MARMARA ÜNİVERSİTESİ YAYINEVİ

MARMARA ÜNİVERSİTESİ YAYIN NO: 541
ATATÜRK EĞİTİM FAKÜLTESİ YAYIN NO: 22

# GENERAL CHEMISTRY

Doç. Dr. Sevil ÜNAL

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# GENERAL CHEMISTRY

by

Doç. Dr. Sevil ÜNAL

UNIVERSITY OF MARMARA
Atatürk Faculty of Education

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# PREFACE

This text has been written as a quide to university level general chemistry studies. It also aims at reducing the difficulties encountered in lecture-note preparation by the lecturers and note-taking by the students in English medium general chemistry courses in Turkey.

I have tried to make a concise presentation of the fundamentals of chemistry. I have followed an order that starts with the atom, its structure and properties. Related topics such as electromagnetic radiation and molecular geometry are covered before the mole concept is introduced and molar systems are discussed. Nuclear chemistry is introduced as a separate chapter at the end of the text. The fourteen chapters comprising the text can be covered in a two-semester course: Chapters 1 to 9 in the first semester, Chapters 10 to 14 in the second. The time allowed for quantitative applications can be varied according to the specific needs of the class and course credit.

I hope this text will be of help to all its users as it has been to me and my students.

Sevil ÜNAL

December, 1992

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# CHAPTER 1

# INTRODUCTION TO CHEMISTRY AND MATTER

## 1-1 What is chemistry?

Chemistry is the study of structure, composition and the properties of the various forms of matter and the transformations that matter may undergo.

## 1.2 Matter, elements and compounds

Matter can be described as any object or material that occupies space.

The quantitiy of matter is measured by a property called mass.

Properties of matter can be grouped into two categories: physical and chemical.

Physical properties may be used to describe the physical appearance of an object e.g. colour, state, boiling point, freezing point.

Chemical properties of materials are their ability to undergo chemical changes which take place in chemical reactons.

Many different kinds of matter, known as substances, exist in the universe. They exist in three states: solid, liquid and gas. However, all matter, irrespective of its state, is composed of elements which may have combined together in the form of a compound.

Elements are a class of substance that cannot be reduced further either by chemical or physical means.

Compounds are substances in which two or more different elements are chemically combined. They retain their identity in physical changes but can be reduced to their elements by appropriate chemical means.

Many combinations of elements and/or compounds with uniform composition are possible. These are said to be homogeneous e.g. sea water, chemical solutions. However these can be separated into their components by appropriate physical means.

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In some mixtures the components are segregated into physically distinct regions. Consequently the physical properties vary from one part of the mixture to the other. Such mixtures are said to be heterogeneous.

A general classification of matter and its transformations from one type to another are illustrated in Figure 1.1

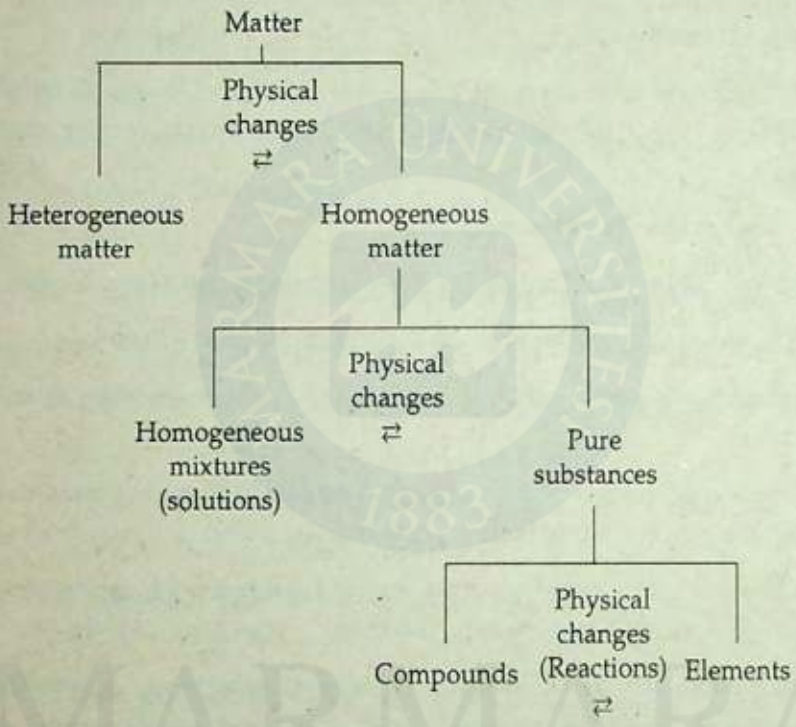


**Figure 1.1** Classification of matter

## 1.3 Units of measurement

The magnitude of a physical quantity is expressed as the product of two quantities: one is the magnitude of the unit, the other is the number of those units. Thus in "10 cm" cm is the magnitude of the unit - it could be m, mm or km - and 10 is the number of those units.

There are number of quantities that are measured and a number of systems in which these measurements are expressed. The three major

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systems of units are the centimeter-gram-second (cgs) system, the Système International d'Unites (SI) and the foot-pound-second (fps), the British system. Units and symbols of the various parameters in each system are listed in Table 1.1. Conversion of units from one system to another is given in Table 1.2. The prefixes for most commonly used decimal fractions and multiples of SI units are listed in Table 1.3. The temperature scale used in each system is shown in Table 1.4.

In the General Chemistry course very small and very large numbers are usually dealt with in the same mathematical operation. It is therefore imperative that these mathematical operations are performed using suitable notations. Scientific notation is strongly recommended.

Scientific notation has the form of

$$N \times 10^{n}$$

where $1.0 \leq N \leq 9.\overline{9}$

e.g. 311 000 ise $3.11 \times 10^{5}$ and 0.000311 is $3.11 \times 10^{-4}$ in scientific notation.

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| Parameter | Dimension | Unit | | |
|---|---|---|---|---|
| | | SI | cgs | fps |
| **Base units** | | | | |
| Length | L | meter (m) | centimeter (cm) | foot (ft) |
| Time | t | second (s) | second (s) | second (s) |
| Mass | M | kilogram (kg) | gram (g) | pound (1b) |
| **Derived units** | | | | |
| Force (F) | $ML/t^2$ | Newton (N) (kg m/$s^2$) | dyne (dyn) (g cm/$s^2$) | pund force ($1b_f$) (1b ft/$s^2$)<br>poundal (pdl) (1b ft/$s^2$) |
| Area (A) | $L^2$ | sq. meters ($m^2$) | sq. centimeters ($cm^2$) | sq. feet ($ft^2$) |
| Volume (V) | $L^3$ | cu. meters ($m^3$) | cu. centimeters ($cm^3$) (cc) | cu. feet ($ft^3$) |
| Velocity (v) | L/t | (m/s) | (cm/s) | (ft/s) |
| Acceleration (a) | $L/t^2$ | ($m/s^2$) | ($cm/s^2$) | ($ft/s^2$) |
| Density (d) | $M/L^3$ | ($kg/m^3$) | (g/cc) | ($1b/ft^3$) |
| Pressure (P) | $F/L^2$ ($M/Lt^2$) | Pascal (Pa) ($N/m^2$) | ($dyn/cm^2$) | ($1b_f/ft^2$) |
| Energy | FL ($ML^2/t^2$) | Joule (J) (N m) | erg (dyn cm) | British thermal units (Btu) |
| Power | FL/t ($ML^2/t^3$) | Watt (W) (J/s) | (erg/s) | (Btu/h)<br>horsepower (h.p) |
| Temperature (T) | | Kelvin (K) | Celsius (°C) | Fahrenheit (°F) |

**Table 1.1** Sstems of units

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| | SI | cgs | fps |
|---|---|---|---|
| gravitational | | | |
| acceleration, $g = 9.8\ m/s^2$ | | | |
| $= 32.174\ ft/s^2$ | 1 m | $10^2$ cm | 3.28 ft |
| 1 poundal = 1 lbx $32.174\ ft/s^2$ | | $10^2$ cm | 39.37 in. |
| $1\ lb_f = 1\ lb \times 32.174\ ft/s^2$ | 1 kg | $10^3$ g | 2.2 lb |
| | 1 N | $10^5$ dyn | 7.216 pdl |
| | | | 0.225 $lb_f$ |
| | 1 Pa | 10 dyn/$cm^2$ | 0.672 pdl/$ft^2$ |
| | | | 0.021 $lb_f/ft^2$ |
| | | | $1.45 \times 10^{-4}\ lb_f/in^2$ |
| | 1 Pa | $10^7$ erg | $9.48 \times 10^{-4}$ Btu |
| | | (0.239 cal) | |
| | 1 W | $10^7$ erg/s | 3.41 Btu/h |
| | | | $1.34 \times 10^{-3}$ h.p |

**Table 1.2** Constant values and conversion factors

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| Prefix | Symbol for prefix | Quantity | Scientific notation |
|---|---|---|---|
| Giga | G | 1 000 000 000 | $10^{9}$ |
| Mega | M | 1 000 000 | $10^{6}$ |
| Kilo | k | 1 000 | $10^{3}$ |
| Hecto | h | 100 | $10^{2}$ |
| Deco | da | 10 | $10^{1}$ |
| | | 1 | $10^{0}$ |
| Deci | d | 0.1 | $10^{-1}$ |
| Centi | c | 0.01 | $10^{-2}$ |
| Milli | m | 0.001 | $10^{-3}$ |
| Micro | μ | 0.000 001 | $10^{-6}$ |
| Nano | n | 0.000 000 001 | $10^{-9}$ |
| Angstrom | A° | | $10^{-10}$ |
| Pico | p | | $10^{-12}$ |

**Table 1.3** Prefixes for multiples and fractions of SI units

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| Scale | K (Kelvin) | °C (Celsius) | °F (Fahrenheit) | °R (Rankin) |
|---|---|---|---|---|
| (@ 1 atm) | | | | |
| Water boils | 373 | 100 | 212 | 672 |
| Water Freezes | 273 | 0 | 32 | 492 |
| | 255 | - 18 | 0 | 460 |
| Helium boils | 0 | - 273 | - 460 | 0 |
| | T (°C) = T (K) - 273 | | | |
| | T (°C) = ( T(F) - 32 ) 5/9 | | | |
| | T (°C) = ( T (R) - 492 ) 5/9 | | | |

**Table 1. 4** Temperature scales and their conversions

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# CHAPTER 2

# THE ATOM

## 2.1 Atomic structure

The atom is the smallest, indivisible part of an element. The smallest atom is the Hydrogen atom. $6.023 \times 10^{23}$ H atoms have a total mass of 1 g. The number $6.023 \times 10^{23}$ has come to be known as the Avogadro's number.

The H atom is composed of two charged particles: a proton and an electron. The former is positively ( + 'ly ) charged, the latter is negatively ( - 'ly ) charged.

The second smallest atom is that of Helium. He has two protons, two electrons and, in the nucleus, two additional particles together with the two protons. They are called neutrons. Neutrons are not charged.

The number of protons in the nucleus of an atom is called its atomic number. The total number of protons and neutrons in the nucleus of an atom is the mass number of that element.

$$\begin{matrix} \text{mass number} \\ \text{atomic number} \end{matrix} \qquad {}^{1}_{1}\mathrm{H},\ {}^{4}_{2}\mathrm{He},\ {}^{12}_{6}\mathrm{C}$$

number of neutrons = mass no. - atomic no.

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| | Mass (kg) | Charge (C) |
|---|---|---|
| Proton | $1.6726 \times 10^{-27}$ | (+) $1.602 \times 10^{-19}$ |
| Neutron | $1.6750 \times 10^{-27}$ | 0 |
| Electron | $9.1096 \times 10^{-31}$ | (-) $1.602 \times 10^{-19}$ |

The atomic mass of any element can be calculated from the masses of the protons, neutrons and electrons its atoms are composed of. The official unit of atomic mass is 1/12 of the the carbon atom that has 6 protons, 6 neutrons and 6 electrons. This unit is called the **unified atomic mass unit** and is given the symbol **u.** $^{12}_{6}C$ has a mass number of 12 u exactly. The important advantage of this unit is that atomic masses have values that are close to the total number of protons and neutrons in the nucleus.

Atoms of an element that have different mases are called **isotopes**. This results from the fact that some atoms of an element hava different number of neutrons in their nuclei than the majority of the atoms of the same element , e.g.

$^{16}_{8}O$, $^{17}_{8}O$, $^{18}_{68}O$, $^{12}_{6}C$, $^{13}_{6}C$ .

In addition to naturally occurring isotopes, isotopes of some elements can be obtained by bombarding the atoms with nuclear particles thus bringing about a change in their number of neutrons.

The average atomic mass of an element which naturally occurs in the form of various isotopes is calculated by taking the weighted average of the atomic masses of the isotopes.

The charge on an elemental atom is zero. This is because the number of electrons in an elemental atom is equal to the number of protons in the nucleus and they are equally but oppositely charged ($q_e = q_p = 1.602 \times 10^{-19}$ C). 6.241 $10^{18}$ electrons and the same number of protons have a total charge of - 1 C and + 1 C respectively. So, an electron has a - 1 electron charge, - e, and a proton has + 1 electron charge, + e, which are both $1.6 \times 10^{-19}$ Coulomb in magnitude.

The atom is held together mainly by the electrostatic forces between the +'ly charged protons and the -'ly charged electrons. This force is expressed by

$$F = k \frac{q_1 q_2}{r^2} \qquad (2.1)$$

and is known as the Coulomb's law where k is a constant ($9 \times 10^9$ N $m^2$ / $C^2$), $q_1$, $q_2$ are charges ( C ) and r is the distance between the two charges ( m ).

Theories on the detailed structure of the atom could be developed only through extensive research on the impact of electromagnetic radiation with atoms. Properties of electromagnetic radiation are therefore briefly mentioned here prior to introducing the various atomic models.

## 2.2. Electromagnetic radiation

Radiowaves, infrared ( IR ) light, visible light and X rays are all tpyes of electromagnetic radiation (Figure 2.1). Waves are described in terms of their velocity, v, wavelength, λ (lambda), Frequency, υ (nu) and amplitude, A. The velocity of visible light and all other types of magnetic radiation is constant at $3 \times 10^8$ m/s. Wavelength is the peak-to-peak distance in a wave (Figure 2.2). The number of wavelengths that pass through a given

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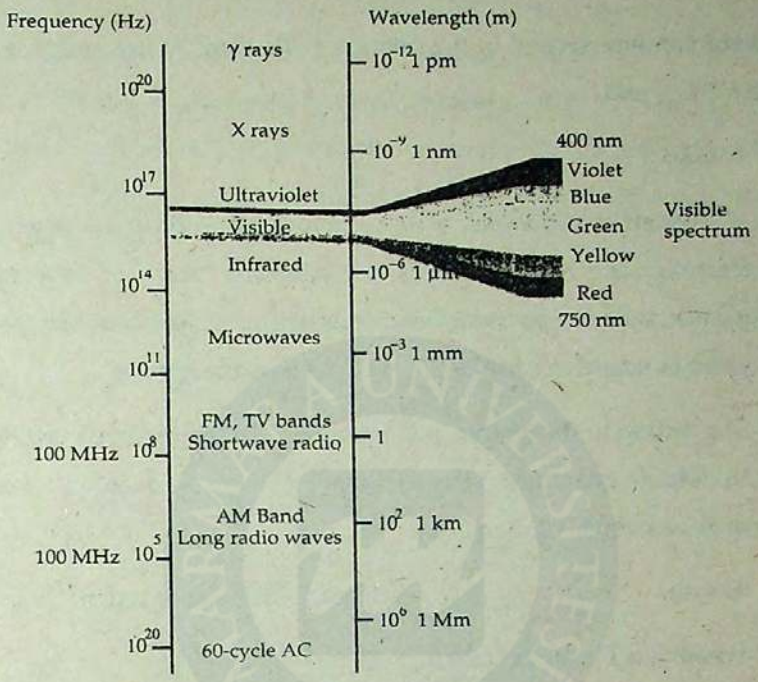


**Figure 2.1** The electromagnetic spectrum

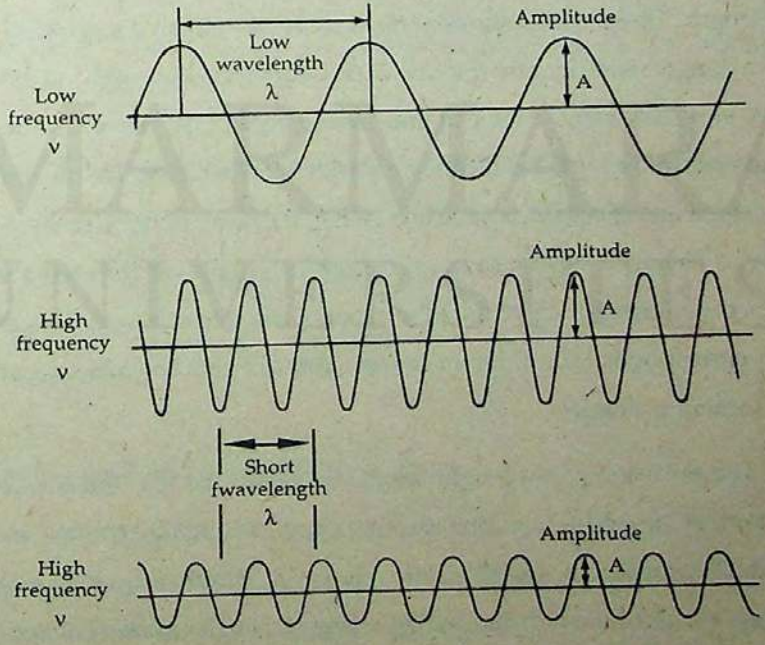


**Figure 2.2** Properties of waves

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fixed point in one second is the frequency. Thu unit of frequency is hertz ($1\ Hz = 1\ s^{-1}$) and

$$v = \lambda\upsilon \qquad (2.2)$$

Although consideration of wave motion can explain many properties of electromagnetic radiation, it is not adequate. Some of its properties require such radiation be considered as consisting of particles. The quantum theory that emerged in early 1900's was able to explain them.

According to this theory radiant energy can be absorbed or given off only in definite quantities called quanta or photons. A quantum of energy, the energy of a single photon i s

$$E = h\upsilon \qquad \text{(Planck/Einstein equation)} \qquad (2.3)$$

where h is Planck's constant, $6.63 \times 10^{-34}$ J s.

When a beam of light is passed through a prism, the beam is bent or refracted. The amount by which a beam is refracted depends upon its wavelength. Those with a shorter wavelength are refracted more than those with a longer wavelength (Figure 2.3). Ordinary white light consists of waves with all wavelengths in the visible region. A ray of white light spreads out into a wide band called a continuous spectrum like the rainbow. However, a line spectrum is produced when the beam of light, emitted upon heating a chemical substance in an electric arc, is passed through a prism. The spectrum consists of a limited number of discrete coloured lines each of which corresponds to a different wavelength of light. The line spectrum of each element is unique.

The emission of such light results from the fact that the electrons in the atom of an element, upon heating, gain additional energy and are excited. They are in an unstable state. However, shortly after they return to their less excited states by dissipating energy through emission of light. The

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discrete line spectrum indicates that the energy emitted in this case is quantized. Energy is quantized because the electrons occupy only certain energy levels and move from one to the other only in discrete or quantum jumps thus emitting or absorbing quanta of energy rather than a continuous spectrum of energy.

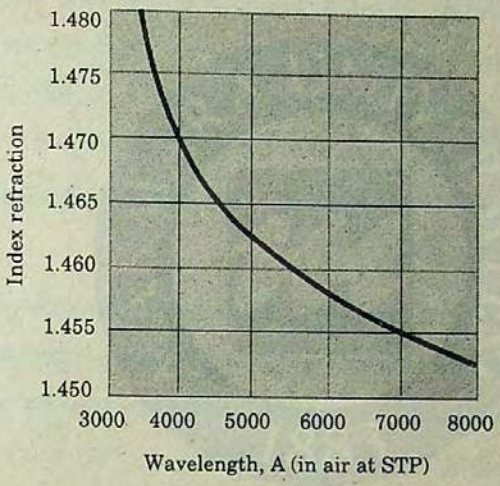


Figure 2.3 The change in the index of refraction of fused quartz with wavelength of beam

In 1885 J.J. Balmer developed an expression for the frequencies that correspond to the lines in the visible region of the Hydrogen spectrum.

$$\upsilon = 3.289 \times 10^{15} (s^{-1}) ( 1 / 2^2 - 1 / n^2 ) \qquad (2.4)$$

where $n = 3, 4, 5....$ (an integer)

## 2.3. Bohr's model of the Hydrogen atom

In 1913 Niels Bohr proposed a theory for the structure of the Hydrogen atom based on the spectrum of the element. According to Bohr's theory the H atom can be visualized as follows:

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1) The electron of the H atom exists in certain spherical orbits (shells, energy levels). These shells are arranged concentricly around the nucleus and are designated by a letter, K, L, M, N..., or a value of n, 1, 2, 3....

2) The electron has a definite energy characteristic of the orbit in which it is moving. The K Level (n = 1), the shell closest to the nucleus, has the smallest radiis. An electron in the K level has the lowest possible energy. With increasing distance from the nucleus the radiis of the shell and the energy of the elecron in the shell increases. The electron cannot have an energy that would place it between the permissible shells.

3) When the electron is as close to the nucleus as possible it is in the condition of lowest possible energy called the ground state. When the H atom is heated in an electric arc the electron absorbs energy and jumps to outer to outer levels which are higher energy states. The atom is then said to be in an excited state.

4) When the electron falls back to a lower energy level it emits a definite amount of energy. The energy difference between the high energy state and the low energy state is emitted in the form of a quantum of light. The light quantum has a characteristic frequency and produces a characteristic spectral line.

## 2.4 Energy levels in the Hydrogen atom

In Balmer's expression of

$$\upsilon = 3.289 \times 10^{15} \, (1 / 2^2 - 1 / n^2) \qquad (2.4)$$

for the H spectrum, $\upsilon$ is the frequency of the photon emitted when the single electron in the atom falls to the 2nd orbit from an outer orbit n. But according to Planck/Einstein equation

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$$E = h\upsilon. \qquad (2.3)$$

The energy emitted in this case is therefore

$$\Delta E = 6.63 \times 10^{-34} \times 3.289 \times 10^{15} (1 / 2^2 - 1 / n^2), \qquad (2.5)$$

and the energy associated with the single electron in each orbit in the H atom can be written as

$$E_n = \frac{-6.63 \times 10^{-34} \times 3.289 \times 10^{15}}{n^2}$$

$$= \frac{-2.179 \times 10^{-18} (J)}{n^2} \qquad (2.6)$$

The minus sign signifies the increase in the energy associated with the orbits as the shell number increases. The value is multiplied by Avogadro's number to obtain the energy associated with a mole of electrons in a mole of H atoms.

The general expression for transfers between all energy levels thus becomes

$$\Delta E = -2.179 \times 10^{-18} (1 / n_f^2 - 1 / n_i^2) \qquad (2.7)$$

where subscripts f and i, stand for final and initial respectively. $\Delta E$ is the energy of the light (photon) emitted or absorbed when the electron in the H atom drops or jumps from the $n_i$ orbit to the $n_f$ orbit.

If $n_f > n_i$ light is absorbed and $\Delta E$ is positive (+),

if $n_f < n_i$ light is emitted and $\Delta E$ is negative (−).

To remove the single electron from the ground state ($1s^1$) H atom altogether i. e.

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$$H^{\circ} \rightarrow H^{+} + e^{-} \quad \text{(IONIZATION)},$$

the energy required is $\Delta E = -2.179 \times 10^{-18} (1 / \infty^2 - 1 / 1^2)$

$$= 2.179 \times 10^{-18} \text{ J}. \qquad (2.8)$$

This is called the Ionization Energy (IE) of Hydrogen.

When a photon strikes an electron in an atom, it imparts all its energy to the electron and disappears from existence. The electron, struck by a photon may either

i) jump to a higher orbit,

ii) escape from the atom altogether (ionize) or

iii) escape from the atom and acquire some kinetic energy.

$$E_{photon} = \varnothing + KE \qquad (2.9)$$

$\varnothing$ (phi) is the energy needed for the electron in any energy level to escape from the atom;

KE is the kinetic energy ( $1 / 2\ mv^2$ ) acquired by the electron.

In multielectron atoms, the electrons in the same energy level (orbit) acquire the same amount of kinetic energy when bombarded with photons of a given frequency. This is the principle used in determining the energy levels that exist in the atoms of elements.

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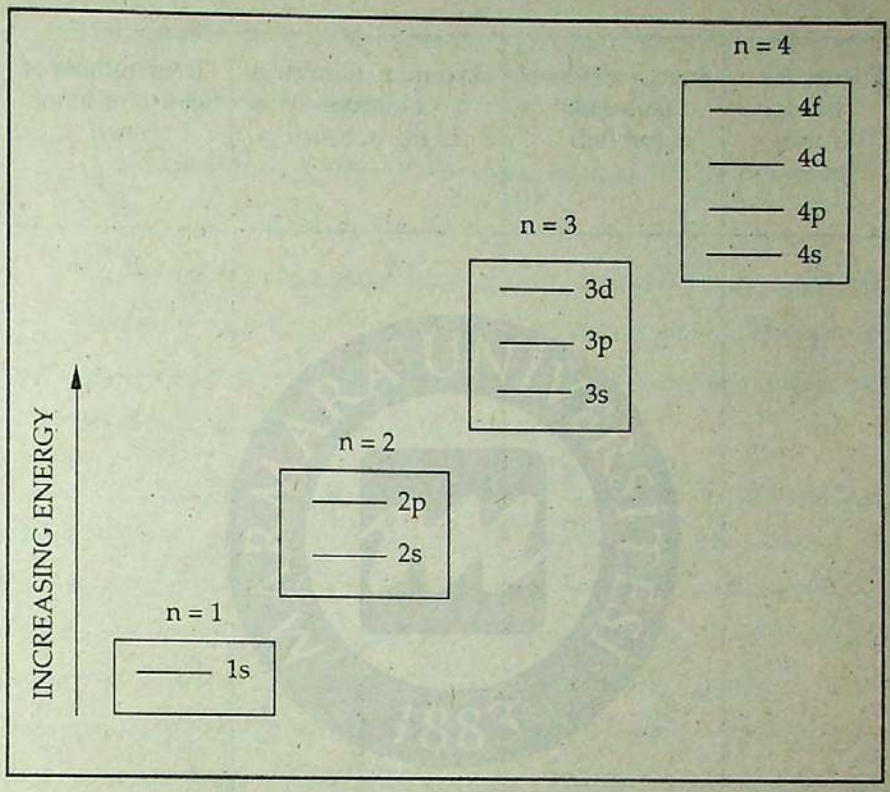


Figure 2.4 Energy levels in atoms

## 2.5. Electronic configurations

The energy levels in the atoms of elements have been determined mostly by employing photoelectron spectrometers. In these instruments the atoms are bombarded with photons of known frequency and the kinetic energy of the ejected electrons are measured. Figure 2.4 illustrates the position of the energy levels with respect to each other.

Table 2.1 lists the number of electrons that each orbit or orbital can accomodate. The following are the basic rules that emerge from the numbers given in the table:

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| Energy level (shell) (orbit) n | Energy sub-level (subshell) (orbital) | Maximum number of electrons in the subshell | Total number of electrons in the shell $2n^2$ |
|---|---|---|---|
| 1 | 1s | 2 | 2 |
| 2 | 2s | 2 | 8 |
| | $2p_x$ | 2 | |
| | 2s $2p_y$ | 2 | |
| | $2p_z$ | 2 | |
| 3 | 3s | 2 | 18 |
| | $3p_x$ | 2 | |
| | 3p $2p_y$ | 2 | |
| | $2p_z$ | 2 | |
| | $3d_{xy}$ | 2 | |
| | $3d_{yz}$ | 2 | |
| | 3d $3d_{xz}$ | 2 | |
| | $3d_{x^2-y^2}$ | 2 | |
| | $3d_{z^2}$ | 2 | |
| 4 | 4s | 2 | 32 |
| | 4p (3 p's) | 6 | |
| | 4d (5 d's) | 10 | |
| | 4f (7 f's) | 14 | |

Table 2.1 Electron holding capacities of orbits and orbitals

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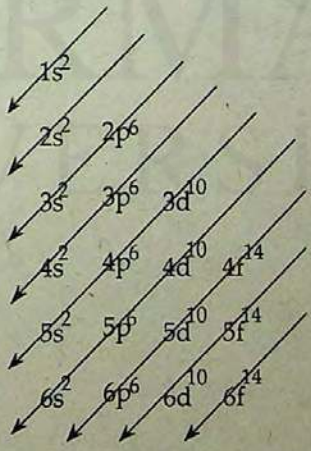
i) the number of subshells in one shell is equal to the shell number, n;

ii) the number of electrons that can occupy one orbital is 2;

iii) the maximum number of electrons that can occupy one orbit is $2n^2$.

The s orbital is considered as a sphere in the centre of a 3- dimensional coordinate system. The three p orbitals, $p_x$, $p_y$ $p_z$, are composed of two lobes around each of the x, y and z axes respectively. The five d orbitals have more complicated shapes as illustrated in Figure 2.5.

It has been already stated that the number of electrons in an elemental atom is equal to the number of protons in the nucleus. The number of protons in the elements identified to date range from 1 for Hydrogen (H) to 103 for Lawrencium (Lr). So, it follows that the same number of electrons are present in these atoms occupying the various energy levels or their subdivisions. The order by which the orbits and orbitals are filled is from the lowest to the highest energy level. Electronic configurations of atoms can be written simply by following the arrows, from tail to head, as shown below.




Accordingly, the following electronic configurations can be written:

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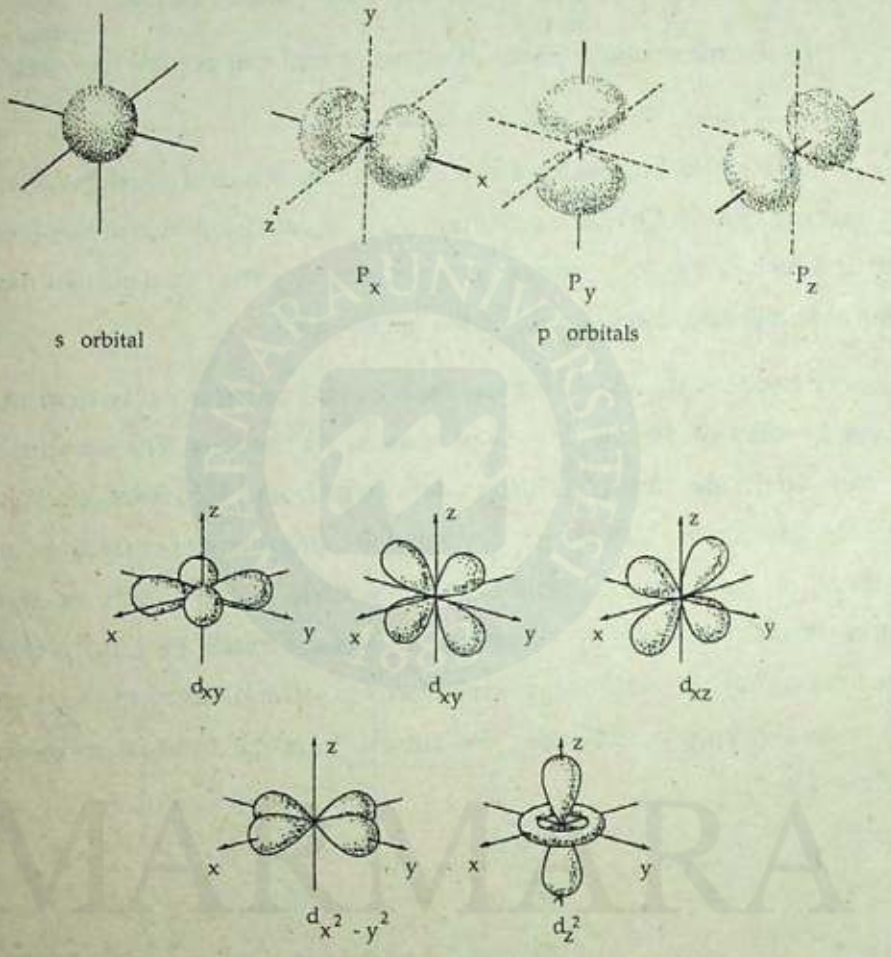


**Figure 2.5** Atomic orbitals

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| | | |
|---|---|---|
| $_1H : 1s^1$ | $_3Li : 1s^2\ 2s^1$ | $_{11}Na : 1s^2\ 2s^2\ 2p^6\ 3s^1$ |
| $_2He : 1s^2$ | $_4Be : 1s^2\ 2s^2$ | $_{12}Mg : 1s^2\ 2s^2\ 2p^6\ 3s^2$ |
| | $_5B : 1s^2\ 2s^2\ 2p^1$ | $_{13}Al : 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$ |
| | $_6C : 1s^2\ 2s^2\ 2p^2$ | $_{14}Si : 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$ |
| | $_7N : 1s^2\ 2s^2\ 2p^3$ | $_{15}P : 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$ |
| | $_8O : 1s^2\ 2s^2\ 2p^4$ | $_{16}S : 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$ |
| | $_9F : 1s^2\ 2s^2\ 2p^5$ | $_{17}Cl : 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$ |
| | $_{10}Ne : 1s^2\ 2s^2\ 2p^6$ | $_{18}Ar : 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ |

The outermost shell of the atom is called the **valence shell**. For the three columns of elements listed above the valence shell numbers are 1, 2 and 3 respectively.

The core of the atom is considered to be the nucleus and all the shells minus the valence shell. The **core charge** is therefore the atomic number, the total + charge on the atom, minus the number of electrons in the nonvalence shells.

Although electronic confgurations of elements are written following the sequence given above, there are some deviations from the configurations thus predicted. Deviations occur because of the magnetic properties of electrons.

The electron is a charged sphere rotating (spinning) around the axis through its centre. The rotating action of a charge generates a magnetic field and the electron behaves like a magnet. The spin of the electron can either be clockwise or anticlockwise. This is deduced from the fact that the former occurs when the axis of rotation of the electron points in the direction of the field it is placed in, and, conversely, the latter occurs when the axis is in the opposite direction. Only two orientations are possible. Clockwise spin is the low energy spin, anticlockwise spin is the high energy spin. Since stability increases as the energy of the species decreases, the electron is in a more stable state when spinning in the clockwise direction.

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There are two principles or rules that explain how the electrons come to occupy the orbitals unpredictable in the usual manner: -

**The Pauli Exclusion Principle**

"Only two electrons can be described by the same orbital and these two electrons must have opposite spin."

**Hund's Rule**

"In the lowest-energy (ground state) electron configuration, electrons in the same energy level, as far as possible occupy separate orbitals and have the same spin."

From the two rules it follows that the electrons are distributed among the orbitals of a subshell in a way that gives the maximum number of unpaired electrons with parallel and lowest energy spins.

Carbon, $_6C$, therefore has an electronic configuration of

$1s^2\ 2s^2\ 2p^2$ ; $\underset{1s}{\uparrow\downarrow}\ \underset{2s}{\uparrow\downarrow}\ \underset{2p_x}{\uparrow}\ \underset{2p_y}{\uparrow}\ \underset{2p_z}{\ }$

NOT ; $\underset{1s}{\uparrow\downarrow}\ \underset{2s}{\uparrow\downarrow}\ \underset{2p_x}{\uparrow\downarrow}\ \underset{2p_y}{\ }\ \underset{2p_z}{\ }$

$_7N$: $1s^2\ 2s^2\ 2p^3$ ; $\underset{1s}{\uparrow\downarrow}\ \underset{2s}{\uparrow\downarrow}\ \underset{2p_x}{\uparrow}\ \underset{2p_y}{\uparrow}\ \underset{2p_z}{\uparrow}$

and $_8O$: $1s^2\ 2s^2\ 2p^4$ ; $\underset{1s}{\uparrow\downarrow}\ \underset{2s}{\uparrow\downarrow}\ \underset{2p_x}{\uparrow\downarrow}\ \underset{2p_y}{\uparrow}\ \underset{2p_z}{\uparrow}$

It should be mentioned here that the configurations above are still ground state configurations. More exceptional ones are encountered with atoms in the excited state and transition metals.

In the excited state, which occurs when the atom is ready to make bonds, the electronic configuration of the carbon atom is

$_6C$ : $\underset{1s}{\uparrow\downarrow}\ \underset{2s}{\uparrow}\ \underset{2p_x}{\uparrow}\ \underset{2p_y}{\uparrow}\ \underset{2p_z}{\uparrow}$

and therefore it makes 4 bonds as in $CH_4$.

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The electronic configuration of transition metals is covered in later sections.

Electronic configurations of elements can also be described in terms of quantum numbers.

Principle quantum number is the shell (orbit, energy level) number: $n = 1, 2, 3, 4...$ (or K, L, M, N ...).

Subsidary quantum number is the subshell or the orbital number:

$\ell = 0, 1, 2, 3.... (n - 1)$.

$\ell = 0$ is the s orbital (s stands for sharp)

$\ell = 1$ is the p orbital (p stands for principle)

$\ell = 2$ is the d orbital ( d stands for diffuse)

$\ell = 3$ is the f orbital ( f stands for fundamental)

Magnetic quantum number identifies the orientation of the orbital : $m_\ell = -\ell, -(\ell - 1), -(\ell - 2) ... 0 ... (\ell - 2), (\ell - 1), \ell$. The total number of orientations of an orbital is $2\ell + 1$, e.g. there are three orientations of the p orbital($\ell = 1$), $p_x$, $p_y$, $p_z$.

Magnetic spin quantum number specifies the direction of the spin of the electron. Only two values are possible: $m_s = 1/2, -1/2$. The positive value usually stands for the lower energy (clockwise) spin, the negative value for the higher energy spin.

Table 2.2 lists the quantum number sets of the two electrons in each orbital in orbits with numbers 1 to 4.

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| Principle quan. no (n) | Subsidary quan. no ($\ell$=0, 1..n-1) | Magnetic quan. no ($m_\ell$=-$\ell$.. 0..$\ell$) | Quantum number sets of the two electrons in each orbital ($n, \ell, m_\ell, m_s$) |
|---|---|---|---|
| 1 | 0 (s) | 0 | (1, 0, 0, 1/2) (1, 0, 0, -1/2) |
| 2 | 0 (s) | 0 | (2, 0, 0, ±1/2) |
| | 1 (p) | -1, 0, 1 | (2, 1, $\begin{bmatrix}-1\\0\\1\end{bmatrix}$, ±1/2) |
| 3 | 0 (s) | 0 | (3, 0, 0, ±1/2) |
| | 1 (p) | -1, 0, 1 | (3, 1, $\begin{bmatrix}-1\\0\\1\end{bmatrix}$, ±1/2) |
| | 2 (d) | -2, -1, 0, 1, 2 | (3, 2, $\begin{bmatrix}-2\\-1\\0\\1\\2\end{bmatrix}$, ±1/2) |
| 4 | 0 (s) | 0 | (4, 0, 0, ±1/2) |
| | 1 (p) | -1, 0, 1 | (4, 1, $\begin{bmatrix}-1\\0\\1\end{bmatrix}$, ±1/2) |
| | 2 (d) | -2, -1, 0, 1, 2 | (4, 2, $\begin{bmatrix}-2\\-1\\0\\1\\2\end{bmatrix}$, ±1/2) |
| | 3 (f) | -3, -2, -1, 0, 1, 2, 3 | (4, 3, $\begin{bmatrix}-3\\-2\\-1\\0\\1\\2\\3\end{bmatrix}$, ±1/2) |

**Table 2.2** Quantum number sets

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## 2.6 The Periodic Table

A tabular arrangement of the elements based on the periodic law is called a periodic table. The periodic law basically states that if the elements are arranged in the order of increasing atomic weight, certain sets of properties are found to recur periodically. The original periodic table that is very similiar to what is used today was developed by two chemists in 1869, one a Russian, Mendeleev, and the other a German, Lothar Meyer. But somehow the former is cited more frequently.

In the modern periodic table, like the original one, the elements are arranged in the order of their increasing atomic weight (Figure 2.6).

On the periodic table the rows are called **periods.** The period number is the number of the outermost shell (valence shell) of the atom.

The columns are called **groups.** The group number is the number of electrons in the valence shell of the atom.

The columns are divided into A-groups and B-groups. The elements in the A-groups are referred to as representative elements. The elements that fall into the B-groups in the center of the table are called transition elements. The two long rows of elements below the table are called the inner transition elements.

The first period consists of only two elements, H and He. Subsequent periods have 8, 8, 18, 18 and 32 elements. The seventh period is not completed.

The periodic table can be used to derive the electronic configuration of elements. In the first two columns of elements on the left it is the s orbital that is filled in the outermost shell. These two columns are therefore referred to as the "s block". Similarly, the six columns on the right are referred to as the "p block" and the ten columns in the middle are referred to as the "d block". The fourteen columns below the table are called the "f block".

