron? Which is better and why?

3-14 Define each of the following

- 1- Transitional element.
- 2- d elements group.
- 3- Coordinated number.
- 4- Ligand.



## Chapter Four Solutions

4

After completing this chapter, the student is expected to:

- Identify solutions and understand the meaning of solubility and the factors affecting it.
- Identify the types of solutions and some methods of classification and distinguish between saturated solutions, unsaturated and supersaturated solutions.
- Recognize some methods of expressing solution concentrations.
- Distinguish between real solutions, plankton and colloidal systems.
- Distinguish between ideal and non-ideal (real) solutions and defines Raoult's law.
- Recognize the reason of solute some effect on some of solvent properties.
- Realize the concept of collective properties of solution and the quantitative relationships of solute concentration.

#### 4-1 Introduction

The solution is generally defined as a homogeneous mixture of substances consisting Solvent and solute of one or more, mixing proportions are different from solution to solution. The largest material quantity In the mixture is the solvent and the least amount is the solute.

The term solutions include different types of mixtures in which Solid, liquid or gaseous materials exhibit either solvent or solute behavior. But the solvent is usually liquid such as water, alcohol, gasoline and ether chloroform, carbon tetrachloride, acetone, etc. For example, sea water contains a number of dissolved substances in addition to other substances suspended in it. Water saturated with carbon dioxide is an example of a gas solution dissolved in a liquid. The blood also contains a plasma solution with suspended substances are blood cells.

On the other hand there are solutions that liquids doesn't formed solvent. The dental fillings that the doctor attends is an example of a solid amalgam, in other words a solution in which liquid mercury is formed liquid substance in the metallic solid phase as zinc, whereas metallic alloys are an example of solid solutions. Atmospheric air is one of the solutions for gases in nature, oxygen as well as other gases dissolved in formed solute while the solvent is nitrogen. Table (4-1) shows different types of solutions and some examples for each type

Table (4-1) different types of solutions and some examples for each type

| Solution status | Solute status | Solvent status | Examples                    |
|-----------------|---------------|----------------|-----------------------------|
| Liquid          | Gas           | Liquid         | Oxygen in water             |
|                 | Liquid        | Liquid         | Ethanol in water            |
|                 | Solid         | Liquid         | Sugar in water              |
| Gas             | Gas           | Gas            | Oxygen in air               |
|                 | Liquid        | Gas            | water droplet in atmosphere |
|                 | Solid         | Gas            | Dust particles in air       |
| Solid           | Gas           | Solid          | Hydrogen in platinum        |
|                 | Liquid        | Solid          | Mercury in zinc             |
|                 | Solid         | Solid          | alloys                      |

## 4-2 Solubility process

The speed and ease of solubility process for any solute in a particular solvent depends on two important factors: Firstly, the change in the temperature of the product mixture (solution) and secondly the extent of dissolution of the solute (in the form of ions or molecules) between the solvent molecules, associated with the solubility process. It can be said that the solubility process takes place more easily:

1. If the solubility process is accompanied by an increase in the temperature of the resulting solution (hottest the solution).
2. If the diffusion of dissolved components in the solvent widely and completely.

The change in energy associated with the solubility process is called heat of solution. The increase (or decrease) in the solution temperature in the melting process depends mainly on the reaction forces (attraction or repulsion) between the solute and solvent molecules. When mixing a solvent with a solute to prepare a solution, each of the solvent molecules will be affected with other solvent molecules surrounding them, in addition to being affected by solute molecules. The same can be said for solute molecules. It is the amount of force of these effects that determines the amount of solubility and ease with which the solubility process takes place. It can be said that the ease of solubility is determined by the following conditions:

1. weak affect between the solute molecules among them.
2. Weak effect between solvent molecules among themselves.
3. Large effect between solute molecules with solvent molecules.

Figure 4.1 shows the energy change associated with each step of the solubility process. For the solubility process to take place, forces must be overcome the attraction force between solute molecules (step A) is accompanied by a heat absorption. (step B) represents the separation and faraway of solvents particles of each other to be ready to receive solute particles. This step needs to be absorbed by the heat, but thermal energy is emitted as a result of the effect between the solute and solvent molecules (step C) and thus the solubility process in this case produces heat and the solution after preparation is hot.

On the other hand, the solubility of a number of solids in liquid solvents is accompanied by heat absorption (cold output solution). this can be explained by widespread and complete diffusion of the solute components between the solvent molecules during the

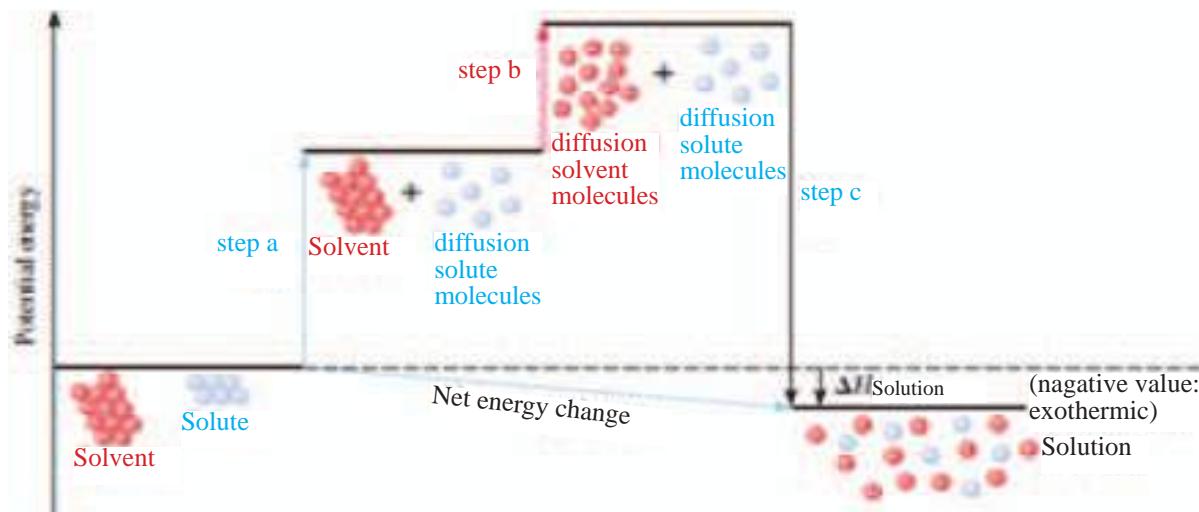


Figure 4-1

Change in system energy content accompanying the steps involved in the melting process.

solubility process and become free to move and randomly in the solution after they were restricted movement in a solid state. Solvent molecules are also more free to move. They become in an environment that contains solute components that surround each molecule, including a mixture of solute and solvent molecules [Figure (4-2)].

### 4-3 Types and properties of solutions

Solutions in which the solvent is liquid can be classified in several ways depending on the concentration or type of solvent or mixture type that forms the solution as follows:

#### 4-3-1 Diluted and concentrated solutions

This classification only depends on the difference in the amount of solute in the solution, ie on the relative masses of solute and solvent. Therefore, it is a descriptive expression of the quantities of solute and solvent. A solution that contains a larger amount of solute is called or described as a concentrated solution, while a solution with a small amount of solute is called with diluted solution.

#### 4-3-2 Expression of concentration

Chemists use the term concentration to refer to the amount of solute in an amount of solvent. The concentration of the solution is expressed as is known amount of solute in a given weight or volume of solvent. There are many ways to express the concentrations of solutions and these are in two ways:

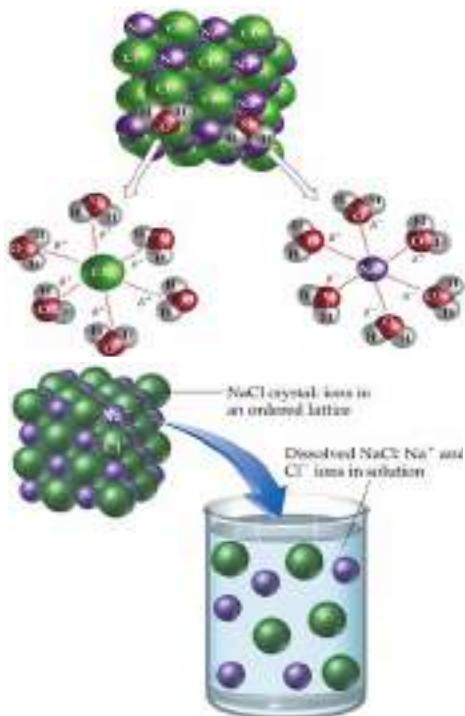


Figure 4-2

Sodium chloride solution (dissolved) in water (solvent).

Firstly. Expression of concentration in terms of mass of solute in mass of solvent (mass in mass) or amount of solute in amount of solvent (amount in amount). most important are:

### 1. Mass percentage of solute

See Figure 4-3, What does the percentage written on the bottle mean?

Percentage (20%) refers to the concentration of sodium hydroxide solution. Each 100g solution contains 20 g sodium hydroxide and the remaining 80 g water. The solution can be prepared with the same concentration if we dissolve 2g of sodium hydroxide in 18g of water. **The mass percentage of solute can be defined as the number of grams of solute in 100g solution** and the mathematical relationship to calculate the mass percentage of solute in a solution :

$$\text{percentage (\%)} = \frac{\text{solute mass (g)}}{\text{solvent mass (g)} + \text{solute mass (g)}} \times 100\%$$

$$\% = \frac{m_2(g)}{(m_1+m_2)(g)} \times 100\%$$

Where  $m_1$  represent solvent mass and  $m_2$  represent solute mass

#### Example 4-1

Calculate the mass percentage of sodium hydroxide in a solution prepared by dissolving 8 g NaOH of 50g of water.

#### Solution

$$\% \text{ NaOH} = \frac{m_{\text{NaOH}}}{m_{\text{NaOH}} + m_{\text{H}_2\text{O}}} \times 100\%$$

$$\% \text{ NaOH} = \frac{8 \text{ g}}{8 \text{ g} + 50 \text{ g}} \times 100\%$$

$$\% \text{ NaOH} = 13.8 \text{ \%}$$

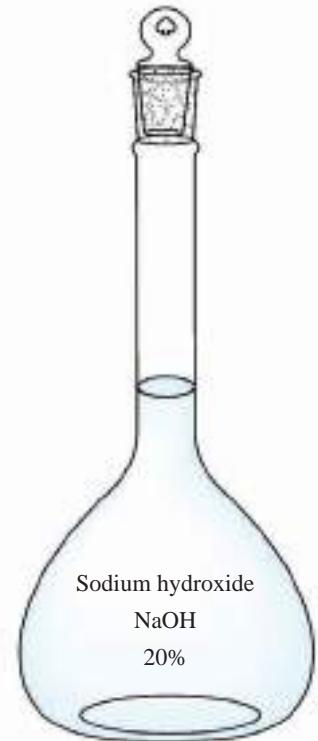


Figure 4-3

Percentage of mass to express of the solution concentration

#### Exercise 4-1

What is the mass of potassium chloride needed to prepare 250 g of a 5% concentration solution by mass?

#### Exercise 4-2

How many grams of sulfuric acid  $\text{H}_2\text{SO}_4$  are contained in one litter of aqueous solution of this acid if the percentage of acid in it is 34% and the density of the aqueous solution of this acid is equal 1.24 g/ml (Note: the density of the solution is defined as the ratio between mass to volume)

## 2. Molality (m\*)

Molality is the number of solute moles that is contained in one kilogram of solvent. If one mole of sugar is dissolved in one kg of distilled water you get a concentration of solution (1mol / kg) or one molali 1m. Molality is known as the following mathematical relationship:

$$\text{Molality}(m) \left( \frac{\text{mole}}{\text{kg}} \right) = \frac{\text{solute moles number (mole)}}{\text{solvent mass (kg)}}$$
$$m \text{ (mol/kg)} = \frac{n \text{ (mol)}}{m \text{ (kg)}}$$

This method of expressing concentration is useful as this expression refers to the ratio between the number of solute particles (i.e., number of moles) to the solvent particles (i.e. its mass) in solution.

The concentration of the solution expressed in molarity is not affected by temperature change. As previously known, Moles are expressed as follows:

$$n \text{ (mol)} = \frac{m \text{ (g)}}{M \text{ (g/mol)}}$$

Where m is the mass of solute in grams and M is the solvent atomic molar

### Example 4-2

Calculate the molarity of the prepared solution by dissolving 36 g of glucose sugar.

Molar mass = 180 g / mol in 360 g distilled water.

#### Solution

Calculate molality of solution through the relation:

$$n \text{ (mol)} = \frac{m \text{ (g)}}{M \text{ (g/mol)}} = \frac{36 \text{ (g)}}{180 \text{ (g/mol)}} = 0.2 \text{ mol}$$

Calculate the number of moles of solute (glucose sugar)

$$m = m \text{ (g)} \times \frac{1 \text{ (kg)}}{1000 \text{ (g)}} = 360 \text{ g} \times \frac{1 \text{ (kg)}}{1000 \text{ (g)}} = 0.36 \text{ kg}$$

Change solvent mass to unit (kg)

$$m \text{ (mol/kg)} = \frac{n \text{ (mol)}}{m \text{ (kg)}} = \frac{0.2 \text{ mol}}{0.36 \text{ kg}} = 0.556 \text{ mol/kg} = 0.556 \text{ m}$$

\* The student should distinguish between the mass symbol (m) and the symbol used to express the molality concentration(m)

### 3. Molar fraction x

Some properties of the solutions depend on the relative quantities of all the components of the solution expressed in terms of the number of moles (molar fractions). A method to express the components of the solution. For two component solution solute (A) and solvent (B), the molar fraction of the component (A) known, **as the ratio of the number of moles of this component  $n_A$  to the total number of moles of all the components of the solution ( $n_A + n_B$ )**, it can be expressed as follows:

$$x_A = \frac{n_A}{n_A + n_B}$$

Thus, the molar fraction of the solvent ( $x_B$ ) is the ratio between the number of solvent ( $n_B$ ) to the total number of solutions ( $n_A + n_B$ )

$$x_B = \frac{n_B}{n_A + n_B}$$

The molar fractions of the components of the solution are always equal to one integer as described below:

$$\frac{n_A}{n_A + n_B} + \frac{n_B}{n_A + n_B} = 1 \Rightarrow (x_A + x_B = 1)$$

#### Example 4-3

Prepare sucrose solution  $C_{12}H_{22}O_{11}$  (molar mass=342 g/mol) by dissolving 34.2 g of it in 180g of distilled water (molar mass=18 g/mol). Express the concentration of sugar and water in the solution in terms of molar fraction for each one.

#### solution

Calculate the number of molars of sugar and water from the relationship:

$$n \text{ (mol)} = \frac{m \text{ (g)}}{M \text{ (g/mol)}}$$

$$n_{C_{12}H_{22}O_{11}} = \frac{34.2 \text{ (g)}}{342 \text{ (g/mol)}} = 0.1 \text{ mol}$$

$$n_{H_2O} = \frac{180 \text{ (g)}}{18 \text{ (g/mol)}} = 10 \text{ mol}$$

$$x_{C_{12}H_{22}O_{11}} = \frac{n_{C_{12}H_{22}O_{11}}}{n_{C_{12}H_{22}O_{11}} + n_{H_2O}} = \frac{0.1 \text{ mol}}{0.1 \text{ mol} + 10 \text{ mol}} = 0.01$$

$$x_{H_2O} = \frac{10 \text{ mol}}{0.1 \text{ mol} + 10 \text{ mol}} = 0.99 \quad \text{In the same way}$$

#### Exercise 4-4

Prepare a solution of sodium hydroxide by dissolving 4 g of solid base at 16.2g of distilled water. Calculate the molar fraction of the components of the solution.

#### Exercise 4-5

Calculate the molar fraction of water in a mixture consists of 9.0 g of water and 120g of acetic acid ( $CH_3COOH$ )

### Exercise 4-6

What the molarity concentration of chloride sodium NaCl solution prepared by dissolving 4.39 g of salt in distilled water to get a solution of 250 mL?

Second. Expression of concentration in terms of solute mass in solvent volume(mass in volume) or amount of solute in solvent volume (amount in volume), the most important of these expressions are:

#### Molarity M\*

Mole denotes the amount of matter, and often there is a need to deal with the substance when is dissolved in a solution, so it is appropriate use of the Molarity concentration to determine the number of moles of material is dissolved in a certain volume of solution. The Molarity are number of the solute that is contained in one liter of solution, ie  
Molarity (M) = 
$$\frac{\text{moles number of solute (mole)}}{\text{solution volume (liter)}}$$

$$M = \frac{n \text{ (mol)}}{V \text{ (L)}}$$

Therefore, the unit of molarity is (mol/L). For example, if one mole (62g) of ethylene glycol ( $C_2H_6O_2$ ) in sufficient quantity from distilled water to obtain one liter of solution, the concentration of the resulting solution is equal to 1mol / L or written in the simplest form 1M.

#### Example 4-4

Calculate the molarity concentration of a solution prepared by dissolving 2.3g of ethanol ( $C_2H_6O$ ) (molar mass = 46 g/mol) in 3.5L of distilled water.

#### Solution

Calculate the number of ethanol moles

$$n_{C_2H_6O} = \frac{m \text{ (g)}}{m \text{ (g/mol)}} = \frac{2.3 \text{ (g)}}{46 \text{ (g/mol)}} = 0.05 \text{ mol}$$

Accordingly, his molarity can be calculated as follows:

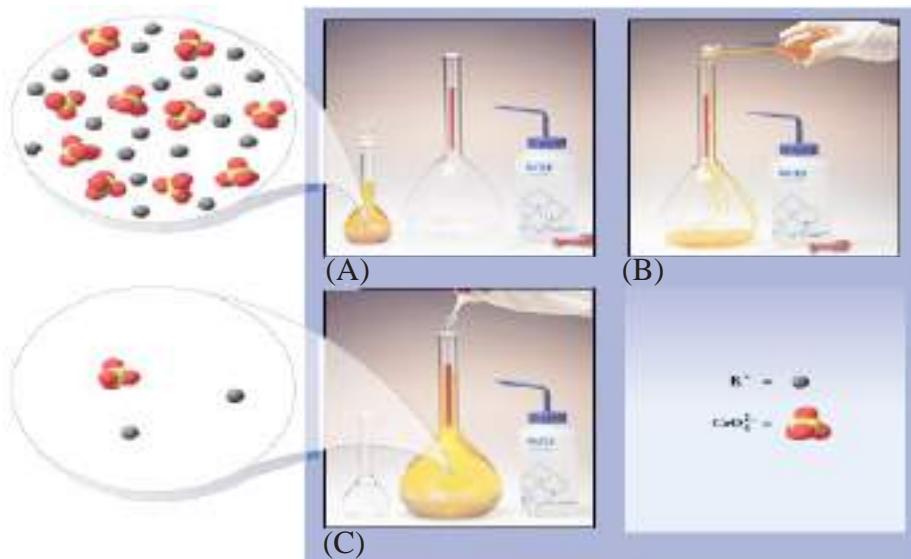
$$M = \frac{n \text{ (mol)}}{V \text{ (L)}} = \frac{0.05 \text{ mol}}{3.5 \text{ L}} = 0.015 \text{ mole/L} = 0.015 \text{ M}$$

In general, a solution can be prepared for any substance in two ways, firstly as it has already been explained in the previous examples by dissolving a known weight of soluble solid or liquid in a known weight of solvent or secondly by dissolving the known weight of the solute in a given volume of solution.

\* The student should distinguish between the molar mass symbol M and the symbol used to express the molarity concentration M.

#### 4-3-4 Dilution law

We often need to prepare a dilute solution (low concentration) from concentrated solution (high concentrated), when diluting the solution (by adding an amount of solvent to it) its volume increases and the concentration of the dissolved material decreases (reduced concentration), but the amount of dissolved material remains constant. That is, the number of solute moles does not change [Figure (4-4)]. And this is mean:



Number of solute moles before dilution = Number of solute moles after dilution

Return to the general relationship to express molarity concentration can say that:

Number of solute moles (n) = solution volume (V) (L)  $\times$  concentration (M) (mol/l)

If we symbolize the volume and concentration of the solution before dilution ( $V_1$ ) and ( $M_1$ ) respectively and its size and concentration after dilution ( $V_2$ ) and ( $M_2$ ) so:

$$V_1 \times M_1 = V_2 \times M_2$$

#### Exercise 4-7

A solution of 2L and a concentration of 1.5M of  $\text{Na}_2\text{CO}_3$ , how many grams of carbonate sodium you need to prepare this solution?

Figure 4-2

Dilute solution:

(A) Volumetric flask fills with 100 mL solution of 0.10 M potassium chromate.  
(B) The solution was completely converted to 1L volumetric flask. (C) Distilled water was added until the beaker reaches the final volume of (1L). The new solution is 0.01 M and its volume is 1L and contains the same amount of  $\text{K}_2\text{CrO}_4$  as if contained in the original solution before dilution.

### Example 4-5

Calculate the molarity concentration of sodium hydroxide in a solution prepared by adding 150 mL of distilled water to 100 mL of NaOH solution with a concentration of 0.2 M.

#### solution

$$V_1 = 100 \text{ mL}, M_1 = 0.2 \text{ M}$$

$$V_2 = 100 \text{ mL} + 150 \text{ mL} = 250 \text{ mL}$$

$$M_2 = ?$$

$$V_1 \times M_1 = V_2 \times M_2$$

$$M_2 = \frac{V_1 \times M_1}{V_2} = \frac{100 \text{ mL} \times 0.2 \text{ mol/L}}{250 \text{ mL}} = 0.08 \text{ mol/L} = 0.08 \text{ M}$$

### 4-3-4 Aqueous and non-aqueous solutions

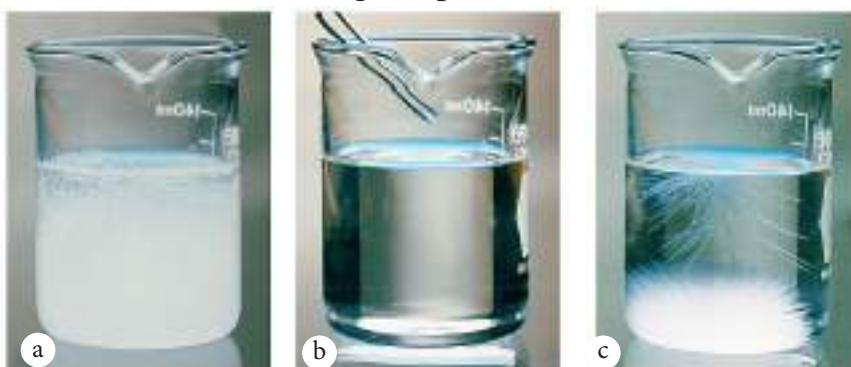
The solution in which water is a solvent is called aqueous solution such as water-sugar solution and sodium chloride in water solution, while a solution in which a liquid other than water is soluble is called a non-aqueous solution, such as sulfur solution in carbon disulfide and naphthalene solution in gasoline.

### 4-3-5 Saturated and unsaturated solutions

The solution that cannot be dissolved an additional amount of solute at a certain temperature, is called a saturated solution, [Figure (4-5a)], while the solution in which a greater amount of solute can be dissolved, at a given temperature, is called an unsaturated solution [Figure 4.5b]. It should be noted here that the saturated solution at a certain temperature can become an unsaturated solution if the temperature increases (considering that solubility of most substances increases with increasing temperature) and vice versa.

Figure 4-5

- a : saturated solution.
- b : unsaturated solution.
- c : supersaturated solution.



A condition that the solution can reach is called an oversaturation state, the solution is therefore called the supersaturated solution [Figure (4-5c)]. It can be defined as a solution that contains an additional amount of solute from that calculated at equilibrium (saturation state) at a certain temperature. The condition above the saturation that the solution may reach, its unstable state in which the solution attempts to reach a stable state (saturation). This can be assisted by adding a crystal of the solute or any other solid or by moving the solution.

#### 4-3-6 Solubility

Solubility of a substance is defined as the largest quantity of the matter (grams or moles ... etc.) that can dissolve in a certain amount (volume or mass) of solvent or solution at specific temperature and pressure. Therefore solubility is often defined as a substance dissolved in a given solvent at any temperature as the number of grams solute which can dissolve to reach the saturation state at 100 g of solvent.

#### 4-3-7 Factors affecting solubility

There are a number of factors affecting solubility:

##### 1. Temperature

Increased temperature often leads to increased solubility and vice versa true, but this rule does not necessarily apply in general. For this reason you should follow the following:

If the process of solute dissolved in specific solvent to low temperature solution (cooler solution) The rate of solubility increases with temperature, an example is that the solubility of potassium nitrate salt increases with temperature increasing. If soluble solubility in a particular solvent leads to overheating of the resulting solution (the resulting solution is hotter), the solubility will decreases by increasing the temperature such as the process of soluble calcium oxide in water. Gas solubility is generally greater in cold solvents than in hot solvents.

##### 2. The nature of the solute and the nature of the solvent

Solubility depends mainly on the nature of both solute and solvent. A general rule of solubility is like dissolves like. The polarized solute dissolves in a polarized solvent (such as solubility of potassium chloride in water), while the non-polarized solute dissolves in a non-polarized solvent (such as iodine solubility in carbon tetrachloride).

### 3. Pressure:

Pressure change has no noticeable effect on solubility solid or liquid materials however, increased pressure leads to increased solubility of gases.

#### 4-3-8 Factors that accelerate the solubility process

There are a number of factors that affect the speed of solubility of the material (but it does not affect solubility):

##### 1. The volume of solute particles

When the solute is dissolved, the solubility process takes place on the outer surface of each particle of the solute, which is in contact with the solution. Therefore, increasing the total surface area of the precipitate (contact area with the solution) will increase the solubility. Solute particles grinding and making them smaller sizes increases the total surface area for these particles which increases the rate of solubility.

##### 2. Stirring and shaking

Stirring or shaking exposes the surface of the solute particles to new batches of solvent continuously and this leads to increased solubility rate.

##### 3. Temperature

Temperature increases lead to solubility increasing of the solids and liquids, which have been described previously, and to increase solubility rate because it increases the movement of the components of the solution by increasing its kinetic energy and creating convection currents in it and thus have the same effect as the mechanical stirring process. On the other hand, the effect of increasing temperature is adversely affecting the solubility rate of gases. Increasing the temperature increases the kinetic energy of the gas molecules leading to overcoming the interconnected forces that bind gas molecules to components, so it can escape the solution.

#### 4-3-9 Real solutions, plankton and colloidal systems

##### 1. Real Solution:

Is a homogeneous solution in which the solute particles have volumes ranging from (0.1-1.0nm) ( $1.0\text{nm}=10^{-9}\text{m}$ ) that is within molecular volumes, so their solubility in the solution form a homogeneous system. They can be seen even with the strongest types of microscopes or separated from the solution by filtration such as sodium chloride solution in water or sugar water solution.

## 2. Colloidal systems

Also called colloidal solutions, colloidal state or colloidal diffusion, it's a case between real solutions and plankton. Solute particles size are ranged between (1.0-100nm). So they form a heterogeneous two-phase system (solid and liquid) in which the solute particles aren't separated by sedimentation. It seems to the naked eye or the use of a normal microscope as the real solution and solute can not be separated by filtration and examples of this type are milk and blood. However, if a high beam of light is projected onto the solution and then viewed from a vertical angle relative to the direction of incident light, it is able to see the light dispersed by the solution. This phenomena is called the "Tyndall effect" and is characteristic of colloidal solutions [Figure 4-6].

## 3. Plankton

They are solid particles stuck in a liquid medium and therefore they are systems consisting of two distinct phases (solid and liquid) with a solute particles size more than (100 nm). The solute particles in these systems may be invisible, but they can be seen with a microscope. It forms a heterogeneous and unstable system (i.e., a temporal state) because of the ability of the solute particles to sediment is stagnated by gravity and can be easily separated by filtration such as sodium chloride is stuck in gasoline and sand is stuck in water. Figure (4-7) and Table (4-2) show the relationship between the solutions properties and solute particles diameter dissolved in them.

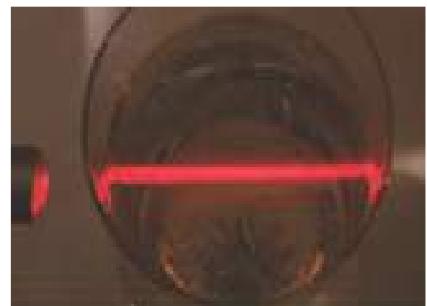


Figure 4-6

It enables us to see the beam of ablation falling on the colloidal solution from a vertical angle relative to the direction of the rays. Because of their reflection from the surface of the suspended particles in the solution.

Table (4-2) Relationship between the solutions and diameter of solute particles

| Mixture       | Particle diameter | Properties   |
|---------------|-------------------|--|
| Real solution | Less than 1.0nm   | The solute particles pass through the precise filter, and cannot distinguish them with a microscope and have a high diffusion capacity.  |
| Colloids      | Between 1.0-100nm | The solute particles pass through the usual filter papers but it does not pass through precise filters and can identify by a microscope and has a weak ability to spread.  |
| Plankton      | More than 100nm   | Plankton granules do not pass through the pores of normal filter papers and has no ability to spread. The usual filtration has no propagation potential. It can be seen with a normal microscope and sometimes with the naked eye. |

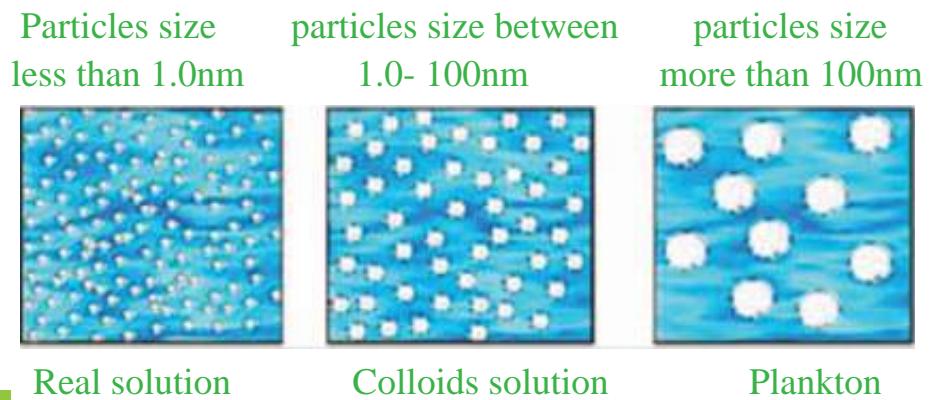


Figure 4-7

Comparing volumes of solute particles in various solutions.

### 4-3 Raoult's law

For a solution containing two components similar in properties such as toluene and benzene or heptane and octane blends, each component behaves if it were pure. This type of solution is approaching behavior of the ideal solution and it is called the ideal solution. If the ideal solution contains volatile components A and B, Raoult law provides as follows:

**“The vapor pressure of any component in an ideal solution is directly proportional with the molar fraction of that component in the solution”** this proportionality can be expressed as the following:

$$P_A \propto x_A$$

or for a relationship of equality

$$P_A = x_A P_A^\circ$$

where  $P_A$  represents the vapor pressure of component A in the solution and fraction  $x_A$  represent the molar of this component.  $P_A^\circ$  represents a constant proportional (vapor pressure of pure component). The same applies to the other component B in the solution.

$$P_B \propto x_B$$

$$P_B = x_B P_B^\circ$$

The total vapor pressure of the solution ( $P_T$ ) is equal to the total sum of the two components partial vapor pressure according to Raoult Law:

$$P_T = P_A + P_B$$

This relationship can be represented by the graph shown in Figure 4-8. All solutions that obey Raoult's law are called ideal solutions, however in fact, most solutions do not exhibit ideal behavior. While called

solutions not obey Raoul's Law are not ideal, which are called real solutions.

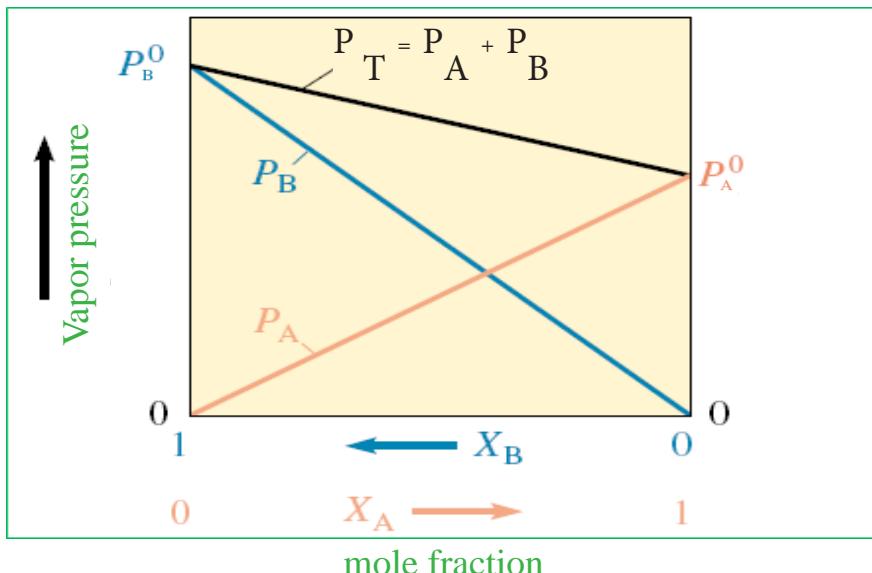


Figure 4-8

Raoul's law of an ideal solution consisting of two volatile components.

### Example 4-6

At 40 °C, the vapor pressure of the pure heptane and octane are 92 Torr and 31 Torr respectively. Calculate the pressure the vapor for each component in the solution and the total vapor pressure of the component solution for solution of 1 mole of heptane and 4 mole of octane?

**solution**

Raoult's law

$$P_A = x_A P_A^0$$

we symbolize heptane with the letter H and octane with the letter O. First, the mole fraction heptane ( $x_H$ ) and octane ( $x_O$ ) in solution

$$x_H = \frac{n_H}{n_H + n_O} = \frac{1 \text{ mol}}{1 \text{ mol} + 4 \text{ mol}} = 0.2$$

Since the sum of the molar fractions of the components of the solution is equal to one,  $x_O$  is equal to:

$$x_O = 1 - x_H = 1 - 0.2 = 0.8$$

By applying the Raoult's law for volatile components, we obtain

$$P_H = x_H P_H^0 = (0.2)(92 \text{ Torr}) = 18.4 \text{ Torr}$$

$$P_O = x_O P_O^0 = (0.8)(31 \text{ Torr}) = 24.8 \text{ Torr}$$

$$P_T = P_H + P_O = 18.4 \text{ Torr} + 24.8 \text{ Torr} = 43.2 \text{ Torr}$$

### Exercise 4-10

Steam pressures for pure benzene ( $C_6H_6$ ) and pure toluene ( $C_7H_8$ ) is 44.5 Torr and 88.7 Torr at a certain temperature. An ideal solution was prepared at the same temperature by mixing 60 g of benzene with 40 g of toluene. Calculate the partial vapor pressure of benzene and toluene in the solution and total vapor pressure (atomic masses H = 1 and C = 12)

## 4-5 Effect of non-volatile solute on some solvent properties

The physical properties of the solution, which depend only on the number of particles of the solute (molecules or ions), and not on the type of those particles, in a certain amount of solvent are called the colligative properties. There are four important properties of this type of solution that are directly proportional to their value with the number of solute particles present, namely:

1. Lowering vapor pressure of solution.
2. Increasing boiling point of solvent.
3. Decreasing freezing point of solvent.
4. Osmosis pressure.

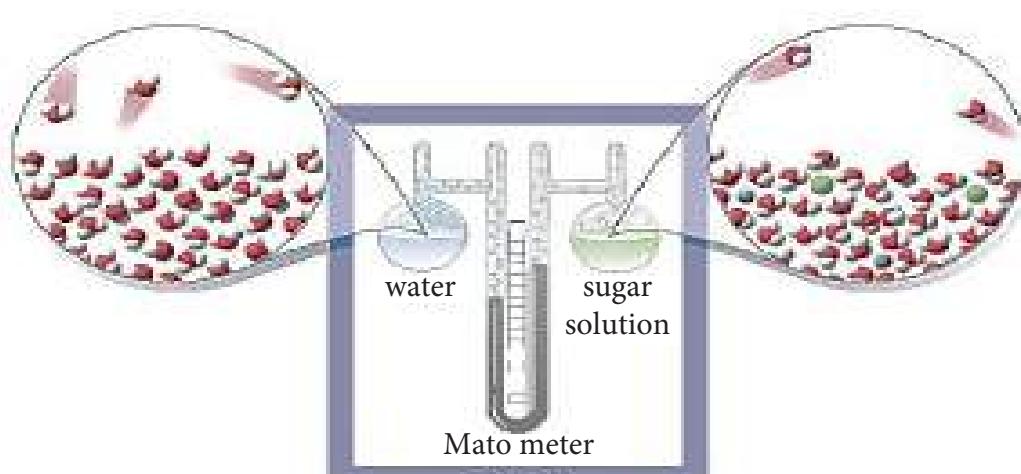
All of these properties depend on the total concentration of the solute particles regardless of the ionic or molecular or charge or volume nature. The effect of solubility of non-electrolyte and non-volatility materials is discussed (which, when it dissolves, that it will produce one mole of soluble species per mole of solute) as follows:

### 1. Lowering vapor pressure of solution

Many experiments have shown that a solution containing a nonvolatile liquid or a solid as a solute always has a lower vapor pressure than the pure solvent (Figure 4-9). The vapor pressure of a liquid depends on the ease with which the molecules are able to escape from the surface of the liquid. When a solute is dissolved in a liquid, some of the total volume of the solution is occupied by solute molecules, and so there are fewer solvent molecules per unit area at the surface of the liquid decreases and the vapor pressure of the solution decreases.

Figure 4-9

Lowering vapor pressure. If no air is present in the apparatus, the pressure above each liquid is due to water vapor. This pressure is less over the solution of sugar and water.



## 2. Increasing boiling point of solvent

The definition of boiling point of a liquid is the temperature at which its vapor pressure equals the applied pressure at its surface. For liquids in open containers, this is atmospheric pressure. We have seen that the vapor pressure of a solvent at a given temperature is lowered by the presence of a nonvolatile solute. Such a solution must be heated to a higher temperature than the pure solvent to cause the vapor pressure of the solvent to equal atmospheric pressure (Figure 4-10). In accord with Raoult's Law, the elevation of the boiling point of a solvent caused by the presence of a nonvolatile, nonionized solute is proportional to the number of moles of solute dissolved in a given mass of solvent. Mathematically, this is expressed as

$$\Delta T_b \propto m$$

$$\Delta T_b = K_b m$$

The term  $\Delta T_b$  represents the elevation of the boiling point of the solvent, that is, the boiling point of the solution minus the boiling point of the pure solvent. The  $m$  is the molality of the solute, and  $K_b$  is a proportionality constant called the molal boiling point elevation constant. This constant is different for different solvents and does not depend on the solute.  $K_b$  corresponds to the change in boiling point produced by a one-molal ideal solution of a nonvolatile nonelectrolyte. The units of  $K_b$  are  $^{\circ}\text{C}/\text{m}$ .

Table (4-3) shows Some properties of common solvents

Table (4-3) shows Some properties of common solvents

| solvent      | Boiling point ( $^{\circ}\text{C}$ )<br>(pure solvent) | Increasing molal boiling<br>constant $K_b$ $^{\circ}\text{C}/\text{m}$ | Freezing point<br>( $^{\circ}\text{C}$ )(pure solvent) | Decreasing molal<br>freezing point $K_f$ $^{\circ}\text{C}/\text{m}$ |
|--------------|--|--|--|--|
| water        | 100  | 0.512  | 0.00   | 1.86   |
| benzene      | 80   | 2.530  | 5.48   | 5.12   |
| acetic acid  | 118  | 3.070  | 16.60  | 3.90   |
| nitrobenzene | 210  | 5.240  | 5.70   | 7.00   |
| phenol       | 182  | 3.560  | 43.00  | 7.40   |
| camphor      | 207  | 5.601  | 178.40   | 40.00  |

We have already identified molality and knowledge of the following relationship with the symbol for solvent 1 and solute 2

$$m \text{ (mol/kg)} = \frac{n_2 \text{ (mol)}}{m_1 \text{ (kg)}}$$

As is known, the number of moles of solute is equal to

$$n_2 = \frac{m_2 \text{ (g)}}{M_2 \text{ (g/mol)}}$$

#### Exercise 4-11

When 0.15 g of a substance is dissolved in 15 g of a solvent, the boiling point of the solvent is increased by 0.216 °C at boiling point of pure solvent. What is the molar mass of the solute if you know that the constant of the increasing boiling point of the solvent is equal to 2.16 °C/m?

Where  $m_2$  is the mass of the solute in unit (g) and  $M_2$  is the molar mass of the solute (g/mol). The mass of the solvent ( $m_1$ ) is converted from the unit (g) to (kg)

$$m_1 \text{ (kg)} = m_1 \text{ (g)} \times \frac{1 \text{ (kg)}}{1000 \text{ (g)}} = \frac{m_1 \text{ (g)}}{1000 \text{ (g/kg)}}$$

Substitute in molality formula, we get

$$m \text{ (mol/kg)} = \frac{\frac{m_2 \text{ (g)}}{M_2 \text{ (g/mol)}}}{\frac{m_1 \text{ (g)}}{1000 \text{ (g/kg)}}} = \frac{1000 \text{ (g/kg)} \times m_2 \text{ (g)}}{m_1 \text{ (g)} \times M_2 \text{ (g/mol)}}$$

Therefore, increasing boiling point equal to

$$\Delta T_b \text{ (°C)} = K_b \text{ (°C/m)} \times \frac{1000 \text{ (g/kg)} \times m_2 \text{ (g)}}{m_1 \text{ (g)} \times M_2 \text{ (g/mol)}}$$

#### Example 4-7

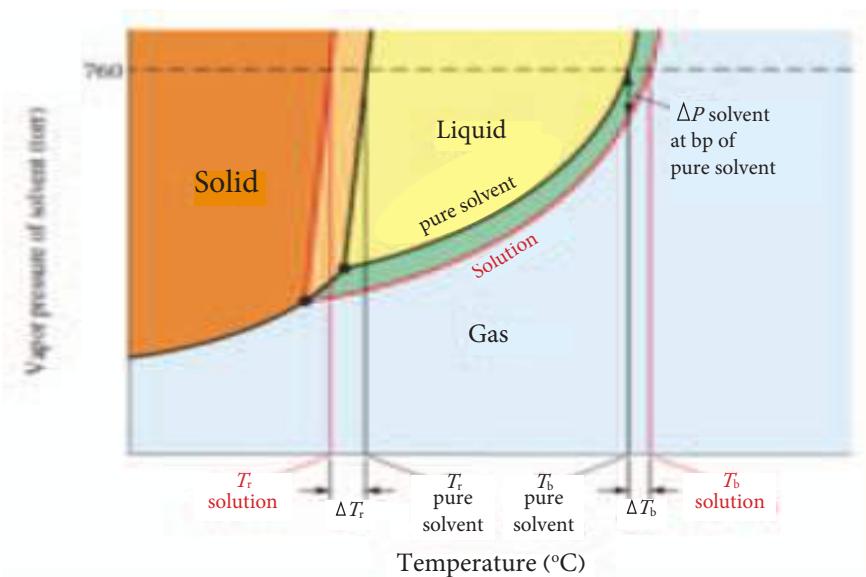
Predict the boiling point of the 1.25 m sucrose solution? Note that The boiling point of pure water is 100 °C and increasing molal boiling point constant for water is 0.512 °C/m.