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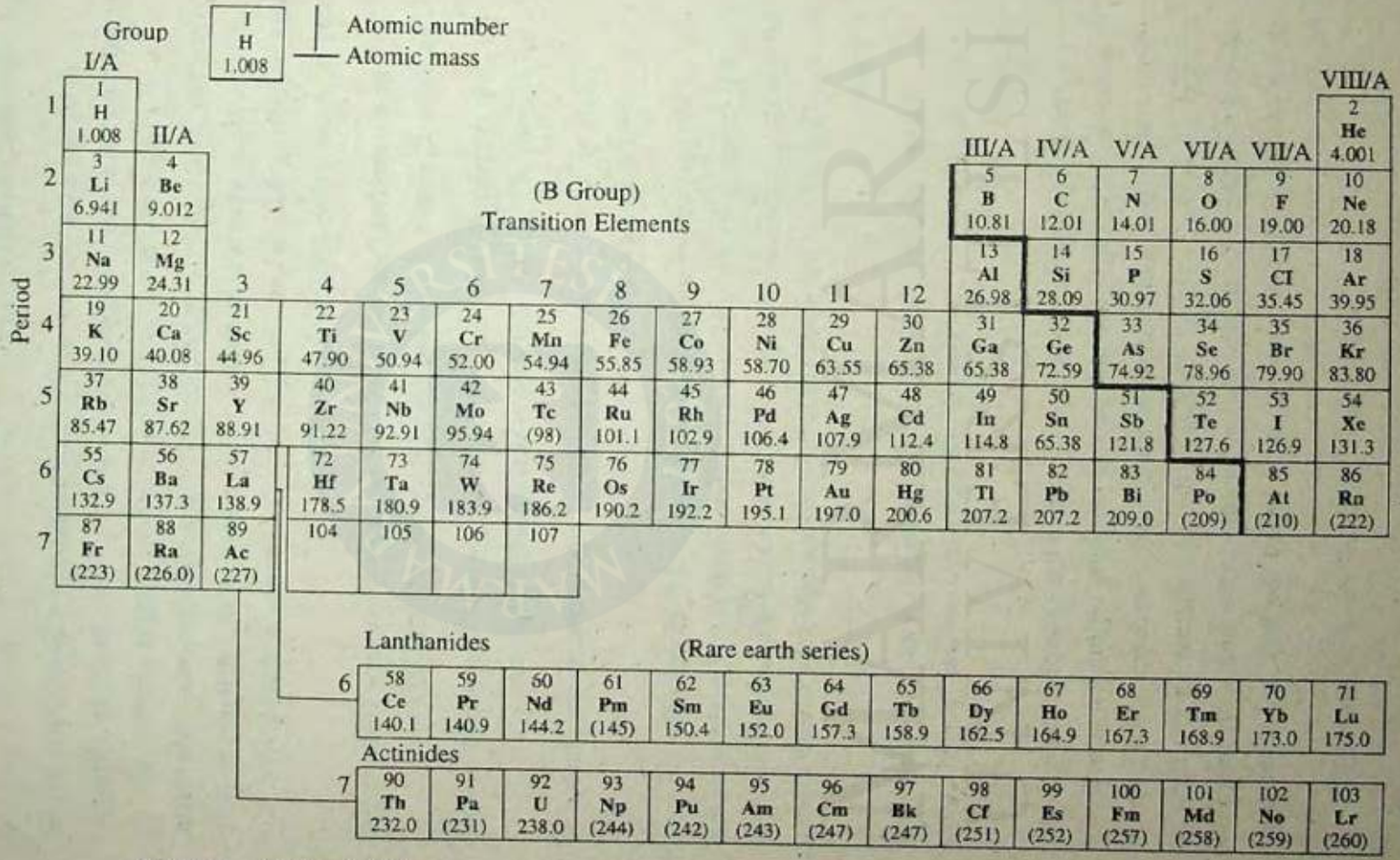


**Figure 2.6** The Periodic Table

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The differentiating electron that makes the electronic configuration of an atom different from that of the atom that precedes it is added to the s orbitals in the s block, to the p orbitals in the p block, to the d orbitals in the d block and to the f orbitals in the f block.

Since the properties of elements are determined largely by the electronic configuration of the outermost shell, elements in the same group have similar physical and chemical properties.

The groups in the periodic table are designated by Roman numerals and the group letter A or B. A number of the groups have characteristic family names.

Group IA elements are called alkali metals. Two characteristic properties of these metals are

1) the are soft, lustrous metals of low melting points and low densities;

2) they are highly reactive. They combine directly with group VIIA elements to form ionic compounds or salts, and with water they yield an aqueous solution of metal hydroxide and hydrogen gas.

Group IIA elements are called alkaline earth metals. Like the alkali metals the group IIA elements are all solids with typical metallic properties. However they are harder, melt at higher temperatures and are somewhat less reactive.

Group VIA elements are called chalcogens. With the exception of oxygen, the chalcogens are all solids. Oxygen and sulphur are nonmetals, the rest bear metallic properties.

Group VIIA elements are called halogens. The term halogen means salt former and describes one of the characteristic properties, the ability to form ionic compounds or salts in combination with metals.

Group VIIIA elements are called noble gases. They are all gases at room temperature. They exist as single atoms i. e. monatomic. They are very inert.

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The change in some properties of elements with position on the periodic table is quite predictable once the causes of these properties are known. These properties are discussed below.

**Atomic radiis**

The outermost shell of an atom has no precise boundary. It gradually thins out and ends at infinity. It is therefore impossible to measure the radiis of an atom exactly. But the distance between the two nuclei in a molecule can be measured by the use of X-Ray diffraction methods. The atomic radiis is taken as half the internuclei distance in the molecule.

Two trends evolve when the atomic radii of the elements on the periodic table are considered. (Figure 2.7):

1) the atomic radiis increases as the period number increases in the same group;

2) the atomic radiis decreases as the group number increases in the same period. This is due to the increased core charge that pulls the electrons closer to the nucleus.

The first trend as expected. The period number designates the number of the outermost shell. As the number of shells on the atom increases the radiis of the atom increases.

The second trend is somewhat violated in the region of the transition elements. In this block of elements the electrons are added to the inner shell, d orbital of the shell preceding the valence shell, thus effectively reducing the effect of the increased core charge.

**Ionization Energy**

Ionization energy is the energy required to remove one electron from the outermost shell of an atom that is in the ground state. Ist Ionization Energy is the energy required to remove the first electron from such an atom. 2nd Ionization Energy is the energy required to remove the the

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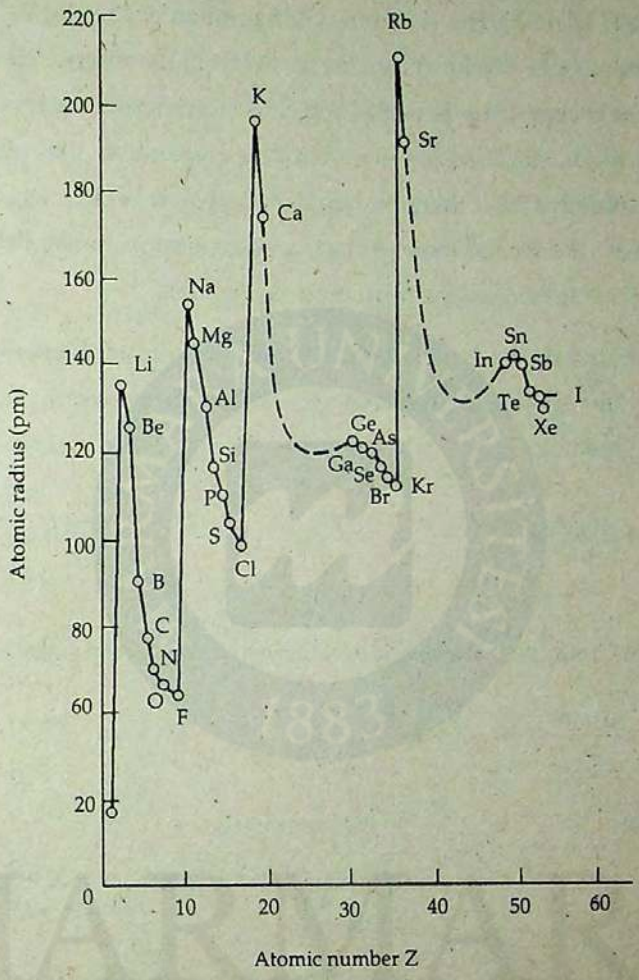


**Figure 2.7** Periodic variation of atomic radii

second electron from the already ionized atom and so on. The succesive ionization energies exceed the ones preceding them since the electron being removed has to move away from an ion that has a greater net positive charge. The ionization energy increases sharply, about ten-fold, when the valence shell electrons are depleted and the inner shell electrons start being removed (Table 2.3). The Ist Ionization Energy (IE) for Li is 520 kJ/mole, the

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2nd IE is 7297 kJ mole. The electronic configuration of Li is $1s^2\ 2s^1$. It takes one mole atom of Li 520 kJ to lose the 2s electron, the valence electron. The next electron occupies the 1s orbital which is closer to the nucleus. The core charge that the 1s electrons are subjected to is greater than that which the 2s electron is subjected to. It therefore takes more than ten-fold energy (7297 kJ) to break away the second mole of electrons and approximately half as much more (11810 kJ) to remove the third mole of electrons.

To predict the variation in the IE of elements from the periodic table, Coulomb's law should be remembered. The force between two charged particles is given by

$$F = \frac{kq_1\ q_2}{r^2} \qquad (2.1)$$

When Coulomb's law is applied to the atom it can be expressed as

$$F = \frac{kq_c\ q_e}{r^2} \qquad (2.10)$$

where $q_c$ is the core charge,
(atomic no - no of electrons in the inner shells)

$q_e$ is the charge on the electron,

r is the atomic radius

The force F increases directly with $q_c$ and inversely with the square of the radiis

As the period number increases on the periodic table within the same group, the atomic radiis increases. The core charge remains constant. There is less attraction on the valence shell electrons by the protons in the nucleus. F decreases and it becomes easier to remove the first electron from the valence shell. The 1st IE therefore decreases as the period number increases within a group (Figure 2.8).

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| | Ist | 2.nd | 3rd | 4th | 5th | 5th | 7th | 8th |
|---|---|---|---|---|---|---|---|---|
| H | 1 312 | | | | | | | |
| He | 2 371 | 5 247 | | | | | | |
| Li | 520 | 7 297 | 11 810 | | | | | |
| Be | 900 | 1 757 | 14 840 | 21 000 | | | | |
| B | 800 | 2 430 | 3 659 | 25 020 | 32 810 | | | |
| C | 1 086 | 2 352 | 4 619 | 6 221 | 37 800 | 47 300 | | |
| N | 1 402 | 2 856 | 4 577 | 7 473 | 9 443 | 53 250 | 64 340 | |
| O | 1 314 | 3 391 | 5 301 | 7 468 | 10 980 | 13 320 | 71 300 | 84 050 |
| F | 1 681 | 3 375 | 6 045 | 8 418 | 11 020 | 15 160 | 17 860 | 92 000 |
| Ne | 2 080 | 3963 | 6 276 | 9 376 | 12 190 | 15 230 | – | – |
| Na | 495.8 | 4 565 | 6 912 | 9 540 | 13 360 | 16 610 | 20 110 | 25 490 |
| Mg | 737.6 | 1 450 | 7 732 | 10 550 | 13 620 | 18 000 | 21 700 | 25 660 |
| Al | 577.4 | 1 816 | 2 744 | 11 580 | 15 030 | 18 370 | 23 290 | 27 460 |
| Si | 786.2 | 1 577 | 3 229 | 4 356 | 16 080 | 19 790 | 23 780 | 29 250 |
| P | 1 012 | 1 896 | 2 910 | 4 954 | 6 272 | 21 270 | 25 410 | 29 840 |
| S | 999.6 | 2 260 | 3 380 | 4 565 | 6 996 | 8 490 | 28 080 | 31 720 |
| Cl | 1 255 | 2 297 | 3 850 | 5 146 | 6 544 | 9 330 | 11 020 | 33 600 |
| Ar | 1 520 | 2 665 | 3 947 | 5 770 | 7 240 | 8 810 | 11 970 | 13 840 |
| K | 418.8 | 3 069 | 4 600 | 5 879 | 7 971 | 9 619 | 11 380 | 14 950 |
| Ca | 589.5 | 1 146 | 4 941 | 6 485 | 8 142 | 10 520 | 12 350 | 13 830 |

**Table 2.3** Successive ionization energies for some elements (kJ/mole)

As the group number increases within the same period, atomic radiis decreases. Furthermore, the core charge increases due to the fact that while the number of protons in the nucleus increases the number of electrons in the nonvalence shells remains constant. The ionization energy therefore increases with group number.

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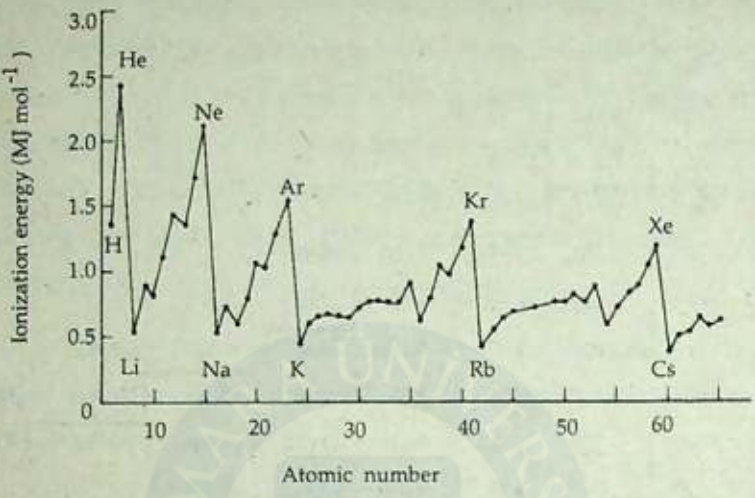


**Figure 2.8** Periodic variation of ionization energies

It is quite obvious from the above that there is a variation in the tendency of the elements to give or take electrons as one moves from left to right on the periodic table suggesting different chemical, and possibly, physical properties. And it is so indeed. A diagonal line that runs across the periodic table from top left to bottom right broadly divides the elements into two classes: metals and nonmetals.

The characteristic properties of these two classes can be summarized as follows:

**Metals.**

* They conduct heat and electricity very well.
* They have a high reflectivity and a shiny metallic luster.
* They are malleable and ductile.
* They are solids at room temperature except for mercury.
* They emit electrons when exposed to radiation of sufficiently high energy or when they are heated.

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**Nonmetals**

* They are poor conductors of heat and electricity.

* They do not have a high reflectivity or a shiny metallic luster.

* They may be gases, liquids, or solids at room temperature.

* They are not malleable or ductile.

* They do not emit electrons when exposed to radiation or heated.

**Electron Affinity**

Electron affinity is the energy released upon addition of an electron to an isolated atom (gaseous) in its ground state.

The force with which an electron is pulled to the valence shell of an atom depends on the core charge and generally increases with it.

The process of electron capture by an atom into its valence shell is exothermic when the valence subshell is partly vacant. Otherwise the process is endothermic. One mole of H atoms releases 72.8 kJ of energy when a mole of electrons is added to the 1s orbital which is half full. 230 kJ

$$M_{(g)} + e^- \longrightarrow M^- + \text{Energy}$$

of energy needs to be supplied in order to add a mole of electrons to a mole of Mg atoms which has an electronic configuration of $1s^2\ 2s^2\ 2p^6\ 3s^2$. The additional electron has to be introduced into the 3p subshell since 3s is already full.

Despite some exceptions the general trend is that electron affinity increases as the group number increases (Group IA to group VIIA) and decreases with period number. The electron affinities of noble gases are very low.

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Table 2.4 lists the electron affinities of some elements. The sign convention is that it is negative when energy is released and positive when energy is absorbed (universal sign convention for energy). Since electron affinity is defined as the energy released upon addition of an electron to an atom, the higher negative value means higher electron affinity and the higher positive value stands for lower electron affinity.

Succesive electron affinities are all positive indicating that energy always needs to be supplied in order to increase the negative charge of the already negatively charged ion, e.g.

$$O_{(g)} + e^- \longrightarrow O^-_{(g)} \qquad -140 \text{ kJ/mole}$$

$$O^-_{(g)} + e^- \longrightarrow O^{-2}_{(g)} \qquad +844 \text{ kJ/mole}$$

$$O_{(g)} + 2e^- \longrightarrow O^{-2}_{(g)} \qquad +702 \text{ kJ/mole}$$

The general variation in atomic radiis (AR), ionization energy (IE) and electron affinity (EA) with location on the periodic table is illustrated in Figure 2.9.

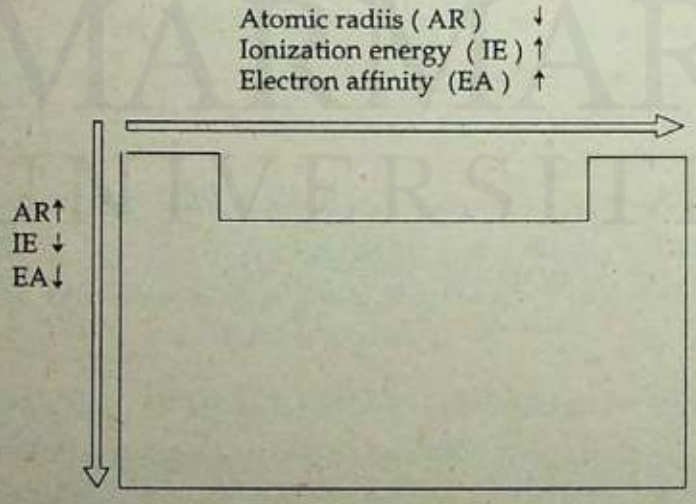


**Figure 2.9** The general trends in AR, IE and EA

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| IA | IIA | IIIA | IVA | VA | VIA | VIIA | VIIIA |
|---|---|---|---|---|---|---|---|
| H | | | | | | | He |
| −73 | | | | | | | 21 |
| Li | Be | B | C | N | O | F | Ne |
| −60 | 240 | −27 | −122 | −+9 | −140 | −333 | 29 |
| Na | Mg | Al | Si | P | S | Cl | Ar |
| −53 | 230 | −44 | −34 | −72 | −200 | −349 | 35 |
| K | Ca | Ga | Ge | As | Se | Br | Kr |
| −48 | 156 | −30 | −120 | −77 | −195 | −325 | 39 |
| Rb | Sr | In | Sn | Sb | Te | I | Xe |
| −47 | 168 | −30 | −121 | −101 | −190 | −297 | 41 |
| Cs | Ba | Ti | Pb | Bi | Po | At | Rn |
| −45 | 52 | −30 | −110 | −110 | −180 | −270 | 41 |

**Table 2.4** Electron affinities of some elements (kJ / mole)

## 2.7. Electronic configuration of transition elements

The first series of transition elements are in the 4th period. In this period the alkali metals K and Ca occupy groups IA and IIA respectively. The electronic configuration of

$$_{19}K \text{ is } 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$$

$$\text{or } [\text{Ar}]\ \underset{4s}{\uparrow}$$

and that of $_{20}Ca \text{ is } 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$

$$\text{or } [\text{Ar}]\ \underset{4s}{\uparrow\downarrow}$$

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The next element in the 4th period is $_{21}Sc$. The additional electron occupies the 3d orbital, the next higher energy level after 4s. The electronic configuration of

$_{21}Sc$ is [Ar] $\underset{4s}{\uparrow\downarrow}$ $\uparrow$ $\underset{3d}{\quad}$ — — —

Similarly,

$_{22}Ti$ is [Ar] $\underset{4s}{\uparrow\downarrow}$ $\uparrow$ $\underset{3d}{\uparrow}$ — — —

$_{23}V$ is [Ar] $\underset{4s}{\uparrow\downarrow}$ $\uparrow$ $\underset{3d}{\uparrow}$ $\uparrow$ — —

but $_{24}Cr$ is [Ar] $\underset{4s}{\uparrow}$ $\uparrow$ $\underset{3d}{\uparrow}$ $\uparrow$ $\uparrow$ $\uparrow$

not [Ar] $\underset{4s}{\uparrow\downarrow}$ $\uparrow$ $\underset{3d}{\uparrow}$ $\uparrow$ $\uparrow$ —

This is because a half-filled orbital or a completely filled orbital provides greater stability to the atom than otherwise. In the same manner, the electronic configuration of

$_{29}Cu$ is [Ar] $\underset{4s}{\uparrow}$ $\uparrow\downarrow$ $\underset{3d}{\uparrow\downarrow}$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$

not [Ar] $\underset{4s}{\uparrow\downarrow}$ $\uparrow\downarrow$ $\underset{3d}{\uparrow\downarrow}$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow$

The electronic configurations of some transition elements (d block elements) are listed in Table 2.5. The deviations from the expected configurations is the subject of more advanced inorganic chemistry studies.

| Atomic no. | Element | shell no. | 1 | 2 | | 3 | | | 4 | | | | 5 | | | | 6 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | subshell | s | s | p | s | p | d | s | p | d | f | s | p | d | f | s | p | d | f |
| 21 | Sc | | 2 | 2 | 6 | 2 | 6 | 1 | 2 | | | | | | | | | | | |
| 22 | Ti | | 2 | 2 | 6 | 2 | 6 | 2 | 2 | | | | | | | | | | | |
| 28 | V | | 2 | 2 | 6 | 2 | 6 | 3 | 2 | | | | | | | | | | | |
| 24 | Cr | | 2 | 2 | 6 | 2 | 6 | 5 | 1 | | | | | | | | | | | |
| 25 | Mn | | 2 | 2 | 6 | 2 | 6 | 5 | 2 | | | | | | | | | | | |
| 26 | Fe | | 2 | 2 | 6 | 2 | 6 | 6 | 2 | | | | | | | | | | | |
| 27 | Co | | 2 | 2 | 6 | 2 | 6 | 7 | 2 | | | | | | | | | | | |
| 28 | Ni | | 2 | 2 | 6 | 2 | 6 | 8 | 2 | | | | | | | | | | | |
| 29 | Cu | | 2 | 2 | 6 | 2 | 6 | 10 | 1 | | | | | | | | | | | |
| 30 | Zn | | 2 | 2 | 6 | 2 | 6 | 10 | 2 | | | | | | | | | | | |
| 39 | Y | | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | 1 | | 2 | | | | | | | |
| 40 | Zr | | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | 2 | | 2 | | | | | | | |
| 41 | Nb | | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | 4 | | 1 | | | | | | | |
| 42 | Mo | | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | 5 | | 1 | | | | | | | |
| 43 | Tc | | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | 6 | | 1 | | | | | | | |
| 47 | Ag | | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | 10 | | 1 | | | | | | | |
| 48 | Cd | | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | 10 | | 2 | | | | | | | |

**Table 2.5** Electronic configuration of some d-block transition elements

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# CHAPTER 3

# THE CHEMICAL BOND

## 3-1 The bond

With the exception of noble gases, elements do not exist as single atoms especially in the gas phase. Atoms combine with other atoms to make molecules. Within a molecule the atoms are held strongly by chemical bonds.

A change in the electron distribution of an atom takes place when it bonds to another atom. Electron transfer (ionic bond) or merger of valence shells (covalent bond) takes place in chemical bonding.

The electrons in the inner shells of an atom are held much more strongly than the electrons in the outermost shell. Therefore, it is generally the valence shell electrons that are involved in a chemical bond.

The valence of an element is described as the combining power of that element. The valence of elements in groups IA to IVA is equal to the number of electrons in the valence shell, that is the group number. The valence of elements in groups VA to VIIIA is equal to 8 minus the group number. Although the general rule is that the maximum number of bonds an atom can make is equal to its valence, as will be seen later, this does not always hold true.

There is a convention developed by Gilbert Lewis (1875-1946) to indicate the electrons in the valence shell of an atom. Each electron in the valence shell is designated by a dot around the symbol of the element. Table 3.1 shows the predicted and the actual electronic configurations, the Lewis structures and the valence of elements in the second period.

| Element | Group | Electronic configuration | | | Lewis structure | Valence |
|---|---|---|---|---|---|---|
| | | | Valence shell | | | |
| | | | Predicted | Actual | | |
| $_{3}Li$ | IA | $1s^2\ 2s^1$ | ↑ 2s | ↑ 2s | Li• | 1 |
| $_{4}Be$ | IIA | $1s^2\ 2s^2$ | ⇅ 2s | ↑ ↑ 2s 2p | •Be• | 2 |
| $_{5}B$ | IIIA | $1s^2\ 2s^2\ 2p^1$ | ⇅ ↑ 2s 2p | ↑ ↑ ↑ 2s 2p | •B• | 3 |
| $_{6}C$ | IVA | $1s^2\ 2s^2\ 2p^2$ | ⇅ ↑ ↑ 2s 2p | ↑ ↑ ↑ ↑ 2s 2p | •C• | 4 |
| $_{7}N$ | VA | $1s^2\ 2s^2\ 2p^3$ | ⇅ ↑ ↑ ↑ 2s 2p | ⇅ ↑ ↑ ↑ 2s 2p | :N• | 3 |
| $_{8}O$ | VIIA | $1s^2\ 2s^2\ 2p^4$ | ⇅ ⇅ ↑ ↑ 2s 2p | ⇅ ⇅ ↑ ↑ 2s 2p | :O: | 2 |
| $_{9}F$ | VIIA | $1s^2\ 2s^2\ 2p^5$ | ⇅ ⇅ ⇅ ↑ 2s 2p | ⇅ ⇅ ⇅ ↑ 2s 2p | :F: | 1 |
| $_{10}Ne$ | VIIIA | $1s^2\ 2s^2\ 2p^6$ | ⇅ ⇅ ⇅ ⇅ 2s 2p | ⇅ ⇅ ⇅ ⇅ 2s 2p | :Ne: | 0 |

**Table 3.1** The valence shells of the 2nd period elements



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As seen in Table 3.1, in the case of Be, B and C, the actual electronic configurations of some elements are different from those predicted by following the order given in the previous chapter. The elements in groups IIA to IVA can form bonds only when they are excited i.e. when one electron has jumped to a slightly higher energy level orbital within the valence shell. Thus, the valence of an element can effectively be described as the number of unpaired (single) electrons in the outermost shell.

Electron transfer or merger of valence shells in chemical bonding occurs such that the electronic configurations of the atoms involved in the bonding resemble that of a noble gas. $_{11}$Na has an electronic configuration of $1s^2\ 2s^2\ 2p^6\ 3s^1$. $_{17}$Cl has an electronic configuration of $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$. The Lewis structures are Na· and Cl respectively. When forming the compound NaCl (table salt), Na loses the 3s single electron thus acquiring the electronic configuration of the noble gas $_{10}$Ne ($1s^2\ 2s^2\ 2p^6$) that precedes it, and Cl acquires the electronic configuration of the noble gas $_{18}$Ar ($1s^2\ 2s^2\ 2p^6\ 1s^2\ 3s^2\ 3p^6$) that follows it.

Hydrogen, H·, bonds to another H· to form H : H, $H_2$. In the $H_2$ molecule, both H's thus acquire the electronic configuration of He, the noble gas in the first period.

In the formation of all simple compounds it appears that an atom tends to lose or gain electrons or to share them until its outermost shell electronic configuration consists of completely filled orbitals like that of the noble gas that either comes before it, as in groups IA to IIIA, or comes after it, groups VA to VIIA (there are same exceptions starting with the 3rd period).

Since all noble gases, with the exception of He, have the valence shell electronic configuration of $ns^2\ np^6$ with 8 electrons, a rule, called the octet rule, has been advanced by Gilbert Lewis:

"in compound formation an atom tends to gain or lose electrons or to share electrons until there are 8 electrons in its valence shell".

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### 3- 2 The ionic bond

An ionic bond is formed between two atoms, or polyatomic structures, when one or more electrons are transferred from the valence shell of one party to that of the other. The party that loses the electrons become positively charged (cations) and the party that gains the electrons become negatively charged (anions). The bonding is due to the attractive forces between the positively and negatively charged ions. The compounds that contain ionic bonds are called ionic compounds. LiF, NaCl, KBr are examples of such compounds.

The electronic configurations of Li and F are $1s^2\ 2s^1$ and $1s^2\ 2s^2\ 2p^5$ respectively. Li loses the 2s electron and converts into $Li^+$ ($1s^2$), F gains the electron lost by Li and converts into $F^-$ ( $1s^2\ 2s^2\ 2p^6$ ). Both atoms thus acquire the electronic configuration of a noble gas: $Li^+$ has the electronic configuration of He, $F^-$ has the electronic configuration of Ne. Since opposite charges attract each other, an attractive force evolves between the lithium and the fluoride ions. The ionic bond in LiF is this electrostatic attraction between the two ions.

Groups IA to IIA elements mostly make ionic compounds with group VIA and VIIA elements.

Ionic compounds are normally solids. Ionic solids consist of positively and negatively charged ions arranged in such a manner that the repulsive forces between identically charged ions are minimized and the attractive forces between the oppositely charged ions are maximized. The bonds in ionic compounds are nondirectional. In the LiF crystal, each $Li^+$ is surrounded by 6 $F^-$ ions and each $F^-$ ion is surrounded by 6 $Li^+$ ions.

### 3- 3 The covalent bond

Two identical atoms form a bond, as in $H_2$, $N_2$, $Cl_2$ etc., by sharing the valence shell electrons. Since the electron affinities of the two atoms are

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the same, electron transfer between the two does not take place.

A single covalent bond consists of a pair electrons, with opposite spin, shared by two atoms.

$H\cdot + \cdot H \qquad H:H;\ H-H\ (H_2)$

$:N\cdot + \cdot N: \qquad :N:::N:;\ N \equiv N;\ (N_2)$

$:\ddot{Cl}\cdot + \cdot\ddot{Cl}: \qquad :\ddot{Cl}:\ddot{Cl}:;\ Cl-Cl\ (Cl_2)$

The two electrons in the $H_2$ molecule, one from each H, can be considered to belong to the molecule rather than one to each H atom. Each proton, as well as exerting an attractive force on its own electron, exerts a force on the electron belonging to the other H atom. The two ls orbitals somehow combine and come to occupy a common orbital between the two nuclei. Such an orbital is called a molecular orbital or a bonding oribital.

The shape of a molecular orbital is different to those of the atomic orbitals that make it up. However, it does depend on their shapes. The molecular orbital in $H_2$ is made up two ls orbitals which are spherical. The molecular orbital is not spherical. It has the shape of an elongated sphere (Figure 3. la).

The covalent bond in HF is the merger of two orbitals, ls from H and a 2p from F, each with a single electron.

$$\underset{1s}{\uparrow} + \underset{2p_x}{\downarrow}\ \underset{2p_y}{\uparrow\downarrow}\ \underset{2p_z}{\uparrow\downarrow}\ \underset{2s}{\uparrow\downarrow} \qquad \underset{\text{bonding orbital}}{\uparrow\downarrow} \qquad \underset{2p_y}{\uparrow\downarrow}\ \underset{2p_z}{\uparrow\downarrow}\ \underset{2p}{\uparrow\downarrow}$$

$H\cdot \qquad \cdot\ddot{F}: \qquad H-F$

The shape of the molecular orbital in this case is a combination of a sphere and a lobe (Figure 3.lb). Therefore it can be said that an atom forms covalent bonds only in certain specific directions.

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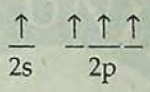
### 3- 4 Hybrid orbitals

An hybrid orbital can be described as a combination of two or more atomic orbitals constructed (mentally?) so as to agree with the observed geometry of the bonds around an atom. The most common example of hybrid orbital concept is encountered in the bonds made by carbon.

The electronic configuration of carbon in the excited state is




In a molecule of methane ( $CH_4$ ) one carbon atom bonds to four hydrogen atoms covalently. Three bonding orbitals are formed between the 1s electrons of the three hydrogen atoms and the three 2p orbitals of the carbon atom. The fourth bonding orbital is a combination of the 2s and the 1s orbitals of the carbon and hydrogen respectively. The fourth bonding orbital is expected to be somewhat different from the three which are constructed from similar orbitals. However, studies of the three bonds reveal that they are identical. This can only be possible if the four unpaired electrons of the carbon atom occupy the same energy level orbitals i.e. the one 2s and the three 2p orbitals of the carbon atom have merged to give four equivalent orbitals, hybrid orbitals.

When carbon bonds to four other atoms, the one 2s and the three 2p orbitals hybridize to form four $sp^3$ hybrid orbitals. With one s and two p orbitals, three $sp^2$ hybrid orbitals; with one s and one p orbital two sp orbitals are formed. The latter two hybrid orbitals are encountered when carbon form covalent multibonds with another atom.

### 3- 5 Polarity of bonds

Although covalent bonding is described as the sharing of electrons, the electrons involved in such a bond are not always equally shared. The

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electron density of the bonding electron pair in some molecules is distributed unequally. One of the two atoms attracts the bonding electron pair more than the other one does and, as a result, a partial negative and a partial positive charge form on the former and the latter one respectively. Such a bond is said to be polar.

The ability of an atom in a molecule to attract the bonding pair electrons to itself is called electronegativity. It is a qualitative concept and, therefore, cannot be directly measured. The term was originally used by R.S. Mullikan in 1934. Later, L. Pauling developed the so called Pauling scale as a quantitative measure of the electronegativities of elements. This is given in Figure 3.2. In view of the ionization energies and the electron affinities of the elements listed the trend is as expected:

i) electronegativity increases with group number,
ii) electronegativity decreases with period number.

The covalent bond in a diatomic molecule of the same element is nonpolar since there is no difference in the abilities of the two atoms to attract the bonding electrons to themselves. $H_2$, $N_2$, $O_2$, $F_2$, $Cl_2$ are all examples of nonpolar covalent bonding.

The bonding between hydrogen and any one of the halogens is polar since there is a considerable difference between the electronegativities of the two.

The extreme case of polarity in chemical bonding is the ionic bond. In ionic bonding, the difference in the electronegativities of the two atoms is large enough to break up the molecule as one positive and one negative ion which are then held together by electrostatic forces (Figure 3.3).

To predict the nature of bonds a well-known rule-of-thumb is used. If the difference in the electronegativities of the two atoms is zero, i.e. the bond is between two identical atoms, the bond is perfectly nonpolar. If the difference is 1.0 or smaller the bond is polar covalent. For differences greater than 2.0 the bonds are considered to be ionic.

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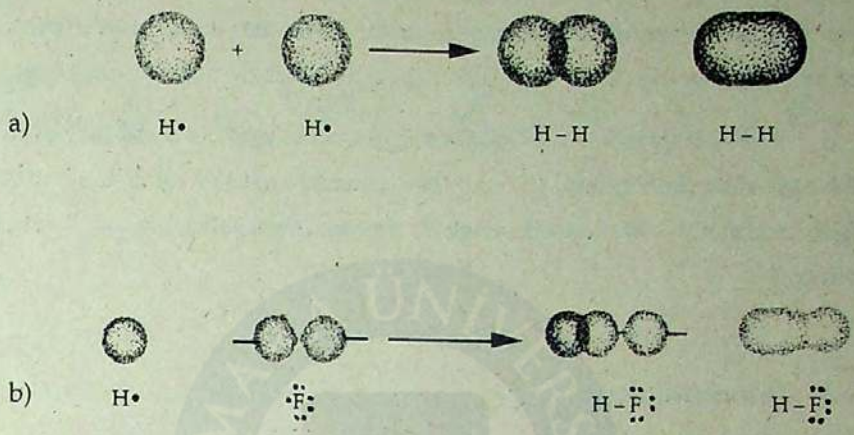


**Figure 3.1** Formation of molecular orbitals

Group

| Period | I | II | II | III | IV | V | VII | VIII |
|---|---|---|---|---|---|---|---|---|
| 1 | H | | | | | | | He |
| | 22 | | | | | | | – |
| 2 | Li | Be | B | C | N | O | F | Ne |
| | 1.0 | 1.5 | 2.0 | 2.5 | 3.1 | 3.5 | 4.1 | – |
| 3 | Na | Mg | Al | Si | P | S | Cl | Ar |
| | 1.0 | 1.2 | 1.3 | 1.7 | 2.1 | 2.4 | 2.8 | – |
| 4 | K | Ca | Ga | Ge | As | Se | Br | Kr |
| | 0.9 | 1.0 | 1.8 | 2.0 | 2.2 | 2.5 | 2.7 | 3.1 |
| 5 | Rb | Sr | In | Sn | Sb | Te | I | Xe |
| | 0.9 | 1.0 | 1.5 | 1.7 | 1.8 | 2.0 | 2.2 | 2.4 |

Electronegativity decreases

Electronegativity increases

**Figure 3.2** Electronegativities of representative elements

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For electronegativity differences between 1.0 and 2.0, the nature of the bond cannot be predicted reliably. In some cases the compound proves to be an ionic one, e.g. NaCl, in others, e.g. $AsF_3$, a polar covalent one.

Another simple way of predicting the nature of the bond is to follow the statement that "group IA and IIA elements usually make ionic bonds with nonmetals whereas nonmetals, among themselves make covalent bonds."

### 3- 6 The metallic bond

Metals, due to their low ionization energies, lose their outer shell electrons easily. However, when metallic atoms of the same element combine, as in metallic sheets, there are no atoms to accept the lost electrons. Metals therefore form a type of bonding that is neither ionic not covalent: it is called metallic bonding.

The phenomenon of metallic bonding is best described by what has come to be called the 'band theory'. According to this theory, the fixed positions in a crystalline metal are occupied by the positive metal ions comprised of atomic nuclei and inner shell electrons (Figure 3.4). Outer shell electrons are not held by any given atom, but are found in higher energy levels which are grouped together into bands. If a greater number of energy levels than electrons exist in a band, electrons can be promoted readily from one level to another within the band. These electrons are said to be delocalized and such bands are called conduction bands since they are responsible for electrical conductivity of metals.

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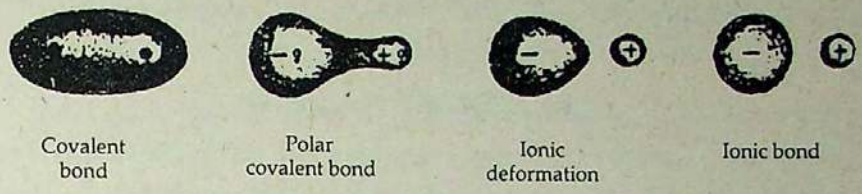
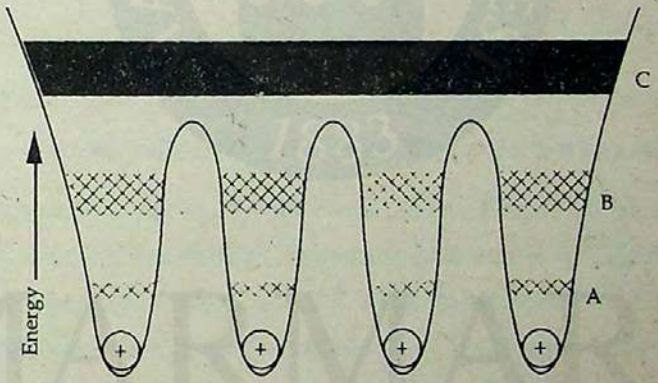



**Figure 3.3** Covalent and ionic bonds




In this schematic representation the circles ⊕ represent metal ions, which occupy fixed positions in a crystalline lattice. Certain electrons are held tightly to these positive ions. These bonding electrons reside in the lowest energy states. These states are grouped together into valence bands (A and B). Another band of closely spaced energy states represented by C is not fully occupied. The electrons in this band are bot associated with any particular metal ion. These delocalized electrons can move freely through the metal crystal and are responsible for its electrical conductivity. The energy band C is called a conduction band.

**Figure 3.4** Metallic bonding

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# CHAPTER 4

# MOLECULAR GEOMETRY

Molecules form in certain geometries when covalent bonds are involved. Ionic bonds are nondirectional. In crystals of ionic compounds, an ion attracts to itself as many ions of positive charge as can be packed around it.

Valence Shell Electron Pair Repulsion (VSEPR) theory explains why and how the covalent bonds form in the directions that are observed experimentally.

## 4-1 Valence Shell Electron Pair Repulsion (VSEPR) theory

The theory basicly states that "The geometrical arrangement of the bonds around an atom in a molecule depends on the total number of electron pairs in the valence shell of the atom, including both the bonding and the nonbonding pairs. The electron pairs in the valence shell of the central atom A in a molecule of $AX_n$ adopt the arrangement that maximizes the angle between any two pairs". n is the number of X atoms (ligands) that are bonded to A.

The maximum angle condition is satisfied when

2 pairs of electrons are 180° apart,

3 pairs of electrons are in a plane and 120° apart,

4 pairs of electrons have a tetrahedral arrangement and are 109.5° apart.

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It should be mentioned here that starting with the 3rd Period elements the octet rule can be violated. Some elements, like phosphorus and sulphur, can make more than 4 bonds, that is they can have more than 8 electrons around them. In such caes other geometric shapes emerge.

In order to determine the structure of a covalently bonded molecule, the Lewis structure of the molecule needs to be drawn up correctly. However, prior to introducing the procedure applied in drawing up Lewis structures, Table 4.1 should be studied carefully. Table 4.2 illustrates the various geometric shapes covalently bonded molecules may adopt. Table 4.3 is "the" table for determining the geometry of a molecule once the Lewis structure has been drawn up and the class of the molecule has been determined.

## 4- 2 Lewis structures

Lewis structures of covalently bonded molecules can be drawn up by following the procedure given below step by step.

1) Draw a diagram of the molecule showing the atoms connected to the central atom by single bonds. The atom of which there is only one can be considered to be the central atom. The others can be considered as ligands

2) Add the number of valence electrons in each atom in the molecule to find the total number of valence electrons. If the molecule is charged, i.e. a polyatomic ion, add one electron for each negative charge and subtract one electron for each positive charge.

3) Subtract the number of electrons needed to form the single bonds between the atom and use the remainder to complete octets around each atom except hydrogen. If there are insufficient electrons to complete all the octets, complete those of the more electronegative atoms first. Then assign formal charges.*

---

* (Formal charge) = (core charge) – ( # of unshared e's) – (# of bonds)

| Group | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| Element | $_{3}Li$ | $_{4}Be$ | $_{5}B$ | $_{6}C$ | $_{7}N$ | $_{8}O$ | $_{9}F$ | $_{10}Ne$ |
| Electronic configuration | $1s^2\ 2s^1$ | $1s^2\ 2s^2$ | $1s^2\ 2s^2\ 2p^1$ | $1s^2\ 2s^2\ 2p^2$ | $1s^2\ 2s^2\ 2p^3$ | $1s^2\ 2s^2\ 2p^4$ | $1s^2\ 2s^2\ 2p^5$ | $1s^2\ 2s^2\ 2p^6$ |
| Electronic configuration of activated valence shell | ↑ 2s | ↑ ↑ 2s 2p | ↑ ↑ ↑ 2s 2p | ↑ ↑ ↑ ↑ 2s 2p | ⇅ ↑ ↑ 2s 2p | ⇅ ⇅ ↑ ↑ 2s 2p | ⇅ ⇅ ⇅ ↑ 2s 2p | ⇅ ⇅ ⇅ ⇅ 2s 2p |
| Lewis structure | Li· | ·Be· | ·B· | ·C· | ·N· | ·O· | :F· | :Ne: |
| Compound with covalent bond | Li:X | X:Be:X | X:B:X<br>X | X:C:X<br>X<br>X | X:N:X<br>X | X:O:X | :F:X | |
| No. of electron pairs in valence shell of the central atom | 1 | 2 | 3 | 4 | 4 | 4 | 4 | |
| Class of molecule | AX | $AX_2$ | $AX_3$ | $AX_4$ | | | | |
| Shape of molecule | linear | linear | eq. triang. | tetrahedral | | | | |
| Predicted bond angle | | 180° | 120° | 109.5° | | | | |

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| NUMBER OF ELECTRON PAIRS | ARRANGEMENT OF ELECTRON PAIRS | NUMBER OF NONBONDING ELECTRON PAIRS | CLASS OF MOLECULE | ARRANGEMENT OF BONDS OF SHAPE OF MOLECULE | EXAMPLES | PREDICTED BOND ANGLE |
|---|---|---|---|---|---|---|
| 2 | Linear | 0 | $AX_2$ | Linear<br>X – A – X | $BeH_2$, $BeCl_2$ | 180° |
| 3 | Equilateral triangular | 0 | $AX_3$ | Equilateral triangular | $BF_3$, $B(OH)_3$, $AlCl_3$ | 120° |
| | | 1 | $AX_2E$ | Angular | $SnCl_2$ | 120° |
| 4 | Tetrahedral | 0 | $AX_4$ | Tetrahedral | $CH_4$, $CCl_4$, $SiH_4$, $NH_4^+$ | 109.5° |
| | | 1 | $AX_3E$ | Triangular pyramidal | $NH_3$, $NF_3$, $PCl_3$, $H_3O^+$ | 109.5° |
| | | 2 | $AX_2E_2$ | Angular | $H_2O$, $H_2S$, $SCl_2$ | 109.5° |
| | | 3 | $AXE_3$ | Linear | HF, HCl | — |
| 5 | Trigonal bipyramid | | | | | |
| 6 | Octahedron | | | | | |

**Table 4. 2** Electron pair arrangements and shapes of molecules

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4) If any atom still has an incomplete octet, convert nonbonding electron pairs to bonding pairs. Nonbonding pairs are used to form double or triple bonds where necessary until each atom has an octet. Then reasign formal charges.

5) If step 4 creates additional formal charges, use the structure obtained in step step 3.

6) If the central atom is from period three and later periods, the octet rule may not apply. Form additional multibonds in order to remove as many formal charges as possible

In the examples below, the Lewis structures of $CO_2$ and $SO_3^{-2}$ are drawn and their are geometries are predicted applying the above procedure and Table 4.3.

$CO_2$: 1. O – C – O

2. On 2xOxygen (Grp VI) 12 e–

Carbon (Grp IV) 4 e–

Total 16 e–

3. Total 16 e–

In two bonds – 4 e–

Remainder 12 e–

The 12 electrons are distributed evenly around the two oxygen which are more electronegative than carbon.

Formal charge on each O: 6 – 6 – 1 = –1

Formal charge on C: 4 – 0 – 2 = + 2

i.e. $:\ddot{O} - C - \ddot{O}:$ (-1, +2, -1), there are three formally charged atoms in the structure.

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| Number of ligands and nonbonding pairs of electrons on the valence shell of the central atom | | | Class of molecule | Shape of molecule | Examples |
|---|---|---|---|---|---|
| Total | No. of ligands | No. of non-bonding pairs | | | |
| 2 | 2 | 0 | $AX_2$ | linear | $BeCl_2$, $CO_2$ $HgCl_2$, $CuCl_2$ |
| 3 | 3 | 0 | $AX_3$ | triangular | $BF_3$, $CO_3^{-2}$, $SO_3$, $AlCl_3$, |
| | 2 | 1 | $AX_2E$ | angular | $SO_2$, $SnCl_2$, $NO_2$ |
| 4 | 4 | 0 | $AX_4$ | tetrahedral | $CH_4$, $BF_4^-$, $BF_4$, $PO_4^{-3}$, |
| | 3 | 1 | $AX_3E$ | triangular pyramidal | $NH_3$, $PF_3$, $SO_3^{-2}$, $H_3O^+$, |
| | 2 | 2 | $AX_2E_2$ | angular | $H_2O$, $ClO_2^-$, $SCl_2$, $F_2O$, |
| | 1 | 3 | $AXE_3$ | linear | $S_2^{-2}$ |
| 5 | 5 | 0 | $AX_5$ | trigonal bipyramid | $PCl_5$, $SnCl_5^-$ |
| | 4 | 1 | $AX_4E$ | irregular tetrahedral | $TeCl_4$ |
| | 3 | 2 | $AX_3E_2$ | triangular (planar) | $XeF_2$, $ICl_2^-$ |
| 6 | 6 | 0 | $AX_6$ | octahedral | $SF_6$, $PF_6^-$ |
| | 5 | 1 | $AX_5E$ | square pyramidal | $IF_5$, $SbF_5^{-2}$ |
| | 4 | 2 | $AX_4E_2$ | square | $BrF_4^-$, $XeF_4$, $IF_4^-$ |

**Table 4. 3** Molecules and their shapes

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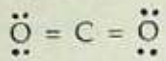
4. Although the overall charge on the molecule is zero (-1 +2 -1), as it should be, carbon has not completed its octet. So, the nonbonding electrons - one from each oxygen - are converted into bonds i.e.



The formal charge on each atom is recalculated:

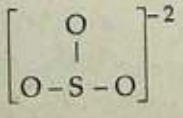
FC on each O $= 6 - 4 - 2 = 0$

FC on C $= 4 - 0 - 4 = 0$

The overall charge on $CO_2$ is again zero and the number of formal charges are minimized to absolute zero.

Now, following Table 4.3 the the geometry of the $CO_2$ molecule can be predicted.

The total number of ligands and nonbonding pairs of electrons on the central atom C is 2. The number of ligands is 2 and the number of nonbonding pairs of electrons is 0. The class of the molecule is therefore $AX_2$ and the shape is linear.

$SO_3^{-2}$ : 1. 

2. On 3xOxygen $18\ e^-$

Sulphur $6\ e^-$

$-2$ charge $2\ e^-$

Total $26\ e^-$

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3. Total $26\ e^-$

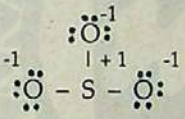
In three bonds $-6\ e^-$

Remainder $20\ e^-$

The 20 electrons are distributed evenly on the three oxygens, the more electronegative atoms, until they complete their octet. The remaining two are assigned to sulphur. Each atom completes its octet.

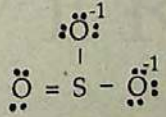
FC on each O : $6-6-1=-1$

FC on S : $6-2-3=+1$



The above structure gives the desired overall charge of -2 but there are 4 formal charges on it.

6. Since sulphur is in the 3rd period, the octet rule can be violated to minimize the number of formal charges on the structure while maintaining the overall charge of -2. So, one pair of nonbonding electrons on one oxygen is converted into a bond forming a double bond.



The formal charges now are;

On doubly bonded O : $6-4-2=0$

On 2 singly bonded O : $6-6-1=-1$

On S : $6-2-4=0$

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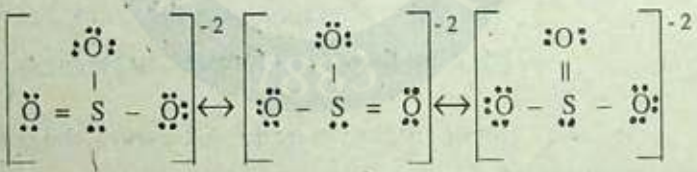
This structure has only two formally charged atoms and has an overall charge of - 2. The total number of ligands and nonbonding pairs of electrons on the central atom is 4. The number of ligands is 3 and the number of nonbonding pairs of electrons is 1. The class of the molecule is therefore $AX_3E$ and the shape is triangular pyramidal.

It should also be noted the second bonding to sulphur could have been formed by any one of the three oxygens and, the same result with regards to formal overall charges would have been obtained. This type of phenomenon is called resonance.

## 4- 3 Resonance structures

Resonance is a method for describing the structures of molecules that



cannot be adequately represented by a single Lewis structure because the electrons are not exactly localized as shown in one Lewis structure. Such a molecule may be represented by a combination of two or more Lewis structures called resonance structures i.e.

## 4- 4 Bond order

Bond order is defined as the total number of electron pairs that constitute the bond. With nonresonance structures, it is an integer number. A single bond has a bond order of 1, a double bond has a bond order of 2 and a triple bond has an order of 3.

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In the case of resonance structures fractional bond orders are encountered. The three resonance structures of the sulphite ion ($SO_3^{-2}$) considered in the preceeding section shows that the double bond between the sulphur atom and one of the oxygen atoms can indeed be on any one of the three oxygens. It is not certain which S – O bond is single, with an order of 1, and which is double, with an order of 2. What is certain is that one pair of electrons that form the second S – O bond in the molecule is effectively shared by all three oxygens (delocalized electrons). It can be said that each S – O bond is comprised of one pair of electrons plus its share of the surplus electron pair which is 1/3. The order of the S – O bonds in the structure is therefore 1 1/3 (1+1/3).

## 4- 5 Bond angles

The angle between any two bonds of an atom is called the bond angle. The bond angles for the first four classes of molecules (irrelevant for the first class) were given in Table 4.1. However, with the $AX_4$ ($AX_3E$, $AX_2E_2$) class of molecules large deviations from these predicted values occur. The predictions are correct for $AX_4$ class of molecules when all four ligands (X's) are identical. In a molecule of $CH_4$ or $SiH_4$ all bond angles are 109.5° as predicted. Deviations occur only when the four ligands are nonidentical, e.g. $CH_2Cl_2$. This is due to the difference in the electronegativities of the two types of ligands, H and Cl.

$AX_3E$ and $AX_2E_2$ subclasses contain nonbonding pair (s) of electrons. The bond angles in such molecules deviate from the predicted angle of 109.5° due to the effect of the nonbonding pairs of electrons

### Effect of electronegativity

In the case of nonidentical ligands, the bond angles decrease with increasing electronegativity of the ligands since the more electronegative ligand exertsa greater force of attraction on the bonding pair than the less

electronegative ligand. The volume of space occupied by the bonding pair of electrons decreases resulting in a smaller bond angle. Figure 4.1 shows the bond angles in various molecules with different ligands. A deviation from the predicted bond angle of 109.5° occurs whenever a ligand other than hydrogen is introduced to the molecule. The angle between two more electronegative ligands or one more electronegative ligand and one hydrogen atom decreases and, consequenly, the angle between two hydrogen bonds increses.

**Effect of nonbonding pairs of electrons**

The deviations from the predicted bond angles in molecules which contain nonbonding pairs of electrons on the central atom is due to the fact that nonbonding electrons take up more space in the valence shell than the bonding electrons.

Figure 4.2 illustrates the effect of the nonbondig pairs of electrons on the bond angles in $NH_3$. The angles between the nonbonding and the bonding pairs have increased but the angle between two bonding pairs has decreased.

## 4- 6 Molecular polarity and dipole moments

Polarity of a molecule is determined by two factors:

i) Polarity of the bonds present in the molecule,

ii) Geometry of the molecule.

Polar bonds, as discussed in Chapter 3, are the covalent bonds between two atoms with different electronegativities.

A dipole is formed by two separated charges (Q) of equal magnitude and opposite sign. Dipole moment ($\mu$) is the product of the magnitude of charges forming the dipole and the distance between the charges i.e.

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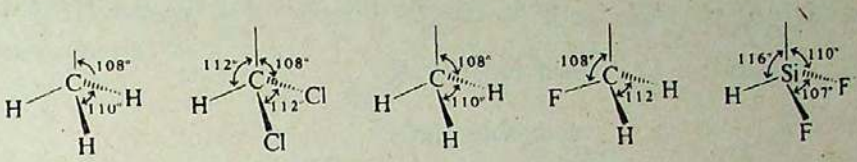


**Figure 4.1** Bond angles in some $AX_4$ molecules

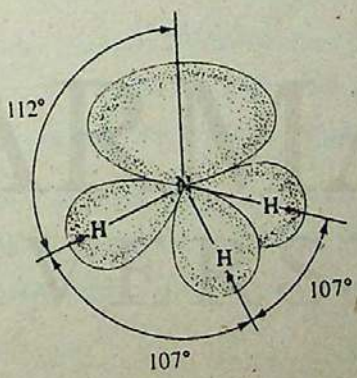


**Figure 4.2** Bonding and nonbonding electron pairs

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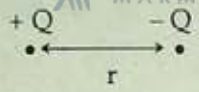


$$\mu = Q\,r$$

where Q is in coulombs (C)

r is in meters (m)

$\mu$ is in C m.

In a diatomic molecule containing a polar bond, a dipole moment is present, viz

$$\overset{\delta+}{H} - \overset{\delta-}{Cl} \quad (\longrightarrow)$$

Dipole moment is a vectoral quantity. When there are more than one dipole moments present in a molecule, the vectoral sum of these yields the dipole of the molecule. If the molecular dipole moment is zero, the molecule is said to be nonpolar; if it is nonzero the molecule is said to be polar.

In the case of HCl, because of its geometry, there is a net dipole moment in the direction of the arrow. Indeed, all diatomic molecules with a polar covalent bond have dipole moments and they are polar.

Other polyatomic molecules with polar covalent bonds are not necessarily polar since the vectoral sum of the dipole moments in the molecule, if geometry allows, may add up to zero. As seen in section 4.2, $CO_2$ is a linear molecule,

$$\delta- \leftarrow \delta+ \rightarrow \delta- \qquad \mu = 0$$
$$O = C = O$$

Oxygen is more electronegative than carbon (Figure 3.2). The dipole moments created on either side of carbon are equal in magnitude but

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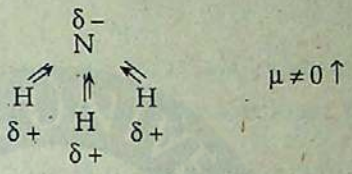
directionally opposite. The vectoral sum of these two dipole moments is therefore zero and, consequently, the $CO_2$ molecule is nonpolar.

The $NH_3$ molecule is triangular pyramidal ($AX_3E$) and the shape is shown in Figure 4.2. The three N - H bonds all are polar and have dipole moments viz.




The vectoral sum of the three dipole moments is directed upwards. The ammonia molecule is therefore polar with effective partial negative and positive charge on nitrogen and the three hydrogens respectively.

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# CHAPTER 5

# STOICHIOMETRY

Stoichiometry is a branch of chemical mathematics. It deals with the quantitative relations determined by chemical formulas and equations.

The word stoichiometry is derived from the Greek word "stoicheion" meaning element. Literally, stoichiometry means measure of elements. However, the term is generally used more broadly to include a rather wide variety of measurements and quantitative relationships involving all substances and mixtures of chemical interest.

The two basic principles that apply in stoichiometric calculations are referred to as "the law of conservation of mass" and "the law of conservation of energy".

The law of conservation of mass indicates that in chemical reactions ATOMS ARE NEITHER CREATED OR DESTROYED; THEY ARE MERELY REARRANGED.

The law of conservation of energy states that

ENERGY CAN NEITHER BE CREATED NOR DESTROYED BUT ONLY CHANGED FROM ONE FORM TO ANOTHER.

## 5.1. Atoms, molecules, moles and STP

The atom is the smallest unit of an element. The mass of an atom is called its atomic weight (AW). Atomic weights of elements are expressed in terms of Unified Atomic Mass Unit's (u).

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$^{12}_{6}C$ has a mass of 12u exactly (section 2.1). Avogadro's number of u's, that is $6.02 \times 10^{23}$ u's, make 1 g.

$$6.02 \times 10^{23}\ u = 1\ g$$

$$1u = 1/6.02 \times 10^{23}\ g$$

$$= 1.67 \times 10^{-24}\ g$$

$$= 1.67 \times 10^{-27}\ kg.$$

Atoms combine to give molecules:

N is the atom; $N_2$ is the molecule,

O is the atom; $O_2$ is the molecule,

C is an atom and O is an atom;

$CO_2$ is a molecule.

$Na^+$ is an ionic atom, $Cl^-$ is an ionic atom;

NaCl is a molecule of an ionic compound.

Avogadro's number of atoms make one mole atom:

$$6.02 \times 10^{23}\ \text{atoms} = 1\ \text{mole atom.}$$

Avogadro's number of molecules make one mole molecule which is briefly called one mole:

$$6.02 \times 10^{23}\ \text{molecules} = 1\ \text{mole molecule}$$

$$= 1\ \text{mole.}$$

In a mole molecule of the compound $Ca(OH)_2$ there are

1 mole atom of Ca,

2 mole atoms of O,

2 mole atoms of H.

The mass of a mole of atoms of an element has the same magnitude as

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the mass of a single atom of that element, but the unit of the former is g, grams, and that of the latter is u, unified atomic mass units.

Another way of denoting the mole is the gram-atom/gram-molecule concept.

1 gram-atom (g-atom) of hydrogen = 1 mole of H atoms
= $6.02 \times 10^{23}$ H atoms
= 1.00 g H

1 gram-molecule (g-mole) of hydrogen = 1 mole of $H_2$ molecules
= $6.02 \times 10^{23}$ $H_2$ molecules
= 2.00 g $H_2$.

Also,

1 kg-atom of hydrogen = 1 kilomoles of H atoms
= 1 kmoles of H atoms
= $6.02 \times 10^{26}$ H atoms
= 1 kg H

1 kg molecule (kg-mole) of hydrogen = 1 kilomoles of $H_2$ molecules
= 1 kmole of $H_2$ molecules
= $6.02 \times 10^{26}$ $H_2$ molecules
= 2.00 kg $H_2$.

STP stands for Standard Temperature and Pressure. Standard temperature is 273 K (0°C). Standard pressure is 1 Atm. The significance of STP is that one mole of any gas under the canditions of STP occupies 22.4 litres and since the volume occupied by a gas is directly proportional to its number of moles as will be seen in later chapters, the volume occupied by

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any number of moles of a gas at STP can be calculated by using the value of 22.4 ℓ.

The concept of STP is introduced prior to the introduction of gas laws since it is frequently encountered in stoichiometric problems solved at this stage of General Chemistry studies.

## 5.2. Chemical formulas and names

### Chemical formulas

The exact combination of elements in a compound, with regards to the number of atoms of each element, is shown by its chemical formula.

Chemical formulas of compounds can be classified in three groups:

1. Simplest (empirical) formula - the simplest formula that expresses the relative numbers of atoms in a substance as whole numbers.
2. Molecular formula - the complete formula that shows the exact number of atoms of each kind in a molecule of a substance. It is always some integral multiple of the empirical formula.
3. Structural formula - the simple schematic formula that shows which atoms are connected to which atoms in a molecule of a substance and how they are approximately arranged in space. It gives an idea of the geometry of the molecule.

The simple and molecular formulas of common inorganic compounds are identical. Organic compounds usually have different simple and molecular formulas. Table 5.1 shows these formulas for some inorganic and organic compounds.

The formulas for chemical compounds are written so as the charges on the combining ions are balanced and the overall charge on the molecule is zero. The common charges on monatomic ions are equal to their valences.

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Group IA to IIIA elements (metals) ionize to give +1, +2, +3 charged ions respectively. These elements are considered to lose their valence electrons thus acquiring positive charges.

Group VA to VIIA elements (nonmetals) are considered to gain electrons to complete their octet thus acquiring -3, -2, -1 charges respectively.

Hydrogen always ionizes to +1 except when it forms hydrides with group IA to IIA metals.

Polyatomic ions are those ions which contain mora than ona atom e.g. $CO_3^{-2}$, $SO_4^{-2}$. The charge on such an ion is calculated from its Lewis structure. The correct structure is drawn according to the procedure given in section 4.2 and the overall charge on the ion is determined by summing up the formal charges on each atom in the ion.

Table 5.2 lists the formulas, charges and names of common ions.

Chemical formulas can be written by following the procedure given below.

1. Write the symbol for the more metallic element or the positively charged polyatomic ion (cation) first.
2. Write the symbol for the nonmetallic element or the negatively charged polyatomic ion (anion) next to the symbol already written.
3. Balance the charges (valences) on the ions such that the net charge on the resulting compound is zero. Write the subscripts to the right of the symbols or, if polyatomic ions are involved, bracket the polyatomic ion and write the subscript to the right of the closing bracket.

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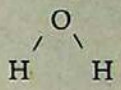
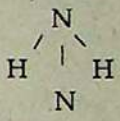
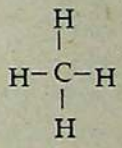
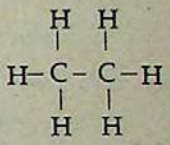
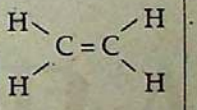
| Name | Simplest Formula | Molecular Formula | Molecular Geometry | Structural Formula |
|---|---|---|---|---|
| Water | $H_2O$ | $H_2O$ | angular |  |
| Ammonia | $NH_3$ | $NH_3$ | triangular pyramidal |  |
| Methane | $CH_4$ | $CH_4$ | tetrahedral |  |
| Ethane | $+[CH_3]+$ | $C_2H_6$ | two intersect. tetrahedra |  |
| Ethyhene | $+[CH_2]+$ | $C_2H_4$ | planar |  |

**Table 5.1** Types of formulas for some compounds

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| | | | |
|---|---|---|---|
| $NH_4^+$ | ammonium | $Fe^{2+}$ | iron (II) of ferrous |
| $Cs^+$ | cesium | $Pb^{2+}$ | lead (II) |
| $Cu^+$ | copper (I) | $Mg^{2+}$ | magnesium |
| $H^+$ | hydrogen | $Hg^{2+}$ | mercury (II) or mercuric |
| $Li^+$ | Lithium | $Ni^{2+}$ | nickel |
| $Hg_2^{2+}$ | Mercury (I) or mercurous | $Sr^{2+}$ | strontium |
| $K^+$ | potassium | $Sn^{2+}$ | tin (II) |
| $Rb^+$ | rubidium | $Zn^{2+}$ | zinc |
| $Na^+$ | sodium | $Al^{3+}$ | aluminum |
| $Ag^+$ | silver | $Sb^{3+}$ | antimony (III) or antimonous |
| $Au^+$ | gold (I) or aurous | $As^{3+}$ | arsenic (III) or arsenious |
| $Ba^{2+}$ | barium | $Bi^{3+}$ | bismuth |
| $Ca^{2+}$ | calcium | $Cr^{3+}$ | chromium (III) or chromic |
| $Cr^{2+}$ | chromium (II)or chromous | $Co^{3+}$ | cobalt (III) or cobaltic |
| $Co^{2+}$ | cobalt (II) or cobaltous | $Fe^{3+}$ | iron (III) of ferric |
| $Cu^{2+}$ | copper (II) or cupric | $Au^{3+}$ | gold (III) or auric |

| | | | |
|---|---|---|---|
| $C_2H_3O_2^-$ | acetate | $CO_3^{2-}$ | Carbonate |
| $HCO_3^-$ | bicarbonate or hydrogen carbonate | $CrO_4^{2-}$ | chromate |
| $HC_2O_4^-$ | bioxalate or hydrogen oxalate | $Cr_2O_7^{2-}$ | dichromate |
| $HSO_4^-$ | bisulfate or hydrogen sulfate | $HPO_4^{2-}$ | mono-hydrogen phosphate |
| $HS^-$ | bisulfide or hydrogen sulfide | $C_2O_4^{2-}$ | oxalate |
| $Br^-$ | bromide | $O^{2-}$ | oxide |
| $ClO_3^-$ | chlorate | $SO_4^{2-}$ | sulfate |
| $Cl^-$ | chloride | $S^{2-}$ | sulfide |
| $ClO_2^-$ | chlorite | $SO_3^{2-}$ | sulfite |
| $CN^-$ | cyanide | $S_2O_3^{2-}$ | thiosulfate |
| $H_2PO_4^-$ | dihydrogen phosphate | $AsO_4^{3-}$ | arsenate |
| $F^-$ | fluoride | $As_3^{3-}$ | arsenite |
| $OH^-$ | hydroxide | $BO_3^{3-}$ | borate |
| $IO_3^-$ | iodate | $PO_4^{3-}$ | phosphate |
| $I^-$ | iodide | $Fe(CN)_6^{3-}$ | ferrycianide |
| $NO_3^-$ | nitrate | | |
| $ClO_4^-$ | perchlorate | $Fe(CN)_6^{4-}$ | ferrocyanide |
| $MnO_4^-$ | permanganate | $SiO_4^{4-}$ | orthosilicate |

**Table 5.2** Some comman positive and negative ions

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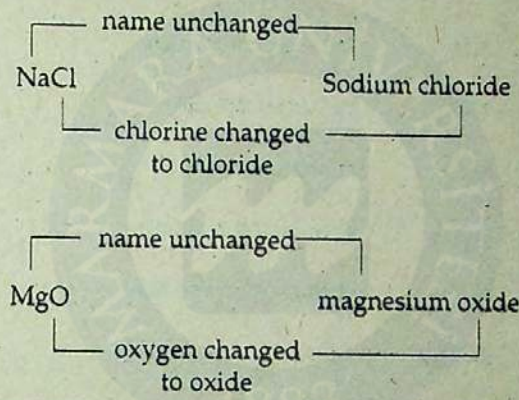
**Naming chemical compounds**

a) **Binary compounds of a metal and a nonmetal**

Salts of a metal and nonmetal are named by stating, first, the the name of the metal and, the name of the nonmetal with the ending changed to "-ide" e.g.




A number of elements, especially the transition metals due to their electronic configurations, can assume valences other than their usual valences. More precisely these are called oxidation states. Roman numerals are used to denote the oxidation state, or the charge, on such metallic ions in a compound:

| | | | |
|---|---|---|---|
| $Fe^{+2}$ | iron (II) (ferrous) | $Cu^{+1}$ | copper (I) |
| $Fe^{+3}$ | iron (III) (ferric) | $Cu^{+2}$ | copper (II) |
| $FeCl_2$ | iron (II) chloride (ferrous chloride) | $Cu_2O$ | copper (I) oxide |
| $FeCl_3$ | iron (III) chloride (ferric chloride) | CuO | copper (II) oxide |

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b) **Binary compounds of two nonmetals**

Two nonmetals can combine to form a compound by way of covalent bonding. In the formulas and names of such compounds the less electronegative element - that is the one with the smaller group number - appears first. In naming them, prefixes are used to designate the relative numbers of atoms of each type in the molecule, e.g.

| | |
|---|---|
| NO | nitrogen monoxide |
| $NO_2$ | nitrogen dioxide |
| $N_2O$ | dinitrogen oxide |
| $N_2O_3$ | dinitrogen trioxide |
| $N_2O_4$ | dinitrogen tetroxide |
| $N_2O_5$ | dinitrogen pentoxide |

If a compound contains one polyatomic ion, or two as in $(NH_4)_2SO_4$, it contains more than two elements. Writing the formulas of and naming such compounds is simple once the procedure given on the previous pages are followed and the names of the polyatomic ions are known (Table 5.2).

## 5.3. Chemical reactions and chemical equations

A chemical reaction is a process whereby new chemical substances, called products, are produced from a given set of substances called reactants. The process involves the breakage of bonds in the reactants, and/or changes in their oxidation states, and formation of new bonds to yield the products.

The following apply in chemical reactions:

1. Mass is conserved. The total mass of the reactants in a reaction is equal to the total mass of the products formed.

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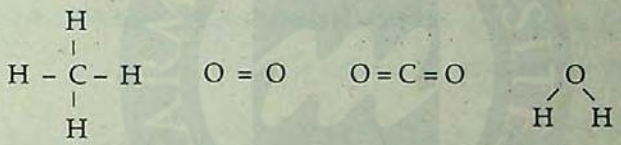
2. Atoms are conserved. The total number of atoms of each element remains unchanged in the rection.

The symbolic representation of a chemical reaction is called a chemical equation. For example, in the combustion of natural gas, methane ($CH_4$) and the oxygen in the air ($O_2$) are the reactants. Assuming complete combustion, the products are carbon dioxide ($CO_2$) and water ($H_2O$).

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$



As can be seen from the structural formulas of the reactants and the products in the equation above, the bonds observed on the left hand side, the reactant side, do not exist on the right hand side, the product side. The bonds in the reactants have broken up and new chemical compounds with different bonds have formed.

The equation is balanced since the number of atoms of each element on the left hand side is the same as what appears on the right hand side.

It should be noted that in order to write the correct balanced equation for a reaction

a) the reactants and the products have to be known,

b) the correct formulas for these substances have to be written.

Balancing of the equation is done simply by performing an elemental balance: the total number of atoms of each element on the left hand side should be equal to that on the right hand side.

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A few common types of reactions that are frequently encountered in stoichiometric problems at this stage of the General Chemistry studies are

i) combustion reactions whereby a hydrocarbon burns to $CO_2$ and $H_2O$,

$$C_2H_6 + 7/2\,O_2 \rightarrow 2\,CO_2 + 3\,H_2O,$$

ii) neutralization reactions whereby an acid is neutralized by a base or vica versa,

$$H_2SO_4 + 2\,NaOH \rightarrow Na_2SO_4 + 2\,H_2O,$$

iii) redox reactions whereby a change in the oxidation number of the elements involved takes place,

$$\overset{(+)}{2\,HCl} + \overset{(o)}{Mg} \rightarrow \overset{(+2)}{MgCl_2} + \overset{(o)}{2\,H_2}$$

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# CHAPTER 6

# THERMOCHEMISTRY

Thermochemistry is the study of heat changes involved in chemical reactions. When two chemical species come together to react, the existing chemical bonds are broken and new ones are formed. Energy is required to break a bond; whereas in the formation of a bond, energy is released.

## 6- 1 Enthalpy changes in chemical reactions

Heat is a form of energy. Heat changes that occur at constant pressure are given a special name: enthalpy changes, $\Delta H$.

It is considered that every substance possesses the property called enthalpy, H. The absolute values of enthalpy cannot be measured. By convention, the enthalpies of pure elements in their most stable forms are taken as zero.

The heat change involved in a reaction at constant pressure is called the enthalpy of reaction, $\Delta H_r$, and can be measured directly by use of calorimeters. It is called the standard enthalpy of reaction, $\Delta H_r^\circ$, when the reaction commences with reactants at standard state (25°C and 1 atm) and is completed with products at standard state.

A positive value of $\Delta H_r$ indicates that heat is absorbed by the reacting system as a result of the reaction. Such reactions are called endothermic reactions.

A negative value of $\Delta H_r$ indicates that heat is released by the reacting system as a result of the reaction. Such reactions are called exothermic reactions.

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In the combustion of methane to carbon dioxide and water,

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(\ell)}$$

the standard enthalpy change, $\Delta H_r^\circ$, is - 890.4 kJ. The minus sign indicates that 890.4 kJ of energy, in the form of heat, evolves upon combustion of one mole of methane.

The enthalpy change of a reaction is the change in the total enthalpy of the reacting system as a result of the reaction. Each of the reactants possesses $H_{Ri}$ amount of enthalpy. The total enthalpy of the system before the reaction is therefore $\Sigma H_{Ri}$.

When the reaction is completed, assuming complete conversion, the reactants have disappeared and products have formed. The total enthalpy of the system is then equal to the sum of the enthalpies of the products, $\Sigma H_{Pi}$. The enthalpy change of the system can be expressed as

$$\Delta H_r = \Sigma H_{Pi} - \Sigma H_{Ri}$$

If, in a reaction, one mole of a pure compound is fomed from its elements in their most stable form and in their standard states, that reaction is called a formation reaction. The enthalpy change for such a reaction is the standard enthalpy of formation, $\Delta H_f^\circ$ of that compound.

In the reaction of

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$$

$\Delta H_r^\circ$ is - 393.5 kJ. This is a formation reaction and, therefore, -393.5 kJ is the enthalpy change upon formation of $CO_2$, $\Delta H_{f(CO_2)}$.

$$\Delta H_{f(CO_2)} = \Delta H_r^\circ$$

$$= \Sigma H_{Pi}^\circ - \Sigma H_{Ri}^\circ$$

Since the reactants are pure elements in their most stable forms in their standard states, $\Sigma H_{Ri}^\circ$ is zero and $\Sigma H_{Pi}^\circ$, the enthalpy of $CO_2$ in its most stable, is equal to its enthalpy of formation, $\Delta H_{f(CO_2)}$. Following similar logic for $\Sigma H_{Ri}^\circ$, the expression for $\Delta H_r$ can be written as

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$$\Delta H_r^\circ = \Sigma (\upsilon \Delta H_f^\circ)_{Pi} - \Sigma (\upsilon \Delta H_f^\circ)_{Ri},$$

where $\upsilon$ is the stoichiometric coefficient of each species in the balanced equation for the reaction.

For the general reaction of

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

$$\Delta H_r^\circ = [\, c\Delta H^\circ_{fC} + d\Delta H^\circ_{fD} \,] - [\, a\Delta H^\circ_{fA} + b\Delta H^\circ_{fB} \,].$$

$\Delta H_f^\circ$'s for some common compounds are listed in Table 6.1.

The reaction between methane and oxygen, given above, is a combustion reaction. The enthalpy changes for such reactions are called enthalpies of combustion, $\Delta H_c^\circ$. The heat evolved upon combustion of a hydrocarbon fuel can be obtained simply from the enthalpies of formation of the specific hydrocarbon and, carbon dioxide and water.

There is no single path to obtain a given set of products from a given set of reactants, actually and theoretically. If it is desired to obtain $CO_2$ and $H_2O$ from $C_2H_6$ (ethane), $C_2H_6$ can either be burnt in excess oxygen completely.

$$C_2H_{6(g)} + 7/2\, O_{2(g)} \rightarrow 2\, CO_{2(g)} + 3H_2O/_{(1)}$$

$$\Delta H_r^\circ = -1560.4 \text{ kJ},$$

or it can be first dehydrogenated and the products $C_2H_4$ (ethene) and $H_2$ can be combusted. The products finally obtained in the latter case are the same as those obtained in the direct combustion of $C_2H_6$.

1. $C_2H_6 \rightarrow C_2H_4 + H_2 \qquad \Delta H_r^\circ = +136.2$ kJ
2. $C_2H_4 + 3\, O_2 \rightarrow 2\, CO_2 + 2H_2O \qquad \Delta H_r^\circ = -1410.8$ kJ
3. $H_2 + 1/2O_2 \rightarrow H_2O \qquad \Delta H_r^\circ = -285.8$ kJ

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$$C_2H_6 + 7/2O_2 \rightarrow 2\, CO_2 + 3H_2O \qquad \Delta H_r^\circ = -1560.4 \text{ kJ}$$

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| SUBSTANCE | $\Delta H_f^\circ$ (kJ mol$^{-1}$) | SUBSTANCE | $\Delta H_f^\circ$ (kJ mol$^{-1}$) |
|---|---|---|---|
| $CH_4$ (g) | − 74.5 | NO (g) | + 90.3 |
| $C_2H_2$ (g) | + 226.8 | $NO_2$ (g) | + 33.2 |
| $C_2H_4$ (g) | + 52.3 | $NH_3$ (g) | − 56.2 |
| $C_2H_6$ (g) | − 84.7 | $SO_2$ (g) | − 296.8 |
| $C_3H_6$ (g) (cyclopropane) | + 53.3 | $SO_3$ (g) | − 395.7 |
| $C_3H_8$ (g) (*n*-propane) | − 103.8 | $O_3$ (g) | + 142.7 |
| $C_4H_8$ (g) (cyclobutane) | + 28.4 | $H_2SO_4$ (ℓ) | − 814.0 |
| $C_4H_{10}$ (g) (*n*-butane) | − 126.1 | $HNO_3$ (ℓ) | − 174.1 |
| $C_5H_{10}$ (g) (cyclopentane) | − 78.4 | $B_5H_9$ (s) | + 73.2 |
| $C_5H_{12}$ (g) (*n*-pentane) | − 146.4 | $B_2O_3$ (s) | − 1273.5 |
| $C_6H_6$ (ℓ) (benzene) | + 49.0 | NaOH (s) | − 425.6 |
| $C_6H_{12}$ (g) (cyclohexane) | − 123.3 | $Na_2O_2$ (s) | − 511.7 |
| CO (g) | − 110.5 | All elements | |
| $CO_2$ (g) | − 393.5 | (most stable form) | 0 |
| $H_2O$ (ℓ) | − 285.8 | C (diamond) | + 1.90 |
| $H_2O$ (g) | − 241.8 | H (g, atomic) | + 218.0 |
| | | C (g, atomic) | + 716.7 |

**Table 6.1** Standard enthalpies of formation

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The Russian chemist Germain Hess (1802 - 1850) found out experimentally that a large number of reactions can be carried out by following different paths and that "the enthalpy change in a reaction is the same regardless of the path by which the reaction occurs". His conclusion has come to be known as Hess's law.

## 6- 2 Bond energies

Bond energy can be described as the energy needed to break a bond. It is also called the dissociation energy. In the case of singly bonded diatomic molecules like $H_2$, the bond energy can be obtained from the enthalpy of reaction whereby the diatomic molecule splits into its atoms.

$$H_{2(g)} \rightarrow 2\,H_{(g,\,atomic)} \quad \Delta H_r^\circ = 436.0\ kJ\ .$$

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The dissociation energies of all bonds cannot be determined as simply as in the case of the H - H bond. Complexities arise as molecules get larger and contain different types of bonds.

**Molecules with multibonds of the same type**

The methane molecule is a good example of this type. In $CH_4$ there are four equivalent C-H bonds. The equation for the reaction whereby all these bonds are broken can be written as

$$CH_4 \rightarrow C_{(g)} + 4\,H_{(g)}.$$

The expression for $\Delta H_r^\circ$ of this reaction is

$$\Delta H_r^\circ = \Delta H_{f\,(C)}^\circ + 4\Delta H_{f\,(H)}^\circ - \Delta H_{f\,(CH_4)}^\circ .$$

Using the values given in Table 6.1, the value of 1663.2 kJ is obtained. 1663.2 kJ is the amount of energy required to break all of the four C-H bonds in a mole of $CH_4$. The average bond energy for the C-H bond is therefore 415.8 kJ/mole.

**Molecules with multibonds of different types**

In a molecule of ethane ($C_2H_6$) there are six C-H bonds and one C-C bond. The reaction whereby all these seven bonds are broken is formulated as

$$C_2H_6 \rightarrow 2C_{(g)} + 6H_{(g)}.$$

The enthalpy of reaction is

$$\Delta H_r^\circ = 2\Delta H_{f\,(c)}^\circ + 6\Delta H_{f\,(H)}^\circ \text{ o} - \Delta H_{f(C_2H_6)}^\circ .$$

Using the $\Delta H_f^\circ$ values given in Table 6.1,

$$\Delta H_r^\circ = 2826.1 .$$

This is the total energy required to break the six C-H bonds and the one C-C bond, i.e.

$$2826.1 = 6\ BE\ (C\text{-}H) + BE\ (C\text{-}C)$$

where BE stands for bond energy.

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Since there are two unknowns in the equation, namely BE (C-H) and BE (C-C), an assumption is necessary. The dissociation energy for each of the C-H bonds is taken as equal to the average value obtained in the case of methane.

$$2826.1 = 6\,(415.8) + BE\,(C\text{-}C)$$

$$BE\,(C\text{-}C) = 331.3\ kJ/mole.$$

**Molecules with double and triple bonds**

The problem is dealt with in the same fashion as the carbon-to-carbon single bond. The simplest molecule that contains the multibond is considered and an assumption is made for the rest of the bond energies based on previous determinations.

The bond energy increases with the number of bonds. The average bond energies for the single, double and the triple bonds between two carbons are 348, 619 and 812 kJ/mole respectively (Table 6.2).

## 6- 3 Reaction enthalpies from bond energies

In section 5.3 a chemical reaction was described as a process whereby existing bonds are broken and new ones are formed. Going from this description, the enthalpy of a reaction can also be described as the difference between the dissociation energies of the existing bonds and those of the ones to be formed.

The example below illustrates this approach to calculating an approximate enthalpy change for a reaction from bond dissociation energies.

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The reaction is

$$OF_{2(g)} + H_2O_{(g)} \rightarrow O_{2(g)} + 2HF_{(g)}$$

| | | | |
|---|---|---|---|
| Energy needed to break the bonds of | F-O-F | 2 x 184 = | 368 kJ |
| | H-O-H | 2 x 463 = | 926 kJ |
| Energy released to form the bonds of | O = O | 1 x 494 = | - 494 kJ |
| | H-F | 2 x 565 = | - 1130 kJ |
| | (approximate) | $\Delta H_r^\circ$ = | - 330 kJ |

In general, the enthalpies of reactions, or formations, determined in this fashion agree reasonably well with those determined experimentally. Differences arise mainly because of the structure of the particular molecule which is not accounted for in the average dissociation energy of a bond.

Table 6.3 lists the experimental and the calculated $\Delta H_f^\circ$'s for some compounds using bond energies.