#### solution

Use the relationship  $\Delta T_b = K_b m$  to find the amount of increase first and then add this increase to the boiling point of pure water:

$$\Delta T_b = (0.512 \text{ °C/m}) (1.25 \text{ m}) = 0.640 \text{ °C}$$

This means that the solution will boil at a temperature higher than the boiling point pure water by a value 0.640 °C, so the boiling point of the solution will be  $100 \text{ °C} + 0.640 \text{ °C} = 100.640 \text{ °C}$



### 3. Decreasing freezing point of solvent

Molecules of liquids move more slowly and approach one another more closely as the temperature is lowered. The freezing point of a liquid is the temperature at which the forces of attraction among molecules are just great enough to overcome their kinetic energies and thus cause a phase change from the liquid to the solid state. Strictly speaking, the freezing (melting) point of a substance is the temperature at which the liquid and solid phases are in equilibrium. When a dilute solution freezes, it is the solvent that begins to solidify first, leaving the solute in a more concentrated solution. Solvent molecules in a solution are somewhat more separated from one another (because of solute particles) than they are in the pure solvent. Consequently, the temperature of a solution must be lowered below the freezing point of the pure solvent to freeze it.

The freezing point depressions ( $\Delta T_f$ ) of solutions of non-electrolytes have been found to be equal to the molality (m) of the solute multiplying constant called the molal freezing point depression constant,  $K_f$ . The values of  $K_f$  for a few solvents are given in Table 4-3.  $K_f$  knows as the freezing point depression of a one-molal ideal solution of a nonelectrolyte in that solvent.

The relationship is as follow and similarly to the relationship of the increasing in boiling point:

$$\Delta T_f (\text{°C}) = K_f (\text{°C/m}) \times \frac{1000 \text{ (g/kg)} \times m_2 \text{ (g)}}{m_1 \text{ (g)} \times M_2 \text{ (g/mol)}}$$

where  $\Delta T_f$  represent freezing point depression (pure solvent freezing point- solution freezing point)

Figure 4-10

Increasing boiling point (by a value  $\Delta T_b$ ) Decreasing freezing point (by a value  $\Delta T_f$ ). Because a nonvolatile solute lowers the vapor pressure of a solvent.

### Example 4-8

When 15.0 grams of ethyl alcohol (atomic mass = 46 g/gmol), is dissolved in 750 grams of formic acid, the freezing point of the solution is 7.21 °C. The freezing point of pure formic acid is 8.40 °C. Evaluate  $K_f$  for formic acid.

#### Solution

We find the value of  $\Delta T_f$  from difference between the freezing point of pure solvent and pure freezing point of solution:

$$\Delta T_f = 8.40^\circ\text{C} - 7.21^\circ\text{C} = 1.19^\circ\text{C}$$

Apply the relationship

$$\Delta T_f (\text{°C}) = K_f (\text{°C/m}) \times \frac{1000 \text{ (g/kg)} \times m_2 \text{ (g)}}{m_1 \text{ (g)} \times M_2 \text{ (g/mol)}}$$

So  $K_f$  value equal

$$K_f = \frac{\Delta T_f (\text{°C}) \times m_1 \text{ (g)} \times M_2 \text{ (g/mol)}}{1000 \text{ (g/kg)} \times m_2 \text{ (g)}}$$

$$K_f = \frac{1.19 \text{ (°C)} \times 750 \text{ (g)} \times 46 \text{ (g/mol)}}{1000 \text{ (g/kg)} \times 15 \text{ (g)}} = 2.74 \text{ °C/m}$$

### Exercise 7-3

What is the freezing point of aqueous solution of 0.05m for non-electrolyte solute? Note that the constant of molal freezing point depression of water is 1.86 °C/m.

### Example 4-9

Soluble 1.2 g of an unknown covalent compound in 50 g of benzene, and the freezing point of the solution was found to be 4.92 °C. Calculate the molar mass of the unknown compound, if you know that the freezing point of pure benzene is 5.48 °C and the value of  $K_f$  is 5.12 °C/m.

#### Solution

Firstly, we find the value of  $\Delta T_f$  which is equal to the freezing point of the pure solvent - the freezing point of the solution:

$$\Delta T_f = 5.48^\circ\text{C} - 4.92^\circ\text{C} = 0.56^\circ\text{C}$$

Use the relationship

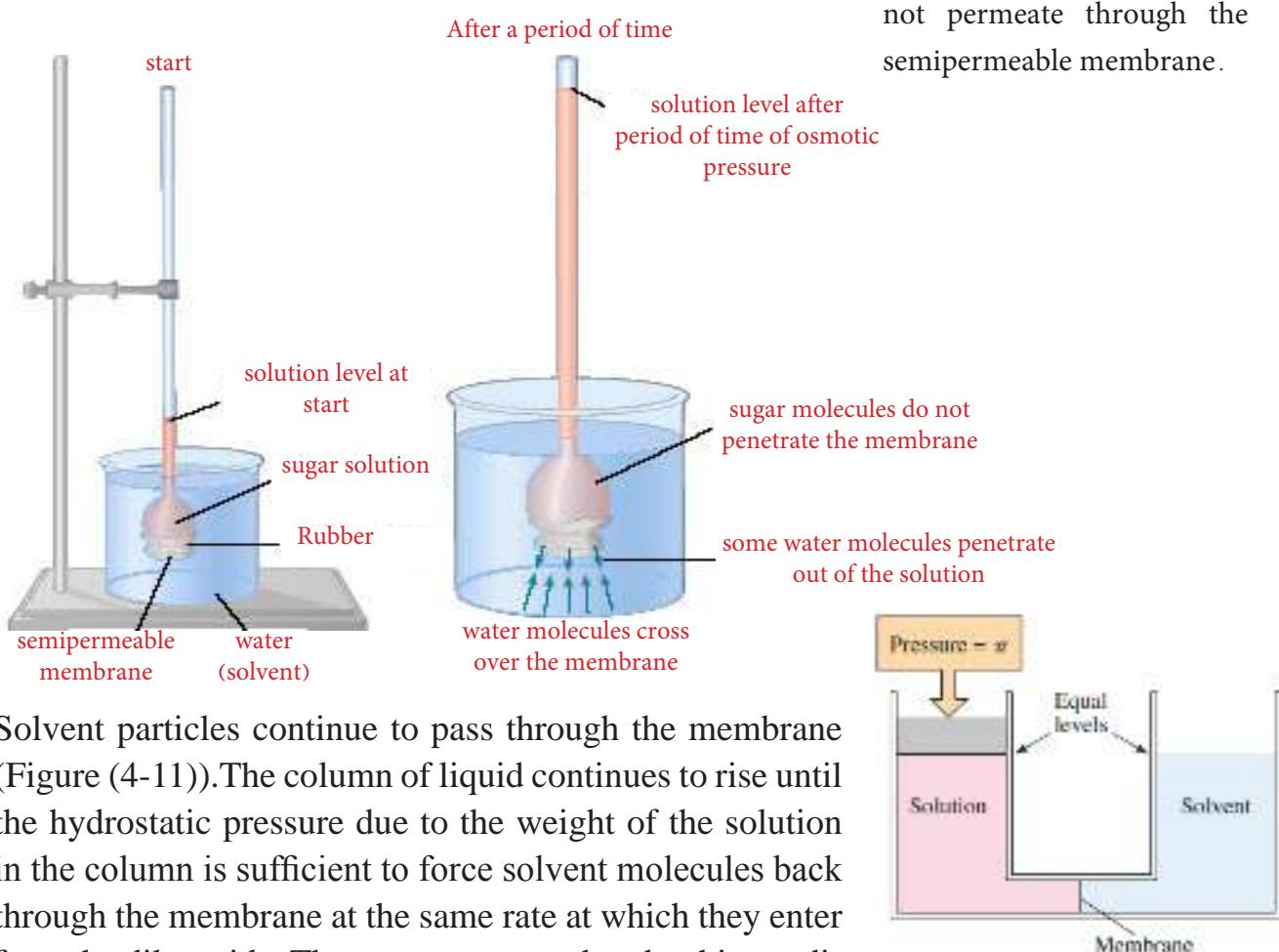
$$\Delta T_f (\text{°C}) = K_f (\text{°C/m}) \times \frac{1000 \text{ (g/kg)} \times m_2 \text{ (g)}}{m_1 \text{ (g)} \times M_2 \text{ (g/mol)}}$$

$M_2$  value will be

$$M_2 \text{ (g/mol)} = \frac{5.12 \text{ (°C/m)} \times 1000 \text{ (g/kg)} \times 1.2 \text{ (g)}}{50 \text{ (g)} \times 0.56^\circ\text{C}} = 219.4 \text{ g/mol}$$

#### 4. Osmosis pressure

Osmosis is the spontaneous process by which the solvent molecules pass through a semi – osmotic (semipermeable) membrane from a solution of lower concentration of solute into a solution of higher concentration of solute). A semipermeable membrane separates two solutions. Solvent molecules may pass through the membrane in either direction, but the rate at which they pass into the more concentrated solution is found to be greater than the rate in the opposite direction. The initial difference between the two rates is directly proportional to the difference in concentration between the two solutions.



Solvent particles continue to pass through the membrane (Figure (4-11)). The column of liquid continues to rise until the hydrostatic pressure due to the weight of the solution in the column is sufficient to force solvent molecules back through the membrane at the same rate at which they enter from the dilute side. The pressure exerted under this condition is called the osmotic pressure of the solution. Osmotic pressure depends on the number, and not the kind, of solute particles in solution; it is therefore a colligative property. The osmotic pressure of a given aqueous solution can be measured by shedding an equal external pressure to it (sufficient pressure to prevent osmosis) as shown in Figure (4-12). The external pressure to be shed is equal to the solution osmotic pressure.

Figure 4-11

Laboratory instruments to display the osmotic property, the solute molecules can not permeate through the semipermeable membrane.

Figure 4-12

The pressure that is just sufficient to prevent solvent flow from the pure solvent side through the semipermeable membrane to the solution side is a measure of the osmotic pressure of the solution.

The osmotic pressure can be calculated using a law-like mathematical relationship for general gases

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

Replace the pressure symbol  $P$  with symbol  $\pi$  which indicates the osmotic pressure, as follows:

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

In this equation  $n$  is the number of moles of solute in volume,  $V$ , (in liters) of the solution.  $R$  is the gas constant (0.0821 L. atm/mol. K) and  $T$  temperature in degree Kelvin. The term  $n/V$  is a concentration term. In terms of molarity,  $M$ ,

$$\pi = MRT$$

Osmotic pressure increases with increasing temperature because  $T$  affects the number of solvent–membrane collisions per unit time. It also increases with increasing molarity because  $M$  affects the difference in the numbers of solvent molecules hitting the membrane from the two sides, and because a higher  $M$  leads to a stronger drive to equalize the concentration difference by dilution and to increase disorder in the solution.

### Solution

In general the solution is defined as a homogeneous mixture of substances consisting of solvent and one solute or more. Mixing ratios among them are different from solution to solution. The largest amount in the mixture is the solvent and the least amount is solute.

### Molality m

Molality is the number of solute moles, which it contains in one kilogram of solvent

$$m \text{ (mol/kg)} = \frac{n \text{ (mol)}}{m \text{ (kg)}}$$

### Mole Fraction x

Defined as the ratio between the number of components of a component ( $n_A$ ) to the total number of components of all components ( $n_A + n_B$ ). They can be expressed as follows:

$$x_A = \frac{n_A}{n_A + n_B} \quad \text{or} \quad x_B = \frac{n_B}{n_A + n_B}$$

### Molarity M

Molarity is the number of solute moles, in one liter of solution

$$M = \frac{n \text{ (mol)}}{V \text{ (L)}}$$

### Solubility

Solubility of a substance is defined as the largest amount of matter (number of grams, number of moles,... etc.) that can dissolve in in certain (volume or weight)

of solvent or solution at specific temperature and pressure.

### Raoult's Law

The vapor pressure of a solvent in an ideal solution is directly proportional to the mole fraction of the solvent in the solution.

$$P_A \propto x_A \Rightarrow P_A = x_A P_A^o$$

$$P_B \propto x_B \Rightarrow P_B = x_B P_B^o$$

### Osmotic Pressure

Osmosis is spontaneity process by which solvent molecules pass through a semi-permeable membrane from a dilute solution into a more concentrated solution in solute. Also solvent molecules pass through the membrane in both directions and The shed pressure at this condition are called the osmotic pressure.

4-1 Give an example of a solution that contains each of the following:

- a solid dissolved in a liquid.
- a gas dissolved in a gas.
- a gas dissolved in a liquid.
- a liquid dissolved in a liquid.
- a solid dissolved in a solid.

4-2 Discuss the following statement: that the heat produced or consumed during the dissolution process are important factor in determining the solubility or dissolution of solute. What is the other important factor? How does it affect the process?

4-3 Define all of the following: the molar fraction of a component in a solution, Raoult's law, the osmotic pressure, Saturated solution.

4-4 How many grams of table salt are needed to dissolve in 40 mL of water to obtain a solution salt where the mass percentage of salt is 15%? (Water density = 1 kg / L).

4-5 How to prepare 250 mL of diluted hydrochloric acid solution a concentration of 0.5 M from concentrated acid solution of 12M? Explain this with the required calculations.

4-6 A 60 mL sample of diethyl ether,  $(C_2H_5)_2O$ , is dissolved in enough methanol,  $CH_3OH$ , to make 300 mL of solution. The density of the ether is 0.714 g/mL. What is the molarity M of this solution?

4-7 Explain, using the necessary calculations, how you can prepare one liter of sodium chloride solution (NaCl) has a concentration of 0.215 m, if you know the resulting solution density is 1.01 g/mL.

4-8 A solution was prepared for potassi-

um hydroxide, by dissolving 1g of KOH in 100 mL of ethyl alcohol ( $C_2H_5OH$ ) (alcohol density = 0.789 g / mL), expressing the concentration of the resulting solution by:

1. Molarity concentration.
2. Molal concentration.
3. Mole fraction of sodium hydroxide.
4. Mass percentage of sodium hydroxide.

4-9 Calculate the boiling point of the aqueous solution of ethylene glycol compound (non-volatile substance) of concentration 2.5 m. (The boiling point of pure water is 100 °C). Note that the molal constant of water increasing boiling point is ( $K_b = 0.512 \text{ } ^\circ\text{C}/\text{m}$ )

4-10 Dissolve 3.75 g of non-volatile substance in 95 g of acetone, the boiling point increased to (56.50 °C), compared to the boiling point of pure acetone (55.95 °C). Note that the molal constant of acetone increasing boiling point is ( $K_b = 1.71 \text{ } ^\circ\text{C}/\text{m}$ ). what is the molar mass of a solute?

4-11 When grinding 0.154 g of sulfur smoothly and dissolved in 4.38 g of camphor, freezing point of camphor is decreased by 5.47 °C. What is molar mass of sulfur and its molecular formula? If you know that molar constant of camphor depression freezing ( $K_f = 40 \text{ } ^\circ\text{C}/\text{m}$ )

4-12 Using the Table (4.3), what is the material that caused the greatest depression in the degree of freezing?

|                |            |
|----------------|------------|
| A. Benzene     | B. Camphor |
| C. Acetic acid | D. Phenol  |

4-13 Using Table 4.3, find the freezing point of a solution prepared by dissolving 1.5 g of matter has a molar mass of 125 g / mol in 30 g of nitrobenzene.



## Chapter Five

## Chemical Kinetics

5

After completing this chapter, the student is expected to:

- Calculates the reaction rate in terms of the change in the concentration of material over time.
- Determine the rate of reaction and deduces the law of reaction speed.
- Explain chemical reactions by collision theory and transition state theory.
- Determine the factors influencing reaction rate and how to control it to increase reaction speed.
- Distinguish between exothermic and endothermic reactions.
- Propose an acceptable reaction mechanism that conforms to the specified conditions.

## 5-1 Introduction

We have learned from our previous study of chemical changes and simplified that they occur between the reactants to form the products, and expressed by a balanced chemical equation, which is useful in calculating the number of moles and masses of materials and the volumes of reactive and resulting gases. But the chemical equation did not tell us other details regarding the speed at which the reactants are converted into products as well as the number of steps that the reaction pass to create the products. All these changes are studied by chemical kinetics and concern by the following points:

1. The rate of the chemical reaction and how to measure it and the factors affecting it.
2. The reaction mechanism, ie the initial reactions that the reactants pass through to reach the final product and how they are expressed in balanced chemical equations. Chemical kinetics is an important science because knowledge speed of the reaction and the factors that affect it, such as concentration, pressure, temperature, and the nature of the reactants, allow students to predict how quickly the reaction will reach equilibrium. Also and that study of the reaction mechanism (the initial steps that the reaction passes through to the reaction of the reactants into the products), enables them, when they know, to control the flow of the reaction to obtain the desired material in the required quantities and in appropriate economic ways.

## 5-2 Chemical reaction speed

The definition of speed is familiar in our daily lives. If a car drives 70 kilometers in one hour, we say it has a speed of 70 Kilometer / hour, or student reads twenty pages of a book in 30 minute, or the people of Baghdad consume one million cubic meters of potable water per day. These expressions of speed share a common explanation that a change occurs over a certain period of time. The speed of the car expresses the change in place measured in kilometers per hour. For a student reading a book, the number of pages read increases twenty pages every 30 minutes. As for the people of Baghdad who consume one million cubic meters of potable water per day, water tanks will decrease by one million cubic meters during this time period.

Similar to chemical reactions, they occur at varying rate according to the change in the quantities of substances entering or leaving the reaction per unit of time. Chemical reactions vary in rates. Some of them are very fast when mixing the reactants in a fraction of a second, such as neutralization reactions between acids and bases and combustion reactions. Others have moderate rates that take several minutes to several months, such as iron rust and reactions that lead to the ripening of fruits and vegetables. There are very slow reactions that take several years or millions of years to occur, such as reactions that lead to human growth and age and turn dead plants into coal. Note the Figure (5-1).

### 5-2-1 Measurement of chemical reaction rate

The rate of a chemical reaction is measured by knowing the concentration change in reactive or product material in unit of time (unit of time may be second (s), minute (min), hour (hr), day (day) or any other units of time). In this chapter we will use the molar concentration exclusively, which is defined as the number of moles of solute in one liter of solution (mole /L) expressed by a square arc [ ], where any symbol inside the arc means molar concentration. For example [X] means the molar concentration of material X. So we will express the rate in the mathematical relationship as the following:

$$\text{Rate} = \frac{\Delta [ ]}{\Delta t}$$

rate of reaction=( Change in concentration of one of the reactants/change in time)

Where  $\Delta$  means change, and [ ] means molar concentration in unit (mol/ L). Therefore have the chemical reaction rate unit:

(mole / L.t )(or).( mole  $L^{-1} t^{-1}$ )

For the following general reaction:



Where R represents any (reactant) and P represents any product substance. The rate of this general reaction is calculated by

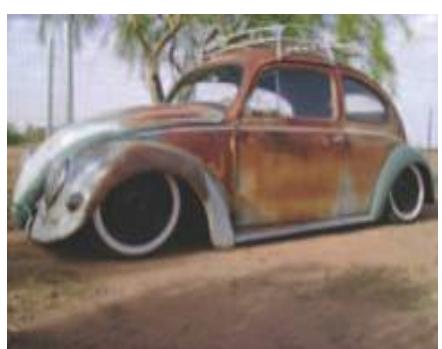
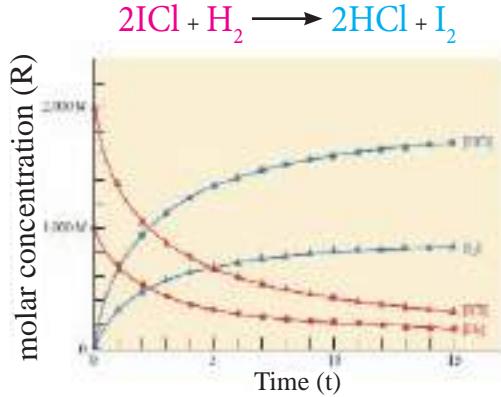


Figure 5-1

Differential reaction rate, from top to bottom: combustion is very fast reaction, ripening fruits and vegetables Moderate reaction rate, rust a iron reaction moderate rate and lower than rate of fruit ripening, human growth reaction is very slow.



The concentration of reactants **ICl** and **H<sub>2</sub>** decreases, while the concentration of the resulting substances **HCl** and **I<sub>2</sub>** increases over time.

**Figure 5-2**

The concentration of reactant R decreases over time.

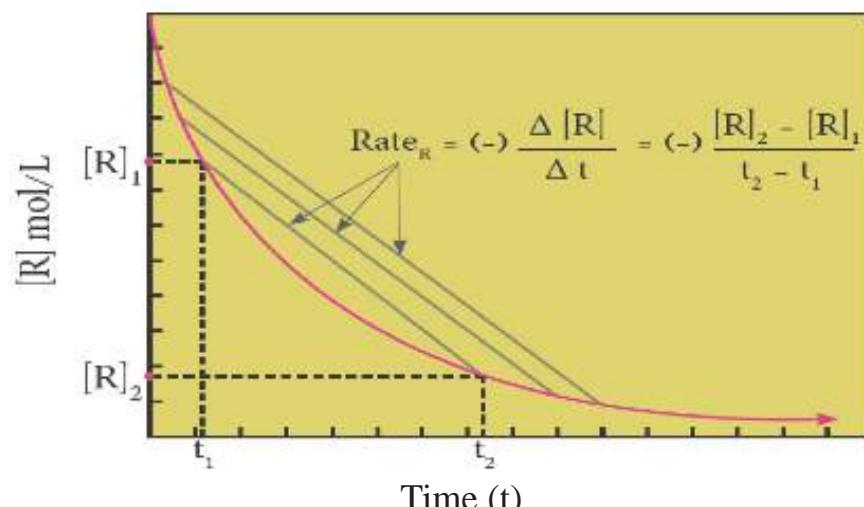
The relationship above and in terms of reactants R and as follows:

Rate of reaction in term R = (-)concentration of R/change in time

$$\text{Rate}_R = (-) \frac{\Delta [R]}{\Delta t}$$

If the reaction starts with a certain concentration of the reactant, let  $[R]_1$  be in the time of  $(t_1)$  and as the reaction progresses, the concentration of the reactant material decreases, while concentration of product material will be increased. In time  $(t_2)$  concentration of the reactant material  $[R]_2$ , Note Figure (5-2), rate of reaction in term of R as follows:

$$\text{Rate}_R = (-) \frac{\Delta [R]}{\Delta t} = (-) \frac{[R]_2 - [R]_1}{t_2 - t_1}$$



The negative signal is added in the law when expressing the reaction rate in terms of the change in the concentration of a reactant, because the reactant is consumed during the reaction and its concentration is lowered, so that the second concentration is less than the first concentration and the change in concentration is negative. so the negative signal was added to make the reaction rate positive signal note Figure (5-2).

When the reaction rate is measured in terms of the change in the concentration of the substance produced by the reaction P, the relationship is as follows:

Rate of reaction in term P = change in P concentration/change in time

$$\text{Rate}_P = \frac{\Delta [P]}{\Delta t} = \frac{[P]_2 - [P]_1}{t_2 - t_1}$$

The change in the concentration of the resulting substance  $\Delta [P]$  is positive because its concentration increases over time and the second concentration is  $[P]_2$  greater than the first concentration  $[P]_1$ , so no negative sign is added in the law. As shown in Figure (5-3).

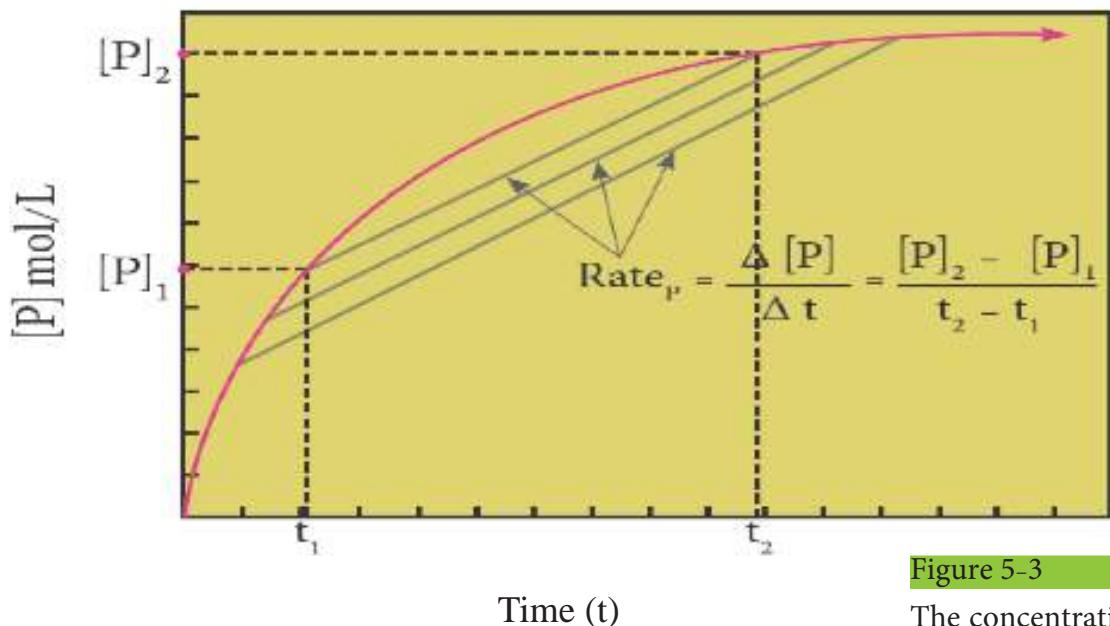
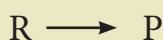


Figure 5-3

The concentration of the resulting substance P increases over time.

### Example 5-1

The concentration of material R changed from 1.2 mole / L to 0.75 mole / L over 125s depending on the following reaction:

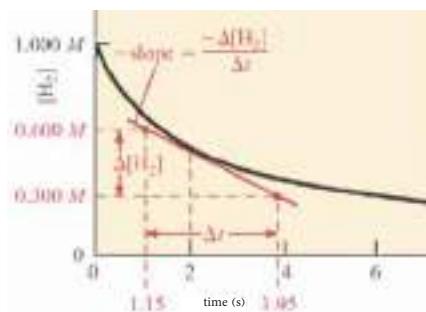


Calculate the reaction rate S as a function R.

**Solution**

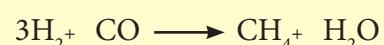
$$\text{Rate}_R = \frac{\Delta [R]}{\Delta t} = \frac{[R]_2 - [R]_1}{t_2 - t_1}$$

$$\text{Rate}_R = \frac{(0.75 - 1.20) \text{ mol/L}}{(125 - 0) \text{ s}} = 0.0036 \text{ mol/L.s}$$



### Exercise 5-1

Assume the following reaction:



The concentration of  $\text{H}_2$  varies according to the above diagram. Find the rate of this reaction and the time needed to decrease the concentration of  $\text{H}_2$  to 0.300 mol / L.

### 5-2-2 The relationship of reaction rate with the number of moles

The reaction rate varies in terms of the change in the concentration of the substance depending on the number of moles of the substance in the balanced reaction equation. For example, the reaction between hydrogen and iodine to form hydrogen iodide as in the following equation:



When one molecule of hydrogen is consumed (one mole), one molecule of iodine is also consumed (one mole), while two molecules (two moles) of hydrogen iodide is formed. ie rate of consumed of hydrogen or  $\text{I}_2$  equal to half the rate of HI formation.

$$\text{Rate} = -\frac{\Delta [\text{H}_2]}{\Delta t} = -\frac{\Delta [\text{I}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta [\text{HI}]}{\Delta t}$$

or the formation rate of HI is twice rate of consumption  $\text{H}_2$  or  $\text{I}_2$

$$\frac{\Delta [\text{HI}]}{\Delta t} = 2 \frac{\Delta [\text{H}_2]}{\Delta t} = 2 \frac{\Delta [\text{I}_2]}{\Delta t}$$

the equation can be write as follows

$$\text{Rate}_{(\text{HI})} = 2\text{Rate}_{(\text{H}_2)} = 2\text{Rate}_{(\text{I}_2)}$$

Rate(HI) means the rate in term product HI concentration, and so on for the rate in terms of the reactants  $\text{H}_2$  and  $\text{I}_2$ , we note that we are not put signals when rate is used because rate is always positive, while change in concentration is negative for reactants and positive for products substances.

For general reaction



Where (a, b, g and h) are the number of moles of substances in the balanced reaction equation, and the rate of this reaction is expressed in terms of the reactants produced as follows:

$$\text{Rate} = -\frac{1}{a} \times \frac{\Delta [\text{A}]}{\Delta t} = -\frac{1}{b} \times \frac{\Delta [\text{B}]}{\Delta t} = -\frac{1}{g} \times \frac{\Delta [\text{G}]}{\Delta t} = -\frac{1}{h} \times \frac{\Delta [\text{H}]}{\Delta t}$$

or

$$-\frac{1}{a} \text{Rate}_{(\text{A})} = -\frac{1}{b} \text{Rate}_{(\text{B})} = -\frac{1}{g} \text{Rate}_{(\text{G})} = -\frac{1}{h} \text{Rate}_{(\text{H})}$$

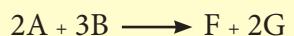
When the rate is expressed in terms of one mole of any substance involved in the reaction overall rate of reaction is used. It is the overall rate of reaction in terms of one mole of reactants or products, and as follow:

$$\text{Rate} = \frac{1}{n_j} \frac{\Delta [J]}{\Delta t}$$

Where  $n_j$  represents the number of moles of  $J$  with its negative sign of the reactants and the positive of the products, it was  $-a$  or  $-b$  or  $g$  or  $h$  in the general reaction above.

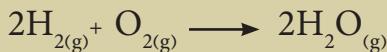
### Exercise 5-3

Which one of the expressions below do not represent the suitable expression for the general rate of reaction



### Example 5-2

For the following reaction



- Express the rate in terms of the change in concentration of  $H_2$ ,  $O_2$  and  $H_2O$ .
- Calculate the  $H_2O$  formation rate if the  $O_2$  consumption rate is equal  $0.023 \text{ mol/L.s}$
- Calculate the amount of  $H_2O$  formed after  $18\text{s}$

### Solution

$$(1) \text{Rate}_{(H_2)} = -\frac{\Delta [H_2]}{\Delta t}$$

$$\text{Rate}_{(O_2)} = -\frac{\Delta [O_2]}{\Delta t}$$

$$\text{Rate}_{(H_2O)} = \frac{\Delta [H_2O]}{\Delta t}$$

$$(2) \quad \frac{1}{2} \frac{\Delta [H_2O]}{\Delta t} = \frac{\Delta [O_2]}{\Delta t}$$

$$\text{Rate}_{(H_2O)} = 2 \text{ Rate}_{(O_2)}$$

$$\text{Rate}_{(H_2O)} = 2 \times 0.023 \text{ mol/L.s} = 0.046 \text{ mol/L.s}$$

$$(3) \text{Rate}_{(H_2O)} = \frac{\Delta [H_2O]}{\Delta t} = \frac{[H_2O]_2 - [H_2O]_1}{t_2 - t_1} = \frac{([H_2O]_2 - 0) \text{ mol/L}}{(18 - 0) \text{ s}}$$

$$[H_2O]_2 = \text{Rate}_{(H_2O)} \text{ mol/L.s} \times 18 \text{ s} = 0.046 \text{ mol/L.s} \times 18 \text{ s}$$

$$[H_2O]_2 = 0.828 \text{ mol/L}$$

### Example 5-3

The reaction between ethylene gas and ozone gas is expressed by:

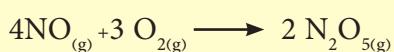


It was found that the concentration of  $\text{O}_3$  changed as the reaction progressed in the table below

| t/(s)                                  | 0    | 10   | 20   | 30   | 40   | 50   | 60   |
|--|------|------|------|------|------|------|------|
| $[\text{O}_3] / 10^{-5}(\text{mol/L})$ | 3.20 | 2.42 | 1.95 | 1.63 | 1.40 | 1.23 | 1.10 |

### Exercise 5-4

For the following reaction:



A- Express the reaction rate in terms of change in the concentration of each substance over time.

B- Calculate the rate of  $\text{O}_2$  consumption if consumption rate of NO was equal

$$1.60 \times 10^{-4} \text{ mol/L.s}$$

A- Calculate the reaction rate during the first 10s of the reaction.

B- Calculate the reaction rate during the last 10s of the reaction.

C- What is the reason for the difference between the rate of reaction in both cases?

### Solution

A- Reaction rate during the first 10s of the reaction.

$$\text{Rate}_{(\text{O}_3)} = \frac{\Delta [\text{O}_3]}{\Delta t} = \frac{[\text{O}_3]_2 - [\text{O}_3]_1}{t_2 - t_1}$$
$$= \frac{(2.42 \times 10^{-5} - 3.20 \times 10^{-5}) \text{ mol/L}}{(10 - 0) \text{ s}} = 7.8 \times 10^{-7} \text{ mol/L.s}$$

B-The reaction rate during the last 10s of the reaction.

$$\text{Rate}_{(\text{O}_3)} = \frac{\Delta [\text{O}_3]}{\Delta t} = \frac{[\text{O}_3]_2 - [\text{O}_3]_1}{t_2 - t_1}$$
$$= \frac{(1.10 \times 10^{-5} - 1.23 \times 10^{-5}) \text{ mol/L}}{(60 - 50) \text{ s}} = 1.3 \times 10^{-7} \text{ mol/L.s}$$

C- The reaction rate during the first 10s is equal to six times as reaction rate during the last 10 s, indicating that the reaction rate is not constant. It decreases over time in terms of the concentration of the reactant as a result of its consumption.

### 5-3 The reaction rate law

In general, the reaction rate is directly proportional to the product the concentrations of the reactants and each concentration are raised to a given exponent.

The following general reaction:



The reaction rate is proportional to the concentrations of the reactants as follows:

$$\text{Rate} \propto [A]^\alpha [G]^\beta [H]^\gamma$$

Or in the form of equality

$$\text{Rate} = K [A]^\alpha [G]^\beta [H]^\gamma$$

The student should note that the number of moles of the reactants  $a$ ,  $g$  and  $h$  is not related to the ranks of the reactants  $\alpha$ ,  $\beta$ , and  $\gamma$ , but are derived from practical experiments only. The general rate of reaction is represented by Rate for any of the reactants on the products as the following:

$$\text{Rate} = \frac{1}{a} \frac{\Delta[A]}{\Delta t}$$

$$\text{Rate} = \frac{1}{g} \frac{\Delta[G]}{\Delta t}$$

$$\text{Rate} = \frac{1}{h} \frac{\Delta[H]}{\Delta t}$$

$$\text{Rate} = \frac{1}{p} \frac{\Delta[P]}{\Delta t}$$

Where  $[A]$ ,  $[G]$  and  $[H]$  are the molar concentrations of A, G and H respectively.

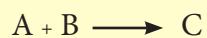
$\alpha$  is called the reactant order A and  $\beta$  is the order of the reactant G and  $\gamma$  is the order of the reactant H. The general order of the reaction  $n$  is defined as being equal to the sum of the orders of the reactants as follows:

$$n = \alpha + \beta + \gamma$$

$n$  values are zero, 1, 2, or 3 and may be fractional.  $K$  is called the reaction rate constant and the relationship above framed by the law of reaction rate.

#### Exercise 5-5

For the following gaseous reaction:



Experimentally found that the law of reaction rate

$$\text{Rate} = K [A]^2 [B]$$

So the order of this reaction

A- First order

B- Second order

C- Third order

D- zero order

E- half order

If the reaction is zero, then the values of  $\alpha$ ,  $\beta$  and  $\gamma$  are equal to zero, meaning that the reactant concentration do not affect the reaction rate and therefore the law of reaction rate for zero-order reactions is as follows:

$$\text{Rate} = K$$

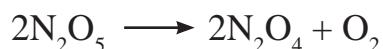
\*The student notes that the rank of the reactant in the law of reaction rate may not correspond to number of moles of that reactant in the balanced equation. so it is necessary to create the term molecular reaction and compare it with the order of reaction.

The reaction molecule is defined as the number of molecules or ions of reactants in the balanced equation that can theoretically be found from the number of moles. Either reaction order is a value that can only be known by experience, and there is another difference that the order of reaction may be zero while the reaction molecule cannot be like this.

If the reaction is a first order, the value  $\alpha = 1$  the value of  $\beta$  and  $\gamma$  is zero, the law of velocity is written as a

$$\text{Rate} = K[A]$$

For example, the following reaction is of the first order \*



The law of reaction rate is:

$$\text{Rate} = K[\text{N}_2\text{O}_5]$$

The general order of the reaction is first ( $n = 1$ )

If the second order reaction, the law of rate can be written as following forms:

$$\text{Rate} = K[A][G]$$

or

$$\text{Rate} = K[A]^2$$

So for other orders. The following examples illustrate the law of rate and orders of some reaction.

The law of reaction rate:



Is

$$\text{Rate} = K[\text{NO}]^2 [\text{H}_2]$$

\* The reaction is of the first order for the  $\text{H}_2$  reactant and the second for the  $\text{NO}$  reactant. So the general reaction rate order is  $n=3$

For the following reaction:

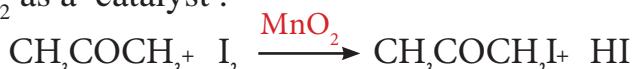


The law of reaction rate is:

$$\text{Rate} = K[(\text{CH}_3)_3\text{CBr}]$$

Reaction rate is first order for the reactant  $(\text{CH}_3)_3\text{CBr}$  and it is zero order for the  $\text{H}_2\text{O}$  reactor and the general order of the reaction is firstly, ie  $n = 1$

The reaction between acetone and iodine has the presence of  $\text{MnO}_2$  as a catalyst .



It was observed that its rate does not depend on the concentrations of reactants and the reaction rate law for this reaction is

$$\text{Rate} = K$$

Thus, this reaction is zero order From the above example, it is clear that the law of reaction rate and its order cannot to be concluded by just considering the chemical equation of the reaction, indeed this should be determined by experiment only.

The values of  $\alpha$ ,  $\beta$  and  $\gamma$  are not determined by the number of moles of the reactants  $a$ ,  $g$  and  $h$  as in the general reaction:  $a\text{A} + g\text{G} + h\text{H} \longrightarrow p\text{P}$

### 5-3-1 Determination of reaction orders

To illustrate how to set the values of  $\alpha$ ,  $\beta$ ,  $\gamma$  experimentally. It is used several experimental methods, we will look at one here. This method involves making a number of experiments in which the concentration of a reactant is altered and maintained the concentrations of the other reactants are constant, so we find the order of the variable reactant, and so on for the other reactants. This method can be explained by the following examples:

#### Example 5-4

The first reaction at a given temperature:



The reaction rate was measured at different concentrations of the reactant  $\text{N}_2\text{O}_5$ . Data were obtained in the table below.

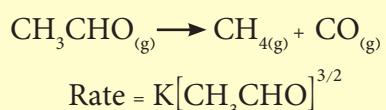
| Exp. No. | $[\text{N}_2\text{O}_5]/\text{mole/L}$ | Rate / mole / L.s    |
|----------|--|----------------------|
| 1        | 0.0113                                 | $6.7 \times 10^{-6}$ |
| 2        | 0.0084                                 | $5.0 \times 10^{-6}$ |
| 3        | 0.0042                                 | $2.5 \times 10^{-6}$ |

Determine the order of the reactant and deduce the law of reaction rate and its general reaction rate order.

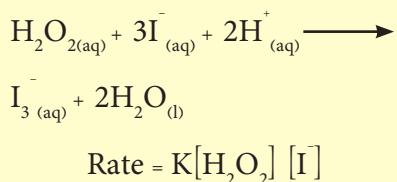
### Exercise 5-6

Determine the orders of the reactants and the general Reactions orders for each of the following reactions:

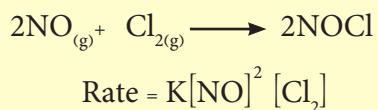
A-



B-



C-



### Exercise 5-7

For the following gaseous reaction:



Experimentally found that the law of his rate

$$\text{Rate} = K [A]^2 [B]$$

If the concentration of A is three times greater than its concentration. B is twice its concentration. The reaction rate is increased by:

A- 6      B- 9      C- 12  
D- 18      E- 36

### Solution

1 - We write the reaction rate law

$$\text{Rate} = K [N_2O_5]^{\alpha}$$

2- To determine the value ( $\alpha$ ) we choose any two experiments such as 1 and 2 and compensate the results of each experiment in the law of reaction rate and divide one equation by the other and simplify of fraction we get ( $\alpha$ ) value

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{K [N_2O_5]_1^{\alpha}}{K [N_2O_5]_2^{\alpha}}$$

$$\frac{6.7 \times 10^{-6}}{5.0 \times 10^{-6}} = K (0.0113)$$

$$1.34 = K (0.0084)$$

$$(1.34)^1 = (1.34)^{\alpha} \Rightarrow \alpha = 1$$

Therefore the value of  $\alpha$  is equal to the integer one, so the reaction is of the first order and its rate law is written as follows:  $\text{Rate} = K [N_2O_5]$

### 5-3-2 Calculating the value of the reaction rate constant

The reaction rate constant is a constant amount that does not change unless the temperature changes. Its value is calculated from the compensation of the results of an experiment in the law of reaction rate, as in the following example:

#### Example 5-5

Calculate the value of the rate constant of the reaction in Example 5.4.