The large discrepancy between the calculated and experimental values of $\Delta H_f^\circ$ for cyclopropane and cyclobutane can be explained in terms of the strain energy possessed by the molecules of these compounds. Both cyclopropane and cyclobutane are in a way packed into the cyclic structure that they are in. The natural geometry of the carbon hybrid obitals ($sp^3$) involved in the bonding in these compounds is such that there be an angle of 109.5° between the bonds. However, in the three carbons define a plane (a triangle) with an angle of 60° between the two C-C bonds. This produces a strain on the molecule. The cyclic molecule is under pressure to open up and, therefore, requires more energy to form than its straight-chain counterpart, $C_3H_8$. The bond energies given in Table 6.2 do not account for such structural features of the molecules where the bonds may exist. Their calculations are based on the simplest structures in which these bonds can be found.

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| BOND | BOND ENERGY[a] ($kJ\ mol^{-1}$) | BOND | AVERAGE BOND ENERGY[b] ($kJ\ mol^{-1}$) | BOND | AVERAGE BOND ENERGY[b] ($kJ\ mol^{-1}$) |
|---|---|---|---|---|---|
| H – H | 436 | O – O | 138 | C – F | 485 |
| H – F | 565 | N – N | 159 | O – Cl | 205 |
| H – Cl | 431 | N = N | 418 | N – Cl | 201 |
| H – Br | 364 | C – C | 348 | C – Cl | 326 |
| H – I | 297 | C = C | 619 | P – Cl | 326 |
| F – F | 155 | C ≡ C | 812 | S – Cl | 276 |
| Cl – Cl | 239 | O – H | 463 | C – O | 335 |
| Br – Br | 190 | N – H | 389 | C = O | 707 |
| I – I | 149 | C – H | 413 | C ≡ O | 1070 |
| O = O | 494 | P – H | 318 | C – N | 293 |
| N ≡ N | 941 | S – H | 364 | C = N | 616 |
| | | O – F | 184 | C ≡ N | 879 |

[a] These bond energies are the dissociation energies of diatomic molecules that have only one bond; they are therefore exact values

[b] These bond energies are obtained, as described in the text, from molecule that contain more than one bond; they are average, not exact, values therefore.

**Table 6.2** Bond energies

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| COMPOUND | $\Delta H_f^\circ$ CALCULATED FROM BOND ENERGIES (kJ Mol $^{-1}$) | $\Delta H_f^\circ$ EXPERIMENTAL (kJ mol $^{-1}$) | $\Delta H_f^\circ$ EXPERIMENTAL $- \Delta H_f^\circ$ CALCULATED (kJ mol$^{-1}$) |
|---|---|---|---|
| Methane, $CH_4$ | - 63 | - 75 | - 12 |
| Ethane, $C_2H_6$ | - 85 | - 85 | 0 |
| Propane, $C_3H_8$ | - 106 | - 104 | + 2 |
| Butane, $C_4H_{10}$ | - 127 | - 126 | + 1 |
| Pentane, $C_5H_{12}$ | - 148 | - 146 | + 2 |
| Hexane, $C_6H_{14}$ | - 170 | - 167 | + 3 |
| 2- Methylpropane, $C_4H_{10}$ | - 127 | - 135 | - 8 |
| 2- Methylbutane, $C_5H_{12}$ | - 148 | - 154 | - 6 |
| 2,2- Dimethylpropane, $C_5H_{12}$ | - 148 | - 167 | - 19 |
| 2- Methylpentane, $C_6H_{14}$ | - 170 | - 175 | - 5 |
| 2, 2-Dimethylbutane, $C_6H_{14}$ | - 170 | - 172 | - 2 |
| Cyclopropane, $C_3H_6$ | - 64 | + 53 | + 117 |
| Cyclobutane, $C_4H_8$ | - 89 | + 28 | + 113 |
| Cyclopentane, $C_5H_{10}$ | - 106 | - 78 | + 28 |
| Cyclohexane, $C_6H_{12}$ | - 128 | - 123 | + 5 |
| Ethene, $C_2H_4$ | + 52 | + 52 | 0 |
| Propene, $C_3H_6$ | + 13 | + 20 | + 7 |
| 1-Butene, $C_4H_8$ | - 8 | 0 | + 8 |
| *cis* 2- Butene, $C_4H_8$ | - 8 | - 8 | 0 |
| *trans* - 2- Butene, $C_4H_8$ | - 8 | - 12 | - 4 |
| Benzene, $C_6H_6$ | + 229 | + 83 | - 146 |

**Table 6.3** Experimental and calculated $\Delta H_f^\circ$ 's for some compounds using bond energies

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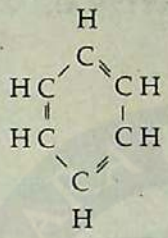
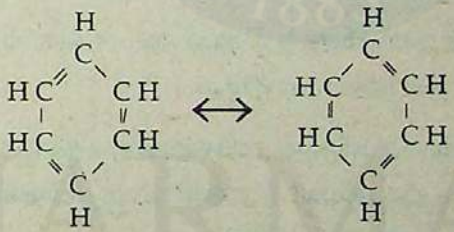
Similar explanation applies to cyclobutane.

One other large discrepancy is exhibited in the case of benzene ($C_6H_6$). Benzene is a cyclic molecule with alternating double bonds, viz



However, the double bonds are not between two particular carbons. The six shared electrons making up the double bonds are shared among the six carbons: they are delocalized over the benzene molecule. Benzene has two resonance strutures, viz



The benzene ring, due to these delocalized electrons, is more stable than that suggested by the value of $\Delta H_f^\circ$ calculated from the energies of the common forms of the bonds involved. The difference between the predicted and the experimental values of $\Delta H_f^\circ$ for benzene is ascribed to its resonance characteristic and is therefore called the resonance energy.

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# CHAPTER 7

# STATES OF MATTER AND SOLIDS

## 7-1 States of matter

Matter exists in three forms: solid, liquid and gas. These forms, or phases, are called the three states of matter.

The atoms, molecules or ions in a solid are constrained to fixed points. They may vibrate about these points but, ordinarily, they may not move from them permanently.

In the liquid state, there is some free volume among the structural units; motions are more vigorous, and the structure is more random.

In the gaseous state, there is a great deal of free volume; motion is chaotic and disorder is at maximum (Figure 7.1).

The state in which a substance exists under a given set of conditions basically depends on the amount of kinetic energy posessed by the molecules of the substance under those conditions.

The transformation of a substance from one state, or phase, to another is called a phase change (Figure 7.2).

When a solid is heated, the kinetic energy of the atoms or molecules increases and they start vibrating vigorously about their fixed positions. Eventually, transformation into the liquid phase commences. The temperature at which solid-liquid equilibrium is attained under 1 atm is called the melting point. It is the same as the freezing point of the substance. The process of melting is also called fusion. The quantity of heat that must be added to melt a mole of a substance is called the molar enthalpy of fusion, $\Delta H_{fus}$.

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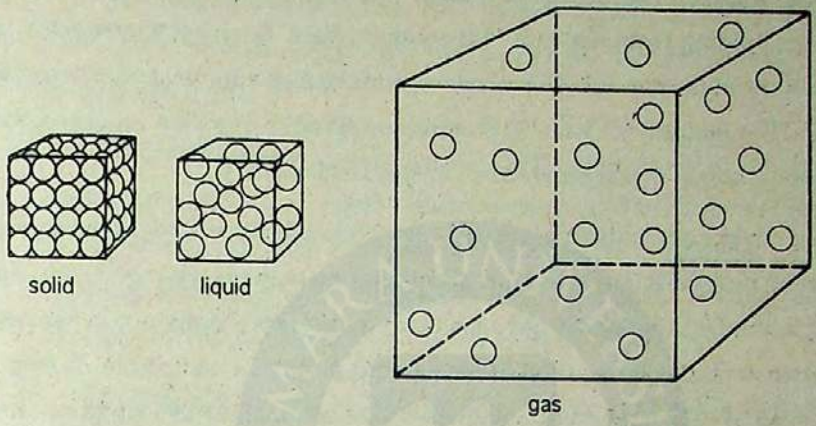


**Figure 7.1** Symbolic representation of the solid, liquid nd the gas states

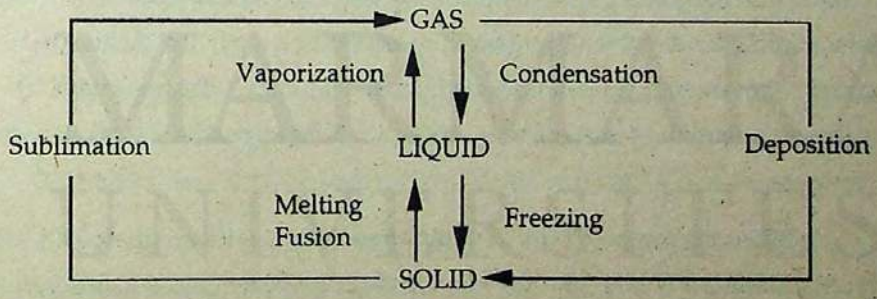


**Figure 7.2** Phase changes

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When a liquid is heated, the kinetic energy of the molecules increases. Those molecule with enough kinetic energy overcome the intermolecular forces holding them together in the liquid phase. They escape from the liquid to form the vapour. This phenomenon is called vaporization or evaporation. The quantity of heat that must be added to vaporize a mole of substance is called the molar enthalpy of vaporization, $\Delta H_v$.

Evaporation takes place even at very low temperatures. The more energetic molecules leave the liquid forming the vapour. However, this does not continue indefinetely. At each temperature, once evaporation reaches a certain extent, condensation of the gaseous molecules commence. A point is reached at each temperature with each substance where the rate of evaporation equals the rate of condensation. This condition is called phase equilibrium. The pressure exerted by the vapour of a liquid in such an equilibrium state is called the vapour pressure of that liquid at that temperature.

In the same manner, when any gas comes in contact with a liquid, the gas will acquire vapour from that liquid. If contact is attained for a considerable length of time the "partial" pressure of the vapour (vaporized liquid) in the gas will equal the vapor pressure of the liquid at the temperature of the system. Regardless of the duration of contact between the liquid and gas, no more net mass transfer will take place from the liquid to the gas phase. The gas is then said to be saturated with the particular vapour at the given temperature.

When the vapour is not in equilibrium with the liquid phase and the partial pressure is less than the vapour pressure of the liquid at the given temperature, the condition is called partial saturation.

Solids and their structures are a major part of Inorganic Chemistry studies. They are, therefore, not covered extensively here. However, a brief introduction is considered appropriate.

The gaseous and the liquid states are discussed in the following two chapters.

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## 7- 2 Solids and their structures

Most solids are crystalline. They have a regular periodic arrangement of their atoms or ions. The crystals they form have flat faces with definite angles between them.

Solids without a regular periodic arrangement of their atoms are called amorphous solids. Some solids can exist in different forms. For example, sulphur is found in three forms: orthorombic crystalline, monoclinic crystalline and amorphous. Such solids are called allotropic and the different forms are called allotropes of that element.

Solids, with regard to their structures, can be basically classified into two categories: molecular solids and network solids (Table 7.1).

Molecular solids consist of individual molecules held together by relatively weak intermolecular forces. Depending on the strength of these forces between the molecules the solid state can prevail even at room temperature. Lower temperatures are required to attain the solid state of those substances with weak intermolecular forces.

Network salids have crystalline structures. They do not consist of individual molecules. They have a continuous network of atoms or ions in which each atom or ion is strongly bound to its neighbours. The regular network extents indefinetely throughout the crystal. The bonding between the atoms or ions of such solids is either covalent, ionic or metallic.

The structure of a solid affects its basic properties like melting point, boiling point and solubility.

Molecular solids, as mentioned above, usually have low melting and boiling points due to the weakness of the forces that hold them together.

On the other hand, network solids usually have high melting and boiling points because of the nature of the bonds that hold its atoms and ions together.

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Molecular solids are often soluble in molecular liquids like carbon disulphide and carbon tetrachloride.

Network solids with covalent and metallic bonding are insoluble in all solvents including water. Many ionic solids, to varying extens, are soluble in water. The reasons for thes phenomenon and the mechanics of dissolution are discussed in Chapter 9.

| | MOLECULAR | NETWORK | | | | | |
|---|---|---|---|---|---|---|---|
| | | 1D CHAINS | 2D LAYERS (SHEETS) | | 3D NETWORKS | | |
| Structural units | Molecules | Atoms | Atoms | Ions of opposite charge | Atoms | Ions of opposite charge | Positive ions and electrons |
| Types of interaction between units | Intermolecular forces | Covalent bonds | Covalent bonds | Ionic bonds | Covalent bonds | Ionic bonds | Metallic bonds |
| Examples | $CH_4$, $CO_2$, HCl, $NH_3$, $I_2$, $S_8$, $P_4$ | $S_n$ $Se_n$ $(SO_3)_n$ $(PO_3^-)_n$ | C(graphite) P(black) | $MgCl_2$ | C(diamond) $SiO_2$ SiC | NaCl MgO $CaF_2$ | Ca Fe Al |

**Table 7.1** Classification of solids

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# CHAPTER 8

# GASEOUS STATE

Gases are in important part of our life. The atmosphere that we live in is a mixture of gases held to earth by gravity. The atmophere is most dense at sea level and thins out with increasing altitude. The lowest level of the atmosphere that extends to about 30 km and is called air is basically a mixture of nitrogen and oxygen. Although there are trace amounts of other components (Table 8.1) it is general practice to assume air 79% $N_2$ and 21 % $O_2$, by volume.

Gases behave in a unique manner. The behaviour of gases has been formulated by the so called gas laws. However, prior to elaboration on these laws, an important property of gases, pressure and its measurements, is reviewed.

## 8- 1 Pressure and its measurements

Gas pressure can be broadly defined as the force exerted by a gas on a unit area of the surface it is in contact with. Pressure, in general mathematical terms, is defined as force per unit area, viz

$$P = F/A \qquad (8.1)$$

The unit of force in the SI system is Newtons (N) and that of area is square meters ($m^2$). The unit of pressure is $N/m^2$ and is called pascal (Pa).

Pressure exerted by a liquid on the base of its container can be evaluated as follows (Figure 8.1):

A force is exerted on the base of the container due to the weight of the liquid,

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| COMPONENT | FORMULA | PERCENT BY VOLUME |
|---|---|---|
| Nitrogen | $N_2$ | 78.084 |
| Oxygen | $O_2$ | 20.948 |
| Argon | Ar | 0.934 |
| Carbon dioxide | $CO_2$ | 0.031 4 |
| Neon | Ne | 0.001 82 |
| Helium | He | 0.000 52 |
| Methane | $CH_4$ | 0.000 2 |
| Krypton | Kr | 0.000 11 |
| Hydrogen | $H_2$ | 0.000 05 |
| Nitrous oxide | $N_2O$ | 0.000 05 |
| Xenon | Xe | 0.000 008 |

**Table 8.1** Composition of dry air

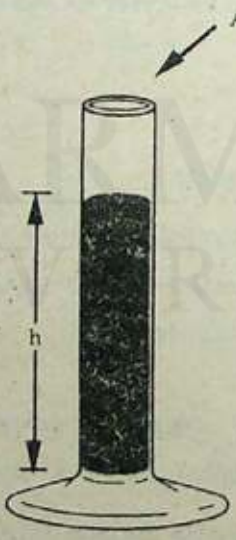


**Figure 8.1** The concept of liquid pressure

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$$P_\ell = mg/A = V\,d\,g/A = A\,h\,d\,g/A$$

$$P_\ell = g\,h\,d \qquad (8.2)$$

where g is the gravitational acceleration,

h is the height of the liquid column,

d is the density of the liquid.

It should be noted that this is the pressure exerted on the base by the liquid only. The total pressure on the base is that plus the barometric pressure ($P_o$) that is exerted by the atmosphere on the liquid.

$$P_t = P_\ell + P_o \qquad (8.3)$$

The pressure of a gas is often measured indirectly by means of a device in comparison with a liquid pressure. One such device is the mercury barometer first used by Toricelli in 1643 (Figure 8.2).

The air pressure on the mercury in the pan forces the mercury up into the evacuated column until the liquid pressure at point A is equal to the air pressure. The pressure of the air in terms of the pressure of the mercury column is

$$P_o = g\,h\,d_{Hg}$$

The pressure of the atmosphere decrease with altitude. The average height of the column at sea level is 760 mm and this value is called the standard atmospheric pressure (1 atmosphere, atm). In terms of pascals and kilopascals,

$$1\ atm = 9.8\ (m/s^2)\ 0.76\ (m)\ 13.6 \times 10^3\ (kg/m^3)$$

$$= 101\,300\ Pa\ (N/m^2)$$

$$= 101.3\ kPa.$$

In recognition of Toricelli's contribution to pressure measurements, 1 mm Hg is also called a torr.

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A simple device that is used to measure the pressure of gases is the manometer. The two basic types of manometers are shown in Figure 8.3.

When the open-end manometer is connected to a gas sample at atmospheric pressure $P_o$, there is no difference between the mercury levels in two arms (AI). When the gas sample is at a different pressure from atmospheric,

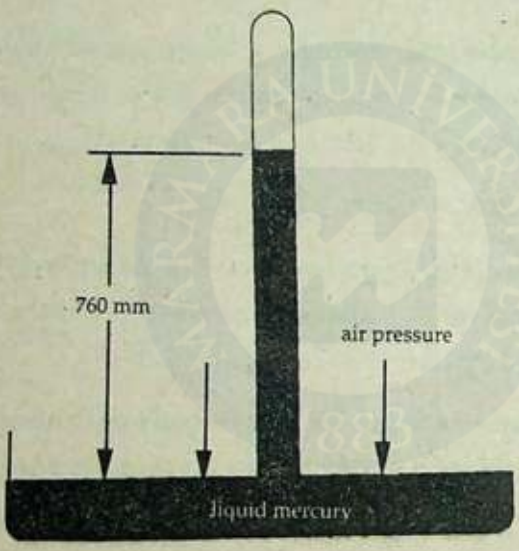


**Figure 8.2** The Toricelli barometer

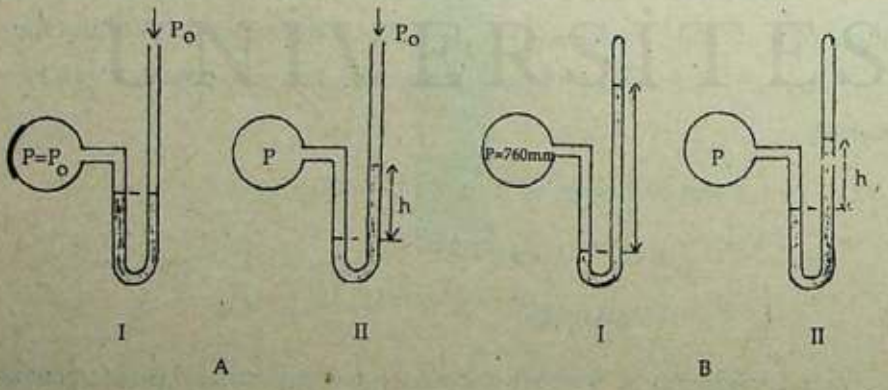


**Figure 8.3** The open-end the closed-end manometers

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the two mercury levels are not the same. In the case of AII, the pressure of the gas is greater than atmospheric by hgd (in Pa) or simply h (in mm Hg). If the mercury level in the left arm of the manometer were to be higher than that in the right arm by h mm, then the pressure of the gas would be measured as $P_0$ - hgd (Pa).

In the closed-end manometer, also called the absolute manometer, there is no gas and, consequently no pressure on top of the mercury column in the closed end arm. The pressure exerted by the mercury vapour is neglegible. This is one reason why mercury is used as a manometer liguid. Also, since it has a very high density, only reasonable heights of the mercury column are required to measure atmospheric pressures. If water is used instead, the height of the water column needed to support a given pressure is 13.6 times the height of the mercury column to support the same pressure.

## 8- 2 Kinetic theory of gases

The theory which explains the behaviour of gases was developed during the nineteenth century and has come to be called the Kinetic Theory of Gases. The theory is based on the following model of a gas:

1. A gas is comprised of extremely small particles called molecules or atoms.
2. The gas molecules themselves hardly occupy any space. They are separated from each other by great distances in the container they are held in.
3. No forces exist between molecules.
4. The molecules move constantly and randomly throughout the gas volume. As a result of their motion they undergo frequent collisions with one another and with the walls of their container.

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5. Collisions between molecules are elastic. Individual molecules may gain or lose momentum as a result of collisions.

6. Kinetic energy of the molecules of a gas is proportional to the absolute temperature. At constant temperature, the total energy of the molecules, consequently the total momentum, in a closed system, remains constant.

In reality, the behaviour of most gases deviate from the above model under most pressure and temperature conditions. The gases which conform with this model are called ideal gases. The various gas laws that are formulated in the following section are based on such ideal gas behaviour.

## 8- 3 Gas laws

The four basic variables in a gaseous system are pressure, temperature, volume and quantity. They cannot be varied independent of each other because of the relations among them.

The first of these relations was discovered by Robert Boyle in 1662. He found that the volume of a constant quantity of gas, at constant temperature, is inversely proportional to its pressure, i.e.

$$V \propto 1/P$$

The relation between gas volume and temperature was discovered by Jacques Charles in 1787 and restated by Gay-lussac in 1802. Their observation was that when a fixed amount of gas is kept under constant pressure by external means in a variable-volume vessel, the gas will expand as temperature increases, i.e.

$$V \propto T$$

The law relating the volume of a gas to the quantity of the gas was developed from Avogadro's original hypothesis that equal volumes of different gases, at the same temperature and pressure, contain equal numbers of molecules. Mathematically this is expressed as

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$$V \propto n.$$

The ideal gas laws combines these three relations in one expression that contains the gas constant R as the overall proportionality constant.

| | | |
|---|---|---|
| Boyle's Law : | $V \propto 1/P$ | (n and T constant) |
| Charles' Law: | $V \propto T$ | (n and P constant) |
| Avogadro's Law: | $V \propto n$ | (P and T constant) |

$$V \propto n\,T/P$$

$$V = R\,n\,T/P$$

Ideal Gas Law: $P\,V = n\,R\,T$ (8.4)

(or Combined Gas Law)

In dealing with problems involving gases, with the assumption of ideal gas behaviour, it is necessary to remember only the last expression rather than each one of the first three.

In the first section of this chapter, although the concept of gas pressure was introduced, its causes were not discussed. This is done below.

The ideal gas model pictures the gas molecules as moving constantly and randomly throughout the gas volume. As a result of their motion the molecules undergo collisions with one another and with the walls of the container they are held in. The pressure exerted by a gas on its container walls is a result of these collisions.

Assuming the container is a cube of side $\ell$, as illustrated in Figure 8.4, and wall A is the surface where the gas pressure is considered, the following mechanism can be described.

The velocity u of one molecule in space is resolved into the components $u_x$, $u_y$, $u_z$ which are perpendicular to the walls of the container. As a

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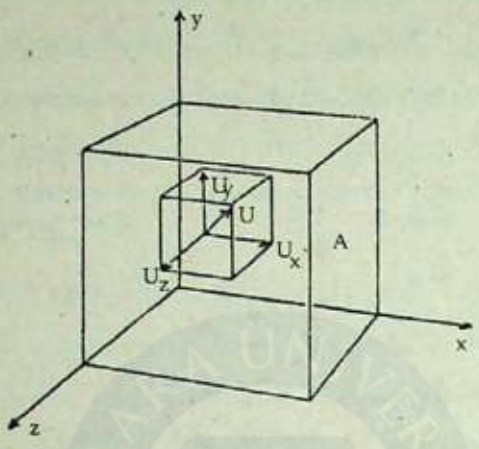


**Figure 8.4** Motion of a gas molecule in a container

result of $u_x$, the molecule collides with surface A, bounces back and subsequently collides with the opposite side of the container.

When an object of mass m travels with a velocity v in a certain direction, the momentum of the object in the same direction is expressed as

$$p = m\,v \tag{8.5}$$

Like energy, momentum is conserved.

The rate of change of momentum is

$$dp/dt = d\,(mv)\,/dt$$

and, since m is constant,

$$dp/dt = m\,dv/dt. \tag{8.6}$$

Acceleration, a, is dv/dt.

$$dp/dt = m\,a = F \qquad \text{(Newtons relation)} \tag{8.7}$$

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In the system considered the molecule, before collision with wall A, has a momentum of $mu_x$ in the x-direction. After collision, the molecule bounces back with velocity $-u_x$. The change in the momentum of the molecule is $2\,mu_x$.

The distance the molecule travels while undergoing this amount of momentum change is $2\ell$ and, the time it takes is $2\ell/u_x$. The rate of change of momentum, i.e. the change of momentum per unit time, is therefore

$$(F = dp/dt = )\ 2\,mu_x\ u_x\ /2\ell = mu_x^2/\ell \qquad (8.8)$$

Pressure is defined as force per unit area and the rate of change of momentum is force. Hence, the pressure exerted on wall A is

$$F/A = p = mu_x^2/\ell\ell^2 = mu_x^2/\ell^3 = mu_x^2/V \qquad (8.9)$$

where V is the volume of the container.

When N number of molecules are considered, the average of the squares of the velocities of all molecules in the x-direction are taken and

$$P = N\,m\overline{u_x^2}/V \qquad (8.10)$$

It is more convenient to write this relation in terms of the average of the magnitude of the velocities of the molecules:

$$u^2 = u_x^2 + u_y^2 + u_z^2.$$

For a large number of molecules moving in random directions,

$$\overline{u_x^2} = \overline{u_y^2} = \overline{u_z^2}.$$

Hence $\quad u^2 = 3\,u_x^2,$

and $\quad P = N\,m\,\overline{u^2}/3\,V$

or $\quad PV = N\,m\overline{u^2}/3. \qquad (8.11)$

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The average kinetic energy of a molecule is

$$\overline{ke} = 1/2\ \overline{mu^2}$$

and

$$\overline{mu^2} = 2\ \overline{ke}.$$

Substituting this expression in 8.11

$$P\,V = 2/3\ N\ \overline{ke} \qquad (8.12)$$

N number of molecules can be expressed as $6.02 \times 10^{23}$ n, n being the number of moles. Equation 8.12 can be written as

$$P\,V = 2/3 \times 6.02 \times 10^{23}\ n\ \overline{ke}.$$

and

$$K\,E = 6.02 \times 10^{23}\ \overline{ke}.$$

then

$$P\,V = 2/3\ n\ KE. \qquad (8.13)$$

The ideal gas law is

$$P\,V = n\,R\,T$$

and therefore

$$2/3\ n\ KE = n\ R\ T$$

$$KE = 3/2\ RT \qquad (8.14)$$

Equation 8.14 is the formulation of the relation between the kinetic energy of the molecules and temperature as mentioned in section 8.2.

### 8- 4 Partial pressure and partial volume

The ideal gas law does not involve the identity of the gas it is used for. As long as its behaviour is ideal, or can be assumed ideal, the law applies to any whether it is in pure form or in a mixture.

When in a mixture each gas distributes itself uniformly throughout the container and exerts the same pressure as it would if it were alone in that container. This pressure is called partial pressure. The total pressure exerted by a mixture of gases is the sum of the partial pressures of the components it is comprised of. It is expressed as

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$$P_t = \sum_{i=1}^{n} p_i \qquad (8.15)$$

where $P_t$ is total pressure,

$p_i$ is the partial pressure of each component,

n is the number of components in the mixture.

The expression has come to be known as Dalton's law of partial pressures after the name of its formulator, John Dalton.

Applying the ideal gas law to a gaseous mixture contained in a fixed-volume vessel,

$$P_t V_t = n_t R T$$

where $V_t$ is the volume of the container or total volume,

$n_t$ is the total number of moles of gas.

Also, for each component at the same temperature,

$$p_i V_t = n_i R T$$

$$\frac{p_i V_t}{P_t V_t} = \frac{n_i R T}{n_t R T}$$

$$p_i / P_t = n_i / n_t = y_i \qquad (8.16)$$

where $y_i$ is the mole fraction of the i'th component in the mixture.

The partial volume of a component in a mixture in a fixed-volume container is a conceptual quantity. It is defined as the volume occupied by a component of the mixture at the same temperature and total pressure of the system, i.e.

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$$P_t v_i = n_i R T$$

and, consequently

$$\sum_{i=1}^{n} v_i = V_t \qquad (8.17)$$

Also

$$v_i / V_t = n_i / n_t = p_i / P_t = y_i \qquad (8.18)$$

## 8- 5 Diffusion and effusion

Molecules of a gas are in constant motion as described by the kinetic theory. When two gases are brought together, they mix. The mixing of one gas with another is called diffusion.

Another phenomenon, called effusion, occurs when gas molecules escape from a container through a very small opening.

The rate of diffusion or effusion of a gas depends on the velocity with which the molecules are moving. The average kinetic energy of molecules has already been shown to depend on temperature. Consequently, at the same temperature, the average kinetic energy of two molecules with masses $m_1$ and $m_2$ are the same, i.e

$$1/2\, m_1 v_1^2 = 1/2\, m_2 v_2^2$$

$$v_1 / v_2 = \sqrt{m_2 / m_1} \qquad (8.19)$$

The relation states that those molecules with lower molecular mass move around with higher velocities than those with greater molecular mass. Consequently, the rate of diffusion and/or effusion of lower mass molecules is higher than those with greater molecular mass:

$$r_1 / r_2 = v_1 / v_2 = \sqrt{m_2 / m_1}$$

This is known as Graham's law.

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# CHAPTER 9

# LIQUID STATE

The liquid is the intermediate state between the solid and the gas states under ordinary atmospheric pressures. The forces between the molecules in a liquid are fairly strong and, consequently, they are not free to move around as in the gaseous state. However, they are not arranged in the rigid regular patterns that are found in solid structures.

The forces that hold molecules together in the liquid stat are called intermolecular forces. These are discussed in the following section. Table 9.1 summarizes the types and occurence of such forces.

## 9- 1 Intermolecular forces

### A. Ionic interactions

**Ion - ion interactions**

The ionic bonding in ionic compounds persist when they are in the liquid state. The ions are still held together by electrostatic forces but somehow more loosely. Unlike their rigid structure in the solid phase the ions can move around in the liquid phase, still holding on to their oppositely charged partners.

**Ion - dipole interactions**

Dipole and polarity of molecules were discussed in Chapter 4.

The ion-dipole interaction is that between an ion and a polar molecule. The ion attracts the oppositely charged end of the polar molecule whereby an attractive force is created.

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The force of attraction between an ion and a dipole varies with $1/r^3$, where r is the distance between the centre of the ion and the midpoint of the dipole. It decreases with r more sharply than the electrostatic force between two ions.

In addition to the dipole encountered in polar molecules, there is another type of dipole called the induced dipole. A dipole can be induced in a nonpolar molecule by a nearby ion and, subsequently, an attractive force is created between the two. This type of force is weaker than the two discussed above and is inversely proportional to the fifth power of the distance between the two charge centres (Figure 9.1).

**B. Molecular interaction**

**Dipole - dipole forces**

When two polar molecules are positioned in a positive end-to-negative-end fashion, an attractive force is set up between the two molecules very similar to the electrostatic forces between two oppositely charged ions. However, these are weaker and decrease more sharply with distance.

**Dipole - induced dipole forces**

The same way as an ion can, a polar molecule can induce a dipole in a nonpolar molecule (Figure 9.2). This resulting force of attraction is a weak one and decreases sharply with distance.

**Induced dipole - induced dipole forces**

Since condensation is a result of intermolecular forces and even nonpolar molecules like $N_2$, $H_2$ and $O_2$ do condense, it has been proposed by Fritz London (1900 - 1954) that molecular interaction does occur between nonpolar molecules. Such interactions are explained in terms of instantaneous dipoles in nonpolar molecules due to the constant motion of electrons and their random orientation in molecules. A molecule which has acquired an instantaneous dipole in this fashion can induce or direct a similar dipole

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| | TYPE OF INTERACTION | USUAL DESCRIPTION OF INTERACTION | DEPENDENCE OF FORCE ON DISTANCE |
|---|---|---|---|
| Ions and ions | Ion-ion | Ionic bonding | $1/r^2$ |
| Ions and polar molecules | Ion-dipole | | $1/r^3$ |
| Ions and nonpolar molecules | Ion-induced dipole | Ion solvation | $1/r^5$ |
| Polar molecules and polar molecules | Dipole-dipole | | |
| Polar molecules and nonpolar molecules | Dipole-induced dipole | Intermolecular forces (van der Waals forces) | $1/r^7$ |
| Nonpolar molecules and nonpolar molecules | Induced dipole-induced dipole | (London forces)* | |

Table 9.1 Interionic and intermolecular forces

*The term intermolecular (van der Waals) forces applies to all types of attractions between molecules. The term London forces is used to describe only induced dipole-induced dipole forces-that is, the forces that act between nonpolar molecules

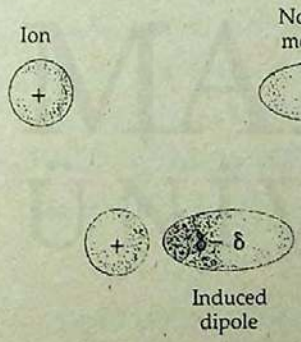


Figure 9.1 Ion - molecule interaction

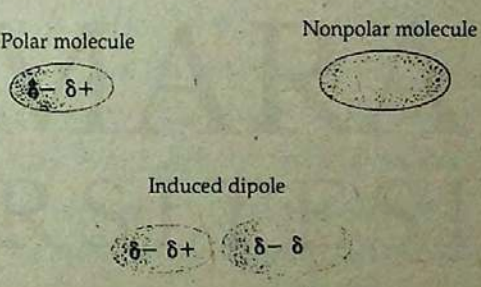


Figure 9.2 Dipole - induced dipole interaction

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in another nonpolar molecule nearby. As a result, an attractive force is created between the two molecules (Figure 9.3).




Figure 9.3 Induced dipole - induced dipole interaction

## C. van der Waal's forces

It was mentioned in the preceeding chapter that all gases under all conditions do not conform with the ideal gas model. Rather than behaving as individual molecules, the molecules of some gases, particularly large ones with dipoles, interact with one another and, therefore deviate from ideal gas behaviour.

The Dutch physicist Johannes van der Waal (1837 - 1923) was the first to identify such forces in the gaseous state. He also postulated that the volume occupied by the molecules of some gases cannot be ignored as is done in the ideal gas model. When these two factors were introduced into the ideal gas equation, he obtained more accurate predictions.

The nonideal gas equation, or van der Waal's equation, is written as

$$(P + an^2 / v^2)(V - nb) = n R T$$

where constant a takes care of the intermolecular forces and

constant b represents the volume occupied by each gas molecule. The constants a and b can be obtained from the critical temperature, pressure and volume of the gas.

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## 9.2 Water

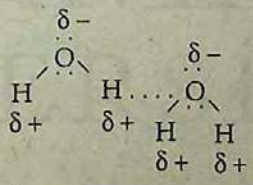
Water is the most abundant liquid on earth. 97 % of it is in the oceans, the remainder is fresh water.

Water has some unusual properties in comparison to other substances with similar chemical structures, e.g. $H_2S$, $H_2Se$ and $H_2Te$. These unusual properties are the high boiling point, lower density of the solid state (ice) than the liquid state and the ability of water to dissolve other substances.

These properties of water can all be attributed to the unusually strong attractive forces between the water molecules, referred to as hydrogen bonding.

The water molecule is polar and has a dipole. Hydrogen bonding, in essence, is a dipole-dipole interaction. However, the interaction between water molecules is much greater than that between molecules with comparable dipoles. This is explained in terms of the very small size of the positively charged (partially) H atom which allows it to get very close to the negatively charged (partially) O atom of another water molecule, i.e.

The H-bond is intermediate in strength between other intermolecular forces and the much stronger ionic and covalent bonds.




Hydrogen bonding exists not only between H and O, but between hydrogens bonded to other small highly electronegative 2nd period elements. The common feature of these elements is the unshared pair of electrons in their valence shell.

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Hydrogen bonding, in general terms, can thus be defined as an intermolecular attraction in which a hydrogen atom that is bonded to an electronegative atom is attracted to the unshared electron pair on another small electronegative atom.

| | | |
|---|---|---|
| F – H · · · · : F | F – H · · · · : O | F – H · · · · : N |
| O – H · · · · : F | O – H · · · · : O | O – H · · · · : N |
| N – H · · · · : F | N – H · · · · : O | N – H · · · · : N |

Figure 9.4 illustrates the boiling points of hydrides of groups IV, V, VI and VII. The effect of H-bonding is clearly displayed in the boiling points of $NH_3$, HF and $H_2O$ in comparison with the trend exhibited by the other elements in the same groups.

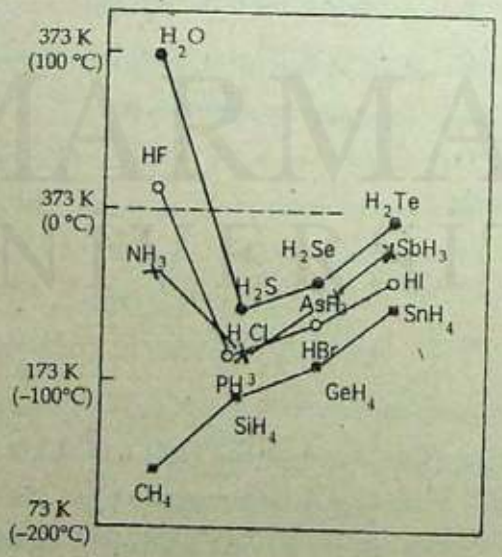


**Figure 9.4** Boiling points of hydrides of groups IV, V, VI and VII

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The density of liquid water increases, as expected, as it is cooled down to 3.98°C. At 3.98 °C, it reaches a maximum of 1.000 g/cc. However, by the time water freezes at 0.00°C, its density decreases to 0.917 g/cc.

Ice has a network structure similar to that of diamond, each oxygen surrounded by four other oxygen atoms in a tetrahedral arrangement.

Each oxygen has two hydrogen atoms covalently bound to it and it has two pairs of unshared electrons, each of which forms a H-bond with the hydrogen atoms of neighbouring water molecules.

Each water molecule could have up to 12 nearest neighbours if they were closely packed together. But the number of neighbours of any water molecule is limited to four because each oxygen atom forms two covalent O - H bonds and two O - H hydrogen bonds. As a result, the structure has physically room for more molecules.

During heating of ice, the H- bonds gradually start to break. By the time the the ice has melted about 15 % of the H - bonds are broken and, consequently, the water molecules become more closely packed resulting in greater desity.

## 9.3 Solutions

A solution is an homogeneous mixture of two or more substances. The substance (s) with lesser quantity in the mixture is called the solute and the one with greater quantity is called the solvent.

The most common solvent is water and its solutions are called aqueous solutions.

For a solution to form, the molecules or the ions of the solute have to be attracted to the solvent molecules more strongly than they are attracted to one another and the solvent molecules have to be attracted to the solute molecules or ions more strongly than they are attracted to one another.

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For aqueous solutions to form, the molecules or ions of the solute have to form bonds with the water molecules that are stronger than the H-bonds between the water molecules themselves. Only whin this condition is satisfied an aqueous solution of a compound is possible.

NaCl, $KNO_3$ and $MgSO_4$ are among the compounds that are soluble in water. Aqueous solutions of these compounds are possible because the ion-dipole interaction between the ions of these compounds and water molecules is stronger than the electrostatic force that is holding the ions of this compound together and the H-bonds between the water molecules.

Many ionic compounds such as MgO, AgCl and $BaSO_4$ are insoluble in water since the ion-ion interaction in the solid is stronger than any other possible interaction.

Polar organic compounds are soluble in water. Alcohol, which have the polar - OH functional group as in $CH_3OH$ and $CH_5OH$, do form aqueous solutions. The H-bonds between the water molecules and the alcohol molecules themselves are replaced by the H-bonds between the molecules of water and alcohol.

Nonpolar compounds, organic or inorganic, dissolve in nonpolar solvents. $CCl_4$ and $C_6H_5CH_3$ are examples of such solvents.

From a thermodynamic point of view, dissolution can be classified as endothermic or exothermic. If more energy is required to overcome the interaction between the solvent molecules and the solute molecules themselves than the energy released upon formation of the interaction between the solute - solvent particles, then the process is endothermic. The solubility of the solute in the solvent will increase with temperature.

If the converse is true, then the process is an exothermic one and solubility will decrease as temperature increases.

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The heat change involved when one mole of a solute dissolves in a solvent at constant pressure is called the molar enthalpy of solution, $\Delta H^\circ_{solution}$.

Figure 9.5 illustrates the thermal effects of the dissolution process.

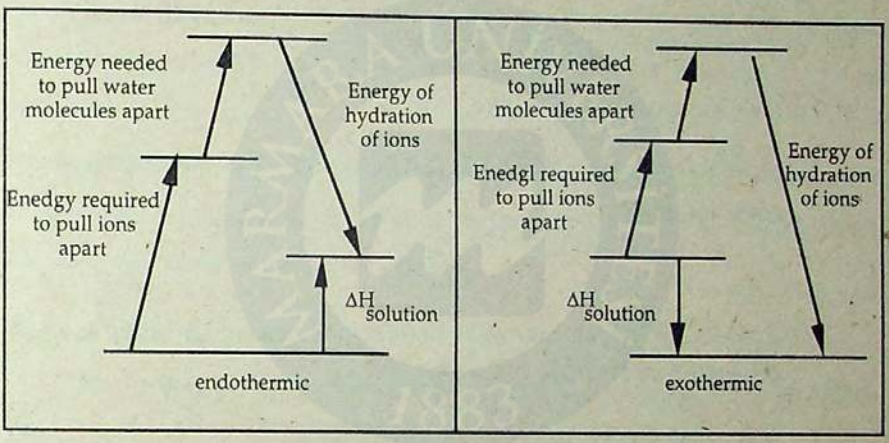


**Figure 9.5** Thermal effects in an aqueous solution

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## 9.4 Concentration of solutions

The specific information needed to describe the composition of a solution is the amount of solute in a given amount of solution.

Concentration of a solution can be expressed in a number of ways. These are

i) molarity (M)

ii) % concentration (by mass or volume)

iii) normality (N)

i) Molarity is defined as the number of moles of solute found in one litre of solution, i.e.

$$M = n/V\ (\ell).$$

ii) Percentage concentration (by mass) is the percentage of the mass of the solute in the mass of the solution, i.e.

$$\%\ \text{concentration (by mass)} = m_{solute} / m_{solution} \times 100.$$

Percentage concentration (by volume) is the percentage of the volume of the solute in the volume of the solution, i.e.

$$\%\ \text{concentration (by volume)} = V_{solute} / V_{solution} \times 100.$$

iii) Normality is defined as the number of equivalent weights of the solute in one litre of solution, i.e.

$$N = (\text{no. of eq. wt's})_{solute} / V(\ell).$$

Equivalent weight can be described as the mass of a substance that furnishes one unit, positive or negative, charge. The equivalent weight of an ionic compound is its molecular weight divided by the total positive, or negative, charges on its ions.

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## 9.5 Colligative properties of solutions

Colligative properties of solutions are those properties that depend only on the number of solute and solvent molecules (or ions) but not on the nature of the solute.

Boiling point elevation and freezing point depression are two such properties of solutions.

These features of solutions could be explained only after the findings of François Raoult (1830 - 1901) on the vapour pressures of componenets in solutions.

Raoult expressed the vapour pressure of each component in a solution in terms of the vapour pressure of the pure component, $P_i^\circ$, and its mole fraction, $x_i$, in the solution as

$$P_i = x_i P_i^\circ .$$

In the case of a two component solutions, i.e. single solute in a solvent,

$$P_{solvent} = x_{solvent} P^\circ_{solvent}$$

$$P_{solute} = x_{solute} P^\circ_{solute}$$

and $$P_{solution} = P_{solvent} + P_{solute}.$$

In the case of nonvolatile solutes, like aqueous solutions of ordinary inorganic salts, the vapour pressure of the solute is zero and

$$P_{solution} = P_{solvent} = x_{solvent} P^\circ_{solvent} .$$

Since $x_{solvent}$ is always less than 1 in a solution, the vapour pressure of the solution becomes less than that of the pure solvent.

Lower vapour pressure means higher boiling point. Hence, the boiling point of a solution, in case of a nonvolatile solute, is higher than that of the substance that acts as a solvent in the solution.

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The elevation of the boiling point is directly proportional to the concentration of the nonvolatile solute in the solution. The derivation of the exact relation is delayed until the Physical Chemistry course. At this stage the relation is expressed as

$$\Delta T = i K_b m$$

where i is the number of ions furnished upon dissociation of the ionic solute. In case of molecular solutes i = 1.

$K_b$ is the boiling point elevation constant, specific for each solvent

m is molality and defined as the number of moles of solute in 1 kg of solvent.

The freezing point of a solution is lower than that of the pure substance that acts as the solvent in the solution. Again, the derivation of the relation between the amount by which the freezing point is depressed and the concentration of the solute is delayed until the Physical Chemistry course. At this stage, the relation is expressed in terms of a constant, $K_b$ called the freezing point depression constant, viz

$$\Delta T = i K_b m \ .$$

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# CHAPTER 10

# CHEMICAL KINETICS

A balanced chemical equation and principles of stoichiometry that have been introduced so far allow us to calculate the amounts of reactants required or the products formed in the case of the expected reaction actually taking place. However, the expected reaction does not take place between every single atom and/or molecule of the reactants. Only some atoms and/or molecules react and that proceeds at a rate that is dependent on a number of factors.

Chemical kinetics is the branch of chemistry that studies these dynamic aspects of chemical reactions.

Chemical reactions can be classified in a number of ways. One of these is to consider the number of phases involved in them. A reaction is homogeneous if it takes place in one phase alone. It is heterogeneous if it requires the presence of at least two phaes, e.g.

$A_{(g)} + B_{(g)} \rightarrow AB_{(g)}$ : Homogeneous

$C_{(s)} + D_{(g)} \rightarrow CD_{(g)}$ : Heterogeneous.

In the discussion of reaction rates in the following section, the homogeneous type is considered first.

## 10- 1 Rates of chemical reactions

The rate of a chemical reaction is defined as the change in the concentration of a reactant, or product, per unit time during the progress of the reaction.

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Consider the homogeneous reaction

$$A + B \rightarrow AB \qquad (10.1)$$

The graphs of concentrations of the species involved versus time of reaction are illustrated in Figure 10.1 The concentration of the reactants decrease as the products are formed and the reaction progresses.

According to the definition of reaction rate given above, the rate of the reaction considered can be expressed as

$$r = -\Delta [A] / \Delta t \qquad (10.2)$$

$$= \frac{[A]_2 - [A]_1}{t_2 - t_1} \qquad (10.3)$$

where $[A]_2 < [A]_1$ and $t_2 > t_1$

hence $\Delta [A] / \Delta t$ is negative and rate, r, is positive.

Similarly, the reaction rate in terms of reactant B is,

$$r = -\Delta [B] / \Delta t \qquad (10.4)$$

The reaction rate in terms of the concentration of product AB is written as

$$r = -\Delta [AB] / \Delta t \qquad (10.5)$$

$$= \frac{[AB]_2 - [AB]_1}{t_2 - t_1} \qquad (10.6)$$

where $[AB]_2 > [AB]_1$ and $t_2 > t_1$

hence $\Delta [AB] / \Delta t$ is positive.

Since equations 10.2, 10.4 and 10.5 are expressions for the rate of the same reaction

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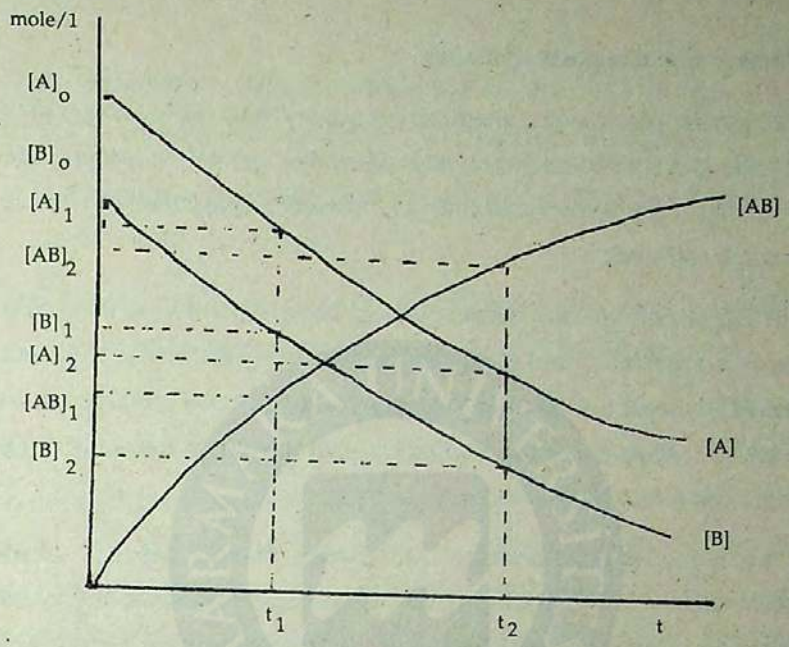


**Figure 10.1** Variation of concentration with time in a reacting system.

$$r = -\Delta [A] / \Delta t = -\Delta [B] / \Delta t = \Delta [AB] / \Delta t \qquad (10.7)$$

For a real reaction,

$$N_2 + 3H_2 \rightarrow 2NH_3 \qquad (10.8)$$

$$r = -\Delta [N_2] / \Delta t = -1/3\, \Delta [H_2] / \Delta t = 1/2\, \Delta [NH_3] / \Delta t.$$

Generalizing, the rate expression for a reaction

$$aA + bB \rightarrow cC \qquad (10.9)$$

is written as

$$r = -1/a\, \Delta [A] / \Delta t = -1/b\, \Delta [B] / \Delta t = 1/c\, \Delta [C] / \Delta t. \qquad (10.10)$$

When the time increment approaches zero

$$r = -1/a\, d [A] / dt = -1/b\, d [B] / dt = 1/c\, d [C] / dt \qquad (10.11)$$

In Figure 10.1, for the reaction (10.1), the rate at time t is the slopes of the tangents to the three curves which are equal in magnitude but opposite in sign, i.e.

$$r_t = -d [A] / dt = -d [B] / dt = d [AB] / dt.$$

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## 10- 2 Factors that affect reaction rates

A reaction between any chemical species involves the breakage of existing bonds and formation of new ones. However, before the reacting species get to that stage they have to come into contact with each other. This occurs through collisions.

In a gaseous reaction system, collisions occur as a result of the continuous motion of the molecules within the container they are held in. Collision between the molecules is the first condition for a reaction to commence. As discussed in Chapter 8, the collision of the molecules with the walls of the container is the cause of gas pressure.

The frequency of collisions molecules will undergo depends on the population density of the reacting molecules in total. That is, the higher the concentration of the reactants the higher the frequency of collisions and therefore a high rate of reaction is expected.

For the simple reaction of A and B expressed as in (10.1), the rate according to the logic above, is proportional to the product of the concentrations of A and B, i.e.

$$r \propto [A][B]$$

or

$$r = k[A][B]$$

where k, for the time being, should be accepted as a proportionality constant implying that all collisions do not result in a reaction. Only a fraction will do so.

For the reaction formulated in a general way as in (10.9), the rate expression, or the rate law, becomes

$$r = k[A]^a[B]^b. \qquad (10.12)$$

The indecies a and b are called the order of the reaction with respect to reactants A and B respectively. (a + b) is the overall order of the reaction.

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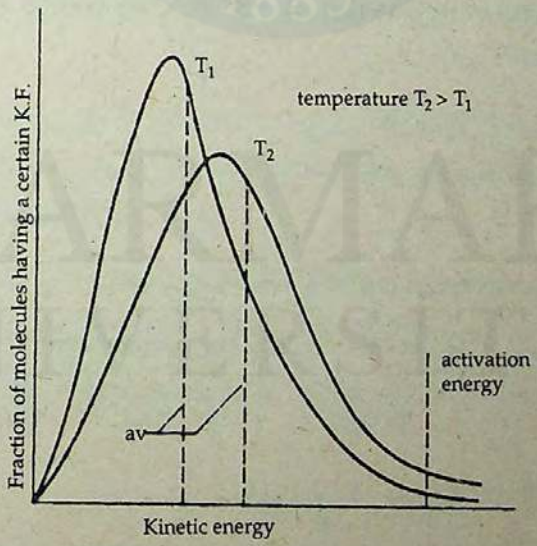
The observation that only a small fraction of molecular collisions are effective in producing a chemical reaction is based on two factors:

(1) Only the more energetic molecules in a mixture undergo reaction as a result of collisions.

(2) The probability of a particular collision resulting in a chemical reaction depends on the orientation of the colliding molecules.

The energy that molecules must possess in order to bring about a reaction is called the activation energy. A hypothetical activation energy and the fraction of molecules possessing energies in excess of this value are indicated on a distribution curve of molecular energies in Figure 10.2. As the temperature increases the average molecular energy increases and a higher fraction of molecules possesses energies greater than the activation energy of the reaction considered.




At the higher temperature $T_2$, the distribution of energies is broadened: the average molecular kinetic energy increases and many more molecules possess energies greater than the activation energy.

**Figure 10.2** Distribution of molecular energies

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The colliding molecules, as well as possesing adequate energy, must have a favourable orientation with respect to each other in order to react. As indicated in Figure 10.3, the number of unfavourable orientations for reaction generally exceeds the number for favourable ones. So, the probability of a particular collision having favourable orientation of the molecules is always less than 1.

According to the discussion above, the rate of a reaction can be expressed as

$$r = p\,f\,Z \qquad (10.13)$$

where p is the probability of favourable orientation of the collisions,

f is the fraction of the molecules with energies greater than the activation energy, EA,

Z is the collision frequency.

Collision frequency, Z, is proportional to the concentration of the reacting molecules. Therefore,

$$r \propto p\,f\,[A]^a\,[B]^b$$

or

$$r = k\,[A]^a\,[B]^b \qquad (10.14)$$

### 10- 2.1 The rate constant and activation energy

The k term, that has been introduced earlier as the proportionality constant, is actually called the reaction rate constant and in terms of temperature and $E_A$

$$k = k_o\,e^{-E_A/RT} \text{ (Arrhenius equation)} \qquad (10.15)$$

where $k_o$ = is called the pre-exponential factor and is a constant for each reaction.

A mathematical analysis of this expression reveals that the value of k

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increases with temperature and decreases with $E_A$ resulting in a higher and a lower reaction rate respectively.

Taking the natural log of both sides of expression (10.15),

$$\ell n\, k = \ell n\, k_o - E_A / RT \qquad (10.16)$$

is obtained.

The graph of $\ell n\ k$ versus $1/T$ is a straight line with $-E_A / R$ as the slope and $\ell n\, k_o$ as the intercept (Figure 10.4). $k_o$ is considered as the rate constant as $T \rightarrow \infty$.

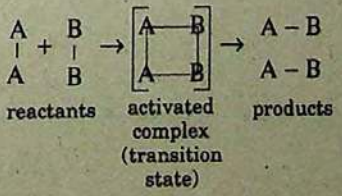
Values of activation energies for reactions are determined by applying this relationship to the values of k obtained experimentally at varying temperatures.

The minimum energy requirement for the colliding molecules to effect a reaction can be explained in terms of the Transition State Theory developed by the American chemist Henry Eyring. In the reaction of

$$A_2 + B_2 \rightarrow 2\,AB,$$

for the two molecules of AB to form, the bonds in the $A_2$ and $B_2$ molecules have to break and a bond in each of the AB molecules have to form. This process is represented as follows:

The activated complex has old bonds stretched to the breaking point and new bonds only partially formed. The formation of the A-B bond releases energy but the breakage of A-A and B-B bonds requires energy. Since the two processes occur simultaneously, all of the energy released in bond for-



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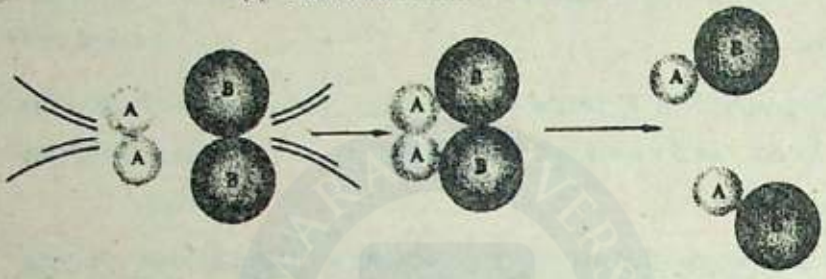
(a) Unfavorable collision for chemical reaction




(b) Favorable collision for chemical reaction

**Figure 10.3** Molecular collisions and chemical reactions

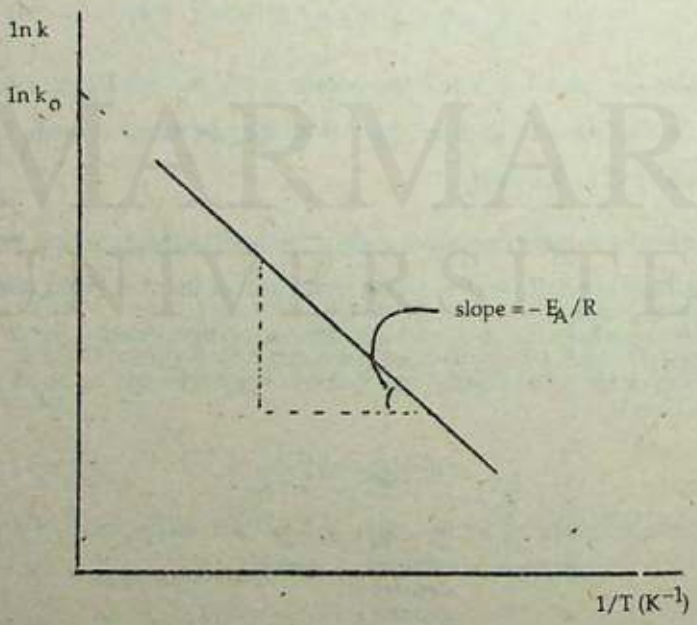



**Figure 10.4** Determination of activation energy

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mation cannot be utilized for the breakage of the bonds in the two reactants. Some energy, therefore, has to be invested, sometimes temporarily, to get to the transition state.

In Figure 10.5 the energy diagrams for two types of reactions are given. Potential energy is plotted versus the reaction coordinate, ε (epsilon), which is defined as the extent of reaction.

Potential energy of a chemical species is its enthalpy of formation, $\Delta H°_f$ . At the beginning of a reaction $\varepsilon = 0$ and only the reactants are present in the system. The total potential energy of the reaction system is therefore the sum of enthalpies of formation of the reactants. In order for the products to form, the energy barrier $E_A$ has to be overcome. The potential energy of the system increases to the level of $E_A$ during the transition state. Once the products are formed, the energy of the system decreases to the level determined by the sum of the enthalpies of formation of the products. The difference between the final and initial energy levels of the system is the enthalpy of reaction, $\Delta H°_r$ .

For an endothermic reaction, the final energy level of the system is higher than the initial one. There is a net energy requirement by the system that has to be supplied from external sources - a positive $\Delta H°_r$ .

For an exothermic reaction the situation is reversed. The final energy level of the system is lower than the initial level. The surplus energy of the system is dissipated to the outside in the form of heat - a negative $\Delta H°_r$ .

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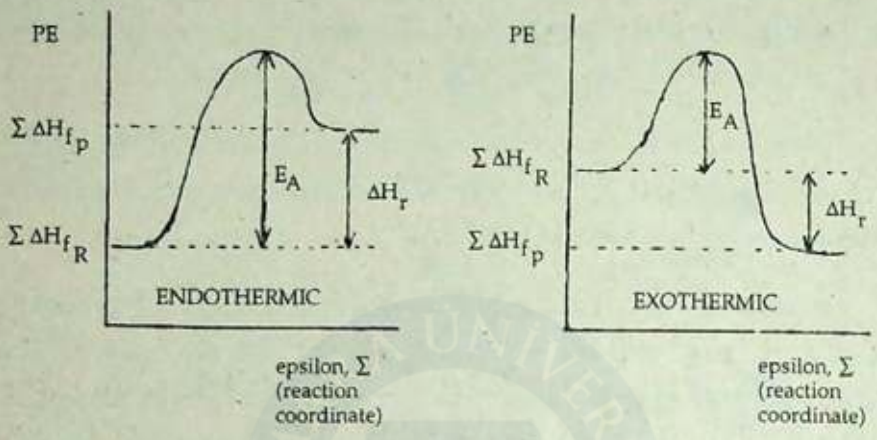


**Figure 10.5** Energy diagrams

### 10- 2. 2 Catalysis

The rate of a homogeneous reaction can be increased with the introduction of a third party to the reaction system that does not take a nett part in in the reaction but makes it easier for the reactants to react. Such a substance is called a catalyst and the process is catalysis.

A catalyst effects an increase in the rate of the reaction by providing an alternative reaction path that has a lower activation energy (Figure 10.6).

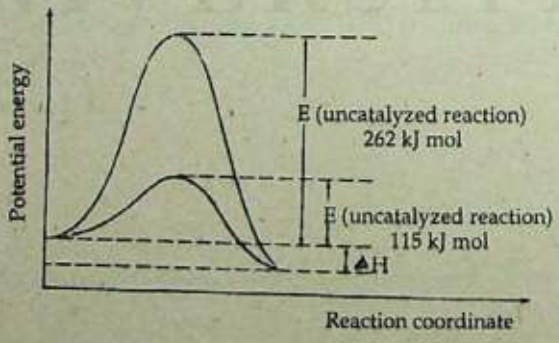


**Figure 10.6** Activation energy of isomerization of cis-2-butene to trans -2- butene

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## 10- 3 Heterogeneous reactions

The factors discussed above affect both homogeneous and heterogeneous reactions. However, the rate of a heterogeneous reaction, in the presence of a solid phase, is further affected by the size of the solid particles.

In heterogeneous reactions two different phases have to come into contact for the reaction to commence. The greater the extent of the contact between the reactants in the two phases, the higher the probability of a reaction. In the case of a solid and a nonsolid reactant, contact is achieved via the surface of the solid to which the nonsolid reactant has access. The reaction rate therefore increases with the surface area of the solid.

The surface area of a given amount of solid increases inversely with the size of the solid particles that make it up. The rate of a heterogeneous reaction involving solids therefore increases inversely with the size of the particles.

## 10- 4 Reaction mechanisms

The balanced equation does not always tell us how a reaction occurs. It merely summarizes the numbers of moles of reactants necessary to produce a given number of moles of products. It does not necessarily mean that in

$$aA + bB \rightarrow cC$$

a moles of A are colliding with b moles of B and yielding c molec of C. It could be that

$$aA \rightarrow a'A' \qquad (10.17A)$$

$$a'A' + bB \rightarrow cC \qquad (10.17B)$$

to yield $aA + bB \rightarrow cC$ as the overall reaction. (10.17C)

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The actual information about the mechanism of a reaction is obtained by studying experimentally the effect of the change in the concentration of each reactant on the rate of the reaction.

With regards to the number of moles of reactants involved reactions can be classified as follows:

**Unimolecular reactions**

$A \rightarrow$ Products

The reactant molecule, under appropriate conditions, dissociates to yield the products.

**Bimolecular reactions**

$A + B \rightarrow$ Products

or $2A \rightarrow$ Products

Reaction occurs upon collision of reactant A molecules with reactant B molecules or among themselves.

**Termolecular reactions**

$2A + B \rightarrow$ Products

or $A + B + C \rightarrow$ Products

or $A + 2B \rightarrow$ Products

In this type of reactions, simultaneous collision of three reactant molecules is required.

Reactions can take place in a single step or in multi steps. Single step reactions whereby the products are formed directly from the original reactants are called elementary reactions. The stoichiometric equation for the reaction also represents the mechanism of the reaction. In multistep reactions, the reaction takes place in a stepwise fashion as in (10.17A) to (10.17C).

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## 10- 5 Rate laws for nonelementary reactions

Consider the reaction

$$aA + bB \rightarrow cC \qquad (10.17C)$$

occuring in two steps at different rates, i.e.

| | | | |
|---|---|---|---|
| Step 1 | $a\,A \rightarrow a'A'$ | SLOW | (10.17A) |
| Step 2 | $a'\,A' + bB \rightarrow cC$ | FAST | (10.17B) |
| | $aA + bB \rightarrow cC$ | | (10.17C) |

The overall reaction (10.17C) proceeds at the rate of the slowest step (10.17A). This step is called the the rate determining, or the rate controlling, or the rate limiting, step. Such reactions, for which the overall balanced equations do not represent the actual mechanisms, are called nonelementary reactions.

The rate expression, or the rate law, for an elementary reaction is based on the stoichiometric equation and that for a nonelementary reaction is based on the slowest reaction step. The rate law for the above reaction is therefore

$$r = k\,[A]^a .$$

## 10- 6 Determination of rate laws

The three methods listed below are generally used:

1) Initial rate method

2) Integrated rate law method

3) Half-life method

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**1) Initial rate method**

The method involves measuring the initial rate of a reaction for different sets of initial concentrations i.e. measuring the slope of the [A], or [B] or [AB] curve in Figure 10.1 at t = 0. The order of the relation between rate and concentration of each of the reactants is established.

Prior to introducing an illustrative example, a first, second and third order relation between the dependent variable y and the independent variable x are reviewed.

| | $y = a$ | $y = ax$ | $y = ax^2$ | $y = ax^3$ |
|---|---|---|---|---|
| $x = 1$ | $y = a$ | $y = a$ | $y = a$ | $y = a$ |
| $x = 2$ | $y = a$ | $y = 2a$ | $y = 4a$ | $y = 8a$ |
| $x = 3$ | $y = a$ | $y = 3a$ | $y = 9a$ | $y = 27a$ |

**Example 1**

The following data are obtained for the reaction between reactants A and B. Determine the rate law for the reaction and the value of k.

| | Run | $[A]_{t=0}$ | $[B]_{t=0}$ | Initial rate (moles/ℓ s) |
|---|---|---|---|---|
| | 1 | 0.2 | 0.1 | 1.0 |
| (Constant temperature) | 2 | 0.2 | 0.3 | 3.0 |
| | 3 | 0.4 | 0.3 | 12.0 |

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**Solution**

Write out the possible chemical equation for the reaction - or the rate determining step.

$$aA + bB \rightarrow \text{products}$$

The rate equation is

$$r = k\,[A]^a\,[B]^b.$$

In Run 2, when the concentration of A is kept constant and the concentration of B is tripled, the rate is tripled. Therefore $b = 1$. In Run 3, the concentration of B is the same as in Run 2 but the concentration of A is doubled. The rate is increased four-fold. Therefore $a=2$. Hence the rate equation.

$$r = k\,[A]^2\,[B]$$

The equation for the rate determining step can be written as

$$2A + B \rightarrow \text{products}$$

To determine the value of k take any one of the three runs and substitute the known values into the rate equation.

Take Run 1: $1\ (\text{moles}/1\ s) = k\ (0.2)^2\ (\text{moles}/1)^2\ (0.1)\ (\text{mole}/1)$

$$k = 250\ (1^2/\text{mole}^2\ s)$$

**2) Integrated rate law method**

The rate law is determined directly from a suitable plot of concentration versus time. The differential expression of rate has to be integrated to determine the correct relation between concentration of a participant in a reaction versus time.

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For a zeroth order reaction, $r = -d[A]/dt = k$

(A) → prod.

$$-d[A] = k\,dt$$

$$-\int_{A_o}^{A} d[A] = k\int_{t=0}^{t} dt$$

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

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

The expression above is in the form of an equation for a straight line i.e. $y = ax + b$. Hence, if the plot of concentration of the reactant vs. time is a straight line, then the reaction is 0th order with respect to reactant A. 0th order reactions are encountered in catalyzed or gas/solid reactions.

For a first order reaction, $r = -d[A]/dt = k[A]$

A → prod.

$$-d[A]/dt = k[A]$$

$$-d[A]/[A] = k\,dt$$

$$-\int_{A_o}^{A} d[A]/[A] = k\int_{t=0}^{t} dt$$

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$$-\,|\,\ell n[A]\,|_{A_o}^{A} = kt$$

$$-\,|\,\ell n[A] - \ell n[A]_o\,| = kt$$

$$-\ell n[A] + \ell n[A]_o = kt$$

$$\ell n[A] = -kt + \ell n[A]_o .$$

The expression above is in the form of an equation for a straight line i.e. $y = ax + b$. Hence, if the plot of concentration ($\ell n$) vs. time is a straight line, then the reaction is first order with respect to reactant A.

For a second order reaction, $r = -\,d[A]/dt = k[A]^2$

$2A \rightarrow$ prod.

$$-\,d[A]/[A]^2 = k\,dt$$

$$-\int_{A_o}^{A} d[A]/[A]^2 = k\int_{t=0}^{t} dt$$

$$-\,|\,-1/[A]\,|_{A_o}^{A} = kt$$

$$1/[A] - 1/[A]_o = kt$$

$$1/[A] = kt + 1/[A]_o$$

Hence, if a plot of reciprocal concentration versus time is a straight line, then the reaction is second order with respect to reactant A.

**3) Half-life method**

Half-life, $t_{1/2}$, is the time required for the concentration of a reactant to decrease to half its initial value. The relation between half-life and concentration of the reactant changes depending on the order of the reaction.

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For a zeroth order reaction

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

$$[A]_o/2 = -kt_{1/2} + [A]_o$$

$$t_{1/2} = [A]_o / 2k$$

For a first order reaction

$$\ell n\,[A] = -kt + \ell n\,[A]_o$$

$$\ell n\,[A]_o/2 = -kt_{1/2} + \ell n\,[A]_o$$

$$\ell n\,[A]_o\,\ell n\,2 = -kt_{1/2} + \ell n\,[A]_o$$

$$t_{1/2} = 0.693/k.$$

For a second order reaction

$$1/[A] = kt + 1/[A]_o$$

$$1/[A]_o/2 = kt_{1/2} + 1/[A]_o$$

$$2/[A]_o - 1/[A]_o = kt_{1/2}$$

$$t_{1/2} = 1/k\,[A]_o$$

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# CHAPTER 11

## CHEMICAL EQUILIBRIUM

The stoichiometric equation for a reaction tells us how much of one reactant combines with how much of the other reactant (s) to yield the amount of product that is does.

The rate equation for a reaction tells us how fast a reaction will proceed using up the reactantants and forming the products in the raitos indicated by the stoichiometric equation. It also expresses the fact that the rate diminishes to zero when the reactants in a reacting system are depleted. However, a phenomenon, called chemical equilibrium, is usually observed before such a state is reached. Once the concentration of products reaches a certain level, the products start reacting to give back the reactants, i.e.

(Homogeneous, elementary)

$$aA + bB \underset{k_r}{\overset{k_f}{\rightleftarrows}} cC + dD \qquad (11.1)$$

(A reversible reaction)

The rate constant for the forward reaction (to the right) and the rate constant for the reverse reaction (to the left) are denoted by $k_f$ and $k_r$ respectively. The state of equilibrium in this reaction system will manifest itself as a constancy in the concentrations of all reactants and products (Figure 11.1).

A system in the state of equilibrium is not static: both forward and reverse reactions are taking place. However, there is no net conversion of one species to another. Forward and reverse reactions proceed at the same rate i.e.

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$$H_2(g) + I_2(g) \rightleftarrows 2HI(g)$$

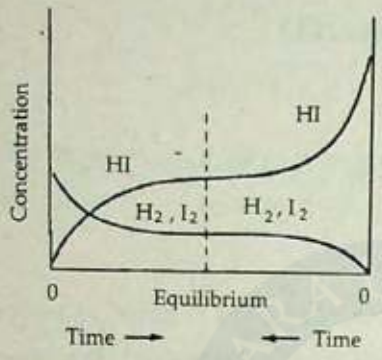


**Figure 11.1** Concentration changes during approach to equilibrium

On the left, we start with equal initial concentrations of $H_2$ and $I_2$. As the reaction proceeds, the concentrations of $H_2$ and $I_2$ decrease and the concentration of HI increases, until each attains a constant value at equilibrium. On the right, we start with HI alone. As the reaction to give $H_2$ and $I_2$ proceeds, the concentration of HI decreases and the concentrations of $H_2$ and $I_2$ increase, until they all become constant when equilibrium is reached. In the figure the initial concentration of HI on the right is twice the initial concentration of $H_2$ and $I_2$ on the left. Under these circumstances the same equilibrium mixture is attained whether we start from the left or from the right.

$$r_f = r_r$$

For the reaction formulated by (11.1),

$$r_f = k_f [A]^a [B]^b \qquad (11.2)$$

$$r_r = k_r [C]^c [D]^d \qquad (11.3)$$

and, at equilibrium

$$k_f [A]^a [B]^b = k_r [C]^c [D]^d$$

$$k_f / k_r = [C]^c [D]^d / [A]^a [B]^b$$

$$= K \qquad (11.4)$$

The ratio of the two rate constants is denoted by K, the equilibrium constant. Since both k's are functions of temperature, K is a function of temperature also.

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## 11-1 Equilibrium in non-precipitating systems

Consider the reversible reaction between hydrogen and iodine:

$$H_2 + I_2 \rightleftarrows 2\,HI \qquad (11.5)$$

(Homogenous, gas phase)

$H_2$ and HI are colourless gases whereas $I_2$ has a distinct violet colour. Under suitable conditions, $H_2$ combines with $I_2$ to form HI. The intensity of the violet colour in the system gradually decreases as more and more $I_2$ is consumed. Eventually no more colour changes are observed: equilibrium is reached. If the concentration values of $H_2$, $I_2$ and HI at this stage are substituted into the expression

$$[HI]_2 / [H_2]\,[I_2],$$

the value of the equilibrium constant K for the reaction, at the reaction temperature, is obtained. Irrespective of the initial concentrations of the reactants, the same value of K (at the same temperature) is obtained once the reaction reaches equilibrium.

For the general reaction formulated by (11.1), the expression

$$[C]^c\,[D]^d / [A]^a\,[B]^b,$$

at any time t during the reaction is called the reaction quotient and is denoted by Q.

Of course, if $t = t_{eq}$

then $Q = K$

and, the reaction is at equilibrium.

If $t < t_{eq}$

then $Q < K$

and, the reaction is proceeding in the forward direction.

If $Q > K$

then, the reaction is proceeding in the reverse direction.

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### 11- 1 .1 Temperature dependence of K

Consider the reversible reaction formulated by (11.1). In the first case let us assume it is an endothermic reaction (Figure 11.2)

By definition $K = k_f / k_r$ .

But $k_f = k_{of} e^{-E_{Af}/RT}$

$k_r = k_{or} e^{-E_{Ar}/RT}$ and

$$K = \frac{k_{of} e^{-E_{Af}/RT}}{k_{or} e^{-E_{Ar}/RT}}$$

Since both $k_{of}$ and $k_{of}$ are constants, their ratio is a constant.

Also $E_{Af} = E_{Ar} + \Delta H_r$ (Figure 11.2). (11.6)

The expression for K therefore reduces to

$$K = \text{const } e^{-\Delta H_r / RT} \quad (11.7)$$

For endothermic reactions, $\Delta H_r$ is a positive value. Hence, K increases with temperature.

Assuming the reaction is exothermic (Figure 11.3) $E_{Af}$ is still expressed by (11.6) and the expression for K reduces to (11.7).

For exothermic reactions, $\Delta H_r$ is a negative value. Hence, K decreases with temperature.

Taking the natural log of both sides of the equality in (11.7)

$$\ell n\, K = \ell n\, (\text{const}) - \Delta H_r / R \;.\; 1/T \quad (11.8)$$

A plot of the natural logs of the K values for a reaction at different temperatures versus 1/T yields a straight line with slope $-\Delta H_r / R$ and $\ell n\, (k_{of} / k_{or})$ as the intercept.

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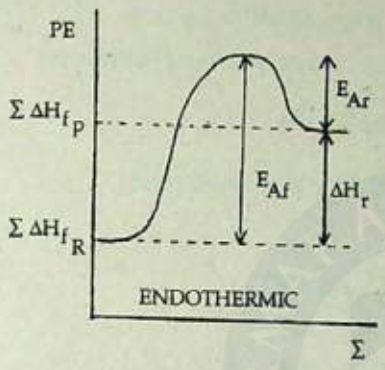


Figure 11.2

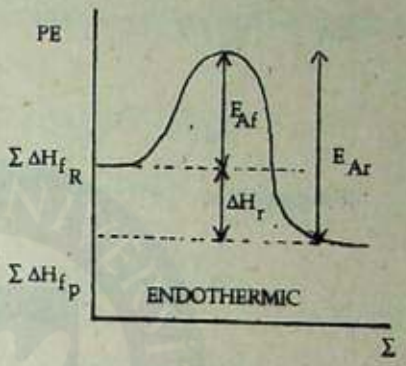


Figure 11.3

### 11- 1 .2 An alternative equilibrium constant in gaseous systems

Assume the homogeneous reaction,

$$aA + bB \rightleftarrows cC + dD \qquad (11.1)$$

is taking place in the gas phase.

The expression for the equilibrium constant, in terms of concentrations, is

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b} \qquad (11.9)$$

The partial pressures of the species in the system at equilibrium are

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$p_C = n_C / V.RT$ $\qquad p_D = n_D / V.RT$

$p_A = n_A / V.RT$ $\qquad p_B = n_B / V.RT$

But $\quad n_C / V = [C] \qquad n_D / V = [D]$

$n_A / V = [A] \qquad n_B / V = [B].$

It follows that

$[C] = p_C / RT \qquad [D] = p_D / RT$

$[A] = p_A / RT \qquad [B] = p_B / RT.$

Substituting these expressions in (11.9)

Let

$$K = \frac{p_C^c \, p_D^d}{p_A^a \, p_B^b} (RT)^{(a+b-c-d)} \qquad (11.10)$$

then

$$K = K_p (RT)^{(a+b-c-d)}$$

$$K_p = \frac{p_C^c \, p_D^d}{p_A^a \, p_B^b}$$

or $\quad K_p = K (RT)^{\Delta n} \qquad (11.11)$

where $\quad \Delta n = c + d - a - b.$

$$= \Sigma n_{prod} - \Sigma n_{react}$$

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### 11-1.3 Heterogeneous equilibrium

If the reacting system is a heterogeneous one, the equilibrium reached in this system is called heterogeneous equilibrium.

The decomposition of calcium carbonate to lime and carbon dioxide is a reversible heterogeneous reaction:

$$CaCO_{3(s)} \rightleftarrows CaO_{(s)} + CO_{2(g)}$$

The expression for the equilibrium constant is

$$K' = \frac{[CaO]_{(s)}\ [CO_2]_{(g)}}{[CaCO]_{(s)}}$$

The concentration of a solid is effectively its density which is constant. Only $[CO_2]$ is a variable in the above expression. Hence,

$$\frac{K'\ [CaO_3]_{(s)}}{[CaO]_{(s)}} = K = [CO_2]_{(g)} \qquad (11.12)$$

The equilibrium constant for a heterogeneous system involving solids can therefore be formulated as

$$K = \frac{\pi\ [Prod_{i\ (nonsolid)}]^{\nu_i}}{\pi\ [Prod_{i\ (nonsolid)}]^{\nu_i}} \qquad (11.13)$$

where $\pi$ is the product (of)

$\nu_i$ is the stoichiometric constant of the i'th species in the in the chemical equation for the elementary reaction (or the rate determining step).

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### 11- 1 .4 Effects of changes in the equilibrium conditions - Le Chatelier's Principle

A qualititative rule about the effects of changes in any one of the factors that affects equilibrium has been stated as follows by the French chemist Henri Le Chatelier (1884):

"If a system at equilibrium is disturbed, the equilibrium condition is upset. The reaction proceeds in the direction that tends to relieve the disturbing influence."

Going from Le Chatelier's principle, increasing the concentration of the reactants in a reacting system is expected to drive the reaction in the forward direction. Conversely, if the concentration of the products is increased, the reaction is driven in the reverse direction.

The concentration of the species in a reacting system can be varied in a number of ways. One obvious method is to inject the desired species into the reacting system externally. Also, in gaseous systems, the concentration of all the species can be modified by varying the volume of the reaction vessel if it is physically possible.

The effect of changes in the concentrations of species on equilibrium can be predicted quantitatively by comparing the new value of Q with that of K.

The effect of changes in the temperature of a system which is already at equilibrium can be predicted depending on whether the reaction is endothermic or exothermic.

Consider an endothermic reaction at equilibrium. The temperature of the system is increased by supplying energy to the system. The equilibrium is upset. The upsetting influence can be relieved by using up the energy that is added to the system. The reaction therefore resumes in the forward direction consuming energy thus relieving the disturbing influence.

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The reverse takes place in an exothermic reaction system. The reaction resumes in the reverse direction, which is endothermic, in order to relieve the system from the additional energy.

The same conclusions can be reached if the mathematical expression of K, in terms of temperature, is considered as in section 11.1.1.

## 11- 2 Precipitating systems

Solutions are homogeneous mixtures of two or more substances. The solute is the component that dissolves in the solvent. The solute considered under the present topic is a solid under atmospheric conditions and the solvent is water.

It is not possible to dissolve an unlimited amount of a solid in a given volume of water. Even those solids which are well known for their solubility in water dissolve only to a certain extent. Once that limit is reached, the additional amount will remain in water as a solid under constant temperature.

A solution that contains the maximum amount of solute that can be dissolved at the prevailing temperature is called a saturated solution. The concentration of the solute in a saturated solution is called the solubility of the solute in that solvent - water in this case.

The dissolution process can be considered as a chemical reaction. Indeed, it fits the description of a chemical reaction: the ionic bond in the solute - solids that dissolve in water are generally ionic compounds - is broken and hydration of the ions takes place. Although no chemical bonds are formed in the hydration process, attractive forces between the ions and the water molecules are created.

For the dissolution of the compound AB in water, the following equation can be written:

$$AB_{(s)} \rightleftarrows A^{+}_{(ag)} + B^{-}_{(ag)} \qquad (11\ 11)$$

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The reaction is reversible. The rate of the reverse reaction exceeds that of the forward reaction once saturation is achieved.

In the reverse reaction, $A^+$ combines with $B^-$ to form the solid- the precipitate - AB. At the saturation point, the concentration of each ion in the solution is at its maximum. The situation is exactly the same as the chemical exuilibrium. The rate of the forward reaction (dissociation) is equal to the rate of the reverse reaction (association or precipitation) i.e.

$$r_{dis} = r_{ass}$$

where $r_{dis} = k_{dis}[AB_{(s)}]$

and $r_{ass} = k_{ass}[A^+][B^-]$.

Let $K' = k_{dis} / k_{ass}$

$$= \frac{[A^+][B^-]}{[AB_{(s)}]}.$$

As discussed in the previous sections, the concentration of a solid that remains as a solid in a reacting systing system is considered constant.

Hence $K'[AB_{(s)}] = [A^+][B^-]$

$$K_{sp} = [A^+][B^-] \text{ (at equilibrium)} \qquad (11.15)$$

The left-hand-side (LSH) still remains a constant but the symbol is now $K_{sp}$ and is called the "solubility product". At a given temperature, once the product of the concentrations of the ions reaches this value, no more net dissolution takes place in the system. The solution is saturated.

The expression and the concept of "Q" is valid in solutions also. For the system considered above

$$Q = [A^+][B^-] \text{ at any time t.}$$

If $t = t_{sat}$

then $Q = K_{sp}$

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and, the solution is saturated (precipitation is just about to start or there is already a precipitate in the system).

If $t < t_{sat}$

then $Q < K_{sp}$

and, the solution is unsatured. Further dissolution can take place.

If $Q > K_{sp}$

then precipitation is occurring and a saturated solution is obtained.