### Solution

To find the value of rate constant we compensate the results of one experiment in the law of reaction rate, that we got in the previous example as follows:

$$\text{Rate} = K [N_2O_5]$$

Suppose we have chosen experiment number 1 and offset its values in the relationship above

$$6.7 \times 10^{-6} \text{ mol/L.s} = K (0.0113) \text{ mol/L}$$

$$K = \frac{6.7 \times 10^{-6} \text{ mol/L.s}}{(0.0113) \text{ mol/L}} = 5.95 \times 10^{-4} \text{ s}^{-1}$$

### 5-3-3 Rate constant units

The units of rate constant vary depending on the general order of the reaction and the unit of time used to express the reaction rate. It can be derived mathematically from compensation in the law of reaction rate, or from the application of the following law:

$$\text{Unit of rate constant} = \frac{[\text{mol}]}{[\text{L}]^{\frac{1}{n}}} \frac{[\text{M}]}{[\text{t}]^{\frac{1}{n}}}$$

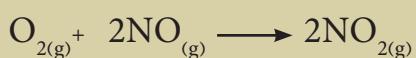
Where  $n$  represents the general reaction order and  $M$  molarity. Table (5-1) shows units of rate constant for different orders if time is expressed in (s)

Table 5-1 Units of rate constant corresponding to the general reaction order

| Order (n) | Units of rate constant corresponding to the general reaction rate  |
|-----------|--|
| 0         | $\text{M} \cdot \text{s}^{-1}$ or $\text{mol L}^{-1} \text{s}^{-1}$ or $\text{mol/L} \cdot \text{s}$   |
| 1         | $\text{s}^{-1}$ or $1/\text{s}$  |
| 2         | $\text{M}^{-1} \cdot \text{s}^{-1}$ or $\text{L} \cdot \text{mol}^{-1} \text{s}^{-1}$ or $\text{L/mol} \cdot \text{s}$                         |
| 3         | $\text{M}^{-2} \cdot \text{s}^{-1}$ or $\text{L}^2 \cdot \text{mol}^{-2} \text{s}^{-1}$ or $\text{L}^2 \cdot \text{mol}^2 \cdot \text{s}^{-1}$ |

### Example 5-6

For the following reaction



Determine the orders of the reactants and deduce the law of reaction rate, general reaction rate, and rate constant of experiments results in the table below:

| Exp. No. | $[\text{O}_2]/ \text{mole/L}$ | $[\text{NO}]/ \text{mole/L}$ | Rate / mole / L.s     |
|----------|-------------------------------|------------------------------|-----------------------|
| 1        | $1.10 \times 10^{-2}$         | $1.30 \times 10^{-2}$        | $3.20 \times 10^{-3}$ |
| 2        | $2.20 \times 10^{-2}$         | $1.30 \times 10^{-2}$        | $6.40 \times 10^{-3}$ |
| 3        | $1.10 \times 10^{-2}$         | $2.60 \times 10^{-2}$        | $12.8 \times 10^{-3}$ |
| 4        | $3.30 \times 10^{-2}$         | $1.30 \times 10^{-2}$        | $9.60 \times 10^{-3}$ |
| 5        | $1.10 \times 10^{-2}$         | $3.90 \times 10^{-2}$        | $28.8 \times 10^{-3}$ |

### Solution

Write reaction rate law  $\text{Rate} = K [\text{O}_2]^\alpha [\text{NO}]^\beta$

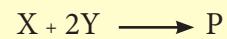
To determine the value of  $(\alpha)$ , select two experiments such as 1 and 2, where  $[\text{NO}]$  is constant in the two experiments while  $[\text{O}_2]$  variable and compensate for the results of each experiment in the law of rate. Divided one equation to the other and simplify the fraction we get  $\alpha$  value

### Exercise 5-9

Use the constant rate value calculated in example 5-5 to calculate the consumption rate of  $\text{N}_2\text{O}_5$ . When its concentration is equal to 0.1 mol/L at the same set temperature.

### Exercise 5-10

For the following reaction



It is found first order for  $\text{X}$  and second order to  $\text{Y}$ .

The units of rate constant of this reaction if time in seconds is:

A-  $\text{M} \cdot \text{s}^{-1}$

B-  $\text{M}^{-2} \cdot \text{s}^{-1}$

C-  $\text{M}^{-3} \cdot \text{s}$

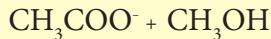
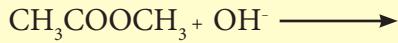
D-  $\text{M}^2 \cdot \text{s}^{-1}$

E-  $\text{M}^{-1} \cdot \text{s}^{-1}$

$$\begin{aligned}
 \text{Rate}_2 &= K [O_2]^{\alpha} [NO]^{\beta} \\
 \text{Rate}_1 &= K [O_2]^{\alpha} [NO]^{\beta} \\
 \frac{6.40 \times 10^{-3}}{3.20 \times 10^{-3}} &= \frac{K (2.20 \times 10^{-2})^{\alpha} (1.30 \times 10^{-2})^{\beta}}{K (1.10 \times 10^{-2})^{\alpha} (1.30 \times 10^{-2})^{\beta}}
 \end{aligned}$$

$$(2)^1 = (2)^{\alpha} \Rightarrow \alpha = 1$$

For the following reaction:



From the results of the three experiments in the table below:

| [C <sub>3</sub> H <sub>6</sub> O <sub>2</sub> ] | [OH <sup>-</sup> ] | Rate/ mol/L. s |
|---|--------------------|----------------|
| 0.040   | 0.040              | 0.000225       |
| 0.040   | 0.080              | 0.00045        |
| 0.080   | 0.080              | 0.00090        |

A- Determine the ranks of the reactants.

B- Deduce the law of reaction rate.

C- Find the value of the constant rate.

So the reaction is first order for O<sub>2</sub>

To determine the value (β) we select experiments 1 and 3 where [O<sub>2</sub>] is constant in both experiments, while [NO] is a variable and we substitute the results of each experiment in the rate law and divided one equation over the other and simplify the fraction, we get a (β) value.

$$\begin{aligned}
 \text{Rate}_3 &= K [O_2]^{\alpha} [NO]^{\beta} \\
 \text{Rate}_1 &= K [O_2]^{\alpha} [NO]^{\beta} \\
 \frac{12.80 \times 10^{-3}}{3.20 \times 10^{-3}} &= \frac{K (1.10 \times 10^{-2})^{\alpha} (2.60 \times 10^{-2})^{\beta}}{K (1.10 \times 10^{-2})^{\alpha} (1.30 \times 10^{-2})^{\beta}} \\
 (4) = (2)^{\beta} &\Rightarrow (2)^2 = (2)^{\beta} \Rightarrow \beta = 2
 \end{aligned}$$

So the reaction is second order for NO.

The general order of the reaction is equal

$$n = \alpha + \beta = 1 + 2 = 3$$

so the reaction rate law is Rate = K[O<sub>2</sub>][NO]<sup>2</sup>

We use the information in one of the experiments in the table above and replace it in the law of reaction rate to get the value of the rate constant. We used information from experiment 2

$$\text{Rate} = K [O_2] [NO]^2$$

$$6.4 \times 10^{-3} \text{ mol/L.s} = K(2.20 \times 10^{-2}) \text{ mol/L} (1.30 \times 10^{-2})^2 \text{ mol}^2/\text{L}^2$$

$$K = \frac{6.4 \times 10^{-3} \text{ mol/L.s}}{(2.20 \times 10^{-2}) \text{ mol/L} (1.30 \times 10^{-2})^2 \text{ mol}^2/\text{L}^2} = 1721.4 \text{ L}^2/\text{mol}^2\text{s}$$

Note that the unit of rate constant for third order reactions is L<sup>2</sup>/ mol<sup>2</sup>.s

## 5-4 Theories of reaction rate

A number of theories have been developed to explain how the reaction occurs. The most important of these theories is the theory of collision and the theory of the transition state or called the theory of activated complex. The first explained how the reaction occurs on the basis of the visible, while the second explained the reaction in a way that happens inside molecules subject to interaction and we will briefly explain both theories.

### 5-4-1 Collision Theory

The rate of chemical reactions varies depending on the properties of the reactants particles (atoms, molecules, or ions) with varying reaction conditions.

To illustrate how chemical reactions occurs and why they differ their rates. Collision theory had been submitted, the hypotheses of which are:

1. The chemical reaction occurs as a result of the collision of the reactants' particles, this theory assumed that the shape of the colliding particle was spherical.
2. The reaction rate is directly proportional to the number of collisions between the reactants particles per unit of time. Where you can say it whenever the number of collisions between the reactants particles increased the probability of the reaction to occur.
3. Not all collisions are effective and lead to the formation of products, in that the number of collisions between particles are enormous and about  $1 \times 10^{27}$  collisions per second between gas particles of 1 liter volume under normal conditions. Therefore, if such a large number of collisions lead to the formation of products to complete all the reactions at the moment of mixing of reactants. So most collisions are ineffective and does not lead to products.

To be effective, the collision must meet the following two conditions:

1. Collision molecules have a minimum of potential energy to overcome the power of repulsion among themselves when colliding and breaks the bonds of materials and turn them into products. This minimum energy Necessary to reaction is called activation energy.
2. The direction of the colliding particles is appropriate, that the particles are in an appropriate geometric space and in the right direction when colliding. This it creates the desired products. To illustrate this, consider Figure (5-4).

### Exercise 5-12

What the texts below are erroneous with regard to hypotheses collision theory:

A- Occurrence of collision between the reactant molecules is a basic condition of the reaction.

B- All intermolecular collisions lead to the formation of products.

C- In order for the products to be formed, the collision molecules must be in a suitable appropriate space.

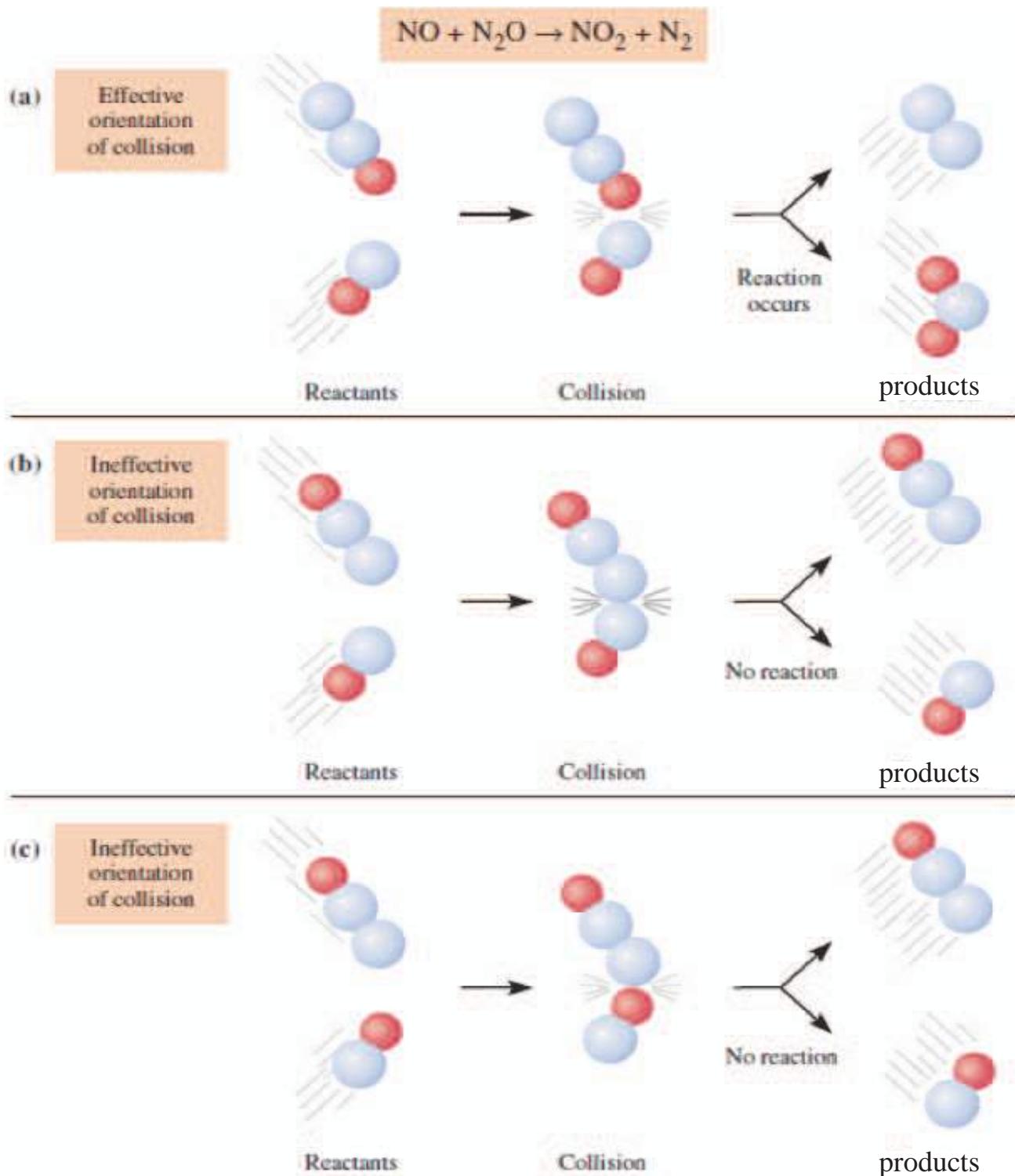


Figure 5-4

Some possible collisions between  $\text{N}_2\text{O}$  and  $\text{NO}$  molecules in the gas phase.

- (a) collision that could be effective in producing the products.
- (b, c) Collisions that would be ineffective orientation.

From the above we find that in order for reaction to occur according to this theory, the molecules must possess the minimum activation energy and that their collision is spatially oriented in the right direction. That's known that the internal (total) energy of any moving molecules are equal to the sum of the kinetic energy and the potential energy it possesses, and the molecules moving very quickly have high kinetic energy and low potential energy. When two moving molecules approach too fast, part

Kinetic energy of each one will convert to potential energy. Because of the repulsion between them is caused by the presence of electrons in their outer shells. At the moment of the collision, the two molecules stop moving and the kinetic energy of each is converted to the potential energy, if that energy is less than energy of the activation energy of the reaction will bounce off each other without any reaction (Non effective Collision) [Figure( 5-4b and c)].

If they have enough kinetic energy, they will rush with great power and high speed, they can overcome the power of repulsion and enter the reaction(Effective Collision) [Figure (5-4a)].

In fact, the collision theory failed to give the true rate of reactions when tested, the reason for the failure of this theory is to assume that the molecules are all spherical. This, in fact, applies only to a small number of molecules that are monatomic. Therefore, other scientists have proposed a new theory to explain how the reaction occurs, namely the theory of the transition state or called the theory of activated complex.

#### 5-4-2 Transition State Theory

This theory showed that in all chemical reactions cannot resulting material consists directly, but must pass through the so-called state active transition, which is where the so-called activated complex. It is a non-static active compound suggested that its synthesis is a compromise between the reactants and the resulting substances, so this theory called activated complex theory. it is also in equilibrium with the reactants [Figure( 5-5)]. The energy of this compound is always greater than that of the reactants and the resulting substances. It should be noted that the activated complex is often inseparable but can disintegrate either to produce products or to give reactants according to reaction conditions.

An important example to illustrate the idea of collision theory and transition state theory is the reaction between the  $\text{I}^-$  ion and methyl chloride  $\text{CH}_3\text{Cl}$ .



This reaction occurs according to the method shown in [Figure (5-6)]. The reaction begins with the collision of the iodide  $\text{I}^-$  ion with the methyl chloride molecule  $\text{CH}_3\text{Cl}$ .

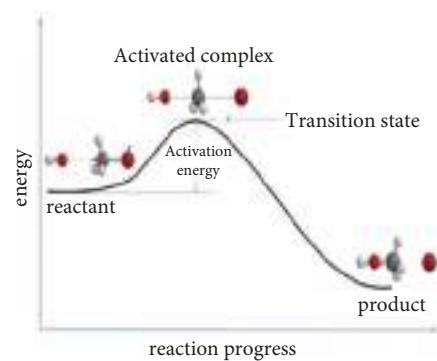
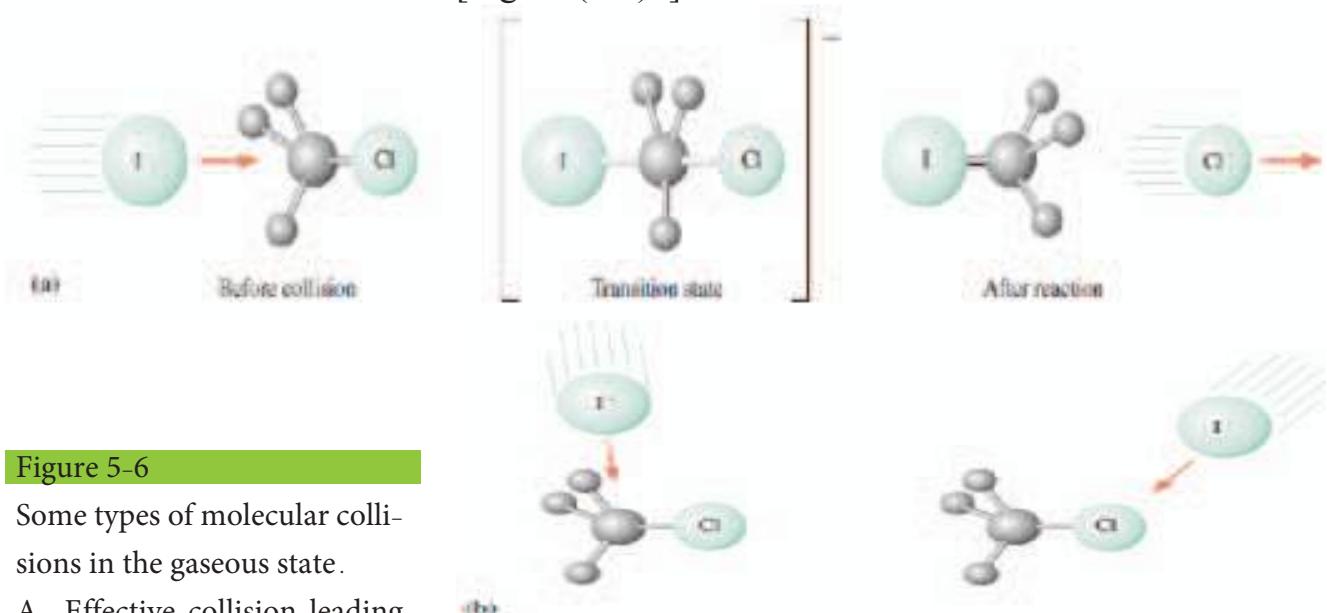


Figure 5-5

Reaction progress according to the theory of transition state.

From behind the C-Cl bond through the center of the three hydrogen atoms, where the bond begins between carbon and iodine while elongating and weakening between carbon and chlorine and the transition state of the reaction (the activated complex) is formed. Activated complex has three standard C-H bonds and two bonds weak (partial bonds) between carbon and iodine, C-I, carbon and chlorine C-Cl. As the bond strength increases between carbon and iodine, the bond is established between them, while the bond breaks down between carbon and chlorine and reaction is done [Figure (5-6)a].

If the collision between the iodide ion and the methyl chloride molecule is in the wrong direction, the reactants remain unchanged. The reaction doesn't occur, note the [Figure (5-6)b].



**Figure 5-6**

Some types of molecular collisions in the gaseous state.

A- Effective collision leading to the formation of products.

B- Collisions are ineffective because the direction of the colliding molecules is incorrect in addition to lack of energy sufficient for an effective collision.

### 5-5 Heat of reaction

The rate of the chemical reaction is related to the activation energy, wherever the activation energy value is large, the reaction is slow, and the reaction is quicker as the activation energy is smaller.

The chemical reaction is accompanied by a change in energy due to the absorption or emission of a quantity of heat. This quantity represents the difference between the energy of the products and the energy of the reactants. They are called reaction temperatures and are calculated as follows:

$$\text{Heat of reaction} = \text{Energy of products} - \text{Energy of reactants}$$

The reaction is endothermic when the reaction temperature is a positive value, ie the energy of the resulting material is greater than that of the reactant. As shown in Figure (5-7).

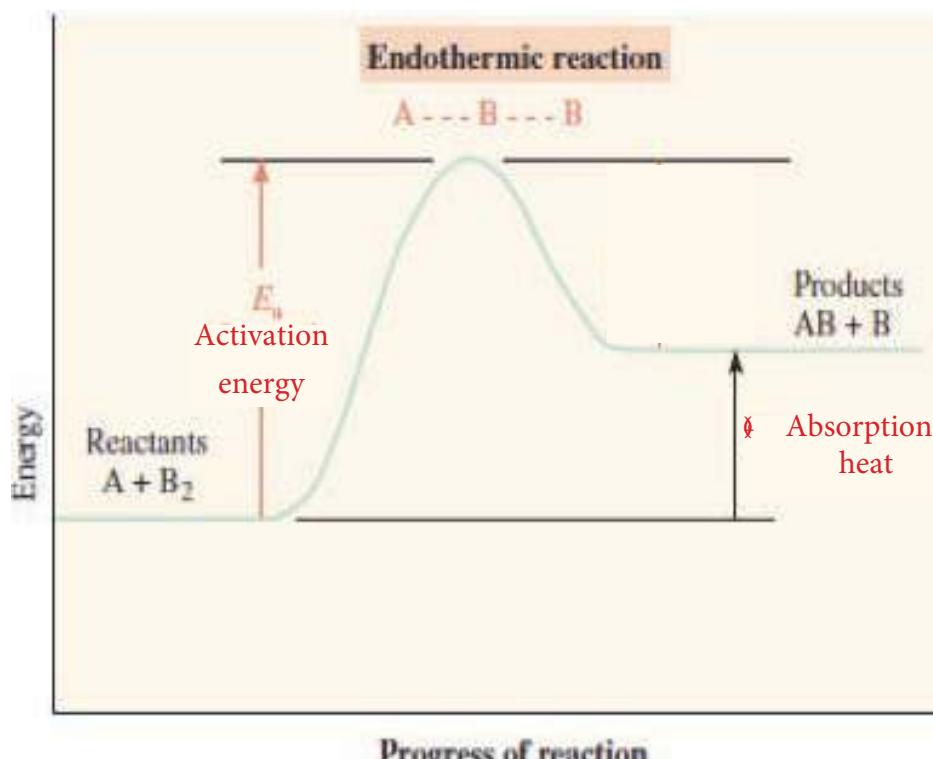


Figure 5-7

The following reaction scheme



When the energy of the products is greater than the energy of the reactants have the reaction endothermic so signal heat value  $\ddagger$

If the amount of reaction temperature is negative value, that is the, energy products > energy of the reactants, so the reaction is Exothermic. As shown in Figure (5-8).

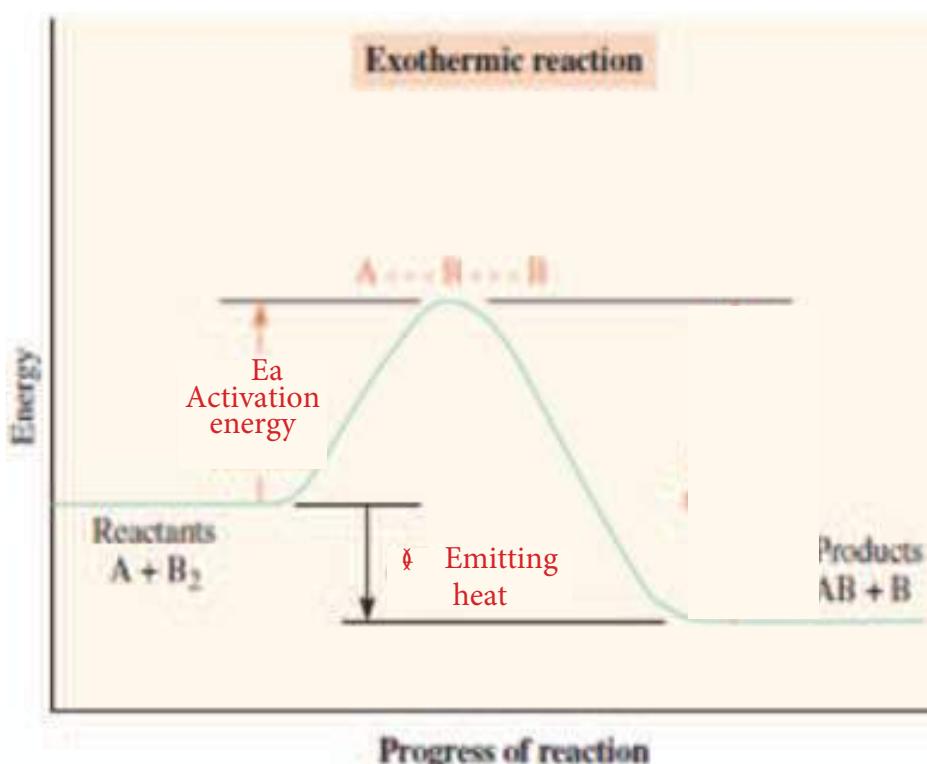


Figure 5-8

The following reaction scheme



When the energy of the resulting material is smaller of the energy of the reactants have the reaction is exothermic, so heat signal heat value  $\ddagger$



Figure 5-9

Increase in the speed of ignition of the splinter by increasing the concentration of oxygen.

(bottom) ignition of the splinter in the air (top) burning flame glow inside a bottle filled with oxygen gas.



Figure 5-10

Phosphorus has two forms. White Phosphorus (above) ignites and burns quickly when exposed to oxygen air therefore, it should be stored under water.

Red phosphorus (under) reacts very slowly severe with air so it can be stored with open bottles.

## 5-6 Activation Energy

Activation energy is defined as the minimum energy required that the reactants must possess them in order for the collision to be effective.

## 5-7 Factors affecting reaction rate

Reactions vary in rate, some slow and others fast and under the same conditions, the reaction rate can be changed by controlling the factors affecting the reaction rate, namely:

### 5-7-1 Concentration

We observed from our study of the reaction rate law that increasing the concentration of a reactant often increases the reaction speed. Figure (5-9) shows effect of increasing oxygen concentration on reaction rate where the burning fragment lights in the air, containing oxygen gas 20%, but flame glow when inserted into a filled bottle with Oxygen gas it caused by an increase in the concentration of oxygen, which leads increased ignition rate.

It also concentration has the effect of increasing the rate of reactions involving on reactants in the liquid state, the pressure has a similar effect on reactions involving reactants in the gaseous state. That increased pressure reduces the volume of gas and thus increases its concentration which increases of the chemical reaction rate.

### 5-7-2 Physical nature and reactant material nature

The rate of chemical reactions depends on the physical state of the reactants. If, for example, we had three pieces of metal, sodium, zinc and tin have the same size and we put each piece in a hydrochloric acid solution has the same concentration. We find that the sodium piece reacts strongly, the zinc piece will react at a lower rate for the tin, it will react very slowly. So it's a physical state of the reactants are very important to determine their effectiveness and their rate of reaction, as well as the effectiveness of white and red phosphorus [Figure (5-10)]

The surface area of a given mass of material increases as it is small the size of the constituent particles, and as the surface area increases, the number of collisions then, reaction rate increases, [Figure (5-11)]. The surface area of the solid can be increased, either by soluble it in a solvent, the solvent separates the particles from each other or grinds them and turn it into a fine powder.

### 5-7-3 Temperature

The reaction rate increases as the temperature rises and it decreases with temperature decreasing. This is because high temperature increases the speed of the reacted molecules, then collision of molecules increases. So the number of molecules has kinetic energy equal to or greater than the activation energy of the reaction, which can react to form the product, as shown in Figure 5-12.



Figure 5-11

The chalk powder (pure carbonate calcium  $\text{CaCO}_3$ ) reacts quickly with diluted hydrochloric acid because it has a large surface area, while the chalk finger with a small surface area reacts much slower.

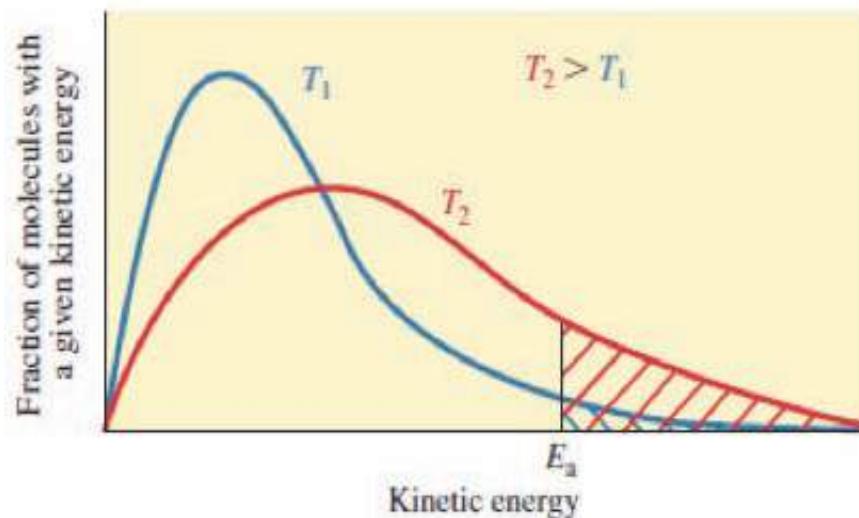


Figure 5-12

Temperature increasing leads to a marked increase in the number of molecules with high energies equal to or greater than activation energy which will increase the number of collisions and the rate of reaction.

#### Do you know

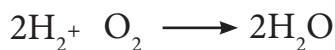
The mixture of coal dust and air is a mixture capable of explosion at high temperature and may cause the explosion of coal mines, as well as the mixture of flour dust and air may cause an explosion for the same reason.

Table 5-2 The reaction rate doubles as the reaction temperature increases ( $10^\circ\text{C}$ )

| Number of molecules involved in the reaction | Temperature                |
|--|----------------------------|
| $1.70 \times 10^{-9}$                        | $25^\circ\text{C}$ (298 K) |
| $3.29 \times 10^{-9}$                        | $35^\circ\text{C}$ (308 K) |
| $6.12 \times 10^{-9}$                        | $45^\circ\text{C}$ (318 K) |

#### 5-7-4 Catalyst

Catalyst is a substance that increases the rate of reaction without consuming it. The effect of adding catalyst is stronger than the effect of high temperature on reaction rate. Since the catalyst reduces the activation energy level of the reaction, the number of colliding particles with kinetic energy is equal to or greater than the energy of activation energy, so that it can react to form the products, as shown in Figure (5-13). Note from the figure that the activation energy is reduced for reaction also leads to the opening of a new line that differs from the first line before adding the catalyst by creating a new activated complex with low energy. The effect of the catalyst on increasing the reaction rate of hydrogen with oxygen can be illustrated:



The reaction is hardly happening at the normal temperature, but is taking place quickly by adding a little platinum powder as a catalyst.

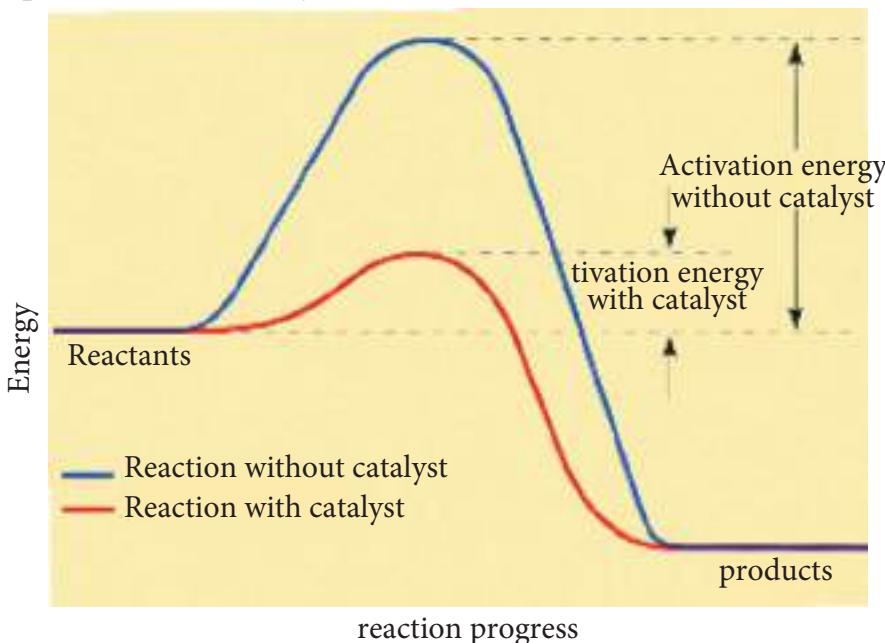


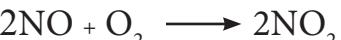
Figure 5-13

The catalyst reduces the activation energy and increases the reaction rate.

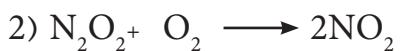
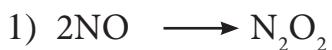
#### 5-8 Reaction mechanism

Most chemical reactions occur through a number of sequential steps represented by so-called reaction mechanics. Reactions occur in more than one step called complex reactions, while one-step reactions are called primary reactions.

A complex reaction involves more than one initial reaction. For example, the interaction between NO and O<sub>2</sub> occurs as follows:

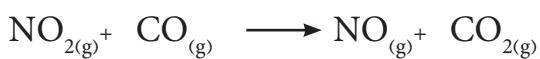


In practice it's found that the reaction take place in two steps:



In practice, this reaction was found to occur in two steps. Each of these steps is a primary reaction. If we combine equations (1) and (2), we would get the above general reaction.

$\text{N}_2\text{O}_2$  is the intermediate compound, which is defined as a compound produced in one step the initial reaction and it is consumed in another step of these reactions. So the intermediate compound does not appear in the general equation of the reaction but it appears in the mechanism steps of the reaction or the so-called primary reaction steps. This is because it is an unstable compound, it is more stable than the activated complex because its atoms are bound together with normal bonds and in some cases can be separated from the reaction. Mechanism steps include the reaction on the specified step for speed (Rate-determining step), defined as the slowest step of reaction mechanism steps. When a primary reaction occurs in the mechanism in a lower rate than any other primary reactions, so this reaction is the rate determined step of reaction rate. The rate of this reaction, it determines the general reaction rate whether this step is at the beginning, end, or intermediate. For example, the reaction of nitrogen dioxide  $\text{NO}_2$  and carbon monoxide  $\text{CO}$  was experimentally found that it is a reaction of second order for  $\text{NO}_2$  compound and zero order for  $\text{CO}$  compound.



This is contrary to what can be deduced at first glance from the above chemical equation as a first order reaction for  $\text{NO}_2$  and  $\text{CO}$  on this it was suggested that this reaction follows the following mechanics:



### Do you know

In 1998 a new science was introduced is called the femtosecond science, by a group of scientists, including the Arab scientist, Dr. Ahmed Zewail. This science enters in many areas including medicine, electronics and science space, chemistry, physics etc.

As a first time and by using this science scientists were able to observe what happens during chemical reaction and slow imaging and see the movement of atoms using super speed camera which helped to suggest a reaction mechanism.

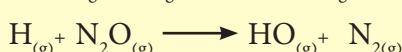
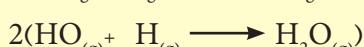
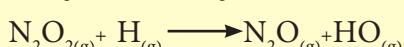
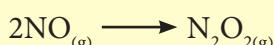
Since the reaction rate is the speed of the slow step, the law of the reaction rate law is:

$$\text{Rate} = K [\text{NO}_2] [\text{NO}_2]$$

or  $\text{Rate} = K [\text{NO}_2]^2$

### Exercise 5-13

A reaction mechanism has been proposed for a given reaction; constitute of five steps are as follows:



1. Write the balanced reaction equation.
2. Write the law of reaction rate for each step.
3. Set the reaction order for each step.
4. determine the intermediate materials.

This is consistent with the law of reaction rate of empirically concluded. Observations of the reaction mechanism is forming intermediate compound  $\text{NO}_3$ . Deduce from previously that any proposed mechanism for any chemical reaction must be agreed with the general chemical equation of reaction. To propose a reaction mechanism must apply the following conditions:

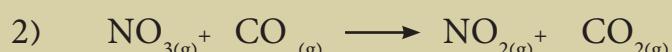
1. When combining the equations of the primary reactions in the proposed reaction mechanism, we obtain the general equation for the reaction.
2. The order of reaction for any primary reaction must be a first or second order and primary reactions are excluded from the third order due to the difficulty of effective collision occurring between three molecules at once.
3. The law of reaction rate for rate-determining step the specified step of velocity must be identical to the law of general reaction rate because the reaction rate will depend on the “rate-determining step” rate.

The following examples illustrate a mechanical steps for reactions according to above point:

### Example 5-8

The law of reaction rate of an reaction:  $\text{Rate} = K [\text{NO}_2]^2$

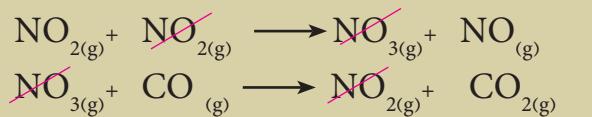
Suggested reaction mechanism:



- A. Write the general balanced equation for the reaction and what is the intermediate compound.
- B. Write the law of rate for each step.
- C. Set the rate-determining step.

### Solution:

A - Combine steps 1 and 2 and cut down similar items to get reaction equation



The intermediate compound is  $\text{NO}_3$  because it did not appear in the general equation of the reaction.

B-The law of reaction rate for the first step Rate=  $k[\text{NO}_2]^2$

The law of reaction rate for the second step Rate=  $k[\text{NO}_3][\text{CO}]$

The first and second steps are second order.

C - The first step is the rate-determining step for rate, because the law of rate of it is matched with the law of reaction rate.

### Example 5-9

For the following reaction:



Reaction rate law is : Rate=  $K[\text{NO}_2][\text{F}_2]$

The reaction mechanism has been proposed in four different ways, explain with the reason being given the right reaction mechanism, and false one.

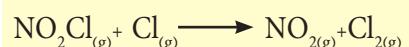
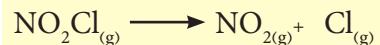


### Solution

(1) False , because reaction rate law of rate-determining step Rate=  $K[\text{NO}_2]^2$  does not matched to the law of reaction rate

### Exercise 5-14

What is the proposed reaction mechanism



Reaction rate law is :

$$\text{Rate} = K[\text{NO}_2\text{Cl}]$$

1. Write the balanced general reaction equation.

2. Write the law of reaction rate for each step.

3. What a general reaction rate

4. which one of the two steps rate-determining step and why.

(2) False, because the sum of the two steps does not produce the reaction equation:



(3) False, because the reaction mechanism is from one step and third order

(4) True, because it meets the following three conditions:

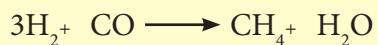
A- When we combine the two steps we get the equation of reaction.

B- The reaction order for each step is of the second general order and it is acceptable.

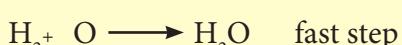
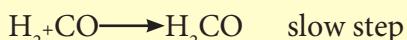
C- The law of the rate-determining step is matched to the law of reaction rate: Rate =  $[NO_2][F_2]$

### Exercise 5-15

Suppose the following reaction



Follows the following mechanism



1. Rate =  $K[\text{H}_2]^2[\text{CO}]^2$

2. Rate =  $K[\text{H}_2]^2[\text{CO}]$

3. Rate =  $K[\text{H}_2][\text{CO}]^2$

4. Rate =  $K[\text{H}_2][\text{CO}]$

5. Rate =  $K[\text{H}_2]^2[\text{CO}]^3$

### Example 5-10

Proposed the following reaction:



And suppose the following mechanism:



A - What is the law of the rate of reaction of this reaction.

B - Does this mechanism satisfy this reaction.

C - What is the general order of reaction.

D - What are the intermediate compounds in this reaction.

### solution

A - Yes, this mechanism achieves this reaction because the combination of the initial reactions leads to the general equation of the reaction.

B - Reaction rate law is Rate =  $K[\text{B}][\text{B}]$  or Rate =  $K[\text{B}]^2$

C - Reaction is of second order

D - Intermediate compound is  $\text{B}_2$  and  $\text{AB}$

## Basic concepts

### The Rate of Chemical Reaction

The amount of decrease in the molar concentration of reactant materials Reaction or increase in molar concentration of product materials with the corresponding change in unit time.

### General reaction rate

The Overall Rate of Chemical Reaction Rate in terms of one mole of any reactant material product material or resulting.

### The Rate Law

Relationship between rate of reaction with the concentrations of reactants A, G and H are powered to their orders respectively and with the constant reaction rate K. For the general reaction:



Rate law is written as follows:

$$\text{Rate} = K [A]^{\alpha} [G]^{\beta} [H]^{\gamma}$$

### The Rate constant

The general rank of the reaction is equal to the sum of the reactants in the law of velocity:

$$n = \alpha + \beta + \gamma$$

### Rate Constant Units

The unit of reaction rate depends on the order of reaction and can be derived by the following relationship:

$$\text{Unit of rate constant} = \left[ \frac{\text{mol}}{\text{L}} \right]^{1-n} \square \frac{\text{M}^{-n}}{\text{t}}$$

### Rate theories

Developed theories are to explain how that reactions occur. There are two theories, collision theory and theory of activated complex or transition state.

### Activation Energy

Is the minimum energy needed for reactant molecules to form products

### Effective Collision

Those collisions in which the two conditions are met: The two basic molecules possess the minimum of activation energy and be geometric vacuum situation for colliding molecules in the right direction.

### Heat of reaction

Heat absorbed (positive value) or emitted (negative value) during the chemical reaction. Their values depend on the difference between the energy of the reactant material energy and product material energy.

### Reaction mechanism

Number primary steps (reactions) that reaction passes to convert reactant material to product.

### Rate-Determining step

The slowest step of the reaction mechanism (primary reactions) and the rate of this step limits the law of reaction rate ie the number of reactants moles in rate-determining step are orders of the reactants themselves.

## Chapter Five Questions

5

5-1 for the following reaction:



The results in the following table:

| t / hr | [N <sub>2</sub> O <sub>5</sub> ]/ mol/L |
|--------|---|
| 0.00   | 0.849                                   |
| 0.50   | 0.733                                   |
| 1.00   | 0.633                                   |
| 2.00   | 0.472                                   |

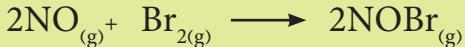
Calculate the rate of reaction in hour unit of the following .

- A- From 0.00 to 0.50
- B-From 0.50 to 1.00
- C-From 1.00 to 2.00

5-2 Explain how the following factors affect chemical reaction rate

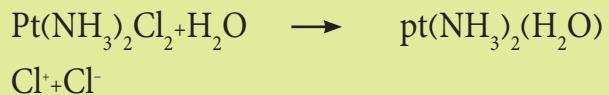
- A-Temperature.
- B- Surface area of reactants.
- C- The nature of the reactants.
- D- Concentration of reactants.

5-3 The following reaction is a first order for Br<sub>2</sub> reactant and it is second order for NO.



- A- Write the reaction rate law
- B- How the reaction rate changes when the concentration of Br<sub>2</sub> is to be three times the initial concentration.
- C- How the reaction rate changes when the NO concentration is doubled only.
- D- How the reaction rate changes when the concentration of both Br<sub>2</sub> and NO is doubled.

5-4 for the following reaction:



Reaction rate law

$$\text{Rate} = K [\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$$

$$\text{Its value } K = 0.090 \text{ hr}^{-1}$$

A-Calculate reaction rate when concentration is

$$\text{pt}(\text{NH}_3)_2\text{Cl}_2 = 0.040\text{M}, 0.020\text{M}, 0.010\text{M}$$

B-How the consumption rate changes of Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> with its concentration changes.