$K_{sp}$, being the ratio of two temperature dependent rate constants, $k_{dis}$ and $k_{ass}$, is a function of temperature in the same manner as K is, i.e.

$$K_{sp} = \text{const}\, e^{-\Delta H^{\circ}_{sol} / RT}.$$

Applying the same mathematical analysis as in the previous section, it can be shown that in a endothermic dissolution process $K_{sp}$ increases with temperature whereas in an exothermic process $K_{sp}$ decreases with temperature.

Most dissolution processes in water are endothermic. Solubility increaes with temperature.

Figure 11.4 illustrates the effect of temperature on the solubility of various ionic compounds in water.

Depending on their solubilities at constant temperutare (usually measured at 25°C) compounds can be broadly classified as soluble, sparingly soluble and insoluble:

| | | | |
|---|---|---|---|
| for | solubility $\geq$ | 0.1 mole/ℓ; | soluble |
| $0.01 \leq$ | solubility $\leq$ | 0.1 mole/ℓ; | sparingly soluble |
| | solubility $<$ | 0.01 mole/ℓ; | insoluble. |

Such a classification is shown in Table 11.1.

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Table 11.2 lists the solubility product constant, at 25°C, for some slightly soluble salts.

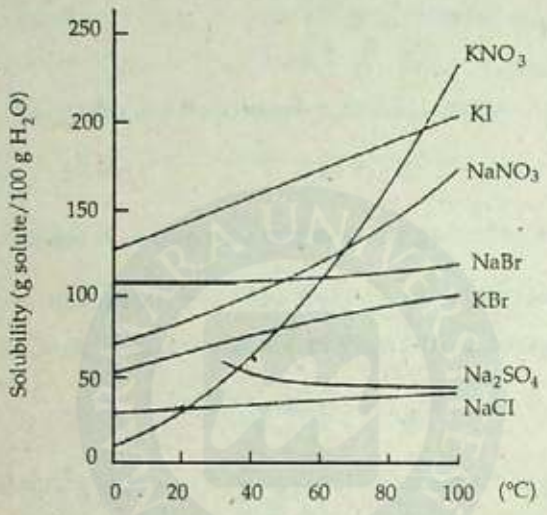


**Figure 11.4** Temperature dependence of solubility

| | | EXCEPTIONS |
|---|---|---|
| SOLUBLE | INSOLUBLE | SPARINGLY SOLUBLE |
| $Na^+$, $K^+$, and $NH_4^+$ salts | | |
| Nitrates | | |
| Perchlorates | | |
| Chlorides, bromides, and iodides | $Ag^+$, $Pb^{2+}$, $Hg_2^{2+}$ | $PbCl_2$, $PbBr_2$ |
| Sulfates | $Sr^{2+}$, $Ba^{2+}$, $Pb^{2+}$ | $Ca^{2+}$, $Ag^+$, $Hg_2^{2+}$ |
| Acetates | $Ag^+$, $Hg_2^{2+}$ | |

| | | EXCEPTIONS |
|---|---|---|
| INSOLUBLE | SOLUBLE | SPARINGLY SOLUBLE |
| Carbonates | $Na^+$, $K^+$, $NH_4^+$ | |
| Phosphates | $Na^+$, $K^+$, $NH_4^+$ | |
| Sulfides | $Na^+$, $K^+$, $NH_4^+$, $Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$ | |
| Hydroxides | $Na^+$, $K^+$, $NH^+$, $Ba^{2+}$ | $Ca^{2+}$, $Sr^{2+}$ |

**Table 11.1** Solubilities of some common salts and hydroxides in water at 25°C.

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| | $K_{sp}$ | | $K_{sp}$ |
|---|---|---|---|
| **Bromides** | | | |
| $PbBr_2$ | $4.6 \times 10^{-5}$ | $Fe(OH)_2$ | $1.8 \times 10^{-15}$ |
| $Hg_2Br_2$ | $1.3 \times 10^{-22}$ | $Fe(OH)_3$ | $1.0 \times 10^{-38}$ |
| $AgBr$ | $5.0 \times 10^{-13}$ | $Pb(OH)_2$ | $4.2 \times 10^{-15}$ |
| **Carbonates** | | $Mg(OH)_2$ | $8.9 \times 10^{-12}$ |
| $BaCO_3$ | $1.6 \times 10^{-9}$ | $Sr(OH)_2$ | $3.2 \times 10^{-4}$ |
| $CaCO_3$ | $4.7 \times 10^{-9}$ | $Zn(OH)_2$ | $4.5 \times 10^{-17}$ |
| $CuCO_3$ | $2.5 \times 10^{-10}$ | Iodides | |
| $FeCO_3$ | $2.1 \times 10^{-11}$ | $PbI_2$ | $8.3 \times 10^{-9}$ |
| $PbCO_3$ | $1.5 \times 10^{-15}$ | $Hg_2I_2$ | $4.5 \times 10^{-29}$ |
| $MgCO_3$ | $1 \times 10^{-15}$ | $AgI$ | $8.5 \times 10^{-17}$ |
| $Ag_2CO_3$ | $8.2 \times 10^{-12}$ | Phosphates | |
| $SrCO_3$ | $7 \times 10^{-10}$ | $Ba_3(PO_4)_2$ | $6 \times 10^{-39}$ |
| $ZnCO_3$ | $2 \times 10^{-10}$ | $Ca_3(PO_4)_2$ | $1.3 \times 10^{-32}$ |
| **Chlorides** | | $Ag_3PO_4$ | $1.8 \times 10^{-18}$ |
| $PbCl_2$ | $1.7 \times 10^{-5}$ | $Sr_3(PO_4)_2$ | $1 \times 10^{-31}$ |
| $Hg_2Cl_2$ | $1.1 \times 10^{-18}$ | Sulfates | |
| $AgCl$ | $1.7 \times 10^{-10}$ | $BaSO_4$ | $1.5 \times 10^{-9}$ |
| **Fluorides** | | $CaSO_4$ | $2.4 \times 10^{-5}$ |
| $BaF_2$ | $2.4 \times 10^{-5}$ | $PbSO_4$ | $1.3 \times 10^{-8}$ |
| $CaF_2$ | $3.4 \times 10^{-11}$ | $Ag_2SO_4$ | $1.2 \times 10^{-5}$ |
| $PbF_2$ | $4 \times 10^{-8}$ | $SrSO_4$ | $7.6 \times 10^{-7}$ |
| $MgF_2$ | $8 \times 10^{-8}$ | Sulfides | |
| $SrF_2$ | $7.9 \times 10^{-10}$ | $CuS$ | $8 \times 10^{-37}$ |
| **Hydroxides** | | $FeS$ | $6.3 \times 10^{-18}$ |
| $Al(OH)_3$ | $5 \times 10^{-33}$ | $PbS$ | $7 \times 10^{-29}$ |
| $Ba(OH)_2$ | $5.0 \times 10^{-3}$ | $HgS$ | $1.6 \times 10^{-54}$ |
| $Ca(OH)_2$ | $1.4 \times 10^{-6}$ | $Ag_2S$ | $5.5 \times 10^{-51}$ |
| $Cu(OH)_2$ | $1.6 \times 10^{-19}$ | $ZnS$ | $1.6 \times 10^{-24}$ |

**Table 11.2** Solubility product constants for some slightly soluble salts at 25°C

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## 11- 3 Equilibrium in aqueous solutions of acids and bases

Prior to the discussion of equilibrium in aqueous solutions of acids and bases three theories on the definitions of acids and bases will be introduced.

### 11- 3 .1 Overview of acid and base theories

According to **Savante Arrhenius** (1859 - 1927) acids are those chemical species which have at least one hydrogen atom attached to an electronegative atom or group of atoms. They dissociate in $H_2O$ to an hydrogen ion (proton) and an anion, i.e.

$$HCl \rightarrow H^+_{(aq)} + Cl^-_{(aq)}.$$

$$\text{In general} \quad HA \rightarrow H^+_{(aq)} + A^-_{(aq)}. \qquad (11.16)$$

The positively charged H atom cannot exist freely. It is attracted to the negatively (partially) charged oxygen atom of a water molecule and becomes attached to one of the unshared electron pairs to form the hydronium ion, $H_3O^+$. It is therefore more appropriate that the dissociation of an acid be expressed as

$$HA \rightarrow H_3O^+ + A^-. \qquad (11.17)$$

In the same manner, bases are described as substances which bear at least one hydroxyl group and dissociate in water as follows:

$$NaOH \rightarrow Na^+_{aq)} + OH^-_{(aq)}.$$

$$\text{In general} \quad BOH \rightarrow B^+_{(aq)} + OH^-_{(aq)}. \qquad (11.18)$$

Johannes **Bronsted** (1879 - 1947) and Thomas **Lowry** (1874 - 1936) defined acids as those chemical species which donate protons and bases as those which accept protons. An acid-base reaction is therefore referred to as a proton transfer reaction.

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When an acid gives up a proton the anion that is formed is a base since it can add a proton to reform the acid i.e.

$$HA \rightleftarrows H^+ + A^-.$$

The anion $A^-$ is called the conjugate ase of acid HA, and HA and $A^-$ are described as a conjugate acid-base pair.

| acid | | | conjugate base |
|---|---|---|---|
| $HCl$ | $\rightleftarrows$ $H^+$ | + | $Cl^-$ |
| $H_2O$ | $\rightleftarrows$ $H^+$ | + | $OH^-$ |
| $NH_4^+$ | $\rightleftarrows$ $H^+$ | + | $NH_3$ |
| $H_3O$ | $\rightleftarrows$ $H^+$ | + | $H_2O$ |

In the same manner, when a base accepts a proton, the cation $BH^+$ that is formed is an acid since it can lose a proton to give back the base B:

$$B + H^+ \rightleftarrows BH^+$$

The cation that is formed, $BH^+$, is called the conjugate acid of base B, and $BH^+$ and B are described as conjugate acid-base pair.

| base | | | conjugate acid |
|---|---|---|---|
| $H_2O$ | $\rightleftarrows$ $H^+$ | + | $H_3O^+$ |
| $NH_3$ | $\rightleftarrows$ $H^+$ | + | $NH_4^+$ |
| $OH^-$ | $\rightleftarrows$ $H^+$ | + | $H_2O$ |
| $F^-$ | $\rightleftarrows$ $H^+$ | + | $HF$ |

Since a base can obtain a proton only from an acid, and an acid can give up a proton only if there is a base to accept it, every Bronsted-Lowry acid-base reaction involves two conjugate acid-base pairs:

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$$HA + B \rightleftarrows BH^+ + A^-$$

$$acid_1 + base_2 \quad acid_2 \quad base_1$$

$$A_1 \quad B_2 \quad A_2 \quad B_1$$

$A_1$ - $B_1$ and $A_2$ - $B_2$ are the the two acid-base pairs, e.g.

$$HF + H_2O \rightleftarrows H_3O^+ + F^-$$

$$A_1 \quad B_2 \quad A_2 \quad B_1$$

Substances which can exhibit both acid and base properties are called amphoteric. For example $H_2O$, in the presence of HCl, behaves as a base but in the presence of $NH_3$ it behaves as an acid:

$$HCl + \underset{\text{(base)}}{H_2O} \rightleftarrows H_3O^+ + Cl^-$$

$$NH_3 + \underset{\text{(acid)}}{H_2O} \rightleftarrows NH_4^+ + OH^-$$

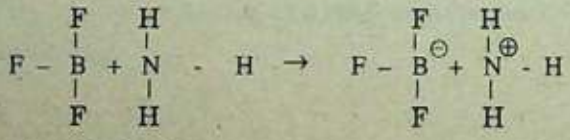
Because of its amphoteric nature water can self-ionize

$$H_2O + H_2O \rightleftarrows H_3O^+ + OH^-$$

$$A_1 \quad B_2 \quad A_2 \quad B_1$$

In 1923 G.N. **Lewis** suggested that all molecules and ions that combine with other molecules and ions accepting an electron pair should be regarded as acids. Similarly, all molecules and ions that provide an electron pair should be regarded as bases. It can therefore be said that Lewis acids are electron pair acceptors whereas Lewis bases are electron pair donars.

An illustrating Lewis acid-base reaction is given below:



Lewis acid Lewis base

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## 11- 3. 2 Equilibrium in aqueous solutions of acids and bases

Dissociation, or ionization, of an acid in water is expressed as

$$HA + H_2O \rightleftarrows H_3O^+ + A^- . \qquad (11.19)$$

The two-way arrow signifies the fact that the process is reversible. Like all other reversible processes the dissociation of an acid entails a state of equilibrium. The equilibrium constant in this

case is expressed as

$$K_a = \frac{[H_3O^+]\,[A^-]}{[HA]\,[H_2O]} .$$

Since $[H_2O]$ is effectively constant,

$$K_a = \frac{[H_3O^+]\,[A^-]}{[HA]} \quad \text{(at equilibrium)} \qquad (11.20)$$

When the extent of dissociation of an acid is large, [HA] reduces to a small value; and $K_a$ assumes very large values.

Acids with $K_a$ values 1 or greater are called strong acids, the others are called weak acids (Table 11.3).

The same logic applies to equilibrium in aqueous solutions of bases also. Large values of $K_b$ indicate strong bases, small values of $K_b$ indicate weak bases (Table 11.4).

The strength of an acid is indirectly related to the strength of the bond that holds the proton within the molecular structure of the acid. In the most common binary acids, the bond strength is in the order of

$$HF > HCl > HBr > HI$$

whereas the order of acid strength is

$$HF < HCl < HBr < HI$$

| ACID | PROTON TRANSFER REACTION | CONJUGATE BASE | $K_a$ (mol $L^{-1}$) | $pK_a$ ($= -\log_{10} K_a$) |
|---|---|---|---|---|
| Perchloric acid | $HClO_4 + H_2O \rightarrow H_3O^+ + ClO_4^-$ | | Very large | – |
| Hydrochloric acid | $HCl + H_2O \rightarrow H_3O^+ + Cl^-$ | | Very large | – |
| Sulfuric acid | $H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-$ | | Very large | – |
| Nitric acid | $HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$ | | Very large | – |
| Hydronium ion | $H_3O^+ + H_2O \rightleftharpoons H_3O^+ + H_2O$ | | 1.0 | 0.0 |
| Sulfurous acid [a] | $SO_2 + 2H_2O \rightleftharpoons H_3O^+ + HSO_3^-$ | | $1.5 \times 10^{-2}$ | 1.8 |
| Hydrogen sulfate ion | $HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$ | | $1.2 \times 10^{-2}$ | 1.9 |
| Phosphoric acid | $H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$ | | $7.5 \times 10^{-3}$ | 2.1 |
| Hydrofluoric acid | $HF + H_2O \rightleftharpoons H_3O^+ + F^-$ | | $3.5 \times 10^{-4}$ | 3.5 |
| Acetic acid | $CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-$ | | $1.8 \times 10^{-5}$ | 4.7 |
| Hydrated aluminum ion | $Al(H_2O)_6^{3+} + H_2O \rightleftharpoons H_3O^+ + Al(H_2O)_5OH^{2+}$ | | $7.2 \times 10^{-6}$ | 5.1 |
| Carbonic acid [b] | $CO_2 + 2H_2O \rightleftharpoons H_3O^+ + HCO_3^-$ | | $4.3 \times 10^{-7}$ | 6.4 |
| Hydrogen sulfide | $H_2S + H_2O \rightleftharpoons H_3O^+ + HS^-$ | | $9.1 \times 10^{-8}$ | 7.0 |
| Dihydrogen phosphate ion | $H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-}$ | | $6.2 \times 10^{-8}$ | 7.2 |
| Hypochlorous acid | $HOCl + H_2O \rightleftharpoons H_3O^+ + OCl^-$ | | $3.1 \times 10^{-8}$ | 7.5 |
| Ammonium ion | $NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$ | | $5.6 \times 10^{-10}$ | 9.3 |
| Hydrocyanic acid | $HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$ | | $5.9 \times 10^{-10}$ | 9.3 |
| Hydrogen phosphate ion | $HPO_4^{2-} + H_2O \rightleftharpoons H_3O^+ + PO_4^{2-}$ | | $2.1 \times 10^{-12}$ | 12.4 |
| Water [c] | $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$ | | $1.8 \times 10^{-13}$ | 15.8 |
| | CONJUGATE ACID | BASE | | |

[a] There is no evidence for formation of the undisscociated acid $H_2SO_3$.

[b] The equilibrium given here is the sum of the two equilibria $H_2O + CO_2 \rightleftarrows H_2CO_3$ and $H_2CO_3 + H_2O \rightleftarrows H_3O^- + HCO_3^-$ because the amount of $H_2CO_3$ formed is small and not accrately konwn.

[c] $K_a(H_2O) = K_w[H_2O]$

**Table 11.3** Dissociation constants for some acids at 25 °C

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| | PROTON TRANSFER REACTION | | | | | | | $K_b$ (mol $L^{-1}$) | $pK_b$ |
|---|---|---|---|---|---|---|---|---|---|
| | BASE | | | | | CONJUGATE ACID | | | |
| Hydride ion | $H^-$ | + | $H_2O$ | ⇄ | $OH^-$ | + | $H_2$ | Very large | |
| Amide ion | $NH_2^-$ | + | $H_2O$ | ⇄ | $OH^-$ | + | $NH_3$ | Very large | – |
| Oxide ion | $O^{2-}$ | + | $H_2O$ | ⇄ | $OH^-$ | + | $OH^-$ | Very large | – |
| Hydroxide ion | $OH^-$ | + | $H_2O$ | ⇄ | $OH^-$ | + | $H_2O$ | 1.00 | 0.0 |
| Phosphate ion | $PO_4^{3-}$ | + | $H_2O$ | ⇄ | $OH^-$ | + | $HPO_4^{2-}$ | $4.8 \times 10^{-2}$ | 1.3 |
| Carbonate ion | $CO_3^{2-}$ | + | $H_2O$ | ⇄ | $OH^-$ | + | $HCO_3^-$ | $2.1 \times 10^{-4}$ | 3.7 |
| Cyanide ion | $CN^-$ | + | $H_2O$ | ⇄ | $OH^-$ | + | $HCN$ | $2.0 \times 10^{-5}$ | 4.7 |
| Ammonia | $NH_3$ | + | $H_2O$ | ⇄ | $OH^-$ | + | $NH_4^+$ | $1.8 \times 10^{-5}$ | 4.7 |
| Hydrogen phosphate ion | $HPO_4^{2-}$ | + | $H_2O$ | ⇄ | $OH^-$ | + | $H_2PO_4^-$ | $1.6 \times 10^{-7}$ | 6.8 |
| Hydrogen carbonate ion | $HCO_3^-$ | + | $H_2O$ | ⇄ | $OH^-$ | + | $H_2CO_3$ | $2.5 \times 10^{-8}$ | 7.6 |
| Aniline | $C_6H_5NH_2$ | + | $H_2O$ | ⇄ | $OH^-$ | + | $C_6H_5NH_3^+$ | $4.3 \times 10^{-10}$ | 9.4 |
| Dihydrogen phosphate ion | $H_2PO_4^-$ | + | $H_2O$ | ⇄ | $OH^-$ | + | $H_3PO_4$ | $1.3 \times 10^{-12}$ | 11.9 |
| | CONJUGATE BASE | | | | | | ACID | | |

**Table 11. 4** Dissociation constants for some weak bases at 25° C



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From the orders given above, it is obvious that as the size of the anion decreases, the bond strength increases thus making it harder for the proton to break away from the molecule - weak acid. As the size of the anion increases, the bond strength decreases and it is not too hard for the proton to break away from the molecule - strong acid.

Acids which contain one or more oxygen atoms are called oxyacids e.g. $HNO_3$ and $H_2SO_4$. They contain an O-H bond. Again, depending on the strength of the O-H bond, the acid becomes a strong one or a weak one.

In oxyacids, the strength of the O-H bond depends on the ability of the nonmetal atom to withdraw electrons from the O-H bond. The more electronegative the nonmetal is, the stronger it will pull the electrons on the oxygen to which the hydrogen atom is bonded thus resulting in a looser hold on the H atom. The attraction of the electrons by the nonmetal atom is also related to to the formal charge on the nonmetal atom in the acid molecule. The formal charge on the nonmetal atom increases with the number of O atoms bonded to it.

| (0) | (+1) |
|---|---|
| H-O-Cl | H-O-Cl-O |
| $K_a = 5 \times 10^{-8}$ | $K_a = 1 \times 10^{-2}$ |
| hypochlorous acid | chlorous acid |
| O (+2) | O (+3) |
| H-O-Cl-O | H-O-Cl-O, O |
| $K_a = 1 \times 10^{3}$ | $K_a = 1 \times 10^{8}$ |
| chloric acid | perchloric acid |

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There are some acids which possess more than one proton. They are called polyprotic acids. The protons are lost in a stepwise fashion with the first proton being the most readily lost, then the second and so on.

### 11- 3. 3 Self-ionization of water

As mentioned in section 11.3.1 water is an amphoteric substance. It can act as as a weak base or a weak acid:

$$H_2O + H_2O \rightleftarrows H_3O^+ + OH^- \qquad (11.21)$$

This reaction is called the self-ionization of water. The equilibrium constant for the reaction is expressed as

$$K'_w = \frac{[H_3O^+]\,[OH^-]}{[H_2O]^2},$$

but since $[H_2O]$ is effectively constant

$$K_w = [H_3O^+]\,[OH^-]$$

The experimentally measured values of $[H_3O^+]$ and $[OH^-]$ in pure $H_2O$ at 25°C, are both $10^{-7}$ moles/ℓ. Hence,

$$K_w = 10^{-14}\ \text{mole}^2/\ell^2 .$$

The hydronium and hydroxide ions exist in equilibrium in any given aqueous solution. In an aqueous solution of an acid, or base, the product of the $[H_3O^+]$ and $[OH^-]$ is equal to $10^{-14}\ \text{mole}^2/\ell^2$.

### 11- 3. 4 pH scale

pH is defined as the negative of the logorithm of the $H_3O^+$ concentration in an equeous solution.

$$pH = -\log [H_3O^+].$$

Similarly $$pOH = -\log [OH^-]$$

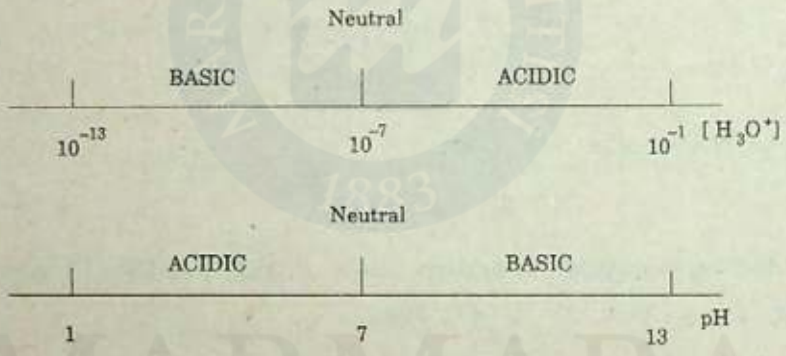
Since $[H_3O^+][OH^-] = 10^{-14}$,

$pH + pOH = 14.$

In pure $H_2O$, $[H_3O^+] = [OH^-] = 10^{-7}$.

Therefore $pH = pOH = 7.$

Pure $H_2O$ is taken as the neutral solution. If $[H_3O^+]$ in a solution is greater than that in pure $H_2O$, the solution is said to be acidic, otherwise it is said to be basic.




### 11- 3. 5 Hydrolysis of cations and anions

Ions can sometimes act as an acid or a base with $H_2O$:

$$NH_4^+ + H_2O \rightleftarrows NH_3 + H_3O^+$$

In the presence of ammonium ions, the $H_3O^+$ concentration in $H_2O$ increases. The pH of the solution falls below 7. The reaction is a hydrolysis reaction whereby $NH_4^+$ acts as an acid. The equilibrium constant is expressed as

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$$K_h = \frac{[NH_3]\,[H_3O^+]}{[NH_4^+]\,[H_2O]}.$$

Self-ionization of $H_2O$ is

$$H_2O + H_2O \rightleftarrows H_3O^+ + HO^-$$

for which

$$K_w = [H_3O^+]\,[OH^-] = 10^{-14}.$$

Ammonia, in water, reacts as a base:

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$$

and

$$K_b = \frac{[NH_4^+]\,[OH^-]}{[NH_3]}.$$

Ammonium ion, in water, hydrolyses:

$$NH_4^+ + H_2O \rightleftarrows NH_3 + H_3O^+$$

for which

$$K_a = \frac{[NH_3]\,[H_3O^+]}{[NH_4^+]}.$$

But

$$\frac{K_w}{K_b} = \frac{[H_3O^+]\,[OH^-]\,[NH_3]}{[NH_4^+]\,[OH^-]}.$$

$$= \frac{[H_3O^+]\,[NH_3]}{[NH_4^+]}$$

$$= K_a.$$

In the same manner,

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$$\frac{K_w}{K_a} = \frac{[H_3O^+][OH^-][NH_4^+]}{[NH_3][H_3O^+]}$$

$$= \frac{[OH^-][NH_4^+]}{[NH_3]}$$

$$= K_b ,$$

and it follows that $K_a K_b = K_w$.

$K_h$ is equal to $K_a$ or $K_b$ depending on whether the ion displays acidic or basic properties respectively.

It is possible to predict the extent of hydrolysis of a species using the numerical values of $K_a$ and $K_b$. For qualitative predictions, the following statements about hydrolysis are helpful.

- In general, salts are completely dissociated into ions in in aqueous solutions.
- Salts of strong acids and strong bases, e.g. NaCl, do not hydrolyse. pH of the solution remains 7.
- Salts of weak acids and strong bases, e.g. $NaC_2H_3O_2$, undergo hydrolysis producing a basic solution with pH >7. It is the anion in such a salt that hydrolyzes.
- Salts of strong acids and weak bases, e.g. $NH_4Cl$, undergo hydrolysis to produce an acidic solution with pH < 7. It is the cation in such a salt that hydrolyzes.
- Salts of weak acids and weak bases, e.g. $NH_4C_2H_3O_2$, hydrolyze but whether the resulting solution is neutral, acidic or basic depends on the relative values of $K_a$ and $K_b$.

Acid-base properties of aqueous solutions of some common salts are listed in Table 11.5.

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| BASIC SOLUTIONS. | NEUTRAL SOLUTIONS. | ACIDIC SOLUTIONS. |
|---|---|---|
| pH > 7 | pH = 7 | pH < 7 |
| Neutral cation | Neutral cation | Acidic cation |
| Basic anion | Neutral anion | Neutral anion |
| NaCN | KCl | $NH_4Cl$ |
| KF | $BaCl_2$ | $Al(H_2O)_6Cl_3$ |
| $Na(CH_3CO_2)$ | $Ca(NO_3)_2$ | $Fe(H_2O)_6(NO_3)_3$ |
| $Na_2CO_3$ | $Mg(ClO_4)_2$ | $C_6H_5NH_3.Cl$ |
| | | Neutral cation |
| | | Acidic anion |
| | | $KHSO_4$ |

**Table 11.5** Acid-base properties of some salts

### 11- 3. 6 Measurement of pH - indicators

The simplest way of measuring the pH of a solution is by means of an indicator. An indicator is a weak acid, denoted by HIn, which has one colour in the nonionized form and another colour in the ionized form.

$$HIn + H_2O \rightleftarrows H_3O^+ + In^-$$

colour (1) colour (2)

If the concentration of the $H_3O^+$ ion in the solution is large enough to suppress the dissociation of HIn, then colour (1) is observed. Otherwise, HIn dissociates to yield $In^-$ and colour (2) prevails.

The colour change in a solution is definetely detected when the indicator is half dissociated. The effective pH range for an indicator can be determined from its ionization c onstant.

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$$K_a = \frac{[H_3O^+]\,[In^-]}{[HIn]}$$

$$[H_3O^+] = K_a \frac{[HIn]}{[In^-]}$$

$$\log [H_3O^+] = \log K_a + \log \frac{[HIn]}{[In^-]}$$

$$-\log [H_3O^+] = -\log K_a - \log \frac{[HIn]}{[In^-]}$$

$$pH = pK_a + \log \frac{[In^-]}{[HIn]}$$

When the indicator is 50 % ionized

$$[In^-] = [HIn]$$

$$pH = pK_a + \log 1$$

But $\log 1 = 0$

$$pH = pK_a .$$

So, the colour change is definetely detectable when the pH of the solution is equal to $pK_a$ .

The pH range in which an indicator is effective can be determined using the following logic.

**Lower limit:** If 90 % or more of the indicator is in the form of HIn, colour (1) will prevail.

$$pH = pK_a + \log 0.1/0.9 (\sim 0.1)$$

$$pH = pK_a - 1$$

**Upper limit:** If 90% or more of the indicator has dissociated to $In^-$, then colour (2) prevails.

$$pH = pK_a + \log 0.9/0.1 (\sim 10)$$

$$pH = pK_a + 1$$

So, the effective pH range of an indicator is

$$pH = pK_a \pm 1 .$$

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Some common indicators and their properties are listed in Table 11.6.

| | $pK_a$ | EFFECTIVE pH (RANGE) | COLOR | |
|---|---|---|---|---|
| | | | ACID FORM | BASE FORM |
| Methly violet | 1.6 | 0.0 – 3.0 | Yellow | Violet |
| Methyl orange | 4.2 | 2.1 – 4.4 | Red | Yellow |
| Methyl red | 5.0 | 4.2 – 6.2 | Red | Yellow |
| Bromothymol blue | 7.1 | 6.0 – 7.8 | Yellow | Blue |
| Thymol blue | 8.2 | 7.9 – 9.4 | Yellow | Blue |
| Phenolphthalein | 9.5 | 8.3 – 10.0 | Colorless | Red |
| Alizarine yellow | 11.0 | 10.0 – 12.1 | Yellow | Red |

**Table 11.6** Properties of some indicators

### 11- 3. 7 Buffer solutions

Maintaining a constant pH is essential in many chemical processes such as treatment of sewage, electroplating and metabolic systems.

Solutions which can maintain a near-constant pH are called buffer solutions. They contain either a weak acid and a salt of a weak acid, or a weak base and a salt of a weak base, in approximately equal concentrations.

Consider an aqueous solution of acetic acid (weak acid) and sodium acetate (salt of a weak acid) in equal concentrations, say 0.1 M.

$$NaC_2H_3O_2 \rightarrow Na^+ + C_2H_3O_2^-$$

0.1 M 0.1 M 0.1 M

(complete dissociation)

$$HC_2H_3O_2 \rightleftarrows H^+ + C_2H_3O_2^-$$

| | | | |
|---|---|---|---|
| initially | 0.1 M | 0 | 0.1 |
| change | -x | x | x |
| equil. | 0.1-x | x | 0.1+x |

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$$K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = 1.74 \times 10^{-5}.$$

$$1.74 \times 10^{-5} = (x)\,(0.1 + x) / (0.1 - x).$$

Solving this quadratic equation

$$[H^+] = 1.74 \times 10^{-5} = K_a \text{ is obtained.}$$

The concentration of $H^+$, therefore pH, is expected not to change when a small amount of an acid, say 0.01 moles of HCl, is added to one litre of this system.

One litre of the system now contains 0.1 moles of $C_2H_3O_2^-$, 0.1 moles of $HC_2H_3O_2$ and 0.01 moles of $H^+$ from the dissociation of the strong acid HCl.

Since the concentrations of $C_2H_3O_2^-$ and $H^+$ are high, the dissociation reaction of $HC_2H_3O_2$ is expected to reverse itself. This can be shown quantitatively by calculating the Q value on the assumption that the 0.1 moles of $HC_2H_3O_2$ does not dissociate at all.

$$Q_{(a)} = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

$$= (0.01)\,(0.1) / (0.1)$$

$$= 10^{-2}$$

i.e. $Q_{(a)} > K_a$ and the reaction is proceeding in the reverse direction.

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| | $HC_2H_3O_2$ | $\rightleftarrows$ | $H^+$ | + | $C_2H_3O_2^-$ |
|---|---|---|---|---|---|
| initially | $(0.1-1.74 \times 10^{-5})$ | | $(0.01 + 1.74 \times 10^{-5})$ | | $(0.1 + 1.74 \times 10^{-5})$ |
| change | $+x$ | | $-x$ | | $-x$ |
| equil. | $(0.1-1.74 \times 10^{-5}+x)$ | | $(0.01+1.74 \times 10^{-5}-x)$ | | $(0.1+1.74 \times 10^{-5}-x)$ |

Solving the quadratic equation obtained by substituting these terms (neglecting any term below the order of –3) the value of x is found to be 0.01 and $[H^+] = 1.74 \times 10^{-5}$ is again obtained.

The constancy of pOH in a basic buffer solution can be shown in the same manner.

### 11- 3. 8 Acid-base titrations

In dealing with acids and bases, it is necessary to determine their exact concentration. This is realized by utilizing the neutralization reaction between an acid and a base in a procedure called titration.

In the case of an acid with unkown concentration, a base with known concentration is progressively added to a measured volume of the acid in the presence of an appropriate indicator until the acid is completely neutralized. The point at which this occurs is called the equivalence point or the end point and is indicated by the colour change in the solution.

At the end point one equivalent of an acid neutralizes one equivalent of a base i.e.

$$V_{acid}N_{acid} = V_{base}N_{base}$$

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# CHAPTER 12

# THERMODYNAMICS

Thermodynamics is the science which deals with transformations of energy of all kinds from one form to another. The general restrictions within which all these transformations are observed to occur are known as the first and second laws of thermodynamics.

Knowledge of thermodynamic principles enables the chemist and the chemical engineer to solve many problems. Among these are

1. determination of heat and work requirements for physical and chemical processes,
2. determination of equilibrium conditions for chemical reactions,
3. determination of equilibrium conditions for transfer of chemical species between phases.

## 12- 1 Forms of energy

The two main forms of energy are

a) kinetic energy - that possessed by a body by virtue of its motion as a whole,

b) potential energy - that possessed by a body by virtue of its position in relation to an object that exerts a force upon it.

There are further types of energy which may or may not fall in these two classes. Chemical energy can be considered as a form of potential energy.

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Heat and work are two distinct forms of energy that are dealt separately from the two forms above.

Heat can be defined as the flow of energy between two bodies due to difference in their temperatures.

Work can be defined as the flow of energy when a given amount of force is applied over a distance.

In the 19th century, the English scientist James P. Joule conducted a series of experiments to demonstrate the relationship between heat and work. The following is a brief description of these experiments.

- He placed measured amounts of water in an insulated container and agitated the water with a rotating stirrer. He measured the amount of work done by the stirrer on the water very accurately. He found that a definite amount of work was required per unit mass of water to cause a temperature rise of one degree. He could also restore the original temperature of water by bringing into contact with a cooler body- .

In these experiments it is obvious that energy is added to water as work but is extracted as heat. But what if this energy is not extracted as heat? It is most probable that it would be contained in the water in some form which is called the internal energy, U.

The internal energy of a substance does not include the form of energy that it may possess as result of its position or movement as a whole. It only refers to the energy of the molecules making up the substance. It is believed that the molecules of a substance are in ceaseless motion and that they possess kinetic energy of translation, rotation and internal vibration. The addition of heat to a substance increases this molecular activity thus causing an increase in internal energy.

In addition to the molecular energy, the molecules of a substance possess potential energy because of interactions among force fields and/or chemical bonds. This energy is on a submolecular scale and is a part of the internal energy.

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It is not possible to determine the total internal energy of a substance. Absolute values of internal energy are therefore not known. However, this is not a disadvantage since only changes in internal energy are required in thermodynamic analysis.

The external forms of energy of a substance are the energies possesed by the body of the substance in the form of potential ($E_p$) and kinetic ($E_K$) energies.

**12- 2 Thermodynamic terminology**

Prior to the introduction of thermodynamic principles, it is considered appropriate that the most frequently used thermodynamic terminology be defined.

UNIVERSE = SYSTEM + SURROUNDING

| | |
|---|---|
| SYSTEM | part of the universe in which we are particularly interested because the process we are investigating is taking place in it. |
| SURROUNDING | the rest of the universe with which the system is in contact directly or indirectly. |
| OPEN System | there is transfer of matter in and out of the system. |
| CLOSED System | there is no transfer of matter in and out of the system. |
| ISOTHERMAL | condition of constant temperature |
| ISOMETRIC | condition of constant volume |
| ISOBARIC | condition of constant pressure |
| ADIABATIC | condition of no heat transfer between a system and its surrounding |

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| | |
|---|---|
| POLYTROPIC | no specific conditions apply |
| REVERSIBLE Change | can be reversed by an infinitesimal modification of a variable |
| IRREVERSIBLE Change | cannot be reversed by an infinitesimal modification of a variable |
| STATE Functions | do not depend on the path chosen to accomplish a change in state e.g. T,P, H,U |
| PATH Functions | depend on the path chosen to accomplish a change in state e.g. Q and W |
| EXTENSIVE Property | depends on the amount of material the system contains e.g. m, V, n |
| INTENSIVE Property | does not depend on the amount of material the system contains e.g. T, P, c |

## 12- 3 1st Law of Thermodynamics

"Although energy assumes many forms, the total energy of the universe is constant and, when energy disappears in one form it appears simultaneously in other forms."

The 1st law can be formulated as

$$\Delta \text{(energy of system)} + \Delta \text{(energy of surrounding)} = 0 \qquad (12.1)$$

The total energy change of the system is

$$\Delta \text{(energy of system)} = \Delta U + \Delta E_K + \Delta E_P \qquad (12.2)$$

The total energy change of the surrounding is equal to the energy transferred to or from it as heat or work.

$$\Delta \text{(energy of surrounding)} = \pm Q \ \pm W \qquad (12.3)$$

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Hence, $\Delta U + \Delta E_K + \Delta E_P = \pm Q \pm W$.

The conventional form of the expression is

$$\Delta U + \Delta E_K + \Delta E_P + Q - W \qquad (12.4)$$

where (+) Q is the heat added TO the system FROM the surrounding

(–) W is the work done BY the system ON the surrounding.

For a closed system that does not undergo any changes in potential or kinetic energy, the lst Law is expressed by

(finite change) $\Delta U = Q - W$ (12.5)

(differential change) $dU = dQ - dW$ (12.6)

The signs of Q and W are reversed if heat is taken away from the system or work is done by the surrounding on the system.

It is emphasised here that internal energy, U, should be accepted as a function of temperature only.

### 12-3.1 Work

The general expression for work is

$$W = Fd \quad (Nm = J) \qquad (12.7)$$

Gaseous systems accomplish work (±) when they expand or contract. Pressure is expressed as

$$P = F/A.$$

Therefore, $F = PA.$

But, $W = Fd.$ (12.7)

$$W = PAd.$$

In the gaseous system illustrated in Figure 12.1,

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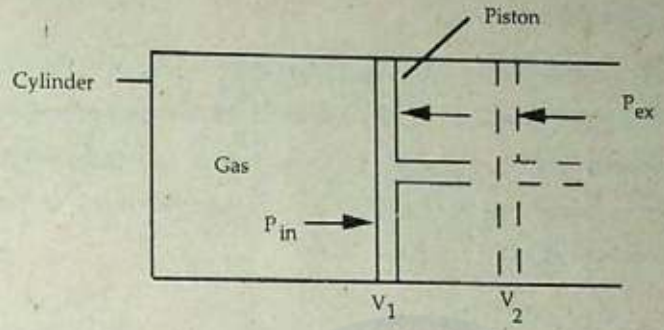


Figure 12.1 Work done by gases - expansion work

$$\Delta V = Ad.$$

Hence, $$W = P\Delta V, \qquad (12.8)$$

or $$dW = PdV.$$

Gaseous systems expand against an external pressure or they contract under the action of an external pressure. So,

$$dW = P_{ex}dV. \qquad (12.9)$$

If dV is positive i.e. gas is expanding, then the gas is doing work on the surrounding.

If dV is negative i.e. gas is compressed, then the surrounding is doing work on the system.

**Free expansion against vacuum:** $P_{ex} = 0$

$$dW = 0 \qquad (12.10)$$

**Expansion against constant pressure** $P_{ex}$:

$$W = \int dW = P_{ex}\int_{V_1}^{V_2} dV \qquad (12.11)$$

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**Reversible expansion (or work):**

To realize a reversible work in the expansion of a confined gas, the external pressure is taken only infinitesimally less than the internal pressure. But the internal pressure may change during the expansion. Therefore, in order to calculate the work done in this case, $P_{ex}$ is set effectively equal to the internal pressure at every stage of the expansion.

$$dW = P_{ex}dV = P_{in}dV$$

But for an ideal gas, $P_{in} = nRT/V$ (Assuming const. T)

$$\int dW = nRT \int_{V_1}^{V_2} dV/V \qquad (12.12A)$$

$$W = nRT \ln V_2/V_1. \qquad (12.12)$$

As illustrated in Figure 1.2.2. the work accomplished reversibly for a volume change of $\Delta V$ by an ideal gas is gerater than that accomplished irreversibly.

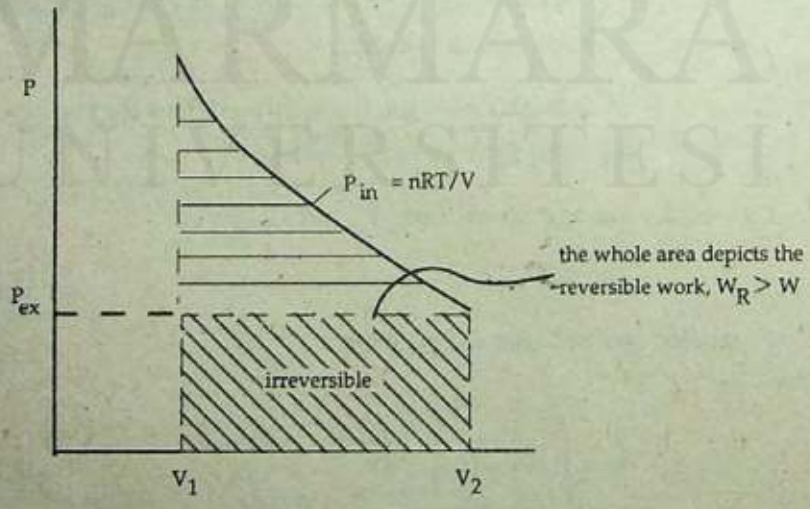


**Figure 12.2** Reversible and irreversible expansion work

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### 12-3.2 Heat

When heat is added to a system its temperature rises. For an infinitesimal amount of heat transferred to a system, an infinitesimal temperature rise, that is proportional to the amont of heat supplied, is observed.

$$dT = (\text{constant})\, dQ$$

or

$$dQ = \underbrace{1/\text{const.}}_{C}\, dT.$$

C is the heat capacity of the system.

Helat capacities at constant volume and constant pressure are both special cases of this general ldefinition.

$$C_V = (\partial Q/\partial T)_V \qquad (12.13)$$

$$CP = (\partial Q/\partial T)_P \qquad (12.14)$$

### 12-4 Enthalpy

In addition to internal energy a number of other thermodynamic functions are in common use because of their practical importance. Enthalpy is explicitly defined for any system by the mathematical expression

$$H = U + PV. \qquad (12.15)$$

Upon changing both pressure and volume infinitesimally

$$H + dH = (U + dU) + (P + dP)\,(V + dV)$$

$$= U + dU + PV + PdV + dPV + \underbrace{dPdV}_{\text{very small}}$$

$$= \underbrace{U + PV}_{H} + dU + PdV + dPV$$

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$$dH = dU + PdV + VdP. \quad (12.15A)$$

For a gaseous system, the lst law is

$$dU = dQ - PdV. \quad (12.16)$$

Hence, $dQ = dU + PdV$

and $dH = dQ + VdP.$

Under constant pressure

$$dH = (dQ)_P.$$

At const.V $dU = (dQ)_V.$

Therefore $C_p = (\partial Q/\partial T)_P = (\partial H/\partial T)_P.$ (12.17)

$$C_V = (\partial Q/\partial T)_V = (\partial U/\partial T)_V. \quad (12.17A)$$

By definition $H = U + PV$ (12.15)

but $PV = n\,R\,T,$

so $H = U + nRT.$

If temperature is raised from T to T + dT,

$$dH = dU + nR\,dT.$$

But $dH = C_p dT$

$dU = C_V dT.$

Therefore $C_p dT = C_V dT + n\,R\,dT$

$$C_P - C_V = nR. \quad (12.18)$$

For one mole

$$C_P - C_V = R \quad (12.19)$$

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## 12- 5 Application of the Ist law to reversible closed systems

### a) Constant - volume (ISOMETRIC) process:

$$dU = dQ - \underbrace{P\,dV}_{0}$$

Form (12.13) $$dU = dQ = C_V dT \qquad (12.20)$$

### b) Constant - pressure (ISOBARIC) process:

$$dU = dQ - P\,dV$$

$$dQ = dU + P\,dV.$$

But $$dH = dU + P\,dV + V\,dP. \qquad (12.15A)$$

At constant P,

$$dH = dU + P\,dV = dQ.$$

Hence $$dH = dQ = C_P dT. \qquad (12.21)$$

$$dU = dQ - dW \qquad (12.6)$$

But $$\int dW = P\int_{V_1}^{V_2} dV, \qquad (12.11)$$

hence $$dU = dH - P\,dV \qquad (12.22)$$

### c) Constant - temperature (ISOTHERMAL) process:

$$dU = dQ - dW \qquad (12.6)$$

At constant temperature

$$dU = 0 \text{ (section 12.3)}$$

$$0 = dQ - dW$$

$$dQ = dW.$$

At constant temperature

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$$dW = nRT \int_{V_1}^{V_2} dV/V, \qquad (12.12A)$$

$$W = nRT \ell n\, V_2/V_1 \qquad (12.12)$$

Hence

$$Q = nRT \ell n\, V_2/V_1. \qquad (12.23)$$

$$dW = nRT\, d\ell n\, V_2/V_1 \qquad (12.12A)$$

But at constant T,

$$P_1V_1 = P_2V_2$$

$$V_2/V_1 = P_1/P_2$$

$$W = nRT \ell n\, P_1/P_2 \qquad (12.12B)$$

$$W = -nRT \ell n\, P_2/P_1 \qquad (12.12C)$$

$$dW = -nRT\, d\ell n\, P \qquad (12.12D)$$

Work performed reversibly is Wmax

$$W_{max} = -nRT \ell n\, P_2/P_1 \qquad (12.12E)$$

**d) ADIABATIC process:**

$$dU = \underbrace{dQ}_{O} - dW$$

$$dU = -dW$$

$$= -P\,dV \qquad (12.24)$$

$$dU = C_V dT \qquad (12.20)$$

$$C_V dT = -P\,dV$$

$$= -RT/V\,dV$$

$$dT/T = -R/C_V dV/V. \qquad (12.25)$$

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Let $C_P/C_V = \gamma$ (gamma)

But $C_P = C_V + R$ (12.19)

$(C_V + R)/C_V = \gamma$

$1 + R/C_V = \gamma$

$R/C_V = \gamma - 1$ (12.26)

Substituting (12.26) in (12.25)

$dT/T = -(\gamma - 1)\, dV/V$

$\ell n\, T_2/T_1 = -(\gamma - 1)\, \ell n\, V_2/V_1$

or $T_2/T_1 = (V_1/V_2)^{\gamma-1}$ (12.27)

Also $P_1V_1/T_1 = P_2V_2/T_2$

or $V_1/V_2 = (P_2/P_1)\,(T_1/T_2)$ (12.28)

Substituting (12.28) in (12.27)

$T_2/T_1 = (P_2/P_1)^{\gamma-1}\,(T_1/T_2)^{\gamma-1}$

$T_2/T_1\ (T_1/T_2)^{-(\gamma-1)} = (P_2/P_1)^{\gamma-1}$

$T_2/T_1\ (T_2/T_1)^{\gamma-1} = (P_2/P_1)^{\gamma-1}$

$(T_2/T_1)^{\gamma} = (P_2/P_1)^{\gamma-1}$

$T_2/T_1 = (P_2/P_1)^{(\gamma-1)/\gamma}$ (12.29)

Substituting (12.27) in (12.29)

$(V_1/V_2)^{\gamma-1} = (P_2/P_1)^{(\gamma-1)/\gamma}$

If both sides of the above equality is raised to the power of $\gamma/(\gamma-1)$

$P_1V_1^{\gamma} = P_2V_2^{\gamma} = \text{Const.}$ (12.30)

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e) POLYTROPIC Process:

$$dU = dQ - dW$$

$$dU = C_V dT$$

$$dH = C_p dT$$

$$dW = P\,dV$$

$$dQ = dU + P\,dV$$

$$dQ = CV dT + P\,dV \qquad (12.31)$$

## 12- 6 2nd Law of Thermodynamics

The first law, stating that energy must be conserved in all ordinary processes, imposes no restriction on the direction of energy transformations.

The differences between the two forms of energy, heat and work, provide some insight into the second law. These differences are not implied by the first law. In an energy balance both work and heat are included as simple additive terms, implying that one unit of heat, such as joule or BTU, is equivalent to the same unit of work. Although this is true with respect to an energy balance, experience teaches us that there is a difference in quality between heat and work.

Consider the efficiency of transformation from one form of work to another, such as electrical to mechanical as accomplished in an electric motor. The efficency of this process can be made to approach 100% as closely a desired by simply exerting more care in eliminating irreversibilities in the apparatus.

Efforts to convert heat into anyone of the forms of work show that this conversion i limited to iow values, around 40%. This experience leads to the conclusion that there is an intrinsic difference between heat and work. On the reverse side, conversion of work into heat with 100% efficiency is

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common. These facts lead to the conclusion that heat is les versatile or more degraded form of energy than work. Work might be termed energy of a higher quality than heat.

Again from experience, it is known that heat always flows from a higher temperature level to a lower one and never in the reverse direction. This suggests that heat itself may be assigned a characteristic quality as well as quantity, and that this quality depends on temperature. As the temperature is raised, an increase in the efficiency is observed when converting heat into work as in power plants.

Based on these observations the second law can be phrased as

1) No apparatus can operate in such a way that its only effect is to convert heat absorbed by a system completely into work in a cyclic process.

2) Any process which consists solely in the transfer of heat from one temperature to a higher one is impossible.

These principles are formulated and discussed in the following section.

To formulate the second law two new thermodynamic functions, entropy (S) and Gibb's free energy (G), are introduced. However, since the working of a heat engine is a perfect illustration of the second law, it will be decribed first.

A heat engine is a device or a machine that produces work from heat in a cyclical process. An example is a steam power plant in which the medium (steam) periodically returns to its original state. In such a power plant the cycle is basicly as follows:

a) Part of the heat from the fuel (heat of combustion of coal, oil, or gas or heat from a nuclear reaction) is transferred to liquid water in the boiler, converting the water to steam at a high pressure and temperature.

b) Energy is transferred from this steam as shaft work by a device such as a turbine.

c) The exhaust steam from the turbine is condensed at a low temperature by the transfer of heat to cooling water.

d) The liquid water is pumped back to the boiler, thus completing the cycle.

Each step in the cycle can be symbolized as follows:

a) $Q_1 \rightarrow$ system @ $T_1$

b) System $\rightarrow$ $W_s$ (shaft work by turbine)

c) System $\rightarrow$ $Q_1$ @ $T_1$ (heat to cooling water) $T_1 > T_2$

d) $W_p$ (pump work) $\rightarrow$ System

Since all thermodynamic functions, with the exception of Q and W, are state functions and in a cyclic process initial state is the same as the final state, for the complete cycle

$$\Delta U_{cycle} = 0 \qquad (12.32)$$

(1st law) $$\Delta U_{cycle} = Q_1 - Q_2 - W_s + Wp$$

$$= 0$$

Let $$W = W_s - W_p$$

$$Q_1 - Q_2 - W = 0$$

$$Q_1 - Q_2 = W.$$

The efficiency of an engine is defined as the ratio of the net work obtained from the engine to the heat input to the engine, i.e.

$$\text{Efficiency} = W/Q_1 \qquad (12.33)$$

As shown in section 12.3.1 work accomplished reversibly is always greater than that accomplished irreversibly. Therefore

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(Efficiency of a reversible heat ingine) > (Efficiency of an irreversible heat engine)

Now, consider two heat engines, one reversible and one irreversible, operating in reverse directions between the same temperatures $T_1$ and $T_2$. The irreversible engine operates in the conventional manner, absorbing heat, $Q_1$, at the high temperature $T_1$, converting part of it into work W, and discarding the remainder $Q_2$ at the low temperature $T_1$.

As illustrated in Figure 12.3, the reversible heat engine runs in the opposite direction and is directly connected to the irreversible one. It uses the work produced by the irreversible engine to absorb the heat $Q_2'$ at the low temperature $T_2$, and discards the heat $Q_1'$ (equal to $Q_2' + W$) at $T_1$.

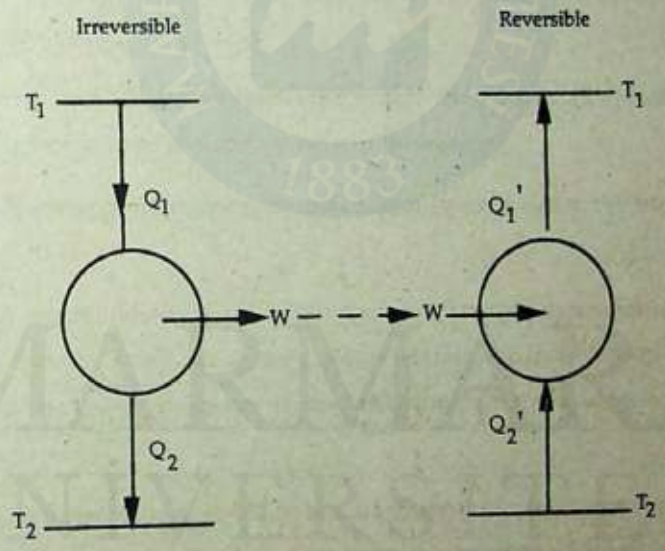


**Figure 12.3** Efficiency of irreversible and reversible heat engines

The efficiency of the irreversible engine is $W/Q_1$.

The efficiency of the reversible engine is $W/Q_1'$.

If it were possible for the irreversible engine to have a higher efficiency than the reversible engine

$$W/Q_1 > W/Q_1'$$

and

$$Q_1 < Q_1'.$$

$$Q_2 = Q_1 - W$$

$$Q_2' = Q_1' - W$$

and, therefore

$$Q_2' > Q_2.$$

But, this means that this two-engine system is transferring heat from a low temperature to a high temperature which is impossible.

## 12-7 Entropy

The thermodynamic function entropy is defined as

$$\Delta S = \int dQ_R/T \qquad (12.33A)$$

where $dQ_R$ is the heat absorbed or released by the system in a reversible process,

T is the temperature of the system.

In cases where only heat transfer is involved - that is no work is produced - $\Delta S$ can be correctly evaluated from $\int dQ_R/T$ applied to the actual process even though the heat transfer is irreversible.

An analysis of the relationship between entropy and reversibility leads to a concise mathematical expression of the limitation on the direction of any actual process.

Consider two heat reservoirs, one at $T_1$, the other at $T_2$ and $T_1 > T_2$. No work is involved. Heat is transferred from the hot one to the cold one irreversibly.

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$$\Delta S_1 = -Q/T_1 \text{ (heat is given up)}$$

$$\Delta S_2 = Q/T_2 \text{ (heat is taken up)}$$

$$\Delta S_t = \Delta S_1 + \Delta S_2$$

$$= Q/T_2 - Q/T_1$$

$$= Q(T_1 - T_2)/(T_2 T_1). \qquad (12.34)$$

Remembering that Q is positive and $T_1 > T_2$,

$\Delta S_t$ = is positive.

Now, let us consider the case where the heat is transferred reversibly from one reservoir to the other,

and $T_1 = T_2 + dT.$

Substituting this expression for $T_1$ in (12.34),

$$\Delta S_t = Q(T_2 + dT - T_2)/(T_2T_1)$$

$$= Q\,dT/(T_2T_1)$$

$$\lim_{dT \to 0} \Delta S_t = 0$$

These two results can be generalized as follows:

$$\Delta S_{sys} + \Delta S_{surr} = \Delta S_t \geq 0. \qquad (12.35)$$

(12.35) is the statement of the general principle reached from the second law.

In the case of a chemical reaction, only at equilibrium the reaction is realized reversibly, $\Delta S_t = 0$. Until equilibrium is reached, the process moves in one direction irreversibly towards equilibrium and the change in total entropy, or entropy of the universe, is always greater that zero, $\Delta S_t > 0$. It should be noted clearly that for all processes that take place spontaneously, like mixing of gases in a container or rusting of iron, $\Delta S_t > 0$ . The physical and chemical equilibria in the universe are reached when $\Delta S_t = 0$.

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If the system is a reacting one,

$$\Delta S_{sys} = \Sigma \upsilon_i S^\circ_{i\,(prod)} - \Sigma \upsilon_i S^\circ_{i\,(react)} \qquad (12.34A)$$

Standard molar entropies for various compounds are given in Table 12.1.

| SOLIDS | | LIQUIDS | | GASES | |
|---|---|---|---|---|---|
| C (diamond) | 2.4 | $H_2O$ | 70.0 | $H_2$ | 130.6 |
| C (graphite) | 5.8 | Hg | 75.9 | $N_2$ | 191.5 |
| Fe | 27.3 | $Br_2$ | 152.2 | $F_2$ | 202.7 |
| S (rhombic) | 32.0 | $CH_3OH$ | 126.8 | $O_2$ | 205.0 |
| Cu | 33.2 | $HNO_3$ | 155.6 | $Cl_2$ | 223.0 |
| P (white) | 41.1 | $CH_3CO_2H$ | 159.8 | $I_2$ | 260.6 |
| Ag | 42.6 | $C_2H_5OH$ | 160.7 | $CH_4$ | 86.1 |
| $I_2$ | 116.1 | $CH_2Cl_2$ | 177.8 | HCl | 186.8 |
| MgO | 27.0 | $CHCl_3$ | 201.7 | $H_2O$ | 188.7 |
| CaO | 38.1 | $CCl_4$ | 216.4 | $NH_3$ | 192.7 |
| $SiO_2$ (quartz) | 41.5 | $SiCl_4$ | 239.7 | $H_2S$ | 205.6 |
| NaF | 51.3 | $C_5H_{12}$ [a] | 263.3 | HI | 206.5 |
| NaCl | 72.5 | $C_6H_6$ [b] | 172.2 | $CO_2$ | 213.7 |
| NaBr | 87.2 | $C_6H_{14}$ [a] | 295.9 | $C_2H_6$ | 229.5 |
| $Fe_2O_3$ | 87.4 | $C_7H_{16}$ [a] | 328.5 | $C_3H_8$ | 269.9 |
| $CaCO_3$ | 92.9 | $C_8H_{18}$ [a] | 361.2 | $C_4H_{10}$ [a] | 310.1 |
| AgCl | 96.2 | | | $C_5H_{12}$ [a] | 348.9 |
| NaI | 98.5 | | | $C_6H_6$ [b] | 269.2 |
| Glucose ($C_6H_{12}O_6$) | 182.4 | | | | |
| $P_4O_{10}$ | 231 | | | | |
| Sucrose ($C_{12}H_{22}O_{11}$) | 360 | | | | |

a Straight-chain alkanes
b) Benzene

**Table 12.1** Standard molar entropies, S°, at 25°C (J $K^{-1}$ $mole^{-1}$)

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## 12- 8 Gibb's free energy, chemical spontaneity and equilibrium

Consider a chemical system (gaseous and ideal) in which both heat exchange and expansion are reversible. According to the second law

$$dS_{sys} + dS_{surr} \geq 0. \qquad (12.35)$$

In the case of reversible heat exchange

$$dS_{surr} = -dQ_{sys}/T_{sys}$$

$$dS_{sys} - dQ_{sys}/T \geq 0$$

$$dS_{sys} \geq dQ/T$$

or

$$dQ \leq T\,dS. \qquad (12.36)$$

According to the first law

$$dU = dQ - dW \qquad (12.6)$$

but $dW = P\,dV.$

Hence,

$$dQ = dU + P\,dV. \qquad (12.37)$$

Substituting (12.37) in (12.36)

$$dU + P\,dV \leq T\,dS$$

$$dU + P\,dV - T\,dS \leq 0. \qquad (12.38)$$

It should be remembered that the equal sign applies to completely reversible, i.e. equilibrium, conditions and less than sign applies to irreversible, i.e. nonequilibrium, conditions under which changes occur spontaneously.

It the temperature and the pressure of the system are kept constant

$$dU_{T,P} + d(PV)_{T,P} - (TS)_{T,P} \leq 0.$$

or $$d(U + PV - TS)_{T,P} \leq 0. \qquad (12.39)$$

The thermodynamic function Gibb's free energy is defined as

$$G = H - TS. \qquad (12.40)$$

$$H = U + PV \qquad (12.15)$$

Therefore $$G = U + PV - TS. \qquad (12.41)$$

Combining (12.41) with (12.39),

$$(dG)_{T,P} = d(U + PV - TS)_{T,P} \leq 0 \qquad (12.42)$$

Equation (12.42) expresses the fact that under conditions of constant temperature and pressure, Gibb's free energy for a reacting system (the **change** in G, $\Delta G$ or dG) at equilibrium is zero and, it is a negative value for all pre-equilibrium (nonequilibrium) conditions.

Equation (12.40) can be written as

$$\Delta G = \Delta H - \Delta(TS)$$

At constant temperature and pressure,

$$\Delta G = \Delta H - T\Delta S. \qquad (12.43)$$

Whether the reacting system is at equilibrium or not, or the direction in which it is proceeding, can be predicted from the sign of $\Delta G$. The sign of $\Delta G$ is determined by the signs of $\Delta H$ and $\Delta S$ (for the reaction) and the magnitude of T in equation (12.43). Table 12.2 lists the possible combinations of $\Delta H$ and $\Delta S$ as related to $\Delta G$ in (12.43).

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Standard Gibb's free energy for a reaction can be calculated according to

$$\Delta G^\circ = \Sigma \upsilon_i G_{f\,(prod)}^\circ - \Sigma \upsilon G_{f\,(react)}^\circ \qquad (12.44)$$

Standard Gibb's free energy of formation of various compounds are listed in Table 12.3.

From (12.40) $dG = dH - d(TS)$

$$= dH - dT\,S - T\,dS. \qquad (12.45)$$

From (12.15) $dH = dU + P\,dV + V\,dP \qquad (12.46)$

From (12.37) $dU = dQ - P\,dV \qquad (12.47)$

From (12.33A) $dQ = T\,dS \qquad (12.48)$

Combining equations 12.46, 12.47 and 12.48 in equation 12.45,

$$dG = -S\,dT + V\,dP. \qquad (12.49)$$

At constant temperature,

$$dG = V\,dP \qquad (12.50)$$

For an ideal gaseous system, (for one mole of it)

$$V = RT/P$$

$$dG = RT\,dP/P$$

$$dG = RT\,d\ell n\,P \qquad (12.51)$$

From (12.12D) $dG = -dW_{max}$

For one of the components in a reaction mixture (ideal) that is expressed as

$$aA + bB \rightleftarrows cC + dD, \qquad (12.52)$$

$$dG_i = RT\,dP_i/P_i \qquad (12.53)$$

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| | ΔH | ΔS | ΔG | | Change |
|---|---|---|---|---|---|
| (1) | – | + | – | | Spontaneous |
| (2) | – | – | – | at low T | Spontaneous |
| | | | + | at high T | Not spontaneous |
| (3) | + | – | + | | Not spontaneous |
| (4) | + | + | + | at low T | Not spontaneous |
| | | | – | at high T | Spontaneous |

**Table 12.2** Prediction of the spontaneity of a reaction

| | $\Delta G_f^a$ (kJ mol$^{-1}$) | | $\Delta G_f^\circ$ (kJ mol$^{-1}$) |
|---|---|---|---|
| AgCl (s) | – 109.8 | $CH_3CO_2H$ (ℓ) | – 390 |
| CO (g) | – 137.2 | $C_6H_6$ (ℓ) | 124.7 |
| $CO_2$ (g) | – 394.4 | $Fe_2O_3$ (s) | – 742.2 |
| $CH_4$ (g) | – 50.8 | $H_2S$ (g) | 33.4 |
| $C_2H_6$ (g) | – 32.9 | HCl (g) | – 95.3 |
| $C_3H_8$ (g) | – 9.6 | HI (g) | – 1.6 |
| $C_4H_{10}$ (g) | – 4.4 | $HNO_3$ (ℓ) | – 80.8 |
| $C_5H_{12}$ (ℓ) | 1.0 | $H_2SO_4$ (g) | – 690.1 |
| $C_6H_{14}$ (ℓ) | 4.4 | $H_2O$ (g) | – 237.2 |
| $C_7H_{16}$ (ℓ) | – 1.0 | $H_2O$ (g) | 228.6 |
| $C_8H_{18}H$ (ℓ) | – 6.4 | $NH_3$ (g) | 16.4 |
| $CH_2O$ (g) | – 113 | NO (g) | 86.6 |
| $CH_3OH$ (ℓ) | – 116.4 | $NO_2$ (s) | 51.3 |
| $C_2H_5OH$ (ℓ) | – 174.9 | $N_2O_4$ (s) | 97.8 |
| $CH_2Cl_2$ (ℓ) | – 67.3 | NaCl (s) | – 384.3 |
| $CH_3Cl$ (g) | – 57.4 | NaBr (s) | – 349.1 |
| $CHI_4$ (ℓ) | – 65.3 | NaI (s) | – 282.4 |
| $C_6H_{12}O$ (s) (glucose) | – 919.2 | CaO (s) | – 603.5 |
| | | $CaCo_3$ (s) | – 1128.8 |

**Table 12.3** Standard Gibb's free energies of formation, $\Delta G_f^\circ$, at 25°C

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$$\int_{P=1\ atm}^{P_i} dG_i = RT \int_{P=1\ atm}^{P_i} d\ell nP_i \qquad (12.54)$$

$$= W_{max} \qquad (12.54A)$$

Gibb's free energy (of formation) of an ideal gas at 1 atmosphere is defined as its standard free energy (of formation), G°.

$$G_i - G_i^\circ = RT\,\ell nP_i - RT\,\underset{0}{\ell n1}$$

$$G_i = G_i^\circ + RT\,\ell nP_i \qquad (12.55)$$

Writing this expression for each component in 12.52,

$$G_A = G_A^\circ + RT\,\ell nP_A \qquad (12.56A)$$

$$G_B = G_B^\circ + RT\,\ell nP_B \qquad (12.56B)$$

$$G_C = G_C^\circ + RT\,\ell nP_B \qquad (12.56C)$$

$$G_D = G_D^\circ + RT\,\ell nP_D \qquad (12.56D)$$

The expression for the nonstandard Gibb's free energy of the reaction becomes

$$\Delta G_r = cG_C^\circ + cRT\,\ell nP_C + dG_D^\circ + dRT\,\ell nP_D$$

$$- aG_A^\circ + aRT\,\ell nP_A - bG_B^\circ - bRT\,\ell nP_B$$

$$\Delta G_r = \Delta G_C^\circ + RT\,\ell n\, P_C{}^c P_D{}^d / P_A{}^a P_B{}^b \qquad (12.57)$$

But $$Q_{(P)} = P_C{}^c P_D{}^d / P_A{}^a P_B{}^b ,$$

hence, $$\Delta G_r = \Delta G^\circ + RT\,\ell n\, Q_{(P)} \qquad (12.58)$$

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At equilibrium, $\Delta G_r$ is zero and Q is equal to K.

$$O = \Delta G^\circ + RT \ln K$$

$$\Delta G^\circ = -RT \ln K \qquad (12.59)$$

$$\Delta G_r = -RT \ln K + RT \ln Q \qquad (12.59A)$$

$$\Delta G_r = RT \ln Q/K \qquad (12.60)$$

The above equality combines the two criteria for equilibrium:

when $Q = K$ $\Delta G_r = 0$

and reaction is at equilibrium;

when $Q < K$ $\Delta G_r < 0$

and reaction is proceeding spontaneously in the forward direction towards equilibrium;

when $Q > K$ $\Delta G_r > 0$

and reaction is proceeding spontaneously in the reverse direction towards equilibrium;

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# CHAPTER 13

# ELECTROCHEMISTRY

Electrochemistry is a field of chemistry that deals with the electrical aspects of chemical reactions.

Since chemical bonds involve electrons, the essence of all chemical reactions is the transfer or rearrangement of electrons around the atoms participating in the reaction.

An electric current is a flow of electrons. Chemical reactions which entail transfer of electrons therefore produce an electric current if they occur spontaneously. Conversely, electrical energy needs to be supplied in order to force the reaction and the electron transfer in the opposite direction.

Prior to the discussion of the electrical effects of chemical reactions, the relevant electrical parameters are reviewed.

## 13- 1 Electricity reviewed

An electric current is the flow of electrons. Remembering that the charge ona single electron is (–) $1.602 \times 10^{-19}$ C (coulomb), a mole of electrons bear a total charge of 96485 C. This value is called the Faraday constant and is denoted by F.

$$F = 96\,485 \text{ C mole}^{-}$$

or

$$F = 96\,500 \text{ C mole}^{-}.$$

The flow of electrons can be viewed as the flow of electrical charge. The change in charge at one point per unit time is the rate of charge flow

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and is simply called the electric current.

$$dq/dt = I$$

If a charge of one coulomb passes a given point in one second then that electric current is one ampere (A).

$$q = I \quad t \qquad (13.1)$$

(C) (A) (s)

The cause of the charge flow between two points is the difference in their electric potentials. If it takes one joule of work to carry a charge of one coulomb from one point to the other, then the potential difference (E) between these two points is one volt (V).

$$W = E \quad q \qquad (13.2)$$

(J) (V) (C)

The relation indicates that greater the potential difference between two given points, the greater amount of work is effected in the transfer of a charge between the two points. If the transfer of charge is from a point of high potential to a lower one, the work effected can be utilized externally. External work is required for the transfer of charge from a low potential to a higher one.

**13- 2 Oxidation - reduction (REDOX) reactions**

Reactions which involve transfer of electrons are called oxidation-reduction (REDOX) reactions.

$$M^\circ \rightarrow M^+ + e^- \qquad \text{oxidation}$$

$$M^+ + e^- \rightarrow M^\circ \qquad \text{reduction}$$

Alternatively, an oxidation reaction can be defined as that process whereby the "oxidation number" or "oxidation state" of an element increases. A reduction process can be described as that process whereby the oxidation number (ON) of an element decreases.

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### 13- 2.1. Oxidation number (state)

Oxidation number is a measure of the extent of oxidation of an element in its compounds. It is assigned by using a set of simple rules:

1. Elements, in their metallic or neutral state, are assigned an oxidation number, ON, of 0.
2. Fluorine, the most electronegative element, has an ON of -1 in all its compounds.
3. Oxygen usually has an ON of -2 in its compounds. There are exceptions:
   i) in $F_2O$, the ON of oxygen is + 2;
   ii) in compounds containing oxygen-oxygen bonds, such as $H_2O_2$, ON of oxygen is -1.
4. All halogens other than F, have an ON of -1 except when they are combined with a more electronegative element, that is with oxygen or more electronegative halogen.
5. Hydrogen in its compounds always has an ON of +1 except in metal hydrides when its ON is -1.
6. The sum of the ON's of all atoms in a neutral compound is 0. The ON of an ion is equal to its charge.
7. The ON of other atoms can be deduced from the rules listed above.

### 13- 2.2. Balancing redox equations

Oxidation and reduction reactions go in pairs: as one party is being oxidized (releasing electrons) the other party is reduced (taking electrons).

The reaction between copper (metallic) land silver ions in an aqueous solution is a redox reaction:

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$$Cu^{(o)}_{(s)} + 2Ag^{(+)}_{(aq)} \rightarrow Cu^{(+2)}_{(aq)} + 2\,Ag^{(o)}_{(s)} \qquad (13.3)$$

The overall reaction can be written as an oxidation half-reaction and a reduction half-reaction:

$$Cu^{\circ}_{(s)} \rightarrow Cu^{+2}_{(aq)} + 2e^{-} \qquad \text{oxidation} \qquad (13.3A)$$

$$Ag^{+}_{(aq)} + e^{-} \rightarrow Ag^{\circ}_{(s)} \qquad \text{reduction} \qquad (13.3B)$$

In order to obtain (13.3) from the equations for the two half-reactions, (13.3B) has to be multiplied by 2 thus balancing the number of electrons taken up by Ag+ with the number of electrons released by Cu°.

There are various procedures for balancing redox reactions. One of these is given below.

1. Write down the reactants and the products of the reaction. Identify the elements which have undergone a change in their ON.
2. Write the equations for the oxidation half-reaction and the reduction half-reaction. Deal with each one separately as in the following steps.
3. Balance all atoms except O and H.
4. Balance the ON by adding the requisite number of electrons to the appropriate side of the equation.
5. Balance the charges on each side of the equation by adding $H^+$ or $OH^-$ (for acidic and basic medium respectively) to the appropriate side of the equations.
6. Balance O and H by adding the requisite number of $H_2O$'s to the appropriate side of the equation.

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7. Multiply each half-reaction by an appropriate coefficient such that the electrons are cancelled out when the two equations are added up.

The example below is solved following this procedure.

**Example**

Write the balanced equation for the reaction between metallic copper and nitric acid as shown below.

$$Cu_{(s)} + HNO_3 \rightarrow Cu(NO_3)_2 + NO_2$$

1. The ON of all atoms are specified. Only those which have undergone a change are shown.

$$\overset{(+5)}{\phantom{x}} \qquad \overset{(+2)}{\phantom{x}} \qquad \overset{(+4)}{\phantom{x}}$$
$$Cu^{(o)} + HNO_3 \rightarrow Cu(NO_3)_2 + NO_2$$

Copper has undergone a change in its oxidation number from 0 to +2 (oxidation).

Some of the nitrogen atoms have undergone a change in their ON from + 5 to + 4 (reduction).

2. The two half-equations are written.

$$Cu^{(o)} \rightarrow Cu^{(+2)}$$

$$\overset{(+5)}{NO_3^-} \rightarrow \overset{(+4)}{NO_2}$$

3. Atoms are already balanced.

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4. Balance the ON.

$$Cu^{(o)} \rightarrow Cu^{(+2)} + 2e^-$$

$$\overset{(+5)}{NO_3} + e^- \rightarrow \overset{(+4)}{NO_2}$$

5. Balance the charges with $H^+$ since an acid is present in the system.

$$Cu^{(o)} \rightarrow Cu^{(+2)} + 2e^-$$

$$\overset{(+5)}{NO_3} + e^- + 2H^+ \rightarrow \overset{(+4)}{NO_2}$$

6. Balance the O and H.

$$Cu^{(o)} \rightarrow Cu^{(+2)} + 2e^-$$

$$\overset{(+5)}{2NO_3} + e^- + 2H^+ \rightarrow \overset{(+4)}{NO_2} + H_2O$$

7. Multiply the reduction half-equation by 2.

$$Cu^{(o)} \rightarrow Cu^{(+2)} + 2e^-$$

$$\overset{(+5)}{2NO_3} + 2e^- + 4H^+ \rightarrow \overset{(+4)}{2NO_2} + 2H_2O$$

$$Cu + 2NO_3^- + 4H^+ \rightarrow Cu^{(+2)} + 2NO_2 + 2H_2O$$

OR

$$Cu + 4HNO_3 + 4H^+ \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

## 13- 3. Oxidation and reduction tendencies of elements and electrochemical cells

In both of the redox reactions presented in the previous section, it was Cu which was oxidized and, $Ag^+$ in the first case and $N^{(+5)}$ in the second case, was reduced.

On the other hand, if a strip of metallic zinc is dipped into a solution of $CuSO_4$, the zinc strip becomes coated with copper ($Cu^{(o)}$) and zinc ions ($Zn^{(+2)}$) start appearing in the solution (Figure 13.la). When the situation is reversed - that is when a strip of metallic copper is dipped into a solution of $ZnSO_4$ - nothing happens (Figure 13.lb).

In the arrangement illustrated in Figure 13.2, the strips of metallic copper and zinc are connected with a wire. A device called a potentiometer, or voltmeter, is introduced between the two connections. The two half-arrangements are further connected with what is called a salt bridge. The deflection observed on the potentiometer indicates a potential difference between the left and the right halves of the system and, consequently, a flow of electrons from the zinc half to the copper half.

In the zinc half, the zinc atoms on the zinc strip oxidize:

$$Zn^\circ \rightarrow Zn^{+2} + 2e^- .$$

The electrons released by the zinc atoms flow to the copper half through the connecting wire. The electrons gathering and discharging at the copper strip are taken up by the copper ions in the $CuSO_4$ solution - they are reduced:

$$Cu^{+2} + 2^{e-} \rightarrow Cu^\circ .$$

The neutrality of the solutions and, therefore, the continuity of the process is maintained by the salt bridge. The ions of the salt, e.g. $NaNO_3$, move towards the appropriate half to relieve any inbalance in charges.

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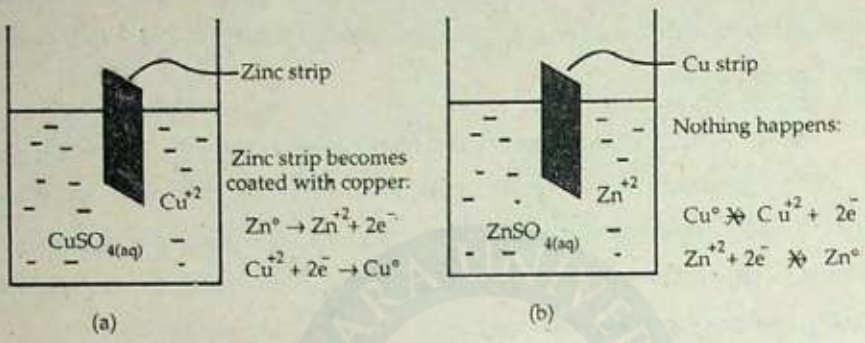


**Figure 13.1.**

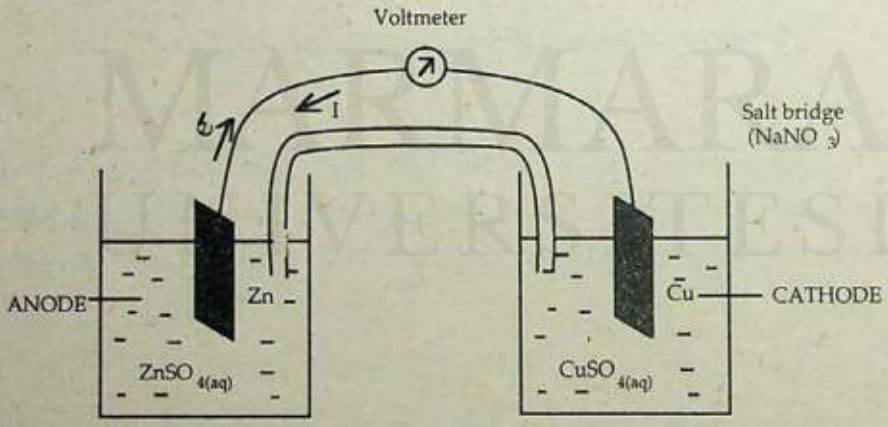


**Figure 13.2.** An electrochemical cell

The arrangement described above is what is called an electrochemical cell and is a perfect example of transformation of chemical energy into electrical energy.

The two metal strips are called the electrodes. The electrode where oxidation takes place, the zinc strip, is called the ANODE; the electrode where reduction takes place, is called the CATHODE.

The electron flow is from the anode to the cathode. Since the electric current was originally considered to be a flow of positive charges, its direction is opposite to that of the electrons.

Cell diagrams are used for simple depiction of electrochemical cells. The diagram for the cell in Figure 13.2 is

$$Zn_{(s)} \mid ZnSO_{4(aq)} \mid\mid CuSO_{4(aq)} \mid Cu_{(s)}$$

The single vertical line separates the electrode from the solution with which it is in contact The double verticle line indicate a salt bridge or a porous barrier between the two solutions. In cell diagrams, the anode appears on the left and the cathode on the right.

This electrochemical cell supplies (direct) electric current (DC) since the tendencies of the parties involved in the process for oxidation and reduction are in the appropriate direction and order. Zn has a gerater tendency for being oxidized than Cu. $Cu^{+2}$ ions have a greater tendency for being reduced than $Zn^{+2}$. Otherwise the electron flow would have been in the opposite direction - from the copper electrode to the zinc electrode.

The tendency of an atom or an ion to be reduced can be measured relative to that of the $H^+$ ion by employing an arrangement as show in Figure 13.3. The potential difference is measured by a potentiometer. The potential of the $H^+$ ion to be reduced is taken as zero. The reading on the potentiometer is therefore taken as the potential of the copper ions, or any other ion, to be reduced.

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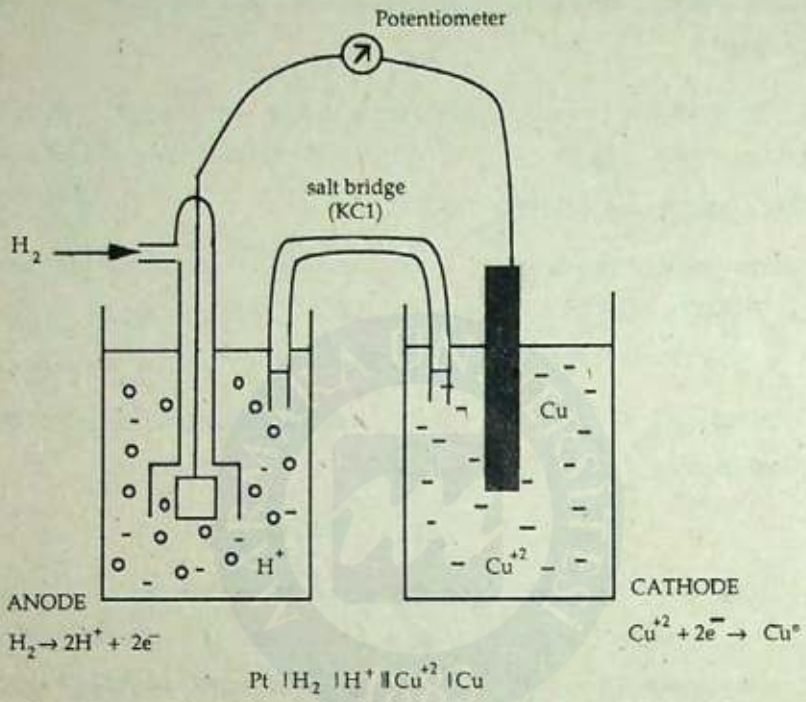


**Figure 13.3.** Measurement of standard reduction potentials

If such measurements are performed with $H_2$ at 1 atm, $[H^+] = 1$ M at 25°C, the standard reduction potentials of atoms, or ions, are obtained.

Table 13.1 lists these values. Since the $E^\circ_{red}$ of $H^+$ ion is taken as zero, negative values of $E^\circ_{red}$ indicates that the tendency of the species to be reduced is less than that of the $H^+$ ion. Positive values indicate a greater tendency.

The potential of the cell illustrated in Figure 13.2 is the difference between the $E^\circ_{red}$ 's of $Zn^{+2}$ and $Cu^{+2}$ or, since the process is one oxidation and one reduction half-reaction,

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$$E^\circ_{cell} = E^\circ_{oxid} + E^\circ_{red} .$$

For $Zn^{+2} + 2e^- \rightarrow Zn^\circ$ $\qquad E^\circ_{red} = -0.76\ V.$

But the reaction that takes place in the zinc half of the cell is the reverse of this reaction - it is an oxidation half-reaction.