C-What is the effect of concentration change of Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> on formation rate of Cl<sup>-</sup>.

5-5 What effect does the catalyst on the following:

- A- Heat of reaction.
- B- Activation energy.
- C- Reactant energy and product energy.

5-6 The reaction below is found that the formation rate at a given time is 0.036M.s<sup>-1</sup> for C.

Rate in terms of change in A,B and D and general reaction rate (all in unit M.s<sup>-1</sup>) is  
 $2\text{A} + 3\text{B} \longrightarrow 4\text{C} + 2\text{D}$

$$\text{A: } 0.018, 0.027, 0.018, 0.009$$

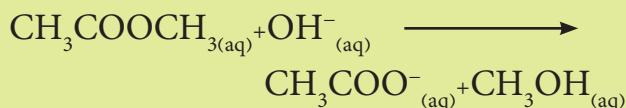
$$\text{B: } -0.018, -0.027, 0.018, 0.009$$

$$\text{C: } -0.072, -0.048, 0.072, 0.144$$

$$\text{D: } -0.036, -0.036, 0.036, 0.009$$

$$\text{E: } -0.018, -0.012, -0.018, -0.018$$

5-7 Methyl acetate decomposes in a basic solution to ion acetate and methyl alcohol, according to the following equation:



Reaction rate law Rate =  $K [CH_3COOCH_3][OH^-]$ ,  $K=0.14\text{L/mol.s}$

A-What is the dissociation rate of methyl acetate when concentration of both  $CH_3COOCH_3$  and  $OH^-$  are  $0.025\text{M}$ .

B-What rate of appearance  $CH_3OH$  in solution.

Reaction rate law

$$\text{Rate} = K [CH_3COOCH_3][OH^-]$$

$$K=0.14\text{L/mol.s}$$

5-8 The following reaction



| Exp. No. | $[\text{H}_2]$        | $[\text{NO}]$         | Rate mol/L.s          |
|----------|-----------------------|-----------------------|-----------------------|
| 1        | $2.5 \times 10^{-3}$  | $5.0 \times 10^{-3}$  | $3.0 \times 10^{-3}$  |
| 2        | $2.5 \times 10^{-3}$  | $15.0 \times 10^{-3}$ | $9.0 \times 10^{-3}$  |
| 3        | $10.0 \times 10^{-3}$ | $15.0 \times 10^{-3}$ | $36.0 \times 10^{-3}$ |

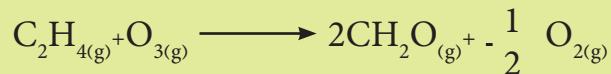
From the results of the experiments in the following table:

A- Conclude the law of reaction rate.  
B- Calculate the value of the rate constant.

C- Calculate the reaction rate when the concentration  $NO$ ,  $H_2$  equal to  $8.0 \times 10^{-3}\text{M}$

B - Calculate the reaction rate when the concentration of each  $O_3$  and  $C_2H_4$  are equal to  $2.0 \times 10^{-7}\text{M}$

5-9 For the following interaction and the results of experiments in the table below:

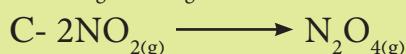
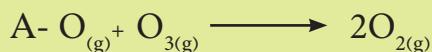


| Exp. No. | $[C_2H_4]$           | $[O_3]$              | Rate mol/L.s          |
|----------|----------------------|----------------------|-----------------------|
| 1        | $1.0 \times 10^{-8}$ | $0.5 \times 10^{-7}$ | $1.0 \times 10^{-12}$ |
| 2        | $1.0 \times 10^{-8}$ | $1.5 \times 10^{-7}$ | $3.0 \times 10^{-12}$ |
| 3        | $2.0 \times 10^{-8}$ | $1.0 \times 10^{-7}$ | $4.0 \times 10^{-12}$ |

A- Deduce the law of reaction rate, then calculate K value.

B- Calculate the reaction rate when the concentration of each  $O_3$  and  $C_2H_4$  are equal to  $2.0 \times 10^{-7}\text{M}$

5-10 Write the law of reaction rate for the following primary reactions:



5-11 The following reaction



From the results of the experiments in the following table:

| Exp. No. | [NO <sub>2</sub> ] | [F <sub>2</sub> ] | Rate mol/L.s         |
|----------|--------------------|-------------------|----------------------|
| 1        | 0.001              | 0.005             | $2.0 \times 10^{-4}$ |
| 2        | 0.002              | 0.005             | $4.0 \times 10^{-4}$ |
| 3        | 0.002              | 0.002             | $1.6 \times 10^{-4}$ |

A- Conclude the law of reaction rate.  
 B- What is the order of the reactants for each substance in the law of rate?  
 C- Calculate the reaction rate constant.

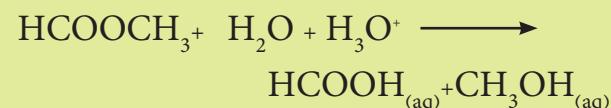
5-12 The following reaction:



From the results of the experiments in the table below, specify the reactants orders, deduced the law of reaction rate and general reaction rate.

| Exp. No. | [NO <sub>2</sub> ] | [CO] | Rate mol/L.s |
|----------|--------------------|------|--------------|
| 1        | 0.10               | 0.10 | 0.005        |
| 2        | 0.40               | 0.10 | 0.080        |
| 3        | 0.10               | 0.20 | 0.005        |

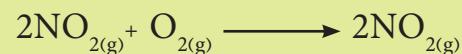
5-13 Methyl format is decomposed in an acid solution Made up of methyl alcohol and formic acid according to the following equation:



$$\text{Rate} = K [HCOOCH_3]$$

Why ion  $H_3O^+$  does not appear in the law of reaction rate though it is found in the reaction equation ?

5-14 The following reaction was done to a 600K



The results of the experiments in the following table:

| Exp. No. | [O <sub>2</sub> ] | [NO] | Rate mol/L.s         |
|----------|-------------------|------|----------------------|
| 1        | 0.01              | 0.01 | $1.2 \times 10^{-5}$ |
| 2        | 0.01              | 0.02 | $4.8 \times 10^{-5}$ |
| 3        | 0.02              | 0.01 | $2.4 \times 10^{-5}$ |

A- Conclude the law of reaction rate.

B- Calculate the reaction rate when the concentration of each of NO and O<sub>2</sub> are equal to 0.025M and 0.05M respectively

C-Calculate the rate of consumption NO, and the composition rate of NO<sub>2</sub> if O<sub>2</sub> consumption rate was  $1.0 \times 10^{-4}$  mol/L

5-15 Select the right statement and the false statement, then correct the error in all of the following:

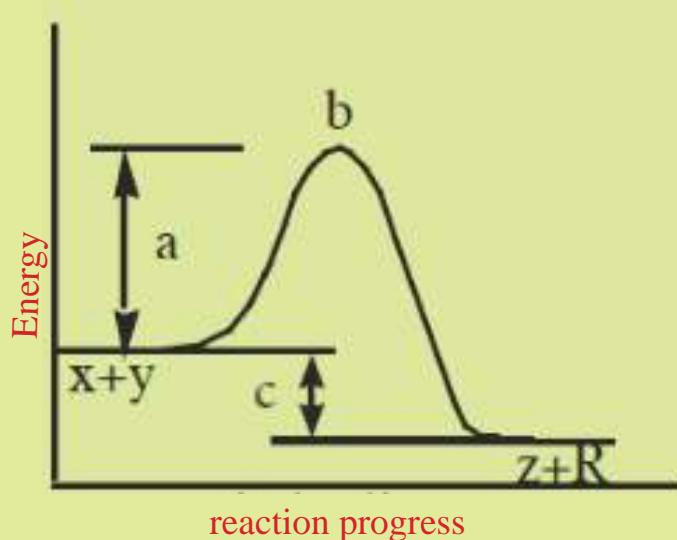
A-The reaction rate constant varies with the reaction temperature and over time.

B - The reaction rate constant varies with the concentration of the reactants.

C-The reaction rate remains constant over time for a first order reaction when the temperature is constant.

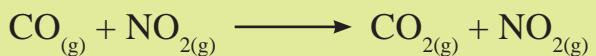
D- The reaction rate is doubled for the reaction of zero order when the concentration of the reactant is doubled.

5-16 In the scheme below is plotted between energy (Y axis) and reaction progress (x axis) for the following reaction:



show what are the letters a, b and c mean and whether the reaction is endothermic reaction or exothermic reaction and why?

5-17 The reaction comes in second order for the  $\text{NO}_2$  reactant and zero order for  $\text{CO}$  reactant:

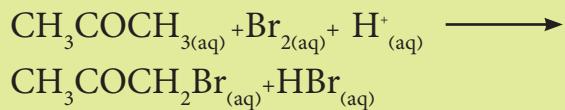


1- Write down the rate law of reaction.

2- How does the rate of the reaction changes when the  $\text{NO}_2$  concentration is halved.

3-How does the rate of the reaction changes when the  $\text{CO}$  concentration is doubled.

5-18 The following reaction and results of the experiments are show in the table below:



| Exp. No. | $[\text{CH}_3\text{COCH}_3]$ | $[\text{Br}_2]$ | $[\text{H}^+]$ | Rate<br>mol/L.s       |
|----------|------------------------------|-----------------|----------------|-----------------------|
| 1        | 0.30                         | 0.05            | 0.05           | $5.7 \times 10^{-5}$  |
| 2        | 0.30                         | 0.10            | 0.05           | $5.7 \times 10^{-5}$  |
| 3        | 0.30                         | 0.05            | 0.10           | $12.0 \times 10^{-5}$ |
| 4        | 0.40                         | 0.05            | 0.05           | $7.6 \times 10^{-5}$  |

1-Write down the rate law of reaction.

2- Calculate the rate order constant value of reaction.

3- How does the rate of the reaction change when:

$$[\text{H}^+] = 0.050\text{M} \quad [\text{CH}_3\text{COCH}_3] = [\text{Br}_2] = 0.10\text{M}$$



## Chapter Six Acids, Bases and Salts

6

After completing this chapter, the student is expected to:

- Recognize the properties of aqueous solutions of acids and bases.
- Identify the different molecular concepts of acids and bases according to Arrhenius and Bronshted-Lauri and Lewis theories.
- Characterize the auto-ionization of water and the amphoteric properties of some substances.
- Recognize the acids and bases reactions in aqueous solutions.
- Distinguish between the types of salts, the method of forming each and the properties of their aqueous solutions.
- Recognize the indicators that used in neutralization reaction.
- Recognize the titration process and understand its importance.

## 6-1 Introduction

In nature, there are many acids, bases and salts that are used in different fields, for example, digestive juices in the human body contain a solution of hydrochloric acid at a concentration of about 0.1 molar and in the blood of human and also water components in body cells have a moderate acid action. The solution in the car battery is composed of 40% by mass of sulfuric acid solution. On the other hand, sodium hydroxide is used in the manufacture of soap, paper industry and a number of other chemical industries. The salt also has extensive uses, baking soda is one of the salts of carbonic acid. Table salt (sodium chloride) uses to give a salty taste to food on the one hand and on the other hand it is used to preserve many types of food. Another example of the use of these substances is the application of calcium chloride salt to dissolve snow accumulated on public roads. This salt is also used in the treatment of people who has heart attacks. Ammonium salts are also used as nitrogen fertilizers to increase soil fertility. Most organic acids and their derivatives are found naturally, the vinegar we use have about 4% of acetic acid in its contents. The pain that you have feel when ants bite you is caused by the formic acid that these insects secrete into the body. Amino acids form protein modules in living organisms. Many other examples illustrate the importance and uses of these substances in everyday life.



## 6-2 Properties of aqueous solutions of acids and bases

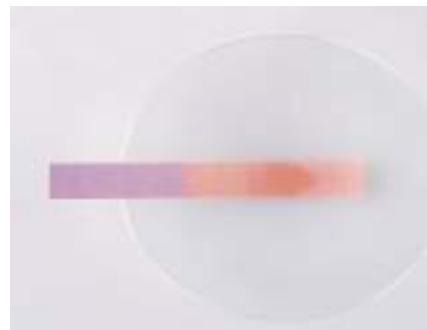
The aqueous solutions of most acids have distinctive characteristics attributed to the presence of positive hydrogen ion ( $H^+$ ) (proton) or crosses about hydronium ion ( $H_3O^+$ ) in its aqueous solution. The properties are:

1. Has an acidic taste.
2. Change the color of a number of indicators (pigments), for example change the pigment of a sunflower tint from blue color to red color
3. Acids react with most metals and release hydrogen gas ( $H_2$ ).

- Reaction with metal oxides and metal hydroxides to form salts and water.
- Its aqueous solutions have the ability to conduct electrical current because of their full or partial ionization. The Table (6-1) shows some common acids.

The aqueous solutions of most bases also have distinctive characteristics, attributed to the presence of hydroxide ion ( $\text{OH}^-$ ) in its aqueous solution and qualities. The properties are:

- Has a pungent taste.
- It has a viscous soapy texture as in the case of aqueous solution of sodium hydroxide.
- Change the color of a number of indicators, for example change the pigment of the sun flower tint from red color to blue color.
- Reacts with acids (neutralize) to form salts and water.
- Its aqueous solutions have the ability to conduct electrical current to their ability to be ions.



The acid solution changes the color of the pigment sunflower to red color.



The basic solution changes the color of the pigment sunflower to blue color.

Table (6-1) Some of the common acids and their uses.

| Acid name                             | Acid name Uses   |
|---------------------------------------|--|
| hydrochloric acid $\text{HCl}$        | Purification of minerals and purification of mineral ores and preparation of some food. It is the main component of stomach acids. |
| Sulfuric acid $\text{H}_2\text{SO}_4$ | Manufacture of fertilizers, explosives, glues and liquid used in the cars batteries.   |
| Nitric acid $\text{HNO}_3$            | Manufacture of fertilizers, explosives and adhesives.  |
| Acetic acid $\text{CH}_3\text{COOH}$  | Plastic and rubber industry and in food preservation is the main component for vinegar.  |
| Carbonic acid $\text{H}_2\text{CO}_3$ | It is present in all carbonated drinks due to the reaction of carbon dioxide with water.   |
| Hydrofluoric acid $\text{HF}$         | Clean the metal and polish the glass and engraving it.   |

## 6-3 Molecular concepts of acids and bases

In this section we will look at the molecular concepts of acids and bases according to the main theories are:

### 6-3-1 The Arrhenius Theory

In 1884 Arrhenius presented his theory of electrolysis dissociation, which later resulted in a theory for naming acids and bases which states on the following:

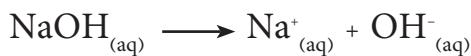
**Acid is the substance that contains hydrogen which is ionized to given hydrogen ions ( $H^+$ ) in the aqueous solution.**

By the definition of Arrhenius, HCl is considered to be Arrhenius acid because it produces  $H^+$  ions in aqueous solution:

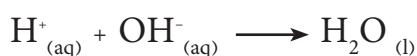


**The base is the substance that contains the hydroxide group ( $OH^-$ ) which ionizes the data of the negative hydroxide ions in the aqueous solution.**

According to Arrhenius' definition of the base, NaOH is the Arrhenius base because it produces hydroxide ions  $OH^-$  in the aqueous solution:



The process of neutralization according to this theory is defined as a union  $H^+$  ions and  $OH^-$  ions to form water molecules:



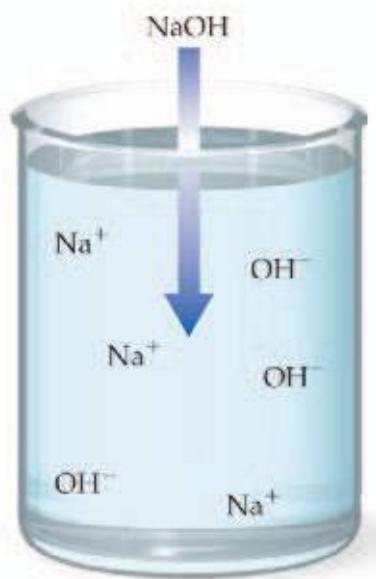
Arrhenius theory successfully explained the acids reactions that have protons with metal hydroxides (hydroxide bases), although the application of this theory is limited, it has led to the development of more comprehensive theories to describe the properties of acids and bases.

### Hydronium ion (hydrated hydrogen ion)

Arrhenius described hydrogen ions in water as  $H^+$  ( $H_2O$ )<sub>n</sub>, (where n is an integer) this is because the attraction between  $H^+$  ions and oxygen atom carrying a negative partial charge,  $\delta^-$  in the polarized water molecule. Although we do not know exactly how hydrogen ions hydrolyze in most aqueous solutions, we usually represent hydrogen ion as hydronium  $H_3O^+$ . Thus, it is argued that the hydrated ion of hydrogen

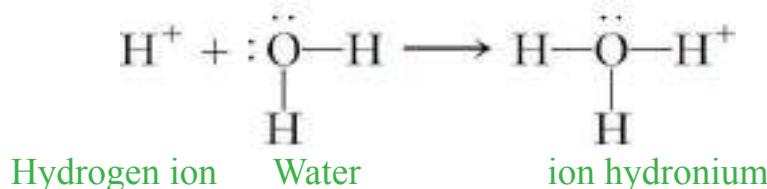


Ionization of hydrochloric acid is in water.



Ionization of sodium hydroxide in water.

is to give aqueous acid solution its specific acidity properties. The hydrogen ion can be expressed as  $\text{H}^+(\text{aq})$  or hydrolyzed  $\text{H}_3\text{O}^+$  as follows:



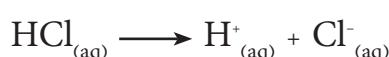
### 6-3-2 The Bronsted – Lowry Theory

In 1923, scientists Bronsted and Lowry introduced the individually developed the theory of Arrhenius and thus emerged new theory known as Bronsted-Lowry theory.

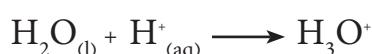
According to this theory, **acid is defined as the donor of the proton, and the base is the proton receptor.**

These definitions of acid and base are highly general as any molecule or ion contains hydrogen and has the capability to release a proton is acid, while any molecule or ion can receive a proton is a base. So an acid reaction with a base can be defined as that the reaction involves the transfer of a proton from the acid to the base. For this reason, the ionization process of hydrochloric acid (strong acid) in water, It is an acid-base reaction in which the water molecule behaves as a base because it acquires a proton. This can be expressed as follows:

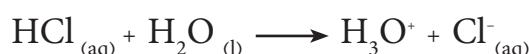
**First step (Arrhenius description)**



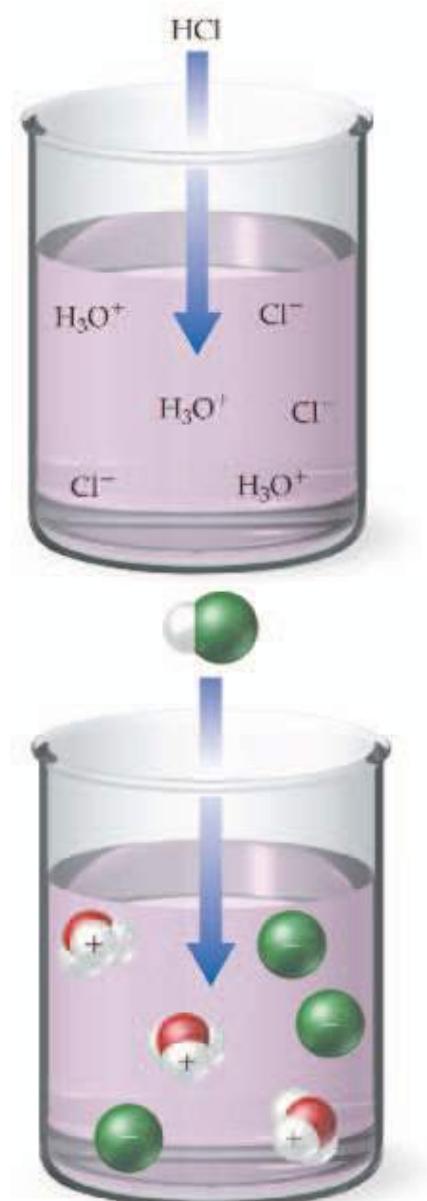
**Second step**



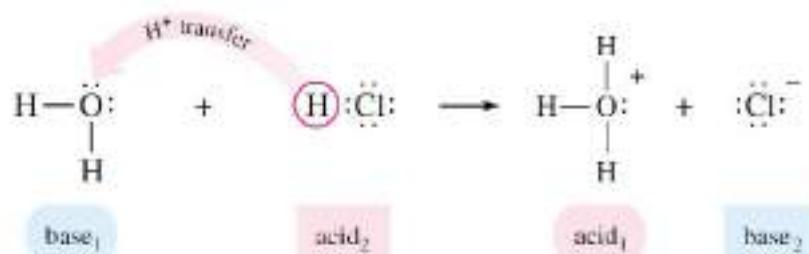
**Overall reaction (Bronsted-Lowry description)**



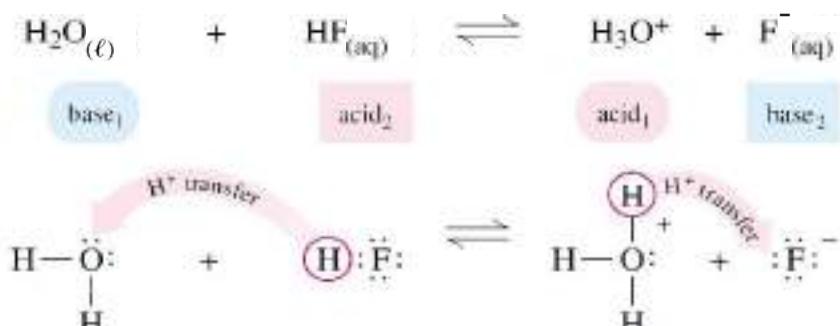
The reactions of acids and bases can be described by the Bronsted-Lowry concept in terms of pairs (conjugate acid-base) and each pair is two different classes in a proton. In the previous equation,  $\text{HCl}$  (acid) with  $\text{Cl}^-$  (conjugate base) is in the sense of a pair (conjugate acid-base), while  $\text{H}_2\text{O}$  (base) with  $\text{H}_3\text{O}^+$  (conjugate acid) ie is another pair of (conjugate base-acid) is as in the following figure:



**Ionization of hydrochloric acid is in water.**

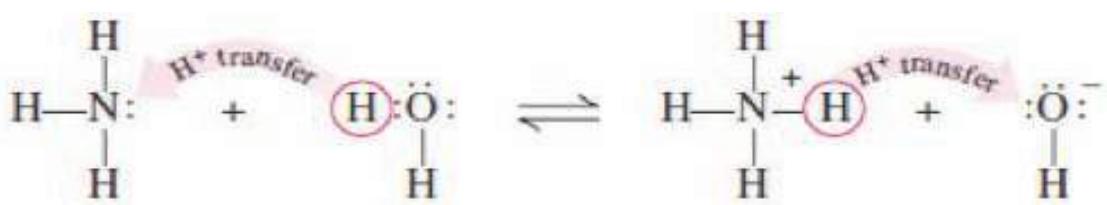
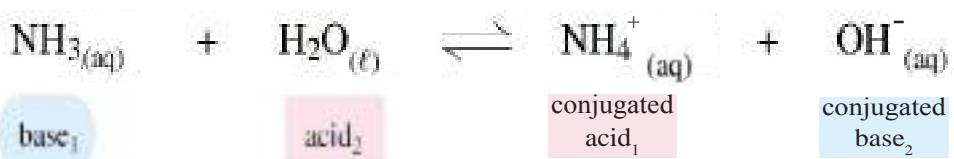


On the other hand, the ionization of hydrogen fluoride (weak acid). It occurs similarly but to a lesser extent and therefore represents the following:



In this equation HF is acid with F<sup>-</sup> conjugate base, while H<sub>2</sub>O represents a base with H<sub>3</sub>O<sup>+</sup> conjugate acid. In the forward reaction ( $\rightleftharpoons$ ) HF and H<sub>2</sub>O exhibit acid and base behavior respectively, while in the reverse reaction ( $\rightleftharpoons$ ) H<sub>3</sub>O<sup>+</sup> exhibits acid behavior (ie, a proton donor) and fluoride ion F<sup>-</sup> exhibits base behavior (ie, a proton receptor). We note from the examples above that when a weak acid (HF) dissolves in water, HF molecules will produce a small amount of H<sup>+</sup> ions. It can be acquired by one of the two basic classes in the solution F<sup>-</sup> or H<sub>2</sub>O. In fact, HF dissociates slightly, indicating that F<sup>-</sup> is a stronger base than H<sub>2</sub>O. When a strong acid (HCl) is dissolved in water, the HCl molecules will produce H<sup>+</sup> ions that can be gained by one of the two basic classes in the solution Cl<sup>-</sup> or H<sub>2</sub>O. Since HCl dissociates completely in diluted aqueous solution, this means that Cl<sup>-</sup> is lower base than H<sub>2</sub>O. **That all means that the weak acid has strong conjugate base and the strong acid has weak conjugate base.** It can be generalized by saying: the greater the strength of acid, the weaker the conjugated base strength of his context and vice versa. These concepts must be used correctly; a strong acid or a weak acid (as well as a base) are qualities that you will use to describe a relative situation. When we say (in the previous example) that F<sup>-</sup> is a strong base, it does not mean that it is so by comparing it with OH<sup>-</sup> for example,

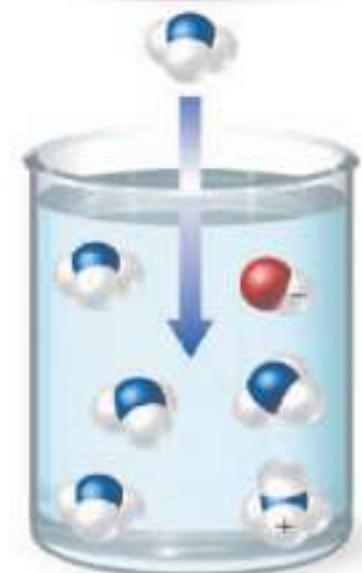
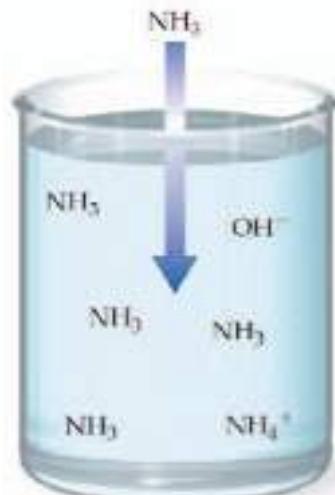
But we mean it is a stronger base relative to the conjugate base of the strong acid in the example ( $\text{H}_2\text{O}$ ). In the aqueous solution of ammonia, the ammonia molecules behave as a weak Bronsted base behavior while the water molecules behave as a acidic behavior and can be expressed as follows



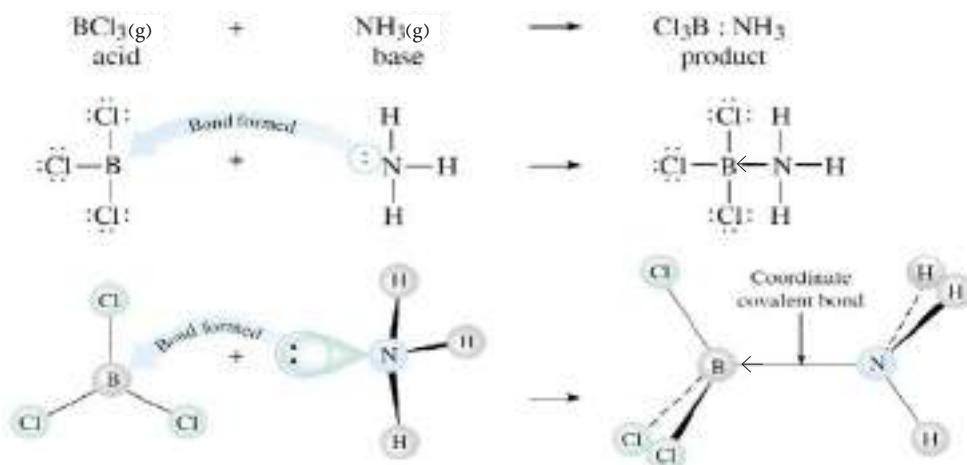
As is evident in the reverse reaction, the ion  $\text{NH}_4^+$  behaves as conjugate acid of ammonia while the  $\text{OH}^-$  exhibits the behavior of a conjugate base of water. It is noted from the above that water exhibits acidic (proton-donor) behavior in its reaction with  $\text{NH}_3$  while its behavior is basic (proton-receptor) at its reaction with  $\text{HCl}$  and  $\text{HF}$ , therefore, the behavior of water as acid or as a base depends on the other class contained in the solution, and this can be described that water has an amphoteric behavior and will explain this later.

### 6-3-3 Lewis Theory

In 1939 Lewis proposed the most comprehensive theory among other theories for the definition of acid and base. The base, according to Lewis' concept is any substance that can donate a non-bonded pair of electrons in their chemical reactions, while the acid is any substance that has a blank orbital and can accept the electronic pair of another class. This theory does not stipulate that the electronic pair must move completely from one atom to another but instead assume that the electronic pair which one atom has, becomes shared between the two atoms. So the neutralization process (acid-base reaction) identify as it is to form coordinate bond, and the reaction between trichloride boron with ammonia is an typical example of the reaction between Lewis acid-base.

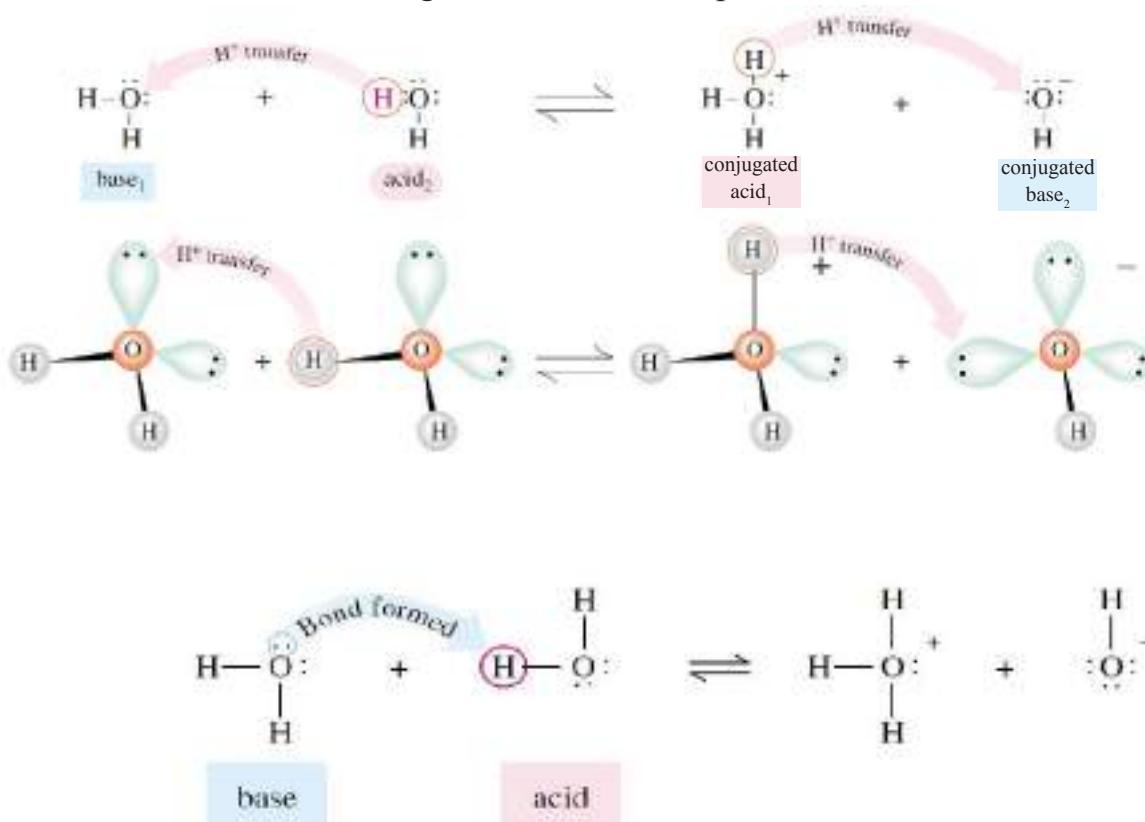


## The dissolution of ammonia in its aqueous solution.



### Self-ionization of water

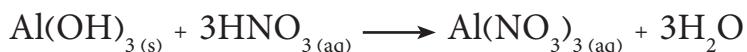
Careful measurements showed that pure water ionizes ever so slightly to produce equal numbers of hydronium ions and hydroxide ions. Where one water molecule donates a proton to another water molecule, and can be expressed this according to Bronsted concept:



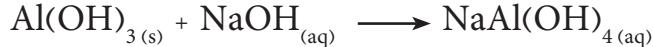
The transition of the proton to the base involves the formation of a coordinate bond. It is clear that in the process of self-ionization, one of the molecules of water behaves acid and other molecule behaves as base behavior so it is said that water behavior is amphoteric behavior.

## 6-4 Amphoteric substances

As we already know, a certain substance can behave as acid or base behavior depending on the medium it is in. Amphoteric is general term describing the reactivity of a substance either as an acid or as a base. The amphoteric behavior describes the state in which the substance has an amphoteric property by gaining or losing a proton ( $H^+$ ). For a number of the metallic hydroxides that low soluble in water are an amphoteric property as they react with acids to form salts dissolved in water but at the same time they can dissolve by reacting with an excess of strong base. For example, aluminum hydroxide is a typical example of metallic hydroxide amphoteric as it exhibits a basic behavior by reacting with nitric acid to form salt as in the following equation:



When a solution of any strong base (such as  $NaOH$ ) is added to the solid aluminum hydroxide powder,  $Al(OH)_3$  exhibits acidic behavior and begins to dissolve, forming dissolved sodium aluminate as in the following equation:



A number of other metal hydroxides have the same behavior, as shown in Table (6-2).

Table (6-2) Some amphoteric hydroxides

| metallic ion metalloids ion |           | Insoluble amphoteric hydroxide | The complex ion is formed with an excess of a strong base |
|-----------------------------|-----------|--------------------------------|---|
| Beryllium ion               | $Be^{2+}$ | $Be(OH)_2$                     | $[Be(OH)_4]^{2-}$   |
| Aluminum ion                | $Al^{3+}$ | $Al(OH)_3$                     | $[Al(OH)_4]^-$  |
| Chrome ion                  | $Cr^{3+}$ | $Cr(OH)_3$                     | $[Cr(OH)_4]^-$  |
| Zinc ion                    | $Zn^{2+}$ | $Zn(OH)_2$                     | $[Zn(OH)_4]^{-2}$   |
| Tin (II) ion                | $Sn^{2+}$ | $Sn(OH)_2$                     | $[Sn(OH)_3]^-$  |
| Tin (IV) ion                | $Sn^{4+}$ | $Sn(OH)_4$                     | $[Sn(OH)_6]^{2-}$   |
| Lead ion                    | $Pb^{2+}$ | $Pb(OH)_2$                     | $[Pb(OH)_4]^{2-}$   |
| Arsenic(III) ion            | $As^{3+}$ | $As(OH)_3$                     | $[As(OH)_4]^-$  |
| Antimony(III) ion           | $Sb^{3+}$ | $Sb(OH)_3$                     | $[Sb(OH)_4]^-$  |
| Silicon ion                 | $Si^{4+}$ | $Si(OH)_4$                     | $SiO_4^{4-}, SiO_3^{2-}$                                  |
| Cobalt ion                  | $Co^{2+}$ | $Co(OH)_2$                     | $[Co(OH)_4]^{2-}$   |
| Copper ion                  | $Cu^{2+}$ | $Cu(OH)_2$                     | $[Cu(OH)_4]^{2-}$   |

## 6-5 Acid and base reactions in aqueous solutions

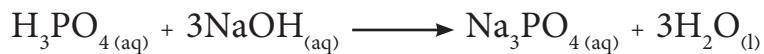
The reaction between acid and base which results salt and water is called neutralization reaction, most salts are ionic compounds. Table (6-3) shows common strong acids and bases

Table (6-3) Common strong acids and bases

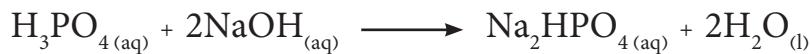
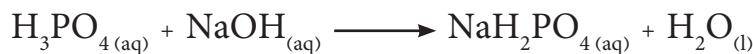
| Base   | Acid   |
|--|--|
| Lithium hydroxide LiOH                       | Hydrochloric acid HCl                          |
| Sodium hydroxide NaOH                        | Hydrobromic acid HBr                           |
| Potassium hydroxide KOH                      | Hydroiodic acid HI                             |
| Rubidium hydroxide RbOH                      | Perchloric acid $\text{HClO}_4$                |
| Cesium hydroxide CsOH                        | Chloric acid $\text{HClO}_3$                   |
| Calcium hydroxide $\text{Ca}(\text{OH})_2$   | Nitric acid $\text{HNO}_3$                     |
| Strontium hydroxide $\text{Sr}(\text{OH})_2$ | Sulfuric acid $\text{H}_2\text{SO}_4$          |
| Barium hydroxide $\text{Ba}(\text{OH})_2$    | Chromic acid $\text{H}_2\text{Cr}_2\text{O}_7$ |

When any acid reacts with a base in stoichiometric will result a normal salt (equivalent). It does not contain hydrogen atoms or ionized hydroxide groups.

For example, the complete neutralization of phosphoric acid ( $\text{H}_3\text{PO}_4$ ) with sodium hydroxide (NaOH) is produced a normal salt sodium phosphate ( $\text{Na}_3\text{PO}_4$ ) according to the following equation:



If base is added less than the equivalent amount required to completely neutralize the acid, it will result acidic salts due to the ability of these salts to react with the base, as shown in the following equations:

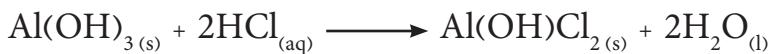


There are many examples of this type of salts, including hydrogenated sodium carbonate (acidic), also called sodium bicarbonate ( $\text{NaHCO}_3$ ).

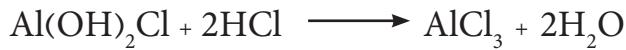
When a polyhydroxide base (a base containing more than one hydroxide group in its chemical formula) is reacted with an equivalent amount of acid, a normal salt is formed as described in the following equation:



When this type of base reacts with less amount of acid than is necessary to equivalent it, then strong base salts are formed (i.e. salts contains non-reactive OH groups (as shown in the following equations:



It should be noted that the basic salts is not necessary to have a basic character, but they can react and neutralize acids as described in the following equation:



## 6-6 Types of salts

As we learned earlier, when a solution of acid is neutralize with the base completely and accurately, the resulting solution is a salt derived from a pair acid-base. That such a situation often occurs in chemical reactions used in chemical analysis processes which will be necessary to calculate the acidic function (pH) or in other words the concentration of hydrogen ion in the solution. Salts are a strong electrolyte, therefore salt will completely dissociated in the solution. If the acid and base are strong, the acidic value of aqueous salt solution remains constant does not change. If one or both pairs (the acid and the base that formed the salt) is weak, then the calculation of the acidic function of solution becomes more complicated, so it is appropriate to address this issue by dividing the salt into four main sections:

### 6-6-1 Salts derived from strong acids and strong base reactions

Example of reaction of hydrochloric acid HCl with sodium hydroxide NaOH



The solubility of this group of salts does not affect the equilibrium process between hydrogen and hydroxide ions in water:



Therefore, the solution remains neutral.

### 6-6-2 Salts derived from weak acids (HA) and strong bases (MOH)

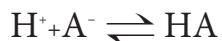
The weak acid HA reacts with the strong base of MOH as follows:



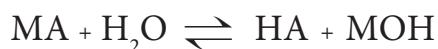
The salt (MA) of this type completely dissociated in its aqueous solution:



As is known, the aqueous solution also contains small amounts of hydrogen and hydroxide ions resulting from dissociation of water molecules. Because acid HA is weak acid, it is partially ionized, so the amount of  $\text{A}^-$  ions that can be present in the solution with  $\text{H}^+$  ions is also small, and to maintain the equilibrium state in the solution,  $\text{A}^-$  ions combine with  $\text{H}^+$  ions to form the weak acid HA



The only source of hydrogen ions in the solution is the dissociation of more water molecules. That the continued dissociation of water molecules will produce quantities of hydroxide ion and hydrogen ion consumed from the solution to form the weak acid HA. All that leads finally to increase in the concentration of hydroxide ions in the solution at the expense of the concentration of hydrogen ions, and the solution becomes basic. This condition in which an ion (or ions) of salt reacts with water ions is called hydrolysis process. The hydrolysis process of a salt derived from a weak acid and a strong base can be expressed by the following equation:



The property of the solution depends on the relative strength of the acid and the base resulting from the hydrolysis process, an example of this type of salts is sodium acetate ( $\text{CH}_3\text{COONa}$ ) and formic potassium ( $\text{HCOOK}$ ).

### 6-6-3 Salts derived from strong acids (HA) and weak bases (B)

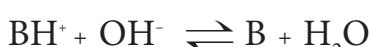
This type of salts is formed according to the following equation:



This salt is fully ionized in the aqueous solution:



In the aqueous solution of salt  $(\text{BH})\text{A}$ , the concentration of  $\text{BH}^+$  ion (formed by the complete dissolution of the salt) decreases, due to its association with the hydroxide ion (resulting from the dissolution of water molecules) to form the weak base B and reach to the equilibrium state, as in the following equation:

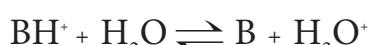
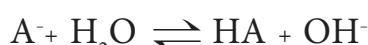


Therefore the concentration of hydrogen ion in the solution will increase at the expense of the hydroxide ion (consumed to form the weak base), so the solution becomes acidic.

An example of this type of salts is ammonium chloride salt  $(\text{NH}_4)\text{Cl}$  and ammonium sulfate salt  $(\text{NH}_4)\text{SO}_4$ .

### 6-6-4 Salts derived from weak acids (HA) and weak bases(B)

In the aqueous solution of this type of salt, the following two instantaneous reactions occur:



The property of the acidic or basic solution depends mainly on this case on the relative strength of acid and base (whichever is stronger than the second). If they are the same strength (acid dissociation constant = base dissociation constant) the aqueous solution of salt is neutral. If the acid dissociation constant is larger than the base dissociation constant. The aqueous solution of the salt is acidic and vice versa.

### Information

Dissociation constant of weak acid and base means (ability of dissociation of weak acid and weak base to produce their ions in the solution).

## 6-7 Acid and bases indicators

Acid and base indicators are organic dyes (organic compounds), the color of which depends on the concentration of  $\text{H}_3\text{O}^+$  ions in the solution. The color of the indicators shows the amount of acidity or basicity of the solution. The first indicators that were used for this purpose were plant dyes such as sunflower (Litmus), but most of the indicators used now are laboratory-made materials. Most of the indicators for acid-base reactions are weak organic acids (symbolized as  $\text{HIn}$ ), which have a color for its non-dissociated formula that differ than the color of dissociated formula  $\text{In}^-$ . For example, the non-dissociated blue bromophenol dye indicator (is a very weak organic acid) have yellow color, while the dissociated dye have a blue color as shown in the following equation for the indicator  $\text{HIn}$ :



The color of the solution is determined by the ratio of the quantities of both dissociated  $\text{In}^-$  and non- dissociated  $\text{HIn}$  available in the solution. A type of indicator used in neutralization reactions is called general or comprehensive indicators (consisting of a combination of a number of acid-base indicators). These indicators show a gradient in color for a wide range of acidic function.

## 6-8 Acid and base solutions

Aqueous solutions of acids and bases are considered to be the most important solutions. These solutions are vitally important, as the biological reactions that occur within our bodies take place in aqueous acidic or basic media, and any difference, even if a slight concentration of these solutions may alter these reactions, it may result in impaired physiology. Acids and bases prepare in the laboratory in different concentrations according to what we have already learned about the preparation of solutions previously. For example, a solution of hydrochloric acid (HCl) can be prepared by dissolving hydrogen chloride gas HCl in water, and solutions of sodium hydroxide can also be prepared by dissolving solid NaOH in water. The preparation process each time is done by dissolving a known quantity (mass or number of moles) of the solute, and precisely, in a specific amount (mass or volume) of the solvent according to calculations made for this purpose.

Figure 6-1

The colors of the three solutions are common indicators at values for the acidic function of the solution (pH) ranging from 3-11 (A) red methyl, (b) blue bromothymol, (c) phenolphthalein.

### Example 6-1

Calculate the molarity of a solution containing 3.65 g HCl in 2 L of solution (molar mass 36.5g/mol).

#### Solution

According to the law of the molar

$$M = \frac{n \text{ (mol)}}{V \text{ (L)}}$$

Calculate the number of moles of HCl from the following relationship:

$$n_{\text{HCl}} = \frac{m \text{ (g)}}{M \text{ (g/mol)}} = \frac{3.65 \text{ (g)}}{36.5 \text{ (g/mol)}} = 0.1 \text{ mol}$$

So molarity is equal to:

$$M = \frac{n \text{ (mol)}}{V \text{ (L)}} = \frac{0.1 \text{ (mol)}}{2.0 \text{ (L)}} = 0.05 \text{ mole/L} = 0.05 \text{ M}$$

### Example 6-2

Calculate the mass of Ba(OH)<sub>2</sub> (molar mass = 171 g / mol) needed to prepare 2.5 L of barium hydroxide solution at a concentration of 0.06 M.

#### Solution

Based on the law of molarity:

$$M \text{ (mol/L)} = \frac{n \text{ (mol)}}{V \text{ (L)}}$$

From the definition of moles numbers

$$n_{\text{HCl}} = \frac{m \text{ (g)}}{M \text{ (g/mol)}}$$

Combining the two relationships above we get:

$$M \text{ (mol/L)} = \frac{\frac{m \text{ (g)}}{M \text{ (g/mol)}}}{V \text{ (L)}}$$

and then we get the mass of Ba(OH)<sub>2</sub>

$$m(g) = M(\text{mol/L}) \times V(\text{L}) \times M \text{ (g/mol)}$$

$$m(g) = 0.06 \text{ (mol/L)} \times 2.5 \text{ (L)} \times 171.3 \text{ (g/mol)}$$

$$m(g) = 25.695 \text{ g}$$

### Exercise 6-1

Calculate the molarity of concentrated sulfuric acid solution in one liter (molar mass = 98 g/mol) if you know the mass percentage of the acid in the solution is 96.4% and the mass of the solution is equal 1.96 kg / L .

## 6-9 Titration

Laboratory (acid-base) reactions are usually used to measure the volume of a solution (known concentration) to react with a certain volume of another solution with unknown concentration and then the measured volume is used to calculate the concentration of the first solution, this process is called titration. Titration is the process in which the solution of one of the two reactants is added gradually from a cylindrical glass instrument inserted in such a way that it can accurately measure the volume of the solution and it is called the burette, to a solution of the other reactant typically found in a conical flask called a (Erlenmeyer flask) until the reaction between the two substances is complete. Then measured the volume of the solution that should added to complete the reaction.



To determine the point at which the titration process is stopped (the point at which the reaction between the acid and the base ends) is called the (end point) or the actual equivalence point where a substance color-changing is added that its color-changing at this point called the indicator.

For example, an acid solution with unknown concentration in the conical flask can be titrated by gradual addition of a standard sodium hydroxide solution (with a known concentration) from the burette [Figure (6-2)] and using the phenolphthalein indicator.



Figure 6-2

Titration of a solution of unknown concentrated acid against a standard solution of the base where the reaction endpoint is determined when the color of the added indicator to the titrated solution changes.

### Example 6-3

What is the molar concentration of an acid solution for hydrochloric acid if know that 36.5 mL of it was necessary to react with 43.2 mL of 0.236M of sodium hydroxide solution?

#### Solution



The reaction equation shows that one mole of acid is equivalent to one mole of the base, or one millimole of acid is equivalent to one millimole of the base, so it calculates the number of millimoles of sodium hydroxide involved in the reaction firstly. Then it can be calculated the molar of hydrochloric acid concentration because the volume of the acid solution is known.

#### Information

$$V_{\text{HCl}} = 36.5 \text{ mL}$$

$$M_{\text{HCl}} = ?$$

$$V_{\text{NaOH}} = 43.2 \text{ mL}$$

$$M_{\text{NaOH}} = 0.236 \text{ M}$$

Using the dilution law of the solution

$$M_{\text{HCl}} \times V_{\text{HCl}} = M_{\text{NaOH}} \times V_{\text{NaOH}}$$

$$M_{\text{HCl}} \times 36.5 \text{ mL} = 0.236 \text{ M} \times 43.2 \text{ mL}$$

$$M_{\text{HCl}} = \frac{0.236 \text{ M} \times 43.2 \text{ mL}}{36.5 \text{ mL}} = 0.278 \text{ M}$$

### Example 6-4

In the process of titration of sulfuric acid solution with standard sodium hydroxide solution. It was found that 43.2 mL of a solution of 0.236 M sodium hydroxide consumes 36.5 mL of acid solution to reach the end reaction point the reaction (changes the color of the blue bromophenol indicator from blue color to yellow color). What is solution molarity of  $\text{H}_2\text{SO}_4$ ?

#### Solution



The chemical equation of the reaction shows that the reaction ratio is 1 mol of  $\text{H}_2\text{SO}_4$  per 2 mol of  $\text{NaOH}$ , so the number millimoles of sulfuric acid are equal to half of the millimoles of sodium hydroxide, so we write the dilution law as follows:

$$M_{\text{H}_2\text{SO}_4} \times V_{\text{H}_2\text{SO}_4} = \frac{1}{2} \times (M_{\text{NaOH}} \times V_{\text{NaOH}})$$

#### Information

$$V_{\text{H}_2\text{SO}_4} = 36.5 \text{ mL}$$

$$M_{\text{H}_2\text{SO}_4} = ?$$

$$V_{\text{NaOH}} = 43.2 \text{ mL}$$

$$M_{\text{NaOH}} = 0.236 \text{ M}$$

#### Substitute in the above relationship

$$M_{\text{H}_2\text{SO}_4} \times 36.5 \text{ mL} = \frac{1}{2} \times (0.236 \text{ M} \times 43.2 \text{ mL})$$

$$M_{\text{H}_2\text{SO}_4} = \frac{0.236 \text{ M} \times 43.2 \text{ mL}}{2 \times 36.5 \text{ mL}} = 0.139 \text{ M}$$

## Basic concepts

### Hydronium ion( $\text{H}_3\text{O}^+$ )

Is a common expression of full hydrogen ion.

### Self – Ionization

Ionization reaction occurs between similar molecules (For the same substance).

#### Ionization in aqueous solution

A process that involves the reaction of a compound molecule with water to form ions.

### Titration

A process by which the standard solution volume (with a known concentration) is required to react with specific amount of material to be estimated.

### Neutralization

Acid reaction with base to form salt and water. Hydrogen ions usually interact with ions hydroxide to form water molecules.

### Arrhenius acid

A substance that produces  $\text{H}_{(\text{aq})}^+$  ions in aqueous solutions. Strong acids ionize completely or almost completely in dilute aqueous solutions, while weak acids are partially deionized.

### Acid Bronshted Laurie

Proton donates class

### Lewis acid

Any item can contribute to receiving a pair of electrons to form a symmetric nucleus.

### Indicator

An organic substance that can show different colors when present in different acid solutions, so it is used to determine the point at which the reaction between two substances is finished( one of them act as acid and the other as a base).

### Arrhenius base

Substance produce ions  $\text{OH}^-$  in aqueous solutions. Strong bases are dissolved in water and completely dissociated, while weak bases are partially deionized.

Base Bronshted Laurie

Proton - acquired class.

### Lewis Base

Any item can contribute by providing (honor) a pair of electrons to form a co-ordinate bond.

### Amphoteric substance

The substance that shows the amphoteric property and that of during their ability to acquire or lose protons, i e, any substance that has the potential to behave either acid or base behavior.

### Equivalence

The point at which equivalent amounts chemical reactants have reacted.

### Standard solution

A solution whose concentration is precisely known.

### Calibration

A process by which the concentration of the solution is determined accurately, it is usually corrected against known control quantity of standard material.

### Hydrolysis

Ionization or dissociation of the substance in water.

## Chapter Six Questions

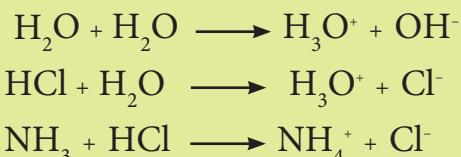
6

6-1 How did Arrhenius define the acid, base and neutralization process? Explain this by example.

6-2 Using the Bronshted and Laurie theory, explain what is meant by each of the following with example:

A- acid                      B- conjugate base  
C- base                      D- conjugate acid  
E- pairs of conjugate acid-base

6-3 Distinguish between acids and bases in each of the following using the theory of Lewis, indicating the donor and acquired of electron pair:



6-4 What is acid salt? Write balanced chemical equations to show how to get the following acidic salts from appropriate acids and bases:

A-  $\text{NaHSO}_3$               B-  $\text{KHCO}_3$   
C-  $\text{NaH}_2\text{PO}_4$               D-  $\text{NaHS}$

6-5 Explain why

A- Salts solutions derived from strong acids and strong bases will be neutral.

B- Salts solutions derived from strong acids and weak bases are acidic.

C- Salts solutions derived from weak acids and strong bases are basic.

6-6 Calculate the molarity of the nitric acid solution if you know that 35.7 mL from it neutralized, in titration process, 0.302g from  $\text{Na}_2\text{CO}_3$ .

6-7 How much the volume of concentrated HCl acid(Its mass percentage = 36% and its density = 1.18 g/mL) is required to prepare 500 mL of dilute solution of the same acid at concentration of 2 M?

6-8 Calculate the mass of  $\text{HNO}_3$  contained in 5 mL of concentrated acid solution( Its mass percentage = 69.8% and its density = 1.42 g / mL).

6-9 How much ammonium sulfate salt  $(\text{NH}_4)_2\text{SO}_4$  (molar mass = 132.8 g/mol) required to prepare 400 mL of solution in a concentration of 0.25 M?

6-10 How much the volume of concentrated sulfuric acid( Its mass percentage = 98% and its density = 1.84 g / mL) is required to prepare 100 mL of diluted acid solution( Its mass percentage 20% and its density = 1.14 g / mL).

6-11 Put (✓) in front of the correct statement and a sign (✗) in front of incorrect statement as follows:

1. All Bronshted-Laurie acids and bases are considered Arrhenius acids and bases.
2. Ammonia reacts with water as Bronshted base.
3. The aluminum chloride ( $\text{AlCl}_3$ ) is an acid Louis.
4. The conjugate base of strong acid behave as strong behavior base.
5. Boron trifluoride is considered Lewis acid.

6-12 Which of the following statements relates to Arrhenius theory are correct?

1. Acid-base reaction according to Bronshted-Lauri theory includes protons transmission.
2. One of the essential requirements for the Bronshted-Lauri statement is the presence of hydroxide ion in its chemical formula.



## Chapter Six Acids, Bases and Salts

6

After completing this chapter, the student is expected to:

- Recognize the properties of aqueous solutions of acids and bases.
- Identify the different molecular concepts of acids and bases according to Arrhenius and Bronshted-Lauri and Lewis theories.
- Characterize the auto-ionization of water and the amphoteric properties of some substances.
- Recognize the acids and bases reactions in aqueous solutions.
- Distinguish between the types of salts, the method of forming each and the properties of their aqueous solutions.
- Recognize the indicators that used in neutralization reaction.
- Recognize the titration process and understand its importance.

## 6-1 Introduction

In nature, there are many acids, bases and salts that are used in different fields, for example, digestive juices in the human body contain a solution of hydrochloric acid at a concentration of about 0.1 molar and in the blood of human and also water components in body cells have a moderate acid action. The solution in the car battery is composed of 40% by mass of sulfuric acid solution. On the other hand, sodium hydroxide is used in the manufacture of soap, paper industry and a number of other chemical industries. The salt also has extensive uses, baking soda is one of the salts of carbonic acid. Table salt (sodium chloride) uses to give a salty taste to food on the one hand and on the other hand it is used to preserve many types of food. Another example of the use of these substances is the application of calcium chloride salt to dissolve snow accumulated on public roads. This salt is also used in the treatment of people who has heart attacks. Ammonium salts are also used as nitrogen fertilizers to increase soil fertility. Most organic acids and their derivatives are found naturally, the vinegar we use have about 4% of acetic acid in its contents. The pain that you have feel when ants bite you is caused by the formic acid that these insects secrete into the body. Amino acids form protein modules in living organisms. Many other examples illustrate the importance and uses of these substances in everyday life.



## 6-2 Properties of aqueous solutions of acids and bases

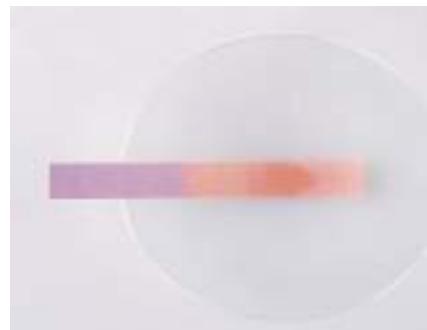
The aqueous solutions of most acids have distinctive characteristics attributed to the presence of positive hydrogen ion ( $H^+$ ) (proton) or crosses about hydronium ion ( $H_3O^+$ ) in its aqueous solution. The properties are:

1. Has an acidic taste.
2. Change the color of a number of indicators (pigments), for example change the pigment of a sunflower tint from blue color to red color
3. Acids react with most metals and release hydrogen gas ( $H_2$ ).

- Reaction with metal oxides and metal hydroxides to form salts and water.
- Its aqueous solutions have the ability to conduct electrical current because of their full or partial ionization. The Table (6-1) shows some common acids.

The aqueous solutions of most bases also have distinctive characteristics, attributed to the presence of hydroxide ion ( $\text{OH}^-$ ) in its aqueous solution and qualities. The properties are:

- Has a pungent taste.
- It has a viscous soapy texture as in the case of aqueous solution of sodium hydroxide.
- Change the color of a number of indicators, for example change the pigment of the sun flower tint from red color to blue color.
- Reacts with acids (neutralize) to form salts and water.
- Its aqueous solutions have the ability to conduct electrical current to their ability to be ions.



The acid solution changes the color of the pigment sunflower to red color.



The basic solution changes the color of the pigment sunflower to blue color.

Table (6-1) Some of the common acids and their uses.

| Acid name                             | Acid name Uses   |
|---------------------------------------|--|
| hydrochloric acid $\text{HCl}$        | Purification of minerals and purification of mineral ores and preparation of some food. It is the main component of stomach acids. |
| Sulfuric acid $\text{H}_2\text{SO}_4$ | Manufacture of fertilizers, explosives, glues and liquid used in the cars batteries.   |
| Nitric acid $\text{HNO}_3$            | Manufacture of fertilizers, explosives and adhesives.  |
| Acetic acid $\text{CH}_3\text{COOH}$  | Plastic and rubber industry and in food preservation is the main component for vinegar.  |
| Carbonic acid $\text{H}_2\text{CO}_3$ | It is present in all carbonated drinks due to the reaction of carbon dioxide with water.   |
| Hydrofluoric acid $\text{HF}$         | Clean the metal and polish the glass and engraving it.   |

## 6-3 Molecular concepts of acids and bases

In this section we will look at the molecular concepts of acids and bases according to the main theories are:

### 6-3-1 The Arrhenius Theory

In 1884 Arrhenius presented his theory of electrolysis dissociation, which later resulted in a theory for naming acids and bases which states on the following:

**Acid is the substance that contains hydrogen which is ionized to given hydrogen ions ( $H^+$ ) in the aqueous solution.**

By the definition of Arrhenius, HCl is considered to be Arrhenius acid because it produces  $H^+$  ions in aqueous solution:

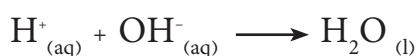


**The base is the substance that contains the hydroxide group ( $OH^-$ ) which ionizes the data of the negative hydroxide ions in the aqueous solution.**

According to Arrhenius' definition of the base, NaOH is the Arrhenius base because it produces hydroxide ions  $OH^-$  in the aqueous solution:



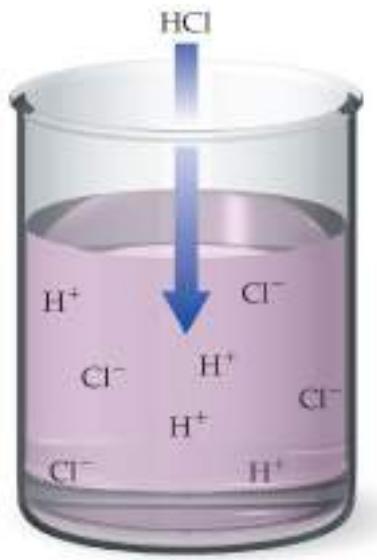
The process of neutralization according to this theory is defined as a union  $H^+$  ions and  $OH^-$  ions to form water molecules:



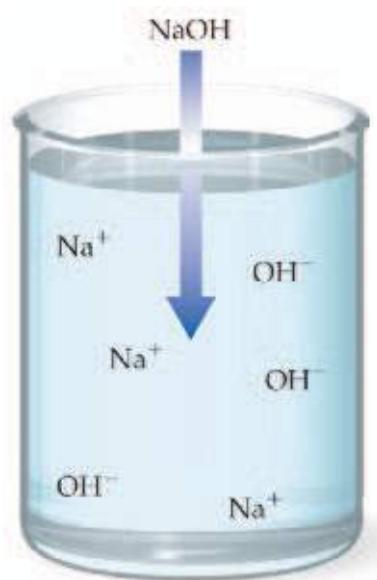
Arrhenius theory successfully explained the acids reactions that have protons with metal hydroxides (hydroxide bases), although the application of this theory is limited, it has led to the development of more comprehensive theories to describe the properties of acids and bases.

### Hydronium ion (hydrated hydrogen ion)

Arrhenius described hydrogen ions in water as  $H^+$  ( $H_2O$ )<sub>n</sub>, (where n is an integer) this is because the attraction between  $H^+$  ions and oxygen atom carrying a negative partial charge,  $\delta^-$  in the polarized water molecule. Although we do not know exactly how hydrogen ions hydrolyze in most aqueous solutions, we usually represent hydrogen ion as hydronium  $H_3O^+$ . Thus, it is argued that the hydrated ion of hydrogen

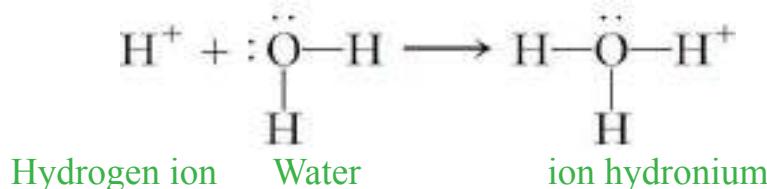


Ionization of hydrochloric acid is in water.



Ionization of sodium hydroxide in water.

is to give aqueous acid solution its specific acidity properties. The hydrogen ion can be expressed as  $\text{H}^+(\text{aq})$  or hydrolyzed  $\text{H}_3\text{O}^+$  as follows:



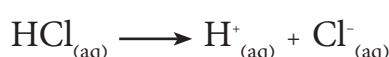
### 6-3-2 The Bronsted – Lowry Theory

In 1923, scientists Bronsted and Lowry introduced the individually developed the theory of Arrhenius and thus emerged new theory known as Bronsted-Lowry theory.

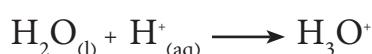
According to this theory, **acid is defined as the donor of the proton, and the base is the proton receptor.**

These definitions of acid and base are highly general as any molecule or ion contains hydrogen and has the capability to release a proton is acid, while any molecule or ion can receive a proton is a base. So an acid reaction with a base can be defined as that the reaction involves the transfer of a proton from the acid to the base. For this reason, the ionization process of hydrochloric acid (strong acid) in water, It is an acid-base reaction in which the water molecule behaves as a base because it acquires a proton. This can be expressed as follows:

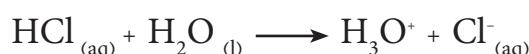
**First step (Arrhenius description)**



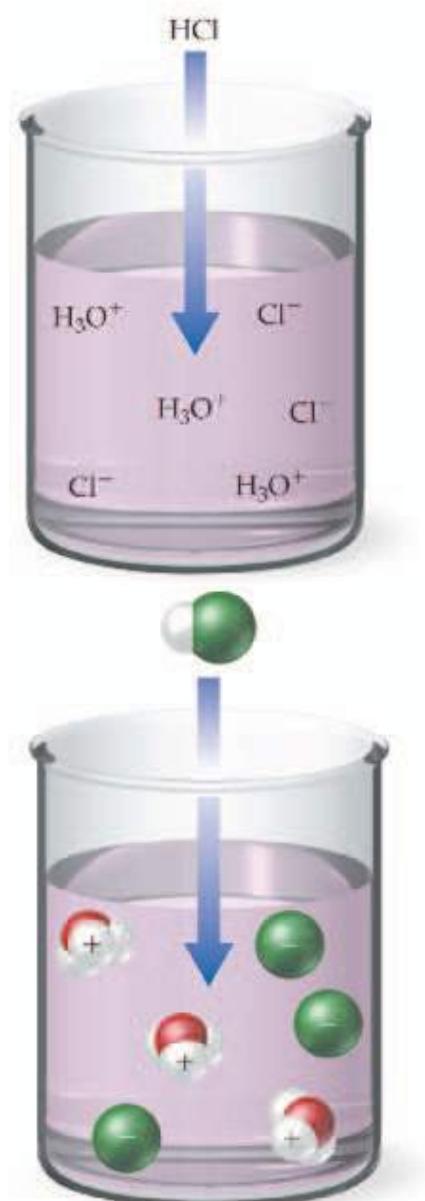
**Second step**



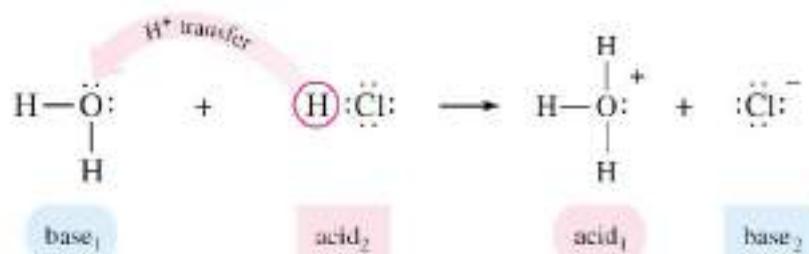
**Overall reaction (Bronsted-Lowry description)**



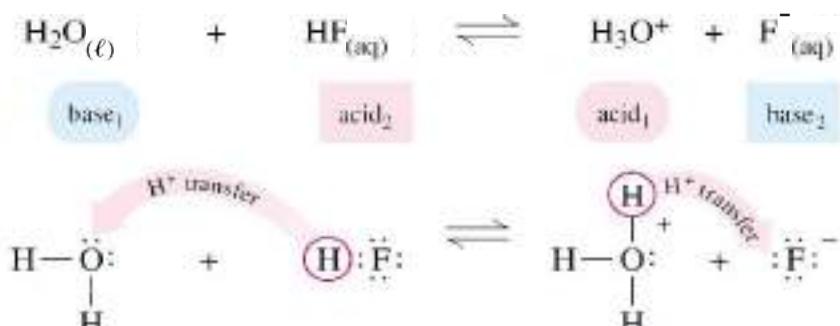
The reactions of acids and bases can be described by the Bronsted-Lowry concept in terms of pairs (conjugate acid-base) and each pair is two different classes in a proton. In the previous equation,  $\text{HCl}$  (acid) with  $\text{Cl}^-$  (conjugate base) is in the sense of a pair (conjugate acid-base), while  $\text{H}_2\text{O}$  (base) with  $\text{H}_3\text{O}^+$  (conjugate acid) ie is another pair of (conjugate base-acid ) is as in the following figure:



**Ionization of hydrochloric acid is in water.**

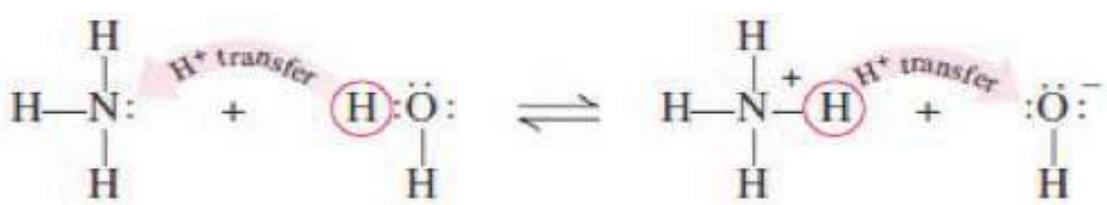
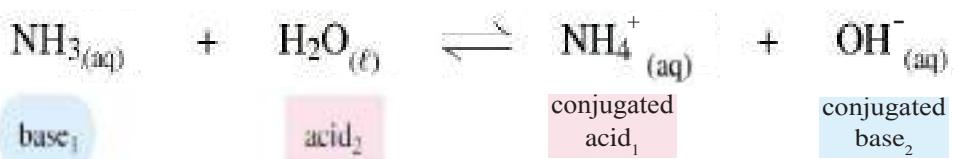


On the other hand, the ionization of hydrogen fluoride (weak acid). It occurs similarly but to a lesser extent and therefore represents the following:



In this equation HF is acid with  $F^-$  conjugate base, while  $H_2O$  represents a base with  $H_3O^+$  conjugate acid. In the forward reaction ( $\rightleftharpoons$ ) HF and  $H_2O$  exhibit acid and base behavior respectively, while in the reverse reaction ( $\rightleftharpoons$ )  $H_3O^+$  exhibits acid behavior (ie, a proton donor) and fluoride ion  $F^-$  exhibits base behavior (ie, a proton receptor). We note from the examples above that when a weak acid (HF) dissolves in water, HF molecules will produce a small amount of  $H^+$  ions. It can be acquired by one of the two basic classes in the solution  $F^-$  or  $H_2O$ . In fact, HF dissociates slightly, indicating that  $F^-$  is a stronger base than  $H_2O$ . When a strong acid (HCl) is dissolved in water, the HCl molecules will produce  $H^+$  ions that can be gained by one of the two basic classes in the solution  $Cl^-$  or  $H_2O$ . Since HCl dissociates completely in diluted aqueous solution, this means that  $Cl^-$  is lower base than  $H_2O$ . **That all means that the weak acid has strong conjugate base and the strong acid has weak conjugate base.** It can be generalized by saying: the greater the strength of acid, the weaker the conjugated base strength of his context and vice versa. These concepts must be used correctly; a strong acid or a weak acid (as well as a base) are qualities that you will use to describe a relative situation. When we say (in the previous example) that  $F^-$  is a strong base, it does not mean that it is so by comparing it with  $OH^-$  for example,

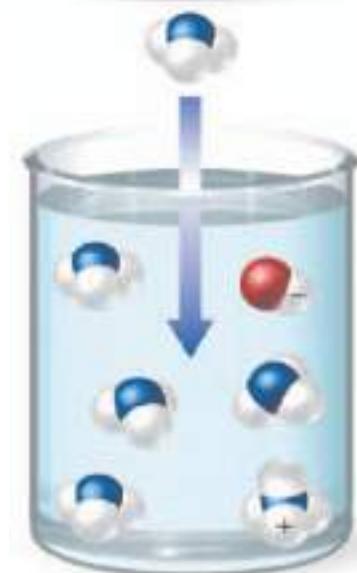
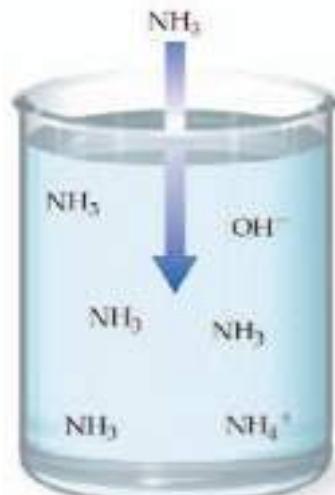
But we mean it is a stronger base relative to the conjugate base of the strong acid in the example ( $\text{H}_2\text{O}$ ). In the aqueous solution of ammonia, the ammonia molecules behave as a weak Bronsted base behavior while the water molecules behave as a acidic behavior and can be expressed as follows



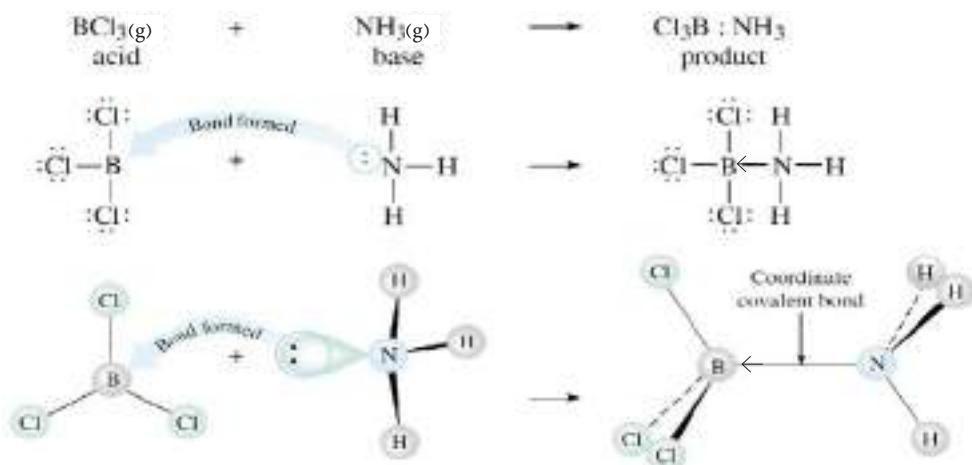
As is evident in the reverse reaction, the ion  $\text{NH}_4^+$  behaves as conjugate acid of ammonia while the  $\text{OH}^-$  exhibits the behavior of a conjugate base of water. It is noted from the above that water exhibits acidic (proton-donor) behavior in its reaction with  $\text{NH}_3$  while its behavior is basic (proton-receptor) at its reaction with  $\text{HCl}$  and  $\text{HF}$ , therefore, the behavior of water as acid or as a base depends on the other class contained in the solution, and this can be described that water has an amphoteric behavior and will explain this later.

### 6-3-3 Lewis Theory

In 1939 Lewis proposed the most comprehensive theory among other theories for the definition of acid and base. The base, according to Lewis' concept is any substance that can donate a non-bonded pair of electrons in their chemical reactions, while the acid is any substance that has a blank orbital and can accept the electronic pair of another class. This theory does not stipulate that the electronic pair must move completely from one atom to another but instead assume that the electronic pair which one atom has, becomes shared between the two atoms. So the neutralization process (acid-base reaction) identify as it is to form coordinate bond, and the reaction between trichloride boron with ammonia is an typical example of the reaction between Lewis acid-base.

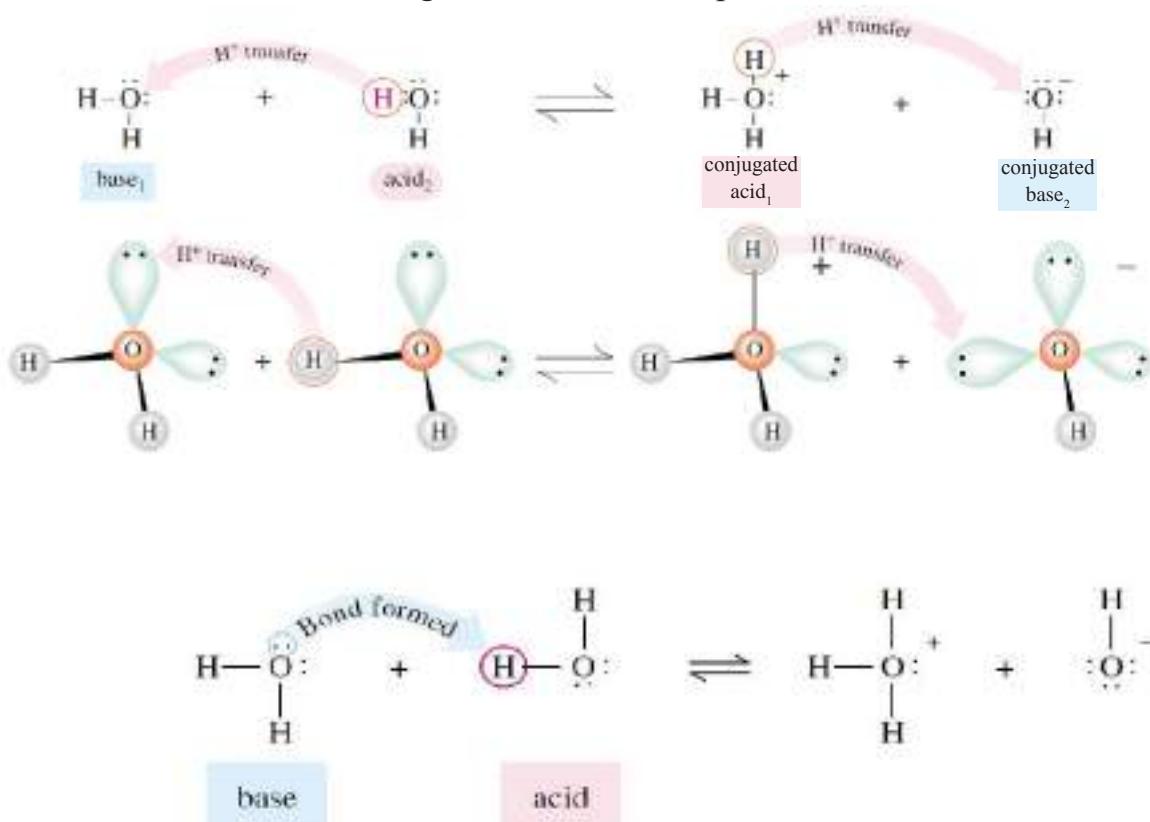


## The dissolution of ammonia in its aqueous solution.



### Self-ionization of water

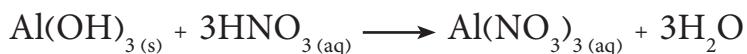
Careful measurements showed that pure water ionizes ever so slightly to produce equal numbers of hydronium ions and hydroxide ions. Where one water molecule donates a proton to another water molecule, and can be expressed this according to Bronsted concept:



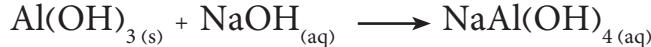
The transition of the proton to the base involves the formation of a coordinate bond. It is clear that in the process of self-ionization, one of the molecules of water behaves acid and other molecule behaves as base behavior so it is said that water behavior is amphoteric behavior.

## 6-4 Amphoteric substances

As we already know, a certain substance can behave as acid or base behavior depending on the medium it is in. Amphoteric is general term describing the reactivity of a substance either as an acid or as a base. The amphoteric behavior describes the state in which the substance has an amphoteric property by gaining or losing a proton ( $H^+$ ). For a number of the metallic hydroxides that low soluble in water are an amphoteric property as they react with acids to form salts dissolved in water but at the same time they can dissolve by reacting with an excess of strong base. For example, aluminum hydroxide is a typical example of metallic hydroxide amphoteric as it exhibits a basic behavior by reacting with nitric acid to form salt as in the following equation:



When a solution of any strong base (such as  $NaOH$ ) is added to the solid aluminum hydroxide powder,  $Al(OH)_3$  exhibits acidic behavior and begins to dissolve, forming dissolved sodium aluminate as in the following equation:



A number of other metal hydroxides have the same behavior, as shown in Table (6-2).

Table (6-2) Some amphoteric hydroxides

| metallic ion metalloids ion |           | Insoluble amphoteric hydroxide | The complex ion is formed with an excess of a strong base |
|-----------------------------|-----------|--------------------------------|---|
| Beryllium ion               | $Be^{2+}$ | $Be(OH)_2$                     | $[Be(OH)_4]^{2-}$   |
| Aluminum ion                | $Al^{3+}$ | $Al(OH)_3$                     | $[Al(OH)_4]^-$  |
| Chrome ion                  | $Cr^{3+}$ | $Cr(OH)_3$                     | $[Cr(OH)_4]^-$  |
| Zinc ion                    | $Zn^{2+}$ | $Zn(OH)_2$                     | $[Zn(OH)_4]^{-2}$   |
| Tin (II) ion                | $Sn^{2+}$ | $Sn(OH)_2$                     | $[Sn(OH)_3]^-$  |
| Tin (IV) ion                | $Sn^{4+}$ | $Sn(OH)_4$                     | $[Sn(OH)_6]^{2-}$   |
| Lead ion                    | $Pb^{2+}$ | $Pb(OH)_2$                     | $[Pb(OH)_4]^{2-}$   |
| Arsenic(III) ion            | $As^{3+}$ | $As(OH)_3$                     | $[As(OH)_4]^-$  |
| Antimony(III) ion           | $Sb^{3+}$ | $Sb(OH)_3$                     | $[Sb(OH)_4]^-$  |
| Silicon ion                 | $Si^{4+}$ | $Si(OH)_4$                     | $SiO_4^{4-}, SiO_3^{2-}$                                  |
| Cobalt ion                  | $Co^{2+}$ | $Co(OH)_2$                     | $[Co(OH)_4]^{2-}$   |
| Copper ion                  | $Cu^{2+}$ | $Cu(OH)_2$                     | $[Cu(OH)_4]^{2-}$   |

## 6-5 Acid and base reactions in aqueous solutions

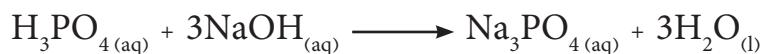
The reaction between acid and base which results salt and water is called neutralization reaction, most salts are ionic compounds. Table (6-3) shows common strong acids and bases

Table (6-3) Common strong acids and bases

| Base   | Acid   |
|--|--|
| Lithium hydroxide LiOH                       | Hydrochloric acid HCl                          |
| Sodium hydroxide NaOH                        | Hydrobromic acid HBr                           |
| Potassium hydroxide KOH                      | Hydroiodic acid HI                             |
| Rubidium hydroxide RbOH                      | Perchloric acid $\text{HClO}_4$                |
| Cesium hydroxide CsOH                        | Chloric acid $\text{HClO}_3$                   |
| Calcium hydroxide $\text{Ca}(\text{OH})_2$   | Nitric acid $\text{HNO}_3$                     |
| Strontium hydroxide $\text{Sr}(\text{OH})_2$ | Sulfuric acid $\text{H}_2\text{SO}_4$          |
| Barium hydroxide $\text{Ba}(\text{OH})_2$    | Chromic acid $\text{H}_2\text{Cr}_2\text{O}_7$ |

When any acid reacts with a base in stoichiometric will result a normal salt (equivalent). It does not contain hydrogen atoms or ionized hydroxide groups.

For example, the complete neutralization of phosphoric acid ( $\text{H}_3\text{PO}_4$ ) with sodium hydroxide (NaOH) is produced a normal salt sodium phosphate ( $\text{Na}_3\text{PO}_4$ ) according to the following equation:

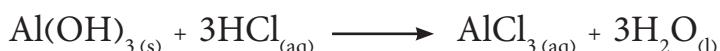


If base is added less than the equivalent amount required to completely neutralize the acid, it will result acidic salts due to the ability of these salts to react with the base, as shown in the following equations:

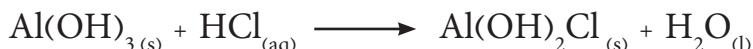


There are many examples of this type of salts, including hydrogenated sodium carbonate (acidic), also called sodium bicarbonate ( $\text{NaHCO}_3$ ).

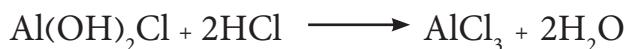
When a polyhydroxide base (a base containing more than one hydroxide group in its chemical formula) is reacted with an equivalent amount of acid, a normal salt is formed as described in the following equation:



When this type of base reacts with less amount of acid than is necessary to equivalent it, then strong base salts are formed (i.e. salts contains non-reactive OH groups (as shown in the following equations:



It should be noted that the basic salts is not necessary to have a basic character, but they can react and neutralize acids as described in the following equation:



## 6-6 Types of salts

As we learned earlier, when a solution of acid is neutralize with the base completely and accurately, the resulting solution is a salt derived from a pair acid-base. That such a situation often occurs in chemical reactions used in chemical analysis processes which will be necessary to calculate the acidic function (pH) or in other words the concentration of hydrogen ion in the solution. Salts are a strong electrolyte, therefore salt will completely dissociated in the solution. If the acid and base are strong, the acidic value of aqueous salt solution remains constant does not change. If one or both pairs (the acid and the base that formed the salt) is weak, then the calculation of the acidic function of solution becomes more complicated, so it is appropriate to address this issue by dividing the salt into four main sections:

### 6-6-1 Salts derived from strong acids and strong base reactions

Example of reaction of hydrochloric acid HCl with sodium hydroxide NaOH



The solubility of this group of salts does not affect the equilibrium process between hydrogen and hydroxide ions in water:



Therefore, the solution remains neutral.