Therefore

$$E^\circ_{oxid(Zn)} = 0.76\ V.$$

For the reduction of $Cu^{+2}$, the value of $E^\circ_{red}$ is 0.34 V. Hence

$$E^\circ_{cell} = 0.76 + 0.34$$

$$= 1.10\ V .$$

For a cell to function as a source of electrical energy, the redox reaction involved has to proceed spontaneously. The spontaniety of a redox reaction is indicated by a positive value of the cell potential.

The work done by an electrochemical cell is expressed by equation (13.2) as

$$W = E\,q .$$

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| OXIDIZING AGENTS | REACTION[a] | REDUCING AGENTS | $E^\circ_{red}$ (V) |
|---|---|---|---|
| Acidic Solution | | | |
| Very weak | $Li^+ + e^- \rightarrow Li\ (s)$ | Very strong | −3.05 |
| | $K^+ + e^- \rightarrow K(s)$ | | −2.93 |
| | $Ca^{2+} + 2e^- \rightarrow Ca\ (s)$ | | −2.87 |
| | $Na^+ + e^- \rightarrow Na\ (s)$ | | −2.71 |
| | $Mg^{2+} + 2e^- \rightarrow Mg\ (s)$ | | −2.36 |
| | $H_2\ (g) + 2e^- \rightarrow 2H^-$ | | −2.25 |
| | $Al^{3+} + 3e^- \rightarrow Al\ (s)$ | | −1.66 |
| | $2H_2O + 2e^- \rightarrow H_2\ (g) + 2OH^-$ | | −0.83 |
| | $Zn^{2+} + 2e^- \rightarrow Zn\ (s)$ | | −0.76 |
| | $Cr^{3+} + 3e^- \rightarrow Cr\ (s)$ | | −0.74 |
| | $Fe^{2+} + 2e^- \rightarrow Fe\ (s)$ | | −0.44 |
| | $Cr^{3+} + e^- \rightarrow Cr^{2+}$ | | −0.41 |
| | $V^{3+} + e^- \rightarrow V^{2+}$ | | −0.26 |
| | $Ni^{2+} + 2e^- \rightarrow Ni\ (s)$ | | −0.25 |
| | $Sn^{2+} + 2e^- \rightarrow Sn$ | | −0.16 |
| | $Pb^{2+} + 2e^- \rightarrow Pb\ (s)$ | | −0.13 |
| | $2H^+ + 2e^- \rightarrow H_2\ (g)$ | | 0 |
| | $AgBr\ (s) + e^- \rightarrow Ag\ (s) + Br^-$ | | +0.10 |
| | $S\ (s) + 2H^+ + 2e^- \rightarrow H_2S\ (aq)$ | | +0.14 |
| | $Cu^{2+} + e^- \rightarrow Cu^+$ | | +0.15 |
| | $AgCl\ (s) + e^- \rightarrow Ag\ (s) + Cl^-$ | | +0.22 |
| | $Cu^{2+} + 2e^- \rightarrow Cu\ (s)$ | | +0.34 |
| | $Cu^+ + e^- \rightarrow Cu\ (s)$ | | +0.52 |
| | $I_2\ (s) + 2e^- \rightarrow 2I^-$ | | +0.54 |
| | $O_2\ (g) + 2H^+ + 2e^- \rightarrow H_2O_2\ (aq)$ | | +0.68 |
| | $Fe^{3+} + e^- \rightarrow Fe^{2+}$ | | +0.77 |
| | $Ag^+ + e^- \rightarrow Ag\ (s)$ | | +0.80 |
| | $2NO_3^- + 4H^+ + 2e^- \rightarrow N_2O_4\ (g) + 2H_2O$ | | +0.80 |
| | $2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$ | | +0.92 |
| | $NO^-_3 + 4H^+ + 3e^- \rightarrow NO(g) + 2H_2O$ | | +0.97 |
| | $Br_2 + 2e^- \rightarrow 2Br^-$ | | +1.09 |
| | $O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O$ | | +1.23 |

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| | | | | |
|---|---|---|---|---|
| | $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ | | | + 1.33 |
| | $Cl_2\,(g) + 2e^- \rightarrow 2Cl^-$ | | | + 1.36 |
| | $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ | | | + 1.49 |
| | $Au^{3+} + 3e^- \rightarrow Au\,(s)$ | | | + 1.50 |
| | $MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 4H_2O$ | | | + 1.61 |
| | $H_2O_2\,(aq) + 2H^+ + 2e^- \rightarrow 2H_2O$ | | | + 1.78 |
| | $Co^{3+} + e^- \rightarrow Co^{2+}$ | | | + 1.81 |
| Very strong | $F_2 + 2e^- \rightarrow 2F^-$ | | Very weak | + 2.87 |
| Basic Solution | | | | |
| | $2H_2O + 2e^- \rightarrow H_2\,(g) + 2OH^-$ | | | − 0.83 |
| | $Fe(OH)_3\,(s) + e^- \rightarrow Fe(OH)_2\,(s) + OH^-$ | | | − 0.56 |
| | $O_2\,(g) + e^- \rightarrow O_2^-\,(aq)$ | | | − 0.56 |
| | $O_2\,(g) + 2H_2O + 4e^- \rightarrow 4OH^-$ | | | + 0.40 |

[a] All ions are in aqueous solution, and H2O is in the liquid state.

**Table 13.1.** Standard Reduction Potentials

$E^\circ_{cell}$ is the maximum electrical potential a cell can provide. In the case of the Zn | $ZnSO_4$ || $CuSO_4$ | Cu cell considered, the $E^\circ_{cell}$ value. is 1.10 V. Since two moles of electrons are involved in the redox reaction of $Zn–Cu^{+2}$, the maximum work such a cell can perform is

$$W_{max} = E^\circ_{cell}\,(\#\text{ moles of e's})\,(96\,500\text{ C mole}^{-1})$$

$$= (1.1\text{ V})\,(2\text{ moles of e's})\,(96\,500\text{ C mole}^{-1})$$

$$= 213\,300\text{ J.}$$

Since the maximum work (reversible) done by a reacting system at constant temperature is equal to the change in its Gibb's free energy, $\Delta G^\circ$ (12.12E and 12.54A),

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$$\Delta G^\circ = -W_{max} = -zFE^\circ$$

and $$\Delta G^\circ = -RT\ell n K \qquad (12.59)$$

$$\Delta G_r = -RT\ell n K + RT\ell n Q \qquad (12.59A)$$

or $$\Delta G_r = \Delta G^\circ + RT\ell n Q.$$

If all the terms in the above expression are divided by - zF

$$E_{cell} = E^\circ_{cell} - RT\ell n Q/zF \qquad \text{(Nernst equation)}$$

is obtained.

At equilibrium, that is when the cell is flat, Q = K and $E_{cell} = 0$.

$$0 = E^\circ_{cell} - RT\ell n K/zF$$

$$\ell n K = E^\circ_{cell}\, zF/RT$$

Or $$E_{cell} = 2.303\, RT \log K/zF = 0.0592 \log K/z \ (@\ 25^\circ C)$$

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# CHAPTER 14

# NUCLEAR CHEMISTRY

In the chemical reactions studied to this point, it was the electrons and the electronic structure of the elements that played the major role. The nuclei of the atoms remained unchanged.

Nuclei of atoms can undergo changes under external influences or naturally. These transformations are called nuclear reactions. Nuclear reactions can be in the form of fusion of smaller nuclei to form more massive nuclei or in the form of fission of a single nucleus to form smaller nuclei.

Nuclear chemistry is the field of chemistry that studies variety of phenomena stemming directly from the nuclei of atoms.

## 14- 1 Law of conservation of mass-energy

By the end of 19th century, the two separate physical conservation laws-conservation of mass and consevation of energy - were well accepted.

In 1905, Albert Einstein (1879-1955) developed his famous theory of relativity relating time, space, mass and motion. The equation which unifies the laws of conservation of mass and energy,

$$E = m c^2 \qquad (14.1)$$

(erg) (g) (cm/s)

is part of this theory of relativity.

The value of c, speed of light, is $3 \times 10^{10}$ cm/s. This means that a very small mass is equivalent to a large amount of energy. The expression also implies that when a system gains energy, it also gains mass. It has been shown experimentally that the faster a particle moves, the greater its effec-

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tive mass is. The mass of a stationary particle is called its rest mass. The mass of a particle in motion is called its relativistic mass. In nuclear processes involving high seped particles, relativistic masses must be considered. In chemical (non-nuclear) processes rest masses are considered.

Einstein used the term mass- energy to illustrate their interchangeability. The law of conservation of mass-energy states that: – "MASS AND ENERGY CAN BE TRANSFORMED BUT MASS-ENERGY CANNOT BE CREATED OR DESTROYED."

Einstein visualized mass as concentrated energy and energy as deconcentrated mass. In a nuclear reaction or explosion - as in the case of the nuclear bomb - a small amount of mass is transformed into an enormous amount of energy.

Einstein's equation applies to non-nuclear reactions also. But in that case, the change in mass is so very small that it can be neglected.

**14- 2 The nucleus and nuclear stability**

The fundamental particles in an atomic nucleus are protons and neutrons. The number of protons is represented by the atomic number Z. The sum of the number of protons and neutrons is represented by the mass number A.

It is the number of protons in the nucleus that defines an element. All nuclei with the same proton number, with different mass numbers, are isotopes of the same element.

$$^{A}_{Z}E.$$

Precise mass measurements can be performed by use of mass spectrometers. A difference is observed between the mass of a nucleus measured in this manner and that calculated from the masses of protons and neutrons that make it up. In the case of the $^{4}_{2}He$ nucleus the measured mass is 4.00150 u (obtained by subtracting the mass of 2 electrons from the mass of the helium atom - Table 14.1). The helium nucleus consists of two protons and two neutrons:

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| PARTICLE OR ISOTOPE | MASS (u) | PERCENT NATURAL ABUNDANCE | ISOPTOPE | MASS(u) | PERCENT NATURAL ABUNDANCE |
|---|---|---|---|---|---|
| $^{1}_{1}H$ | 1.007 83 | 99.985 | $^{23}_{11}Na$ | 22.989 77 | 100 |
| $^{2}_{1}H$ | 2.014 10 | 0.015 | $^{24}_{12}Mg$ | 23.985 04 | 78.7 |
| $^{4}_{2}He$ | 4.002 60 | 99.999 87 | $^{25}_{12}Mg$ | 24.985 84 | 10.2 |
| $^{6}_{3}Li$ | 6.015 12 | 7.42 | $^{26}_{12}Mg$ | 25.986 36 | 11.1 |
| $^{7}_{3}Li$ | 7.016 00 | 92.58 | $^{27}_{13}Al$ | 26.981 53 | 100 |
| $^{9}_{4}Be$ | 9.012 19 | 100 | $^{29}_{14}Si$ | 28.976 50 | 4.71 |
| $^{10}_{5}B$ | 10.012 94 | 19.77 | $^{30}_{14}Si$ | 29.973 77 | 3.12 |
| $^{11}_{5}B$ | 11.009 31 | 80.23 | $^{31}_{15}P$ | 30.973 77 | 100 |
| $^{12}_{6}C$ | 12.000 00 | 98.892 | $^{32}_{16}S$ | 31.972 07 | 95.02 |
| $^{13}_{6}C$ | 13.003 36 | 1.108 | $^{33}_{16}S$ | 32.971 46 | 0.76 |
| $^{14}_{7}N$ | 14.003 07 | 99.635 | $^{34}_{16}S$ | 33.976 86 | 4.22 |
| $^{15}_{7}N$ | 15.000 11 | 0.365 | $^{36}_{16}S$ | 35.976 10 | 0.014 |
| $^{16}_{8}O$ | 15.994 91 | 99.759 | $^{35}_{17}Cl$ | 34.968 85 | 75.53 |
| $^{17}_{8}O$ | 16.999 13 | 0.037 | $^{37}_{17}CL$ | 36.965 90 | 24.47 |
| $^{18}_{8}O$ | 17.999 16 | 0.204 | $^{36}_{18}Ar$ | 35.967 54 | 0.337 |
| $^{19}_{9}F$ | 18.998.40 | 100 | $^{38}_{18}Ar$ | 37.962 73 | 0.063 |
| $^{20}_{10}Ne$ | 19.992 44 | 90.92 | $^{40}_{18}Ar$ | 39.962 38 | 99.60 |
| $^{21}_{10}Ne$ | 20.993 85 | 0.257 | $^{39}_{19}K$ | 38.963 71 | 93.22 |
| $^{22}_{10}Ne$ | 21.991 38 | 8.82 | $^{40}_{19}K$ | 39.964 01 | 0.012 |
| | | | $^{41}_{19}K$ | 40.961 83 | 6.77 |

$$1\ u = 1.660\ 05655 \times 10^{-27}\ kg$$

1 proton = 1.00751 u = $1.672\ 52 \times 10^{-27}$ kg

1 neutron = 1.00894 u = $1.675\ 41 \times 10^{-27}$ kg

1 electron = 0.000549 u = $0.910\ 9534 \times 10^{-30}$ kg

Table 14.1. Mass and natural abundance of some isotopes and particles

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| | |
|---|---|
| 2 protons | 2 x 1.00751 u |
| 2 neutrons | 2 x 1.00894 u |
| | 4.03290 u |

The difference between two masses is (4.03290 - 4.00150 u) 0.03140 u. According to Einstein's theory, 0.03140 u of mass is transformed into energy each time two protons and two neutrons merge to form the helium nucleus.

$$E = mc^2$$

$$= 0.0314\ u \times 1.660\,057 \times 10^{-24}\ g/u \times (3 \times 10^{10}\ cm/s)^2$$

$$= (0.0314)\,(1.660\,057 \times 10^{-24})\,(9 \times 10^{20})\ erg$$

$$= 0.50798 \times 10^{-4}\ erg\ (energy\ released).$$

In the formation of 1 mole of helium nuclei, (~ 4 g of helium)

$$E = 0.50798 \times 10^{-4}\ erg \times 6.023 \times 10^{23} \times 1\ J/10^{7}\ erg$$

$$= 3.05956 \times 10^{12}\ J/mole$$

$$= 3.05956 \times 10^{9}\ kJ/mole$$

$$E = 0.76489 \times 10^{9}\ kJ/g\ helium.$$

$$(\Delta H^{\circ}_{c} = 0.55640 \times 10^{2}\ kJ/g\ methane).$$

The value of the energy released upon formation of one mole of helium nucleus shows the magnitude of the force that holds the protons and neutrons together. It also reflects the severity of the conditions necessary to effect a nuclear reaction. It is referred to as the binding energy of the nucleus.

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It is common practice to quote binding energies in electron volts (eV). In the preceeding chapter, one joule of work was presented as the work, or potential energy change, effected when a charge of one coulomb is transferred across a potential difference of one volt. One electron volt (eV) is defined as the work, or potential energy change, effected when a charge of one electron (~ $1.6 \times 10^{-19}$ C) is transferred across a potential difference of 1 V.

$$W = E\,q$$

$$1\ (J) = 1\ (V)\ 1\ (C)$$

$$10^7\ (erg) = 1\ (V)\ 1\ (C)$$

$$1\ (eV) = 1\ (V)\ 1.6 \times 10^{-19}\ (C)$$

$$1\ (eV) = 1.6 \times 10^{-12}\ erg.$$

The energy associated with a change of 1 u in mass, in eV, is

(take 1u = $1.66 \times 10^{-24}$ g)

$$E = 1.66 \times 10^{-24}\ g \times 9 \times 10^{20}\ cm^2/s^2 \qquad \text{(from 14.1)}$$

$$= 1.49 \times 10^{-3}\ erg$$

$$= 1.49 \times 10^{-3}\ erg \times 1\ eV / 1.60 \times 10^{-12}\ erg$$

$$= 931 \times 10^6\ eV$$

$$= 931\ MeV.$$

The binding energy of the helium nucleus can now be quoted in MeV as

$$E = 0.0314 \times 931$$

$$= 29.23\ MeV$$

The binding energy per nucleon is obtained by dividing this value by the total number of nucleons.

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29.23 MeV/4 nucleons = 7.31 MeV/nucleon.

The greater the binding energy per nucleon, the more stable is the nucleus. Figure 14.1 shows the variation of nuclear stability with atomic number. $^{56}_{26}Fe$, with the largest binding energy per nucleon, has the most stable nucleus. Formation of a $^{56}_{26}Fe$ nucleus from component particles liberates more energy than the formation of any other nuclei.

$^{4}_{2}H$, $^{12}_{6}C$ and $^{16}_{8}O$ lie above the curve. They have higher binding energies per nucleon than other elements with comparable masses. The fact that the mass numbers of these three elements can be divided by 4 suggests that helium nuclei which have 4 nucleons (2 protons and 2 neutrons) may be the building block of other nuclei.

Going from this observation, a nuclear shell model, analogous to the electron shell model, has been developed. According to this model, certain numbers of nucleons are assigned to different energy levels in the nucleus as in the case of electronic configurations. Nuclear stability is observed to be especially high when proton and neutron numbers are equal and they are 2, 8, 20, 28, 50 and 82. In nuclear chemistry, these numsers are referred to as "magic numbers".

Figure 14.2 shows a plot of number of neutrons versus number of protons in all known elements. The straight line is the N = Z line. The stable nuclei are found in the narrow band above the N = Z line after Z = 20. As Z increases, the number of neutrons exceeds the number of protons and the N to Z ratio in creases to 1.5 for the for the heaviest stable nucleus, bismuth nucleus.

Nuclei are made up of protons and neutrons. Protons are positively charged and neutrons are neutral. Similarly charged particles repel each other. The repulsive forces between the protons, which are effective only when the distance between the protons is gerater than $10^{-15}$ m, are reduced by the neutrons in the nucleus. The nuclei that lie outside the band of stabili-

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ty are unstable and transform to nuclei with more stable neutron-to-proton ratio. However, above the atomic number of 83, no matter how man neutrons are present and whatever the binding energy is, it is not possible to reduce these repulsive forces so as such nuclei are stable. All nuclei with $Z > 83$ are unstable. They acquire their stability by emitting particles that will decrease the number of protons in them.

Nuclei above the band of stability with $Z < 83$ achieve stability by emitting particles so as to reduce their neutron-to-proton ratios.

Nuclei below the band of stability with $Z < 83$ achieve stability by emtting particles so as to reduce their proton-to-neutron ratios.

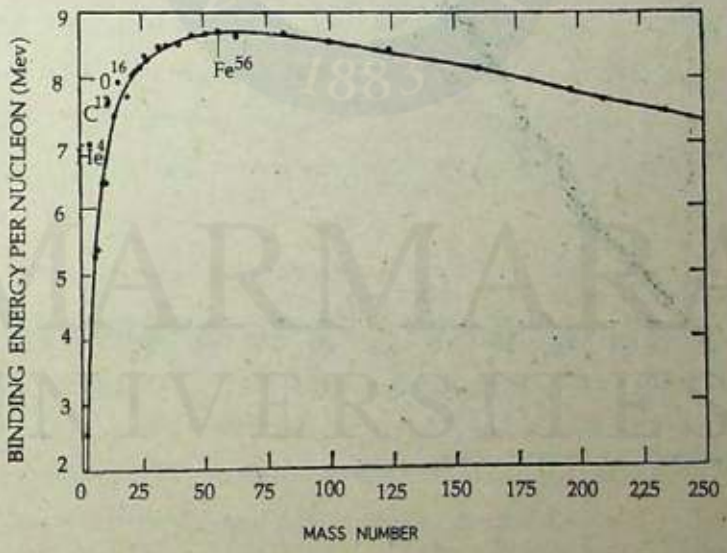


**Figure 14.1** Binding energy per nucleon of stable nuclei

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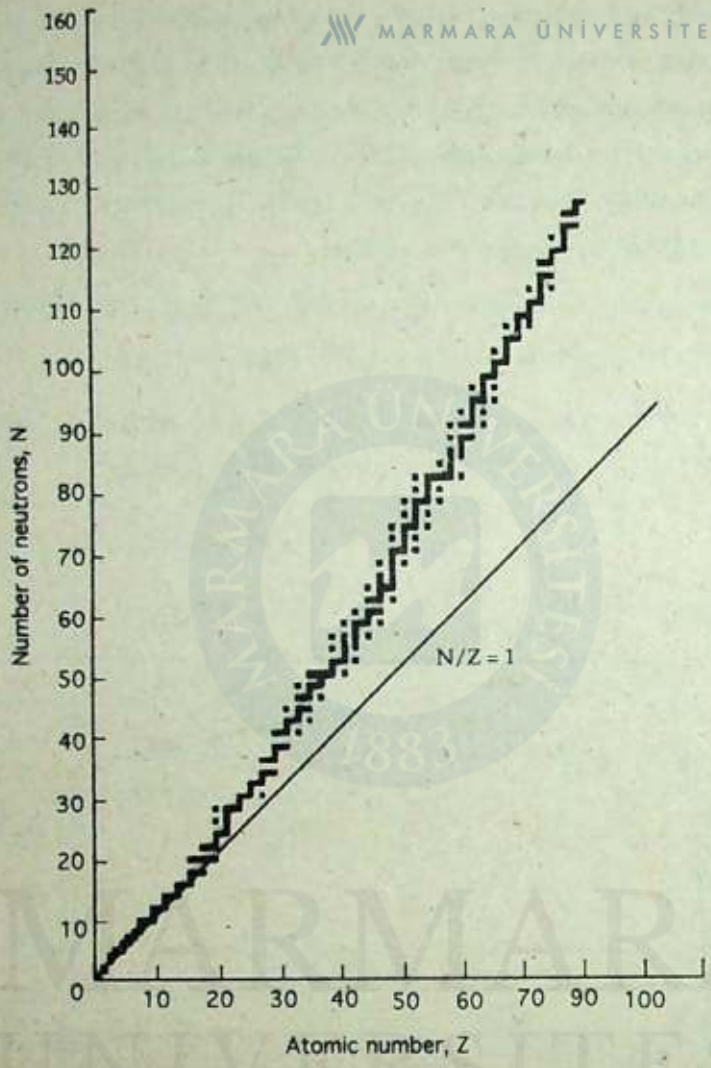


**Figure 14.2** The band of stability

## 14- 3 Radioactivity

In order to achieve stability, unstable nuclei undergo transformations emitting some form of radiation that can be particulate or nonparticulate.

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**Alpha-particles (α – particles)**

α – particle is a $^{4}_{2}He$ nucleus. It has a charge of +2 and a mass number of 4. A heavy nucleus with atomic number greater than 83 can alter its neutron-toproton ratio, its mass and charge by emitting an α – particle.

In the α –decay of radium,

$$^{226}_{80}Ra \rightarrow ^{4}_{2}He + ^{222}_{86}Rn,$$

one helium nucleus is emitted and a radon nucleus is formed. The neutron to-proton ratio is increased and mass and charge are decreased. Both changes are favourable for achieving higher stability.

α –particles are relatively massive particles that travel at about one-tenth the speed of light. They have little penetrating power. They can be stopped by a sheet of paper. On the other hand, since they have a charge of +2, they have high ionizing ability. One α –particle can dislodge approximately 100 000 electrons and, therefore, produce the same number of ion pairs (one electron and the positive ion) in its existance. α –particles present a serious internal hazard.

**Beta - particles ( β- particles)**

Nulei with unfavourable neutron-toproton ratios emit β- particles. β-particles are high energy point charges like electrons. They are denoted by e, like the electrons. However, they can bear both negative ($_{-1}°e$ or $\beta^{-}$ ) and positive ($+1°e$ or $\beta^{+}$ ) charges. The negatively charged ones are called electrons. The positively charged ones are called positrons.

β – decay of $^{234}_{90}Th$ is an example of $_{-1}°e$ emission whereby one neutron is transformed into a proton thus forming a $^{234}_{91}Pa$ nucleus.

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$$^{234}_{90}Th \rightarrow ^{234}_{91}Pa + ^{0}_{-1}e$$

$$^{1}_{0}n \rightarrow ^{1}_{1}P + ^{0}_{-1}e$$

When the neutron-to proton ratio is low - which can be the case with artificial isotopes of elements with Z < 20 – positron emission is encountered. In positron emission, a proton is converted into a neutron.

$$^{30}_{15}P \rightarrow ^{30}_{14}Si + ^{0}_{+1}e$$

$$(^{1}_{1}p \rightarrow ^{1}_{0}n + ^{0}_{+1}e).$$

Positron emission can also be accomplished when the nucleus captures an electron from the inner most shell (n = 1 or K shell) of the atom (Electron Capture - E.C.). The negative charge of the captured electron effectively transforms a proton into a neutron. Following that, an electron from an outer shell falls into the vacated K-shell releasing a photon (X - ray).

β – particles have very small masses. They have higher penetrating power than β – particles but less ionizing power.

**Gamma-rays (γ-rays)**

Some radioactive decay processes emitting α or β particles leave the nucleus in an energetic state. The nucleus then loses this excess energy in the form of electromagnetic radiation. γ – rays are highly penetrating form of radiation. They have shorter wavelengths than any other magnetic radiation (< 1 nm).

$$^{234}_{92}U \rightarrow ^{230}_{90}Th^{*} + ^{4}_{2}He$$

$$^{230}_{90}Th^{*} \rightarrow ^{230}_{90}Th + \gamma.$$

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## 14- 3.1 Natural radioactivity

$^{209}_{83}Bi$ is the nucleus with the highest atomic and mass number that is stable. All nuclei with greater atomic and mass numbers are naturally radioactive.

Naturally occuring $^{238}_{92}U$ is radioactive and disintegrates progessively to $^{236}_{92}U$ Pb by emitting $\alpha$ is $\beta$ particles.

$$^{238}_{92}U \rightarrow {}^{230}_{90}Th + {}^{4}_{2}He$$

$$^{234}_{90}Th \rightarrow {}^{234}_{91}Pa + {}^{0}_{-1}e$$

$$^{234}_{91}Pa \rightarrow {}^{234}_{92}U + {}^{0}_{-1}e .$$

The series continues until $^{206}_{82}Pb$ is obtained. This is called the uranium decay series. In the same manner, the disintegration of naturally occuring thorium and actinium are called the thorium and actinium series (Tables 14.2, 3, 4).

The lighter nuclei that are radioactive are $^{40}K$, $^{50}V$ and $^{138}La$.

$^{40}K$ decays by electron emission or electron capture.

$$^{40}_{19}K \rightarrow {}^{40}_{20}Ca + {}^{0}_{-1}e$$

$$^{40}_{19}K \xrightarrow{E.C.} {}^{40}_{18}Ar .$$

It is believed that the high argon content of the atmosphere (0.934 % by volume) has been derived from $^{40}K$.

## THE URANIUM SERIES

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| Radioelement | Corresponding Element | Symbol | Radiation | Half Life |
|---|---|---|---|---|
| Uranium I | Uranium | $U^{238}$ | α | $4.51 \times 10^{9}$ yr. |
| ↓ | | | | |
| Uranium $X_1$ | Thorium | $Th^{234}$ | β | 24.1 days |
| ↓ | | | | |
| Uranium $X_2$* | Protactinium | $Pa^{234}$ | β | 1.18 min. |
| ↓ | | | | |
| Uranium II | Uranium | $U^{234}$ | α | $2.48 \times 10^{5}$ yr. |
| ↓ | | | | |
| Ionium | Thorium | $Th^{230}$ | α | $8.0 \times 10^{4}$ yr. |
| ↓ | | | | |
| Radium | Radium | $Ra^{226}$ | α | $1.62 \times 10^{3}$ yr. |
| ↓ | | | | |
| Ra Emanation | Radon | $Rn^{222}$ | α | 3.82 days |
| ↓ | | | | |
| Radium A | Polonium | $Po^{218}$ | α and β | 3.05 min. |
| 99.98% \| 0.02% | | | | |
| Radium B | Lead | $Pb^{214}$ | β | 26.8 min. |
| ↓ | | | | |
| Astatine-218 | Astatine | $At^{218}$ | α | 2 sec |
| ↓ | | | | |
| Radium C | Bismuth | $Bi^{214}$ | β and α | 19.7 min. |
| 99.95% \| 0.04 % | | | | |
| Radium C' | Polonium | $Po^{214}$ | α | $1.6 \times 10^{-4}$ sec. |
| ↓ | | | | |
| Radium C'' | Thallium | $Tl^{210}$ | β | 1.32 min. |
| ↓ | | | | |
| Radium D | Lead | $Pb^{210}$ | β | 19.4 yr. |
| ↓ | | | | |
| Radium E | Bismuth | $Bi^{210}$ | β and α | 5.0 days |
| ~ 100% \| $2 \times 10^{-4}$% | | | | |
| Radium F | Polonium | $Po^{210}$ | α | 138.4 days |
| ↓ | | | | |
| Thallium-206 | Thallium | $Tl^{206}$ | β | 4.20 min |
| ↓ | | | | |
| Radium G (End Product) | Lead | $Pb^{206}$ | Stable | - |

**Table 14.2.** The Uranium series

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## THE THORIUM SERIES

| Radioelement | Corresponding Element | Symbol | Radiation | Half Life |
|---|---|---|---|---|
| Thorium | Thorium | $Th^{232}$ | α | $1.39 \times 10^{10}$ yr. |
| ↓ | | | | |
| Mesothorium I | Radium | $Ra^{228}$ | β | 6.7 yr. |
| ↓ | | | | |
| Mesothorium II | Actinium | $Ac^{228}$ | β | 6.13 hr. |
| ↓ | | | | |
| Radiothorium | Thorium | $Th^{228}$ | α | 1.91 yr. |
| ↓ | | | | |
| Thorium X | Radium | $Ra^{224}$ | α | 3.64 days |
| ↓ | | | | |
| Th Emanation | Radon | $Rn^{220}$ | α | 52 sec. |
| ↓ | | | | |
| Thorium A | Polonium | $Poa^{216}$ | α | 0.16 sec. |
| ↓ | | | | |
| Thorium B | Lead | $Pb^{212}$ | β | 10.6 hr. |
| ↓ | | | | |
| Thorium C | Bismuth | $Bi^{212}$ | β and α | 60.5 min. |
| 66.3% \| 33.7 % | | | | |
| Thorium C' | Polonium | $Po^{212}$ | α | $3 \times 10^{-7}$ sec. |
| Thorium C'' | Thallium | $Tl^{212}$ | β | 3.1 min. |
| ↓ | | | | |
| Thorium D (End Product) | Lead | $Pb^{208}$ | Stable | – |

**Table 14.3** The Thorium series

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## THE ACTINIUM SERIES

| Radioelement | Corresponding Element | Symbol | Radiation | Half Life |
|---|---|---|---|---|
| Actinouranium | Uranium | $U^{235}$ | α | $7.13 \times 10^{8}$ yr. |
| ↓ | | | | |
| Uranium Y | Thorium | $Th^{231}$ | β | 25.6 hr. |
| ↓ | | | | |
| Protactinium | Protactinium | $Pa^{231}$ | α | $3.43 \times 10^{4}$ yr. |
| ↓ | | | | |
| Actinium | Actinium | $Ac^{227}$ | β and α | 21.8 yr. |
| 98.8% \| 1.2 % | | | | |
| Radioactinium | Thorium | $Th^{227}$ | α | 18.4 days |
| Actinium K | Francium | $Fr^{223}$ | β | 21 min. |
| ↓ | | | | |
| Actinium X | Radium | $Ra^{223}$ | α | 11.7 days. |
| ↓ | | | | |
| Ac Emanation | Radon | $Rn^{219}$ | α | 3.92 sec. |
| ↓ | | | | |
| Actinium A | Polonium | $Po^{215}$ | α and β | $1.83 \times 10^{-3}$ sec. |
| ~ 100% \| ~ $5 \times 10^{-4}$% | | | | |
| Actinium B | Lead | $Pb^{211}$ | β | 36.1 min.. |
| Astatine-215 | Astatine | $At^{215}$ | α | $\sim 10^{-4}$ sec. |
| ↓ | | | | |
| Actinium C | Bismuth | $Bi^{211}$ | α and β | 2.16 min. |
| 99.7% \| 0.3% | | | | |
| Actinium C' | Polonium | $Po^{211}$ | α | 0.52 sec. |
| Actinium C'' | Thallium | $Tl^{207}$ | β | 4.78 min. |
| ↓ | | | | |
| Actinium D (End Product) | Lead | $Pb^{207}$ | Stable | – |

**Table 14.4** The Actinium series

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### 14- 3.2 Artificial radioactivity

Bombardment of the nuclei of nonradioactive elements by nuclear particles produce isotopic nuclei which can be radioactive or nonradioactive.

$$^{14}_{7}N + ^{4}_{2}He \rightarrow ^{17}_{8}O + ^{1}_{1}H.$$

An alternative notation for this nuclear reaction is

$$^{14}N(\alpha, p)^{17}O$$

symbolizing the fact that $^{14}_{7}N$ is bombarded with $\alpha$ - particles and a proton and $^{17}_{8}O$ are obtained. $^{17}_{8}O$ is nonradioactive. However, in

$$^{27}Al(\alpha, n)^{30}P,$$

$^{30}_{15}P$ is radioactive and decays further to $^{30}_{14}Si$ .

$$^{30}_{15}P \rightarrow ^{30}_{14}Si + ^{0}_{+1}e.$$

### 14- 4 Radioactive decay rates

It has been observed that the rate of disintegration of a radioactive material is directly proportional to the number of atoms present in the sample.

$$\text{rate of decay} \propto N$$

or

$$\text{rate of decay} = \lambda N$$

where N is the number of radioactive atoms present

$\lambda$ is the radioactive constant or decay constant.

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rate of decay, $-dN/dt = \lambda N$ (14.2)

$$-\int_{N_0}^{N_t} dN/N = \lambda \int_0^t dt$$

$$\ell n\, N_t / N_o = -\lambda t. \qquad (14.3)$$

At half-life, $N_t = N_o/2$ and $t = t_{1/2}$.

$$\ell n\, 1/2 = \lambda_{t1/2}.$$

$$t_{1/2} = 0.692/\lambda. \qquad (14.4)$$

This expression of radioactive decay rate is widely utilized in determining the age of substances as will be seen in the following section.

**14- 5 Applications of radioactivity**

**14.4.1 Nuclear reactors**

A good example of utilization of energy released by nuclear reactions is nuclear reactors.

In the fission of $^{235}_{92}U$ upon bonbardment with neutrons,

$$^{235}_{92}U + {}^{1}_{o}n \rightarrow {}^{236}_{92}U \rightarrow \underset{\text{fragments}}{\text{Fission}} + \text{neutrons} + (\sim) 3.2 \times 10^{-11} J,$$

an average of 2.5 neutrons are released per fission of each $^{235}_{92}U$ nucleus. The neutrons produced by the second round of fission produce another 4 or 5 neutrons and so on. The result is a chain reaction whereby enormous amount of enegy is released. If the reaction is uncontrolled, the total energy released causes an explosion as in the case of the nuclear bomb. If the reaction is monitored, the energy released can be utilized.

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The most common design of a nuclear reactor is shown in Figure 14.3. In the core of the reactor, rods of uranium-rich fuel are suspended in a liquid or gas - $H_2O$, $D_2O$, Na, Na-K alloy or $CO_2$, He. The most common reactor media are $H_2O$ and $D_2O$ (heavy water).

The water in the reactor serves a dual purpose. First it slows down the neutrons released in the fission process thus controlling the rate of the reaction and the rate of energy release. As such, water acts as a moderator. The second function of the water is to transfer the heat it has absorbed to the outside of the reactor for utilization. It foes through a heat-exchanger whereby it transfers the heat to the incoming water at a lower temperature. As a result of the heat transferred, the incoming water is converted to steam. The steam drives the turbine which generates electricity. Lower enthalpy steam goes through the condenser and recycles back to the heat exchanger.

The control rods are usually cadmium or boron metal rods. They absorb neutrons and their isotopes are not radioactive.

$$^{113}_{48}Cd + ^{1}_{0}n \rightarrow ^{114}_{48}Cd + \gamma$$

$$^{10}_{5}Cd + ^{1}_{0}n \rightarrow ^{11}_{5}B + \gamma$$

When the rods are lowered into the reactor, the fission process is slowed down. When the rods are raised, the density of the neutrons and, therefore, the rate of fission increases.

**14-5.2 Radioachemical dating**

A important application of radioactive decay is the dating of rocks, fossils and ancient objects.

As stated in section 14.3.1, the final stable nucleus in the decay series of $^{238}_{92}U$ is $^{206}_{82}Pb$ . The half-life of U-238 is $4.5 \times 10^9$ years. For the natural decay scheme of U-238, the net equation is written as

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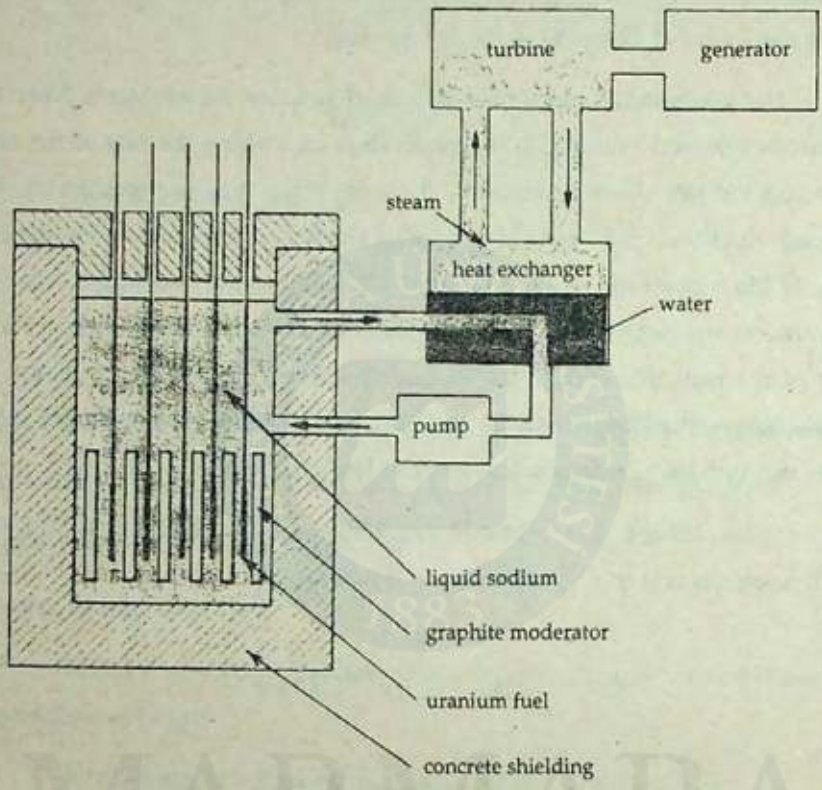


**Figure 14.3** A nuclear reactor

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$$^{238}_{92}U \rightarrow {}^{206}_{82}Pb + 6\,{}^{0}_{-1}e .$$

Ignoring the mass associated with the electrons emitted, for every 238 g of U-238 that undergoes complete decay, 206 g of Pb-206 and 32 g of He-4 are produced.

The age of a fossil that has a U-238 to Pb-206 ratio of 1 : 6 (by mass) can be calculated as follows.

$$t_{1/2} = 0.692/\lambda$$

$$\lambda = 0.692/4.5 \times 10^{9}\ y^{-1}$$

$$= 0.154 \times 10^{-9} \quad y^{-1}.$$

$$\ell n\, N_t / N_o = -\lambda t \qquad (14.3)$$

Consider the sample as 1 g of U-238 and 6 g of Pb-206.

238 g of U-238 yields 206 g of Pb-206

x ← 6 g of Pb-206

x = 6.93 g.

Therefore

$$N_o = (1 + 6.93) / 238$$

$$N_t = 1/238$$

$$\ell n\, 1/7.93 = 0.154 \times 10^{-9}\ t$$

$$-2.07 = -0.154 \times 10^{-9}\ t$$

$$t = -6.5 \times 10^{9}\ y .$$

### 14-5.3 Medical applications

Radiation causes ionization, excitation and, therefore, dissociation of molecules. In a biological system like the human body, such severe chemical changes may distrupt the normal operation of some cells. They may even

cause some abnormal cells to grow at abnormal rates finally annihilating the entire biological system - CANCER.

Cancerous cells, although may be induced by radiation, can at the same time be killed off selectively by $\gamma$ or X rays. Usually $\gamma$ or $\beta$ rays from Co-59 or Co-60 are applied at the appropriate dosage.

The units of radiation are given in Table 14.5.

Radiation emitted from an isotope is easily detected by suitable equipment. This feature of radioisotopes is widely utilized in medical diagnosis. The radiation emitted by a radioisotope introduced to the human body in subhazardous dosages can give the image of the organ in which it cnocentrates or circulates. Na-24 is used for blood circulation, Tc-99 is used for brain and liver scans, I-123 is used for thyroid imaging.

### 14-5.4 Labeling of elements

Reactions can take in multisteps. In order to determine the exact sequence of steps in complex reactions, a fraction of the atoms of one element in the chemical species is exchanged with its isotope. Since a radioactive isotope has the same chemical properties as the stable isotopes of an element, it will follow the same sequence of reactions. However, the movement of the radioctive isotope can be determined by suitable equipment and thus the mechanism of the reaction can be determined.

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| Unit | Definition |
|---|---|
| Curie | An amount of radioactive material decaying at the same rate as 1 g of radium ($3.7 \times 10^{10}$ dis/s). |
| Rad | A dosage of radiation capable of depositing $1 \times 10^{-2}$ J of energy per kilogram of matter. |
| Rem | A unit related to the rad, but taking into account the varying effects of differen t types of radiation of the same energy on biological matter. This relationship is through a "quality factor", which may be taken as equal to one for x ray, $\gamma$ rays $\beta$ particles. For protons and slow neutrons the factor has a value of 5; and for $\alpha$ - particles, 10. THus, an exposure to 1 rad of x rays is about equal to 1 rem, but 1 rad of $\alpha$ - particles is about equal to 10 rem. |

**Table 14.5** Units of radiation

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