### 6-6-2 Salts derived from weak acids (HA) and strong bases (MOH)

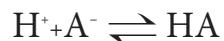
The weak acid HA reacts with the strong base of MOH as follows:



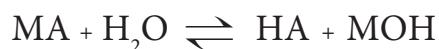
The salt (MA) of this type completely dissociated in its aqueous solution:



As is known, the aqueous solution also contains small amounts of hydrogen and hydroxide ions resulting from dissociation of water molecules. Because acid HA is weak acid, it is partially ionized, so the amount of  $\text{A}^-$  ions that can be present in the solution with  $\text{H}^+$  ions is also small, and to maintain the equilibrium state in the solution,  $\text{A}^-$  ions combine with  $\text{H}^+$  ions to form the weak acid HA



The only source of hydrogen ions in the solution is the dissociation of more water molecules. That the continued dissociation of water molecules will produce quantities of hydroxide ion and hydrogen ion consumed from the solution to form the weak acid HA. All that leads finally to increase in the concentration of hydroxide ions in the solution at the expense of the concentration of hydrogen ions, and the solution becomes basic. This condition in which an ion (or ions) of salt reacts with water ions is called hydrolysis process. The hydrolysis process of a salt derived from a weak acid and a strong base can be expressed by the following equation:



The property of the solution depends on the relative strength of the acid and the base resulting from the hydrolysis process, an example of this type of salts is sodium acetate ( $\text{CH}_3\text{COONa}$ ) and formic potassium ( $\text{HCOOK}$ ).

### 6-6-3 Salts derived from strong acids (HA) and weak bases (B)

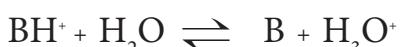
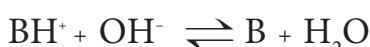
This type of salts is formed according to the following equation:



This salt is fully ionized in the aqueous solution:



In the aqueous solution of salt  $(\text{BH})\text{A}$ , the concentration of  $\text{BH}^+$  ion (formed by the complete dissolution of the salt) decreases, due to its association with the hydroxide ion (resulting from the dissolution of water molecules) to form the weak base B and reach to the equilibrium state, as in the following equation:

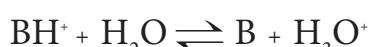


Therefore the concentration of hydrogen ion in the solution will increase at the expense of the hydroxide ion (consumed to form the weak base), so the solution becomes acidic.

An example of this type of salts is ammonium chloride salt  $(\text{NH}_4)\text{Cl}$  and ammonium sulfate salt  $(\text{NH}_4)\text{SO}_4$ .

### 6-6-4 Salts derived from weak acids (HA) and weak bases(B)

In the aqueous solution of this type of salt, the following two instantaneous reactions occur:



The property of the acidic or basic solution depends mainly on this case on the relative strength of acid and base (whichever is stronger than the second). If they are the same strength (acid dissociation constant = base dissociation constant) the aqueous solution of salt is neutral. If the acid dissociation constant is larger than the base dissociation constant. The aqueous solution of the salt is acidic and vice versa.

### Information

Dissociation constant of weak acid and base means (ability of dissociation of weak acid and weak base to produce their ions in the solution).

## 6-7 Acid and bases indicators

Acid and base indicators are organic dyes (organic compounds), the color of which depends on the concentration of  $\text{H}_3\text{O}^+$  ions in the solution. The color of the indicators shows the amount of acidity or basicity of the solution. The first indicators that were used for this purpose were plant dyes such as sunflower (Litmus), but most of the indicators used now are laboratory-made materials. Most of the indicators for acid-base reactions are weak organic acids (symbolized as  $\text{HIn}$ ), which have a color for its non-dissociated formula that differ than the color of dissociated formula  $\text{In}^-$ . For example, the non-dissociated blue bromophenol dye indicator (is a very weak organic acid) have yellow color, while the dissociated dye have a blue color as shown in the following equation for the indicator  $\text{HIn}$ :



The color of the solution is determined by the ratio of the quantities of both dissociated  $\text{In}^-$  and non- dissociated  $\text{HIn}$  available in the solution. A type of indicator used in neutralization reactions is called general or comprehensive indicators (consisting of a combination of a number of acid-base indicators). These indicators show a gradient in color for a wide range of acidic function.

## 6-8 Acid and base solutions

Aqueous solutions of acids and bases are considered to be the most important solutions. These solutions are vitally important, as the biological reactions that occur within our bodies take place in aqueous acidic or basic media, and any difference, even if a slight concentration of these solutions may alter these reactions, it may result in impaired physiology. Acids and bases prepare in the laboratory in different concentrations according to what we have already learned about the preparation of solutions previously. For example, a solution of hydrochloric acid (HCl) can be prepared by dissolving hydrogen chloride gas HCl in water, and solutions of sodium hydroxide can also be prepared by dissolving solid NaOH in water. The preparation process each time is done by dissolving a known quantity (mass or number of moles) of the solute, and precisely, in a specific amount (mass or volume) of the solvent according to calculations made for this purpose.

Figure 6-1

The colors of the three solutions are common indicators at values for the acidic function of the solution (pH) ranging from 3-11 (A) red methyl, (b) blue bromothymol, (c) phenolphthalein.

### Example 6-1

Calculate the molarity of a solution containing 3.65 g HCl in 2 L of solution (molar mass 36.5g/mol).

#### Solution

According to the law of the molar

$$M = \frac{n \text{ (mol)}}{V \text{ (L)}}$$

Calculate the number of moles of HCl from the following relationship:

$$n_{\text{HCl}} = \frac{m \text{ (g)}}{M \text{ (g/mol)}} = \frac{3.65 \text{ (g)}}{36.5 \text{ (g/mol)}} = 0.1 \text{ mol}$$

So molarity is equal to:

$$M = \frac{n \text{ (mol)}}{V \text{ (L)}} = \frac{0.1 \text{ (mol)}}{2.0 \text{ (L)}} = 0.05 \text{ mole/L} = 0.05 \text{ M}$$

### Example 6-2

Calculate the mass of Ba(OH)<sub>2</sub> (molar mass = 171 g / mol) needed to prepare 2.5 L of barium hydroxide solution at a concentration of 0.06 M.

#### Solution

Based on the law of molarity:

$$M \text{ (mol/L)} = \frac{n \text{ (mol)}}{V \text{ (L)}}$$

From the definition of moles numbers

$$n_{\text{HCl}} = \frac{m \text{ (g)}}{M \text{ (g/mol)}}$$

Combining the two relationships above we get:

$$M \text{ (mol/L)} = \frac{\frac{m \text{ (g)}}{M \text{ (g/mol)}}}{V \text{ (L)}}$$

and then we get the mass of Ba(OH)<sub>2</sub>

$$m(g) = M(\text{mol/L}) \times V(\text{L}) \times M \text{ (g/mol)}$$

$$m(g) = 0.06 \text{ (mol/L)} \times 2.5 \text{ (L)} \times 171.3 \text{ (g/mol)}$$

$$m(g) = 25.695 \text{ g}$$

### Exercise 6-1

Calculate the molarity of concentrated sulfuric acid solution in one liter (molar mass = 98 g/mol) if you know the mass percentage of the acid in the solution is 96.4% and the mass of the solution is equal 1.96 kg / L .

## 6-9 Titration

Laboratory (acid-base) reactions are usually used to measure the volume of a solution (known concentration) to react with a certain volume of another solution with unknown concentration and then the measured volume is used to calculate the concentration of the first solution, this process is called titration. Titration is the process in which the solution of one of the two reactants is added gradually from a cylindrical glass instrument inserted in such a way that it can accurately measure the volume of the solution and it is called the burette, to a solution of the other reactant typically found in a conical flask called a (Erlenmeyer flask) until the reaction between the two substances is complete. Then measured the volume of the solution that should added to complete the reaction.



To determine the point at which the titration process is stopped (the point at which the reaction between the acid and the base ends) is called the (end point) or the actual equivalence point where a substance color-changing is added that its color-changing at this point called the indicator.

For example, an acid solution with unknown concentration in the conical flask can be titrated by gradual addition of a standard sodium hydroxide solution (with a known concentration) from the burette [Figure (6-2)] and using the phenolphthalein indicator.

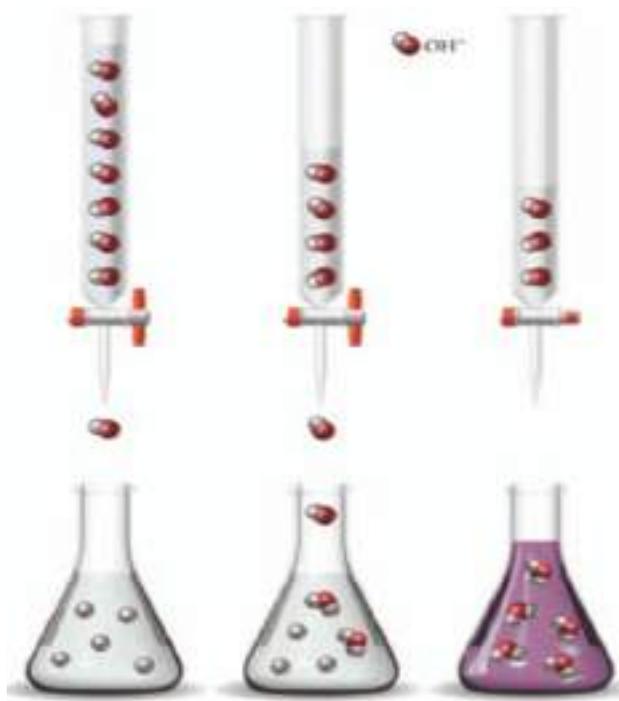


Figure 6-2

Titration of a solution of unknown concentrated acid against a standard solution of the base where the reaction endpoint is determined when the color of the added indicator to the titrated solution changes.

### Example 6-3

What is the molar concentration of an acid solution for hydrochloric acid if know that 36.5 mL of it was necessary to react with 43.2 mL of 0.236M of sodium hydroxide solution?

#### Solution



The reaction equation shows that one mole of acid is equivalent to one mole of the base, or one millimole of acid is equivalent to one millimole of the base, so it calculates the number of millimoles of sodium hydroxide involved in the reaction firstly. Then it can be calculated the molar of hydrochloric acid concentration because the volume of the acid solution is known.

#### Information

$$V_{\text{HCl}} = 36.5 \text{ mL}$$

$$M_{\text{HCl}} = ?$$

$$V_{\text{NaOH}} = 43.2 \text{ mL}$$

$$M_{\text{NaOH}} = 0.236 \text{ M}$$

Using the dilution law of the solution

$$M_{\text{HCl}} \times V_{\text{HCl}} = M_{\text{NaOH}} \times V_{\text{NaOH}}$$

$$M_{\text{HCl}} \times 36.5 \text{ mL} = 0.236 \text{ M} \times 43.2 \text{ mL}$$

$$M_{\text{HCl}} = \frac{0.236 \text{ M} \times 43.2 \text{ mL}}{36.5 \text{ mL}} = 0.278 \text{ M}$$

### Example 6-4

In the process of titration of sulfuric acid solution with standard sodium hydroxide solution. It was found that 43.2 mL of a solution of 0.236 M sodium hydroxide consumes 36.5 mL of acid solution to reach the end reaction point (changes the color of the blue bromophenol indicator from blue color to yellow color). What is solution molarity of  $\text{H}_2\text{SO}_4$ ?

#### Solution



The chemical equation of the reaction shows that the reaction ratio is 1 mol of  $\text{H}_2\text{SO}_4$  per 2 mol of  $\text{NaOH}$ , so the number millimoles of sulfuric acid are equal to half of the millimoles of sodium hydroxide, so we write the dilution law as follows:

$$M_{\text{H}_2\text{SO}_4} \times V_{\text{H}_2\text{SO}_4} = \frac{1}{2} \times (M_{\text{NaOH}} \times V_{\text{NaOH}})$$

#### Information

$$V_{\text{H}_2\text{SO}_4} = 36.5 \text{ mL}$$

$$M_{\text{H}_2\text{SO}_4} = ?$$

$$V_{\text{NaOH}} = 43.2 \text{ mL}$$

$$M_{\text{NaOH}} = 0.236 \text{ M}$$

#### Substitute in the above relationship

$$M_{\text{H}_2\text{SO}_4} \times 36.5 \text{ mL} = \frac{1}{2} \times (0.236 \text{ M} \times 43.2 \text{ mL})$$

$$M_{\text{H}_2\text{SO}_4} = \frac{0.236 \text{ M} \times 43.2 \text{ mL}}{2 \times 36.5 \text{ mL}} = 0.139 \text{ M}$$

## Basic concepts

### Hydronium ion( $\text{H}_3\text{O}^+$ )

Is a common expression of full hydrogen ion.

### Self – Ionization

Ionization reaction occurs between similar molecules (For the same substance).

#### Ionization in aqueous solution

A process that involves the reaction of a compound molecule with water to form ions.

### Titration

A process by which the standard solution volume (with a known concentration) is required to react with specific amount of material to be estimated.

### Neutralization

Acid reaction with base to form salt and water. Hydrogen ions usually interact with ions hydroxide to form water molecules.

### Arrhenius acid

A substance that produces  $\text{H}_{(\text{aq})}^+$  ions in aqueous solutions. Strong acids ionize completely or almost completely in dilute aqueous solutions, while weak acids are partially deionized.

### Acid Bronshted Laurie

Proton donates class

### Lewis acid

Any item can contribute to receiving a pair of electrons to form a symmetric nucleus.

### Indicator

An organic substance that can show different colors when present in different acid solutions, so it is used to determine the point at which the reaction between two substances is finished( one of them act as acid and the other as a base).

### Arrhenius base

Substance produce ions  $\text{OH}^-$  in aqueous solutions. Strong bases are dissolved in water and completely dissociated, while weak bases are partially deionized.

Base Bronshted Laurie

Proton - acquired class.

### Lewis Base

Any item can contribute by providing (honor) a pair of electrons to form a co-ordinate bond.

### Amphoteric substance

The substance that shows the amphoteric property and that of during their ability to acquire or lose protons, i e, any substance that has the potential to behave either acid or base behavior.

### Equivalence

The point at which equivalent amounts chemical reactants have reacted.

### Standard solution

A solution whose concentration is precisely known.

### Calibration

A process by which the concentration of the solution is determined accurately, it is usually corrected against known control quantity of standard material.

### Hydrolysis

Ionization or dissociation of the substance in water.

## Chapter Six Questions

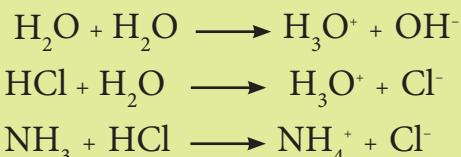
6

6-1 How did Arrhenius define the acid, base and neutralization process? Explain this by example.

6-2 Using the Bronshted and Laurie theory, explain what is meant by each of the following with example:

A- acid                      B- conjugate base  
C- base                      D- conjugate acid  
E- pairs of conjugate acid-base

6-3 Distinguish between acids and bases in each of the following using the theory of Lewis, indicating the donor and acquired of electron pair:



6-4 What is acid salt? Write balanced chemical equations to show how to get the following acidic salts from appropriate acids and bases:

A-  $\text{NaHSO}_3$               B-  $\text{KHCO}_3$   
C-  $\text{NaH}_2\text{PO}_4$               D-  $\text{NaHS}$

6-5 Explain why

A- Salts solutions derived from strong acids and strong bases will be neutral.

B- Salts solutions derived from strong acids and weak bases are acidic.

C- Salts solutions derived from weak acids and strong bases are basic.

6-6 Calculate the molarity of the nitric acid solution if you know that 35.7 mL from it neutralized, in titration process, 0.302g from  $\text{Na}_2\text{CO}_3$ .

6-7 How much the volume of concentrated HCl acid(Its mass percentage = 36% and its density = 1.18 g/mL) is required to prepare 500 mL of dilute solution of the same acid at concentration of 2 M?

6-8 Calculate the mass of  $\text{HNO}_3$  contained in 5 mL of concentrated acid solution( Its mass percentage = 69.8% and its density = 1.42 g / mL).

6-9 How much ammonium sulfate salt  $(\text{NH}_4)_2\text{SO}_4$  (molar mass = 132.8 g/mol) required to prepare 400 mL of solution in a concentration of 0.25 M?

6-10 How much the volume of concentrated sulfuric acid( Its mass percentage = 98% and its density = 1.84 g / mL) is required to prepare 100 mL of diluted acid solution( Its mass percentage 20% and its density = 1.14 g / mL).

6-11 Put (✓) in front of the correct statement and a sign (✗) in front of incorrect statement as follows:

1. All Bronshted-Laurie acids and bases are considered Arrhenius acids and bases.
2. Ammonia reacts with water as Bronshted base.
3. The aluminum chloride ( $\text{AlCl}_3$ ) is an acid Louis.
4. The conjugate base of strong acid behave as strong behavior base.
5. Boron trifluoride is considered Lewis acid.

6-12 Which of the following statements relates to Arrhenius theory are correct?

1. Acid-base reaction according to Bronshted-Lauri theory includes protons transmission.
2. One of the essential requirements for the Bronshted-Lauri statement is the presence of hydroxide ion in its chemical formula.



## Chapter Seven

## Polymer Chemistry

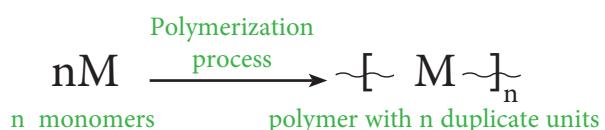
7

After completing this chapter, the student is expected to:

- Recognize molecules (polymers) as large molecules built from small units called monomers.
- Understand polymerization of monomers process for the formation of polymers.
- Recognize some types of natural and synthetic polymers.
- Explain the effect of different general structural composition of polymers on their properties.
- Specify the types of polymers (polymers of addition and condensation polymers) and how they are prepared in laboratory.
- Describe the formation of polymers by addition polymerization as well as by condensation polymerization .
- Recognize rubber (as a type of polymer) and distinguish between natural rubber and synthetic polymer.
- Know some of common uses of synthetic polymers like plastics synthetic and fibers.

## 7-1 Polymers (plastics)

Plastics, synthetic fibers, rubber, cellulose and proteins, the clothes we wear all these materials are polymers, starch and fatty are other examples of polymers. The word polymer consists of two segments, (poly) the Greek word means multi and the word (mer) is a molecule, and so on, polymer means polymorphic(multi-molecules). Polymers are huge molecules composed of a large number of small molecules called (monomers). These monomers were connected by mostly covalent bonds in the form of long chains according to organic chemical reactions. One of the polymers contains approximately 1000 to 200,000 atoms, mostly carbon and hydrogen. The monomers are small molecules that may be organic or inorganic compounds that combine with each other by chemical reaction to form huge chains, which is polymer. A polymer consisting of units of these duplicate molecules is called duplicated unit, and the reaction process of these monomers of the formation of polymers is called polymerization process. So polymerization is a bonding process of small molecules called monomers come together to form huge molecules called polymers. If the monomer is denoted by the letter M and the number of monomers is n (n values are between 5 and 50,000), the polymerization process can be represented to form polymer (M)<sub>n</sub> as in the following equation:



## 7-2 Polymers types

Polymers were initially classified into two types:

### 7-2-1 Natural Polymers

They are found in nature such as starch, cellulose, proteins and natural rubber.

### 7-2-2 Synthetic Polymers

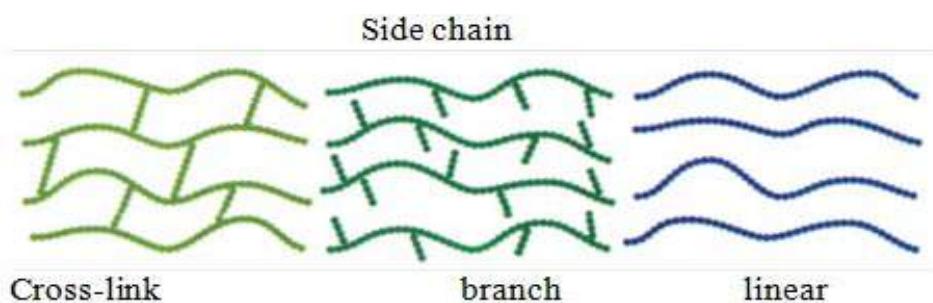
Which was prepared laboratorial or synthetically by human such as polyethylene, polyamide (nylon), polyvinyl chloride and other thousands of polymers are known nowadays. Polymers may be classified according to the effect of temperature on:

## A-Thermoplastic polymers

This type of polymer is softened when it is heated where it can be reformed several times and then it hardens at a low temperature. These polymers are named plastics. The most famous examples are: polyethylene, polypropylene, polyvinyl chloride and polystyrene.

## B-Thermosetting polymers

Do not soften when heated, but maintain its original shape. One of the famous example melamine, synthetic rubber. Polymers may also be classified according to their structural composition and effect of heating on, it is either linear or branched or crosses - linked as shown in Figure 7-1. When linear polymer is heating the molecules are free to move and slide easily forward and backward on top of each other as they are thermally unstable. As for heating the branching polymer and its molecules contain side chains that prevent the particles slide off each other easily but are likely still not thermally stable. The cross-link polymer has molecules adjacent are interrelated so it cannot slide over each other by heating. It remains in this state to maintain its shape thermally.



### 7-3 Synthetic polymers

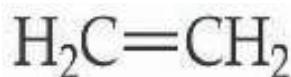
synthetic polymers (which are made by Human) can be made by two types of polymerization, namely:

#### 7-3-1 Addition Polymerization

A chemical reaction in which too many small unsaturated molecules (monomer containing double bond) are added to form one huge molecule, which is a polymer without any by-product (those polymers may be made of one type monomer). Examples of addition polymers are polyethylene (PE), polyvinyl chloride (PVC), polystyrene (PS) and polypropylene (PP), and we will look at the methods of preparation and compositions in a brief summary.

Figure 7-1

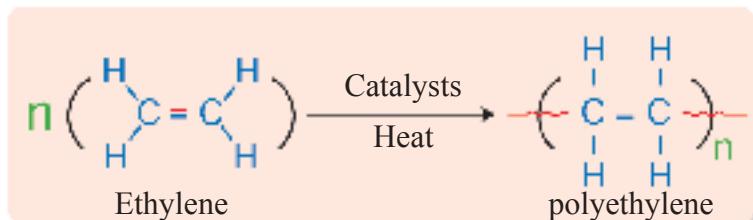
Types of polymer according to their structural composition.



Ethylene Molecule

### 1. polyethylene (PE)

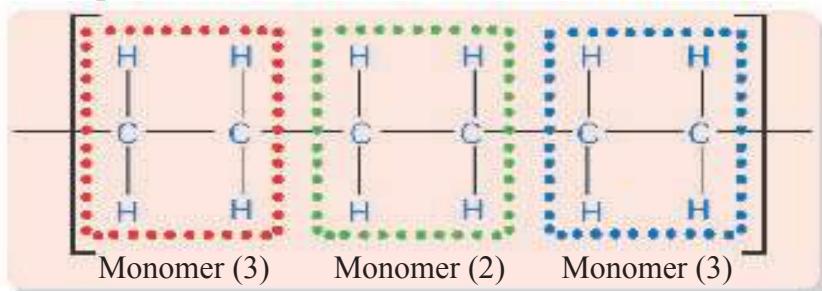
Polyethylene is prepared from the addition of ethylene molecules ( $\text{CH}_2=\text{CH}_2$ ) for some of them to be a polyethylene molecule. As shown in the following equation:



The letter (n) represents the number of polymerized ethylene molecules which may be a number repeated units of approximately 50,000 or more. The addition reaction is repeated many times to form a polymer with length n of monomers (very long molecular chain). This reaction can be repeated hundreds or even thousands of times, the ethylene unit in the polymer chain is called the repeated unit, where one of the two bonds breaks between the two carbon atoms in the ethylene molecule ( $\pi$  bond). Each atom is bound to a carbon atom of another molecule, and this process is repeated until thousands of ethylene molecules are bonded to form polyethylene as follows:



This equation can be written briefly as in the previous equation and figure 7-2 shows how the number of units of a molecule is known polymer (polyethylene), consisting of three repeated units.



### Forms of ethylene

Polyethylene is usually prepared in various forms according to the conditions of the polymerization reaction. There are three forms of polyethylene according to temperature, pressure and catalysts used in the preparation:

Figure 7-2

Number of units of polymer molecule (polyethylene).

## A-High-Density polyethylene (HDPE)

It is formed when ethylene is heated to  $100^{\circ}\text{C}$  in a hydrocarbon solvent at normal atmospheric pressure a high density linear polymer is formed. Because linear molecules are very closely aligned, their size is small this makes the density is high, so the polymer remains strong and solid, making it plastic containers such as milk containers and juices.

## B-Low-Density polyethylene (LDPE)

It is formed when ethylene is heated to  $200^{\circ}\text{C}$  at high pressures (approximately 1000 atm) with little oxygen as the initiator of the reaction. Branched polymer is formed when removal of hydrogen atoms from the molecule and the addition of ethylene molecules instead in these sites, unlike the linear molecules because their molecules cannot converge. So the density of branching chain is less than the density of the linear chain. So the polymer is less rigid than high density polyethylene and therefore used in making ordinary plastic bags.

## C- Cross-linked polyethylene (CPE)

This type of polyethylene can be obtained when removed hydrogen atoms of polyethylene molecules, where two adjacent molecules in the chain are bonded and form an cross-link bonding between two molecules. The cross-type is known to be stiffer and stronger than high-density polyethylene, making things that require extreme stiffness. Figure (7-3) shows the different forms of polyethylene with their different uses.



### Do you know

The polymer chain is in adhesive tapes. low density polyethylene with a value of  $n$  about 10.000 units each series has an average molar mass of about 300.000.



Figure 7-3

Properties of various forms of polyethylene and some special uses to them.

Figure 7.4 shows some of the different uses of polyethylene.

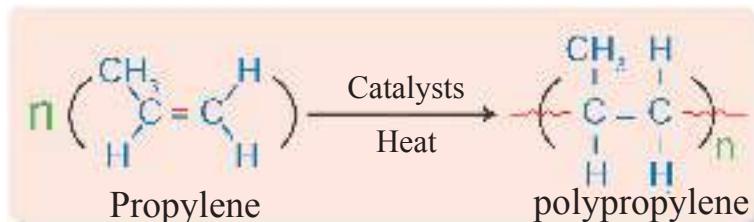


Figure 7-4

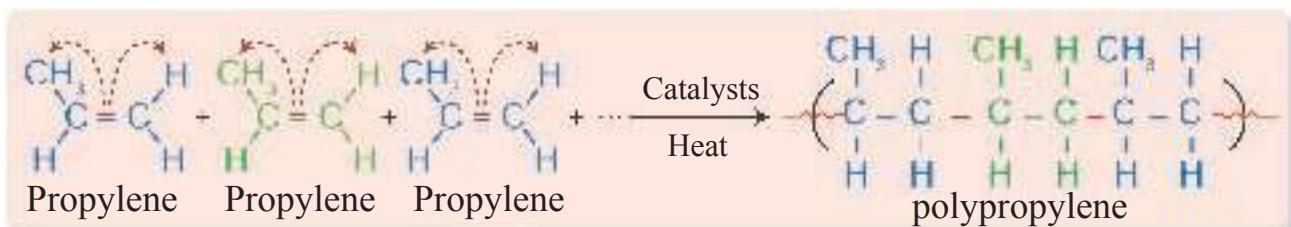
Different uses of polyethylene.

## 2. polypropylene (pp)

It forms of the union of a large number of propylene molecules( $\text{CH}_2=\text{CH}-\text{CH}_3$ ) with catalysts in the following equation written briefly as follows:



This process can be repeated until thousands of propylene molecules bind to the polypropylene as follows:



Polypropylene has the following characteristics:

1. Easily formed, poured and resistant to heat and chemicals.
2. Unbreakable
3. Transparent and odorless
4. Used in the manufacture of medical instruments, toys, tubes and Figure (7-5)

Shows some different uses of polypropylene.

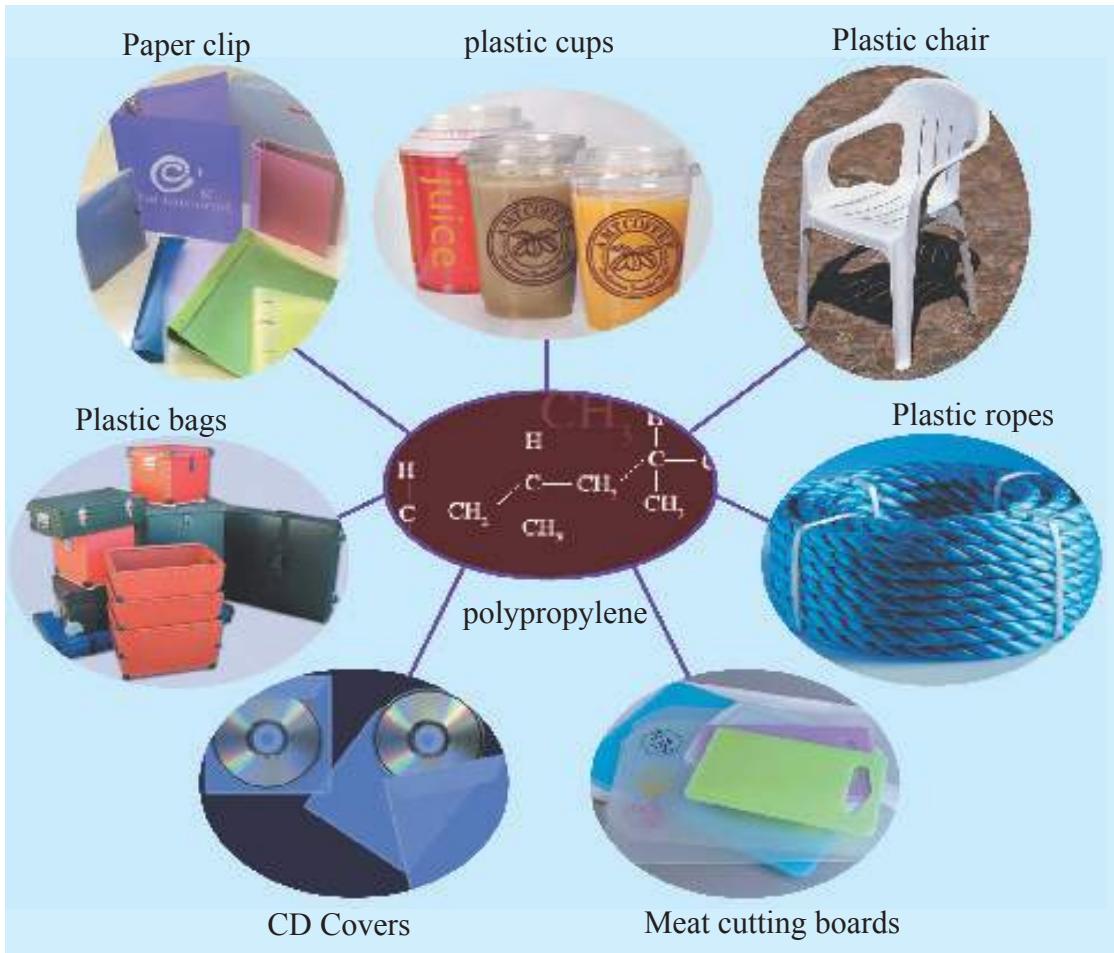
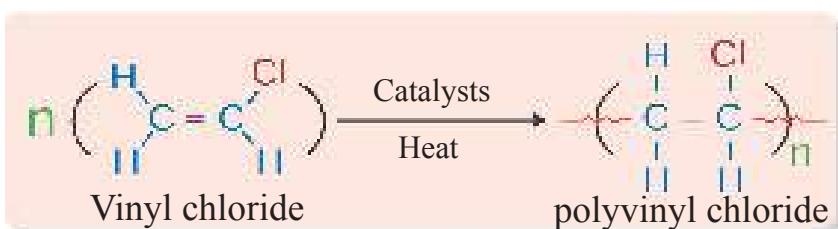


Figure 7-5

Some different uses of polypropylene.

### 3. Polyvinyl chloride (PVC)

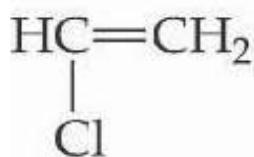
It consists of the bonding of a large number of vinyl chloride molecules ( $\text{CH}_2 = \text{CH-Cl}$ ) with catalysts, as the following simplified reaction:



PVC has the following qualities:

1. More durable, heat resistant and chemicals than polyethylene and propylene.
2. Cheaper
3. It is used instead of metal pipes in the manufacture of water pipes.
4. Water resistant and insulator so it enters the car brushless and raincoats industry.

Figure (7-6) show some uses of polyvinyl chloride.



Molecular structure of vinyl chloride

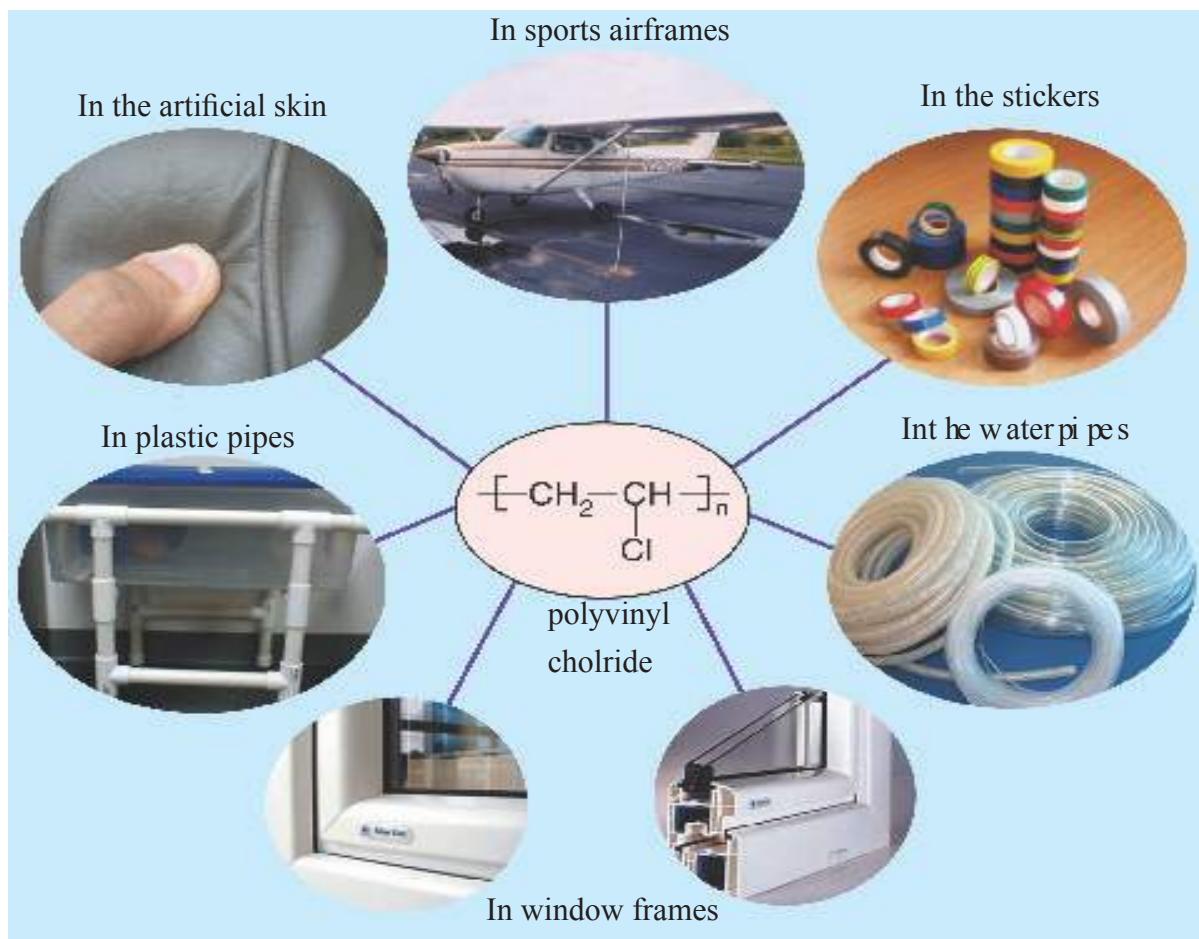
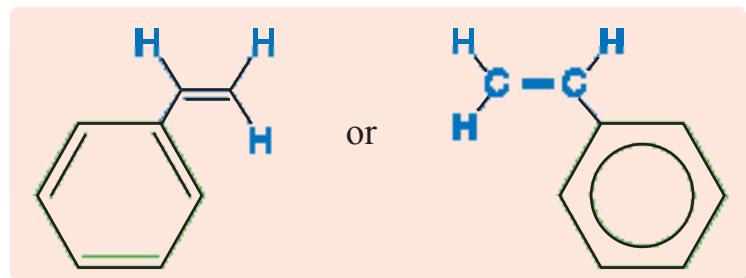


Figure 7-6

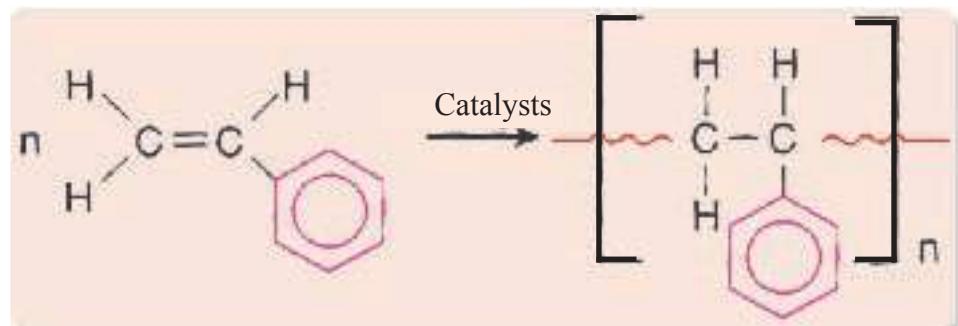
Various uses of polyvinyl chloride.

#### 4. Polystyrene (PS)

Polystyrene consists of the polymerization of a polymer molecule called styrene with the presence of suitable catalysts and the structural formula of styrene is as follows:



Polymer styrene to form polystyrene according to the following formula:



Polystyrene is a white solid that is easy to form and resist for acids and alkalis, used in the manufacture of synthetic sponge (cork), insulators, pipes, some household utensils and vegetable containers. Figure 7-7 illustrates some uses of polystyrene.

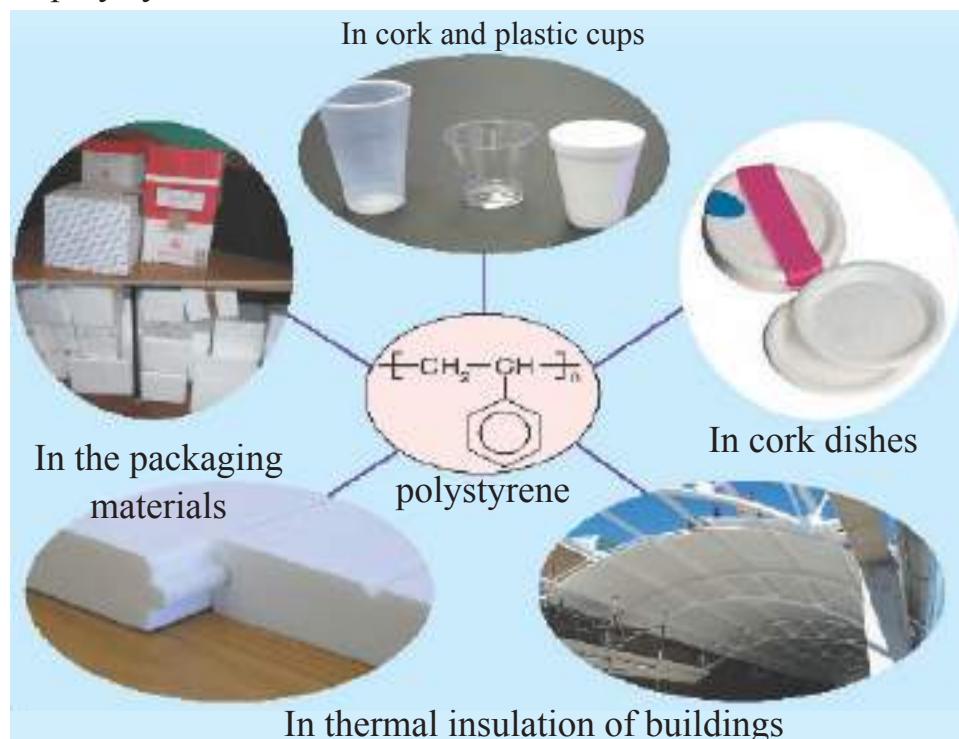


Figure 7-7  
Different uses of polystyrene.

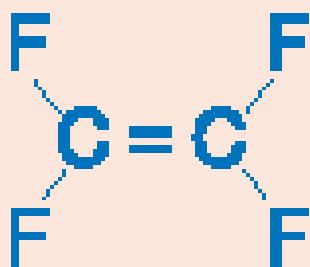
Cork is made of polystyrene, which is small balls as shown in Figure (7-8). Its size varies depending on the type of cork and there is a monolith together. When it is exposed to flame in an atmosphere saturated with oxygen (at least 30%), it ignites and because of this characteristic cork is used in the manufacture of high-temperature resistant materials, note Figure (7-9), which made polystyrene to compete with many other polymers prepared.



Figure 7-8  
Cork is a small balls.



Figure 7-9  
Cork resistance to heat in the normal atmosphere.



Structural formula of tetrafluoroethylene.

## 5. Poly tetrafluoroethylene (Teflon)

This polymer is prepared from the tetrafluoroethylene monomer ( $\text{CF}_2 = \text{CF}_2$ ), note the structural formula adjacent to the polymer.

Where molecules bonded to this monomer in the form of a long chain to form a substance known as Teflon. This substance contains a non-reactive and stable carbon fluorine bond at temperature is  $325^\circ\text{C}$ . It has a very low friction coefficient and this it means that the material slides easily off the surface, making it an important material in the manufacture of parts of heat-resistant machines in addition to use in the manufacture of kitchen utensils that do not stick food (Tefal) Figure (7-10).

Teflon has the following characteristics:

1. Its extreme resistance to heat and chemicals
2. More fixed than any polymer material, whether natural or manufactured.
3. It does not burn and is not corroded by weathering.

The most important uses are:

1. In the manufacture of tools exposed to heat.
2. In coating cooking utensils to prevent food sticking to them.
3. In the manufacture of heat resistant clothing.



Figure 7-10

Frying pan coated with Teflon.

Note from the examples above that added polymers are all from hydrocarbons, which they are very similar in form and chain the method of composition, differ in terms of groups that are related to the carbon atom; for example, the hydrogen atom in ethylene is replaced by the methyl group  $-\text{CH}_3$  as in propylene, chlorine atom  $-\text{Cl}$  as in vinyl chloride, and the phenyl ring  $-\text{C}_6\text{H}_5$  as in styrene. The four atom of hydrogen may be replaced by fluorine atoms  $-\text{F}$  as in tetrafluoroethylene. This causes a difference in the qualities of plastics produced from them.

Table(7-1) illustrate the monomer structures and refind units of addition polymers and some of their uses.



Teflon uses

Table 7-1 Structures of monomers and refined units of addition polymers and their names

| Monomer name                        | The repeated unit form in the polymer | Polymer name              | Monomer form | uses   |
|-------------------------------------|---------------------------------------|---------------------------|--------------|--|
| Ethylene                            |                                       | Polyethylene              |              | plastic bags<br>.slices, strips<br>.etc.     |
| Propylene                           |                                       | Polypropylene             |              | Glasses, Plastic bottles, etc                |
| Chloro ethylene<br>(vinyl chloride) |                                       | Poly chloride vinyl (PVC) |              | Waterproof materials<br>isolators, cylinders |
| Styrene                             |                                       | Polystyrene               |              | Canning, roofing of buildings                |
| Tetrafluoroethylene                 |                                       | Teflon                    |              | Non - stickutensils                          |

### 7-3-2 Condensation Polymerization

Monomers are bonded together with the removal of a simple molecule (by-product) such as water. Each polymer may contain two types of monomer molecules. It contains two functional groups which make each monomer associate with another and withdrawn a molecule as a by-product. One of the most important examples of this polymers type are polyamides (nylon) and polyester polymers (Terylene) and will show the preparation and properties of these polymers in brief.

#### 1. Polyamide

Nylone (nylon) is the first common manufactured condensation polymer derived from New York and London. It was made of two monomers, one of which has the amine group ( $-\text{NH}_2$ ) at both ends, The other monomer has a carboxyl group ( $-\text{COOH}$ ) at both ends. These two monomers are easily linked together with removal molecule of water and they are formed polyamide and the bond roup between the two monomers for the nylon chain  $\text{O} \text{---} \text{C} \text{---} \text{N} \text{---}$  is called amide group. The following equation shows the nylon industry:

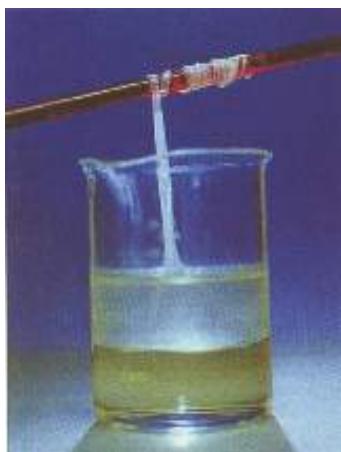


Figure 7-11

Nylon when prepared from hexagonal methylene Di-amine and adipic acid and pull it in the form of filaments.

## Do you know

One type of polyamide is called fiber (Kevlar) is used in armor bulletproof worn by military personnel.

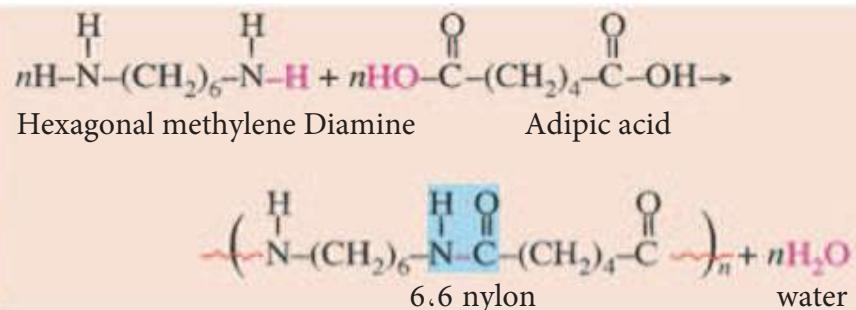


Figure 7-11 shows nylon 6,6 wrapping around the glass leg. We conclude from the equation that the reaction comprises two types of monomers: adipic acid monomer ( $\text{HOOC}(\text{CH}_2)_4\text{COOH}$ ). The second monomer is hexamethylene diamine ( $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$ ) and the resulting polymer is called (6,6 nylon), which is to contain each carbon monomer (6) carbon atoms. This is one of the most manufactured polymers frequently used. Nylon is characterized by its low water absorption, which makes it limited to use in body contact clothes, but is also used in the manufacture of moisture resistant fabrics such as coats and umbrellas. Figure (7-12) shows the most important uses of nylon.



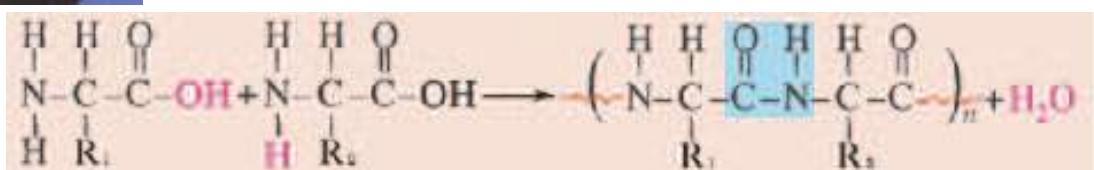
Figure 7-12

## Nylon uses.



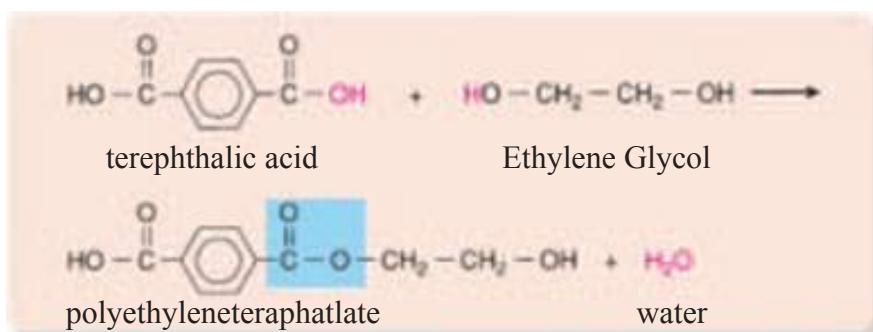
## 2 Proteins

When we mention polyamides we have to look at proteins. They are polymers that contain thousands of  $(H_2N-X-COOH)$  molecules that bind together and have the same bonding groups in Nylon, it is an amide group. It removes water from amino acids when it polymerized, so it is one of the condensation polymerization reactions. The polymerization of these acids can be represented as follows:



### 3. Polyesters

An example of polyesters is polyethyleneteraphthalate (PET). It is polyster is one of the most famous condensate polymers where it is prepared from the reaction of ethylene glycol ( $\text{HOCH}_2\text{CH}_2\text{OH}$ ) with with terephthalic acid ( $\text{COOH-C}_6\text{H}_4\text{-COOH}$ ) in the presence of catalysts according to the following reaction:



A water molecule is removed during the polymerization process and the bonding group between the repeated units in the polyesters is the ester group. Polyethylene terephthalate is used in most bottles of carbonated beverages and water because it is a synthetic polymer that does not pollute these beverages.

Do you know that the cartoons that withdraw cash and those used to mobilize phones Mobile charge and credit cards in banks and others are all made of the plastic is light, long-lasting, strong, cheap and easy to print and save magnetic information (CD) on them.

Table 7-2 Structures of condensate polymers, their repeated units and some of their uses

| Table 7-2 Structures of condensate polymers, their repeated units and some of their uses |  |   |
|--|--|---|
| Polymer name   | Repeated polymer unit form   | Uses  |
| Polyurethane   | $\left[ \text{C} \begin{array}{c} \text{NH} \\ \parallel \\ \text{O} \end{array} - \text{R} - \text{NH} \begin{array}{c} \text{C} \begin{array}{c} \text{O} \\ \parallel \\ \text{O} \end{array} - \text{O} - \text{R} - \text{O} \end{array} \right]_n$ <p>As example <math>\text{R}, \text{R}' = -\text{CH}_2 - \text{CH}_2 -</math></p> | Foam filler for bedding, seats and composition, spray insulators, spare parts for cars and industry, footwear and packaging materials, waterproof |
| Polyethylene<br>Terephthalate<br>(Polyester)   | $\left[ -\text{O} - \text{CH}_2 - \text{CH}_2 - \text{O} - \text{C} \begin{array}{c} \parallel \\ \text{O} \end{array} - \text{C}_6\text{H}_4 - \text{C} \begin{array}{c} \parallel \\ \text{O} \end{array} \right]_n$   | Tire, tapes, clothes and bottles and soft drinks  |
| 6.6 Nylon<br>(Polyamide)   | $\left[ -\text{NH} \begin{array}{c} \leftarrow \\ \text{CH}_2 \end{array} \right]_6 \left[ \text{NH} \begin{array}{c} \text{C} \begin{array}{c} \parallel \\ \text{O} \end{array} \end{array} - (\text{CH}_2)_4 - \text{C} \begin{array}{c} \parallel \\ \text{O} \end{array} \right]_n$   | Home furniture, clothes, fiber carpets and fishing nets, Fish   |



Extraction of natural rubber from the rubber tree



Figure 7-13

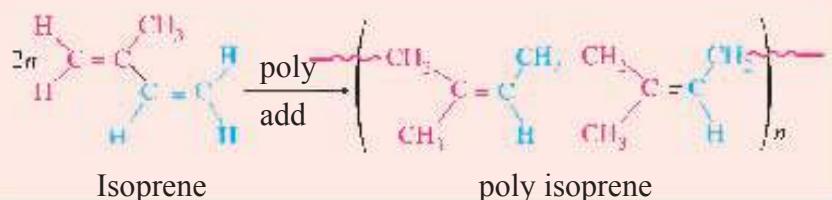
Some uses of synthetic rubber.

**Do you know**

That the material Bakelite, the first plastic material, was discovered by Bakeland 1908, so attributed to him and uses bakelite in making hard tools such as Radio, television and telephone instruments.

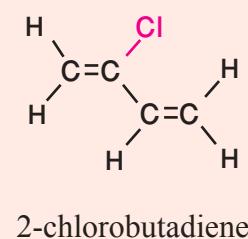
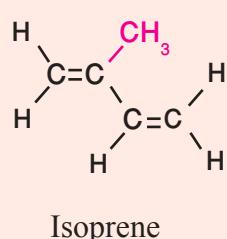
#### 4. Natural rubber and synthetic rubber

Natural rubber is extracted from the rubber tree (available in Malaysia and Brazil). Natural rubber is composed of a repeated unit called isoprene in its cis form (cis-isoprene): a 2-methyl 1,3-butadiene, which is polymerized in the following form:



Rubber produced from other monomers, in addition to isoprene, such as butadiene and styrene.

Note that the applications of pure natural rubber and syntheses relatively few because when it heated, individual molecules slide easily into front and back and on each other, so that the rubber become soft and viscous. It cannot be used to make needs, so sulfur is added to the rubber. It cannot be used to make needs, so sulfur is added to the rubber in its manufacturing processes turn it into a solid and strong material. Adding sulfur to rubber is called vulcanization. It is a process that leads to the entanglement of adjacent rubber molecules through sulfur atoms. Vulcanization makes the rubber usable in a wide field as rubber pipe industry, automotive tires ...etc. Note Figure (7-13). Another example is the rubber made from polymerization of Neoprene, which is 2-Chlorobutadiene with the following structural structure similar to isoprene. Note that 2-chlorobutadiene is similar to natural rubber isoprene monomer, except that the chlorine atom has replaced the methyl group in carbon atom number (2). As described below



## 7-4 The world of plastics

Since the Second World War, plastics have become increasingly important. Plastics has many advantages compared to other materials are clean, cheap and transparent and easy to form and non-corrosive and insulating good lightweight, easy to shape and stays long and can be extremely strong. But they have one serious flaw. They do not degrade and cause environmental pollution because they can remain in the earth indefinitely.

### Plastic waste

It is known that waste is of two types:

A- Organic waste from natural products around us that is biodegradable (naturally occurring in the presence of the sun), such as paper and cardboard, which can be decomposed by bacteria into their essential components during the days and months or years.

Plastic waste, which does not degrade naturally even in natural conditions (sun and temperature) except during decades unlike organic waste. For example, plastic bags affect marine and terrestrial organisms because they are impermeable to air, causing many of these organisms to suffocate as they enter the bags.

There are positive things to follow to reduce contamination of plastics waste as follows:

1. Reduce the use of plastic bags for everyday purchases
2. Reuse bags more than once instead of throwing them directly
3. Throw the plastic bags in the designated places.
4. Collection of the plastic products that have been discarded and delivered to the companies that recycle them from waste to new raw materials.

Recycled products can be found in the presence of the recycling mark. Most natural materials, such as cartons and paper, are degraded by microorganisms such as bacteria in the soil. Plastic containers do not degrade naturally and they are said to be non-biodegradable. Therefore, plastic waste is an environmental problem, even if disposed of by burning. They produce toxic fumes such as hydrogen chloride from burning polyvinyl chloride and also toxic cyanogen gas from burning polyurethane.



Plastic waste causes killing many revival



plastic waste

### Do you know

Research is still ongoing to obtain biodegradable (natural) plastics so they can be eliminated and thus eliminate the problem of pollution plastic waste. Research is conducted on the development of biodegradable plastics called (degradable biopolymer).

It is made from fermentation of sugar by bacteria. It is a typical plastic and can be formed into molds or slices.

It costs 15 times the cost of its manufacture and its chemical name is polyhydroxybutyrate (PHB).

### Addition polymerization

Chemical reaction in which too many small unsaturated particles (monomers) are added to be one huge and large molecule, a polymer. Like adding ethylene molecules to each other to be a polyethylene molecule.

### Condensation Polymerisation

Bonding of monomers to polymer composition with extract a small molecule like water. Such as the formation of nylon and terylene polymers.

### Polymer

A macromolecule consists of the bonding of a large number of small molecules (monomers) such as polyethylene.

### Monomer

A small molecule can bond to a large number of it (polymerize) as ethylene is a monomer of polyethylene.

### Thermosetting polymer

A polymer that does not melt after its formation and cannot be reshaped.

### Natural polymer

A huge macromolecule like carbohydrates Proteins and fats.

### Synthetic Polymer

Man-made polymer such as plastic, synthetic fiber.... etc.

### Biodegradable

Natural decomposition of substances mediated by bacteria and light the sun.

### Pollution

Damage to the environment as a result of the use of dangerous chemical materials which are called pollutants.

### Catalyst

A substance that accelerates the rate of chemical reaction and its composition does not change at the end of the reaction.

### Dehydration

Pull up water from the material.

### Thermoplastic polymer

It is a polymer that melts more than once so it can be reshaped many times.

### Plastics

Polymers are easy to form for low melting point, they have relative properties. So that they are used for many purposes in contemporary life and sometimes called plastic materials.

### Plastic

A large molecule is often a polymer that can be cast and formed such as polyethylene PE and polyvinyl chloride PVC ..... etc.

### Vulcanization

Is the process of overlap between contiguous polyisoprene molecules that it occurs, when these molecules are heated with sulfur atoms.

### Polymerization

Is the process of combining the number of n monomers with some of them to form a polymer molecule.

### Polymerization process



## Chapter seven Questions

7

7-1 Circle the correct answer symbol in all of the following:

1. Which of the following materials is used for non-stick surfaces?

- A- Dichloro difluoromethane
- B- Polychlorofluoroethylene (Teflon).
- C- Tetrachloromethane
- D- Polyvinyl chloride

2. During the condensation polymerization reaction.

- A-The output becomes saturated
- B- Often forms of water
- C- Didn't form by- product

3. Which of the following molecules is heated with sulfur atoms during the vulcanization process.

- A- Isoprene
- B -Polyisoprene
- C- 2-methyl 1,3Butadiene
- D- Butadiene

4. In the vulcanization process, what happens to the contiguous molecules when heated with sulfur atoms.

- A- branching
- B- interrelated cross-link
- C- slip over each other
- D- collide

5. Any polymers of the following is added polymer.

- A- Nylon
- B- Polystyrene
- C- protein
- D- terlene

6. Any of the following hydrocarbon molecules can polymerize it.

- A-  $\text{CH}_4$
- B-  $\text{C}_2\text{H}_6$
- C-  $\text{C}_3\text{H}_6$
- D-  $\text{C}_4\text{H}_{10}$

7. Biodegradable plastic.

- A- It burns easily and produces toxic fumes.
- B- can be absorbed through the roots of plants
- C-break down by bacterial decomposition.

8. Plastic has pollution problem because many plastics are plastic.

- A- Very flammable
- B- burns to create toxic fumes
- C- decomposes into toxic products

9. The polymer that does not melt when heated but it retains its original form.

- A-Thermally unstable
- B-Thermally stable
- C- linear
- D- branching

10. Large molecules consist of a number of units the small ones are related in organic reactions are.

- A- Monomers
- B- Polymers
- C- Functional groups
- D- carboxylic acids

11. Which of the following are small units associated to each other in a polymer during organic chemical reactions.

- A- Monomers
- B- Micropolymers
- C- branched polymers
- D- linear polymers

12. Small units that are associated during organic reactions to be large molecules.

- A- Must be similar
- B- must be different
- C- can be similar or different

13. Linear polymers

- A- They have freely moving molecules
- B- Have molecules that slide easily when heated

C- (a) and (b) together

14. The polymers are associated in cross-link shape

- A- Thermally unstable
- B- retains its shape when it is heated
- C- have side chains.

15 . In an cross-link polymer, contiguous molecules.

- A- linked to by chains
- B- slide forward and back on each other

when heated

C- regular in layers that can slip apart when heated

**16. Either of the following forms the two main types for polymers?**

A- Thermally unstable and thermally fixed plastic

B- Linear and branching polymers

C- Adding polymers and condensation polymers

**17. A polymer is formed during a chain addition reaction among the monomers that have a bilateral bond?**

A - polymer addition

B- condensation polymer

C- Branched polymer

D- Cross-link polymer

**18. In the addition reaction, monomers associated through reaction involved**

A- Identical functional groups

B- Different functional groups

C- Bilateral links

**19. A polymer usually consists of two alternating monomers**

A - polymers added

B- Condensation polymers

C- Branched polymers

**20. Linear molecules are stacked together**

A- Cross-link polyethylene

B - high density polyethylene

C - low density polyethylene

D - Neoprene

**7-2 Explain why:**

1. Natural rubber is thermally unstable polymer.

2. Alkane is not suitable as a polymer for the added polymer.

3. Cooking handles are made of a fixed thermally polymer.

4. No single functional group molecule

for a condensation reaction to form a polymer.

5. Branched polymer needs to be fused to quantity of heat is greater than the quantity it needs linear polymer.

6. Vulcanized rubber withstand higher temperatures of synthetic rubber.

**7-3 Classify the following polymers into polymers natural or synthetic .**

1. cellulose                    2. nylon

3. proteins                    4. Polyisoprene

5. Polypropylene

**7-4 Draw the structural composition of vinyl chloride.**

**7-5 Write the polymerization reaction of vinyl chloride to form polyvinyl chloride.**

**7-6 Teflon is proven from any other polymeric material, whether synthetic or natural.**

**7-7 Define the following: vulcanization, plastics, polymers, monomers, polymers, addition polymer.**

**7-8 In a chemical reaction, two small molecules were bound, a water molecule produced what type of reaction occurred.**

**7-9 Does the reaction of addition increase the saturation of a molecule or reduces it.**

**7-10 What are the two reactions can be produced polymers.**

**7-11 What are the difference in Structural compositions of the three types of polyethylene HDPE, LDPE, CPE**

**7-12 What does the molecular structure of neoprene differs structure of natural rubber.**

**7-13 Can ethanol acid be used as a monomer in a condensation polymer. Justify your answer.**



## Chapter Eight

# Aromatic Hydrocarbons

8

After completing this chapter, the student is expected to:

- Understand what's aromatic compounds and their characteristics and identify benzene and its composition. Draw its shape and accommodates its own properties.
- Recognize the meaning of resonance in chemical compounds and draw the resonant shape of some aromatic compounds.
- Named aromatic derivatives of benzene.
- Distinguish between additive and substitution reactions in aromatic compounds.
- Recognize electrophilic substitution reactions in benzene and some of its derivatives.
- Recognize phenols and their properties and some uses.
- Understand what are nonhomogeneous heterocyclic compounds and some examples.

## 8-1 Introduction

### Do you know

that the name of aromatic compounds is derived from the Latin word (aroma), which means fragrance or smell because these compounds have distinctive scents. Though that is a lot of these compounds are toxic and some of them are considered carcinogens as some compounds produced from tobacco smoking. Some of these compounds have great importance in the pharmaceutical industry such as aspirin and tetracycline.

A group of organic compounds have been discovered with a great deal of unsaturation, but they are unique in their stability and since the derivatives of these compounds have aromatic odors called aromatic compounds or aromatics. This label has lost its actual meaning and gained a theoretical significance to describe the properties of that type of unsaturated compounds.

The first compound in this group is benzene that enables the scientist Faraday to obtain it for the first time in 1825 from lighting gas. Coal tar is an important source of gasoline and large quantities are produced from petroleum hydrocarbons. This type includes organic compounds such as benzene and its derivatives and similar compounds in terms of chemical composition and effectiveness, such as naphthalene and anthracene.



anthracene



naphthalene



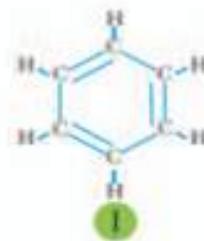
benzene



Schematic representation of a benzene molecule.

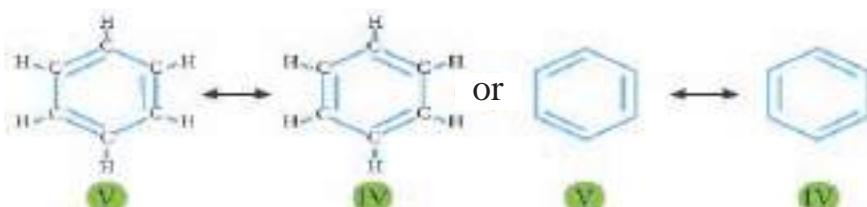
## 8-2 Benzene composition

Benzene is the first aromatic compound and its molecule consists of six carbon atoms linked together in the form of a regular hexagonal ring and each carbon atom is connected to a hydrogen atom and double bonds and single-carbon atoms alternate between carbon atoms (composition I). Or each angle in the hexagon symbolizes a carbon atom with a sphere combines with hydrogen and rotates the double and single bonds (II), and can compensate for the rotation of the double and a single by a circle inside the loop installation(III).



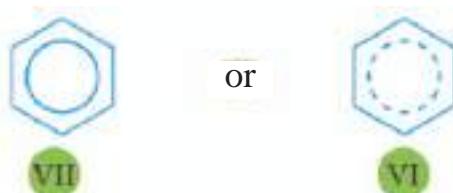
## 8-2-1 Resonance in benzene

In 1865, the scientific Kekule proposed the two formulas (IV) or (V) for benzene as follows

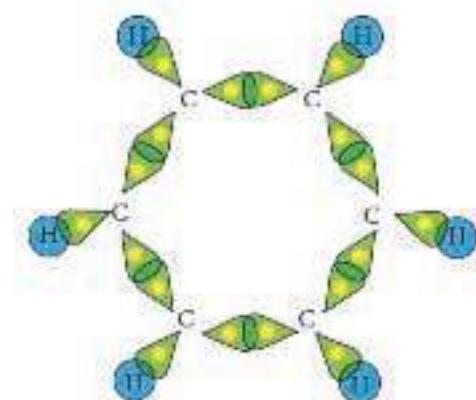


It is clear that the carbon atoms in the formulas (IV and V) occupy similar places but differ in the places assigned to the double bonds. The exchange of these link sites is called resonance (Ringing). That benzene is actually not a reciprocal state between the two states of resonance IV and V are not part of the molecules in the form of resonance and another part of the molecules in the form of the other resonance. But the real form of benzene is modified for the two shapes is called the resonance hybrid. Where we observe it's in place there is a double bond in one of the shapes, it will be single in other shape. When the average is taken, we get a hybrid form of resonance containing of six carbon -carbon bonds, which are identical and of equal length as the average case between the length of the single bond and the length of the double bond.

Therefore, the shape of benzene is usually painted in the form of a hexagonal ring, it has an inner loop (VI and VII composition) rather than in the form of successive double and double aces (IV and V composition) because it describes the situation is more accurate. However, drawing in the form of double bonds and individual successive is better in the case of monitoring the movement of electrons as in reaction mechanism state.



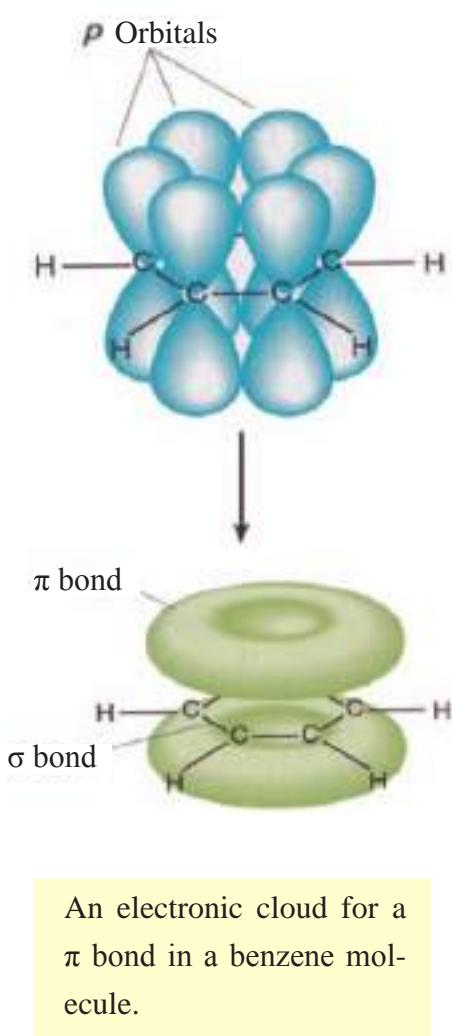
In brief, benzene is a molecular formula  $C_6H_6$  containing six identical carbon atoms and six hydrogen atoms. The C-C bonds have equal lengths and it is in a median case between the length of the single bond and the length of the double bond.



A diagram of how carbon atoms bonded in a benzene molecule.

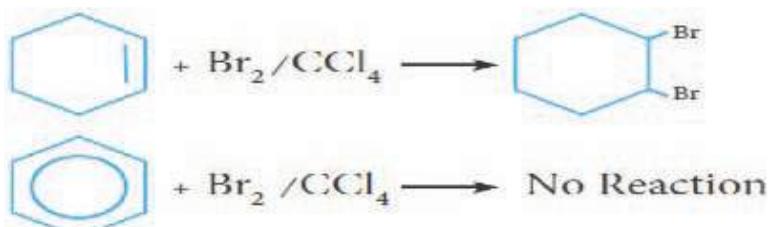
### Do you know

The  $C_6H_6$  benzene, we are studying is completely different from gasoline used in internal combustion engines. The latter is a mixture of 5 to 10 carbon hydrocarbons.

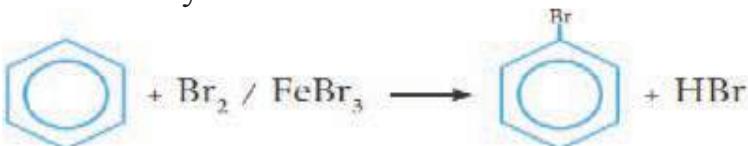


### 1. Stability

It is a stable compound as indicated by its reactive properties and relative resistance to chemical changes. That most unsaturated compounds tend to engage in addition reactions in which binary or triple bonds are saturated into individual bonds. Note that cyclohexane reacts easily with the bromine dissolved in carbon tetrachloride, forming 1,2-Dibromocyclohexane, whereas benzene does not fully react under the same conditions.



In order for benzene to react with bromine, a catalyst ( $\text{FeBr}_3$ ) must be used to enter a substitution reaction (substitution) and not an addition interaction where the loop remains preserved in its shape and this is evidence on the stability of benzene.



### 2. Resonance Energy

To understand the energy of the resonance, we explain the following:

When a chemical reaction occurs, a change in thermal energy. For example, cyclohexane hydrogenation is a heat-emitting reaction, releasing 120 kJ energy per mole of cyclohexane.



At the hydrogenation of 1,3 cyclohexane (cyclohexane containing two  $\pi$ -bonds) we expect the amount of energy to be released 240 kJ per mole, twice the liberated energy at the hydrogenation of cyclohexene because there is twice the number of double bonds in the cyclohexene. The real energy measured for this reaction was 232 kJ Per mole, it is very close to expected.



According to the same logic, we expect that the energy released by hydrogenation of gasoline is three times the liberated energy at hydrogenation of cyclohexane, ie 360 kJ per mole. The actual energy of this has been found. The reaction is 208 kJ per mole and is very different to our expectation.



The difference between the expected energy value and the real energy value is 152 kJ per mole and this amount of energy is called a resonance energy. This means that benzene contains 152 kJ per mole of energy is less than expected. So that gasoline is more stable than expected by 152 kJ per mole.

### 3. Carbon-Carbon Bonds Length

Physical measurements showed that the lengths of carbon-carbon bonds in benzene are equal and are of average length between the length of a single C-C and double C=C.

| C-C    | C=C    | C-C         |
|--------|--------|-------------|
| Single | double | for benzene |
| 1.54A° | 1.34A° | 1.40A°      |

#### 8-2-3 Benzene Derivatives Names

There are some systems in the label as follows:

**1.1 Monocompensation Components:** These compounds are called as derivatives of benzene such as:



Ethylbenzene



bromobenzene



chlorobenzene



Nitrobenzene

#### Exercise 8-1

Type the following compounds names as derivatives of benzene.



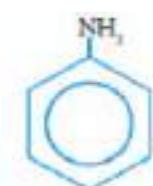
as:



methylbenzene  
(Toluene)



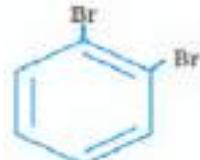
hydroxybenzene  
(Phenol)



amine benzene  
(Aniline)

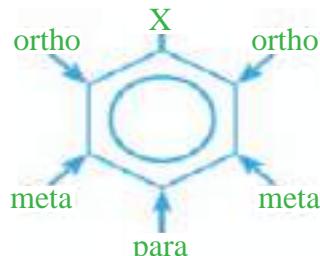
## 2. Dual-compensation Compounds:

When there are two groups on the benzene ring, it is not enough to mention the names of the two groups only, but they must be located on the benzene ring. Where the carbon atoms are numbered for the benzene ring and the two groups take the smallest figures, for example, 1,2 Dibromobenzene is:



1,2 dibromobenzene

The terms **ortho** may be used to denote the site 2 and (meta) to denote site 3 or (para) to denote on site 4 for the main compensator



If the two groups are different, they are mentioned in the nomenclature according to the alphabets one after the other and followed by the word benzene with its location at the beginning of the name or called the compound as a derivative

1,4 chloronitrobenzene  
para nitrochlorobenzene  
para chloronitrobenzene



Where we notice in the second label we considered that the molecule of chlorobenzene is a benzene monocompensation by chlorine. In the third label it was considered that the benzene mono-compensation in nitro group, so it is the basis in the designation. Dual-compensation benzene compounds are named in this way and as in the following examples:

1,3 Nitro hydroxybenzene  
Meta-nitrophenol  
Meta-hydroxy nitrobenzene



1,2 Bromo iodide benzene  
Ortho iodide bromo benzene  
Ortho bromo iodide benzene



### 3. Multiple Compensation Compounds:

When there are more than two groups on the benzene ring in which case it should be numbered the locations of these groups, where the name Ortho, Barra and Meta are unacceptable. These groups are named as a derivative of benzene or as a derivative of common names if any. If the associated group are large, the compound is named in the general designation of hydrocarbons. It takes the longest hydrocarbon chain as the base of the name and benzene is named as a compensating group, where it is called Phenyl. If benzene is replaced by a group, it is called Aryl.

We will be satisfied with this stage by naming mono and dual-compensation compounds. We postpone the designation of multi-compensation compounds to advanced levels.

#### 8-2-4 Preparation of benzene

##### A-In laboratory

Benzene is prepared in laboratory by heating sodium benzoate with sodium hydroxide (NaOH) in a glass distillation device where, benzene is obtained from the distillate at 80°C.



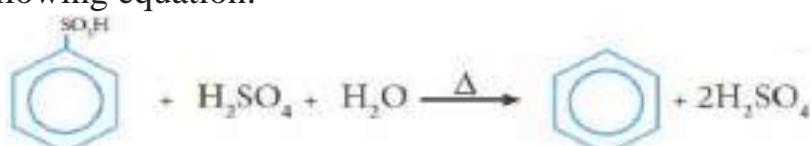
##### B- Industrially:

Benzene industrially is prepared in several ways, the most important of which are:

1. **From phenol:** Phenol is heated with Zn-dust in a distillation apparatus and then benzene is obtained from an 80°C distillate.



2. **From benzene sulfonic acid:** benzene sulfonic acid is heated with dilute hydrochloric acid or dilute sulfuric acid to boiling point and under high pressure according to the following equation:



## 8-2-5 Properties of benzene

### 1. Physical properties

- A- Colorless liquid, flammable, has a specific aromatic smell and it is toxic.
- B - boiling point 80 °C and freezing point 5 °C.
- C - Its density is less than the density of water and didn't mixed with it.
- D - a good solvent for non-polar organic materials such as grease, oils, resins and others.

### 2. Chemical properties

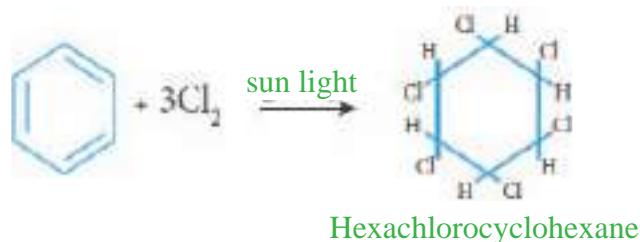
Benzene is a relatively stable chemical compound compared to unsaturated compounds for the presence of resonance phenomenon.

It is not affected by concentrated bases or concentrated hydrochloric acid nor by strong oxidizing agents such as potassium permanganate but suffers from a number of reactions, such as combustion and addition and substitution.

**A- Combustion:** Benzene is burned with a bright and flame due to the ratio of its high carbon content 92.3% and gives carbon dioxide and water with heat liberation.

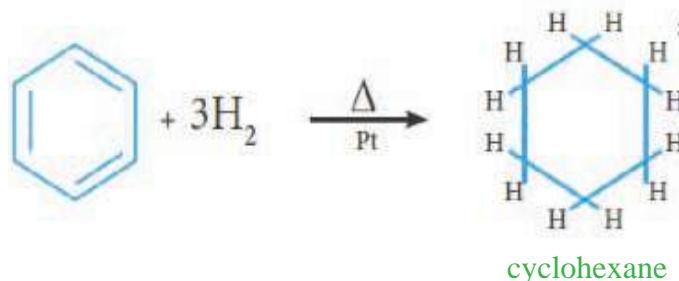


**B- Additive reactions:** Chlorine is added to benzene in the presence of light and there is a reaction accompanied by popping the reactants leading to the formation Hexachlorocyclohexane as described in equation A:



Burning of benzene with a bright and flame.

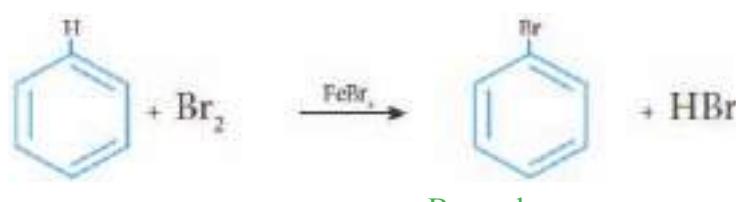
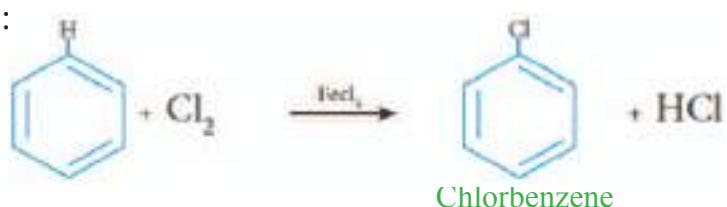
Benzene is also reduced to hydrogen at high temperatures and under high pressure in the presence of a catalyst such as platinum to cyclohexane, as in the following equation:



**C-Substitution reactions (compensation):** One of the most important reactions of benzene and its derivatives is the possibility of replacing (compensation) one of the hydrogen atoms by atom or different group (e.g. alkyl group R, nitro group  $\text{NO}_2$ , sulfonic group  $\text{SO}_3\text{H}$ , halide X or acetyl group  $\text{C}(\text{O})\text{CH}_3$ ) in the presence of an appropriate catalyst, which is helpful for the reaction. Examples of substitution reactions are:

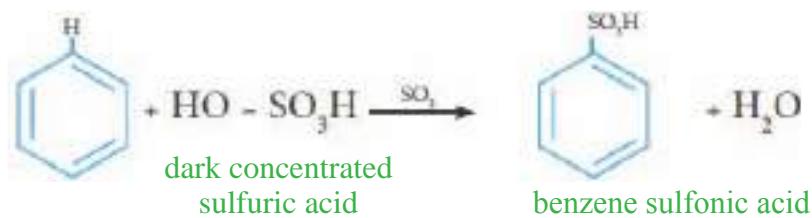
### A- Halogenation

It is the process of replacing one of the hydrogen atoms with a halogen atom (such as chlorine  $\text{Cl}_2$  or  $\text{Br}_2$ ) with a catalyst such as ferric chloride  $\text{FeCl}_3$  or ferric bromide  $\text{FeBr}_3$ :



### B- Sulfonation

It is the process of replacing one of the hydrogen atoms with the sulfonic group  $\text{SO}_3\text{H}$ , for example benzene reacts with the dark concentrated sulfuric acid at room temperature to form benzene sulfonic acid.



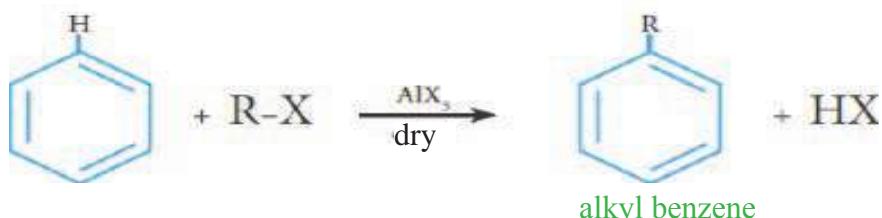
### C- Nitration

Replace a hydrogen atom with a nitro group  $\text{NO}_2$  where benzene reacts with a mixture of concentrated nitric and sulfuric acid at a temperature of  $45^\circ\text{C}$  to form nitrobenzene.



## D- Friedle- Crafts reactions

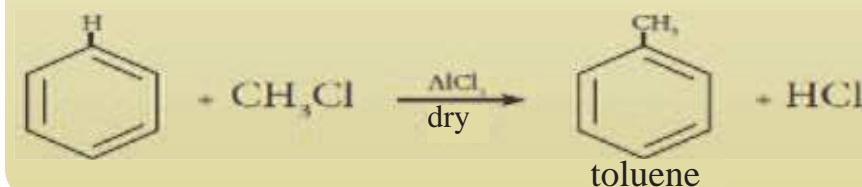
**1. Friedel-crafts Al-kylation:** It is the process of replacing one hydrogen atom in the alkyl group (R) with an appropriate catalyst. When benzene reacts with alkyl halide (R-X) in presence of catalyst like dry aluminum chloride ( $\text{AlCl}_3$ ) lead to compose of alkyl benzene



### Example 8-1

Type the Friedel-crafts Al-kylation for benzene using methyl chloride ( $\text{CH}_3\text{Cl}$ ) in the presence of dry aluminum chloride as a catalyst and named the produced compound.

**Solution** Benzene reacts with  $\text{CH}_3\text{Cl}$  in the presence of dry  $\text{AlCl}_3$  according to the following reaction:



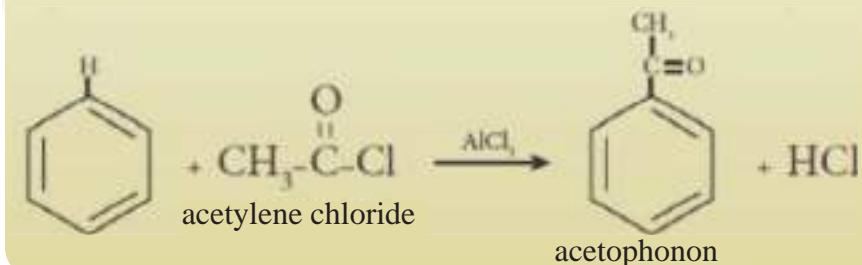
**2. Friedel-Kraft acetylation:** is the process of replacing an atom hydrogen in the acetyl group ( $\text{CH}_3\text{C}=\text{O}$ ). Benzene reacts with acetyl chloride ( $\text{CH}_3\text{C}(\text{O-Cl})$ ) in the presence of dry aluminum chloride to compose of acetyl benzene.



### Example 8-2

Type the Friedel-kraft acetylation of benzene and name the produced compound.

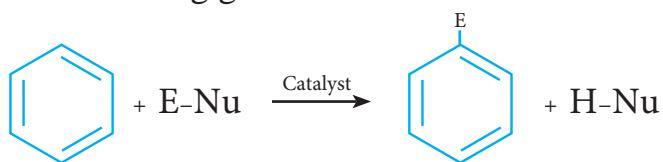
**Solution** Benzene reacts with in the presence of dry  $\text{AlCl}_3$  according to the following reaction:



### 8-3 Mechanism of electrophilic substitution reactions

The substitution reactions above are called electrophilic substitution reactions. Where there are electrons detectors is also called electrophilic reagent (E). The electron electrophilic reagent is a reagent that needs electrons and can be in the form of a positive charge that can form covalent bonds with carbon atoms like  $X^+$ ,  $NO_2^+$ ,  $R^+$ ,  $RC^+O$ .

A double link is rich in electrons therefore, it is a source of electrons for the reagent that electrophilic reagents need it. Electron-rich reagent are called Neocluphilic reagents (Nu)(see chemistry book for the fourth stage). By reviewing these reactions we can symbolize all these reactions by the following general reaction:



These include three steps:

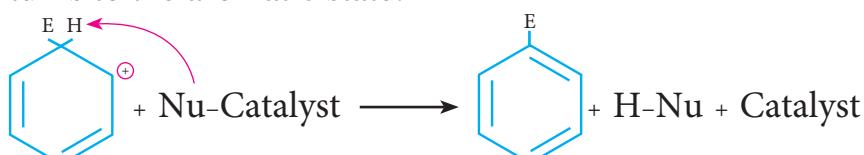
A-In the first step, the catalyst converts the reactant into an electron reagent ( $E^+$ ) according to the equation:



B- In the second step, one of the double bonds of the reagent benzene ring attacks the electron, forming a positive carbonium ion.



C- In the third step, a proton (positive hydrogen atom  $H^+$ ) is withdrawn by Nu-Catalyst. The output from the first step forms the other output  $H-Nu$  while the benzene ring returns to the aromatic state.



This mechanism, known as electrophilic compensation mechanism is a complex subject which we believe is above

### Do you know

That photography is black and white, it mainly depends on the oxidation of a phenol. It is hydroquinone by silver bromide with a photosensitive reaction. Since the film contains small granules of silver bromide, the light-grained particles are active and then the film is treated with hydroquinone solution which is called the looking solution. Where the activated granules are reduced from silver bromide, leaving black silver deposits in light-exposed places. As a result, we get the negative image with dark areas in places hit by light.

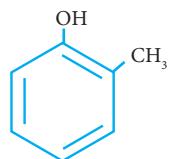
the level of student understanding at this stage. So we were limited to describe general mechanical only to explain how the reaction occurs in a briefly method, these mechanics are studied in detail in advanced stages.

## 8-4 Phenols

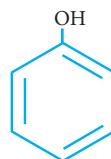
Aromatic organic compounds derived from benzene, which are formed the hydroxyl group (OH) is directly linked to the benzene ring like :-



1,4 dihydroxybenzene



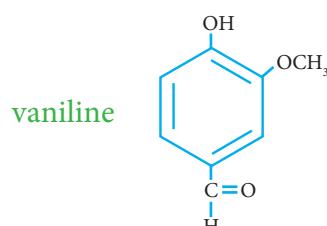
Ortho methylphenol



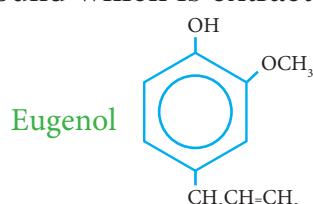
Phenol

It is a material with wide application, it has wide pharmaceutical properties such as its ability to act as an anti-mildew, antibacterial and anesthetic or topical analgesic. That's why they are used in spray products ointments, antiseptics, soaps, first aid materials and gargle solutions. They are also used as antioxidants as they are added to most foods and cosmetics, because of the easy oxidation of phenols. They are used in the developer in photography black and white kind.

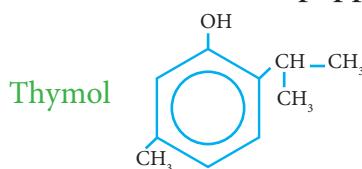
Some phenols are found in natural sources such as for example, vaniline gives vanilla, which is used as a food moisturizer.



and Eugenol compound which is extracted from clove oil.



and Thymol which is extracted from peppermint plant

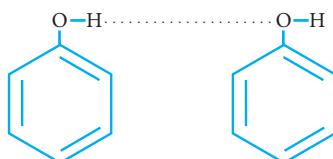


Some plants contain phenols consisting of three rings, these compounds are called flavanoids. They are antioxidant and extracted of green tea.

### 8-4-1 Properties of phenols

Physical properties: - The hydroxyl OH group found in phenols has a significant effect in determining physical properties, due to the formation of hydrogen bonds between their molecules. The high melting point and boiling point of these molecules, which are higher than the melting point and boiling point of alcohols (ROH), phenols are easily dissolved in water due to the formation of hydrogen bonds with water molecules .

Hydrogen bond

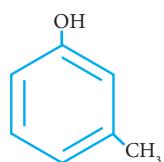


### Do you know

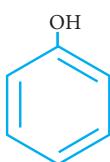
That there are bacteria in the soil feed on aromatic compounds where you turn them first to phenols and then it breaks the aromatic ring and breaks the resulting compounds into water and carbon dioxide. These bacteria abound in the soil on the roadsides where they feed on compounds that fall from their carrier vehicles and pedestrians on these roads.

### 8-4-2 Naming of phenolic compounds

According to the International Union of Pure and Applied Chemistry (IUPAC) system, whose abbreviation (IUPAC), phenols are named by addition section (ol) to the name of the mother hydrocarbons such as:



3-methyl benzeneol



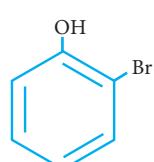
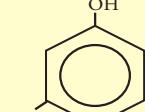
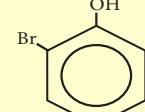
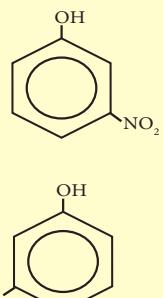
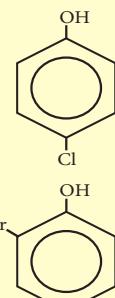
Benzeneol



Benzene

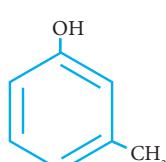
### Exercise 8-3

Type the names of the vehicles below by the system of naming IUPAC time and common names one more time



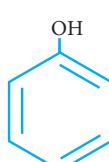
2- Bromo Phenol

or ortho bromo phenol



3-Methylphenol

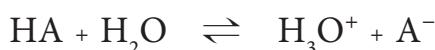
or meta methylphenol



Phenol

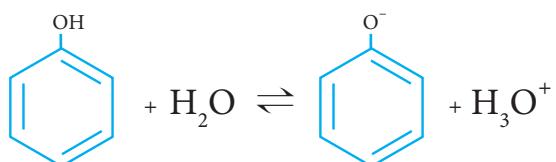
### 8-4-3 Phenolic acid

Phenols are organic acids and their acidic strength is compared by measuring their ionization in water. Acids that are fully ionized with water, such as HCl and HNO<sub>3</sub>, are called strong acids. The weak acids are partly ionized in the aqueous solution where there is equilibrium between the ionizing state and the non ionizing state as in the following equation (see chapter four of this book):



Most organic acids are weak acids with little ionization in water,

phenol is one of them and is ionized in water according to the following formula:



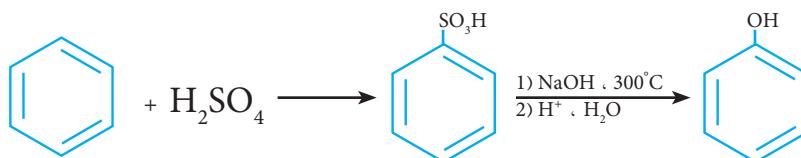
### 8-4-4 Phenol

Phenol was separated in the 19th century from coal tar. Phenol has been used in most countries of the world as a feedstock for the preparation of aspirin, dyes, writing ink, glue, plastic industries and most commercial phenols can be prepared in the laboratory or in the industry.

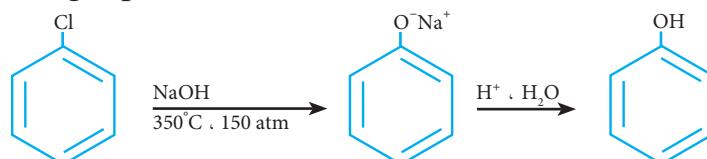
#### 1-Phenol preparation

##### A- From Benzene sulfonic acid

This method is an old method used in the industry to prepare phenol where benzene can be sulfonized first to obtain benzene sulfonic treated with sodium hydroxide solution (NaOH) and then make acid solution We get phenol as in the following equation:

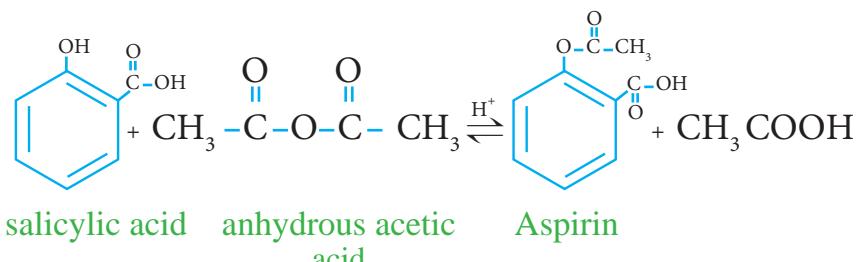


B) From heating chlorobenzene with sodium hydroxide solution under high pressure and then making the solution acidic we get phenol.



## 8-5 Preparation of aspirin

Aspirin is prepared industrially in laboratory by the reaction of salicylic acid with organic acid, which is anhydrous acetic acid to produce the corresponding ester, , which is acetylsalicylic acid, which is known commercially as aspirin.



## 8-6 Detection of phenols

For the detection of phenols, iron salts (III) are added to their solutions, the solution color is dark blue or dark green depending on the chemical composition of phenol. When iron potassium cyanide solution (III) is added to their solutions, the solution is colored in red.

## 8-7 Heterocyclic compounds

### 8-7-1 Introduction

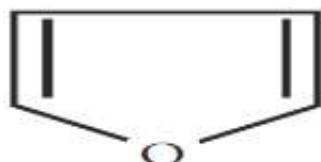
A heterocyclic compound is a compound in which one or more atoms of the ring or more are carbon, and most common species contain one nitrogen, oxygen, or sulfur atoms in addition to carbon which makes up the high percentage. Heterocyclic compounds can be aliphatic or aromatic in nature depending on electronic structure.

The heterocyclic aliphatic compounds are chemically similar to a large degree with their corresponding compounds open-chain aliphatic, as the cyclic heterogenous aromatic compounds have a similarities with their corresponding of aromatic carbon compounds.

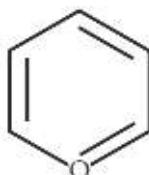
Heterocyclic compounds are widespread in nature is essential for life in multiple shapes. Most sugars and their derivatives, including vitamin C (for example), are present often in the form of heterocyclic compounds either pentagonal like Furan (composition VIII) or hexagonal such as Piran (composition IX) where the ring contains one atom of oxygen. Most alkaloids, nitrogenous bases found in plants

### Do you know

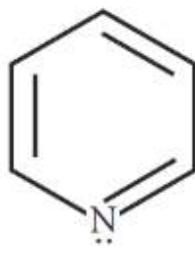
That there is a kind of ladybug, which is called ejector beetle. When the insect is threatened, the ladybug defends itself with a hot, irritating solution of quinone (a phenol) on its enemies. The beetle mixes hydroquinone with hydrogen peroxide with a special enzyme, during that hydroquinone oxide to quinone and this reaction emits high heat lead to boiling solution and strongly emitted from the insect's abdomen.



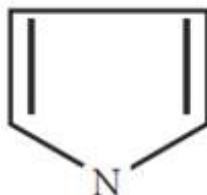
Furan VIII



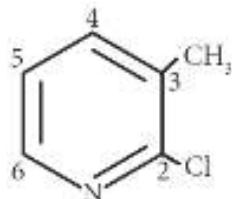
Piran



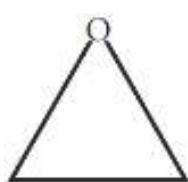
X Pruden



XI Pyrol



XII 2-chloro - 3 methylpredine



XIII Ethylene Epoxide



XIV oxctane

and many antibiotics, including penicillins, contain heterogeneous cyclic systems. It was found that Pruden (composition X) a heterocyclic hexagonal compound containing one nitrogen atom that is part of the nicotine structure. It was found pyrol (composition XI) is a pentagonal compound containing one nitrogen atom that is a unit of hemoglobin and chlorophyll. There are also a large number of heterocyclic compounds that can be obtained through laboratory preparations having valuable qualities as therapeutic chemical compounds and as drugs, dyes and copolymers.

### 8-7-2 Naming of heterocyclic compounds

There are many ways to number the atoms and compensated groups in the heterocyclic compounds. In monocyclic compounds the atoms are numbered starting from heterogeneous atom which then carries the number -1- and then revolves around the ring so that the compensating groups in this ring give the lowest numbered and then arrange them according to the order of the letters the alphabet for example compound number(XII) named 2-chloro-3-methyl predine

### 8-7-3 Type of heterocyclic compounds

To facilitate the study of this type of compounds were divided into the following:

#### 1. Heterogeneous triple ring compounds:

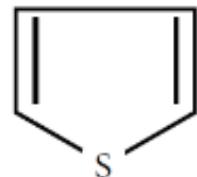
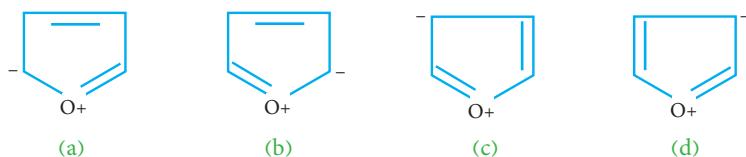
They are the cyclic compounds corresponding to the cyclic propane, but they contain one differ atom. Examples of these compounds are epoxides such as composition formula (XIII).

#### 2. Heterogeneous quadrilateral compounds:

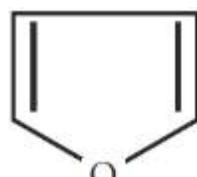
These are the heterocyclic compounds corresponding to the cyclic butane. These compounds are more stable than triple-ring compounds, such as the composition formula oxctane (XIV).

### 3. Heterocyclic five-ring compounds:

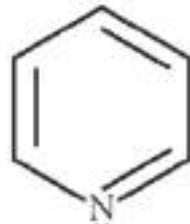
They are the heterocyclic compounds corresponding to cyclopentadiene. The most common examples of these compounds are thiophene (XV) and furan mentioned earlier (VIII). Furan is a colorless liquid, boiling at 31 °C. It has a chloroform-like odor and dissolves scarcely in water and is completely soluble in organic solvents. In 1877, Bayer proved furan structure and composition. It is best to look at the furan molecule as a resonance hybrid because of the not positional of the oxygen atom electron pair where the a to d hypothetical structures form, where a and b are the most important.



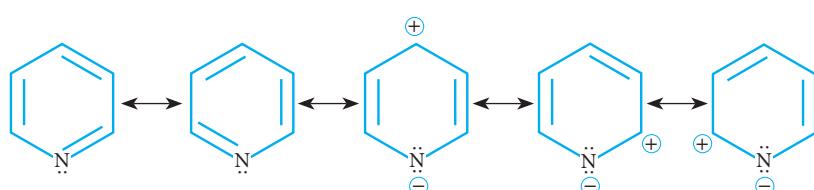
XV Thiophene



VIII furan



X predine



It is a weak base because nitrogen contains two unshared electrons that greatly affect its chemical properties, introducing more compensating reactions than additive reactions.

### Aromatic Hydrocarbons

It is a group of organic compounds on some degree of unsaturation is only unique in its stability, therefore these compounds tend to engage in substitution (compensate) reactions where the aromatic ring remains preserving their form and not additional reactions as in most unsaturated compounds. This type of organic compounds includes benzene and its derivatives and similar compounds in terms of composition and chemical reactivity.

### Resonance

It is a phenomenon of the lack of concentration of electrons around nuclei of specific atoms in the molecule or ion making them more stable. In the case of benzene and in order to justify strictly the fact the composition formula of the benzene molecule, so that the bonds of the  $\pi$ -bonds appear in the double carbon atoms like they are in continuous motion, we draw the hexagonal form of benzene and inside it moving electrons in the form of sequential points or closed loop instead of the double elements. That is, we make the electrons of these bonds the property of all six carbon atoms, this type of electronic motion so-called resonance.

### Benzene Derivatives Names

Monocomponent compounds are called as derivatives of benzene or called by their common names. In the case of derivatives of dual compensation must be located on the ring either numbering where the two groups take the smallest a numbers and then mention the names of the two groups by alphabets Ortho, Meta and Barra to indicate the location of the groups. In com-

pounds case with multiple compensation should be used numbering method where the term ortho and meta parra is unacceptable.

### Electrophilic Substitution

It is the process of replacing one of the hydrogen atoms in the ring in atom or different group such as halogenation, sulfonation, Nitration, alkylation , and acylation , and is made by presence reagent looking for electrons (electrophilic reagent), especially in each process.

### Phenols

Aromatic organic compounds derived from benzene it consists of the bonding of the hydroxyl group to benzene ring directly. The presence of the hydroxyl group has a significant effect in determining its physical properties due to the formation of hydrogen bonds between their molecules, which causes the high degree of boiling point and melting point.

### Heterocyclic Compounds

A heterocyclic compound is a compound in which one or more atoms of the ring are not carbon may be an atom of nitrogen or oxygen or sulfur. It can be a heterogeneous ring triple, quadruple, pentagonal or hexagonal.

### Benzene

Benzene is a molecular formula with six identical carbon atoms and six identical hydrogen atoms, and the lengths of the C-C are equal. It is an intermediate state between the length of the single bond and the double bond.

## Chapter eight Questions

8

8-1 How did the concept of aromatic changed?

8-2 What is the source of aromatic hydrocarbons?

8-3 Why is the composition of benzene a resonance hybrid?

8-4 When benzene behaves as a non-saturated hydrocarbon?

8-5 How can you distinguish of benzene in its reactions from alkanes and alkenes? What caused the relative stability of its molecule?

8-6 What are the possible isomers of nitrochlorobenzene?

8-7 How do you distinguish between cyclohexane and benzene?

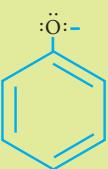
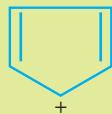
8-8 Write the chemical equations for the reaction of benzene with :

A-  $\text{Cl}_2/\text{FeCl}_3$

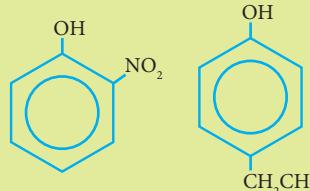
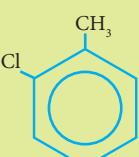
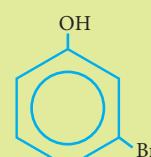
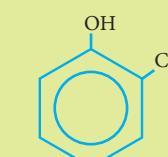
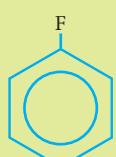
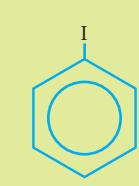
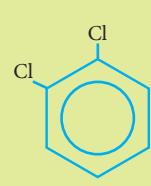
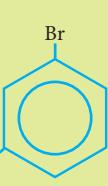
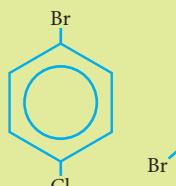
B-  $\text{CH}_3\text{CH}_2\text{Cl}/\text{AlCl}_3$

C-  $\text{CH}_3\text{COCl}/\text{AlCl}_3$

8-9 Draw Resonance shape for the following



8-10 Named the following components



8-11 Draw the formulas for the following compounds:

1. Para-dichlorobenzene

2. 1, 3 - difluorobenzene

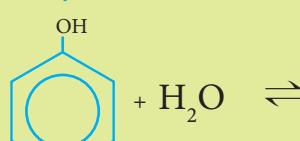
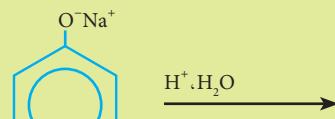
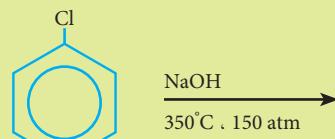
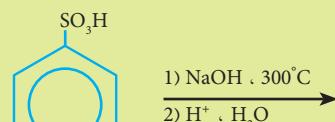
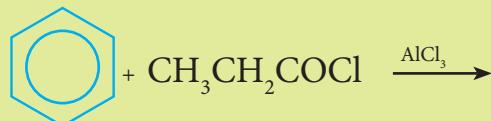
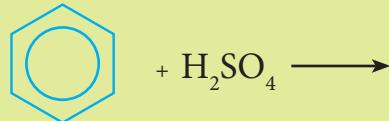
3. 1, 2 - iodochlorobenzene

4. Para bromochlorobenzene

5. Meta-bromo sulfonic acid

6. Para nitrophenol

8-12 Complete the following equations?



**8-13** What are the Industrially methods for preparing benzene? Write them in detail?

**8-14** Write the composition formulas of the following compounds

1. 1, 3, 5 Tri-Bromo Benzene.
2. Meta - Chloro Toluene.
3. Ethyl-benzene.
4. Para - dichlorobenzene.

**8-15** Expressed in composition formulas the reaction of benzene with ethyl chloride?

**8-16** By chemical equation and composition formulas, write the product reduction process of benzene by hydrogen and with the presence of platinum?

**8-17** Write the reaction of chlorine addition to benzene in presence of light ?

**8-18** Draw of the following compounds:

- A- Meta-fluoro-chlorobenzene
- B- 2 - Bromo - 4 - Chloropridine
- C- Ortho Ethylphenol

**8-19** Place a (✓) in front of the correct statement and (✗) in front of the wrong statement:

1. Aromatic compounds are organic compounds with high nonsaturation.
2. The compensation reactions introduced by benzene are evidence on its high stability.
3. The terms Ortho, Meta and Para are used in the designation of binary and multiple benzene derivatives.
4. Benzene burns with a bright and smoky flame due high carbon content.
5. Benzene is easily reduced by hydrogen to cyclohexane.
6. Halogenation is the process of replac-

ing an Hydrogen atom in benzene by sulfonic group  $\text{SO}_3\text{H}$

7. Reagents rich in electrons are called reagents looking for electrons.

8. The Furan molecule is made of five carbon atoms bonded to form a pentagonal ring.

9. Benzene Molecular formula  $\text{C}_6\text{H}_6$  contains of six bonds three of which are single and the other three being double.

10. The ester resulting from the reaction of salicylic acid and acetic acid is commercially called aspirin.

11. Phenols are detected by mercury salt solutions.

12. Predine is a heterocyclic compound that contains one oxygen.

13. In nonhomogeneous heterocyclic compounds the numbering begins starting with the heterocyclic atom which is given the number1.

14. The heterocyclic triple-ring compounds are the corresponding cyclic compounds of Butane.

**8-20** What are nonhomogeneous heterocyclic compounds and how are they divided?

**8-21** What are the physical properties of furan and what are resonance shaps for it?

**8-22** What is Predine and what are its resonance shaps?

**8-23** When did phenol first isolated and what are its uses.

**8-24** write down the general electrophilic substitution reaction and what are its three steps.

# المصطلحات

| المصطلح باللغة الانكليزية | المصطلح باللغة العربية   |
|---------------------------|--------------------------|
| Cathod ray                | أشعة الكاثود             |
| Electromagnetic ray       | أشعة كهرومغناطيسية       |
| Metalloids                | أشباء الفلزات            |
| Ionic bond                | آصرة ايونية              |
| Covalent bond             | آصرة تساهمية             |
| Polar covalent bond       | آصرة تساهمية مستقطبة     |
| Single bond               | آصرة منفردة (احادية)     |
| Double bond               | آصرة مزدوجة              |
| Triple bond               | آصرة ثلاثية              |
| Coordinate bond           | آصرة تناسقية             |
| Metalic bond              | آصرة فلزية               |
| Hydrogen bond             | آصرة هيدروجينية          |
| Quantaum numbers          | اعداد الكم               |
| Electron                  | الكترون                  |
| Valence electrons         | الكترونات التكافؤ        |
| Resonance                 | الرنين (ظاهره الروزنانس) |
| Electron affimty          | الفة الكترونية           |
| Nonmetal                  | اللافلزات                |
| Soulblity                 | الذوبانية                |
| Overall rate of reaction  | السرعة العامة للتفاعل    |
| s - Orbital               | اوربيتال s               |
| p - Orbital               | اوربيتال p               |
| d - Orbital               | اوربيتال d               |
| f - Orbital               | اوربيتال f               |
| Ion                       | ايون                     |
| Hydronium ion             | آيون الهيدرونيوم         |
| Paramagnetic              | بارا مغناطيسية           |
| Proton                    | بروتون                   |
| Polymer                   | بوليمير                  |

## المصطلحات

| المصطلح باللغة الانكليزية | المصطلح باللغة العربية      |
|---------------------------|-----------------------------|
| Plastics                  | بلاستيك (لدائن)             |
| Addition Polymers         | بوليمرات الأضافة            |
| Condensation polymers     | بوليمرات التكافف            |
| Thermoplastic polymers    | بوليمرات مطاوعة للحرارة     |
| Thermoset polymers        | بوليمرات غير مطاوعة للحرارة |
| Synthetic polymers        | بوليمرات مصنعة              |
| Chemical bonding          | تآثر كيميائي                |
| Hydrolysis                | تحلل مائي                   |
| Concentration             | تركيز                       |
| Molar concentration       | تركيز مولاري M              |
| Molal concentration       | تركيز مولالي m              |
| Effective collision       | تصادم فعال                  |
| Noneffective collision    | تصادم غير فعال              |
| Nutrlization              | تعادل                       |
| Hyperdiazation            | تهجين                       |
| Orbital hyperdiazation    | تهجين اوربitalي             |
| Frequency                 | تردد                        |
| Electron configuration    | ترتيب الكتروني              |
| Titration                 | تسحیج                       |
| Chemical reaction         | تفاعل كيميائي               |
| Pollution                 | تلويث                       |
| Rate constant             | ثابت سرعة التفاعل           |
| Plank constant            | ثابت بلانك                  |
| Perodic Table             | جدول دوري                   |
| Acid                      | حامض                        |
| Conjugated acid           | حامض قرين                   |
| Excited state             | حالة مستثارة                |
| oxidiation state          | حالة التأكسد                |
| Atomic volume             | حجم ذري                     |

## المصطلحات

| المصطلح باللغة الانكليزية | المصطلح باللغة العربية   |
|---------------------------|--------------------------|
| Heat of solution          | حرارة محلول              |
| Chemical kinetics         | حركيات كيميائية          |
| Linear                    | خطي                      |
| Golligative properties    | خواص جماعية              |
| Diamagnatic               | دايا مغناطيسية           |
| Temperature               | درجة الحرارة             |
| Boiling point             | درجة حرارة الغليان       |
| Freezing point            | درجة حرارة الانجماد      |
| Indicators                | دلائل                    |
| Lewis symbol              | رمز لويس                 |
| Burret                    | سحاحة                    |
| Rate of reaction          | سرعة التفاعل             |
| Light speed               | سرعة الضوء               |
| Crystal lattice           | شبكة بلورية              |
| Tetrahedral               | شكل رباعي الاوجه منتظم   |
| Trigonal                  | شكل مثلثي منتظم          |
| Pressure                  | ضغط                      |
| Partial pressure          | ضغط جزئي                 |
| Total pressure            | ضغط كلي                  |
| Vapour pressure           | ضغط بخاري                |
| Osmotis pressure          | ضغط ازموزي               |
| Activation energy         | طاقة التنشيط             |
| Resonance energy          | طاقة الرنين              |
| Ionization energy         | طاقة التأين              |
| Wave length               | طول الموجة               |
| Flame spectrum            | طيف اللهب                |
| Line emisson spectrum     | طيف الانبعاث الخطى       |
| Nucleophilic reagent      | عامل باحث عن النواة      |
| Electrophilic reagent     | عامل باحث عن الألكترونات |

## المصطلحات

| المصطلح باللغة الانكليزية | المصطلح باللغة العربية    |
|---------------------------|---------------------------|
| d - Block                 | مجموعة d                  |
| s - Block                 | مجموعة s                  |
| f - Block                 | مجموعة f                  |
| Solutions                 | محاليل                    |
| Aqueous solution          | محاليل مائية              |
| Nonaqueous solution       | محاليل غير مائية          |
| Colliodal solution        | محاليل غروية              |
| Saturated solution        | محلول مشبع                |
| Unsaturated solution      | محلول غير مشبع            |
| Supesaturated solution    | محلول فوق المشبع          |
| Ideal solution            | محلول مثالي               |
| Standard solution         | محلول قياسي               |
| Solute                    | مذاب                      |
| Solvent                   | مذيب                      |
| Reaction order            | مرتبة التفاعل             |
| Intermediate              | مركب وسطي                 |
| Hetrocyclic compouds      | مركبات حلقية غير متتجانسة |
| Ground state              | مستوى ارضي (مستقر)        |
| Rubber                    | مطاط                      |
| Coordination complexes    | معقدات تناسقية            |
| Activated-Complex         | معقد منشط                 |
| Salt                      | ملح                       |
| Amphoteric substances     | مواد أمفوتييرية           |
| Molarity                  | مولارية M                 |
| Molality                  | مولالية m                 |
| Monomer                   | مونمر                     |
| Quntaum mechanics         | مكانيكيا كمية             |
| Reaction Mechanism        | ميكانيكية التفاعل         |
| Ionic radius              | نصف قطر الايون            |

## المصطلحات

| المصطلح باللغة الانكليزية | المصطلح باللغة العربية   |
|---------------------------|--------------------------|
| Catalyst                  | عامل مساعد               |
| Atomic number             | عدد ذري                  |
| Atomic mass               | عدد الكتلة               |
| Principal quantum number  | عدد الكم الرئيس          |
| Magnetic quantum number   | عدد الكم المغناطيسي      |
| Spin quantum number       | عدد الكم المغزلي         |
| Momentum quantum number   | عدد الكم الشانوي (الزخم) |
| Polymerization            | عملية البلمرة            |
| Element                   | عنصر                     |
| Transition element        | عناصر انتقالية           |
| Inner Transition element  | عناصر انتقالية داخلية    |
| Rare -earth elements      | عناصر الاتربه النادرة    |
| Coordinated number        | عدد تناصفي               |
| Alkaline -earth elements  | عناصر الاتربة القلوية    |
| Metal                     | فلز                      |
| Vulcanization             | فلكونة                   |
| Photon                    | فوتون                    |
| Ferromagnetic             | فيرومغناطيسية            |
| Base                      | قاعدة                    |
| Hund's rule               | قاعدة هوند               |
| Pauli- excluded principle | قاعدة الاستثناء الباوي   |
| Octate rule               | قاعدة الثمان             |
| Congugated base           | قاعدة قرينة              |
| Rate law                  | قانون سرعة التفاعل       |
| Raoult's law              | قانون راؤلت              |
| Electron mass             | كتلة الالكترون           |
| Atomic mass               | كتلة ذرية                |
| Mole fraction             | كسر مولى $X$             |
| Electronegativity         | كهرسلبية                 |

## المصطلحات

| المصطلح باللغة الانكليزية                    | المصطلح باللغة العربية                     |
|--|--|
| Collision Theory                             | نظرية التصادم                              |
| Transition- state theory                     | نظرية الحالة الانتقالية                    |
| Activated- complex theory                    | نظرية المعقد المنشط                        |
| Arrhenius Theory                             | نظرية ارينوس                               |
| Bronsted lowry theory                        | نظرية برونشتاد - لوري                      |
| Lewis theory                                 | نظرية لويس                                 |
| Quantum theory                               | نظرية الكم                                 |
| Valence - bond theory                        | نظرية اصرة التكافؤ                         |
| Valence shell electron pair repulsion theory | نظرية تنافر وازدواج الكترونات غلاف التكافؤ |
| Equivalent point                             | نقطة التكافؤ                               |
| End point                                    | نقطة الانتهاء                              |
| Neutron                                      | نيوترون                                    |
| Armatic hydrocarbon                          | هيدروكربونات اروماتية                      |
| Rate-determining step                        | الخطوة المحددة للسرعة                      |
| Electron charge                              | شحنة الالكترون                             |
| Dilution Law                                 | ( قانون التخفيف ) $V_1 M_1 = V_2 M_2$      |

| Elements      |  | sublevels |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
|---------------|--|-----------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
|               |  | 1s        | 2s | 2p | 3s | 3p | 3d | 4s | 4p | 4d | 4f | 5s | 5p | 5d | 5f | 6s | 6p | 6d | 7s |
| 1-Hydrogen    |  | 1         |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 2-Helium      |  | 2         |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 3-Lithium     |  | 2         | 1  |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 4-Beryllium   |  | 2         | 2  |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 5-Boron       |  | 2         | 2  | 1  |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 6-Carbon      |  | 2         | 2  | 2  |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 7-Nitrogen    |  | 2         | 2  | 3  |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 8-Oxygen      |  | 2         | 2  | 4  |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 9-Fluorine    |  | 2         | 2  | 5  |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 10-Neon       |  | 2         | 2  | 6  |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 11-Sodium     |  | 2         | 2  | 6  | 1  |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 12-Magnesium  |  | 2         | 2  | 6  | 2  |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 13-Aluminum   |  | 2         | 2  | 6  | 2  | 1  |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 14-Silicon    |  | 2         | 2  | 6  | 2  | 2  |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 15-Phosphorus |  | 2         | 2  | 6  | 2  | 3  |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 16-Sulfur     |  | 2         | 2  | 6  | 2  | 4  |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 17-Chlorine   |  | 2         | 2  | 6  | 2  | 5  |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 18-Argon      |  | 2         | 2  | 6  | 2  | 6  |    |    |    |    |    |    |    |    |    |    |    |    |    |
| 19-Potassium  |  | 2         | 2  | 6  | 2  | 6  |    |    |    |    | 1  |    |    |    |    |    |    |    |    |
| 20-Calcium    |  | 2         | 2  | 6  | 2  | 6  |    |    |    |    | 2  |    |    |    |    |    |    |    |    |
| 21-Scandium   |  | 2         | 2  | 6  | 2  | 6  |    |    |    | 1  | 2  |    |    |    |    |    |    |    |    |
| 22-Titanium   |  | 2         | 2  | 6  | 2  | 6  |    |    | 2  | 2  | 2  |    |    |    |    |    |    |    |    |
| 23-Vanadium   |  | 2         | 2  | 6  | 2  | 6  |    |    | 3  | 2  |    |    |    |    |    |    |    |    |    |
| 24-Chromium   |  | 2         | 2  | 6  | 2  | 6  |    |    | 5  | 1  |    |    |    |    |    |    |    |    |    |
| 25-Manganese  |  | 2         | 2  | 6  | 2  | 6  |    |    | 5  | 2  |    |    |    |    |    |    |    |    |    |
| 26-Iron       |  | 2         | 2  | 6  | 2  | 6  |    |    | 6  | 2  | 2  |    |    |    |    |    |    |    |    |
| 27-Cobalt     |  | 2         | 2  | 6  | 2  | 6  |    |    | 7  | 2  |    |    |    |    |    |    |    |    |    |
| 28-Nickel     |  | 2         | 2  | 6  | 2  | 6  |    |    | 8  | 2  |    |    |    |    |    |    |    |    |    |
| 29-Copper     |  | 2         | 2  | 6  | 2  | 6  |    |    | 10 | 1  |    |    |    |    |    |    |    |    |    |
| 30-Zinc       |  | 2         | 2  | 6  | 2  | 6  |    |    | 10 | 2  |    |    |    |    |    |    |    |    |    |
| 31-Gallium    |  | 2         | 2  | 6  | 2  | 6  |    |    | 10 | 2  | 1  |    |    |    |    |    |    |    |    |
| 32-Germanium  |  | 2         | 2  | 6  | 2  | 6  |    |    | 10 | 2  | 2  |    |    |    |    |    |    |    |    |
| 33-Arsenic    |  | 2         | 2  | 6  | 2  | 6  |    |    | 10 | 2  | 3  |    |    |    |    |    |    |    |    |
| 34-Selenium   |  | 2         | 2  | 6  | 2  | 6  |    |    | 10 | 2  | 4  |    |    |    |    |    |    |    |    |
| 35-Bromium    |  | 2         | 2  | 6  | 2  | 6  |    |    | 10 | 2  | 5  |    |    |    |    |    |    |    |    |
| 36-Krypton    |  | 2         | 2  | 6  | 2  | 6  |    |    | 10 | 2  | 6  |    |    |    |    |    |    |    |    |
| 37-Rubidium   |  | 2         | 2  | 6  | 2  | 6  |    |    | 10 | 2  | 6  |    |    | 1  |    |    |    |    |    |
| 38-Strontium  |  | 2         | 2  | 6  | 2  | 6  |    |    | 10 | 2  | 6  |    |    | 2  |    |    |    |    |    |
| 39-Yttrium    |  | 2         | 2  | 6  | 2  | 6  |    |    | 10 | 2  | 6  | 1  |    | 2  |    |    |    |    |    |
| 40-Zirconium  |  | 2         | 2  | 6  | 2  | 6  |    |    | 10 | 2  | 6  | 2  |    | 2  |    |    |    |    |    |

| Element Electronic Configurations |           |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |   |
|-----------------------------------|-----------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|---|
| Elements                          | sublevels |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |   |
|                                   | 1s        | 2s | 2p | 3s | 3p | 3d | 4s | 4p | 4d | 4f | 5s | 5p | 5d | 5f | 6s | 6p | 6d | 7s | 7p |   |
| 41-Niobium                        | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 4  |    | 1  |    |    |    |    |    |    |    |    |   |
| 42-Molybdenum                     | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 5  |    | 1  |    |    |    |    |    |    |    |    |   |
| 43-Technetium                     | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 5  |    | 2  |    |    |    |    |    |    |    |    |   |
| 44-Ruthenum                       | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 7  |    | 1  |    |    |    |    |    |    |    |    |   |
| 45-Rhodium                        | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 8  |    | 1  |    |    |    |    |    |    |    |    |   |
| 46-Palladium                      | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 |    |    |    |    |    |    |    |    |    |    |   |
| 47-Silver                         | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 |    | 1  |    |    |    |    |    |    |    |    |   |
| 48-Cadmium                        | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 |    | 2  |    |    |    |    |    |    |    |    |   |
| 49-Indium                         | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 |    | 2  | 1  |    |    |    |    |    |    |    |   |
| 50-Tin                            | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 |    | 2  | 2  |    |    |    |    |    |    |    |   |
| 51-Antimony                       | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 |    | 2  | 3  |    |    |    |    |    |    |    |   |
| 52-Tellurium                      | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 |    | 2  | 4  |    |    |    |    |    |    |    |   |
| 53-Iodine                         | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 |    | 2  | 5  |    |    |    |    |    |    |    |   |
| 54-Xenon                          | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 |    | 2  | 6  |    |    |    |    |    |    |    |   |
| 55-Cesium                         | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 |    | 2  | 6  |    |    |    |    |    |    |    | 1 |
| 56-Barium                         | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 |    | 2  | 6  |    |    |    |    |    |    |    | 2 |
| 57-Lanthanum                      | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 |    | 2  | 6  | 1  |    |    |    |    |    |    | 2 |
| 58-Cerium                         | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 1  | 2  | 6  | 1  |    |    |    |    |    |    | 2 |
| 59-Prasedoymium                   | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 3  | 2  | 6  |    |    |    |    |    |    |    | 2 |
| 60-Neodymium                      | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 4  | 2  | 6  |    |    |    |    |    |    |    | 2 |
| 61-Promethium                     | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 5  | 2  | 6  |    |    |    |    |    |    |    | 2 |
| 62-Samarium                       | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 6  | 2  | 6  |    |    |    |    |    |    |    | 2 |
| 63-Europium                       | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 7  | 2  | 6  |    |    |    |    |    |    |    | 2 |
| 64-Gadolinum                      | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 7  | 2  | 6  | 1  |    |    |    |    |    |    | 2 |
| 65-Terbium                        | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 9  | 2  | 6  |    |    |    |    |    |    |    | 2 |
| 66-Dysprosium                     | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 10 | 2  | 6  |    |    |    |    |    |    |    | 2 |
| 67-Holmium                        | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 11 | 2  | 6  |    |    |    |    |    |    |    | 2 |
| 68-Erbium                         | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 12 | 2  | 6  |    |    |    |    |    |    |    | 2 |
| 69-Thulium                        | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 13 | 2  | 6  |    |    |    |    |    |    |    | 2 |
| 70-Yetterbium                     | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  |    |    |    |    |    |    |    | 2 |
| 71-Luteium                        | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 1  |    |    |    |    |    |    | 2 |
| 72-Hafanium                       | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 2  |    |    |    |    |    |    | 2 |
| 73-Tantalium                      | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 3  |    |    |    |    |    |    | 2 |
| 74-Tungesten                      | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 4  |    |    |    |    |    |    | 2 |
| 75-Rhenium                        | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 5  |    |    |    |    |    |    | 2 |
| 76-Osmium                         | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 6  |    |    |    |    |    |    | 2 |
| 77-Iridium                        | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 7  |    |    |    |    |    |    | 2 |
| 78-Platinum                       | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 9  |    |    |    |    |    |    | 1 |
| 79-Gold                           | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 |    |    |    |    |    |    | 1 |
| 80-Mercury                        | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 |    |    |    |    |    |    | 2 |

| Elements          |  | sublevels |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
|-------------------|--|-----------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
|                   |  | 1s        | 2s | 2p | 3s | 3p | 3d | 4s | 4p | 4d | 4f | 5s | 5p | 5d | 5f | 6s | 6p | 6d | 7s | 7p |
| 81-Thalium        |  | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 |    |    | 2  | 1  |    |    |
| 82-Lanthanum      |  | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 |    |    | 2  | 2  |    |    |
| 83-Bismuth        |  | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 |    |    | 2  | 3  |    |    |
| 84-Polonium       |  | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 |    |    | 2  | 4  |    |    |
| 85-Astatine       |  | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 |    |    | 2  | 5  |    |    |
| 86-Radon          |  | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 |    |    | 2  | 6  |    |    |
| 87-Francium       |  | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 |    |    | 2  | 6  | 1  |    |
| 88-Radium         |  | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 |    |    | 2  | 6  | 2  |    |
| 89-Actinium       |  | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 |    |    | 2  | 6  | 1  | 2  |
| 90-Thorium        |  | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 |    |    | 2  | 6  | 2  | 2  |
| 91-Protactinium   |  | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 | 2  | 2  | 6  | 1  | 2  |    |
| 92-Uranium        |  | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 | 3  | 2  | 6  | 1  | 2  |    |
| 93-Neptunium      |  | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 | 4  | 2  | 6  | 1  | 2  |    |
| 94-Plutonium      |  | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 | 6  | 2  | 6  | 1  | 2  |    |
| 95-Amerecium      |  | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 | 7  | 2  | 6  | 1  | 2  |    |
| 96-Curium         |  | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 | 7  | 2  | 6  | 1  | 2  |    |
| 97-Berkelium      |  | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 | 9  | 2  | 6  | 1  | 2  |    |
| 98-Californium    |  | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 | 10 | 2  | 6  | 1  | 2  |    |
| 99-Einestanium    |  | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 | 11 | 2  | 6  | 1  | 2  |    |
| 100-Fermium       |  | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 | 12 | 2  | 6  | 1  | 2  |    |
| 101-Mendelevium   |  | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 | 13 | 2  | 6  | 1  | 2  |    |
| 102-Nobelium      |  | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 | 14 | 2  | 6  | 1  | 2  |    |
| 103-Lawrencium    |  | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 | 14 | 2  | 6  | 1  | 2  |    |
| 104-Rutherfordium |  | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 | 14 | 2  | 6  | 2  | 2  |    |
| 105-Dubinum       |  | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 | 14 | 2  | 6  | 3  | 2  |    |
| 106-Seaborgium    |  | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 | 14 | 2  | 6  | 4  | 2  |    |
| 107-Bohrium       |  | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 | 14 | 2  | 6  | 5  | 2  |    |
| 108-Hassium       |  | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 | 14 | 2  | 6  | 6  | 2  |    |
| 109-Meitnerium    |  | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 | 14 | 2  | 6  | 7  | 2  |    |
| 110-Darmstadtium  |  | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 | 14 | 2  | 6  | 9  | 1  |    |
| 111-Unununium     |  | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 | 14 | 2  | 6  | 10 | 1  |    |
| 112-Unubium       |  | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 | 14 | 2  | 6  | 10 | 2  |    |
| 113-Ununquadium   |  | 2         | 2  | 6  | 2  | 6  | 10 | 2  | 6  | 10 | 14 | 2  | 6  | 10 | 14 | 2  | 6  | 10 | 2  | 2  |

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